A Mechanistic Study of Pulsed Corona Processing of Hydrocarbons in Air at Ambient Temperature and Pressure

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ABSTRACT—A large wire/cylinder bench-top corona reactor has been developed for mechanistic studies of the decomposition of volatile organic compounds (VOCs) in air at room temperature and pressure induced by different types of corona. A model hydrocarbon, *n*-hexane, was used to chemically characterize the process induced by positive pulsed corona, by monitoring efficiency, products and reactive intermediates in dry as well as humid air. Chemical diagnostics included qualitative and quantitative GC/FID, GC/MS and on-line FT/IR analyses which provided coherent data and mass balance for all volatile products and intermediates: CO_2, CO, minor quantities of organic byproducts (propane, butane and simple aldehydes, ketones and alcohols) but also a few more complex oxygen and nitrogen-containing compounds. A considerable amount of carbon is unaccounted for, thus indicating that non-volatile products, not detected by GC analyses, are also formed. Interestingly, the extent of undetected carbon depends on the extent of VOC conversion. Thus, CO_2 production increases with energy density also after complete *n*-hexane consumption. Humidity has a beneficial effect on hydrocarbon processing with positive pulsed corona: an increment in efficiency of 30% is gained in going from dry air to humid air with 40%RH. The most important neutral reactive species, $O(^3P)$ for dry air and $^\bullet OH$ for humid air, were also investigated using chemical probes (ozone formation and CO oxidation, respectively). The results are consistent with the proposal that the decomposition of hydrocarbons induced by +pulsed corona is initiated by radical reactions. A preliminary comparison with results obtained with +DC corona is also presented.

Keywords—**VOC removal, corona discharge, non-thermal plasma, pulsed corona, pollution control, hydrocarbon removal**

I. INTRODUCTION

Non-thermal plasma catalysis is being actively pursued for the abatement of volatile organic compounds (VOCs) [1-5]. In non-thermal plasmas (NTPs), which are conveniently produced by electric corona discharges in air at atmospheric pressure, high energy electrons induce ionization, excitation and dissociation of the bulk gas molecules (N_2 and O_2). The resulting reactive species, ionic and neutral, as well as thermalized electrons, can attack VOC molecules and initiate a chain of reactions leading eventually to their oxidation. The goal of exhaustive oxidation to CO_2 is however seldom reached [1]. Undesirable VOC-derived byproducts include CO, volatile and non-volatile organic compounds, and nanosized particles [6,7]. Additional components of air NTP processing which need to be controlled are NO_x, ozone and hydrogen peroxide. More recent developments concern various combinations of NTP with heterogeneous catalysts to achieve better energy efficiencies and product selectivities [1]. However, it is usually impossible to compare the results from different laboratories due to the widely different experimental set-ups used and, especially, to the non-linear nature of the corona phenomena. Moreover, despite the numerous well-established applications of NTP and the important recent technological advancements in the field of combined catalysis, fundamental knowledge of the underlying chemical processes is still insufficient: product analysis and mass balance data are not often available, particularly as far as the aerosol and non-volatile fractions are concerned, and the reactions and mechanisms involved in VOCs decay are far from being well understood and characterized. It is generally accepted that NTP-induced VOC oxidation proceeds via VOC-derived organic radicals, $R^\bullet$, which are trapped by molecular oxygen and further decomposed in a similar manner to that accounting for their tropospheric oxidation [8]. As for the origin of such radicals, i.e. the nature of the initiation steps of NTP-induced VOC decay, the general consensus favors reaction with neutral and radical reactive species, notably $O(^3P)$ and $^\bullet OH$. However, a few literature reports have suggested that in some cases ionic initiation steps might prevail [9-14].

With the intent to gain insight into the chemistry of corona induced VOC abatement, especially with regard to the crucial initiation steps, we have recently undertaken a systematic study of the processing of model hydrocarbons with different types of corona, but otherwise under identical experimental conditions. To this end we have built a large corona reactor which can be energized with DC or with pulsed voltage of either polarity, and have developed standard protocols for chemical and electrical diagnostics. With this experimental apparatus we intend to explore the chemistry of some model VOC under different energization conditions and to interpret it in the light of known chemical and physical features pertaining to the ensuing specific corona regimes. Thus, although the general features of the overall decomposition process might be very similar, different initiation steps may well prevail under different corona regimes. A knowledge of what these initiation steps are will not only contribute to

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our fundamental understanding of NTP plasma chemistry but will also help optimizing the process and mastering it towards the desired end products. Originally we turned our attention to pulsed corona since current research and development are focussed on such type of NTP sources [1,6,7,15]. This paper reports and discusses the results of a mechanistic study on pulsed corona processing of a model hydrocarbon VOC, *n*-hexane. A preliminary comparison with +DC processing is also presented.

II. EXPERIMENTAL SECTION

The reactor is a stainless steel cylinder (38.5 mm i.d. x 600 mm) with a coaxial stainless steel emitting electrode (1 mm i.d.). The stainless steel cylinder, which has a window (1 cm x 10 cm) for the observation of the corona luminescence, is contained into a Pyrex glass cylinder of slightly larger diameter held in place by two teflon caps connected by steel guys and viton o-rings.

For pulsed corona the reactor is energized by a pulsed high voltage power with DC bias (PHVDC), based on a spark gap switch with air blowing, with the following specifications: DC bias 0 - 14kV (input voltage 0 - 100V), peak voltage 25 - 35kV with DC bias (input voltage 120 - 220V) peak current 100A, maximum frequency 300Hz, rise-time of pulses less than 50ns.

For DC corona experiments the reactor is energized with a DC (- 30 kV to + 30 kV) power supply.

Measurements of power input are made using a digital oscilloscope (Tektronix type 410A, bandwidth 200 MHz, two channels), a high voltage probe by Tektronix (ratio 1000:1, bandwidth 75 MHz, peak voltage 40 kV), and two homemade current probes with 10 resistors in parallel housed in an electromagnetic shield (1.1 Ω for PHVDC current measurement and 52 for DC only current measurement).

For pulsed corona experiments, considering the short duration of the voltage pulses, the mean power input produced by PHVDC is the sum of the mean DC power of the DC bias (P_{DC}), calculated as the product of the current measured during the interval between two pulses multiplied by the DC bias voltage, plus the mean pulsed power (P_{pulsed}), which is the product of pulse frequency times the energy per pulse. The energy per pulse is obtained by integrating the product of the current waveform times the voltage waveform which are monitored during the experiment.

The DC corona experiments, the mean power input is the product of the mean current times DC high voltage when only DC power supply is applied to the reactor.

Energy density (E, $J\cdot L^{-1}$), i.e. the energy delivered to the gas per volume unit, is defined as the mean power input divided by the gas flow rate.

The reactor is inserted in a continuous gas flow line made of teflon tubing (4 mm i.d.) and equipped with flowmeters, a loop for air humidification and a probe to measure the humidity. Cylinders of synthetic air and of synthetic air containing the compound to be treated (*n*-hexane, CO or CO_2) in 500 ppm concentration (Airliquide) are connected to the gas line. Gas flow-rates are in the range 150 - 800 $mL\cdot min^{-1}$. The gas exiting the reactor goes through a small glass reservoir equipped with a sampling port from which samples are withdrawn with a gas tight syringe for off-line chemical analysis by GC/MS (HP 5973) and GC/FID (Varian 3600). On-line IR analysis is performed with an FTIR Nicolet 5700 spectrophotometer using a 10 cm long gas cell with NaCl windows. The IR signals were calibrated by means of standards for CO_2 and CO (Airliquide) and by means of iodometric titration for ozone.

The carbon mass balance is calculated as the ratio between the recovered carbon (the sum of contributions due to residual *n*-hexane, abbreviated here as VOC, CO, CO_2 and all volatile organic byproducts) and the carbon initially present in the VOC. The percentage of undetected carbon ($\%C_{undet}$) is, therefore, expressed by equation (1)

$$\%C_{undet} = \left(1 - \frac{[VOC]\cdot n_{VOC} + [CO] + [CO_2] + \Sigma[byproduct]\cdot n_{byproduct}}{[VOC]_0 \cdot n_{VOC}}\right)\cdot 100 \tag{1}$$

where n_{VOC} and $n_{byproduct}$ are the number of carbon atoms present in *n*-hexane and in each one of the various byproducts, respectively.

The process efficiency is evaluated by interpolating the fraction of residual VOC as a function of the energy density using the exponential equation (2)

$$[VOC] = [VOC]_0 \cdot e^{-k_E \cdot E} \tag{2}$$

where $[VOC]_0$ is the initial VOC concentration, [VOC] is its concentration after applying the energy density E and k_E ($kJ^{-1}\cdot L$) is the characteristic energy constant for the given VOC under the specific experimental conditions used [1].

III. RESULTS AND DISCUSSION

Preliminary experiments with positive pulsed corona were devoted to investigate the effects on process efficiency due to the different electric variables: the DC bias voltage (V_{DC}), the voltage of the pulses (V_{pulsed}) and the frequency of the pulses (f). Numerous experiments showed that the higher efficiencies are obtained when the contribution by the DC bias power (P_{DC}) is negligible with respect to that by the pulsed power (P_{pulsed}). Thus, in order to maximize the P_{pulsed}/P_{DC} ratio, V_{DC} was usually set at a value lower than the corona onset and was further reduced for frequencies higher than 75 Hz. Another system variable which was used to change the energy input is the gas residence time within the reactor, i.e. the gas flow-rate.

Fig. 1 collects in a single plot of *n*-hexane (500 ppm in dry air) conversion *vs* energy density the results of a number of experiments in which the energy density was changed by adjusting any of the variables listed above. A reasonably good fit of the data to the exponential decay of equation 2 is evident, from which an energy constant of 3.47 $kJ^{-1}·L$ is derived for +pulsed corona processing of *n*-hexane in dry air. Expectedly, the corresponding +DC corona induced process is significantly less efficient, k_E being in this case 0.17 $kJ^{-1}·L$.

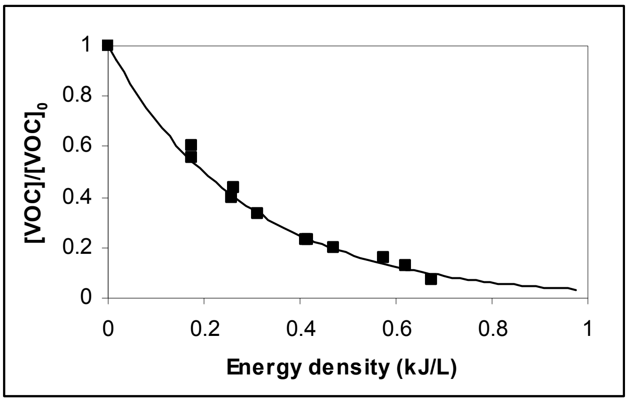

Fig. 1. Removal of *n*-hexane (500ppm in dry air) by +pulsed corona at room temperature and pressure.

A full characterization and quantification of the products formed in these processes is, in our view, even more important than efficiency evaluations, considering that these are air-cleaning treatments. Exhaustive hydrocarbon oxidation would lead to H_2O and CO_2. However, as mentioned in the introduction, numerous byproducts are usually formed in NTP processing of VOCs in air. We used FT/IR analysis for monitoring CO_2, CO, O_3 and NO_x and quantitative GC/FID and GC/MS analysis for volatile organic byproducts.

Fig. 2 shows typical FT/IR spectra recorded before and after processing of *n*-hexane in dry air with +pulsed corona. Besides CO_2, the characteristic bands of CO, N_2O and O_3 are also seen. Moreover, a band due to C-H stretching is also evident, which is due mainly to residual *n*-hexane (the conversion was 84% in this particular experiment) but also possibly to minor amounts of VOC byproducts as detailed later. Plots of CO_2 and CO production as a function of *n*-hexane conversion in dry and humid air (40% RH) show that the concentration of both increases as the fraction of consumed *n*-hexane is increased (Fig. 3). Interestingly, the data also show further increases of both CO_2 and CO concentrations when energy densities are used which are in excess to that required for the total consumption of *n*-hexane (points marked with arrows in the plots).

Besides CO_2 and CO, numerous volatile organic compounds form, although in very small amounts, from +pulsed corona processing of *n*-hexane. A list is shown in Table 1. They include small organic molecules like the hydrocarbons propane, butane, the alcohols methanol and ethanol and several aldehydes and ketones of various chain lenghts ranging from 2 to 11. In addition, more complex organic compounds of lower volatility, most of which contain nitrogen have also been detected (entries 10-24 in Table 1). The concentration of byproducts 1-9 was monitored as a function of energy density. As an example, a plot of byproduct concentration *vs* *n*-hexane conversion is shown in Fig. 4 for two of the most abundant byproducts, acetaldehyde and 3-hexanone. It should be noted that when the conversion of *n*-hexane is complete, the byproducts concentration also drops to zero. Similar trends were found for the other volatile organic byproducts.

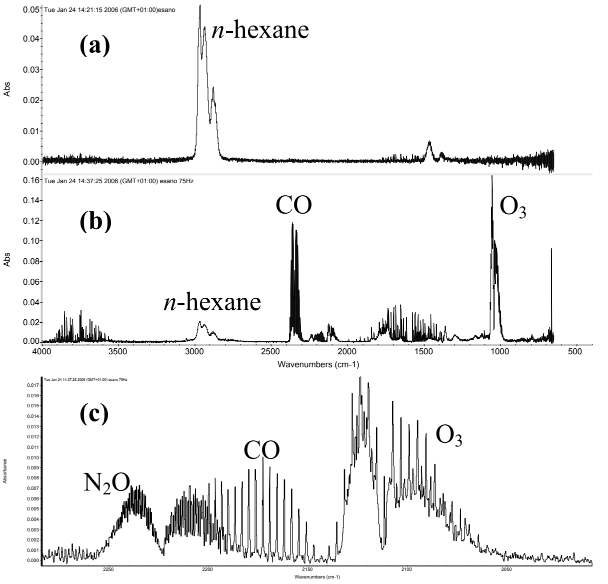

Fig. 2. FT/IR spectra of the gas mixture (a) before and (b) after treatment of *n*-hexane with +pulsed corona. (c) Expansion of spectrum (b) from 2300 to 2000 cm^{-1}.

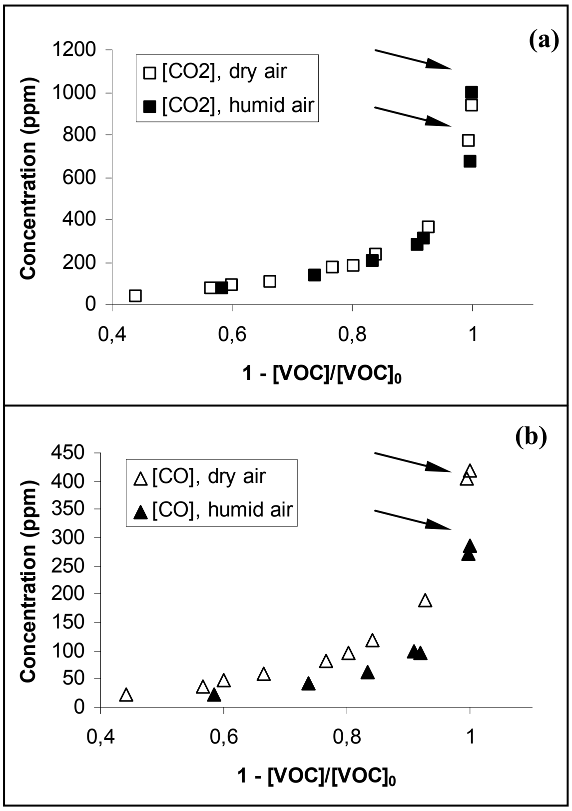

Fig. 3. CO_2 and CO production as a function of *n*-hexane (VOC) conversion in +pulsed corona processing.

TABLE I
VOLATILE ORGANIC BYPRODUCTS
FOR *N*-HEXANE PROCESSING WITH PULSED POSITIVE CORONA
IN AIR AT ROOM TEMPERATURE AND PRESSURE

Entry	Byproducts	Entry	Byproducts
1	Lower hydrocarbons	13	Heptanal
2	Acetaldehyde	14	Octanal
3	Propanaldehyde	15	Nonanal
4	Acetone	16	Decanal
5	Butyraldehyde	17	Undecanal
6	Methanol	18	Butyl octanoate
7	Ethanol	19	8-Pentadecanone
8	2-Hexanone	20	Hexadecanoic acid
9	3-Hexanone	21	Methylnitrate[a]
10	Pentanal	22	Ethylnitrate[a]
11	Hexanal	23	Butylisocianate[a]
12	Hexanol	24	N-Butylformamide[b]

[a] Detected only for energies > 1 $kJ \cdot L^{-1}$.

[b] Detected only in dry air for energy > 1 $kJ \cdot L^{-1}$

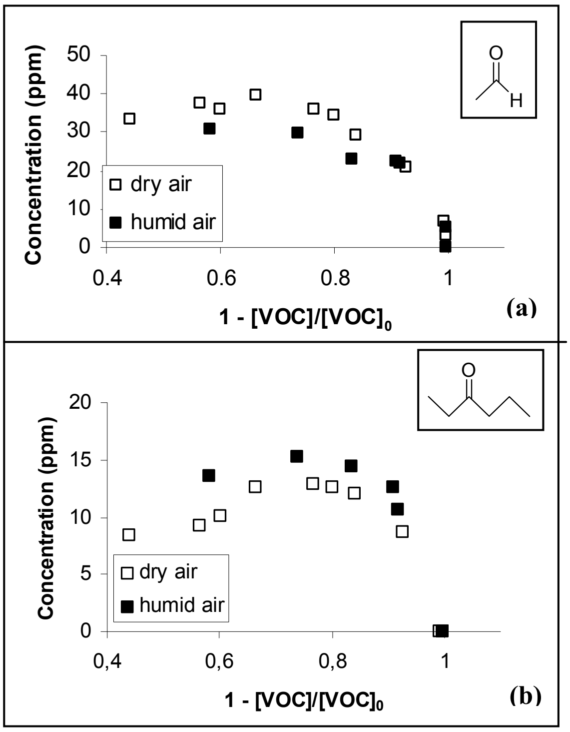

Fig. 4. Concentration of (a) acetaldehyde and (b) 3-hexanone as a function of *n*-hexane (VOC) conversion in +pulsed corona processing.

The quantitative results from these integrated chemical analyses were used to calculate the carbon mass balance with respect to the amount initially present as *n*-hexane. Fig. 5 shows that, both in dry and humid air, the percentage of undetected carbon (defined by (1) in the Experimental Section) increases with energy density reaching a maximum value of over 70%. However, as the energy is increased above 1 kJ L^{-1}, at which stage the conversion of *n*-hexane is complete, the fraction of unaccounted carbon begins to decrease. This result is consistent with the data of Fig. 3, which show that as more and more energy is provided, the production of CO and CO_2 continues, well after the complete consumption of *n*-hexane. This must be due to the oxidation at high energy densities of non-volatile organic byproducts which are not detected by GC analysis.

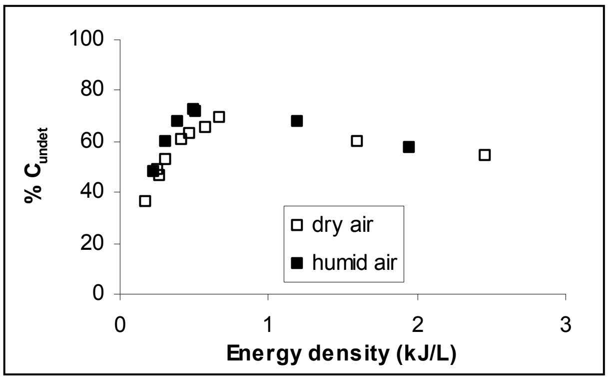

Fig. 5. Percentage of undetected carbon as a function of energy density in +pulsed corona processing of *n*-hexane in dry and humid air

The rate constants for reaction of *n*-hexane with the most important neutral reactive species in dry and humid air plasma, i.e. $O(^3P)$ and $^{\bullet}OH$, are known and reported in eq.s (3) [16] and (4) [17].

$$C_6H_{14} + O(^3P) \rightarrow {}^{\bullet}OH + \text{products}$$

$$k = 9.06 \cdot 10^{-14}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}\ (T = 300\ K) \tag{3}$$

$$C_6H_{14} + {}^{\bullet}OH \rightarrow H_2O + \text{products}$$

$$k = 5.2 \cdot 10^{-12}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}\ (T = 298\ K) \tag{4}$$

The $^{\bullet}OH$ radical, which is significantly more reactive than $O(^3P)$, is formed from water via electron dissociation (eq. 5) and via reaction with $O(^1D)$ (eq. 6)

$$H_2O + e^- \rightarrow {}^{\bullet}OH + {}^{\bullet}H + e^- \tag{5}$$

$$O(^1D) + H_2O \rightarrow 2\,{}^{\bullet}OH \tag{6}$$

as well as via ionic paths (eq.s 7-11)

$$N_2^{+\bullet} + H_2O \rightarrow N_2H^+ + {}^{\bullet}OH \tag{7}$$

$$\rightarrow H_2O^{+\bullet} + N_2 \tag{8}$$

$$H_2O^{+\bullet} + H_2O \rightarrow H_3O^+ + {}^{\bullet}OH \tag{9}$$

$$O_2^{+\bullet} + H_2O + M \rightarrow O_2^{+\bullet}(H_2O) + M \tag{10}$$

$$O_2^{+\bullet}(H_2O) + H_2O \rightarrow H_3O^+ + {}^{\bullet}OH + O_2 \tag{11}$$

Therefore, it is reasonable to conclude that while in dry air reaction (3) is probably prevailing, in humid air reaction with $^\bullet$OH radicals (eq. 4) is largely responsible for the abatement of n-hexane.

Support for this interpretation comes from the application of a chemical reactivity probe [18-20] based on the well known oxidation of CO (eq. 12) [21].

$$CO + {}^\bullet OH \rightarrow CO_2 + {}^\bullet H$$
$$k = 1.66\cdot 10^{-13}\ \text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1}\ (T = 296\ \text{K}) \qquad (12)$$

Under the effect of +pulsed corona in humid air (40% RH) we found that CO is oxidized to CO_2, its concentration decaying exponentially with energy density as shown in Fig. 6. In contrast, in dry air reaction (12) is not observed due to the very low concentration of $^\bullet$OH radicals, which can be formed only from trace amounts of residual water in the apparatus. Assuming that all conditions outlined in the literature are fulfilled [19], one can attempt to estimate rough average concentration values for $^\bullet$OH under any specific energy regime (single points in the plot of Fig. 6) by use of (13)

$$\frac{[CO]}{[CO]_0} = e^{-k_\psi \cdot t} \qquad (13)$$

where t is the residence time in the reactor, given by the ratio of reactor volume over flow rate, and k_ψ is a pseudo-first order rate constant given by

$$k_\psi = k \cdot \left[{}^\bullet OH\right] \qquad (14)$$

In (14), k is the rate constant for reaction (12) and [$^\bullet$OH] is a stationary concentration, averaged in time and space, of the hydroxyl radical under the specific energy regime considered.

Thus, using the experimentally determined k_E of 1.07 kJ^{-1}·L (data of Fig. 6), one calculates that the ratio $[CO]/[CO]_0$ is equal to 0.5 (50% conversion) for an energy density of 0.65 kJ·L^{-1}. Under these specific energy conditions a stationary $^\bullet$OH concentration, averaged in space, of 4.5x10^{10} molecule·cm^{-3} is calculated using (13) and (14).

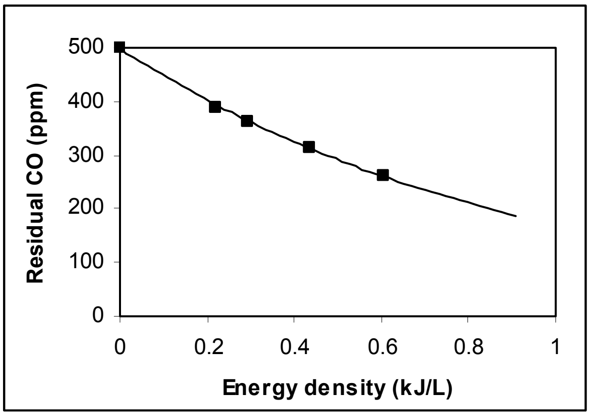

Fig. 6. Conversion of CO (500 ppm in humid air, RH: 40%) as a function of energy density in experiments performed with +pulsed corona at a constant flow rate of 450 mL·min^{-1}

One can now use this data to estimate whether the observed conversion of *n*-hexane at this specific energy density is reasonably attributed to reaction with the $^\bullet$OH radical (eq. 4).

By using (2) with the experimentally determined k_E = 4.52 kJ^{-1}·L for humid (40% RH) air, one finds that at E = 0.65 kJ·L^{-1}, the fraction of unreacted *n*-hexane, $[VOC]/[VOC]_0$, is 5.2x10^{-2}.

Under the assumption that reaction (4) is the only decay route for *n*-hexane one obtains (15)

$$-\frac{d[VOC]}{dt} = k[OH][VOC] \qquad (15)$$

from which a value of 6.1x10^9 molecule cm^{-3} is calculated for [$^\bullet$OH] using the following data: $[VOC]/[VOC]_0$=5.2x10^{-2}, k = 5.2·10^{-12} cm^3·molecule^{-1}·s^{-1} and t = 93 s (reaction time is equal to the residence time, i. e. reactor volume over flow rate). This [$^\bullet$OH] value is ca. 7 times smaller than the [$^\bullet$OH] density of 4.5x10^{10} molecule·cm^{-3} derived from the experiment on CO oxidation described above. Considering the rather gross assumptions used in applying this very simplified model, the match is remarkable and supports the conclusion that in humid air the decay of *n*-hexane is largely due to reaction with $^\bullet$OH radicals.

We have also monitored the concentration of ozone obtained by +pulsed corona in dry and in humid air as a function of energy density. Ozone was measured by integration of the corresponding FT/IR band, after calibration of the spectrometer response by simultaneous iodometric titration. The data show that ozone concentration increases with energy density up to a plateau value of ca 5000 ppm in dry air and ca 3500 ppm in humid air (40% RH), respectively (Fig. 7).

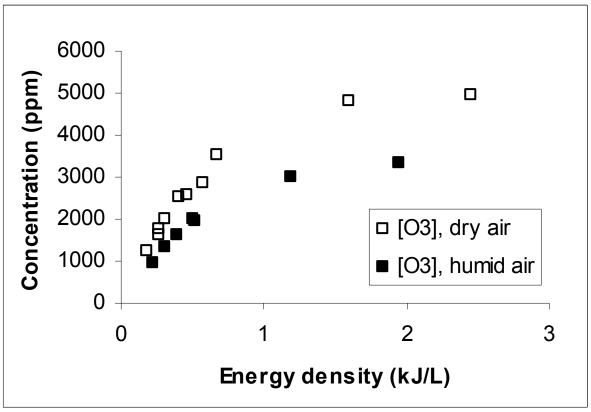

Fig. 7. Ozone production as a function of energy density in +pulsed corona processing in dry and humid air

Since ozone is produced by the reaction of O(^{3}P) with O_2, it is probably safe to conclude that, at a given energy density, a higher concentration of O(^{3}P) is achieved in dry air than in humid air. Our ozone concentration of 5000 ppm at 1.6 kJ·L^{-1} in dry air compares reasonably well with the data reported recently for a similar experiment [22].

IV. CONCLUSION

A large corona reactor was developed for mechanistic studies of non-thermal plasma VOC abatement. The reactor can be energized with pulsed as well as DC voltage, thus allowing for a direct comparison of removal processes induced by either pulsed or DC corona but otherwise under identical experimental conditions. Specifically, this work has investigated the +pulsed corona processing of *n*-hexane by monitoring efficiency and products in dry as well as in humid air. As reported by other authors [7], pulsed corona processing is scarcely selective in the production of CO_2. Although formed in very minor amounts, numeorus volatile organic byproducts have been detected and identified. Their concentration profile with respect to energy density shows consistently a rising portion followed by steep decay at higher energies. Interestingly, a few such byproducts, detected only at high energy densities, contain nitrogen. Notably, a significant fraction of the total carbon initially present as *n*-hexane ends up as non-volatile organic material. It appears, however, that at energy densities higher than required for complete *n*-hexane conversion, at least part of such organic materials are oxidized to release CO_2 and CO.

Expectedly, pulsed corona is more efficient than DC corona processing both in dry and in humid air. Most interestingly, while for +pulsed corona the efficiency is better in humid than in dry air, the opposite is true for +DC corona. These findings are hard to reconcile with the hypothesis of a common mechanism under the two corona regimes. For +pulsed corona in humid air, both the favorable effect of water and the estimated mean $^{\bullet}OH$ concentration are consistent with radical initiation steps involving $^{\bullet}OH$. This conclusion is consistent with literature reports [1, 2]. As for the +DC corona induced process, recent results from our laboratory, comprising also analysis of the ions present within the plasma, support a proposal that ionic initiation steps are involved in this case [23].

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REFERENCES

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[1] H.-H. Kim, "Nonthermal plasma processing for air-pollution control: a historical review, current issues, and future prospects", *Plasma Processes Polym.*, vol. 1, pp. 91-110, 2004.

[2] E. M. van Veldhuizen, *Electrical Discharges for Environmental Purposes, Fundamentals and Applications*. Huntington, Nova Science Publishers, Inc., New York, 2000.

[3] S. Pasquiers, "Removal of pollutants by plasma catalytic processes", *Eur. Phys. J. Appl. Phys.*, vol. 28, pp. 319-324, 2004.

[4] B. M. Penetrante and S. E. Schultheis, *Nonthermal plasma techniques for pollution control.* New York: Springer Verlag, 1993.

[5] K. L. L.Vercammen, A. A. Berezin, F. Lox, and J.-S. Chang. "Non thermal plasma techniques for the reduction of VOC in air streams: a critical review", *J. Adv. Oxid. Technol.*, vol. 2, pp. 312-329, 1997.

[6] J. Jarrige and P. Vervisch, "Decomposition of three volatile organic compounds by nanosceond pulsed corona discharge: study of by-product formation and influence of high voltage pulse parameters", *J. Appl. Phys.*, vol. 99, art. no. 113303 (10 pages), 2006.

[7] H. H. Kim, H. Kobara, A. Ogata, and S. Futamura, "Comparative assessment of different nonthermal plasma reactors on energy efficiency and aerosol formation from the decomposition of gas-phase benzene", *IEEE Trans. Ind. Appl.*, vol. 41, pp. 206-214, 2005.

[8] R. Atkinson, "Gas-phase degradation of organic compounds in the troposphere", *Pure Appl. Chem.*, vol. 70, pp. 1327-1334, 1998.

[9] B. M. Penetrante, M. C. Hsiao, J. N. Bardsley, B. T. Merritt, G. E. Vogtlin, and P. H. Wallmann, "Electron beam and pulsed corona processing of volatile organic compounds in gas streams", *Pure Appl. Chem.*, vol. 68, pp. 1083-1087, 1996.

[10] L. N. Krasnoperov, L. G. Krishtopa, and J. W. Bozzelli, "Study of volatile organic compounds destruction by dielectric barrier corona discharge", *J. Adv. Oxid. Technol.*, vol. 2, pp. 248-256, 1997.

[11] R. Rudolph, K.-P. Francke, and H. Miessner, "Concentration dependance of VOC decomposition by dielectric barrier discharges", *Plasma Chem. Plasma Process.*, vol. 22, pp. 401-412, 2002.

[12] E. Marotta, G. Scorrano, and C. Paradisi, "Ionic reactions of chlorinated VOCs in air plasma at atmospheric pressure", *Plasma Processes Polym.*, vol. 2, pp. 209-217, 2005.

[13] (a) A. Donò, C. Paradisi, and G. Scorrano. "Abatement of VOCs by corona discharge. A study of the reactivity of trichloroethylene under atmospheric pressure ionization conditions", *Rapid Commun. Mass Spectrom.*, vol. 11, pp. 1687-1694, 1997; (b) E. Odic, C. Paradisi, M. Rea, L. Parissi, A. Goldman, and M. Goldman, "Treatment of Organic Pollutants by Corona Discharge Plasma", in *The Modern Problems of Electrostatics with Applications in Environment Protection*. NATO Science Series, 2. Environmental Security, Vol. 63, I. I. Inculet, F. T. Tanasescu and R. Cramariuc, Eds. Kluwer Academic Publishers, Dordrecht, 1999, p. 143; (c) E. Marotta and C. Paradisi, "Positive ion chemistry of esters of carboxylic acids in air plasma at atmospheric pressure", *J. Mass Spectrom.*, vol. 40, pp. 1583-1589, 2005. (d) E. Marotta, R.G. Cooks, and C. Paradisi, "Novel CFCs-substitutes recommended by EPA (hydrofluorocarbon-245fa and hydrofluoroether-7100): ion chemistry in air plasma and reactions with atmospheric ions", *J. Am. Soc. Mass Spectrom.*, vol. 16, pp. 1081-1092, 2005.

[14] M. Pavlik, and J. D. Skalny, "Generation of $[H_3O]^+\cdot(H_2O)_n$ clusters by positive corona discharge in air," *Rapid Commun. Mass Spectrom.*, vol. 11, pp. 1757-1766, 1997.

[15] (a) A. Mizuno, J. S. Clements, and R. H. Davis, "A method for the removal of sulfur dioxide from exhaust gas utilising pulsed streamer corona for electron energization", *IEEE Trans. Ind. Appl.*, vol. 22, pp. 516-522, 1996; (b) A. Mizuno, Y. Kisanuki, M. Noguchi, S. Katsura, S. H. Lee, Y. K. Hong, S. Y. Shin, and J. H. Kang, "Indoor Air Cleaning Using a Pulsed Discharge Plasma", *IEEE Trans. Ind. Appl.*, vol. 35, pp. 1284-1288, 1999.

[16] J.T. Herron, "Evaluated chemical kinetic data for the reactions of atomic oxygen $O(^3P)$ with saturated organic compounds in the gas phase", *J. Phys. Chem. Ref. Data*, vol. 17, pp. 967-1026, 1988.

[17] R. Atkinson, "Kinetics of the gas-phase reactions of OH radicals with alkanes and cycloalkanes", *Atmos. Chem. Phys*, vol. 3, pp. 2233-2307, 2003.

[18] M. J. Campbell, J. C. Farmer, C. A. Fitzner, M. N. Henry, J. C. Sheppard, R. J. Hardy, J. F. Hopper, and V. Muralidhar, "Radiocarbon tracer measurements of atmospheric hydroxyl radical concentrations", *J. Atmos. Chem.*, vol. 4, pp. 413-427, 1986.

[19] Z.-Z. Su, K. Ito, K. Takashima, S. Katsura, K. Onda, and A. Mizuno, "OH radical generation by atmospheric pressure pulsed discharge plasma and its quantitative analysis by monitoring CO oxidation", *J. Phys. D: Appl. Phys.*, vol. 35, pp. 3192-3198, 2002.

[20] R. Rudolph, K.-P. Francke, and H. Miessner, "OH radicals as oxidizing agent for the abatement of organic pollutants in gas flows by dielectric barrier discharges", *Plasmas Polym.*, vol. 8, pp. 153-161, 2003.

[21] S. G. Lias, "Ionization Energy Evaluation", in *NIST ChemistryWebBook, NIST Standard Reference Database No. 69*; Maillard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD; http://webbook.nist.gov/chemistry/, 2006.

[22] M. Simek and M. Clupek, "Efficiency of ozone production by pulsed positive corona discharge in synthetic air", *J. Phys. D: Appl. Phys.*, vol. 35, pp. 1171-1175, 2002.

[23] E. Marotta, A. Callea, M. Rea, and C. Paradisi, "DC corona electric discharges for air pollution control. Part 2. Ionic intermediates and mechanisms of hydrocarbon processing." unpublished.