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Exhaust Remediation Using Non-thermal (Plasma) Aftertreatments: a review

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Abstract

There are four post combustion (non-thermal) plasma treatments on the table for reducing NOx in exhaust streams. In this paper we compare these techniques, and suggest what appears to be a novel (eight inventions) and optimum path for development of a useful exhaust treatment system. We propose to employ 5 GHz microwaves which will have a risetime of 20 ps - 100 times shorter than present state of the art and result in the best chemistry path by: reduction of plasma shielding, greater availability of atomic nitrogen, elimination of surface charging of dielectrics, avoidance of (low) threshold fields, and higher breakdown limit. We also propose combining a surface intrinsically into the plasma discharge. Novel embodiments are proposed for the pebble bed discharge allowing an order of magnitude increase of field-volume over the closest packing configuration.

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Background

Plasma aftertreatments have been identified as a possible reduction treatment to NOx since nonthermal plasmas can induce a host of new chemical reactions due to the abundant production of radicals and excited state molecules.

All of the plasma aftertreatments rely on high local electric fields which directly produce energetic electrons. These energetic electrons can influence the chemistry, even in the ambient collision dominated regime, because they do not lose much energy in elastic collision due to their small mass. Instead they bounce around and transfer most of their energy to molecules, either dissociating, ionizing, or 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).

A combination of oxidation and reduction reaction pathways is possible. Oxidation leads to the production of such compounds as N_2O and nitric acid. Reduction leads to dissociative attachment eventually forming N_2. Nitric acid is toxic, both to lungs and fenders, and is to be avoided in mobile applications.

The four plasma aftertreatments considered here differ in the chemical reaction pathways mentioned above. It is found that at high electric field to pressure ratio (E/P) the reduction pathway predominates, while at low E/P the oxidation pathway predominates. Therefore 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 shielding of the applied fields. This space charge shielding is due to the charge imbalance arising caused by the higher mobility of electrons compared to the positive ions.

The difficulty of reaching high E/P in the existing embodiments of these discharges has led to exploration of electron beam technology which appears to have major barriers to commercial implementability. We will propose an alternative method to achieve high E/P.

Rather general kinetic calculations have shown that the energetics in volume plasma exhaust aftertreatments is quite unfavorable. Electron beams also offer a partial advantage in this regard. We will propose configurations, outside the range of these calculations, which offer the possibility of ameliorating this defect also.

There are four post-combustion (non-thermal) plasma treatments considered for reducing NOx in exhaust streams. They are reviewed below.

(A): Corona Discharge

A feature of the corona discharge which differentiates it from the other discharges considered is that no dielectric is involved.

Instead an avalanche is initiated from a sharp metallic surface where the radius of curvature is small and where the local vacuum electric field is high (up to 100 keV/cm.). The discharge, once initiated, propagates throughout the volume by creation of a space charge wave led by ionization at the wave front.

Pulse risetimes on the order of 3 ns with low duty factor are usually employed. Two problems with this approach are that while 3 ns is short enough so that the ions (and therefore the gas) are not unnecessarily heated up, it is sufficiently long so that a space charge shielded plasma builds up thus lowering the electric fields inside the plasma. Furthermore by having a low duty factor the crucial radical, atomic nitrogen, is present only a small fraction of the time since it forms within a microsecond and decays on a time scale much faster than the interval between pulses (see the paper of Kushner et al, these proceedings). Therefore the undesirable oxidizing reaction pathway dominates. From these comments, it is obvious what needs to be done and we will bring it up explicitly later.

(B): Dielectric Barrier Discharge

Dielectric barrier discharges (DBD) have a commonality with the corona discharge in that small scale streamers are formed. When the electric field is perpendicular to the dielectric, streamers form with a density of about 100/cc. A feature of technological convenience for dielectric barrier plasma discharges is that it can run without pulsed power since in several nanoseconds of operation space charge builds up on the dielectric surface which reduces the external electric field, extinguishing the discharge (locally). Unfortunately this convenience, when employed, tend to favor the oxidation channel over the desirable reduction channel since the electric field is relatively low (discharge starts only at threshold).

(C): Surface Plasma Discharges

In this configuration, the electric fields are parallel to the surface and the plasma is created adjacent to this dielectric surface. In operation the surface plasma covers the entire dielectric surface during the pulse. This plasma produces the high energy electrons that start the chain reactions mentioned earlier.

The surface discharge differs from those of discharges A and B, mentioned above, in that a surface is in contact with a large part of the plasma. This contact has the possibility of inducing or enhancing surface catalytic effects and mitigating the effects of plasma shielding.

To illustrate the configuration of the surface discharge and the role of the dielectric Fig 1 is constructed from a solution of Laplace's equation including the boundary conditions appropriate to a dielectric but neglecting any effect of the plasma. Labeled in the figure are: the location of the dielectric, which in this case has a dielectric constant of 9 (alumina); the location of the conducting electrodes, one of which resides on the surface of the dielectric, and the other residing within the dielectric (the configuration shown is not optimum, but rather is illustrative -

Surface Plasma Discharge

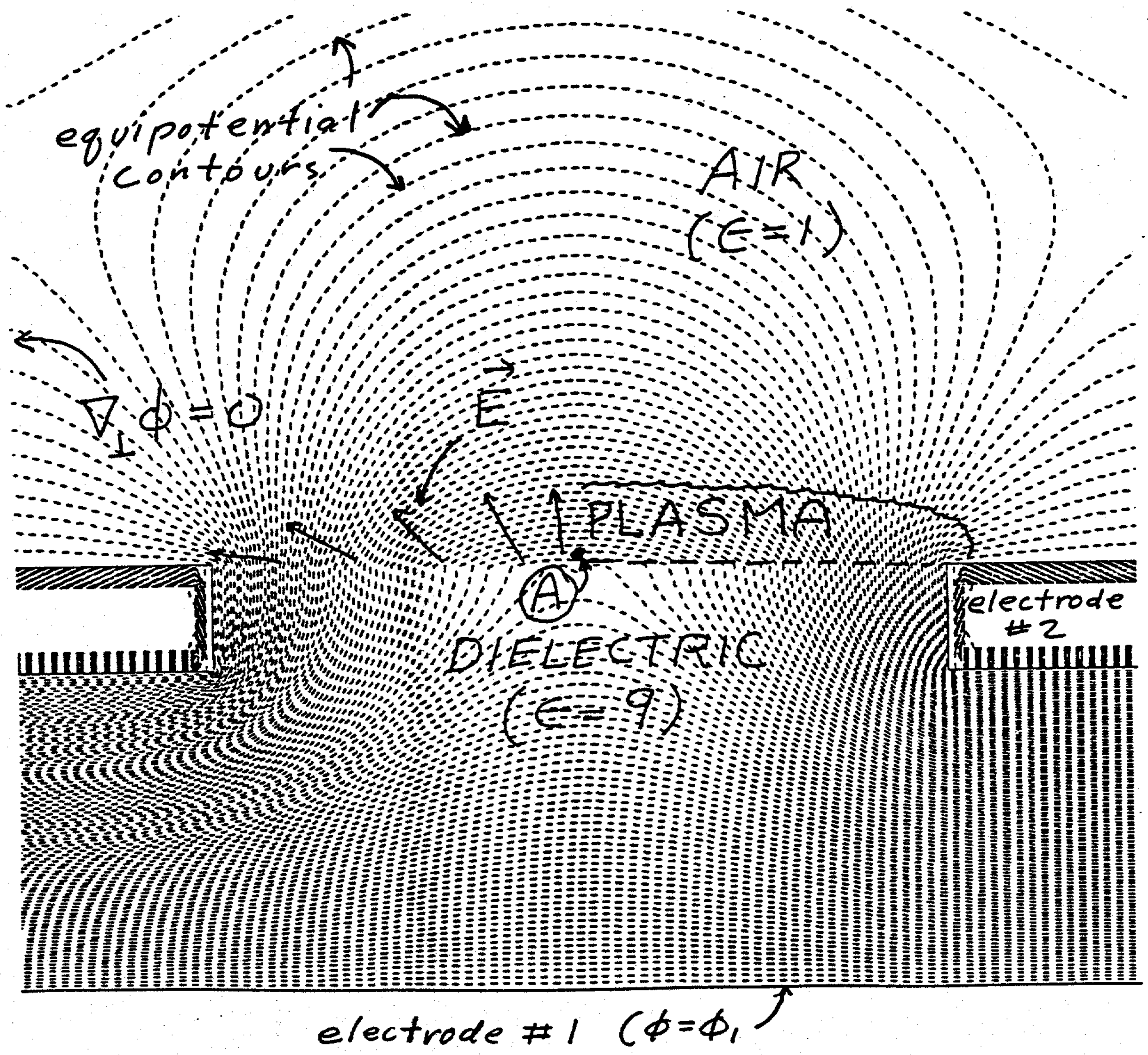

Fig 1: To illustrate the configuration of the surface discharge and the role of the dielectric this figure is constructed from a solution of Laplace's equation including the boundary conditions appropriate to a dielectric but neglecting any effect of the plasma. Labeled in the figure are: the location of the dielectric, which in this case has a dielectric constant of 9 (alumina); the location of the conducting electrodes, one of which resides on the surface of the dielectric, and the other residing within the dielectric (the configuration shown is not optimum, but rather is illustrative - see Gunderson, these proceedings, for optimal configurations); the direction of the electric fields on the surface of the dielectric; and other boundary conditions. A feature of this discharge is that after a few ns charge starts to build up on point "A" (labeled on the figure) which has the effect of reducing the electric fields outside of the dielectric, eventually extinguishing the discharge.

(D1): Dielectric packed bed reactor (DBD view)

The dielectric packed bed reactor is like the dielectric barrier discharge but with a different configuration of dielectrics as illustrated in Fig 2. Between a parallel plate discharge, pebble shaped (or smaller) chunks of dielectric. (A ferroelectric is claimed to be used wherein the relationship between D and E is nonlinear and an electric dipole can be retained even in the absence of an applied field. This appears to be unnecessary and we will only treat the case of dielectrics.) Local field enhancement is a natural consequence of Gauss's Law combined with the fact that the dielectric has a dielectric constant much larger than the intervening space (See Fig 3).

Fig . 3 illustrates several features of the electric field structure from solutions (equipotentials shown by dotted lines) to the Laplace's equation. For example: (a), the electric field inside the dielectric (P4) is lower than the voids between the dielectrics (P1 & P5); (b), the voids between dielectrics along electric field lines (P1) have higher electric fields than other voids (e.g. P5); (c) field penetration into the dielectric (P3), near these high field points (P1) can be significant and can reduce the potential drop (and therefore the electric field) within the gaps; (d), this field penetration becomes more significant as the gaps between the dielectrics decreases, (see e.g. P3 of Fig. 3C compared to Fig. 3A or 3B); (e), for touching dielectrics (e.g. Fig 3C) where the gap is closed, the field enhancement is reduced substantially (Compare E_{a1} to E_{b2} and E_{c1}); (f), field penetration perpendicular to the electric field (P2) also increases the field in the dielectric leaving less of a potential difference in the gap P1. This fact leads to the improvement indicated in the next section. Items (c-e, f) represent advancements over the state of the art.

According to the local high field explanation of the pebble bed discharge mechanism, there are some disadvantages compared to the standard DBD: (a), a higher total voltage is required since dielectrics are in series, and (b), there are wasted regions of lower electric fields (see Fig 3). From the standpoint of maximizing electric field and volume: pebble size, shape, and configuration can make a big difference in the performance of the device. For example, (a), pellets which actually touch may not be as effective as those which come close but don't touch (see Fig 3b & 3c), (b), the number of gaps along an electric field line should be minimized. Therefore, closest packing of dielectric spheres (commonly employed) is not the best (see Figs 3 & 4).

Dielectric packed bed discharge 0

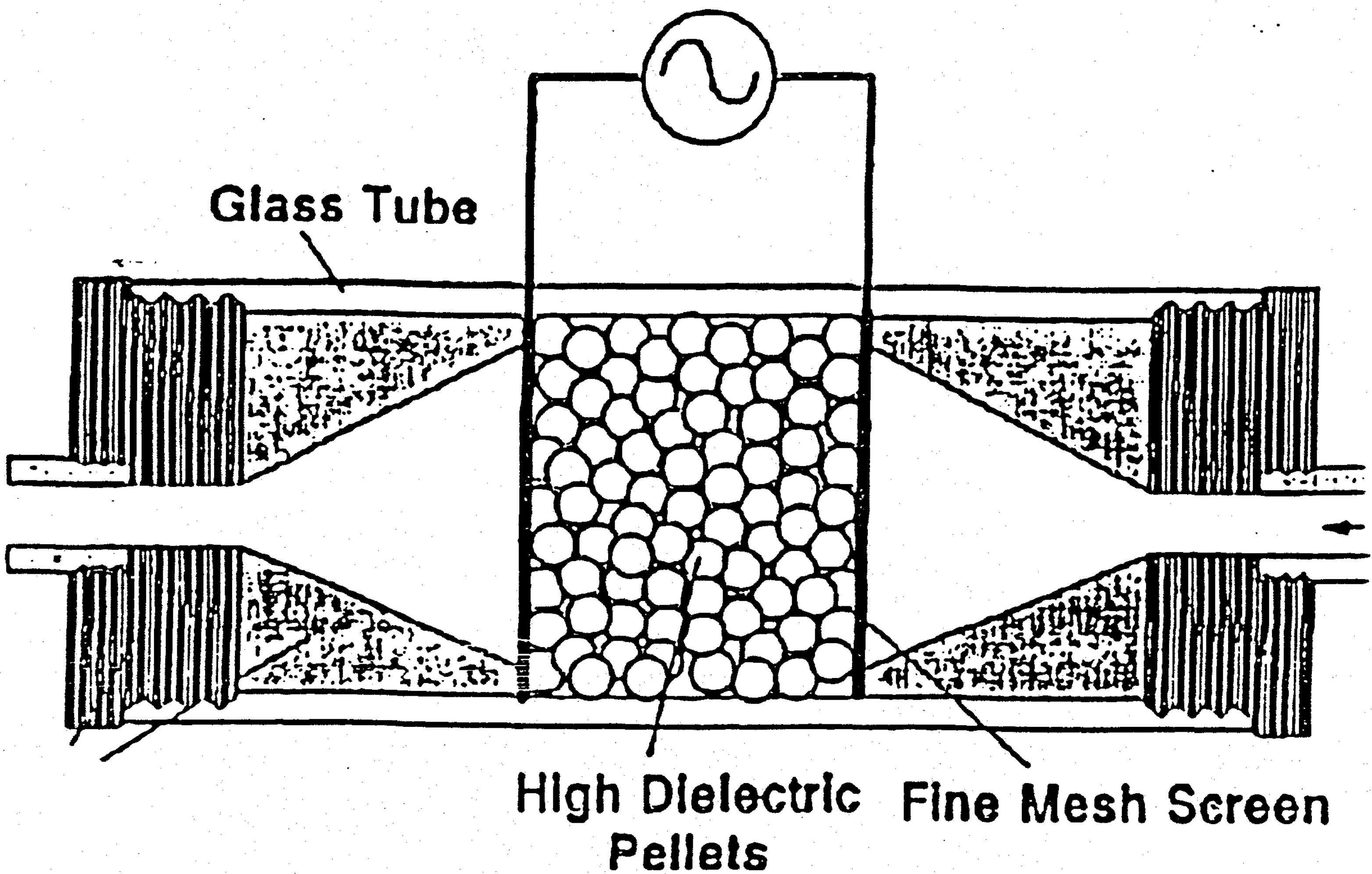

Fig 2: embodiment of invention by Bayliss, Raybone, and Hall

Dielectric packed bed discharge I

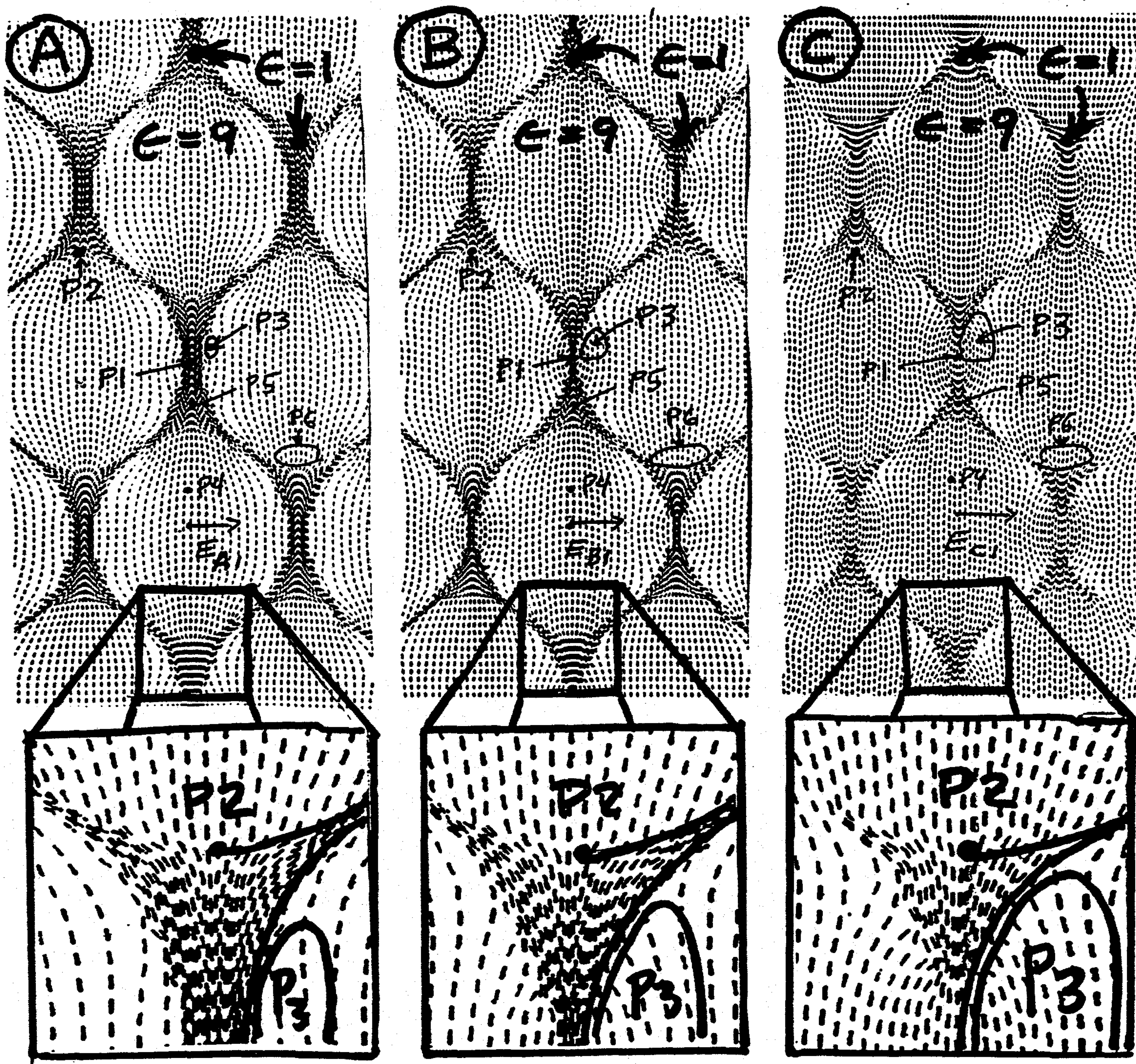

Fig 3: Local field enhancement is a natural consequence of Gauss's Law - Pebbles have a dielectric constant much larger than the intervening space. If the pebbles actually touch, however, the effect of the high dielectric is reduced, as shown in the figure on the right hand side.

Dielectric packed bed discharge II

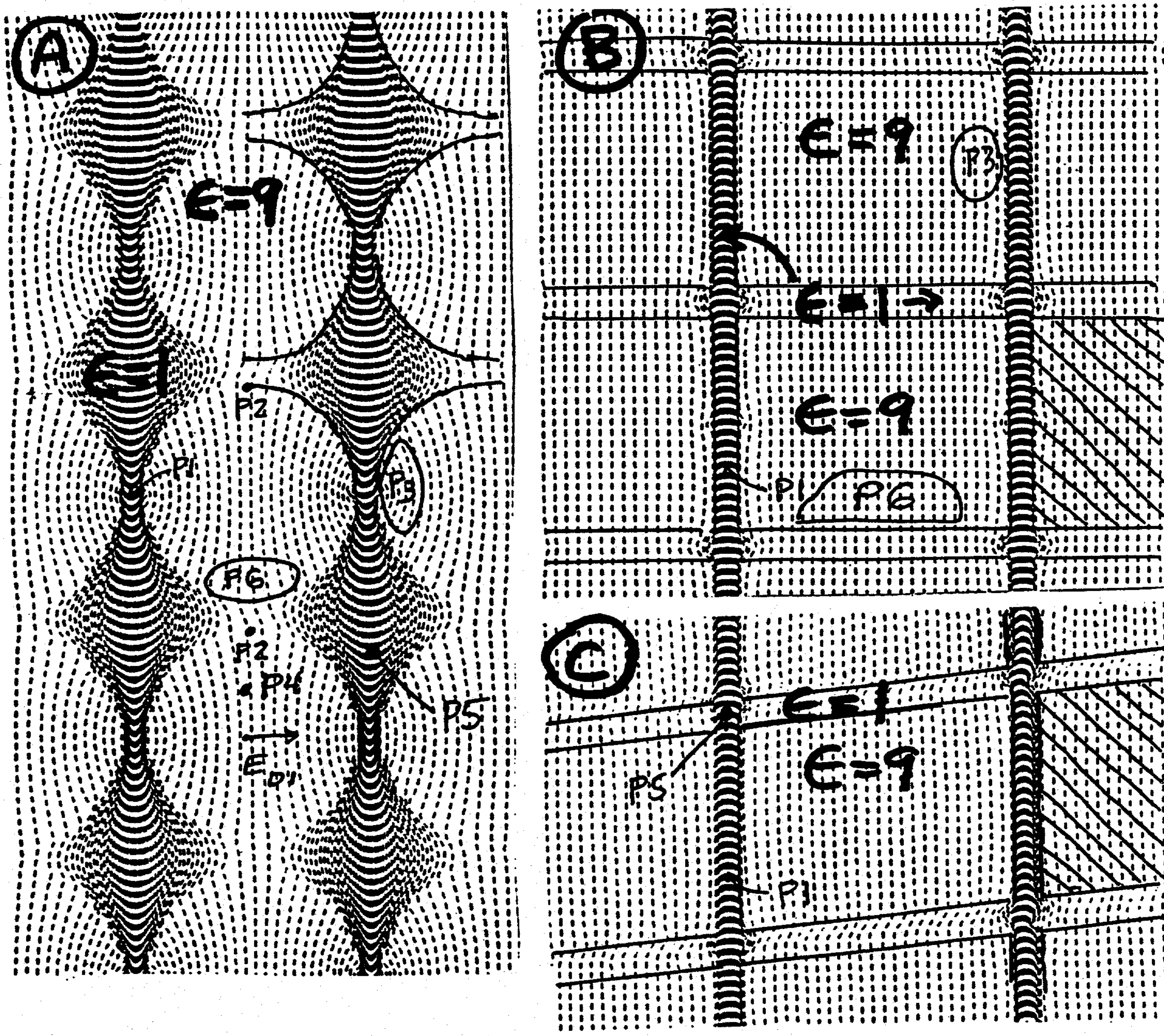

Fig 4: Left figure shows effect of planar packing instead of closest packing as shown in figure 3. Greater fields are achieved in this configuration, but less volume has high fields. An embodiment achieving both relatively high volume and high fields is shown on the figure on the right.

(D2): Dielectric packed bed discharge (surface discharge view)

If, however, we think of a pebble discharge as a surface discharge, instead of as a dielectric barrier discharge, then the situation is different: (a), the discharge sees the total voltage instead of the voltage between each pebble (capacitors in parallel instead of capacitors in series); (b), the discharge occurs over a large volume, perhaps most of the region between the pebbles.

Fig . 4 illustrates several additional features of the electric field structure. For example: (a), nonuniform field penetration perpendicular to the electric field (P2, P6), which was a problem in the embodiments of Fig. 3, is significantly reduced in the rearrangement of Fig 4a (and eliminated in optimal geometry of Fig 4B or 4C) therefore resulting in an increased electric field at P1; (b), the end field penetration, P3, which results in P1 field degradation for embodiments represented in Fig 3 and 4a, is eliminated in the embodiments represented in Fig 4b and c; (c),the relatively low field void region (P5) of Fig 3 and 4a is also eliminated in the embodiments of Fig 4b and 4c;(d), a controllable field-surface angle is exhibited in Fig 4c, compared to the uncontrolled variations illustrated in Fig 1, 3, and 4a. Items (a, b, c, d) represent advancements over the state of the art.

From this standpoint: pebble size, shape, and configuration can also make a big difference: (a), the channel width between pebbles should be optimized. (see Fig 4b), (b), channel length must also be optimized (see Fig 4b), (c), again, closest packing of spheres arrangement not the best.

The dielectric bed reactor can be viewed as a forced surface discharge, different from the conventional discharge because it will not self-extinguish due to charge buildup.

Efficiency

Energy efficiency is important because it is tightly budgeted from the commercial aspect and at best difficult to achieve due to technological constraints. From economic considerations, no more than 5 percent of the engine power can be devoted to pollution removal at the exhaust. To develop reasonable expectations on what is possible or practical, one must look into atomic physics / chemistry limitations as was done by Penetrante et al. and is summarized below.

The dissociation energy of NO is 6.5 eV. This by itself translates into a power sink of 1 percent for 300 ppm NO_X in the exhaust stream. However, not all the energy pumped into the formation of the aftertreatment plasma is obediently channeled into NOx dissociation. Chemical reactions occur, some of which eventually lead to reduction of NO_X, and others lead to less benign byproducts. Penetrante, Bardsley, and Phelps have marshaled together atomic physics cross-section data and a validated electron kinetic description to establish, at least to first order in, the ways the electron energy is channeled. Their conclusion is that one should expect a cost of 62 eV/NO_X, up an order of magnitude from the 6.5 eV dissociation energy of NO. If one wanted the energetic cost of just the reduced NO rather than the milder condition, above, of the dissociated NO, the energy cost would be significantly higher.

It should be noted that for e-beam treatment, the efficiency in reducing NO_X is considerably higher : 14 eV/NO_X vs. 62 eV/NO_X.

Conclusions

There are two issues which inhibit development of plasma discharge aftertreatments: undesirable chemistry path and low electrical efficiency. Both of these issues are addressed herein.

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 NOx as opposed to oxidation. To enable much higher E/N, we propose to employ 5 GHz microwaves which will have a risetime of 20 ps - 100 times shorter than present state of the art in this application. The net benefit of this approach to increase the fields are as follows:

A--to the extent that the fields turn on with a time scale short compared with 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 duty cycle is high.

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 limitations due to breakdowns (Paschen limit) will be almost entirely avoided 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 two orders of magnitude increase in the strength / efficacy of the applied fields. In addition, the six incremental inventions contained in the discussions surrounding Figs. 3 and 4 for the pebble bed discharge allow an order of magnitude increase of field-volume over the conventional embodiments. The above improvements result in a tilt of the reaction pathway towards the desirable reduction of NO_X to N_2.

Rather general kinetic calculations have shown that the energetics in volume plasma exhaust aftertreatments is quite unfavorable. However these rather pessimistic results are only valid in the plasma volume itself. They do not refer to surface catalytic plasma chemistry effects. For this and several other reasons we propose combining a surface intrinsically into the plasma discharge. Of the above mentioned discharges, only the surface plasma discharge (C) or the pebble bed discharge (D) fit this description. Of these, the pebble bed discharge is preferred, at least in the improved embodiments suggested in Fig. 4, since the electrical connection is forced and not dependent of the whims of space charge buildup. Also the surface connection with the plasma can be two sided, instead of one sided, and the angle of incidence of the electric field can be controlled. There are other embodiments at least as interesting as the variants to (D) that we have mentioned, which are obvious to anyone familiar with the state of the art.

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ABSTRACTS

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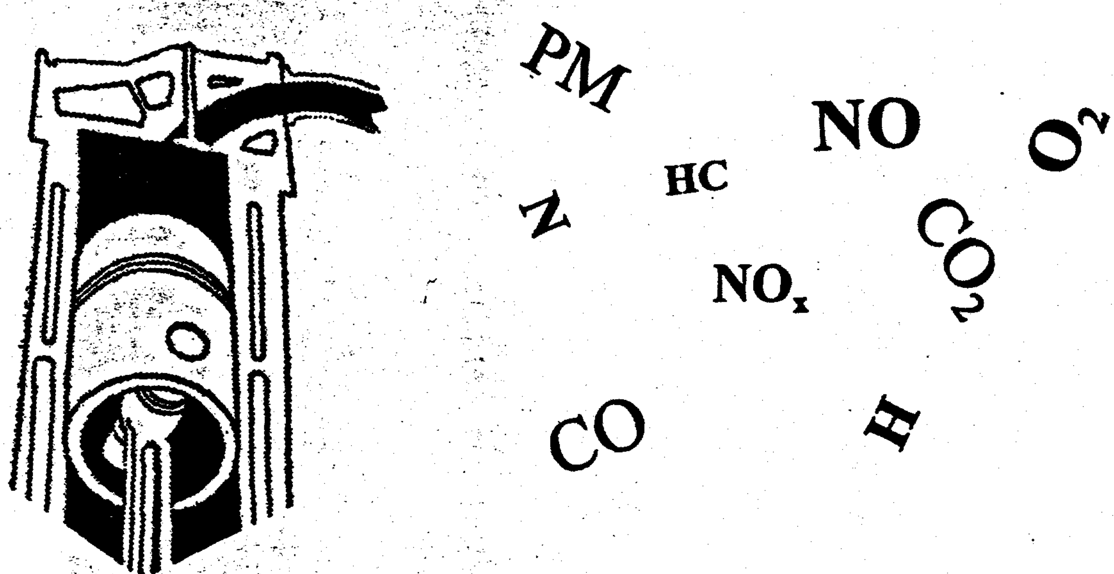

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