Ethanol/Acetone Mixtures Conversion in Air Dielectric Barrier Discharges

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Abstract—This work aims to get inside the plasma treatment of VOCs mixtures. At this purpose ethanol/acetone blends in air fed Dielectric Barrier Discharges have been studied. The two pollutants plasma removal does not seem to be affected by their coexistence into the discharge. Experimental investigations in dry and humid air DBDs show that water vapor content does not significantly improve the VOCs abatement; instead exceeding feeding gas humidity inhibits the two target molecules conversion. The ethanol/acetone mixtures exhausts showed the same chemical composition of each plasma treated compound singularly considered. The feeding gas humidity does not affect the by-products nature, but it seems to promote the complete oxidation chemical paths.

Keywords—DBD, ethanol, acetone, VOCs

I. INTRODUCTION

The industrial development of many countries has promoted, along with their economic growth, increasing environmental concerns due to atmospheric pollutants emitted from human activities. In addition to NOx, SOx and inorganic acids, Volatiles Organic Compounds (VOCs) are a large group of pollutants often hazardous both to human and earth’s health. Adsorption, thermal and thermal-catalytic oxidation are well established technologies for VOCs abatement, but due to the required energy supply and their effectiveness for VOCs concentrations higher than 1000 ppm, more efficient and low energy consumption technologies are demanded [1].

Over the last two decades an increasing scientific investigation has been focused on atmospheric pressure non-thermal plasmas (NTPs), as they revealed to be an interesting alternative to traditional thermal technologies. The attractive point of NTPs technique is that it is not necessary to heat the entire gas flow. Electron-molecule collisions in the plasma phase produce unstable reactive species able to promote VOCs conversion at the bulk gas temperature. Moreover the technique is suitable for a wide range of VOCs contents (1-10000 ppm) and it is especially effective for diluted VOCs concentrations [2].

One drawback of NTP technology is the non-complete VOC oxidation resulting in a low CO2 selectivity and in the formation of by-products as O3, CO, NOx, and other organic compounds. Recent trends in the field show that higher removal efficiency and increased oxidation rate are obtained coupling plasma treatment with heterogeneous catalysis. Catalyst can be placed either in the discharge zone or in the post-plasma zone: the synergism of the active species creation in the plasma phase and of the adsorption of target molecules on catalyst surface makes the hybrid plasma catalysis technology a more effective tool for air purification [3].

In order to achieve the best performances in the NTP-catalyst coupling, a full characterization of the plasma induced decomposition mechanism for some target molecules is worth of interest. Many studies have been carried out on the VOC removal in dry or humid air fed plasmas. A large variety of NTP reactors, differing in type of discharge or power supply or electrode configuration have been employed for environmental purpose: in all cases the main issued by-products and the dominant reaction pathways involving single pollutant molecules have been often investigated [4]. By the way, due to the complexity of real samples, the occurrence of additive or synergic effects in the plasma treatment of VOCs blends requires attention.

Some studies concerning the treatment of binary or multi-component VOCs mixtures by different kind of discharges [5-13] have shown that the process performance strongly depends on the pollutant nature. Sobacchi and co-workers, investigating the corona treatment of a methanol/acetone/dimethyl sulfide/α-pinene mixture simulating a brownstock washer emission from paper and pulp plants, found that the all VOCs high removal efficiency is decreased by the presence of α-pinene [5]. Wang and co-workers showed that m-xylene conversion in a silent discharge is quite unaffected, whereas acetone, benzene and tetrachloroethylene removal decreases a lot when such VOCs are mixed together [6]. Similar results were obtained by Zhang and co-workers who studied the benzene/m-xylene treatment by multi-pin-mesh corona discharges [7] and by Ogata and co-workers who investigated a benzene/toluene/o-xylene mixture in a packed-bed reactor [8]. On the other hand, Karuppiah and co-workers found a general conversion improvement for benzene / chlorobenzene / toluene mixtures by a DBD driven by a catalytic electrode [9].

This work focus on the conversion of ethanol-acetone mixtures in dry and humid air fed Dielectric Barrier Discharges (DBDs). Both ethanol and acetone are VOCs emitted from natural and anthropogenic sources, as painting and tanning hide processes, fine chemical industry [14]. Acetone removal in NTP, eventually coupled with catalysis, has been often investigated [6, 15-17], whereas ethanol oxidation has been mainly
studied in catalytic and photo-catalytic systems [18-20] and in low-pressure plasma [21]. The aim of this work is to provide a complete characterization for the simultaneous plasma treatment of the two VOCs: the effect of the mixtures composition on the removal efficiency and the by-products distribution, along with hypothesis on possible chemical pathways, are discussed. As interesting for practical industrial application, the effect of water vapor addition to the feeding gas has been also investigated.

II. EXPERIMENTAL

Experimental work was carried out in a symmetric pin-to-pin DBD reactor: a linear array of 17 equidistant groups of 4 pins was placed onto each stainless steel electrode. Pins onto opposite electrodes face each other at 3 mm inter-electrode pin-to-pin distance and are separated by a 1 mm thick mica plate acting as floating dielectric. Electrodes were connected to a pulsed power supply able to generate positive voltage pulses up to 25 kV, with a 1 kV/ns pulse rise time rate: discharges were driven by 1 µs width pulses of 15 kV and 20 kV, in the 100 Hz–1800 Hz working frequencies range [22, 23]. 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 energy deposited in the plasma volume per current pulse ($E_p$). The specific input energy ($SIE$), was simply evaluated as

$$SIE \ (J/L) = \nu E_p / F$$  \hspace{1cm} (1)$$

where $\nu$ is the working frequency and $F$ the gas flow rate. At the used working conditions SIE up to 150 J/L were investigated.

Synthetic dry air was used as carrier gas. Ethanol and water vapors were added to the air flow by means of controlled evaporation and mixing systems (CEM, Bronkhorst), each one consisting of a liquid flow meter, a mass flow controller for the carrier gas and a gas-liquid mixing chamber. Acetone vapors, instead, were introduced into the gas flow by an air stream bubbling through a liquid reservoir kept at 0°C. The air flow rate ($F$) was kept constant at 2 L/min NTP. Two ethanol-to-acetone ratios, 1:1 and 5:1, for a total VOCs concentration of 600 ppm, were investigated; the water vapor concentration was varied in the 0-2.5% range. Feeding gas was split and injected into each electrode-dielectric gap, then the exhaust gas was collected at the reactor exit for further chemical analysis; the inlet and the exit gas lines were kept at the constant temperature of 35°C.

By-products detection was performed by means of a gas chromatograph equipped with a thermal conductivity detector (Varian 490-GC), a Fourier transform infrared spectrometer (Nicolet-Nexus FT-IR), an O₃ UV-absorption based detector (BMT 964) and a CO₂-H₂O infrared gas analyzer (LI-840) placed in the exhaust gas line. Infrared spectra were recorded with a spectral resolution of 0.125 cm⁻¹, allowing exhaust gas to pass through a 10.6 m long path cell. For a more complete characterization gas chromatography-mass spectroscopy (GC-MS Varian Saturn 2000) out-line analysis were also employed. After a proper calibration, ethanol, acetone and some by-products were quantified by means of in-line GC analysis, while O₃, CO₂ and H₂O concentrations were evaluated by the respective detectors. The destruction and removal efficiency (DRE) of each pollutant was evaluated as:

$$DRE \ (%) = 100(C_0 - C)/C_0$$  \hspace{1cm} (2)$$

where $C_0$ is the initial concentration and $C$ the final concentration of examined VOCs in ppm.

III. RESULTS

A. VOCs removal

The VOCs removal obtained in the 1:1 and 5:1 ethanol-to-acetone mixtures were compared to the removal of each molecule singularly considered in the same experimental conditions. Fig. 1 shows the ethanol and acetone DRE in dry air mixtures, starting from an...
initial VOCs concentration of 300 ppm, both alone and in a 1:1 mixture. The conversion rate efficiency for each pollutant does not seem affected by the simultaneous presence of the two target molecules in the discharge: at a SIE of 120 J/L an ethanol removal of 55% and an acetone removal of 15% were obtained in both cases. A similar trend was found for the 5:1 ethanol-to-acetone mixtures: despite the initial concentrations of 500 ppm for ethanol and 100 ppm for acetone, the same DRE as in the 1:1 and singularly considered molecules mixtures were measured.

As shown in Fig. 2, water vapor addition to the feeding gas does not seem to improve the acetone conversion, whereas really slighter ethanol removal efficiency is observed at 1% water vapor content. At higher feeding gas humidity, instead, the plasma removal seems slightly less efficient for both VOCs.

B. By-products

A complete list of the identified by-products, along with the analytical technique which allowed their identification, is given in Table 1. Apart the complete oxidation products as CO$_2$ and H$_2$O (water issued from the discharge was quantified only in dry mixtures), CO and other partially oxidized species were found.

Aldehydes containing up to six carbon atoms, ketones and carboxylic acids, in amounts less than 10 ppm, were detected in the ethanol-air exhausts: after CO and CO$_2$, acetaldehyde was the most abundant by-product (concentrations up to 50 ppm were quantified) and presumably the first ethanol oxidation step [18, 24]. As expected in air fed DBDs, ozone, nitrogen oxides (N$_2$O, N$_2$O$_5$), nitric acid and organic nitrate were found. The detection of peroxyacetyl nitrate (PAN) suggests that the discharge has no significant heating effect. H$_2$ amounts less than 10 ppm were also detected.

From the qualitative point of view, the analysis of acetone-air exhausts showed a very similar composition. Nevertheless, very low amounts of all by-products were found, due to the lower acetone decomposition rate and to the presumable different plasma induced chemical paths. The formaldehyde, at concentrations not higher than 13 ppm, was, in this case, the most abundant detected by-product after CO and CO$_2$.

At any examined ethanol-to-acetone ratio the VOCs mixtures exhausts showed the same chemical composition of each plasma treated compound; the concentration level of major by-products enhances almost as the sum of the amounts detected in the singularly considered target molecules discharges.

The water vapor addition to the feeding gas in any case seems to affect the number and the nature of detected by-products. Nevertheless, although the target molecules removal efficiency is quite constant at increasing feeding gas humidity, the concentration of some partially oxidized species decreases.

![Fig. 3. Formaldehyde concentration in (a) ethanol-to-acetone 1:1 and (b) 5:1 mixtures exhausts of dry and humid air DBDs.](image-url)
higher humidity levels. Moreover, although formaldehyde was found to be the major by-product in acetone exhausts, especially at a water vapor content of 2.5%, higher concentrations were detected in the ethanol richer feeding mixture.

Humidity of the feeding gas similarly affects the acetaldehyde production in the discharge. As only acetaldehyde traces were found in acetone exhausts, it can be stated that in the examined mixtures ethanol is the main acetaldehyde source: indeed its trend is the same as in ethanol-air exhausts.

In all examined working conditions water vapor content also dramatically reduces the CO production in favor of the CO2 formation. As shown in Fig. 4, the [CO]/[CO2] ratio for the 1:1 ethanol-to-acetone mixture moves from about 2 in dry air to about 0.8 in the moistest air discharges: at a SIE of 120 J/L about 60 ppm of CO2 and 110 ppm of CO were found in the first case, whereas at 2.5% water vapor content in the feeding gas CO2 concentration enhances at about 100 ppm and CO amount decreases at 75 ppm.

A different behavior was observed for methanol (CH3OH), a by-product found in both ethanol and acetone exhausts, as, for all examined mixtures, the CH3OH concentration increases with the feeding gas humidity. The methanol trend observed for the 1:1 ethanol-to-acetone blends is presented in Fig. 5.

For all examined mixtures the evaluated carbon balance ranges from 99% to 90% at higher SIE: as not all identified by-products listed in Table 1 were quantified, compounds like carboxylic acids and organic nitrates could account for the missing carbon.

IV. DISCUSSION

In the here studied air fed DBDs, ethanol and acetone mixtures decomposition shows an additive effect both in each starting pollutant conversion efficiency and in the by-products distribution. As, comparing the mixed VOCs and the single-component discharges, any DRE suppression or enhancement was observed, it can be supposed that the two molecules activation paths in the plasma phase are not competitive.

Ethanol removal in dry air fed DBDs could be initiated by O atoms produced by dissociative electron attachment and nitrogen metastables collisions:

\[
C_2H_5OH + O \rightarrow Q + OH \quad (R1)
\]

Q being CH3CHOH, CH3CH2O or CH2CH2OH radicals.

The produced OH radicals can also be involved in ethanol activation:

\[
C_2H_5OH + OH \rightarrow Q + H_2O \quad (R2)
\]

The Q radicals can undergo further oxidation processes leading to the acetaldehyde production, which was found to be the main ethanol by-product, as:

\[
\text{CH}_3\text{CHOH} + \text{O} (\text{O}_2) \rightarrow \text{CH}_3\text{CHO} + \text{OH} (\text{HO}_2) \quad (R3)
\]

\[
\text{CH}_3\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2 \quad (R4)
\]

Similarly acetone could react with O atoms and OH radicals:

\[
\text{CH}_3\text{COCH}_3 + \text{O} (\text{OH}) \rightarrow \text{CH}_3\text{COCH}_2 + \text{OH} (\text{H}_2\text{O}) \quad (R5)
\]

The CH3COCH2 radical can be further oxidized up to formaldehyde:

\[
\text{CH}_3\text{COCH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{O}_2 \quad (R6)
\]

\[
\text{CH}_3\text{COCH}_2\text{O}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{O} + \text{O} \quad (R7)
\]

\[
\text{CH}_3\text{COCH}_2\text{O} \rightarrow \text{CH}_3\text{CO} + \text{CH}_2\text{O} \quad (R8)
\]

Anyway Sarroukh and co-workers, studying a photo-triggered discharge carried on in N2/O2 mixtures at 460 mbar, showed that an increase of feeding gas oxygen content up to 10% reduced the acetone conversion efficiency: as the R5 rate constants are quite low at ambient temperature, nitrogen metastables were much more efficient in acetone removal (R9-R10) [25].
By the way, as in the present work air was the carrier gas, the quenching reactions of nitrogen excited states by O2 are competitive with R9 and R10. The H2 detection suggests that such dissociative paths, which are also a source of H atoms, could occur. Furthermore due to the very low rate constant of oxidation reactions R5, the acetone removal could not be explained without taking into account dissociation processes. As H2 is also a by-product of ethanol decomposition, the role of dissociative paths in ethanol activation remains an open question.

The other main detected by-products could issue not only from reactions involving the radicals formed in R1-R2 and R5, R9-R10, but also from acetaldehyde degradation in the plasma phase. Some reactions are given as example.

Acetaldehyde oxidation by both O atoms and OH radicals (R11) can easily generate the CH3CO radical [26] (also produced in the acetone activation) which is a source of CO (R12, R16), CO2 (R13) and a precursor of formaldehyde (R15 – R17):

\[
\text{CH}_3\text{CHO} + O(\text{OH}) \rightarrow \text{CH}_3\text{CO} + \text{OH} (\text{H}_2\text{O}) \quad \text{(R11)}
\]

\[
\text{CH}_3\text{CO} \rightarrow \text{CH}_3 + \text{CO} \quad \text{(R12)}
\]

\[
\text{CH}_3\text{CO} + O \rightarrow \text{CH}_3 + \text{CO}_2 \quad \text{(R13)}
\]

\[
\text{CH}_3\text{CO} + \text{O} (\text{OH}) \rightarrow \text{CH}_2\text{CO} + \text{OH} (\text{H}_2\text{O}) \quad \text{(R14)}
\]

\[
\text{CH}_2\text{CO} + \text{OH} \rightarrow \text{CH}_2\text{H}_2 + \text{CH}_2\text{O} \quad \text{(R16)}
\]

\[
\text{CH}_3\text{OH} + O(\text{OH}) \rightarrow \text{CH}_3\text{O} + \text{OH} (\text{H}_2\text{O}) \quad \text{(R17)}
\]
The CH₃ radical can be directly oxidized to formaldehyde (R18) or converted into the methoxy radical CH₃O (R19):

\[
\text{CH}_3 + \text{O (O}_2) \rightarrow \text{CH}_2\text{O} + \text{H (OH)} \quad \text{(R18)}
\]

\[
\text{CH}_3 + \text{O} \rightarrow \text{CH}_3\text{O} \quad \text{(R19)}
\]

The CH₃CO radical can be also directly converted to CO₂ and methoxy radical by the following reaction:

\[
\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{CO}_2 \quad \text{(R20)}
\]

The CH₃O radical can undergo further oxidation to CH₂O (R21-R22):

\[
\text{CH}_3\text{O} + \text{O (OH)} \rightarrow \text{CH}_2\text{O} + \text{OH (H}_2\text{O)} \quad \text{(R21)}
\]

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2 \quad \text{(R22)}
\]

The methoxy and ethoxy radicals are also NO₂ scavengers as they form the methyl- and the ethyl-nitrate, respectively [27]; on the other hand the CH₃CO radical is a PAN precursor as it can be converted into the CH₃C(O)O₂ radical (R23) [28]. Indeed any NO₂ trace was detected in the exhausts: as observed in air fed DBDs NO₂ is consumed in N₂O, N₂O₅, HNO₃ and organic nitrates production.

\[
\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{C(O)O}_2 \quad \text{(R23)}
\]

It is known from the literature that the effect of feeding gas humidity on pollutants removal and plasma phase reactions strongly depends on water vapor concentration, discharge type and target VOC [4]. In NTP water decomposes into OH and H radical by the following reactions:

\[
\text{H}_2\text{O} + e^- \rightarrow \text{OH} + \text{H} + e^- \quad \text{(R24)}
\]

\[
\text{H}_2\text{O} + \text{O}^\text{(1D)} \rightarrow \text{OH} + \text{OH} \quad \text{(R25)}
\]

\[
\text{H}_2\text{O} + \text{N}_2 (\text{A}_3\Sigma^+ + \text{u}) \rightarrow \text{N}_2 + \text{OH} + \text{H} \quad \text{(R26)}
\]

Due to the electron-impact dissociation, H₂O is an electron scavenger, thus inducing the consequent decrease of O atoms density in the plasma phase [4, 29-31]. Water is anyway an O atom sink, as proved by the strong reduction of O₃ concentration at increasing feeding gas humidity, as observed also in the current experimental work. Furthermore O₃ reaction with OH radicals is a source of peroxide radicals HO₂.

Although OH and HO₂ radicals are strong oxidant, it has been often found that H₂O could have a negative effect on VOCs removal as it quenches the activated chemical species (R25-R26) [4, 29-30]. Some studies have shown that there is an optimum water vapor content to maximize the VOCs removal efficiency [4]. Almost the same trend has been observed for ethanol removal: at lower feeding gas humidity ethanol activation by oxidation pathways seems to be enhanced. As it was previously stated that oxidative paths are not crucial in the acetone removal, competition between H₂O-nitrogen metastables collisions and acetone activation mechanisms could account for the not improved acetone removal. The negative effect observed for both molecules removal at higher water vapor content in the feeding gas could suggest that also for ethanol activation dissociation reactions involving nitrogen metastables and nitrogen atoms could be not negligible. Another point that could account for this negative effect is the increasing OH sink pathways via recombination at increasing feeding gas humidity.

As shown by the reaction rate constants (Table 2), OH and HO₂ radicals can faster react with the radical issued from the primary pollutants activation and the main produced by-products to further produce lower molecular weight compounds. Oxidation reactions like R11 and R14-R17 can be promoted in moist air DBDs. Intermediate radicals as CH₃CO, CH₂OH and CH₃O can be easily oxidized up to formaldehyde by OH and HO₂ radicals. The HCO radical, an intermediate in CH₃OH production (R28-R29), could derive by formaldehyde reactions with OH and HO₂ radicals.

\[
\text{CH}_3\text{O} + \text{OH (HO}_2) \rightarrow \text{HCO} + \text{H}_2\text{O (H}_2\text{O}_2) \quad \text{(R27)}
\]

\[
\text{HCO} + \text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{OH} + \text{CO} \quad \text{(R28)}
\]

\[
\text{HCO} + \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH} + \text{CO} \quad \text{(R29)}
\]

These chemical pathways could account for the acetaldehyde and formaldehyde depletion in humid air discharges. The higher amount of formaldehyde found in humid 5:1 ethanol-to-acetone mixtures further support the previous discussed low acetone reactivity, as formaldehyde seems to issue mainly by the ethanol-acetaldehyde plasma conversion.

Apart the chemical pathways involving the HCO radical, the methanol formation could be improved by the following reactions:

\[
\text{CH}_3\text{OH} + \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{O} \quad \text{(R30)}
\]

\[
\text{CH}_3\text{O} + \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{O} \quad \text{(R31)}
\]

As observed in other works, the feeding gas humidity inhibits the CO formation enhancing the CO₂ production. As OH radical is much more efficient than O atom in CO oxidation to CO₂, the CO₂ selectivity is enhanced [29, 30-32].
V. CONCLUSION

The simultaneous non-thermal plasma treatment of ethanol and acetone exhibits an additive behavior: the coexistence of the two pollutants in the plasma phase does not improve nor suppress their removal plasma efficiency.

Detected by-products, mainly consisting of partially oxidized compounds, show the same additive effect: main by-products concentrations in the ethanol/acetone mixture exhausts are almost the sum of the amounts detected in the singularly considered molecules.

Plasma treatment in humid air slightly affects the primary VOCs removal, but strongly promotes the main by-products oxidation and enhances the CO2 selectivity.

Just a kinetic pathway has been proposed in order to explain the exhaust gases composition. A kinetic modeling is necessary to analyze the relative importance of the different chemical steps.

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