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**Non-Thermal Plasma (NTP) Session Overview:
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**Non-Thermal Plasma (NTP) Session Overview:
2nd International Symposium on
Environmental Applications of Advanced Oxidation Technologies (AOTs)**

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Abstract

Because of increased interest in pollution control and the treatment of hazardous wastes, the field of Advanced Oxidation Technologies (AOTs) has grown in the past several years. Originally, AOTs dealt with the use of hydroxyl radicals OH in treating organic compounds in water. The field has now expanded to encompass processes based on reductive as well as oxidative free radicals and is applied to pollutants in both gas-phase and aqueous-phase media.

This session deals with the particular AOT called Non-Thermal Plasma (NTP) technology. NTPs use electrical energy to create highly reactive species, e.g., oxygen atoms $O(^3P)$, OH-radicals, N-radicals, and plasma electrons, in gaseous media at near-ambient temperature. The NTP is usually created in by an electrical discharge in a gas, or the injection of energetic electrons (e.g., 100 keV - 1 MeV) into a gas. Both processes create secondary plasma electrons, with a distribution of electron energies defined by an average electron energy (or electron temperature). In contrast to a thermal plasma, a non-thermal (non-equilibrium) plasma, is characterized by electrons which are not in thermal equilibrium with the other gas species. The electrons are "hot" (few to tens of eV), while the ions and neutral gas species are "cold" (near-ambient temperature). The active species generated by the NTP subsequently react with entrained hazardous organic chemicals in the gas, converting them to non-hazardous mineralized compounds (CO_2 , H_2O , and acids) or other easily-managed compounds. Because NTP processing may be able to simultaneously remove different types of pollutants (e.g., volatile organic compounds - VOCs and oxides of sulfur and nitrogen frequently found in flue gases - SO_x and NO_x), it is particularly attractive for many present and future environmental applications.

In this paper, an overview of NTP technology as it applies to pollution control and hazardous waste treatment in gas streams will be presented. It is intended as an introduction to the Non-Thermal Plasma Session of the Symposium. In the session, the papers to be presented principally deal with electrical discharge-driven NTPs (corona, silent discharge - or dielectric barrier discharge, surface discharges) and electron-beam-driven NTPs for the treatment of gas-based pollutants.

Introduction

Historically the field of Advanced Oxidation Technologies (AOTs) has encompassed processes which decompose organic compounds via the hydroxyl radical OH. AOTs were first used in the treatment of water using OH radicals generated from the photolysis of ozone (O_3) or hydrogen peroxide (H_2O_2), or the direct combination of O_3 and H_2O_2 . In the past several years, the field has been expanded to include processes which involve other free radicals, some of which are reductive rather than oxidative, and to the treatment of gaseous as well as aqueous-based effluents. During the past five years, interest in AOTs has grown considerably because of their applications to pollution control and waste treatment. In many cases this interest has been stimulated by a heightened concern over the pollution of our environment and more stringent environmental regulations (e.g., the Clean Air Act Amendments of 1990 and the Clean Water Act, in the U.S.). AOTs show particular promise for the treatment of hazardous and toxic pollutants (e.g., volatile hydrocarbons and halocarbons) because the reaction rates of free radicals with organic compounds can be orders of magnitude larger than a strong oxidizer like O_3 . Highly reactive species, such as free radicals, can be generated with plasmas.

A plasma (in electrical terminology) is an ionized state of matter (sometimes called the *fourth state of matter*) containing electrons and ions. A plasma behaves much like an *electrical gas*, where the individual charged particles which compose the plasma interact collectively with applied and self-generated electromagnetic fields. Plasmas can be created thermally by heating ordinary matter to a temperature greater than about 10,000 C. In such a *thermal plasma*, all the species - electrons, ions, neutral atoms and molecules - are all in thermal equilibrium (i.e., at the same temperature). Considerable heat energy (enthalpy) must be added to the gas to achieve such an equilibrium. In contrast to a thermal plasma, a *non-thermal plasma* (or non-equilibrium plasma) is characterized by electrons which are not in thermal equilibrium with the other gas species. The electrons are *hot* (few to tens of eV temperature), while the ions and neutral gas species are *cold* (near-ambient temperature). The key idea in NTP processing is to direct electrical energy into favorable gas chemistry through energetic electrons, rather than using the energy to heat the gas. Two common ways of creating an NTP are by an electrical discharge in a gas or the injection of energetic electrons (e.g., 100 keV - 1 MeV) into a gas. Both processes create secondary plasma electrons, with a distribution of electron energies defined by an average electron energy (or electron temperature).

Electrical energy coupled into an NTP can be used to create highly reactive species, e.g., oxygen atoms $O(^3P)$, OH-radicals, N-radicals, and plasma electrons, in gaseous media at near-ambient temperatures and pressures. These active species subsequently react with entrained hazardous organic chemicals in the gas, converting them to non-hazardous mineralized compounds (CO_2 , H_2O , and acids) or other easily-managed compounds. Because NTP processing shows promise for simultaneously removing different types of pollutants (e.g., volatile organic compounds - VOCs and oxides of

sulfur and nitrogen frequently found in flue gases - SO_x and NO_x), it is particularly attractive for many present and future environmental applications.

In a thermal process (like incineration of equilibrium plasma), thousands of electron volts of energy are typically required to decompose one pollutant molecule, because it is a non-selective process. Compared to a thermal process, non-thermal plasmas typically require energies of order 10's - 100's eV per decomposed pollutant molecule, because the chemistry can be more selective.

Technical Overview

Non-Thermal Plasma Reactors

NTPs for gas-phase pollutant processing are normally created in one of two ways: by an electrical discharge (where a high voltage is applied across electrodes in a gas or along a surface adjacent to a gas) or by the injection of a beam of energetic electrons (e.g., 100 keV - 1 MeV) into a gas. The key idea of both methods is to direct electrical energy into favorable gas chemistry through energetic electrons, rather than using the energy to heat the gas (i.e., add enthalpy). The energetic plasma electrons are sometimes themselves dominant in the process of pollutant decomposition, while under other conditions, the electrons create free radicals that attack the pollutants.

Figure 1 shows several electrical-discharge plasma reactor configurations commonly employed for NTP processing. Because the glow- and RF-discharge reactors usually operate with high efficiency at lower pressures and, consequently, lower throughput, they are not strong candidates for pollutant processing. The other four reactors - silent discharge (dielectric barrier), corona, electrified packed bed, and surface discharge - are the subject of several international investigations for environmental applications.

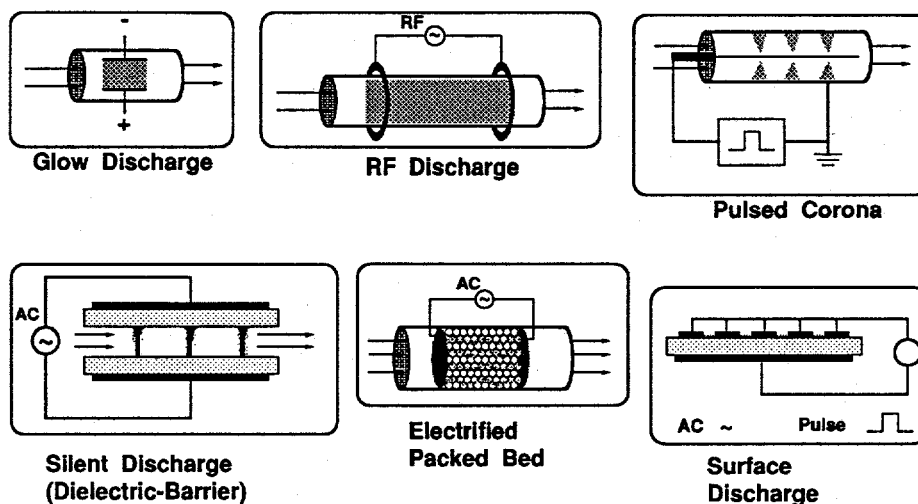


Figure 1: Schematic diagrams of electrical discharge non-thermal plasma reactors.

In corona a non-homogeneous electric field is used to stabilize the discharge and prevent thermal arc formation. Silent discharges use charge buildup on a capacitive barrier to achieve a similar end result. The surface discharge and electrified packed bed are closely related to a barrier discharge. All four of these methods create transient electrical-discharge streamers in the gas. The streamer is the source of energetic electrons and other active species. A relatively high voltage (determined by the reactor geometry, gas composition, and gas pressure) is required to cause electrical breakdown in the gas. The necessary voltage is supplied by a drive circuit connected to the reactor.

Figure 2 shows a schematic diagram of an electron-beam-driven NTP reactor. An electron-beam reactor requires an electron accelerator to produce the beam that is injected into the process gas. The source of electrons (the cathode) can be separate from the accelerating-field section (as in thermionic-cathode and plasma-cathode devices) or integrated with the accelerating-field section (as in a field-emission-cathode electron gun).

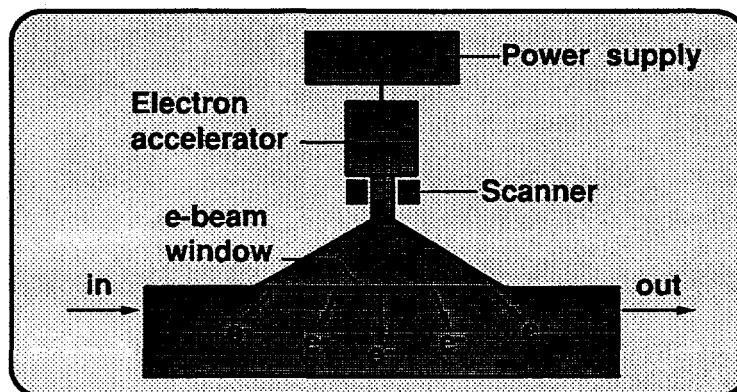


Figure 2: Schematic diagram of electron beam non-thermal plasma reactor.

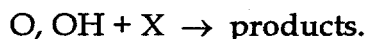
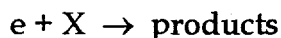
Active Species Generation and Pollutant Decomposition

In the decomposition process, plasma physics and plasma chemistry are interconnected. The NTP is created by the electrical discharge or electron beam and the active species are generated in the pollutant-containing gas by plasma-initiated processes (starting from energetic electrons). The active species (O-atoms, N-atoms, OH-radicals, electrons, etc.) then react with and decompose the chemical pollutants.

The yield of a particular radical species (i.e., the number of radicals produced per unit deposited plasma energy) will depend on factors such as the gas composition, the gas pressure, and the average electron temperature. One major difference between discharge reactors and electron-beam reactors is that discharge reactors are very efficient producers of oxygen atoms, while electron-beam reactors are very efficient producers of hydroxyl radicals and nitrogen atoms. This means that oxidation reactions with O-atoms have the highest efficiency in discharges, while electron beams

can more efficiently promote N-atom-driven reductive reactions in addition to OH-radical-driven oxidation reactions.

The two main ways for a gas-phase chemical pollutant X to be decomposed in an NTP are direct electron impact or chemical (radical-promoted) attack,



The first path is dominant at large contaminant concentrations, while the second dominates at smaller concentrations. The reason for this is because more electrical energy is directly absorbed by the contaminant at higher concentrations. Some researchers also emphasize the importance of ion-molecule reactions in pollutant decomposition.

The decomposition chemistry for NO is tractable and can be largely described in terms of oxidation and reduction reactions. Oxidative-mode reactions involving O-atoms can trap total NO_x as NO and NO₂. Oxidative-mode reactions involving OH-radicals produce nitric acid HNO₃, which can be easily removed by a caustic scrubber. Reductive-mode reactions involving N-atoms drive more NO_x to N₂ and O₂. This reduces the scrubber requirements, but depends on higher average energy electrons (a condition presently favored by electron-beam reactors). SO_x removal is favorably driven by O-atom and OH-radical oxidative reactions, producing sulfuric acid as a terminal product.

The removal of chlorocarbons involves rather complicated reaction chemistry. Complex molecules, like many VOCs, will often undergo a series of reactions before the final products result. A discussion of chlorocarbon removal is too lengthy for this overview and the reader is referred to the literature for more information on this subject.

The most desirable goal of plasma processing is to fully mineralize the pollutant. Unfortunately, this is not usually possible because undesired hazardous byproducts can sometimes result. For example, much of the chlorine resulting from the decomposition of trichloroethylene (TCE, C₂HCl₃) and carbon tetrachloride (CCl₄) is converted to HCl, Cl₂, and COCl₂. Phosgene (COCl₂) is a toxic compound that is made in thermal combustion as well as in nonthermal plasma remediation. Fortunately, it can be easily and quickly decomposed by reacting with water or water vapor. It can also be further destroyed by increasing the plasma energy density.

Practical success can be achieved by treating the parent hazardous compound to produce compounds which can be more easily treated by conventional methods. One promising technique for dealing with toxic byproducts is a closed-loop processing

system, where the byproducts are cycled back through the plasma processor and held or captured.

Removal Scaling Relationships

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. To increase the destruction ratio $[X]/[X]_0$ for a given gas mixture, \bar{E} must be increased. This can be done by either increasing its power or decreasing its flow rate.

In ideal 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 $\alpha = 2.303 \beta$. For real cases, the removal expression is not necessarily an ideal exponential, so the use of the β -value is only an approximation. Nevertheless, it is still quite useful over a limited range of e-folds. β -values for representative compounds are usually determined by laboratory experiments. For TCE in dry air, β is about 10 -15 J/lit for discharge reactors and 3 J/lit for electron beam reactors.

Applications & Expected Advantages

Motivation for Technology

The roots of treating hazardous and/or toxic chemicals with NTPs go back about two decades to military applications for destroying toxic chemical warfare agents with electric discharge reactors and civilian applications for treating flue gases (SO_x and NO_x) from electric power plants and other installations (e.g., steel mills) with electron beams. At that time, a lack of understanding of the plasma chemistry, a lack of knowledge and measurement of important reactor parameters, the formation of undesirable byproducts, and unfavorable economics compared to conventional systems contributed to a loss of interest in the technology.

More recently in the United States, the Clean Air Act Amendments of 1990 (which targets 189 chemicals and groups of chemicals for more stringent emissions standards) and the Clean Water Act have served as motivators for the development of new

technologies for destroying hazardous chemicals. Technical and regulatory difficulties associated with current air-pollutant treatment methods, such as dilution/air-stripping, activated-carbon absorption, and incineration have prompted the search for alternatives. Drawbacks with current methods result in the generation of large secondary waste streams (e.g., the greenhouse gases CO_2 , N_2O , CH_4 , scrubber liquids, and activated carbon canisters), the emission of other atmospheric contaminants (e.g., NO_x , dioxins and furans), the use of expensive and/or poisonous catalysts, hard-to-permit installations, and increased costs.

Example Applications

NTP 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.

One can also stage an NTP processor with a conventional technology like granular activated carbon (GAC) absorption. By removing a sizeable fraction (e.g., 75%) of the pollutant before the GAC unit, the overall economics of the process becomes much more favorable. The primary drawback of GAC is its disposal cost.

Status

Non-thermal plasma processing of pollutants is an emerging field; it is not represented by off-the-shelf technology. Many laboratory-based investigations, several small-scale field demonstrations, and a few large-scale demonstrations (primarily with electron beams) have been carried out, but little, if any, commercial non-thermal plasma processing equipment for industrial applications is presently available.

Laboratory investigations and field demonstrations have shown that the energy cost of decomposing SO_x/NO_x as well as VOCs is usually lower in electron beam reactors than in electrical discharge reactors (frequently by an order of magnitude or more). The reason for this in most cases is because an electron beam reactor can produce a plasma electron energy distribution with a higher average electron energy (electron temperature) than a discharge reactor, e.g., 10's eV for an electron beam vs. a few eV for a discharge. For an electron beam reactor, this results in higher N and OH radical production efficiencies or the enhanced production of lower-energy secondary electrons that are dominant in dissociative-attachment-driven decomposition.

For example, for dry air, the removal of SO_x and NO_x is about six times as efficient with electron beams than with discharges (order 10 J/lit vs. 60 J/lit for one e-fold); for VOCs such as TCE, benzene, and carbon tetrachloride, removal efficiencies are of order 5 - 50 times better with electron beams than with discharges. TCE takes roughly 10-15 J/lit for one e-fold in discharges, but only about 3 J/lit with electron beams. Similar trends are expected for humid air as well.

Presently, there is no compelling reason to establish any particular reactor as the technology of choice for flue gases or VOCs - because each has its own advantages and disadvantages and because commercial scaling and feasibility has not been established for any reactor. Electron beam reactors appear to have an energy-efficiency advantage (based upon power into the plasma) but electrical discharge reactors usually have a higher coupling efficiency from power supply energy to that deposited in the plasma (e.g., 60-90% vs. 40-60%). The capital cost of a typical electrical discharge reactor is also expected to be considerably less than a comparable electron beam reactor. Electron beams can excite a larger volume with a single reactor due to the high penetration of the primary electrons into a gas. However, the foil materials used to separate the electron-beam generation section from the treated gas are still a practical issue.

Many factors can influence the effectiveness, economics, and larger environmental benefits of treating air pollutants with non-thermal plasma processing. At the first AOT Symposium held in 1992, the following factors were emphasized:

- Electrical driver pulse width/rise time
- Gas mixture (temperature, humidity, oxygen content, etc.)
- Circuit coupling (how the driver follows the load)
- Role of UV light in plasma chemistry, discharge process
- Effects/mechanisms related to additives (e.g., hydrocarbons).
- Reaction chemistry mechanisms (radical attack vs. fragmentation)
- Radical production and utilization efficiencies
- Contaminant removal/conversion efficiencies
- By-products
- Power and energy density measurements
- Reactor and process scaling
- Consistent nomenclature and parameters.

Since the last conference, there has been considerable progress in the understanding of the plasma and reaction chemistry and measurements needed to compare different reactors on similar footings (e.g., measurements of the plasma energy density required for an e-fold removal).

Summary/Conclusions

Non-thermal plasmas show promise for the treating flue gases (SO_x/NO_x) and hazardous air pollutants (VOCs). Many laboratory experiments and controlled field demonstrations (primarily small-scale) have been carried out and removal figures of merit have been established for various reactors and pollutants. Basic understanding of the plasma chemistry has evolved to the point where trends and equipment scaling can be predicted with reasonable confidence and reactors have been scaled to energy density levels that will permit industrial service. Several efforts are in progress to demonstrate industrial-scale equipment and commercialize the process, but the technology is not yet a commercial reality. Electron beam systems have achieved better removal energy costs for many compounds, so they should have lower energy operating costs than electrical discharge reactors, but their system complexity and capital costs are expected to be higher. In spite of all the experience so far with NTP technology, much data for comparing different reactors under identical operating conditions is still lacking as is comprehensive data on system costs. Nevertheless, because non-thermal plasma processing can simultaneously remove different types of pollutants without added fuel or catalysts, it is still considered promising and is expected to have advantages over conventional technologies.

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