

# Plasma-Catalysis for Toluene destruction in one pass process

Graciela Prieto, *Member IEEE*, Oscar Prieto, Carlos R. Gay, Tomoyuki Kuroki, Masaaki Okubo, Toshiaki Yamamoto, *Member IEEE*

**Abstract**—A Chemical Process can be conducted at cold temperatures by using the techniques of Nonthermal Plasma that enable operations at room temperatures and atmospheric pressures. The main goal of the present investigation is the development of a process for the treatment of gaseous effluents in industrial painting factories or graphical printings facilities. The reactor is fed with a gaseous stream rich in toluene, as the major representative of the emitted Volatile Organic Compounds (VOCs). A high gaseous flow rate with a low toluene concentration is processed employing an intense electric field from a cold plasma as a source of energy. The development of this practical and effective process that combines the effect of the cold plasma with the effect of adsorption followed by chemical catalytic reactions facilitates the achievement of high levels of toluene destruction enabling the compliment of the stringent legislation for the VOCs contents in flue gases from stationary sources.

**Index Terms**— Nonthermal plasma, Toluene destruction, Catalysis assisted nonthermal plasma

Manuscript received April 17, 2009.

Graciela Prieto. Author was with the Department of Mechanical Engineering, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, 599-8531, Japan, on leave from the Department of Chemical Engineering, National University of Tucuman, Argentine Republic, Ave. Independencia 1800, (4000) San Miguel de Tucuman, Argentina, (email: gprieto@herrera.unt.edu.ar).

Oscar Prieto. Author is with the Department of Chemical Engineering, National University of Tucuman, Argentine Republic, Ave. Independencia 1800, (4000) San Miguel de Tucuman, Argentina, (email: oprieto@herrera.unt.edu.ar).

Carlos R. Gay. Author is with the Department of Chemical Engineering, National University of Tucuman, Argentine Republic, Ave. Independencia 1800, (4000) San Miguel de Tucuman, Argentina, (email: cgay@herrera.unt.edu.ar).

Tomoyuki Kuroki. Author is with the Department of Mechanical Engineering, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, 599-8531, Japan, (email:kuroki@me.osakafu-u.ac.jp).

Masaaki Okubo. Author is with the Department of Mechanical Engineering, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, 599-8531, Japan, (email:mokubo@me.osakafu-u.ac.jp).

Toshiaki Yamamoto. Author is with the Department of Electrical Engineering, Tokyo City University, 1-28-1 Tamatsutsumi, Setagaya-ku, Tokyo 155-8557, Japan, (email:yamamoto@ee.musashi-tech.ac.jp).

## I. INTRODUCTION

VARIOUS technologies have been investigated to remove the Volatile Organic Compounds (VOCs) produced in a great extent by stationary sources like the painting and printing industries. The concentration of VOCs emitted by these industries are in the order of one hundred part per million, which makes the traditional incineration processes very costly due to the necessity of heating enormous amounts of flue gas for burning only small amounts of pollutants. In the search for better VOCs control strategies, more practical and cost effective, the adsorption processes are being considered. In a first step the flue gases are adsorbed during a long time, and the second step consists in treating the concentrated gases with the conventional after treatment technologies such as thermal decomposition, catalytic decomposition, and the novel technologies such as nonthermal plasma, and plasma assisted catalysis or the hybrid techniques that combine plasma with adsorbents [1-10].

For the adsorption processes the materials employed are activated carbon, alumina and zeolites, all of them disposed or destroyed after use. Some other materials can be regenerated by heating or adding steam or by treatments that combine pressure and temperature such as the PSA (Pressure Swing Adsorption) or the TSA (Temperature Swing Adsorption), all of them requiring additional costs for the auxiliary services needed.

The techniques of nonthermal plasma work at ambient temperature and hence, have as an advantage the no need of heating. The main goal of the present research is to develop a flue gases aftertreatment process for the printing and painting facilities that have in common the use of VOCs as solvents. The reactor is feed with gaseous stream rich in toluene as the representative of VOCs. A high flow rate, in the range of 20-60 L/min, with a low toluene concentration, in the range of 20-300 ppm is processed in a nonthermal plasma reactor equipped with two surface discharge electrodes and connected in series with a second reactor packed with a bed of a hydrophobic adsorbent material. The development of this process, practical and effective that combines the effect of the intense electric field from the nonthermal plasma with the effect of adsorption-catalytic reaction, makes possible to get high efficiencies in converting the VOCs up to levels that can reach the stringent regulations.

## II. EXPERIMENTAL SETUP

### Experimental Methodology

The methodology developed consists in feeding the plasma tubular reactor with a square section with a gaseous mixture of air-toluene for about 5 minutes until stationary conditions, controlled by sampling at the reactor outlet and analyzing by GC chromatography. Once the stationary conditions have been reached, another reactor with the adsorbent material is placed in series with the plasma reactor, named the catalytic reactor. Nonthermal plasma is generated and two samples are taken, one at the exit of the plasma reactor and the other at the exit of the catalytic reactor. The samples are collected every 5 minutes during 1 hour of experimental run. The purpose of sampling before the catalytic reactor is for evaluating only the plasma effect. Sampling after the catalytic reactor is for evaluating both, the plasma effect and the catalytic adsorption-reaction effect. Both samples are taken at the same time with 2 syringes of 5000 microliters for gas sampling for analysis with a Gas Chromatograph.

The adsorbent material is a hydrophobic zeolite in pellets of 1/16 inches, packed in a reactor of 4 cm in diameter and 2 cm in height, in between two copper metallic meshes able to contain 17 grams of the zeolitic material.

The reactor flue gases were analyzed by a gas chromatograph and a gas analyzer (Horiba Ltd. PG-235, VIA-510, and FIA-510). The compounds analyzed were: carbon monoxide, carbon dioxide, toluene, and total hydrocarbons.

The schematic of the experimental setup is displayed in Fig. 1, and details of the surface discharge electrode are displayed in Fig. 2.

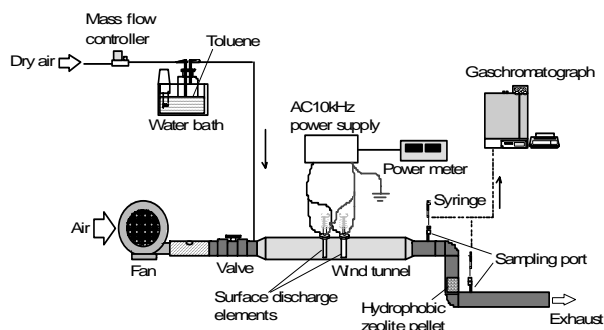


Fig.1. Schematic of the experimental setup .

### Experimental conditions:

- Primary input power: Primary Voltage: 100 Volt, and Primary Power: 50-60 W
- Peak to peak voltage: 6~10 kV
- Frequency: ~10 kHz
- Maximum input: 100 V, 1.3A, 90W
- Walls temperature: about 30-50 degrees Celsius.
- Flow rate range (L/min): 20-60

- Concentration range (ppm): 20-300
- Speed Meter (m/sec) (ANEMOCHECK, KANOMAX Model 6413) equivalence according to the Flow Rate (L/min) is: 0.27 (m/sec) = 20 (L/min); 0.53 (m/sec) = 40 (L/min); 0.80 (m/sec) = 60 (L/min); 1.06 (m/sec) = 80 (L/min).

### Experimental setup:

- Gas chromatograph: Shimadzu Co., GC-14B
- Digital power meter: Hioki E.E. Co., 3186
- Adsorbent material: Union Showa K. K., HiSiv 1000 (pellets: 1/16 inch in diameter; pore diameter: 0.6~0.9 nm)
- Blower: Yodogawa Denki Seisakusho Co., Y1
- AC high voltage power supply: Masuda Research Inc., EP-0.2/9
- Surface discharge element: Masuda Research Inc., OC-002

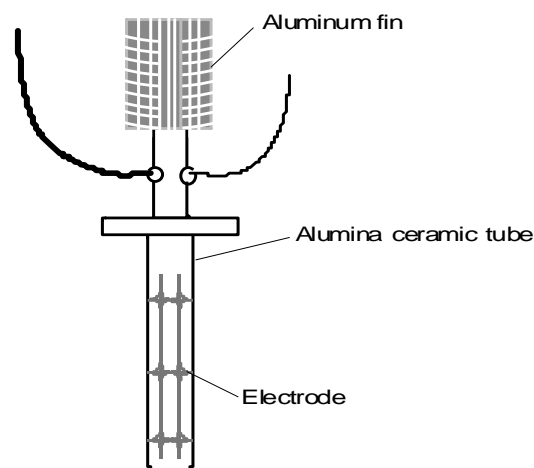


Fig.2. Surface discharge electrode

For the experimental plan a complete factorial experimental design at two levels was used. In this design the parameters assume only two values which are the extremes of the range selected for each one. For calculation of the experimental error, experiments at the conditions of the center of the range for each variable assayed were repeated 5 times [11-13].

The input variables selected were "initial toluene concentration, C", in the range of 20-60 ppm, and the "inlet carrier gas flow rate, FR", in the range of 20-300 L/min.

## III. RESULTS AND DISCUSSION

For the experimental design analysis the selected output variable was the "reaction efficiency %" after one hour of reaction time. This variable is calculated from the toluene

concentration measured upstream and downstream the reaction zone.

$$Efficiency = \frac{InitialConcentration - FinalConcentration}{InitialConcentration} \cdot 100$$

The Efficiency will be named:

Y60(OP) = Efficiency measured at 60 min, after the reaction initiation (only Plasma)

Y60(PA) = Efficiency measured at 60 min, after the reaction initiation (Plasma-Adsorption)

Table I shows the values assumed for the input operating variables: Inlet flow rate (FR), measured in (L/min), Initial Toluene concentration (C), measured in (ppm), and the values obtained for the output variable, the Efficiency, expressed in (%), and calculated as a function of the toluene concentration measured at the exit of each reactor.

TABLE I  
VALUES OBTAINED FROM THE EXPERIMENTAL DESIGN

run	FR [L/min]	C [ppm]	Y60(OP) [%]	Y60(PA) [%]
1	20	20	46,699	87,884
2	60	20	37,293	77,916
3	20	300	34,598	55,058
4	60	300	11,339	19,834
5	40	160	23,430	59,209
6	40	160	27,313	54,891
7	40	160	30,260	54,427
8	40	160	25,183	52,704
9	40	160	39,073	45,253

The statistical analysis of the present experimental results express that when only plasma is employed, the variable concentration has a marked negative effect, which means that the Efficiency decreases when concentration increases from 20 ppm to 60 ppm. From this point of view, these results would indicate the convenience of working with the lowest values of initial toluene concentration.

Analyzing the effect of the flow rate, it can be observed that when it increases the efficiency considerably decreases, as it was expected because an increase in the flow rate means a decrease in the residence time of the reactants inside the reactor.

Both effects are powered when besides the plasma reactor, the catalytic reactor is connected in series, and the conclusions

are the same as before, when only the plasma reactor was considered.

For getting the best efficiencies in converting Toluene, it would be convenient to work with the minimum flow rate and the minimum toluene concentration in the feed employing the system which combines the plasma reactor with the adsorbent-catalytic reactor.

The statistical analysis of the experimental design enables us to obtain the empirical model for the Efficiency as a function of parameters flow rate (FR) and initial toluene concentration (C) and the interaction among them, if there exists.

When working only with plasma the model is:

$$YOP(60\text{ min}) = 30.58 - 9.51 \cdot C - 8.17 \cdot FR - 3.46 \cdot FR \cdot C$$

When working with the combined system, plasma-catalyst the model is:

$$YOP(60\text{ min}) = 56.35 - 22.73 \cdot C - 11.30 \cdot FR - 6.31 \cdot FR \cdot C$$

These models can be represented, each one, by a response surface graphic. Due to the similarity of both models the surface responses are almost overlapped and the surface for the system plasma-adsorption is over the surface for the system only plasma. Figure 3 shows the response surface for the Efficiency in the system plasma-adsorption.

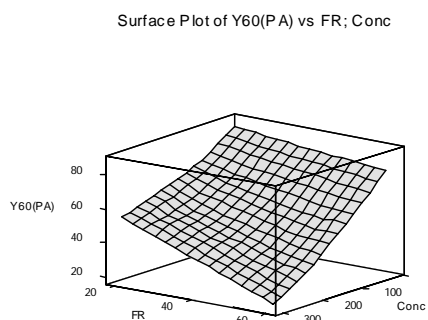


Fig. 3. Response surface for the Efficiency in the system plasma-adsorption

Figure 4 shows the graphic for the Efficiency as a function of time when the process is operated in two stages, what means the catalytic reactor connected in series with the plasma reactor (plasma-adsorption). Figure 5 shows the graphic for the Efficiency as a function of time when only the plasma reactor is considered. It is observed in both figures that after one hour of experimental range the system reaches the steady state and this is the reason why one hour is the reaction time selected for the evaluation of results. Both graphics clearly show that the higher efficiencies for toluene destruction are

obtained for the lower flow rates (higher residence times) and for the lower concentrations.

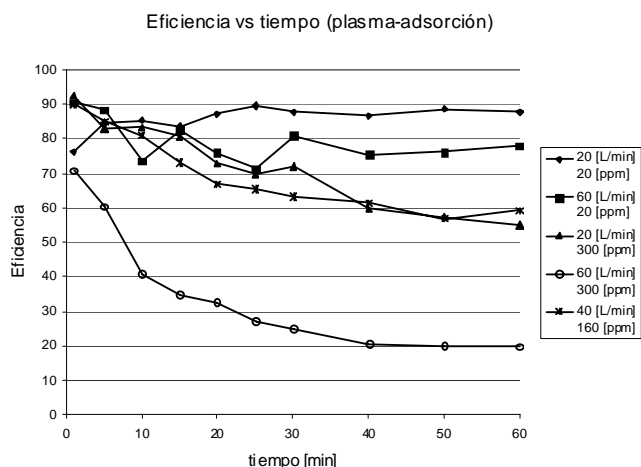


Fig. 4. Efficiency (%) as a function of the time elapsed in the run for the different combinations of Flow Rates and Toluene initial Concentration. System plasma-adsorption.

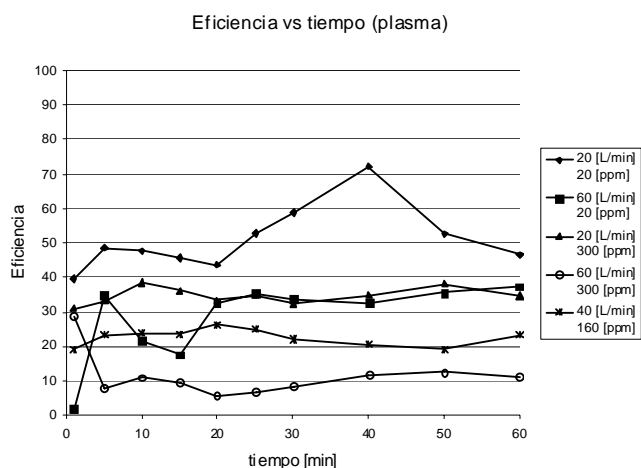


Fig. 5. Efficiency (%) as a function of the time elapsed in the run for the different combinations of Flow Rates and Toluene initial Concentration. System only plasma.

Much more evident is this effect, as it is observed in Fig. 5, for the system plasma-adsorption with chemical reaction, for the higher flow rate and the higher concentration. The importance of comparing both figures is for clearly show the catalytic effect when the catalytic reactor is coupled with the plasma reactor.

#### 4. CONCLUSIONS

A non-thermal plasma tubular reactor equipped with a surface discharge electrodes reach a higher efficiency in toluene destruction (50%), working at ambient pressure and temperature. When another tubular reactor, packed with a pellets of hydrophobic zeolites, is connected in series, the destruction efficiency increases up to 90%. The intense electric field developed into de reactor produces ions, excited molecules, and free radicals that in turn are the initiators of other sequence of chemical reactions. In this way, the system designed that combines the plasma reactor with a catalytic reactor results practical and very effective for the toluene destruction.

#### REFERENCES

- [1] J. Blanco, P. Avila, A. Bahamonde, E. Alvarez, B. Sánchez and M. Romero "Photocatalytic destruction of toluene and xylene at gas phase on a titania based monolithic catalyst", *Catalysis Today*, Vol. 29, 1-4, pp.437-442, 1996.
- [2] G. Taralas, M.G. Kontominas, X. Kakatsios, "Modeling the Thermal Destruction of Toluene (C<sub>7</sub>H<sub>8</sub>) as Tar-Related Species for Fuel Gas Cleanup", *Energy Fuels*, 17 (2), pp.329-337, 2003.
- [3] T. Ibusuki, S. Futamura, Trans. ASME, *J. Solar Energy Eng.*, 126, 2, pp.789-793, 2004.
- [4] K. Urashima, J.S: Chang, *IEEE Trans. Dielect. and Elect. Ins.* 7, 5 pp.602-614, 2000.
- [5] H. Cono, A.A. Berezein, J.S. Chang, M. Tamura, T. Yamamoto, A. Shibuya, S. Hondo, *IEEE Trans. Ind. Applicat.*, 34, 5, pp.953-966, 1998.
- [6] T. Oda, T. Takahashi, T. Yamaji, *IEEE Trans. Ind. Applicat.*, 38, 3, pp.873-878, 2002.
- [7] S.M. Oh, H.H. Kim, A. Ogata, H. Einaga, S. Futamura, D.W Park, *Catal. Letters*, 99, 1-2, pp.101-104, 2005.
- [8] A. Ogata, K. Yamanouchi, K. Mizuno, S. Kushiya, T. Yamamoto, *IEEE Trans. Ind. Applicat.*, 35, 6, pp.1289-1295, 1999.
- [9] D.W. Park, S.H. Yoon, G.L. Kim, H. Sekiguchi, *J. Ind. And Eng. Chem.*, 8, 4, pp.393-398, 2002.
- [10] T. Oda, K. Yamaji, T. Takahashi, *IEEE Trans. Ind, Applicat.* 40, 2, pp.430-436, 2004.
- [11] R.H. Myers, D.C. Montgomery, *Surface Response Methodology: Process and Product Optimization Using Designed Experiments*, Second Edition, John Wiley & Sons, Inc., New York, 2002.
- [12] G.E.P. Box, W.G. Hunter, J.S. Hunter, *Statistics for Experimenters*, John Wiley & Sons, Inc., New York, 1978.
- [13] D.C. Montgomery, *Design and Analysis of experiments*, Third Edition, John Wiley & Sons, Inc., 1991.