Packed Bed Corona Discharge reactor for gas-phase acetaldehyde decomposition at atmospheric pressure and ambient temperature

C. Klett, M. Redolfi, A. Vega, S. Touchard, X. Duten, K. Hassouni

1LIMHP, CNRS UPR 1311, Université Paris 13, 99 Av. JB Clément, 93430 Villetaneuse, France

Abstract: The aim of this study is to investigate the effect of a packed bed on the acetaldehyde degradation in atmospheric pulsed plasma. Acetaldehyde was chosen as this pollutant is produced during the biofuels combustion. Nano-TiO$_2$ deposited on SiO$_2$ or $\gamma$-Al$_2$O$_3$ balls will be used as packed bed. Major sub-products of acetaldehyde degradation will be identified and major reaction paths will be discussed.

Keywords: corona, packed bed, acetaldehyde, oxidation, atmospheric pressure

1. Introduction

The emission of Volatile Organic Compounds (VOCs) in the atmosphere is restricted by environmental regulations to very low values, due to the toxicity of these compounds and their contribution to global warming mechanisms. We investigate the remediation of acetaldehyde (CH$_3$CHO), as a model VOC, using different Packed Bed Corona Discharge systems (PBCD). PBCD takes advantage of a synergy between non-thermal plasma chemistry and surface chemistry in the porous bed at relatively low temperature conditions.

VOCs include many toxic species and are, with nitrogen oxide, the main ozone precursors. VOCs emission limits are therefore becoming more stringent and development of new VOC removal process is needed to satisfy the limits projected in the near future either in industrial activities (solvent industry) or transport application (mobile emission). Several studies were carried out to investigate the potentiality of non-thermal plasma as a tool for an advanced oxidation of VOC [1-5].

Most of the systems discussed in the literature made use of dielectric barrier discharge [6]. Corona coupled discharges were rarely considered in these studies. Corona systems operated in a pulsed mode give the possibility of a very precise control of the energy deposition in the system. They also enable achieving high activation efficiency when processed with very short rise time voltage chocks [7].

The aim of the work presented in this paper is to investigate the efficiency of a pulsed corona system for the oxidation of acetaldehyde molecule. Our choice of acetaldehyde was motivated by the fact that the oxidation of this species under discharge conditions has almost never been investigated.

The corona systems considered here include Packed Bed Wire-To-Cylinder configurations. Catalytic packed materials were considered in this study. The oxidation efficiencies of the corona systems were characterized in term of CO$_2$ and CO production yield.

2. Gas flow system and chemical analysis

The feed gas considered in this study mainly consists of N2/O2 mixture. The flow rate entering the discharge cell is monitored with three digital mass flow-meters (Fig.1). The base values of oxygen and acetaldehyde concentrations in the feed gas are 0%-10% and 1000 ppmC (i.e. 500 ppm of acetaldehyde). The total flow rate is fixed at 100 mL/min, corresponding to a residence time in the empty reactor of 64 seconds.

Fig.1 Experimental setup for acetaldehyde removal in the Packed Bed Corona Discharge Reactor.

The oxidation of acetaldehyde was evaluated by measuring the CO, CO$_2$ using an infra-red absorption analyser (Environnement SA MIR 9000), and the residual acetaldehyde by gas chromatography (Shimadzu GC 2010) at the cell exit. The gas phase chromatograph is also used to detect and quantify the hydrocarbons that may result from the
interaction between acetaldehyde and the atmospheric pressure pulsed corona discharges. Ozone concentration at the cell exit was measured by ultra-violet absorption spectroscopy using an InUSA IN 2000 analyser.

3. Packed Bed Corona Reactor

The reactor consists of two coaxial electrodes and small sized beds. The outer electrode is a stainless steel tube, and the inner electrode is a 100 µm diameter tungsten wire. The inner diameter of the reactor is 20 mm, resulting in a 10 mm discharge gap. The discharge length is 200 mm. Two packing material were used in the packed bed wire-to-cylinder configuration: (i) a 2 mm diameter spherical SiO$_2$ glass particles, (ii) a 2 mm diameter spherical non porous γ-Al$_2$O$_3$ particles as a packing material.

TiO$_2$ catalyst was deposited [8] on both packing materials to enhance the degradation efficiency or modify the degradation kinetics of acetaldehyde.

The Packed Bed material is analysed before and after being used in the corona reactor, by Scanning Electron Microscopy (SEM – Figure 2), BET, X-ray diffraction, IR-absorption and Raman spectroscopy.

The energy deposited during one discharge pulse is estimated from the measured voltage and current. Figure 3(a) and 3(b) show a typical voltage and current waveforms associated respectively to a pulsed corona discharge and a SiO$_2$ packed bed corona discharge. In both configurations, the discharge voltage and current reaches a maximum of 22 kV and 65 A. They cancel after 200 ns duration. The typical value for the energy deposited in the discharge ranges between 20 mJ and 60 mJ per pulse, corresponding to a maximum power of 3 W for a ten Hz frequency.

We observe that the use of a packed bed does not significantly modify the current and voltage waveforms.

4. Degradation of acetaldehyde in different packing material.

We propose here to present some of the results that will be discussed during the poster session. In the following, the oxygen content was fixed at 5%, acetaldehyde was introduced at 1000 ppmC and experiments were performed at room temperature. Results obtained with plasma alone and with SiO$_2$ packed bed plasma reactor will be compared. The Figure 4 presents the residual acetaldehyde measured at the exit of the reactor using a plasma discharge (open symbols) and a plasma coupled with a SiO$_2$ packed bed. At low specific energy, the residual acetaldehyde decreases at the same rate with and without a packed bed.

The fact that residual acetaldehyde is the same at low energy using plasma and plasma packed bed reactors means that the main species responsible for the degradation of acetaldehyde is not much influenced by the packing material (i.e. SiO$_2$ in this example). In corona discharges, active species that may degrade acetaldehyde are mostly O, OH radicals, O$_3$ and N and N$_2$ metastable.
Fig 4: Residual acetaldehyde measured at the exit of the system in a plasma or a packed bed SiO$_2$ plasma configuration, as a function of the specific energy.

We have here to consider two kinds of active species, depending on their lifetimes. For example, O atoms are produced in the streamer volume [9] and do not diffuse outside the streamer diameter (around 200 microns) due to its short lifetime (10 microseconds). This means that only a very small part of produced O atoms will reach the SiO$_2$ surface and interact with the packing material.

On the other hand, OH radical, ozone or N$_2$(A) have a longer lifetime (respectively hundreds of microseconds, several seconds) and diffuse in the entire reactor volume. This long lifetime active species can adsorb on the packed bed material, recombine, …

The fact that the acetaldehyde removal is not influenced by a SiO$_2$ packed bed material means that the net production of these active species is not modified by the use of the SiO$_2$ material. Considering ozone, this is clearly shown in the Figure 5, where the concentration of O$_3$ at the exit of the cell as a function of the specific energy is presented using the “with” and “without” packed bed configurations.

Fig 5: Ozone concentration at the exit of the discharge cell in both configurations.

We can also note that the variation of the logarithm of the residual acetaldehyde is linear at low specific energy (below 100 J/L), but then trends to decrease faster than the linear variation. This means that the removal kinetic of acetaldehyde at low and high specific energy might differ. As previously shown in [10], a linear decrease indicated that the removal kinetic follows the Yan simple model ([9], [11]).

The difference of degradation of acetaldehyde in term of major reaction paths will be discussed in the poster.

5. Degradation products of acetaldehyde in different packing material.

Figures 6 and 7 show respectively the CO and CO$_2$ concentrations, and total COx concentration, at the reactor exit using the two configurations. One can note that CO and CO$_2$ increase with increasing almost linearly at low energy (bellow 100 J/L). At high specific energy, the CO$_2$ concentration in plasma reactor tends to saturate. Moreover, the CO and CO$_2$ concentrations in the plasma coupled with a SiO$_2$ packed bed increase by almost 25% in comparison with plasma reactor (open symbols). The total COx concentration increases linearly with the specific energy and reaches almost 400 ppm. In all the studied conditions, the COx in plasma Packed Bed reactor is higher (up to 20% more at 120 J/L) than in the plasma system.

The major paths of production of CO and CO$_2$ will be discussed in the poster.

Fig 6: CO and CO$_2$ concentrations as a function of the specific energy using the plasma Packed Bed and the plasma systems.

Fig 7: Total COx in both configurations.

Several sub-products of acetaldehyde degradation have been identified using gas chromatography and fourier
transform infra-red spectroscopy. As an example, the variation of methanol (CH$_4$O) and acetone (C$_3$H$_6$O) as a function of the specific energy are presented on Fig 8. In plasma reactor, the methanol is the major sub-product, and its concentration increases linearly with the specific energy up to 270 ppm at 100 J/L and tends to saturate at higher energies. Acetone is produced at a maximum level of 30 ppm (90 ppmC) at 100 J/L and decreases at higher energy. In plasma Packed Bed configuration, the methanol is produced at a lower concentration (up to 150 ppm) and acetone is not detected.

![Fig 8: Methanol and acetone concentrations in both configurations.](image)

The methanol can be produced from the acetaldehyde through the following reaction paths:

$$\text{CH}_3 - \text{CHO} + \text{O}, \text{OH}, \text{N}_2(\text{A}), \text{O}_3, \ldots \rightarrow \text{CH}_3 + \text{products}$$

$$\text{CH}_3 + \text{O} \rightarrow \text{CH}_3\text{O}$$

$$\text{CH}_3\text{O} + \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{O}$$

Contributions of the different paths of production of methanol and acetone will be discussed in the poster.

6. Conclusion.

The aim of this paper is to study the effect of a packed bed on the acetaldehyde degradation in atmospheric pulsed plasma. In the paper, we focused our attention on the use of SiO$_2$ as material. We observe that the voltage and current waveforms, which are linked to the production of active species (O especially) were not modified by the SiO$_2$ packed bed. Moreover, the ozone concentration at the exit of the reactor was the same using or not a SiO$_2$ packed bed.

Considering the acetaldehyde degradation, we observed that the SiO$_2$ packed bed did not change the residual acetaldehyde at the reactor exit. However, concentrations of sub-products (CO, CO$_2$, methanol, acetone) were modified when coupling the plasma with the SiO$_2$ packed bed.

Major reaction paths will be discussed on the poster. Effects of a γ-Al$_2$O$_3$, and TiO$_2$ deposited on packed bed, will be presented and discussed.

7. Acknowledgement.

This work is financially supported by “Agence Nationale de la Recherche” (JCIC BIOPAC) and Région Ile-de-France (CNANO NanoCAT).

8. References.