Odorous volatile compounds conversion by electro-ceramic barrier discharge

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Abstract: Decomposition of butyric acid and dimethyl sulphide diluted in dry air is studied in coaxial cylindrical geometry of Electro-ceramic Barrier Discharge (EBD). Removal rates are measured for different initial concentrations and electrical parameters. By products are identified using FTIR spectroscopy and PTR-MS diagnostic.

Keywords:VOCs, dimethylsulfid, butyric acid, PTRMS, electroceramic barrier discharge.

1. Introduction

Volatile organic compounds (VOC) emitted by industrial processes may have a strong odorant impact, even at weak levels, and therefore must be correctly handled. Techniques such as activated carbon filters, scrubbing or thermal oxidation may be used to either remove or destroy these compounds. However, these techniques are not always suited to strong flow rates and/or weak concentrations found in some VOC-emitting industrial processes. Non-thermal plasmas, eventually coupled to catalysis, are promising alternatives to these techniques [1]. The most common plasma used for these applications is dielectric barrier discharge (DBD). In this work, electro ceramic barrier discharges (EBD) are studied. Electro-ceramics materials allow working under lower voltage than pure alumina [2, 3]. The plasma conversion of two molecules, used as olfactory pollutant models were studied: butyric acid ($CH_3(CH_2)_2COOH$) and dimethyl sulfide (DMS, $(CH_3)_2S$). In order to follow the removal of these odorous molecules and the formation of some by-products, optical absorption in the infra-red (FTIR) has been employed. In complement Proton Transfer Reaction Mass Spectrometry, PTR-MS was used. This technique is currently used for academic research [4] or industrial applications [5], it has proved to be very effective for studies of VOCs removal by plasmas [6].

2. Experimental conditions

The EBD reactor consists of an electro-ceramic tube with a length of 8 cm, an internal diameter of 21.6 mm and an external diameter of 25.3 mm. A copper grid tape (L = 40 mm) surrounding the electro-ceramic tube was grounded, while the high voltage pulse was applied on a central stainless steel rod (diameter 2 mm). The electro-ceramic reactor was placed in a thermoregulated oven allowing conversion studies at temperatures from 25°C up to 200°C. Butyric acid or dimethyl sulfide were fed into the reactor by means of an evaporation system. It allows working with concentrations of 50 ppm or 100 ppm in case of the acid, with a total air flow of 1 $l.min^{-1}$. In case of the sulfide, its physical properties, in particular its vapor pressure, limited us to a study at a high concentration, 500 ppm, obtained using a low flow of 0.2 $l.min^{-1}$.

The discharge may be described by two operating modes: i/ a first regime, corresponding to "low deposited energy", which is characterized by a single current impulse and a filamentary plasma well distributed over all the inter-electrode volume for each HV-pulse; ii/ a second one, corresponding to "high deposited energy", which is characterized by two current impulses. This last regime was previously found detrimental to formaldehyde or toluene removal in studies with the same reactor design [2, 3]. In the present study, the electrical parameters were chosen to work in the first regime: the peak value of the applied voltage was fixed to 16 kV, while the pulse repetition frequency, ν, was chosen ranging from 50 Hz up to 500 Hz in order to vary the specific input energy, SIE. This energy is given by:

$$SIE = Ep \, . \, \nu \, / \, F \qquad (1)$$

where E_p is the electrical energy deposited in the discharge per HV-pulse and F is the total volume flow rate. E_p was determined through measurements of the voltage and current time evolutions using adapted probes connected to a fast digital oscilloscope. As a typical example, in figure 1 are plotted the values of E_p measured for a sample of 1000 pulses, for a frequency equal to 100 Hz and for a gas mixture containing 500 ppm of dimethyl sulfide.

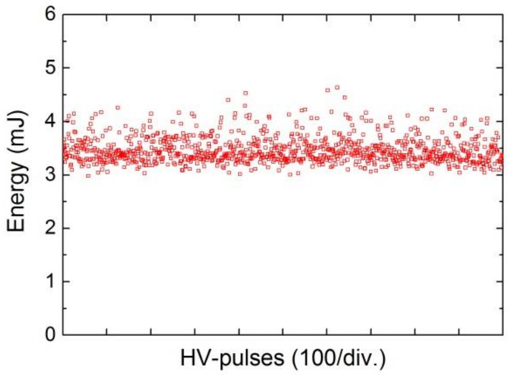

Fig. 1. Energy per pulse for a sample of 1000 HV-pulses at a repetition frequency of 100 Hz. DMS inlet concentration: 500 ppm.

For this example, the mean energy over ten thousands of pulses is 3.4 mJ with a small standard deviation equal to 0.2 mJ, emphasizing the good stability of the discharge operation in the first regime for the chosen applied voltage value.

3. Diagnostics

FTIR spectroscopy allowed measuring primary molecules and by-products concentration. A Nicolet Nexus Model 670 was used with spectral resolution of 0.5 cm^{-1}. Effluents pass through a long path cell with an optical length of 10.6 m kept at 50° C. This diagnostic allowed quantifying butyric acid, DMS and some of by-products issued from their conversion by plasma.

Time resolved measurement of butyric acid and by-products concentrations at the exit of the EBD, were also performed using chemical ionization (CI) in a compact FT-ICR mass spectrometer based on a permanent magnet, referred to as BTrap, developed by the company AlyXan in collaboration with the LCP laboratory. This diagnostic was already described in a previous study [6]. Mass spectrometry is a versatile and sensitive tool for on line detection of VOCs, provided it is associated with a soft and selective ionization technique such as controlled chemical ionization. This term means that the sample interacts with a unique, well-identified precursor ion under well-defined pressure and time conditions so that quantitative information is obtained. Proton transfer reaction with H_3O^+ as precursor has been used in this work. Since it is a soft ionization technique resulting in little or no fragmentation, identification is made directly from the mass of the observed ions and can benefit from high mass resolution techniques leading to the molecular formula of the ions. The gas flow from the exit of reactor was sampled through a capillary tube followed by a three-way pulsed valve generating the controlled gas pulses sent to the mass spectrometer. For each pulse the mass spectrum was recorded after PTR and the concentrations of the detected VOCs were derived. The analyses were performed with a minimum sampling rate of 3 seconds.

In the absence of absolute calibration, the value of the constant of the ionization reaction (CI) between H_3O^+ and butyric acid is used. Its value, $k = 3.0x10^{-9}$ $cm^3.s^{-1}$, comes from literature [7].

4. Experimental results

In case of butyric acid experiments were made at 160°C for an initial concentration of 100 ppm and at 25°C for initial concentrations of 50 and 100 ppm. Conversion rates of the acid, measured by both diagnostics (at ± 15%) are : 22% and 37% at 25°C for respectively 100 ppm and 50 ppm, and 39% at 160°C for 100 ppm. These results are coherent with studies on other molecules where conversion rates are observed to be higher for the lowest concentrations.

Several by–products are identified by FTIR analysis during butyric acid conversion. Concentrations of quantified species appeared in table 1.

Table 1 :By-products concentrations (ppm) measured by FTIR in butyric acid conversion for two initial concentrations, C_0.

SIE ($J.l^{-1}$)	T (°C)	C_0	O_3	CH_2O	HCN
85	25	100	334	7.5	6
82	25	50	400	0.6	3
62	160	100	34	13	2

The measured ozone concentration, 334 ppm à 25°C and 34 ppm at 160° C, is directly linked to oxygen atoms available in the discharge [8]. At higher temperature ozone decomposes to form oxygen atoms available for oxidation. This could be related with the fact that, at 25°C, even if the SIE is higher, butyric acid is less converted than at 160° C. Other species identified by FTIR are : HCOOH, HNO_3, N_2O and N_2O_5 and a heavy mass nitrate, in low concentration; no quantification of these species was made with this diagnostic. Carbon oxides have already been observed to be the main by-products [9]. The presence of a few ppm of HCN shows that dissociation processes by quenching of nitrogen metastable states occurs in the discharge, even in air, as already observed for other molecules, as ethanol for example [10].

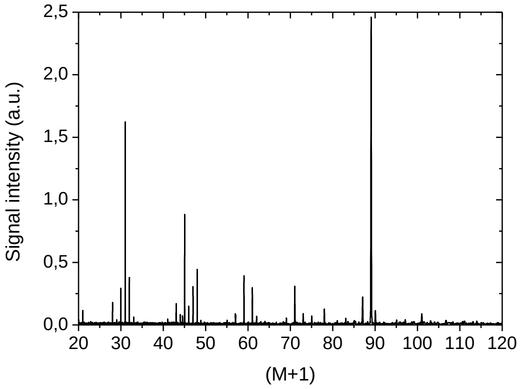

Fig. 2. Mass spectrum following treatment of 100 ppm of butyric acid at T = 160°C, SIE = 62 $J.l^{-1}$

Measurements by PTR-MS were made under the same conditions and at the same time as those made by FTIR. Fig. 2 gives an example of mass spectrum obtained in case of plasma treatment of 100 ppm of butyric acid at T = 160°C. Pics at m/z 89, $(C_3H_7COOH)H^+$, and m/z 71, $(C_2H_5CH=C=O)H^+$, correspond to ions directly issued from chemical ionization of butyric acid respectively by ionization and fragmentation. Numerous by-products were also observed and quantifications were made. The concentration of CH_2O, for example, is the same as that measured by FTIR.

PTR-MS analysis allowed observing the time evolution in the discharge of a lot of by-products in very low concentrations. In Fig.3 are plotted, for example, the results obtained for the plasma conversion of 100 ppm of acid (m/z 89) at 25°C and a SIE of 85 $J.l^{-1}$. Butyric acid is introduced in the reactor and after 30 min the discharge is put into operation for 44 minutes and, 4.5 minutes later, the butyric acid injection is cut off. Fig.3 exhibits also evolution as function of time of the intensity of the main products formed during the discharge. Those products are identified as formaldehyde (CH_2O) (m/z 31), acetaldehyde (CH_3CHO) (m/z 45), propanal (CH_3CH_2CHO) (m/z 59) and a molecule, $C_4H_6O_2$ (m/z 87), which could be: CH_3-CH=CH-C(=O)OH, the crotonic acid.

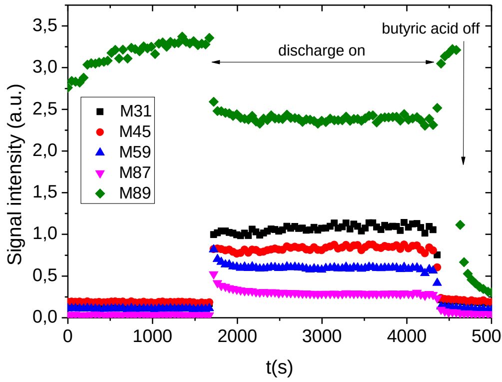

Fig 3. Time evolution of butyric acid and main by-products intensities measured by PTR-MS (C_0 = 100 ppm, T=25°C, SIE = 85 $J.l^{-1}$)

Possible reactional paths explaining the formation of these by-products are proposed in figure 4.

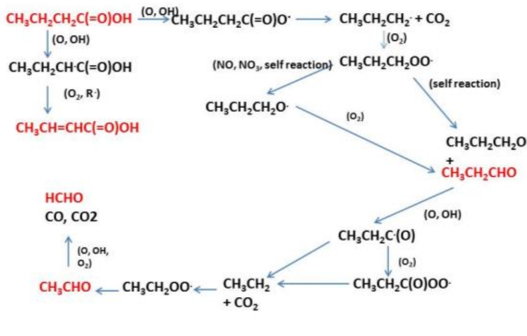

Fig 4. Scheme of some reactional paths explaining the formation of main products observed during butyric acid conversion (in red).

By reaction with O or OH, H abstraction can occur on carbon 3 and then lead to formation of crotonic acid. Concerning the formation of aldehydes, studies on oxidation of propionic acid suggest H-atom abstraction from the -COOH group followed by lost of CO_2 as schematized on Fig.4 [11]. In case of butyric acid this mechanism could explain the formation of propanal and, by successive oxidations, the formation of lighter aldehydes.

The capacity of the EBD reactor to degrade DMS was also tested. Several by-products were identified and quantified by FTIR, results at 25°C are presented in Table 2.

Table 2 :By-products concentrations (ppm) measured by FTIR in DMS removal at 25°C (C_0 = 500 ppm).

SIE ($J.l^{-1}$)	DMS	CH_4	CH_3OH	CH_2O	HCN
371	0	10	97	200	6
95	245	10	143	280	3
58	315	7	119	188	2

In addition to dimethyl sulphide, the products quantified by FTIR are methane CH_4, methanol CH_3OH, formaldehyde CH_2O, and hydrocyanic acid HCN. In the FTIR spectra of by-products from the treatment of dimethyl sulphide are also identified several molecules that have not been quantified : carbon oxides, methyl nitrate CH_3ONO_2, formic acid HCOOH, nitric acid HNO_3, nitrous oxide N_2O, carbonyl sulphide O=C=S and sulfur dioxide SO_2 which absorbance is very important, especially at 25 ° C for a frequency of 500Hz.

The conversion of all the DMS is reached at 25 ° C for an energy of 371 $J.l^{-1}$.

Among the quantified identified products, the formation of methanol can be explained by this reactional path:

$(CH_3)_2S + O \rightarrow CH_3 + CH_3SO$
$(CH_3)_2S + OH \rightarrow CH_3SCH_2 + H_2O$
$(CH3)_2S + OH \rightarrow \mathbf{CH_3OH} + CH_3S$

The oxidation of methanol by OH, for example, is then a direct reaction leading to formaldehyde.

5. Conclusion

The removal of odorous molecules by EBD is quite efficient, even for high concentrations of pollutants, and plasma treatment is improved by lowering the initial concentration and increasing the temperature; these conditions better correspond to industrial application conditions.

In addition to carbon oxides, which are the most abundant by-products, several by–products are identified by FTIR during butyric acid or dimethyl sulphide conversion. PTR-MS is a diagnostic which gives concordant and complementary results to the FTIR, in case of butyric acid study. It allows to identify very low concentrations of by-products and to follow their time evolution. These results give information about possible reactional paths explaining the formation of main by-products. Work is in progress to discuss further about those paths.

6. Acknowledgment:

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7. References

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