

Destruction of 1,1,1-trichloroethane (TCA) using Non-Thermal Plasma (NTP)

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ABSTRACT

This study utilizes empirical and numerical approaches to determine the feasibility of using non-thermal plasma (NTP) for destruction of 1,1,1-trichloroethane (TCA). In this research NTP was produced in a planar dielectric-barrier discharge (DBD) reactor through which TCA laden air streams were passed and effects of various operational parameters on the destruction removal efficiency (DRE) of TCA were determined. Experiments indicated that water vapor concentration had a great effect on TCA destruction and on overall carbon balance of the system. DRE as high as 99.9% could be achieved at very low relative humidity (RH) conditions. Analysis of CO/CO₂ concentrations in the reactor effluent indicated a decrease in the amount of CO generated with increasing RH with low CO/CO₂ ratio of 1:3 at 88% RH. Numerical analysis of experimental data was conducted to determine cost and energy requirements of the operation and, most importantly, to calculate a scale-up parameter, β for TCA destruction in a DBD reactor. The calculated β values ranged between 1478 to 3010 J/L for RH ranging from 0 to 88%.

INTRODUCTION

The 1990 Clean Air Act Amendments required the Environmental Protection Agency to mandate more stringent emission standards for 188 hazardous air pollutants (HAPs) that are associated with approximately 300 major source categories. Most of the listed HAPs are volatile organic compounds (VOCs) that are known for their adverse effects on human health and recalcitrant persistence in the atmosphere. HAPs need to be controlled according to maximum achievable control technology (MACT) standards. Conventional MACT for removing VOCs from air streams include adsorption, absorption, incineration and condensation processes. Depending on the source of contaminants, the concentrations of VOCs in the resulting gas streams may vary from very low values (tens of ppbv) to very high values (few percent by volume), which can render some of the control technologies ineffective for certain pollutant concentrations. In view of the constraints of

existing control technologies, it would be highly desirable to have a control technology capable of effectively and efficiently removing multiple gas-phase pollutants present in varying concentrations.

This research investigated the use of NTP for destruction of 1,1,1-trichloroethane (commonly known as methyl chloroform or TCA, $C_2H_3Cl_3$), a colorless, man-made chemical often found as a liquid in water and soil, and as a vapor in the air at hazardous waste sites. TCA is extensively used in dry cleaning operations. It is also used industrially for removing grease and oil from manufactured metal parts. In 1998, 167 facilities released 3.4×10^5 kg of TCA in the United States alone, of which nearly 96% was emitted into the atmosphere.¹ TCA is classified as a class C possible human carcinogen, and is known to have other health effects as well. It is considered to be a HAP, which means that its emissions from stationary sources must be monitored and controlled.

Non-Thermal Plasma

Non-thermal plasma (NTP) is a new concept of application of gas-phase oxidation processes that can destroy air pollutants. It is an extensively studied advanced oxidation technology (AOT) that envisions production of highly reactive gas-phase free radicals, such as $\cdot O(^3P)$ and $\cdot OH$ that can initiate and sustain a complex chemistry of pollutant destruction reactions. It is often produced by creating electrical discharges in a dielectric barrier electrode arrangement (commonly known as DBD or SDP reactor) and is referred to as a discharge occurring in an open space between two insulated electrodes connected to a source of high voltage alternating current. The geometry of such reactors is either planar or cylindrical with a configuration similar to that of a parallel-plate or a cylindrical capacitor, respectively. Usually, one or both metal electrodes are covered with a dielectric material (pyrex, quartz, ceramics etc.) that separates them from a thin gas layer. The presence of a dielectric splits the electrical discharges into numerous microdischarges of high instantaneous current and spatially distributes them over the discharge area and, hence, increases the homogeneity of NTP.

The use of NTP for pollutant destruction has been studied for over a decade now but it is still in its early stages of research and development. NTP is expected to work well for both high (> 1000 ppmv) and low (< 100 ppmv) concentrations of pollutants.² To date, much research has been focused on using NTP for destruction of NO_x and SO_x and some research has been performed in the area of hydrocarbons, chlorocarbons, and chlorofluorocarbon destruction.³⁻⁸ NTP is now known to offer several advantages for controlling HAPs emitted from various source categories.⁹

Plasma Chemistry and Modeling

Numerous reactions may take place in non-thermal plasma that can lead to the formation of active species capable of reacting with pollutant molecules.⁹ These species react with pollutant molecules, which can result in near complete oxidation of hydrocarbons into CO_2 and H_2O and conversion of species such as Cl, S and NO into HCl, Cl_2 , SO_2 , H_2SO_4

and HNO₃. Once the concentration of active species is high enough to initiate the destruction reaction, the pollutant concentration begins to decrease. The complete reaction chemistry is extremely complicated and has posed a great challenge for plasma modelers. Even for small molecules, the overall reaction mechanism can be very complex. Large molecules, on the other hand, are known to undergo a series of intricate intermediate reactions before completely destroying into common combustion products. However, it is known that at high electron temperatures, the decomposition of gas-phase hydrocarbons is dominated by gas-phase radicals, $\cdot\text{O}(^3\text{P})$ and $\cdot\text{OH}$.⁶



Due to the complexities of this mechanism for pollutant destruction in NTPs, much research still needs to be done in this area. Fortunately, it is not necessary to completely understand the mechanism of plasma destruction of pollutants to gain valuable information about the pollutant destruction process.

Recent research has shown that simplified kinetic models can be used to describe the rate of radical-initiated decomposition of the pollutant molecules in a DBD reactor. The first step in plasma modeling is the calculation of average power delivered to the plasma reactor, which can be obtained by using following relation.¹⁰

$$P = 4f C_d V_i [V_o - \frac{(C_d + C_g)}{C_d} V_i] \quad (1)$$

where f is the repetition frequency of the applied voltage in Hz, C_d and C_g are the dielectric and gas-gap capacitance, respectively, in Farads, and V_o and V_i are the peak applied voltages and gas discharge ignition voltage, respectively, in Volts. V_o is empirically measured across the discharge cell and V_i can be calculated by using following relation.¹¹

$$V_i = 24.4 (\rho d) + 6.53 (\rho d)^{1/2} \quad (2)$$

where V_i is in kV, ρ is the air density relative to 1013 mb pressure and 20 °C temperature, and d is the gap length in cm. The value of V_i can be affected by presence of water vapor in the gas, the effect of which can be incorporated accordingly.¹¹

The approach to obtain a simplified pollutant destruction model involves the calculation of a scale-up parameter β , which relates the destruction removal efficiency (DRE) with the power density (also called energy density, E_d), P/Q , where P is the power delivered to the reactor in watts and Q is the flowrate of gas in liters/second.¹² The knowledge of an approximate value of β can be used to determine the power requirements for a given DRE and flowrate of gas stream. The β (Joules/liter) parameter signifies a relationship between the radicals responsible for destruction of pollutant molecules and the scavengers of such radicals. In short, the β parameter provides an approximate picture of the important reaction chemistry in a NTP environment. For low DRE (lower than 95%) the relationship between DRE and power density can be expressed as

$$\frac{[X]}{[X_0]} = \exp\left(-\frac{P}{Q\beta}\right) \quad (3)$$

$$\beta = 1/G ([X]_o + \{ \sum_i k_{si} [S]_i \}/k) \quad (4)$$

where $[X]$ and $[X_0]$ are pollutant concentrations in the outlet and inlet streams in ppmv, respectively, P is the average power delivered to the plasma cell in Watts, Q is the flowrate of gas in liters/second, β is the scaling parameter for pollutant X in Joules/liter, G is the production efficiency of the radical species responsible for pollutant destruction, k is the radical-pollutant kinetic rate constant, $[S]_i$ is the concentration of i^{th} scavenger, and k_{si} is the scavenging rate constant for the i^{th} species.

The β parameter can be calculated by plotting P/Q vs. $-\ln [X]/[X_0]$ and fitting a straight line to the data points and passing the line through the origin. The slope of straight line of the P/Q vs. $-\ln [X]/[X_0]$ plot gives the value of β . Typical values for β parameters for some common pollutants calculated for a DBD reactor are shown in the Table 1.

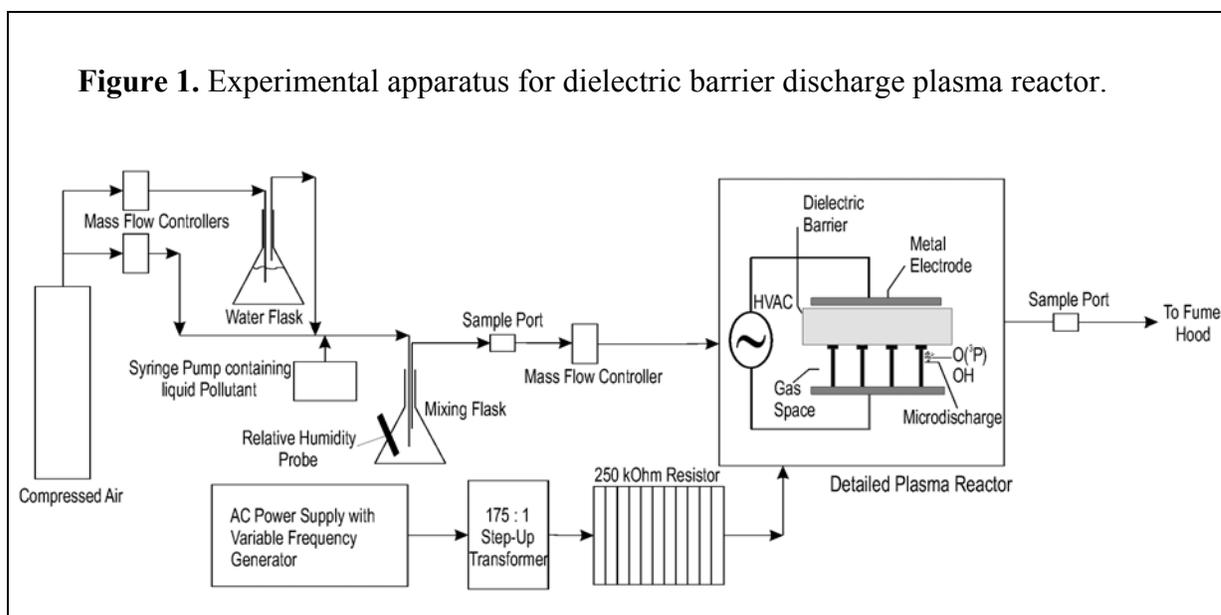
Table 1. Scale up Parameter, β for Various Compounds.

Compound	β (Joules/liter)	Source
Perchloroethylene, PCE	1500	12
NO _x	66	12
Trichloroethylene, TCE	33	13
Carbon Tetrachloride, CCl ₄	2500	13

EXPERIMENTATION

Planar dielectric barrier discharge reactor was constructed to investigate the destruction of TCA under various process conditions. The DBD schematic used in this study is presented in Figure 1.

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



The reactor consisted of two aluminum plates, each covered with a 3mm thick pyrex dielectric plate. Plasma was generated in the space between the two dielectric plates by applying high voltage across the two electrodes. Dimensional information for the reactor is presented in Table 2.

Table 2. Plasma reactor dimensions.

Parameter	Value
Gas gap spacing (H)	0.3 cm
Electrode width (W)	5.7 cm
Electrode length (L)	12 cm
Inlet Area	1.7 cm ²
Reactor volume	20.5 cm ³

The power supply system for the experiments consisted of a Compact Power Series AC Power System, a 175:1 step-up transformer, a 250 k Ω resistor, a high voltage probe, and an oscilloscope. The Compact Power Series AC Power System was connected to the domestic power supply and was used to deliver voltages that could be varied in the range of 0 to 130 VAC; the frequency could be varied between 45 to 15,000 Hz. The output of the system was connected to the 175:1 step-up transformer (Corona Magnetics), which could deliver maximum RMS voltages of about 23 kV_{rms}. The operating voltages for this configuration varied between 11.9 kV_{rms} to 19.7 kV_{rms}, and were measured with the Tektronix high voltage probe (Model P6015A) and a Tektronix oscilloscope (Model TDS 210). RMS voltage was calculated from the oscilloscope, assuming that the voltage waveform was a sine curve.

The gas generation system consisted of ultra-zero compressed air flowing over a syringe pump containing TCA. By adjusting the flow rate of the syringe pump and the total gas flow rate, different gas-phase TCA concentrations were achieved. In these experiments,

the gas residence time ranged from 1 to 6 seconds, and the TCA concentration varied from 500 to 1500 ppmv. Calibration standards from Matheson or MG Industries were used to calibrate the Varian gas chromatograph/ mass spectrometer (Model 3800 GC/2000 MS) for determining the influent and effluent TCA concentrations. The syringe pump was capable of producing steady gas-phase TCA concentrations over long time periods.

Variation in the inlet TCA concentration was measured to be within 2% of the calibration standard during the course of an experiment. All measurements of the effluent TCA concentrations were averaged over three measurements taken when the plasma reactor was at steady state. CO and CO₂ were measured with a Liston Scientific NDIR gas analyzer (Model Enviomax). As with the TCA measurements, average of three CO/CO₂ samples were taken at each voltage.

RESULTS AND DISCUSSION

Destruction of TCA in the DBD reactor was evaluated at several gas residence times, water vapor concentrations, and influent TCA concentrations (Table 3). Flow through the reactor was laminar at all conditions, with a maximum Reynolds number of 17. Under the reaction conditions, uniform plasma was developed between the two aluminum electrodes.

Table 3. Experimental conditions for DBD reactor.

Parameter	Value
Gas Temperature	293 K
Gas Pressure	0.85 atm
Gas Residence Time	1.2 seconds to 6.0 seconds
Gas Flowrate	0.2 to 1.0 L/min
Applied Voltage (RMS)	11.9 to 19.7 KV _{rms}
Applied Electrical Frequency	1000 Hz
Relative Humidity	0 to 88%
TCA Inlet Concentration	500 to 1500 ppmv
Reynolds Number	4 to 17

In general, as the applied voltage was increased from 11.9 to 19.7 kV_{rms} for any combination of other parameters, an increase in TCA destruction removal efficiency (DRE) was observed (Figure 2 to Figure 6). This trend was observed in all experiments conducted in this research. The DBD reactor was capable of destroying > 99.9% TCA in dry air at a residence time of 6 seconds (Figure 2). As the residence time was decreased from 6 seconds to 1 second, a decrease in DRE was observed and a higher voltage was needed to achieve higher removal efficiency (Figure 2 and Figure 3). Increasing the inlet TCA concentration from 500 to 1500 ppmv showed a decrease in the DRE (Figure 4), however, the effect of increasing water vapor content was more pronounced. Experimental results showed that DRE of TCA was greatly affected by the presence of water vapor in the gas mixture (Figure 5 and Figure 6). It is speculated that the DRE

decreases because the presence of water decreases the concentration of $\cdot\text{O}(\text{}^3\text{P})$, which is important for oxidation of TCA molecules. Electrons generated in a microdischarge often collide with O_2 to produce $\cdot\text{O}(\text{}^3\text{P})$ and $\cdot\text{O}(\text{}^1\text{D})$ --key oxidizing radicals for hydrocarbons (Equation 1). $\cdot\text{O}(\text{}^1\text{D})$ possesses higher energy and is a less stable species in comparison to $\cdot\text{O}(\text{}^3\text{P})$ and often converts to $\cdot\text{O}(\text{}^3\text{P})$ by losing excess energy with collisions with other species, and, hence, increases the final concentration of reactive $\cdot\text{O}(\text{}^3\text{P})$ available for destruction of TCA molecules (Equation 2). However, the presence of water molecules decreases the concentration of $\cdot\text{O}(\text{}^1\text{D})$ available for producing more $\cdot\text{O}(\text{}^3\text{P})$ by reacting with $\cdot\text{O}(\text{}^1\text{D})$ to produce $\cdot\text{OH}$ radicals (Equation 3), and, hence, decreases the concentration of $\cdot\text{O}(\text{}^3\text{P})$ that could have been available for oxidation of TCA molecules.

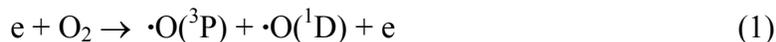


Figure 2. Effect of residence time on TCA destruction in 3 mm gap spacing DBD reactor. 500 ppmv, 1 kHz, 0% RH

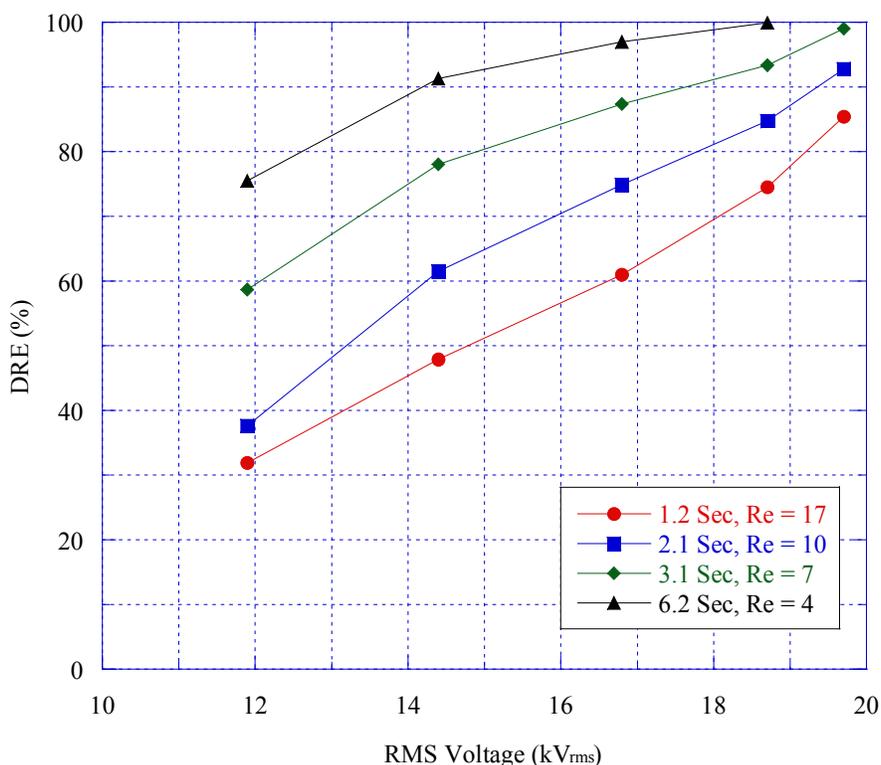


Figure 3. Effect of residence time on TCA destruction in 3 mm gap spacing DBD reactor. 1000 ppmv, 1kHz, 88% RH.

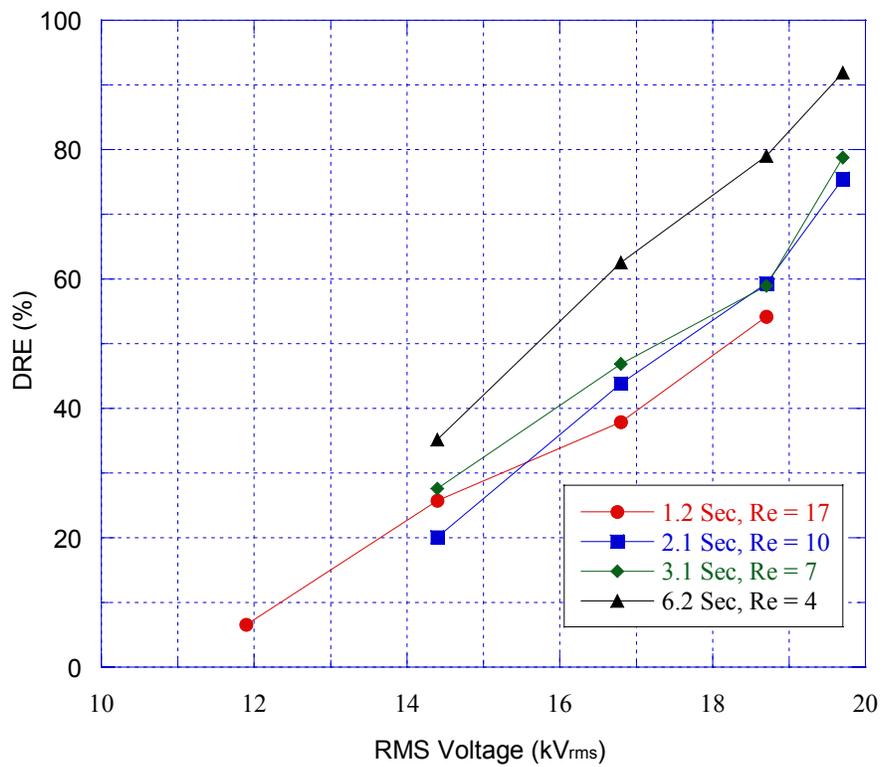


Figure 4. Effect of influent TCA concentration on TCA destruction in 3mm gap spacing DBD reactor. 0% RH, 1 kHz, $t_r = 3.1$ sec.

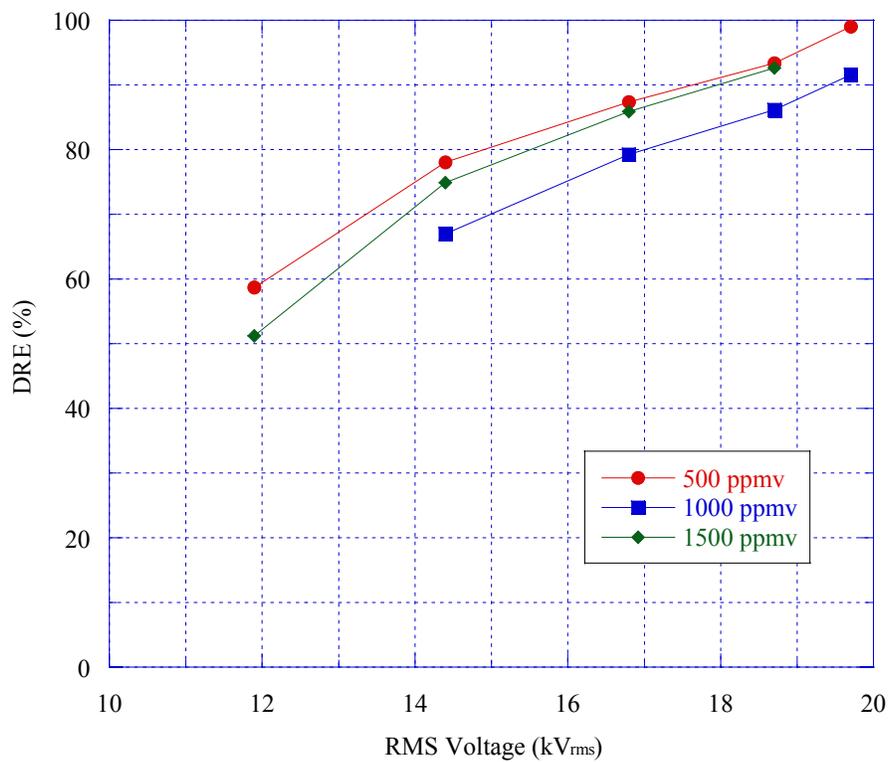


Figure 5. Effect of RH on TCA destruction in 3 mm gap spacing DBD reactor. 500 ppmv, 1 kHz, $t_r = 1.2$ sec.

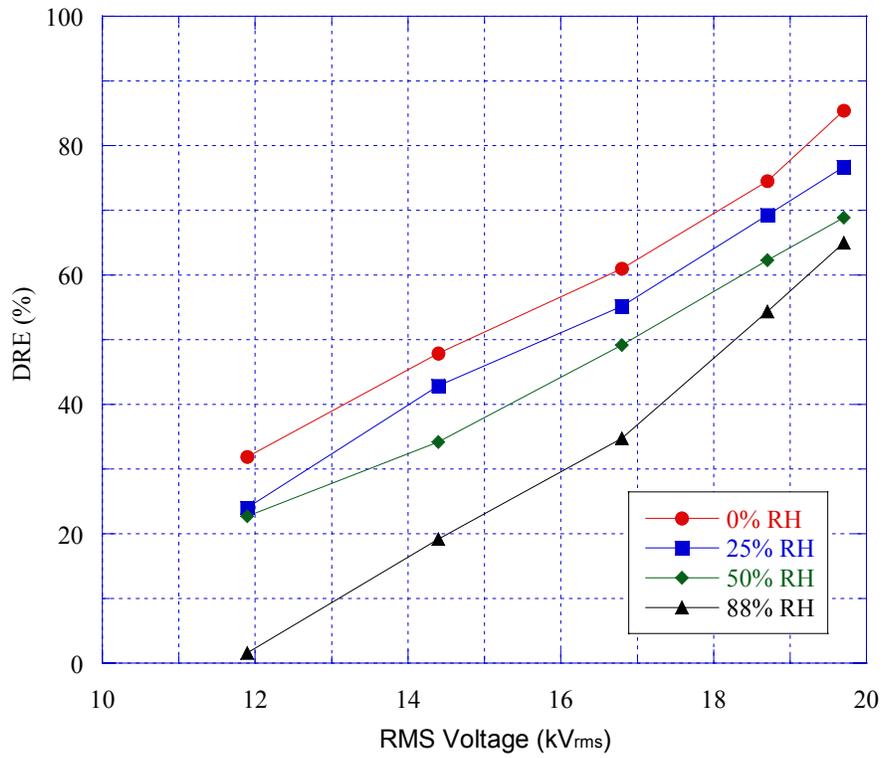
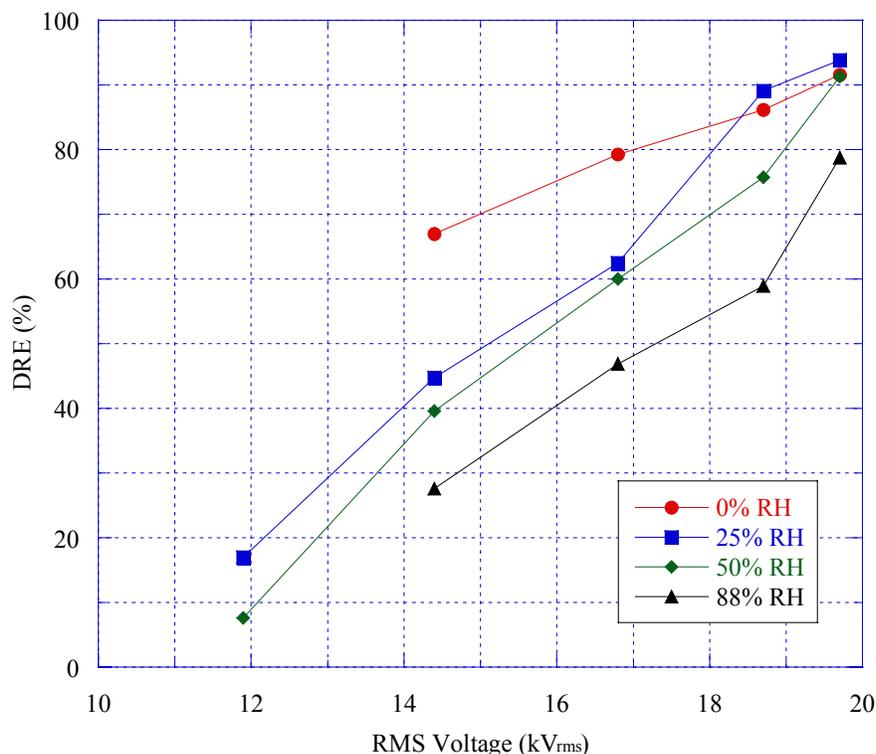
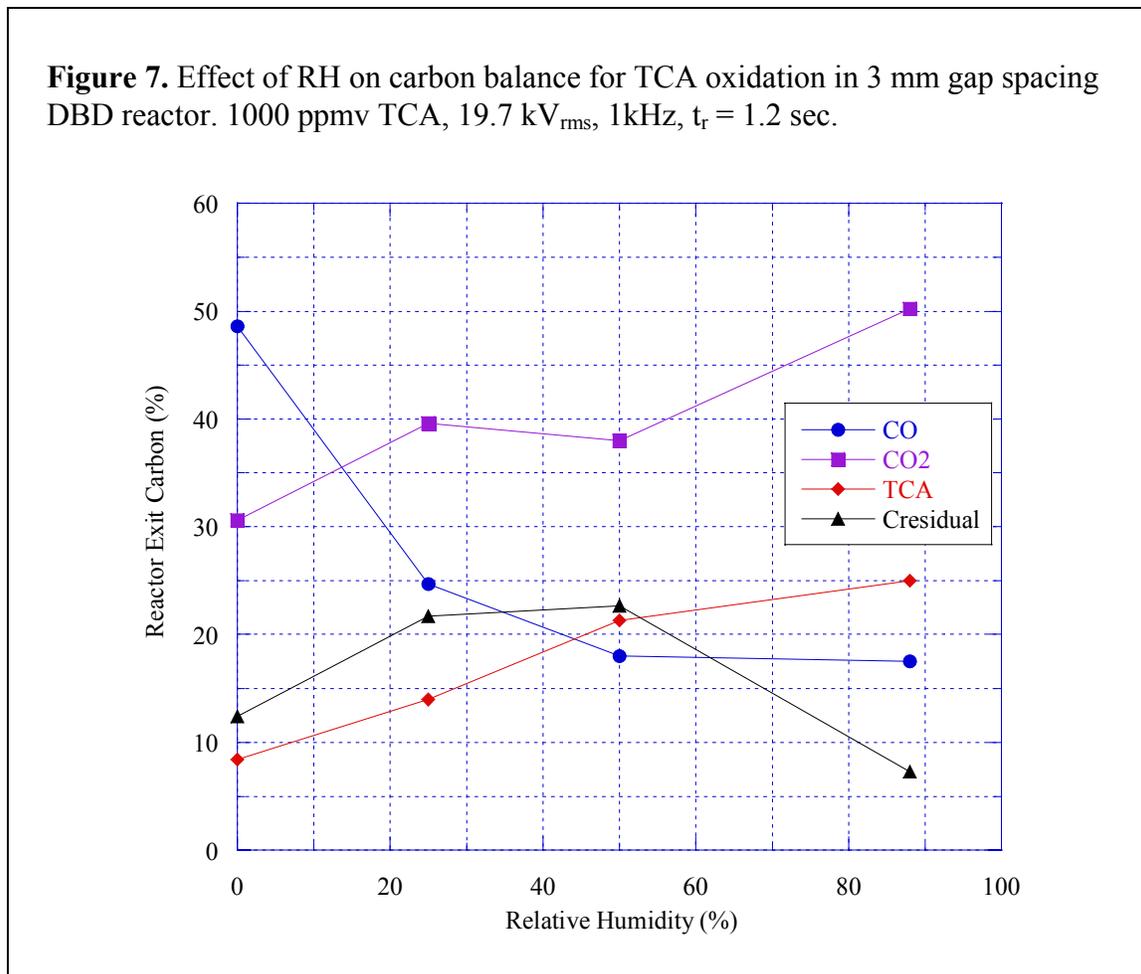


Figure 6. Effect of RH on TCA destruction in 3 mm gap spacing DBD reactor. 1000 ppmv, 1 kHz, $t_r = 3.1$ sec.



A carbon mass balance was measured for the products exiting and entering the plasma reactor during the oxidation of 1000 ppmv of TCA (Figure 7). Residual carbon (C_{residual}) was measured by subtracting the total measurable carbon present in exiting carbon species, TCA, CO and CO₂ from total inlet carbon in 1000 ppmv of TCA. The results indicate the effect of water vapor concentrations on distribution of carbon in TCA destruction products. It was noted that an increased RH, though decreases the DRE of TCA, decreases the CO/CO₂ ratio and also reduces the concentration of residual carbon. For varying applied voltages, the CO/CO₂ ratio decreased from approximately 3:2 to 1:3 for RH ranging from 0 to 88%, respectively. Therefore, much less CO was produced with water vapor being present in gas streams. Higher RH favored TCA destruction into CO and CO₂ as the major carbon species in reactor outlet. However, at lower RH conditions, mass balance revealed a substantial amount of carbon present as unaccountable residual carbon, which signifies incomplete oxidation of TCA. The percentage of carbon present as residual carbon steadily decreased to minimal values by increasing the RH. The presence of residual carbon can be explained by the possibility of many other carbon containing products present in very small concentrations that are typical for oxidation of hydrocarbons in NTP. This hypothesis was further supported by observation of few occasional peaks corresponding to COCl₂ in the GC/MS analysis of exit gases. However, an exact quantification of other carbon containing species was not feasible due to

experimental limitations and possibility of errors being introduced in measurement of CO and CO₂ concentrations. Therefore, an approximate carbon balance suggests that higher concentration of water vapor is beneficial for conversion of TCA into common combustion products, CO and CO₂.



Destruction of chlorocarbons in a DBD reactor is expected to generate chlorinated species such as HCl, Cl₂ and oxygenated-Cl compounds.⁷ Due to limitations of the experimental set up an exact quantification of chlorine distribution in DBD exit streams could not be carried out. However, a preliminary TCA incineration model coupled with HCl-Cl₂ equilibrium showed that at near ambient conditions most of the chlorine present in TCA would convert to Cl₂ (> 99.9 %). This implies that at present operating conditions 1000 ppmv of TCA is expected to produce approximately 1498 ppmv of Cl₂ and 4 ppmv of HCl. It is surmised that chlorinated species can be removed by passing the reactor exhaust through a water scrubber. The model did not take into account production of intermediate oxygenated-Cl species that can greatly contribute to the overall Cl balance and produce substantial amounts of oxygenated-Cl species such as COCl₂, COCl and ClO⁷ and, hence, indicates the need for a detailed reaction chemistry model for TCA destruction in a DBD reactor.

Numerical analysis of experimental data included calculation of specific energy density, cost of destruction of 1 kg of TCA in the system and calculation of scale-up parameter, β . The specific energy density, E_d was calculated as a function of applied voltage, RH and flowrate of gas. It was observed that keeping the applied voltage and flowrate constant, the presence of water in the gas stream slightly reduced (< 5% decrease at maximum RH) the energy density of the reactor. This happens because an increase in water content of gas increases the ignition voltage, V_i required for producing electrical sparks (Table 4), and hence, decreases the amount of actual power delivered to the reactor.

Table 4. Ignition voltages, V_i calculated as a function of RH.

V_i (kV)	RH (%)
8.98	0
9.23	25
9.38	50
9.49	88

Energy density calculations were used to calculate the cost of power required for destruction of 1 kg of TCA in the DBD reactor (Figure 8) and the DBD reactor scale-up parameter, β for TCA destruction (Figure 9). Cost calculations indicated the importance of RH, inlet TCA concentration and flowrate of gas streams. Most cost effective operation was achieved for low RH, high inlet TCA concentrations and low residence times. β calculations were performed for each experimental run using relation (3). Statistically correlated β values were averaged for 0, 25, 50 and 88% RH conditions. β ranged between 1478 to 3010 J/L for RH ranging from 0 to 88%. The values also showed a positive linear dependence of β on RH.

$$\beta = 1478.5 + 17.416*(\%RH) \quad (5)$$

An increase in the value of β with increasing RH indicates that in order to achieve an equivalent DRE for TCA in a DBD reactor, humid conditions will require more energy per unit volume of gas processed than that required in dry conditions. The dependence of β on the RH of the inlet gas mixture can be explained using relation (4). As explained earlier, $\cdot\text{O}(\text{}^3\text{P})$ is the main radical species responsible for TCA destruction, and H_2O is the main species accounted for a lower destruction of TCA with increasing RH conditions. This implies that the H_2O molecules or some other species generated from H_2O molecules, can be considered as the major scavengers of $\cdot\text{O}(\text{}^3\text{P})$. When RH increases, the concentration of H_2O molecules increases which leads to a concomitant increase in the concentration of other scavenging species as well. Mathematically, this implies that an increase in the amount of water vapor in the gas mixture, increases the numerical value of $\{\sum_i k_{si} [\text{S}]_i\}$ in relation (4), which is an expression for overall reactivity of scavenger species. Hence, the value of β increases with increasing RH. In short, it can be suggested that since the value of β parameter indicates the amount of energy required for TCA destruction in a DBD reactor, an increase in water concentration in inlet gas mixture reduces the DRE, which increases the amount of energy required to achieve the same DRE, and, hence, increases the value of β parameter for increasing water concentrations.

Figure 8. Electrical energy cost for TCA destruction with respect to energy density in a DBD reactor. Flowrate = 1 liter/minute, TCA concentration = 500 to 1500 ppmv, Relative humidity = 0 to 88%.

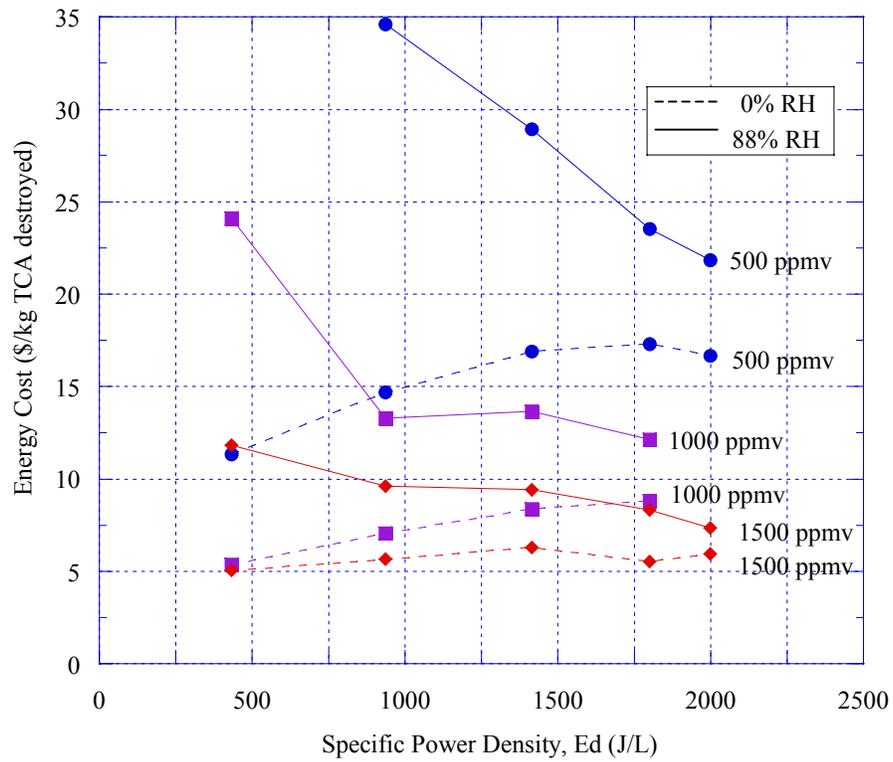
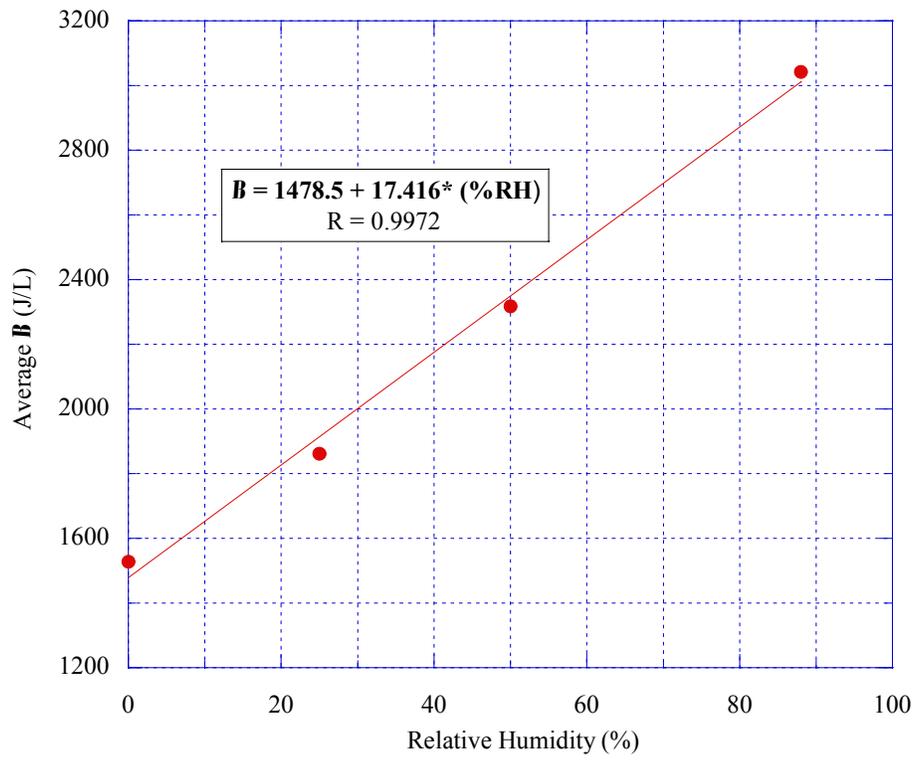


Figure 9. β parameter calculated for TCA destruction in DBD reactor.



CONCLUSIONS

These experiments conclude that NTP generated in a DBD reactor was capable of destroying high air borne TCA concentrations with a DRE of higher than 99%. The destruction of TCA molecules produced less harmful products such as CO, CO₂, H₂O, and HCl and Cl₂, which suggests that TCA destruction in a DBD reactor generates products that are similar to those formed by incineration of TCA.

The experiments indicated that concentration of water vapor present in gas streams is an important parameter for TCA destruction in a DBD reactor. Although high concentration of water can substantially reduce the TCA destruction efficiency, it is, in fact, beneficial for complete oxidation of TCA and lower CO/CO₂ concentration ratio in the reactor outlet.

The scale-up parameter, β , for TCA destruction in a DBD reactor was numerically calculated. It was observed that the value of β for TCA was a linear function of RH of the gas mixture, and it ranged between 1478 and 3010 J/L for RH ranging between 0 to 88%, respectively. Since the value of β is an indicator of amount of energy required for TCA destruction, it was surmised that an increase in the value of β with increasing RH was due to lower DRE at higher RH conditions. β is an important parameter for evaluating the feasibility for scale-up of the system. For example, it is estimated that in order to achieve 90% DRE from an air stream containing 500 ppmv of TCA at 60% RH conditions and flowing at 100 liters per minute in ambient conditions of Socorro, NM; 9.68 kW of power will be required. This power can be achieved by applying 12.5 kV_{rms} to a DBD reactor of 9.6 m² area (1000 times bigger than experimental reactor) and 3mm gap spacing between pyrex glass plates, and it will take nearly 80 hours of continuous DBD reactor operation and an electrical power worth \$ 46 to destroy 1 kg of TCA at such operating conditions.

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