

1 Efficient plasma-catalysis coupling for CH₄ and CO₂ transformation in a
2 fluidized bed reactor: comparison with a fixed bed reactor

3 Nassim Bouchoul, Houcine Touati, Elodie Fourré, Jean-Marc Clacens, Catherine Batiot-
4 Dupeyrat*

5 *IC2MP, ENSIP, Université de Poitiers - UMR CNRS 7285*
6 *1 rue Marcel Doré, TSA 41105, 86073 Poitiers cedex 9 (France)*

7 *E-mail : catherine.batiot.dupeyrat@univ-poitiers.fr

8
9 **Abstract**

10 The transformation of methane and carbon dioxide by coupling plasma and catalysis was
11 investigated using a fluidized bed reactor and the results, in terms of reactant conversion and
12 yields in products, were compared with those obtained in a fixed bed reactor. A series of
13 alumina, including a commercial sample and various meso-macro materials synthesized in the
14 laboratory, was tested in this study. Their surface areas varied from 260 to 312 m² g⁻¹ depending
15 on their calcination temperature. A correlation between reactant conversion and surface area of
16 alumina was highlighted for the plasma-fluidized bed, the best conversions being reached with
17 the alumina presenting the highest surface area. CH₄ conversion increased from 8.5 to 12.1 %
18 for S=260 and 312 m² g⁻¹ respectively and the CO₂ conversion from 3.4 to 6.2 % for a deposited
19 power of 4W, in an excess of CO₂. This correlation was not corroborated for the fixed bed
20 reactor. It proves that an efficient coupling of plasma and catalysis can be expected as soon as
21 solid particle are moving in the gas flow, enhancing the plasma-surface interaction.

22
23 **Keywords**

24 CH₄ and CO₂, Non-thermal plasma, fluidized bed, plasma - catalyst interaction, alumina

25 **1 Introduction**

26 The need to develop renewable energy sources in order to reduce greenhouse gas emission is a
27 major contemporary concern, leading to a continuous increase of research activities. To this
28 end, methane and carbon dioxide, the two main constituent of biogas, are particularly studied
29 since the reaction between them (dry reforming) lead to the formation of syngas ($H_2 + CO$), an
30 important raw material in liquid fuel processes such as Fischer-Tropsch synthesis and methanol
31 synthesis. However, the reaction presents two serious problems: it is very endothermic,
32 requiring temperatures above $700^\circ C$ and the catalysts deactivate rapidly due to carbon
33 deposition [1]. Consequently, new methods of activation are still needed to perform the reaction
34 in conditions reaching today's economic and environmental constraints.

35 Non-thermal plasma (NTP) has been the subject of a large array of publications showing that
36 atmospheric pressure and low-temperature plasmas offer an interesting alternative to
37 conventional catalytic thermal processes in the dry reforming reaction [2-6]. Different types of
38 NTP were investigated, the most common being microwave [7], gliding arc discharges [8, 9]
39 and Dielectric Barrier Discharges (DBDs) [10]. DBD reactors present the advantages of
40 operating at atmospheric pressure with a simple design suitable for upscaling. The strong
41 electric field generated by the application of a high voltage (several kV) between two electrodes
42 (one of which being protected by a dielectric material) leads to the formation of highly energetic
43 electrons. These electrons collide with surrounding gas molecules, creating reactive species
44 such as ions, excited species and radicals.

45 Many reactions occur under non-thermal plasma, leading to valuable products such as
46 hydrocarbons [6] or oxygenates [11] but a poor selectivity towards the targeted products is often
47 referenced. A way to promote the efficiency of the process is to combine plasma with catalysis
48 [12]. However, some antagonist effects were reported. If the interaction between the gas
49 discharge and the surface of the catalyst may lead, in some cases, to significant improvement

50 when compared to pure plasma system [13], in other cases, lower performances were described.
51 For example, the presence of a reduced Ni/Al₂O₃ catalyst [14] or a zeolite A [15] in the plasma
52 discharge decreased CH₄ and CO₂ conversion. It was suggested that the insertion of a solid in
53 the plasma zone modifies significantly the propagation of the discharge. A shift of the discharge
54 mode from filamentary to a combination of surface discharges, in addition to spatially limited
55 micro-discharges at the contact point of the catalyst pellets were observed [16]. Moreover, the
56 presence of conductive Ni sites decreased the electric field strength and consequently the
57 electron density, reducing reactants conversion [17].

58 Looking at the catalyst grain size effect, the highest reaction conversions were reached when
59 using the smallest grain size, which was partly attributed to a maximum number of contact
60 points [18, 19]. The main conclusion deriving from the studies combining non-thermal plasma
61 and catalysis would suggest that the volume of gas in the plasma zone is too low to efficiently
62 perform the reactants activation.

63 The purpose of this paper is to examine the combination of plasma and catalysis in a fluidized
64 bed, considering that the contact between the external surface of grains and plasma discharge
65 can be improved when compared to a fixed bed reactor. Fluidized bed plasmas have been used
66 for pre-treatment of catalysts, under reduced pressure [20] and at atmospheric pressure [21-23]
67 for catalyst surface modification. Wang *et al.* [24] reported the dry reforming of methane in an
68 atmospheric pressure plasma fluidized bed with Ni/Al₂O₃. The authors investigated the reaction
69 at temperatures varying from 648 to 798 K and showed a clear positive effect of the plasma
70 fluidized bed compared to plasma packed bed. Currently, more insight on the understanding of
71 plasma - catalysis interactions in a fluidized bed is needed and particularly on the influence of
72 the materials textural properties on CH₄ and CO₂ reactivities. For that purpose, the study of a
73 series of alumina materials possessing surface areas from 65 m² g⁻¹ to 312 m² g⁻¹ was achieved
74 in this work. Alumina was chosen due to its low dielectric constant (9-30), favorable to plasma

75 –catalysis coupling [25]. Indeed, we show in a previous paper that CH₄ and CO₂ conversions
76 can be correlated with the dielectric constant of the material, the lower the dielectric constant,
77 the higher the conversions for both CO₂ and CH₄ [26].

78 The goals defined here are to determine the influence of 1- the type of reactor (fixed bed versus
79 fluidized bed) and 2- the textural and structural properties of alumina on the CH₄ and CO₂
80 reactivities.

81

82 **2 Experimental part**

83

84 **2.1 Experimental setup**

85 The reaction was performed at room temperature and atmospheric pressure under a mixture of
86 helium, methane and carbon dioxide at a total flow rate of 40 mL min⁻¹ using a CO₂/CH₄ ratio
87 of 2, with a constant concentration in He: 75%. All the experiments were performed twice with
88 a good accuracy of the measurements within an error of 5%.

89 The two plasma reactors are described below:

90 1) Fixed bed plasma: a coaxial dielectric barrier discharges (DBD) reactor (figure 1a). The
91 non-thermal plasma reactor (dielectric barrier discharge) consists in an alumina tube
92 (ID: 4mm; ED: 6mm), a stainless steel electrode centered inside the reactor (1.0mm)
93 and a copper electrode wrapped around the alumina tube (10 cm long). It corresponds
94 to a volume of plasma equal to 1.2 cm³.

95 2) Fluidized bed reactor (figure 1b): A fritted glass (2 mm) was inserted in a quartz tube to
96 support the sieved catalyst and favor the fluidization of the catalyst. The reactor
97 possesses an inner diameter of 9 mm and the inner electrode was 3.8 mm in diameter.
98 The external electrode length was chosen in order to obtain the same plasma volume
99 (1.2 cm³) as for the fixed bed reactor, so the length of the outer electrode was 2.2 cm.

100 The gas flow, sent from the bottom, was fixed at 40 mL min⁻¹. The catalyst grains
101 remained static on the fritted glass (figure 1b: without plasma). A point to be highlighted
102 is that, the minimum gas flow to reach fluidization is 300mL/min, corresponding to an
103 experimental minimum fluidization velocity of 0.23m.s⁻¹. The theoretical minimum
104 fluidization velocity was also calculated by the Ergun's equation [27] and the simplified
105 formula for Reynolds number proposed by Wen and Yu [28]. A value of $U_m = 0.29$
106 m.s⁻¹ was obtained, not too far from the experimental value.

107 As soon as the plasma discharge is generated into the reactor, at a low flow of 40
108 mL.min⁻¹, it is remarkable to observe that fluidization occurs, which can be explained
109 by the presence of electrostatic charges under plasma. The particles move into the
110 reactor with up/down and left/ right movements. (figure 1b: with plasma). Similar
111 observation was reported by Currier et al. using a radio-frequency generator at low
112 pressure (100-500 mTorr) [29]. The authors showed a much higher particle density
113 (SiO₂) in the plasma fluidized bed compared to the experiment without plasma at the
114 same gas-flow rate. They explained that it could result from the interaction of the highly
115 charged particles and the electric and magnetic fields and also to a significant change in
116 the physical properties of the fluidizing agent.

117 A sinusoidal supply of power was applied across the electrodes (TG1010A Aim-TTi, Thurlby
118 Thandar Instruments Brand). The discharge power, calculated from the Lissajous figures, was
119 fixed at 4 W, keeping the frequency constant at 800 Hz while the voltage was adjusted to keep
120 the deposited power constant. The electrical signals were monitored with high voltage probes
121 (PMK, model PHV4-2757) connected to an oscilloscope (waveRunner 62 Xi, Lecroy). A low
122 power was chosen in order to avoid a thermal effect, which could be caused by joule effect. In
123 that case, the reaction in the reactor remained close to room temperature.

124

125 **2.2 Gamma alumina**

126 A commercial γ -Al₂O₃ provided by Alfa Aesar was tested. The mesoporous alumina was
127 prepared according to the following procedure, inspired by Z-Y. Yuan et al. [30]: 20.5 g of
128 cetyltrimethylammonium bromide (CTMABr) (purity > 96 %, Sigma-Aldrich) were dissolved
129 in 93.93 g of deionized water. The suspension was stirred at 40 °C for about 1 h, before the
130 addition, under stirring, of 24.12 g of aluminium isopropoxide (Sigma-Aldrich). The resulting
131 sol was further matured under stirring for 3 h. It was then autoclaved under static conditions in
132 a polypropylene bottle at 80°C for 24h. The bottle was cooled to room temperature and the
133 suspension was filtered. The obtained paste was washed 3 times with 200 mL of water. The
134 washed paste was dried at 100 °C overnight. The solids were calcined at three different
135 temperatures: 400, 600 and 800 °C in order to vary the surface area as shown in table 1.

136 The solids were characterized before and after plasma treatments. Surface areas were measured
137 according to the BET procedure. The nitrogen adsorption-desorption isotherms were
138 determined with a Micromeritics Flowsorb II 2300 apparatus at -196°C. Thermogravimetric
139 analysis were performed with a TA Instruments SDT-Q600 analyzer under a 100 mL/min flow
140 of air up to 900°C.

141

142 **2.3 Gas phase analysis and calculation**

143 The gas phase was analyzed on-line by gas chromatography equipped with FID (oxygenated
144 products) and TCD detectors (hydrogen, carbon monoxide, carbon dioxide, methane). The
145 reaction was performed during one hour.

146 All the experiments were performed three times after cleaning the inner electrode and changing
147 the catalyst (when used), a margin error of ± 3 % was calculated.

148 The conversion, selectivity, yields and energy efficiency were defined as:

149 Conversion (%) of CH₄ and CO₂ = 100 × mole of CH₄ (or CO₂) converted/ mole of CH₄ (or
150 CO₂) in the feed (1)

151 The selectivity was calculated based on carbon atoms:

152 Selectivity to C_nH_y (%) = 100 × n × mole of C_nH_y / (mole of CH₄ converted + mole of CO₂
153 converted) (2)

154 Selectivity to CO (%) = 100 × mole of CO / (mole of CH₄ + mole of CO₂) converted

155 Yield in H₂ (%) = 100 × mole of H₂ / 2 x (mole of CH₄) introduced (3)

156 Carbon Balance: CB (%) = 100 × (mole of CO + ∑ n × mole of C_nH_y) / (mole of CH₄
157 converted + mole of CO₂ converted) (4)

158 Energy Efficiency: EE (mmol kJ⁻¹) = total mol of CH₄ + CO₂ converted (mmol min⁻¹) / input
159 power (kJ min⁻¹) (5)

160

161 3 Results and discussion

162 3.1 Influence of the geometry of the reactor on the plasma discharge

163 The geometry of the two reactors (fixed and fluidized bed) differs strongly since a larger gap is
164 required to obtain a fluidized bed and a quartz tube was used as dielectric material to visualize
165 the catalyst in motion. The first experiments were performed in presence of quartz wool in the
166 plasma zone, without catalyst. A constant flow rate of 40 mL min⁻¹ was kept through all the
167 experimentations with the same gas composition: He/CO₂/CH₄: 75/17/8%. The deposited
168 power was fixed at 4W.

169 The influence of the reactor geometry on the reactant conversion is a known effect, described
170 by different authors. It is admitted in the literature that, at constant input power, the larger the
171 electrode gap distance, the weaker the electric field strength [31], a lower reactant conversion
172 being thus expected. However, for the two reactors defined in this study, the results in terms of
173 CH₄ and CO₂ conversions, reported in fig. 2, show that methane conversions are similar, closed

174 to 9%, while CO₂ conversion in the fixed bed is slightly higher than in the fluidized bed reactor.
175 Such behavior is a consequence of two concomitant effects. First, the gap distance reduction,
176 which increases the plasma energy. The second effect results from the electrode length
177 modification. When the electrode length is increased, the plasma energy lost as heat increases.
178 Indeed, Nozaki et al. [32] showed that 60% of input power was dissipated as heat to the
179 dielectric barrier due to the formation of surface discharge in a DBD reactor fed with methane.
180 For this study, those two effects are counteracting each other, leading to similar methane
181 conversion despite the different gap distances. The higher conversion of CO₂ is followed by a
182 higher yield of CO, while the formation of hydrocarbons is not favored, due to a CO₂/CH₄ ratio
183 higher than unity. Under these experimental conditions, it appears that the residence time,
184 identical and close to 1.1 s for both reactors, is the key parameter on which depends the
185 conversions and this independently of the reactor geometry. The effect of residence time was
186 reported in different studies, at atmospheric pressure, increasing the residence time leads to an
187 increase of reactants conversions [33, 34], while in low pressure system, Uner and Thimsen
188 [35] showed little effect of residence time for CO₂ transformation due to fast reaction rate
189 (approximately 1000 times shorter than in atmospheric pressure DBD). The higher CO₂
190 conversion in the fixed reactor could be due to the presence of alumina as dielectric material.
191 Mora et al. [36] described a better performance for CO₂ hydrogenation with alumina instead of
192 quartz. This effect was attributed to the higher relative dielectric permittivity coefficient of
193 alumina compared to quartz. Additionally, in the dry reforming of methane, higher yield in CO
194 and higher energy efficiency were obtained by Khoja et al. [37] in an alumina reactor compared
195 to a quartz one, which is in agreement with this study.
196 In presence of a catalyst, the experimental conditions were significantly different for the two
197 reactors. About one gram of alumina powder was necessary to fill completely the plasma zone
198 of the fixed bed while 150 mg of material were required for the fluidized bed.

199 Lissajous figures of the discharge for the fixed and fluidized bed reactors packed with alumina
200 pellets (γ Al_2O_3 calcined at 400°C), for the same deposited power ($P=4\text{W}\pm 5\%$) are plotted in
201 Fig. 3. In the fluidized bed reactor, the catalyst does not occupy the entire plasma zone, it is
202 thus expected that filamentary microdischarges dominate while, for the fixed bed reactor, the
203 complete packing of the reactor with alumina pellets results in the combination of filamentary
204 and surface discharges. The breakdown of gas is expected to be lower in the presence of alumina
205 powder and the electric field should be more intense at the contact points between pellets [14].
206 As a result, the applied voltage differs strongly between the two reactors to keep a constant
207 power of 4 W. It is $\sim 10 \text{ kV}_{\text{pk-pk}}$ for the fixed bed and $\sim 30 \text{ kV}_{\text{pk-pk}}$ for the fluidized bed at
208 constant frequency, 800Hz (Table 2).

209

210 **3.2 Influence of the surface area of alumina**

211 3.2.1 Chemical and physical properties of alumina

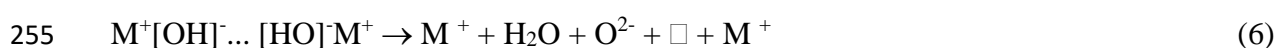
212 The alumina material was calcined at different temperatures from 400 to 800°C to vary the
213 specific surface area and porous volume. The values obtained are gathered in Table 1. Prior to
214 the reaction, all the solids were sieved in the range: 355 - $650 \mu\text{m}$ to eliminate the impact of the
215 grain size on the reactivity, as shown in previous studies [19].

216 The total equivalent capacitance of the DBD (C_{cell}) and the effective capacitance (C_{eff}),
217 corresponding to the capacitances in the plasma-off period and plasma-on period respectively,
218 were determined from the Lissajous figures with the different alumina materials (Table 2). The
219 value of C_{cell} is slightly higher for the fixed bed reactor compared to the fluidized bed,
220 whatever the Al_2O_3 material. The reactor capacitances were approximately the same with or
221 without material in the discharge zone, so the differences observed in C_{cell} values depend
222 mainly on the reactor geometry, the packing with alumina having no significant impact on

223 C_{cell}. The effective capacitances are strongly higher for the fixed bed than for the fluidized
224 bed, which can be explained by the expansion of the discharge across the gap [38].
225 Conversions of CH₄ and CO₂ are plotted as a function of the surface areas of alumina in figure
226 4. The data were collected after 30 minutes on stream since no significant modification of
227 reactants transformation was observed within one hour under plasma. A different trend,
228 occurring between the two reactors, was noticed. As soon as the surface area of alumina
229 increases, CH₄ and CO₂ conversion decrease in the fixed bed reactor, while a significant
230 increase for both CH₄ and CO₂ conversion is observed in the fluidized bed reactor. It is the first
231 time, to our knowledge, that the influence of a material surface area is evidenced in the plasma-
232 catalysis coupling. The results show undoubtedly that the combination of plasma and catalysis
233 in a fluidized bed reactor can be efficient for methane and carbon dioxide conversion. Despite
234 predominant gas phase reactions, these results highlight the importance of the surface reactivity
235 of the material. No improvement is observed comparing the commercial γ -Al₂O₃ (S= 65 m² g⁻¹)
236 ¹) to the material prepared in the laboratory (S= 260 m² g⁻¹). Differences in the synthesis
237 procedure, which would induce different surface properties in terms of number of surface -OH
238 groups per surface unit, would explain this result.

239 It is expected that in the fixed bed reactor, the reaction proceeds mainly at the contact point of
240 the catalyst where the electric field is stronger but in a very limited reactional volume.
241 Consequently, the porosity of the oxide is rapidly blocked by the deposition of heavy products
242 such as C₃ aldehydes and C₅ ketones, detected after reaction by pyrolysis coupled with mass
243 spectrometry. In a fixed bed reactor, the decrease of CH₄ and CO₂ conversions using porous
244 materials such as zeolite was reported by Jiang et al. [39]. Inversely, in the fluidized bed reactor,
245 the reaction can proceed on the overall surface of the moving catalyst grains in the plasma zone,
246 thus favoring CH₄ and CO₂ conversions. This results in an increase of the analyzed products:
247 CO, H₂ and hydrocarbons (mainly C₂H₆) as shown in figure 5.

248 A mechanism can be proposed for plasma- γ -Al₂O₃ assisted reaction according to the results we
 249 obtained and based on the published paper of N.N. Gadzhieva [40] and Liu et al. [41], and is
 250 presented in figure 6. This reaction cannot be dissociated from reaction in homogeneous phase.
 251 The dissociative adsorption of CH₄ at the surface of alumina is expected to proceed under
 252 plasma, which depends on the concentration of surface OH groups. Since Alumina is a material
 253 with a strong dipolar character, it contains numerous OH groups and becomes easily charged
 254 [35]. Reactions at the surface of Al₂O₃ could be written according to Eqs. (6) - (9):



259 With \square being an active site

260 The energy Efficiency (EE) is the highest using the fluidized bed reactor with the alumina
 261 possessing the highest surface area (Fig. 7). The trend of the energy efficiency is similar to the
 262 reactant conversions one, which is coherent since the reactions were performed at the same
 263 specific input energy (6 kJ L⁻¹) and both CH₄ and CO₂ conversions were favored using a
 264 fluidized bed reactor. The energy efficiencies were 0.07 and 0.14 mmol kJ⁻¹ for the fixed bed
 265 and fluidized bed, respectively.

266

267 3.2.2 Structural and textural characterization of alumina materials before and after reaction 268 under plasma

269 TGA analysis of the Al₂O₃ materials were performed after one hour of reaction under plasma
 270 for both reactors (Fig. 8). A continuous weight loss proceeds from low temperatures (T<100°C)
 271 to 600°C. It comes from the desorption of products, which were condensed into the porosity of
 272 alumina during the reaction under plasma. The yellowish color of the plasma treated samples

273 confirms the presence of organic compounds at the surface of alumina, except for the
274 commercial Al_2O_3 (surface area $65 \text{ m}^2 \text{ g}^{-1}$) after treatment in the fixed bed reactor. Moreover
275 the presence of carbon deposit by methane cracking under plasma cannot be excluded, it would
276 be removed at the highest temperature. The total weight loss is particularly significant (closed
277 to 20%) for the alumina with the highest surface areas (301 and $312 \text{ m}^2 \text{ g}^{-1}$) with the fluidized
278 bed. It is in accordance with the carbon balance (Fig. 5d), which is the lowest for alumina with
279 the highest surface area. The adsorption of heavy compounds at the surface of alumina would
280 depend on the accessible surface. Indeed, it is expected that these products, formed in the
281 plasma gas phase, are deposited in the porosity of alumina. However this effect depends on the
282 catalyst pore size. According to Bogaerts et al. [42, 43], from a modeling investigation, plasma
283 can only penetrate in pores larger than 50 nm and the alumina synthesized in this study possess
284 pores from 4 to 8 nm (Table 1). Considering that their calculations were based on a glow mode,
285 which differs strongly from the DBD plasma used in the present work, it would explain our
286 results. In fact, when comparing the two reactors, no significant differences in terms of weight
287 loss are observed for the alumina $\gamma\text{Al}_2\text{O}_3\text{-600}$ and $\gamma\text{Al}_2\text{O}_3\text{-800}$ while significant differences are
288 obtained for $\gamma\text{Al}_2\text{O}_3\text{-400}$ and particularly for the commercial $\gamma\text{Al}_2\text{O}_3$. If we consider that the
289 surface reaction proceeds only at contact point of grains in the fixed bed reactor, the low weight
290 loss is due to the low accessible surface for products deposition. Contrarily, as soon as the
291 alumina particles are fluidized, the product condensation proceeds on the entire accessible
292 surface and possibly into the porosity of the commercial alumina which is significantly larger
293 than the porosity of alumina synthesized in the laboratory.

294 The measurement of surface area after reaction (Table 1) reveals a significant loss for the meso-
295 macro alumina materials synthesized in the laboratory, which is more intense for the fluidized
296 bed than for the fixed bed. The exposition of the entire surface area of the material in the
297 fluidized bed reactor, while localized at the contact point in the fixed bed reactor, would explain

298 these observations. Note that the value of pore size after reaction do not take into account
299 organic compounds adsorbed during reaction, since the measurements require a thermal
300 treatment under reduce pressure, leading to products elimination.

301

302 **4. Conclusion**

303 The transformation of a mixture of methane and carbon dioxide under plasma discharge in the
304 presence of alumina was investigated in fluidized and static bed reactors.

305 Methane and carbon dioxide conversions depend on the surface area, a significant increase
306 being obtained with alumina of large surface area in the fluidized bed reactor. CH₄ conversion
307 increases from 8.5 to 12.1 % for S=260 and 312 m² g⁻¹, respectively and the CO₂ conversion
308 from 3.4 to 6.2 % for a deposited power of 4 W, in an excess of CO₂. An opposite trend is
309 obtained between fluidized and fixed bed reactors. This effect is to the limited accessible
310 catalyst surface in the fixed bed, at the contact point of grains, were the electric field is the most
311 intense. In the fluidized bed, the overall grain surface is involved in the plasma-catalytic
312 reaction and higher conversions to products such as CO and ethane are obtained. Reactions at
313 the surface of Al₂O₃ under plasma discharge are proposed. Condensation of organic products
314 into the porosity of alumina was evidenced whatever the surface area of alumina. The
315 deposition of organic products is favored in the alumina of largest porosity (23 nm), in fluidized
316 mode. The stacking of grains in the fixed bed mode limits this effect.

317 To conclude the use of a plasma fluidized bed might be considered as an attractive process to
318 enhance performances of plasma-catalysis coupling. It opens new routes for the investigation
319 of a wide variety of reactions thermodynamically unfavorable.

320

321 **Acknowledgements**

322 The authors grateful acknowledge the ANR for the financial support of the PRC program
323 VALCO2PLAS and the financial support from the European Union (ERDF) and "Région
324 Nouvelle Aquitaine".

325

326

327 **References**

328 [1] E. Ruckenstein, H.Y. Wang, *J. Catal.* 205 (2002) 289-293

329 [2] M. Usman, W.M.A. Wan Daud, H. F. Abbas, *Renew. Sust. Energy Rev.* 45 (2015) 710-
330 744

331 [3] A.J. Zhang, A.M. Zhu, J. Guo, Y. Xu, C. Shi, *Chem. Eng. J.* 156 (2010) 601–606

332 [4] M. Kraus, W. Egli, K. Haffner, B. Eliasson, U. Kogelschatz, A. Wokaun, *Phys. Chem.*
333 *Chem. Phys.* 4 (2002) 668–675

334 [5] X. Tao, M. Bai, X. Li, H. Long, S. Shang, Y. Yin, X. Dai, *Prog. Energy Combust. Sci.*
335 37 (2011) 113–124

336 [6] B. Wang B, G. Xu (2003) *J Nat Gas Chem* 12 (2003) 178–182

337 [7] B. Fidalgo, J.A. Menéndez, *Fuel processing technology*, 95 (2012) 55-61

338 [8] X. Tu, J.C. Whitehead, *Int. J. Hydrogen Energy*, 39 (2014) 9658-9669

339 [9] N. Rueangjitt, T. Sreethawong, S. Chavadej, H. Sekiguchic, *Chem. Eng. J.* 155 (2009)
340 874-880

341 [10] M. Kraus, B. Eliasson, U. Kogelschatz, A. Wokaun, *Phys. Chem.Chem. Phys.* 3 (2001)
342 294-300

343 [11] B. Eliasson W. Egli, U. Kogelschatz *Pure Appl Chem* 66(6) (1994) 1275–1286

344 [12] H. Puliyalil, D.L. Jurkovic, V.D. Dasireddy, B. Likozar, *RSC Adv.* 8 (2018) 27481-
345 27508

346 [13] E.C. Neyts, K. Ostrikov, M. K. Sunkara, A. Bogaerts, *Chem. Rev.* 115 (2015) 13408-
347 13446

- 348 [14] X. Tu, H.J. Gallon, M. V. Twigg, P. A. Gorry, J.C. Whitehead, *J.Phys. D: Appl. Phys.* 44
349 (2011) 274007-274017
- 350 [15] T. Jiang, Y. Li, C.J. Liu, G.H. Xu, B. Eliasson, B. Xue, *Catal. Today*, 72 (2002) 229-235
- 351 [16] H.J. Gallon, X. Tu, J.C. Whitehead, *Plasma Process and Polymer*, 9 (2012) 90-97
- 352 [17] X. Tu, H.J. Gallon, M. V. Twigg, P. A. Gorry, J.C. Whitehead, *J.Phys. D: Appl. Phys.* 44
353 (2011) 274007-274017
- 354 [18] P. Kasinathan, S. Park, W.C. Choi, Y.K. Hwang, J.S. Chang, Y.K. Park, *Plasma Chem.*
355 *Plasma process.* 34 (2014) 1317-1330
- 356 [19] N. Bouchoul, J.M. Tatibouët, E. Fourré, C. Batiot-Dupeyrat, *Plasma Chem. and Plasma*
357 *Process.*, 39 (2019) 713-727
- 358 [20] R. Bartolomeu, M. Foix, A. Fernandes, M. Tatoulian, M.F. Ribeiro, C. Henriques, P. da
359 Costa, *Catal. Today*, 176 (2011) 234-238
- 360 [21] G. Hee Kim, S. D. Kim, S. H. Park, *Chem. Eng. Process.* 48 (2009) 1135-1139
- 361 [22] G. Chen, S. Chen, M. Zhou, W. Feng, W. Gu, S. Yang, *J. Phys. D: Appl. Phys.* 39 (2006)
362 5211-5215
- 363 [23] G. Chen, S. Chen, W. Feng, W. Chen, S. Yang, *Appl. Surf. Sci.* 254 (2008) 3915-3920
- 364 [24] Q. Wang, Y. Cheng, Y. Jin, *Catal. Today*, 148 (2009) 275-282
- 365 [25] W. Wang, H.H. Kim, K. Van Laer, A. Bogaerts, *Chem. Eng. J.* 334 (2018) 2467-2479
- 366 [26] N. Bouchoul, E. Fourré, A. Duarte, N. Tanchoux, C. Louste, C. Batiot-Dupeyrat, *Catal.*
367 *Today*, in press 2020, doi.org/10.1016/j.cattod.2020.06.058
- 368 [27] S. Ergun, *Chem. Engrg. Progress*, 48, No. 2, (1952) 89-94
- 369 [28] Wen, C. Y. and Yu, Y. H., *Chem. Engrg. Progress Symp. Series*, Vol. 62 (1966) 100-111
- 370 [29] R.P. Currier, M. Trkula, H.R. Snyder, *The plasma fluidized bed, a report*,
371 DOI:10.2172/758321
- 372 [30] Z-Y. Yuan, T-Z. Ren, A. Vantomme, B-L. Su, *Chem. Mater* 16 (2004) 5096-5106

- 373 [31] N. Rueangjitt, T. Sreethawong, S. Chavadej, H. Sekiguchi, Plasma Chem. Plasma
374 Process (2011) 31, 517-534
- 375 [32] Nozaki T, Miyazaki Y, Unno Y and Okazaki K. (2001) Journal of Physics D: Applied
376 Physics 34, 3383-90
- 377 [33] V. Goujard, J.M. Tatibouët, C. Batiot-Dupeyrat, Appl. Catal. A : Gen, 353 (2009) 228-
378 235
- 379 [34] J. Sentek, K. Krawczyk, M. Mlotek, M. Kalczwska, T. Kroker, T. Kolb, A. Schenk, K.H.
380 Gericke, K. S. Szalowski, Appl. Catal. B: Env. 94 (2010) 19-26
- 381 [35] N.B. Uner, E. Thimsem, Aiche J. 2020,;66e16948
- 382 [36] E.Y. Mora, A. Sarmiento, E. Vera, J. Phys.: Conf. series 687 (2016) 012020
- 383 [37] A. H. Khoja, M. Tahir, N. A. S. Amin, Energy Conv. And Management, 144 (2017) 262-
384 274
- 385 [38] S. Jo, D. H. Lee, W. S. Kang, Y.H. Song, Physics of plasmas, 20 (2013)123507
- 386 [39] Y. Jiang, Y. Li, C.J. Liu, G.H. Xu, B. Eliasson, B. Xue, Catal Today 72 (2002) 229–235
- 387 [40] N.N. Gadzhieva, High Energy Chemistry, 37 (2003) 38-43
- 388 [41] C. Liu, A. Marafee, R. Mallinson, L. Lobban, Appl. Catal. A: gen 164 (1997) 21-33
- 389 [42] Y.R. Zhang, K.Van Laer, E. C. Neyts, A. Bogaerts, Appl. Catal. B: Env 185 (2016) 56-
390 67
- 391 [43] Q.Z. Zhang, A. Bogaerts, Plasma Sources Sci. Technol. 27 (2018) 35009-35019

Table 1: Properties of the gamma alumina: surface area and pore volume before and after reaction under plasma (1 hour, grain size: 355-650 μm , P=4 W, total flow: 40 mL min^{-1} , $\text{CO}_2/\text{CH}_4=2$, He: 75%)

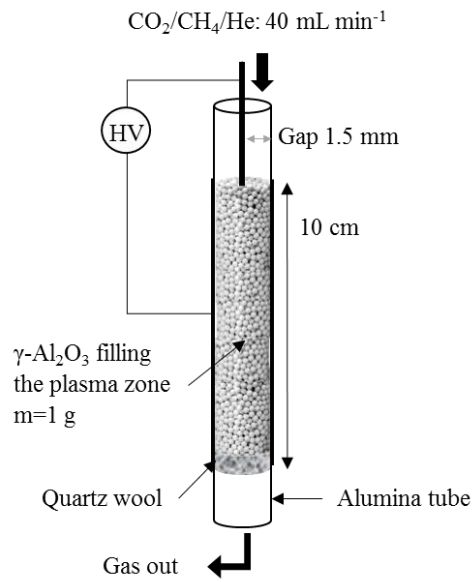
Oxide	S BET ($\text{m}^2 \text{g}^{-1}$)			Pore size (\AA)		
	Before plasma	After plasma		Before plasma	After plasma	
		Fixed bed	Fluidized bed		Fixed bed	Fluidized bed
$\gamma\text{Al}_2\text{O}_3\text{-AA}$	65	64	64	230	230	230
$\gamma\text{Al}_2\text{O}_3\text{-400}$	312	305	298	64	64	64
$\gamma\text{Al}_2\text{O}_3\text{-600}$	301	282	275	76	75	76
$\gamma\text{Al}_2\text{O}_3\text{-800}$	260	183	165	41	42	41

Table 2: Characteristics of the discharge for the two plasma reactors: fixed and fluidized bed at a constant deposited power: P=4 W, grain size: 355-650 μm , total flow: 40 mL min^{-1} , $\text{CO}_2/\text{CH}_4=2$, He: 75%

Catalyst bed	U peak-peak (kV)		C_cell (pF)		C_eff (pF)	
	Fixed	Fluidized	Fixed	Fluidized	Fixed	Fluidized
$\gamma\text{Al}_2\text{O}_3\text{-AA}$	10.4	30.5	1.3	0.9	32.9	3.9
$\gamma\text{Al}_2\text{O}_3\text{-400}$	10.2	30.8	1.2	0.8	33.7	3.7
$\gamma\text{Al}_2\text{O}_3\text{-600}$	10.2	30.6	1.4	1.0	32.7	4.1
$\gamma\text{Al}_2\text{O}_3\text{-800}$	10.5	30.4	1.6	0.9	31.2	3.8

Figure 1: Reactor scheme a) Fixed bed reactor, b) fluidized bed reactor

a)



b)

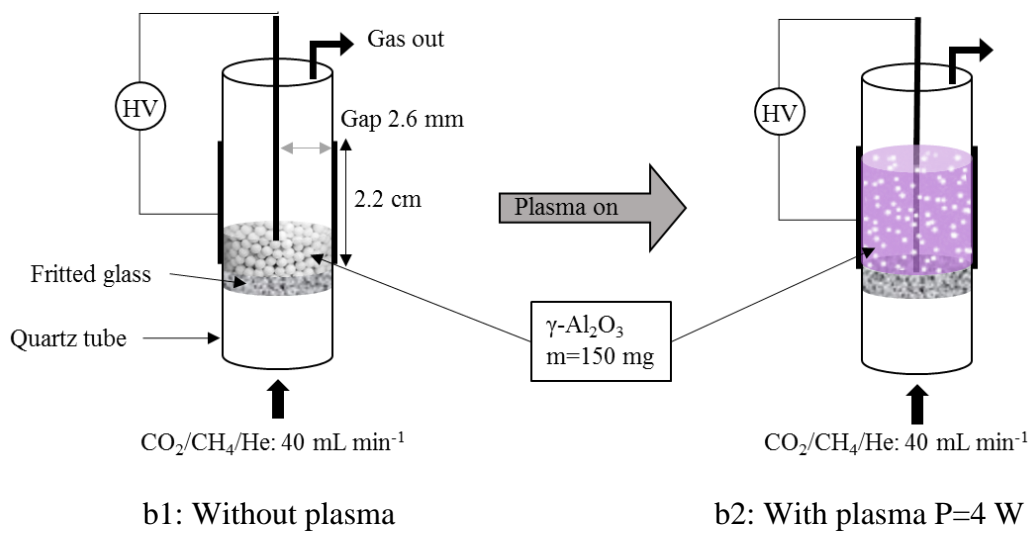


Figure 2: CO₂ and CH₄ conversion, yield into CO, H₂ and hydrocarbons (mainly C₂H₆): influence of reactor geometry. P=4 W, total flow: 40 mL min⁻¹, CO₂/CH₄=2, He: 75% (data after 30 minutes on stream) ■ fluidized bed, □ fixed bed

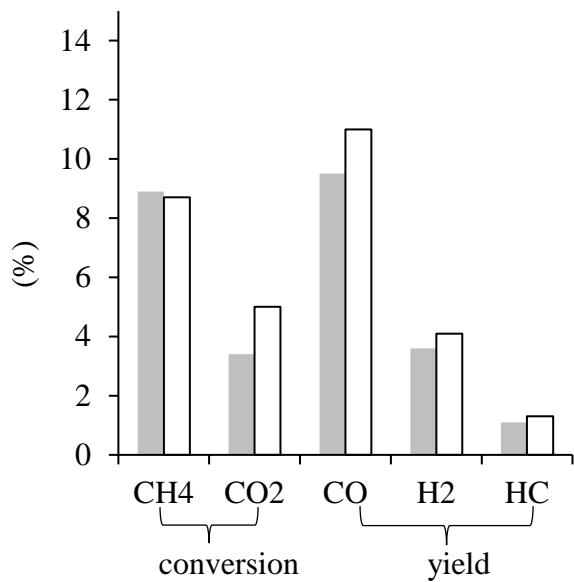
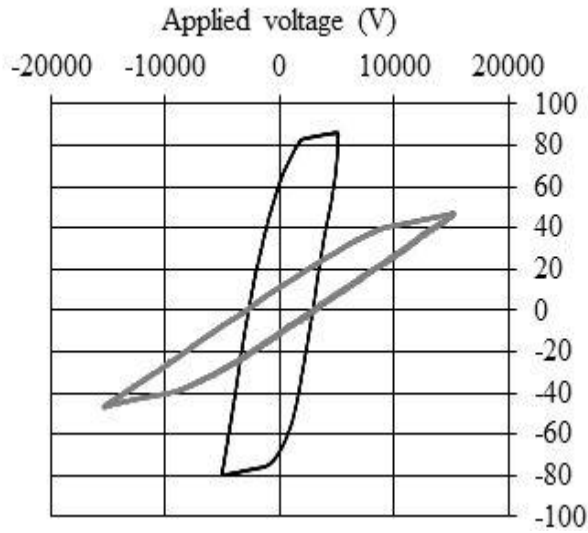


Figure 3: a) Lissajous figures of the CO₂/CH₄ DBD with alumina pellets for the fixed bed and fluidized bed reactor at a constant discharge power of 4 W (total flow: 40 mL min⁻¹, CO₂/CH₄=2, He: 75%), b) typical Lissajous figures, determination of C_{cell} and C_{eff}

a)



b)

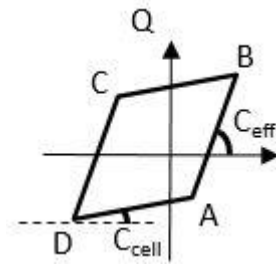


Figure 4: CO₂ and CH₄ conversion over gamma alumina: influence of surface area and reactor geometry. Grain size: 355-650 μm, P=4 W, total flow: 40 mL min⁻¹, CO₂/CH₄=2, He: 75% (data after 30 minutes on stream) —× fluidized bed, —+ fixed bed

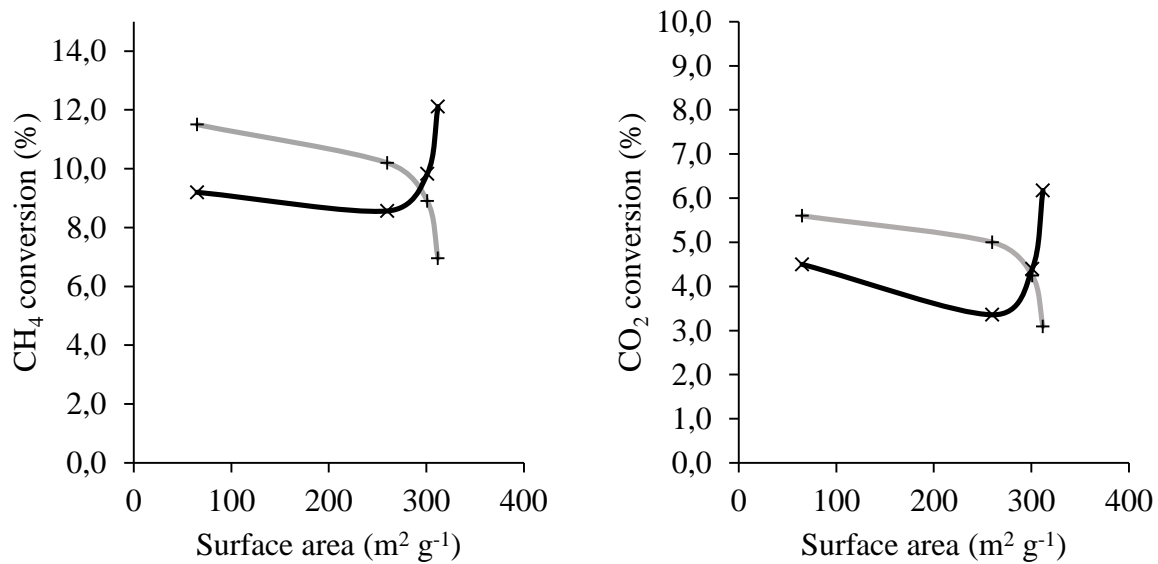


Figure 5: CO, H₂, hydrocarbon yield and carbon balance over gamma alumina: influence of surface area and reactor geometry. Grain size: 355-650 μm, P=4 W, total flow: 40 mL min⁻¹, CO₂/CH₄=2, He: 75%, (data after 30 minutes on stream) × fluidized bed, + fixed bed

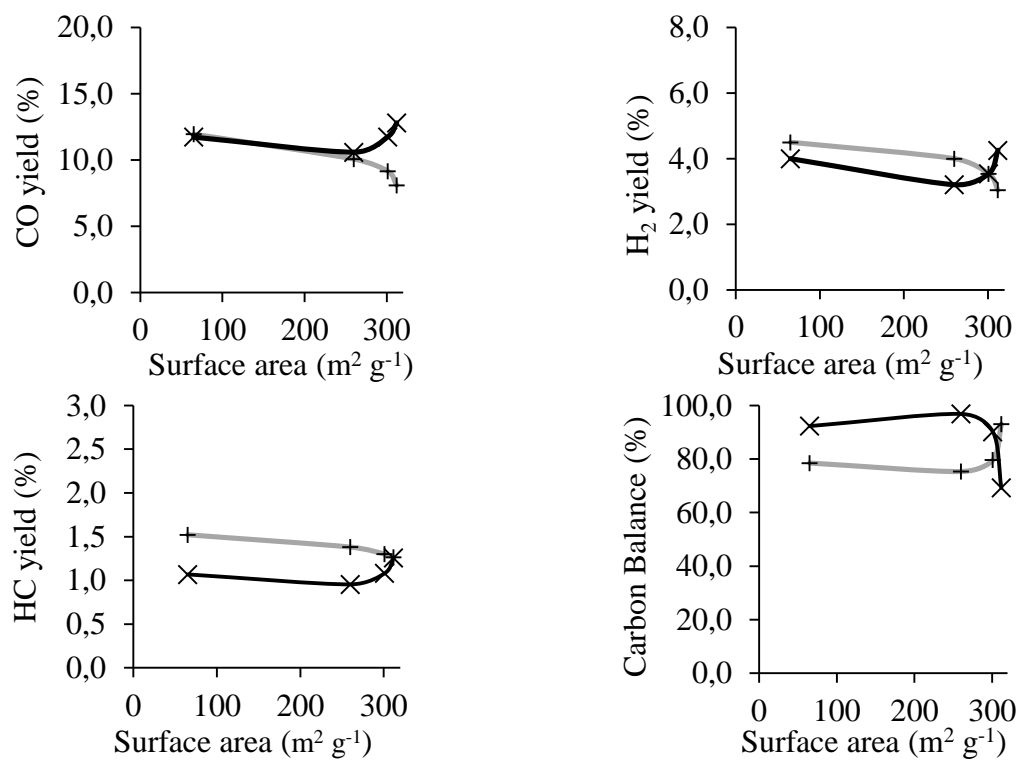


Figure 6: Schematic illustration of plasma discharge and reaction at the surface of $\gamma\text{-Al}_2\text{O}_3$ in fixed bed and fluidized bed reactor (not to scale)

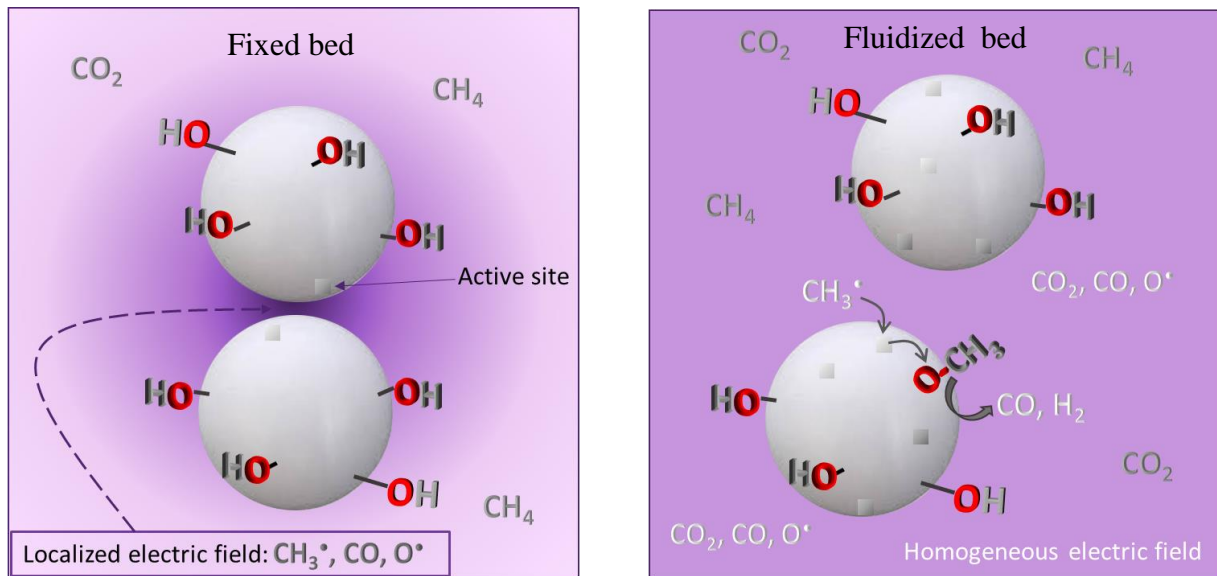


Figure 7: Effect of surface area of gamma alumina on Energy Efficiency for the two reactors geometry. Grain size: 355-650 μm , $P=4\text{ W}$, total flow: 40 mL min^{-1} , $\text{CO}_2/\text{CH}_4=2$, He: 75%, (data after 30 minutes on stream) \times fluidized bed, $+$ fixed bed

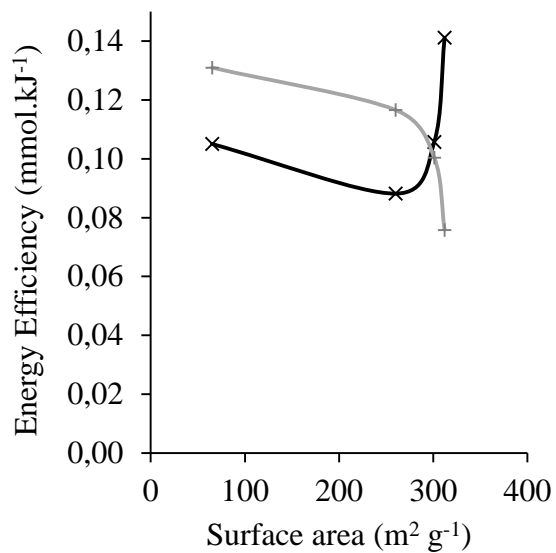


Figure 8: TGA analysis of alumina calcined at different temperatures, after reaction under plasma (60 minutes), grain size: 355-650 μm , P=4 W, total flow: 40 mL min^{-1} , $\text{CO}_2/\text{CH}_4=2$, He: 75%, — fixed bed reactor, — fluidized bed reactor

