ELECTRON BEAM AND PULSED CORONA PROCESSING OF VOLATILE ORGANIC COMPOUNDS AND NITROGEN OXIDES

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INTRODUCTION

Non-thermal plasma processing is an emerging technology for the abatement of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) 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 reduce the pollutant molecules. The potential of electron beam and electrical discharge methods has been demonstrated for the abatement of NO_x and many kinds of 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.

There are many types of non-thermal plama reactors that are being investigated for pollution control applications. Whatever the type of reactor, the plasma can induce four basic types of reactions with the pollutant molecules, as shown in Fig. 1. For stationary applications, it may be sufficient to oxidize NO to NO_2; the latter is then further oxidized by OH radicals to nitric acid. Some form of scrubbing is required to collect the final products. For mobile engine applications, it is very important to make a distinction between NO removal by chemical oxidation and NO removal by chemical reduction. To avoid the need for scrubbing of process products, the desired method of NO removal is by chemical reduction; i.e. the conversion of NO to the benign products N_2 and O_2. For typical exhaust gases without additives, the only species that the plasma can produce to implement NO reduction is the N atom. For some VOCs such as carbon tetrachloride, the electrons play a key role in the direct decomposition of the VOC molecules.

The electron mean energy in a plasma reactor is very important because it determines the types of radicals produced in the plasma and the input electrical energy required to produce those radicals. Fig. 2 shows the dissipation of the input electrical power in a dry air discharge. Note that at low electron mean energies (< 5 eV) a large fraction of the input electrical energy is consumed in the vibrational excitation of N_2. Electron mean energies around 5 eV are optimum for the electron-impact dissociation of O_2, which is important for the production of O radicals. These oxidizing radicals play a key role in the initial decomposition of some types of VOCs. To implement the chemical reduction of NO to benign molecules such as N_2 and O_2, the important reducing species

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is the N atom, which is produced through the electron-impact dissociation of N_2. High electron mean energies are required to efficiently implement the dissociation of N_2. For VOCs that take advantage of electron-induced or ion-induced decomposition, high electron mean energies are also required to efficiently implement the ionization of the background gas.

- ***Oxidation***

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

  $O(^3P) + NO + M \Rightarrow NO_2 + M$

  $O(^1D) + H_2O \Rightarrow OH + OH$

  $OH + NO_2 \Rightarrow HNO_3$

- ***Reduction***

  $e + N_2 \Rightarrow e + N + N$

  $N + NO \Rightarrow N_2 + O$

- ***Electron-induced decomposition***

  $e + N_2 \Rightarrow e + e + N_2^+$

  $e + O_2 \Rightarrow e + e + O_2^+$

  $e + CCl_4 \Rightarrow CCl_3 + Cl^-$

- ***Ion-induced decomposition***

  $N_2^+ + CH_3OH \Rightarrow CH_3^+ + OH + N_2$

Fig. 1. The plasma can induce four basic types of reactions with the pollutant molecules.

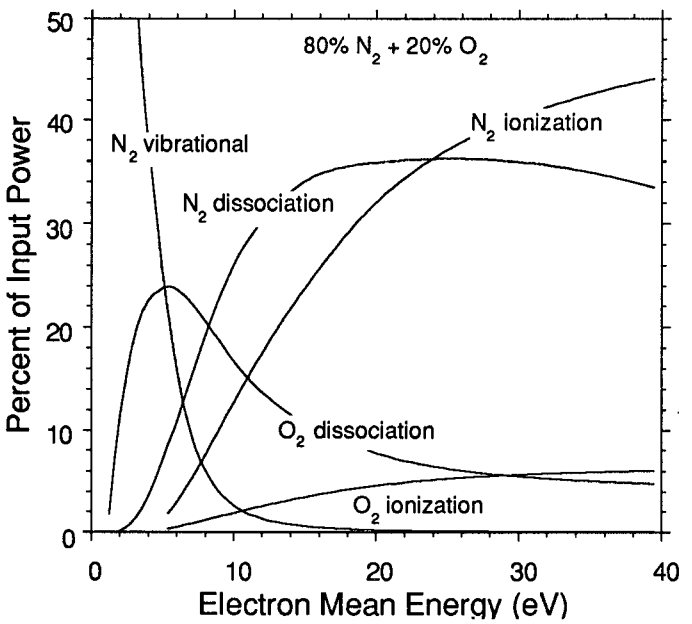

Fig. 2. Power dissipation in a dry air discharge, showing the percent of input power consumed in the electron-impact processes leading to vibrational excitation, dissociation and ionization of N_2 and O_2.

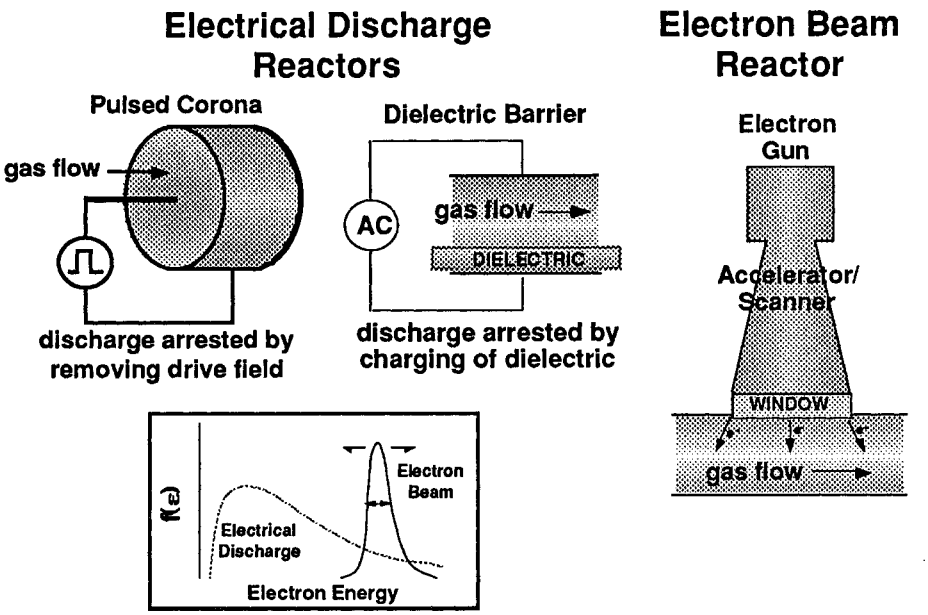

Fig. 3. There are basically two types of non-thermal atmospheric-pressure plasma reactors: electrical discharge reactors and electron beam reactors.

Much of our work has been devoted to the characterization of the electron mean energy in the plasma. In terms of the electron energy distribution produced in the plasma, we believe there are basically only two types of non-thermal atmospheric-pressure plasma reactors: electrical discharge reactors and electron beam reactors. Electrical discharge techniques can be implemented in many ways, depending on the electrode configuration and electrical power supply (pulsed, AC or DC). Two of the more extensively investigated types of electrical discharge reactors are the pulsed corona and the dielectric-barrier discharge, shown in Fig. 3. For most electrical discharge reactors our results suggest that the attainable electron mean energy is rather limited and cannot be significantly 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 NO_x and various VOCs using a pulsed corona reactor and an electron beam reactor.

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 NO_x or VOC was quantified using a chemiluminescent NO_x meter, 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.

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 FWHM pulses at repetition rates from 15 Hz to 1.5 kHz. 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 can be maintained at a temperature that can be controlled from 25°C to 300°C.

RESULTS

Fig. 4 shows a comparison between electron beam and pulsed corona processing of 100 ppm of NO in N_2. The concentration of NO is presented as a function of the input energy density deposited into the gas. In the NO-N_2 mixture the removal of NO is dominated by the reduction reaction N + NO => N_2 + O. These experiments therefore provide a good measure of the electron-impact dissociation rate of N_2. Fig. 4 shows that the energy consumption for NO reduction by electron beam processing is six times less than that of pulsed corona processing. The energy density required to reduce NO is around 20 Joules/liter and 120 Joules/liter by electron beam and pulsed corona processing, respectively.

Fig. 5 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 + CCl_4 => Cl^- + CCl_3. During the creation of the plasma, electron-ion pairs are produced through primary electron-impact ionization of the bulk molecules,

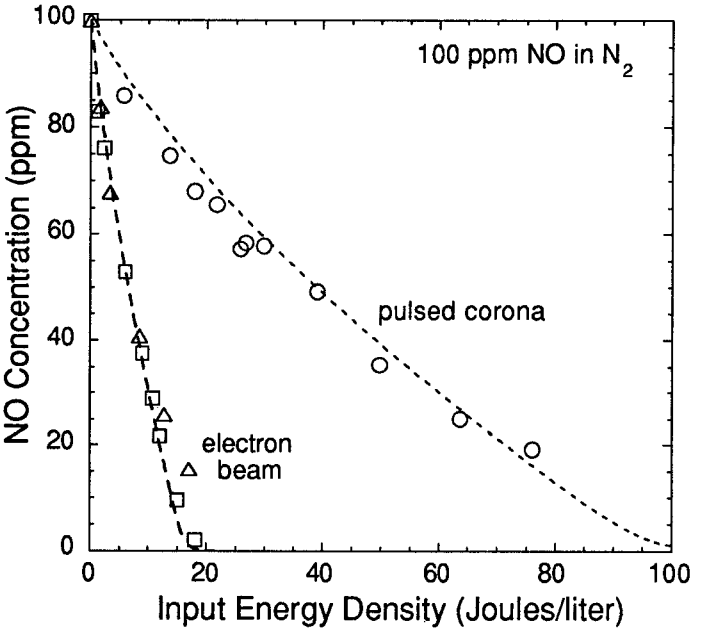

Fig. 4. Electron beam and pulsed corona processing of 100 ppm NO in N_2.

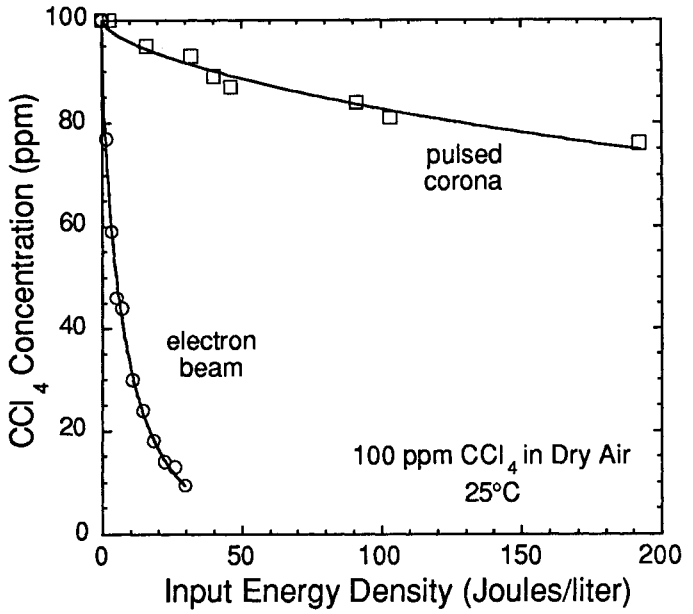

Fig. 5. Electron beam and pulsed corona processing of 100 ppm CCl_4 in dry air.

such as $e + N_2 \Rightarrow e + N_2^+$ and $e + O_2 \Rightarrow e + O_2^+$, and the corresponding dissociative ionization processes for N_2 and O_2. 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 for creating electron-ion pairs. Fig. 5 shows that the energy consumption for CCl_4 decomposition by electron beam processing is around sixty times less than that of pulsed corona processing. The energy density required to decompose CCl_4 by 90% is around 20 Joules/liter and 1270 Joules/liter by electron beam and pulsed corona processing, respectively. This result demonstrates that for VOCs requiring copious amounts of electrons for decomposition, electron beam processing is much more energy efficient than electrical discharge processing.

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. 6 shows the effect of gas temperature on pulsed corona processing of methylene chloride (CH_2Cl_2) in dry air. Note that the energy efficiency for CH_2Cl_2 removal increases dramatically with gas temperature. The energy density required to decompose CH_2Cl_2 by 90% is 3425 Joules/liter and 106 Joules/liter at 25°C and 300°C, respectively.

CONCLUSIONS

Electrical discharge reactors are most suitable for processes requiring O radicals. For processes requiring copious amounts of electrons or N atoms, the use of electron beam reactors is generally the best way of minimizing the electrical energy consumption. For many of the VOCs we have investigated, we found that 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.

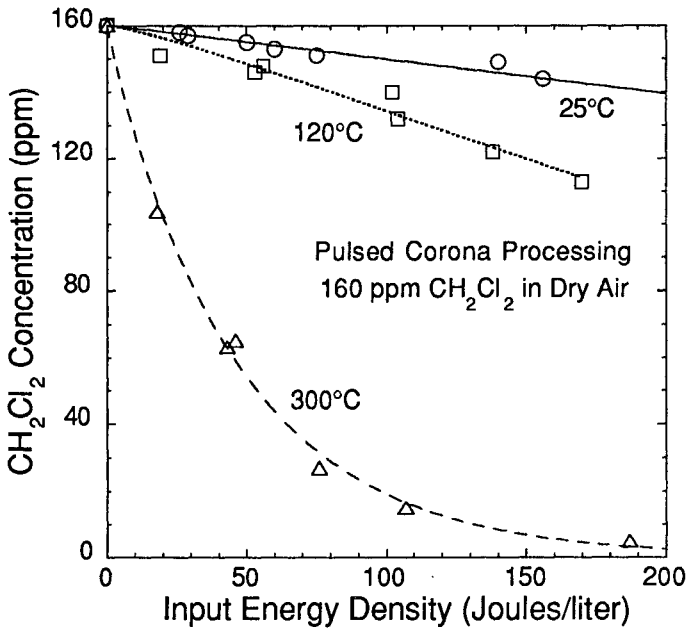

Fig. 6. Effect of gas temperature on pulsed corona processing of methylene chloride.

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REFERENCES

1. A collection of papers on various types of non-thermal plasma reactors being investigated for VOC and NO_x abatement appears in *Non-Thermal Plasma Techniques for Pollution Control: Part A - Overview, Fundamentals and Supporting Technologies*, edited by B. M. Penetrante and S. E. Schultheis (Springer-Verlag, Heidelberg, 1993) and *Non-Thermal Plasma Techniques for Pollution Control: Part B - Electron Beam and Electrical Discharge Processing*, edited by B. M. Penetrante and S. E. Schultheis (Springer-Verlag, Heidelberg, 1993).