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Removal of trimethylamine and isovaleric acid from gas streams in a continuous flow surface discharge plasma reactor

Aymen Amine ASSADI^{a,b}, Abdelkrim BOUZAZA^{a,b*}, Marguerite LEMASLE^{a,b}, Dominique WOLBERT^{a,b}

^a Laboratoire Sciences Chimiques de Rennes - équipe Chimie et Ingénierie des Procédés, UMR 6226 CNRS, ENSCR, 11 allée de Beaulieu, 35700 Rennes, France.

^b Université Européenne de Bretagne.

* Corresponding author. Tel.: +33 2 23238056; fax: +33 2 23238120.

E-mail address: Abdelkrim.bouzaza@ensc-rennes.fr (A. Bouzaza)

Abstract

The removal of isovaleric acid (IVA) and trimethylamine (TMA) using nonthermal plasma (NTP) in a continuous surface discharge reactor is investigated. The influence of the energy density shows that its increment is accompanied by the increase of the removal rate. At flow rate equal to $2 \text{ m}^3 \cdot \text{h}^{-1}$, when energy density extends three times, the removal rates of IVA and TMA are increased from 5 to 15 $\text{mmol} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and from 4 to 11 $\text{mmol} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, respectively. The impact of relative humidity (RH) is also studied. An increase in % RH (up to 20%) leads to a decrease of the removal rate. Additionally, the formation of by-products in the surface discharge reactor and the plausible reaction mechanism of the two VOC were also detected and discussed. Moreover, a kinetic model taking into account the mass transfer step is developed in order to represent the experimental results. The model shows a good agreement with experimental results.

Keywords

Surface discharge, VOCs, mass transfer, relative humidity

1. Introduction

VOCs are hazardous to health and environment; their emission causes serious environmental problems such as stratospheric ozone depletion, photochemical smog, greenhouse effect and so on (US EPA, 2008; Le Cloirec, 1998). Increasing awareness of these emissions has resulted in legislation requiring stringent enforcement of new regulations to improve the quality of the environment (US EPA, 2008). To remove those gaseous

37 pollutants, many technologies have been developed but they are not very successful and do
38 not satisfy the strict social demands of the present (**Harling et al., 2008**). One of the methods
39 which are developed for the control of VOCs is nonthermal plasma processing. This latest
40 process is a major area of research in both industry and academia (**Le Cloirec, 1998; Harling**
41 **et al., 2008; Mista et al., 2008**).

42 It is characterized by the formation of electrons, ions and neutral molecules. Energetic
43 electrons ionize and dissociate background molecules resulting in the formation of highly
44 reactive chemical species (radicals, ions, excited molecules and ozone) (**Khani et al., 2011**).
45 Literature has also shown that various types of electrical discharge have been investigated for
46 the oxidation of hydrocarbons: pulsed corona discharge(**Ouni et al., 2009**), atmospheric
47 pressure glow discharge(**Yan et al., 2013**), dielectric barrier discharge (DBD)(**Mfopara et**
48 **al., 2009; Ye et al., 2013**], packed-bed discharge(**Jiang et al., 2013, Goujard et al., 2011;**
49 **Schmid et al., 2010**) and surface discharge(**Maciuca et al., 2012, Allegraud, 2007; Jolibois**
50 **et al., 2012**).

51 Recently, many research attempts have been made to make up for the advantages of DBD
52 plasma reactors for particularly effective control of hazardous gas emissions and treating gas
53 streams with low VOC concentrations at low temperature[**Ouni et al., 2009; Jolibois et al.,**
54 **2012**). In fact, DBD plasmareactorshavebeen widely studied in the area of hazardous and
55 toxic gases control, VOC abatement such as toluene (**Mok et al., 2011; Huang et al., 20011;**
56 **Subrahmanyama et al., 2010**) and dimethylamine(**Ye et al., 2013**), H₂S and NH₃ removal
57 (**Ma et al., 2001**), NO_x removal from the flue gas (**Jolibois et al., 2012; Yoshida, 2013**).

58 The aim of our study is to improve understanding of the physical and chemical mechanisms
59 involved during nonthermal plasma (NTP) removal process of a typical VOC. In this work,
60 isovaleric acid and trimethylamine are chosen as representative of odorous compounds. These
61 compounds are the main molecules detected in the exhaust gases from animal quartering
62 centers (**ADEME, 2005**).

63 The focus is put on the study of kinetic removal of these pollutants and the effect of relative
64 humidity and some operating parameters. Moreover, in most cases, steady-state kinetic models
65 with plasma process in the literature ignore the effect of mass transfer (**Mokt et al, 2001**). That
66 could be presumed if turbulences in the system are high enough to consider the
67 surfacereaction as the limiting step in the apparent removal rate(**Redolfi et al., 2009**). Thus,
68 the influence of the mass transfer on the performance of NTP process will also be discussed.

69

70 **2. Experimental**

71

72 **2.1. DBD plasma reactor**

73

74 The used DBD plasmareactor is composed principally of a glass tube (58 mm id and 100 cm
75 length) (Fig. 1). To generate the DBDplasma, the reactor is covered by a copper grid forming
76 the outer electrode. The glass tube, 4 mm thickness, acts as the dielectric media. The inner
77 electrode is on aluminum. The applied high voltage is about 30 kV/40 mA and is a sine
78 waveform. The DBD plasma is obtained by submitting the electrodes to a sinusoidal high
79 voltage ranging from 0 to 30 kV at a 50 Hz frequency(Fig.1). The outer electrode is connected
80 to the ground through a 2.5 nFin order to collect the charges transferred through the
81 reactor(Manley, 1943). Theapplied voltage (U_a) and high capacitance voltage (U_m) are
82 measured by LeCroy high voltage probes and recorded by a digital oscilloscope (Lecroy
83 Wave Surfer 24 Xs, 200 MHz) (Fig.1).

84 The design of this reactor (Fig.1) is the subject of a Patent Application BFF11L1041/MFH
85 (CIAT Patent, 2013).

86 The pollutants, isovaleric acid (IVA)andtrimethylamine (TMA), are injected continuously
87 using a syringe/syringe driver system (Kd Scientific Model 100) through a septum into the
88 gas stream. A heating system covering the injection zone sets the gas temperature and
89 facilitates the VOC vaporization ahead of the static mixer (Fig.2.a). The treated
90 flowratestream varies from 2 to 10 m³.h⁻¹.

91

92 **Fig.1**

93 **Fig.2.b**

94

95 **2.2. Product analysis**

96

97 IVA analysisisperformed by FID-Gas chromatography (Fisons Chromatograph). A Chrompack
98 FFAP-CB column (25 m of length 0.32 mm of external diameter 0.32mm), which is specially
99 adapted for volatile fatty acids is used. Nitrogen gas constitutes the mobile phase. All injections
100 are performed manually with a syringe of 250 µl.

101

102 The TMAis analyzed by a gas chromatograph equipped with a nitrogen-phosphor detector
103 (NPD). The column is a capillary column VOLAMINE, its length is 60 m. The sample
104 injection is done with a syringe of 500 µl.

105 The experiments which are repeated two times; show a good reproducibility with 5% standard
106 deviation. This standard deviation is represents by vertical bars in the experimental results in all
107 figures.

108 An effort is also made to quantify the major reaction intermediates present in gas phase in
109 order to determine the main reaction routes and to better understand the mechanisms
110 involved.

111 The byproducts generated during the DBD plasma oxidation of IVA and TMAare identified
112 and evaluated by Gas Chromatograph-Mass spectrometer (GC-MS) (Perkin Elmer Clarus
113 500) equipped with an infrared (IR) detector. The temperature conditions in the oven, the
114 injection chamber and the detector are, respectively, 100, 120 and 200 °C.

115 Due to their low concentrations, byproducts are concentrated in a Carbotrap (25 ml) then
116 removed by thermal desorption unit coupled with GC-MS.

117 At the exit of the DBD plasmareactor a constant flowrate of 200 L/h is bubbled on iodine
118 solution. Standard iodometric titration method is used to estimate the downstream ozone
119 formation (**Rakness et al., 1996**). NO_x and CO concentrations are measured by an NO/CO
120 ZRE gas analyzer. The CO₂ concentration is analyzed by a Fourier Transform Infrared (FTIR)
121 spectrophotometer brand Environnement SA (Cosma Beryl reference 100). The measurement
122 accuracy is about 5%.

123 The removal rate (R) of IVA and TMA at any value of specific energy is calculated as:

$$124 \quad R = \left(\frac{Q}{S_{plasma}} \right) \cdot (C_{in} - C_{out}) \quad (1)$$

125 Where C_{in} and C_{out} are the inlet and the outlet pollutant concentrations (mmol.m⁻³),
126 respectively; Q is the volumetric flowrate (m³.h⁻¹) and S_{plasma} the active surface of plasma
127 (m²).

128 Moreover we use the Lissajous plot method (**Manley, 1943**) for estimating mathematically
129 the power input (P) (fig. 2.b). P is obtained by multiplying the pulse frequency (Hz) and the
130 specific energy (SE) over a period (eq.3).

$$131 \quad P (W) = SE (J) \times \text{frequency (Hz)} \quad (2)$$

132 The energy density (ED) is then calculated as:

$$133 \quad ED(J/L) = (3600 \times P(W) / Q(m^3 \cdot h^{-1})) / 1000 \quad (3)$$

134 The energy density (ED) value is varied by changing the applied voltage (U_a).

135

136

Fig.2.b

137

138 The removal of isovaleric acid and trimethylamine in the DBD plasma reactor is evaluated at
139 several gas residence times, water vapor concentrations and influent pollutant concentrations
140 (Table 1).

141

Table 1

142 N.B.: The corresponding residence times in the annular plug-flow reactor for gas flowrates
143 equal to 2, 4 and 6 $\text{m}^3 \cdot \text{h}^{-1}$ are respectively 1.2, 0.8 and 0.5 s.

144 The CO_2 overall selectivity (CO overall selectivity can also be defined) may be a useful
145 parameter to assess the performance of the DBD plasma reactor towards VOC removal. It
146 allows an estimation the mineralization rate i.e. the ultimate reaction step, of the process.

147 The CO_x overall selectivity is expressed as follow (eq. 4&5):

$$148 \quad \{CO_x \text{'s overall selectivity } (\%) \}_{IVA} = \frac{[CO_x]_{IVA}^{out} - [CO_x]_{IVA}^{in}}{5 \times [IVA]^{in} \times \{ \% \text{ conversion} \}_{IVA}} \times 10^4 \quad (4)$$

$$149 \quad \{CO_x \text{'s overall selectivity } (\%) \}_{TMA} = \frac{[CO_x]_{TMA}^{out} - [CO_x]_{TMA}^{in}}{3 \times [TMA]^{in} \times \{ \% \text{ conversion} \}_{TMA}} \times 10^4 \quad (5)$$

150

151 where $x = 1$ for CO and $x = 2$ for CO_2 . $[CO_x]_{IVA}$, $[CO_x]_{TMA}$ are respectively obtained after the
152 removal of IVA and TMA. $[IVA]^{in}$ and $[TMA]^{in}$ are respectively the inlet concentration of
153 IVA and TMA.

154 The coefficients 5 and 3 are the stoichiometric coefficients of the removal reaction.

155 The carbon balance (CB) is defined as the ratio (expressed in percentage) of the number of
156 moles of carbon present in the reaction products relative to their respective moles in each
157 pollutant removed.

158 CB values of IVA and TMA are expressed as:

$$159 \quad [CB(\%)]_{IVA} = \frac{[CO_x] + \sum [other \ byproducts]}{5 \times [IVA]^{in} \times \{ \% \text{ IRE} \}_{IVA}} \times 100\% \quad (6)$$

$$160 \quad [CB(\%)]_{TMA} = \frac{[CO_x] + \sum [other \ byproducts]}{3 \times [TMA]^{in} \times \{ \% \text{ IRE} \}_{TMA}} \times 100\% \quad (7)$$

161

162 **3. Results and Discussion**

163

164 **3.1. Flowrate and energy density**

165

166 **3.1.1. The removal rate**

167

168 The removal rate of each VOC is studied by varying the energy density and flowrate (Fig.3a
169 and 3.b).

170

171

Fig. 3.a

172

Fig. 3.b

173 In the first instance, the effect of ED shows that when this parameter increases the removal
174 rates of IVA and TMA increase also (Fig.3.a & b). In fact, at flowrate equal to 2 m³/h, when
175 ED extends three times, the removal rates of IVA and TMA are increased from 5 to 15
176 mmol.m⁻².h⁻¹ and from 4 to 11 mmol.m⁻².h⁻¹, respectively. This result is similar to those
177 reported for trichloromethane (Schmidt-Szalowski et al., 2011) acetylene (Redolfi et al.,
178 2009) and toluene (Vandenbroucke et al., 2011),

179 This behavior was expected, as increasing the electric voltage across the reactor leads to
180 higher degree of ionization and higher reactive species production (Thevenetet al., 2008;
181 Wang et al., 2009). Therefore the pollutant has more probability to be attacked by electrons
182 or radicals, resulting in enhancing removal rates of IVA and TMA. Similar results have been
183 reported in the literature for some VOCs (Fridman, 2008; Vandenbroucke et al., 2011).

184 By comparing the removal rate of each VOC, Fig. 3.a & b show that IVA is easier to be
185 removed. In fact, at an ED of 17 J/L and flowrate of 6 m³.h⁻¹, the removal rate of IVA can
186 reach 39 mmol.m⁻².h⁻¹ where the removal rate of TMA is equal to 27 mmol.m⁻².h⁻¹.

187 The chemical bond strength and molecule stability are the main factors that can affect the
188 removal rate of VOCs in the NTP process (Schmidt-Szalowski et al., 2011; Wang et al.,
189 2009; Assadi, 2012).

190 We note that, at a low value of ED, the effect of the flowrate is not important. This effect can
191 be explained that, at these conditions, low electrons and reactive species (such as ·O and ·OH)
192 are formed. Thus, the removal rate is probably limited by the chemical step.

193 A similar trend is observed for the two studied VOCs.

194 Thus, at high values of ED, the flowrate has more influence on the removal rate. The mass
195 transfer becomes the limited step. This is due to that, in laminar regime, the flowrate
196 increase involves higher values of the Reynolds number (R_e) from 368 to 1103 and mass
197 transfer coefficient (k_m) (Assadi et al.,2012).

198

199 3.1.2. The overall selectivities of CO and CO₂

200

201 The increase of ED leads to an increase of the overall selectivities (Fig 4.a&b). This is
202 due to the fact that more electrons and reactive species (such as $\cdot\text{O}$ and $\cdot\text{OH}$) are formed when
203 the ED increases and then more pollutants molecules are oxidized into CO₂ and CO (Guaitella
204 et al., 2008). In fact, with TMA, an increase in ED from 9 to 17 J/L leads to CO and CO₂
205 overall selectivity increase from 4 to 11 % and from 16 to 25 %, respectively. These results
206 are in agreement with works on removal of toluene with plasma (Guo et al., 2006; Huang et
207 al., 2011; Liang et al., 2009), isovaleraldehyde (Maciucă et al., 2012), acetylene (Thevenet
208 et al., 2008 ; Guaitella et al.,2008), acetone (Schmid et al., 2010), benzene (Jiang et al.,
209 2013; Fan et al., 2009) and dimethylamine (Ye et al., 2013).

210

211 **Fig. 4.a**

212 **Fig. 4.b**

213

214 In other hand, the mineralization of TMA is better than that of IVA. This can be explained by
215 the fact that less TMA is converted to intermediate compared to isovaleric acid. Thus the
216 intermediates have more probability to be attacked by electrons and active species.

217

218 3.2. Relative humidity

219

220 Many works (Thevenet et al.,2008;Vandenbroucke et al., 2011) reported that relative
221 humidity (RH) can considerably alter the performances of NTP.

222 Water plays a very important role in the reaction since it decomposes into $\cdot\text{OH}$ and $\cdot\text{H}$ free
223 radicals in the plasma system (Ogata et al., 2004; Atkinson et al., 2003):



225 When RH is high, more H₂O molecules collide with high energy electrons and $\cdot\text{OH}$ radicals
226 are formed.

227 Generally, VOCs can be removed by NTP via two pathways including (a) direct electron
228 attack and (b) indirect gas phase radical reactions (reactions between VOC molecules and
229 atomic oxygen $\cdot\text{O}$ or gas phase radicals such as $\cdot\text{OH}$)(Ogata et al., 2002). On one side, water
230 molecules partially dissociate to form reactive species (Khani et al., 2011; Ouni et al.,
231 2009;Vandenbroucke et al., 2011). On the other side, water negatively influences VOC
232 removal due to its electronegative characteristics. Due to high water concentrations, increased
233 plasma attachment processes result in a reduced hydroxyl radical ($\cdot\text{OH}$) production. It can be
234 concluded that two opposite phenomena are involved: water partially dissociates in the
235 plasma leading to reactive species, but humidity also negatively influences the plasma
236 characteristics. (Mista and Kacprzyk, 2008; Goujard et al., 2008;Capitelli, 1965).
237 So it will be interesting to study the influence of RH on the IVA and TMA removal.

238

239 3.2.1. The removal rate

240

241 The variation of removal rate of IVA and TMA with respect to RH is represented on Fig.5.a
242 and 5.b. Tests are performed at 20%, 55-60% and 85–90% RH.

243

244 **Fig. 5.a.**

245 **Fig. 5.b.**

246

247 We note that increasing water in the stream leads to a decrease of TMA's removal rate
248 (Fig.5.b).

249 It is unlikely that $\cdot\text{OH}$ radicals produced from water dissociation are responsible for TMA
250 removal. As a result of decreased electron density with increasing RH, the removal rate of
251 TMA decreases.

252 As reported by Guaitella et al (Guaitella et al, 2008) and Thevenet et al (Thevenet et al,
253 2008), oxygen atomic plays an important role on VOC oxidation under dry plasma treatment.
254 The disappearance of this specie due to H_2O electron scavenging could explain the decrease
255 of the removal rate of VOC with an increasing H_2O amount.

256 On the contrary, the removal rate of IVA by NTP is slightly promoted by increasing of RH
257 from 20% to 50–60% (Fig. 5.a). This is probably due to the enhanced production of $\cdot\text{OH}$
258 radicals, since the C-O substituent in isovaleric acid molecule can be more easily oxidized by
259 radicals as compared to the N-C link.

260 Adding more water in inlet gas mixture (RH> 60 %) has a negative effect on the removal rate
261 of IVA due to its electronegative characteristics. At higher RH electron density is reduced and
262 some reactive species are then quenched(Ogata et al., 2004; Thevenet et al., 2008).

263

264 3.2.2. The overall selectivity of CO₂

265

266 The water vapour seems to play an important role on byproducts formation. CO₂ overall
267 selectivity increases when RH increases. This tendency is the same for the two pollutants
268 studied (Fig 6 a. & b).

269

270

Fig.6.a

271

Fig 6.b

272

273 When RH raises from 25 to 90 %, at ED equal to 16.5 J/L, CO₂'s overall selectivity of IVA
274 and TMA increases from 25 to 34 % and from 21% to 30%, respectively.

275 As described previously, the water vapor is essential to the formation of [•]OH and [•]O which
276 promotes the mineralization of byproducts (Thevenet et al., 2008; Futamura et al.,
277 1997).Moreover, several authors (Thevenet et al., 2008; Ogata et al., 2004) report that CO
278 and CO₂ would be related by equilibrium under plasma action. In fact, water would be
279 supposed to favor the oxidation of CO leading to CO₂. In fact, the presence of [•]OH radicals
280 shifts the equilibrium towards the formation of CO₂.

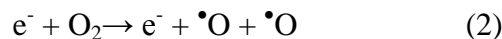
281

282 3.2.3. On the ozone formation

283

284 Ozone is an inevitable byproduct in a NTP. Atomic oxygen [•]O is generated by molecular
285 dissociation due to an impact with high energy electrons (reaction 2).

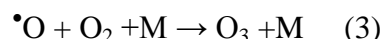
286



287 Atomic oxygen is a strong oxidizer, but its stability is very limited. Due to fast recombination
288 processes, the lifetime is only few microseconds at atmospheric pressure (Aggadi,
289 2006;Atkinson et al., 2003).

290 Atomic oxygen reacts with molecular oxygen in three-body collisions, forming ozone by the
291 following reaction:

292



293 where M can be either molecular oxygen or molecular nitrogen (Atkinson et al., 2003).
294 The effect of ED on ozone formation is presented in Fig. 7.a and b. Whatever the value of RH
295 and the used VOC, the ozone formation follows the same trend i.e. it increases with the ED.
296 This can be explained by the fact that more electrons and reactive species (such as $\bullet\text{O}$) are
297 formed and then atomic oxygen reacts with molecular oxygen in three-body collisions,
298 (reactions 2 & 3) leading to ozone production (Redolfi et al., 2009).

299 Moreover, the decrease in ozone formation is also observed when RH increases. The quantity
300 of the produced ozone is reduced two times when the RH increases from 25 to 90%.

301 In fact, the formation of ozone is inhibited due to a series of radical reactions leading to fast
302 ozone consumption (Atkinson et al., 2003). The presence of water molecules activates the
303 reaction giving $\bullet\text{OH}$ and $\bullet\text{O}_2\text{H}$ radicals which react with ozone.

304 • First, water acts as electron acceptor, following this pathway (Atkinson et al., 2003):



306 • Then ozone is decomposed by $\bullet\text{H}$ and $\bullet\text{HO}$ radicals (Atkinson et al., 2003; Braci et al.,
307 2011):



310 Globally, the effect of RH on the ozone production is relatively important.

311 **Fig.7.a**

312 **Fig.7.b**

313

314 **3.3. Gas phase reaction intermediates**

315

316 Byproducts formation is an important factor to be taken into account when NTP process is
317 carried out. VOCs removal often leads to the formation of some byproducts (Thevenet et al.,
318 2008; Vandenbroucke et al., 2011).

319 Fig.4.a and 4.b show that CBof each pollutant is achieved. This means that the majority of
320 organic byproducts are released from the DBD plasma reactor.

321 The gas stream in the exit of DBD plasma reactor is analyzed in order to identify the formed
322 byproducts. This is done in order to understand the reaction mechanism.

323

324 **3.3.1. Case of IVA**

325

326 An air stream of $2 \text{ m}^3 \cdot \text{h}^{-1}$ containing 55 ppm of IVA is treated in DBD plasma reactor. Six
327 byproducts are identified (Fig.8.a): acetone (CH_3COCH_3), isobutyric acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{-}$
328 COOH), methanol (CH_3OH), acetic acid (CH_3COOH), CO and CO_2 .

329

330

Fig.8.a

331

332 A removal pathway is proposed from literature study and is checked through experimental
333 investigations (Assadi, 2012; Aggadi, 2006). The oxidation scheme of IVA consists of the
334 simultaneous carboxylic function removal and new function carried on an ' $n-1$ ' carbon
335 molecule. So a possible removal pathway in series, which leads to a complete mineralization,
336 is proposed in Fig. 8.b.

337

Fig.8.b

338

339 Standard plasma radical kinetics based on $\cdot\text{O}$ and $\cdot\text{OH}$ oxidation of the compounds fails to
340 explain this distribution of the byproducts. Therefore the decomposition of $\text{C}_5\text{H}_{10}\text{O}_2$ in the
341 discharge must proceed through a fast cleavage of the C-C and C-O bonds. Several processes
342 can be implied in the removal mechanism: direct electronic impact and chemical reactions
343 with ions or nitrogen excited states (Huang et al., 2011; Atkinson et al., 2003).

344

3.3.2. Case of TMA

345

346
347 Byproducts due to TMA removal are also analyzed. Thus (Dimethylamino) acetonitrile, N, N-
348 Dimethyl formamide, Nitromethane, acetone, acetic acid, methanol and ethanol are identified
349 (Fig.8.a).

350 The removal mechanism of trimethylamine seems to be more complex than isovaleric acid.
351 Byproducts containing nitrogen would be formed at different removal steps.

352

353

Fig. 9.a

354

355 Moreover the oxidation of the trimethylamine leads to the formation of NO_x . The amounts of
356 these byproducts are represented in Fig.9.b

357

358

Fig.9.b

359

360 Therefore, in our opinion, the possible removal pathway is that (Dimethylamino)
361 acetonitrile, N, N-Dimethyl formamide, Nitromethane at atmospheric pressure are essentially
362 produced by the reaction of methyl radical with NO₂ (Braci et al., 2011, Harling et al., 2009,
363 Aggadi, 2006).

364 Moreover it is possible that after the main oxidation reactions another “combination-
365 reactions” can occur between byproducts (Schmidt-Szalowski et al., 2011; Yoshida, 2013).
366 Maybe acetone and acetic acid are essentially due to TMA “fragments” oxidation by CO.
367 While methanol and ethanol formation is due to acetic acid oxidation.

368

369 3.4. Modelling of kinetics and influence of the mass transfer

370

371 3.4.1. Model without mass transfer (WMT)

372

373 During the oxidation process in DBD plasma reactor two main steps can be considered: the
374 mass transfer step and the chemical reaction step. Usually the mass transfer step is neglected.
375 Many authors (Goujard et al., 2011; Mokt et al., 2001; Wang et al., 2009; Redolfi et al.,
376 2009) work only in batch reactor where mass transfer does not impact the kinetics, due to a
377 perfectly mixed gas phase.

378 By applying a mass balance over the entire length of the reactor we obtain:

$$379 D_e \frac{d(C_b)^2}{dz^2} - u_0 \frac{dC_b}{dz} = R \quad (8)$$

380 where D_e is the axial dispersion coefficient, C_b is the concentration of VOC on the gas phase,
381 u_0 is the linear velocity in the reactor, z is any position along the reactor longitudinal axis and
382 R is the removal rate.

383 Moreover, here, the reactor has been confirmed as a plug-flow reactor (Assadi et al., 2012).
384 In fact, a residence time distribution (RTD) experiment was carried out using carbon dioxide
385 as a tracer substance. This last was injected during a very short time interval into the reactor
386 (Dirac function). The outlet carbon dioxide concentration is measured at the exit of reactor.
387 The tanks in series model were used to describe the response of the system. The experiments
388 of RTD revealed that our annular reactor could be assimilated to a cascade of 22 elementary
389 continuously stirred tank reactors. It is generally accepted that above a number of 20
390 elementary reactors, the experimental reactor can be considered as a plug flow
391 reactor (Vincent et al., 2008). Thus, the continuous pollutant removal along the radial

392 direction should not be ignored (Assadi, 2012; Guaitella et al., 2008). On the other side, the
393 axial dispersion can be neglected and the equation (9) can be expressed as:

394
$$-u_0 \frac{dC_d}{dz} = R \quad (9)$$

395 Moreover, many authors use the relation (10) to identify the removal rate of toluene and
396 acetone (Schmid et al., 2010; Chang et al., 2005), nitric oxide (Mokt et al.,
397 2001), cyclohexane (Harling et al., 2009) and isovaleraldehyde (Maciucă et al., 2012) on the
398 DBD plasma reactors. This removal rate can be written as:

399
$$R = k_d C_d \frac{P}{V_{reactor}} = k_d C_d \frac{E_{inj}}{V_{reactor}} \cdot Q = k_d C_d \frac{E_{inj}}{\tau} \quad (10)$$

400 where k_d is the apparent rate constant, C_b and C_d are concentrations of VOC on the bulk and
401 discharge phases respectively, $V_{reactor}$ is the reactor volume and P is the discharge power, τ is
402 the residence time of the pollutant on the DBD plasma reactor and Q is the flowrate.

403 Experimentally, the plot of $\ln(C_{in}/C_{out})$ vs. E_{inj} will allow determining the constant of
404 model WMT. The values of the apparent rate constants (k_d) are represented on table 2. We note
405 that the model WMT represents the experimental results with a good approach. However the
406 apparent constants of this model are flowrate dependent. Thus, we can conclude that the mass
407 transfer step cannot be neglected in this present study. Therefore the model that will be
408 developed below will reflect the influence of the transfer step.

409

410

Table 2

411

412 3.4.2. Model with mass transfer (MT)

413

414 In air, under atmospheric pressure, the electrical discharge is considered as filamentary. Each
415 time the discharge takes place, electrons and active species such as ions, radicals and excited
416 species are generated at the surface of glass tube. They recombine rapidly into more stable
417 species and can further diffuse in the bulk phase (Allegraud et al., 2007; Capitelli et al.,
418 2000). The short life duration of radicals such as atomic oxygen $\cdot\text{O}$ makes that, in the bulk
419 phase, only the ozone is present (Allegraud et al., 2007; Vandenbrouck et al., 2011).

420 Thus, the plasma process is broken down into two phases:

- 421
- 422 • Transfer of gaseous reagents from gas phase to the discharge phase
 - 423 • Oxidation reaction between gaseous reagents on the discharge phase.

423 By applying a mass balance over the two phases of the reactor we obtain:

424 Gas phase:
$$-u_0 \frac{dC_b}{dz} = T \quad (11)$$

425 Discharge phase:
$$T = k_d C_d \frac{P}{V} \quad (12)$$

426 Where T is the mass transfer between the two phases. It can be estimated as (Bouzaza et al.,
427 2006):

428
$$T = k_m a_v (C_b - C_d) \quad (13)$$

429 where k_m is the mass transfer coefficient (m.s^{-1}) and a_v is the area of discharge per unit
430 volume of the reactor ($\text{m}^2.\text{m}^{-3}$). a_v is kept constant and is equal to $134 \text{ m}^2.\text{m}^{-3}$.

431 The external mass-transfer coefficient, k_m is estimated using a correlation developed for
432 laminar flow in annular reactors (Mobarak et al., 1997):

433
$$Sh = 1,029 \times Sc^{0.33} \times Re^{0.55} \times \left(\frac{L_{tot}}{d} \right)^{-0.472} \quad (14)$$

434 where L_{tot} is the length of the annular reactor, d is its equivalent diameter, and Sh, Sc and Re
435 are respectively Sherwood, Schmidt and Reynolds dimensionless numbers.

436 The values of Re and k_m are given in table 3.

437

438 **Table 3**

439

440 By combining equations (11) and (12), an algebraic resolution from $z = 0$ to $z = L$ and C from
441 C_{in} to C_{out} , gives:

442
$$C_b(z=L) = C_0 \cdot \exp \left[- \left(\frac{k_m a_v}{u_0} \right) \cdot \left(1 - \left(\frac{1}{1 + \frac{k_d \cdot E_{inj}}{\tau \cdot k_m a_v}} \right) \right) \cdot L \right] \quad (15)$$

443

444 The constant k_d of each pollutant is determined by numeric resolution using solver Excel. For
445 each experimental point, a target cell is defined as the difference between the experimental
446 and the theoretical removal rate.

447 The value of the apparent rate constant k_d obtained is summarized in Table 4.

448

449 **Table 4**

450 Fig. 3.a and 3.b show that the model is adequate to correlate the experimental results.
451 According to the literature, these results are in agreement with those reported for some VOCs
452 (Subrahmanyama et al., 2010,Wang et al., 2009; Redolfi et al., 2009).

453 In addition, it is interesting to note that this constant is not flowrate dependent. The influence
454 of this last parameter is integrated on the expression of k_m . In fact, the separation between the
455 mass transfer and the chemical reaction steps is obtained.

456

457 **4. Conclusions**

458

459 We have unambiguously shown that the removal rate of IVA and TMA can be improved by
460 increasing the energy density. The increase of flowrate leads to a better removal rate of tested
461 VOCs.

462 On the other hand, at higher levels of RH, an inverted trend occurs and the removal of the two
463 VOCs becomes slightly lower. Intermediates byproducts are also identified. Thus, removal
464 pathways of the pollutants are also proposed.

465 Moreover, a model based on chemical and mass transfer steps is developed to represent the
466 experimental results. The influence of mass transfer is estimated by using semi-empirical
467 model. Thus an apparent rate (k_d) and mass transfer (k_m) constants are determined
468 independently.

469 This model describes successfully the removal of IVA and TMA by DBD plasma.

470

471 **Acknowledgment**

472

473 The authors gratefully acknowledge the financial support provided by the French National
474 Research Agency (ANR) for this research work.

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484 **References**

485

486 ADEME, 2005. Pollutions olfactives : origine, législation, analyse, traitement, Ademe,
487 Dunod, Angers.

488

489 Allegraud K., 2008. Décharge à barrière diélectrique de surface : physique et procédé, thèse
490 Ecole polytechnique de Paris.

491

492 Aggadi N., 2006. Étude de la réactivité de suies modèles de n-hexane sous décharge couronne
493 pulsée à la pression atmosphérique, Université de Paris Nord-France

494

495 Assadi A.A., 2012. Développement d'un procédé de couplage réacteur plasma DBD-réacteur
496 photocatalytique pour le traitement des effluents gazeux : du laboratoire à l'application
497 industrielle, Thèse n ° 009. Rennes: ENSC Rennes.

498

499 Atkinson R., Baulch D. L., Cox R. A., Crowley J. N., Hampson R. F., Hynes R. G., Jenkin M.
500 E., Rossi M. J., Troe J., 2003. Evaluated kinetic and photochemical data for atmospheric
501 chemistry: Part 1 - gas phase reactions of Ox, HOx, NOx and SOx species Atmospheric
502 chemistry and Physics Discussions, 3, 6179–6699.

503

504 Bouzaza, A., Vallet, C., Laplanche, A., 2006. Photocatalytic removal of some VOCs in the gas
505 phase using an annular flow reactor determination of the contribution of mass transfer and
506 chemical reaction steps in the photodegradation process. J. Photochem. Photobiol. A: Chem.
507 177, 212–217.

508

509 Braci L., Ognier S., Liu Y.N., Cavadias S., 2011. Post-discharge treatment of air effluents
510 polluted by butyl-mercaptan: role of nitrate radical, Conference Series 275, 12-13.

511

512 Capitelli M., Ferreira C.-M., Gordiets B., Osipov A., 2000. Plasma kinetics in atmospheric
513 gases, C.-M. Ferreira, B. Gordiets, A. Osipov (Eds.), in: Springer Series on Atomic, Optical,
514 and Plasma Physics, Eds 31, Springer-Verlag, Berlin.

515

516 Capitelli M., 1965. Plasma Kinetics in Atmospheric Gases, New York -Springer.
517
518
519 Chang Ch.-L., Lin T.-Sh., 2005. Decomposition of Toluene and Acetone in Packed Dielectric
520 Barrier discharge Reactor, Plasma Chemistry and Plasma Processing, 25, 227-243.
521
522 Derakhshesh M., Abedi J., Hassanzadeh H., 2010, Mechanism of methanol decomposition by
523 non-thermal plasma, Journal of Electrostatics 68, 424-428.
524
525 Fan H.Y., Shi C. , Li X.S. , Zhao D. Z., Xu Y. , Zhu A.M., 2009. High-efficiency plasma
526 catalytic removal of dilute benzene from air, Journal of Physics D—Applied Physics 42
527 225105- 225110.
528
529 Fridman A. 2008. Plasma chemistry. New York: Cambridge University Press.
530
531 Futamura S., Zhang A. H., Yamamoto T., 1997. the dependence of non thermal plasma
532 behavior of VOCs on their chemical structures Jwournal of Electrostatics 42, 51-62.
533
534 Goujard V., Tatibouet J-M., Batiot-Dupeyra C., 2011. Carbon Dioxide Reforming of Methane
535 Using a Dielectric Barrier Discharge Reactor: Effect of Helium Dilution and Kinetic Mode,
536 Plasma Chem Plasma Process 31, 315–325.
537
538 Guaitella O., Thevenet F., Puzenat E., Guillard C., Rousseau A., 2008. C₂H₂ oxidation by
539 plasma/TiO₂ combination: Influence of the porosity, and photocatalytic mechanisms under
540 plasma exposure, Applied Catalysis B: Environmental, 80, 296–305.
541
542 Guo Y. F., Ye D.-Q., Chen K.-F, Tian Y.F., 2006. Humidity Effect on Toluene
543 Decomposition in aWire-plate Dielectric Barrier Discharge Reactor, Plasma Chem Plasma
544 Process 26, 237–249.
545
546 Harling A. M., Glover D. J., Whitehead J. C., Zhang, K., 2008. Industrial Scale Destruction of
547 Environmental Pollutants using a Novel Plasma Reactor, Ind. Eng. Chem. Res. 47, 5856–586.
548

549 Jolibois J., Takashima K., Mizuno A., 2012. Application of a non-thermal surface plasma
550 discharge in wet condition for gas exhaust treatment: NO_x removal, *Journal of Electrostatics*,
551 70, 300-308.
552

553 Harling A.M., Glover D. J., Whitehead J. Ch., Zhang K., 2009. The role of ozone in the
554 plasma-catalytic destruction of environmental pollutants, *Applied Catalysis B: Environmental*
555 90, 157–161.
556

557 Huang H., Ye D., Leung D. Y. C., 2011. Abatement of Toluene in the Plasma-Driven
558 Catalysis: Mechanism and Reaction Kinetics, *IEEE transactions on plasma science*, 39, 877-
559 882.
560

561 Jiang N., Lu N., Shang K., Li J., Wu Y., 2013. Effects of electrode geometry on the
562 performance of dielectric barrier/packed-bed discharge plasmas in benzene degradation.
563 *Journal of Hazardous Materials* 262, 387–393
564

565 Jiwu L., Lei F., 2013. Modeling of corona discharge combined with Mn²⁺ catalysis for the
566 removal of SO₂ from simulated flue gas, *Chemosphere* 91, 1374–1379
567

568 Khani M.R., RazaviBarzoki S.H., SahbaYaghmaee M., Hosseini S.I., Shariat M., Shokri B.,
569 Fakhari A.R., Nojavan S., Tabani H., Ghaedian M., 2011. Investigation of cracking by
570 cylindrical dielectric barrier discharge reactor on the n-hexadecane as a model compound,
571 *IEEE Trans. Plasma Sci.* 39, 1807–1813.
572

573 Le Cloirec P., 1998. *Les composés organiques volatils dans l’environnement*, Lavoisier, Paris
574

575 Liang W., Li J., Li J., Jin Y., 2009. Abatement of toluene from gas streams via ferro-electric
576 packed bed dielectric barrier discharge plasma, *Journal of Hazardous Materials* 170, 633–638.
577

578 Maciuca A., Batiot-Dupeyrat C., Tatibouet J-M., 2012. Synergetic effect by coupling
579 photocatalysis with plasma for low VOCs concentration removal from air *Applied Catalysis B:*
580 *Environmental*, 125, 432-438.
581

582 Ma H., Chen P., Ruan R., 2001. H₂S and NH₃ Removal by Silent Discharge Plasma and
583 Ozone Combo-System, Plasma Chemistry and Plasma Processing 21, 611-624.
584

585 Manley T.C., 1943. Transactions of the electrochemical society,. Proceedings of the 84th
586 General Meeting, New York 84, p. 83.
587

588 Mfopara A., Kirkpatrick M. J., Odic E., 2009. Dilute methane treatment by atmospheric
589 pressure dielectric barrier discharge: effects of water vapor, Plasma Chemistry and Plasma
590 Processing 29, 91–102.
591

592 Mista W., Kacprzyk R., 2008. Decomposition of toluene using non-thermal plasma reactor at
593 room temperature, Catalysis Today 137, 345–349.
594

595 Mobarak A. A., Farag H. A., Sedahmed G.H., 1997. Mass transfer in smooth and rough
596 annular ducts under developing flow conditions Journal of applied electrochemistry. 27, 201-
597 207.
598

599 Mok Y. S., Lee Ho W., Hyun Y. J., Ham S. W., Nam I. S., 2001. Determination of
600 Decomposition Rate Constants of Volatile Organic Compounds and Nitric Oxide in a
601 Pulsed Corona Discharge Reactor, Korean J. Chem. Eng, 18, 711-718.
602

603 Mok Y.S., Kim D.H., 2011. Treatment of toluene by using adsorption and nonthermal plasma
604 oxidation process Current applied physics, 11,S58–S62.
605

606 Ogata A., Ito D., Mizuno K., Kushiyama S., Gal A., Yamamoto T., 2002. Effect of coexisting
607 components on aromatic decomposition in a packed-bed plasma reactor, Applied Catalysis A:
608 General, 236, 9–15.
609

610 Ogata A., Ito D., Mizuno K., Kushiyama S., Gal A., Yamamoto T., 2004. Effect of coexisting
611 components on aromatic decomposition in a packed-bed plasma reactor, Radiation Physics
612 and Chemistry 69, 281–287.
613

614 Ouni F., Khacef A., Cormier J. M., 2009. Gas Production from Propane Using Atmospheric
615 Non-thermal Plasma PlasmaChem Plasma Process, 29, 119–130.
616

617 Petit P., Vialle P.-J., Maciucă A., Batiot-Dupeyrat C., Tatibouet J.-M., Assadi A., Bouzaza A.,
618 Wolbert D., Vallet C., 2013. Dispositif, système et procédé de traitement de gaz. CIAT,
619 ENSCR, CNRS. France. N°1350906.
620

621 Rakness K., Gordon G., Langlais B., Masschelein W., Matsumoto N., Richard Y., Robson C.
622 M., Somiy I., 1996. Guideline for Measurement of Ozone Concentration in the Process Gas
623 From an Ozone Generator, 18, 209-229.
624

625 Redolfi M., Aggadi N., Duten X., Touchard S., Pasquiers S., Hassouni K., 2009. Oxidation of
626 Acetylene in Atmospheric Pressure Pulsed Corona Discharge Cell Working in the
627 Nanosecond Regime, Plasma Chem Plasma Process 29, 173–195.
628

629 Schmidt-Szałowski K., Krawczyk K., Sentek J., Ulejczyk B., Górska A., Młotek M., 2011,
630 Hybrid plasma-catalytic systems for converting substances of high stability, greenhouse gases
631 and VOC. chemical engineering research and design 89, 2643–2651
632

633 Schmid S., Jecklin M.C., Zenobi R., 2010. Degradation of volatile organic compounds in a
634 non-thermal plasma air purifier, Chemosphere, 79, 124–130.
635

636 Subrahmanyama Ch., Renken A., Kiwi-Minsker L., 2010. Catalytic non-thermal plasma
637 reactor for abatement of toluene, Chemical Engineering Journal 160, 677–682.
638

639 Subrahmanyam Ch., Magureanu M., Kiwi-Minsker L., Renken A., 2006. Catalytic abatement
640 of volatile organic compounds assisted by non-thermal plasma: part II. Optimized catalytic
641 electrode and operating conditions. ApplCatal B, 65, 157-162.
642

643 Thevenet F., Guaitella O., Puzenat E., Guillard C., Rousseau A., 2008. Influence of water
644 vapour on plasma/photocatalytic oxidation efficiency of acetylene, Applied Catalysis B:
645 Environmental, 84, 813–820.
646

647 US EPA, 2008. Clean Air Act. US Code. Environmental Protection Agency. Washington, DC.
648

649 Vandebroucke A. M., Morent R., De Geyter N., Leys Ch., 2011. Non-thermal plasmas for
650 non-catalytic and catalytic VOC abatement, *Journal of Hazardous Materials* 195, 30–54.
651

652 Vincent G., Marquaire P.M., Zahraa O., 2008. Abatement of volatile organic compounds
653 using an annular photocatalytic reactor: study of gaseous acetone, *J.Photochem. Photobiol. A:
654 Chem.* 197, 177–189.
655

656 Wang H., Li D., Wu Y., Li J., Guofeng L., 2009. Removal of four kinds of volatile organic
657 compounds mixture in air using silent discharge reactor driven by bipolar pulsed power,
658 *Journal of Electrostatics* 67, 547–555.
659

660 Yang H., An B., Wang Sh., Li L., Jin W., Li L., 2013. Destruction of 4-phenolsulfonic acid in
661 water by anodic contact glow discharge electrolysis, *Journal of Environmental Sciences*, 25(6)
662 1063–1070
663

664 YeZh., Zhao J., Huang H. y., Ma F., Zhang R., 2013. Decomposition of dimethylamine gas
665 with dielectric barrier discharge, *Journal of Hazardous Materials* 260, 32–39
666

667 Yoshida K., 2013, Diesel NO_x aftertreatment by combined process using temperature swing
668 adsorption, nonthermal plasma, and NO_x recirculation: NO_x removal accelerated by
669 conversion of NO to NO₂, *Journal of the Taiwan Institute of Chemical Engineers*, 44,1054–
670 1059.
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683 **Table captions**

684

685 Table 1: Parameters of DBD plasma reactor

Parameter	Value and domain
Gastemperature	Ambient (293 K)
Gas pressure	Atmospheric pressure (1 atm)
Relative humidity	20–90%
Trimethylamineinlet concentration	55 ppm
Isovalericacidinlet concentration	55 ppm
Applied voltage	12–29 kV
Gasflowrate	2–6 m ³ h ⁻¹

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687

688 Table 2: Values of the kinetic coefficient with the model WMT

Flow rate (m³ h⁻¹)	2		4		6	
	TMA	IVA	TMA	IVA	TMA	IVA
Pollutant						
$k_d \times 10^2$ (m ² W ⁻¹ s ⁻¹)	3.6	4.1	3.1	3.4	2.6	2.9
R^2 (%)	97.91	98.68	98.95	99.24	97.00	99.05

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691 Table 3: Reynolds number and mass transfer coefficients

Flow rate (Q, m³ h⁻¹)	Reynolds number	Mass transfer coefficient ($k_m \times 10^3$, m s⁻¹)	
		IVA	TMA
2	380	2.2	3.0
4	760	3.6	4.3
6	1140	4.4	5.4

692

693

694 Table 4: Values of parameters k_d of model TM

Isovalericacid		Trimethylamine	
$k_d \times 10^2$ (m ² (W s)) ⁻¹	Correlation (%)	$k_d \times 10^2$ (m ² (W s)) ⁻¹	Correlation (%)
3.9	99	3.5	99

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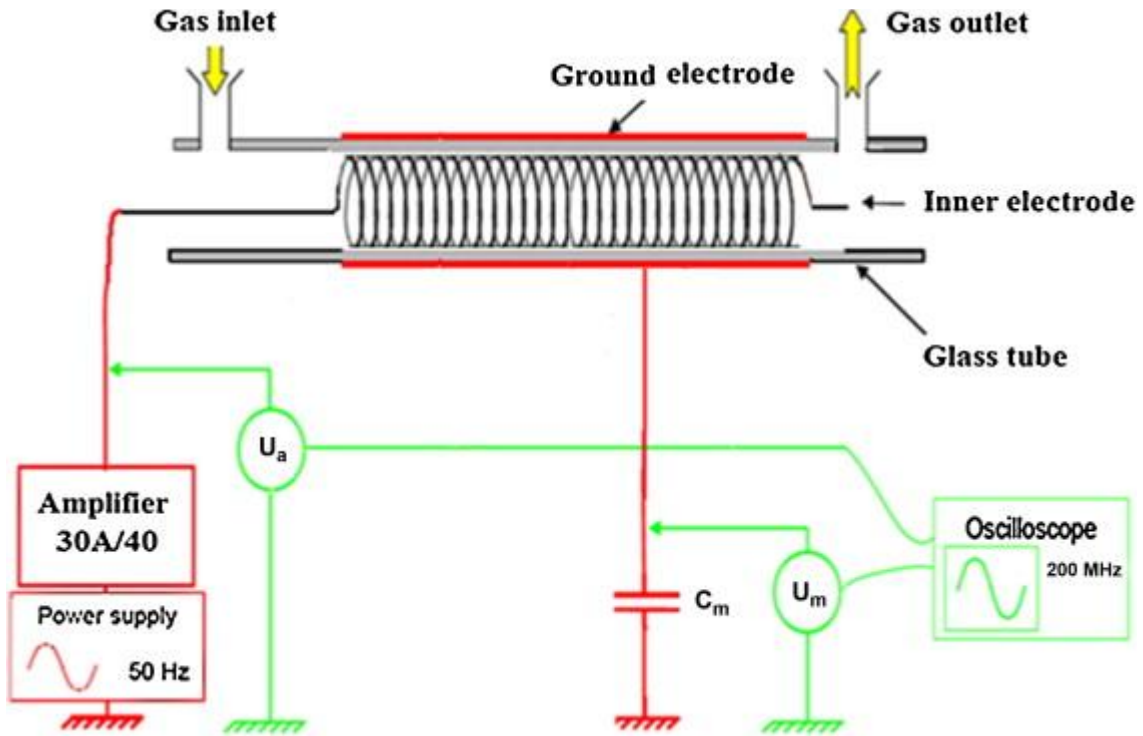
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698 **Figure captions**

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700 Fig. 1: General electric schema of the DBD plasma reactor



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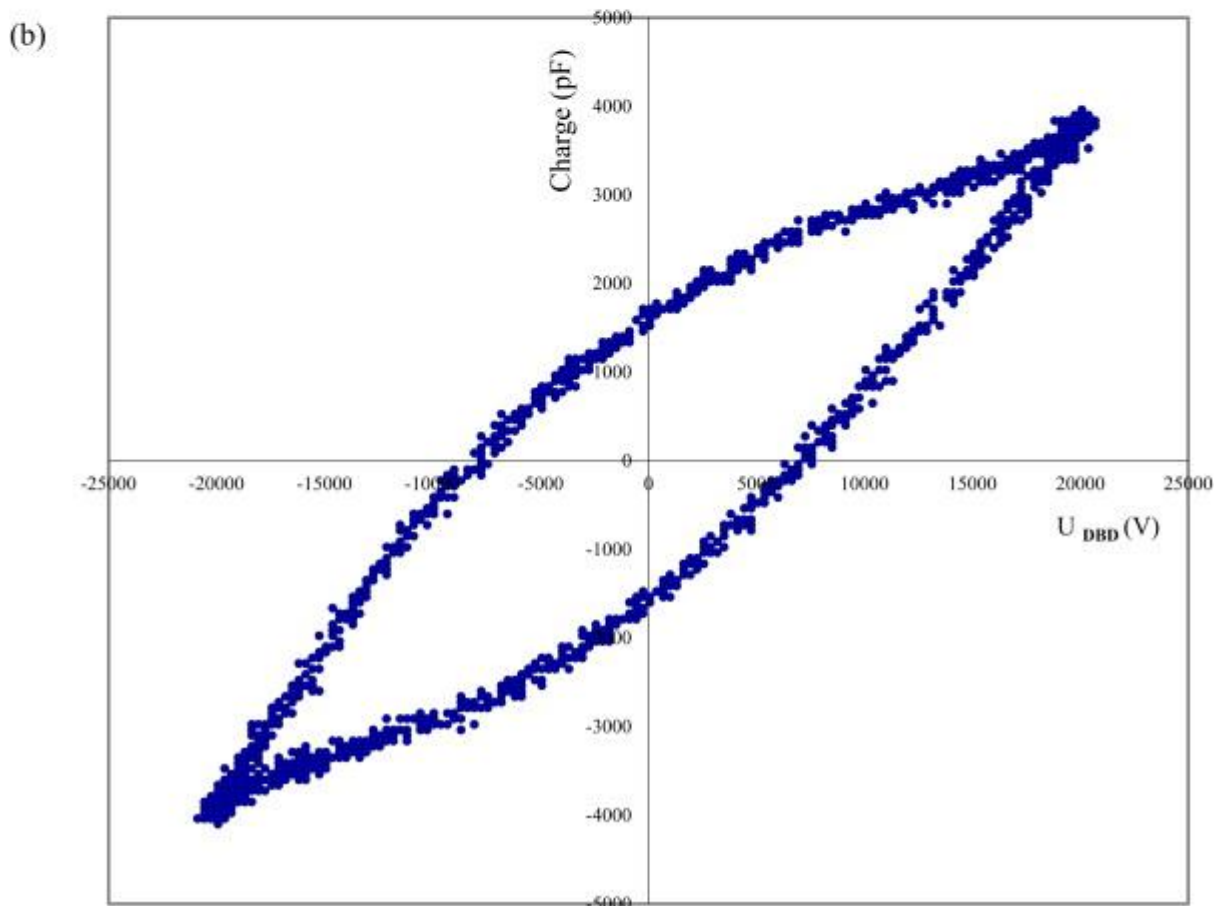
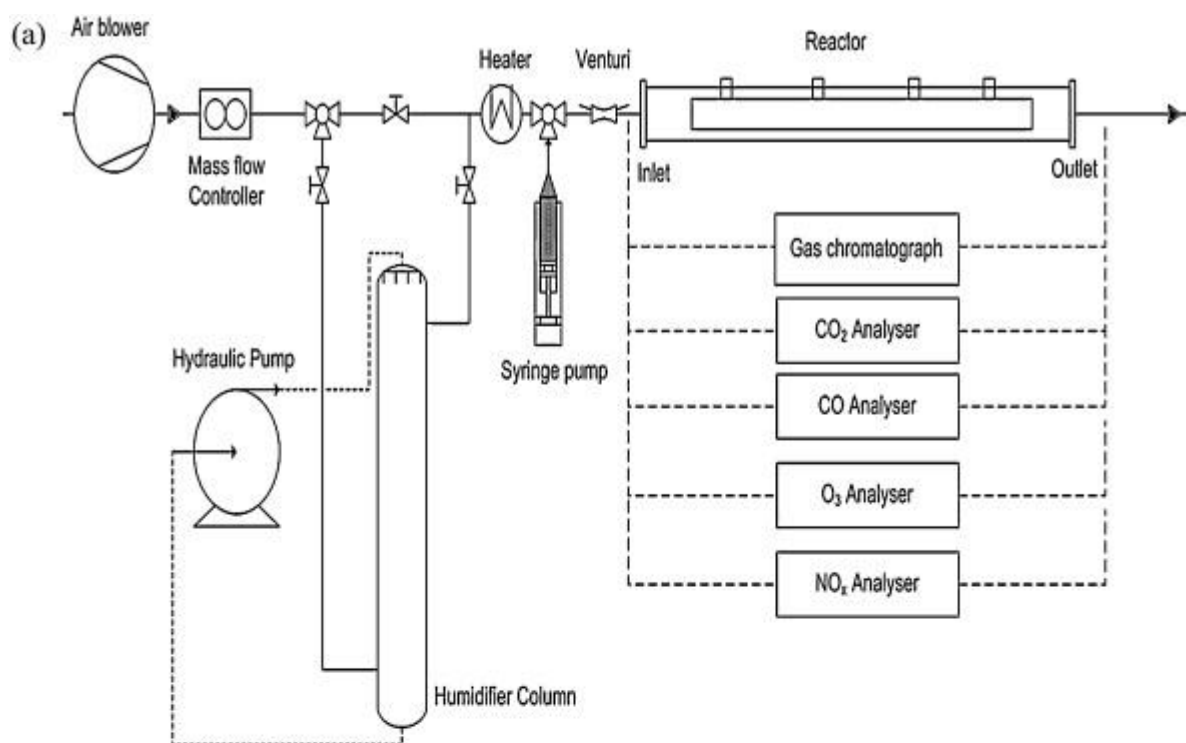
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719 Fig. 2.a: Experimental Set-Up

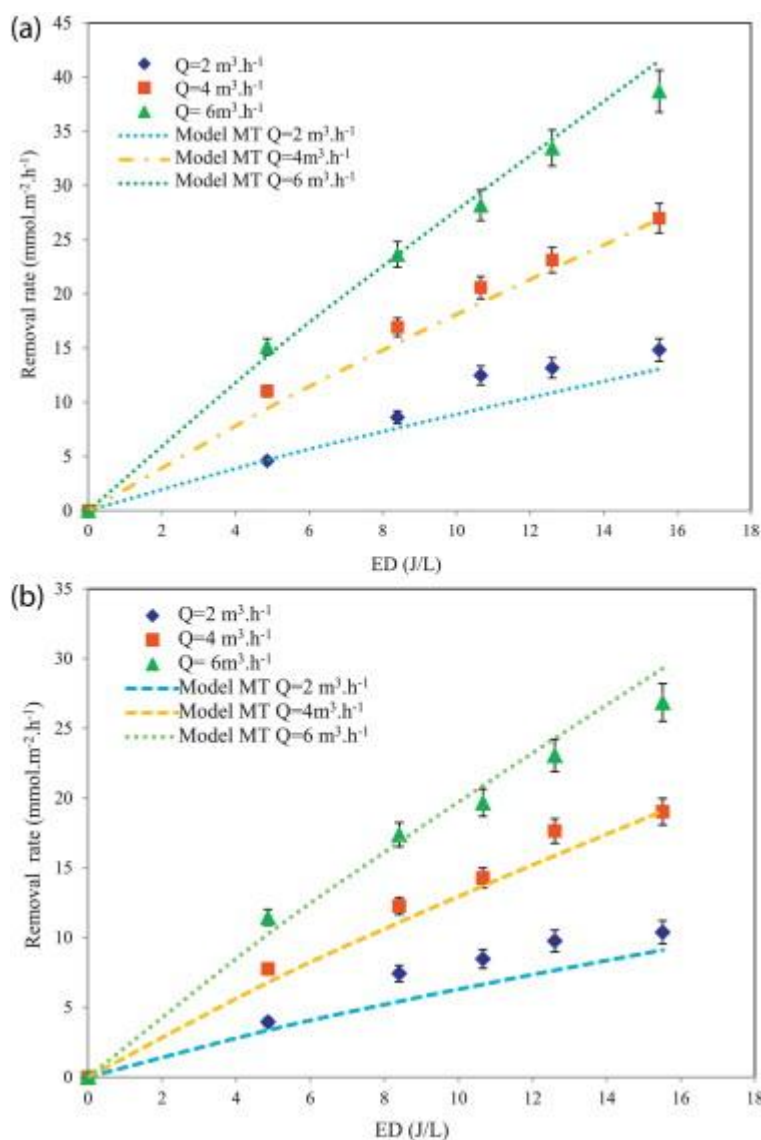
720 Fig. 2.b: Lissajous curve obtained at 50 Hz.



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722 Fig. 3.a: Removal rate of IVA on the plasma reactor with the ED at different flowrate (Model:
 723 MT, [IVA] = 55 ppm, T= 20 °C, RH = 50 ± 5 %).

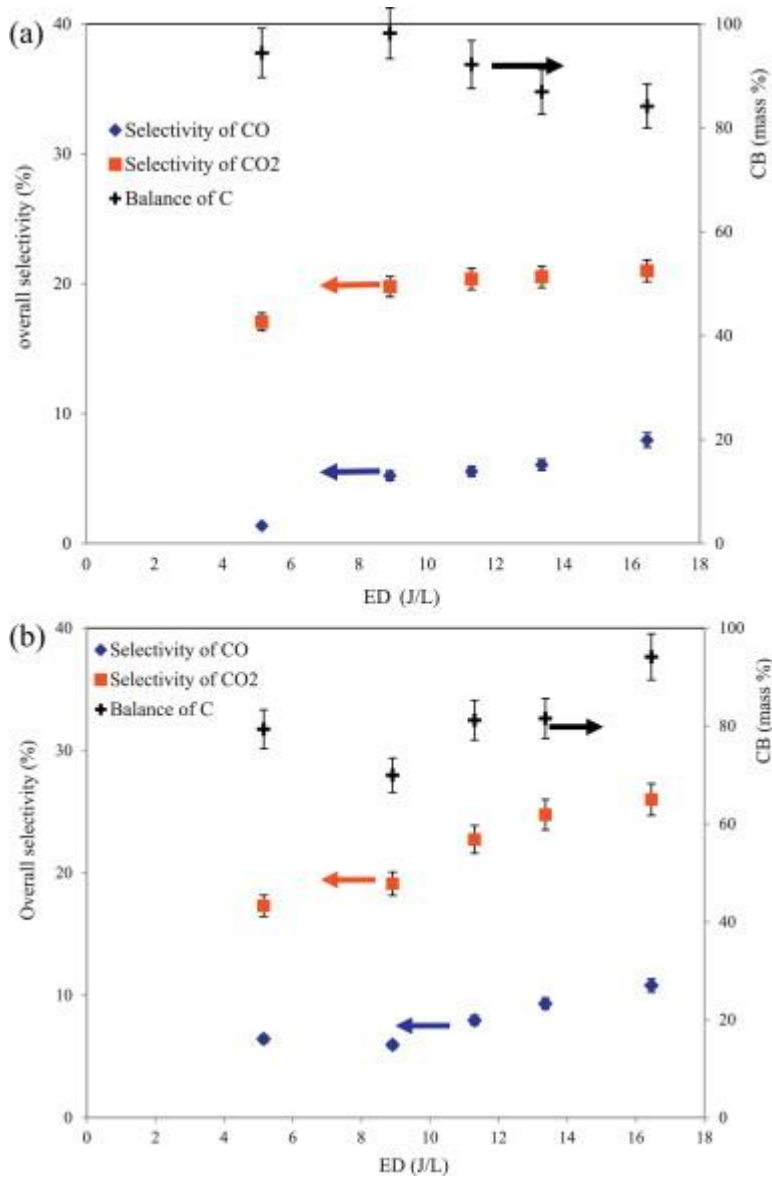
724 Fig. 3.b: Removal rate of TMA on the plasma reactor with ED at different flowrate (Model:
 725 MT, [TMA] = 55 ppm, T= 20 °C, RH = 50 ± 5 %).



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735 Fig. 4.a: Variation of the CO's and CO₂'s selectivities (%) and balance of Carbon vs. ED -
 736 Isovaleric acid (T= 20 °C, RH = 25%, Q=2 m³.h⁻¹, [IVA] = 55 ppm).

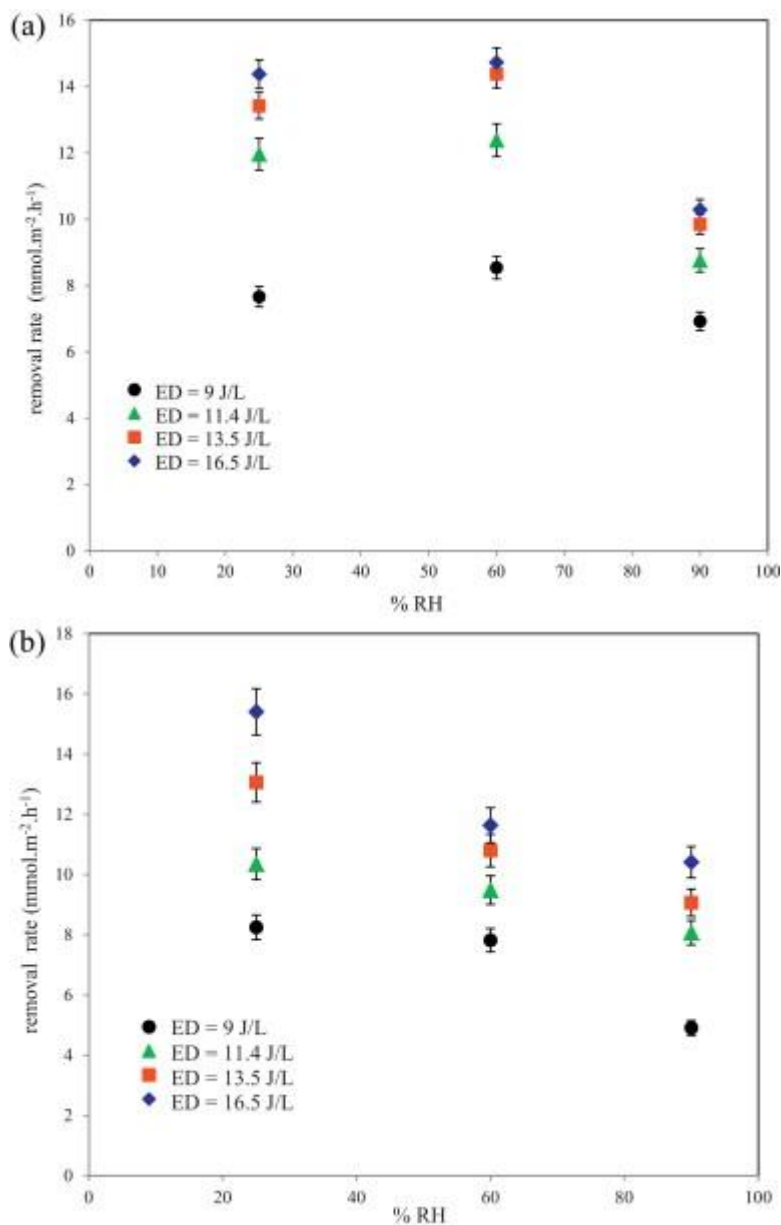
737 Fig. 4.b: Variation of the CO's and CO₂'s selectivities (%) and balance of Carbon vs. ED -
 738 Trimethylamine (T= 20 °C, RH = 25%, Q=2 m³.h⁻¹, [TMA] = 55 ppm).



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747 Fig.5.a.Variation of removal rate of IVA on the plasma reactor with relative humidity at
 748 different ED ([IVA] = 55 ppm, T= 20 °C, Q= 2 m³.h⁻¹).

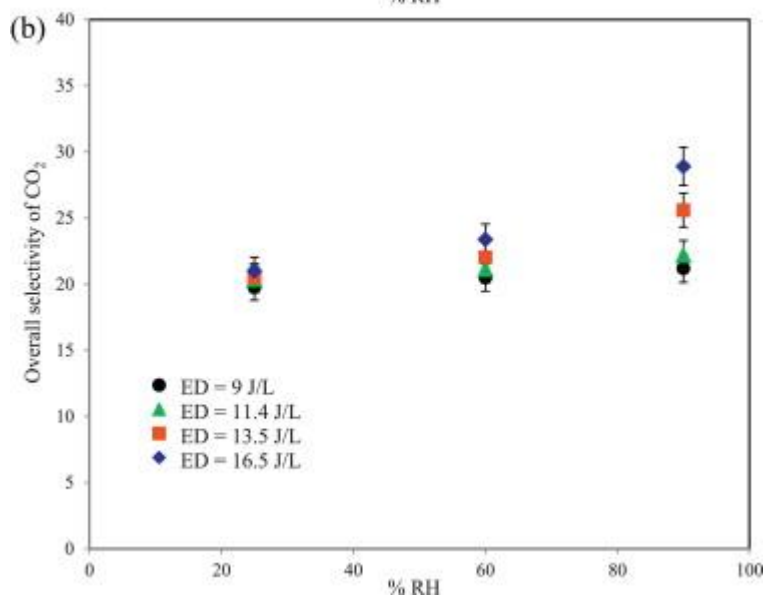
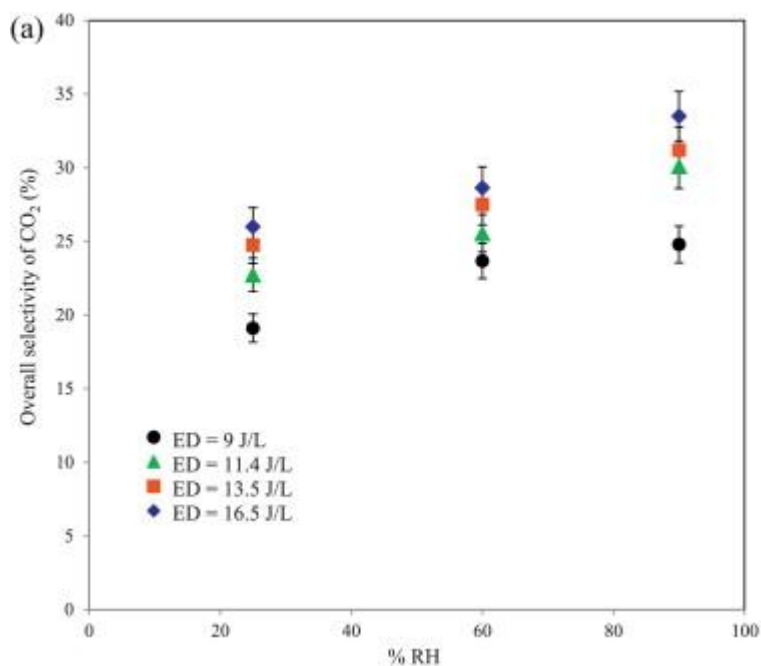
749 Fig.5.b.Variation of removal rate of TMA on the plasma reactor with relative humidity at
 750 different density energy ([TMA] = 55 ppm, T= 20 °C, Q= 2 m³.h⁻¹)



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758 Fig. 6a Variation of CO₂ selectivity vs % RH at different values of ED([TMA] = 55 ppm, T=
 759 20 °C, Q = 2 m³.h⁻¹).

760 Fig 6.b Variation of CO₂ selectivity vs % RH at different values of ED([IVA] = 55 ppm, T=
761 20 °C, Q = 2 m³.h⁻¹).



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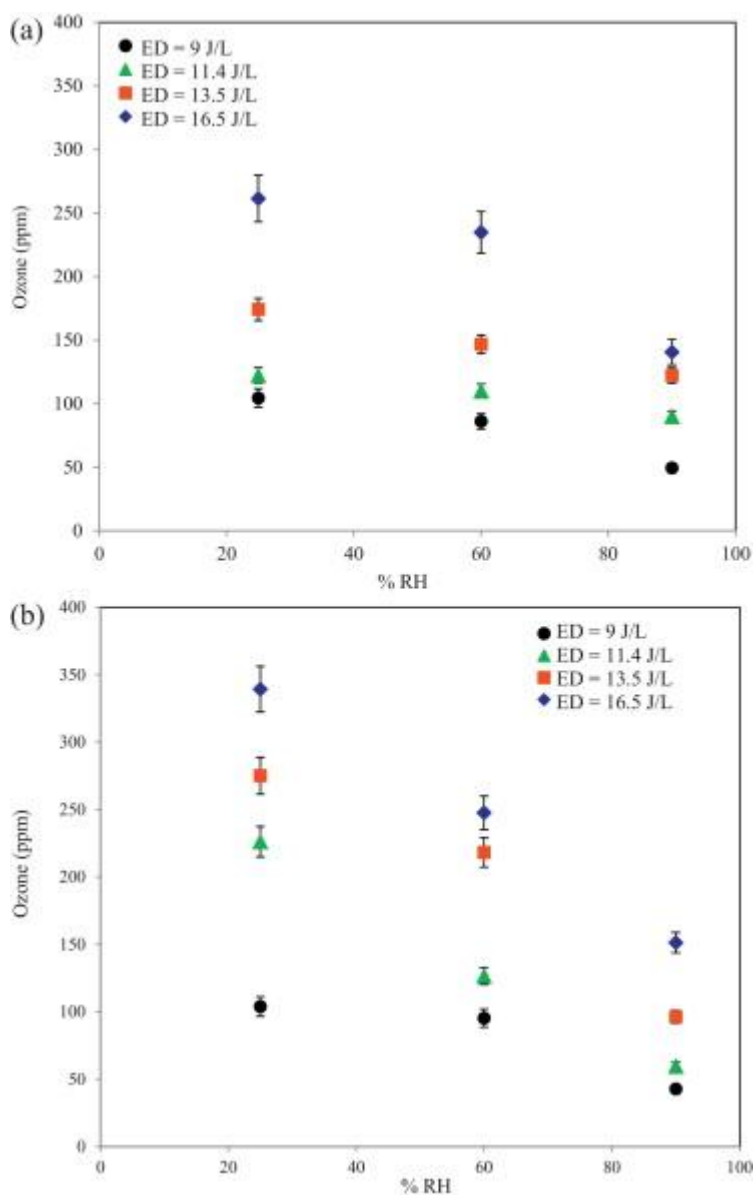
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768 Fig 7.a Variation of ozone production vs % RH at different values of ED ([TMA] = 55 ppm,
769 T= 20 °C, Q = 2 m³.h⁻¹).

770 Fig 7.b.:Variation of the ozone production vs % RH at different values of ED ([IVA] = 55
771 ppm, T= 20 °C, Q = 2 m³.h⁻¹).



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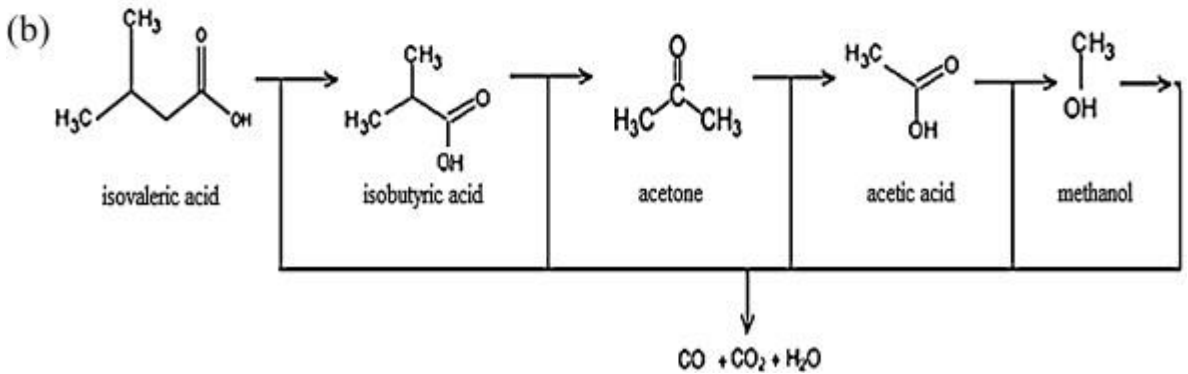
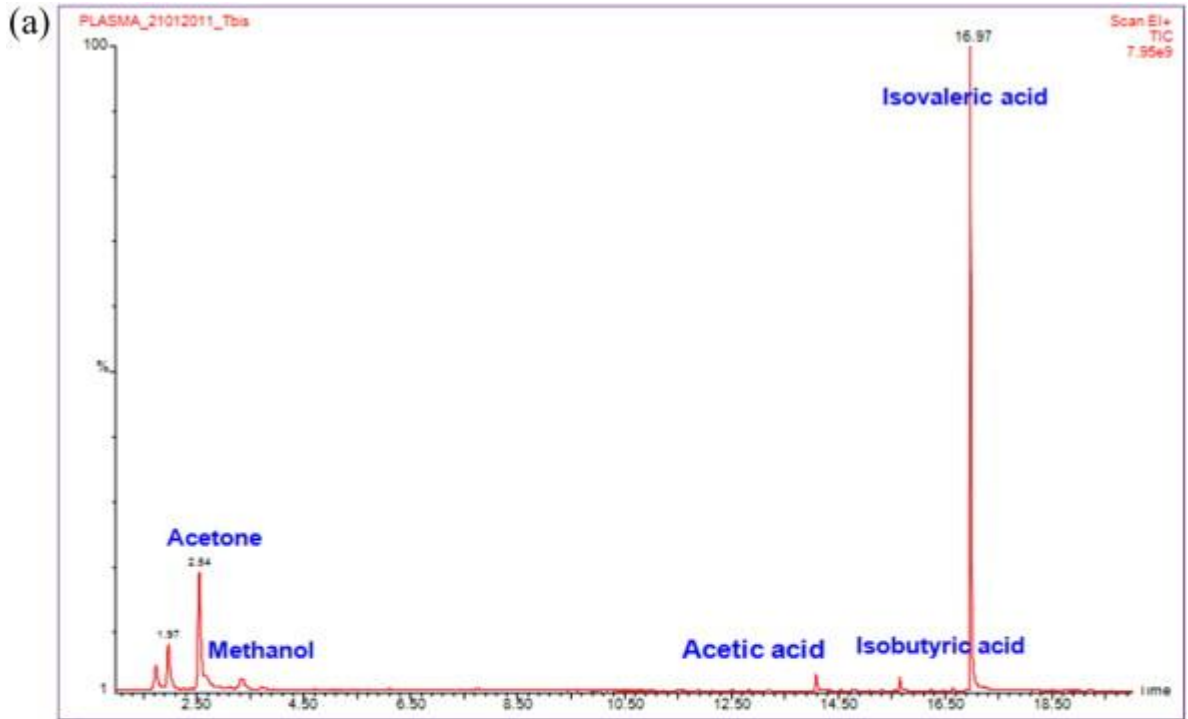
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779 Figure 8.a: GC-MS spectrum of IVA byproducts(ED = 13.4 J/L, [IVA] = 55 ppm, T= 20 °C,
780 Q = 2 m³.h⁻¹).

781 Fig. 8.b: A possible pathway of isovaleric acid destruction on DBD plasma reactor.



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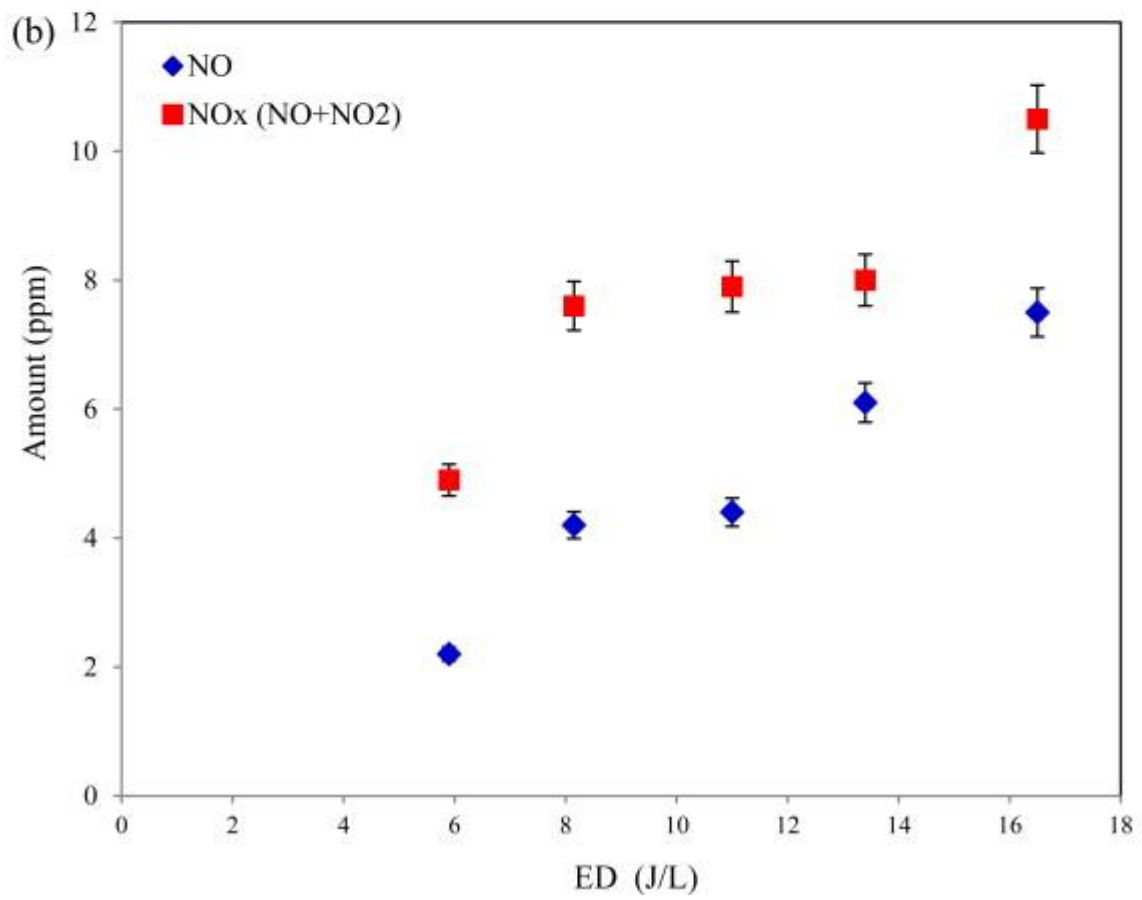
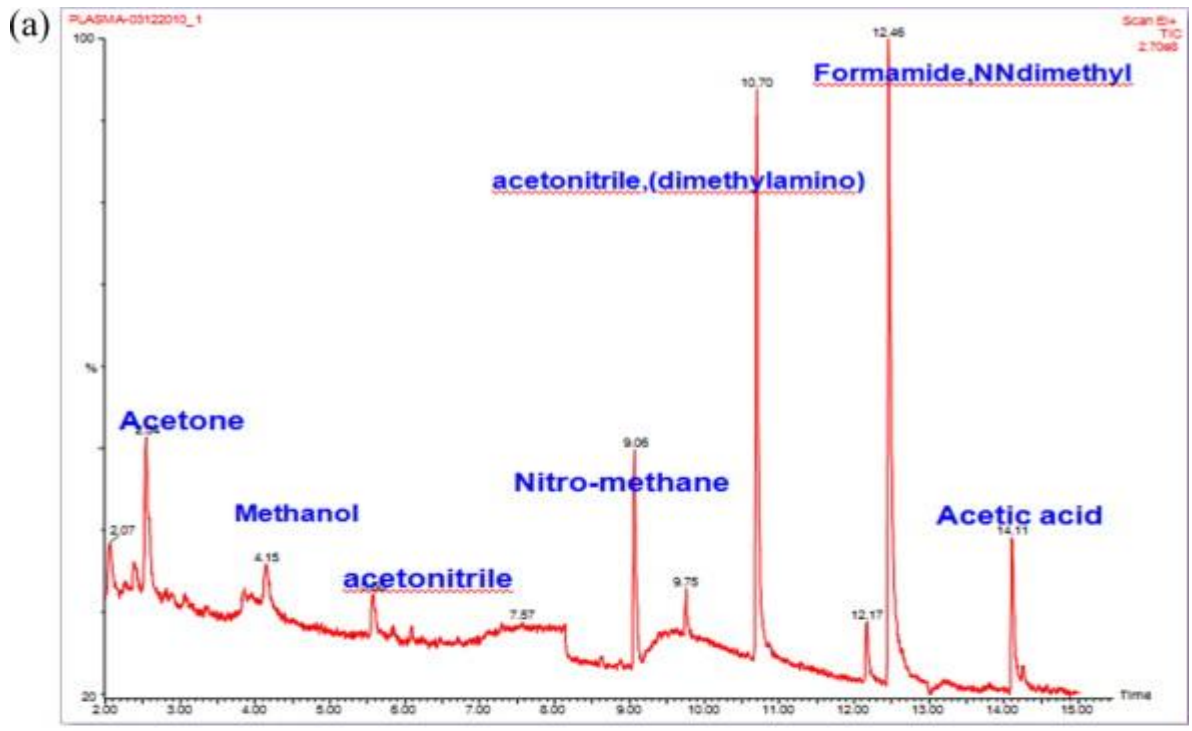
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787 Fig.9.a: GC-MS spectrum of TMA by-products (ED=13.4 J/L, [TMA] = 55 ppm, T= 20 °C, Q
788 = 2 m³.h⁻¹).

789 Fig. 9.b: Variation of amount of NO and NO_x vs ED(% RH= 50 %, [TMA] = 55 ppm, T= 20
790 °C, Q = 2 m³.h⁻¹).



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