

Optimization of nonthermal plasma for the treatment of gas streams

Toshiaki Yamamoto *

*Department of Energy Systems Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai,
Osaka 599-8531, Japan*

Received 1 December 1998; received in revised form 1 March 1999; accepted 4 March 1999

Abstract

The decomposition of hazardous air pollutants (HAPs) has been described by using the ratio of power input to flow rate or of energy to gas flow rate (or specific energy density (SED), in joules/liter). However, we found that HAP decomposition was not constant for a given SED but rather depends on SED. Data were plotted to examine HAP decomposition with constant SEDs. The results indicated for most HAPs tested the soft plasma (the low voltage and high residence time) is the preferred operation for most HAP decomposition applications. This concept can lead to new insights for HAP decomposition and to the optimization of nonthermal plasma for the treatment of HAPs. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Nonthermal plasma; Hazardous air pollutants; Decomposition; Soft plasma; Air pollution

1. Introduction

Traditionally, hazardous air pollutant (HAP) decomposition has been predicted from the power required at a given flow rate or the energy per unit gas volume, which is called ‘specific energy density (SED)’ and is measured in joules/liter. Various nonthermal plasma devices have been evaluated using SED but we found that the decomposition of certain HAPs did not depend on SED [1].

In the plasma chemical process, the ideal final product would be CO₂, N₂ and H₂O, and hydrogen halides (HX where X is F, Cl and Br). However, most nonthermal plasma processes produce reaction byproducts whose selectivity is not controllable. Reaction byproducts consist of organic byproducts and inorganic byproducts. Examples of

* Tel./fax: +81-722-54-9230; E-mail: yamamoto@ava.osakafu-u.ac.jp

inorganic byproducts are CO, NO, NO₂, N₂O, and O₃, while the generation of organic byproducts depends on the types of HAPs and the reactor, input energy, background gas, residence time, and humidity. In general, the amounts of reaction organic byproducts decrease with increased power and become highest with a dry hydrogen background gas, followed by dry nitrogen, humidified nitrogen, wet air, and dry air [2,3]. We found that the decomposition of aerated HAP produces a negligibly low concentration of organic byproducts. These concentrations are usually far below the threshold values when compared with other background gases such as nitrogen and hydrogen [2,3].

On the other hand, the concentration of inorganic byproducts is significantly higher than that of organic byproducts. Fig. 1 shows a typical concentration of inorganic byproducts for HAP decomposition as a function of applied voltage (or power). Thus, the major concern for the successful application of nonthermal plasma technology should be that of minimizing inorganic byproducts.

One strategy for an integrated HAP control technology is to control the background gas constituents; for example, the oxygen concentration is controlled at about 3% or less to minimize NO_x emissions so that secondary control devices become unnecessary although this approach is impractical for most of applications. Another strategy would be to operate the plasma with lower voltage and a longer residence time. This new approach is called 'soft plasma,' as opposed to 'hard plasma,' which is operated with high power and short residence time. The soft plasma operation produces significantly less inorganic byproducts than the hard plasma even though the reactor size increases linearly with residence time.

In addition, the author proposed a new way of increasing HAP decomposition [1]. Previous discussions for HAP decomposition have considered only the balance of energies acting on HAPs. In contrast, the new approach recognized the influence of electron impact to accumulate the energy to excite HAP molecules in plasma and to

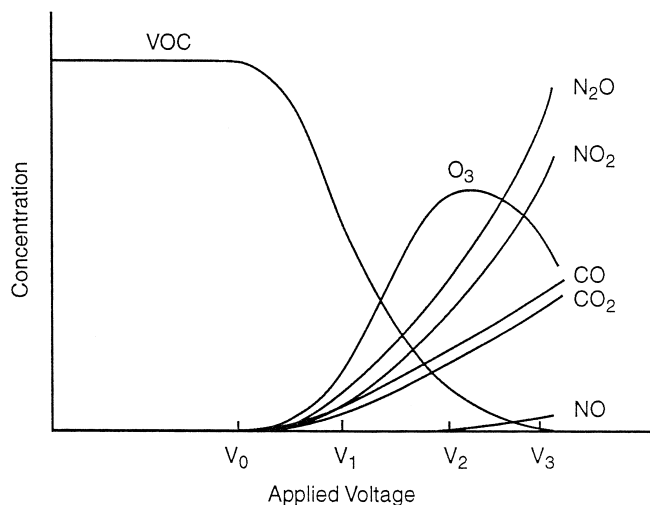


Fig. 1. Typical concentration of inorganic byproducts for HAP decomposition.

form radicals, which proceed homolytically via their excited states, leading to HAP decomposition. In other words, the decomposition rate is affected by the residence time, i.e. a HAP molecule can be decomposed with much lower energy than is required to break a HAP bond [1].

In this paper, data were plotted in order to evaluate the soft plasma concept. This concept can lead to new insights regarding HAP decomposition and the optimization of the nonthermal plasma technology for the treatment of HAPs.

2. Experiments

Laboratory-scale experiments were performed using a ferroelectric plasma reactor. The ferroelectric plasma reactor employed an AC power supply at 50/60 Hz and was a coaxial type: the inner cylindrical electrode was 16.6 mm in diameter and the outer electrode was 47.3 mm in diameter, resulting in a gap distance of 15.4 mm where 1-mm diameter BaTiO₃ pellets were packed as shown in Fig. 2. High AC voltage was applied between the two concentric electrodes. The gas streams passed through the 6.4-mm entry tube and were dispersed into the plasma zone. The operating characteristics of a ferroelectric plasma reactor have been previously reported [5].

The desired HAP concentration and background conditions were obtained with zero air or nitrogen in a gas cylinder. The flow rate was adjusted with a flowmeter. The decomposition efficiencies of the HAPs were determined on a Hewlett Packard (HP) 5880A with a capillary column of 5% OV 101 on Chromosorb WHP. The concentrations of NO, NO₂, and total NO_x were measured by a chemiluminescence NO–NO₂–NO_x analyzer (Model 42), and the concentration of ozone was measured by a UV photometric O₃ analyzer (Model 49 of Thermo Environmental Instruments). The concentrations of CO, CO₂, and N₂O were determined on a GC-9A with combined columns of Porapak Q + N and Molecular Sieve 13X.

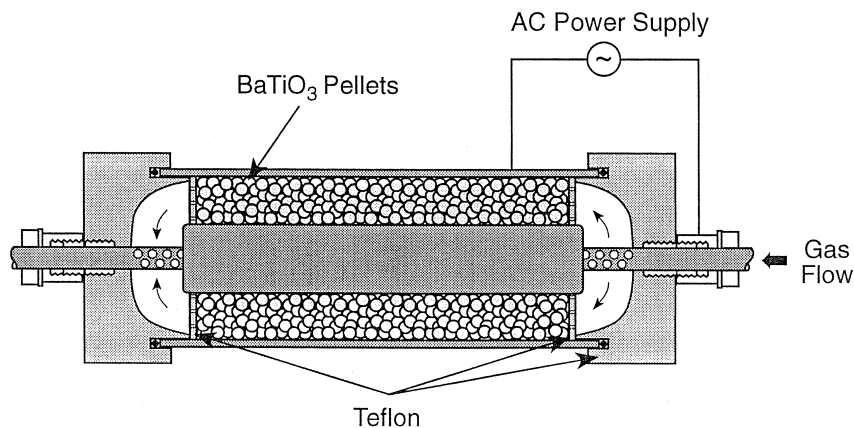


Fig. 2. Schematic of ferroelectric packed-bed plasma reactor (FPR).

The effects of three different levels of applied voltage and residence time (or flow rate) on the decomposition of various HAPs were investigated, while the SED was kept constant for different levels. The HAPs tested were trichloroethylene (TCE, $\text{Cl}_2\text{C}=\text{CHCl}$), trichloroethane (Cl_3CCH_3), methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), butane (C_4H_{10}), CFC-113 ($\text{Cl}_2\text{FCCF}_2\text{Cl}$), tetrachloroethylene (C_2Cl_4) and halon FC-12B (CClBrF_2) in both dry nitrogen and dry air. By maintaining the SED constant, the comparison between soft plasma and hard plasma on HAP decomposition was made in order to help understand the optimum operating characteristics of the plasma reactor.

3. Results and discussion

3.1. Inorganic byproducts

The quantification of byproducts is extremely important for the engineering evaluation of nonthermal plasma technologies. Fig. 3a and b show O_3 , NO, NO_2 and NO_x concentrations as a function of applied voltage for the packed-bed plasma reactor with and without TCE, respectively. The flow rate was set at 1.0 l/min. Under dry air without TCE as shown in Fig. 3a, O_3 concentration increased at around 4 kV and reached a maximum (48 ppm) at 5 kV, followed by a sharp decrease to nearly 0 ppm at 6 kV. The concentrations of NO, NO_2 and total NO_x increased and was accompanied by the formation of O_3 , and those of show NO_2 and NO_x increased linearly even after the O_3 concentration decreased. The NO concentration stayed extremely low due to successive oxidation of NO by O and O_3 compared to NO_2 . When TCE was introduced, O_3 , NO_2 , and NO_x all decreased.

A significant amount of nitrous oxides (N_2O) was generated for both the pulsed-corona and packed-bed plasma reactors [2]. For example, 50 ppm of N_2O was measured at 5 kV and 600 ppm at 7.8 kV for the packed-bed reactor when the flow rate was 1.0 l/min. Some other nonthermal reactors are also expected to generate a significant amount of N_2O . The power level can be tuned to minimize NO_x , N_2O and O_3 concentrations.

3.2. Voltage and power relationship

Fig. 4 shows the plug power vs. applied voltage. The power consumption for the reactor was approximately 27% of the plug power. SED is defined as the ratio of power (P) to flow rate (Q). When we select a certain power of $P_1 = 68$ W and the flow rate of $Q_1 = 1.5$ l/min (SED = 2700 J/l), the corresponding applied voltage is $V_1 = 6.5$ kV from Fig. 2. For $Q_2 = 1.0$ l/min and $Q_3 = 0.5$ l/min, P_2 and P_3 become 45 and 22.7 W, respectively, for SED = 2700 J/l. The corresponding applied voltages are $V_2 = 5.9$ kV and $V_3 = 5.3$ kV because $P_1/Q_1 = P_2/Q_2 = P_3/Q_3 = (68 \text{ W})/(1.5 \text{ l/min})$. The flow rates selected were 0.5, 1.0, and 1.5 l/min and correspond to residence times of 8.9, 4.4, and 3.3 s, respectively. Similarly, the plasma operating conditions can be determined in the same manner for different SED levels (4020 and 1440 J/l). Note that

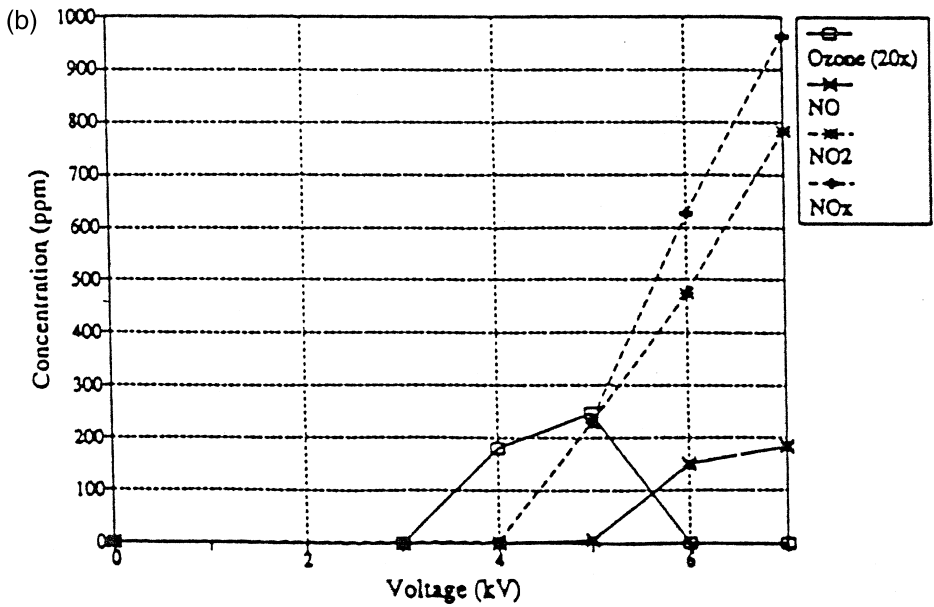
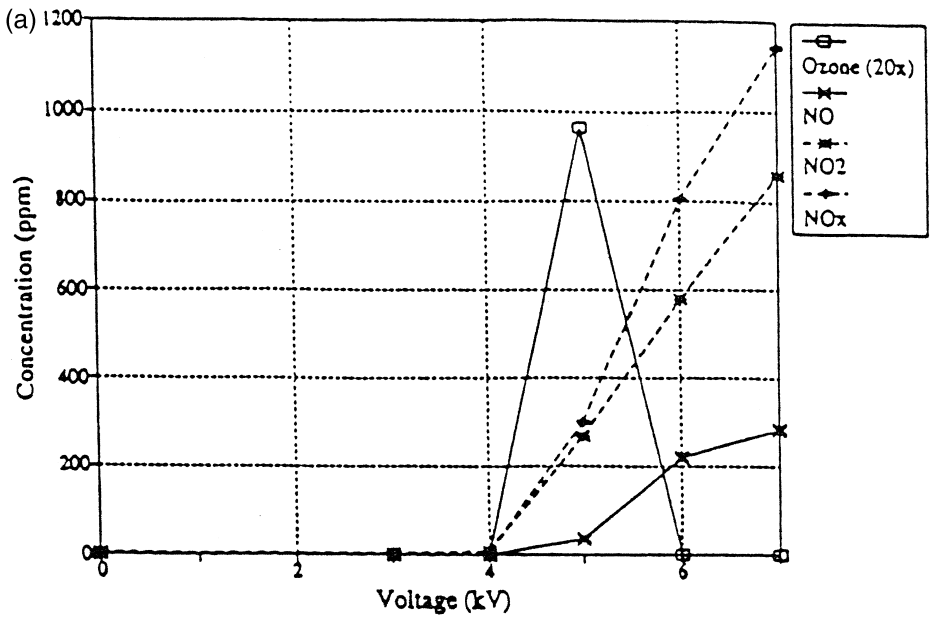


Fig. 3. (a) The concentration of O₃, NO, NO₂ and NO_x in dry air for FPR (1.0 l/min). (b) The concentration of O₃, NO, NO₂ and NO_x in dry air with TCE (1.0 l/min)

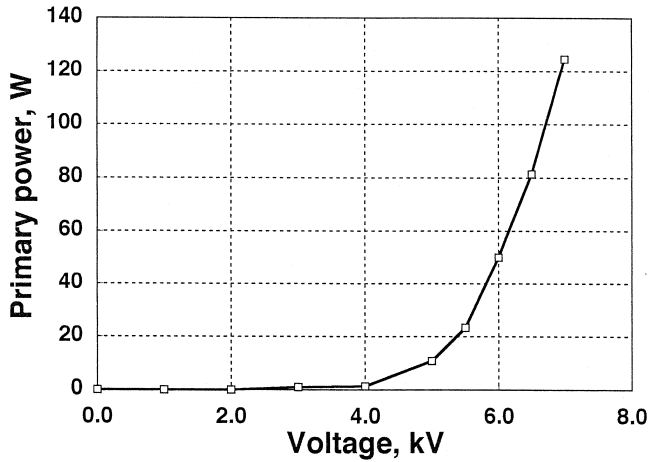


Fig. 4. Voltage and current relationship.

these data points were based on duplicate experiments conducted (not three experimental data points) and also noted that the applied voltages become different for each SED level.

3.3. HAP decomposition

3.3.1. Trichloroethylene decomposition

Fig. 5a and b show the decomposition efficiency for TCE in dry N_2 and dry air, while SED was kept constant at three levels (1440, 2700, and 4020 J/l). The TCE concentrations were maintained between 1020 and 1110 ppm during the tests.

With the SED of 2700 J/l, applied voltage of 6.5 kV, and flow rate of 1.5 l/min, TCE decomposition efficiency in N_2 was 70%. As the flow rate was reduced to 1.0 l/min with applied voltage of 5.9 kV, TCE decomposition efficiency was increased to 81%. When the flow rate was reduced to 0.5 l/min with applied voltage of 5.3 kV, TCE decomposition was further increased to 84% without changing the SED. The TCE decomposition efficiency increased with the decreasing flow rate and voltage (negative slope or $\partial\eta/\partial V < 0$).

When the SED was set at a higher level (4020 J/l), the decomposition efficiency was 82% with 1.5 l/min and 6.7 kV, 90% with 1.0 l/min and 6.3 kV, and 89% with 0.5 l/min and 5.7 kV, respectively. Similarly, when the SED was set at a lower level (1440 J/l), the decomposition efficiency was 47% with 1.5 l/min and 5.8 kV, 65% for 1.0 l/min and 5.5 kV, and 65% for 0.5 l/min with 5.0 kV, respectively. A similar trend was observed, although the decomposition efficiency levelled off below 6.3 kV for a SED of 4020 J/l and 5.5 kV for a SED of 1440 J/l. It is clear that the decomposition efficiency was significantly higher for 1.0 l/min than for 1.5 l/min for all SED levels.

TCE decomposition efficiencies in dry air with three different levels of SED are shown in Fig. 5b. Decomposition efficiency decreases with increased voltage or reduced

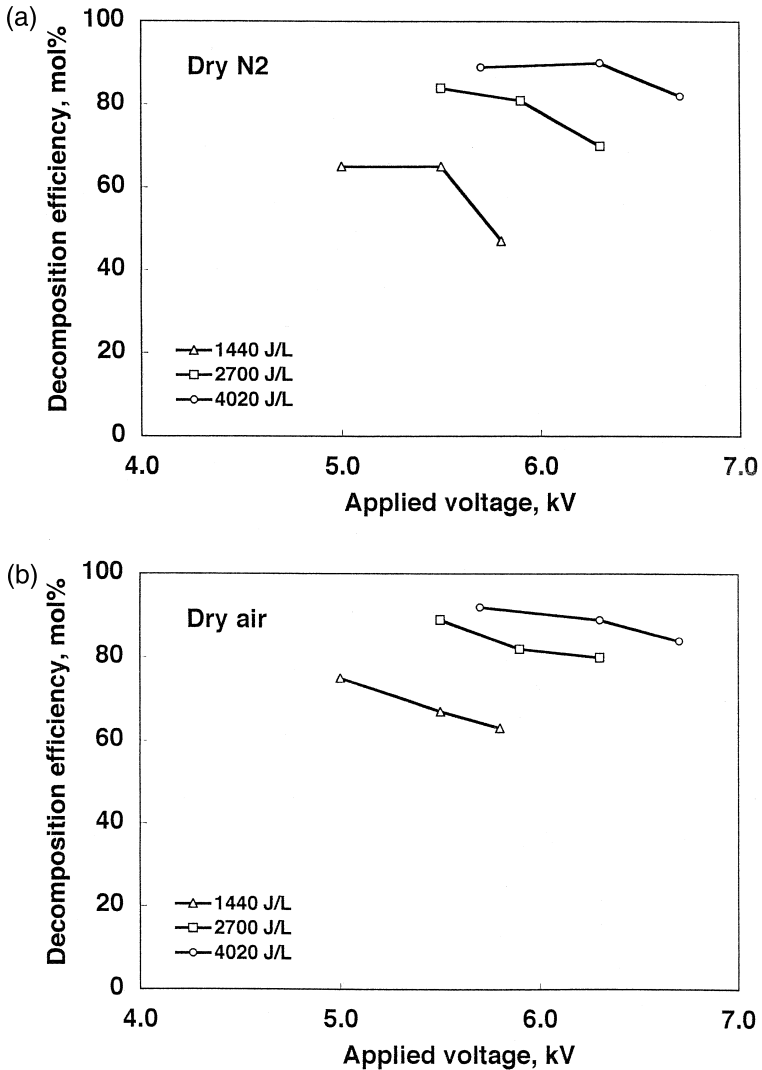


Fig. 5. (a) TCE decomposition in dry N₂. (b) TCE decomposition in dry air.

now rate (increased residence time). It is interesting to note that decomposition efficiency is somewhat higher for dry air than for N₂ although the maximum efficiency that was achieved was higher for the case of N₂.

These results indicate that residence time has an additional effect on TCE decomposition. In other words, the TCE decomposition rate is not constant even when SED is constant, but it is a function of residence time, for which a new decomposition rate equation developed was validated [1]. The results of higher TCE decomposition at low voltage and longer residence time support the soft plasma operation. In addition, TCE can be decomposed with much lower energy.

3.3.2. Trichloroethane decomposition

The decomposition efficiencies for trichloroethane (Cl_3CCH_3) in dry N_2 and in dry air are shown in Fig. 6a and b. The concentrations were maintained between 970 and 1020 ppm during the experiments.

For trichloroethane in dry N_2 , the decomposition efficiency was significantly lower compared with TCE. The decomposition efficiency decreased with increased applied voltage for all SED levels, indicating that soft plasma is superior to hard plasma. The increase of decomposition efficiency is more significant for trichloroethane decomposition at higher SEDs.

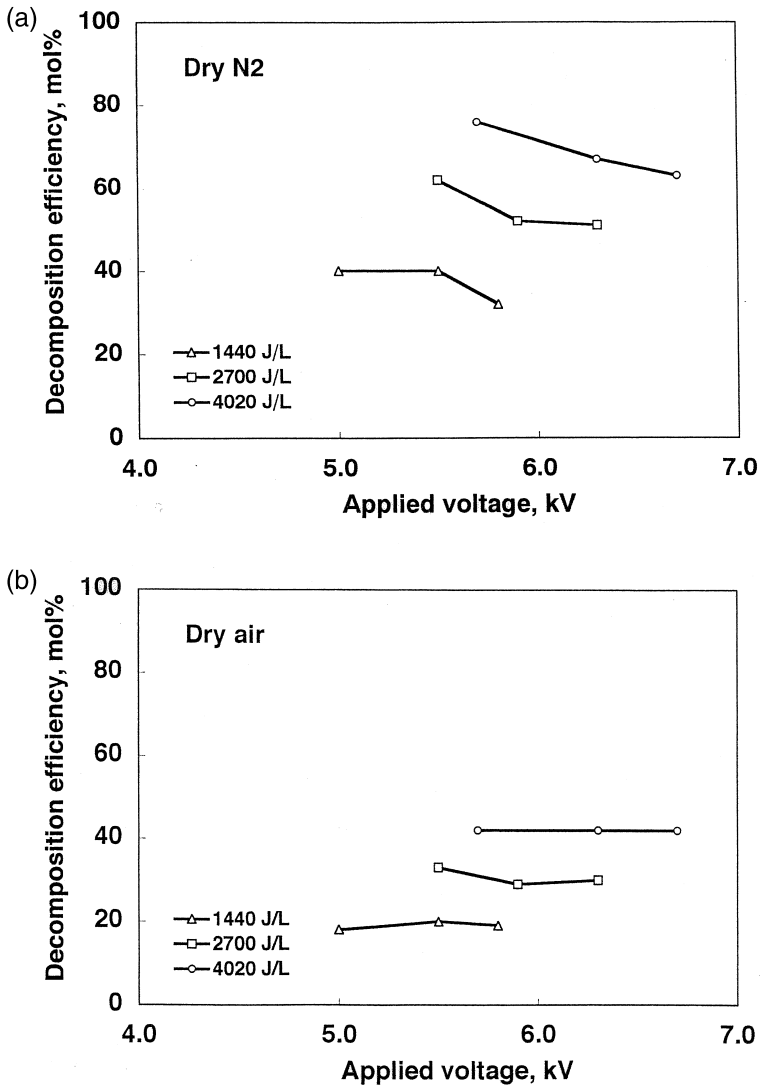


Fig. 6. (a) Cl_3CCH_3 decomposition in dry N_2 . (b) Cl_3CCH_3 decomposition in dry air.

However, the decomposition efficiency for trichloroethane in dry air showed no significant difference. In other words, the advantage of soft plasma is not obvious here except for minimizing inorganic byproducts.

3.3.3. Methane decomposition

The decomposition efficiencies for methane (CH_4) in dry N_2 and in dry air at three SED levels are shown in Fig. 7a and b. The concentrations were maintained between 980 and 1000 ppm during the experiments. The decomposition efficiency in dry N_2

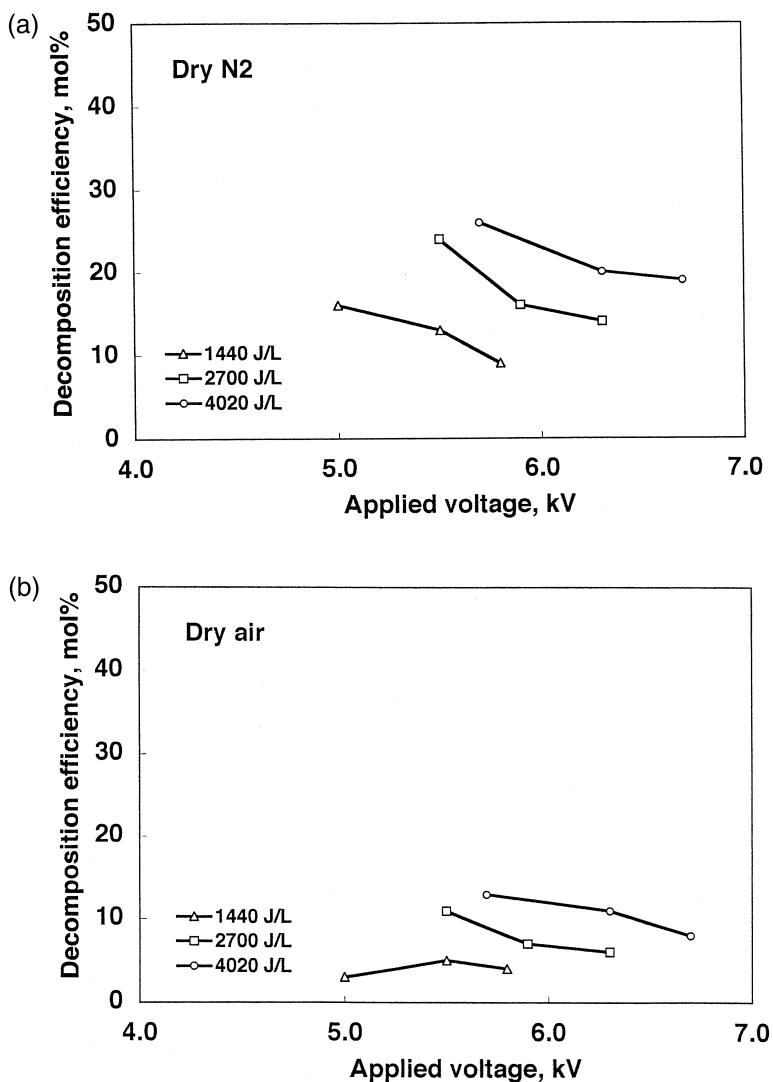


Fig. 7. (a) CH_4 decomposition in dry N_2 . (b) CH_4 decomposition in dry air.

decreased with increased applied voltage for all SED levels but the decomposition efficiency in dry air showed a modest improvement only for high SEDs.

3.3.4. Ethane decomposition

The decomposition efficiencies for ethane (C_2H_6) in dry N_2 and in dry air are shown in Fig. 8a and b. The concentrations were maintained between 1000 and 1020 ppm during the experiments. The decomposition efficiencies for ethane in N_2 were significantly higher than in dry air. The decomposition efficiency in dry N_2 decreased with increased applied voltage for all SED levels but the increase of decomposition is

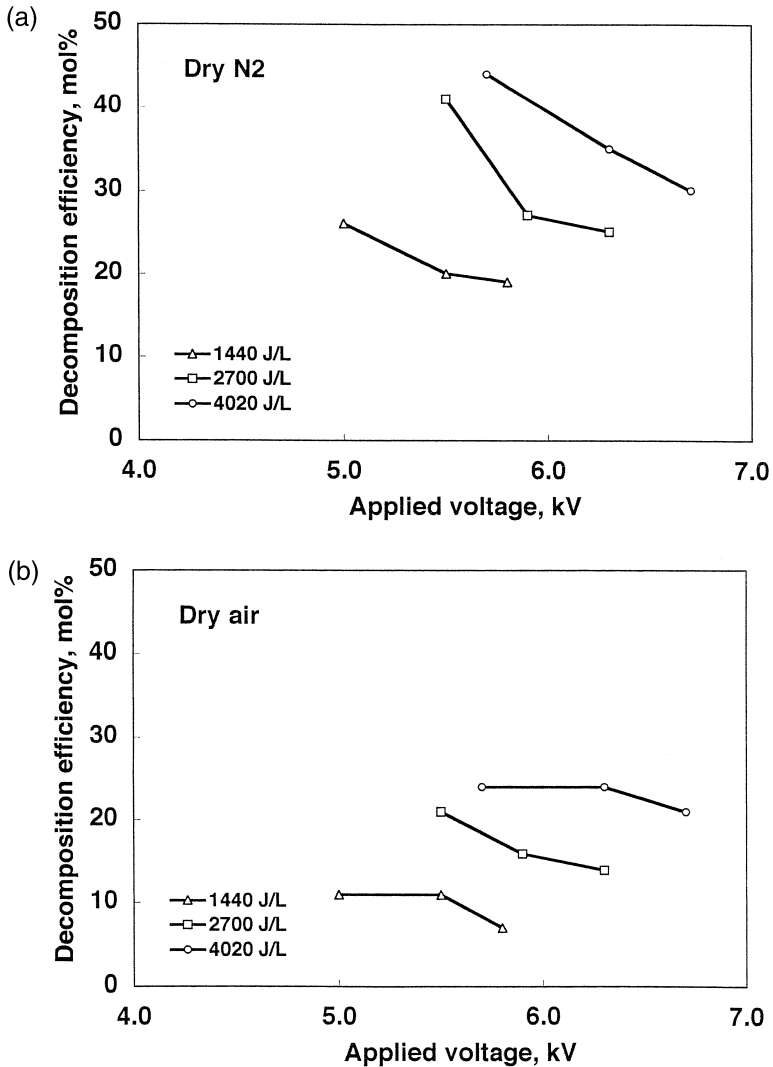


Fig. 8. (a) C_2H_6 decomposition in dry N_2 . (b) C_2H_6 decomposition in dry air.

significant for higher SEDs. The decomposition efficiency in dry air showed modest SED dependency although the trend is obvious, indicating the preferred soft plasma mode.

3.3.5. Ethylene decomposition

Fig. 9a and b show the decomposition efficiencies for ethylene (C_2H_4) in dry N_2 and in dry air. The concentrations were between 1000 and 1010 ppm during the experiments. The decomposition efficiencies for ethylene in dry N_2 were significantly higher than in

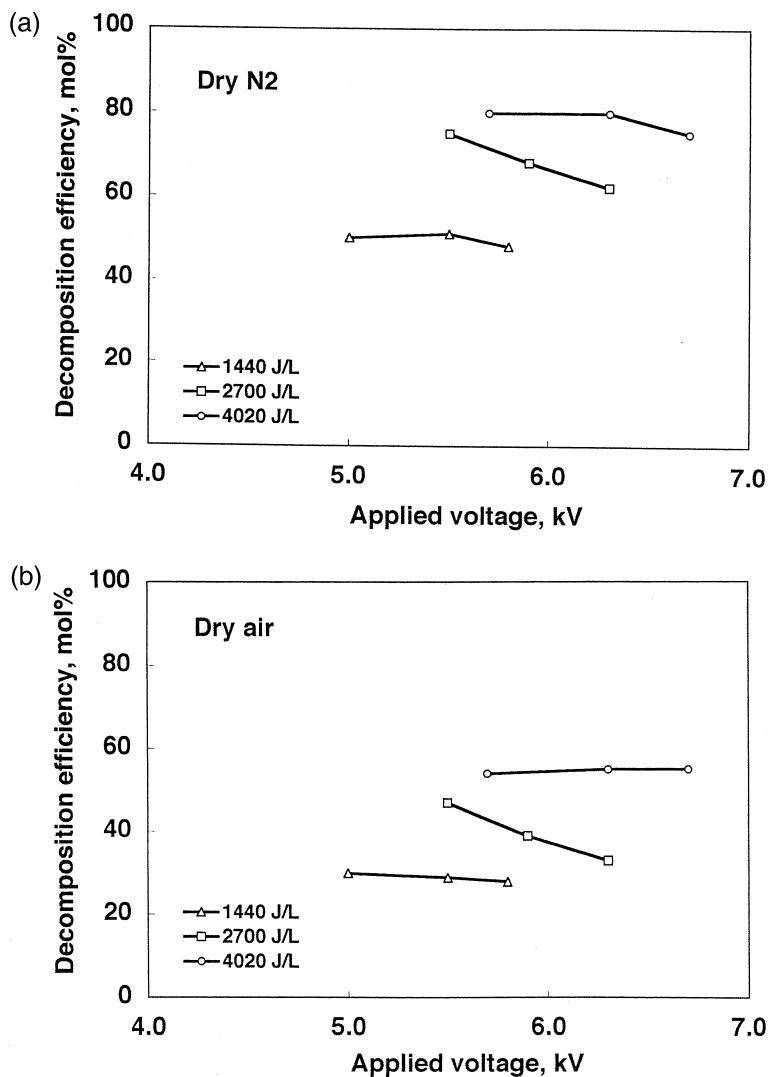


Fig. 9. (a) C_2H_4 decomposition in dry N_2 . (b) C_2H_4 decomposition in dry air.

dry air. The decomposition efficiencies in both N_2 and air showed weak SED (residence time) dependency except for the 2700-J/l level.

3.3.6. Butane decomposition

Fig. 10a and b show the decomposition efficiency for butane (C_4H_{10}) in dry N_2 and in dry air. The concentrations were maintained between 990 and 1040 ppm during the experiments. The decomposition efficiencies in both dry N_2 and air shows a decrease

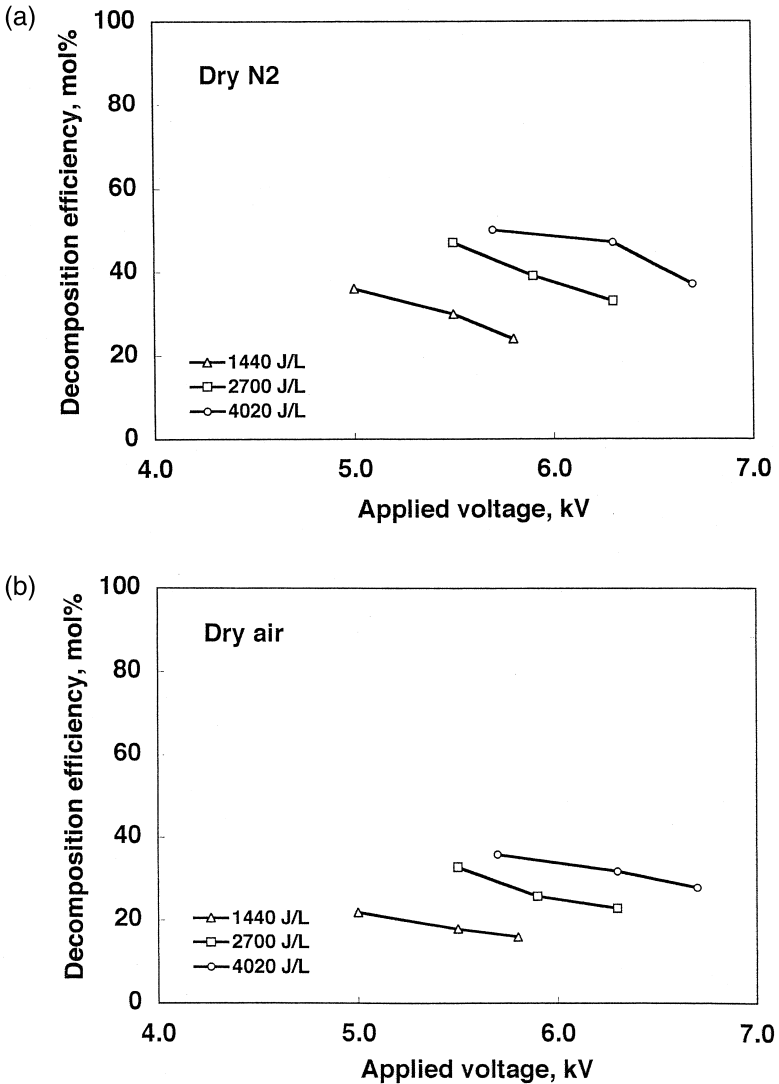


Fig. 10. (a) C_4H_{10} decomposition in dry N_2 . (b) C_4H_{10} decomposition in dry air.

with increased applied voltage for all SED levels, indicating that the soft plasma is the preferred mode for C_4H_{10} decomposition.

3.3.7. CFC-113 decomposition

The decomposition efficiency for 1000 ppm CFC-113, varying the flow rates and voltages while maintaining SED at a constant value ($SED = 2700 \text{ J/l}$), is shown in Fig. 11. The concentration of CFC-113 was maintained at 1000 ppm.

With an applied voltage of 6.6 kV and flow rate of 2.2 l/min (2.0 s in residence time), CFC-113 decomposition efficiency was in the range of 25.9%–28.5%. As the flow rate decreased to 1.0 l/min and the applied voltage was decreased to 6.0 kV, the decomposition efficiency improved significantly from 51.7% to 53.5%. The applied voltage of 5.2 kV is just above the corona onset voltage (approximately 4.0 kV); the plasma was very weak and only a very small fraction of the volume was recognized as an active plasma zone. Yet, CFC-113 decomposition further increased to 65.4% to 77.3% with a lower flow rate (or longer residence time) despite the constant SED.

These results indicate that decomposition is affected by treatment time even when the SED is maintained at the same level. As a consequence, CFC-113 molecules are decomposed more easily than when the force required for CFC-113 molecule cleavage is applied, which supports our new theory [1].

3.3.8. Tetrachloroethylene decomposition

Fig. 12 shows the C_2Cl_4 decomposition efficiency in dry air and in humidified air, while the SED was kept constant at two levels (1200 and 2820 J/l). With a SED of 2820 J/l, applied voltage of 8.0 kV, and flow rate of 2.0 l/min, C_2Cl_4 decomposition efficiency in dry air was 95.0%. As the flow rate was reduced to 1.0 l/min with an applied voltage of 7.0 kV, C_2Cl_4 decomposition efficiency increased to 96.0%. When the flow rate was reduced to 0.5 l/min with an applied voltage of 6.1 kV, C_2Cl_4 decomposition efficiency was 94.4% without changing the SED. The C_2Cl_4 decomposi-

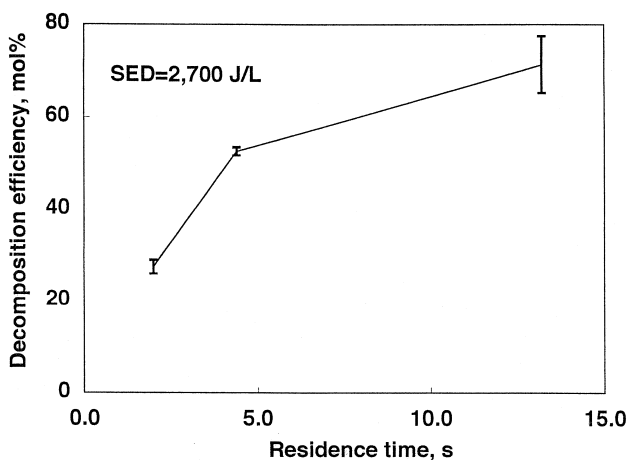


Fig. 11. CFC-113 decomposition in dry air.

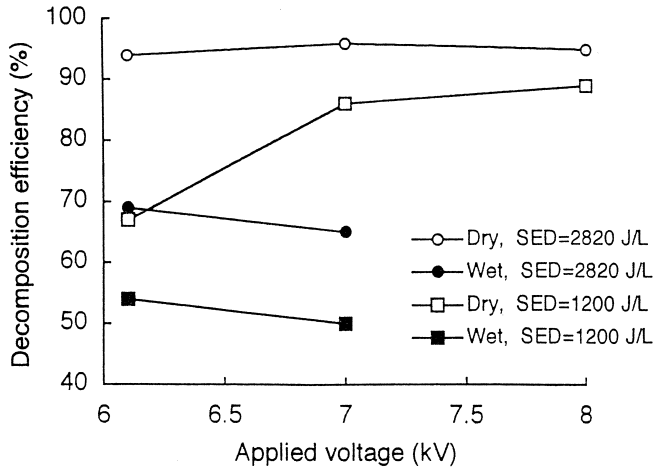


Fig. 12. C₂H₄ decomposition in dry and in humidified air.

tion efficiency peaked at 7.0 kV for SED = 2820 J/l but was not significantly affected by the operating conditions. When the SED was at a lower level (1200 J/l), the decomposition efficiency decreased with a decrease in the flow rate (increased residence time). The decomposition efficiency was significantly lower for 0.5 l/min than for 2.0 l/min at this SED level. The C₂Cl₄ decomposition is not constant but is rather significantly affected even with a constant SED. The decomposition efficiency in the humidified case showed no dependency on applied voltage. Clearly, the high voltage and short residence time operation (hard plasma) was the preferred operation for C₂Cl₄ decomposition as opposed to the low voltage and longer residence time operation (soft

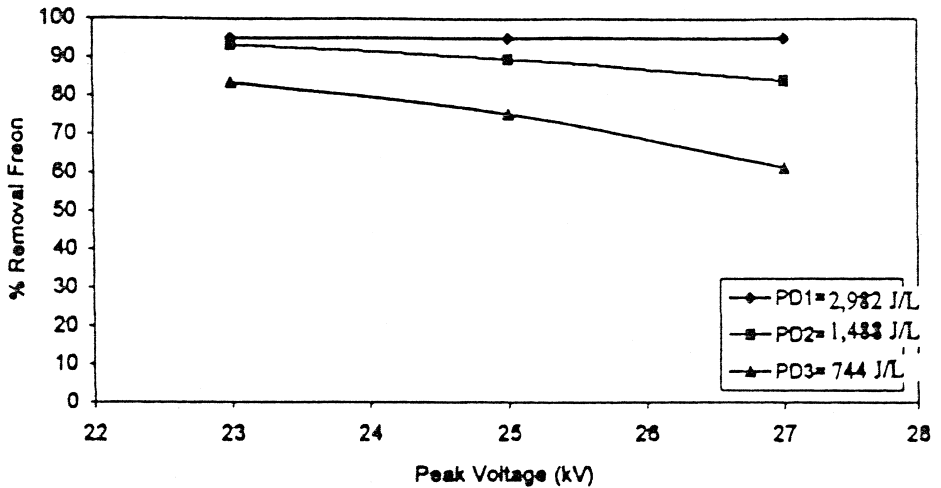


Fig. 13. Halon decomposition in dry air.

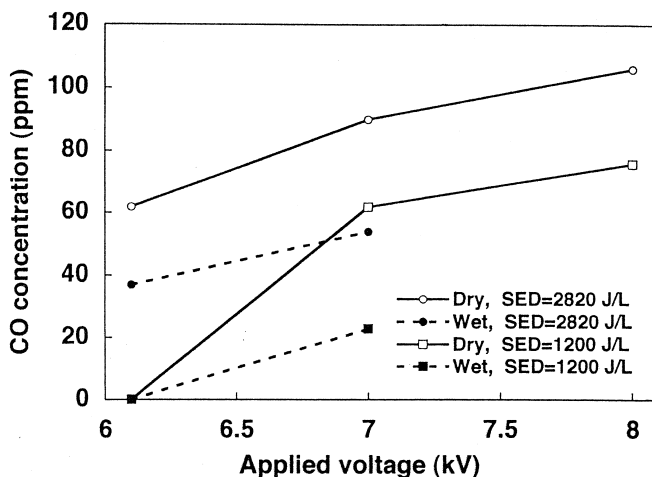


Fig. 14. CO concentration in dry air and in humidified air.

plasma) which is a preferred plasma operation, especially with regard to hard-to-decompose HAPs [4,6]. However, the hard plasma produces a large amount of inorganic byproducts.

3.3.9. Halon decomposition

Fig. 13 shows the Halon FC-12B (CClBrF_2) decomposition efficiency in dry air, while the SED was kept constant at three levels (744, 1448, and 2982 J/l) using the pulsed corona reactor [7]. With a high SED of 2982 J/l, halon decomposition efficiency was independent of applied voltage. However, with a low SED of 744 J/l, the

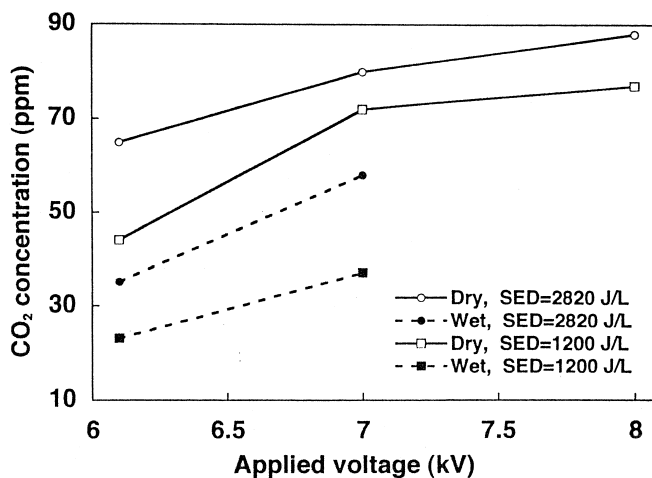


Fig. 15. CO₂ concentration in dry air and in humidified air.

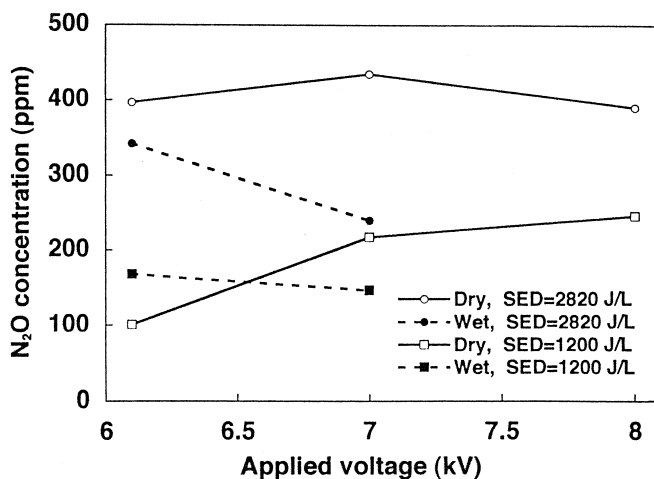


Fig. 16. N₂O concentration in dry air and in humidified air.

decomposition efficiency was 63% at 27 kV and increased to 83% at 23 kV despite the constant SED. It is clear that as the SED decreased, halon decomposition efficiency decreased with increased voltage, i.e. soft plasma is preferred.

3.3.10. Inorganic byproducts

Fig. 14 shows the CO concentration for the case of tetrachloroethylene decomposition in dry air and in humidified air when the SED was constant at two levels (1200 and 2820 J/l). It is clear that the soft plasma was a preferred operation to minimize the CO concentration in dry air and in humidified air. Figs. 15 and 16 also show the CO₂ and N₂O concentrations under the same conditions described above. Data showed that inorganic byproducts were minimized by soft plasma although N₂O data in humidified air showed some contradiction. This was attributed to the reduction of decomposition efficiency due to local breakdown with moisture.

4. Conclusions

Experimental data were replotted to examine HAP decomposition with constant SEDs. The results indicate that the HAP decomposition rate is not constant even with a constant SED but it is a fraction of residence time for most HAPs tested. The soft plasma operation is preferred for most of the HAPs, considering decomposition efficiency and minimizing inorganic byproducts. This concept can lead to the optimization of nonthermal plasma for the treatment of HAPs.

Acknowledgements

I would like to acknowledge Dr. Shigeru Futamura, Dr. Aihua Zhang, Dr. Atushi Ogata and Dr. Koichi Mizuno at National Institute for Resources and Environment for valuable discussion. This study was partly supported by the International Joint Research

Grants sponsored by the New Energy and Industrial Technology Development Organization (QVEDO), the Ministry of International Trade and Industry (MITI) of Japan.

References

- [1] T. Yamamoto, *J. Electrostat.* 40 (1997) 227–238.
- [2] S. Futamura et al., *IEEE Trans. Ind. Appl.* 34 (1998) 967–974.
- [3] T. Yamamoto et al., *Proc. NEDO Symp.*, Univ. of Tokyo, Tokyo, 1996, pp. 15–32.
- [4] T. Oda et al., *Proc. IEEE-IAS Annu. Meeting*, Denver, CO, 1994, pp. 1563–1569
- [5] T. Yamamoto et al., *IEEE Trans. Ind. Appl.* 28 (1992) 528–534.
- [6] T. Yamamoto et al., *Proc. 2nd Int. Symp. on Nonthermal Plasma Tech. for Pollution Control*, Salvador, Brazil, 1997.
- [7] G. Saithamoorthy et al., *Proc. 4th Int. Conf. on Adv. Oxid. Tech. for Water and Air Remediation*, Orlando, FL, 1997.