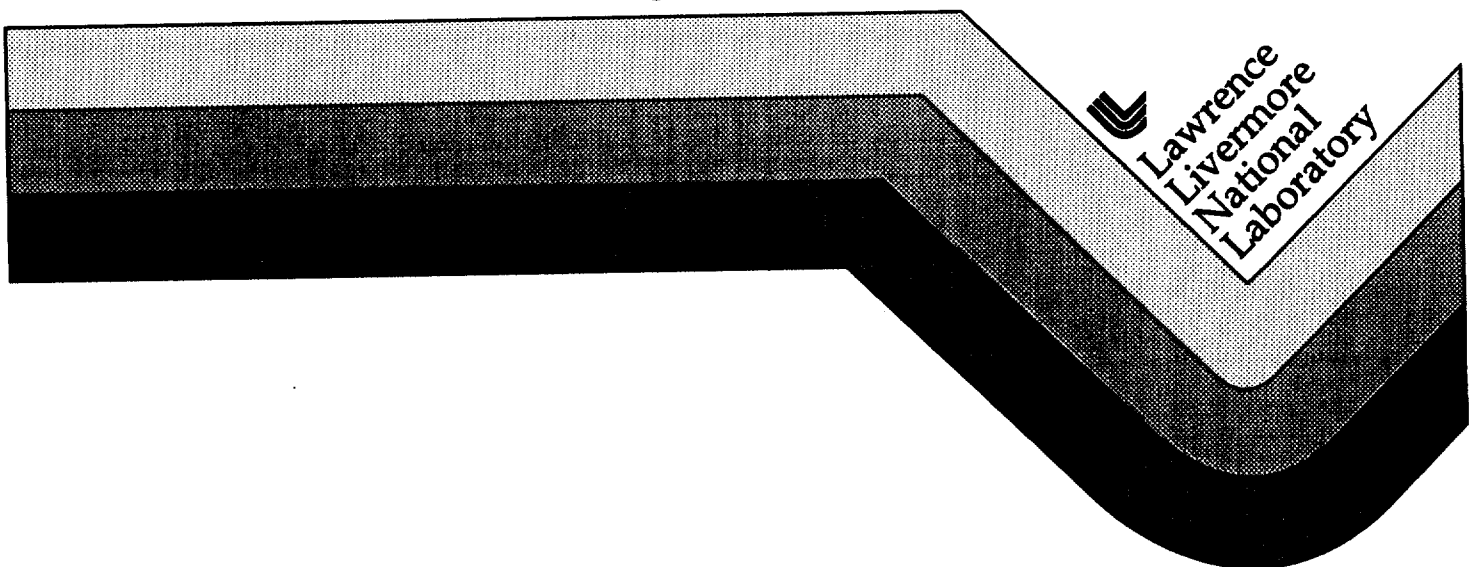


# **Final Report Pulsed Plasma Processing of Effluent Pollutants and Hazardous Chemicals**

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# **Final Report – Pulsed Plasma Processing of Effluent Pollutants and Hazardous Chemicals \***

LDRD Project 92-sr-018

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## **Abstract**

The electrical discharge techniques, called non-thermal, utilize high voltage breakdown of gases using short pulses of one to a few hundred nanoseconds. These short pulses between metal electrodes generate energetic electrons without appreciable thermal heating of the gas. The energetic electrons collide with gas molecules to form radicals. The radicals then react with pollutants to form harmless compounds.

Our non-thermal experimental device used a wire in a pipe geometry. The wire was driven by a 40 kilovolt pulse 100 nanoseconds long. Gas was circulated in a loop through the pipe geometry in a closed system. This system permitted the introduction of various gas combinations prior to testing. The recirculated gas was heated to determine the effect on the electrical discharge, and chemical reactions. Additives were introduced to improve the efficiency (defined as energy input per unit molecule destroyed).

The efficiency was found to be the most important parameter in that the experiments generally required high energy inputs. However, we were able to significantly improve the efficiency of NO removal by the addition of hydrocarbons. Nitric oxide has been removed with an energy cost of 15 ev per NO molecule. We believe the hydrocarbon additive serves by recycling the hydroxyl radicals during the oxidation of NO. The implementation of this process will depend largely on how much additives, electrical power consumption, and final NO<sub>x</sub> concentration are acceptable for a particular application.

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## 1. INTRODUCTION

The Clean Air Act of 1990 introduced new regulations restricting the emission of pollutants to the atmosphere. LLNL is engaged in research to help industry and government meet these new regulations. Our approach is to use an electrical discharge to change the pollutants into harmless or useful chemicals. We call the action of this discharge, pulse plasma processing. Our primary goal has been the efficient removal of nitric oxide which is created by combustion processes. Nitric oxide is an essential ingredient in the formation of lower atmospheric ozone, and contributes to about half of acid rain.

Pulsed plasma processing is a method of electrically creating chemical radicals that assist in the conversion of gaseous pollutants to harmless or useful compounds. The radicals are created by electrons from an electrical discharge. The optimum discharge occurs from a positive highly stressed small electrode to a large low stress electrode. The discharge is driven from a high power, high repetition rate pulsed modulator.

It is known that non-thermal techniques are efficient only when the pollutant is present in very small concentrations. At higher initial pollutant concentrations, the electrical energy consumption becomes comparable, or may even exceed, that of thermal techniques. For most applications, the energy consumption can only be reduced by using reagents that effectively recycle the active radicals. The removal of  $\text{NO}_x$  using non-thermal plasmas can be implemented without using catalysts or additives, but only at a high electrical energy cost. The use of additives, such as ammonia or urea-based substances, becomes necessary in most cases just as in commercially available "conventional"  $\text{NO}_x$  control technologies. In our most recent work, we investigated the use of hydrocarbon additives to reduce the non-thermal De $\text{NO}_x$  energy consumption's.

## 2. EXPERIMENTAL SETUP

The principal experimental apparatus utilized by this effort was a closed loop gas system. A drawing of the system is shown in Figure 1. This system permits the introduction of various gas combinations prior to testing. Analysis can be conducted during or after these tests. This processor can accommodate electrode geometries up to two inches in diameter. The recirculated gas was heated as hot as  $240^\circ\text{C}$  in some experiments. Temperature and water content have been studied in terms of their effect on the electrical discharges and the overall chemical reactions.

The discharge device is a wire in a tube. High voltage is applied in pulses shorter than 200 nanoseconds. These high voltage pulses achieve non-thermal conditions through the production of short-lived microdischarges. Non-thermal means the electrons are heated, not the gas molecules. These microdischarges yield a large improvement in the power efficiency because, within the short lifetime of each microdischarge, the ions do not experience significant movement and therefore do not contribute to the power consumption. The short lifetime of these microdischarges is accomplished with the use

of very-short high-voltage pulses (pulsed corona discharge) and/or with the use of dielectric coatings on the electrodes (dielectric barrier discharge).

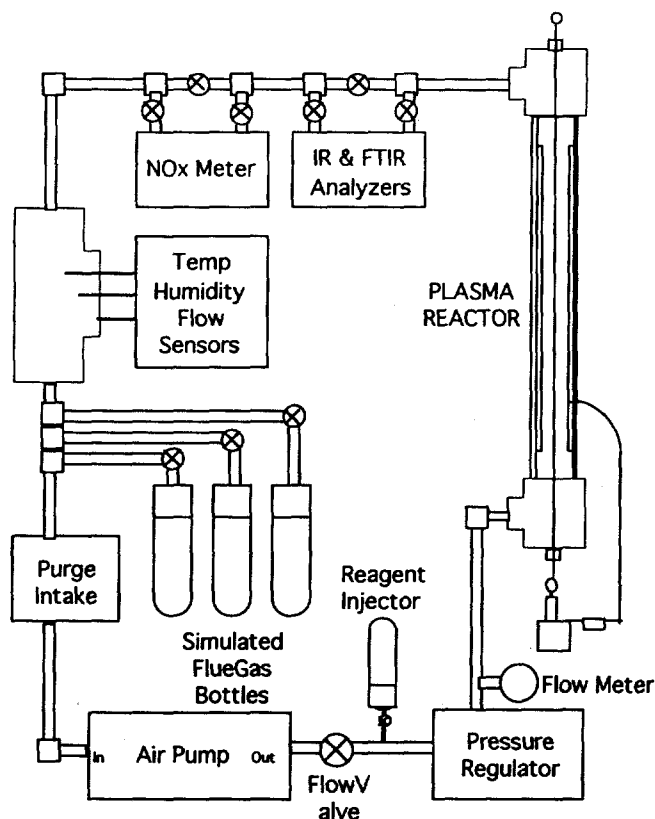


Figure 1. Schematic of the gas system.

## 2.1 Structure of Plasma Reactor

A drawing of the gas system is shown in Figure 1. The processing chamber has been designed with an outer pipe of two inches in diameter. This tube can be used as an electrode, other geometries of smaller dimensions can be placed inside. A cross section is shown in Figure 2. This processor can accommodate electrode geometries up to two inches in diameter. The current reaction chamber is 15.24 cm in length, but can be increased as needed to match the impedance of the cable to that of the processor for maximum energy transfer.

## 2.2 Electrode Geometries

The corona discharge that we are investigating is generated from electrodes one of which has a stress on its surface that is greater than five times the average stress. This ratio is commonly called  $f^*$  (peak E field/average E field). Below an  $f^*$  of five, breakdown occurs before corona occurs [Alston 1968](Ref. 1). We have used  $f^*$ 's of 7.7 or greater. Breakdown after the onset of corona discharge can occur but is a function of the stress and pulse length.

Figure 3 shows a discharge of a 1.5 millimeter diameter wire 2 centimeters from a ground plane. This discharge was a 100 nanosecond pulse at 40 kv. The structure of the corona is a streamer originating at the positive wire. The wire is bent up at the ends and the streamers follow the electric field. A cathode spot is visible at the lower end on the ground plane. One or more of the streamers is much brighter and will eventually result in a high temperature arc. This arc formation results in a low impedance short circuit and creates nitric oxides.

### 2.3 Voltage And Pulse Length Parameters

The voltage and pulse length applied to electrodes determine the time to breakdown if the  $f^*$  is above five. As the voltage increases, breakdown occurs at an earlier time. Open shutter photographic imaging of this process using different pulse lengths shows first faint streamers that have crossed the gap except for a small space at the cathode, low stress electrode. These streamers then grow in intensity and a spot appears on the cathode surface opposite the streamer. One of the streamers and its spot grows brighter than the others and then proceeds to breakdown.

One scenario for this process is as follows: The streamers have an impedance greater than tens of kilo-ohms. As the streamer approaches the cathode it must charge an increasing capacitance. The limited charging current through the streamer reduces the potential across the streamer to

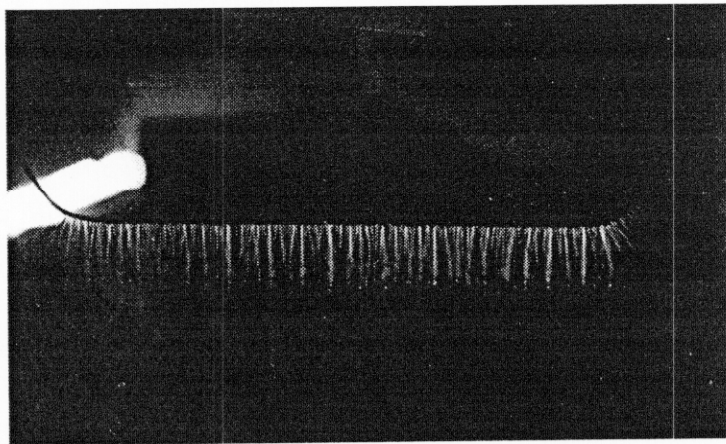


Figure 3. Coronal discharge showing early arc formation

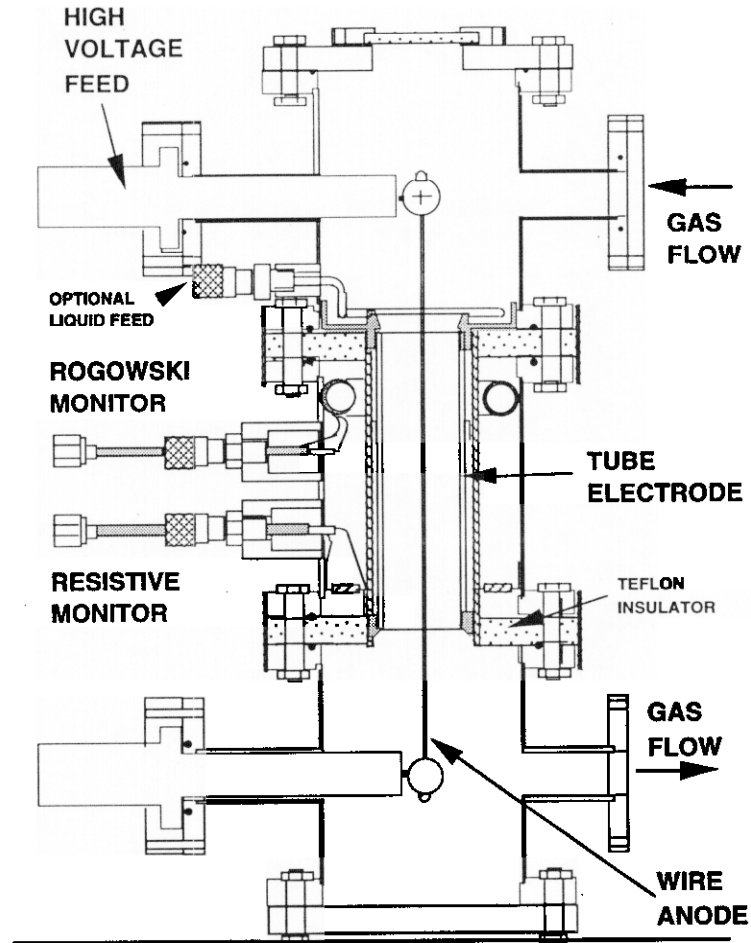


Figure 2. Structure of the pulsed plasma reactor.

cathode gap. This slows the streamer progress. The approaching streamer increases the stress on the cathode which develops a cathode spot. Breakdown is then due to the heating of the cathode spot.

It has been observed that if the voltage exceeds the breakdown voltage, NO is produced, not removed. In other cases, even though the NO removal rate increases with

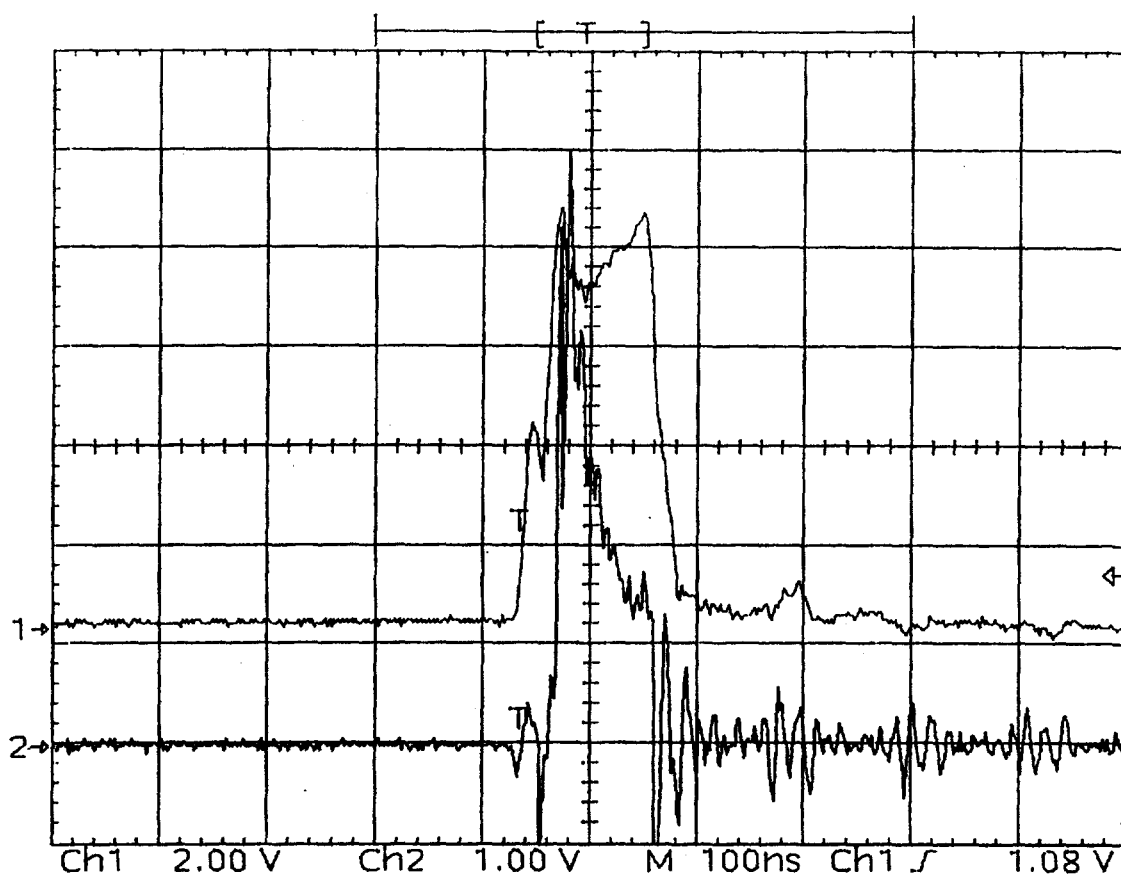


Figure 4 Typical voltage and current waveforms in our plasma reactor. The voltage (upper curve) is 10 kV per division. The current (lower curve) is 98 A per division. The time is 100 ns per division.

voltage, the efficiency decreases. This implies that the optimum voltage for efficient NO removal be much less than the breakdown threshold.

The pulse generator used in our tests is capable of 50 kV into a matched load or 100 kV into a high impedance load. Pulse lengths can be varied from 10 ns to greater than 1  $\mu$ sec depending on the charging cable length. The risetime from this cable pulser is 5 ns (10 - 90%). The risetime of the pulse can be varied by the addition of an R-C network, and the pulse rate can be increased up to 100 pps. Most of the data presented here were taken using a pulse rate of around 20 pps and a pulse length of around 80 ns. Typical voltage and current waveforms are shown in Figure 4.

## 2.4 Diagnostics

Diagnostic systems have been used to analyze the light emissions of the discharge. These include a monochromator and an open shutter camera. Devices to measure the

results of chemical reactions include a chemical  $\text{NO}_x$  meter, a chemiluminescence  $\text{NO}_x$  meter, and an IR and FTIR analyzer.

The chemical  $\text{NO}_x$  meter was calibrated frequently using a calibration bottle of 100 ppmv of nitric oxide in dry nitrogen. The chemiluminescence  $\text{NO}_x$  meter was checked for linearity against a bottle of 100 and 510 ppmv of NO in nitrogen and was linear to one percent.

We used the IR and FTIR analyzers to monitor the levels of secondary pollutants and harmful by-products, for example  $\text{N}_2\text{O}$ , that may be produced by the plasma processing. The FTIR analyzer provided quantitative determination of several components because it measured the infrared absorption spectrum over a wide range of wavelengths.

We measured the energy by measuring the voltage and current as a function of time, and then integrated the product as a function of time. The pulse rate was measured by a counter. To prevent reflections a load resistor was included at the end of a short transmission line. This was where the voltage is measured with a Physics International voltage divider. The current was measured with a 0.1 ohm resistor in the return path.

We have imaged the discharge using an open shutter camera. This, combined with the ability to generate pulse lengths of from 20 ns to 1000 ns, permitted time resolution

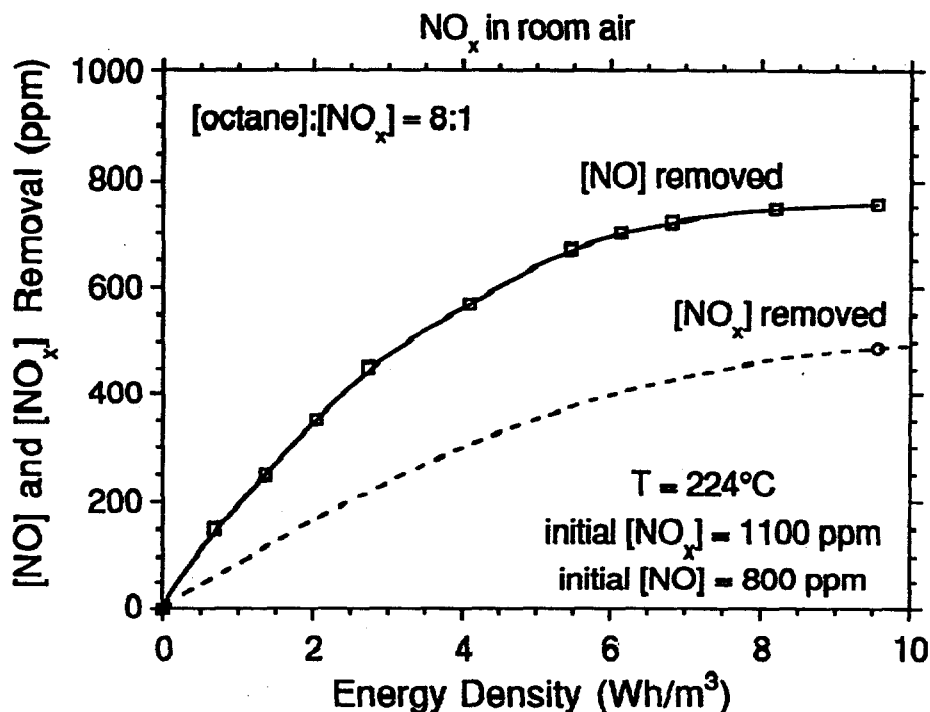


Figure 5. Measured NO and  $\text{NO}_x$  removal as a function of energy density input into the discharge. The gas temperature was 224°C. The gas was room air containing initial concentrations of 1100 ppm and 800 ppm of  $\text{NO}_x$  and NO, respectively. The n-octane additive was added at a molar ratio to initial  $[\text{NO}_x]$  of 8:1.



studies of the streamer evolution. We also imaged the discharge with a monochrometer to measure the electron temperature.

### 3. EXPERIMENTAL RESULTS

The following results were obtained using the wire-cylinder pulsed corona system. The gas flow was recirculated in turbulent flow through the plasma reactor. Figure 5 shows the removal of NO and NO<sub>x</sub> in air at a gas temperature of 224°C, using a relatively large amount of n-octane additive. The molar ratio of n-octane to initial NO<sub>x</sub> used in this run was 8:1. About 750 ppm of the initial 800 ppm NO was removed with an energy consumption of 9.5 Wh/m<sup>3</sup>. About 500 ppm of the initial 1100 ppm NO<sub>x</sub> was removed with the same energy consumption. This energy consumption corresponds to 18 eV per removed NO molecule, and 29 eV per removed NO<sub>x</sub> molecule.

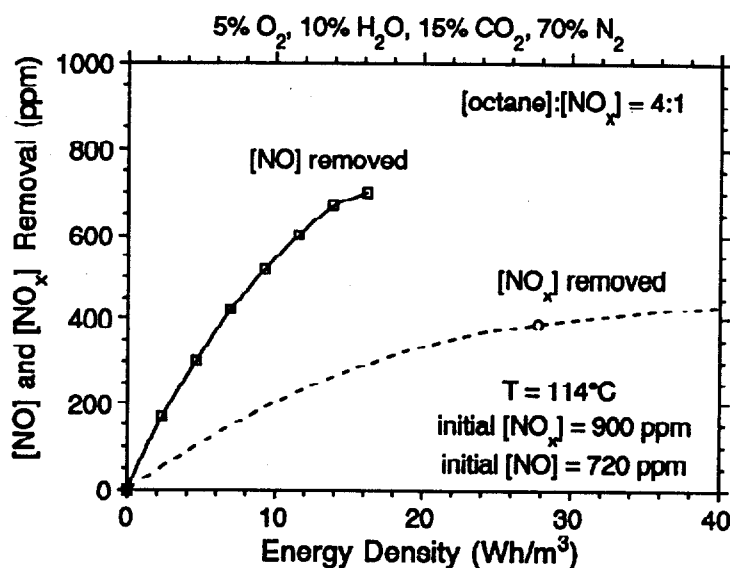


Figure 6. Measured NO and NO<sub>x</sub> removal as a function of energy density input into the discharge. The gas temperature was 114°C. The gas consisted of 5% O<sub>2</sub>, 10% H<sub>2</sub>O, 15% CO<sub>2</sub>, and 70% N<sub>2</sub>, with initial NO<sub>x</sub> and NO concentrations of 900 ppm and 720 ppm, respectively. The n-octane additive was added at a molar ratio to initial [NO<sub>x</sub>] of 4:1.

Figure 6 shows the removal of NO and NO<sub>x</sub> in a gas mixture consisting of 5% O<sub>2</sub>, 10% H<sub>2</sub>O, 15% CO<sub>2</sub> and 70% N<sub>2</sub>. The gas temperature was 114°C. The molar ratio of n-octane to initial NO<sub>x</sub> used in this run was 4:1. Almost 100% of the initial 720 ppm NO was removed at an energy consumption of 16 Wh/m<sup>3</sup>, corresponding to 28 eV per removed NO molecule. About 45% of the initial 900 ppm NO<sub>x</sub> was removed at an energy consumption of 28 Wh/m<sup>3</sup>, corresponding to 80 eV per removed NO<sub>x</sub> molecule.

The results in Figure 6 show that hydrocarbon additives could be very effective in reducing the energy cost for non-thermal DeNO<sub>x</sub>. For the same energy input, higher NO<sub>x</sub> reductions are observed with higher hydrocarbon additive concentrations. However, care has to be taken with regards to secondary pollution production due to unreacted hydrocarbons ("slip"). It is therefore desirable to achieve the NO<sub>x</sub> reduction using the least amount of additive at an acceptable energy consumption. These results show that it is rather energy intensive to remove large amounts (> 500 ppm) of NO<sub>x</sub> at acceptable injection levels of additives (molar ratios of 1:1 or less).

We believe the hydrocarbon additive serves by recycling the hydroxyl radicals during the oxidation of NO. The efficiency of a particular hydrocarbon is therefore limited by the reaction rate of this hydrocarbon with hydroxyl radicals. Table 1 shows the reaction rates for a variety of hydrocarbons. Note that n-octane and C<sub>2</sub>H<sub>4</sub> have almost the same reaction rate with OH at room temperature. However, at higher gas temperatures, C<sub>2</sub>H<sub>4</sub> becomes less effective because of its negative activation energy.

Table 1. Interaction of hydroxyl radicals with hydrocarbons [Atkinson 1986].

Species	Rate (cm <sup>3</sup> /molecule-s)	Rate (298°K) (cm <sup>3</sup> /molecule-s)	Rate (400°K) (cm <sup>3</sup> /molecule-s)
CH <sub>4</sub>	$6.95 \times 10^{18} T^2 \exp(-1280/T)$	$8.41 \times 10^{15}$	$4.53 \times 10^{14}$
C <sub>2</sub> H <sub>6</sub>	$1.37 \times 10^{17} T^2 \exp(-444/T)$	$2.74 \times 10^{13}$	$7.22 \times 10^{13}$
C <sub>3</sub> H <sub>8</sub>	$1.27 \times 10^{17} T^2 \exp(+14/T)$	$1.18 \times 10^{12}$	$2.10 \times 10^{12}$
C <sub>4</sub> H <sub>10</sub>	$1.55 \times 10^{11} \exp(-540/T)$	$2.55 \times 10^{12}$	$4.02 \times 10^{12}$
CH(CH <sub>3</sub> ) <sub>3</sub>	$9.58 \times 10^{18} T^2 \exp(+305/T)$	$2.37 \times 10^{12}$	$3.29 \times 10^{12}$
Cyclohexane	$2.73 \times 10^{11} \exp(-390/T)$	$7.38 \times 10^{12}$	$1.03 \times 10^{11}$
n-Octane	$3.12 \times 10^{11} \exp(-380/T)$	$8.72 \times 10^{12}$	$1.21 \times 10^{11}$
C <sub>2</sub> H <sub>4</sub>	$2.15 \times 10^{12} \exp(+411/T)$	$8.53 \times 10^{12}$	$6.01 \times 10^{12}$

A product of the NO<sub>x</sub> conversion that proved difficult to quantify was nitric acid (NO<sub>x</sub> removal cited above is literally a decrease in the NO+NO<sub>2</sub> concentration only. The "removed" NO<sub>x</sub> is converted to HNO<sub>3</sub> and N<sub>2</sub>). To test removal of the HNO<sub>3</sub> product some experiments with added ammonia were performed. However, these experiments were unsuccessful in establishing a removal mechanism for HNO<sub>3</sub> in that the added ammonia appeared to adsorb on the processor walls. HNO<sub>3</sub> may have been subject to the same adsorption phenomenon.

Water was recirculated through the processor and sprayed into the processor intake with little improvement in the nitrogen dioxide removal. When ammonia was added to the water the removal of nitrogen dioxide improved significantly. The addition of n-octane and the ammonia solution at 70 degrees Centigrade resulted in an efficiency of  $\text{NO}_x$  removal of better than 15 ev/molecule.

Several volatile organic hydrocarbons were also tested in similar experiments. The removal of benzene and trichloroethylene was found to be 60 to 70 ev/molecule for a fifty percent conversion. This does not mean that the compounds were made harmless. No measurements were made to determine the reaction products. Carbon tetrachloride was tested but with negative results: if it were removed several thousand ev were required per molecule.

Sulfur dioxide removal was not affected by the addition of hydrocarbons.  $\text{SO}_2$  was not removed efficiently either by the discharge, the addition of gaseous ammonia or both. It would appear that at the temperatures tested that ammonia must be dissolved in liquid water to be effective in the removal of either nitrogen dioxide or sulfur dioxide.

Additional details of the experimental results can be found in References 3-6.

#### 4. DISCLOSURES AND RECORD OF INVENTIONS

During the course of the project several disclosures of inventions were made. These inventions may have some commercial value. The following is a list of these inventions and a brief description.

*Pulse Plasma Array, IL-8796, George E. Vogtlin,*

Pulsed plasma processors have been constructed in coaxial tube or wire to plane geometries. These configurations result in high friction losses and uneven processing of pollutants. This invention alternates large cylinders with small cylinders which gives low friction losses and uniform treatment of the flowing gas. This geometry also permits easy access for cleaning.

*Reduction of  $\text{NO}_x$  by Means of Pulsed-Plasma Processing in the Presence of a Carbonaceous Fuel, IL-9119, P. Henrik Wallman, George E. Vogtlin*

Diesel exhaust gas is treated in a pulsed-plasma processor such that soot particles (and absorbed hydrocarbons) are collected on the electrode surface for a period long enough to allow complete oxidation of said particles.

*Barrier Flashover Discharge Processing, IL-9048, George E. Vogtlin*

The barrier flashover discharge starts as the barrier process from a voltage enhanced electrode to a insulator surface. Before the electrode is charged and the corona extinguished the surface of the insulator flashes over an edge and discharges the insulator surface. Once the barrier surface is discharged the next pulse can be applied. This permits a barrier discharge that can be driven by a single polarity pulse. The pulse voltage and shape can be optimized for maximum energy efficiency.

*Pulsed Plasma Processing of Pollutants with Hydrocarbons, IL-9052, Roger Atkinson (UC Riverside), George E. Vogtlin, Henrik Wallman*

We have improved the efficiency of nitric oxide removal by at least a factor of two by the addition of n-octane to the processed gas. We introduced 0.5 cc of n-octane into eight liters of air prior to processing. N-octane is a hydrocarbon with eight carbon atoms, and is similar to gasoline. When introduced it vaporizes and mixes uniformly with the air. We believe the process involves the formation and regeneration of the hydroxyl radical (Ref. 2). This process should work with many other hydrocarbons and other pollutants. It should be possible to use hydrocarbons that can be vaporized during the process then condensed at a later time and be recovered from the gas stream. Many pollutant gas streams may have sufficient hydrocarbons to remove pollutants without their addition.

*Electrical Discharge Fuel Injection, IL-9136, George E. Vogtlin*

This invention uses the pressure wave from an electrical discharge to inject fuel into cylinders of an internal combustion engine. The small capillaries inhibit the flow except during the pressure wave. There are no moving parts and will have a long life limited only to electrode wear.

*Conversion of Natural Gas to Methanol by Pulsed-Plasma Processing, IL-9157, P. Henrik Wallman, George E. Vogtlin*

The invented process is a simple preprocessing step applicable to natural gas fired power plants where a fraction of the natural gas feed is converted to methanol while the remaining gas is burned for power generation.

*Improvement of Ozone Production Efficiency Using a Pulsed Power Supply, IL-9361, George E. Vogtlin, W. Ray Cravey*

The application of a fast rise pulse to a barrier discharge ozone generator can result in the simultaneous generation of coronal streamers. A pulse forming line can then be designed to efficiently couple the energy into the load by matching the source impedance to the load impedance and maintaining the voltage across the discharge.

## 5. CONCLUSIONS

We have investigated the reactions of  $\text{NO}_x$  and to a lesser extent volatile organic compounds (VOC) in non-thermal discharges. Overall, the non-thermal discharge was found to accelerate oxidation reactions such the oxidation of NO to  $\text{NO}_2$  and nitric acid. VOCs were oxidized even at room temperature. However, energy consumption, expressed for example as eV/molecule reacted, was generally quite high.

Despite difficulties in closing the material balance for the  $\text{NO}_x$  experiments we found that part of the  $\text{NO}_x$  was actually reduced to  $\text{N}_2$ , and not oxidized to  $\text{NO}_2$  and acids. Again, this was achieved at high energy costs. The addition of hydrocarbons seemed to lower the energy input required for reduction of  $\text{NO}_x$ . This was an important finding that called for more work in the form of a research project devoted to  $\text{NO}_x$  reduction by means of non-thermal plasmas. This project is now under way.

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