Processing of Pollutants in Dielectric-Barrier Plasma Reactors

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Abstract

Atmospheric-pressure dielectric barrier electrical discharges (silent discharges) can produce large-volume nonthermal plasmas and energetic electrons which can create substantial concentrations of free radicals. Gas-phase pollutants can be decomposed by these free radicals or by electron-induced dissociation. Basic plasma chemistry, laboratory-scale testing, reactor scale up, example applications, and specific electrical energy requirements for representative compounds are discussed in this paper.

Introduction

Gas-phase hazardous chemicals are readily attacked by free radicals which can be efficiently generated in the gas phase by nonequilibrium (or nonthermal) plasmas. Nonthermal plasmas are characterized by conditions in which the various plasma species are not in thermal equilibrium - that is, electrons, ions, and neutral species have different temperatures, with the less massive electrons having the highest temperature (e.g., 1-10 eV). Large-volume, atmospheric-pressure nonequilibrium plasmas suitable for chemical processing can be easily created using dielectric-barrier or pulsed corona discharges. Nonthermal plasmas show promise for simultaneously treating different types of pollutants such as volatile organic compounds (VOCs) and flue gases (SO_x and NO_x).

A dielectric-barrier electrical discharge is produced when one or both electrodes are covered with a dielectric. This arrangement provides a self-terminating discharge which is relatively independent of applied voltage waveshape. At gas pressures of order one atmosphere, gap spacings of order millimeters, and the application of alternating high voltage (e.g., 50 Hz to several kHz), a large number of "microdischarges", statistically spread in space and time over the electrode area, are created in the gas. Most evidence suggests that barrier discharges are generally described by a Townsend avalanche followed by a discharge streamer. The microdischarge streamers (cylindrical current filaments with typical radius of order 100 μm) are transient discharges (e.g.,

lasting only a few nanoseconds for oxygen or air), fed by ionization and detachment and then arrested when charge build-up on the dielectric reduces the electric field in the streamer to the point where electron attachment becomes dominant.

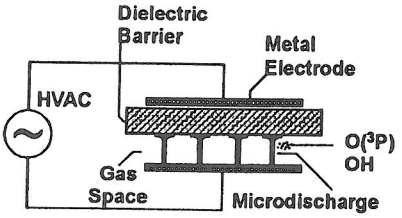

Fig. 1 Diagram of a single-dielectric-barrier discharge plasma reactor.

The barrier configuration was developed in 1857 by von Siemens, was named the silent discharge by Warburg who investigated it around the turn of the century, and has been widely used for the generation of ozone. Fig. 1 shows a single-barrier reactor schematic diagram. Corona discharges produce plasmas similar to barrier discharges but take advantage of their natural electric-field inhomogeneity to terminate the discharge, rather than charge buildup on a dielectric barrier.

Summary of Plasma Chemistry

In nonthermal plasmas, electrical energy is used to create large quantities of highly reactive free radicals (especially atomic oxygen, $O(^3P)$ and hydroxyls, OH) in a gaseous medium. At the relatively high reduced electric field E/N of an atmospheric-pressure barrier discharge, O-atoms and OH radicals are produced by reactions such as

$$e + O_2 \rightarrow O(^3P) + O(^1D) + e$$

$$O(^1D) + H_2O \rightarrow 2OH\,.$$

Radical yield estimates for example gas mixtures are given in Table 1 [1, 2].

Table 1
Estimated Radical Yields (per 100 eV) at E/N = 100 Td

Mixture	G[$O(^3P)$]	G[OH]
Ar/O_2 (80/20)	22.3	0.0
$Ar/O_2/H_2O$ (78/20/2)	18.2	7.5
N_2/O_2 (80/20)	6.8	0.0
$N_2/O_2/H_2O$ (78/20/2)	6.7	0.5

Complex molecules, like many VOCs, will often undergo a series of reactions before the final products result. The decomposition of a gas-phase chemical species (e.g., a chlorocarbon like TCE) is dominated by free-radical reactions at high E/N [3]:

$$O(^3P) \text{ or } OH + C_2HCl_3 \rightarrow CO_2 + HCl + Cl_2 + COCl_2 + ...$$

Fortunately, some commonly formed hazardous byproducts (like phosgene - $COCl_2$) are unstable and are quickly destroyed by reacting with liquid water or water vapor.

Strongly electron-attaching molecules, like CCl_4, are preferentially decomposed by dissociative attachment at low E/N. Electron-induced dissociation and radical attack dominate at high E/N. Unfortunately, Cl and ClO radicals resulting from O and OH reactions with CCl_4 drive circular kinetics which reforms CCl_4 at high E/N.

Typical Laboratory Equipment

Much of our past work at Los Alamos [1,2] has focused on the nonthermal plasma destruction of chlorocarbons (e.g., TCE - C_2HCl_3, TCA - $C_2H_3Cl_3$, PCE - C_2Cl_4, and CCl_4), using dielectric-barrier discharges. Most experiments have used rectangular planar reactor cells (in both single-barrier and double-barrier configurations), although cylindrical reactors (using metal and dielectric tubes) have also been used for some tests. At low temperatures (i.e., < 200 C), glass (e.g., Pyrex) is used for the dielectric barriers. For higher temperatures, we have considered ceramics, but these are harder to use and also have a larger dielectric-loss factor, which increases with increasing temperature.

A representative planar reactor has approximate dimensions of 71-cm length, 18-cm width, and 2.5-mm gap, giving a mean discharge area of 1236 cm^2 and an active discharge volume of 310 cm^3. In typical laboratory tests, the contaminant concentrations and individual-cell gas flows are a few ppm to a few 1000 ppm (by volume) and 10 - 20 std lit/min, respectively. Representative operating conditions (e.g., tests with TCE and CCl_4) are a flow rate Q of 10 std lit/min and average powers P of 20 to 200 W (average plasma energy densities of 0.12 to 1.2 J/cm^3). The average power per unit area can be as high as 0.5 W/cm^2. Reactors are usually driven by an electrical power supply coupled to a high voltage transformer. Two different types of power supplies have been employed: a variable-frequency, sinusoidal-waveform generator and amplifier or a series inverter which switches charged capacitors through a pulse transformer using high-power thyristors. Typical power ranges are from 500W to 3 KW for laboratory sinusoidal units and nearly 4 kW of power at repetition frequencies up to 4.5 kHz for our inverter. Fig. 2 shows a circuit diagram for a laboratory setup.

Electrical power deposited into the discharge plasma is measured with a high-voltage probe combined with a current-viewing resistor. Integration of a voltage-charge (Q-V) plot obtained from these instruments gives the power [4]. A standard commercial flow-meter is used to measure the gas flow.

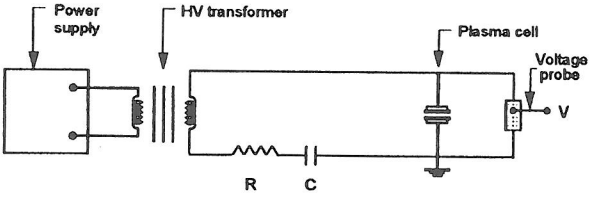

Fig. 2 Circuit schematic for typical laboratory dielectric-barrier discharge reactor.

The influent stream is usually humidified so that water will be available for the generation of OH radicals. Humidity (e.g., typical range of 1 to 3%) is supplied by bubbling the influent stream through a water contactor or by a vapor injector. In practical cases, water will normally be present in the influent. Effluent from the test reactor is distributed to a gas manifold for analysis by a gas chromatograph, which employs either a mass spectrometer or a flame ionization detector and an electron capture detector. An FTIR (Fourier Transform Infrared) spectrometer, $CO/CO_2/O_2$ detectors, a SO_2/NO_x analyzer, and a total hydrocarbon analyzer are also used for analysis and product identification.

Reactor Scaling

Removal Scaling Relationships: In many cases (when first-order chemistry dominates), the removal of a contaminant X can be described by an exponential function

$$[X] = [X]_0 \exp(-\bar{E}/\beta),$$

where [X] is the resulting concentration, $[X]_0$ is the initial concentration, $\bar{E}$ is the applied specific energy, and β is the e-fold energy density. Supplying one β of energy density to the reactor reduces the concentration by 1/e, two β's reduces it by $1/e^2$, and so on. β is given in base e units. In base ten units, the removal, $1 - ([X]/[X]_0)$, is often expressed in terms of a destruction and removal efficiency (DRE) of so many "nines"; e.g., three "nines" removal (or 99.9%) is achieved by supplying the reactor with three ten-fold $\bar{E}$'s. For base ten units, the exponential function is replaced by powers of ten and β by the ten-fold factor given by $\alpha = 2.303\ \beta$. In an ideal case, when $\bar{E}$ is plotted versus $-\ln([X]/[X]_0)$, a straight line of slope β results. Therefore, the β-value can be easily determined from data presented in such a removal plot. For real cases, the plot is not necessarily a straight line, so such a slope-determined β-value is only an approximation. Nevertheless, it is still quite useful over a limited range of e-folds. Table 2 gives example β-values for representative compounds.

System Architecture and Scaling: The key reactor scaling parameter is the specific energy $\bar{E}$ or, equivalently, the power per unit gas flow P/Q. To increase the gas flow and maintain a fixed destruction ratio $[X]/[X]_0$, the power must be increased in proportion to the flow rate. There are two basic system architectures for scaling up

the gas flow while keeping P/Q fixed: 1) Monolithic (using a single, physically-larger reactor and increasing the applied power P in proportion to the flow rate); 2) Modular (increasing the number of reactors, or cells. For N cells, each cell handles a flow of Q/N and receives a power P/N).

To increase the destruction ratio $[X]/[X]_0$ for a given gas mixture, $\bar{E}$ must be increased. $\bar{E}$ for an individual reactor can be increased by either increasing its power or decreasing its flow rate. We prefer the modular architecture whereby a cell of desirable properties is replicated many times and the total gas flow is divided among a bank of parallel-flow cells. Such modularization is commonly used for the industrial-scale synthesis of ozone, where municipal water treatment plants frequently require the on-site generation of thousands of kilograms per day. Our typical single cells are capable of flowing more than 100 std lit/min, but are limited in applied power to 500 - 1,000 W by the rate at which heat is removed (to prevent mechanical damage to dielectrics).

Table 2
Exponential-folding values β for example gas mixtures (straight-line removal plot approximations).

Gas Mixture	β-value (J/std lit)
TCE (C_2HCl_3) in Ar/O_2	12 (dry), 95 (humid)
CCl_4 in Ar/O_2	520 (dry), 1824 (humid)
TCA ($C_2H_3Cl_3$) in dry N_2	208 (at ≤ 4 e-folds)
Toluene ($C_6H_5CH_3$) in dry N_2	300
TCE in humid air/TCA/PCE (C_2Cl_4)	121
TCE/TCA/PCE in humid air	1500

Applications

Dielectric-barrier reactors can be used to treat stack-gas or flue-gas emissions (air streams), off-gases from incinerators or other primary treatment units, or industrial-process gas streams. Heterogeneous wastes (e.g., solvent-contaminated solids) can also be treated by applying heat to volatilize the solvents and then flushing with an inert gas (e.g., Ar or N_2). In this case, a closed-loop cycle can be employed so that reaction byproducts are further destroyed by the plasma unit or removed in a water contactor (for Cl_2 and $COCl_2$) and an acid-scrubber (for HCl). Another potential application is the treatment of solvents or other volatile chemicals in soil or groundwater. In this case, the plasma processor is coupled to a soil vapor extractor that pumps volatile compounds out of the soil through wells drilled in the ground. Fig. 3 is a conceptual drawing of field-demonstration, barrier-discharge equipment that was used for tests carried out to treat TCE (trichloroethylene), TCA (trichloroethane), and PCE (perchloroethylene) extracted from the ground at the U.S. Department of Energy Savannah River Site in 1993.

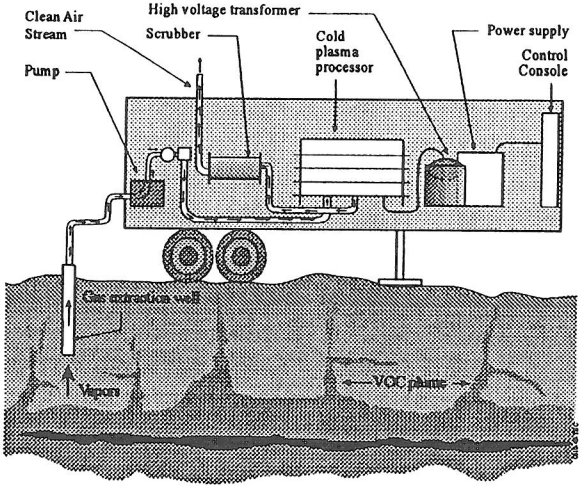

Fig. 3 Field-demonstration equipment for treating extracted solvent vapors with Los Alamos mobile barrier-discharge processor.

Summary

Many hazardous organic chemicals and the flue gas constituents SO_x and NO_x are readily attacked by the free radicals generated in barrier-discharge plasmas. We have briefly discussed basic plasma chemical reaction mechanisms and have presented experimental data and scaling relationships for the decomposition of representative compounds. In general, the degree of removal of a particular chemical species scales exponentially with the plasma energy density. The characteristic e-fold energy density depends on the specific pollutant and the carrier gas composition. More work is in progress at our laboratory to study the decomposition of a variety of compounds in different gas mixtures.

References

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