DESTRUCTION OF VOCs IN A NON-THERMAL PLASMA REACTOR

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ABSTRACT

The work presented herein investigates the effectiveness and efficiency of a novel, non-thermal large-volume ambient pressure diffuse plasma for destruction of environmental air contaminants. The plasma characteristics, plasma chemistry, and contaminant destruction efficiency for selected contaminants including benzene, toluene, n-heptane, iso-octane, and methanol were investigated. Plasma spectroscopic studies employing gas mixtures of He with N_2 of 1-20% yielded electron temperatures in the range 60,000 – 66,000 K (corresponding to average electron energies of 5.0 – 5.5 eV). The observed contaminant destruction efficiency exceeded 99% at a reactor power density of approximately 4 watts/cc at residence times less than 0.1 sec.

ΔΙΑΣΠΑΣΗ ΠΤΗΤΙΚΩΝ ΣΕ ΑΝΤΙΔΡΑΣΤΗΡΕΣ ΜΗ-ΘΕΡΜΙΚΟΥ ΠΛΑΣΜΑΤΟΣ

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ΠΕΡΙΛΗΨΗ

Στην παρούσα εργασία ερευνήθηκαν η αποτελεσματικότητα και απόδοση μιας νέας μεδόθου καταστροφής αερίων ρύπων βασισμένη στη τεχνολογία διάχυτων, μεγάλου όγκου, μη-θερμικών πλασμάτων σε ατμοσφαιρική πίεση. Μελετήθηκαν τα χαρακτηριστικά, οι χημικές ιδιοτητές και η απόδοση καταστροφής αερίων ρύπων όπως βενζόλιο, τολουόλιο, επτάνιο, οκτάνιο και μεθανόλη. Φασματογραφικές μελέτες του πλάσματος σε αέρια μίγματα He και N_2 έδειξαν οτι η θερμακρασία των ηλεκτρονίων κυμαίνεται μεταξύ 60.000 – 66.000 K (αντιστοιχούσα σε μέση τιμή ενέργειας των ηλεκτρονίων μεταξύ 5,0 και 5,5 eV). Η απόδοση καταστροφής των ρύπων υπερέβει το 99%, με παρατηρούμενη πυκνότητα ισχύος στον αντιδραστήρα πλάσματος περίπου 4 watts/cc σε χρόνο παραμονής <0,1 sec.

1. INTRODUCTION

Air decontamination and revitalization in the confined areas of spacecrafts and space stations present special challenges that are not adequately addressed by conventional air treatment technologies. Air contaminants are traditionally removed from the crew cabin atmosphere and the living quarters of spaceships by adhesion to an adsorptive medium or high temperature catalytic oxidation. Space application of these technologies are inherently difficult due to technical and economic reasons. Adsorption requires regeneration or replacement of the exhausted medium, both difficult to accomplish in space, and catalytic oxidation is associated with high energy expenditures. A low energy, low cost technology that does not rely on expendable materials for continuous operation is highly desirable for maintaining a contaminant-free breathable atmosphere, especially during long duration space flights where material re-supply is not feasible or cost effective. The work presented in this paper focuses on the development of a novel technique which has the potential of replacing existing treatment methods for the control of air contaminants in the closed environment of a spacecraft. This method is based on the utilization of large volume non-thermal diffused plasmas, generated at ambient pressures, for contaminant conversion to innocuous products [1].

Diffused non-thermal plasmas are regions of ionized gases produced by electrical discharges across two electrodes to which high voltages are applied. The electrical energy in these systems generates high energy electrons which are capable of producing, via electron impact, radicals that can convert organic contaminants to harmless products. The method of plasma generation and the plasma characteristics are extremely important for successful implementation of this technology to environmental applications. Diffused plasmas are ideal for processing gaseous streams since they occupy larger reactor volumes compared to corona discharges which are filamentary in nature and very thus inefficient for gas treatment.

The flow regime and gas distribution within the reaction volume are important parameters that influence the contaminant destruction efficiency. Three different reactor configurations were constructed and tested of varying reaction volume and geometry. These are: a cylindrical parallel plate reactor with circular electrodes, an adjustable gap cylindrical reactor with rectangular electrodes, and an annular reactor with cylindrical electrodes. Gas flow is perpendicular to the capillary holes, which generate the plasma discharge, in all three configurations. The first two configurations were used primarily for plasma characterization and testing of dielectric materials. A set of rotational, vibrational, and electron temperatures (T_R, T_V, T_E) can serve as a window into the microscopic processes that determine the properties of the plasma. Plasma emission spectroscopic measurements were used to determine the rotational, vibrational, and electronic temperatures of the plasma components from a detailed analysis of the various spectral features emitted by a discharge plasma in a steady state. The characteristic emission spectra of various gas mixtures were obtained and their average electron temperatures were calculated. The destruction efficiency of various volatile organic compounds (VOCs) obtained in plasma reactors exceeded 99% at a reactor power density that ranged from 3 to 4 watts/cc.

2. MATERIALS AND METHODS

The main components of the experimental apparatus used in our experiments are the power supply and the plasma reactor. Various analytical and diagnostic equipment are also employed for determination of the electrical and plasma characteristics of the discharge, and quantification of contaminant removal. The destruction of five VOCs namely, benzene, toluene, heptane, iso-octane

and methanol was tested using the annular plasma reactor configuration shown in Figure 1. For each compound various runs were performed at different air flow rates, contaminant concentration and power input. The contaminant mass destroyed was measured and the destruction efficiency was estimated for each steady state. Only the contaminant mass was quantified during these experiments. Formation of organic byproducts and plasma generated inorganic compounds were not monitored.

Third generation reactor

1. Electrode (*Aluminum bar*)
2. Electrode (*Aluminum screen*)
3. Dielectric material (*Cotronics 902 Alumina silicate*)
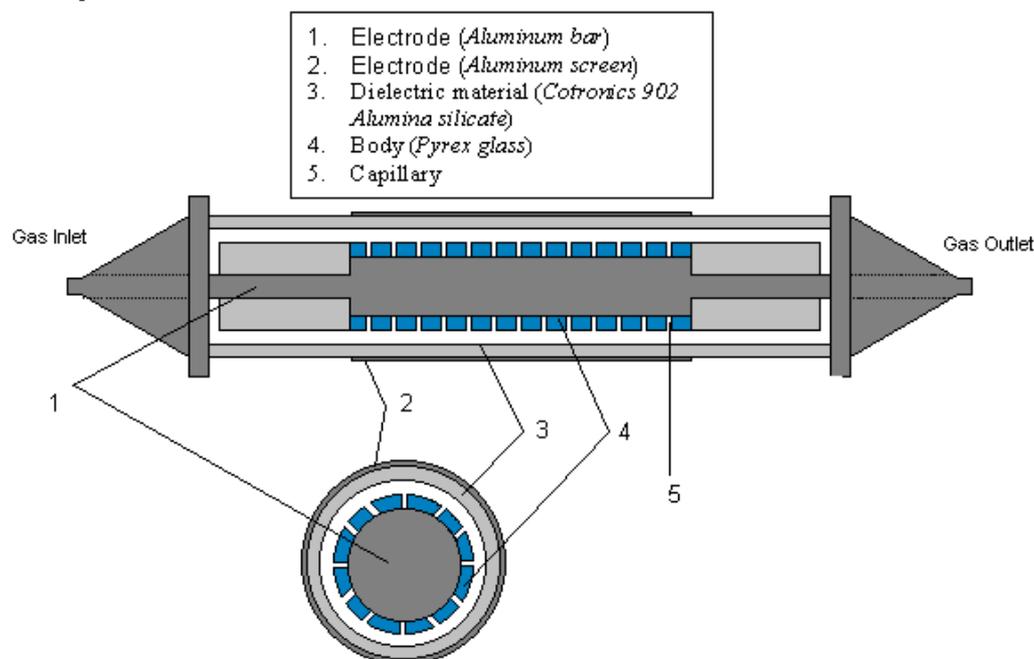4. Body (*Pyrex glass*)
5. Capillary

Figure 1: Annular plasma reactor with cylindrical electrodes

The experimental set-up for the emission spectroscopic studies carried out comprised of a medium-resolution 0.25 m double-grating scanning monochromator in conjunction with a thermoelectrically cooled photomultiplier (Hamamatsu R955A). The monochromator can be operated with three sets of fixed slits corresponding to an optical resolution (full width at half maximum, FWHM) of 2 nm, 0.5 nm, and 0.2 nm, respectively. The useful spectral range of the monochromator-photomultipler detection system spans from 200 nm to 800 nm. The wavelength-dependent sensitivity of the detection system was determined previously [2]. The detection system has its maximum sensitivity around 400 nm and exhibits a fairly flat response in the 330-450 nm region. Emission spectra were recorded by scanning the wavelength of the monochromator with the help a computer-controlled stepper motor. The output of the photomultiplier after proper amplification and discrimination was fed into the same computer for data storage and analysis.

The analytical methods used to analyze the target compounds involved both on-line UV/visible and IR absorbance spectroscopy and GC/MS analysis using carbon traps. The effluent gas from the plasma reactor flows through a quartz UV/visible cell, where an HP8452A diode array spectrophotometer is used to detect aromatic organics as well as certain inorganic species with strong electronic absorption peaks, such as nitrogen dioxide and ozone. The effluent gas is then carried through a Foxboro MIRAN 1A-fixed wavelength (3.4 micron) IR absorption spectrophotometer, equipped with a 10.0 cm pathlength cell. The IR spectrophotometer is used to

detect aliphatic organic target molecules and by-products with a strong vibrational band at 3.4 microns. This absorption peak is characteristic of any compound with aliphatic C-H bonds. Both instruments are calibrated on-line for a particular target molecule, by passing a series of known concentrations of the gas through the system and measuring the absorbance of the gas in the absence of a plasma discharge. We have shown that the discharge itself doesn't provide any appreciable interference in either of these spectral windows. Calibration runs as well as, plasma experiments are routinely verified using time averaged carbon trap GC/MS analysis.

3. RESULTS AND DISCUSSION

3.1 Emission Spectroscopy

A typical emission spectrum from 200-450 nm (corrected for the wavelength-dependent sensitivity of the detection system) nm is shown in Figure 2. This spectrum was obtained from a high-pressure discharge plasma in He with a 1% N_2 admixture. The characteristic features of the spectrum in the far ultraviolet are the NO γ-bands near 250 nm. The excited NO results from the recombination of N with O atoms which are produced by sputtering from the reactor surfaces and the dielectric covers. The most prominent emission are due to the N_2 and N_2^+ in the 300- 450 nm region. The emission spectrum above 500 nm (not shown) shows some of the characteristic atomic He lines (which are much narrower than the molecular emission bands).
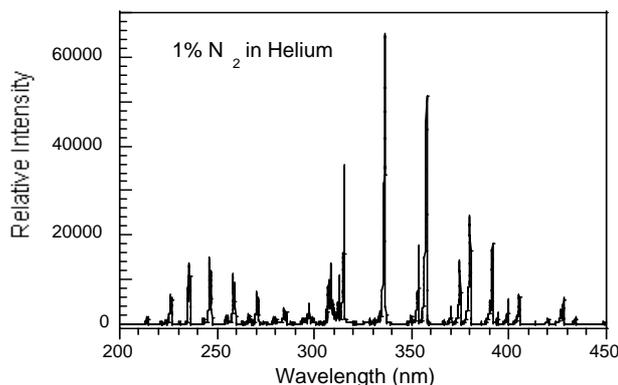

Figure 2: Emission spectrum from a high-pressure discharge plasma in He with a 1% N_2 admixture in the spectral region from 200 – 450 nm.

The rotational temperature T_R of a radiating molecular species can be determined from the analysis of a single vibrational band. This can be done, for instance, by recording the fully rotationally resolved structure of the band (i.e. by recording the emission intensity of individual rotational lines) and by fitting the intensities of the rotational lines to a "rotational Boltzmann factor" from which one can obtain T_R. As an alternative, one can record a rotationally unresolved vibrational band with high statistical accuracy and then obtain an estimate for the rotational temperature from a comparison of the envelope of the measured vibrational band with a calculated band envelope. The calculated band envelope has the rotational temperature as the only free parameter. We used this second approach in determining an estimate for the rotational temperatures of the N_2 molecules and the N_2^+ ions. Figure 3 shows the comparison between a measured and a calculated (0,3) vibrational band of the N_2 second positive system centered at 406 nm. The measured spectrum is indicated by the individual data points. The calculated spectra were obtained by

convoluting a calculated intensity distribution of all rotational lines corresponding to a given rotational temperature with a monochromator slit function. Two calculated curves are shown in Figure 3, one corresponding to a rotational temperature T_R of 330 K (best fit) and the other one corresponding to T_R = 450 K. It is evident that the calculated curve corresponding to T_R = 330 K fits the measured spectrum perfectly, whereas the curve corresponding to T_R = 450 K clearly overestimates the short wavelength part of the band. In almost all cases, the rotational temperatures were found to be slightly above room temperature (in the 320-350 K range) which is not unexpected. The precision with which we can determine the rotational temperature is about 30K or 10%.
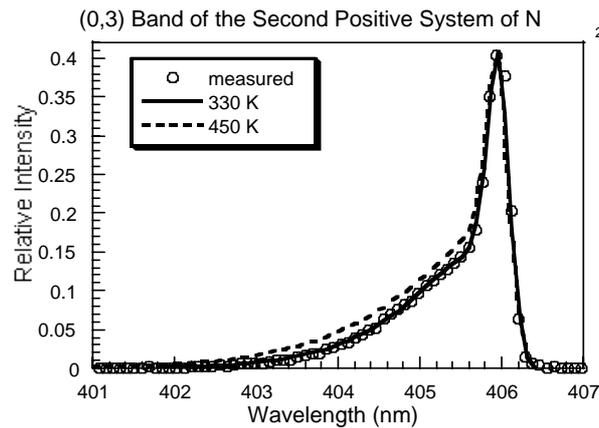

Figure 3: Comparison of measured and calculated rotational envelope of the (0,3) band of the N second positive system.

The determination of the vibrational temperature T_V requires the analysis of several vibrational bands that belong to a given electronic transition and that differ in the vibrational quantum numbers v'(upper vibrational level) and v" (lower vibrational level). If the analysis involves several Δv=constant sequences, the comparison of the various T_V values from the different Δv=constant sequences provides a consistency check. We note that typical vibrational temperatures obtained from the N_2 2nd positive and the N_2^+ 1st negative system were in the range from 2,450 – 2,700 K.

The determination of the electron temperature requires the analysis of emission bands from at least 2 different electronic states. We obtained estimated electron temperatures for various discharge plasmas in atmospheric-pressure He with 1-20% N_2 admixtures in the range from 60,000 to 66,000 K corresponding to average electron energies of 5 – 5.5 eV. Moreover, the electron temperature was found to decrease systematically as the N_2 admixture was increased. This is to be expected, since the presence of N_2 introduces a variety of additional energy loss channels in the low-energy regime (e.g. vibrational excitation) which tend to shift the peak in the electron energy distribution to lower average values.

In summary, the plasma spectroscopic studies of the discharge plasmas used in our experiments employing gas mixtures of near-atmospheric pressure He with N_2 admixtures of 1-20% yielded rotational temperatures around 350 K, vibrational temperatures around 2,600 K and electron temperatures in the range 60,000 – 66,000 K (corresponding to average electron energies of 5.0 – 5.5 eV). The rotational (T_R), vibrational (T_V), and electron (T_E) temperatures demonstrate the highly non-thermal character of the discharge plasmas under all operating conditions ($T_E \gg T_V$, T_R).

The vibrational and rotational temperatures of our discharge plasmas under typical operating conditions of approximately 350 K (T_R) and 2,600 K (T_V) are significantly lower than the comparable temperatures for other high-pressure plasmas (e.g. microhollow cathode discharge (MHCD) plasmas, filamentary dielectric barrier discharge (F-DBD) plasmas). By comparison, atmospheric-pressure MHCD plasmas have rotational temperatures of up to 2,000 K and vibrational temperatures of up to 4,000 K, while the average electron energies of the MHCD plasma with values in the 5-6 eV range (K.H. Schoenbach, private communication (1999)) are comparable to our values. This indicates that in our discharge plasma much less input energy is converted into gas heating (lower T_R and T_V values). Equivalently, the overall input energy requirement to achieve a comparable electron temperature, which can serve as a measure for the ability of the plasma to initiate plasma chemical reactions [3] is considerably lower in our case. F-DBD plasmas at or near atmospheric pressure typically have rotational and vibrational temperatures comparable to those of MHCD plasmas, but their average electron energy rarely exceed 3 eV which renders F-DBD reactors much less efficient than our atmospheric-pressure discharge plasmas.

The presence of the prominent NO γ-band emissions around 250 nm indicates the efficient formation of NO (and NO_x) in our discharge plasma, which are highly undesirable by-products. The formation of NO (NO_x) results from the recombination of atomic nitrogen and oxygen produced by the dissociation of N_2 (which is a desired feed gas constituent) and O_2 (which is an unavoidable, albeit unwanted contaminant). The only way to minimize the formation of NO/NO_x short of eliminating all O_2 from the plasma reactor, a highly impractical, if not unrealistic proposition, is via a modification of the operating conditions of our discharge plasma in such a way that the average electron energy is drastically reduced. This is due to the fact that the minimum energy required to dissociate O_2 is much lower than the minimum energy to dissociate N_2 (5.08 eV vs. 9.75 eV)[4]. With average electron energies in the 5.0-5.5 eV range under present operating conditions, the electron energy distribution function (eedf) of the plasma electrons has a significant fraction of energetic electrons with energies up to an above 15 eV. These electrons can efficiently dissociate N_2 and thus stimulate the NO/NO_x formation. If we reduce the average electron energy to values below 2 eV, the high-energy tail can be significantly reduced and the rate of N_2 dissociation will decline sharply. A shift in the average electron energy can be accomplished by reducing the input power into the discharge plasma. In addition, the high-energy tail of the eedf can be suppressed further by adding a molecular gas to the feed gas mixture which is know to have large cross sections for e.g. vibrational excitation and/or dissociative attachment. This introduces efficient energy-loss channels in the low-energy regime for the plasma electrons and thus shifts the eedf to lower values [3]. The results of the plasma spectroscopic measurements provide guidance to the establishment of optimum operating conditions of our atmospheric-pressure discharge plasma for the various applications that are addressed as part of this project. As discussed before, up to now all plasma spectroscopic measurements have been "integrated" measurements, in which the light was collected from the entire plasma volume. We are currently designing a single-capillary, quasi one-dimensional plasma reactor with a light collection system that will enable the selective analysis of light coming from small spatial regions of the plasmas. These spatially resolved plasma spectroscopic studies will provide insight into the variation of the rotational, vibrational, and electron temperatures along the direction of propagation of the plasma emerging from the capillary. Should there be significant spatial variations in T_R, T_V, and T_E, the results of the spatially-resolved plasma spectroscopy will help us identify regions of higher plasma chemical reactivity and regions of lower plasma chemical reactivity. By modifying the plasma operating conditions accordingly we will we able to tailor the plasma chemical reactivity in such a way as to

enhance the desired remediation of a given pollutant in certain regions, while at the same time minimizing the formation of unwanted by-products such as NO and NO_x.

3.2 VOC Destruction

Preliminary experiments for the destruction of specific volatile organic toxins were conducted in the annular reactor configuration. The experimental results reported here were quantified using the on-line UV/visible spectroscopy (aromatic compounds) and fixed wavelength IR spectroscopy (aliphatic compounds). Time averaged carbon trap/GCMS analysis was conducted for each system to verify mass balance and detect the formation of byproducts.

Figures 4, and 5 show the destruction efficiency vs. discharge power density and energy cost per molecule vs. discharge power density respectively, for benzene. Figure 4 shows that the destruction efficiency curves are a function of the product of the contaminant concentration and the carrier gas flow rate through the system. The product can be easily converted into the flow rate of toxic gas treated in cc/min. at STP. As expected the efficiency curves drop as this flow rate increases, mostly because the residence time for treatment is shorter. The second trend is that all of the curves seem to converge at efficiency above 90 %, this is because above this threshold value increased power density alone can no longer be used to treat more contaminant. The system has reached a saturation point. Above this saturation point the excess power input is not efficiently directed to benzene destruction. For benzene the threshold efficiency occurs at 90 %, the energy cost per molecule below that point remains constant at ~ 500 eV per molecule. Our results show that this saturation point comes at power densities of five to six watts/cc for these systems.

Figure 5 shows the energy cost as a function of power density, for a series of different flow rates of benzene vapor at STP. The relationship between energy cost and power density is linear for a particular flow rate (residence time). This is expected, because the power increase corresponds directly to the amount of energy expended per molecule. An important point regarding this graph is that the highest energy cost lines correspond to the lowest rate of benzene transfer (highest efficiency). This shows that treatment becomes more difficult and more expensive at low contaminant concentrations.
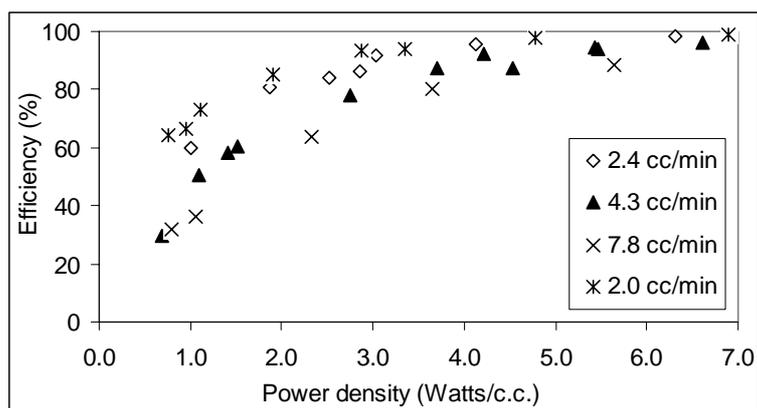

Figure 4: Efficiency vs. power density for the treatment of Benzene vapor in air, at various benzene flow rates.
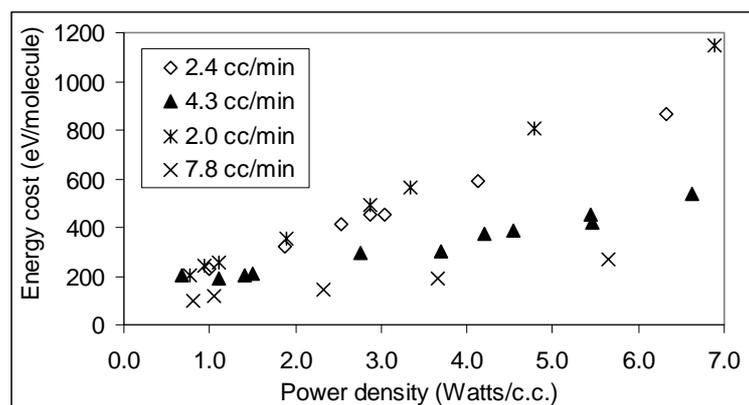
Figure 5: Energy cost per molecule vs. power density for the treatment of benzene in air, at various benzene flow rates.

The results obtained from destruction experiments performed with the model compounds are summarized in Table 1. It can be concluded from these results that the efficiency threshold and power density required for saturation are independent of the compound being treated. These parameters are dependent on the design of the reactor, limitation of the power supply and selected conditions of flow rate and concentration. In each case of each target molecule over 99 % efficiency has been achieved simply by adjusting these parameters. You must, however work at conditions below the threshold efficiency to determine the energy cost effectively.

Table1: Results of plasma treatment for selected VOCs.

Target compound	Energy Cost (eV / molecule)	Efficiency Threshold (%)	Power Density Required for Saturation. (watts/cc)
Benzene	500	90	3
Toluene	900	75	4
n-Heptane	1700	85	3
iso-Octane	1600	75	3
Methanol	150	90	3.5

Our results for energy cost per molecule show that a typical alcohol like methanol is the most reactive toward plasma oxidation. The aromatic compounds, benzene and toluene have intermediate reactivity, and the saturated hydrocarbons, n-heptane and iso-octane are the least reactive. There are probably only small differences between the reactivity of compounds within each class, and these differences are probably very hard to detect in harsh oxidative conditions associated with plasma treatment.

4. CONCLUSIONS

The results obtained from the spectrometric measurements and the destruction of the model compounds lead to the following conclusions:

➢ The discharge plasmas used in our experiments employing gas mixtures of near-atmospheric pressure He with N_2 admixtures of 1-20% yielded rotational temperatures around 350 K,

vibrational temperatures around 2,600 K and electron temperatures in the range 60,000 – 66,000 K (corresponding to average electron energies of 5.0 – 5.5 eV). The rotational (T_R), vibrational (T_V), and electron (T_E) temperatures demonstrate the highly non-thermal character of the discharge plasmas under all operating conditions ($T_E \gg T_V, T_R$).

➢ The non-thermal plasma reactor has successfully decomposed individual organic compounds in pure air at very high concentrations and satisfactory power expenditures.

AKNOWLEDGMENTS

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