RADICAL OXIDATION AUTOMOTIVE DE-NO_x

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We describe an experiment to remove NO_x from air-like gas flows by optimizing its oxidation to nitric acid. Our aim is to demonstrate an efficient de-NO_x process that can replace the catalytic converter of today's automobiles and recover greater engine performance. NO is oxidized to HNO_3 by injecting O_3 from an auxiliary air discharge unit, and the acid is scrubbed by a granular NaOH filter, the final product being $NaNO_3$. In theory this scheme requires less engine power than the enthalpy loss through the catalytic converter, and permits engine operation with oxygen-rich fuel mixtures at high compression ratios for peak thermodynamic efficiency. Experiments utilize a glass tube flow reactor with a 20 liter/minute flow mixed from the separate injections of compressed ozonized air and an admixture of 200 ppm of NO in nitrogen from a small pressurized bottle, for net proportions of 89% N_2, 11% O_2, 120 ppm NO. Ozone concentration is selected by adjusting the frequency of the repetitive-pulsed coaxial-barrier air discharge cell. For O_3:NO ratios greater than unity a chain of reactions successively produce NO_2, NO_3, and N_2O_5 which then combines with ambient H_2O to form HNO_3. The overall efficiency is dominated by the electrical efficiency of the ozonizer, at present about 30 eV/O_3 within the discharge.

Introduction

We describe an experiment on NO_x oxidation by ozone in a gas flow, in order to demonstrate the potential of a proposed de-NO_x process. The intent of the scheme is to capture all the NO_x generated by engines operating with oxygen-rich fuel mixtures at high compression ratios for peak thermodynamic efficiency, and with minimal unburned hydrocarbon emission. Replacing the catalytic converter would also have the benefit of eliminating a future toxic waste to be reprocessed.

The scheme is to optimize NO oxidation to HNO_3 by injecting O_3 into the exhaust, and then scrub the acid out through a granular NaOH filter, the final product being $NaNO_3$. The ozone is produced from air by an auxiliary discharge unit, and the filter would be replaced periodically. In theory this scheme could require less engine power than the net enthalpy loss represented by operating at low compression ratio with a catalytic converter.

Pulsed plasma de-NO_x schemes [1] that employ discharges through the exhaust gas mixture are inefficient because they are not chemically specific, the electrical energy initiates a welter of competing chemical reactions. Also while the reduction of NO_x to N_2 and O_2 would be ideal, this process requires more energy than its oxidation to nitric acid, its natural thermodynamic sink. The scheme presented here aims at chemical specificity by injecting radicals produced outside of the exhaust stream to both select the oxidation process and accelerate it. Figure 1 is a schematic of a model system.

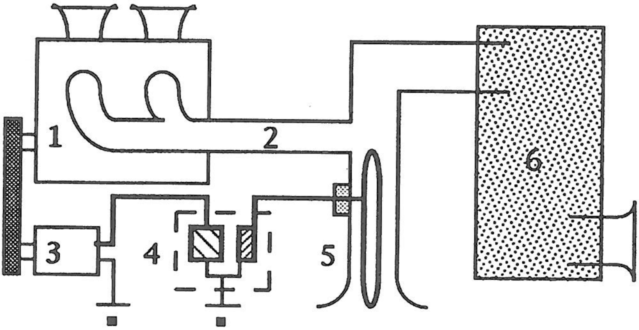

Figure 1: Schematic of model de-NOx system.
1: engine, 2: exhaust pipe, 3: generator,
4: transformer, 5: air ozonizer, 6: acid filter

A Model System

The first three items in Fig. 1, the engine, exhaust pipe and generator, would be typical automotive components. In this system the engine is assumed to operate at high temperature (high compression ratio) and on lean fuel-air mixtures. The exhaust from such an engine would have higher NO_x, but negligible hydrocarbon concentration.

Item 4 is shown as a simple step-up voltage transformer, in reality it would more likely be a compact, repetitive-pulsed source producing tens of kV near 1 kHz. Item 5 is the air-discharge ozone generator. Most of the electrical energy delivered to the ozonizer produces waste heat which counteracts ozone accumulation. The efficient removal of this waste heat, in conjunction with the electrical efficiency of the pulsed power source, constitute the majority of the energy losses to this de-NO_x process.

The mixed flow of ozonized air and exhaust gas react as follows:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (2)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad (3)$$

$$N_2O_5 + H_20 \rightarrow 2\ HNO_3 \qquad (4)$$

The water involved in this reaction sequence is normally a component of the exhaust flow. Were it possible to generate and transport OH radicals efficiently, they could be added to the flow after reaction (1) had reached completion for a rapid oxidation of NO_2:

$$NO_2 + OH \rightarrow HNO_3 \qquad (5)$$

Removing the acid from the exhaust flow could be accomplished by a granular base filter column, shown as item 6 in Fig. 1. The agitation of gas molecules as they percolate through this filter would also cause the breakup of O_3 prior to venting the flow to atmosphere.

A specific example of a model system could be as follows. A 3 liter engine at 4000 rpm produces 135 hp and 1000 ppm NO in an exhaust flow of 100 liters/s. The ozonizer produces 5000 ppm O_3 in a 20 liter/s airflow with an efficiency of 60 gm-O_3/kWh, or equivalently 30 eV/O_3. This ozonizer is expending just under 13% of the engine power, or 17 hp (12.8 kW) to produce a one-to-one ratio of O_3 to NO in the exhaust flow. The ozonizer discharge in our laboratory experiments can exceed the efficiency used in the above example, while the 3 liter engine performance estimate may be conservative.

Experiment

Experiments utilize a 10 cm diameter glass tube flow reactor with a 20 liter/minute flow mixed from the separate injections of compressed air and an admixture of 200 ppm of NO in nitrogen from a small pressurized bottle, for net proportions of 89% N_2, 11% O_2, 120 ppm NO. Ozone was produced in the airflow prior to its injection into the flow reactor by a coaxial barrier discharge. The discharge unit operates with an adjustable-frequency repetitive-pulsed power supply, and in this way initial ozone concentration could be selected. Figure 2 summarizes the essential data.

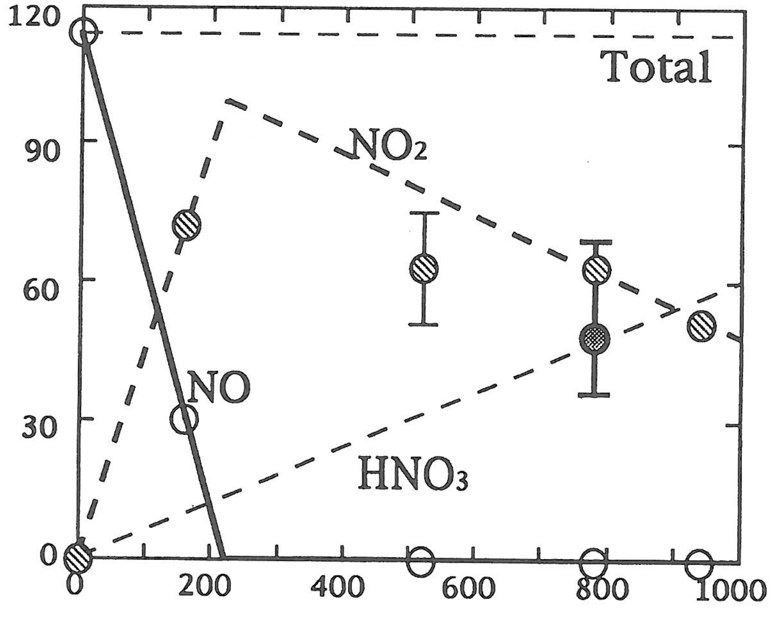

Figure 2: NO_x mass balance at ozone concentration, (ppm)

NO quickly oxidizes to NO_2 when the injected ozone concentration exceeds that of NO, and for O_3 above 200 ppm no NO was detectable at the NO-NO_2 measurement station 46 cm downstream of the mixing zone. When O_3 increases beyond 100 ppm the concentration of NO_2 always exceeds that of NO, and it peaks at about 80 ppm near the 200 to 300 ppm O_3 level. With ozone between 800 to 1000 ppm the concentration of NO_2 is between 50 to 60 ppm, and nitric acid is now seen at this same concentration. These measurements were accomplished by using a continuously operating commercial NO and NO_2 meter in conjunction with manually obtained gas samples analyzed by Dräger tube indicators. Ozone concentration exiting the ozonizer was measured by a commercial meter.

An unsuccessful effort was made to exploit reaction (5) by generating OH radicals in a pulsed corona discharge cell with an air-steam mixture, and then introducing this stream into the flow reactor. Analysis of OH production measurements indicates that the efficiency for producing this radical by pulsed discharge is at best eight times lower than for generating ozone. A companion paper describes this work [2].

NO is inevitably formed in an air ozonizer because some nitrogen is dissociated. In efficient ozonizers with dry air this NO_x concentration is about one percent that of ozone [3]. Though total NO_x and ozone formation are reportedly insensitive to humidity, [3] and [4], we observed significant nitric acid and NO_x formation, and reduced ozone production, in our ozonizer discharge after steam and fog were introduced. This may be due to the combined electrical and aqueous chemical effects of water droplets in the discharge.

Conclusion

The process of engine exhaust NO_x removal by radical injection and oxidation, followed by a granular acid scrubbing filter, could lead to lower emission engines with possibly no net efficiency loss. An optimized air ozonizing system is key to this development.

Acknowledgements

Phil Arnold, Jim Hill, and Jeff Robinson provided invaluable pulsed power, laboratory, and mechanical expertise. We are grateful to the LDRD program at LLNL for project sponsorship. This work was performed under the auspices of the U.S. DOE by LLNL under contract no. W-7405-Eng-48.

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