

VOCs REMOVAL BY COMBINED USE OF ELECTRON BEAM, MICROWAVE AND CATALYST

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A new hybrid technique for the volatile organic compound decomposition, based on combined use of electron beam (EB) induced non-thermal plasma (NTP), microwave (MW) induced NTP and catalytic oxidation, named “EB+MW-plasma catalysis”, is presented. Real synergistic effects between NTP and catalysis were obtained by introducing the catalyst into the irradiation zone, *i.e.* into the MW reactor or EB reactor. The main goal of our research was to combine the features of each known technique used in gas pollution control, *i.e.* the very high efficiency of EB in converting VOCs to intermediate products, the ability of MW to produce and sustain NTP in large electrodeless reaction vessels, and the important role of catalysts in the complete conversion of the intermediate products to carbon dioxide and water.

INTRODUCTION

The main sources of volatile organic compounds (VOCs) emissions in Roumania from industry are the following: the use of solvents in various activities (protection coatings, cleaning and trimming of surfaces, wood impregnation); various production processes (manufacturing of lacquers and adhesives, extraction and refining of vegetable oils) and combustion units. VOCs must be removed from industrial waste streams to meet the more and more stringent regulations of discharge limits. To eliminate the gaseous pollutants, many approaches are possible. Non-thermal plasma (NTP), in which the mean energy of the electrons is substantially higher than that of the ions and the neutrals, offers a considerable advantage in reducing the energy requirements to remove the pollutants.¹⁻³

There are three promising methods for generating non-thermal plasmas (NTP) in atmospheric gas pressure containing the pollutants, namely electron beam (EB) irradiation, microwave (MW) irradiation and electrical discharge (DC, AC and pulsed fields) techniques.¹⁻⁵ Also, the combination of a NTP with in situ heterogeneous

catalysis (denoted as “plasma catalysis”) is considered as a promising method to improve the oxidation of volatile organic compounds (VOCs) and the energy efficiency of the plasma process.^{3, 6, 7} A new hybrid technique for the VOCs decomposition, based on combined use of EB induced NTP, MW induced NTP and catalytic oxidation, named “EB+MW-plasma catalysis”, is presented. Real synergistic effects between NTP and catalysis is expected by introducing the catalyst into the irradiation zone, *i.e.* into the MW reactor, EB reactor or into a reactor in which both EB and MW are injected. The main goal of our research was to combine the features of each known technique used in gas pollution control, *i.e.* the very high efficiency of EB in converting VOCs to intermediate products, the ability of MW to produce and sustain NTP in large electrodeless reaction vessels, and the important role of catalysts in the complete conversion of the intermediate products to carbon dioxide and water. There is not any previous work in the literature examining the effect of successive or simultaneous EB irradiation, MW irradiation and catalysts for VOCs decomposition.

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EXPERIMENTAL

A laboratory hybrid installation (LHI) was designed and built for the comparative studies of VOCs decomposition using separate and combined microwave irradiation, electron beam irradiation and catalyst. The installation consists mainly of the following units: a gaseous mixture preparation system (VOC dosing pump, water dosing pump, air compressor, circulating pumps, flowmeters, valves, etc.); a microwave reactor (MWRc) - an elongated cylindrical cavity containing a concentric quartz tube with a V_2O_5 catalyst bed placed inside; an electron beam reactor (EBR) containing inside a V_2O_5 catalyst and a electrical heating system; a microwave injection

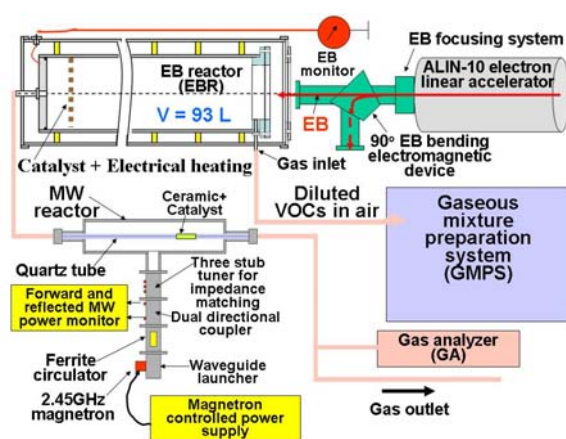


Fig. 1 – Schematic drawing of the LHI.

The catalyst that has been used is of the V_2O_5 type (an industrial catalyst used for the oxidation of butane to maleic anhydride). This type of catalyst has been chosen because it is resistant to acid pollutants from gases and because it could be used for removal of both acid oxides and VOC's. Toluene and hexane were used as VOC's, either individually or in a mixture.

RESULTS AND DISCUSSION

In all experiments, the VOCs decomposition process was observed, by determining the concentrations of carbon oxides and of volatile organic compounds (the initial ones, but also the newly appeared ones). In order to achieve a better assessment of the oxidation process, two indices have been determined: **the conversion of VOCs to any product**, denoted **Conv** (removal efficiency) and **the selectivity of VOCs conversion into carbon oxides and water**, denoted **Sel** (oxidation efficiency).

$$\text{Conv} = \frac{[\text{VOC}]_0 - [\text{VOC}]_t}{[\text{VOC}]_0} * 100 \quad (1)$$

system of 2.45 GHz and 850 W maximum output power, an electron beam injection system (an EB linear accelerator of 6.23 MeV and 164 W maximum EB output power, built in the Electron Accelerator Laboratory, NILPR, Bucharest, Romania) and gas analysers (three gas analyser types: TLV Panther Industrial Precision PID Monitor; Gas chromatograph Fisons 8330; Buck Scientific, Multiple Gas Analyser #1). The MWRc and the EBR were connected in two configurations: first MWRc and then EBR (MW+EB – plasma catalysis) or first EBR and then MWRc (EB+MW-plasma catalysis). Fig. 1 and Fig. 2 show the schematic drawing and photograph of the LHI, respectively.

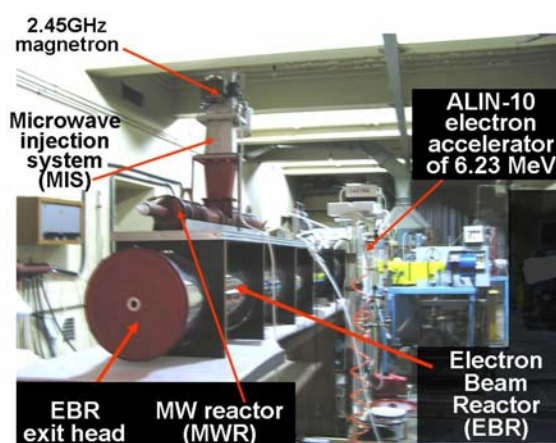


Fig. 2 – Photograph of the LHI.

$$\text{Sel} = \frac{[\text{CO}_2]_t - [\text{CO}_2]_0 + [\text{CO}]_t}{[\text{VOC}]_0 - [\text{VOC}]_t} * 100 \quad (2)$$

Where: $[\text{VOC}]_0$ is the initial concentration of VOC, (ppmv); $[\text{VOC}]_t$ is the concentration of VOC after treatment, (ppmv); $[\text{CO}_2]_t$ is the concentration of CO_2 after treatment, (ppmv); $[\text{CO}_2]_0$ is the initial concentration of CO_2 from air, (ppmv); $[\text{CO}]_t$ is the concentration of CO after treatment, (ppmv); N.C. is the number of carbon atoms from VOC.

The main purpose of our research was to determine the irradiation conditions that allow the VOCs removal with a high efficiency simultaneously with a complete oxidation.

The research was made in several steps. In the first step, a series of reactors was used: a catalytic reactor irradiated with MW (MWRc) and a second reactor, irradiated with EB, but without a catalyst (EBR). These reactors were connected in two configurations: EBR+MWRc or MWRc+EBR. The results obtained for toluene – air mixture, are presented in Fig. 3.

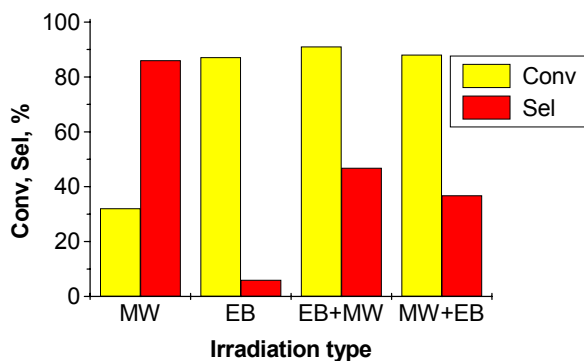


Fig. 3 – Results obtained for toluene removal from gases by MW, EB, EB+MW or MW+EB treatment, continuous air flow (400 l/h); [toluene]₀=608 ppmv.

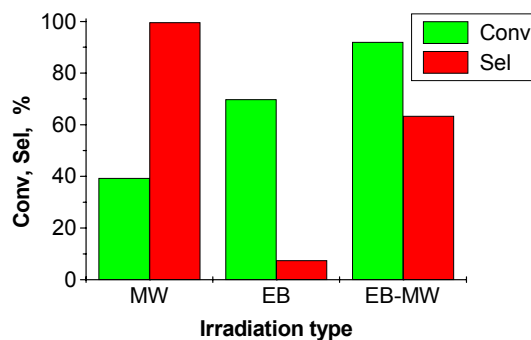


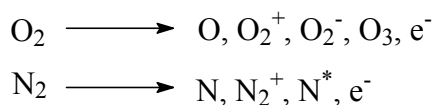
Fig. 4 – Results obtained for hexane removal from gases by MW, EB or EB+MW treatment, continuous air flow (400 l/h); [hexane]₀=608 ppmv.

When the catalytic reactor irradiated with MW (MWRc) is used, it can be noticed that the catalyst is heated by MW and this makes possible the VOCs oxidation without preheating of the gaseous mixture. The VOCs conversions are small, however (30-40%), and the selectivities for total oxidation process are quite good (90-99%).

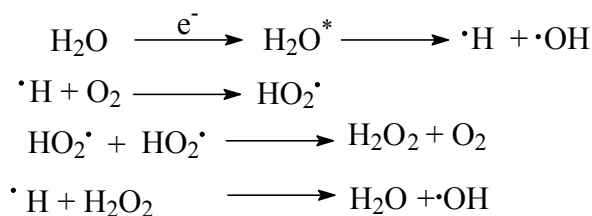
The EB irradiation (without catalyst inside EBR) gives higher conversions (70-90%) but lower selectivities (10%). In the EB irradiation case a large portion of the EB energy input is consumed by processes of excitation, ionization and dissociation resulting in species which are not directly usable for the VOCs total oxidation and which lead to the formation of harmful by-products.

These results show that the successive treatment of the type EB+MW leads to better results. This fact may be caused by the formation of active radical species (during the EB treatment) which can be easily transformed into total oxidation products after being exposed to the MW reactor.

Primary electrons interact with the background air gas molecules and this reaction produces free radicals and electron-ion pairs through electron-impact dissociation and ionization. The products of the primary electron-molecule reactions are atomic oxygen and atomic nitrogen. These radicals react with VOCs.^{8,9} Ionization and excitation of N₂, O₂ produce ions, electrons, and radicals as follows:



In the presence of moisture, the formation of OH radical by electron beam irradiation is as follows:



OH radical is so reactive that it plays a significant role in the VOC decomposition reaction.⁸

Fig. 4 presents the results obtained at the treatment of an air and hexane mixture. In this case, also, the same feature that was noticed at toluene treatment applies: the successive use of the EBR and MWR reactors with a catalyst allows us to obtain the highest conversion possible and quite high selectivity for total oxidation.

During the second step, a series of two reactors was used, and they both contained a catalyst – the first was irradiated with EB and the second was irradiated by MW.

The electron beam reactor was used, and inside it a 4 cm thick catalyst layer was placed. In front of this catalyst layer there is an electric system of gas heating (this heating system is useful only when low-power accelerators are used). Only a hot catalyst was used for the experiments into this reactor. If the catalyst is cold, the VOCs might be adsorbed by its surface, which would cause errors in the determination of the conversion of VOCs. For this reason, throughout the whole experiment, the hot catalyst was maintained, having a temperature of 200-220⁰C (the temperature in the catalyst layer was continuously measured using a thermocouple introduced inside the catalyst layer).

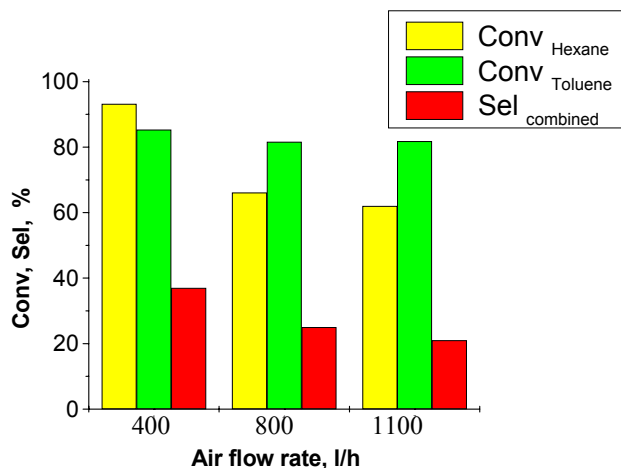


Fig. 5 – Results obtained for toluene and hexane removal from gases by catalytic oxidation. $[\text{toluene}]_0 = [\text{hexane}]_0 = 285$ ppmv, catalyst temperature = 220°C .

In the first set of experiments, a mixture of toluene, hexane and air was used, in similar concentrations (285 ppmv), and the influence of the gas flow rate upon the VOCs conversion and selectivity was observed. Figure 5 presents the results obtained at the treatment of the gas in the presence of the catalyst (electrically heated) inside the EBR reactor, without irradiation. One can notice how the V_2O_5 catalyst becomes active in the VOCs removal from air at relatively low temperatures, of approx. 200°C . In these conditions, the conversions of hexane and toluene are quite high (93.2 at 60% for hexane and 85.3 at 81.8% for toluene), but they decline with the increase of the air flow rate (at the same VOCs concentration). However, in these conditions, the selectivity for oxidation to carbon oxides is quite

low (37 at 21%), and it declines with the increase of the gas flow rate.

Figure 6 presents, comparatively, the results obtained at the treatment of the gas in the following conditions: in a catalytic reactor irradiated with microwave (MWRc), in a catalytic reactor irradiated with electron beam (EBRc) or into a series of two reactors EBRc+MWRc. The experiments were obtained for the same initial concentrations of hexane and toluene and for different air flow rates.

It can be noticed that when the two catalytic EBR and MWR reactors are used successively, the efficiency of the process is significantly improved. At low flow rates, it is especially the selectivity of VOCs total oxidation that increases, while at high flow rates, both conversion and selectivity increase.

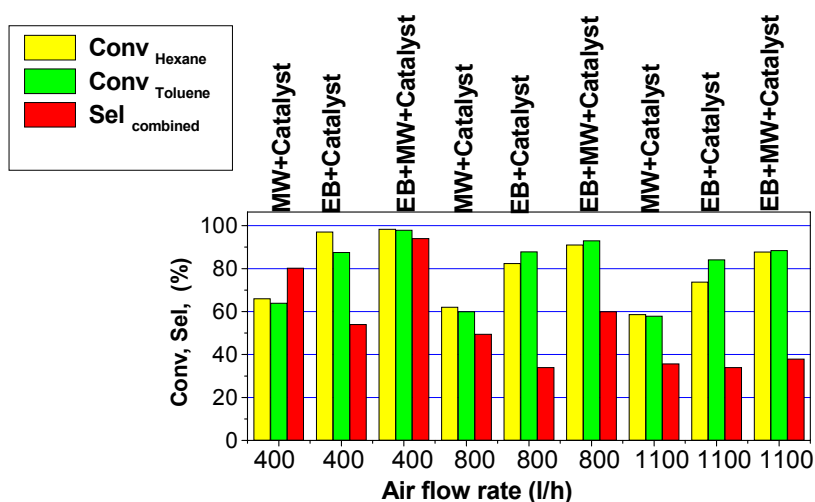


Fig. 6 – The effects of different treatments and air flow rates on hexane + toluene mixture conversion and selectivity for total oxidation. MW power = 400 W; EB power = 106 W; Catalyst temperature in EBR and MWRc $\sim 200^\circ\text{C}$.

Further on, toluene was used for the experiments, in various concentrations (100-580 ppmv). Subsequently, several experiments were carried out, and they included the treatment of the gaseous mixture inside the EBR reactor, and then inside the series of EBR and MWR reactors.

The results presented in Fig. 7, show that the conversion of the hexane and toluene mixture and

the selectivity for total oxidation, are higher for the EB+MW+catalyst treatment than the conversion and selectivity obtained with the EB+catalyst treatment. The conversion decreases slowly while the selectivity decreases rapidly versus air flow rate for both treatment types, EB+catalyst and EB+MW+catalyst.

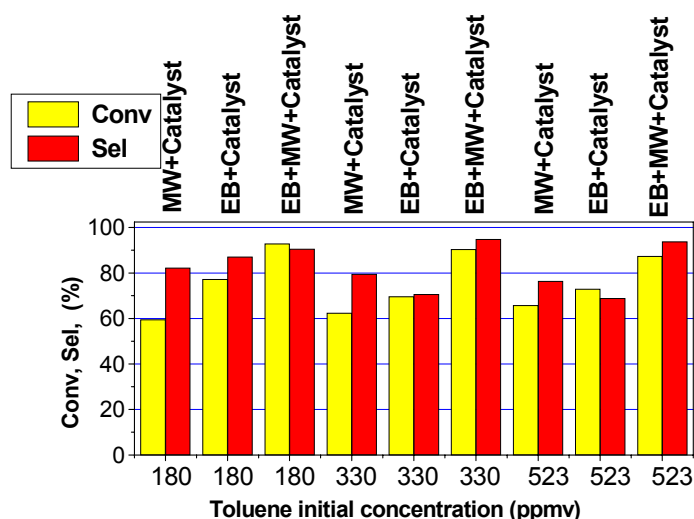


Fig. 7 – The effects of different treatments and initial toluene concentrations on conversion and selectivity for total oxidation. MW power = 400 W; EB power = 106 W; Catalyst temperature inside EBR and MWRc ~200° C; Flow rate = 400 l/h.

The experimental results demonstrate that the treatment of gases in a series of two reactors, in which there is a catalyst which is subject to EB irradiation (in the first one), and to MW irradiation (in the second one), led to the obtaining of the best results for VOCs conversion and complete oxidation. Moreover, this technique can be applied on large concentration ranges and flow rates, as well as on a wide range of VOCs.

Our future objective is to continue this research with the study of the catalytic VOCs oxidation process by the simultaneous presence of EB, MW and catalysts in the same reactor, a multimode rectangular cavity named MRC-EB+MW+Catalyst.

CONCLUSIONS

The hybrid technique based on combined use of EB induced NTP, MW induced NTP and catalytic oxidation, named “EB+MW-plasma catalysis”, could be considered as a promising method to improve the process of removal of volatile organic compounds (VOCs) from air by oxidation.

The main conclusion of this work is that EB+MW+catalyst treatment improves both, removal efficiency and oxidation efficiency with respect to those obtained by EB+catalyst only or MW+catalyst only. The EB+MW+Catalysis method demonstrated good results at low VOC initial concentrations and low flow rates as well as at high VOC concentrations and high flow rates.

List of symbols

- VOC – volatile organic compounds
- EB – electron beam
- NTP – non-thermal plasma
- MW – microwave
- Conv – the conversion of VOCs to any product
- Sel – the selectivity of VOCs conversion into carbon oxides and water
- LHI – laboratory hybrid installation
- MWRc – catalytic reactor irradiated with microwaves
- EBR – reactor irradiated with electron beam
- EBRc – catalytic reactor irradiated with electron beam

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