Influence of Temperature on the Removal of Toluene by Dielectric Barrier Discharge

N. Blin-Simiand*, F. Jorand, Z. Belhadj-Miled, S. Pasquiers, C. Postel
Laboratoire de Physique des Gaz et des Plasmas, CNRS, Orsay cedex, France

Abstract—The decomposition of toluene is investigated using a pulsed high voltage energised Dielectric Barrier Discharge (DBD) reactor, under temperature from 20°C up to 250°C in N₂ and N₂/O₂ (90/10) dry or humid (5% H₂O) gaseous mixtures. For all mixtures studied, the concentration of toluene at the exit of the reactor decreases exponentially when the specific deposited energy increases at constant temperature. Decomposition is easier in the N₂/O₂(90/10) mixture than in N₂, but the characteristic energy values differ only by a factor of two at 250°C. In the mixture with oxygen, the removal efficiency increases when the temperature increases, as does the rate constant for reaction of O with toluene. At 250°C water vapour seems to have no effect on toluene decomposition. Besides carbon oxides, various aromatic by-products are observed, which concentrations depend on experimental conditions: benzene, benzaldehyde, benzyl alcohol, phenol, cresols.

Keywords—toluene; dielectric barrier discharges (DBD); non thermal plasma; volatile organic compounds (VOC)

I. INTRODUCTION

Combustion engine exhausts gases contain several types of unburned hydrocarbons, in particular aromatic ones such as benzene, toluene, xylens.... Such toxic atmospheric pollutants need to be removed from flue gas streams. Therefore the removal of these molecules by non-thermal plasmas is under investigation since the beginning of the eighties [1-5]. The use of plasma reactors showed that an efficient removal can be obtained, in particular for toluene. Since the first work by T. Yamamoto et al. [6], electron beams as well as several types of discharge such as dielectric barrier or corona discharges, capillary discharge, DC glow discharge, multi hollow needle discharge, and also various types of packed-bed reactors, have been studied for the treatment of toluene [6-23]. The combining of a non-thermal plasma and a catalyst, i.e. an electrical discharge coupled to a catalyst deposited on various supports as honeycomb monoliths or pellets, seems to improve the efficiency of conversion processes [19-23].

Temperature values of flue gases for lean burn gasoline, or diesel compression ignition, range typically from 80°C up to 800°C. For starting phase conditions, the temperature does not exceed 300°C. Very few studies have been performed up to now on the effect of the gas mixture temperature on VOCs removal by non-thermal plasmas, except for some light olefins (ethene, propene) in the course of the numerous works on NOx removal by the plasma-catalytic reduction process. About VOCs, Hsiao et al. [24], using a pulsed corona reactor, demonstrated that the plasma removes some molecules (ethene, acetone, benzene) more effectively as the reactor is warmed up to 300°C. They explained their results with the increased reaction rate constants of oxygen atoms with molecules when the temperature increases. For toluene, Chang and Chang (10) indicated that increasing the temperature, up to 100°C, could improve the molecule removal by a DBD. However, also using such a discharge in the same temperature range but with a packed-bed reactor filled with glass pellets, Song et al. [21] did not see any effect.

The aim of our study is to investigate the decomposition of toluene in dry air using a pulse high voltage energised Dielectric Barrier Discharge (DBD) reactor in order to get insight the physical and chemical mechanisms involved in the degradation of toluene by the N₂/O₂ plasma, in particular, to investigate the effect of the gas mixture temperature in the range 25°C-250°C. We also study the effect of oxygen and water vapour at a constant temperature value of 250°C.

II. EXPERIMENTAL SET-UP

The DBD reactor is operated in a cylindrical coaxial geometry. It is made of a quartz tube (15 mm inner diameter and 2 mm wall thickness) surrounded by a stainless steel tape connected to the earth, and a central stainless steel rod (e.d. 5 mm) on which is applied a high voltage pulse with a repetition frequency value up to 100 Hz. The discharge volume is 23 cm³. The reactor is located in a thermo regulated oven. Experiments have been performed under temperature from 20°C up to 250°C in N₂, N₂/O₂ (90/10), or N₂/O₂/H₂O (85/10/5, only for T=250°C) gaseous mixtures. The electrical energy deposited in the discharge has been measured through measurements of the voltage and current time evolutions using adapted electrical probes connected to a fast digital oscilloscope (Lecroy LT584, 1 GHz, 4 GS/s).

Toluene is vaporised through an air flow by making it stream along a rod located at the centre of a heated tube. In this way, vapours of hydrocarbon are produced in the range of 100 to 275 ppm, the total gaseous flow being 1
Products issued from discharge reactions are collected directly at the outlet of the discharge by means of a microprobe which allows a small amount of the mixture of gaseous products to be trapped under low pressure on a Dewar finger cooled to 77 K. This microprobe, placed at 3 cm of the discharge end, allows setting free from reactions occurring in the afterglow. The condensable species are then dissolved in methanol and analysed by gas chromatography (column WCOT ulti-metal 25 mx 0.25 mm, coating CP SIL PAH-CB Varian) coupled to an ion trap mass detector (GC-MS Varian Saturn 2200). Carbon oxides concentrations are measured at the outlet of the oven (i.e. in the late afterglow, 6 s after the discharge). Carbon monoxide is quantified by an electrochemical cell analyser (Testo 330) and carbon dioxide by an infrared gas analyser (Li-840 LI-COR). FTIR spectroscopy (MIR8000 spectrometer from Oriel, with a long path cell from Infrared Analysis) is used to check presence of nitrogen oxides in effluents coming from the discharge. Measurements are only performed in the N₂/O₂ mixture. NO, NO₂, and N₂O₅ concentrations are measured in absolute values. N₂O is also detected, but not precisely quantified.

III. ELECTRICAL PARAMETERS

Fig. 1 shows typical examples of measured voltage and current time evolutions, for a discharge in the N₂/O₂ mixture with 10% oxygen at 20°C and 250°C and for a pulse repetition frequency of 50 Hz. The applied voltage pulse has a total increase time (from 0 V) of 500 ns, with an increase between 5 kV up to the discharge breakdown in about 55 ns. The breakdown voltage value depends on the oxygen concentration (hydrocarbon concentration has no influence in our working conditions), the gas temperature, and the pulse repetition frequency, ν. The temperature has a noticeable influence on the electrical parameters of the DBD discharge, as it is emphasised in fig. 1. The increase of the temperature leads to modify current and voltage time shapes. It induces the decrease of the breakdown voltage (from 21.7 kV down to 19.3 kV for the chosen parameters of the figure) and the increase of the peak current (from 44.5 A up to 76.5 A in fig.1). Consequently, the deposited energy per pulse increases when the temperature increases, at a given value of the repetition frequency (from 51.0 mJ up to 64.5 mJ in fig.1). Such an effect should be related to variation of the total molecule density, N, leading to a change of the local reduced electric field value, E/N, as soon as the temperature is changed. Previous experiments performed in air at ambient temperature, as function of the total pressure and for the same discharge device and electrical excitation type [25], have shown similar behaviour of the electrical parameters than those plotted for example in fig. 1. However more detailed studies are necessary to determine the effect of the temperature on the energy deposition in the gas and the consecutive production of reactive species such as atomic oxygen. Dependence with temperature of the spatial repartition of the energy in the inter-electrode volume should be determined, in particular the volumic extension of each micro-discharge following propagation of streamers and the volumic density of these micro-discharges (number of plasma filaments per unit volume).
IV. CHARACTERISTIC ENERGY

In fig. 2, the removal of toluene is displayed for four values of the temperature, as a function of the specific energy, and for an initial toluene concentration of 100 ppm. Note that results are not available for all repetition frequency values at ambient temperature because numerous deposits are formed on the central rod in such conditions, and this entailed a malfunction in the discharge (breakdown at very irreproducible voltage value from pulse to pulse, leading to very different values of $E_{\text{pulse}}$); only some measurements have been performed after careful cleaning of the rod.

For all temperature values studied, the toluene concentration at the reactor exit, $[\text{TOL}]_{\text{exit}}$, exhibits a single exponential decrease when the specific energy increases up to 200 J/L. It follows that its evolution may be written as:

$$[\text{TOL}]_{\text{exit}} = [\text{TOL}]_0 \exp (- E_{\text{dep}} / \beta)$$

In (2), $[\text{TOL}]_0$ is the initial toluene concentration at the reactor entrance and the parameter $\beta$ is further called the characteristic energy. Such a law has been established already for various VOCs and discharge types [1-5]. Fig. 2 shows that $\beta$ is a strongly decreasing function of the temperature as soon as the DBD reactor is warmed above 100 °C.

Evolution of the characteristic energy, versus the temperature, is plotted in fig. 3. It is constant, 140 J/L, for temperature values lower or equal than 100 °C. This has been also obtained by Song et al. [21] using an AC-energised DBD packed-bed reactor containing chemically inactive glass pellets, and at 20 % O₂.

Experiments at specific energies higher than 200 J/L have been performed at ambient temperature and at 100 °C. Equation (2) remains valid in the first case, but not in the second case for which a lower characteristic energy is measured, 70 J/L, for high specific energy values. This effect could be related to an increase of the temperature owing to the discharge itself (Joule effect and plasma chemistry).

The decrease of the $\beta$-value, when the temperature increases, has been also reported by Hsiao et al. [24] in a study about removal of acetone, benzene and ethylene by a corona discharge in dry air. In this work the same effect is observed for the removal of toluene by a DBD. This could be explained by the physics of micro-discharges created in the inter-electrode volume. For example, one may answer to the following questions for our discharge geometry: what is the effect of an increase of the temperature on the oxygen atom production during streamer propagation, on the diameter of the micro-discharge, and on micro-discharges volume density? However it is known that rate constant for the oxidation reaction:

$$\text{O} + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{products} \quad (R1)$$

is an increasing function of the temperature [26]:

$$k_{R1} = 5.3 \times 10^{15} T^{1/21} \exp(-1260/T) \text{ cm}^3\text{s}^{-1} \quad (3)$$

which gives $2.3 \times 10^{13} \text{ cm}^3\text{s}^{-1}$ at 100 °C and $9.3 \times 10^{13} \text{ cm}^3\text{s}^{-1}$ at 250 °C. It is obvious that such an increase must have an influence on toluene removal.
V. EFFECT OF GAS MIXTURE COMPOSITION

The logarithmic evolution of $[\text{TOL}]_{\text{exit}}$ over $[\text{TOL}]_0$ is shown in fig. 4 as function of the specific energy, for the $\text{N}_2/\text{O}_2$ (10 %) and $\text{N}_2/\text{O}_2/\text{H}_2\text{O}$ (+ 5% water vapour) mixtures and for nitrogen, at 250°C and for $[\text{TOL}]_0 = 100$ ppm.

The parameter $\beta$ is equal to 50 J/L in $\text{N}_2/\text{O}_2$ mixture and to 90 J/L in $\text{N}_2$. In a previous study about the effect of the $\text{O}_2$ concentration on the removal efficiency of toluene, in a plane-to-plane DBD, Falkenstein [13] has emphasised that addition of 2 % $\text{O}_2$ to $\text{N}_2$ is sufficient to increase considerably the removal efficiency at ambient temperature. Our results show that removal of toluene is also easier at 250 °C when oxygen is present in the mixture, but the difference between $\beta$ parameter values measured in $\text{N}_2$ and in $\text{N}_2/\text{O}_2$ with 10 % $\text{O}_2$ is not very important, i.e. less then a factor of 2. Thus, on the condition that the spatial distribution and energetic characteristics of micro-discharges will not be too influenced by the presence of oxygen, it seems that oxidation reaction (R1) is just a little bit more effective than toluene reactions with electrons, or with nitrogen ions and metastable states. This remark can also be made for the reaction:

$$\text{OH} + \text{C}_6\text{H}_5\text{CH}_3 \rightarrow \text{products} \quad (\text{R2})$$

Indeed, addition of 5 % of $\text{H}_2\text{O}$ does not improve the removal efficiency. We measured the same $\beta$-value in dry and wet mixtures for $[\text{TOL}]_0 = 100$ ppm, see fig. 4. Hydroxyl radicals coming from the dissociation of the water molecule are probably lost by other kinetic processes than (R2).

At 250°C in $\text{N}_2/\text{O}_2$ (90/10) mixture, the effect of the initial concentration on the removal efficiency was studied by comparison of $\beta$-values obtained for $[\text{TOL}]_0 = 100$ ppm and 275 ppm. It was observed that $\beta$ increases from 50 J/L at 100 ppm, up to 70 J/L at 275 ppm. The increase of $\beta$ with an increasing toluene concentration has been also established for DBDs running at ambient temperature [16].

To compare with our experiment, table 1 gives characteristic energies previously measured for different types of discharges in the air-like dry mixture and for an initial toluene concentration between 100 and 450 ppm.

Results of the present work show that the pulsed-HV excited cylindrical DBD reactor allows to remove toluene quite efficiently, although the $\text{O}_2$ concentration is only 10 % in our experiment. Future studies will be performed at different oxygen content in the mixture.

<table>
<thead>
<tr>
<th>Discharge type</th>
<th>Temperature</th>
<th>Concentration</th>
<th>$\beta$ (J/L)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBD</td>
<td>ambient</td>
<td>100 ppm</td>
<td>80</td>
<td>(11)</td>
</tr>
<tr>
<td>corona</td>
<td>ambient</td>
<td>125 – 450 ppm</td>
<td>99</td>
<td>(3, 12)</td>
</tr>
<tr>
<td>DBD</td>
<td>ambient</td>
<td>100 ppm</td>
<td>498</td>
<td>(16)</td>
</tr>
<tr>
<td>DBD</td>
<td>ambient</td>
<td>350 ppm</td>
<td>233</td>
<td>(21)</td>
</tr>
<tr>
<td>Packed-bed with glass pellets</td>
<td>ambient</td>
<td>100 °C</td>
<td>200</td>
<td>214 J/L</td>
</tr>
<tr>
<td>DBD and corona</td>
<td>ambient</td>
<td>200 ppm</td>
<td>214</td>
<td>(4)</td>
</tr>
<tr>
<td>Packed-bed with glass pellets</td>
<td>ambient</td>
<td>up to 270 ppm</td>
<td>1150 J/L</td>
<td>(17)</td>
</tr>
<tr>
<td>Pin-to-plate capillary</td>
<td>ambient</td>
<td>100 ppm</td>
<td>140 down to 50 ppm</td>
<td>50 up to 70 J/L</td>
</tr>
<tr>
<td>DBD</td>
<td>250 °C</td>
<td>100 – 275 J/L</td>
<td>50 up to 70 J/L</td>
<td>(17)</td>
</tr>
</tbody>
</table>
VI. BY-PRODUCTS

Formation of carbon oxides was studied for 100 ppm of toluene in a N\textsubscript{2}/O\textsubscript{2} (90/10) mixture at 20°C, 100°C and 250°C. Observation of the evolution of the CO and CO\textsubscript{2} concentration as a function of time at 25 Hz (50/J/L) (fig. 5) shows a mean concentration of 132 ppm while CO concentration is higher with 186 ppm. At 1500 s the discharge and the vaporization of toluene were stopped. Then the discharge was operating at 100 Hz (180 J/L) without toluene and a peak of 46 ppm CO\textsubscript{2} is observed while the CO concentration is only 10 ppm.

![Fig. 5. Carbon dioxide concentration measured as a function of time for 100 ppm of toluene oxidized at 250°C in N\textsubscript{2}/O\textsubscript{2} (90/10) for 25 Hz.](image)

The formation of carbon oxides when no toluene is injected in the discharge should be explained by the treatment of deposits on the walls of the reactor. When the discharge is operating in the mixture with toluene, the carbon oxides formation should be explained by the treatment of both the hydrocarbon and its by-products, and deposits.

In a previous study, oxidation products generated by the treatment of 25 ppm and 400 ppm of toluene in a dielectric barrier discharge at 25°C were analyzed [14]. In dry air the major oxidation products were aerosol deposit, CO\textsubscript{2} and organic acids. Carbon monoxide, a major oxidation product, was not measured. Benzyl alcohol, benzaldehyde, benzoic acid and cresol were formed, but in very small amounts, except for benzoic acid. Very small amounts of aliphatic aldehydes were also detected. Chromatograms of the products issued from the conversion of toluene at 50 Hz (100 J/L) and 250°C in N\textsubscript{2} and in N\textsubscript{2}/O\textsubscript{2} (90/10) in this work are shown in fig. 6. The removal efficiency of toluene is easier with O\textsubscript{2} (peak 1) is smaller in N\textsubscript{2}/O\textsubscript{2} mixture then in N\textsubscript{2} as observed above (fig. 4). Products observed are different in the two chromatograms. Reactions of toluene with nitrogen metastable states and electrons lead to the formation of nitrile (peaks 6) and (7)) which could be explained by reaction of CN radical (or HCN) upon phenyl or methylphenyl radical. Di-phenyl species (peaks (8), (9) and (10)) are also observed, their formation could be explained by recombination of phenyl, methyl phenyl or benzyl radicals. Products formed in presence of O\textsubscript{2} are oxygenated species. In this case, the most important peak corresponds to benzaldehyde dimethyl acetal (peak 5); no poly phenyl species are observed. The same experiment of toluene conversion was performed where the products trapped on the cold finger were collected in n-pentane as solvent instead of methanol; in this case the main product is benzaldehyde while benzaldehyde dimethyl acetal is not observed. This shows that benzaldehyde dimethyl acetal is issued from addition reaction of CH\textsubscript{2}OH on the carbonyl bond of benzaldehyde, in the liquid phase, when products are collected by methanol for analysis. Reaction of toluene with O atom (or OH after the first attack) leads to the formation of benzyl radical C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}\textsuperscript{°} which generates benzy1 peroxy radical C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}OO\textsuperscript{°} by reaction with O\textsubscript{2}. Reactions of C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}OO\textsuperscript{°} lead to benzaldehyde and benzyl alcohol formation. Phenol formation may be explained by oxidation of benzene issued from toluene dissociation. Other by-products are observed for specific deposit energy lower than 100 J/L (benzene, cresols). The removal efficiency of toluene at 250°C in N\textsubscript{2}/O\textsubscript{2} or N\textsubscript{2}/O\textsubscript{2}/H\textsubscript{2}O mixtures is quite the same in case of 5% H\textsubscript{2}O. Nevertheless, the comparison of by-products obtained for the conversion of 100 ppm of toluene at 250°C in dry N\textsubscript{2}/O\textsubscript{2} (90/10) or with 5% H\textsubscript{2}O shows that the amount of by-products depends on the presence of water. In case of wet air an increase of phenol and benzyl alcohol is observed. It seems that, under our experimental conditions, the higher amount of OH radicals due to water decomposition has no influence on toluene consumption but on the by-products reactions; as noted above OH radicals coming from the dissociation of the water molecule are probably lost by other kinetic processes than (R2).

Moreover, as explained above, in dry air the main peak observed belongs to benzaldehyde dimethyl acetal, whereas in wet air the amount of this product is very weak, the main by product being benzaldehyde. This may be explained by hydrolysis of the acetol which regenerates benzaldehyde in liquid phase when the trapped species, including water, are dissolved in methanol. Fig. 7 shows the evolution of the concentration of toluene, carbon oxides and benzaldehyde when 100 ppm toluene is removed in N\textsubscript{2}/O\textsubscript{2} at 250°C. The concentration of benzaldehyde increases with the energy, reaches a maximum value, then decreases. This shows that it is converted by the discharge. The sum of these three amounts, in ppmC, shows that below 50 J/L carbon recovery is near 100%, almost all toluene being converted into carbon oxides and benzaldehyde identified by the formation of its acetol in methanol. The evolution of CO\textsubscript{2} is a linear function of energy for specific deposit energy below 150 J/L. Then a saturation is obtained, for higher energy values, CO\textsubscript{2} reaching 650 ppm. The little lost of carbon, with respect to initial 700 ppmC, could be explain by the formation of deposits or by conversion of toluene.
into light hydrocarbons non identified under our chromatographic conditions. From the measures plotted in fig. 5 and 7, the total carbon deposits are about 1% of the total carbon measured at the exit of the reactor for 50 J/L, at 250°C.

Nitrogen oxides have been detected in the N2/O2 mixture by FTIR spectroscopy. Their concentrations are strongly dependant upon parameters such as the mixture temperature and the deposited electrical energy. There is no NO nor NO2 molecules for a temperature lower than 150°C and for a deposited energy lower than 100 J/L. However N2O5 is clearly seen in the absorption spectra, which concentration has been estimated from absorption cross section data [27]; no more than 10 ppm of N2O5 is produced in the whole range of temperature and deposited energy values studied. For a high temperature and a high deposited energy (typically for energy values higher than 300 J/L at 175°C, 170 J/L at 250°C), N2O5 disappear from effluents whereas NO and NO2 concentrations are in the range 100-250 ppm and 40-70 ppm respectively. No measurement on nitrogen oxides have been performed in mixtures containing toluene. It is probable that presence of the hydrocarbon molecule should lead to minimise NO concentration, owing to oxidation of this molecule to produce NO2 during reactions with some radicals such as benzyl peroxy, C6H5CH2OO°, or C6H5(OH)(OO°)CH3, or the dioxyphenyl, C6H5OO° [28], which could be produced in the discharge volume or during the flowing afterglow. On the other hand, NO2 should add to the benzyl peroxy, or to benzoate C6H5CO(OO°), to form nitrates [28]. However such compounds have not been clearly identified by GC-MS analysis, so that it is believed that the NO2 concentration produced is lower than the concentration measured in the toluene free mixture. This deserves to be checked by other experiments in the future.

III. CONCLUSION

From 100°C, the increase of the temperature enhances the toluene removal by a pulse HV energised DBD. Toluene removal is efficient in N2/O2 (10%) at 250°C, but the hydrocarbon is also decomposed in the oxygen free mixture with an efficiency just a factor of two lower than for N2/O2. For mixture with oxygen, benzaldehyde is the main by-product. Further chemical analysis are planned to precise the kinetic scheme involved.

REFERENCES


[26] W. Mallard, F. Westley, J. Herron, R. Hampson, and D. Frizzell.