On the Destruction of Volatile Organic Compounds using a Dielectric Pellet Bed Reactor

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Abstract. Volatile organic compounds (VOC) are known to be dangerous for human health. If they are part of a precursor gas mixture undesired effects in e.g. industrial processes may occur. Therefore, the destruction of unwanted VOCs in a gas stream is an important aim. For that purpose a five stage planar dielectric barrier discharge reactor working at atmospheric pressure has been developed and tested. Each stage consists of two parallel stainless steel meshes serving as electrodes. The space between them is filled with dielectric beads. The ac voltage applied to the electrodes is in the kV and kHz range and several gas flow rates are possible. The gases of interest have been measured using a Fourier Transform Infrared Spectrometer (FTIR) combined with a 32.5m long path cell. First result showed, that the VOC ethylene (C₂H₄) can be removed.

1. Introduction
Volatile Organic Compounds (VOCs) are chemical substances which are easy to vaporise and therefore, when exhausted, are present in the gas phase at room temperature and ambient pressure. Although no unique and precise definition exists these substances can be roughly classified into four groups based on their boiling points [1]:

| Name                                                      | Boiling Point [°C] |
|------------------------------------------------------------|--------------------|
| Very Volatile Organic Compounds (VVOC)                     | <0 - 50...100      |
| Volatile Organic Compounds (VOC)                           | 50...100 - 240...260|
| Semi Volatile Organic Compound (SVOC)                      | 240...260 - 380...400|
| Organic compound associated with particulate matter or particulate organic matter (POM) | 380                |

As one can see from table 1 a lot of these substances are vaporised at room temperature and therefore, if present, easy to breath.
Nowadays two main sources can be distinguished: natural sources such as wetlands, ruminants or rice agriculture and anthropogenic sources such as paint thinners, petroleum fuels or solvents. Whereas natural sources are considered to be unproblematic the man-made VOCs emitted e.g. from chemical industries are considered to be critical because some of these VOCs are suspected or known to cause cancer or to damage the central nervous system of humans. Therefore anthropogenic emission
of VOCs into the atmosphere or into ground water can lead to certain health problems for humans. For example, the VOC toluene is suspected to harm the embryo. Accumulation of VOCs in the atmosphere or in the ground water has to be avoided because of these facts. Therefore waste gas exhaust from industry has to be cleaned.

Plasma processing for air pollution control has a high potential for industrial applications. Based on a new approach by Whitehead and co-workers [2] a new five stage packed-bed dielectric barrier discharge reactor working at atmospheric pressure has been designed and tested. Harling et. al. found that such an arrangement is appropriate for efficient destruction of VOCs inside a gas stream without NOx production and that three stages working in series are more efficient compared to a parallel arrangement [2]. This synergistic effect will be investigated in more detail using infrared absorption experiments. Fourier Transform Infrared Spectrometry (FTIR) is used for overview spectra, and for higher sensitive species concentration measurements Tuneable Diode Laser Absorption Spectroscopy (TDLAS) and Quantum Cascade Laser Absorption Spectroscopy (QCLAS) will be applied. Within the last years both techniques have been successfully established for studying molecular phenomena in plasmas and gases, in particular in kinetic and chemical processes [3, 4, 5].

In the present work the VOC ethylene (C2H4) was used as a pollutant. Ethylene is gaseous at ambient conditions with a boiling point of -103°C and a melting point of -169°C [6]. When humans are exposed to low concentrations of ethylene narcotic effects like headache, vertigo and loss of coordination may occur.

This paper describes a new five stage reactor and presents first results about the ethylene destruction in an air stream.

2. Experimental Setup

The new five stage packed-bed plasma reactor is made of acryl glass as shown in figure 1. The dimensions over all are 390 mm x 130mm x 130mm. The main units are the five stages. Each stage is made of two stainless steel meshes which serves as electrodes. The space between them is filled with glass beads with a diameter d = 6mm. The dimension of one electrode is 109mm x 109mm x 1.1mm. The space between two electrodes is approximately 15mm. The distance between the stages is about 45mm, figure 2. The top cover is removable. The gas supply can be realized by a tube connection at the front walls (left and right side in figure 1). Gas samples can be taken via tube connections between each stage. Additionally, IR transparent windows (KBr) are placed between each stage for absorption spectroscopy (AS) purposes.
Each stage was separately driven by a NeonPro (NP-10000-30) ac power supply with a voltage of $U_{HV} = 6500V$ ac and a frequency of $f_{HV} = 20kHz$. The power was measured with a commercial power meter connected before the NeonPro power supply. The power measured in this way is the system power for one stage. It was measured to be $P_{system} = 8W$ per stage.

The gas flow guided into the inlet valve of the reactor consisted of 1slm air and 1sccm $C_2H_4$ (99.95 vol. % purity) which is equivalent to an ethylene concentration of about $1\%$. It was controlled with mass flow controller units (MKS), premixed and then guided into the reactor. The outlet gas stream was guided into a 32.5m long path cell (White cell) and investigated using a Fourier Transform
Infrared Spectrometer (Bruker IFS66/v). A vacuum pump was used to stabilize the pressure inside the long path cell at 50mbarr.

3. Results
Two FTIR spectra of the gas at the outlet of the reactor are shown in figure 4. One is from C\textsubscript{2}H\textsubscript{4} after gas flow stabilisation and the second was recorded 10min after the plasma was ignited. As one can see in figure 4, ethylene has been almost completely removed.

![FTIR spectra](image)

**Figure 4.** FTIR spectra of (i) the gas stream with ethylene without plasma and (ii) of the outlet gas flow treated by plasma in the reactor. \( \Phi = 1 \text{slm air} + 1 \text{sccm C}_2\text{H}_4, P = 8W. \)

The identification of the species produced in the plasma was done using the HITRAN [7] database and the software IGOR was used to simulate the spectra. The parameters for the simulation were: pressure \( p = 50 \text{mbar}, \) absorption length \( l = 3250 \text{cm}, \) temperature \( T = 296 \text{ K}, \) and line width \( l_w = 1 \text{cm}^{-1}. \)

Typical products of the plasma treatment were found to be CO, CO\textsubscript{2}, N\textsubscript{2}O, O\textsubscript{3}, H\textsubscript{2}CO and H\textsubscript{2}CO\textsubscript{2}. In figures 5-7 detailed parts of measured FTIR spectra are shown and compared with simulated spectra to identify the products of the plasma treatment and to estimate their concentrations.
Figure 5. Identification of $\text{H}_2\text{CO}$. Species concentration used for spectrum simulation: 280 ppm $\text{H}_2\text{CO}$.

Figure 6. Identification of $\text{CO}_2$, $\text{N}_2\text{O}$, CO and $\text{O}_3$. Species concentration used for spectrum simulation: 170 ppm $\text{CO}_2$, 900 ppm $\text{O}_3$, 100 ppm $\text{N}_2\text{O}$ and 0.4% CO.
Figure 7. Identification of O\textsubscript{3} and H\textsubscript{2}CO\textsubscript{2}. Species concentration used for spectrum simulation: 900ppm O\textsubscript{3}, 0.15% H\textsubscript{2}CO\textsubscript{2}.

4. Conclusion / Outlook
This work has shown that the new packed-bed plasma reactor works in principle and can be used to remove ethylene from a gas stream. Typical products of the plasma treatment were found to be CO, CO\textsubscript{2}, N\textsubscript{2}O, O\textsubscript{3}, H\textsubscript{2}CO and H\textsubscript{2}CO\textsubscript{2}.

Further work will focus on a detailed investigation about the ethylene destruction. One experiment will use a different number of stages to investigate the synergistic effect reported by [2, 8]. For that purpose the new reactor permits an easy variation in the number of stages as well as different distances between them. This allows one to realize different residence times of the chemicals between consecutive stages. Whitehead and co-workers assume that one stage produces for example O\textsubscript{3} which destroys the pollutant chemically on the way through the reactor.

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