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FUNDAMENTAL LIMITATIONS OF NON-THERMAL PLASMA PROCESSING FOR INTERNAL COMBUSTION ENGINE NO_x CONTROL

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Abstract: This paper discusses the physics and chemistry of non-thermal plasma processing for post-combustion NO_x control in internal combustion engines. A comparison of electron beam and electrical discharge processing is made regarding their power consumption, radical production, NO_x removal mechanisms, and by-product formation. Can non-thermal deNO_x operate efficiently without additives or catalysts? How much electrical power does it cost to operate? What are the by-products of the process? This paper addresses these fundamental issues based on an analysis of the electron-molecule processes and chemical kinetics.

I. Introduction

Post-combustion control of NO_x from the exhaust of internal combustion engines is now considered an important problem that needs to be tackled by the transportation sector. In the USA about 40% of the NO_x emitted to the atmosphere are from mobile sources. Of the various environmental laws, the ones covering NO_x are the most sweeping.

Among the best available post-combustion NO_x control technologies are Selective Catalytic Reduction (SCR), Selective Non-Catalytic Reduction (SNCR, also known as thermal deNO_x), RAPRENO_x, and Non-Selective Catalytic Reduction (NSCR). The SCR process, which involves injection of ammonia and subsequent reduction of NO to N₂ on a catalyst, has been under development for at least three decades [1]. The NSCR process, which involves the use of hydrocarbon and carbon monoxide to implement NO reduction in the presence of a catalyst, has been available as early as 1945 [2]. Thermal deNO_x (or

SNCR), which does not use a catalyst but requires a higher operating gas temperature, has been implemented using either ammonia [3] or urea-based agents [4,5]. RAPRENO_x works similar to thermal and surface-catalyzed deNO_x but uses isocyanic acid as an additive [6]. These "conventional" technologies have already gained commercial acceptance in a number of countries. For natural-gas-fired rich-burn engines, NSCR is the most common and widely preferred NO_x control alternative. SCR is currently in use in several diesel engine units in Europe, Japan and the USA [7,8]. RAPRENO_x may soon be commercially available for stationary engines.

There is currently a lot of enthusiasm about using non-thermal plasma techniques – in particular, electrical discharge techniques – for possible applications to both stationary and mobile engines. There are speculations that these techniques could reduce NO_x emissions with reasonable power consumption, and without the use of chemical additives or catalysts. If true, these techniques would be a significant advance in post-combustion NO_x control technology. So far, however, it has not been demonstrated that these plasma techniques are technically and economically competitive to the "conventional" techniques. In the past, most studies of non-thermal deNO_x – using electron-beam irradiation or pulsed corona – have been focused on the treatment of flue gases from power plants. For this application, the desired process involves the *oxidation* of NO_x to form nitric acid, which is then neutralized to ammonium nitrate in the presence of ammonia. For internal combustion engine applications – in particular, for mobile sources – it may be impractical to have to collect solid (or liquid) by-products, and so the

desired process is the *reduction* of NO to N₂, as in conventional NO_x reduction techniques.

Some forms of discharge reactors can be implemented with simple power supplies. The main drawbacks of electrical discharge techniques are: (1) the processing is mainly oxidative, and (2) a large amount of the input electrical energy is spent on the vibrational excitation of molecules. Electron beam processing is more effective in producing the radicals responsible for NO_x reduction chemistry. Unfortunately, the high capital cost and x-ray hazard associated with electron beam accelerators have discouraged researchers from using this technique in small scale applications. This drawback stems from the use of conventional accelerators in a high-pressure high-volume application. Plasma cathodes, such as those developed originally for gas discharge switches, could possibly be used to implement compact, windowless electron beam sources for internal combustion engine applications. Of course, the bottomline is the price since the cost of implementation underlies almost all the decision-making in selecting the technology for pollution control.

In order to properly evaluate the economics of non-thermal plasma processing, it is important to understand the physics and the chemistry that controls the power consumption, radical production, NO_x removal mechanisms, and by-product formation. In this paper I will try to address these economics issues based on an analysis of the electron-molecule processes [9,10] and chemical kinetics [11].

Can non-thermal deNO_x operate efficiently without additives or catalysts? How much electrical power does it cost to operate? What are the by-products of the process?

II. Physics of Non-Thermal DeNO_x

Non-thermal plasmas are plasmas in which the electron mean energy is considerably higher than those of the bulk-gas molecules. The essence of non-thermal plasma techniques is the efficient use of electrical energy through the selective decomposition of the pollutant molecules.

Let us assume for the moment that all the input electrical energy is consumed in the electron-impact dissociation of NO molecules, and that all the dissociated N and O atoms recombine to form N₂ and O₂ only. Of course these assumptions cannot be realized in a real application; however, they will provide an estimate of the minimum power consumption that can be achieved in a reactor that does not use catalysts or additives.

Take for example a 100 hp engine; assume an exhaust gas flow rate of 1 liter/s per hp and an initial NO concentration of 400 ppm. The required NO removal rate is

$$\begin{aligned} &= (400 \times 10^{-6}) \times (2 \times 10^{19} \text{ cm}^{-3}) \times (10^5 \text{ cm}^3/\text{s}) \\ &= 8 \times 10^{20} \text{ NO-molecules/s} \end{aligned}$$

The energy required to dissociate an NO molecule is 6.5 eV. Thus the power required is

$$\begin{aligned} &= (8 \times 10^{20} \text{ NO/s}) \times (6.5 \text{ eV/NO}) = 5.2 \times 10^{21} \text{ eV/s} \\ &= 832 \text{ W} \end{aligned}$$

This corresponds to only 1.1% of the engine power output! This kind of performance makes non-thermal deNO_x favorable over conventional deNO_x techniques, especially since no catalysts or additives would be required. Unfortunately, the energy supplied to the electrons is spent in many processes other than the direct dissociation of NO. More than 99% of the input energy is transferred to the main exhaust gas components, i.e., to N₂, O₂, H₂O and CO₂. The purpose of the plasma is to efficiently produce radicals from these dominant background gas molecules.

The typical average electric fields in atmospheric-pressure air discharges are less than 50 kV/cm. For a wire-cylinder corona discharge reactor, the threshold voltage for corona ignition in dry air is 25 kV for a 1 mm-radius wire and a 6 cm-radius cylinder. The corresponding maximum field is 61 kV/cm. The minimum field for local sustainment of the discharge is 25 kV/cm. To fill a significant volume of the reactor with a plasma, the reactor has to produce microdischarges via ionization waves known as streamers. Under stable operating conditions, the plasma produced in the reactor is space-charge shielded and the self-consistent field within

the plasma is close to the sustainment field of 25 kV/cm. The presence of H₂O and CO₂ increases the sustainment field slightly because of the effect of electron attachment. A fair estimate of the spatial and temporal average of the electric field would be 20 - 40 kV/cm. At lower fields the discharge cannot be sustained. At higher fields the discharge becomes unstable (leads to arcing). The corresponding electron mean energies are around 2 - 5 eV, as shown in Fig. 1. The electric field strength, E, shown in this figure correspond to a gas pressure of 1 atm and a gas temperature of 300°K. The electron mean energy is invariable with respect to the ratio E/N, where N is the total gas density.

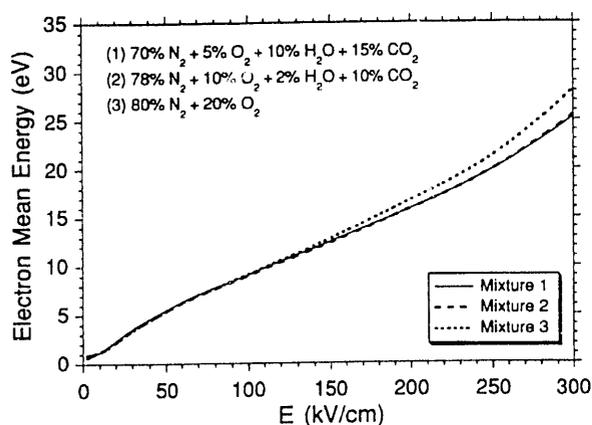


Figure 1. Electron mean energy in a discharge for various mixtures of N₂, O₂, H₂O and CO₂. The electric field strengths correspond to a gas pressure of 1 atm and a gas temperature of 300°K. The electron mean energy is invariable with respect to the ratio E/N, where E is the electric field strength and N is the total gas density.

Fig. 2 shows the energy dissipation in a dry air discharge. For a discharge reactor with an average electric field of 40 kV/cm in the plasma, 30% of the power is spent on the vibrational excitation of N₂, 25% on the dissociation of O₂ and 5% on the dissociation of N₂. At lower fields, the input energy is consumed predominantly by the vibrational excitation of N₂.

Table 1 shows the energy dissipation in the plasma produced by electron-beam irradiation of various gas mixtures. Note that only 6% or less of the input power is dissipated

in vibrational excitation of the molecules. A large portion of the input power is consumed in the dissociation and ionization of N₂.

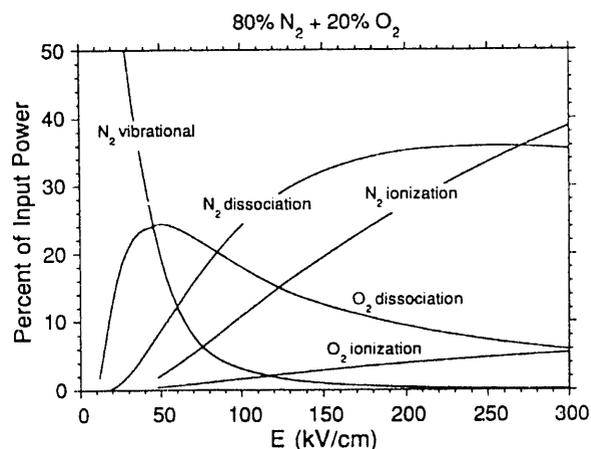


Figure 2. Energy dissipation in a dry air discharge, showing the percent of input power consumed in the electron-impact processes leading to vibrational excitation, dissociation and ionization of N₂ and O₂.

Table 1. Energy dissipation in the plasma produced by electron-beam irradiation of dry air (80% N₂ + 20% O₂).

PROCESS	Energy Dissipation (% of Input Power)
N ₂ Vibrational	5.3
N ₂ (A ³ Σ _u ⁺)	1.1
N ₂ (B ³ Π _g)	1.8
N ₂ Dissociation	24.0
N ₂ Dissociative Ionization	13.9
N ₂ Molecular Ionization	28.3
O ₂ Vibrational	0.6
O ₂ (a ¹ Δ _g)	0.7
O ₂ Dissociation	8.7
O ₂ Dissociative Ionization	2.9
O ₂ Molecular Ionization	2.8
Others	10.3

Some of the excited atoms and molecules react rapidly with the background molecules to produce additional dissociation. For example, the excited oxygen atoms, O(¹D), react rapidly with H₂O to form additional OH radicals. Most of the positive ions react rapidly to

produce additional O_2^+ ions, which then also react with H_2O to form additional OH radicals. Fig. 3 shows the contributions of various rapid processes to the production of OH as a function of the effective field strength in the discharge.

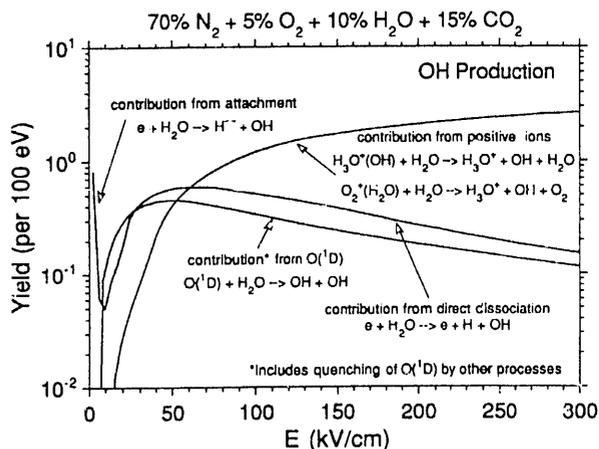


Figure 3. Contributions to the production of OH radicals in an electrical discharge by (i) electron attachment to H_2O , (ii) positive ions clustering with H_2O , (iii) excited oxygen atoms dissociating H_2O , and (iv) direct dissociation of H_2O by electrons, in a gas mixture consisting of 70% N_2 + 5% O_2 + 10% H_2O + 15% CO_2 .

The OH radical production mechanisms in electrical discharge reactors are different than that in electron beam reactors. For discharge reactors, the OH radicals are formed both from direct dissociation of H_2O by electrons and from dissociation of H_2O by excited oxygen atoms. For electron beam reactors, the OH radicals are formed predominantly from positive ions. Fig. 3 also implies that an electron-beam reactor is at least twice as efficient in producing OH radicals compared to a discharge reactor.

Fig. 4 shows the effective primary process yields for N, OH and $O(^3P)$ radicals for two different gas mixtures.

III. Chemistry of Non-Thermal De NO_x

The N atom is the most important reducing species in the absence of additives. The reduction of NO by N proceeds via:

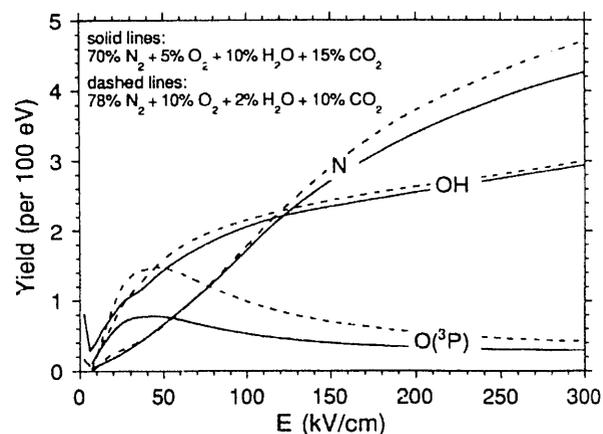
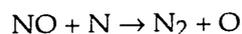
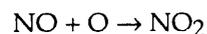
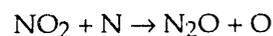


Figure 4. Effective yields of N, OH and $O(^3P)$ produced by an electrical discharge in gas mixtures consisting of (i) 70% N_2 + 5% O_2 + 10% H_2O + 15% CO_2 (solid lines) and (ii) 78% N_2 + 10% O_2 + 2% H_2O + 10% CO_2 (dashed lines).

This reaction is rapid ($k = 3.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and almost independent of gas temperature, as its activation energy is virtually zero. Part of the initial NO will also be oxidized by the O atoms via the oxidation process:



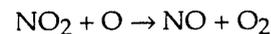
($k = 3.0 \times 10^{-11} (T/300)^{0.3} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$). Part of the NO_2 that was formed will be reduced by N to form N_2O :



($k = 3 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$), and part of the NO_2 will be converted by OH to HNO_3 :



($k \cdot [M] \approx 5.2 \times 10^{-11} (300/T)^{2.9} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$). The O atoms could also reduce NO_2 to NO:



($k = 6.5 \times 10^{-12} \exp(120/T) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$). Under certain conditions, the O atoms serve to trap NO_x in the oxidation-reduction cycle between NO and NO_2 .

Fig. 5 shows the evolution of the concentration of various species during the

discharge processing of 400 ppm NO in a gas mixture of 70% N₂ + 5% O₂ + 10% H₂O + 15% CO₂. The gas temperature is 400°K and the power input is assumed to be 0.05 W/cm³. During the first phase of NO_x removal, out of the 400 ppm of initial NO, about 250 ppm is reduced to N₂, and 150 ppm is oxidized to NO₂. During the second phase of NO_x removal, most of the NO₂ is converted to HNO₃, and some is reduced to N₂O (about 30 ppm).

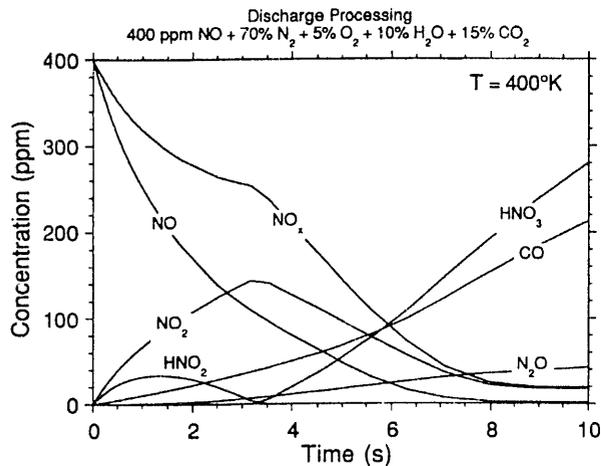


Figure 5. Evolution of the concentration of various species during the discharge processing of 400 ppm NO in a gas mixture of 70% N₂ + 5% O₂ + 10% H₂O + 15% CO₂. The gas pressure is 1 atm and the temperature is 400°K. The power input is assumed to be 0.05 W/cm³.

Fig. 6 shows the evolution of the concentration of various species during the electron beam processing of 400 ppm NO in a gas mixture of 70% N₂ + 5% O₂ + 10% H₂O + 15% CO₂. The gas temperature is 400°K and the power input is assumed to be 0.05 W/cm³. Note that the removal rate of NO_x is four times faster compared to discharge processing. The maximum amount of NO₂ formed is less than 80 ppm. Around 75% of the initial NO is reduced to N₂.

IV. Power Consumption

For the particular mixture used in Fig. 5, the result shows an energy consumption of around 310 eV per removed NO_x molecule. Let us go back to the example of a 100 hp engine with an exhaust gas flow rate of 1 liter/s per hp. The power required by an electrical

discharge reactor to remove 400 ppm of NO is thus

$$= (8 \times 10^{20} \text{ NO}_x / \text{s}) \times (310 \text{ eV} / \text{NO}_x) = 2.5 \times 10^{23} \text{ eV} / \text{s} \\ = 40 \text{ kW.}$$

This corresponds to 54% of the engine power output!

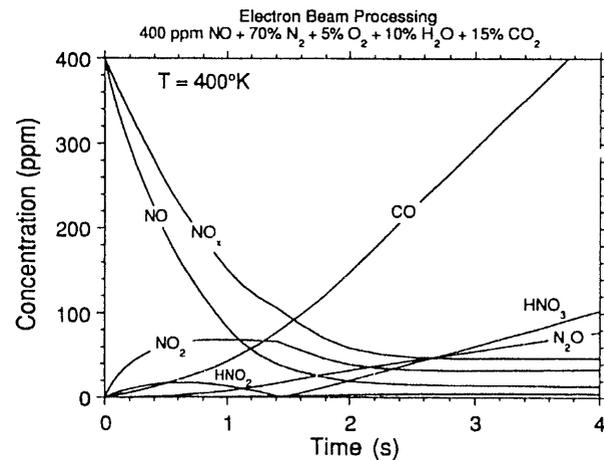


Figure 6. Evolution of the concentration of various species during the electron beam processing of 400 ppm NO in a gas mixture of 70% N₂ + 5% O₂ + 10% H₂O + 15% CO₂. The gas pressure is 1 atm and the temperature is 400°K. The power input is assumed to be 0.05 W/cm³.

For the same mixture, Fig. 6 shows that the energy consumption of electron beam processing is 78 eV per NO_x molecule. The power required by an electron beam reactor to remove 400 ppm of NO is thus

$$= 10 \text{ kW.}$$

This corresponds to 13% of the engine power output!

V. Conclusions

Can non-thermal deNO_x operate efficiently without catalysts or additives? The power consumption requirement of a discharge reactor is too high. The power consumption of an electron beam reactor is about four times less than that of a discharge reactor, but would still require greater than 10% of the engine output power to achieve NO_x removal of

400 ppm. Unless the initial NO_x concentration is already low (perhaps 200 ppm or less), the operating cost of non-thermal deNO_x without catalysts or additives may not be acceptable. The other issue is the cost of the reactor. How much is a 10 kW electron beam system or pulsed power generator compared to the price of a 100 hp engine?

The formation of secondary pollutants from the by-products of the plasma reactions also needs to be addressed. Discharge reactors for deNO_x will tend to produce a lot of nitric acid and some nitrous oxide. Electron beam reactors can be used to maximize NO reduction to N_2 , but will also produce some nitric acid and nitrous oxide and a lot of carbon monoxide. For stationary engines, scrubbing of the nitric acid may not present a problem. For mobile engines, scrubbing of unwanted by-products may not be convenient.

The use of chemical additives (such as ammonia or hydrocarbons) and surface catalysts in combination with a non-thermal plasma is not taken into account in the present analysis. The use of hybrid methods have to be considered carefully in order to reduce the operating and capital costs of non-thermal deNO_x . Quantitative experimental and theoretical analyses of the physics and chemistry of the plasma processing are essential to determine the power consumption, NO_x removal mechanisms, and hazardous by-products.

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