Gaseous Pollutants Removal by Combined Ionizing and Non-ionizing Radiation Treatment

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Abstract : The paper presents the test results obtained for SO_2, NO_x and VOCs removal at semi-pilot scale by combined electron beams (EB) and microwaves (MW) induced non-thermal plasma processes, named EB+MW-NTP. Also, it is described a demonstrative installation consisting of an EB source of 1.8 MeV and 10.8 kW, a microwave source of 2.45 GHz and 4.2 kW and a reaction chamber of 1.102 m x 0.73 m x 0.243 m inner dimensions, in which are injected both, EB and MW. For VOCs removal is used combined EB+MW-NTP and catalytic oxidation, named EB+MW-plasma catalysis, by introducing a catalyst bed at the bottom end of the reaction chamber. The high power EB and MW sources are able to activate the catalyst without additional heat supply. The EB+MW-NTP process, compared with separate EB-NTP or separate MW-NTP process, provides higher pollutants removal efficiencies. The results suggest that chemical reactions driven in both types of plasma, EB-plasma and MW-plasma, complete and sustain each other at a higher rate level in the case of pollutants treatment by EB+MW-plasma.

Keywords: - SO_2, NO_x, VOC, Catalyst, Electron Beams, Microwaves, Combined Treatment.

1 Introduction

During the combustion process of fossil fuels, (coal, natural gas, petroleum, shale oil and bitumem) that are the main source of heat and electrical energy producing, different pollutants as fly ash, sulphur oxides (SO_2 and SO_3), nitrogen oxides ($NO_x = NO_2 + NO$) and VOCs are emitted [1-4]. These pollutants not only affect directly on environment, but also contaminated water and soil and leads to their degradation. The VOCs emission cause ozone layer depletion, ground level photochemical ozone formation, and toxic or carcinogenic human health effect, contribute to the global greenhouse effect. The Romanian emission ceilings for SO_2, NO_x and VOCs, established for 2010 according to the Gothemburg protocol (GO 1856/2005) are for SO_2, NO_x and VOCs as follows: 918 000 tons/year (30% emissions reduction compared to 1990), 437 000 tons/year (20% emissions reduction compared to 1990) and 523 000 tons/year (15% emissions reduction compared to 1990), respectively. 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 considerable advantages in reducing the energy requirements to remove the pollutants [5-8].

There are three promising methods for generating non-thermal plasmas in atmospheric gas pressure containing the pollutants, namely electron beam (EB) irradiation (EB-NTP), microwave (MW) irradiation (MW-NTP) and electrical discharge (DC, AC and pulsed fields) techniques [9-16]. Also, the combination of a NTP with in situ heterogeneous catalysis (denoted as "NTP- catalysis") is considered as a promising method to improve the oxidation of VOCs and the energy efficiency of the plasma process [17, 18]. The catalyst presence induces an increase of the effective reaction time due to adsorbtion of VOCs and intermediates on the catalyst surface, resulting in a shift of the reaction selectivity towards total oxidation.

The fundamental feature of non-thermal plasma [12, 15] is that the electron temperature, T_e ($T_e \gg 1eV$) is much higher than the gas temperature T_g (including vibrational and rotational temperature of molecules; $T_g \ll 0.1eV$). High energetic electrons induce the molecules excitation, ionization and dissociation, and at the same time, lower energy electrons attach to neutrals to form negative ions in the discharge area. In the downstream afterglow discharge region secondary plasma reactions take place. These reactions are initiated by dissociated molecules, radicals and ions by radical-molecule

reactions and ion-molecule reactions [12, 15]. Aerosol particles will be generated and surface reactions involving aerosol particles can also occur. Therefore, plasma treatment of pollutant gases can consist of direct electron reactions, ion reactions, radical reaction, or aerosol generation and surface reactions [12].

EB technology for simultaneously removal of SO_2 and NO_x was investigated and demonstrated at pilot scale in the USA, Germany, Japan, China, Korea, Poland and Bulgaria. The advantage of EB process in pollutants removal is connected to its high efficiency to transfer high amount of energy directly into the matter under treatment. Disadvantage which is mostly related to high investment cost of accelerator may be effectively overcome in future as the result of use accelerator new developments. Thus potential use of medium-energy high power EB accelerators (1.5 - 2.5 MeV) is demonstrated in [19]. The useful EB energy is under 50% for EB of 0.5 MeV and above 90% for at least 1.5 MeV.

EB energy losses in the dual beam windows (accelerator exit window and reaction chamber input window) and in the intervening air space are substantially lower with higher EB incident energy. Useful EB energy is under 50 % for EB of 0.5 MeV and above 90% for at least 1.5 MeV.

However, the EB doses required are generally too high with EB treatment. Low irradiation doses are required for the process efficiency and a high dose rate must be used to give large production capacities. Thus, for industrial scale processing, the problem of reducing the electrical energy consumption as well as the electron beam cost is especially important.

Microwave induced non-thermal plasma, which is quite different from the thermal plasma, could be a source of free electrons with a high density, which can create conditions for chemical reaction under a mild temperature and atmospheric pressure [6]. MW excited non-thermal plasma produces a high degree of ionization and disassociation that commonly gives higher yield of active species and higher electron temperature to gas temperature ratio (T_e/T_g) than other types of electrically excited plasma (AC, DC and pulsed fields) and the absence of internal electrodes makes reaction vessels simpler [12,15]. This consideration suggests that both externally accelerated EB and MW can be regarded as sources of generating free electrons and active species.

When the external electron accelerator is used, the active species are concentrated on the accelerated electron path. At low and medium dose rate, the chemical reactions consuming those radicals proceed fast enough to balance their production by electron beam transfer energy. At large dose rates, the radical concentration is much higher and radical recombination reactions may no longer be neglected, leading to the decreasing efficiency of the pollutants removal. With microwave energy applied in properly designed applicators promising results are expected because the microwaves penetrate large volumes and lead to creation of a volume active species. Thus, fast radical recombination reactions may be avoided.

The examination of the reported results suggest that further studies are still necessary to establish the optimum operational conditions for the gaseous pollutants removal with high efficiency and low costs at the industrial scale level. In view of this argument we have decided to continue our previous experimental research [20-26], regarding SO_2, NOx and VOC removal by combined EB-NTP and MW-NTP processes, performed at laboratory scale (EB source of 100 W, 2.45 GHz MW source of 850 W and small EB and MW reaction vessels), at a higher level by using the simultaneous high power EB (10.8 kW) and high power MW (4.2 kW) induced NTP in the same reactor containing o a catalyst bed.

The main idea of our previous research was to combine the features of both, EB (as ionizing radiation) and MW (as non-ionizing radiation) used in gas energization process, i.e.:

➢ The high EB efficiency to transfer high amount of energy into the gaseous effluents, forming abundant quantities of active species that are consumed in chemical reactions, part of them leading to the desired conversion of pollutants;

➢ The ability of MW to produce and sustain NTP in large electrodeless reaction vessels.

In addition, our previous experiments performed at laboratory scale showed that generally the pollutants removal efficiency by MW-NTP increases with increasing initial concentration but strongly decreases with the gas flow rate increasing. This contrasts with the pollutants removal by EB-NTP that decreases with initial concentration increasing but the flue gas flow rate has much less impact on the removal efficiency. By combined EB-NTP with MW-NTP processes we expected to obtain high removal efficiency at low and high initial pollutant concentrations as well at low and high flow rates. Also, in our opinion, the additional use of MW to the EB energy could increase the number of active species due to the presence of a higher number of free electrons induced by a possible free electron multiplication mechanism. This effect depends on several parameters, such as MW electric field amplitude, field distribution, energy distribution, and MW applicator geometry. Under these circumstances, although extensive prior art exists in the field of MW

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technology, our attention was focused on the improved design of a microwave applicator which are especially adapted to plasma processes at high power level for both, MW and EB. In view of these arguments we decided to perform the following research steps:

1) To design a demonstrative installation for gaseous pollutants treatment at semi-pilot scale level by combined EB-NTP and MW-NTP, named DI-EB+MW;

2) To establish the DI-EB+MW optimum operational conditions for simultaneous removal of SO_2 and NOx. Source of pollutants: simulated flue gas consisting of air, SO_2, NO_x, CO_2, water vapors and NH_3;

3) To establish the DI-EB+MW optimum operational conditions for VOCs removal. Source of pollutants: synthetic gaseous mixture made up of air, one or several VOCs, and water vapors;

4) To establish the DI-EB+MW optimum operational conditions for mixtures of SO_2, NO_x and VOCs removal. Source of pollutants: synthetic gaseous mixture made up of air, one or several VOCs, SO_2, NO_x, CO_2, water vapors and NH_3;

5) To test the maximum capacity of the DI-EB+MW, i.e., up to 180 Nm^3/h for simultaneous irradiation with EB and MW. Source of pollutants: oil boiler, systems for supplementary loading with several VOCs, SO_2, NO_x, CO_2, water vapors and NH_3;

6) To design a new equipment, up to 1620 Nm^3/h, which permits the medium-energy high power EB accelerator, ILU-6M (1.8 MeV and 10.8 kW), available in our country. The estimated MW power is of about 25 kW. Source of pollutants: oil boiler, systems for supplementary loading with several VOCs, SO_2, NO_x, CO_2, water vapors and NH_3.

This work presents only experimental results of the research steps 1-3.

2 Experimental Installations and Procedures

The DI-MW+EB consists mainly of the following units: a gaseous mixture preparation system (GMPS), an electron beam source (EBS) of 1.8 MeV and adjustable output power up to 10.8 kW, a microwave source (MWS) of 2.45 GHz and adjustable output power up to 4.2 kW and a multimode rectangular cavity (MRC), used as reaction chamber, in which are injected both, MW and EB (Figs. 1 and 2). The EBS is a resonator-type accelerator operating at 115±5 MHz, ILU-6M, built in Russia, Institute of Nuclear Physics-Novosibirsk. It is placed at Electrical Project and Research Institute from Bucharest, Romania. This accelerator generates electron beam pulses of 1.8 MeV, 0.375 ms duration and 0.32 A current peak intensity. The maximum output EB average current and EB output power is of 6 mA and 10.8 kW, respectively. The cross-sectional size of the scanned EB at the ILU-6M vacuum window exit is 1100 mm x 6 mm. The inner dimensions of the MRC are of 1.102 m x 0.730 m x 0.243 m. The scanned EB of the ILU-6M accelerator is introduced perpendicular to the MRC upper-end plate through a 100 μm thick aluminum rectangular foil of 1 m x 0.065 m (Fig. 1, 2). For the experiments with DI-EB+ME for VOCs removal by combined EB+MW-NTP and catalytic oxidation (EB+MW-plasma catalysis) a V_2O_5 catalyst bed of 6.5 kg and 3.5 cm thick was introduced into the EB and MW irradiation zone, i.e. at the bottom end of the MRC [Fig. 3].

The MW power is introduced through MRC upper-end plate via six magnetrons of 2.45 GHz and 700 W maximum output power each. Each magnetron is supplied by a separate power controlled electrical source (PCES). Each PCES is a modified magnetron power supply of a domestic oven. In the PCES configuration, the conventional operation of 2.45 GHz oven magnetron supplied by an L.C. single-phase-half-wave doubler (L.C. HWD) was properly modified in order to permit MW power adjustment. The magnetron main power units consisting of a high voltage diode, a high voltage capacitor and a high voltage anode transformer (HVAT) are similar to the units used for the conventional magnetron supplying system. The difference consists in the use of a separate transformer for the filament supply (HVFT) and of a controlled regulator added to the HVAT primary circuit. Each PCES permits preset adjustment and measurement of the MW exposure time and MW output power. Microwaves are generated as 10 ms pulses at 50 Hz repetition rate. Fig. 4 shows the photograph of the MRC and power controlled electrical supplies for six 2.45 GHz magnetrons.

The gas mixture entrance and exit systems are branched to the MRC through sieve metallic plates. A system for taking samples of the gas made up of a solenoid valve and of a Tedlar bag, is branched to gaseous mixture inlet and outlet. A polyethylene tube with circulating water was placed into MRC to absorb the excess energy when working with poor microwave absorbing samples (without catalyst inside MRC). The gaseous mixture temperature (t_{GM}) is measured with a fibber optic thermometer (Luxtron)

for separate MW irradiation and with a CrAl thermocouple for simultaneous MW+EB irradiation. The high power EB and MW sources are able to activate the catalyst without additional heat supply under the condition that both, MW and EB, reaching the catalyst bed, are converted into heat energy to activate the inside catalyst. Therefore, the residual VOCs and other by-products could be total oxidized. Fig. 5 shows the photograph of the MRC placed under ILU-6M electron beam scanner. Fig. 6 presents the photograph of the DI-EB+MW ensemble (ILU-6M accelerator, EB scanner and MRC).
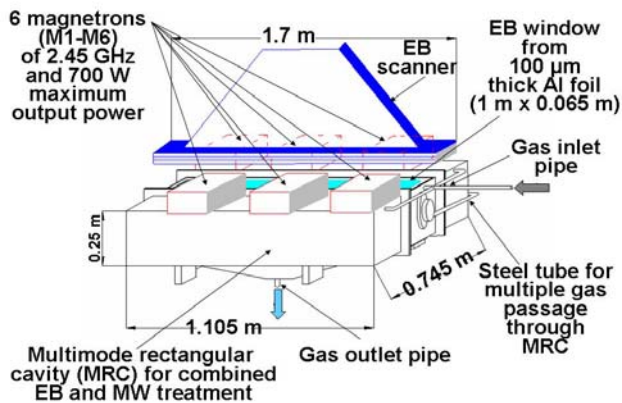
Fig. 1. The schematic drawing of the DI-EB+MW
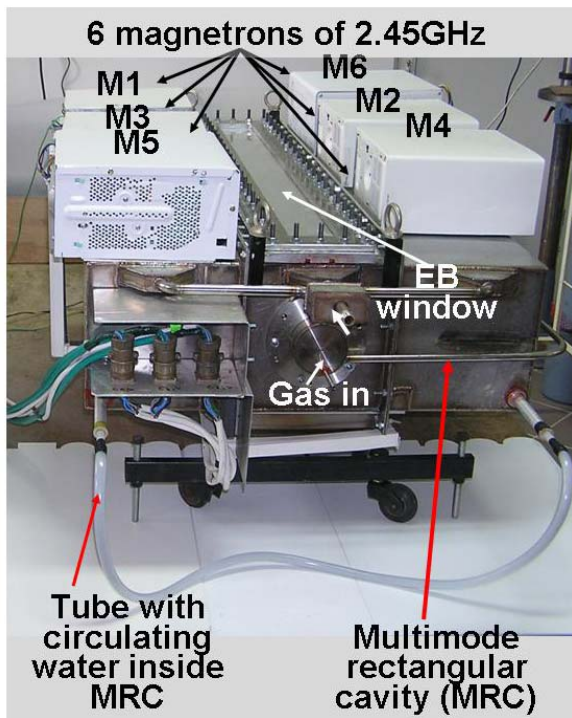
Fig. 2. The photograph of the MRC and magnetrons
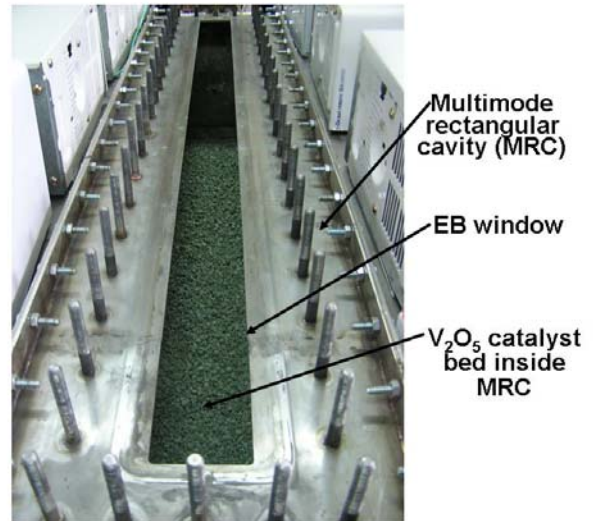
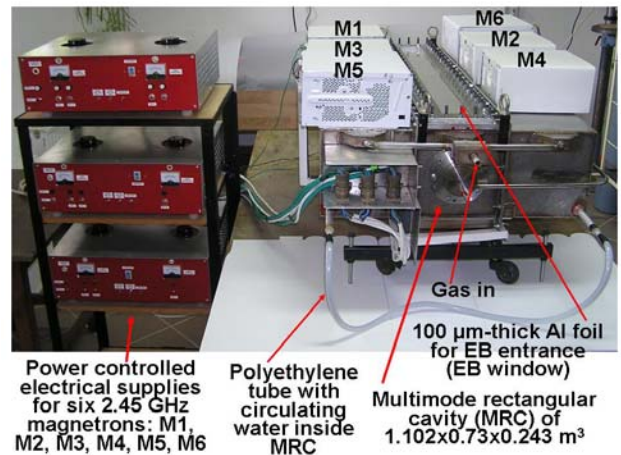Fig. 3. The photograph of the MRC with V_2O_5 catalyst bed inside

Fig. 4. Photograph of the MRC and power controlled electrical supplies for six 2.45 GHz magnetrons
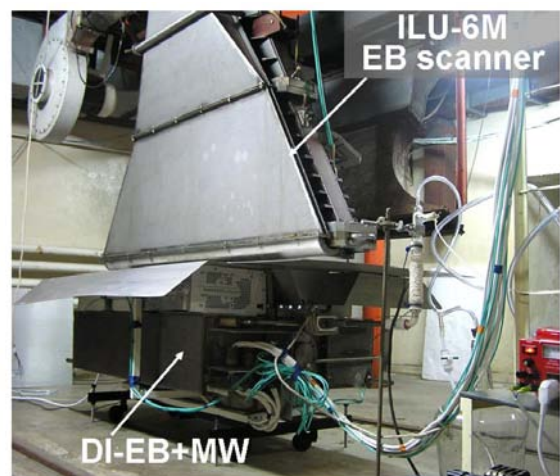

Fig. 5. The photograph of the MRC placed under ILU-6M scanner
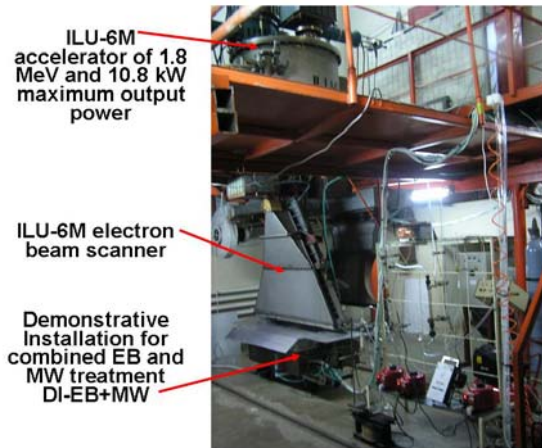
Fig. 6. Photograph of the DI-EB+MW (ILU-6M accelerator, EB scanner and MRC)

3 Results and Discussions

3.1 SO_2 and NO_x Removal

The SO_2, NO_X and NO concentrations were measured with TESTO 350-XL gas analyzer. Several results showing the effects of NH_3, H_2O and microwave power (P_{MW}) on SO_2, NO_X and NO removal efficiency (η_r) for separate MW exposure are presented in Figs. 7-8. Fig. 9 presents the results obtained by simultaneous MW+EB irradiation. The analysis of these results led to the following main observations:

➢ The most important parameters for high $\eta_r(SO_2)$ obtained by MW exposure are H_2O and NH_3 concentrations, t_{GM} and P_{MW}. As seen in Fig. 4, at P_{MW} = 2265 W, $\eta_r(SO_2)$ is only 48% for NH_3 = 71% and H_2O = 8% but increases to 92.5 % for NH_3 = 116% (with 16% excess than stoichiometric amount) and H_2O = 18%. Also, at higher P_{MW} of 2833 W, $\eta_r(SO_2)$ increases from 46.5% for NH_3 = 71% and H_2O = 8% to 87% for NH_3 = 116% and H_2O = 8% (Fig. 7). It was observed that $\eta_r(SO_2)$ diminishes at high MW power level simultaneously with the increase of the gaseous mixture temperature over 60-70°C.

➢ The most important parameter for high $\eta_r(NOx)$ is P_{MW}. The effects of NH_3 and H_2O presence in the gaseous mixture on the $\eta_r(NO_X)$ and $\eta_r(NO)$ are not yet very clearly. The increasing of NH_3 and H_2O concentrations unchanged or diminished the $\eta_r(NO_X)$ and $\eta_r(NO)$ values. However, a clear conclusion is that the P_{MW} increasing from 2265 W to 2833 W, at the same NH_3 and H_2O concentrations, enhances $\eta_r(NO_X)$ and $\eta_r(NO)$ values (Fig. 7 and Fig. 8): from 40.33% to 55.5 % for NO_x and from 8.5% to 39.33% for NO at NH_3 = 71% and H_2O = 8%, and from 22% to 36.5%

for NOx and from 8.5% to 29% for NO, at NH_3 = 116% and H_2O = 8%.

➢ The additional use of EB irradiation to MW exposure strongly increases NO_x and NO removal efficiencies in comparison with MW exposure only (Fig. 9). The values of 100% for $\eta_r(SO_2)$ and up to 95% for $\eta_r(NO_X)$ and $\eta_r(NO)$ are easily obtained by MW+EB processing.
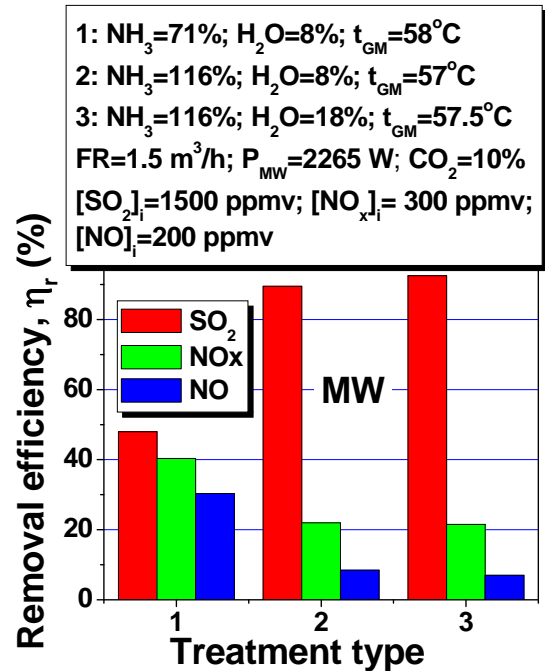

Fig. 7. The effects of NH_3 and H_2O on η_r (SO_2), η_r (NOx) and η_r (NO) at P_{MW} = 2265 W
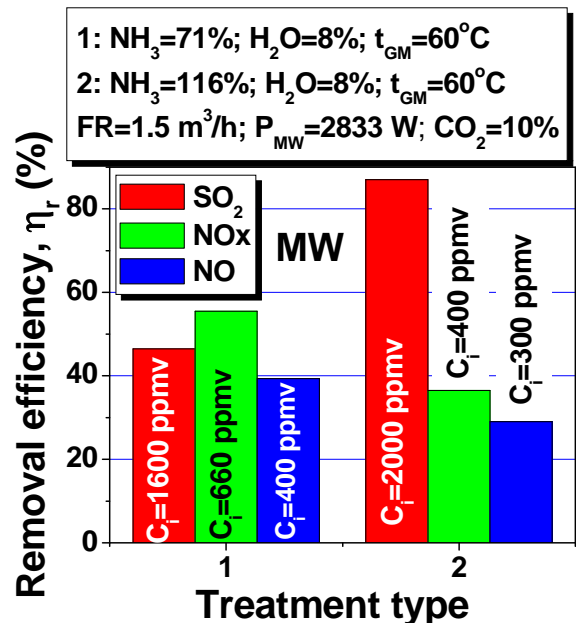
Fig. 8. The effects of NH_3 on η_r (SO_2), η_r (NOx) and η_r (NO) at P_{MW} = 2833 W
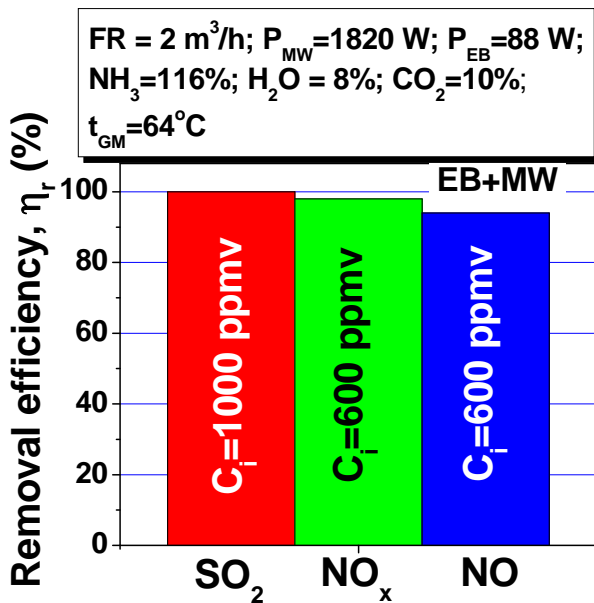
Fig. 9: The effect of MW+EB on η_r (SO$_2$),
η_r (NOx) and η_r (NO)

3.1 VOCs Removal

For the removal of VOCs their total oxidation is preferred, resulting only in H_2O and CO_2. For many EB-NTP technologies, processes of excitation, ionization and dissociation resulting in species, which are not directly usable for the VOC oxidation, consume a large portion of the input energy. Thus, the incomplete oxidation, leading to partially oxidized possible toxic by-products plays an important role in VOCs removal based on the EB-NTP technology. In order to overcome these limitations, for the VOCs removal, we have proposed a hybrid technique based on combined use of EB-NTP, MW-NTP and catalytic oxidation, named "EB+MW-plasma catalysis" [26]. A mixture of hexane (H) and toluene (T) with a initial concentration of $[H]_i$ + $[T]_i$ = 1000 ppmv +1000 ppmv diluted in air containing 7% water vapor was used in experiments. In all experiments, the VOCs removal process was observed by determining the concentrations of carbon oxides and of VOCs.

In order to achieve a better assessment of both, decomposition process and oxidation process, two efficiency types have been determined: decomposition efficiency, Ed (the efficiency in converting VOCs to intermediate products) and oxidation efficiency, Eo (the efficiency for the conversion of VOCs into carbon oxides):

$$Ed = 100 \times \{[VOC]_i - [VOC]_t\}/[VOC]_i \qquad (1)$$

where $[VOC]_i$ is the initial concentration of VOC (ppmv) and $[VOC]_t$ is the concentration of VOC (ppmv) after treatment.

$$Eo = 100 \times \{[CO_2]_t - [CO_2]_i + [CO]_t\}/No. \text{ Catoms} /$$

$$\{[VOC]_i - [VOC]_t\} \qquad (2)$$

where $[CO_2]_i$ is the initial concentration of CO_2 from air (ppmv), $[CO_2]_t$ is the concentration of CO_2 after treatment (ppmv) and $[CO]_t$ is the concentration of CO after treatment (ppmv).

The system for taking samples of the gas is made up of a solenoid valve and of a Tedlar bag. The system for the analysis of gaseous samples, which is used for determining the concentrations of carbon oxides and of organic compounds in vapor state, contains three gas analyzers: TLV Panther Industrial Precision PID Monitor; Gas chromatograph Fisons 8330; Buck Scientific, Multiple Gas Analyzer #1. The experimental results performed at different MW power (P_{MW}), different EB power (P_{EB}), different gas flow rate (FR) and catalyst temperatures are presented in Figs. 10-16. The analysis of these results led to the following main observations:

a) For MW-plasma catalysis

➤ All efficiencies, E_d (H), E_d (T), E_d(H+T) and E_o(H+T) increase continuously versus P_{MW} level but Eo(H+T) increases strongly versus P_{MW} beginning with 2.2 kW (Fig. 10). E_d(T) is always higher than E_d (H) in the P_{MW} tested range from 1.75 kW to 2.6 kW (Fig. 10). Up to P_{MW} of 1.95 kW, E_o (H+T) < E_d(H+T), after then, at 2.2 KW and 2.6 kW, E_o(H+T) > E_d(H+T);

➤ At low FR (0.5 m^3/h) and high P_{MW} levels (2.2 kW and 2.6 kW) there is no a notable difference between E_d (H), E_d (T) and E_d(H+T) but E_o(H+T) strongly increases compared with values obtained at FR of 1 m^3/h and 2 m^3/h (Fig. 11). The FR increase from 1 m^3/h to 2 m^3/h no substantially modifies the level of E_d(H), E_d(T), E_d(H+T) and especially of E_o(H+T) (Fig. 11). It seems that at high FR simultaneously with high P_{MW} could be possible to obtain sufficiently high values for E_o;

➤ The CO and CO_2 concentrations increase strongly versus P_{MW} (Fig. 12). This effect demonstrates that MW-plasma catalysis has an important role on the oxidation process enhance, i.e. on the VOCs complete oxidation;

➤ The CO and CO_2 concentrations decrease strongly for the FR increase from 0.5 m^3/h to 1 m^3/h but the decreasing rate of the carbon oxides concentration diminishes for the FR increase from 1 m^3/h to 2 m^3/h (Fig. 13).

b)For EB+MW-plasma catalysis

➤ $E_o[H+T]$ increases strongly, up to 100%, versus $P_{EB}+P_{MW}$ (Fig. 14). For a given level of $P_{EB}+P_{MW}$ there are little differences between $E_d(H)$, $E_d(T)$ and $E_d(H+T)$, that means EB+MW-plasma catalysis performs the same E_d for two different pollutants, H and T (Fig.11). This contrasts with MW-plasma catalysis (Fig. 10).

➤ CO and CO_2 concentrations increase strongly versus $P_{EB}+P_{MW}$ (Fig. 15) and are higher, by a factor of two as compared with results obtained by MW-plasma catalysis (Fig. 12). This effect demonstrates that EB+MW-plasma catalysis is more efficient on the VOCs oxidation than MW-plasma catalysis that is preferred for the VOCs removal from flue gas;

➤ The comparative results obtained by catalytic oxidation with classical heating (CH), MW-plasma catalysis and EB+MW-plasma catalysis (Fig. 16) demonstrates that satisfactory removal efficiencies are obtained with CH only when the temperature of the catalyst exceeds 350^0C. With MW-plasma catalysis the oxidation process begins at a lower temperature and good efficiencies can be obtained in the range of 250-270^0C. With EB+MW-plasma catalysis, high removal efficiencies start in the range of 175-200^0C.
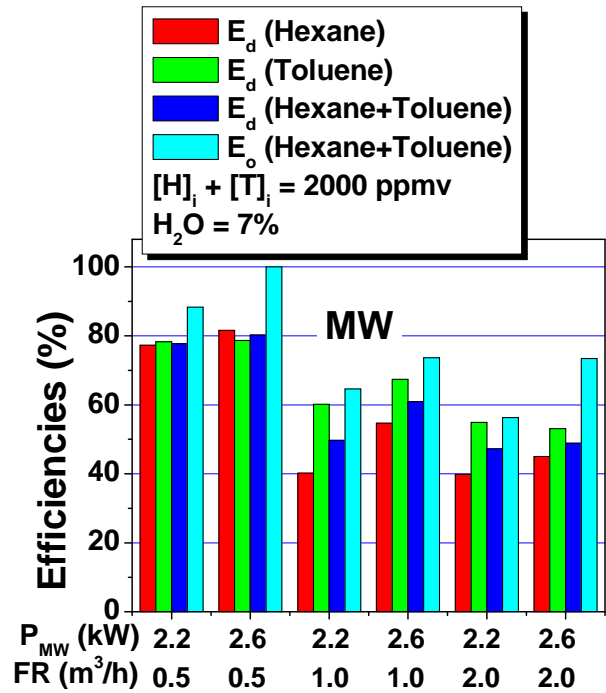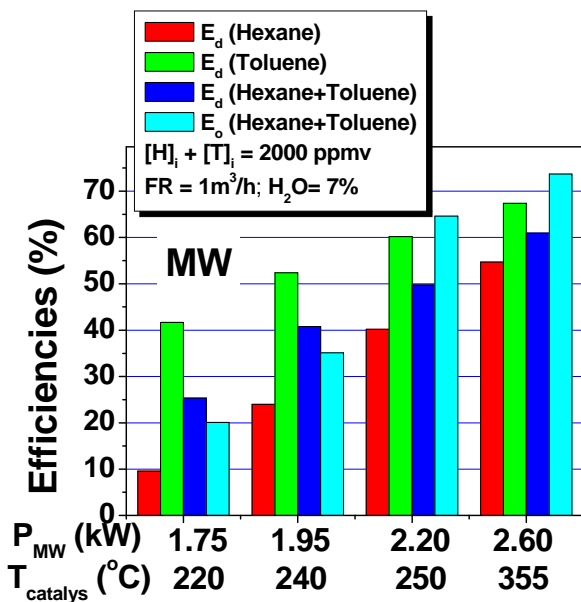

Fig. 11. The effect of FR on the E_d and E_o

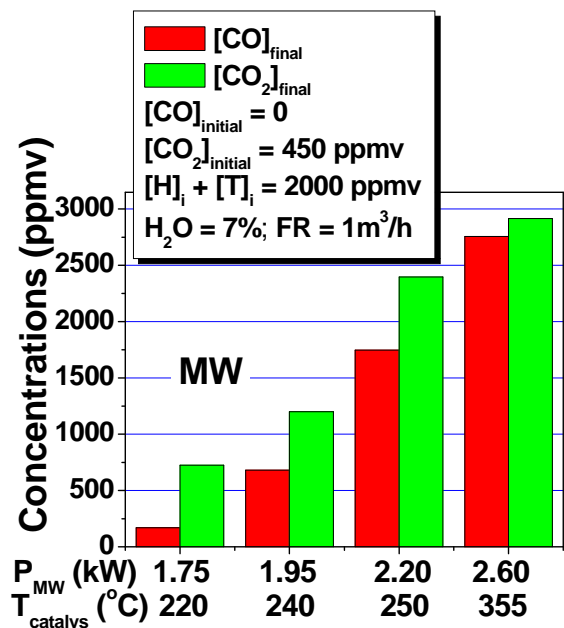Fig. 10. The effect of P_{MW} on the E_d and E_o

Fig. 12: The effect of P_{MW} on the CO and CO_2 concentrations after MW exposure.

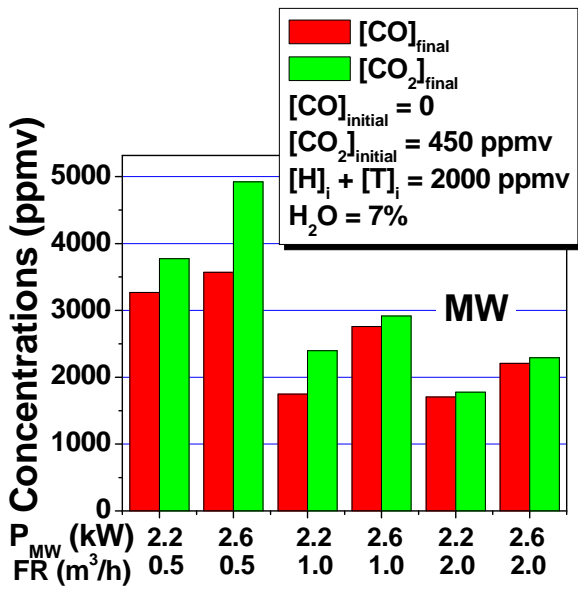Daniel Ighigeanu, Diana Martin,
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Fig. 13. The effect of FR on the CO and CO_2 concentrations after MW exposure.
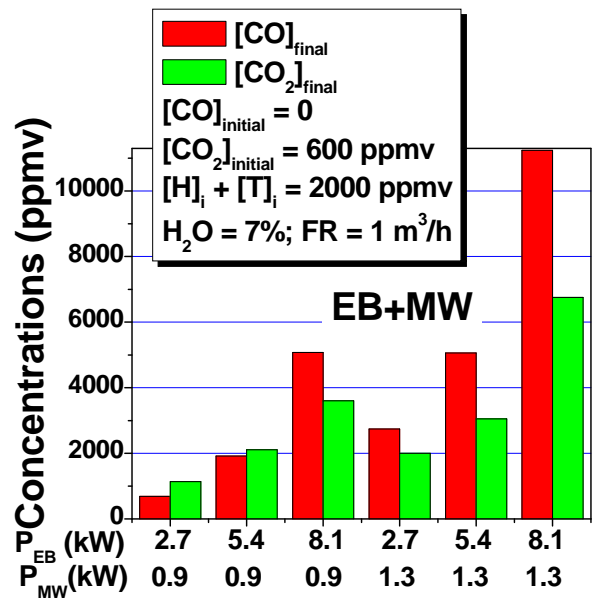

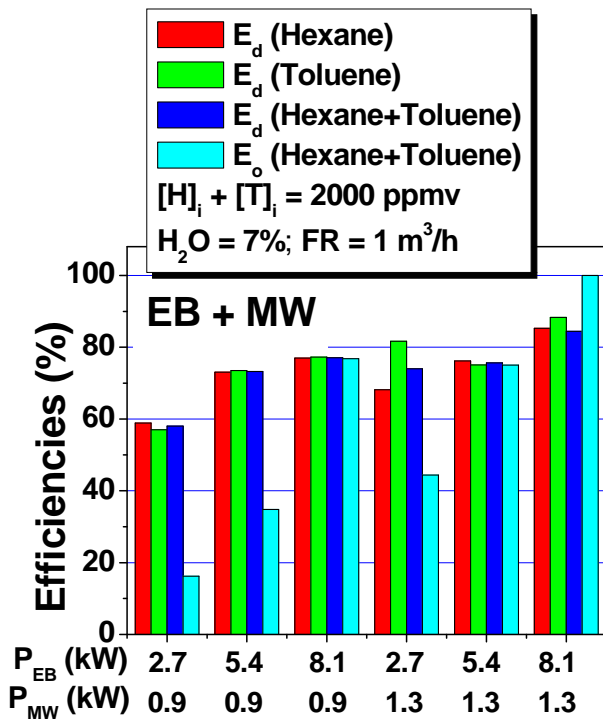Fig. 15. The effect of $P_{EB} + P_{MW}$ on the CO_2 and CO concentration after treatment with EB+MW

Fig. 14. The effect of $P_{EB} + P_{MW}$ on the E_d and E_o
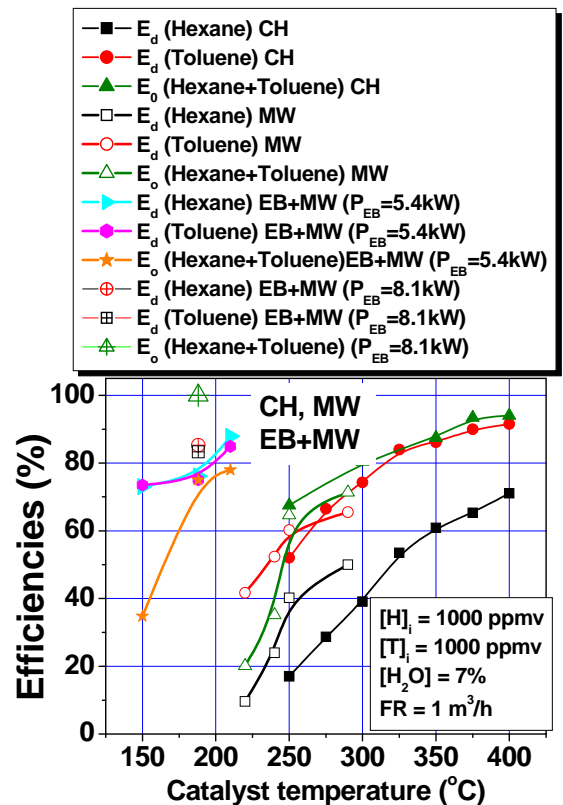

Fig. 16. The effect of catalyst temperature heated by CH, MW and EB+MW on the E_d and E_o

4 Conclusions

The MW treatment is a viable method for flue gas cleaning, especially for SO_2 removal at very high efficiencies. The removal efficiencies obtained by MW processing were up to 95 % for SO_2 and up to 55 % for NO_X. The MW+EB processing increases strongly NO_x removal efficiency, up to 95%, compared with MW treatment only, simultaneously providing high values for the SO_2 removal efficiency, near 100%. The MW+EB processing could be a promising method for flue gas cleaning, especially for simultaneous SO_2 and NO_X removal at very high efficiencies.

The oxidation process of the hexane and toluene mixture enhanced by the simultaneous high power EB and high power MW irradiation in the same reactor containing a catalyst bed. The high power EB and MW sources are able to activate the catalyst without additional heat supply.

It seems that chemical reactions driven in both types of plasma, EB-plasma and MW-plasma, complete and sustain each other at a higher rate level in the case of pollutants treatment by EB+MW-plasma.

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