TCE abatement with a plasma-catalysis combined system using MnO_2 as catalyst

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International Symposium on Plasma Chemistry

Introduction…

The condition of our environment is increasingly endangered by air pollution which poses serious risks to ecological life and public health. In this regard, **volatile organic compounds** (VOCs) are a large group of chemical compounds that significantly contribute to poor air quality. Therefore, air quality regulations are tightened and new remediation technologies are consequently being explored in order to overcome these issues.

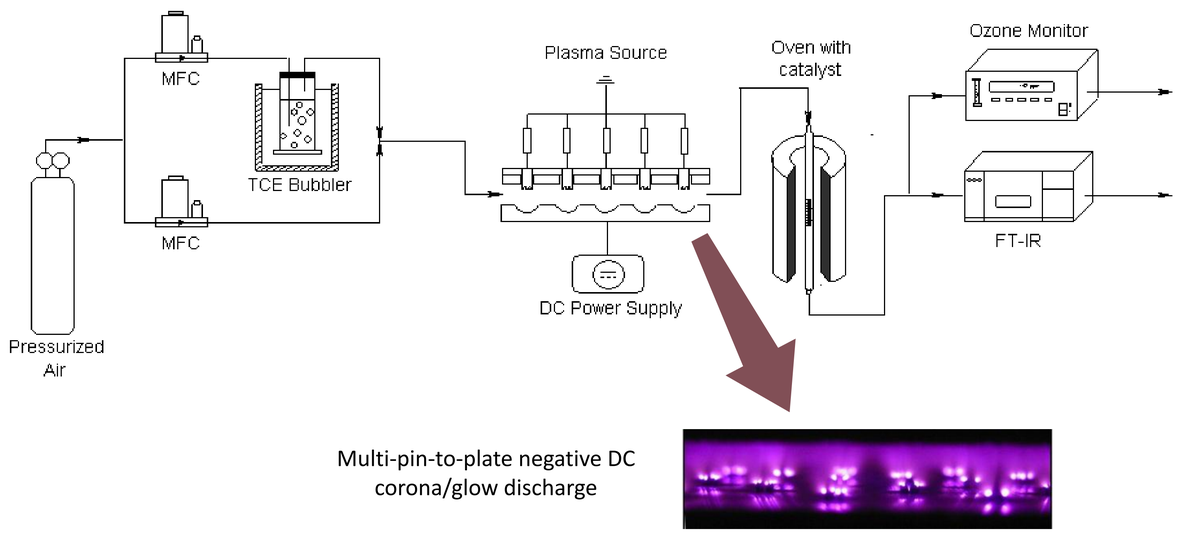
As an alternative to existing air remediation methods, **non-thermal plasma** (NTP) technology has been investigated for the removal of dilute VOCs (< 1000 ppm) from waste gases and indoor air since the last 2 decades [1, 2]. In a NTP, highly energetic electrons (1-10 eV) trigger multiple chemical processes such as ionization, excitation and dissociation through collisions with neutral background molecules (N_2, O_2, H_2O). Hence, pollutants are being exposed to a **reactive chemical environment** containing ions, radicals, excited species and metastable states by which they are converted to less harmful products.

The **combination of NTP with heterogeneous catalysis** has attracted increased attention since the last decade. The introduction of a catalyst, either inside or downstream of a NTP reactor, leads to an **enhancement of the energy efficiency, carbon balance and CO_2-selectivity** compared to plasma alone systems. Recently, Vandenbroucke *et al.* have extensively reviewed the recent achievements and current status of this hybrid technology for VOC abatement [3].

The aim of this study is…

…to investigate the opportunities of a plasma-catalytic system with MnO_2 downstream for the abatement of a typical chlorinated VOC, trichloroethylene (TCE), in terms of conversion and CO_x-selectivity. The effect of catalyst temperature has been studied in detail. A degradation scheme is proposed for the destruction of TCE in the gas-phase and on the catalyst surface.

Experimental…

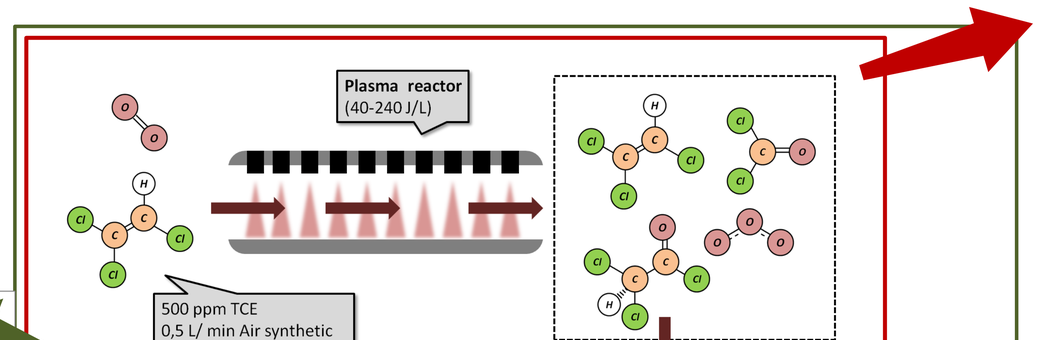


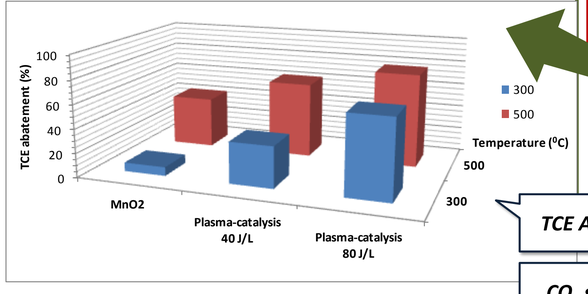
Multi-pin-to-plate negative DC corona/glow discharge

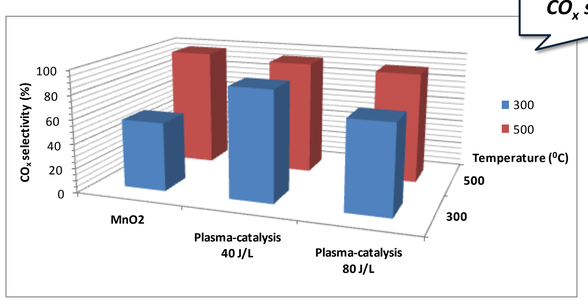
Results and discussion…

TCE abatement using plasma-catalytic combined system

In order to **improve the energy efficiency** of the entire system, we investigated the plasma-catalytic abatement of TCE using the same temperature range (300-500 ^{0}C) but applying **low energy density** (40 and 80 J/L).

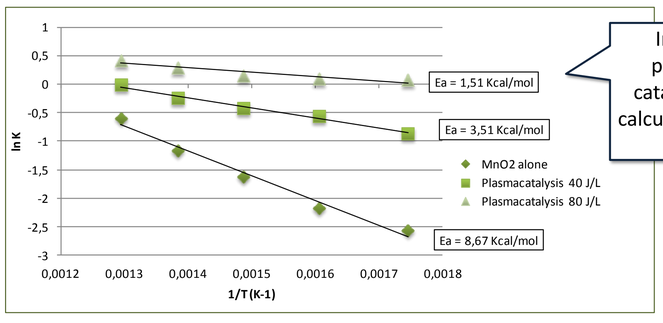






The TCE abatement increased with respect to the catalyst temperature, obtaining the best value (78 %) for an energy density of 80 J/L and maximum temperature of 500 ^{0}C. For these conditions, the **CO_2-selectivity reached 40 %** while the formation of unwanted chlorinated byproducts was greatly suppressed. Therefore, we can conclude that the plasma-catalytic system is an effective method for the abatement of TCE.

For the case of MnO_2 without plasma, a large temperature dependence is observed with respect to the total conversion.. However, in case of plasma-catalysis, there is only a small temperature dependence on the total conversion. From these results it seems clear that the plasma participates in the transformation of TCE. Although the mechanism is not yet elucidated, it is reasonable to consider that the **oxygenated intermediates** produced by the plasma (phosgene, DCAC) reach the catalyst surface. Because these molecules are **more susceptible to catalytic oxidation by MnO_2**, the **activation energy is significantly reduced** when compared to the catalyst alone system.



In order to examine if the plasma provides an extra activation of the catalyst, **Arrhenius plots** were used to calculate the **activation energy** (E_a) of the three systems

$$f_{TCE} = \frac{(\text{TCE abatament})_{\text{plasma-catalysis}}}{[(\text{TCE abatament})_{\text{plasma}} + (\text{TCE abatament})_{\text{catalysis}}]}$$

$$f_{CO} = \frac{(Y_{CO})_{\text{plasma-catalysis}}}{[(Y_{CO})_{\text{plasma}} + (Y_{CO})_{\text{catalysis}}]}$$

$$f_{CO_2} = \frac{(Y_{CO_2})_{\text{plasma-catalysis}}}{[(Y_{CO_2})_{\text{plasma}} + (Y_{CO_2})_{\text{catalysis}}]}$$

The **synergy factor** gives the relation of the studied parameter for plasma-catalysis with respect to the sum of its individual values for plasma and catalyst alone conditions. If this value exceeds 1, a synergetic effect is observed.

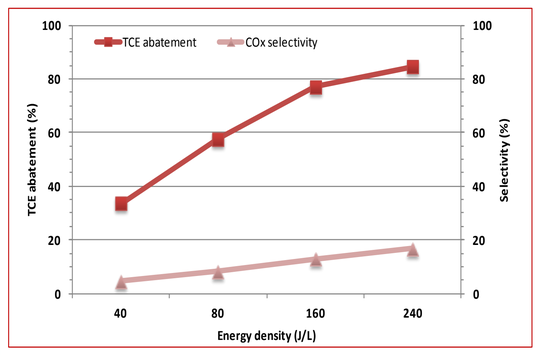
Temp. (°C)	f_{TCE}		f_{CO}		f_{CO2}	
	40 J/L	80 J/L	40 J/L	80 J/L	40 J/L	80 J/L
300	0,84	1,01	8	6,47	3,72	4,22
350	0,99	0,97	5,9	5,2	3,57	4,06
400	0,92	0,91	3,29	3,56	1,96	2,28
450	0,89	0,87	2,26	2,63	1,56	1,78
500	0,83	0,78	1,53	1,72	1,29	1,44

$$Y_{CO_2}(\%) = \frac{[CO_2]_{out}}{2 \times [TCE]_{in}} \times 100$$

$$Y_{CO}(\%) = \frac{[CO]_{out}}{2 \times [TCE]_{in}} \times 100$$

The synergy factor for TCE abatement is in the range of 0.78 – 1, which indicates that the plasma-catalytic system does not offer any synergy with respect to the TCE abatement. Moreover, this factor decreases with increasing catalyst temperature. This is understandable because at higher temperatures, the catalyst efficiency for VOC removal increases. However, **the synergy factors for the yields to CO and CO_2 range from 1.3 to 8**, indicating that the plasma-catalytic system greatly improves the selectivity of the process towards total oxidation.

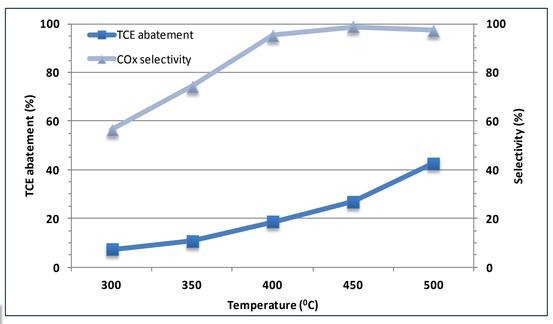
TCE abatement using non-thermal plasma



For a maximum energy density of 240 J/L the TCE abatement reached 85 %. This conversion was however related to the **formation of undesirable chlorinated by-products** such as phosgene ($COCl_2$) and dichloroacetyl chloride (DCAC) [5]. Also, an increase of the energy density gave a slight increase of the selectivity to CO_x, reaching 18 % at 240 J/L. According to Kirkpatrick *et al.* [6], DCAC is the major by-product of TCE decomposition with NTP due to reaction of TCE with ClO radicals (generated *in situ* by decomposition of the same VOC in the plasma) according to the following reaction:

$$C_2HCl_3 + ClO \rightarrow CHCl_2COCl + Cl$$

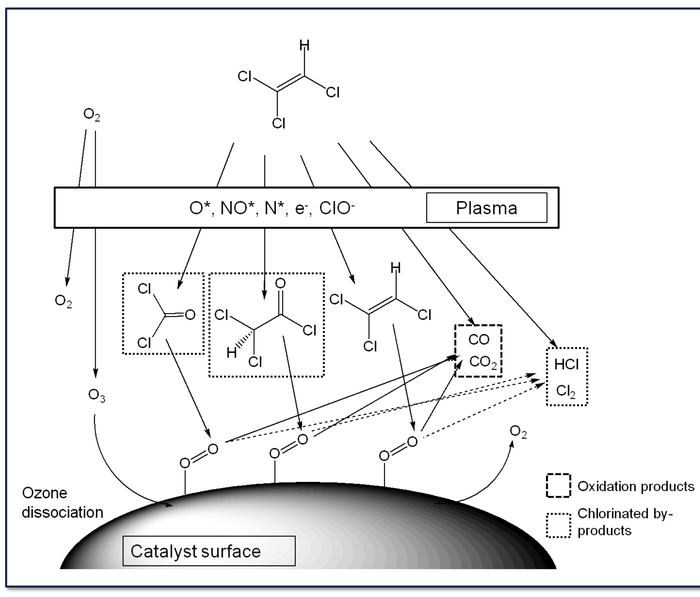
TCE abatement using MnO_2



A **higher catalyst temperature** favors the TCE abatement, reaching a maximum of 42.6 % at 500 $^\circ$ C. Also, the CO_x-selectivity significantly increased when comparing both the NTP and catalytic reactor, reaching 98 % at higher catalyst temperature, thereby **minimizing the formation of unwanted chlorinated byproducts**. This result is quite expected considering that MnO_2 can induce the following total oxidation reactions for TCE [10]:

$$C_2HCl_3 + 2\,O_2 \rightarrow 2\,CO_2 + HCl + Cl_2$$
$$C_2HCl_3 + O_2 \rightarrow 2\,CO + HCl + Cl_2$$

Reaction pathway in the plasma-catalytic TCE abatement…



1. The energy transferred to the plasma converts N_2 and O_2 molecules to ionized species that are able to decompose TCE to a **mixture of oxygenated intermediates and final oxidation products.**
2. Ozone dissociates on the catalyst surface to form **peroxide groups** and molecular oxygen in the gas phase. These surface species **promote the complete oxidation of TCE** to CO, CO_2, HCl and Cl_2. This oxidation is more efficient if oxygenated molecules, like phosgene and DCAC, arrive to the surface of the catalyst.

and the conclusions…

Our results prove that the combined system greatly improves the selectivity of the process towards total oxidation. This can be attributed to the fact that the plasma provides extra activation of the catalyst. The plasma converts TCE to a mixture of oxygenated intermediates and final oxidation products. The ozone produced by the plasma dissociates on the catalyst surface to form peroxide groups. These surface species promote the complete oxidation of TCE.

Acknowledgements…

R. Morent acknowledges the support of the Research Foundation Flanders (FWO, Belgium) through a post-doctoral research fellowship.
The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement n. 279022.
M. Mora acknowledges funding form Junta de Andalucia (FQM-6181), Ministry of Science and Innovation (MAT 2010-18778) and Fondos Feder.

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