NON-THERMAL PLASMA EXHAUST AFTERTREATMENT : ARE ALL PLASMAS THE SAME?

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BACKGROUND

Plasma aftertreatments have been identified as a possible exhaust remediation technique since non-thermal plasma (NTP) can induce a host of new chemical reactions due to electron excitation resulting in the abundant production of radicals and excited state molecules. Present plasma aftertreatments rely on high local electric fields which directly produce energetic electrons. These energetic electrons can influence the chemistry, even in the collision dominated regime, because they do not lose much energy in elastic collision due to their small mass, but instead bounce around and transfer most of their energy to molecules; either dissociating, ionizing, or otherwise exciting them. The excitation and radical production can cause vast changes in reaction rates (as much as a hundred thousand-fold increase in some instances). Oxidation and reduction reaction pathways are possible for the dissociation of NO_x. Oxidation leads to the production of such compounds as N_2O and nitric acid. Nitric acid is toxic and is to be avoided in mobile applications. Reduction, on the other hand, leads to dissociative attachment eventually forming N_2.

To explore excited state chemistry, it is desirable to produce as high an electric field as possible. This would at first seem to entail applying high enough voltages to a suitably arranged configuration of electrodes. However, for plasma densities of interest, there is considerable plasma shielding of the applied fields even in the collision dominated regime and field limits due to low impedance arcing (Ref. 1). This space charge shielding is due to the charge imbalances arising within the plasma because of the higher mobility of electrons compared to the positive ions.

PROPOSED TECHNOLOGY

The efficiency of NTP is limited by several factors as indicated in Ref. 2. One limitation is that the electric fields are generally limited by high voltage breakdown which leads to a low impedance discharge. Significant increases in this arc transition electric field should be possible by incorporating high frequency power (5Ghz) implying 40 ps risetime. Another problem, probably not incorporated into the analysis of Ref. 2, is that plasma shielding effects take place for fields at frequencies below the electron plasma frequency. As a result of plasma shielding, the volume of the plasma where high field enhanced reduction reactions is reduced to within a few Debye lengths or an electron energy relaxation distance of the plasma edge which can reduce the high field reaction volume by orders of magnitude. This plasma shielding effect is significantly reduced by using high frequency power. Resonance cavities enable an efficient coupling of high frequency power to produce high electric fields. Surface charging of dielectrics, to the extent it occurs at all at high frequencies, will likely enhance rather than diminish (as occurs for low frequency) the fields in the next (reverse field) half cycle. Better chemistry (reduction as opposed to oxidation) is obtained by having the electric fields ramp up so fast

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(~40ps) that the probability of the discharge initiating near threshold is substantially reduced.

There are two issues which inhibit development of plasma discharge aftertreatment, undesirable chemistry path and low electrical efficiency. Both of these issues are addressed in the proposed technology.

Chemistry Path: The difficulty of reaching high E/N in the existing embodiments of the above mentioned discharges has resulted in an inability for a plasma aftertreatment device to achieve a high fraction of reduction of NO_x as opposed to oxidation. To enable much higher E/N, and a continuous production of atomic Nitrogen, we propose to employ bursts of high frequency ac electric fields with fast risetimes and many cycles per burst. Specifically, high-power microsecond bursts of 5GHz microwaves will be used which have a risetime of ~40ps (100 times shorter than present state-of-the-art pulse risetimes in this application) and allow thousands of electric field oscillations per burst of microwave power.

The net benefit of this approach in producing the best chemistry is as follows:

(A) For 40ps risetime, the fields turn on with a time scale short compared with the time an electron drifts toward the edge of the plasma; strict space charge neutrality is achieved in the plasma preventing field reduction due to plasma shielding; (B) Atomic nitrogen will be produced and available during the entire treatment since the time between microwave bursts is small compared to the recombination time; (C) Surface charging of dielectrics, to the extent it occurs at all, will enhance the fields in the next (reverse field) half cycle; (D) Field limits due to arc breakdowns (e.g., Paschen limit) will be significantly increased due to the high frequency; (E) Higher fields by having the electric fields ramp up so fast that the probability of the discharge initiating near threshold is substantially reduced.

These improvements should allow a substantial increase in the strength/efficacy of the applied fields and result in a tilt of the reaction pathway toward the desirable reduction of NO_x to N_2. This technology is intended to be used in conjunction with solid catalyst surfaces in proximity to the plasma. For a certain class of such catalysts, the surface reactivity can be enhanced by the microwave fields in addition to the effect of higher reactivity in the plasma itself.

In some cases, it could be desirable to heat the catalyst to increase its reactivity only very locally in places just where the reactions are taking place. One of the features of the proposed technology is to introduce such a scheme of controlled and highly localized enhanced catalyst reactivity.

Consider an inhomogeneous high dielectric material in the presence of low dielectric voids. If an oscillating electric field is applied to such a mixture, the potential distribution could look something like that shown in Fig.2 at an instant of time. Notice the concentration of equipotentials at certain points on the surface of the dielectric indicating the presence of high fields. The heating rate of the dielectric is dependent on these field strengths and so would be very localized even if the absorption of the electric field was uniform; however, the power absorbed is proportional to the square of the electric field. The field absorption at the edges of the dielectric is in fact made greater than that within the bulk of the dielectric by considering the polarizability catastrophe. The polarizability catastrophe occurs in the transition between vibrational excitation (small displacement and, therefore, small field absorption) and rotational excitation (large displacement and, therefore, large field absorption). When a material gets hot enough, lattice excursions become sufficiently frequent so that there is occasionally room for a rotational excitation. When this happens, the heating rate increases a hundredfold and produces more excursions producing yet more rotational excitation and so on. Unless one turns off the rf power quickly enough, a nonlinear catastrophe occurs - hence the name (effect discovered by Debye). The reason for mentioning this bit of historical trivia here is that on the edge of the dielectric, rotational excitation can always occur even at low temperatures since there is no lattice

to get in the way. Therefore, even if the electric field was uniform there could be preferential heating at the very edge of the dielectric. Figure 2a shows that this heating would become even more preferential since that is exactly the place where the electric field is strongest.

EXPERIMENTAL DETERMINATIONS

We describe initial experiments employing 5.5GHz pulsed microwave power, which should result in enhanced chemistry compared to present state-of-the-art plasma aftertreatments by; reducing plasma electric field shielding, increasing availability of atomic nitrogen, exploiting surface charging of dielectrics, avoiding (low field) threshold initiated discharges, and achieving a higher high energy tail on the electron distribution function. As an example, we decided to test for NO reduction in N_2. While this reaction is not a complete description of the exhaust issues by any means, we thought it would demonstrate the technology proposed.

PROCESS

The fast rise time non-thermal plasma NO_x control reactor uses a 5.5 GHz pulsed microwave source to generate a DBD with electric field rise times of less than 50 ps. A gas mixture is fed to the reactor from a flow bench that can mix up to eight gases and cycle certain gases with time. The microwave source is a magnetron tube and power supply with a frequency output tunable from 5.3 GHz to 5.8 GHz, a peak output power of 200 kW, and an average power output of 200 W. The output pulse widths can be 0.5, 1.5, and 2.25 μs with a duty factor up to 0.001. The microwave applicator or reactor, see Fig. 1, consists of a 43 cm length of WR-187 waveguide with a 16 mm OD, 14 mm ID quartz tube penetrating through the wave guide at a 15° angle. The microwave electric field is generated between the top and bottom walls of the waveguide and thus passes through the quartz tube in the region where the tube is within the waveguide. The tube is angled to provide a slow change in dielectric constant in the waveguide. The outlet end of the waveguide, as shown in Fig. 2, is shorted with a plate to reflect any power not absorbed in the first pass back into the reaction volume. The waveguide is pressurized with sulfur-hexaflouride to prevent breakdown around the outside of the quartz tube, rather than inside the tube. The quartz tube is filled with 4 mm dielectric beads to provide electric field enhancement and electrical breakdown. A DBD is generated when an arc is initiated between dielectric surfaces. The electrons at the leading edge of the arc are trapped on the surface of the dielectric, locally canceling out the electric field and extinguishing the arc. A new arc is then immediately formed but intersecting the dielectric surface at a different location. Figure 2 shows the basic waveguide layout from the microwave source to the reactor. A signal sampling coupler is used with coaxial detectors is used to measure the applied and reflected power levels at the reactor.

Gas concentrations of NO_x were determined by chemiluminescence (Rosemount model 951) operated in the NO_x mode. No attempt was made to quantify O3 and N_2O, although this capability will be available for future efforts.

EXPERIMENTAL RESULTS AND DISCUSSION

The set of experiments performed with the described setup involved a simple mixture of NO in N_2. Initial concentrations of NO were set at 1000 ppm and 2000 ppm with flow rates of 4.6 lpm and 10.6 lpm. This gave a residence time of 100 ms and 44 ms respectively in the active zone of the discharge, or space velocities of 36,000 h^{-1} and 83,000 h^{-1}. Because no H_2O was present, the outlet of the reactor was fed directly into the analyzers.

For these experiments, an average pulse width of 1.5 ps and period of 3 ms were used resulting in a duty factor of 0.0005 to 0.001. Several different power levels were investigated resulting in peak transmitted powers of 22 to 150 kW and average transmitted powers of 3 to 100 W. Transmitted and reflected powers were monitored using a calibrated waveguide signal sampler with coaxial detectors. The absorbed power was taken as the difference of applied and reflected power. This is an upper bound for absorbed power because other losses are neglected. Input energy density in joules/liter is calculated from the absorbed power and the flow rate. To put the results in perspective of others'

work, the results are scaled linearly to 100 ppm input NO concentration and the input energy densities are plotted vs ppm NO in Figure 3. Penetrante et al. presented modeling and experimental results on similar axes for pulsed corona discharge generated electrons.[ref]. The resulting energy per molecule NO converted was found to be 238 eVmolecules. The microwave generated plasma is converting at a lower energy per molecule.

The high peak power, low repetition rate data appears to indicate a high efficiency of conversion with low energy densities. This is explained perhaps by the efficiency at which microwave energy can penetrate a plasma and heat the electrons as long as the microwave frequency remains higher than the characteristic electron plasma frequency (cutoff is avoided). For the 5.5GHz typically used in these experiments, the corresponding electron cutoff density is approximately 3.5 x 10-11 cm-3.

DISCUSSION OF ERRORS

The errors in these data have three contributions: NO concentration measurements, gas flow measurements, and microwave power measurements. The transmitted and reflected microwave powers are measured by means of coaxial detectors on a signal sampling coupler in the waveguide system. Random uncertainties in the power measurements result from the reading of the detector voltages, the pulse width and the pulse period are estimated to be ± 15% in the average absorbed power (transmitted power - reflected power). The power measurements are also subject to systematic errors resulting from the signal sampler and coaxial detector calibration. These errors are estimated to be >10% and would offset all of the data in the same way and so not affect any trends displayed in the data here.

The errors in the measurement of NO and NO_2 are small relative to the errors in power measurement. The particular chemiluminescence instrument used for this study drifts less than 1% in a day and was spanned before each set of runs. Similarly, NO_2 response was checked with a standard mixture. The standard deviation over the ten samples taken for each run is also incorporated into the error, for an overall error of concentration of ± 7%. The errors in flow measurement, which is incorporated into the input energy density determination is also small. The mass flow controllers are specified at ± 2% accuracy. The contribution of this error to the overall error in calculating the input energy density is negligible.

CONCLUSIONS

As an illustration, this plasma generator was applied to the removal of NO in N_2. Instead of the usual 238 eV per removed NO obtained with other slower rise time plasmas, a 70% reduction (75 eV per removed NO) was obtained.

The electron temperature was 6.5 eV vs the usual 4 eV, see Fig. 4 [3].

A new plasma generator for NTP treatment of exhaust gases was investigated. It features a fast rise time (40 ps) discharge which is comparable to electron transport times in the plasma. This is obtained from a 5.5GHz microwave generator coupled to a suitable resonance cavity. Thus, plasma shielding is reduced and a higher E/N in the bulk of the plasma achievable. This may reduce the N_2 vibrational excitation risk and allow for high electron temperatures. As an illustration, this plasma generator was applied to the removal of NO in N_2. Instead of the usual 238 eV per removed NO obtained with other slower rise time plasmas, a 25% reduction (167 eV per removed NO) was obtained. This improvement is in and of itself hardly sufficient to admit the stand alone commercial feasibility of the technique, but offers possibilities when combined with smart catalytic converters. With such catalytic converters, the higher electron temperature and concomitant different reaction kinetics (enhanced excited state molecular production) offer a synergistic and enhanced improvement in exhaust remediation. This is in addition to the expected enhanced reactivity of the catalyst itself due to the microwave induced rotational excitation at the catalyst surface edges.

REFERENCES

1. J. H. WHEALTON AND R. L. GRAVES, "EX-

HAUST REMEDIATION USING NON-THERMAL (PLASMA) AFTERTREATMENT: A REVIEW," *PROCEEDINGS OF THE 1995 DIESEL ENGINE EM/SS/ONS REDUCTION WORKSHOP,* V-25, LAJOLLA.

2. B. M. PENETRANTE ET AL., "COMPARISON OF ELECTRICAL DISCHARGE TECHNIQUES FOR NONTHERMAL PLASMA PROCESSING OF NO IN N_2," PP. 679 - 687 IN *IEEE TRANSACTIONS IN PLASMA SCIENCE,* VOL. 23, NO. 4, 1995.

3. B.M. PENETRANTE, PREVIOUS PAPER DEER '97

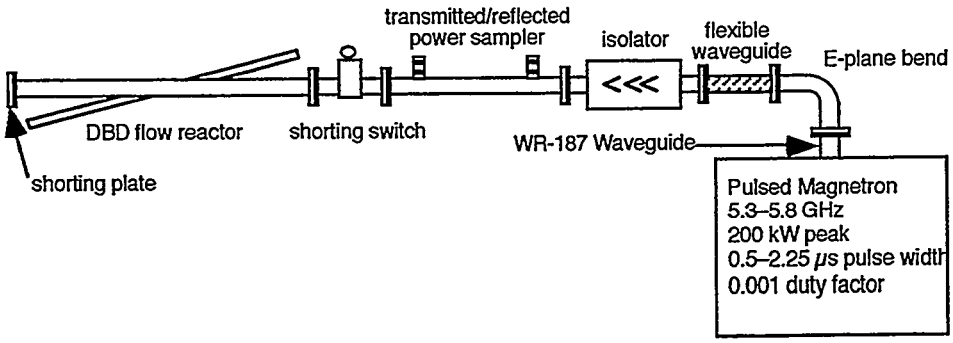


Fig. 1. Waveguide reactor for microwave generated DBD non-thermal plasma treatment of exhaust gases. The microwave energy causes breakdown in the portion of the quartz tube within the waveguide. The quartz tube is filled with dielectric beads through which the gases flow. Electric field enhancement along the surfaces of the dielectric beads leads to the DBD.

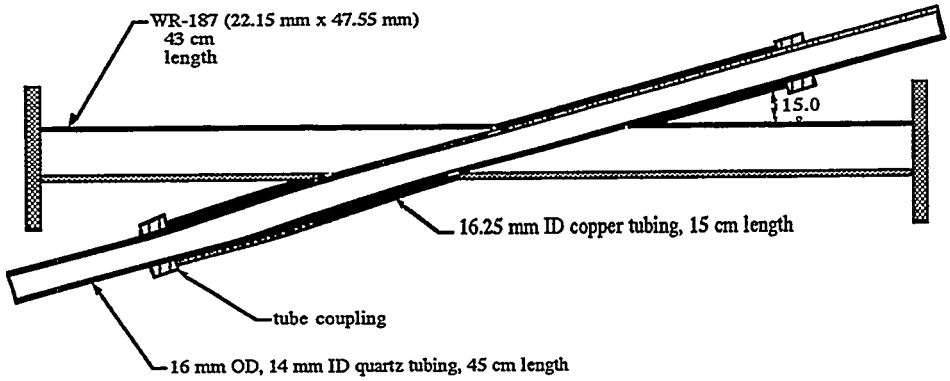


Fig. 2. Microwave generated DBD flow reactor waveguide layout. The microwave energy is generated by a pulsed magnetron tube and conveyed to the waveguide reactor by WR-187 waveguide.

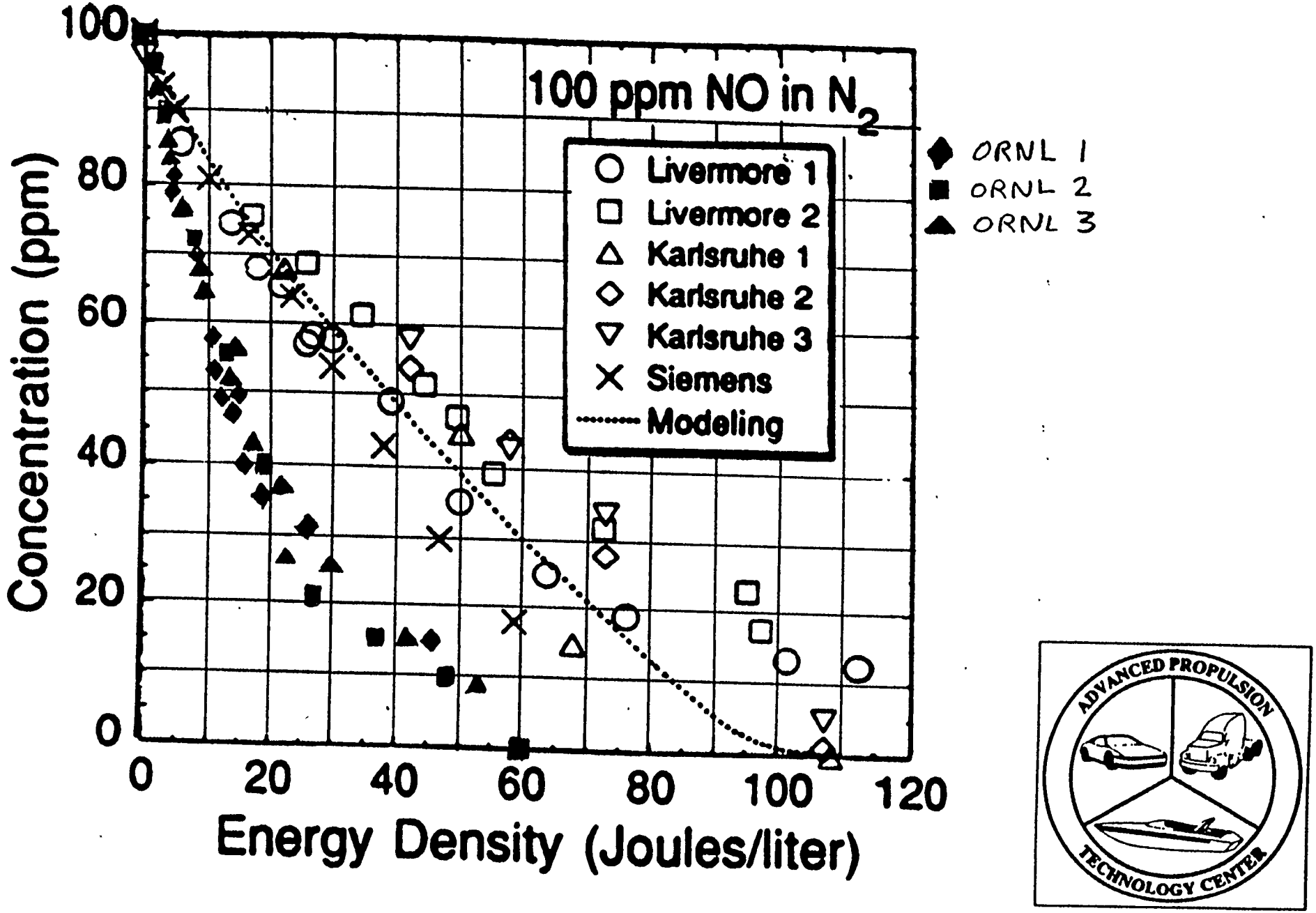
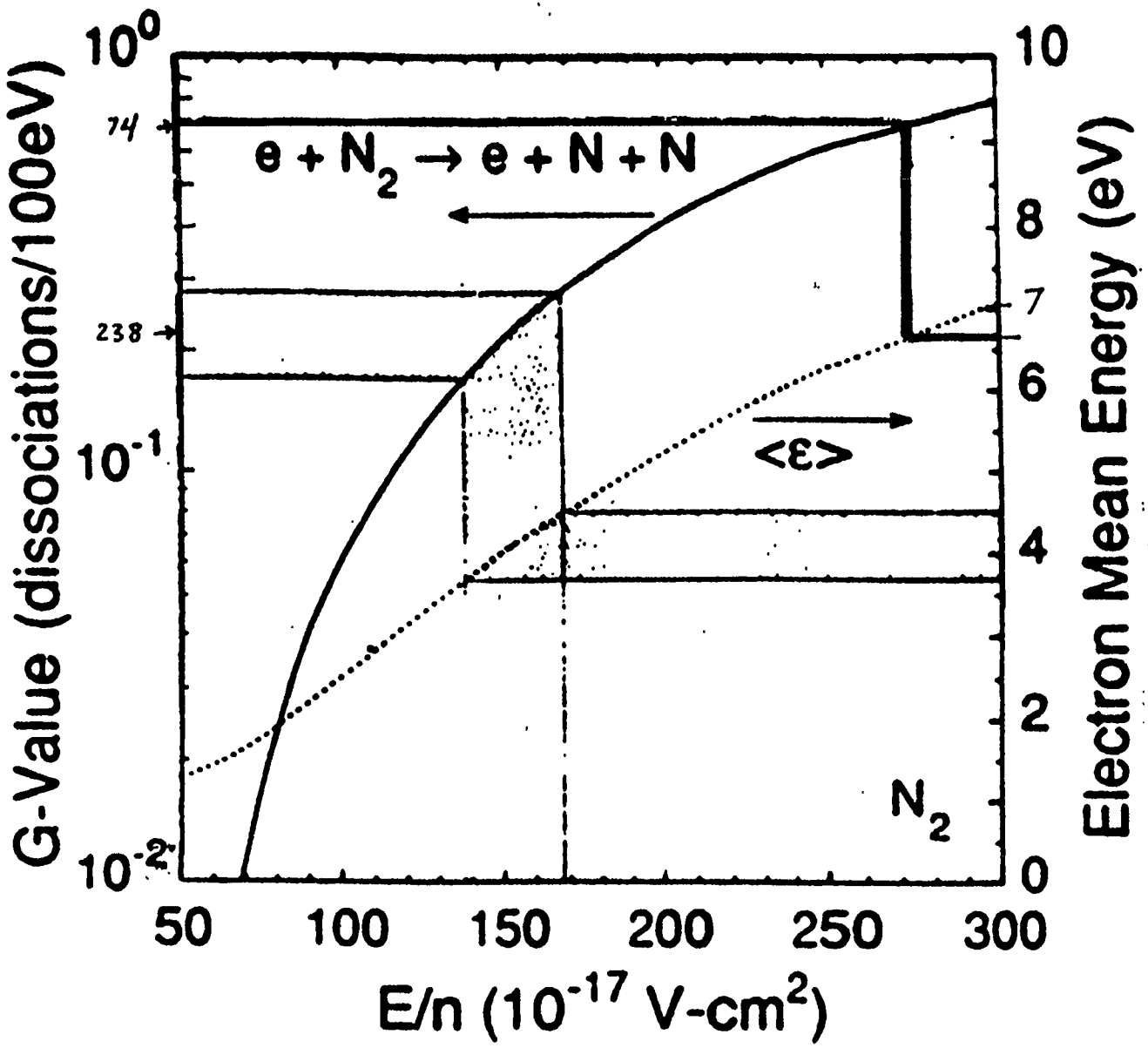


FIG. 3. Pulsed corona and dielectric-barrier discharge processing of 100 ppm NO in N_2.



	$\bar{\varepsilon}$
ORNL	6.6
LIVERMORE	4.2
KARLSRUHE	4.2
Siemens	4.2

FIG. 4. Calculated G value (number of dissociations per 100 eV of energy input) for electron-impact dissociation of N_2, and electron mean energy, as functions of the reduced electric field E/n.