Non-thermal Plasma Processing for Dilute VOCs Decomposition Combined with the Catalyst

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Abstract: Atmospheric pressure non-thermal plasma process combined with the new catalyst for volatile organic compounds, especially dilute tricholorethylene (TCE) in synthesized dry air is discussed. TCE decomposition efficiency is very good and more than 95% of TCE is easily decomposed at SED (specific energy density) of 18 Joule/litter which is practical value. However, more discharge energy is necessary to the full oxidization, which means that almost carbon included in TCE can be oxidized to carbon oxide (CO and CO_2) named as the carbon balance. For better carbon balance, SED of the electric discharge is more than 90 J/L which is pretty large. We would like to find more efficient catalyst for that purpose. The decomposition mechanisms by the non-thermal plasma should be clear and the new catalyst which decomposes the ozone and TCE simultaneously will be developed. Byproduct analysis suggested that nonthermal plasma direct process generates DCAC byproducts from TCE but the catalyst process do not generates any DCAC and the generation of only TCAA is detected indicating the atomic oxygen radical can oxidize TCE to TCAA only. The new catalyst is inserted in the plasma reactor where the diameter of the discharge electrode is thin and the catalyst can be filled in that space between the electrode and the tube wall. The electric field effect and radical life time effects are examined also.

Keywords: Non-thermal plasma, trichloroethylene, catalyst, plasma reactor

1 INTRODUCTION

The atmospheric pressure non-thermal plasma is very effective technique in decomposing various kinds of toxic materials, especially gaseous contaminants (famous gasses of them are volatile organic compounds including chloro-fluorocarbons: CFC which destroy the ozone layer in the stratosphere) in the air, SF_6 or some oxides such as nitric oxide in the combustion flue gas. Late Prof. Senichi Masuda proposed PPCP (pulsed plasma chemical processing) and SPCP (surface discharge plasma chemical processing) [1,2] whose technologies were originated from the Electrostatic Precipitation technology. As the $DeNO_x$ process, Keizo Ohtsuka and others reported the oxidation process of nitric monoxide to nitric-dioxide in the ESP occurs if the Corona discharge current is large enough compared with the typical operation conditions but Hitachi group gave up that technology as the $DeNO_x$ technology because the electric discharge power consumption is much higher than that of ESP operation because of DC discharge needs rather high power[3]. Masuda and Mizuno used pulse discharge corona to decompose nitric oxide in the combustion flue gas by using pulse discharge plasma which generate strong plasma with very small discharge energy[4,5]. Very short pulse can generate high energy electrons but ion heating is not sufficient because of short time of the applied high electric field. Various those experiments were summarized by Chang, Lawless and Yamamoto[6]. Yamamoto and others in RTI group also investigated the decomposition of VOCs. They reported the first decomposition of dilute CFC-113 in the air by using pulse-excited non-thermal plasma in the batch process. At that time, continuous gas flow process could not decompose CFC-113[7]. The authors succeeded in decomposing CFC-113 more than 99% in continuous flowing condition by using the surface discharge non-thermal plasma reactor where the input discharge power is much enhanced[8]. After that report, the authors tested the non-thermal plasma decomposition for various kinds of VOCs in air and all organic compounds can be decomposed where PFC (perfluoro carbon, such as CF_4, C_2F_6 etc)[9,10]. Now many researchers reported VOCs decomposition by using the non-thermal plasma[11,12]and review paper is also exists[13].

At present, main targets of the non-thermal plasma application for VOCs decomposition research are how to improve the energy efficiency compared with the conventional treatment process and how to remove toxic byproducts as the post-process. The authors investigated the plasma reactor configuration for realizing the high energy efficiency and convinced that the short gap discharge reactor with the needle-type discharge electrode is important parameters for better energy efficiency. However, the improvement of the energy efficiency by modification of the plasma reactor is not enough and further energy efficiency improvement should be done. For that purpose, some researchers would like to check the catalyst combination process. The authors also investigated various kinds of catalysts, such as titania (TiO_2), vanadium-oxide (V_2O_5), tungsten oxide (W_2O_3) and others. Einaga [12] group reported the usage of the manganese-dioxide catalyst as the ozone decomposer and that will enhance the VOCs decomposition efficiency. We also tested manganese-dioxide to decompose the ozone which is main byproduct and poison for us[14]. Recently manganese-dioxide supported alumina spheres which have large surface area were tested as the catalyst which works even at the room temperature to decompose the ozone. At that ozone decomposition, VOCs are also well-decomposed to carbon-oxide and maybe water. Those test results will be discussed in this paper

2 EXPERIMENTAL

2.1 Experimental System

The experimental system used is shown in Fig. 1 which is the same as that reported last time. The balance gas is the synthesized air (4 nitrogen + 1 oxygen without carbon-dioxide and others). As the VOCs, typically trichloroethylene (TCE: CCl_2CHCl). Two main processes, Direct Process and Indirect Process are still tested together. For the first case (Direct Process), synthesized dry air passes TCE (TCE injection syringe with a low flow pump with heater for evaporation of TCE) and flow into the plasma reactor. If need, plasma processed TCE-contaminated air passes through the catalyst in the Figure (with the catalyst). For the second case (Indirect Process), only the pure synthesized air passes through the reactor and mixed the TCE-contaminated air after the reactor. In this case, if need, the mixed air passes through the tube filled with the catalyst after the mixing process. The GC-MS (Shimadzu GCMS-PQ5000A) with 25 m long capillary column and normal FTIR (Shimadzu Prestage 21) with multi-reflecting long absorption test cell are used for byproduct analysis. The UV absorption ozone meter and the chemical luminescence NO_x meter are also equipped. Main contaminant gas is the trichloroethylene (TCE: $CCl_2{=}CHCl$ whose molecular weight is 131.39 and boiling temperature is 87 ℃). Formaldehyde (HCHO) is also examined.

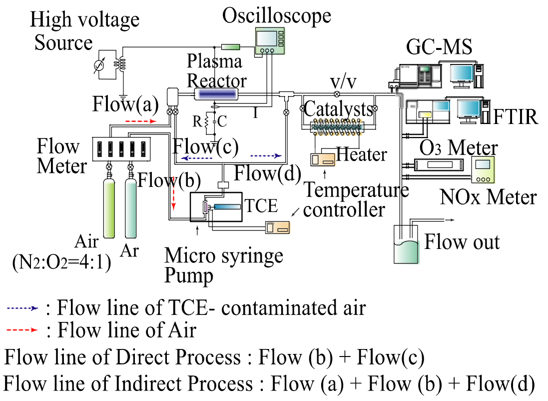


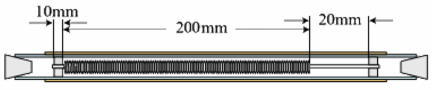
Fig. 1 Experimental system used in the paper

2.1 Catalyst

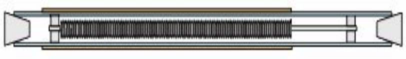
Manganese-dioxide supported alumina spheres were manufactured and tested. Host material (alumina sphere used) is neobeed (made by Mizusawa Chemistry: 2 or 3 mm in diameter) and manganese-dioxide weight ratio to the total catalyst is 5% where total specific surface area is about 190 m^2/g that manganese-dioxide supporting process was done by ourselves. We tested several kinds of manganese-dioxide ratio and several different host materials and concluded that the upper catalyst is the best among them.

2.3 Plasma Reactor

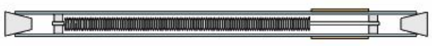
The typical plasma reactor tested is a bolt-type barrier reactor which is made of Pyrex glass tube with the inner diameter of 16.8 mm and the discharge gap of 0.4 mm between the inner glass tube wall and top of the bolt. The discharge length is 20 cm long and the total length of more than 300 mm which is shown in Fig.2 as (a). If need, the catalyst is stored in another glass tube which can be heated up for recovery. Other two new type is also manufactured. One is shown in Fig. 2(b) where the outer ground electrode is cu and covers only the discharge area. On the other hand, conventional type A has long ground electrode which covers all catalyst filling area in Fig.2 (a). In other word, the electric fields is applied to the catalyst for type (a) but not for type (b). As the special reference, type (c) was also tested where no electrode for the plasma region and the outer ground electrode covers only over the catalyst area meaning that the catalyst has no influence of the electric field in type (b) but the electric field is applied only over the catalyst and no plasma will be generated in the plasma region. In the case of outer catalyst, the total weight of the catalyst is 1,000 mg.



(a) type A (all area covered with earth film)



(b) type B (earth plate covers only bolt area



(c) type C (earth film covers only catalyst area)

Fig. 2 Catalyst position and discharge area

The discharge energy is measured by typical Lissajous' method or the direct integration of the product of the current and voltage recorded by the digital oscilloscope.

3 EXPERIMENTAL RESULTS AND DISCUSSIONS

3.1 Electrical Power Consumption

The discharge power consumption versus the applied voltage for three reactors shown in Fig. 2 is shown in Fig. 3 with/without the catalyst. Type A without the catalyst (typical plasma reactor used) consumes the largest discharge energy but the catalyst effect is very small. Type A with the catalyst consumes the 2nd largest energy as shown in the Figure. The discharge power consumption for type B is a little bit smaller than that for type A in general which is easily understood that the catalyst zone is also applied voltage in type A and some power loss by that field may be such as surface discharge loss and surface leakage current loss. If the catalyst exists between the two electrodes, the electric field in gas area should be high and some discharge can occur easily because the dielectric constant of the catalyst is much larger than the gas. That causes surface discharge loss. However, the energy loss in the catalyst is much smaller than that estimated or rather negligibly small. The power loss for type C is also very large compared with our assumption value. As the edge of the ground plate is sharp, the electric field concentration at that edge is large and that will cause the discharge inside the glass tube where the discharge electrode is fine. If the catalyst filled in that space between the glass and the thin electrode that is easily charged and stops the discharge which explains why the catalyst filled reactor has small discharge energy consumption. However, the energy loss for type C is rather reverse but the loss difference is very small (maybe negligible). This suggests there exists some energy loss factor not only in the gap space between the discharge electrode and the glass wall but also other part, surface loss discharge and so on.

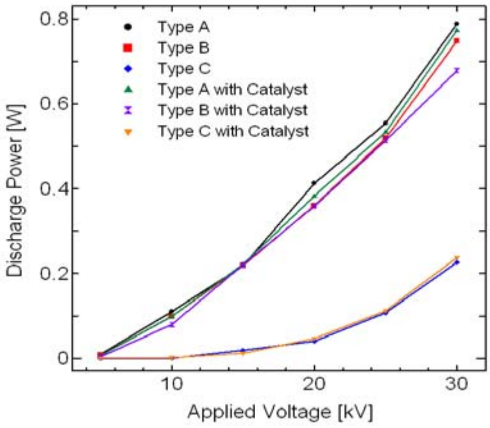


Fig. 3 The discharge power consumption for different reactors

3.2 TCE (Trichloethylene) Decomposition

TCE decomposition efficiency (how many percentage of the original TCE is removed) versus specific discharge energy (SED = discharge energy [W] / gas flow rate [litter/second] = [J/L]) for different reactors is shown in Fig. 4. The catalyst affects very well to decompose TCE and type B without the catalyst (only the plasma process) where non plasma region is not covered with ground electrode shows the worst performance among 5 different operations. Type A which is also without the catalyst shows second poor performance but rather better than type B indicating the electric field between the glass inner wall and the thin discharge electrode may works to decompose TCE where the mechanism of TCE decomposition is not yet clear. Type A with the catalyst works very well and is always better than type B with the catalyst. The electric field between the glass inner wall and the thin electrode should contribute TCE decomposition. It is very interesting that two-stage reactor (time delay from the plasma to the catalyst is very large) shows a little bit bad performance at small SED but is rather compatible at high SED of more than 30 J/l. Exact discussion about that performance is not yet done but the discharge between the ground electrode and the high voltage outside the glass tube may contribute as energy loss because that cannot contribute the TCE decomposition.

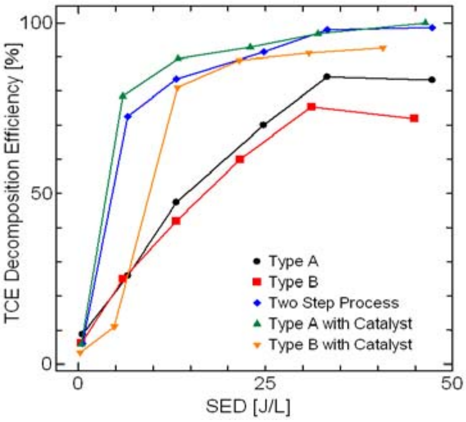


Fig. 4 TCE decomposition efficiency versus discharge energy (SED)

3.3 Byproduct Analysis

Byproduct analysis of TCAA and DCAC produced by the non-thermal plasma process for different conditions is shown in Figs. 5 and 6.

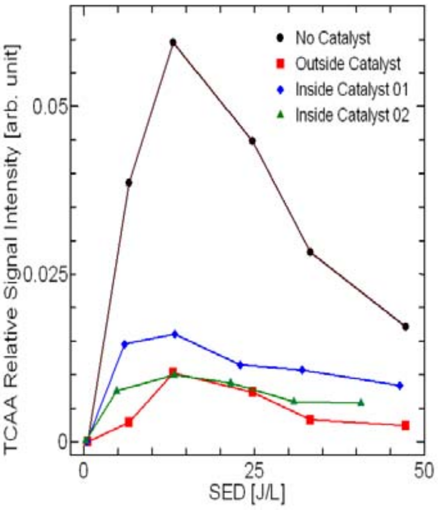


Fig. 5 TCAA byproductsa versus SED

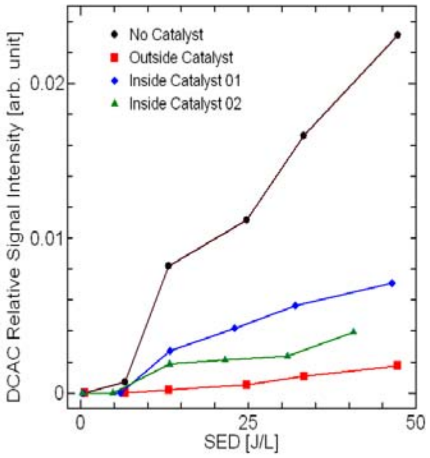


Fig. 6 DCAC byproduct versus SED

No catalyst data (type A without the catalyst) suggested that TCAA is generated greatly with the slight plasma reaction and decreases if the discharge power, SED, increases more than 15 J/L. Weak non-thermal plasma oxidizes TCE to TCAA and rather strong non-thermal plasma oxidizes TCE and TCAA further. Oxidation process is not yet clear but maybe atomic oxygen generated by the plasma oxidizes TCE and TCAA. TCAA is trichloro-acetaldehide, (CCl_3CHO), whose molecular weight is 147.4. Similarly, DCAC is dichloro-acetylchloride ($CHCl_2CClO$), whose molecular weight is also 147.4. Their difference is only the position of H and Cl. Outside catalyst (two-stage) process generates the smallest TCAA among four different processes shown in Fig. 5, if SED is small, and the generated amount of TCAA increases a little bit with SED increase. The TCAA decreases gradually, if SED exceeds 15 J/L. Not so large difference of TCAA generation for other type A or type B with the catalyst. In any case, TCAA generation will decreases with the increase of the SED. DCAC increases with the increase of SED in any case but this tendency is the largest for without the catalyst (type A without the catalyst) as shown in Fig. 6. Two-stage process (in the figure, that is shown as outer catalyst) generates the smallest DCAC among four different plasma processes as shown in Fig. 6. Chlorine generation versus SED is very instructive which is shown in Fig.7 where the large amount of chlorine is produced by two-stage plasma process and type A without the catalyst generates smallest chlorine among four processes suggesting that the cool catalyst-(manganese-dioxide) decomposition of the ozone at room temperature decomposes TCE with a large amount of chlorine generation but rather small amount of phosgene is produced. Concerning with the phosgene generation, type A without the catalyst produces the largest amount of phosgene among four plasma processes as shown in Fig.8. Comparison with Figs. 7 and 8 suggests that the plasma process changes TCE to phosgene but the manganese-dioxide catalyst works to remove chlorine (Cl_2) from TCE. For both non-thermal plasma process and catalyst process, main oxidation process should depend on the oxygen attachment caused by the atomic oxygen radical effect. However, in the plasma region, bonding condition may be changed from the catalyst effect. The real oxidation process on the catalyst surface is not yet known but some absorption effect on the TCE should affect the oxidation performance. There is one opinion that the ozone decomposes on the manganese-dioxide catalyst surface and atomic oxygen is produced. That atomic oxygen oxidizes VOCs (volatile organic compounds). In that model, that atomic oxygen is also generated in the plasma which was already convinced by authors by using TALIF technique. This simple model cannot explain the difference between the plasma process and the ozone-decomposition process on the catalyst. In this case, the difference should be dependent on other electrons and ions effects produced in the plasma but we have no evidence on that. Another explanation is that catalyst absorbs TCE and concentration of TCE on the catalyst surface becomes large. When the ozone come to that absorbed TCE, that ozone decomposes and oxidizes TCE simultaneously. In this case, still it is unknown why the chlorine molecule can be removed from TCE. For phosgene generation, it was assumed that the atomic chlorine radical attacks TCE (double bonding) to $CHCl_2CCl_2$* which will be oxidized by oxygen molecule and finally becomes phosgene and dichloromethane with emission of atomic chlorine (that works as the catalyst).

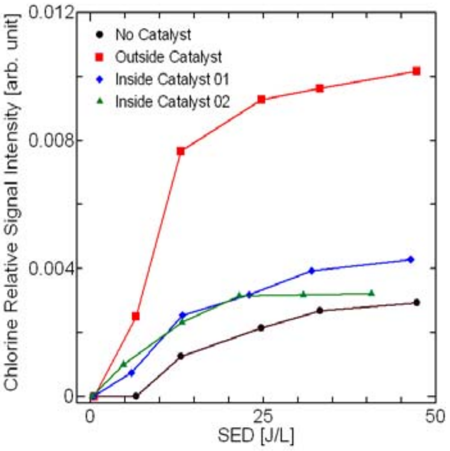


Fig. 7 Chlorine generation by the process versus SED

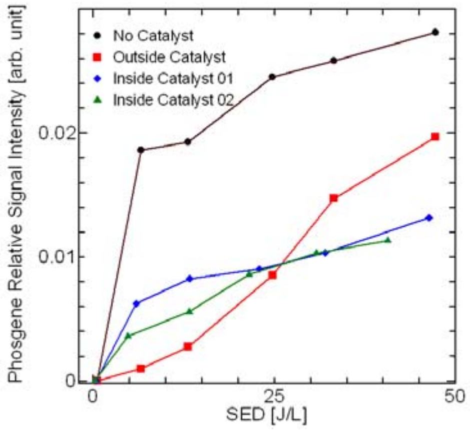


Fig. 8 Phosgene generation versus specific discharge power consumption (SED)

The generation of carbon-monoxide for different processes versus discharge energy (SED) is shown in Fig. 9. Outside catalyst (the catalyst is located at the down flow of the reactor; old style) process produces the largest amount of carbon-monoxide and inside catalyst process (catalyst is filled in the same tube of the reactor) generates the smallest amount of carbon- monoxide. In every case, carbon-monoxide increases with the increase of the SED till SED of 50 J/L. On the other hand, production of carbon-dioxide is rather different. The inside catalyst process (reactor is type filled with the catalyst) generates the largest amount of carbon-dioxide among 4 different processes and without catalyst process or the outside catalyst process generates smaller than other inner catalyst processes. In any case, the generation of the carbon-dioxide is rather saturated with the increase of SED.

3.4 Carbon Balance

The carbon balance versus SED for different reactor systems (practically proportional to the sum of carbon-monoxide and carbon-dioxide) can be discussed from Fig. 9 (carbon-monoxide) and carbon-dioxide (not shown in this paper which will be shown at the Conference).

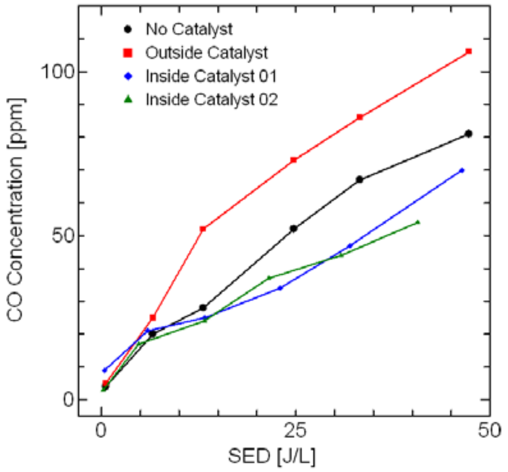


Fig. 9 Generation of carbon-monoxide versus SED for different processes

The superiority of the catalyst (in the plasma reactor) is apparently shown[15]. The carbon balances for two processes (types A and B with no catalyst in the reactor) are not good and less than 50 % even SED is close to 50 J/L. On the other hand, those for three processes with the catalyst (types A or B with the catalyst inside the reactor or type A with the catalyst at the down flow) are very good and more than 100 % which may be caused calibration value error. It is not so easy to make clear difference between type A and type B with the catalyst from the experimental results. Concerning with the carbon monoxide production, type A and type B with the catalyst are well and two-stage process generates the largest amount of carbon-monoxide (that is not preferable for human health).

4 CONCLUSIONS

Low concentration trichloroethylene of 100 ppm in air was decomposed by the non-thermal plasma reactors with/without the catalyst (manganese-dioxide supported alumina spheres). The position of the catalyst, just after the plasma region or with several meter distance between the plasma region and the catalyst was examined concerning with the decomposition efficiency, byproducts and carbon balance and following results are obtained.

1. Carbon balance for plasma process with the catalyst is very well for three different plasma systems and the difference is pretty small concerning with the catalyst position and the electric field in the catalyst area.

2. For TCE decomposition efficiency, type A with catalyst where the electric field is also applied in the catalyst zone just after the plasma area, show best performance versus consumption energy but the two-stage reactor (plasma region and the catalyst is far separated) shows also very good performance concerning with the TCE decomposition efficiency.

3. TCAA and DCAC byproducts are rich in the plasma process without the catalyst but the two-stage process generates smallest TCAA and DCAC.

4. Concerning with the chlorine production, no catalyst process is the best and the two-stage process is very bad compared with other two with the catalyst. However, the phosgene generation is very small for type A and type B with the catalyst, which is recommended.

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REFERENCES

1. Masuda, S. Akutsu, K. Kuroda, M. Awatsu, A. and Shibuya, Y. A ceramic-based ozonizer using high-frequency discharge. IEEE Trans. Ind. Appl., 1988(24): 223-231.
2. Masuda, S. Nakao, H. Control of NO_x by positive and negative pulsed corona discharges, Conference Records of the IEEE/IAS Annual Meeting, Denver. (1986), 1173–1182.
3. Ohtsuka, K. Yukitake, T. and Shimoda, M. Oxidation characteristics of nitrogen monoxide in Corona discharge field, J. Inst. Electrost. Jpn., 9, 1985(5): 346-351 (in Japanese).
4. Masuda, S. Nakao, H. Control of NO_x by positive and negative pulsed corona discharges, Conference Records of the IEEE/IAS Annual Meeting, Denver. (1986), 1173–1182.
5. Mizuno, A. Clements, J.S. Davis, R. H. A device for the removal of sulfur dioxide from exhaust gas by pulsed energization of free electrons, Conference Records of the IEEE/IAS Annual Meeting. (1984), 1015-1020.
6. Chang, J. S. Lawless P.A. and Yamamoto, T. Corona Discharge Processes, IEEE Trans. Plasma Sci.,1991(19): 1152-1166.
7. Yamamoto, T. Kramanathan, R. Lawless, P. A. Ensor, D. S. Newsome, J. R. Control of volatile organic compounds by an AC energized ferroelectric pellet reactor and a pulsed corona reactor, IEEE Trans. Ind. Appl., 1992(28): 528–534.
8. Oda, T. Takahashi, T. Nakano, H. Masuda, S. Decomposition of fluorocarbon gaseous contaminants by surface discharge-induced plasma chemical processing, IEEE Trans. Ind. Appl. 1993(29): 787–792.
9. Oda, T. Yamashita, R. Takahashi, T. and Masuda, S. Decomposition of gaseous organic contaminants by surface discharge plasma chemical processing – SPCP, IEEE Trans. Ind. Appl., 1996 (32): 118-124.

10. Oda, T. Yamashita, R. Takahashi, T. and Masuda, S. Atmospheric pressure discharge plasma decomposition for gaseousair contaminants–trichloroethane and trichloroethylene, IEEE Trans. Ind. Appl., 1996(32): 227-232.
11. Ogata, A. Shintani, N. Mizuno, K. Kushiyama, K. Effect of water on benze12512ne decomposition using packed-bed plasma reactor, Proceedings of the Asia-Pacific Workshop on Advances in Oxidation Technology, Tsukuba, (1998), 91–96.
12. Einagar, H. Ibusuki,T. and Futamura, S. Performance evaluation of hybrid systems comprising silent discharge Pasma and catalysts for VOC Control, IEEE Trans. Ind. Appl., vol.37, (2000), 1476-1482.
13. Urashima, K. Misaka, T. Ito, T. and Chang, J.S. Destruction of volatile organic compounds in air by a superimposed barrier discharge plasma reactor and activated carbon filter hybrid system, J. Adv. Oxid. Technol., 2002(5): 135-140.
14. T. Oda, T. Takahashi and K. Yamaji. TCE Decomposition by the Nonthermal Plasma Process Concerning Ozone Effect. IEEE Trans. Ind. Appl., vol. 40: 1249-1256 (2004).
15. Oda, T. Kuramochi, H. and Ono, R. Non-Thermal Plasma Process for Dilute Trichloroehtylene Decomposition Combined with Catalyst Position Effect of Plasma Reactor and Catalyst, Proc. IEEE/IAS Ann. Meeting, Edmonton, in October, (2008).