DIRECT CHEMICAL REDUCTION OF NOx IN DIESEL EHAUST USING NONTHERMAL PLASMAS AND GAS JET INJECTION

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BACKGROUND

The control of NO_x in diesel engines is of increasing concern as regulatory restrictions on emissions continue to tighten. Conventional catalytic materials are unsuitable for diesel NO_x aftertreatment due to limitations associated with combustion stoichiometry, particulate contamination, and exhaust temperature control. Nonthermal plasma technology is widely considered to have the potential to control NO_x in combustion exhaust without these restrictions, by electrically inducing the thermodynamically unstable NO_x species to decompose into nitrogen and oxygen. The principal chemical mechanism targeted for this process is the reaction of exhaust nitric oxide (NO) with ground state atomic nitrogen, reaction (1). The atomic nitrogen reactant is generated by dissociative collisions of electrons in the nonthermal plasma with molecular nitrogen, the majority chemical species in exhaust.

$$N + NO \rightarrow N_2 + O \qquad (1)$$

Many researchers worldwide have been working toward this end, but a practical diesel NO_x reduction system has yet to be introduced. The principal technological issue working against the success of nonthermal plasmas for NO_x chemical reduction has been that the electric discharges that generate atomic nitrogen for chemical reduction of NO_x also generate atomic oxygen and hydroxyl, which drive chemical processes to oxidize NO_x.

The cross section for dissociating molecular nitrogen in a nonthermal plasma discharge is lower than that for oxygen at typical electron collision energies of ~4.5 eV (dissociation energy 9.7 eV for N_2 compared with 5.2 eV for O_2). In addition to the resulting prevalence of oxidizing species in the discharge, nearly gas kinetic rates of some of the subsequent gas phase oxidation reactions results in the overall chemistry being dominated by NO oxidation to nitrogen dioxide (NO_2) and nitric acid (HNO_3). This chemical outcome is unacceptable for diesel engine NO_x removal.

In addition to the chemical problems described above, most nonthermal plasma devices are subject to serious performance problems when operated in the harsh environment of diesel exhaust. Any commercially viable NO_x reduction technology for mobile diesel engines must tolerate regular exposure to particulates (soot) and water condensation. It must also operate over a wide range of oxygen concentrations, exhaust flow velocities, and temperatures from near ambient up to several hundred degrees Celsius. Meeting these environ-mental operating requirements has been found by many researchers to be as much of a challenge as establishing the appro-priate chemical processes for chemical reduction.

Recent efforts have been made to develop two-step processes which first oxidize NO to NO_2, followed by catalytic reduction of NO_2 to nitrogen and oxygen,[1] but even if such processes succeed chemically, other less positive aspects of catalytic exhaust treatment technology will likely carry forward with the new approach.

NITROGEN JET INJECTION

Since 1989, Thermo Power has demonstrated ever more efficient and reliable technology for generating homogeneously volume-filling nonthermal plasmas for combustion gas treatment, culminating in the engineering of its barrier-discharge based *TecoLytic*[2] nonthermal plasma technology for utility-scale oxidative NO_x

removal. It became clear during this development work that the direct plasma treatment approach would not be commercially viable for the chemical reduction of NO_x particularly in the diesel exhaust environment discussed above. The principal factors contributing to this conclusion were:

1. Non-selective reactant generation
Relatively inefficient production by the discharge of atomic nitrogen compared with oxidizing species.

2. Kinetic competition
Very fast oxidative kinetics dominate over reductive chemical paths. Even if the electron energy distribution in the discharge could be skewed to higher energies to favor nitrogen dissociation, many oxidative reactions are faster than the reductive analogs.

3. Variable operating conditions
Nonthermal plasma discharge properties are dependent on gas composition, humidity and temperature.

4. Fouling
Dielectric barrier electrodes immersed in sooty exhaust are readily fouled by the deposition of a conductive surface layer.

Thermo Power addresses all of these technical problems with its *TecoJet* approach by generating atomic nitrogen external to the exhaust stream, followed by rapid injection and mixing to achieve chemical NO_x reduction.

The persistent yellow-orange glow of "active nitrogen" has been recognized for decades to be emission from electronically excited molecular nitrogen which has only slowly recombined from atomic nitrogen generated in a low-pressure electric discharge.[3] Of particular interest to gas-phase chemists is active nitrogen's extreme reactivity with other chemical species despite multi-second stability in isolation.

Although most work with active nitrogen in the past was done in vacuum vessels, the property of relatively long recombination time coexisting with very high reactivity continues to hold true at higher pressures. Atomic nitrogen recombines to form N_2 on the timescale of a few milliseconds at atmospheric pressure, but the reaction of atomic nitrogen with NO is one to two orders of magnitude faster than recombination, so external generation of atomic nitrogen followed by rapid mixing with exhaust gas can yield useful quantities of chemical reduction.

To deliver atomic nitrogen rapidly and efficiently, the dissociating discharge is located immediately adjacent, but not directly exposed to the exhaust stream. Isolation of the discharge from the exhaust eliminates the direct dissociation of oxygen and other exhaust gases, and practical delivery times on the order of 10-50 μs followed by turbulent mixing in the exhaust stream largely preserves the nascent atomic nitrogen concentration for NO_x reduction. We have observed the characteristic light emission from nitrogen recombination to extend as far as 7 cm beyond a 1 mm diameter jet orifice in a laminar treatment stream containing no NO. The physical extent of the light emission in such a stream is reduced dramatically by the addition of NO. Optimum mixing for diesel NO_x treatment is achieved by using multiple jets injected into a turbulent exhaust stream. The jet injectors themselves need not physically penetrate into the exhaust channel, facilitating the design of NO_x reactors with unobstructed exhaust flow and very small pressure drops.

The *TecoJet* approach specifically addresses each of the concerns listed above for nonthermal plasma techniques:

1. Selectivity in reactant generation
The use of nitrogen jets to generate atomic nitrogen eliminates issues regarding the relative efficiency of nitrogen and oxygen dissociation.

2. Reduced kinetic competition
With nitrogen as the only molecular species dissociated in the discharge, chemical reduction of NO by atomic nitrogen can dominate the chemistry. The relatively small quantity of atomic oxygen produced by

reaction (1) does not contribute significantly to oxidation of NO. Measurements in diesel fuel combustion exhaust have demonstrated >80% of the chemical reaction achieved going to chemical reduction of NO_x. Our measurements of the action of conventional nonthermal plasma methods to treat diesel exhaust yield no significant chemical reduction: nitrogen dioxide and nitric acid are the principal products.

3. Stable operating conditions
The *TecoJet* discharge external to the exhaust stream is not affected by the chemical composition of the stream. Discharge properties are no longer dependent on gas composition, humidity or exhaust temperature.

4. Non-fouling electrodes
The discharge electrodes are isolated from the exhaust stream, making them inherently non-fouling. *TecoJet* reactors operate successfully in wet and sooty environments.

FACILITY

Initial laboratory tests of *TecoJet* were performed using a diesel fuel fired combustor. to provide an exhaust stream of up to 60 scfm. Exhaust from the combustor could be diverted through a heat exchanger to control the working temperature at the *TecoJet* reactor, which was comprised of up to 24 indiviually adjustable jets. Firgure 1 shows an operating 18 jet *TecoJet reactor*. NO could be added to the exhaust stream to extend the test range to high NO_x conditions (typically 60-600 ppmv NO). Exhaust gas composition was monitored at locations before and after the *TecoJet* reactor. Particular attention was paid to measuring nitric acid and nitrogen dioxide formation relative to chemical reduction of NO. Additional analytical capabilities included measure-Mert of oxygen, carbon dioxide, carbon monoxide, total hydrocarbons, and sulfur dioxide.

DISCUSSION

Modeling of the nitrogen jet injection technique for NO_x reduction suggests ultimate attainable overall efficiencies (parasitic power) on the

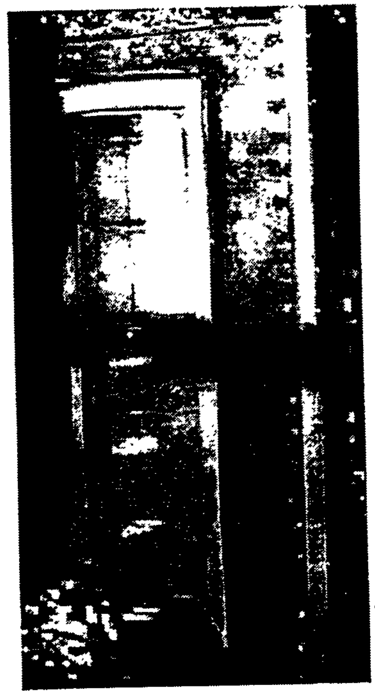

Figure 1. 18-jet *TecoJet* reactor with observation window

order of 1.2% of the output of the engine for each g/bhp-h of NO_x removed. This includes power required to separate nitrogen from air or exhaust gas. Work has begun to evaluate practical tradeoffs among nitrogen preparation methods, purity, and the efficiency of the chemical reduction process.

While external production of atomic nitrogen for NO_x chemical reduction with *TecoJet* dramatically reduces competition from most NO_x oxidation processes, some kinetic competition with reaction (1) remains at high temperatures and high exhaust oxygen concentrations from the reaction of atomic nitrogen with exhaust oxygen, reaction (2).

$$N + O_2 \rightarrow NO + O \qquad (2)$$

Temperature dependent competition between these reactions arises because the rate of reaction (1) varies only slightly with temperature (very low activation energy) while that of reaction (2) increases with temperature (activation energy approximately 7 kcal/mole #). To date, Thermo Power has measured chemical reduction of NO in diesel fuel combustion exhaust at temperatures up to approximately

210°C, and work is in progress to extend these measurements toward an estimated practical limit of 500-600°C.

SUMMARY

TecoJet is the first nonthermal plasma method to achieve practical quantities of chemical reduction of NO_x in diesel exhaust. It achieves this by isolating the plasma from the exhaust stream while maintaining the chemical activity of discharge-generated free radicals. *TecoJet* is inherently non-fouling and has been demonstrated to operate in wet and sooty exhaust. Further qualification of the process is in progress, to validate the performance and economics for mobile diesel engines.

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