

Electron beam and pulsed corona processing of volatile organic compounds in gas streams

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Abstract: This paper presents experimental results on non-thermal plasma processing of atmospheric-pressure gas streams containing dilute concentrations of various volatile organic compounds (VOCs). This investigation used a compact electron beam reactor and a pulsed corona reactor to study the effects of background gas composition and gas temperature on the decomposition chemistry and electrical energy efficiency. The electrical energy consumption is characterized for the decomposition of a variety of VOCs, including carbon tetrachloride, trichloroethylene, methylene chloride, benzene, acetone and methanol. For most of the VOCs investigated, electron beam processing is more energy efficient than pulsed corona processing. For VOCs (such as carbon tetrachloride) that require copious amounts of electrons for its decomposition, electron beam processing is remarkably more energy efficient. For some VOCs the decomposition process is limited by their reaction rate with the plasma-produced radicals and/or by the occurrence of back reactions. In these cases, the energy consumption can be minimized by operating at high (but non-combusting) temperatures.

INTRODUCTION

Non-thermal plasma processing is an emerging technology for the abatement of volatile organic compounds (VOCs) in atmospheric-pressure gas streams. Either electron beam irradiation or electrical discharge methods can produce these plasmas. The basic principle that these techniques have in common is to produce a plasma in which a majority of the electrical energy goes into the production of energetic electrons, rather than into gas heating. Through electron-impact dissociation and ionization of the background gas molecules, the energetic electrons produce free radicals and additional electrons which, in turn, oxidize or decompose the VOC molecules. The potential of electron beam and electrical discharge methods has been demonstrated for the decomposition of many VOCs (1).

To apply non-thermal plasma processing to pollution control, the electrical energy consumption and byproduct formation need to be addressed. The thrust of our work has been to understand the scalability of the non-thermal plasma technique by focusing on the energy efficiency of the process and identifying the byproducts.

The electron mean energy in a plasma reactor determines the yields of radicals and other plasma generated species. Much of our work has been devoted to a characterization of the electron mean energy in the plasma. For most electrical discharge reactors our results suggest that the attainable electron mean energy is rather limited and cannot be easily enhanced by changing the electrode configuration or voltage pulse parameters. This has driven our efforts to improve the efficiency of the non-thermal plasma process by using a compact electron beam source. In this paper we present data on non-thermal plasma processing of various VOCs using a pulsed corona reactor and an electron beam reactor. For most of the VOCs investigated, electron beam processing is more energy efficient than pulsed corona processing. For VOCs (such as carbon tetrachloride) that require copious amounts of electrons for its decomposition, electron beam processing is remarkably more energy efficient. For some VOCs the decomposition process is limited by their reaction rate with the plasma-produced radicals and/or by the occurrence of back reactions. In these cases, the energy consumption can be minimized by operating at high (but non-combusting) temperatures.

TEST FACILITY

All the experiments were performed in a flow-through configuration. To characterize the energy consumption of the process for each VOC, the composition of the effluent gas was recorded as a function of the input energy density. The input energy density, Joules per standard liter, is the ratio of the power (deposited into the gas) to gas flow rate at standard conditions (25°C and 1 atm). The amount of VOC was quantified using an FTIR analyzer and a gas chromatograph/mass spectrometer.

Our electron beam reactor used a cylindrical electron gun designed to deliver a cylindrically symmetric electron beam that is projected radially inward through a 5 cm wide annular window into a 17 cm diameter flow duct. An electron beam of 125 keV energy was introduced into the reaction chamber through a 0.7 mil thick titanium window. The electron beam current was produced from a low-pressure helium plasma in an annular vacuum chamber surrounding the flow duct. A combined experimental and computer modeling approach was used to estimate the electron beam power deposition into the reaction chamber. Two sets of beam current measurements were performed to accurately determine the current delivery efficiency of the cylindrical electron gun. The first was made with a small area probe which provided azimuthal and axial resolution of the beam current density in the absence of the vacuum window. These were followed by measurements with a large area probe which collected the entire beam in the presence of the vacuum window. Electron transport through the window and deposition into the probe was modeled with the 2-D CYLTRAN code to correct for electron energy losses in the window, the probe view factor to the scattered electron distribution, and secondary electron emission from the probe surface. This 2-D Monte Carlo simulation was used to determine the dose distribution in the cylindrical duct as a function of the electron beam energy, window design (material and thickness) and duct diameter. The small probe results were averaged azimuthally and axially, and the averaged signal was corrected for geometrical effects such that it could be compared with the data obtained with the large area probe. The two measurements agreed to better than 6%, thus indicating an accurate measure of the current delivery efficiency from which the dose in the process gas was determined.

Our pulsed corona reactor is a 1.5 mm diameter wire in a 60 mm diameter metal tube 300 mm long. The power supply is a magnetic pulse compression system capable of delivering up to 15-35 kV output into 100 ns pulses at repetition rates from 100 Hz to 1 kHz. The resultant current ranges from milliamperes to hundreds of amperes. Both the voltage and current profiles are recorded. The current that is measured consists of both the discharge current and the current associated with charging the capacitance of the reactor. To obtain the energy deposition into the plasma, the capacitor charging current is subtracted from the total current waveform before integrating the voltage current product over the pulse duration to yield the pulse energy. In these experiments the power input to the processor was varied by changing either the pulse energy or pulse repetition frequency. For the same energy density input, either method produced almost identical results. The gas mixtures were set with mass flow controllers. The gas and processor temperatures were maintained at a temperature that can be controlled from 25°C to 300°C.

RESULTS

Fig. 1a shows a comparison between electron beam and pulsed corona processing of 100 ppm carbon tetrachloride (CCl_4) in dry air (20% O_2 80% N_2) at 25°C. The rate limiting step in the decomposition of CCl_4 is determined by the dissociative attachment of CCl_4 to the thermalized electrons in the created plasma: $e + \text{CCl}_4 \Rightarrow \text{Cl}^- + \text{CCl}_3$. During the creation of the plasma, electron-ion pairs are produced through primary electron-impact ionization of the bulk molecules, such as $e + \text{N}_2 \Rightarrow e + \text{N}_2^+$ and $e + \text{O}_2 \Rightarrow e + \text{O}_2^+$, and the corresponding dissociative ionization processes for N_2 and O_2 . The charge exchange reaction of positive ions, such as N_2^+ , with the background O_2 is fast, resulting in mostly O_2^+ ions: $\text{N}_2^+ + \text{O}_2 \Rightarrow \text{N}_2 + \text{O}_2^+$. The positive ions react with Cl^- through the neutralization reactions: $\text{Cl}^- + \text{O}_2^+ \Rightarrow \text{Cl} + \text{O}_2$ and $\text{Cl}^- + \text{O}_2^+ \Rightarrow \text{Cl} + 2\text{O}$. In the absence of scavenging reactions for CCl_3 , the input energy would be wasted because Cl and CCl_3 would simply recombine quickly to reform the original pollutant: $\text{Cl} + \text{CCl}_3 \Rightarrow \text{CCl}_4$. Fortunately, the presence of O_2 scavenges the CCl_3 through the fast reaction: $\text{CCl}_3 + \text{O}_2 \Rightarrow \text{CCl}_3\text{O}_2$. The CCl_3O_2 species reacts with Cl and, through a series of reactions, eventually produces COCl_2 (phosgene) as one of the main organic products. The other major product is Cl_2 which is formed by the reaction $\text{Cl} + \text{Cl} + \text{M} \Rightarrow \text{Cl}_2 + \text{M}$. An analysis of the rates of the reactions discussed above suggests that the energy consumption for CCl_4 removal is determined by the energy consumption (or G-value) for creating electron-ion pairs. For electron beam processing of dry air, the ionization G-value corresponds to an energy consumption of 33 eV per electron-ion pair produced. For

pulsed corona processing, we calculate an ionization G-value of around 1440 eV per electron-ion pair, based on known electron-impact ionization cross section and assuming an electron mean energy of 4 eV. These values agree very well with our experimentally observed energy consumption values for CCl_4 removal in dry air. The result shown in Fig. 1a demonstrates that for VOCs requiring copious amounts of electrons for decomposition, electron beam processing is much more energy efficient than electrical discharge processing.

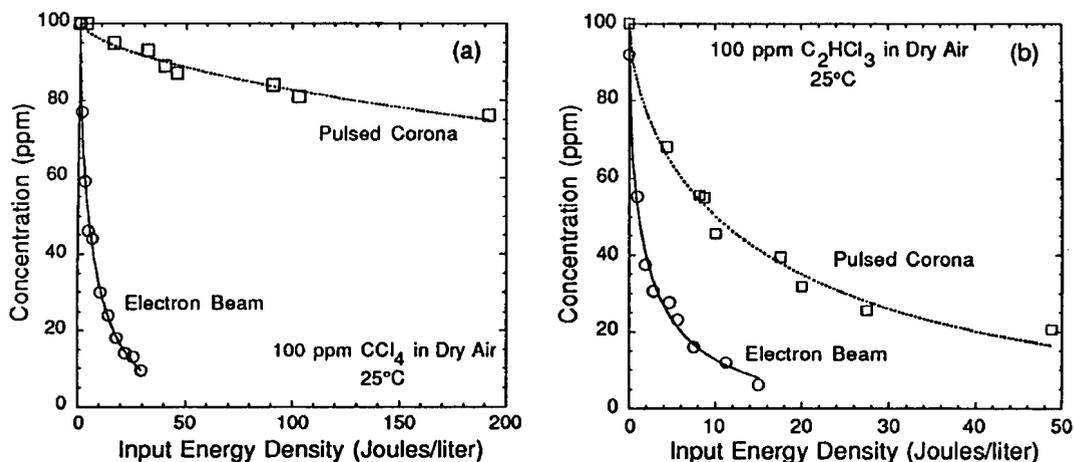


Fig. 1. Comparison between electron beam and pulsed corona processing of 100 ppm of (a) carbon tetrachloride and (b) trichloroethylene, in dry air at 25°C.

Fig. 1b compares electron beam and pulsed corona processing of 100 ppm trichloroethylene (TCE or C_2HCl_3) in dry air at 25°C. Compared to the other VOCs investigated, TCE is easy to decompose and the energy consumption is low in either electron beam or pulsed corona processing. Although the energy efficiency for electron beam processing of TCE is also higher than pulsed corona processing, the difference in processing efficiencies is not as dramatic as that for CCl_4 . Our byproduct measurements and material balance analysis point to significant amounts of dichloroacetyl chloride (DCAC), phosgene, and hydrochloric acid in addition to smaller amounts of CO and CO_2 in the effluent (2). The high efficiency in decomposing TCE has been explained on the basis of a chain reaction propagated by Cl (3,4).

For some VOCs the energy efficiency of the decomposition process is limited by their reaction rate with the plasma-produced radicals and/or by the occurrence of back reactions. The data on the gas temperature dependence provide a good basis for elucidating the chemical kinetics of VOC decomposition in the plasma. Fig. 2 shows the effect of gas temperature on pulsed corona processing of CCl_4 and methylene chloride (CH_2Cl_2) in dry air. The gas temperature does not have a significant effect on the decomposition of CCl_4 , as expected, since the decomposition rate of CCl_4 is determined mainly by the number of electrons produced in the plasma. In contrast the energy efficiency for CH_2Cl_2 increases dramatically with gas temperature.

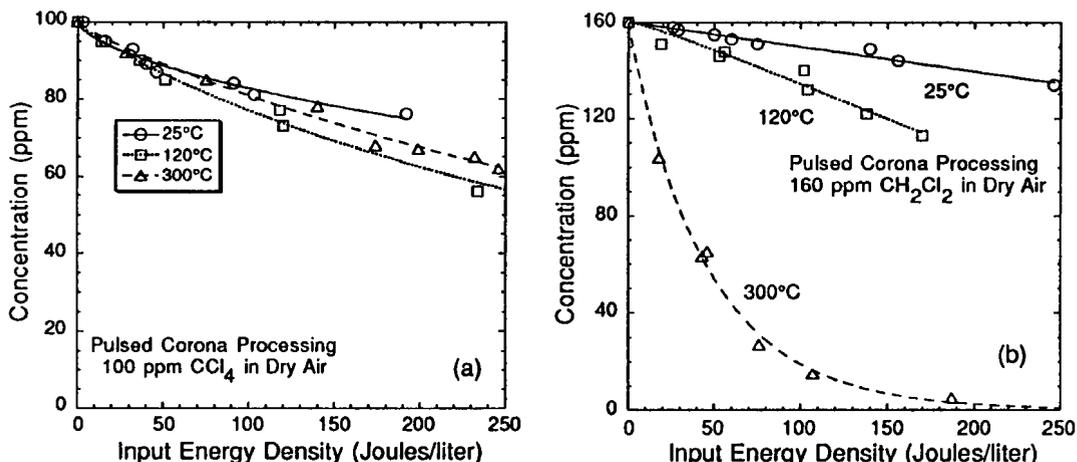


Fig. 2. Effect of gas temperature on pulsed corona processing of (a) 100 ppm carbon tetrachloride in dry air, and (b) 160 ppm methylene chloride in dry air.

TABLE 1. Comparison between electron beam and pulsed corona processing of carbon tetrachloride, benzene and trichloroethylene.

Pollutant	Initial (ppm)	Background Gas	Processor	Temp (°C)	Beta (Joules/liter)
Comparison between Electron Beam and Pulsed Corona Processing of Carbon Tetrachloride					
CCl ₄	100	Dry Air	Pulsed Corona	25	555
CCl ₄	100	Dry Air	Electron Beam	25	9
Comparison between Electron Beam and Pulsed Corona Processing of Benzene					
C ₆ H ₆	100	Dry Air	Pulsed Corona	25	500
C ₆ H ₆	100	Dry Air	Electron Beam	25	39
Comparison between Electron Beam and Pulsed Corona Processing of Trichloroethylene					
C ₂ HCl ₃	100	Dry Air	Pulsed Corona	25	16
C ₂ HCl ₃	100	Dry Air	Electron Beam	25	3

TABLE 2. Effect of background gas composition on electron beam and pulsed corona processing of carbon tetrachloride and methylene chloride.

Pollutant	Initial (ppm)	Background Gas	Processor	Temp (°C)	Beta (Joules/liter)
Effect of Background Gas (at 25°C) on Electron Beam Processing of Carbon Tetrachloride					
CCl ₄	100	Dry Air	Electron Beam	25	9
CCl ₄	100	N ₂	Electron Beam	25	44
Effect of Background Gas (at 25°C) on Pulsed Corona Processing of Carbon Tetrachloride					
CCl ₄	100	Dry Air	Pulsed Corona	25	555
CCl ₄	100	N ₂	Pulsed Corona	25	224
Effect of Background Gas (at 300°C) on Pulsed Corona Processing of Carbon Tetrachloride					
CCl ₄	100	Dry Air	Pulsed Corona	300	506
CCl ₄	100	N ₂	Pulsed Corona	300	219
Effect of Background Gas (at 25°C) on Pulsed Corona Processing of Methylene Chloride					
CH ₂ Cl ₂	100	Dry Air	Pulsed Corona	25	3170
CH ₂ Cl ₂	100	N ₂	Pulsed Corona	25	46
Effect of Background Gas (at 300°C) on Pulsed Corona Processing of Methylene Chloride					
CH ₂ Cl ₂	100	Dry Air	Pulsed Corona	300	45
CH ₂ Cl ₂	100	N ₂	Pulsed Corona	300	52

A figure of merit for expressing the energy efficiency of VOC removal is the β parameter suggested by Rosocha *et al.* (5). For many cases the VOC removal can be described with relatively good accuracy by the form $[X] = [X]_0 \exp(-E/\beta)$, where $[X]_0$ is the initial concentration of VOC molecules, E is the input energy density (Joules per standard liter) and β is the exponential-folding factor. We have summarized our data in terms of this β parameter. Table 1 shows a comparison between electron beam and pulsed corona processing of CCl₄, benzene and TCE in dry air at 25°C. Note that for these three VOCs electron beam processing is more energy efficient than pulsed corona processing, the difference being greatest for CCl₄. Table 2 shows the effect of the background gas composition on electron beam and pulsed corona processing of CCl₄ and CH₂Cl₂. Table 3 shows the effect of gas temperature on pulsed corona processing of CCl₄, CH₂Cl₂, TCE, benzene, methanol and acetone. A detailed discussion of the chemical kinetics of the plasma-assisted decomposition of these VOCs is outside the scope of this paper and will be addressed in a separate publication. The effect of water vapor will also be addressed elsewhere.

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TABLE 3. Effect of gas temperature on pulsed corona processing of carbon tetrachloride, methylene chloride, trichloroethylene, benzene, methanol and acetone.

Pollutant	Initial (ppm)	Background Gas	Processor	Temp (°C)	Beta (Joules/liter)
Effect of Temperature on Pulsed Corona Processing of Carbon Tetrachloride in Dry Air					
CCl ₄	100	Dry Air	Pulsed Corona	25	555
CCl ₄	100	Dry Air	Pulsed Corona	120	430
CCl ₄	100	Dry Air	Pulsed Corona	300	506
Effect of Temperature on Pulsed Corona Processing of Carbon Tetrachloride in N₂					
CCl ₄	100	N ₂	Pulsed Corona	25	224
CCl ₄	100	N ₂	Pulsed Corona	300	219
Effect of Temperature on Pulsed Corona Processing of Methylene Chloride in Dry Air					
CH ₂ Cl ₂	160	Dry Air	Pulsed Corona	25	1488
CH ₂ Cl ₂	160	Dry Air	Pulsed Corona	120	545
CH ₂ Cl ₂	160	Dry Air	Pulsed Corona	300	46
Effect of Temperature on Pulsed Corona Processing of Methylene Chloride in N₂					
CH ₂ Cl ₂	100	N ₂	Pulsed Corona	25	46
CH ₂ Cl ₂	100	N ₂	Pulsed Corona	300	52
Effect of Temperature on Pulsed Corona Processing of Trichloroethylene					
C ₂ HCl ₃	160	Dry Air	Pulsed Corona	25	27
C ₂ HCl ₃	160	Dry Air	Pulsed Corona	120	6
C ₂ HCl ₃	160	Dry Air	Pulsed Corona	300	71
Effect of Temperature on Pulsed Corona Processing of Benzene					
C ₆ H ₆	150	Dry Air	Pulsed Corona	25	671
C ₆ H ₆	150	Dry Air	Pulsed Corona	120	369
C ₆ H ₆	150	Dry Air	Pulsed Corona	300	138
Effect of Temperature on Pulsed Corona Processing of Methanol					
CH ₃ OH	100	Dry Air	Pulsed Corona	25	195
CH ₃ OH	400	Dry Air	Pulsed Corona	120	257
CH ₃ OH	400	Dry Air	Pulsed Corona	300	75
Effect of Temperature on Pulsed Corona Processing of Acetone					
CH ₃ COCH ₃	800	Dry Air	Pulsed Corona	25	3543
CH ₃ COCH ₃	800	Dry Air	Pulsed Corona	120	1391
CH ₃ COCH ₃	800	Dry Air	Pulsed Corona	300	285

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