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**NITROGEN OXIDE DECOMPOSITION
BY BARRIER DISCHARGE**

BY

CHRISTOPHER R. McLARNON

**B.S. University of New Hampshire, 1987
M.S. University of New Hampshire, 1989**

DISSERTATION

**Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirement for the Degree of**

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in

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May 2, 1996

Date

Dedicated to my wife, Debra,
whose patience and support made this work possible.

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ABSTRACT

NITROGEN OXIDE DECOMPOSITION BY BARRIER DISCHARGE

by

Christopher R. McLarnon
University of New Hampshire, May, 1996

Nitrogen oxides have been linked to numerous air pollution problems including the production of ozone in the troposphere and acid rain. Annual nitrogen oxides emissions in the United States exceed 21 million tons and are primarily a result of the high temperature combustion of fossil fuel. Recent regulations in the U.S., both federal and state, require that nitrogen oxides emissions be reduced over the next several years.

Control of nitrogen oxide emissions is difficult in combustion exhaust gases because of their low concentration and reactivity. Numerous technologies have been developed to reduce emissions but the costs are generally high and the technologies are not applicable to many of the combustion systems in use today.

Electrical discharges provide a means of producing active chemical species such as ions, radicals and metastable compounds that can react with oxides of nitrogen and cause their decomposition and removal from the gas stream. This study investigates the use of one such electrical discharge technique, barrier discharges. Experiments were conducted in a bench top apparatus and in a larger scale process development unit. The variables controlling the operation of the barrier discharge process and the products

produced were identified and studied. They included electrical parameters such as applied voltage and frequency, the chemical composition of the gas stream, and flow conditions in the barrier discharge reactor.

Experimental results showed that greater than 95% conversion of nitric oxide could be achieved using both simulated and combustion generated flue gas. Products of the reactions leading to nitric oxide destruction were non-polluting nitrogen and oxygen when dry, simulated flue gas was used. Nitric acid was produced when the gas stream contained water vapor. Operation of the barrier discharge system established on the bench scale apparatus was verified on the process development unit.

Results of this work have the potential to establish the foundation for a nitrogen oxides control technology that is more versatile and may cost less to install and operate than existing control techniques.

CHAPTER I

INTRODUCTION

Release of nitrogen oxides to the atmosphere has been linked to several air pollution problems. They include the destruction of ozone in the stratosphere, photochemical production of ozone in the troposphere, formation of nitric acid leading to acid rain and the formation of hazardous airborne compounds such as nitrosoamines.

Sources of NO_x include both naturally occurring and man-made processes. In nature NO_x is produced in forest fires, in lightning strikes and from volcanic activities. Man made or anthropogenic sources of NO_x include nitric acid manufacture and its use in steel pickling, plating and catalyst recovery operations and chemical manufacture. However, the largest source of anthropogenic NO_x is the combustion of fossil fuels. It is estimated that the annual NO_x emissions in the United States are 21 million tons due to fossil fuel combustion for electricity generation, industrial processes and transportation [Spengler, 1990]. These emissions can result in high local concentrations of airborne NO_x , giving rise to urban area concentrations of 10 to 100 times that found in rural regions.

Many compounds are categorized as oxides of nitrogen. They include nitrous oxide (N_2O), nitric oxide (NO), dinitrogen trioxide (N_2O_3), nitrogen dioxide (NO_2), dinitrogen tetroxide (N_2O_4) and dinitrogen pentoxide (N_2O_5). Nitrous oxide is a relatively

unreactive compound commonly used as an anaesthetic (laughing gas). Dinitrogen trioxide dissociates to NO and NO₂ at temperatures above -30°C. Dinitrogen tetroxide establishes an equilibrium with NO₂ which is temperature dependent, favoring NO₂ formation with increasing temperature. Dinitrogen pentoxide is unstable as a gas, dissociating to NO and NO₃, which is also unstable [Cotton, 1988]. Therefore, the two principal oxides of nitrogen, in terms of emissions to the environment, are nitric oxide (NO) and nitrogen dioxide (NO₂), collectively called NO_x.

Regulations pertaining to NO_x emissions in the United States come from both Federal and State agencies. NO_x emissions are regulated on a Federal level under Title I and Title IV of the Clean Air Act Amendments (CAAA) of 1990. These regulations are to limit NO_x emissions in order to reduce ground level ozone concentrations (Title I) and to reduce their contribution to acid deposition (Title IV). Currently, Title I of the Clean Air Act Amendments requires controls on large sources of NO_x. However, continuing increases in ground level ozone concentrations and its adverse effects may result in regulations governing the operation of small NO_x sources. The U.S. Environmental Protection Agency (EPA) estimates that a 50% reduction in NO_x emissions will be required in the northeastern states of the U.S. to make significant progress towards meeting the national ambient air quality standards for ozone [NESCAUM, 1992]. Estimates by the northeastern states themselves indicate that a 60 to 65% reduction will be required [Dunn, 1994].

State regulations, including those enacted to comply with the requirements of Titles I and IV of the CAAA, vary widely from one state to the next. California's are the most

stringent in the nation. Unusual meteorological conditions in the Los Angeles basin, where compounds emitted to the atmosphere disperse slowly, require strict controls on pollutant release to maintain ambient air standards. Therefore, regulations in California go beyond the federal limits on NO_x emissions required by the CAAA.

Efforts to reduce NO_x emissions are focused on fossil fuel combustion since it is the main source of anthropogenic NO_x. Under current regulations it is the large stationary combustion devices such as utility boilers that are or will be required to implement NO_x control. However, regulations in the future are expected to apply to smaller devices such as industrial boilers, process heaters and furnaces [Wood, 1994]. In New Hampshire the NO_x RACT (reasonably available control technology) rule adopted by the state governs boilers as small as 50 MMBtu/hr (million BTU's per hour heat input based on higher heating value of the fuel). Stationary internal combustion engines with heat inputs as low as 4.5 MMBtu/hr are also regulated [New Hampshire Code of Administrative Rules, 1994].

Several factors inhibit the development of a NO_x control technology that can meet the emissions regulations in place, as well as those expected to be enacted in the near future. Two primary problems are the properties of nitric oxide, the predominant form of NO_x produced in combustion, and the wide variety of combustion processes where NO_x is formed. Nitric oxide is a unreactive molecule and on dissociation it releases oxygen. This has hindered the development of a NO_x reduction catalyst for wide use since the activity of new catalyst for nitric oxide is low and is quickly lost as the surface is poisoned by oxygen.

The wide array of combustion systems in use for power generation, transportation, industrial needs and heating and cooling purposes are the second obstacle to the development of a general NO_x control technology. A variety of fuels is burned in these devices, including natural gas, propane, gasoline, fuel oil (both light and heavy), and coal. Combustion conditions under which each of these fuels is burned can vary considerably from one device to the next. Rich burn engines in which the amount of oxygen supplied to the combustion process is insufficient to completely burn the fuel are in use. At the other end of the spectrum are gas turbines where much larger amounts of air than needed for complete combustion are used to keep combustor exhaust temperatures low enough to prevent damage to turbine blades.

Fuel type and how it is burned significantly affects the mechanism by which NO_x is formed in the combustor. A major path is through fixation of atmospheric nitrogen which occurs at high temperature (thermal NO_x). It is the predominant NO_x formation mechanism in the combustion of gaseous fuels. A second major formation mode is through the fixation of fuel bound nitrogen and is a significant contributor to NO_x formation in solid and liquid fuel combustion. A third, and relatively minor mechanism is the fixation of atmospheric nitrogen through reactions with carbon in the fuel which eventually leads to nitric oxide formation [Seinfeld, 1988]. Called prompt NO , this form is a small contributor to overall NO_x emissions, but it takes on greater importance as emissions limits become more restrictive.

A vast array of NO_x control technologies are under development in an attempt to overcome the problems associated with controlling NO_x emissions. They fall into two

general categories: (1) preventing the formation of NO_x in the combustor and (2) post combustion treatment. The first strategy, preventing NO_x formation, is the most desirable since it eliminates the need for any post combustion processing. Technologies to prevent NO_x formation include load reduction, fuel switching, fuel biasing, air staging, water injection, burners out of service, low- NO_x burners, overfire air, gas reburning, flue gas recirculation, reduced air preheat and low NO_x concentric firing systems. Each of these systems aims to reduce the temperature of the combustion process and/or the length of time the combustion gas spends at high temperature. Lower combustion temperatures reduce the equilibrium concentration in the exhaust gas and the rate at which NO_x is formed. Short combustion time periods at high temperature limit the time available to approach the equilibrium concentration.

Substantial reductions in NO_x emissions, often over 50%, have been achieved through the use of combustion modifications and fuel switching. However, three significant drawbacks to this form of NO_x control exist. First, the capital cost involved in retrofitting existing devices is often prohibitive. Second, rated output of the combustion device is often reduced when combustion modifications or fuel switching are employed. Third, in many instances there are no guarantees that the modifications will result in reduced NO_x at desired levels in the exhaust. Engineers at the steam generating plant at the University of New Hampshire investigated installing Low- NO_x burners to fire number 6 fuel oil in the steam boilers. It was found that no vendor would guarantee reduction in NO_x emissions with the use of their specific burners. It is mainly in new system design that combustion modifications can be relied upon for reducing NO_x emissions.

Downstream destruction or removal of NO_x , once it is formed by the combustion process, is the second major area of NO_x control technology. Catalytic reduction of nitric oxide (NO) and nitrogen dioxide (NO_2) to nitrogen and oxygen was the first post combustion method explored in depth. Nitric oxide's thermodynamic instability at low temperature [Shelef, 1971] indicated that a means of overcoming the activation energy for the decomposition reaction through the use of a catalyst would provide the basis for an effective control technology. Catalytic systems for NO_x control also appeared to be a natural fit with the oxidation catalysts under development to reduce emissions of hydrocarbons and carbon monoxide from internal combustion engines. Three-way catalyst systems for NO_x reduction and hydrocarbon and carbon monoxide oxidation have been successfully deployed [Mahaligam, 1981]. However, their use is limited to rich burn combustors where the exhaust gas leaving the combustion process contains significant amounts of hydrocarbons and carbon dioxide with no oxygen. Successful development of a NO_x reduction catalyst for fuel lean combustion has eluded researchers due to the two principal problems discussed earlier: the low activity of catalysts for NO_x and oxygen, contained in the gas stream or released on reduction of NO and NO_2 , poisoning the catalyst surface. Research conducted using over 600 catalyst and support combinations has yet to produce a commercially successful catalytic reduction system for lean burn combustion systems [Mahaligam, 1981].

Use of catalysts in conjunction with a reducing agent, generally ammonia, is the most successful commercial control technology for NO_x to date. Commonly known as selective catalytic reduction (SCR), this technology is being implemented on large scale

combustion systems such as those used for electrical power production. Public Service Company of New Hampshire, at the time of this writing, is in the process of installing an SCR system pulverized coal fired power plant in Bow, New Hampshire at an estimated cost of \$44 million [Power Engineering, 1995].

NO_x reacts with ammonia (or urea) over SCR catalysts to form nitrogen and water. High levels of NO_x removal (up to 90%) can be achieved at a wide range of operating temperatures, but several disadvantages exist. Operating and capital costs are high with the SCR technique and the storage and handling of anhydrous ammonia can be troublesome. In addition, achieving greater than 90% removal requires high inlet ammonia to NO_x ratios, which can result in secondary emissions of unreacted ammonia.

Reducing agents such as ammonia are also used without a catalyst. Called selective non-catalytic reduction (SNCR), this technology can achieve up to 50% reduction in NO_x emissions and does not require expensive catalytic materials. The disadvantages are relatively low NO_x reduction levels as compared to SCR, and a restricted temperature range for operation. Ammonia is oxidized to NO_x at temperatures above the maximum for operation, while it is passed through the system and released directly to the environment if too low a temperature is maintained. Use of multiple injection ports or restrictions on the heat output of the combustion device are often necessary to ensure that the NH_3 - NO_x interactions occur at the proper temperature.

The expense and limitations of existing commercial NO_x control technologies have made the development of new technology economically attractive. Several systems are presently under development. They include new designs for low NO_x burners, catalytic

combustors, and downstream treatment methods. One of the most promising classes of new technologies for post-combustion treatment of NO_x is non-thermal plasma processing of flue gas. Several techniques fall under this category, including electron beam irradiation, corona discharges, pulsed corona discharges, glow discharges and barrier discharges. Each of these methods uses energetic electrons produced by an electrical discharge to initiate a series of reactions leading to the destruction of nitric oxide and nitrogen dioxide. The major differences between these non-thermal plasma techniques are in the way energetic electrons are generated to initiate the chemical reactions and the energy consumption of each process.

The objective of this investigation was to conduct a study of one promising non-thermal plasma method for NO_x removal from gas streams, the barrier discharge process. This required the completion of several tasks. One was construction of a bench scale experimental apparatus, using simulated flue gas where the composition of NO_x and other constituents could be varied. The bench scale system allowed for identification of and good control over the major parameters governing the process. Incorporated into its design was the ability to control electrical parameters, the composition of the gas stream and flow conditions in the reactor. The apparatus also included analytical instrumentation adequate to quantify the effects of the major parameters on the discharge process.

Identifying the important variables controlling the operation of the barrier discharge process was the second task in the study. A key factor here was understanding the reactions by which NO_x is converted to compounds such as N_2 and O_2 . Towards this objective reaction mechanisms proposed in the literature were checked for consistency

with the experimental results obtained in this study under various conditions. Additionally, parameters that impact the efficiency of the process or energy utilization in the discharge system were identified and studied. They included those variables which govern the electrical operation of the process and the chemical reactions occurring in the discharge, such as the reactor geometry, magnitude and frequency of the applied voltage, chemical composition of the gas stream and flow conditions in the discharge reactor.

Use of catalysts materials in conjunction with the barrier discharge was investigated in an effort to control the rate of reaction and the product slate. A final task, completion of which was made possible due to an effort by Tecogen, Inc. to commercialize this technology for NO_x control, was to gain an understanding of scale-up of this process based on the barrier discharge experimental data obtained from the bench scale system and a larger process development system.

The results of this work laid a foundation for understanding the use of barrier discharges for NO_x control and for evaluating its potential for commercial application. The parameters of importance to the process identified and studied in this work are expected to provide information necessary for efficient reactor design and determination of the optimum operating conditions for an effective NO_x control technology.

CHAPTER II

LITERATURE REVIEW

Release of nitrogen oxides to the atmosphere has been known for many years to have adverse effects on the environment [Spengler, 1990]. Research into technologies capable of reducing NO_x emissions from combustion systems has been under way since the 1960's in response to this information. Over the years many technologies have been brought to bear on limiting NO_x emissions, testifying to the difficulty and expense in treating low concentrations of NO_x in gas streams.

A relatively new approach to NO_x removal has been the use of electrical techniques to overcome some of the difficulties associated with NO catalysis or to initiate the reactions leading to the decomposition of NO. These techniques fall into two categories; (1) the use of electrostatic fields (without an electrical discharge) applied to NO catalysts, (2) the use of energetic electrons to initiate chemical reactions leading to NO_x removal.

Several authors [Hoenig, 1968; Devyatov, 1975; and Domke, 1968] have shown that the application of external electric fields to semi-conducting and conducting surfaces can effectively control the adsorption of oxygen on to these surfaces. As discussed earlier, oxygen adsorption is a major problem in the catalytic decomposition of NO. Wooten and Mangold [1971] in a U.S. Patent reported that NO reduction can be achieved

using high voltages applied to a metal catalyst. The metals tested were in the form of metal wools and included aluminum, bronze, brass, steel, stainless steel, stainless steel plated with nickel, and stainless steel plated with gold. In each case NO removal was reported when a negative potential of between 6,000 and 50,000 volts was applied to the catalysts being tested. Each catalyst was reported to lose its NO removal capability after only a few minutes except gold plated stainless steel, which was reported to have maintained a high level of NO removal (>90%) for periods up to forty hours. The gas containing NO was obtained directly from the exhaust of an automobile engine.

Wooten and Mangold's patent represents the only investigation found in the literature in which the technique of applying negative potentials to metal surfaces was used to achieve NO removal. The patent provided few details of the experiments conducted. Personal discussions with Mr. Wooten shed no additional light on the exact procedures used to obtain these results. Attempts by the author to reproduce these results were not successful and the claims made in the patent could not be verified [McLarnon, 1989].

Recent work on the reduction of NO_x emissions in combustion exhaust gas is making use of the free electrons generated by electrical discharges. The ability to initiate chemical reactions through the use of electrical discharges has been known for many years. In the 1850's Siemens produced a capacitively coupled electrical discharge device for the production of ozone (O₃), subsequently named the Siemens Ozonator. It is still in use today to generate ozone for use in water purification systems [Eliasson, 1987].

Investigation of the electrical discharge-initiated reactions of nitrogen oxides was

first undertaken by Joshi [1927, 1929a, 1929b, 1929c]. Decomposition of nitrous oxide (N_2O) to its elements in a Siemens Ozonator at 6,000-12,000 volts and 150 Hz was studied. Complete decomposition of N_2O to its elements was achieved in this work but the rate of reaction varied considerably over the course of the experiment. It was proposed that the rate varied due to the production of nitrogen dioxide (NO_2) as an intermediate product.

Visvanathan [1952, 1953] applied the same discharge process as that used by Joshi to study the decomposition of pure gaseous nitric oxide (NO). It was found that NO decomposed to N_2 and O_2 with nitrogen dioxide (NO_2) as an intermediate. It was also reported that the decomposition was complete at low initial pressures (< 400 mmHg) but that at higher pressures the reaction stopped before all of the NO could be decomposed to N_2 and O_2 . These results were consistent with the theory of electron activation developed by Elliot et al. [1927]. Electron activation theory proposed that the rate of chemical reaction in the discharge was dependent upon the gas pressure, electron and ion current in the gas, the potential gradient across the gas and the critical energy of the colliding ions and electrons. High concentrations of electronegative NO_2 produced in Visvanathan's work at high initial pressures was considered to have reduced the electron velocity, at the pressure and voltage applied to the system, to a value below the critical velocity needed for NO_2 decomposition.

Bes [1970, 1973, 1977, 1978] and Lacoste and Bes [1974] also studied the decomposition of NO and NO_2 in an electric discharge. The ozonator arrangement originally configured by Siemens to produce the discharge was also used in this work.

It was reported that the product of voltage and frequency was a main parameter in determining the rate of the decomposition reactions taking place. Further, it was found that when the product of the voltage and frequency was below 10^6 V/s the reaction proceeded with the formation of NO_2 as an intermediate product. However, when the voltage-frequency product exceeded 10^6 V/s no formation of intermediate NO_2 was observed.

The work performed on the electrical discharge-initiated decomposition of nitrogen oxides discussed so far was done using individually pure nitrous oxide, nitric oxide and nitrogen dioxide. These studies made significant advancements in the use of the electrical discharge technique for initiation of chemical reactions. However, the conditions under which the experiments were performed were not representative of those found in the electrical discharge processing of NO_x in combustion flue gas, where NO and NO_2 are minor constituents of the gas. The major constituents in flue gas are nitrogen (N_2), water vapor (H_2O), carbon dioxide (CO_2) and oxygen (O_2). The amounts of each component depends upon the combustion conditions and fuel used. Due to their properties and abundance in the gas N_2 , O_2 , H_2O , and CO_2 can significantly alter the pathways by which NO and NO_2 react in the discharge.

Several studies on the radiation induced chemistry of gases such as those found in combustion exhaust have been undertaken. Willis and Boyd [1976] conducted an in-depth study and review of the radiation chemistry of N_2 , O_2 , H_2O , CO_2 , CO (carbon monoxide), N_2O , NH_3 , and H_2S (hydrogen sulfide). Electron impact probabilities for ionization and neutral excitation were determined in this work using a high intensity

electron pulse. Reaction rate data, reaction mechanisms and the yield of excited and ionized species per unit of radiation energy deposited in the reactor were also determined. Ions and excited chemical species (radicals and metastable compounds) generated by the discharge pulse were responsible for chemical reactions occurring in the system. Portions of this work relevant to the present study are discussed in later chapters.

Knowledge of the chemical reactions initiated by interactions of discharge produced electrons with molecules in the gas led to the development of corona discharge systems for NO_x control. Used extensively for the capture of particulate matter in combustion exhaust systems, corona discharges appeared to be a viable NO_x control technology. Reactions induced by the corona discharge are primarily those discussed by Willis and Boyd. However, the yield of ions and excited species produced per unit of electrical energy deposited in the reactor by the corona discharge varied from that determined using the electron pulse. Corona discharges had a lower yield of active chemical species, making the process energy intensive and expensive [Person, 1985; Pashaie, 1994].

There are essentially two principal drawbacks in the corona discharge technology which contribute to the high energy consumption of the process. First, the relatively small volume of the gas in which the discharge takes place limits the exposure of the gas to the active chemical species produced by the corona. Secondly, significant heating of the gas occurs due to acceleration of ions by the electric field imposed to create the discharge.

Pulsed corona discharge systems for flue gas treatment have been developed in an attempt to reduce the energy consumption of the corona discharge process. This is done

by increasing the yield of ions and excited compounds leading to NO_x removal [Masuda 1987, 1990; Civitano, 1992; Vogtlin, 1992]. The active chemical species in this technique are produced by short, strong voltage pulses. The length of the pulse is on the order of tens of nanoseconds, which produces two significant effects. First, the strength of the pulse can be higher than that possible in a continuous corona discharge, creating greater amounts of the active chemical species in a larger discharge volume. In a continuous corona the upper limit on the strength of the discharge is the point where an arc occurs, resulting in loss of large quantities of electrical energy as heat. The short duration of the voltage pulse, even at high voltages, does not allow enough time for an arc to form, yet it produces large amounts of the active chemical species for subsequent reaction.

The second effect brought about by the pulsed corona technique is the limited acceleration of ions produced in the discharge. In a typical corona discharge voltage is applied to the system continuously, establishing a constant electric field in the gas. Ions produced by the discharge are accelerated by the field. They collide with other molecules, giving up some of their energy, or in other words, heating the gas. The gas density, mass of the ions and limited electric field strength (to inhibit arcing) prevent ions from gaining sufficient energy between collisions to create more active chemical species needed to initiate chemical reactions. In a nanosecond pulse the acceleration of ions is severely limited, reducing the amount of energy that goes into heating the gas.

It has been reported that positive pulse corona discharges are more effective at producing the active species for chemical reaction [Masuda, 1992]. A positive discharge is formed by applying a positive potential to one electrode with the second electrode at

ground. A positive pulse discharge tends to bridge the gap between electrodes whereas a negative discharge is restricted to the area surrounding the high voltage electrode. Positive pulsed corona discharges represent a significant advancement over conventional corona discharges for use in NO_x control systems, but the cost of the nanosecond pulse power supply is a significant drawback to the commercialization of this technique. Development of improved and less costly power supplies is continuing.

A second method of generating electrons to initiate chemical reactions, developed to overcome the problems associated with corona discharge methods of NO_x control, is the electron beam (or E-beam) process for flue gas treatment. Developed in Japan by Ebara Corporation in the early 1970's, the E-beam process has undergone extensive experimental investigation and commercial development [Frank, 1992]. It is currently in use in pilot plants in Japan, Europe and the United States.

Free electrons produced by an electrical discharge (separate from the gas stream containing oxides of nitrogen) are accelerated to high energy levels in the E-beam process. They are then introduced into the NO_x laden gas. Extensive studies, performed by several workers [Tokunaga, 1978a, 1978b, 1978c, 1978d, 1979a, 1979b; Suzuki, 1978, 1979, 1980a, 1980b; and Nishimura, 1979, 1981a, 1981b] on the use of the electron beam technology for the removal of oxides of sulfur and nitrogen were undertaken. These studies investigated the effects of gases added to an NO-N_2 stream such as those found in combustion exhaust, including O_2 , H_2O , and SO_2 . It was found that in the dry gas mixtures NO and NO_2 were reduced to N_2 and O_2 by the E-beam process. However, when water vapor was present in the gas the predominant reactions of NO_x resulted in the

formation of HNO_3 . Reaction mechanisms proposed in this work are discussed in detail in later chapters.

The E-Beam process significantly improves with the addition of ammonia (NH_3) to the reactor. Ammonia injection results in the formation of ammonium nitrate (NH_4NO_3) by reaction with gaseous nitric acid. Sulfur dioxide in the gas reacts to form sulfuric acid, which then combines with ammonia to produce ammonium sulfate (NH_4SO_3). Ammonium nitrate and ammonium sulfate are captured downstream of the E-beam reactor using electrostatic precipitators. A small portion of the NO_x in the system is reduced to N_2 and O_2 through reaction with OH and NH_2 radicals produced by interaction of water vapor and ammonia, respectively, with electrons [Matzing, 1991]. It is reported that the efficiency of removal of NO_x with ammonia is enhanced by the presence of SO_2 in the gas stream [Frank, 1993a], making the E-beam technique more attractive for combustion systems burning fuels such as high sulfur coal.

Economic analyses of the E-beam process show that it is competitive with combined flue gas desulfurization-selective catalytic reduction (FGD-SCR) systems for emissions control in exhaust of large combustion facilities such as utility power plants and large industrial boilers [Frank, 1993b]. The cost of the accelerators producing the energetic electrons is still high and represents the major cost in the installation of E-beam systems. Development efforts to reduce this cost and increase reliability of the accelerators are presently underway. High installation costs, the need for ammonia and equipment to capture ammonium nitrate and ammonium sulfate make the E-beam process unattractive for use on small combustion systems.

An electrical technique which produces energetic electrons without the complicated and expensive power supplies required by the pulsed corona discharge and E-beam methods is the dielectric barrier discharge technique. This is essentially the same process developed by Siemens for ozone generation mentioned earlier. Recent advances in diagnostic tools have facilitated a better understanding of processes that occur in the dielectric barrier discharge. Renewed interest in this form of electrical discharge has resulted in many investigations of the fundamental processes that take place.

The only investigation reported in the literature in which an electrical discharge in the presence of a non-conducting catalytic material was used to remove NO from a gas stream is reported by Henis [1976]. In this investigation, an NO-N₂ gas stream was subjected to a barrier discharge with low conductivity catalyst materials in the gas space between coaxial electrodes. Several catalyst support materials were used including alumina, silica, macroporous silica, silica gel, silica-alumina, 1% potassium hydroxide on silica, zirconium silicate and thoria.

Henis found that the use of non-conducting catalyst materials increased the NO removal over that achieved in the unpacked barrier discharge reactor. The maximum NO removal was reported to be 79% using zirconium silicate at an inlet NO concentration of 1500 ppm and a gas residence time of approximately 2.8 seconds against a removal of 18% when no packing material was used under similar conditions. Henis reported that the enhanced removal may have been due to a combination of induced discharge and surface reactions to decompose NO. It was also reported that the presence of oxygen in the gas stream reduced the removal of NO. Use of catalysts in conjunction with dielectric

barrier discharges is investigated in the current work.

Extensive research and development activity in the field of electrical discharge-initiated reactions for the control of NO_x in flue gas streams is underway. It is an indication of the potential of such a technology for the control of NO_x emissions from the vast array of combustion devices currently employed. The present investigation is an attempt to gain an understanding of the barrier discharge process for NO_x control which could lead to the development of a safe, effective and economical technology.

CHAPTER III

BARRIER DISCHARGE THEORY

Barrier discharges are one of several types of electrical breakdowns that fall under the classification of nonequilibrium discharges, also called non-thermal plasmas. This chapter discusses the general characteristics of both equilibrium and nonequilibrium discharges, the types of nonequilibrium discharges and the chemical reactions they initiate. Emphasis is placed on barrier discharges for chemical processing.

An electrical discharge is a phenomenon wherein free electrons are produced and accelerated under the influence of an electric field. Free electrons can be generated by any number of sources including cosmic rays, a source of radiation, or cold cathode emission from an electrode surrounded by a strong electric field. Once generated, free electrons are accelerated by the field [Fite, 1969]. Through collisions with molecules in the gas, electrons cause excitation, ionization, electron multiplication and the formation of atoms and metastable compounds. It is the formation of these atoms and compounds that gives an electrical discharge its unique chemical environment and makes it useful for chemical processing.

Two major categories of electrical discharges are equilibrium and non-equilibrium discharges. Equilibrium discharges (also known as plasmas or thermal plasmas) are those in which there is an equipartition of energy among the charged and neutral species in the

gas. That is, electrons and ions in the gas are at the same temperature as the neutral gas atoms and molecules. An example of an equilibrium discharge is the arc produced in electric arc welding. Typically, the gas temperature in an equilibrium discharge is high, on the order of thousands of degrees. Large amounts of electrical energy must be supplied to the gas to achieve the high temperature condition, making it expensive for use in chemical processing.

Non-equilibrium discharges (also called non-thermal plasmas or partial discharges) are those in which there is a significant difference in temperature between the charged and neutral species in the gas. Free electrons produced in the gas are at high temperature while the gas is maintained at low temperature. As stated earlier, electrons give up some of their energy through collisions with the neutral gas molecules, resulting in excitation and ionization of the gas. This causes a condition where the chemical species produced by the discharge are those that would be expected at temperatures closer to the electron temperature than that of the bulk gas. For example, in the case of a corona discharge (one form of non-equilibrium discharge) in hydrogen at room temperature, the dissociation of hydrogen found is that which would be expected under equilibrium conditions at 4000 K [Fite, 1969]. Producing a chemical environment that behaves as if it is at high temperature without having to supply the energy needed to heat the gas is an attractive feature of non-thermal plasma chemical processing.

Electrical Discharge Physics

In order to initiate an electrical discharge an electric field must be established that

is strong enough to cause breakdown of the gas, freeing electrons, which are then accelerated by the electric field. The field is generally established by applying a high voltage across two electrodes separated by a gas gap.

Electrical discharges, once initiated, are complex phenomena whose behavior depend on numerous variables. They include but are not limited to, the nature of the gas in the discharge gap, gas pressure and temperature, the size, geometry and spacing of the electrodes, conditions at the surface of the electrodes and the polarity and frequency of the applied voltage. In addition, the discharge can be affected by what has happened previously in the gas (memory effects). For example, residual ions in the gas produced during the previous cycle in an ac discharge. The complexity of the discharge has made modelling of the physical system rather difficult. A reasonably complete model of the discharge must provide simultaneous solutions to the Boltzmann equation for electron energy distribution, the continuity equation for the conservation of charge and the Poisson equation for the electric field distribution. A complete physical model must also take into account the chemical species produced and their properties. Progress has been made in developing accurate models, but knowledge of the initial or boundary conditions needed to solve the coupled differential equations describing the system are available for only the simplest situations. Much of the work relies on empirical equations specific to a given situation.

An example of an empirical formula proposed to predict initiation of an electrical discharge is Peek's law [Peek, 1929]. Developed to determine the electric field strength for discharge initiation in air, Peek's law takes on several forms depending upon the

electrode geometry used. For a coaxial cylinder electrode geometry the field strength at the surface of the center electrode for initiation of the discharge is given by:

$$E_{r,s} = E_0 m \delta \left[1 + \frac{k}{(\delta r)^{1/2}} \right] \quad (3.1)$$

where: $E_{r,s}$ = Threshold electric field strength for discharge initiation (KV/cm)
 E_0 = 31 KV/cm
 m = Coefficient describing the center electrode surface ($0.6 < m < 1$)
 δ = $0.392p/(273+T)$ ($\delta = 1$, for $p = 760$ torr, $t = 25^\circ\text{C}$)
 k = $0.308 \text{ cm}^{1/2}$
 r = radius of the center electrode (cm)

Peek's law has been found to be valid for air at several torr to several atmospheres, for center electrode radii between 0.1 mm to several centimeters, and for applied voltages from dc to several kilohertz. The general form of Peek's law has also been found to be valid for gases other than air [Goldman, 1978].

It can be seen from equation (3.1) that the threshold field strength for discharge initiation is dependent upon the temperature and pressure of the gas. It also depends on the radius and surface properties of the center electrode in the coaxial cylinder electrode system. Equation (3.2) gives the electric field distribution in the coaxial electrode geometry:

$$E_r = \frac{0.001 \lambda}{2 \pi \epsilon_0 r} \quad (3.2)$$

where: E_r = Electric field strength at radius r (KV/cm)
 ϵ_0 = Permittivity constant ($= 8.85 \times 10^{-12} \text{ C}^2/\text{N}\cdot\text{m}^2$)
 λ = Charge per unit length of the electrode (C/m)
 r = radius of the center electrode (cm)

Equations (3.1) and (3.2) can then be used to determine the threshold voltage for

discharge initiation (V_s) with electrodes of radii r (center electrode) and R (outer electrode):

$$V_s = E_{r,s} r \ln(R/r) \quad (3.3)$$

For example, in a system with an outer electrode radius of 2.5 cm, an air pressure of 1 atmosphere (760 torr) and a temperature of 25°C, the threshold field strength ($E_{r,s}$) and threshold voltage (V_s) using a smooth ($m=1$) 0.1 cm center electrode are calculated to be 61.2 KV/cm and 19.7 KV, respectively. The threshold values change to 40.6 KV/cm and 37.2 KV when the center electrode radius is increased to 1 cm. A decrease in the threshold field strength but an increase in the voltage are needed to initiate the discharge due to the increase in electrode diameter.

Once the discharge is initiated current flow between the electrodes depends on several variables. For all but the weakest discharges, the electric field established by the applied voltage is distorted by the space charge present in the gas. In some cases the space charge increases the field strength, enhancing the flow of current. For weak discharges, those where the degree of ionization of the gas is low, an empirical equation developed by Townsend for use with coaxial electrodes of radii r (center electrode) and R is:

$$I = \frac{2KV(V-V_s)}{R^2} \ln(R/r) \quad (3.4)$$

where: I = current flow per unit length of the electrode (A/cm²)
 K = mobility of the charge carrier
 V = Applied voltage (V)

This form of equation (3.4) holds for other geometries as well. In each case the current

is proportional to the product of the mobility (K), voltage (V) and excess voltage ($V-V_s$).

The electric field (E) imposed on the gas by applying a voltage initiates the discharge. However, the resulting discharge is dependent on the reduced field, the electric field (E , V/cm) divided by the number density of molecules in the gas (n , molecules/cm³). The reduced field is used to provide a measure of the breakdown strength of a gas. For example, air breaks down at a reduced field of approximately 100 Td (Townsend, 1 Td = 10^{-17} V-cm²). From the calculations of the threshold field for the two coaxial electrode examples discussed above, the reduced field at the surface of the center electrode and the point of corona initiation is 248 Td for the 0.1 cm center electrode and 80 Td for the 1 cm center electrode.

The reduced field (E/n) also provides a measure of the electron energy in the plasma and whether or not the discharge is an equilibrium discharge. The electric field strength (E) determines the force on an electron, accelerating it to high velocity ($a = eE/m$ where a = acceleration, e = electron charge, E = electric field strength, and m = mass of the electron). The number density (n) is inversely proportional to the distance an electron travels before colliding with an atom or molecule (mean free path between collisions). At low values of E/n (<1 Td) the electrons do not gain a significant amount of energy between collisions, allowing them to equilibrate with the surrounding gas, producing an equilibrium plasma [Eliasson, 1992]. High pressure systems (atmospheric pressure or above), because of their high number density, generally result in equilibrium discharges. Only through the use of special electrode configurations, which will be discussed later, can a non-equilibrium discharge be created at high pressure.

Table 3.1
Characteristics of Non-Equilibrium Discharges

Parameter	Type of Discharge		
	Glow	Corona	Barrier
Pressure (Bar)	$<10^{-2}$	1	1
Electric Field (KV/cm)	.010	0.5 - 50	0.1 - 100
Reduced Field (Td)	50	2 - 200	1 - 500
Electron Energy (eV)	.5 - 2	5	1 - 10
Electron Density (cm^{-3})	$10^8 - 10^{11}$	10^{13}	10^{14}
Degree of Ionization	$10^{-6} - 10^{-5}$	small	10^{-4}

Nonequilibrium Plasma Discharges

Several categories of nonequilibrium discharges exist, each with its characteristic properties. These include glow, corona, barrier, RF and microwave discharges. RF (or radio frequency) and microwave discharges have limited use in chemical processing due to the low electron energies in the discharge [Dhali, 1991] and will not be discussed further. Table 3.1 lists order of magnitude values of the pressure, electric field intensity, reduced field, electron energy, electron density and degree of ionization for glow, corona and barrier discharges [Eliasson, 1992], those most often used for chemical processing. The degree of ionization listed in the table is the ratio of the number density of charged species in the gas to the number density of neutral species.

Glow discharges are stationary discharges produced at low pressure. They can be initiated at low voltage and therefore in a relatively weak electric field. Low number density, due to the low pressure, produces a high reduced field. Electron energy in a glow discharge is low, from 0.5 to 2 eV, equivalent to a temperature of 5,000 to 20,000

K. The electron density and degree of ionization are also low but the discharge is a volume discharge, meaning that it completely fills the gap between electrodes, exposing large volumes of gas to the discharge. Low voltage needed to initiate the discharge is advantageous but the low pressure required in the system limits the industrial usefulness of this type of discharge for chemical processing. Glow discharges are widely used for laboratory studies of discharge initiated chemical reactions.

Corona discharges, unlike glow discharges, can be operated at atmospheric or higher pressures, requiring strong electric fields to initiate the discharge. As discussed previously, at high pressure the reduced field is low because of the high number density of molecules in the gas. Electrode arrangements must be such that the electric field is not uniform throughout the gas space to prevent an equilibrium discharge from occurring. That is, at some point in the gas the field strength must drop below that needed for ionization. Electrons in the low field strength region then attach themselves to the gas, and the current between electrodes is limited by the relatively slow movement of ions through this region. Curved electrodes, such as a wire in a wire-cylinder arrangement or a pointed electrode in a point to plane arrangement, establish the needed electric field distribution. The field strength in the vicinity of the curved electrode, when sufficient voltage is applied, is high enough to create the discharge but the field weakens rapidly as one moves away from the electrode. Another way of stating this is that the electron ionization coefficient in a portion of the gas space close to the highly curved electrode exceeds the electron attachment coefficient, but in the remainder of the gas space the attachment coefficient dominates.

Creating an active discharge region in only a portion of the gas space limits the applicability of the corona discharge technique for chemical processing [Pashaie, 1994]. Active chemical species are produced in the region immediately surrounding the curved electrode, allowing large volumes of gas to bypass this region and limiting the amount of gas that can contact the reaction initiating species. A second disadvantage of the corona discharge technique is the energy consumed in accelerating ions produced in the gas. In typical corona discharge applications such as in electrostatic precipitators, a dc voltage is applied and a continuous corona is produced. The electric field is constant and ions produced in the discharge are accelerated by the field, heating the gas. To reduce the energy consumption due to heating, fast rising pulse corona reactors are under development [Verhaart, 1989]. In these systems voltage is applied in a pulse of a few nanoseconds. This is long enough to create the discharge and resulting active chemical species, but so long as to significantly heat the gas through acceleration of ions.

Barrier discharges, also known as silent or dielectric barrier discharges, exhibit properties of both the glow and corona discharges, making them attractive for use in producing active chemical species on a large scale. Operation at atmospheric pressure can be accomplished using barrier discharges. Also, the barrier discharge is a volume breakdown in the gas, exposing large amounts of gas to the action of the discharge. Both of these properties are made possible by the presence of a dielectric barrier between the electrodes in the system.

A dielectric barrier allows operation of the barrier discharge under conditions which would, in the absence of the dielectric material, lead to an equilibrium discharge

(arc) with its high power consumption. The barrier accomplishes this by limiting the current flow between the electrodes due to its high resistivity. A second important effect of the barrier is to change the discharge to a pulsing, non-stationary discharge randomly distributed over the surface of the electrodes. In other words, a series of microdischarges spread out about the gas space results from the presence of the dielectric barrier [Eliasson, 1992].

Microdischarges come about in the barrier discharge because charge traveling between electrodes builds up on the surface of the dielectric material, reducing the local electric field strength and extinguishing the local discharge. Surface charge accumulated due to the discharge is opposite in polarity to that induced by the applied voltage. The discharge site can only become active again by renewal of the induced surface charge density, or by change in polarity of the applied voltage, reestablishing the electric field needed for breakdown of the gas.

Microdischarge intensity and frequency are governed by several parameters such as the barrier's dielectric constant, dielectric strength, volume resistivity and surface resistivity as well as the magnitude and frequency of the applied voltage. Continuous, or direct current voltages can not be used in the barrier discharge since the charge build up on the dielectric barrier weakens the electric field, extinguishing the discharge [Van Brunt, 1994]. Also, a constant current through the dielectric material produces heat, reducing the resistivity of the dielectric, further increasing the current and producing even more heat. The process continues until the dielectric material breaks down, usually resulting in an arc.

The action of the charge buildup on the surface of the dielectric limits the duration of the microdischarge to only a few nanoseconds. But in that time a cylindrical discharge region, reaching completely across the gas space between electrodes is created [Pietsch, 1992]. This effect, in combination with the random distribution of microdischarges in space and time enables large amounts of gas to be exposed to the discharge. Short duration microdischarges also limit the amount of energy expended in accelerating ions and heating the gas, as well as limiting the heat generation in the barrier.

Catalyst Material in the Gas Space Between Electrodes

The presence of solid materials in the gas space between the discharge electrodes alters the operation of the barrier discharge. Changes in the physical characteristics of the discharge can cause variations in chemical reactions to occur. Potential effects of packing the gas space between electrodes are not fully understood. Use of these materials is to enhance the rate of the desired reactions, reduce the rate of undesirable reactions, or increase the energy efficiency of the production of the desired active species. Properties of the materials important to the process are the volume and surface resistivity of the material, dielectric properties such as the dielectric constant for highly resistive materials, shape and specific surface area, and catalytic properties for the reactions of interest.

Solid packing materials affect the physical characteristics of the discharge. A highly conductive material eliminates the discharge through the bulk of the gas region by eliminating the potential difference across the gas. Any discharge that occurs will take place at the dielectric boundary, the region of high electric field strength. In effect, a

conductive packing material "short circuits" the discharge around the gas space. This was observed in earlier work by the author when gold plated metal wool was placed in the gas space between the electrodes [McLarnon, 1989].

Dielectric materials in the gas space do not "short circuit" the discharge. However, they do provide a greater induced surface charge in the gas space for a given electrode geometry and applied voltage, or in other words they increase the capacitance of the electrode system. Additionally, dielectric materials may provide numerous points for the microdischarges to occur, depending upon the shape of the material. A high field intensity around the tip of a fiber with an high induced surface charge density can produce a microdischarge.

A potential disadvantage in the use of solid packing materials in barrier discharge systems is the restriction on gas mixing presented by the packing. Microdischarges occur for only a few nanoseconds in a relatively small volume, but the active species produced can survive for much longer periods of time, on the order of milliseconds to seconds. This allows these species time to mix with the gas, but the packing material can severely limit their movement, changing the hydrodynamic character and thus reducing the rate of reaction and energy efficiency of the process. The use of dielectric packing materials is investigated in the present work.

Chemical Reactions in Electrical Discharges

It is the chemical action initiated by the free electrons in non-thermal plasmas which make electrical discharge systems useful in chemical processing. A discussion of

the general classes of reactions occurring in nonequilibrium discharges is presented here.

Chemical reactions in an electrical discharge are initiated by the interaction of electrons with a neutral gas molecules. Several types of interactions can result from electrons collisions with molecules. One such interaction is excitation, where some of the electron energy is imparted to the molecules resulting in excited species. A second interaction is dissociation of the molecules, e.g. production of two nitrogen atoms through electron collision with a nitrogen molecule (N_2). A third possibility is that the electrons can attach to the gas molecules, producing negatively charged ions. Attachment can also occur with dissociation producing a neutral atom and one with a negative charge.

Electron collisions with molecules can also result in ionization, where collisions free additional electrons from the gas molecules, leaving behind positively charged ions. Ionization can occur with dissociation, resulting in positively charged atoms, neutral atoms and free electrons. Ions produced in the discharge can undergo collisions with electrons resulting in recombination of positive ions with electrons or detachment of electrons from negatively charged ions. In both cases neutral gas molecules result. The electron-molecular reactions are summarized in the first section of Table 3.2, General Nonequilibrium Plasma Reactions. The symbols A and B used in the table represent atoms, A_2 and B_2 molecules, e indicates an electron and M is a temporary collision partner. An * indicates excited species while + or - denotes positive or negative ions.

Excited ions and atoms undergo further reactions through many paths. The principal pathways are classified as atomic-molecular reactions, decomposition and synthesis. Major reactions in each classification are listed in Table 3.2. Atomic-

Table 3.2
General Nonequilibrium Plasma Reactions

Electron/Molecular Reactions			
Excitation	$e + A_2$	$\rightarrow$	$A_2^* + e$
Dissociation	$e + A_2$	$\rightarrow$	$2A + e$
Attachment	$e + A_2$	$\rightarrow$	A_2^-
Dissociative Attachment	$e + A_2$	$\rightarrow$	$A^- + A$
Ionization	$e + A_2$	$\rightarrow$	$A_2^+ + 2e$
Dissociative Ionization	$e + A_2$	$\rightarrow$	$A^+ + A^- + e$
Recombination	$e + A_2^+$	$\rightarrow$	A_2
Detachment	$e + A_2^-$	$\rightarrow$	$A_2 + 2e$
Atomic/Molecular Reactions			
Penning Dissociation	$M^* + A_2$	$\rightarrow$	$2A + M$
Penning Ionization	$M^* + A_2$	$\rightarrow$	$A_2^+ + M + e$
Charge Transfer	$A^* + B$	$\rightarrow$	$B^* + A$
Ion Recombination	$A^- + B^+$	$\rightarrow$	AB
Neutral Recombination	$A + B + M$	$\rightarrow$	$AB + M$
Decomposition			
Electronic	$e + AB$	$\rightarrow$	$A + B + e$
Atomic	$A^* + B_2$	$\rightarrow$	$AB + B$
Synthesis			
Electronic	$e + A$	$\rightarrow$	$A^* + e$
	$A^* + B$	$\rightarrow$	AB
Atomic	$A + B$	$\rightarrow$	AB

molecular reactions include Penning dissociation and ionization where excited collision partners interact with gas molecules to produce atoms or ions and free electrons. Atoms and ions can react to transfer charge, or combine as listed in the table. Potential decomposition reactions include interactions with electrons to form the decomposition products and excited species interactions, listed as atomic decomposition in Table 3.2. Electronic and atomic synthesis reactions also cause electron-atom interactions, excited atom-atom interactions and neutral-atom interactions.

Modelling of the chemical reactions in a specific system is difficult since several entities such as the distribution of electron energies and reaction cross sections for electron-molecule interactions must be known to determine reaction rate coefficients. It may be pointed out that the overwhelming majority of electron interactions occur with the bulk gas, not with the minor constituents in the gas. In a nitrogen gas stream containing a low nitric oxide concentration (parts per million) the reactions leading to the destruction of nitric oxide are likely initiated by electron interaction with nitrogen. Electron-nitric oxide reactions are a minor contributor to the overall destruction process because of their infrequent occurrence.

In this investigation efforts have been made to gain an understanding of the electric, chemical and hydrodynamic effects in the decomposition process of nitric oxide by barrier discharge. The chemical reactions initiated by microdischarges in the gas are studied and the effects of several operating parameters investigated.

CHAPTER IV

EXPERIMENTAL APPARATUS AND PROCEDURE

The equipment used to identify the major parameters affecting the operation of the barrier discharge process for NO_x control and study their effects on the process consisted of two separate assemblies. Each assembly consisted of a discharge reactor with at least one dielectric barrier between the high voltage electrodes to produce the microdischarges characteristic of the barrier discharge technique.

A benchtop assembly, located at the University of New Hampshire, was designed and operated to establish the basic parameters of importance in the use of barrier discharges to destroy NO_x. It consisted of a single tube reactor using simulated flue gases for accurate control of gas composition.

The second assembly, a larger scale process development unit located at Tecogen, Inc., Waltham, MA., was designed as part of the commercial development effort that resulted from the work conducted at UNH. Built to treat flue gas from an actual combustion system burning natural gas, Tecogen's process development unit allowed for higher gas throughput and higher gas velocities than those obtainable in UNH's benchtop system. The process development unit made possible a study of the effects of actual combustion-generated flue gas and high gas velocity on the barrier discharge process. It also provided a means of conducting scale-up analysis of the information gained from the

benchtop and larger scale systems.

There were many similarities between the benchtop and process development systems including the basic reactor design. The equipment in both systems were made up of several sections consisting of the barrier discharge reactor, a gas mixing or flue gas supply section, an analytical instrumentation section and an electrical power supply and measurement section.

Bench Top Reactor System

A schematic diagram of the benchtop reactor system at UNH is shown in Figure 4.1. The barrier discharge reactor is shown in the center of the figure. The electrical supply equipment is in the upper left corner of the diagram, the gas supply and mixing equipment is in the lower left and the analytical equipment is shown in the lower right. A description of the equipment and the procedures used to obtain experimental results are presented below.

Barrier Discharge Reactor

The reactor geometry used to initiate a barrier discharge in a gas space containing oxides of nitrogen was one of concentric cylinders as shown in Figure 4.2(a) and (b). The center and outer cylinders were a solid stainless steel rod and stainless steel tube, respectively. Each of these cylinders served as an electrode while the outer cylinder also served as the pressure boundary. A high voltage was applied between the electrodes, with the outer electrode (tube) at ground potential for safety reasons. Various diameter center

Figure 4. 1: Schematic Diagram of Benchtop System

(a) Concentric Cylinder Electrode System

(b) Concentric Cylinder Electrodes - End View

(c) Bench Top Barrier Discharge Reactor

Figure 4.2: Barrier Discharge Reactor

electrodes were used, ranging from 0.1 mm to 4 mm. The inner diameter (ID) of the outer electrode (tube) ranged from 22 mm to 25 mm.

Dielectric barriers were placed adjacent to the center and outer electrodes as shown in Figure 4.2(b). One was used to cover the inner electrode and the other was used to cover the inside of the outer electrode. In some instances barriers covered both electrodes whereas in other cases only one was employed. As previously discussed in Chapter III, a dielectric barrier between the electrodes was necessary to create the microdischarges along the length of the electrodes. Dielectric materials used were mostly quartz and vycor. Tests were also conducted using Omegatite 450, a commercial insulating material consisting primarily of alumina. Each of the materials has a high electrical resistivity, low dielectric loss, and good temperature stability. Their properties are listed in Table 4.1. Quartz was used for the majority of experiments because of its high dielectric strength, low dielectric loss, and high volume resistivity. Also, the volume resistivity of quartz decreases less than that of vycor as the temperature is increased.

Reactor packing material, when used, filled the gas space between the dielectric barriers or between dielectric barrier and electrode when only one barrier was in use. Packing materials consisted of glass wool, silanized glass wool, Kaowool® (a commercial refractory material), and Linde 4A molecular sieves. The density of the glass wool packing was altered by loosely or more tightly packing the material into the reactor.

The length of the barrier discharge reactor tube, as shown in Figure 4.2(c), was 0.305 m (12"). The discharge region could be made shorter than the tube by limiting the length of the center electrode inside of the center dielectric barrier, which ran the full

Table 4.1
Properties of Dielectric Barrier Materials

	Quartz	Vycor	Omegatite 450
Composition	>99.9% SiO ₂	96% SiO ₂	99.8% Al ₂ O ₃
Thermal Expansion (m/m-°C)	5.5×10 ⁻⁷	8×10 ⁻⁷	4.4×10 ⁻⁶
Density (g/cm ³)	3.6	3.5	3.7
Log ₁₀ Volume Resistivity			
25°C	>17	17	11-14
250°C	11.8	9.7	
350°C	10.2	8.1	
Dielectric Properties at 1MHz, 20°C			
Power Factor	0.001	0.05	
Dielectric Constant	3.8	3.8	9.29
Loss Factor	0.0038	0.19	
Strength (V/m)	1.67×10 ⁷		>9.1×10 ⁶
Dissipation Factor (1MHz)	0.0002	0.0005	

length of the reactor and provided mechanical support for the electrode. The end of the reactor where the high voltage electrode entered the inlet plenum was made of Teflon, an inert, resistive material.

Gas entered the inlet plenum of the reactor, as shown in Figure 4.2(c), and travelled axially along the center electrode, exiting through the outlet plenum. A view port was installed in the exit plenum in line with the center electrode to observe the discharge. The outer stainless steel electrode for the benchtop reactor was wrapped with copper tubing fed by a constant temperature bath, cooling or heating the electrode as necessary for temperature control. Also, the entire reactor could be contained in an oven which could be heated to 100°C to prevent condensation in either the inlet or outlet plenum. Experiments at temperatures higher than 100°C could not be conducted because

of softening of the Teflon in the inlet plenum.

Gas Mixing Section

Simulated flue gas was produced for the benchtop system using cylinders of nitrogen, oxygen, carbon dioxide and nitric oxide in nitrogen as shown in the lower left portion of Figure 4.1. Water vapor was introduced to the system by passing the nitrogen stream through a stainless steel bubbler containing water. The bubbler was heated with tapes to vary the moisture content of the nitrogen stream. Gas flow lines leading to and from the reactor (0.64 cm) were also heated to prevent condensation of water vapor. Hastings model ST mass flow meters, calibrated for the bulk gas flowing through the meter, were used to measure the flowrates of dry gases from each of the cylinders.

The tubing used throughout the system was either stainless steel or Teflon, with the exception of the N₂, O₂ and CO₂ supply lines to the mass flow meters, where Tygon® tubing was employed. Teflon and stainless steel minimized the adsorption on the walls of nitric oxide or any of the products of the discharge initiated reactions. Ungrounded, type K thermocouples were installed at the inlet and outlet of the reactor to measure the temperature of the gas entering and leaving the reactor.

High Voltage Power Supply and Measurement

High voltage AC power was supplied to the reactor through the electrical system shown in the upper left corner of Figure 4.1. A Powertron 500S variable voltage (0-120 V), variable frequency (20-20,000 Hz) power supply was used to power a Neeltran high

voltage transformer. The transformer was rated at a primary voltage of 120 V, a secondary voltage of 25,000 V and a power limit of 0.5 KVA. The secondary windings of the transformer contained high, low and center point taps which allowed the device to be used in either a mid-point ground or cold cathode mode. The center tap was allowed to float and the low voltage tap was grounded for this work, supplying high voltage to only the center electrode of the reactor.

In parallel with the high voltage transformer was a set of inductors to tune the circuit to the power supply. The inductors, individually ranging from 10 to 25 mH, were arranged in series-parallel configurations to reduce the reactive current draw on the power supply. This was necessary due to the fact that the reactor appeared to the power supply as a cylindrical capacitor with its capacitance dependent upon the reactor length, electrode spacing, size and type of dielectric barrier(s), and the amount and type of catalyst packing used. The impedance seen by the power supply, which was dependent on the frequency of the applied voltage, was the reactor impedance multiplied by the square of the windings ratio of the high voltage transformer.

High voltage supplied to the reactor was measured using a Tektronix P6015 high voltage probe (1000x) in series with a Tektronix P6109 probe (10x), effectively dividing the voltage by a factor of 10,000. The signal from the probe was fed to a Tektronix 2211 digital storage oscilloscope sampling at 20 MHz. The current in the secondary circuit of the high voltage transformer was measured using a series resistor as shown in Figure 4.1 and a Tektronix P6027 (1x) probe. The resistors used varied from 25 to 50 ohms. This signal was fed to channel 2 of the oscilloscope.

Power consumption in the reactor (discharge power) was measured using the voltage and current traces recorded and stored by the oscilloscope [Manley, 1943]. Digital storage in the oscilloscope was done using an 8 bit analog to digital converter for the voltage measurements. 4000 samples per channel were recorded by the oscilloscope. A FORTRAN computer program, included in Appendix A, was written to read the values recorded by the oscilloscope, convert them to the proper units based on the oscilloscope settings and series resistance value, and calculate the power input to the reactor.

A schematic diagram of the high voltage electrical circuit is shown in Figure 4.3. The capacitors C_{ab} and C_{cd} shown in the figure were made up of the inner and outer dielectric barriers while the capacitor C_{bc} was due to the gas space. The resistance R_{bc} was essentially infinite before the onset of the discharge but took on a finite value after breakdown of the gas and the discharge is initiated.

A typical voltage-current trace for the benchtop reactor at UNH is shown in Figure 4.4. The measured current trace was inverted to maintain the proper polarity between the

Figure 4.3: Schematic Diagram of Barrier Discharge Reactor Circuit

Figure 4.4: Voltage and Current Traces for 400 Hz

voltage and current for power calculations. The measurements presented in Figure 4.4 were recorded at a frequency of 400 Hz and a peak voltage of 27.6 KV.

A second voltage-current trace, shown in Figure 4.5, was obtained at a frequency of 1000 Hz and a peak voltage of 22.0 KV. The trace shows that at elevated frequencies the reactor electrical system distorted the applied voltage waveform from the sinusoidal shape seen in Figure 4.4. This was characteristic of the system response and could not be corrected by changing the inductors in parallel with the high voltage transformer.

Product Analysis

The inlet gases to the reactor and the reactor exhaust were analyzed using several commercial gas analyzers, a gas chromatograph and specific ion probes. Before gases

Figure 4.5: Voltage and Current Traces for 1000 Hz

entered the analyzers moisture was removed through the use of cold traps submerged in ice water. Condensate collected in the trap could then be analyzed using the specific ion probes or ion test strips. The sample lines leading to the cold trap were heated using heat tapes to minimize adsorption to the walls and prevent condensation. The inlet gas composition was measured by opening a bypass valve to stop the gas flow through the reactor and instead go directly to the analyzers.

NO-NO₂-NO_x Analysis - A Thermo-Electron model 10A/R Chemiluminescent NO-NO₂-NO_x analyzer was used to measure the concentration of oxides of nitrogen in the gas stream entering or exiting from the reactor. The method of analysis used by the device was the well known reaction of nitric oxide with ozone to produce excited nitrogen dioxide. Light emitted from excited NO₂ was measured by a photomultiplier tube. Total

NO_x concentration was determined by first passing the sample through a high temperature (650°C) stainless steel converter which reduced oxides of nitrogen (NO_2 , N_2O_4 , and N_2O_5) [Winer, 1974] to NO , which was subsequently measured as discussed earlier. The difference between NO and NO_x readings was taken to be NO_2 .

Nitrous oxide (N_2O), a possible product in the barrier discharge initiated reactions of NO , could not be detected by the $\text{NO-NO}_2\text{-NO}_x$ analyzer. A Hewlett-Packard 5890 Series II gas chromatograph with a thermal conductivity detector was employed to determine if N_2O was present in the reactor exit gas. A 9' by 1/8" stainless steel column packed with 50/80 mesh Porapak T, obtained from Supelco, Inc. was used to separate N_2O from the other gases in the stream.

Oxygen, Carbon Dioxide and Carbon Monoxide Measurement - A Nova model 375 portable combustion analyzer was used to measure the O_2 , CO_2 and CO concentrations in the gas stream. The oxygen and carbon monoxide analyses were performed in the analyzer using electrochemical cells while the carbon dioxide analysis was performed using an infrared cell.

Water Vapor Measurement - An EG&G Environmental model 911 digital humidity analyzer was used in the benchtop system to measure the water vapor content of the inlet gas. The instrument used the chilled mirror dew point condensation principle. It was installed upstream of the reactor to prevent condensation of acids or other potentially damaging compounds on the mirror surfaces.

Nitric Acid Measurement - The analysis of nitric acid produced in the barrier discharge presented several problems during the course of this investigation. Nitric acid

strongly adsorbed to the Teflon and stainless steel tubing used in the reactor supply and exhaust lines. If allowed to enter the NO-NO₂-NO_x analyzer it decomposed in the high temperature converter and was picked up as NO_x. Use of the cold traps at the immediate exit of the reactor condensed the acid, preventing contamination of the downstream sampling lines. The nitrate concentration in the condensate was measured using specific ion probes and specific ion test strips, but this proved troublesome and accurate results could not be obtained. A simpler procedure was developed in which the sample gas was passed through a 1 meter length of 3.2 mm stainless steel tubing enclosed in a high temperature furnace at 700°C. The nitric acid present in the gas stream was completely decomposed to NO and NO₂. The gas was then passed through a cold trap to remove moisture and delivered to the NO-NO₂-NO_x analyzer where the NO_x concentration was measured. This concentration was then compared to the NO_x concentration of a sample stream which was not passed through the high temperature furnace. The difference was taken to be HNO₃. Tests performed on nitric acid laden gas streams, prepared by introducing acid into the gas stream, showed that the temperature and residence time of the gas in the high temperature furnace was sufficient to completely decompose all of the acid to NO. The nitric oxide could then pass through the cold trap to the NO-NO₂-NO_x analyzer.

Process Development Reactor System

The size of the benchtop system constructed at UNH was small and the gas flowrates that could be used were limited. A process development reactor system was

constructed at Tecogen, Inc. to test higher gas flowrates and to test the barrier discharge technique on actual combustion generated flue gas. A schematic diagram of the development system is shown in Figure 4.6. As previously stated, there were many similarities between the benchtop and development systems. Discussed here are those components of the development system that differed from the benchtop apparatus.

Process Development Reactor

The benchtop reactor consisted of a single pass as shown in Figures 4.1 and 4.2, which limited the residence time and flowrates that could be achieved. To increase the overall length of the reactor a multi-tube reactor was constructed at Tecogen. It consisted of seven, parallel, 1.22 m long stainless steel tubes with an ID of 28.6 mm. Surrounding the tubes was a jacket through which a fluid (water or ethylene glycol) could be pumped to control temperature. The reactor was configured so that flow could be directed through the seven parallel tubes or through three sets of tubes in series, each set consisting of two parallel tubes. The seventh tube in the series arrangement was plugged. Provisions were made to obtain samples after each set of tubes. By this arrangement samples could be obtained after 1.22, 2.44, and 3.66 m lengths. The process development reactor volume (when the three sets of two tubes were employed) was over 30 times greater than the volume of the benchtop reactor.

Two additional single tube reactors were constructed for use in the development system, a 25.4 mm ID reactor with a length of 0.61 m and a 51 mm ID reactor that was 1.3 m long. The length of the discharge zone could be shortened by shortening the length

Figure 4.6: Schematic Diagram of Development System

of the center electrode inside the dielectric barrier. For each of the development reactors only a center dielectric barrier was used.

The multi-tube development reactor used polysulfone insulators at the point where the high voltage electrode penetrated the reactor. The two single tube reactors used a ceramic high voltage insulator.

Flue Gas Supply

The flue gas supply section for the development system consisted of a small gas burner fired with natural gas. A line bleeding pure NO into the system was also installed to provide a means of increasing the NO_x concentration to desired levels. Natural gas flow was measured using a standard gas meter and stopwatch, and the air flow through the burner was controlled using a slide valve at the suction of an induced draft fan, located at the outlet of the reactor. Water cooling at the exit of the burner reduced the gas temperature to the desired value, preventing damage to the reactor and exhaust gas lines which were insulated and heated to maintain temperature and prevent water vapor from condensing. The inlet gas was sampled by switching a three way valve to draw gas directly from the reactor inlet.

Power Supply and Measurement

A Powertron 3000S variable voltage, variable frequency power supply was used to feed the high voltage transformer as shown in Figure 4.6. Essentially a larger version of the model used in the benchtop system, the power supply was rated for an output of

0-260 V and 3 KVA at frequencies from 20 to 20,000 Hz. A Boston Transformer cold cathode transformer, rated at 35,000 V and 5 KVA, was used to supply high voltage to the reactor.

The voltage and current measurement circuits for the development reactor were similar to those used on the benchtop system with the exception that the current and voltage signals were recorded using a Soltec 1220 digital storage oscilloscope board in an IBM PC/AT computer. The Soltec board used an 8 bit analog to digital converter and was able to store 128,000 samples per channel. A FORTRAN program written to calculate power consumption is included in Appendix B.

Gas Analysis

NO-NO₂-NO_x analysis for all of the development system testing utilized the Thermo-Electron model 10A/R analyzer as discussed previously. O₂-CO₂-CO analysis was performed using a Nova model 375T analyzer, identical to the model 375 analyzer utilized for the benchtop testing with the exception that an electrochemical cell was used for the CO₂ analysis instead of the infrared cell. Testing performed on the 51 mm ID reactor made use of Anarad infrared CO and CO₂ analyzers and a Beckman paramagnetic oxygen analyzer.

The water vapor content of the flue gas was calculated using the fuel composition and the measured O₂ concentration, corrected for water vapor removal in the cold traps.

CHAPTER V

RESULTS AND DISCUSSION

The successful development of a barrier or silent discharge technology for NO_x control requires that several criteria be met. First and foremost is that the technology effectively fulfill its objective of destroying nitrogen oxides. An important second criteria is that the reactions occurring in the process do not create and release other potentially harmful compounds, thereby substituting one pollutant for another. In addition, the technology must be cost effective and competitive with other technologies. For barrier discharge technologies the energy consumption of the discharge reactor must be kept to a minimum. High energy consumption has been the major obstacle to the successful development and acceptance of any electrical technique for combustion exhaust cleaning.

This study identifies the important variables in the barrier discharge process and their effect on the operation of the process to destroy NO_x . Understanding the process variables is necessary to optimize the performance of the technology and to make it commercially viable. Several of the variables investigated are of importance in any process which utilizes barrier discharges. These basic parameters include frequency, electrode size and spacing, and properties of the dielectric barrier. Other variables studied are specific to the use of electrical discharges to destroy NO_x in flue gas exhaust streams, including the NO_x content in the presence of oxygen and water vapor.

The results presented in this chapter are subdivided into three sections; namely electrical effects, chemical effects and hydrodynamic effects in the barrier discharge process. Electrical parameters include frequency and voltage applied to the reactor, reactor dimensions such as electrode size and spacing, and materials of construction which determine dielectric and resistive properties of the reactor. Chemical parameters include the gaseous feed composition to the system such as nitric oxide (NO), nitrogen dioxide (NO₂), oxygen (O₂) and water vapor (H₂O) concentrations. Hydrodynamic parameters include gas residence time in the discharge reactor and degree of turbulence in the flowstream. Electrical and hydrodynamic variables can be controlled through the design of the reactor and its operating conditions while chemical parameters are essentially controlled by the combustion process where NO_x is generated.

Destruction of nitrogen oxides is measured in this study in terms of NO and NO_x conversion. NO conversion represents the amount of nitric oxide in the inlet gas that is converted to some other compound, including NO₂. NO_x conversion is a measure of the amount of NO and NO₂ entering the reactor converted to compounds other than NO and NO₂. In mathematical form they are defined as:

$$NO \text{ Conversion } (\%) = \frac{NO_i - NO_o}{NO_i} \times 100 \quad (5.1)$$

$$NO_x \text{ Conversion } (\%) = \frac{NO_{x,i} - NO_{x,o}}{NO_{x,i}} \times 100 \quad (5.2)$$

Where the subscripts i and o represent the inlet and outlet concentrations, respectively.

Several parameters are used to measure the level of electrical activity to which the gas in the reactor is subjected. High voltage applied to the electrodes along with the reactor geometry establishes the electric field distribution in the reactor while the discharge power measures the rate of electrical energy absorbed by the gas. Discharge power is a key measurement in describing the operation of the process. In combination with the gas flowrate and NO_x concentration, power is a component of two parameters that measure the efficiency of the process, the specific energy and the destruction energy. Specific energy (SE) is defined as the energy absorbed per mole of NO_x entering the reactor. The destruction energy (DE) is the energy absorbed in the reactor per mole of NO_x converted in the discharge. Specific energy is given as:

$$SE = \frac{P C_1}{NO_{x,i} Q} \quad (5.3)$$

where:

SE	=	Specific Energy (KJ/mole)
P	=	Discharge Power (W)
NO _{x,i}	=	Inlet NO _x Concentration (ppm)
Q	=	Gas flowrate (l/min at STP)
C ₁	=	Conversion Factor (1.345x10 ⁶ KJ ppm l / mole W min)

Destruction energy is:

$$DE = \frac{P C_1}{Q (NO_{x,o} - NO_{x,i})} \quad (5.4)$$

where:

DE	=	Destruction Energy (KJ/mole)
NO _{x,o}	=	Outlet NO _x concentration (ppm)

The first of the following four sections covers the effect of electrical parameters on the discharge process. The second section deals with the effects of changing the chemical composition of the reactor inlet gas. The benchtop reactor system with simulated flue gas made up from cylinder gases was used to obtain the results discussed

in the first two sections. The third section covers the effect of the hydrodynamic parameters, using experimental data from the development reactor system utilizing combustion-generated flue gas as the inlet stream. The fourth section discusses the electrical and chemical models developed to gain an understanding of the process for scaling up the barrier discharge technology to larger systems.

Electrical Parameters

The electrical variables, in a barrier discharge, affect the operation of the system in two major ways. First, the effective use of these parameters can enhance the efficiency of the discharge process as measured by the NO_x conversion, voltage and energy requirements, to achieve an optimal design. Secondly, the reaction path sequence and consequently the product slate can be controlled. In this section the effects of voltage, frequency, catalyst packing materials and electrode spacing on NO_x conversion and energy requirements are discussed. All of the experimental results presented here are obtained using a mixture of nitric oxide (NO) in nitrogen (N_2). In this system the destruction of NO results in the formation of molecular nitrogen (N_2), molecular oxygen (O_2) and small amounts of nitrogen dioxide (NO_2). NO_x conversion for the NO- N_2 system can therefore be taken as the percentage of the inlet nitric oxide which is converted to N_2 and O_2 .

Effect of Voltage on NO_x Conversion

The effect of voltage on NO and NO_x was studied in a reactor with the configuration shown in Figure 4.2. The length of the reactor used was 30.5 cm with an

center electrode diameter of 4 mm and an outer electrode diameter (ID) of 25 mm. A vycor dielectric barrier, adjacent to the outer electrode, was used with an ID of 22 mm and an OD of 25 mm. The reactor was packed with glass wool at a density of 0.20 g/cm³. Nitric oxide, at a concentration of 500 ppm in N₂, was passed through the reactor at 25°C and at a flowrate resulting in a residence time of 2 seconds.

NO and NO_x conversions as a function of voltage at a frequency of 60 Hz are shown in Figure 5.1. The "S" shape of the two curves is representative of the system response when conversion is plotted in terms of voltage. At voltages below the discharge onset voltage, approximately 7 KV (peak voltage) for the conditions shown in Figure 5.1, no discharge takes place (as seen by the current draw of the system) and no reactions

Figure 5.1: Effect of Peak Voltage on NO and NO_x Conversion

leading to the decomposition of nitric oxide occurred. Increasing the voltage above the onset voltage increased the intensity of the discharge, which was observed visually, and increased the NO conversion, which asymptotically approached 100%. Figure 5.1 also shows that for a fixed reactor configuration and set of operating conditions, the voltage applied to the electrodes controlled the conversion achieved in the reactor.

Only a small difference between the NO and NO_x conversion shown in the figure was observed when the gas mixture is composed of nitrogen and nitric oxide. For example, at 15 KV for the given reactor configuration and operating conditions, 90% NO conversion was achieved versus 88.2% NO_x conversion. The 1.8% difference in NO and NO_x conversion resulted in an outlet NO₂ concentration of 9 ppm. Visvanathan [1952] showed that the decomposition of nitric oxide in the barrier discharge, using NO in N₂, proceeded through an NO₂ intermediate and it was this intermediate that resulted in the difference between NO and NO_x conversion. Throughout the remainder of this section NO_x conversion, the lower of the two conversion values, was used in the presentation of results. It may be assumed that NO conversion was only marginally higher than the NO_x conversion and that the formation of NO₂ was minimal. Wherever a significant difference between NO and NO_x conversion existed both values are presented.

Effect of Frequency on NO_x Conversion

The effect of frequency on NO_x conversion was studied in a second set of experiments. The reactor system used was the same as that employed to study the effect of voltage discussed above. The experiments were conducted using a glass wool packing

Figure 5.2: Effect of Peak Voltage and Frequency on NO_x Conversion

of density 0.12 g/cm³, an inlet gas containing 250 ppm NO in N₂, a gas residence time of 1.1 seconds, a temperature of 30°C and a Reynolds number of 300. The results, presented in Figure 5.2, show that as voltage applied to the center electrode was increased for each frequency, the NO_x conversion increased. Furthermore, NO_x conversion increased with frequency for a given voltage as the frequency was raised from 60 to 1000 Hz. At 20 KV (kilovolts) conversion values of 12, 13, 20, 30, 54, 87, and 99.5% were obtained at frequencies of 60, 110, 150, 200, 400, 800 and 1000 Hz, respectively. The rate of increase in NO_x conversion with voltage also increased as the frequency was increased from 60 to 1000 Hz. This can be seen from the slope of each of the curves fit through the data points for each frequency.

Figure 5.3: NO_x Conversion versus Discharge Power and Frequency

The results shown in Figure 5.2 are plotted again in Figure 5.3 using the discharge power, measured using the voltage and current values as described earlier, instead of peak voltage as the abscissa. It can be seen that NO_x conversion increased with discharge power. However, the effect of frequency as seen in Figure 5.2 was apparently diminished when the conversion was plotted in terms of discharge power. At frequencies ranging from 60 to 1000 Hz there was little distinguishable difference in NO_x conversion for comparable power levels. From Figures 5.1 and 5.2 it is apparent that the voltage applied to the reactor controlled the discharge power for a given reactor geometry and set of operating conditions. The effect of increasing frequency was to increase the power input for a given peak voltage or to reduce the voltage required to achieve a given discharge

Figure 5.4: Discharge Power versus Peak Voltage and Frequency

power. This is shown in Figure 5.4 where the peak voltage versus discharge power was plotted for frequencies of 60 to 1000 Hz.

Effect of Packing Material in the Barrier Discharge Process

Solid materials, generally metal compounds, are often used as a catalyst to increase the rate of reaction in many chemical systems for given operating conditions. Numerous attempts at development of a catalyst system for NO_x control have been made using several catalytic compounds and support systems as discussed in Chapter I. Three-way catalytic converters (e.g. for automobiles) are the only catalytic NO_x control systems in

commercial use which do not need an added reducing agent. The three-way systems are used to treat combustion exhaust in which the gas stream contains carbon monoxide and no oxygen. Carbon monoxide in the combustion exhaust acts as the reducing compound, stripping oxygen away from NO_x , forming CO_2 and N_2 .

The author investigated the use of gold plated metal wools in conjunction with strong electric fields (positive and negative) to decompose NO to its elements [McLarnon, 1989]. No significant effect on NO reduction was observed with the use of these materials.

Experiments using several non-conducting catalyst materials were performed in this study to investigate their effect in conjunction with a barrier discharge on the decomposition of nitric oxide. The materials included cylindrical molecular sieves (Linde 4A) as well as glass wool and Kaowool in fiber form. Kaowool is a commercial refractory material. The glass wool and Kaowool used were composed primarily of silica, while the molecular sieves were composed of aluminosilicates. The reactor configuration, inlet NO_x concentration, temperature and gas residence time were the same as in the experiments investigating the effect of voltage discussed earlier.

The NO_x conversions achieved using the catalyst materials in fiber form were higher than that obtained using cylindrical molecular sieves, as shown in Figure 5.5. Additionally, the use of any of the three catalyst packing materials resulted in higher conversion than when no packing was used. At a peak voltage of 21 KV, the NO_x conversion achieved was 98% using glass wool, 97% using Kaowool packing, 82% for the system packed with molecular sieves, and 24% for the unpacked reactor. It is also

Figure 5.5: Effect of Dielectric Packing Materials on NO_x Conversion

important to note that the conversion achieved using molecular sieves reached a maximum at 21 KV. Increasing the voltage to 22.5 KV did not result in a further increase in NO_x conversion. On the other hand, the conversion achieved with the fibrous materials asymptotically approached 100% while that obtained in the empty bed increased with increasing voltage over the entire voltage range tested.

The results presented in Figure 5.5 show that catalyst packing materials in fiber form (glass wool and Kaowool) yielded a higher NO_x conversion than the cylindrical molecular sieves. The use of glass wool and Kaowool packing also resulted in higher conversion than the maximum of 79.6% reported by Henis [1976] when cylindrical and spherical catalyst materials were used in the barrier discharge system with an NO

Figure 5.6: Effect of Glass Wool Packing on NO_x Conversion

concentration of 1500 ppm.

The effect of glass wool packing on NO_x conversion was further investigated in a reactor at room temperature with an inlet NO concentration of 250 ppm and a gas residence time of 1.1 seconds. Glass wool packings with densities of 0.30 and 0.12 g/cm³, as well as a system with no packing, were used. The results showing NO_x conversion versus discharge power for the three sets of experiments are presented in Figure 5.6. It can be seen that in terms of the power input to the reactor there was no significant difference in NO_x conversion achieved in systems with no catalyst packing material and those with glass wool packing.

The results of the experiments indicate little surface catalytic effect of the glass

wool packing material as measured in terms of reduction in power requirements for a given level of conversion. An increase in the density of the glass wool packing, and therefore an increase in glass wool surface area in the reactor, did not increase the NO_x conversion for a given discharge power.

Packing the reactor gas space with materials having dielectric properties discussed above increased the capacitance of the reactor, which produced a greater charge concentration on the surface of the reactor electrodes for a given voltage. This was seen in the higher current measured for the packed reactor systems, prior to the onset of the discharge, than that measured without packing material in the reactor. The packed reactor's higher charge build-up also resulted in a higher discharge current and therefore a higher power input to the reactor. It was this increase in discharge power that was likely responsible for the higher levels of NO_x conversion achieved when the glass wool and Kaowool packings were used.

While the use of catalyst packing did not result in higher NO_x conversion for a given power, the presence of the packing material allowed for a greater power input to the reactor without arcing between the electrodes and breakdown of the dielectric barrier(s). Packing material increased the pressure drop across the reactor, which would result in increased operating cost in a commercial barrier discharge system. However, the decrease in reactor size resulting from the use of dielectric packing may offset the increased operating cost with a reduced equipment cost. Dielectric packing material provides one more option in the reactor design for an effective chemical processing system using barrier discharges.

Effect of Gap Distance Between the Electrodes on NO_x Conversion

Visual observation of the barrier discharge showed that the region of greatest discharge intensity occurred around the center electrode, where an intense blue glow was seen in the N₂-NO system. At the outer electrode the visible glow was faint if it could be seen at all. This was due to the reduced current flux at the outer electrode brought about by the coaxial cylinder geometry. It was recognized that because of the coaxial cylinder electrode geometry, shown in Figure 4.2, most of the gas in the reactor was outside the intense discharge region. Experiments with outer electrodes of reduced diameter were conducted in an attempt to increase the percentage of the gas in the most discharge region.

The effect on NO_x conversion of reducing the distance between electrodes by decreasing the outer electrode diameter from 25 to 22 mm was studied. A center electrode with a diameter of 4 mm, surrounded by a quartz dielectric barrier (4 mm ID by 6 mm OD) was used in each set of experiments. A second (outer) quartz dielectric barrier, with a wall thickness of 1.5 mm, was placed adjacent to the outer electrode in each configuration. The resulting annulus had an inner diameter of 6 mm for both configurations, an outer diameter of 22 mm for the 25 mm outer electrode, and an outer diameter of 19 mm for the 22 mm outer electrode. Therefore, reducing the outer electrode diameter from 25 to 22 mm reduced the distance between the two electrodes (gas space gap) from 8 mm to 6.5 mm. The following conditions were used in both sets of experiments: room temperature, a gas residence time of 1.0 seconds, a Reynolds number between 225 and 290, no reactor packing, and an inlet NO concentration of 250

Figure 5.7: Effect of Varying the Outer Electrode Diameter on NO_x Conversion

ppm.

The decrease in the gap distance was found to increase the NO_x conversion as is shown in Figure 5.7. At a discharge power of 25 watts the NO_x conversion was 78% using the 25 mm outer electrode and increased to 94% with the 22 mm electrode. However, this comparison on a conversion and power basis can be misleading. In order to keep the same degree of mixing (Reynolds number) and residence time in the reactor for the two sets of experiments, the mass treated in the case of the 22 mm outer electrode was less than when the 25 mm electrode was used. To take into account the difference in mass flow between the two cases the NO_x conversion versus specific energy, as defined in equation 5.3, was calculated and plotted in Figure 5.8. It is clear that reducing the diameter of the outer electrode or decreasing the gas gap distance did not increase the

Figure 5.8: NO_x Conversion versus Specific Energy for Varying Outer Electrode Diameters

NO_x conversion on a specific energy basis.

The electrical effect of reducing the gap spacing between the electrodes by reducing the outer electrode diameter was to increase the power input to the reactor for a given voltage. Since the same center electrode system was used in both sets of experiments, the voltage at which the barrier discharge initiated did not change. This was expected and discussed in Chapter III. However, because of the reduced distance between the electrodes, the resistance of the gas was decreased and the induced surface charge for a given voltage increased (the capacitance increased) over that for the larger gap space. This resulted in a higher discharge current and greater discharge power for the smaller gap between electrodes.

Another method of changing the electric field distribution and therefore the amount of gas in the active discharge region could be to alter the diameter of the inner electrode while maintaining the outer electrode diameter constant. This was attempted using the process development reactor system at Tecogen with combustion-generated flue gas and will be discussed later in this chapter.

Effect of Gas Residence Time

Gas residence time in the reactor is not an electrical parameter but is presented here for reasons to be discussed. Figure 5.9 presents the NO_x conversion versus discharge power for tests run at three different gas residence times in a glass wool packed reactor. The residence times were varied by changing the length of the inner (high voltage) electrode, thereby changing the length of the barrier discharge region. This was done to maintain the same flow conditions for each of the three sets of experiments. The experiments were conducted in a glass wool packed reactor (0.11 g/cm^3) at room temperature with an inlet NO concentration of 50 ppm in N_2 and a Reynolds number of 300. Figure 5.9 shows that residence time in the reactor did not effect the level of NO_x conversion. Instead, the NO_x conversion was seen to be dependent only on the discharge power.

The results obtained by varying the electrical parameters and reactor configuration showed that the discharge power was the main parameter governing the conversion of nitric oxide to N_2 and O_2 in the barrier discharge reactor under the conditions tested. The effect of varying the electrical parameters was to alter the discharge power supplied to the

Figure 5.9: Effect of Gas Residence Time on NO_x Conversion

reactor. The data showed that the power input to the reactor could be controlled by several variables. Increased voltage or frequency resulted in an increased discharge power for a given reactor configuration. Reduced gas gap distance, accomplished by reducing the diameter of the outer electrode, increased the discharge power over that obtained with a larger outer electrode. The experiments also showed that increasing the gas residence time in the barrier discharge reactor increased the discharge energy per mole of gas treated. It was the increase in this energy that resulted in greater conversion as the residence time was increased.

Packing the gas space with non-conducting, fibrous material increased the discharge current, and therefore the power, for a given applied voltage and frequency.

The use of these materials allowed conversion levels of nearly 100% to be achieved in the benchtop reactor, showing that there was no other limitation to complete conversion in the system as was seen in work performed by Visvanathan [1952, 1953] discussed in Chapter II. It also enabled lower voltages to be used which prevented breakdown of the dielectric barrier and arcing in the reactor which would sometimes occur when high power levels were attempted in the unpacked system.

The use of cylindrical molecular sieves appeared to limit the maximum conversion obtainable in the benchtop barrier discharge system to values less than 100%. This may have been due to limited distribution of the microdischarges produced in the barrier discharge by the large volume surrounding a single molecular sieve pellet. Poor microdischarge distribution may have allowed some of the gas to bypass the discharge regions, preventing complete conversion of the nitric oxide.

Chemical Effects

The make up of the gas entering the barrier discharge reactor can significantly affect the performance of the reactor and thus the products of the discharge initiated reactions. This could be due to the fact that the reactions of NO and NO₂ are not primarily a result of direct interaction of NO and NO₂ molecules with the electrons generated by the discharge. Instead, the reactions may result from the interaction of NO and NO₂ with ions, metastable molecules and radicals which are produced from the action of the discharge on the bulk gas. Consequently, the composition of the bulk inlet gas as well as the concentration of NO_x in the gas can play an important role in determining the

Figure 5.10: Flue Gas Composition versus Excess Air for Natural Gas Combustion

make up of the products and the efficiency of the process.

Exhaust gas from fossil fuel combustion generally contains several compounds in large concentrations including nitrogen, water vapor, carbon dioxide and oxygen. The amount of each compound depends on the fuel burned and the amount of air used in the combustor. Figure 5.10 presents the flue gas composition from the burning of natural gas as a function of the excess air used. Exhaust from natural gas combustion contains higher concentrations of water vapor and lower concentrations of carbon dioxide than that from the combustion of gasoline, fuel oil or coal due to its high hydrogen to carbon ratio (~4:1). Combustion exhaust gas will also contain carbon monoxide, sulfur dioxide, and of course, nitrogen oxides. The amount of sulfur dioxide depends primarily on the concentration of

sulfur in the fuel while CO and NO_x concentrations are dependent on the specific combustion conditions.

Because it is the interaction of the barrier discharge with the bulk gas that largely affects the reaction sequence and products of the barrier discharge NO_x destruction process, the effect of each of the gases making up the bulk gas was studied individually. This was done by adding additional gases to the NO-N₂ mixture. Experiments were also performed using combustion-generated flue gas which, when used in this work, was generated through the burning of natural gas.

Nitrogen - Nitric Oxide Mixtures

In most of the NO-N₂ mixtures used throughout this work, N₂ made up in excess of 99.9% of the total gas. The main action of the electric discharge is essentially on the bulk nitrogen in the gas. Over 15 reactions occur from the interaction of N₂ with energetic electrons as was shown by Willis and Boyd [1976] and Harteck and Dondes [1957] using high energy electron pulses. The following reactions have been proposed to be primarily responsible for the destruction of NO in the NO-N₂ mixture [Suzuki, 1978]:

The species produced by reactions (5.5) through (5.7) react rapidly with NO as follows:

The small amount of NO₂ formed in the electrical discharge treatment of an NO-N₂ mixture is due to the reaction of atomic oxygen, formed by (5.8) and (5.11), with NO:

In addition to reaction (5.12), atomic oxygen formed by (5.8) and (5.11) combines to form O₂.

The products of the reactions leading to the reduction of NO listed in equations (5.5) through (5.11) are consistent with those found in the present work where a barrier discharge was used instead of an electron beam used by Suzuki, et al. However, the energy use of the barrier discharge method varied from that reported for the electron beam process. The energy requirements as well as the product of the reactions are discussed in the following sections.

Effect of NO Concentration in the Inlet Gas

The benchtop apparatus described in Chapter IV and shown in Figure 4.1 was used to investigate the effect of the NO concentration in the NO-N₂ inlet gas mixture on NO_x conversion. The reactor electrode configuration was as follows: a 4 mm OD center electrode, a 25 mm ID outer electrode, a 22 mm ID by 25 mm OD vycor dielectric barrier and a reactor length of 30.5 cm (12"). The experiments were performed at room

Figure 5.11: Effect of NO Concentration and Discharge Power on NO_x Conversion

temperature at a gas residence time of 1.1 seconds in a reactor packed with 0.11 g/cm³ of glass wool, allowing high levels of conversion as was shown earlier in this chapter.

Increasing the inlet NO concentration reduced the NO_x conversion attained for a comparable power input to the reactor as shown in Figure 5.11. At a discharge power of 35 watts the NO_x conversion obtained was 99.4% when the inlet NO concentration ranged from 42 to 47 ppm, 93% at 242-250 ppm, and 74% at 480-490 ppm.

The experimental data presented in Figure 5.11 are plotted again in Figure 5.12, showing the NO_x conversion versus specific energy as defined in equation (5.3). It can be seen that when NO_x conversion is plotted in terms of the energy input per mole of NO_x entering the reactor (specific energy), there is essentially no difference in the percent conversion obtained for the three concentration ranges tested. These experiments were

Figure 5.12: NO_x Conversion versus Specific Energy; Effect of NO Concentration with Glass Wool Packing

repeated for a system containing no glass wool packing and similar results were obtained as shown in Figure 5.13.

A comparison of the results obtained for the effect of NO concentration on NO_x conversion for both the glass wool packed and unpacked reactor systems indicated that the use of fibrous packing material did not increase the NO_x conversion for a given specific energy. At a specific energy of 40,000 KJ/mole the NO_x conversion achieved in the glass wool packed reactor (Figure 5.12) was 96%, equal to that achieved in the unpacked reactor (Figure 5.13). As stated earlier, the presence of the packing material increased the discharge power for a given reactor size and set of operating conditions, allowing for less severe conditions (lower voltages) than necessary without the packing,

Figure 5.13: NO_x Conversion versus Specific Energy; Effect of NO Concentration with No Reactor Packing

preventing damage to the reactor.

Effect of Oxygen in the Inlet Gas

Many fossil fuel combustion systems introduce more air to the combustion process than is necessary to completely burn the fuel. This excess air is to ensure that there is sufficient oxygen to fully consume the fuel and results in oxygen in the exhaust gas. The amount of oxygen present in the exhaust depends considerably on the combustion device and fuel used. Natural gas fired systems generally require low amounts of excess air (1-3%) to achieve high combustion efficiency while coal fired systems use 20% or more.

Shown in Figures 5.14 and 5.15 are the NO and NO_x conversions versus specific

Figure 5.14: Effect of Oxygen on NO Conversion

energy for NO-N₂ mixture with oxygen contents ranging from 0 to 6% O₂. The experiments were conducted at room temperature in a glass wool packed reactor (0.26g/cm³) at gas residence time of 1.7 sec with an inlet NO concentration ranging from 470 to 510 ppm.

Figure 5.14 shows that as the O₂ concentration increased, the NO conversion decreased with the largest drop occurring between 0 and 1% O₂. At a specific energy of approximately 36,000 KJ/mole the NO conversion dropped from 97% at 0% O₂ to 77% conversion at 1% O₂ and 66% conversion at 4% O₂. Increasing the oxygen content to 6% only slightly decreased the NO conversion below that obtained at 4% for the same specific energy.

NO_x conversion also decreased as the oxygen concentration increased, but the

Figure 5.15: Effect of Oxygen on NO_x Conversion

decrease in conversion levels was much greater than that seen for NO conversion. Figure 5.15 shows that at a specific energy of 36,000 KJ/mole the NO_x conversion decreased from 95% at 0% O₂ to 65% conversion at 1% O₂, 51% conversion at 2% O₂, 38% conversion at 4% O₂, and 32% conversion at 6% O₂. The difference between NO and NO_x conversion at a comparable oxygen level and specific energy (Figures 5.14 and 5.15) increased as the oxygen content increased. This was due to the production of NO₂ which was determined by the difference in NO and NO_x concentrations discussed in Chapter IV.

The reduced NO and NO_x conversions and increased production of NO₂ were due to the presence of oxygen in appreciable amounts in the NO-N₂ mixture, causing scavenging of N and N₂⁺ by the following proposed reactions [Suzuki, 1978]:

Additionally, the action of the discharge on oxygen resulted in the formation of atomic and excited oxygen [Willis and Boyd, 1976] through:

The effects of reactions (5.13) and (5.14) were to decrease the amount of N, N⁺, and N₂⁺ available to react with NO through (5.8), (5.9) and (5.10). This scavenging of active nitrogen species by oxygen explained the increase in energy required to convert NO as seen in Figure 5.14 for increasing O₂ concentrations. The production of O by reactions (5.15) through (5.17) increased the active oxygen species concentration resulting in greater NO₂ production through (5.12).

The presence of oxygen in the gas entering the barrier discharge reactor significantly altered the reaction pathways leading to the destruction of NO_x. Without oxygen in the gas stream the products of the discharge initiated reactions were N₂ and O₂, with a small amount of NO₂. With oxygen at a concentration of 6% in the gas the production of NO₂ from NO was substantially increased and only a small portion of the inlet NO was converted to N₂ and O₂.

Effect of Carbon Dioxide

Fossil fuel combustion results in the formation of carbon dioxide (CO₂) which is then present in the exhaust gas. The effects of CO₂ in an NO-N₂-O₂ mixture on NO and

Figure 5.16: Effect of CO₂ on NO and NO_x Conversion

NO_x conversion are presented in Figure 5.16. The experiments were performed without CO₂ and with 10% CO₂ in the gas stream. The CO₂ cylinder gas used in the experiments contained oxygen, and therefore O₂ was also included in the gas stream which did not contain carbon dioxide. The O₂ level in both sets of experiments was 1% and the inlet NO concentration was 500 ppm. The addition of 10% CO₂ resulted in a decrease in both the NO and NO_x conversion. At a specific energy of 60,000 KJ/mole the NO conversion dropped from 90% with no CO₂ to 76% when 10% CO₂ was present in the gas stream. NO_x conversion also decreased, from 82% to 68%, when CO₂ was added. In addition to the decrease in NO and NO_x conversions there was significant production of CO, with reactor outlet concentrations exceeding 1000 ppm (the upper limit on the CO analyzer) at specific energy values above 20,000 KJ/mol.

In the NO-N₂ gas mixture the presence of CO₂ resulted in the formation of carbon monoxide through the following proposed reactions [Willis and Boyd, 1976]:

The production of CO also produced oxygen, which can react as discussed previously, reducing the NO and NO_x conversions and increasing the specific energy required for destruction of NO_x. An increase in the outlet oxygen content over the inlet concentration was seen in the experiments at higher specific energy levels (>20,000 KJ/mole). However, an accurate measurement of the amount of oxygen produced by reduction of CO₂ to CO could not be made due to the limited sensitivity of the O₂ analyzer (±0.1% or 1000 ppm).

Effect of Water Vapor

Combustion of fossil fuels can result in considerable amounts of water vapor in the exhaust gas. In natural gas combustion the exhaust can contain up to 18.5% water vapor at a stoichiometric feed ratio of fuel and air. In order to understand the impact of water vapor on the barrier discharge process experiments in which the inlet NO-N₂ gas contained water vapor were performed. Shown in Figure 5.17 are the NO and NO_x conversions for experiments conducted with 1% water vapor and without water vapor. A glass wool packed reactor (0.27 g/cm³) with an inlet NO concentration of 500 ppm and

Figure 5.17: Effect of 1% Water on NO and NO_x Conversion

a gas residence time of 1.7 seconds was used.

It can be seen in the figure that both the NO and NO_x conversions decreased for a given specific energy as the water vapor content was raised from 0 to 1%. At a specific energy of 40,000 KJ/mole the NO conversion decreased from 98% to 49% when 1% water vapor was added to the gas stream. NO_x conversion decreased from 96% to 42%.

The following proposed reactions occurred due to the interaction of the barrier discharge with water vapor in the gas stream [Willis and Boyd, 1976]:

Reactions (5.22) through (5.24) did not contribute directly to destruction of NO_x.

However, they did compete for the discharge energy with the reactions forming the active species resulting in the oxidation and reduction of NO. This caused higher energy requirements for a given level of conversion when the gas stream contained water vapor. The specific energy required to achieve 40% NO_x conversion increased from 10,000 KJ/mole to 34,000 KJ/mole when the water vapor content was increased from 0 to 1%.

The presence of water vapor, in addition to increasing the specific energy requirements needed to achieve a given NO_x conversion, changed the reaction pathways followed in the NO_x destruction process. This altered the products of the barrier discharge technique for NO_x removal. Without water vapor in the gas stream the NO_x conversion, measuring the percentage of NO converted to compounds other than NO and NO₂, indicated the amount of NO_x reduced to N₂ and O₂. When water vapor and oxygen were present NO_x reduction did not take place to any appreciable extent. Instead, nitric oxide was converted to nitric acid (HNO₃). This was a significant shift as the product of the process were no longer benign compounds but was instead a pollutant, requiring controls on its release to the environment. However, nitric acid in the exit stream can be captured and neutralized in an easier way than NO and NO₂ due to its greater reactivity.

The formation of nitric acid can be attributed to the reactions proposed in equations (5.25) and (5.26) in which NO₂, formed by equation (5.12), reacted with an OH radical, formed in (5.24), or with atomic oxygen, formed through equations (5.13) and (5.17) [Tokunaga, 1978].

NO_3 reacted rapidly with NO and NO_2 to form NO_2 and HNO_3 as follows:

In addition to nitric acid formation a small amount of nitrous acid (HNO_2) may have been formed. However, HNO_2 is an unstable compound which would have rapidly decomposed to NO and NO_2 [Tokunaga, 1978], and could have undergone further reaction.

Equations (5.25) through (5.30) show that both water vapor and oxygen in the gas stream contributed to the formation of HNO_3 . In order to study the effect of water vapor and oxygen in the NO - N_2 mixture, experiments were conducted with a gas stream containing 1% water vapor and 6% oxygen. The data are shown in Figure 5.18, including results obtained without the presence of oxygen for comparison. There are several noteworthy differences between the two sets of experimental results, those with and without oxygen in the NO - N_2 - H_2O gas stream. First, at low specific energies (<30,000 KJ/mol) the presence of oxygen increased the NO and NO_x conversion. For example, at 10,000 KJ/mol the NO conversion with and without O_2 was 34 and 25%, respectively, and the NO_x conversion was 31 and 22%. This may have been due to the additional reactive species formed when oxygen was present, leading to the oxidation of NO_2 to NO_3 through equation (5.26). At high energy levels (>30,000 KJ/mol) the trend was reversed and the

Figure 5.18: Effect of Oxygen and Water Vapor on NO and NO_x Conversion and NO Reduction

conversion values obtained for the system without O₂ were higher than those with O₂. At a specific energy of 60,000 KJ/mol, the NO conversion was 55% without O₂ and 45% with 6% O₂. The NO_x conversion at the same specific energy level was 48 and 41%, for the cases without and with oxygen, respectively.

The NO_x conversion for the system containing oxygen and water vapor reached a maximum at a specific energy of approximately 35,000 KJ/mol, which can be explained in terms of the reactions previously discussed. At high specific energies the production of O through equations (5.16) and (5.17) was high, resulting in greater formation of NO₃ through (5.26). This increased the production of NO, NO₂ and O₂ through equations (5.27) and (5.28). These compounds could then react as discussed earlier. The net result

was that the NO_x conversion did not increase as the specific energy increased.

Figure 5.18 also shows the NO_x reduction obtained for the two sets of experiments. NO_x reduction is a measure of the inlet NO_x that is reduced to N_2 and O_2 . To clarify the difference between NO conversion, NO_x conversion and NO_x reduction the following examples are given. If 1 mole of NO is fed to the reactor and the outlet gas contains 0.5 moles NO and 0.25 moles NO_2 , the NO conversion is 50%, NO_x conversion is 25% and the NO reduction is 25%. If, however, in addition to 0.5 moles of NO and 0.25 moles of NO_2 , the outlet gas contained 0.25 moles of HNO_3 , the NO and NO_x conversions are still 50 and 25%, respectively, but the NO_x reduction is 0%. That is, all of the NO fed to the system that underwent reaction in the second case contributed to the formation of NO_2 or HNO_3 . None of the inlet NO was reduced to N_2 and O_2 . Therefore, the difference between NO_x conversion and NO_x reduction is the production of HNO_3 .

Without O_2 in the $\text{NO-N}_2\text{-H}_2\text{O}$ gas stream the NO_x reduction was essentially 0% at all specific energy levels. That is, all of the NO_x converted in the reactor formed HNO_3 , primarily through equation (5.25). With 6% oxygen in the gas stream the NO_x reduction at high energy levels ($>30,000$ KJ/mol) was negative, meaning that some of the inlet N_2 was converted to HNO_3 . For example, at 60,000 KJ/mol the NO_x reduction was -5%.

Experiments with $\text{NO-N}_2\text{-H}_2\text{O}$ inlet gas mixtures containing greater than 1% water vapor could not be performed with the benchtop system using simulated flue gas due to problems in producing, maintaining and measuring streams with higher water content. Experiments at higher water vapor concentrations were conducted with the process

Figure 5.19: Effect of Exhaust Gas Composition on NO_x Conversion

development system using a single tube reactor and exhaust from a natural gas combustor as the inlet gas. The experiments were performed with an inlet gas NO_x concentration of 225 to 350 ppm and with flow rates resulting in Reynold's numbers in the range of 100 to 500. The results obtained using this system are presented in Figure 5.19. The oxygen content of the exhaust gas was varied from 1.9 to 5.8%, with the water vapor content ranging from 16.9 to 13.4%. The oxygen, water vapor and carbon dioxide content of the inlet gas stream for each set of data is listed on the figure. The results show that as the oxygen level of the exhaust gas was increased, thereby reducing the water vapor and carbon dioxide concentrations, the NO_x conversion increased for a given specific energy. At 15,000 KJ/mol, the NO_x conversion increased from 60% at 1.9% O₂ to 69% at 2.3%

O₂ and 92% at 5.8% O₂.

Another significant feature of the results obtained using actual flue gas, containing water vapor, oxygen and carbon dioxide, was that the NO_x conversion for a given specific energy value increased over that obtained when simulated flue gas was used. The NO_x conversion for each of the three conditions using combustion-generated flue gas is higher than that obtained when 1% water vapor (with and without oxygen) was present in an NO-N₂ mixture. At a specific energy of 15,000 KJ/mol the NO_x conversion was 60, 69 and 92% for the three sets of data using combustion-generated inlet gas (Figure 5.19). The NO_x conversion in the simulated flue gas system (NO-N₂-H₂O) with and without O₂ was 27 and 34%, respectively (Figure 5.18). In fact, the NO_x conversion obtained using combustion-generated inlet gas was higher than that obtained at the same specific energy when the inlet gas was made up of only N₂ and NO (54% at 15,000 KJ/mol as seen in Figure 5.13).

These results do not follow the trends shown in Figures 5.15 through 5.18, namely that the addition of gases (CO₂, O₂, H₂O) to the NO-N₂ stream each reduced the NO_x conversion for a given specific energy. When all of the major constituents of combustion exhaust were found in the inlet gas the energy requirement for a given level of NO_x destruction dropped dramatically. This may have been due to a combination of reactions leading to the destruction of NO_x, which occurred only when several or all of the compounds found in combustion exhaust gas were present in the inlet gas. For example, when water vapor and oxygen are contained in the gas O and OH may be formed in significant quantities by the action of the discharge due to the relatively low energy

needed for their production. The dissociation of oxygen to O atoms (through reaction 5.17) needs 12 eV and OH formation (through reactions 5.23 and 5.24) requires 8.8 eV while the formation of N atoms (through reaction 5.7) requires 12.2 to 14.5 eV. [Willis and Boyd, 1976]. Greater quantities of O atoms may result in formation of NO₂ from NO by reaction (5.12). Nitric acid can then be readily formed from OH and NO₂ through (5.25). The overall effect of the combination of gases in the discharge may be to reduce the energy required to convert NO_x to HNO₃ as was seen in Figures 5.12 through 5.19.

The reactions presented up to this point are considered to be the major ones occurring in the barrier discharge process. However, many more have been reported in the literature. Matzing [1991] lists over 700 reactions that occur as a result of the electron beam irradiation (E-beam) of combustion flue gas. While many of these additional reactions may also take place in the barrier discharge process it can not be assumed that they do occur. The probability of forming the active species (such as N, O, and OH) that initiate these reactions is dependant on the energy of the electrons colliding with the gas. This dependence is particularly sensitive to energy at the low electron energy levels typical of the barrier discharge process (<20 eV as compared to 300 to 800 KeV electrons in the E-beam process [Matzing, 1991]).

Water vapor in the gas stream at levels greater than 1% and at the temperatures used in this study (from room temperature to 160°C) prevented the satisfactory use of glass wool packing in the reactor. This was likely a result of the adsorption of water on the surface of the glass packing material. The layer of water produced a conductive path (due to the presence of impurities) that effectively shorted out the discharge. This caused

sparkling throughout the reactor with high energy consumption and little NO_x destruction.

The results presented in this section show that the mechanisms proposed for the reactions occurring in the E-beam irradiation of flue gases are consistent with the reactions seen in the barrier discharge treatment of NO_x . This allows for a greater understanding of the process and can shorten time needed for development of this technology since extensive work on the E-beam process has been undertaken.

It is important to note that water vapor in the gas stream had the most adverse impact of any major combustion exhaust compound (N_2 , O_2 , H_2O , CO_2) on the operation of the barrier discharge process for NO_x removal. The production of nitric acid from NO_x and water vapor in the gas stream presents a significant challenge in the commercial implementation of this technique. Substituting nitric acid emissions for NO_x emissions is not an acceptable method of NO_x control and therefore additional measures must be taken. Possibilities exist such as scrubbing the acid from the gas in either a wet or dry scrubber or reacting the acid with ammonia as in the E-beam process. Another alternative is to remove water vapor from the gas before it enters the barrier discharge reactor. However, this appears to be a costly alternative for typical combustion systems due to the energy requirements for the discharge process and the need for gas drying.

Oxygen in the dry gas mixture resulted in reduced conversion of NO_x with the bulk of the inlet NO converted to NO_2 . However, when combined with water vapor, high levels of conversion to nitric acid (>95%) were achieved. Additionally, the energy requirements were lower with O_2 and H_2O in the gas than when the gas mixture contained either O_2 or H_2O without the other.

Exhaust from combustion of many types of fuel contains sulfur dioxide in significant concentrations. Coal and heavy fuel oil are examples of two such fuels. To investigate the effect of sulfur dioxide on the operation of the barrier discharge process additional tests were conducted. Natural gas combustion generated flue gas with sulfur dioxide (SO_2) added to the gas stream was used. The experiments were performed in an unpacked reactor. The presence of SO_2 resulted in considerable sparking in the reactor with little NO_x conversion. It is felt that SO_2 is oxidized to SO_3 by the action of the discharge [Tokunaga, 1978]. SO_3 then condensed on the surfaces of the reactor resulting in a conductive layer on the dielectric barrier surface, causing the sparking to occur. Eliminating SO_2 from the inlet gas did not stop the sparking. The reactor had to be disassembled and all surfaces cleaned before a barrier discharge without sparking could be produced. Higher temperatures, beyond that attainable in the reactors used for this work, must be maintained to prevent the condensation of SO_3 and the sparking that results.

Hydrodynamic Effects

The work discussed so far was primarily done in a benchtop reactor using simulated flue gas. The flow rates in this system were limited by the size of the reactor and power supply. In order to investigate the effects of gas turbulence on the operation of the barrier discharge technique, a process development system at Tecogen, Inc. was used. It was built for the commercial development of the barrier discharge process for NO_x control, based on the technology developed at UNH and discussed in this thesis. The

process development unit also provided the opportunity to investigate the barrier discharge technique for NO_x control on a larger scale than was possible with the facilities at UNH.

The apparatus contained a multi-tube reactor with seven tubes as discussed in Chapter IV. Each reactor tube was 1.2 m long with an inner diameter of 29 mm. The reactor inlet gas was produced from combustion of natural gas. A schematic diagram of the system is shown in Figure 4.6.

Results given here are in terms of NO_x conversion only. NO conversion is not used since both NO and NO_2 are produced when burning natural gas, with the NO_2 concentration accounting for up to 5% of the total NO_x concentration. To use inlet NO_x concentrations greater than that produced in the combustion process, pure NO was fed into the system as discussed earlier.

Effect of Gas Turbulence on NO_x Conversion

The experiments discussed in previous sections, namely those conducted to study the effects of electrical and chemical parameters on NO_x conversion, were all performed at relatively low flow rates resulting in Reynold's numbers up to 500, that is, in the laminar flow regime for the coaxial electrode system. The effect of increasing the gas flowrate, and therefore the degree of turbulence in the reactor, is presented in Figure 5.20. It shows the NO_x conversion as a function of specific energy for Reynold's numbers of 100-750, 2600-3000, 6000-7000 and 9000-10000. The experiments were conducted with inlet gas NO_x concentrations of 250 to 300 ppm and O_2 levels of 2.5 to 3.3%, resulting in water vapor and carbon dioxide contents of 16.4 to 15.7% and 8.6 to 8.4%,

Figure 5.20: Effect of Gas Mixing on NO_x Conversion

respectively. No reactor packing material was used.

The figure shows that increasing the degree of turbulence in the reactor reduced the specific energy required to achieve a given level of NO_x conversion. In the laminar flow regime ($100 < Re < 750$) the specific energy required to obtain 70% conversion was 14,500 KJ/mol. This dropped to 10,500 KJ/mol when the gas velocity was raised to attain Reynolds numbers in the range of 2600 to 10000. The decrease represents a 28% reduction in energy consumption for the case of turbulent flow over operation of the reactor in the laminar flow regime. Since the gas stream contained oxygen and water vapor the product of the barrier discharge initiated NO_x reactions was HNO₃, as was previously discussed.

The nature of the barrier discharge in a coaxial electrode system is such that the

discharge intensity is greatest in the region surrounding the center electrode. The electron current flux in the gas as one moves away from the center electrode decreases, reducing the concentration of ions and other chemically active species. Therefore it was considered essential that a high degree of mixing be maintained, ensuring that all of elements of the gas are exposed to the active chemical species during some portion of their travel through the reactor.

A high degree of turbulence had two effects on the operation of the barrier discharge reactor. First, the mixing due to turbulence effectively brought NO and NO₂ into contact with the active species which lead to their destruction. A second effect was that the active species produced by the microdischarges were removed from the discharge region, keeping their concentration in this region low and resulting in a higher production rate. The overall reduction in the energy requirements observed experimentally (Figure 5.20) may be due to one or both of these factors.

The importance of the effect of mixing and the increased NO_x conversion achieved when combustion-generated exhaust gas was used instead of simulated flue gases led to the further study of the effect of parameters such as reactor configuration and gas composition. These experiments were similar to those conducted in the laminar flow regime using simulated flue gas except that the inlet gas was produced from the burning of natural gas and the gas velocity through the reactor was high enough to result in turbulent flow.

Comparison of Corona and Barrier Discharges

It was stated in Chapter III that the use of a dielectric barrier enables higher discharge power levels to be achieved over that obtainable without the barrier. Also, the diameter of the barrier discharge electrode can be greater, without arcing, than the largest that can be used with no the dielectric material. In addition, the use of the dielectric barrier changes the discharge mechanism from a continuous discharge (while the applied voltage exceeds the threshold voltage for corona initiation) to a series of localized micro-discharges along the length of the electrode. This change in operation from a continuous discharge to a series of micro-discharges due to the presence of the dielectric barrier is expected to result in greater energy efficiency since the micro-discharges produce the active chemical species across the entire gas gap in a brief period. The short duration of the micro-discharges, during which the local electric field strength is high, limits acceleration of ions produced in the discharge, thereby limiting the amount of energy wasted as heat in the gas.

The differences between the barrier discharge and corona discharge techniques were investigated in a 29 mm ID reactor. In the corona discharge system the center electrode consisted of 0.2 mm diameter wire without a dielectric barrier. In the barrier discharge configuration the center electrode was a 4 mm stainless steel rod covered by a 4 mm ID by 6 mm OD quartz tube. The gas flow rates for both sets of experiments resulted in Reynolds numbers ranging from 4000 to 6000, inlet NO_x concentrations of 225 to 305 ppm, oxygen levels of 2.0 to 3.5%, water vapor contents between 16.8 and 15.5% and CO₂ concentrations between 8.8 and 8.1%.

Figure 5.21: Comparison of Corona and Barrier Discharge Techniques for NO_x Removal

The barrier dielectric system showed greater conversion levels for comparable specific energies as seen in Figure 5.21. At a specific energy of 1400 KJ/mol the NO_x conversion achieved with the corona discharge technique was 12% while 20% conversion was obtained using the barrier discharge. Also, the specific energy levels achieved in the corona discharge electrode system were limited to a maximum of approximately 1500 KJ/mol for the conditions tested. Increasing the discharge power to raise the specific energy above 1500 KJ/mol resulted in arcing between the center and outer electrodes. Tests performed using a bare 3.5 mm electrode in a 29 mm ID tube resulted in arcing between the electrodes before a stable corona discharge could be established.

Effect of Electrode Spacing on NO_x Conversion

The distance between the center and outer electrodes can be reduced in two ways. One is to decrease the diameter of the outer electrode. This was done in the benchtop reactor testing and discussed earlier. The second method is to increase the diameter of the center electrode and its surrounding dielectric barrier. This is expected to effect the discharge onset voltage and resulting discharge power as discussed in Chapter III. It is also expected to increase the percentage of the gas in the highest discharge intensity region of the reactor, that which immediately surrounds the center electrode.

The effect of increasing the center electrode diameter was investigated and the results presented in Figure 5.22. It shows the experimental NO_x conversion versus specific

Figure 5.22: Effect of Center Electrode Diameter on NO_x Conversion

energy for tests conducted on three center electrode systems; a 1 mm electrode, a 4 mm electrode, and a 10 mm electrode. In each case the center electrode was surrounded by a quartz dielectric barrier with an inner diameter equal to the outer diameter of the electrode and a wall thickness of 1 mm. The tests were conducted in a 29 mm ID reactor with Reynolds numbers ranging from 5000 to 7000.

The 4 mm and 10 mm center electrode systems resulted in higher conversion levels for a comparable specific energy than that obtained with the 1 mm electrode system. In addition, the 4 mm system gave consistently higher conversion levels than the 10 mm configuration but scatter in the data for the latter system prevented drawing definitive conclusions. The scatter resulted from intermittent sparking in the reactor where the discharge power was momentarily high and a greater portion of the discharge energy was wasted as heat.

Use of a large electrode system such as the 10 mm electrode in a 29 mm tube reduces the voltage interval between the onset of the discharge and the point where failure of the dielectric barrier occurs. The discharge onset voltage was approximately 19 KV for the 4 mm electrode system experiments shown in Figure 5.22. A stable discharge was maintained at voltages up to 34 KV for this system. Greater voltages may have been possible with the 4 mm electrode but the limit on the power supply prevented operation at voltages greater than 34 KV. However, when the 10 mm electrode system was used the discharge initiated at a voltage of 21 KV and considerable sparking occurred at 29 KV. Leaving an effective operating range of 8 KV. The large electrode system is much more sensitive to local conditions in the reactor because of reduced operating region

between onset of the discharge and the formation of arcs.

The effect of reactor diameter (outer electrode) on NO_x conversion, studied for benchtop system using simulated flue gas and low Reynolds numbers, was also investigated under turbulent flow conditions and with combustion-generated flue gas. A 4 mm center electrode with a 4 mm ID by 6 mm OD quartz barrier was used in two reactor tubes; a 29 mm ID tube and a 51 mm ID tube. The results are shown in Figure 5.23. The inlet NO_x concentration for the tests was in the range of 70 to 250 ppm, the O_2 content was between 1 and 4%, and the Reynolds number ranged from 6000 to 9000.

The smaller ID reactor (29 mm) produced higher NO_x conversion values for a comparable specific energy. This may have been due to the fact that the gas at the outer edge of the reactor in the 51 mm system was unable to travel across the longer distance

Figure 5.23: Effect of Reactor ID on NO_x Conversion

needed to reach the high intensity discharge region than in the 29 mm reactor. An increase in the level of turbulence in the larger outer electrode system may have achieved comparable NO_x conversion for a given specific energy but limitations on the process development system prevented testing at higher flow rates.

A second potential effect of the longer gas gap created by the use of the larger outer electrode diameter is an increase in the amount of energy wasted as heat. Increasing the gap distance may extinguish the discharge before it completely bridges the gap between electrodes. Portions of the gas do not see the discharge and the amount of energy lost through attachment of electrons to gas molecules in a weak electric field increases as a percentage of the total discharge energy. Similarly, reducing the outer electrode too much may create a situation where the gas in the region of the microdischarge may be "overexposed". That is, the discharge intensity and duration may be more than adequate to completely react the NO_x in the region. The additional active chemical species, unable to react with NO or NO_2 , recombine or react with other compounds, wasting the energy used in their production.

The hydrodynamic results, along with those obtained with changing electrode diameters, indicate that the Reynolds number or degree of mixing, in conjunction with the electrode geometry, is of primary importance in the efficient production and use of the active chemical species leading to the removal of NO_x from the gas stream. Increasing the diameter of the inner electrode or reducing the reactor ID can increase the efficiency of the production of active species. This was shown by changes in specific energy at a given NO_x conversion resulting from a change in electrode diameter. A high degree of

mixing in the reactor due to turbulence can help to promote interaction between the active species produced by the discharge and NO and NO₂ in the gas.

Design of a commercial barrier discharge reactor must take advantage of the knowledge gained from the results obtained in the benchtop and process development testing discussed so far. The efficient production and use of the active species causing NO_x destruction is dependent upon several features of the system. Reactor geometry (diameter of the center electrode and distance between electrodes) may be of utmost importance in the efficient generation of the ions, radicals and excited compounds while hydrodynamic effects can be used to ensure that these species are brought into contact with the NO_x molecules. Consideration must also be given to the range of operation provided by the reactor geometry, for example, the voltage range between discharge initiation and arcing. Making the center electrode large in diameter may decrease the level of turbulence required for efficient use of the discharge power but also results in a small window where the reactor can operate without arcing, which wastes electrical energy as heat and can damage the dielectric barrier.

A small electrode diameter mandates that the mixing in the reactor be effective, requiring high gas velocities for efficient operation. Since the power density that can be achieved with a small electrode is limited due to its small size, long reactors are necessary to achieve the needed gas residence time and specific energy at high gas flow rates.

The process development unit constructed at Tecogen enabled testing of the barrier discharge system on a larger scale than possible with the benchtop system. In addition to tests performed to study the effect of gas turbulence already discussed, the system was

used to conduct experiments on the effect of gas composition, inlet NO_x concentration and temperature on the barrier discharge process.

Effect of Inlet Gas Composition

The composition of the flue gas entering the reactor was varied by changing the amount of excess air supplied to the gas burner, changing the composition of N_2 , O_2 , CO_2 and H_2O . Figure 5.24 shows the NO_x conversion versus specific energy at flow rates resulting in Reynolds numbers of 6000-7000 and at four different oxygen contents; 0 to 0.4%, 1.5 to 1.7%, 2.6 to 2.8% and 4.2 to 4.5%. From Figure 5.10 the remaining component compositions for the average O_2 content in each of the four ranges were calculated and listed in Table 5.1.

Figure 5.24: Effect of Oxygen on NO_x Conversion

Table 5.1
Gas Composition for Several Oxygen Contents

Oxygen (%)	Excess Air (%)	Carbon Dioxide (%)	Water Vapor (%)	Nitrogen (%)
0.20	1.0	9.62	18.43	71.75
1.60	9.1	8.97	17.19	72.25
2.70	16.4	8.46	16.20	72.64
4.35	29.0	7.69	14.73	73.23

It can be seen that in turbulent flow (Figure 5.24) there was no significant effect on NO_x conversion when the flue gas composition was varied over the range of concentrations listed in the table. These results differed significantly from those obtained in laminar flow tests where the Reynolds numbers ranged from 100 to 500 (Figures 5.15 through 5.19). The results obtained at low Reynolds numbers showed that the composition of the gas stream had a noticeable effect on the energy requirements to achieve a given NO_x conversion. This was observed for the simulated flue gas as well as for flue gas from natural gas combustion. The addition of compounds such as oxygen, water vapor or carbon dioxide to the NO-N_2 stream in simulated flue gas reduced the NO_x conversion for a comparable given specific energy below that measured when the gas stream was composed of NO and N_2 only (Figures 5.15 to 5.18). When actual combustion-generated exhaust gas was used in laminar flow the NO_x conversion for a given specific energy was higher than that obtained with the NO-N_2 system but there was still an effect of gas composition on NO_x conversion (Figure 5.19); NO_x conversion increased for a given specific energy as the oxygen content was increased.

NO_x conversion dependence on inlet gas composition was not observed in turbulent flow (Figure 5.24). The conversion for a given specific energy under turbulent flow at oxygen levels of 0 to 4.5% was comparable to that obtained in laminar flow at 5.8% O_2 , the most energy efficient laminar flow condition tested. The NO_x conversion under turbulent flow conditions and a specific energy of 7000 KJ/mol was 65% (Figure 5.24). At the same specific energy under laminar flow and an O_2 concentration of 5.8% the NO_x conversion was 68% (Figure 5.19). The dependence on gas composition in laminar flow may have been due to a concentration gradient of active species across the gas gap. Turbulent flow carries the gas into and out of the intense discharge region quickly, which may have significantly reduced the concentration gradient in the gas and increased the reaction efficiency and utilization of the active species as previously discussed.

It was also noted that the production of carbon monoxide (CO) in the barrier discharge reactor was substantially reduced when combustion-generated flue gas was used. Typical CO concentrations at the reactor inlet were 20 to 25 ppm. These values increased by 3 to 5 ppm, to approximately 23 to 30 ppm in the exit gas of the reactor.

In addition to studying the effect of the composition of the bulk inlet gases on NO_x conversion, tests were conducted to investigate the effect of varying inlet NO_x concentrations under turbulent flow conditions. The experiments were conducted at inlet NO_x concentrations of 30 to 65 ppm, 120 to 155 ppm and 200 to 355 ppm. The oxygen concentration ranged from 5.5 to 10% and Reynolds numbers were in the range of 6,000 to 10,000.

The inlet NO_x concentration had no effect on the NO_x conversion achieved for a given specific energy as seen in Figure 5.25. This was also seen in the laminar flow, simulated flue gas results (Figures 5.12 and 5.13). However, the specific energy requirements for the actual flue gas system in turbulent flow were lower than those measured for the simulated gas system in laminar flow; 14,000 KJ/mol at a NO_x conversion of 80% for the turbulent flow, combustion-generated inlet gas versus 26,000 KJ/mol for the $\text{NO}-\text{N}_2$ mixture in laminar flow.

The experiments performed with exhaust gas under turbulent flow conditions for a given reactor configuration showed that the NO_x conversion in terms of specific energy was independent of the flue gas composition (O_2 , H_2O and CO_2 concentrations) and the inlet NO_x concentration. This is an important feature of the barrier discharge process and

Figure 5.25: Effect of Inlet NO_x Concentration

indicates that the technology is attractive to commercial installations where high conversion levels must be achieved at relatively low inlet NO_x concentrations. The following example is given. A 293 KW (thermal) combustion device (=1 MMBtu/hr) burning natural gas at 3% excess air produces 3.4 moles of exhaust gas per second. At 80% NO_x conversion the specific energy requirement is 14,000 KJ/mole of NO_x (Figure 5.25). An inlet NO_x concentration of 300 ppm requires 14 KW (electric) to achieve 80% NO_x conversion. Multiplying this by 3 for the electric to thermal power conversion, the output of the combustor that is needed to supply the discharge process is 42 KW (thermal) which represents 14% of the combustor's rated output power, an extremely high percentage for an emissions control device. However, only 1.4% of the combustor's output power, 4.2 KW (thermal) or 1.2 KW (electric), is needed to achieve 80% conversion if the inlet NO_x concentration was 30 ppm instead of 300 ppm. This represents a much more acceptable drain on the combustor to achieve control of NO_x emissions.

Effect of Gas Temperature on NO_x Conversion

Temperature was not expected to substantially effect the reactions taking place in the barrier discharge process for the destruction of NO_x . As discussed in Chapter III, the electron temperature in an electrical discharge is much higher than the bulk gas temperature. However, the effect of temperature on NO_x conversion was investigated experimentally. Tests were conducted at three temperatures, ranging from 105 to 160°C, in the multi-tube process development reactor using combustion-generated exhaust gas. The NO_x concentration ranged from 50 to 350 ppm, O_2 from 5 to 8%, and the Reynolds

numbers were in the range of 6000 to 10,000. The center electrode diameter was 4 mm with a 4 mm ID by 6 mm OD quartz dielectric barrier.

Figure 5.26 shows that as the temperature was increased the NO_x conversion decreased for the same specific energy. At 105°C the NO_x conversion at a specific energy of 6500 KJ/mol was 61%. This decreased slightly to 55% at 130°C and dropped substantially, to 37% when the temperature was raised to 160°C .

The decrease in NO_x conversion for a given specific energy was likely due to the decrease in electrical resistivity of the quartz barrier as the temperature was increased. At 105°C the electrical resistivity of quartz is approximately 1×10^{16} ohm-cm. This decreased by a factor of five, to approximately 2×10^{15} ohm-cm when the temperature was raised to 130°C , and by a factor of 100, to 1×10^{14} ohm-cm when the temperature increased

Figure 5.26: Effect of Gas Temperature on NO_x Conversion

from 105 to 160°C. The reduced resistivity allowed a greater current through the dielectric barrier resulting in greater heat losses (I^2R) in the barrier. Temperatures higher than 160°C could not be tested due to breakdown of the dielectric barrier and the polysulphone insulators at the top of the reactor.

The experiments performed on the process development unit showed that the basic concepts established with the bench scale unit were sound. The effects of electrical parameters such as voltage and frequency seen in the benchtop system were verified on the larger scale unit. The reaction products measured in the process development unit were the same as those established during the benchtop testing when the simulated gas contained all of the major compounds found in flue gas. The significant difference between the bench scale and process development scale results was the diminished effect of gas composition on NO_x conversion seen in turbulent flow with the process development unit. The conditions that led to this observation could not be established in the bench scale system.

Specific energy requirements for a given level of NO_x conversion were reduced dramatically when actual flue gas in turbulent flow was used in the process development reactor. A significant decrease in the operating cost of the system will result from the reduced energy needs, making the technology more competitive with other NO_x control processes. For example, a northeastern paper mill typically incurs a cost of \$950 per ton of NO_x removed from hog boiler exhaust streams using urea injection (the name of the company is withheld at their request). NO_x conversion achieved in this system is approximately 25%. Using the barrier discharge technique at a level of 25% conversion

and an energy charge of \$0.10 per kilowatt-hour, the electrical energy cost of NO_x removal would be approximately \$930 per ton. Improvements to the process could further reduce this cost.

Modelling of the Barrier Discharge Reactor

A complete understanding of the operation of the barrier discharge reactor for the destruction of nitrogen oxides requires a mathematical description of the physical and chemical processes. As discussed in Chapter III, this description must include the Boltzmann, Poisson and Continuity equations along with a knowledge of the chemical species produced by the discharge. However, useful engineering information can be obtained from simplified models based on empirical equations such as Peek's law discussed earlier. Two such simplified models were developed to predict the electrical behavior of the discharge process and to predict the NO_x conversion for a given set of reactor conditions.

Electrical Model

The electrical model of the discharge reactor was developed based on corona discharges, then modified to apply to the barrier discharge technique under investigation [McLarnon, 1992]. It was used to predict the current and power input to the reactor resulting from the application of high voltage to the center electrode of the coaxial electrode system and to characterize the significance of parameters controlling the discharge such as reactor geometry and properties of the dielectric barrier.

The electrical circuit powered by the high voltage transformer is shown in Figure 4.3. The reactor was considered to have only one dielectric barrier, surrounding the center electrode for this model. The outer dielectric barrier, shown in Figure 4.2 and forming the capacitor labeled C_{cd} in Figure 4.3, was incorporated in C_{ab} . This was done to match the reactor configuration used in the process development reactor testing and the bulk of the benchtop experimentation. The model does not cover the use of packing materials in the reactor as these were not used in the development reactor testing.

The single dielectric reactor circuit consists of a capacitor (C_{ab}) in series with the parallel combination of a capacitor (C_{bc}) and a resistor (R_{bc}). The series capacitor (C_{ab}) is formed by the dielectric barrier in the reactor. The parallel resistance (R_{bc}) and capacitance (C_{bc}) are formed by the gas that occupies the space between the dielectric barrier and the grounded outer electrode.

Four basic assumptions are made in the development of the model. The first is that the circuit can be described in terms of pure capacitive and resistive elements. Second, the circuit is piecewise linear. There is a linear circuit before discharge and another during discharge. The third assumption is that the gas has an infinite resistance prior to discharge initiation, taking on a finite value after onset of the discharge. Fourth, the applied voltage is pure sinusoidal.

The reactance and resistance of each of the elements in the circuit is given by:

$$X_{Cab} = - \frac{\ln b/a}{2\pi\epsilon_0\omega k_{ab}L} \quad (5.31)$$

$$X_{cbc} = - \frac{\ln c/b}{2\pi\epsilon_0\omega k_{bc}L} \quad (5.32)$$

$$R_{bc} = \frac{\rho \ln c/b}{2\pi L} \quad (5.33)$$

where:

X_c	=	Capacitive reactance of glass barrier (ab) and gas space (bc), (ohms)
R_{bc}	=	Resistance of the gas space (ohms)
a, b, c	=	Diameters as shown in Figure 4.2(b), (cm)
L	=	Length of the discharge region of the reactor (cm)
ϵ_0	=	Permittivity of free space ($= 8.854 \times 10^{-12} \text{ C}^2/\text{N-m}^2$)
ω	=	Angular frequency ($= 2\pi f$ radian/sec)
f	=	Frequency (Hz)
k	=	Dielectric constants of the glass barrier (ab) and gas space (bc)
ρ	=	Resistivity of the gas (ohms-cm)

The total current through the circuit is given by:

$$I = \frac{V}{jX_{cab} + \frac{jX_{cbc} R_{bc}}{jX_{cbc} + R_{bc}}} \quad (5.34)$$

where the voltage (V) is:

$$V = V_{\max} \sin(\omega t + \phi) \quad (5.35)$$

and ϕ = Phase Angle (radian)
 t = time (sec)

Before the onset of the discharge the resistance of the gas is essentially infinite, resulting in a purely reactive circuit with the phase shift (ϕ) between the voltage and current equal to $\pi/2$ radian. The current before initiation of the discharge is given by:

$$I = \frac{2\pi L k_{ab} k_{bc} \epsilon_0 \omega V_{\max} \sin(\omega t + \pi/2)}{k_{bc} \ln b/a + k_{ab} \ln c/b} \quad (5.36)$$

The point of discharge initiation is determined by the electric field strength at the outer surface of the dielectric barrier surrounding the center electrode. The threshold field

strength is given by:

$$E_{r,s} = \left(30 \delta + 9 \sqrt{\frac{\delta}{b}} \right) \left(\frac{300}{f} \right)^{.16} \quad (5.37)$$

Where:

$$\begin{aligned} E_{r,s} &= \text{Threshold field strength for discharge initiation (KV/cm)} \\ \delta &= 0.392p/(273+T) \quad (\delta = 1, \text{ for } p = 760 \text{ torr, } t = 25^\circ\text{C}) \end{aligned}$$

Equation (5.37), developed for use with electrostatic precipitators, a modified version of Peek's law discussed in Chapter III, includes a frequency correction factor [White, 1963].

After onset of the discharge, the resistivity of the gas is a function of the difference between the voltage at the outer surface of the glass barrier (V_b) and the voltage required for discharge initiation (V_s). It is given by:

$$\rho = \frac{\pi V_b \delta c^2}{2k^* (V_b - V_s)^2 \ln c/b} \quad (5.38)$$

Where: $k^* = 2.2 \times 10^{-12}$ amp-cm/volt²

The current through the circuit after initiation of the discharge and the phase angle between the voltage and current are:

$$I = \frac{\left(\frac{1}{\epsilon_0 \omega} + k_{bc}^2 \rho^2 \epsilon_0 \omega \right) 2\pi L V_{\max} \sin(\omega t + \phi)}{\left\{ \left(\frac{\rho \ln c/b}{\epsilon_0 \omega} \right)^2 + \left[\frac{\ln b/a}{k_{ab} \epsilon_0^2 \omega^2} + k_{bc}^2 \rho^2 \left(\frac{\ln b/a}{k_{ab}} + \frac{\ln c/b}{k_{bc}} \right) \right]^2 \right\}^{\frac{1}{2}}} \quad (5.39)$$

$$\phi = \tan^{-1} \left[\frac{\ln b/a}{k_{ab} \ln c/b} \left(\frac{1}{\epsilon_0 \omega \rho} + k_{bc}^2 \epsilon_0 \omega \rho \right) + k_{bc} \epsilon_0 \omega \rho \right] \quad (5.40)$$

The phase angle (ωt_s) at which discharge initiation takes place is given by:

$$\omega t_s = \cos^{-1} \left[- \left(\frac{300}{F} \right)^{.16} \left(\frac{30\delta \frac{b}{2} + 9\sqrt{\delta \frac{b}{2}}}{V_{\max}} \right) \left(\frac{k_{bc} \ln \frac{b}{a}}{k_{ab}} + \ln \frac{c}{b} \right) \right] - \frac{\pi}{2} \quad (5.41)$$

The power consumed in the discharge can be calculated by numerically integrating the product of the voltage and current over a complete cycle. However, this model does not distinguish between polarity of the electrodes. Therefore, the power calculation is carried out over only a half cycle and the value multiplied by two to get the total power. The computer code written to perform the voltage, current and power calculations is included in Appendix C [Balsavitch, 1992].

Figures 5.27 and 5.28 show a comparison of the predicted and experimentally measured voltage and current for two sets of reactor operating conditions using the

Figure 5.27: Predicted and Measured Voltage and Current at a Frequency of 152 Hz

Figure 5.28: Predicted and Measured Voltage and Current at a Frequency of 252 Hz

multitube reactor configuration, $a = 4$ mm, $b = 6$ mm, $d = 29$ mm. The dimensions given are for those shown in Figure 4.2(b). The length of the reactor was 1.2 m. Figure 5.27 shows operation at 152 Hz and 96°C. The frequency for the traces shown in Figure 5.28 was 252 Hz at a temperature of 110°C. The figures show good agreement between the calculated and experimental values of current, with some large deviations due to the difference between the sinusoidal voltage used in the model and the actual voltage applied to the reactor. There is also good agreement between the predicted and measured power of 241 and 245 watts, respectively, for the conditions shown in Figure 5.27, and 361 and 368 watts respectively, for those shown in Figure 5.28. A comparison of experimentally measured and predicted discharge power values (Figure 5.29) for twenty four data sets ranging in frequency from 60 to 1200 Hz resulted in an absolute average percent deviation

Figure 5.29: Comparison of Experimentally Measured and Predicted Discharge Power

(AAPD) in predicted discharge power from measured power of 18.6%.

The electrical model was also used to determine the maximum voltage gradients in the dielectric barrier and gas space during reactor operation. This information is necessary to ensure that the discharge reactor is not operated at conditions of voltage and frequency that would result in failure of the barrier causing arcing across the gas space. Figure 5.30 presents the power consumed and the voltage gradients in the quartz dielectric barrier varying voltages and frequencies applied to the multitube reactor configuration, ($a = 4 \text{ mm}$, $b = 6 \text{ mm}$, $d = 29 \text{ mm}$, $L = 1.22 \text{ m}$) operating at 104°C .

The results obtained from the electrical modelling performed with various reactor configurations (electrode sizes and dielectric barrier properties) provided the impetus for

Figure 5.30: Predicted Power and Dielectric Voltage Gradient for Multitube Reactor

tests conducted with varying electrode diameters discussed previously (Figures 5.22 and 5.23). The model results led to designing experiments which provided a better understanding of the barrier discharge process and showed the need for a more comprehensive mathematical description of the process. A more complete model of the process can indicate reactor configurations and operating conditions that will produce and utilize the active chemical species needed for NO_x decomposition with greater efficiency.

Reaction Kinetics Modelling

The chemical environment produced by the barrier discharge leading to the destruction of nitric oxide and nitrogen dioxide is complex, simultaneously containing

ions, radicals and excited compounds. Models to predict the rates and products of the reactions initiated by the discharge must include several hundred reactions to completely describe the system [Matzing, 1991]. However, a simplified model of the barrier discharge for NO_x control was developed as part of the process development reactor testing [Breault, 1992] and used to predict the conversion of NO_x in a larger scale discharge reactor.

The model assumes a first order dependence of NO conversion on residence time in the barrier discharge reactor. It uses collision theory, in conjunction with the electrical model discussed earlier, to predict the conversion versus residence time for a given set of discharge reactor conditions: reactor configuration (a,b,d,L), temperature, and applied voltage and frequency. A description of the model is contained in the paper "Reaction Kinetics for Flue Gas Treatment of NO_x" [Breault, 1992], included in Appendix D.

The results of the kinetic modelling were compared to experimental results obtained at three different voltages in the process development reactor. The comparison was made on a NO_x conversion versus residence time basis. The electrical model discussed previously was used to predict the power input to the reactor, and therefore the specific power for the experimental flow conditions. The experimental and predicted results are shown in Figure 5.31. The agreement between experimental and predicted values of conversion is good. The absolute average percent deviation (AAPD) for the nine sets of data shown in the figure is 3.3%.

As stated earlier, a more complete model, including electrical and chemical effects is needed to accurately represent the processes occurring in the barrier discharge technique

Figure 5.31: Comparison of Experimental and Kinetic Modelling Results

for NO_x control. Development of an accurate model, and the understanding needed to produce it, would represent a significant step towards improving the barrier discharge process and commercialization of this technology for NO_x control.

CHAPTER VI

CONCLUSIONS

The study conducted to investigate the barrier discharge technique for decomposition of oxides of nitrogen, using both a bench scale apparatus and a larger process development unit, has led to several conclusions. They pertain to the parameters controlling the operation of the barrier discharge process, the products formed by the discharge initiated reactions, and the efficiency by which electrical energy is used in the barrier discharge destruction of NO_x .

This study showed that high levels of NO_x conversion, greater than 95%, could be achieved using the barrier discharge process. These high conversion levels were seen using both simulated flue gas and flue gas generated from the combustion of natural gas. The conversion levels demonstrated in this study are higher than those obtained in commercial NO_x control systems such as selective catalytic reduction and selective non-catalytic reduction.

Several conclusions drawn from the work conducted in this study apply to the electrical operation of the barrier discharge system. They are listed below:

1. Power supplied to the discharge reactor is a key variable in the destruction of NO_x in the gas stream. Several parameters are available to control the discharge power, including the magnitude and frequency of the applied voltage

and reactor configuration.

2. Reducing the electrode gap spacing increased the discharge power for a given voltage and frequency. Increasing the voltage or frequency increased the discharge power for a given reactor configuration.
3. The presence of non-conducting, fibrous packing materials provided higher discharge power levels than when no packing material was used. However, it did not increase the efficiency of the process. Increased efficiency would have been seen by a reduced specific energy for a given level of conversion, specific energy values below that needed when no packing was employed.

Experimentation on the chemical aspects of the barrier discharge destruction of NO_x has led to the following conclusions pertaining to effects of various gases (typically found in flue gas streams) on the energy consumption of the discharge process and the products formed in the discharge.

1. The major products of the discharge initiated reactions were nitrogen and oxygen, benign compounds that can be released to the environment, when the simulated flue gas was composed of NO in N_2 . Small amounts of nitrogen dioxide were formed under these conditions. At an inlet concentration of 500 ppm NO in N_2 , an NO conversion of 90% was achieved with the formation of only 9 ppm NO_2 (88.2% NO_x conversion).
2. Oxygen in the simulated flue gas stream increased the formation of NO_2 , reducing the NO_x conversion. A decrease in conversion from 95% to 32% at a specific energy of 36,000 KJ/mole was seen when the oxygen content was

raised from 0 to 6% in the gas.

3. Water vapor at a 1% concentration in the simulated flue gas stream (NO in N₂) resulted in the formation of nitric acid instead of the nitrogen and oxygen. It also increased the specific energy needed to achieve 40% NO_x conversion from 10,000 KJ/mol when no water was present to 34,000 KJ/mol.
4. The presence of water vapor limited the use of non-conducting packing materials at the reactor temperatures employed in this study (room temperature to 110°C). This was due to sparking in the reactor when packing materials were employed with water vapor in the gas stream, which resulted in high power consumption and low NO_x conversion.
5. The addition of 10% carbon dioxide to the simulated flue gas stream containing NO, N₂ and O₂ resulted in a decrease in the NO_x conversion, from 90% to 76% at a specific energy of 60,000 KJ/mole. Carbon dioxide in the simulated flue gas stream also resulted in greater than 1000 ppm CO in the exit gas. CO concentration increases of only 3 to 5 ppm were observed in systems where combustion-generated flue gas was used.
6. The reactions occurring in the barrier discharge process for NO_x control appeared to be consistent with the mechanisms proposed for the electron pulse and electron beam irradiation of flue gases reported in the literature.
7. Increasing the nitric oxide concentration in the simulated or combustion-generated flue gas did not change the NO_x conversion achieved for a given specific energy. For example, at a specific energy of 42,000 KJ/mol in

simulated flue gas composed of NO in N₂, 97% NO_x conversion was achieved at NO_x concentrations of 42 to 490 ppm.

8. The NO_x conversion achieved for a given specific energy was higher when combustion-generated flue gas containing nitric oxide was treated than when simulated flue gas was used. At a specific energy of 15,000 KJ/mol the NO_x conversion was 92 percent using combustion-generated flue gas versus 54% in the simulated flue gas composed of NO in N₂.

The process development system (at a scale of over 30 times greater than the benchtop system) enabled experiments to be performed under conditions of high gas flow not attainable in the benchtop reactor. The conclusions drawn from experiments conducted on the process development unit are listed below.

1. Gas turbulence in the barrier discharge reactor improved the energy efficiency of the process. Increasing the Reynolds number from 500 to a value in the range of 2600 to 10,000 reduced the energy consumption per mole of NO_x entering the reactor by 28% (14,000 KJ/mol versus 10,500 KJ/mol) at a NO_x conversion of 70%.
2. Turbulence in the reactor limited the effect of flue gas composition (N₂, O₂, CO₂, H₂O) on NO_x conversion. No significant change in conversion was observed under turbulent flow conditions when the flue gas composition was changed by altering the air supply to the natural gas fired furnace, resulting in oxygen concentrations of 0 to 4.5%.
3. Reduced gap spacing (by increasing the center electrode diameter from 4 to

10 mm) at high gas flow rates increased the voltage required to initiate the barrier discharge and the rate at which discharge power increased with voltage. The reduced gap also narrowed the voltage range between initiation of the barrier discharge and arcing between the electrodes with breakdown of the dielectric barrier.

4. Increased electrode gap spacing (by reducing the center electrode diameter from 4 to 1 mm in the 29 mm outer electrode) reduced the NO_x conversion from 57% (4 mm electrode) to 40% (1 mm electrode) at a specific energy of 7000 KJ/mole.
5. The barrier discharge process was successfully scaled up from a benchtop apparatus to a process development unit. The reactor volume of the process development unit was over 30 times greater than the benchtop reactor volume.

This study has shown that the barrier discharge is an attractive technology for the control of NO_x emissions through generation of the active chemical species (ion, radicals and metastable compounds) that leads to NO_x destruction. Reduction of nitric oxide to nitrogen and oxygen is achievable with this technique. In addition, low levels of NO_x in the outlet of the barrier discharge reactor (< 2 ppm) can be achieved. The formation of nitric acid, in the presence of water vapor in the gas stream, presents a scientific challenge for the application of this technology. However, further work, to gain a better understanding of the reactions that occur in the discharge, may overcome this problem.

The discharge reactor inlet gas composition had little effect in turbulent flow on the NO_x conversion achieved for a given specific energy. This characteristic makes the

technology applicable to the wide variety of combustion systems in use today. In addition, the high conversion levels achieved without a performance penalty (higher specific energy) when the gas stream contained low concentrations of NO_x is an attractive feature of this technology. Application of this process to combustion systems that can not use currently existing NO_x control technologies due to the low NO_x levels in the exhaust is feasible.

The barrier discharge technology has been scaled up from the benchtop system to a larger process development unit, indicating that it is amenable to use in large combustion systems (such as utility power plants) as well as small systems (automobile engines). This makes the barrier discharge process more versatile than the NO_x control technologies available today. The understanding of these and other characteristics of the technology gained through this study indicate that the barrier discharge process has a high potential for commercial use.

CHAPTER VII

RECOMMENDATIONS

The use of barrier discharge technology for the destruction of nitrogen oxides in combustion exhaust gas is feasible. The high levels of NO_x conversion achieved in this study using simulated flue gas in a bench scale apparatus and combustion-generated flue gas in a process development unit indicate that commercial application of the technology is possible. However, additional work on the fundamental aspects of the barrier discharge process and on reaction kinetics is necessary. The following recommendations are made:

1. A significant challenge presented by this technique is the production of nitric acid when the treated gas contains water vapor. Addressing this problem requires extensive information on the discharge initiated reactions that does not currently exist in the literature. An investigation of the discharge or reactor conditions that promote the reduction of nitric oxide to nitrogen and oxygen and prevents the formation of nitric acid is needed. A separate approach to the problem is drying of the flue gas stream before it enters the discharge reactor. However, this does not appear to be economically feasible.
2. Electrical techniques for chemical processing have been plagued by the high energy requirements of the systems. The work conducted in this study showed that several possibilities exist for improvement of the energy efficiency of the

technique. Additional reactor configurations, including various electrode geometries and dielectric boundary properties, should be further investigated to identify optimum configurations.

3. A comprehensive model of the barrier discharge process is needed to provide the basis for understanding the efficient production of the active chemical species that result in NO_x destruction. The model can also help identify the conditions that would result in nitric oxide reduction instead of oxidation and formation of nitric acid. Development of the model will require a significant effort since it should include the electrical, chemical and hydrodynamic effects on the process. The Boltzmann, Poisson and Continuity equations are needed to model the electrical aspects of the discharge, including the electric field and electron energy distributions. The chemical species produced by electron collisions with neutral and excited gas compounds are effected by the electrical conditions in the discharge region. They also affect the electrical conditions in the discharge and must be taken into account. Finally, transport of the active species from the microdischarge zone, which effects the production of these species in subsequent discharges and their interactions with nitric oxide and nitrogen dioxide in the gas, should be included in the model.
4. The barrier discharge technique is attractive for production of species that can lead to chemical reaction. The oxidation of nitric oxide seen in this work indicates that oxidation of other polluting compounds, particularly volatile organic compounds and halogenated hydrocarbons, can be efficiently

accomplished using barrier discharges. The ability to achieve high levels of conversion at low concentrations makes this technique particularly promising in environmental applications where high levels of control are required. Work in this area has recently been undertaken but a substantial effort will be needed to identify compounds that can be efficiently destroyed, the reactions taking place in the destruction process, the products produced, and the parameters that control the efficiency of the process.

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APPENDICES

APPENDIX A

PROGRAM POWER

!Program to calculate the power from data generated by a
!Tektronix 2211 Oscilloscope using P6015 High Voltage Probes
!(1000X).

```
character*13 vname, iname, outfile, recfile ,numlist*9, check*1
character*4 outname, recname, fnum*2, fnum_a*1, fnum_b*1
real volt(4000), crnt(4000), powr(4000), angle(1000)
integer*2 ndpt, ndpta, count, vref, iref, n_cycles
integer*2 fnum_i, fnum_1, fnum_2
real spd, vvpd, cvpd, freq, sres, del_angle
real vpp, app, tbs, ndpts, tpowr, vmax, cycles, t_total
```

!Values of O-Scope settings. spd is sec/div, vvpd is kvolts/div
!for the voltage across the reactor, cvpd is volts/div for the
!current measurement.

```
open (7,file='power.in',status='old',err=500)
read (7,600,err=505) recname
read (7,600,err=510) outname
read (7,*)
```

```
if( recname .eq. 'NONE') goto 100
recfile = 'p' // recname // '.prn'
open (10,file=recfile,status='new',err=515)
goto 90
```

```
80  read (*,600) check
    if( check .eq. 'y' ) then
        open (10,file=recfile,status='old',err=516)
    else
        goto 590
    endif
90  continue
    write (10,700)
```

```

write (10,710)
numlist = '123456789'

100  read (7,*,err=510) fnum_i,freq,spd,vvpd,cvdp,sres,vref,iref
      if( fnum_i .eq. 999) goto 520

      fnum_1 = fnum_i/10
      fnum_2 = fnum_i - 10*fnum_1

      if( fnum_1 .eq. 0 ) then
          fnum_a = '0'
      else
          fnum_a = numlist(fnum_1:fnum_1)
      endif

      if( fnum_2 .eq. 0 ) then
          fnum_b = '0'
      else
          fnum_b = numlist(fnum_2:fnum_2)
      endif

      fnum = fnum_a // fnum_b
      vname = 'acq1.' // fnum
      iname = 'acq2.' // fnum
      outfile = 'p' // outname // '_' // fnum // '.prn'

      !vpp is volts per point, app is amps per point

      vpp = vvpd * 1000 / 25
      app = cvpd / sres / 25

      !Calculate time between samples (tbs), number of cycles,
      !and number of samples (ndpts)
      t_total = 10 * spd
      tbs = spd / 400
      cycles = freq * t_total
      if (cycles .lt. 1.0) cycles = 1.0
      n_cycles = int(cycles)

200  ndpts = n_cycles / (tbs * freq)
      if (n_cycles .gt. 1) then
          if (ndpts .gt. 4000) then
              n_cycles = n_cycles-1
              write (*,*) n_cycles
          
```

```

        goto 200
    end if
end if

if (ndpts .le. 0.0) goto 550
ndpt = int (ndpts+0.5)
if (ndpt .gt. 4000) ndpt = 4000

!Read in data from two data files

call readdata (vname, volt, vref)
call readdata (iname, crnt, iref)

!Calculate the instantaneous voltage across the reactor (VOLT),
!circuit current (CRNT), and power (POWR).

tpowr = 0.0

do i=1, 4000
    volt(i) = volt(i) * vpp
    crnt(i) = crnt(i) * app
    powr(i) = volt(i) * crnt(i)
end do

do i=1, ndpt
    tpowr = tpowr + powr(i)
end do

tpowr = tpowr / ndpt

if( outname .eq. 'NONE') goto 400

vmax = 0.0
Count = 1
ndpta = ndpt
if ( ndpta .lt. 3997) ndpta = ndpta + 4

do i=1, ndpta-4, 4
    volt(count) = (volt(i)+volt(i+1)+volt(i+2)+volt(i+3))/4
    crnt(count) = (crnt(i)+crnt(i+1)+crnt(i+2)+crnt(i+3))/4
    powr(count) = (powr(i)+powr(i+1)+powr(i+2)+powr(i+3))/4
    if ( abs(volt(count)) .gt. Vmax ) vmax=abs(volt(count))
    count = count + 1
end do

```



```

    open (9, file=outfile)
    write (9,620) outfile
    write (9,625) freq
    write (9,630) vmax
    write (9,640) tpowr
    write (9,645) count-1
    del_angle = 360.0 * n_cycles / (count-2)

    do i=1, count-1
        angle(i) = del_angle * (i-1)
        write (9,650) angle (i), volt(i), crnt(i), powr(i)
    end do
    close (9)
400 continue

    if( recname .eq. 'NONE') goto 410
    write (10,720) fnum, freq, n_cycles, tpowr

410 write (*,660) fnum, ndpt, tpowr

    goto 100

!Error Messages
500 write (*,900)
    goto 590
505 write (*,905)
    goto 590
510 write (*,910)
    goto 590
515 write (*,915)
    goto 80
516 write (*,916) recfile
    goto 590
520 write (*,920)
    goto 590
550 write (*,950)
    goto 590

590 continue

    stop

600 format (a)
610 format (f9.4)

```

```

615 format (i5)
620 format (1x,a)
625 format (f10.0,3X,'hz')
630 format (1pe10.3,3X,'volts max')
640 format (1pe10.3,3X,'watts total')
645 format (i5,3x,'data sets written',/,/,/)
650 format (f8.3,1x,1pe10.3,1X,1pe10.3,1X,1pe10.3)
660 format (/,'file =' ,a3,2x,'# data points = ',i4,3x,
+       'total power = ',1pe10.2, ' Watts')

700 format ('Power program Output')
710 format ('file #',6x,'freq',3x,'Cycles',4x,'Power')
720 format (a3,3x,f10.0,3x,i3,3x,1pe10.2)

900 format (/, 'error opening power.in')
905 format (/, 'error reading record filename in power.in')
910 format (/, 'error reading output filename in power.in')
915 format (/, 'Output file already exists, Overwrite? (y/n)')
916 format (/, 'error opening output record file:',1x,a13)
920 format (/, 'end of input file')
950 format (/, 'error: # of data points less than 0')
end

```

SUBROUTINE READDATA (signam, data, refn)

!Subroutine to read the data generated by a Tektronix 2211 O-Scope
!and stored using the GRABBER program. The data is contained in
!binary files generated from the grabber plot file.

```

integer j, nsamp
integer*1 intdata
integer*2 sig(4000), refn
character*13 signam
real data(4000)

nsamp = 4000
open( unit=11, file=signam,
+     access='sequential',
+     form='unformatted',
+     recordtype='fixed' )

do j = 1, nsamp
    read( 11 ) intdata
    sig( j ) = intdata

```

```
end do

do j = 1, nsamp
    if( sig( j ) .lt. 0 ) sig( j ) = sig( j ) + 256
    data( j ) = sig( j ) - refn
end do

return
end
```

APPENDIX B

PROGRAM TPOWER

```
C
C
C   Program To Calculate the power from a voltage and current
C   input using an SCC1220 data acquisition system with the
C   data files converted to ASCII. Program uses batch file
C   inputs (control.pwr and 'file'.tst) to process data.
C   For current probe set current multiplier in .TST file to
C   the proper value and set resistance value to 1.
C   For series resistance set the resistance to the proper
C   value and the current multiplier to the multiplier for
C   the voltage probe in use.
C
REAL VOLT, CURR, FREQ, RES, CYCL, SPS
REAL PWR, PWRI, PRWB, SUMPWR, TOTPWR
REAL BLOCKS, REMDR, PMULT, VMULT, IMULT, IVMULT
REAL AVSUM, AISUM, VAVE, IAVE
INTEGER I, J, K, SPB, NBLOCK, NREMDR
INTEGER NPOINTS, CNT1, CNT2, CNT3, CNT4, CNT5
CHARACTER*13 DATAFILE, FVOLT, FCURR, FPOWER
C
DIMENSION VOLT(4000), CURR(4000), PWR(50)
DIMENSION VAVE(1500), IAVE(1500)
C
OPEN (3, FILE='CONTROL.PWR', STATUS='OLD')
10 CONTINUE
READ (3,910,END=899) DATAFILE
C
OPEN (4, FILE=DATAFILE, STATUS='OLD')
READ (4,910) FVOLT
READ (4,910) FCURR
READ (4,910) FPOWER
READ (4,*) FREQ, RES, VMULT, IVMULT
READ (4,*) SPS, SPB, CYCL, NPOINTS
C
IMULT = 1/RES * IVMULT
```

```

    PMULT = VMULT * IMULT
    BLOCKS = CYCL * (1/FREQ) * SPS/SPB
    NBLOCKS = BLOCKS
    REMDR = (BLOCKS - NBLOCKS) * SPB
    NREMDR = REMDR
    CNT1 = SPB/NPOINTS
    CNT5 = CYCL * (1/FREQ) * SPS/NPOINTS
C
    OPEN (5, FILE=FVOLT, STATUS='OLD')
    OPEN (6, FILE=FCURR, STATUS='OLD')
C
    DO 150 J=1, NBLOCKS
        PWRB = 0.0
        DO 100 I=1, SPB
            READ (5,*) VOLT(I)
100    CONTINUE
        DO 110 I=1, SPB
            READ (6,*) CURR(I)
110    CONTINUE
        DO 120 I=1, SPB
            PWRI = VOLT(I) * CURR(I)
            PWRB = PWRB + PWRI
120    CONTINUE
        PWR(J) = PWRB * PMULT / SPB
        WRITE (*,920) J, PWR(J)
C
        DO 140 I=1, CNT1
            CNT2 = (I-1)*NPOINTS
            AVSUM = 0.0
            AISUM = 0.0
            DO 130 K=1, NPOINTS
                CNT3 = CNT2+K
                AVSUM = AVSUM + VOLT(CNT3)
                AISUM = AISUM + CURR(CNT3)
130    CONTINUE
            CNT4 = (J-1)*CNT1+I
            VAVE(CNT4) = AVSUM/NPOINTS*VMULT/1000
            IAVE(CNT4) = AISUM/NPOINTS*IMULT*1000
140    CONTINUE
150 CONTINUE
C
    IF (REMDR.GT.0) THEN
        PWRB = 0.0
        NBLOCKS = NBLOCKS + 1

```

```

        DO 200 I=1, NREMDR
            READ (5,*) VOLT(I)
200    CONTINUE
        DO 210 I=1, NREMDR
            READ (6,*) CURR(I)
210    CONTINUE
        DO 220 I=1, NREMDR
            PWRI = VOLT(I) * CURR(I)
            PWRB = PWRB + PWRI
220    CONTINUE
        PWR(NBLOCKS) = PWRB * PMULT / REMDR
        WRITE (*,920) NBLOCKS, PWR(NBLOCKS)
C
        DO 240 I=1, NREMDR/NPOINTS
            CNT2 = (I-1)*NPOINTS
            AVSUM = 0.0
            AISUM = 0.0
            DO 230 K=1, NPOINTS
                CNT3 = CNT2+K
                AVSUM = AVSUM + VOLT(CNT3)
                AISUM = AISUM + CURR(CNT3)
230        CONTINUE
            CNT4 = (NBLOCKS-1)*CNT1+I
            VAVE(CNT4) = AVSUM/NPOINTS*VMULT/1000
            IAVE(CNT4) = AISUM/NPOINTS*IMULT*1000
240    CONTINUE
        ENDIF
C
        CLOSE (5)
        CLOSE (6)
C
        SUMPWR = 0.0
        DO 500 J=1, NBLOCKS
            SUMPWR = SUMPWR + PWR(J)
500    CONTINUE
C
        TOTPWR = SUMPWR / NBLOCKS
        WRITE (*,960) TOTPWR
        OPEN (7, FILE=FPOWR, STATUS='NEW')
C
        WRITE (7,930) FREQ
        WRITE (7,940) CYCL
        WRITE (7,950) SPS
        WRITE (7,960) TOTPWR

```

```

        WRITE (7,970)
        DO 300 I=1, CNT5
            WRITE (7,980) VAVE(I), IAVE(I)
300 CONTINUE
        CLOSE (7)
C
        GOTO 10
899 CONTINUE
C
        STOP
C
910 FORMAT (A)
920 FORMAT (I3, 3X, 1PE10.2)
930 FORMAT (' Freq = ', F6.2, 1X, 'Hz')
940 FORMAT (' # Cycles = ', F3.0)
950 FORMAT (' Sample Rate = ' 1PE10.1, 1X, 'Hz')
960 FORMAT (' Total Power = ', 1PE10.2, 1X, 'Watts')
970 FORMAT (3X, ' KV ', 10X, ' mA ')
980 FORMAT (F10.4, 3X, F10.5)
C
        END

```

APPENDIX C

```

/*****
/*      model_3.d: Electrical model of the corona reactor.      */
/*                                                              */
/*      Date: May 1992                                          */
/*      Rev (1) Dielectric constant of the gas was added.      */
/*              Date: June 9, 1992                             */
/*      Rev (2) Maximum loop criteria added to prevent crashing */
/*              Under Relaxation added.                        */
/*      Rev (3) Looping on voltage and frequency added in order to */
/*              perform parametric investigations.              */
/*              Date: June 17, 1992                             */
/*      Rev (3A) Critical radius, volume and Power added.      */
/*              Date: December 28, 1992                        */
*****/

#include <math.h>
#include <stdio.h>

/* define constants */

#define K_STAR 2.2e-12
#define EPSILON 8.85e-14
#define TRUE 1

/* function prototypes */

double I_i (double a, double b, double c, double l, double Vmax, double k,
            double w, double wt, double k_o);
double wt_1 (double a, double b, double c, double del, double Vmax, double k, double
            k_o, double f);
double V_2_i (double a, double b, double c, double Vmax, double k, double wt,
            double k_o);
double I_f (double a, double b, double c, double l, double Vmax, double k,
            double w, double rho, double wt, double theta_1, double k_o);
double phase_1 (double a, double b, double c, double k, double w, double rho, double
            k_o);
double V_2_f (double a, double b, double c, double Vmax, double k, double w,
            double rho, double wt, double theta_2, double k_o);
double phase_2 (double a, double b, double c, double k, double w, double rho, double
            k_o);

```



```
double rho_corona (double c, double del, double g, double v2f, double v2i_o);
double d_abs(double);
```

```
void main(void)
{
    FILE *fptr2;
    char string[40];
    char file_name[40];
    double a, b, c, l, f, Vmax, k, T, del, w, Vo, wt, wt1, wt2, wt_jump, step;
    double i_i, i_f, v2f, v2i, rho, theta_1, theta_2, v2fo, resistance;
    double dv_dr_gap, dv_dr_di, power, power_sum, dv_dr_max, dv_dr_di_cri;
    double g, v2i_o, i_f_old, rho_old, theta_1_old, theta_2_old, k_o;
    double check_i_f, check_rho, check_theta_1, check_theta_2, con_check;
    double gamma, r_crit, p_crit, res_crit, p_crit_sum;
    double v_crit, v_crit_sum;
    int itest, icount;
    int i_freq = 0;

    clrscr();
    con_check = 0.01;
    fptr2 = fopen("results.prn","a");
                                /* input data */
    printf("\n\nEnter Reactor Geometry:\n\n");
    printf("Enter a (cm): ");
    gets(string);
    a = atof(string);
    printf("Enter b (cm): ");
    gets(string);
    b = atof(string);
    printf("Enter c (cm): ");
    gets(string);
    c = atof(string);
    printf("Enter l (cm): ");
    gets(string);
    l = atof(string);
    printf("\n\nEnter Operating Conditions:\n\n");

    printf("Enter operating temperature (F): ");
    gets(string);
    T = atof(string);
    printf("\n\nEnter kd : ");
    gets(string);
    k = atof(string);
```

```

printf("Enter kg : ");
gets(string);
k_o = atof(string);
printf("Enter g : ");
gets(string);
g = atof(string);

fprintf(fp2, "%lf %lf %lf %lf %lf %lf %lf %lf",a,b,c,l,T,k_o,g);

step = 0.1*2.0*M_PI/360.0;
for (f=100.0; f<=1500; f+=100)
{
    for (Vmax=15000.0; Vmax<=45000.0; Vmax+=1000.0)
    {
        /* initial calculations */

        w = 2*M_PI*f;
        del = 530/(T + 460);
        wt1 = wt_1 (a,b,c,del,Vmax,k,k_o,f);
        wt2 = M_PI-wt1;

        v2fo = V_2_i (a,b,c,Vmax,k,wt1,k_o);
        dv_dr_max = 0.0;
        dv_dr_di_cri = 0.0;
        v2i_o = v2fo;

        for (wt = 0; wt <= wt1; wt += step)          /* no corona */
        {
            i_i = I_i (a,b,c,l,Vmax,k,w,wt,k_o);
            v2i = V_2_i (a,b,c,Vmax,k,wt,k_o);
            dv_dr_gap = v2i/c/log(c/b);
            if (b/a == 1)
                dv_dr_di = 0.;
            else
                dv_dr_di = (Vmax*sin(wt)-v2i)/b/log(b/a);
            if (dv_dr_gap > dv_dr_max)
                dv_dr_max = dv_dr_gap;
            if (dv_dr_di > dv_dr_di_cri)
                dv_dr_di_cri = dv_dr_di;
        }

        power_sum = 0.0;
        p_crit_sum = 0.0;
        v_crit_sum = 0.0;
    }
}

```

```

if (!wt2<=0.0)
{
    rho_old = 1e20;
    rho = 1e20;
    i_f = 0.01;
    theta_1 = 10.0/360.0*2.0*M_PI;
    theta_2 = 15.0/360.0*2.0*M_PI;
    gamma = 0.1;
    for (wt = wt1+step; wt < wt2-20.0*step; wt+=step)          /* main loop */
    {
        icount = 0;
        i_f_old = i_f;                                          /* initial guess */
        rho_old = (rho+rho_old)/2;
        theta_1_old = theta_1;
        theta_2_old = theta_2;
        while (TRUE)
        {
            icount++;
            v2f = V_2_f(a,b,c,Vmax,k,w,rho_old,wt,theta_2_old,k_o);
            rho = rho_old + gamma*(rho_corona(c,delta,g,v2f,v2i_o)-rho_old);
            i_f = i_f_old + gamma*(I_f(a,b,c,l,Vmax,k,w,rho,wt,theta_1_old,k_o)
                -i_f_old);
            theta_1 = theta_1_old + gamma*(phase_1(a,b,c,k,w,rho,k_o)-theta_1_old);
            theta_2 = theta_2_old + gamma*(phase_2(a,b,c,k,w,rho,k_o)-theta_2_old);
            check_i_f = d_abs((i_f-i_f_old)/i_f_old);          /* con check */
            check_rho = d_abs((rho-rho_old)/rho_old);
            check_theta_1 = d_abs((theta_1-theta_1_old)/theta_1_old);
            if (check_i_f > con_check || check_rho > con_check ||
                check_theta_1 > con_check)
            {
                i_f_old = i_f;
                rho_old = rho;
                theta_1_old = theta_1;
                theta_2_old = theta_2;
            }
            else
                break;
            if (icount>5000)
                break;
        }
        dv_dr_gap = v2f/c/log(c/b);
        if (b/a == 1)
            dv_dr_di = 0.;
        else

```

```

        dv_dr_di = (Vmax*sin(wt)-v2f)/b/log(b/a);
        if (dv_dr_gap > dv_dr_max)
            dv_dr_max = dv_dr_gap;
        if (dv_dr_di > dv_dr_di_cri)
            dv_dr_di_cri = dv_dr_di;
        resistance = rho/2/M_PI/l*log(c/b);
        power = v2f*v2f/resistance;
        r_crit = 1/del*pow(-0.15+pow(0.0225+v2f/30000/pow(300/f,0.16)/log(c/b),0.5),2);
        v_crit = 2.0*M_PI*l*(pow(r_crit,2)-pow(b,2));
        res_crit = rho/2/M_PI/l*log(r_crit/b);
        p_crit = pow(v2f,2)*res_crit/resistance/resistance;
        power_sum += power;
        p_crit_sum += p_crit;
        v_crit_sum += v_crit;
    }

for (wt = wt2-20.0*step; wt <= M_PI; wt += step)        /* no corona */
{
    i_i = I_i (a,b,c,l,Vmax,k,w,wt,k_o);
    v2i = V_2_i (a,b,c,Vmax,k,wt,k_o);
    dv_dr_gap = v2i/c/log(c/b);
    if (b/a == 1)
        dv_dr_di = 0.;
    else
        dv_dr_di = (Vmax*sin(wt)-v2i)/b/log(b/a);
    if (dv_dr_gap > dv_dr_max)
        dv_dr_max = dv_dr_gap;
    if (dv_dr_di > dv_dr_di_cri)
        dv_dr_di_cri = dv_dr_di;
}

power_sum = power_sum/180;
p_crit_sum = p_crit_sum/180;
v_crit_sum = v_crit_sum/180;
printf("\n\nFrequency (Hz): %lf", f);
printf("\nVoltage (volts): %lf", Vmax);
printf("\nPower (watts): %lf", power_sum*step*360.0/2/M_PI);
printf("\nCritical Power (watts): %lf", p_crit_sum*step*360.0/2/M_PI);
printf("\nCritical Volume (cm3): %lf", v_crit_sum*step*360.0/2/M_PI);
printf("\ndv_dr (gas) = %lf", dv_dr_max);
printf("\ndv_dr (die) = %lf", dv_dr_di_cri);
fprintf(fp2, "\n %lf %lf %lf %lf %lf %lf %lf",
        f,Vmax,dv_dr_max,dv_dr_di_cri,power_sum*step*360.0/2/M_PI,

```

```

        p_crit_sum*step*360.0/2/M_PI,v_crit_sum*step*360.0/2/M_PI);
    }
    if (i_freq==0)
    {
        i_freq=1;
        f+=0;
    }
}
fclose(fp2);
}

/*****
/* Function I_i:   Electric current before corona          */
*****/

double I_i (double a, double b, double c, double l, double Vmax, double k,
            double w, double wt, double k_o)
{
    double i;
    i = 2*M_PI*EPSILON*w*l*Vmax*sin(wt+M_PI/2)/(1/k*log(b/a) + 1/k_o*log(c/b));
    return i;
}

/*****
/* Function wt_1:  Angle where critical field is reached    */
*****/

double wt_1 (double a, double b, double c, double del, double Vmax, double k, double
k_o,
            double f)
{
    double wt,term;
    term = pow(300./f,0.16)*(-(30000*del*b + 9000*pow(del*b,0.5))/Vmax *
        (1/k*log(b/a) + 1/k_o*log(c/b)));
    if ( term*term > 1.0)
        wt = 180./360.*2.*M_PI;
    else
        wt = acos(term) - M_PI/2;
    return wt;
}

/*****

```

```

/* Function V_2_i: Reactor Voltage before corona */
/*****

double V_2_i (double a, double b, double c, double Vmax, double k, double wt,
double k_o)
{
    double v;
    v = Vmax*sin(wt)/(1+1/k*log(b/a)/(1/k_o*log(c/b)));
    return v;
}

/*****
/* Function I_f: Current after corona */
/*****

double I_f (double a, double b, double c, double l, double Vmax, double k,
double w, double rho, double wt, double theta_1, double k_o)
{
    double i;
    i =
(1/EPSILON/w+pow(k_o,2.)*pow(rho,2)*EPSILON*w)*2*M_PI*l*Vmax*sin(wt+theta
_1)/
    pow( pow(rho*log(c/b)/EPSILON/w,2) +
        pow ( 1/k*log(b/a)*pow(1/EPSILON/w,2) + k_o*k_o*rho*rho*(1/k*log(b/a)
+
        1/k_o*log(c/b)),2),0.5);
    return i;
}

/*****
/* Function phase_1: phase angle 1 after corona */
/*****

double phase_1 (double a, double b, double c, double k, double w, double rho, double
k_o)
{
    double theta;
    theta = atan(1/k*log(b/a)/log(c/b)*(1/EPSILON/w/rho+k_o*k_o*EPSILON*w*rho)
+ k_o*EPSILON*w*rho);
    return theta;
}

/*****
/* Function V_2_f: corona voltage */
/*****

```

```

double V_2_f (double a, double b, double c, double Vmax, double k, double w,
              double rho, double wt, double theta_2, double k_o)
{
    double v;
    v = Vmax*sin(wt+theta_2)/pow( pow(1+1/k*log(b/a)/(1/k_o*log(c/b)),2) +
    pow(1/k*log(b/a)/EPSILON/w/rho/log(c/b),2),0.5);
    return v;
}

/*****
/* Function phase_2: phase angle 2 after corona */
*****/

double phase_2 (double a, double b, double c, double k, double w, double rho, double
k_o)
{
    double theta;
    theta = atan(1/k*log(b/a)/(EPSILON*w*rho*(log(c/b)+k_o/k*log(b/a))));
    return theta;
}

/*****
/* Function rho_corona: corona resistivity */
*****/

double rho_corona (double c, double del, double g, double v2f, double v2i_o)
{
    double rho;
    rho = del*M_PI*pow(c,2.0)/K_STAR/g/d_abs((v2f-v2i_o));
    return rho;
}

/*****
/* Function d_abs(double value) */
*****/

double d_abs(double value)
{
    if (value < 0)
        value = value * (-1.0);
    return value;
}

```

APPENDIX D

**REACTION KINETICS FOR FLUE GAS
TREATMENT OF NO_x**

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REACTION KINETICS FOR FLUE GAS TREATMENT OF NO_x

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SoCal Gas Company

ABSTRACT

The control of NO_x emissions has become a national issue during the past few years. NO_x emissions are a leading contributor to acid rain as well as contributing strongly to photochemical smog and ground level ozone. Current state-of-the-art technologies have essentially reached their maximum potential. To overcome these problems, advanced processes have been developed utilizing plasmas that generate large numbers of various radical species that promote the removal of NO_x. Considerable research has been conducted on e-beam and laser generated plasmas (1,2). However, low energy efficiencies associated with the generation of high energy plasmas has kept these processes from moving rapidly into commercial operation. Recognizing the benefits of advanced high energy techniques, a new process based on the generation of a low energy plasma, a soft corona discharge has been developed that has demonstrated NO_x emission control approaching 99 percent reduction (3,4). The process is an electro-catalytic process in which the electrons generated by the soft distributed corona discharge promote the dissociation of NO_x molecules.

The performance of the current state-of-the-art systems is dependent upon the oxygen level in the flue gas. This is not the case for this process. NO_x reduction with this process is relatively insensitive to oxygen level. Greater than 90% reduction is maintained with flue gas oxygen levels ranging from 2 to 15 percent. Cost estimates for this technology achieving 96% reduction are slightly less than that of an SCR system achieving only 90 percent. This paper discusses the data and the system operation in detail and presents preliminary cost data compared with current state-of-the-art technologies.

INTRODUCTION

During the past several years, control of NO_x emissions has become an international issue. NO_x emissions are a leading contributor to acid rain as well as contributing strongly to photochemical smog. In this regard, NO_x emissions have the most widely spread detrimental impact on air quality, vegetation and human health of any regulated emission. Current state-of-the-art technologies either the combustion zone in an effort to control the temperature, residence time and stoichiometry thereby lowering the NO_x formation or provide a post combustion reducing agent that consumes the oxygen in the NO_x molecule producing nitrogen and water. These two approaches have essentially reached their maximum potential. Combustion modifications alone can no longer achieve the emissions levels required in specific regions throughout the U.S., namely southern California and the North East. Therefore, processes are required to add post

combustion control as well. These technologies function either with or without the aid of a catalyst. A major problem with these techniques is that secondary pollution by the reducing agent (preferably NH_3 due to its reactivity and selectivity) is becoming an issue and monitoring its emissions required (1). Furthermore, oils and other compounds can reduce the effectiveness of an expensive catalyst, eventually requiring the replacement of it.

To overcome these problems, advanced processes have been developed utilizing plasmas that generate large numbers of various radical species that promote the decomposition of NO_x into molecular nitrogen and oxygen. Considerable research has been conducted on e-beam and laser generated plasmas. However, low energy efficiencies associated with generation of the high energy plasmas has kept these processes from moving rapidly into commercial operation (2). In addition, the cost of producing these high energy power supplies further inhibits the commercial introduction of these systems. Recognizing the benefits of the advanced high energy techniques, a new process based on the generation of a low energy plasma, a soft corona discharge, has been developed that has demonstrated NO_x emission control approaching 99 percent reduction. The process is an electro-catalytic process in which the electrons generated by the soft distributed corona discharge promote the dissociation of the NO_x molecules (3,4,5). It does not require a reducing agent or a catalyst. NO_x containing flue gas flows through the annular region of the reactor between the high voltage electrode and the outer wall. In this regard, the reactor is electrically a capacitor. Since capacitors consume little real power, i.e., their reactive power can be recovered. Thus, the only power that is consumed is by the resistive load associated with the low energy discharge.

The performance of the current state-of-the-art Systems is dependent upon the oxygen level in the flue gas and generally modifications are necessary to get these systems to work well away from the design point. This is not the case for this process; NO_x reduction with this process is relatively insensitive to oxygen level. Greater than 90% reduction is maintained with flue gas oxygen levels ranging from 2 to 15 percent. This shows the potential of this process for wide application.

NO_x CONTROL TECHNOLOGIES

A number of approaches, grouped into pre-combustion, In-combustion and post-combustion modifications, can be used to control NO_x emissions. In general, all these approaches attempt to control flame temperature, fuel and gas chemistry at each location in the combustion process. The optimum combination of these approaches can expect to yield emission reductions of 40 to 70 percent. However, no matter how much effort is used to limit the production of NO_x in the first place, some form of post-combustion clean-up will ultimately be required.

Pre-combustion Control Typical fuel oils contain approximately 0.1 percent bound nitrogen while most coals contain from 0.5 to 2 percent bound nitrogen. Pre-treatment of these fuels to reduce their nitrogen content and resulting NO_x formation is very costly and not considered practical today. However, fuel oil/water emulsions and coal/water slurries have been used to reduce NO_x emissions, largely due to lowering of the flame temperature. Stability of oil emulsions or coal/water slurries can be achieved for long periods of time using various additives. As an alternative, emulsification hardware is available to provide controlled metering of the water

prior to atomization.

In-combustion Control In-combustion control of NO_x actually represents the first major opportunity to control emissions. These techniques can generally be grouped as: (1) low- NO_x burners (LNB) or (2) in-furnace modifications which includes air staging, fuel staging (reburning) and flue gas recirculation. LNB burners have been developed by most boiler and burner manufacturers. While the design details differ from manufacturer to manufacturer, they all generally modify the means of introducing the air and fuel to slow the rate of mixing, reduce oxygen availability in critical NO_x formation zones, and reduce the amount of fuel burned at peak temperatures.

A full LNB retrofit can be expected to reduce NO_x emissions from uncontrolled baseline levels by up to 50%. Capital-cost requirements are modest compared to downstream techniques but retrofit is rarely a straightforward proposition. Invariably, air and fuel flow controls, registers, dampers, and other components are significantly more elaborate and have to be properly adjusted. Reliability of these auxiliary systems is critical, resulting in more operator attention, and higher maintenance costs than other designs.

For clean gaseous fuels, another LNB technology known as catalytic combustion is most effective for minimizing NO_x formation. In this approach, the fuel is burned within or on the surface of a porous ceramic substrate. The ceramic transfers the heat of combustion to the process mainly by radiation, and as such, this type of burner is also often called an infrared or IR burner. Because of the low temperatures at which the combustion takes place, typically between 1090 and 1649 K, and the catalytic effects of the porous substrate, the NO_x emissions are able to be minimized. However, very low gas velocities are necessary to keep the flame on or within the porous surface. As such, specific heat release rates are typically very low compared to conventional burners. Also, care must be taken not to plug the substrate.

Air staging, often called two-stage combustion is a technique used to minimize the formation of NO_x by burning the fuel in an initially rich or substoichiometric zone. Here, the furnace is divided into upper and lower combustion zones. The lower zone is operated fuel-rich to control NO_x formation, the upper zone fuel-lean to complete burnout. The amount of fuel supplied to the upper burners depends on the unit load.

Reburning, commonly called fuel staging, involves diverting 10-20% percent of the furnace's total fuel input to create a second combustion zone downstream of the primary zone. The second zone is operated sub-stoichiometrically. NO from the primary zone is then converted to elemental N_2 in the second zone. The general idea is to provide a chemical path for the NO to convert into N_2 instead of NO_2 . Hydro-carbon radicals formed during combustion of the reburn fuel provide this path.

Mixing of the reburn fuel in the wide expanse of the furnace is critical as is mixing of the combustion air above the reburn zone. Theoretically, any fuel can serve as a reburn fuel. However, it helps if it is low in nitrogen and exhibits high volatility to be compatible with tight upper-furnace dimensions.

Flue gas recirculation (FGR) is used to reduce the flame temperature by dilution of the

combustion air. It has been applied to gas, oil and coal systems from commercial to utility scales. Flue gas recirculation can also be used to improve mixing and in so doing reduce excess air requirements. A type of flame-quenching strategy, the flue gas acts as a thermal diluent to reduce combustion temperatures. In the process, it significantly reduces excess-air requirements and provides a means of staging the combustion process. Hardware modifications to implement FGR include new ductwork, recirculation fan, devices to mix flue gas with combustion air, and added controls.

Another technique traditionally associated with minimizing NO_x emissions from gas turbines, is adding water or steam in the combustion zone. This is a flame quenching strategy, and can suppress NO_x formation by up to 70%. Care must be taken to properly integrate the injection system into the turbine. However, there are a number of consequences of water/steam injection: (1) CO and unburned-hydrocarbon emission increase, especially at low load; (2) fuel consumption increases by up to 5% to make up for the heat of vaporization of water (use of steam avoids this penalty but about 50% more of it is needed on a mass basis for equivalent reduction); (3) water that has been extensively treated is lost up the stack; and (4) turbine control and monitoring are more complex.

Post-Combustion Control Techniques Where the limits on NO_x emission cannot be met by in-combustion control, post-combustion treatment is required. The two technologies in commercial use for process gas, boiler and gas turbine applications are selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). In addition, there are a number of combined sulfur and NO_x reduction processes under development using various sorbents as well as irradiation and electron beam technologies. These new technologies all strive to reduce system capital and operating costs. SCR and SNCR processes are termed "selective" because the reducing agent, ammonia, urea, or other nitrogen-containing compound selectively reacts with the NO_x molecule to reduce the oxidative state of the nitrogen rather than reacting with the O_2 , which also present in the flue gas at substantially higher concentrations. With SNCR, the reagent is injected into the flue gas in a temperature regime of 1140 to 1370 K to reduce the NO_x to nitrogen and water. As such, SNCR is limited to process gas and boiler applications where reagent injection ports can be provided. Adequate temperature control and mixing of the reducing agent with the flue gas is key to high reduction. However, reduction levels are typically 60 percent with levels above 80 percent hard to achieve without increasing CO and unreacted reagent (slip) above acceptable limits. In fact, if care is not taken, the slip can exceed the NO_x emissions.

Selective catalytic reduction (SCR) is similar to SNCR except that a catalyst is used to make the reactions proceed within a lower temperature regime. The most popular catalysts include vanadium, platinum or titanium compounds impregnated on a metallic or ceramic substrate.

The process temperature range is typically 590-670°K, which makes it more easily adaptable to post-combustion retrofit. The reagent, ammonia for example, is supplied through a nozzle grid located in the flue gas path. Critical to the process are adequate mixing of the streams. SCR systems can expect to reduce NO_x emissions generally by 80 percent and 90 percent in a few selected tests. However, because no reaction goes to completion and because catalysts lose activity with time, ammonia slip also tends to increase with time. As a result, catalysts must be replaced periodically which may range from one to five years and these catalysts are hazardous waste due to the catalytic metals present. There are also several side reactions when ammonia slip is high. For one, the catalysts tend to convert SO_2 to SO_3 , which reacts with any residual

ammonia and water to form ammonium sulfate and ammonium bisulfate. These are solids that can foul or plug downstream components.

Post combustion NO_x reduction systems for internal combustion engines are also typically catalyst based. For lean-burn engines where the exhaust gas contains substantial amounts (5-13 percent) of oxygen, a complete SCR system, with ammonia injection is necessary. For stoichiometric or rich-burn engines where the oxygen level is less than 0.5 percent, three-way (CO , NO_x and hydrocarbons) catalytic-converter technology called non-selective catalytic reduction (NSCR) can be applied without the need for ammonia. By operating the engine at stoichiometric conditions, a reducing atmosphere high in CO is produced. The catalyst then uses this CO to reduce the NO_x to form CO_2 plus N_2 . Any remaining CO and hydrocarbons are oxidized to CO_2 and water if sufficient oxygen is present; otherwise, additional air can be introduced in a latter stage of the reaction. Typically, NSCR systems can reduce NO_x levels by 90 percent. However, when the starting NO_x concentration is greater than 3000 ppm, this still leaves 300 ppm in the exhaust gas.

Governing factors which effect the performance of three-way NSCR systems include poisoning by degenerating substances such as sulfur compounds, fouling by solid particles, excessive reaction temperatures resulting from engine misfiring and subsequent combustion of the unburnt fuel and oxygen at the catalyst, and masking or coating of the catalyst by heavy metals in the engine lubricant.

THE TECOLYTIC™ CONCEPT

At this point, a thorough background discussion of corona initiated reactions and the status of the work in this area by Tecogen will be given. Tecogen has been involved in developing corona initiated reactions for pollution control for the past four years. During that time, work has focussed on developing that technology for NO_x control. With respect to NO_x control, the technology has very wide applications - from lean burn engines, to high-efficiency gas burners, to utility power plants burning a variety of fossil-based fuels - and Tecogen is dedicated to the development and subsequent commercialization of the TECOLYTIC™ De NO_x process. The wide applicability of the corona based process for NO_x control, from reducing conditions to oxidizing conditions, from dry systems to wet systems, gives evidence to the ability of the reactor to be used for gas as well as oil and coal fired systems. Data on this subject will be discussed later. The uniqueness of the process is the generation of a low energy gaseous plasma, or "corona," within a chemical reactor. Corona is a general term that describes the state of a gaseous mixture. Within a corona, gases may show a wide variety of physical and chemical properties that are entirely different from their normal properties. This is because they exist in a variety of chemical forms, including but not limited to atoms, free radicals, and ions.

One feature common to many of the species generated within the corona is extreme chemical reactivity. On a more fundamental basis, the process could be termed an electro-catalytic process because it is free electrons that initiate the NO_x decomposition reactions much the same way as conventional catalysts. Randomly occurring free electrons within the corona reactor are accelerated in an electric field until they attain sufficient energy to cause ionization of some of the gas molecules. Very soon, a steady state is reached whereby the rate of formation of ions is equal to the rate of recombination. At this point, an equilibrium conducting state, i.e., a self-sustained discharge, is maintained within the reactor.

The corona or electrical discharge can be initiated by one of several methods. Either direct current, low-frequency (audio), radio-frequency (MHz), or microwave-frequency (GHz) electric power can be used effectively as a power source for sustaining a glow discharge, or corona. To date, only low-frequency electric current has been used extensively by Tecogen in the development of the TECOLYTIC™ process.

The Reactor A simplified schematic of the concept as applied to NO_x control is shown in Figure 1. A high voltage potential is applied to the inner electrode as shown in Figure 2. The inner electrode is axially aligned within an outer tube normally maintained at ground potential. Located between the inner and outer electrode is a quartz tube, which serves as a dielectric barrier, allowing a silent glow discharge (corona) rather than a spark to be generated between the two electrodes. It is important to distinguish between spark and corona discharge mechanisms.

Sparks are characterized by extremely high temperatures and large current densities comparable to high energy plasmas such as those produced by e-beam and laser techniques. The electrical current is carried by the ionized gas. A spark is basically a miniature lightning bolt. Within a corona, many spark-like, electrical fibers or streamers are formed. These streamers are similar in appearance to lightning bolts; however, the current density is much lower. In addition, the physical appearance of a spark is usually bright yellow, whereas a corona (with any significant amount of nitrogen present) is characterized by a deep purple color, which is unique to the nitrogen molecule. In general, although a corona is inherently a random process, it is still more predictable and controllable than a spark. The ion current density within a corona can be varied over a wide range simply by varying the applied high voltage potential. This is a convenient control parameter.

In some instances, the void volume of the corona reactor is packed in whole or in part with a fibrous dielectric packing material. The purpose of the dielectric packing is to distribute and enhance the local electric fields set up within the corona reactor during sustained glow discharge. Also, the fibrous packings may provide additional catalytic-like surface for the NO_x decomposition reactions to occur. With respect to fundamental chemical reaction mechanisms, the addition of a fibrous material may possibly divert the decomposition reaction mechanisms from purely homogeneous gas phase reactions to ones that are more heterogeneous in nature. In other words, in the presence of the dielectric packing material, the NO_x decomposition reactions may preferably take place on solid surface active sites rather than solely in the gas phase. The basic concept of packing a corona reactor with dielectric materials to enhance corona generation and optimize the oxidation processes has been thoroughly investigated by Tecogen as well as others.

The Chemistry Presented below are a series of chemical reactions, all of which are likely to occur to an appreciable extent within the TECOLYTIC™ DeNO_x reactor. Experiments conducted to date have been conducted on three types of systems. These are; 1) NO in nitrogen, 2) NO in nitrogen and oxygen and 3) gas combustion flue gas. All of these systems have demonstrated very high NO_x reduction efficiencies, greater than 99 percent. There are, however, some differences in the conditions that have existed when these high reduction efficiencies were demonstrated. For example, dry simulated flue gas mixtures indicated a decline in process conversion efficiency with an increase in oxygen level. However, recent experiments with actual flue gas have shown that NO_x reduction efficiency increases with increasing oxygen level. This

phenomena may be explained by the fact that different chemical reactions take place between the two sets of experiments. Another area that has indicated that the NO_x removal reactions are probably quite different in the different sets of experiments is that using a packing enhances NO_x reduction in the simulated flue gas where as it inhibits NO_x reduction with combustion flue gas. Even though these phenomena appear to be quite opposing, a simple mechanistic model for the system can explain the apparent contradictions.

Looking first at the simulated tests, the gas mixture fed to the corona reactor contained primarily nitrogen and nitric oxide. In this situation, the probable mechanism involves the generation of free radical nitrogen and oxygen species that generate a NO_2 molecule that dissociates into molecular nitrogen and oxygen. The major reactions for this NO_x reduction mechanism are given below.

where "e" is a free electron generated by the corona. This mechanism is substantiated by the near 100 percent conversion of NO into NO_2 in almost all experiments (6).

By adding oxygen to the reactor feed gas, several additional reactions are quite possible. These are:

The greater concentration of oxygen increases the reaction rates of reactions 9 and 10 and subsequently reactions 5 and 7. The net effect of this is an apparent decrease in the rate of reaction 8. This mechanism is supported by data. Experiments have also looked at the effect of CO_2 . The conclusion from these at this time is that CO_2 probably does not enter into the reaction sequence so as to improve or interfere with the process.

The difference between the simulated tests and the combustion flue gas test data is primarily in the chemical makeup of the gas. Water vapor is present in the combustion products. It is therefore postulated that the combined effect of oxygen and water vapor lead to findings for combustion products that higher levels of oxygen are not detrimental. Therefore, a mechanism can account for this effect is as follows. The decomposition of NO to nitrogen and oxygen is through an NO_2 intermediate step, a mechanism which explains the data involves the reaction of NO_2 and water vapor to form HNO_3 which is completely absorbed in the water trap (which is normally required for the NO_x analyzer). The reaction mechanism that would account for this process is:

By finding conditions that enhance the rate of reaction 12, the rate of NO destruction into nitrogen and oxygen can be increased and the overall conversion be maintained at a high level.

The Performance The performance of the TECOLYTIC™ DeNO_x system is shown in Figure 3. This figure shows the general trends in performance of some selected data. In particular, this curve shows the general effect of oxygen, voltage, frequency, and residence time as these variables are changed throughout their range. The responses shown in this figure are for particular conditions, and performance can be improved by coupling effects. Specific test data is discussed below.

Figure 4 shows the performance of the reactor system as a function of the oxygen concentration in the flue gas. These tests were run with inlet NO_x concentrations of approximately 300 ppm and a reactor residence time of 2 seconds. As can be seen, the NO_x reduction shows the performance to always be greater than 90 percent and approximately 95 percent for flue gas streams with an oxygen concentration greater than 3 percent. The effect of applied voltage is shown in Figure 5. Examination of the curve shows that at low voltage levels essentially no reduction occurs. At higher levels, an ignition of the reduction process occurs when a soft discharge is present. The reduction drops off at substantially high voltages due to the generation of non-uniformities in the discharge, the generation of sparks. It is this corona that initiates the series of chemical reactions that ultimately leads to the destruction process. Figure 6, shows how the performance changes with reactor residence time. As the reactor residence time increases for constant gas velocities, the NO_x reduction increases. The highest level of NO_x reduction measured to date is 99.3 percent, as indicated. Also shown on this plot is the effect of NO_x inlet concentration. At least within a small band surrounding these levels on NO_x, lower inlet concentrations give better reduction.

NO_x reduction as a function of the specific energy applied can be seen in Figures 7 and 8. In Figure 7, the percent NO_x conversion is plotted versus the specific applied energy normalized with the energy required for 80 percent conversion with low reynolds numbers and an intermediate oxygen level. This particular plot shows that it requires higher specific energies to obtain the same level of conversion for low oxygen systems than it does for high oxygen systems. That is for the same specific energy greater conversions can be achieved for process streams with higher oxygen levels. For example, the conversion for 100 percent normalized energy and 2.7 percent oxygen can be increased from 69 to 94 percent by increasing the oxygen level to 6.7 percent. Figure 8 shows the effect of Reynolds number on NO_x conversion. Again, this plot shows the percent NO_x conversion plotted versus the specific applied energy normalized with the energy required for 80 percent conversion with low reynolds numbers and an intermediate oxygen level. As can be seen, the effect of Reynolds number is pronounced over the range tested. For example, at a normalized specific energy of 25 percent NO_x conversion can be increased from 45 percent to 75 percent by increasing the Reynolds number by approximately 50 percent from about 2000 to about 2800.

SYSTEM KINETICS

In order to scale the Tecolytic™ Reactor system it is important to understand the reaction kinetics and model rate of conversion. With this regard, the development of a simple engineering model is of the utmost concern. A key word in this model development is simple. The set of chemical reactions discussed in the previous section is at best only a simplified subject of all the probable reactions to occur in this system. The total set numbers in excess of 100 (3).

The data behaves as a first order system for NO_x conversion. Attempts to model the system with a first order Arrhenius rate expression were a dismal failure. The Arrhenius model, which has its roots based on molecular energies having a boltzman distribution with temperature, cannot account for the electron induced energies. Since the Arrhenius expression can be developed from collision theory, it therefore, made sense to model the system using collision theory.

From collision theory, the reactor rate can be expressed as:

$$Rate = q Z_{AB}$$

where "q" is the fraction of effective collisions and "Z_{AB}" is the collision number (7). The collision number "Z_{AB}" is the number of collisions per unit time. In this case, it is the number of collisions of NO with electrons. The value can be determined from the product of the cross section for collision, the relative speed of the two species and the concentration of each species. This can be expressed mathematically as:

$$Z_{AB} = S V N_A N_B$$

where "S" is the reaction cross section, 'V' is the relative velocity, "N_A" is the concentration of species "A" and "N_B" is the concentration of species "B". If we consider that the NO molecule is relatively stationery in the oscillating electric field, then "V" is simply the electron speed, "c". The reaction cross section is a function of the velocity, thus:

$$S = S(c) = Bc$$

Taking species "A" to be NO and species "B" to be the electrons, "Z_{AB}" can be expressed as:

$$Z_{AB} = Z N_B$$

where "Z" is the collision frequency, and is expressed as:

$$Z = S_{(c)} C N_A$$

It has been shown that the speed of the electron can be expressed as:

where "T" is the mean free path, "a" is the electron acceleration and "h" is the mass ratio of the electron to NO molecule. The acceleration of the electron is:

where "q_e" is the electron charge, "E₀" is the field strength and "m" is the electron mass. The

$$c = \left(\frac{4 T^2 C^2}{h} \right)^{1/4}$$

$$a = \frac{q_e E_0}{m}$$

field strength "E₀" is a function of the applied voltage, the geometry and the dielectric constants of the materials within the applied voltage field.

The concentration of electrons is found from the current, the geometry and the electron speed. For the tubular system, the electron concentration is found from:

$$i = \frac{I \ln r_a / r_b}{2 (r_a / r_b) L e C A_0}$$

where "I" is the current, "r_{a,b}" are system radii, "L" is the reactor length, "e" is the electron charge and "A₀" is Avogadro's number.

Substituting and simplifying the rate expression as

$$\frac{d[NO]}{dt} = q' c^n [NO]_i$$

where "q" is a composite constant.

The conversion is then given by:

$$X = 1 - e^{-q' c^n t}$$

where the only unknowns are "q" and "n". Evaluating "q" and "n" from one set of data, the comparison of model predictions to two other sets of data are shown in Figure 2. The data at an applied voltage of 21500 was used to evaluate the constants. The agreement with the other data sets is very good.

SYSTEM ECONOMIC ANALYSIS

An economic analysis for the TECOLYTIC™ DeNO_x control process is being conducted. To date the comparison for an industrial gas fired boiler has been completed. This system has a thermal input of 100 million Btu/hr. The exit NO_x concentration is 80 ppm. Ninety percent removal of the NO_x from the flue gas is required. The economic analysis compares three cases of the technology based on the data obtained to date with three cases of the technology that can be achieved with a low level technology breakthrough. That is operating the reactor at 60 Hz as opposed to 400 Hz. These are both compared to the reference BACT technology, SCR. The conditions for these cases are summarized in Table 1.

The three cases at each frequency differ by the type of acid gas control system utilized. The "A" and "B" cases utilize acid vapor condensers similar to the laboratory experimental facility, and are shown in Figures 10 and 11. The "C" cases, Figure 12, utilize a spray dryer to remove the HNO_3 and 80 percent of the NO_2 to give a combined removal of 90 %. The "C" cases have a considerably lower operating cost since lower powers are required to form NO_2 rather than HNO_3 . The annual life cycle costs for these systems are shown in Figure 9. As can be seen, the high frequency spray dryer system has a considerably lower life cycle cost than the SCR system, approximately 33 percent lower, and the low frequency spray dryer system is approximately 40 percent lower.

SUMMARY

The work conducted to date has identified a reactor configuration and process that can achieve greater than 99 percent removal of NO_x from the flue gas. The level of performance has been identified as a function of system geometry, flow rate, residence time, temperature, flue gas composition and electrical properties such as frequency. The system is economically attractive as compared to SCR systems. In addition, a kinetic model to allow scale-up of the system has been developed and shown to model the system accurately.

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Figure 2. TECOLYTIC™ Corona Reactor for Single Tube Laboratory Version

Figure 3. Performance of TECOLYTIC™ Reactor

Figure 4. Removal Efficiency Effect of Oxygen

Figure 5. Effect of Voltage on NO_x Reduction

Figure 6. NO_x Reduction as a Function of Residence Time

Figure 7. Effect of Oxygen Content on NO_x Conversion

Figure 8. Effect of Reynolds Number on the NO_x Conversion
 (Conditions: freq. = 250 to 420 Hz, NO_x = 250 to 300 ppm, O₂ = 2.5 to 3.3%)

Figure 9. Comparison of Kinetic Model and Data

Table 1.

ECONOMIC COMPARISON CASE STUDIES

100,000,000 Btu/hr INDUSTRIAL BOILER

90 PERCENT NO_x REMOVAL

CASE #	FREQUENCY hz	ACID GAS CONTROL SYSTEM TYPE
1A	400	AIR COOLED CONDENSOR
1B	400	WATER COOLED CONDESE.
1C	400	SPRAY DRYER
2A	60	AIR COOLED CONDENSOR
2B	60	WATER COOLED CONDESE.
2C	60	SPRAY DRYER

Figure 10. Cost Comparison System Configuration for Air Cooled Condenser

Figure 11. Cost Comparison System Configuration for Water Cooled Condenser

Figure 12. Cost Comparison System Configuration for Spay Dryer

Figure 13. Annual Life Cycle Costs