Abstract: This study investigates the feasibility of using nonthermal plasma produced in a dielectric barrier discharge reactor to destroy 1,1,1-trichloroethane (TCA) in a stream of air. The effects of various operating parameters on the destruction and removal efficiency (DRE) of TCA were examined. The experiments indicated that the water vapor concentration greatly influenced the destruction of TCA and the relative amount of oxidation by-products. DRE as high as 99.9% could be achieved at very low relative humidity (RH) conditions. Analysis of the CO/CO\(_2\) concentrations in the reactor effluent indicated a decrease in the amount of CO generated as the RH was increased. The lowest CO/CO\(_2\) ratio, 1:3, was observed at 88% RH. The estimated cost and energy requirement for operation were also determined. The calculated energy density values (\(\beta\)) varied with respect to the RH, and ranged from 1,478 to 3,010 J/L over a RH range of 0–88%.

DOI: 10.1061/(ASCE)0733-9372(2004)130:3(349)

CE Database subject headings: Emission standards; Air pollution; Volatile organic chemicals; Research; Pollutants.

Introduction

The 1990 Clean Air Act Amendment allowed the Environmental Protection Agency (EPA) to mandate more stringent emission standards for 188 hazardous air pollutants (HAPs) associated with approximately 300 major categories of sources. Most of the HAPs listed are volatile organic compounds (VOCs) that are known to have adverse effects on human health and to persist in the atmosphere. HAPs must be controlled according to maximum achievable control technology (MACT) standards. Conventional pollution control technologies used to remove VOCs from industrial gas streams include adsorption, absorption, incineration, and condensation processes. Depending on the source of the contaminants, pollutant concentrations in the resulting gas streams may vary from tens of ppbv to a few percent by volume. This large range of pollutant concentrations in industrial gas streams can render some control technologies ineffective or impractical (Chang and Lee 1995). Because of limitations in existing control technologies, much current research has been directed towards developing technologies capable of effectively and efficiently removing multiple gas-phase pollutants present at a variety of concentrations.

In this research we investigate the use of nonthermal plasma (NTP) generated in a dielectric barrier discharge (DBD) reactor to destroy 1,1,1-trichloroethane (TCA) (also referred to as methyl chloroform and C\(_2\)H\(_3\)Cl). TCA is a colorless manufactured chemical that is often found as a liquid contaminant in soil and water, and is present as vapor at hazardous waste sites. The two largest sources of TCA pollution in the United States are dry cleaning operations and metal degreasing. In 1998, 167 facilities released 3.4\times10^5 kg of TCA in the United States, of which nearly 96% was emitted into the atmosphere (NSC 2001). TCA is a class C contaminant—a possible human carcinogen—and is known to have other adverse health effects. It is considered a HAP and, as such, its emission from stationary sources must be monitored and controlled to make certain that it does not exceed the mandated threshold emission rate.

Nonthermal Plasma

Plasma is a gaseous state of matter in which molecules or atoms are broken apart and form ions. Nonthermal plasma is characterized by conditions in which plasma species are not in thermal equilibrium. In nonthermal plasma, electrons, ions, and neutral species have different temperatures and kinetic energies, with the electrons having the highest temperature due to their small mass. The electrons in nonthermal plasmas are chemically very energetic (1–10 eV), allowing them to create free radicals [O(\(^1D\)), O(\(^3P\)), OH-, and H-] form gas-phase species, such as H\(_2\)O and O\(_2\). These free radicals can then be used to destroy pollutants.

The term “silent discharge plasma” (SDP) refers to a type of electrical discharge that occurs in an open space between two insulated electrodes connected to a source of high voltage alternating current. Such discharges are commonly created in a dielectric barrier electrode arrangement in which one or both metal electrodes are usually covered with materials with a high dielectric constant (Pyrex, quartz, ceramics, etc.). The electrodes are separated from one another by a thin gas layer. The dielectric material may also be placed between the electrodes to separate two gas layers. The geometry is commonly either planar or cylindrical. The electrical discharge consists of a large number of microdischarges of short duration but with high instantaneous
current. The dielectric barrier configuration provides a self-terminating electrical discharge, which is relatively independent of the drive voltage wave shape. Without the barrier and at gas pressures of about 1 atm., and a gap of a few millimeters, only a few localized intense arcs would develop in the gas between the metal electrodes. With a dielectric between the electrodes and at voltages between about 8 and 30 kV at frequencies between 50 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 nonthermal plasma, which is characterized by energetic electrons capable of generating highly reactive free radicals in the gas.

Although the use of NTP for pollutant destruction has been studied for over a decade, many areas for research and development still remain. NTP is known to offer several advantages for controlling HAPs emitted from various categories of sources (Cal and Schluep 2001). It is expected to work well for both high (>1,000 ppmv) and low (<100 ppmv) concentrations of pollutants (Nunez et al. 1993). To date, much research has been focused on using NTP for the destruction of NOx and SO2 (Chang et al. 1993) and some research has been performed for the destruction of hydrocarbons (Chang and Lee 1995); chlorocarbons, and chlorofluorocarbons (McCulla et al. 1991; Rosocha 1991; Evans et al. 1993; Rosocha et al. 1993; Chang and Lee 1995; Snyder and Anderson 1998).

**Plasma Chemistry**

Hundreds of reactions can take place in a NTP that can lead to the formation of species capable of reacting with pollutant molecules (Cal and Schluep 2001). These species can react with target molecules, and result in nearly complete oxidation of hydrocarbons into CO2 and H2O, and conversion of species such as Cl, S, and NO into HCl, H2SO4, and HNO3. The complete reaction chemistry is extremely complex, and modeling the chemistry of plasmas presents a great challenge to researchers. Even small molecules present in simple gas mixtures can exhibit complex overall chemical reaction mechanisms. Large molecules are known to undergo a series of complex intermediate reactions before being completely converted into simple oxidation products.

Even though pollutant destruction in NTP can be very complex, and much research still remains to be done in this area, it is not necessary to completely understand the mechanism of plasma destruction of pollutants in order to gain valuable information about the pollutant destruction process. At relatively high electron temperatures, the decomposition of gas-phase hydrocarbons is mainly dominated by gas-phase radicals, ·O(3P) and ·OH in addition to direct electron impacts (Snyder and Anderson 1998):

\[ C_2H_5Cl_3 + ·O(3P) \rightarrow CO + CO_2 + H_2O + HCl + Cl_2 + COCl_2 + \ldots \]

**Effect of Energy Density on Pollutant Destruction**

Previous research has shown that simplified chemical kinetic models can be used to describe the rate of radical-initiated decomposition of pollutant molecules in a DBD reactor. The first step in plasma modeling is calculation of the average power delivered to the plasma reactor, which can be obtained using the following relationship developed by Manley (1943):

\[ P = 4 f C_d V_i V_o \left( \frac{C_d + C_e}{C_d} \right) V_i \]

where \( P = \) power in W; \( f = \) repetition frequency of voltage applied in Hz; \( C_d \) and \( C_e \) = dielectric and gas–gas capacitance, respectively, in F; and \( V_o \) and \( V_i \) = peak applied voltage and gas discharge ignition voltage, respectively, in V. \( V_o \) is empirically measured across the discharge cell and \( V_i \) can be calculated using the following relation for dry air (Meek and Craggs 1953):

\[ V_i = 24.2(p d) + 6.53(p d)^{1/2} \]

where \( V_i \) is in kV; \( p = \) density of air relative to its density at 1,013 mbar pressure and 20°C temperature; and \( d = \) gap length in cm. The value of \( V_i \) can be affected by the presence of water vapor in the gas, the effect of which can also be incorporated accordingly (Meek and Craggs 1953).

The approach for obtaining a simplified pollutant destruction model involves calculation of a scaling parameter (\( \beta \)) which relates the destruction removal efficiency (DRE) with the power density (related to energy density, \( E_d \)), \( P/Q \), where \( P = \) power delivered to the reactor in W and \( Q = \) flow rate of gas in L/s (Rosocha and Korzekwa 1999a,b). Knowledge of an approximate value of \( \beta (J/L) \) can be used to determine the power requirements for a given DRE and flow rate of the gas stream. The \( \beta \) parameter signifies a relationship between the radicals responsible for destruction of pollutant molecules and scavengers of such radicals and, hence, provides an approximate picture of the important reaction chemistry in a NTP environment. For DRE less than 95% the relationship between DRE and power density can be expressed as

\[ \frac{[X]}{[X_o]} = \exp \left( - \frac{P}{Q \beta} \right) \]

\[ \beta = \frac{1}{G} \left( [X_o] + \frac{\{S_i k_i [S_i]\}}{k} \right) \]

where \([X]\) and \([X_o]\) = pollutant concentrations in outlet and inlet streams in ppmv, respectively; \( P = \) average power delivered to the plasma cell in W; \( Q = \) flow rate of gas in L/s; \( \beta = \) scaling parameter for pollutant \( X \) expressed in terms of J/L; \( G = \) production efficiency of the radical species responsible for pollutant destruction; \( k = \) radical-pollutant kinetic rate constant; \( [S_i] = \) concentration of the \( i \)-th scavenger; and \( k_{s_i} = \) scavenging rate constant for the \( i \)-th species.

The \( \beta \) parameter is calculated by plotting \( E_d \) versus \( \ln[X]/[X_o] \), fitting a straight line to the data points, and passing a line through the origin. The slope of the line of the \( E_d = P/Q \) versus \( \ln[X]/[X_o] \) plot determines the value of \( \beta \). Typical \( \beta \) parameters from some previous studies of pollutant destruction in a nonthermal SDP reactor are shown in Table 1.

**Experimental Procedure**

A planar DBD reactor was constructed to investigate the destruction of TCA under various process conditions (Fig. 1). The reactor

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \beta ) (J/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx</td>
<td>66</td>
<td>Rosocha and Korzekwa (1999a)</td>
</tr>
<tr>
<td>PCE</td>
<td>1,500</td>
<td>Rosocha and Korzekwa (1999a)</td>
</tr>
<tr>
<td>TCE</td>
<td>33</td>
<td>Coogan and Jassal (1997)</td>
</tr>
<tr>
<td>CCl4</td>
<td>2,500</td>
<td>Coogan and Jassal (1997)</td>
</tr>
</tbody>
</table>

where \( P = \) power in W; \( f = \) repetition frequency of voltage applied in Hz; \( C_d \) and \( C_e \) = dielectric and gas–gas capacitance, respectively, in F; and \( V_o \) and \( V_i \) = peak applied voltage and gas discharge ignition voltage, respectively, in V. \( V_o \) is empirically measured across the discharge cell and \( V_i \) can be calculated using the following relation for dry air (Meek and Craggs 1953):

\[ V_i = 24.2(p d) + 6.53(p d)^{1/2} \]
consisted of two aluminum plates each covered with a 3-mm thick Pyrex glass dielectric plate. Plasma was generated in the space between the two dielectric plates by applying high voltage across the two electrodes. Information on the dimensions of the reactor is presented in Table 2. The power supply system for the experiments consisted of a compact power series ac power system (model MAC-01HSH), a 175:1 step-up transformer (Corona Magnetics), a 250-kΩ resistor, a high voltage probe (Tektronix model P6015A), and an oscilloscope (Tektronix model TDS 210). The compact power series ac power system was used to deliver voltages that could be varied in the range of 0–130 VAC; the frequency could be varied between 45 and 15,000 Hz. The output of the system was connected to 175:1 step-up transformer, which could deliver maximum root mean square (RMS) voltages of about 23 kV RMS. At an operating electrical frequency of 1 kHz, the operating voltages for this configuration varied between 11.9 and 19.7 kV RMS, and were measured using a high voltage probe and an oscilloscope. RMS voltage was calculated from the oscilloscope, assuming that the voltage waveform was a sine wave.

The gas generation system consisted of ultrazero compressed air flowing over a syringe pump containing TCA. The syringe pump was capable of producing steady gas-phase TCA concentrations over a long period of time. 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 in the DBD reactor ranged from 1 to 6 s, and the TCA concentration varied from 500 to 1,500 ppmv. TCA gas concentrations were averaged over three measurements taken when the plasma reactor was at steady state. CO and CO2 were measured at the reactor outlet with a Liston Scientific non-destructive infrared (NDIR) gas analyzer (model Enviomax). As with the TCA measurements, three CO/CO2 samples were taken at each voltage and were then averaged.

### 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 under all conditions with a maximum Reynolds number of 17. Under these operating conditions, fairly uniform plasma was developed between the two aluminum electrodes.

In general, as the applied voltage was increased from 11.9 to 19.7 kV RMS, nearly linear correlation with TCA DRE was observed until complete destruction was achieved [Figs. 2(a)–4(b)]. The DBD reactor was capable of destroying more than 99.9% of the TCA in dry air at a residence time of 6 s [Fig. 2(a)]. As the residence time decreased from 6 to 1 s, a decrease in DRE was observed and higher voltage was needed to achieve a higher degree of destruction [Figs. 2(a and b)]. Increasing the inlet TCA concentration from 500 to 1,500 ppmv also decreased the DRE (Fig. 3). However, the effect of an increase in water vapor content on the DRE of TCA was more pronounced. DRE was greatly reduced by water vapor being present in the gas mixture [Figs. 4(a and b)]. The detrimental effect of the presence of water vapor on trichloroethylene (TCE) destruction has also been noted by Futamura et al. (2002).

### Table 3. Experimental Conditions for Dielectric Barrier Discharge Reactor Operation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas temperature (reactor inlet)</td>
<td>293 K</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>0.85 atm</td>
</tr>
<tr>
<td>Gas residence time</td>
<td>1.2–6.0 s</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>0.2–1.0 L/min</td>
</tr>
<tr>
<td>Voltage applied (RMS)</td>
<td>11.9–19.7 kV RMS</td>
</tr>
<tr>
<td>Electrical frequency applied</td>
<td>1,000 Hz</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>0–88%</td>
</tr>
<tr>
<td>TCA inlet concentration</td>
<td>500–1,500 ppmv</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>4–17</td>
</tr>
</tbody>
</table>

Note: RMS=root mean square; TCA=1,1,1-trichloroethane
The decrease in DRE with an increase in RH could be the result of a combined effect of a reduction in charge transferred from electrical discharges and a decrease in the concentration of important oxidizing radicals, such as \( \cdot O(3P) \) and \( \cdot O(1D) \). In double dielectric barrier discharge arrangements, such as the one used in this study, the presence of water vapor is known to reduce the total charge transferred in a microdischarge. This means that increasing the water vapor concentration could reduce the possibility of destruction of TCA molecules by direct electron impact, which could be one of the reasons for the observed effects. Additionally, electrons generated in a microdischarge often collide with \( O_2 \) and \( H_2O \) in the gas mixture and produce \( \cdot O(3P) \), \( \cdot O(1D) \), and \( \cdot OH \), which are key radicals for oxidation of hydrocarbons. \( \cdot O(1D) \) possesses higher energy and is less stable than \( \cdot O(3P) \). It often converts to \( \cdot O(3P) \) by losing excess energy upon collisions with other species, and, hence, increases the overall concentration of \( \cdot O(3P) \). However, the presence of water molecules decreases the concentration of \( \cdot O(1D) \) available that could be used to produce additional \( \cdot O(3P) \) by consuming \( \cdot O(1D) \) and producing \( \cdot OH \) radicals. Therefore this mechanism could result in a decrease of the concentration of \( \cdot O(3P) \) that would be available to oxidize TCA molecules. However, this explanation is most likely incomplete, since overall TCA destruction is expected to depend on a number of factors, such as the concentration of electrons and free radicals and electron impact and radical–radical rate coefficients.

\[
e + O_2 \rightarrow \cdot O(3P) + \cdot O(1D) + e \tag{5}
\]

\[
\cdot O(1D) + M \rightarrow \cdot O(3P) + M \tag{6}
\]

\[
H_2O + \cdot O(1D) \rightarrow \cdot OH + \cdot OH \tag{7}
\]

In addition to experiments conducted to determine the dependence of TCA DRE on reactor operating parameters, additional experiments were conducted to evaluate the distribution of carbon in the reactor effluent gas stream. A carbon mass balance was measured for products exiting and entering the plasma reactor during the oxidation of 1,000 ppmv of TCA (Fig. 5). Residual carbon \( (C_{\text{residual}}) \) was measured by subtracting the total measurable carbon present in exiting carbon species, such as unconverted TCA, CO, and CO\(_2\), from the total amount of inlet carbon present in 1,000 ppmv of TCA. The results indicate the effect of water vapor concentrations on the distribution of carbon in TCA destruction products. At higher RH, which results in a decrease in the TCA DRE, the CO/CO\(_2\) ratio decreases, as does the concentration of residual carbon. For varying voltages applied, the CO/CO\(_2\) ratio decreased from approximately 3:2 to 1:3 for RH increasing from 0 to 88%, respectively. Therefore, much less CO was produced when water vapor was present in the gas streams. Higher RH favored TCA destruction into CO and CO\(_2\), the major carbon species in the reactor outlet. However, at intermediate RH conditions, the mass balance revealed a substantial amount of carbon present as residual carbon, which signifies incomplete oxidation of TCA. Increasing the RH values above 50% steadily decreased the percentage of residual carbon to minimal values. The presence of residual carbon may be explained by the fact that many other carbon-containing products could be present in small quantities.
concentrations, which is typical for oxidation of hydrocarbons in NTP. This hypothesis is further supported by the appearance of a few occasional peaks that correspond to COCl₂ in the GC/MS analysis of exit gases. Exact quantification of the other carbon-containing species in the reactor effluent was not possible due to the lack of calibration standards for the trace by-products. An approximate carbon balance suggests that a higher concentration of water vapor is beneficial for conversion of TCA into the common oxidation products, CO and CO₂, while minimizing the CO/CO₂ concentration ratio.

Destruction of chlorocarbons in a DBD reactor is expected to produce chlorinated species such as HCl, Cl₂, and oxygenated-Cl compounds (Evans et al. 1993). Due to limitations in the analytical measurement capabilities, exact quantification of the chlorine distribution in the DBD exit streams could not be completed. However, a preliminary TCA thermal oxidation model coupled with HCl–Cl₂ equilibrium showed that at near ambient conditions most of the chlorine present in TCA would convert into Cl₂ (>99.9% of inlet chlorine). This implies that at the present operating conditions, 1,000 ppmv of TCA is expected to produce approximately 1,498 ppmv of Cl₂ and 4 ppmv of HCl. Chlorinated species may be removed by venting the reactor exhaust into a water scrubber. The model did not take into account the production of intermediate oxygenated-Cl species that can greatly contribute to the overall Cl balance and could produce substantial amounts of species such as COCl₂, COCl, and ClO (Evans et al. 1993) 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 the specific energy density ($E_d$), the cost of destruction of 1 kg of TCA in the system, and calculation of the scaling parameter ($\beta$). $E_d$ was calculated as a function of the voltage applied, total reactor gas flow rate, and RH. It was observed that increasing the RH while maintaining a constant applied voltage and gas flow rate slightly reduced ($<5\%$ decrease at maximum RH) the energy density of the reactor. This occurs because an increase in the water content of the air stream reduces the number of microdischarges (Falkenstein and Coogan 1997), thereby increasing the ignition voltage ($V_i$) required to produce electrical sparks (Table 4) and, hence, decreases the amount of actual power delivered to the reactor. Power and energy density calculations were used to calculate the cost of power required for destruction of 1 kg of TCA in the DBD reactor (Fig. 6) and the DBD reactor scaling parameter ($\beta$) for TCA destruction [Figs. 7(a and b) and 8].

Table 4. Ignition Voltages ($V_i$) Calculated as a Function of Relative Humidity

<table>
<thead>
<tr>
<th>Relative humidity (%)</th>
<th>$V_i$ (kV RMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.98</td>
</tr>
<tr>
<td>25</td>
<td>9.23</td>
</tr>
<tr>
<td>50</td>
<td>9.38</td>
</tr>
<tr>
<td>88</td>
<td>9.49</td>
</tr>
</tbody>
</table>
The cost of the power required to operate the DBD reactor was calculated, with a unit electricity cost estimated at $0.06/kWh. The cost calculations showed insight into the economic effects of varying the RH, inlet TCA concentration, and gas residence time. The most cost-effective destruction of TCA was achieved at low RH, high inlet TCA concentrations, and short residence times. β was calculated for each experimental run using the procedure described in Experimental Procedure. While the dependence of TCA destruction on the specific energy density at varying RH is very complex, it is common practice to approximate this dependence using a straight fitted line [Figs. 7(a and b)] (Rosocha 1994). Statistically correlated β values (0.83 < R² < 0.99) were averaged for 0, 25, 50, and 88% RH conditions [Figs. 7(a and b)] for approximately 36 experimental runs at varying operating conditions. The β values calculated for TCA destruction ranged between 1,480 and 3,010 J/L for RH ranging from 0 to 88% and indicated a linear dependence of β on the RH [Fig. 8 and Eq. (8)].

$$\beta = 1,480 + 17.4(\% \text{RH}) \quad (8)$$

The decrease in TCA destruction with an increase in RH illustrates that a higher applied energy density (β) would be required to achieve the same TCA destruction at high RH. This conclusion is consistent with experimental observations [Figs. 4(a and b)]. The dependence of β on the RH of the inlet gas mixture can be explained using relation (4). If $\cdot$ O($^3$P) is assumed to be the main radical species responsible for TCA destruction, and H₂O is assumed to be the main species that accounts for lower destruction of TCA, then this implies that the H₂O molecules, or some other species generated from H₂O molecules, can be considered the major scavengers of $\cdot$ O($^3$P). When the RH increases, the concentration of H₂O molecules increases, which leads to an increase in the value of $[S_r]$ in relation (4), which increases the value of β.

**Conclusions**

In this research we concluded that nonthermal plasma produced in a dielectric barrier discharge reactor was capable of destroying TCA. The electrical energy cost for 1,1,1-trichloroethane (TCA) destruction with respect to energy density in dielectric barrier discharge reactor: [TCA] = 500–1,500 ppmv, RH = 0–88%, Q = 1 L/min; Unit electricity cost = $0.06 kWh (RH=relative humidity).
gas-phase TCA concentrations in the 500–1,500 ppmv range, with destruction efficiency of up to nearly 100%, depending on the reactor operating conditions. The destruction of TCA molecules produced oxidation products, such as CO, CO₂, H₂O, and Cl₂. The concentration of water vapor present in gas streams was determined to be an important factor for TCA destruction in a DBD reactor. While a high concentration of water vapor was shown to substantially reduce the TCA destruction efficiency, it also decreased the CO concentration at the reactor effluent. Since both TCA and CO are regulated air pollutants, optimization of the TCA plasma oxidation process warrants further study. The scaling energy density parameter (ß) for TCA destruction in a DBD reactor was observed to vary between 1,478 and 3,010 J/L for RH between 0 and 88%, and it increased with an increase in RH due to lower DRE at higher RH conditions. This parameter and its dependence on the RH can be used to determine the specific energy required (J/L) to achieve a certain degree of TCA destruction in NTP systems, and can also be used to evaluate the applicability of NTP to destroy TCA in an industrial setting.

References