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DEGRADATION OF VOC'S BY A TWO STAGE THERMAL AND HIGH FREQUENCY DBDC SYSTEM

DEGRADACIJA VOC Z DVOSTOPENJSKIM TERMIČNIM IN VISOKOFREKVENČNIM DBDC-SISTEMOM

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The design and construction of a packed-bed thermal reactor and a high frequency operated Dielectric Barrier Discharge Cell (DBCD) based dual system conceived to carry out the degradation of hazardous organic compounds both in liquid and gaseous phases are described. The main components of this system are: i) Thermal treatment system, ii) DBCD, and iii) Specifically developed high frequency (100 kHz) resonant inverter. The power consumed by the cell during the discharges was determined, theoretically and experimentally, through Manley's method. Using this dual system, along with gas chromatography diagnostics, high degradation efficiencies of test compounds such as toluene, benzene and carbon tetrachloride have been achieved which reach 99.976 %, 99.946 % and 99.998 %, respectively.

Key words: degradation of organic compounds two stages high frequency system discharge, design, construction, efficiency

Opisana sta načrt in konstrukcija termičnega reaktorja z gostim ležiščem in z dvojnim sistemom visokofrekvenčne dielektrične razelektritve, zasnovanim za razgradnjo nevarnih organskih tekočih in plinastih spojin. Glavni deli sistema so: i) sistem za toplotno obdelavo, ii) DBCD in iii) posebno razvit visokofrekvenčni (100 kHz) resonančni inverter. Teoretično in eksperimentalno je bila določena energija, ki jo je celica porabila pri razelektritvi z metodo Monley. Z uporabo tega dualnega sistema in plinsko kromatografsko diagnostiko so bile dosežene visoke stopnje degradacije preizkusnih sestavin toluena, bencena in ogljikovega tetraklorida 99,976 %, 99,946 % in 99,998 %.

Ključne besede: razgradnja organskih spojin, dvostopenjski visokofrekvenčni sistem, razelektritev, načrt, konstrukcija, učinkovitost

1 INTRODUCTION

An advantageous waste treatment technology often relies on two techniques: an advanced thermal method, which vaporizes and/or combusts liquid organic waste, and an advanced oxidation process which treats gas streams. A packed bed reactor may be the first stage used to volatilize and/or combust organic liquids. The output can then be treated with a Dielectric Barrier Discharge Cell (DBDC) plasma treatment second stage, to reduce hazardous organic compounds to lower levels of concentration [12,5,10]. Such non-equilibrium plasma processes have demonstrated to be highly efficient as an advanced oxidation technology for the reduction of organic volatile compound [3,4]. The plasma discharge is produced by means of alternating high voltages (from 50 or 60 Hz [1] to several kHz [6,7]. In general, when the dielectric barrier discharge cell (DBDC) is excited at the line frequency with a high voltage transformer, the latter is often considerably heavy and cumbersome, with high leakage inductances that limit its excitation at higher frequencies. Therefore, it is necessary to develop static inverters able to operate at frequencies higher than the line's.

The design and construction of the main electrical, electronic, and mechanical components of a thermal packed-bed reactor, DBDC, and of a high power resonant inverter at a 94.3 kHz operating frequency required to apply the bias voltage to these, are presented in this work. Experimental tests have been performed on toluene, benzene and carbon tetrachloride, whose degradations were analyzed by means of gas chromatography.

2 EXPERIMENTAL SEP-UP

In order to carry out the degradation of hazardous organic compounds in their liquid phase, a system consisting of a thermal treatment stage and an electron discharge stage was designed and constructed. As a first stage, the compound is gasified by means of a rise in temperature in the presence of an oxidizing gas. At the electron discharge stage, the gas mixture is injected, at room temperature and at atmospheric pressure, in a DBDC where the electron discharge takes place. Here, the compound experiments a second degradation. **Figure 1** shows the components of the system.

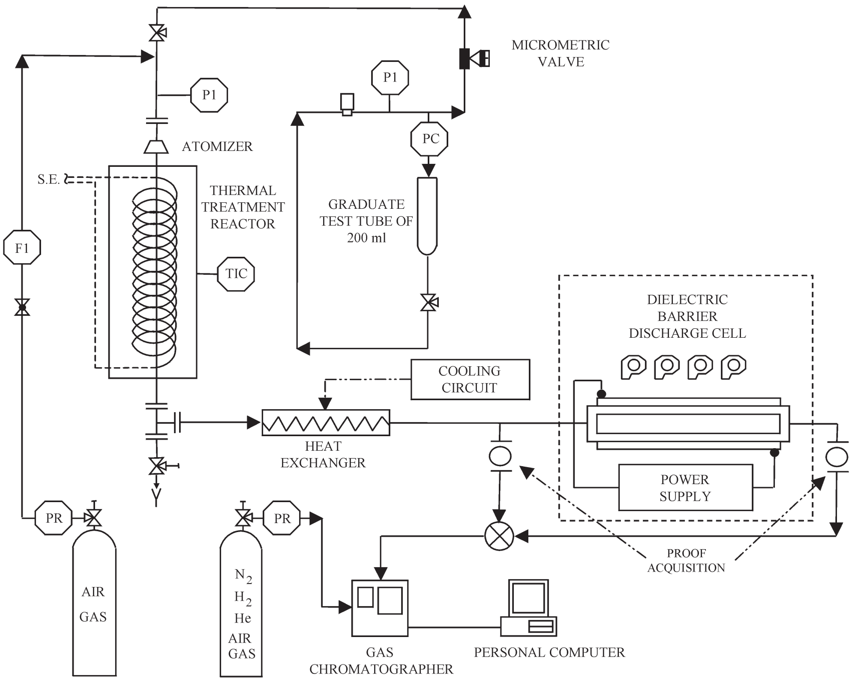

Figure 1: General scheme of the system for the degradation of hazardous compounds
Slika 1: Splošna shema sistema za degradacijo nevarnih snovi

2.1 Thermal Treatment Reactor (TTR) and Heat Exchanger (HX)

The hazardous liquid organic compound is mixed with a liquid carrier such as demineralized light oil (DTE), since many organic compounds are mixed with light oils, at a predefined flow. The liquid compound is combined with the oxidizing gas through an injector which atomizes the mixture. This is injected into a packed bed column and heated up with a high temperature electric furnace. The temperature can be controlled up to 1000 °C, thus taking the organic compound to a gas form. The mixture passes through a cylindrical container made of Hastallowed and Hayes type stainless steel. The container is 0.076 m in diameter and 1.524 m long. Alumina ceramic pellets are used as packing material. In this column, the atomized hydrocarbons are partially converted into simpler chemical compounds by means of thermal combustion. The ensemble formed by the packed column and the electric furnace has been called the Thermal Treatment Reactor (TTR) and delivers, in our case, 1.5 kW. Five K-type thermocouples are used to measure temperatures on different points within the column.

A heat exchanger (HX) is located at the output of the TTR. The function of the HX is to cool the gaseous compound down to room temperature. The HX consists of two coaxial stainless steel tubes. The gaseous compound flows inside the internal tube ($\phi = 0.00127$ m) whereas the external one carries water in counter flow. The cooling circuit consists of a radiator, a pump, and a flow meter. The water flow can be controlled within the 0-10 L/min range.

2.2 Dielectric Barrier Discharge Cell (DBDC)

Several processes are present in each microdischarge that occurs within the DBDC: (a) generation of oxygen atoms from the molecular oxygen due to the impact of electrons, (b) reaction of the oxygen atoms with the toxic compound forming degradation products, and (c) loss of oxygen atoms due to recombination. The chemistry of the process begins with the microdischarge and finishes, some microseconds later, with the recombination of oxygen atoms, forming the main reactive species.

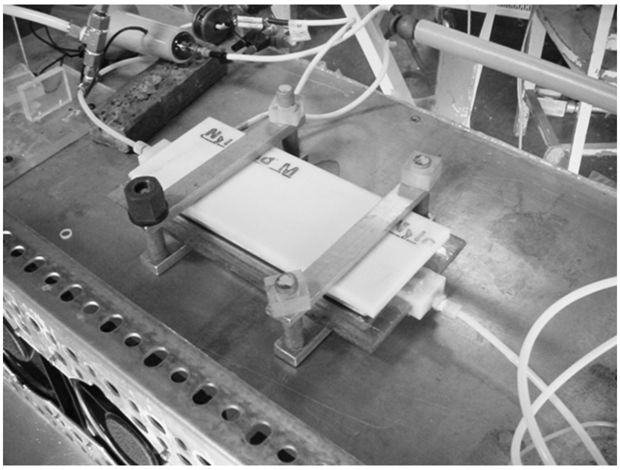

Figure 2: Discharge cell volume 62.25 cm^3
Slika 2: Volumen razbremenitvene celice

The cell was constructed out of tempered glass, sealed with high temperature silicon rubber (300 °C). The heat generated in the cell, when discharges are being produced, is transferred to the aluminum plates. These are used both as electrodes and as heat sinks. Their thickness is 1.2 cm, their length d_2 = 29 cm and width d_1 = 11.25 cm. The space between then is d = 0.2 cm, that is, a 65.25 cm^3 volume. The surfaces are polished up to a mirror finishing, and their corners rounded to prevent the point effect. During the operation, they are kept cool with forced air by means of a fan array. The physical arrangement and aspect of the DBDC are shown in **Figure 2**.

2.3 Power supply

The dielectric barrier discharge cell possesses a 65.25 cm^3 volume (**Figure 2**) and is biased by a high frequency (100 kHz) high voltage (10 kV) resonant inverter which was designed and built purposely. A resonant frequency tracking digital phase locked loop (DPLL) circuit was also designed for this inverter. The block diagram of it is shown in **Figure 3**, displaying: a high speed transition circuit, a digital phase detector, a loop filter, a controlled voltage oscillator, a resonant bridge, and a high voltage transformer coupled to the DBDC which constitutes the resonant load circuit of the inverter.

The reference resonant signal μ_s (t) is detected through a current sensor. This sinusoidal signal is converted to a pulse train by means of a high speed transition circuit (LM308), where frequency and phase are synchronized with the resonant signal. This pulse train is sent to a digital phase detector (CD4046), which compares this reference signal μ_1 (t) with the output voltage controlled oscillator (VCO) signal μ_2 (t). The phase detector produces a linear ramp voltage signal μ_d (t) which is proportional to the phase error (θ_e).

The undesired harmonics present in μ_d (t) are eliminated by a low pass filter. The filter output μ_f (t) becomes the input signal to the VCO, which, in turn, generates the pulse train μ_2 (t). The frequency of the latter is adjusted according to the fluctuations in θ_e. The signal μ_2 (t) is sent as a negative feedback to the phase detector. The VCO output signal activates the full bridge resonant circuit formed by the four power MOSFET modules (IRFK4H350) and four fast recovery power diodes. In this bridge, the voltage signal that is applied to the pulse transformer to excite the DBDC is produced.

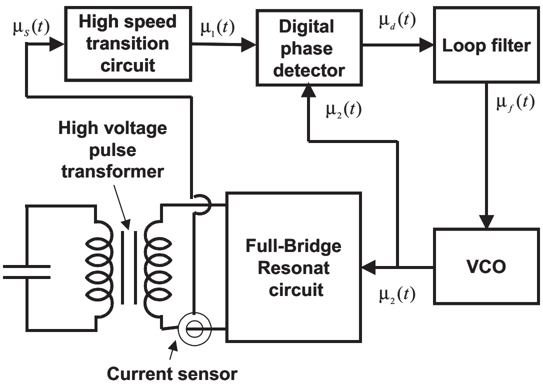

Figure 3: Schematic diagram of the DBDC power supply
Slika 3: Shematičen diagram DBDC-napajanja

3 RESULTS

The high voltage signal was measured with a Tektronix model P6015A test probe, and the resonant current in the DBDC with a Stangenes current monitor whose sensitivity reaches 0.1 V/A. The voltage (top trace) and current (bottom trace) in the cell are shown in **Figure 4(a)**, the most significant electrical parametric values being V_{ig} = 3 kV, V_x = 7.5 kV and f = 94.3 kHz. **Figure 4(b)** portrays the respective Q-V Lissajous plot as a curve relaxed into an elliptic shape due to the frequency rise, as predicted for this condition by Kogelschatz and collaborators [8].

These results were obtained while keeping the same constant gas flux in the cell (Q = 18 L/min). It outstands that a better power transference from the supply to the plasma is achieved at the higher frequency. To gain a better insight into the internal mechanisms responsible for this, let us consider the microscopic nature of the discharge. Once the cell gap spacing and its effective gas density have been established, then the breakdown potential slot, limited by V_{ig} and V_x, for one micro-discharge plasma filament is approximately constant. Furthermore, under the same gas and gap conditions and within the silent discharge regime, the reduced electric

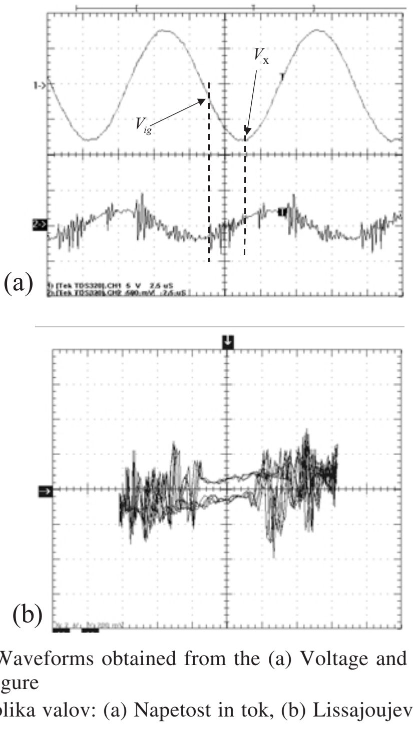

Figure 4: Waveforms obtained from the (a) Voltage and current, (b) Lissajous figure
Slika 4: Oblika valov: (a) Napetost in tok, (b) Lissajoujeva slika

field through the microdischarge can be expected to remain nearly constant. Thus, if the specific power per micro-discharge $\overline{P}_{\mu}$ is also assumed statistically constant, then the specific energy per microdischarge $\overline{E}_{\mu}$ is proportional to the microdischarge mean lifetime t_u [11]. Therefore, a rise in frequency leads to a decrease in the number of microdischarges per half cycle $n_{1/2}$ (or an equivalent number of microdischarges per half cycle per unit area σ) but a consequent growth in the number of charged particles per second dissociating the degrading gas molecules.

Therefore, the microdischarge specific power was $\overline{P}_{\mu}$ = 7.5 MW/cm^3 and the reduced electric field 1.875×10^{-15} V cm^2 (187.5 Td) within the cell. As for the microdischarge specific energy $\overline{E}_{\mu}$ = 15 mJ/cm^3 the microdischarge duration t_u was adopted as 2 ns [2,9]. The residence time was t_r = 0.208 s (**Table 1**).

Table 1: Cell parameters
Tabela 1: Parametri celice

Parameter	Cell	Units
E	4	mJ
$\overline{E}$	1.257	J/cm^3
$\overline{P}$	5.78	W/cm^3
σ	6.793	cm^{-2}
X/X_0	0.087	
V_{ig}	3	kV
V_x	7.5	kV
f	94.3	kHz
P	377.2	W
t_r	0.208	s
$\overline{P}_{\mu}$	7.5	MW/cm^3
$\overline{E}_{\mu}$	15	mJ/cm^3
σ	6.793	cm^{-2}
$n_{1/2}$	2216	
V	65.25	cm^3

The whole system described above was put in operation in order to treat some specific hazardous products. The compound uses in the process were Benzene, Toluene and carbon tetrachloride at a 1000 µg/g concentration. In this case, DTE oil – 28 was used as a liquid carrier. Another fluid involved in the degradation is air that provides the oxygen (O_2) required for recombining organic molecules. The oxygen concentration was 20 % versus 80 % of Nitrogen (N_2), without the presence of water, so one can assume this fluid to be extra dry air. The Benzene, Toluene and Carbon Tetrachloride degradation was carried out to test the performance of the system. Typical spectra are shown in **Figures 5(a, b), 6(a, b) and 7(a, b)**. The gas chromatographer VARIAN 3400CX, together with a flame ionizing detector (FID), was used to determine the degraded compound concentrations.

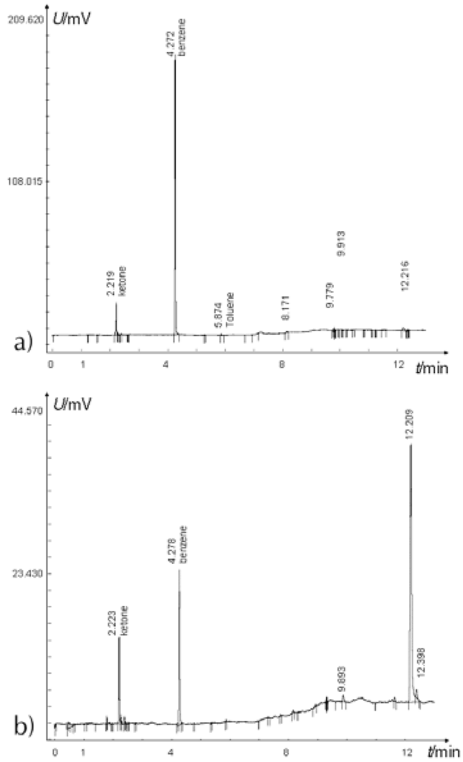

Figure 5: Benzene degradation chromatogram: (a) First stage, (b) Second stage.
Slika 5: Diagram razgradnje bencena: (a) prva stopnja, (b) druga stopnja

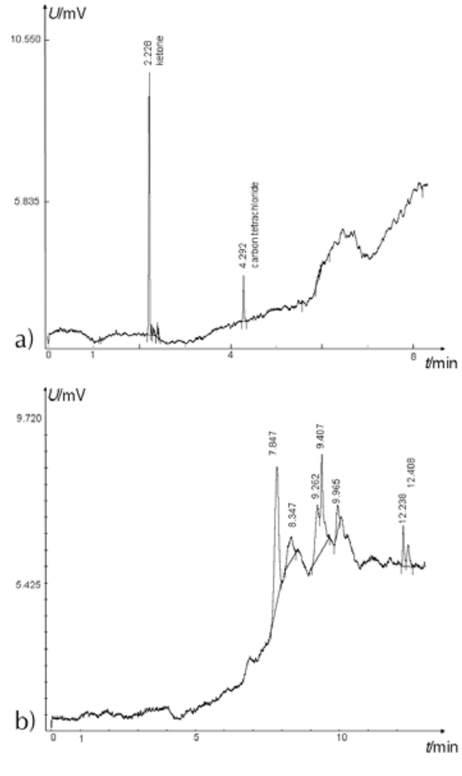

Figure 6: Carbon Tetrachloride degradation chromatogram: (a) First stage, (b) Second stage.
Slika 6: Diagram razgradnje ogljikovega tetraklorida: (a) prva stopnja, (b) druga stopnja

Figure 5 (a) corresponds to the first degradation stage for Benzene, whose efficiency was 98.58 %. This first stage is made in the oven of thermal treatment where the molecules of benzene are fractured and

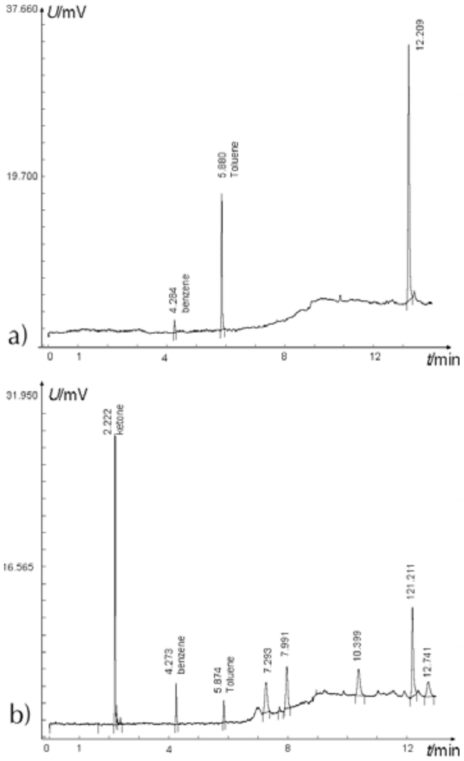

Figure 7: Toluene degradation chromatogram: (a) First stage, (b) Second stage.

Slika 7: Diagram razgradnje toluena: (a) prva stopnja, (b) druga stopnja

divided in short segments to produce lighter molecules. At this stage the light oil molecules are also partially degraded. It is important to highlight that under this first stage conditions the liquid is transformed into phase vapor to pass onto the next stage, by means of the dielectric barrier discharge.

The second stage, as shown in **Figure 5(b)**, operated at high frequency; the degradation was 87.251 % and for the combination of the two stages at high frequency the result attains 99.946 %.

At the second stage, the molecular oxygen is excited and dissociated by means of electronic interactions to produce species known as reactive oxygen species (ROS) capable to oxidize through very complex mechanisms that can be represented in the following way:

a) Molecular oxygen dissociation takes place:

$$e + O_2 \rightarrow O + O + e \tag{1}$$

b) The oxygen atoms can be in a fundamental or excited level collide with the molecules of benzene to oxidize them:

$$C_6H_6 + O \rightarrow C_6H_5O + H \tag{2}$$

$$C_6H_5O + O \rightarrow HCO + 2C_2H_2 + CO \tag{3}$$

Also, the radical C_6H_5O being unstable, breaks down quickly in:

$$C_6H_5O \rightarrow CO + C_5H_5 \tag{4}$$

and this last molecule is oxidized continually until a lineal chain:

$$C_5H_5 + O \rightarrow nC_4H_4 + CO \tag{5}$$

$$nC_4H_5 + O_2 \rightarrow C_2H_4 + CO + HCO \tag{6}$$

$$C_2H_4 + O \rightarrow CH_3 + HCO \tag{7}$$

c) Other degradation mechanisms studied by some authors, involve the direct division of benzene molecule by the electronic interactions; the electrons with energy levels below 10 eV are able to ionize and to dissociate the benzene in linear molecules able to be oxidized by the ROS.

In **Figure 6(a)**, the degradation of 1000 µg/g Carbon Tetrachloride corresponding to the first stage was carried out by the thermal treatment, there the compound suffered a preliminary degradation of 99.9905 %. At the second stage, where the residual gases are subjected to dielectric barrier discharges, it was not possible to determine with sufficient accuracy the degradation grade. Starting from the initial composition of 1000 µg/g and after the plasma process, the sensibility of the chromatography device was not capable to detect the residual CCl_4, as it can be observed in the **Figure 6(b)**. So, the concentration of CCl_4 was duplicated in the mixture until the degradation percentage could be determined. Finally, it was obtained that the degradation of carbon tetrachloride is approximately 99.998 %.

Several authord [9,13] suggest that highly electronegative molecules such as CCl_4 have the dissociative electron attachment as their dominant dissociation mechanism:

$$e + CCl_4 \rightarrow Cl^- + CCl_3 \tag{8}$$

This process dominates on others like attachment electron by oxygen. In the presence of oxygen, the produced CCl_3 is quickly removed:

$$CCl_3 + O \rightarrow COCl_2 \tag{9}$$

This last compound, well-known as phosgene, is eliminated via the following reactions:

$$COCl_2 + O \rightarrow ClO + COCl \tag{10}$$

$$COCl + O_2 \rightarrow CO_2 + ClO \tag{11}$$

$$ClO + O \rightarrow Cl + O_2 \tag{12}$$

$$Cl + Cl \rightarrow Cl_2 \tag{13}$$

The main products of the degradation of CCl_4, are CO_2 and Cl_2.

In **Figure 7(a, b)**, the degradation of 1000 µg/g of Toluene is depicted. After the treatment by dielectric barrier discharge, a degradation near 99.97 % was obtained. For an aromatic compound, it is possible to describe a general degradation mechanism, which consists on the reaction of the organic compound with the reactive oxygen species (ROS):

$$C_xH_y + (x + y/2)O_2 \rightarrow xCO_2 + (y/2)H_2O \tag{14}$$

In this simplistic reaction mechanism, the active ROS species are included in O_2. For the case of Toluene the complete reaction is:

$$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O \tag{15}$$

Equation (15) also applies for Benzene. As it can appreciated, high efficiencies can be obtained when combining processes, namely, the packed thermal reactor and the dielectric barrier discharges. Further research work is being developed into the mechanisms and chemical processes of degradation using optic emission spectroscopy (OES) diagnostics which allows determining average electron energies.

4 CONCLUSIONS

With an aim to carry out the hazardous organic compound (VOC) degradation, a system based on the thermal packed-bed reactor and DBDC technology has been designed and constructed. A substantial growth in the number of charged particles per second, dissociating the degrading gas molecules, has been achieved. Therefore, it is confirmed that the energy density becomes increased by the frequency rise, provided that the residence time remains shorter, up to ≈ 530 %, with a consequent considerable potential for future applications of this design.

In these earlier experiments carried out on Benzene, Toluene and Carbon Tetrachloride using the packed bed reactor exclusively, degradation efficiencies, measured by means of gas chromatography, reached the 90–96 % range. The use of two stages (thermal treatment and cell electron discharge) increases the degradation performance.

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