EFFICIENT, EFFECTIVE, NON-THERMAL PLASMA AFTERTREATMENT OF DIESEL NOx

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INTRODUCTION

Plasma processing for control of effluents from many different sources including diesel engines, incinerators, and power plants is currently receiving considerable attention because these approaches have potentially broad impact on the reduction of harmful gaseous pollutants. For example, the removal of nitrogen oxides (NO_x) is an important problem, and has led to rigid regulation on the level of NO_x emission[1]. E-beam, pulsed corona, surface and silent discharges have been implemented to study efficiency of NO_x removal in many experiments[2]. In this project we are studying underlying physics issues, and limitations to practical applications. We have obtained data showing that advanced pulsed modulator technology used in conjunction with pulsed plasma devices can be used to initiate favorable plasma chemistry to reduce emittants for a variety of these applications.

There are several issues that affect the practical application of pulsed plasma devices including: i) energy cost, ii) by-products emission, iii) pulsed power implementation, and iv) reactor design.

Energy costs that have been reported vary considerably - for example, in terms of energy cost per treated molecule from Å3 to 500 eV/molecule (this approach to calculating energy costs is discussed in ref. 2). To be competitive for remediation of diesel engine emission, the energy cost should be <10-20 eV per NO molecule for concentrations Å1000 ppm, which would correspond to an overall power consumption < 5% of the total engine power, although power requirements will depend on the application. Electron beam processing has been reported to have low energy cost following injection of highly energetic electrons requiring, however, a level of sophistication in implementation that is impractical at present for diesel exhaust treatment. Reactors based on corona and silent discharges have the advantages of relative simplicity, scalability, and lower capital cost than existing e-beam technology. Thus it is of interest to understand the physical mechanisms and practical limits to energy cost for this competing, simpler technology. Here we report evidence that plasma processing with a corona discharge can be applied to the problem of NO_x reduction with an energy cost previously considered attainable only by sophisticated electron beam methods.

APPROACH

The experimental apparatus reported here incorporated discharge chambers, pulsed power modulator, and gas manifold with controller gauges and emission analyzer. A number of reactors were studied; a typical pulsed corona reactor consisted of a cylindrical chamber length of 0.4 m and varying diameter inner electrode 2-34 mm and outer electrode 20-62 mm. It was possible to vary the current density and "active" plasma volume by varying the electrode surface area. The reactor cathode surface was typically threaded to ensure a high local electric field with increasing radius. The current density entering the plasma volume was estimated for a nominal cylinder surface 1 mm above the surface of central electrode. The term "active" plasma volume is used to mean the volume which is within this cylindrical surface (e.g. volume enclosing the maximum electric field).

A pulse generator supplied high voltage pulses with amplitude ²40 kV, pulse duration of 50-100 ns (rise time 20 ns), and repetition rate up to 1 kHz.

Pulses reflected from an unmatched load (the reactor and discharge) were absorbed in a matched pulse generator load. By monitoring voltage and current signals related to the discharge it was possible to determine the energy deposition into the gas. The total current contains both the discharge current and the current associated with charging the capacitance of the reactor. The product of the discharge current and voltage during the corona discharge yields the pulse energy, so that the displacement current is not included in the energy delivered to the gas (although it is included in the overall energy expended). This is an important effect at low current density because for short pulse conditions, which are important for this work, the displacement current is larger (typically 3-6 times) than the conduction current.

The power input into the discharge was varied as a function of pulse length, voltage amplitude and repetition rate. Two types of diesel engines were used: a) 60 kW (Volkswagen Rabbit), b) 300 kW Cummins. Typical data were obtained with the 60 kW engine operated at idle speed and NO emission concentrations of 100-130 ppm. Here the exhaust temperature was 40-50° C. We monitored the outlet gas composition using a NO analyzer (Bacharach, Nonoxor II). The 300 kW engine was operated under load with NO emission (600-1000) ppm. The exhaust temperature was varied from 85 to 180° C. A Horiba analyzer was used for emission monitoring. This system allowed detection of the following components: NO, NO2, HC, CO, CO2, SO2. The flow rate through the reactors was varied between 100 and 1500 standard liters per minute (flow velocity was from 1 to 10 m/s).

On varying discharge parameters (pulse width, voltage amplitude, frequency, pulse polarity) it was found that the energy cost changes considerably, and that short pulses (50 ns) are more advantageous in energy cost than longer pulses, in part because short pulses allow operation with a higher pulse voltage during the time of treatment of the effluent. We found that the energy cost for NO removal is affected by pulse polarity. The energy cost for positive corona (plus at the central electrode) is 1.5-2 times that for negative charging of the central electrode. This difference is even more pronounced at higher repetition rates over Å1000 Hz. This is because positive corona carry higher current at a given pulse voltage than negative, and current is found here to be a crucial parameter for determination of energy cost. Data hereafter refer to negative corona and a pulse duration of 50 ns.

ACCOMPLISHMENTS:

We performed experiments to compare the efficiency of pulsed corona discharges with and without a dielectric insert under otherwise identical experimental conditions, in order to compare barrier discharge efficiencies with corona discharges. Previous studies under this project had shown surface discharges to be less efficient. The voltage amplitude and the frequency were adjusted in such a way that these approaches could be compared for the same level of NO reduction. It was found that a dielectric insert results in higher current and current density. Reduction of NO is approximately equal, but energy cost with the dielectric insert is 2-3 times greater than for the discharge without dielectric. A high repetition rate regime is found to be advantageous for both cases. It was also found in our data that the energy cost decreases with increasing frequency. Energy cost lowering occurs basically due to the decrease of energy per pulse with increasing of repetition rate. To increase NO removal by increasing voltage and current results in a growth of energy cost. For example, almost the same NO removal -- 55 and 65 ppm -- can be obtained at 8 and 30 eV/molecule respectively; however, in the first case, the current Å15 A and the repetition rate is 1000 Hz, while in the latter case Å200 A, and f=300 Hz, with a voltage drop across the discharge Å15 kV in both experiments.

Plasma aftertreatment of diesel exhaust principally relies on the removal of nitrogen oxides (NO_x) and other hazardous components by highly reactive radicals produced in corona discharge by energetic electrons. During the high voltage short pulse, energetic electrons and radicals are generated and subsequently initiate chemical reactions. For this, pulsed parameters (voltage amplitude and pulse width) must be optimized in accordance with the reactor design, and it is observed that these depend in subtle ways on small variations in design. Short pulse excitation is followed by a post-pulse period which lasts from 10s of microseconds to 100s of ms or longer.[4] During this time various remediation and oxidation reactions occur, which are as yet not well characterized, although calculated optimal time intervals for post-pulse chemical reactions are Å1 ms.

The chemical reactions occur mainly in the gas phase, but the plasma composition and charac-teristics can be affected by heterogeneous reac-tions of ions, electrons, and radicals. These reac-tions can considerably decrease the energy cost. For example, the lowest energy cost of several eV per molecule has been measured using e-beam for SO_2 decomposition[5,6]. The authors found that the energy consumption is affected by pulse durations and current density[6], decreasing with decreasing current density. Further, Deminskii et. al. dis- cussed the kinetics of a heterogeneous oxidation process which involves chemical reactions between gas and aerosol particles with consider-ation of dissolved components, transfer processes in gas and the dynamics of the formation and decay of aerosol particles. They found good agree-ment with experimental data and predicted even less energy cost ˜0.3 eV/molecule. In this work we attempted to study the relation between cur-rent density and energy cost for corona discharge-based reactors. The energy cost of NO removal by pulsed corona discharge is also driven by current density similar to e-beam processing of SO_2. A reactor with a dielectric insert exhibits however much higher energy cost. We had anticipated increased NO reduction with low energy cost be-cause this reactor had a large plasma volume and large area cathode: the ratio of inner-to-outer elec-trode diameter was 0.58 (34 - 58 mm). Here the dielectric barrier was supposed to prevent arcing. Despite that we found that the discharge trends to contract into bright filaments at high repetition rates. One should note that a homogeneous plas-ma is a major problem for the use of a corona discharge. Due to a strong nonlinear dependence of field emission on the local electric field the number of starting streamers is an extremely sensitive function of electric field and cathode micro geometry, which is hard to control. It may be that at high currents, the current is carried by a finite number of filaments, rather than equally distributed over the cathode surface. The high repetition rate and flow appears to help smoothing the current irregularities. This result is still the subject of further study.

In a pulsed corona discharge NO is partly converted into NO_2. The production of NO_2 was found to vary with current density, and be minimal at a low current density ˜0.2 A/cm², correspond-ing also to energy efficient operation of the reactor. It was found that NO_2 production drops with decreasing of current: at current density 2 A/cm² the ratio of NO_x reduction to NO_2 production $NO_x/NO_2 = 1.2$, and at current density 0.2 A/cm $NO_x/NO_2 = 1.4$.

Chemistry in heterogeneous media may also have beneficial effects. It was found that there is a higher energy cost for hot exhaust - 180° C, above the vaporization temperature for water, corre-sponding to elimination of droplets. A similar result was previously re-ported.

Energy cost measurements of NO removal from diesel exhaust with a pulsed corona discharge have been experimentally studied. After optimiza-tion of pulsed parameters (polarity, pulse width) we found that the energy cost is driven by current decreasing with corresponding current density de-crease. Best efficiency (< 10 eV/mol) is obtained at current density <0.2 A/cm² and repetition rate (˜1 kHz). With increasing current density (energy deposition into gas) the removal efficiency decreases. Our results indicate that a pulsed coro-na discharge provides effective NO remediation with energy cost comparable to e-beam proces-sing. The cost effective regime was realized, however, at low NO concentration (100 ppm), and it was seen that the spatial and temporal charac-teristics of streamer discharge impose limitations on the removal efficiency at high NO concentration so that reactor design is an important consider-ation

CONCLUSION

Efficient reduction of NO emission with a transient, non-equilibrium plasma created by pulsed corona discharge was shown to be energy efficient. The transient plasma (Å50 ns) is found to reduce NO emission by 50% in a flow of 2-25 liters/second with energy cost Å10-20 eV/molecule, corresponding to a fraction of source power of As %. The efficiency of NO_x reduction is a complex function of parameters that include pulse width, pulse polarity, current density, repetition rate, and reactor design. It was found that best efficiencies are correlated with a low current density (0.2A/-cm^2) and high repetition rate (1 kHz) under high flow rate. Careful optimization of all these parameters is required to reach cost effective NO_x reduction.

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