

## PLASMA-CATALYTIC TREATMENT OF HYDROCARBONS IN AIR FLOWS

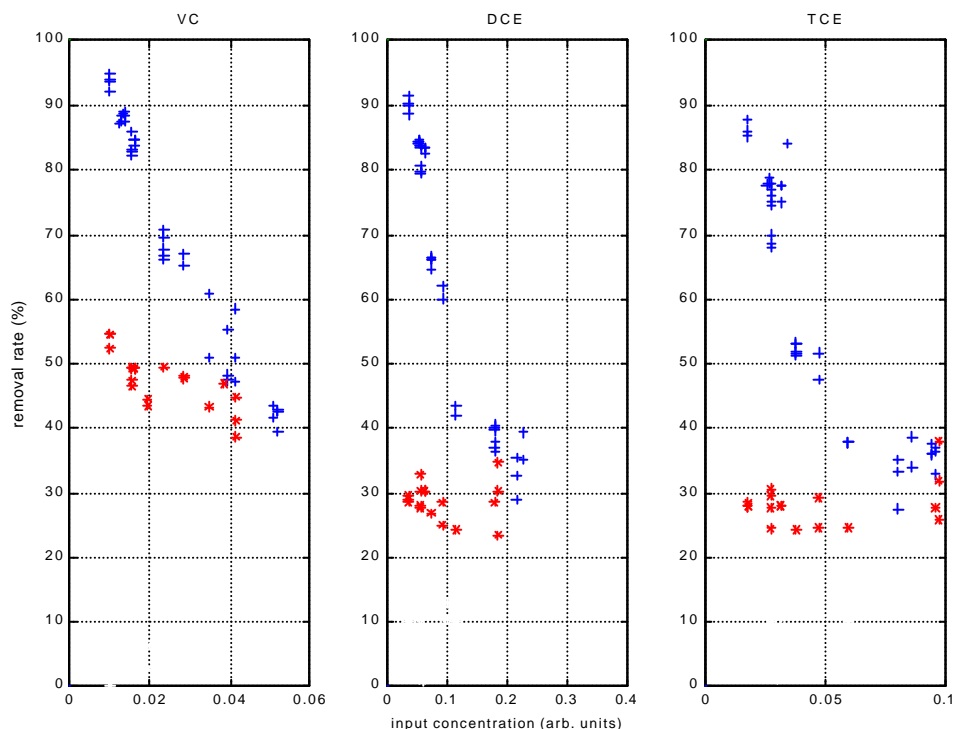
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### 1. Introduction

In a field experiment described in [1,2] a plasma-catalytic treatment procedure (non-thermal plasma followed by low-temperature catalytic oxidation) was applied to contaminated stripper air at an industrial groundwater treatment facility. The organic pollution consisted of a mixture of aromates and halogenated ethylenes. A flow of 60 m<sup>3</sup>/h was treated at a plasma energy density of appr. 12 Wh/m<sup>3</sup>, the Mn-Fe oxide catalyst was held at 110 °C. The experiment revealed, that removal efficiencies for some compounds like vinyl chloride (VC), 1,2-cis dichloroethylene (DCE) and tri-chloroethylene strongly depend on input concentration (fig. 1).

Whereas at low concentrations 80...90 % of these compounds could be removed, removal rates decrease considerably with increasing input load. Moreover, a certain influence of the unstable flow humidity was assumed, but could not be verified in detail.



**Fig. 1:** Removal rates for plasma (\*) and plasma-catalytic treatment (+) as function of input load

These findings motivated us to study the effects of input concentration and air flow humidity on the decomposition of volatile organic compounds (VOCs) at more defined laboratory conditions. The aim of these studies was to learn something about the destruction process of the organic molecules by active species generated within the plasma. Given the complicated reaction chains in case of halogenated hydrocarbons (see [3] for example) we at first studied the decomposition of typical representatives of

halogen-free VOCs by plasma alone. This paper presents results for ethyl acetate (EA), acetone and toluene.

## 2. Experimental set-up

The laboratory set-up consisted of a blower for 10...150 m<sup>3</sup>/h of outdoor air, a barrier discharge reactor, a temperature controlled gas heater and a catalytic converter. The converter contained 5 l of Fe-Mn mixed oxide catalyst. Flow humidity was measured by a capacitive detector and could be set up by means of a water vapour mass flow controller. A small flow of synthetic air was saturated with ethyl acetate and added to the main flow upstream to the plasma reactor. The total amount of organic carbon was measured as CO<sub>2</sub> by means of an NDIR detector after oxidation of a small sample flow in a high temperature furnace.

The compact, planar barrier discharge reactor had a total active volume of 3.1 l. Borofloat glass of 2 mm thickness was used as dielectric barriers in combination with stainless steel plates as electrodes leaving a discharge gap of 2x2 mm. The discharge was operated at 400 Hz sinusoidal voltage at 8...10 kV<sub>rms</sub> and delivered up to 1500 W into the plasma. Power measurements were based on voltage-current recording by a hv-probe and a Rogowski coil.

A photoionisation detector (PID) and a small process gas chromatograph (GC-PID) with integrated gas pumps were used for on line gas analysis. While the PID monitored the integral organic load, the GC-PID measured the concentration of the individual organic components. A short multicapillary column and an internal air based gas loop ensured short measuring times (2 min) without the need of a carrier gas. For the results presented below samples were taken via 6 mm PTFE pipes upstream (raw air) and downstream (plasma treated air) to the discharge reactor. Before entering the analytic equipment the sample flow passed through a gas cooling unit in order to minimise the influence of air humidity.

## 3. Results and Discussion

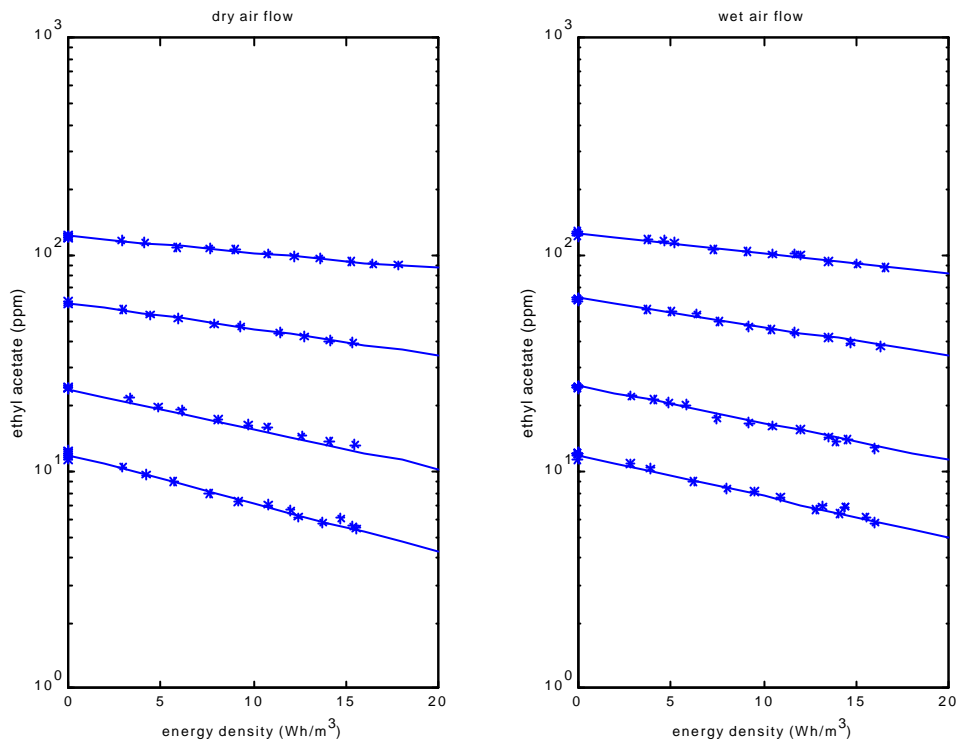
The concentration of ethyl acetate in dependence on energy density E - employed to a 30 m<sup>3</sup>/h flow of polluted dry (7,7...9,4 mbar of water vapour) and wet (26,4...28,4 mbar of water vapour) air - is shown in fig. 2. At least for low and medium removal EA is degraded by

$$S(E) = S_0 \exp[-E/\beta(S_0)]$$

with characteristic  $\beta$ -parameter depending on initial concentration  $S_0$ . Fig. 3 shows the concentration dependence of  $\beta$ . It obeys linear behaviour in  $S_0$  with nonzero value  $\beta_0$  for the limit  $S_0 \rightarrow 0$ . The slope of the straight line is lower for the wet air flow, but  $\beta_0$  becomes somewhat larger in this case. Moreover, a similar linear dependence  $\beta(S_0)$  was found for other hydrocarbons like acetone and toluene (fig. 3).

In order to get a mechanistic understanding of these phenomena we propose a model based on the following assumptions:

1. The organic molecules S are attacked by active species R (radicals), which are produced within the barrier discharge:  $S + R \rightarrow \text{products}$ .
2. The production rate of R is proportional to the energy density employed to the gas flow:  $Q = qE/\tau$  (q - production rate per energy density,  $\tau$  - transit time through the



**Fig. 2:** Destruction of ethyl acetate versus energy density

barrier discharge reactor).

- Losses of R result from plasmachemical reactions with carrier gas species (lifetime  $\tau_R$ ), with S and with its products. The last two losses might be combined in a single loss process by replacing S&products by the initial concentration  $S_0$ . This assumption is the more true the lower the fraction of decomposed  $S_0$  is.

Now the mass conservation equations for species S and R are given by

$$dS/dt = -k_S R S, \quad dR/dt = Q - R/\tau_R - k_S R S_0, \quad 0 \leq t \leq \tau.$$

Assuming that R is short living ( $\tau_R \ll \tau$ ), what was proofed experimentally, R becomes independent of time ( $R = \text{const}$ ). Then, after integration from reactor inlet ( $t = 0$ ) to reactor outlet ( $t = \tau$ ) a pseudo-first-order destruction law is obtained:

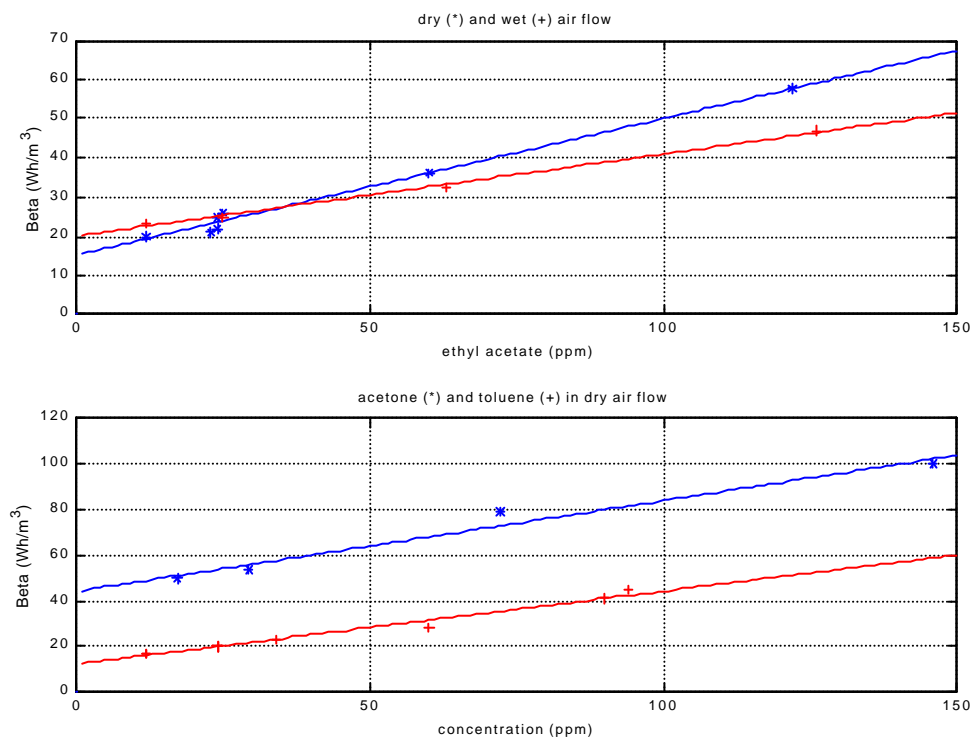
$$S = S_0 \exp[-E/\beta(S_0)], \quad \beta(S_0) = [(k_S \tau_R)^{-1} + S_0]/q = \beta_0 + S_0/q.$$

The obtained  $\beta$ -parameter is a linear function of  $S_0$  with a slope depending only on radical production efficiency.  $\beta_0$  is determined by the reaction rate  $k_S$  in relation to the radical lifetime  $\tau_R$ . Comparing this  $\beta$ -function with the experimental data the parameters  $q$  and  $(k_S \tau_R)$  can be deduced. They are summarised in the table below.

What are the consequences if this simple model is assumed to be qualitatively correct?

- The concentration dependence of  $\beta$  results from competition of molecules S with each other and with its destruction products for limited R.

2.  $\beta_o$  is a consequence of losses of radicals R due to collisions with carrier gas species.
3. Atomic oxygen is not a favourable candidate for R. The main loss process for O is ozone build up. We measured an ozone production rate of 15...30 ppm/(Wh/m<sup>3</sup>) in unpolluted air at the same flow conditions. This value is too high in order to explain the experimental results for q. The failure of atomic oxygen as a VOC destruction radical was always pointed out in [4].
4. OH radicals may be responsible for the primary destruction process. Indeed, the different slope of the  $\beta$ -function in case of EA in dry and wet air flows qualitatively agrees with this assumption. And so does the similar slopes of  $\beta(S_o)$  for EA, acetone and toluene. Nevertheless the known OH reaction rates (last line in the table) do not fit all experimental data in a unique manner.



**Fig. 3:**  $\beta$ -parameter versus initial concentration

	EA in dry air	EA in wet air	acetone	toluene
q (ppm/(Wh/m <sup>3</sup> ))	2,86	4,77	2,51	3,14
$k_S \tau_R$ (cm <sup>3</sup> )	9,38e-16	4,27e-16	3,68e-16	1,05e-15
$k_{OH}$ (cm <sup>3</sup> /h)	1,94e-12 [5]	1,94e-12	1,9e-13 [6]	6,03e-12 [7]

#### 4. Summary

Concentration dependent decomposition of VOC molecules in plasma of a dielectric barrier discharge was studied. Removal efficiencies decrease linearly with initial VOC concentration and depend on flow humidity.

A simple kinetic model was derived, which can explain the linear dependence  $\beta(S_o)$ . Starting from this, atomic oxygen could be ruled out as a candidate for VOC decomposition. The OH radical hypothesis is in better agreement with experimental

data but cannot fit them quantitatively.

### **5. Acknowledgements**

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