

TOLUENE OXIDATION IN A PULSED DIELECTRIC BARRIER DISCHARGE

M. Magureanu*, N. B. Mandache, V. I. Pârvulescu^a

National Institute for Lasers, Plasma and Radiation Physics, 409 Atomistilor Str.,
P.O.Box MG-36, 77125 Bucharest-Magurele, Romania

^aUniversity of Bucharest, Dept. of Chemical Technology and Catalysis, Bd. Regina
Elisabeta 4-12, Bucharest 030016, Romania

A dielectric barrier discharge in coaxial geometry, operated in pulsed mode, was investigated with the aim of total oxidation of volatile organic compounds, in particular toluene. For voltage pulses with amplitudes in the range 23-35 kV and 100 ns duration, the values of the peak discharge current were 90-157 A. The energy per pulse is higher at lower pulse frequency (92 mJ at 96 Hz) and decreases when the frequency is increased (20 mJ at 250 Hz). A less pronounced decrease is observed for the average power, which varies between 9 and 5 W in this frequency range. Toluene oxidation was investigated under the following experimental conditions: voltage pulses amplitude 29 kV, discharge current 109 A, energy per pulse 59 mJ and average power 7 W. Toluene conversions of 60-70% were obtained, roughly independent on flow rate and toluene input concentration. The total oxidation of toluene to carbon dioxide and water is enhanced at low flow rate, or high input energy, and low toluene concentration.

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1. Introduction

Air pollution by volatile organic compounds (VOC) is an issue of major concern due to both environmental and medical reasons. VOC are precursors of photochemical smog and contribute to the greenhouse effect. Some VOC are toxic or even carcinogenic, representing a risk for human health. Conventional techniques for VOC abatement are thermal and catalytic oxidation and carbon adsorption. Thermal and catalytic methods have a drawback in the high operating temperatures required. Catalyst poisoning, followed by deactivation represents also a problem. Carbon adsorption takes place at low temperature, however thermal treatment is also involved when the adsorbed contaminants must be finally destroyed.

As an alternative to conventional VOC abatement techniques, a non-thermal approach, based on non-equilibrium plasmas, receives increasing interest [1-3]. The advantage of these plasmas consists in the ability to generate high-energy electrons, while keeping the background gas close to room temperature. The energetic electrons excite, dissociate and ionize the gas molecules producing chemically active species. Thus, a highly reactive environment is created without spending energy on gas heating as in thermal processes.

This contribution presents results concerning toluene oxidation in a dielectric barrier discharge (DBD). The discharge characteristics were investigated, and the toluene complete oxidation in the plasma was evaluated.

* Corresponding author: monimag@infim.ro

2. Experimental arrangement

The experiments were carried out in a dielectric barrier discharge reactor made of glass, in coaxial geometry (Fig. 1a), of 15 cm length and 2 mm discharge gap. High voltage pulses were generated with the electrical circuit shown in Fig. 1b, based on a coaxial cable of 50 Ω impedance and 10 m length, and a spark-gap switch operating in self-breakdown mode.

The discharge voltage was measured by a high voltage probe (Tektronix P6015) and the discharge current was determined from the voltage fall on the resistor R_C . The voltage and current waveforms were continuously monitored by an oscilloscope (Tektronix TDS 320).

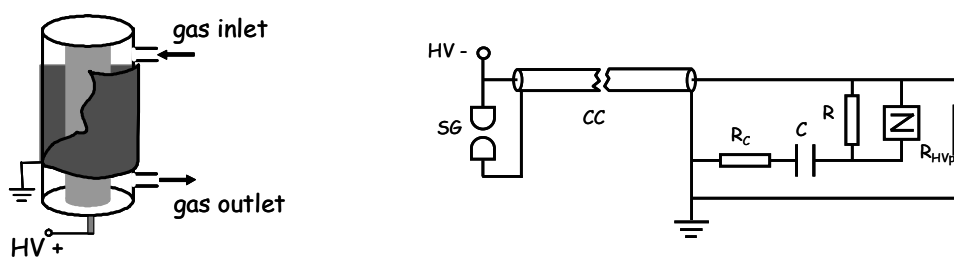


Fig. 1. a. Discharge reactor: $\Phi_i = 8$ mm, $\Phi_o = 14$ mm, $d_{\text{gap}} = 2$ mm, $L = 15$ cm; b. Electrical circuit. CC – coaxial cable (50 Ω , 10 m); SG – self - triggered spark - gap switch; Z – discharge reactor; $R_{\text{HVprobe}} = 100$ M Ω ; $R = 50$ k Ω ; $R_C = 3$ Ω ; $C = 1$ nF.

The experiments were performed at atmospheric pressure, and the working gas was air with small amounts of toluene (400-2250 ppm). The gas flow rate, in the range 110-330 sccm, was regulated by mass flow controllers. A gas chromatograph (HP 5890) with flame ionisation detector (FID) was used to evaluate the toluene conversion in the discharge and to analyse the reaction products. The concentration of CO_2 resulting from complete oxidation of toluene was continuously monitored by a gas analyser (Fischer-Rosemount MLT 4T).

3. Results and discussion

Initially the coaxial cable is charged at a negative potential equal to the applied voltage ($-V_S$). When the spark-gap switch closes the circuit the potential on the cable starts to oscillate and reaches a positive value approximately equal to the applied voltage ($+V_S$). Due to the resistor R and capacitor C , the outer electrode of the discharge reactor is kept at $-V_S$, while the inner electrode follows the potential on the cable. Therefore, the voltage pulses generated have amplitudes of almost twice the value of the applied voltage.

Voltage and current waveforms for several values of the applied voltage are shown in Fig.2.

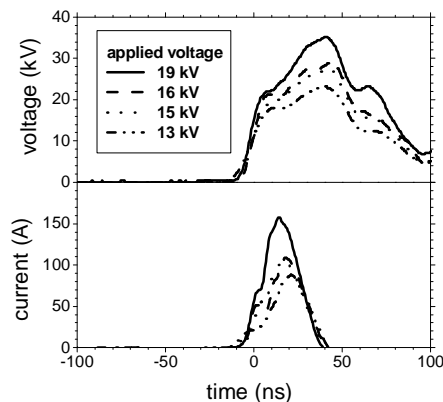


Fig. 2. Voltage and current waveforms.

The rise time of the voltage pulses was 10-11 ns, corresponding to a rise rate of approximately 1.5 kV/ns. The duration of the pulses is equal to twice the time needed for propagation on the coaxial cable, 100 ns. The current pulses have durations of about 50 ns and their amplitude increases with voltage in the range 90-157 A. The shoulder observed on the rising slope of the current pulse, corresponding temporally to the voltage rise, is the capacitive current [4]. The pulse repetition rate is determined by the spark-gap switch operation. In the present experiments, frequencies in the range 96-250 Hz were used.

The energy per pulse, calculated from the time-integral of the current-voltage product (equation 1), and the average power dissipated in the discharge are shown in Fig. 3 as a function of frequency.

$$E_p = \int I(t)V(t) dt \quad (1)$$

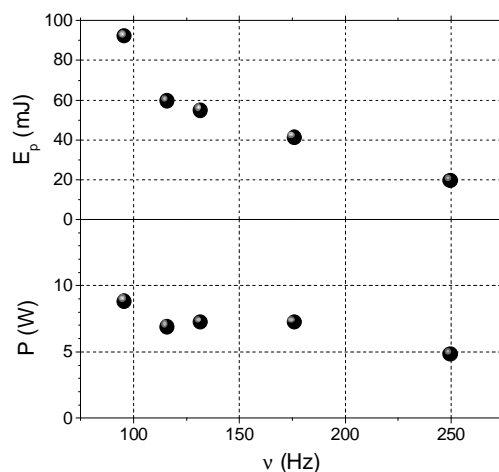


Fig. 3. Energy per pulse and average power in the discharge as a function of pulse frequency.

As the frequency increases the energy per pulse decreases significantly, from 92 mJ at the minimum frequency used, of 96 Hz, to 20 mJ, at 250 Hz. The increase of the pulse repetition rate is obtained by reducing the distance between the electrodes of the spark-gap switch, which leads to lower amplitude of the voltage pulses and, consequently, to lower discharge currents. This interdependency of the pulse frequency on one hand and the discharge voltage and current on the other hand explains the decrease in energy per pulse observed with increasing frequency.

The variation of the average power with pulse frequency is less pronounced, since the increase in frequency compensates to some extent the decrease in energy per pulse. Therefore, the average power shows only a slightly decreasing tendency with increasing frequency, the values ranging between 9 and 5 W.

In the toluene oxidation experiments a pulse repetition rate of 116 Hz was used. The amplitude of the voltage pulses was 29 kV and the peak discharge current was 109 A. In these conditions the energy per pulse was 59 mJ and the average power in the discharge was 7 W.

The toluene conversion in the plasma was evaluated for several gas flow rates in the range 110-330 sccm and toluene input concentrations in the range 415-2227 ppm. The parameter which reflects the ability of plasma to oxidize toluene completely to carbon dioxide and water is the selectivity towards CO₂, defined as the percentage of converted toluene, which was transformed into CO₂ (equation 2).

$$S_{\text{CO}_2}(\%) = \frac{[\text{CO}_2]}{7 \cdot \text{conv} \cdot [\text{C}_6\text{H}_5 - \text{CH}_3]} \quad (2)$$

where $[CO_2]$ is the concentration of carbon dioxide formed, $[C_6H_5-CH_3]$ is the concentration of toluene introduced in the discharge and $conv$ is toluene conversion.

At the discharge power used, the variation in flow corresponds to a variation of input energy (defined as the ratio of average power over flow rate – equation 3) between 0.30 and 0.89 eV/molecule.

$$E_{in} (\text{eV/molecule}) = 13.944 \cdot \frac{P(W)}{\text{flow}(\text{sccm})} \quad (3)$$

The toluene conversion in the discharge and the selectivity to CO_2 are shown in Fig. 4 as a function of flow rate, at a constant toluene input concentration of 1300 ppm.

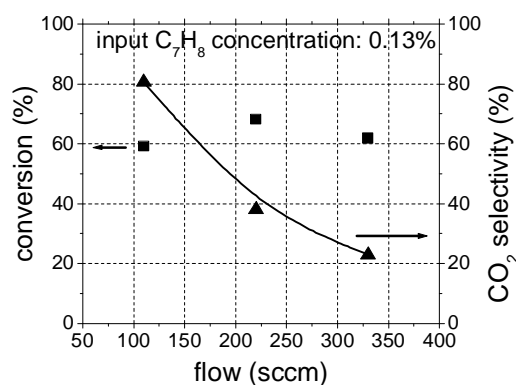


Fig. 4. Toluene conversion and selectivity to CO_2 as a function of flow rate, at constant $C_6H_5-CH_3$ input concentration.

Toluene conversions in the range 60-70% were obtained, roughly independent on flow rate. The selectivity to CO_2 increased significantly towards lower flow rates. At 330 sccm only 23% of the converted toluene was transformed to CO_2 , while at 100 sccm, the selectivity reached 81%. No other hydrocarbons except $C_6H_5-CH_3$ were detected in the effluent gas by gas chromatography. Polymeric deposits were also observed on the walls of the discharge reactor. The selectivity towards these by-products was estimated by weighing the discharge tube before and after the reaction. It increased with decreasing flow rate and increasing C_7H_8 concentration, however it remained below 5% under all experimental conditions. Carbon monoxide was not measured, however it is expected to account for the rest of the carbon that fulfills the carbon balance. In similar discharges in dilute mixtures of air and organic compounds the formation of relatively high amounts of CO was also reported [5-7].

Fig. 5 shows the toluene conversion in the discharge and the selectivity to CO_2 as a function of toluene input concentration, at a constant flow rate of 220 sccm.

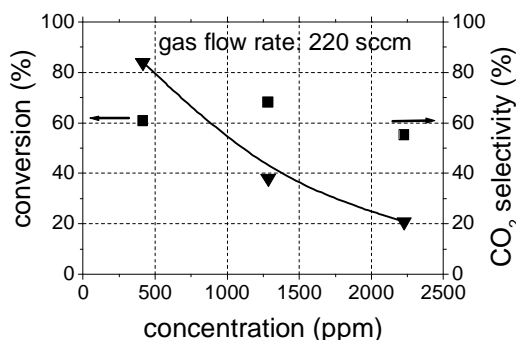


Fig. 5. Toluene conversion and selectivity to CO_2 as a function of $C_6H_5-CH_3$ input concentration, at constant flow rate.

No major influence of the input concentration on toluene conversion was observed. The values obtained ranged between 55 and 70%. The CO₂ selectivity was significantly affected by the toluene concentration. For 220 sccm flow rate, it increased from 21% to 84% when decreasing the C₇H₈ concentration from 2227 ppm to 415 ppm. As in the previous experiments, no other gaseous hydrocarbons were detected as reaction products and the polymeric deposits account to less than 5% of the converted toluene. CO accounts for the remaining carbon, being formed in high amounts especially at high toluene concentration. Most likely, the addition of an appropriate catalyst would lead to the shift in product distribution towards total oxidation, due to oxidation with ozone on the catalyst surface [5,7,8].

4. Conclusions

A DBD with short high voltage pulses (up to 35 kV, duration 100 ns) was used for the oxidation of small amounts of toluene in air. For 59 mJ energy per pulse and 7 W average power in the discharge, toluene conversions in the range 60-70% were obtained. At low flow rate total oxidation was dominant, most likely due to the higher input energy. Less energetic conditions lead to a drastic reduction of CO₂ selectivity. Decreasing the toluene input concentration was found to favor total oxidation, up to 84% of the converted toluene being completely oxidized.

This experimental study shows the feasibility of complete oxidation of toluene with air in a dielectric barrier discharge, especially for highly diluted mixtures, where thermal and thermo-catalytic techniques are not economically attractive.

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