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Compact De-NOxer for Automotive Exhaust

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FY95 Final Report for 94-LW-046

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Our two year project concluded with mixed results. The basic idea of using ozone and hydroxyl radical in a two stage plasma chemical reactor to remove NO_x from automotive exhaust proved to be correct. However we found the energy needed to operate the plasma chemical reactor is 30% of the engine's output, which is three times larger than that of the conventional catalytic converter. Our project is a partial success. If compactness is dropped as a requirement for our plasma-chemical reactor so that it is applicable to stationary rather than mobile power generators, then the reactor needs only 5% of the engine's power.. The energy inefficient component of the reactor, the part which makes our reactor compact, would be unneccesary. Thus our reactor has the potential for being a practical device to remove the NO_x from the emissions of power plants.

This project has given LLNL visibility in plasma chemistry and toxic waste engineering. We reported our findings in two papers at the International Symposium on Plasma Chemistry, held in Minnesota from Aug. 23, 1995 to Aug 26, 1995. We found outside interest for our work, and received proposals for collaboration. However this interest did not materialize into funding, so our project is now dormant. Our project is also suffering for having an environmental flavor. In these times, environmental research and development projecta are viewed as wasteful governmental spending which sows the seeds for new unnecessary regulations.

Let me summarize our successes and failures. We built and tested the OH generator. The production of OH by the breakdown of water cannot be maintained in a silent discharge tube, because OH rapidly destroys the glass lining of the tube (on the order of hours). As our experiment progressed, the production rate of the generator decreased, because of the degeneration of the glass lining. Even when the degenration is accounted for, we found that the OH production rate of the silent discharge is about one third of what we expected. We failed to examine the effect of other combustion product gases (such as CO, H_2O, ketones, etc.) on the oxidation of NO_x by ozone and OH radicals, because we spent our time looking for the reason of the unexpected performance

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. A chain of reactions involving O_3 successively produce NO_2, NO_3, and N_2O_5 which then combines with ambient H_20 to form HNO_3.

The oxidation process could be accelerated even further by injecting OH into the NO_2 flow to form HNO_3 at a point sufficiently downstream of the ozone inlet that no NO remained. We have yet to produce a practical OH generator. Measurements of OH production in a pulsed corona discharge cell with an air-steam mixture indicate that the efficiency for producing this radical is at best eight times lower than for generating ozone.

We now turn to the OH generator. We will describe our measurement of OH concentration in a pulsed corona discharge through a steam-air mixture, and will also describe our model for the chemical kinetics of the OH generation. The motivation for the OH generater is to develop a the accelerator for the NO oxidation.

Time dependent measurements of the 3064 Å emission of OH indicate a production of nearly 4 ppm ($^{\bullet}10^{14}$ cm^{-3}) within a spark. This measurement was accomplished by a 1 ns resolution photomultiplier with a 100 Å filter centered at 3080 Å. The discharge occurs across a 1 cm coaxial gap between a central anode tube and an outer cylindrical cathode cased in glass and at ground potential. The water-air mixture is of equal proportions and at 1 atmosphere. Pulsed voltage of 38 kV and 60 ns risetime produces a 60 A, 20 ns FWHM spark.

The chemical kinetics model predicts the same OH production from the air-water mixture after 100 ns of 10^{12} electrons/cm^3. The electron density is set to zero during the subsequent interval of 100 ms in the model, and OH is seen to be produced by reactions of HO_2 with oxygen and nitrogen atoms until these atoms have recombined into molecules, and the HO_2 has been converted to H_2O_2.

The chemical kinetics model includes thirty four reactions involving the twelve species: H_2, O_2, NO, N_2, H_2O, H, O, N, OH, HO_2, H_2O_2, and O_3. Dissociation reactions predominate during the initial 100 ns discharge interval, and rate coefficients for dissociation are calculated from a Boltzmann model.

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