Ethanol decomposition in Air Dielectric Barrier Discharges: experimental study and kinetic modeling

S. Lovascio[(*)], N. Blin-Simiand, L. Magne, F. Jorand, P. Jeanney, S. Pasquiers

Laboratoire de Physique des Gaz et des Plasma, CNRS (UMR8578), Université Paris-Sud, Bât 210, F91405 Orsay Cedex, France
[(*)] sara.lovascio@u-psud.fr

This work is a fundamental study on ethanol conversion in air fed Dielectric Barrier Discharges. Experimental investigations in dry and humid air/ethanol mixtures show that water vapor content slightly improves the VOC removal and it does not affect the by-products nature, but it seems to promote the complete oxydation chemical paths. The predictions of a 0D kinetic model suggest that, in order to explain experimental data, dissociative reactions cannot be neglected.

Air quality has become one of the main environmental issues, as the growing density of human activities all over the world promote the increase of Volatile Organic Compounds (VOCs) emission in the atmosphere. In the last decades atmospheric pressure non-thermal plasmas (NTPs) have been investigated as a promising tool for VOCs abatement: thanks to their ability to induce different chemical reactions at room temperature and atmospheric pressure, NTPs are considered a more efficient and economically interesting alternative to traditional gas cleaning techniques [1]. Recent trends in the field show that higher energy efficiency and CO_2 selectivity can be achieved by coupling plasma processes and heterogeneous catalysis [2]. At this purpose a better understanding of the plasma induced VOCs conversion mechanism would be helpful.

The aim of this study is a full characterization of the ethanol conversion in air fed Dielectric Barrier Discharges (DBDs): experimental investigations were carried out in order to provide complete informations on removal efficiency and by-products distribution. In order to achieve a deeper insight of the kinetic mechanism occuring in the plasma phase, the experimental data were analyzed by mean of a 0D kinetic model.

Experimental work was carried out in a symmetric pin-to-pin DBD reactor: 17 aligned pins onto each metal electrode were placed at 3mm inter-electrode pin-to-pin distance and separated by a 1mm thick mica plate acting as floating dielectric. Electrodes were connected to a pulsed power supply able to generate positive voltage pulses up to 25kV, with a 1kV/ns pulse rise time rate: discharges were driven by 1μs width pulses of 15kV and 20kV, in the 100Hz – 1800Hz working frequencies range [3-4]. The applied voltage and the driven current were respectively measured by mean of a LeCroy PMK-14kVAC HV probe and a T&M Research Product CNB-5-2 current probe; the current and voltage signals, recorded by a LeCroy WaveRunner 204MXi-A digital oscilloscope, were multiplied and integrated to calculate the specific input energy (SIE).

Synthetic dry air, ethanol and water vapors flows were regulated by mean of a Bronkhorst CEM (Controlled Evaporation and Mixing) system: the ethanol concentration was kept constant at 300ppm in 2slm of air, while the water vapor concentration was varied in the 0-2.5% range. By-products detection and quantification were performed by means of a gas chromatograph (Varian 490-GC), a Fourier transform infrared spectrometer (Nicolet-Nexus FT-IR), an O_3 detector (BMT 964) and a CO_2-H_2O analyzer (LI-840) placed in the exhaust gas line; gas chromatography-mass spectroscopy (GC-MS) out-line analysis were also employed.

An ethanol removal of 70% was attained in dry air at the higher investigated SIE of 200 J/l. A humidity level of 1% in the feeding gas seems to slightly improve the ethanol conversion, while a higher water vapor addition, i.e. 2.5%, does not affect the VOC abatement (Fig. 1).

Apart the complete oxidation products as CO_2 and H_2O, CO and other oxidized species as aldehydes containing up to six carbon atoms, ketones and carboxylic acids were detected in the ethanol-air exhausts: acetaldehyde was the most abundant by-product and presumably the first ethanol oxidation step [5]. As expected in air fed DBDs, ozone, nitrogen oxides (N_2O, N_2O_5), nitric acid and organic nitrate were found.

The number and the nature of detected by-products is not influenced by the water vapor content in the treated mixture. Anyway lower by-products concentrations and higher CO_2 selectivity were obtained increasing the feed humidity.
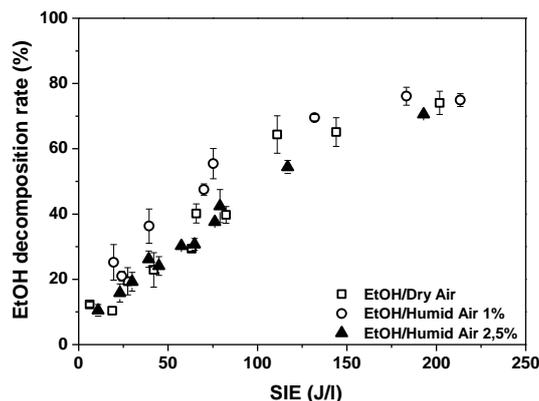

Fig. 1: Decomposition rate of ethanol in dry and humid air mixtures

The identification of H_2 amounts less than 10 ppm suggests that dissociative paths cannot be neglected. The predictions of the 0D discharge and kinetic model L0DKiS [6], which takes into account all relevant reactions for the VOC molecule, show that the measured ethanol conversion cannot be explained only by oxydation reactions (Fig. 2): dissociation processes of the VOC molecule induced by electrons and nitrogen excited states collisions and post-discharge chemical path should be invoked.
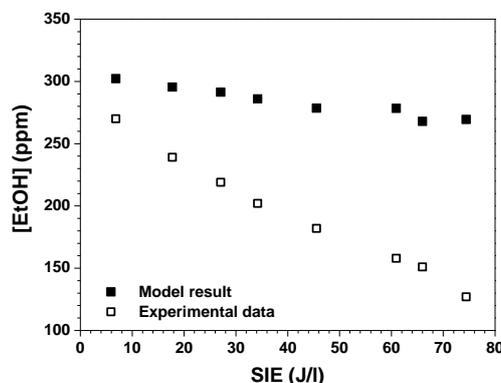

Fig. 2: Residual ethanol concentration in dry air mixtures: experimental results and model prediction based on the single contribution of oxydation reactions.

References

[1] H-H. Kim, *Plasma Process. Polym.* **1** (2004) 91-110
[2] H.L. Chen, H.M. Lee, S.H. Chen, M.B. Chang, S.J. Yu, S.N. Li, *Environ. Sci. Technol.*, **43** (2009) 2216-2227
[3] N. Méricam-Bourdet, M.J. Kirkpatrick, E. Odic, D. Frochot, F. Tuvache, *Proc. 63rd Annual Gaseous Electronics Conference and 7th International Conference on Reactive Plasmas*, Paris France (2010)
[4] N. Méricam-Bourdet, M.J. Kirkpatrick, F. Tuvache, E. Odic, D. Frochot, *Proc. 30th International Conference on Phenomena in Ionized Gases (ICPIG),* Belfast, Northern Ireland, UK, D14 (2011)
[5] W. Wang, C. Zhu, Y. Cao, *Int. J. Hydrogen Energy*, **35** (2010) 1951-1956
[6] N. Blin-Simiand, S. Pasquiers, F. Jorand, L. Magne, C. Postel, *International Symposium on Non-Thermal/Thermal Plasma Pollution Control Technology & Sustainable Energy (ISNTP-7)* St. John's, Terre Neuve, Canada, (2010)