

1 ((please add journal code and manuscript number, e.g., DOI: 10.1002/ppap.201100001))

2 **Article type: Full paper**

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4 **Optimization of CO₂ conversion in a cylindrical dielectric barrier discharge**
5 **reactor using design of experiments**

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37 **Abstract**

38 In this work, a coaxial dielectric barrier discharge reactor has been developed for the
39 decomposition of CO₂ at atmospheric pressure. The response surface methodology based on a
40 three-factor, three-level Box-Behnken design has been developed to investigate the effects of
41 key independent process parameters (discharge power, feed flow rate and discharge length)
42 and their interactions on the reaction performance in terms of CO₂ conversion and the energy
43 efficiency of the plasma process. Two quadratic polynomial regression models have been
44 established to understand the relationships between the plasma process parameters and the
45 performance of the CO₂ conversion process. The results indicate that the discharge power is
46 the most important factor affecting CO₂ conversion, while the feed flow rate has the most
47 significant impact on the energy efficiency of the process. The interactions between different
48 plasma process parameters have a very weak effect on the conversion of CO₂. However, the
49 interactions of the discharge length with either discharge power or gas flow rate have a
50 significant effect on the energy efficiency of the plasma process. The optimal process
51 performance - CO₂ conversion (14.3%) and energy efficiency (8.0%) for the plasma CO₂
52 conversion process is achieved at a discharge power of 15.8 W, a feed flow rate of 41.9
53 ml min⁻¹ and a discharge length of 150 mm as the highest global desirability of 0.816 is
54 obtained at these conditions. The reproducibility of the experimental results successfully
55 demonstrates the feasibility and reliability of the design of experiments approach for the
56 optimization of the plasma CO₂ conversion process.

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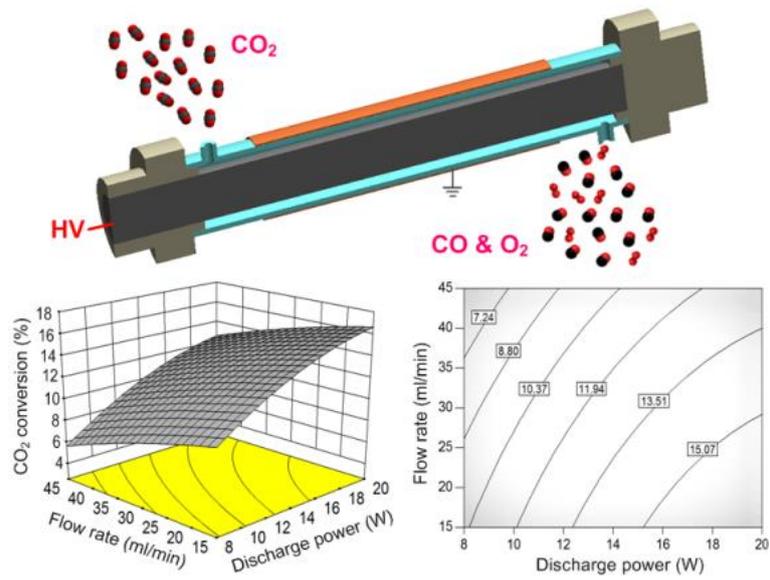
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Graphic for the abstract



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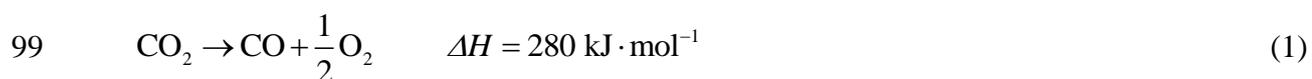
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82 **1. Introduction**

83 The increasing energy demand of the growing population has led to the rapid consumption of
84 fossil fuels, inevitably releasing carbon dioxide (CO₂) which is a prime contributor to global
85 warming and climate change. For instance, the UK emits more than 470 million tons of CO₂
86 per year and of this 39 % is emitted by the energy and chemistry sectors.^[1] The UK
87 government has committed to reduce greenhouse gas emissions by at least 80% (from the
88 1990 baseline) by 2050.^[2] Significant efforts have been devoted to develop innovative and
89 cost-effective technologies to deal with the global challenge of CO₂ emissions. One promising
90 solution is to use wasteful CO₂ emissions as feedstock for the production of value-added fuels
91 and chemicals (e.g. CO, CH₄ and methanol). For instance, direct conversion of CO₂ into CO
92 is an interesting chemical process, as CO is a useful chemical feedstock and can be used as a
93 reactant to produce higher energy products such as hydrocarbons and liquid fuels. This will
94 ultimately not only make full use of CO₂, but will also minimize the negative environment
95 impacts due to carbon emissions. However, it is very challenging to convert CO₂ in an
96 energy-efficient and cost-effective way due to the high stability of CO₂ molecules. A large
97 amount of energy is required for thermal or catalytic decomposition of CO₂ into CO as it is an
98 endothermic reaction due to the positive reaction enthalpy change ΔH as shown in Equation 1.



100 Extensive efforts have been made to convert CO₂ with or without hydrogen into higher
101 value fuels and chemicals using photochemical and electrochemical catalytic reactions.^[3, 4]
102 Despite their great potential, significant fundamental work is still required to further improve
103 the overall energy efficiency and product selectivity of the processes by developing new
104 reactor systems and novel catalytic materials with higher reactivity and stability, especially
105 the generation of cost-effective renewable hydrogen.

106 Non-thermal plasma technology has been regarded as a promising alternative to the thermal
107 catalytic route for converting low value and inert carbon emissions, such as CH₄ and CO₂,
108 into value-added fuels and chemicals at atmospheric pressure due to its non-equilibrium
109 characteristic, low energy cost and unique capability to induce both physical and chemical
110 reactions at ambient conditions.^[5-7] In non-thermal plasmas, the overall plasma gas
111 temperature can be as low as room temperature, while the electrons are highly energetic with
112 an average electron energy of 1-10 eV which can easily break down most chemical bonds of
113 inert molecules and produce chemically reactive species such as radicals, excited atoms,
114 molecules and ions for chemical reactions. The non-equilibrium character of such plasmas
115 could enable thermodynamically unfavourable reactions (e.g. CO₂ splitting) to occur at low
116 temperatures (e.g. <200 °C). Up to now, different plasma sources have been used for CO₂
117 conversion, including dielectric barrier discharge (DBD),^[8-16] corona discharge,^[17-19] glow
118 discharge,^[20, 21] microwave discharge,^[22-24] radio frequency discharge,^[25, 26] and gliding arc
119 discharge.^[27, 28] However, previous works mainly focused on the plasma conversion of CO₂
120 diluted with high volumes of inert gases such as helium and argon,^[11, 29, 30] which are not
121 favourable for industry applications due to the cost of these gases, especially helium, while
122 direct conversion of pure CO₂ into value-added chemicals could be valuable if integrated with
123 carbon capture or bio-oil upgrading processes. Plasma conversion of CO₂ is a complex and
124 challenging process involving a large number of physical and chemical reactions. The
125 reaction performance (CO₂ conversion and energy efficiency) of the process is totally
126 controlled by a wide range of plasma process parameters such as the discharge power, gas
127 flow rate, gas residence time, reactor configuration and frequency.^[31] It is often of primary
128 interest to explore the relationships between these key independent input variables and the
129 output performance characteristics of the plasma process.

130 Standard experiments are designed to look at one of these parameters in isolation from the
131 others and so screening a large number of process parameters is time-consuming and costly

132 due to large numbers of experiments which need to be performed. This type of
133 experimentation requires large quantities of resources to obtain a limited amount of
134 information about the process. A fundamental understanding of the importance of different
135 process parameters, especially the combined effects of these parameters on the performance
136 of plasma processing of CO₂, is very limited and not clear, which makes it difficult to
137 determine the set of operating parameters that will optimize and maximize the performance of
138 the plasma process. Plasma chemical modelling offers an alternative route for solving this
139 problem. De Bie et al. developed a one-dimensional (1D) fluid model to investigate the effect
140 of different plasma process conditions on the plasma decomposition of CH₄ in a DBD
141 reactor.^[32] The model consisted of 36 species (electrons, atoms, ions, molecules) and 367 gas
142 phase reactions. This model was recently extended to simulate plasma methane conversion in
143 CH₄/CO₂ and CH₄/O₂ mixtures.^[33] Snoeckx et al. developed a zero-dimensional (0D) kinetics
144 model to understand the influence of different operating parameters (gas mixture ratio,
145 discharge power, residence time and frequency) on the conversion and energy efficiency of
146 plasma dry reforming of CO₂ and CH₄ in a similar DBD reactor, and to investigate which of
147 these parameters lead to the most promising results.^[31, 34] However, although model
148 calculations can be fast, depending on the type of model, the development of a comprehensive
149 model takes time and is thus not always useful for fast and cost-effective optimization of
150 highly complex plasma chemical processes.

151 Design of experiments (DoE) is a powerful tool for process optimization since it allows
152 multiple input factors to be manipulated, determining their individual and combined effects on
153 the process performance in the form of one or more output responses, whilst significantly
154 reducing the number of experiments compared to conventional experiments with one factor at
155 a time.^[35] Response surface methodology (RSM) is one of the most useful experimental
156 designing methodologies for building the relationship between the multiple input parameters
157 and output responses, which enable us to get a better understanding of the effect of individual

158 factors and their interactions on the responses by three-dimensional and contour
159 interpretations. Two design approaches, central composite design (CCD) and Box-Behnken
160 design (BBD), have been commonly used in response surface methodology.^[36] It has been
161 demonstrated that BBD is more efficient than CCD for a three-factor and three-level design
162 since fewer experiments are required using the BBD approach.^[37, 38] Until now, there has been
163 only very limited work focussing on the optimization of plasma processing of materials using
164 the DoE method,^[37, 39] while the use of DoE for quick optimization of plasma chemical
165 reactions, such as CO₂ conversion and utilization, has not been done before.

166 In this study, a coaxial DBD reactor has been developed for the conversion of pure CO₂
167 into CO and O₂ at atmospheric pressure. Response surface methodology based on Box-
168 Behnken design has been used to establish the relationship between the key plasma process
169 parameters and the process performance, and to optimize the performance of the plasma
170 processing of CO₂ in terms of CO₂ conversion and energy efficiency. Moreover, the influence
171 of different process parameters and their interactions on the reaction performance has been
172 investigated and discussed.

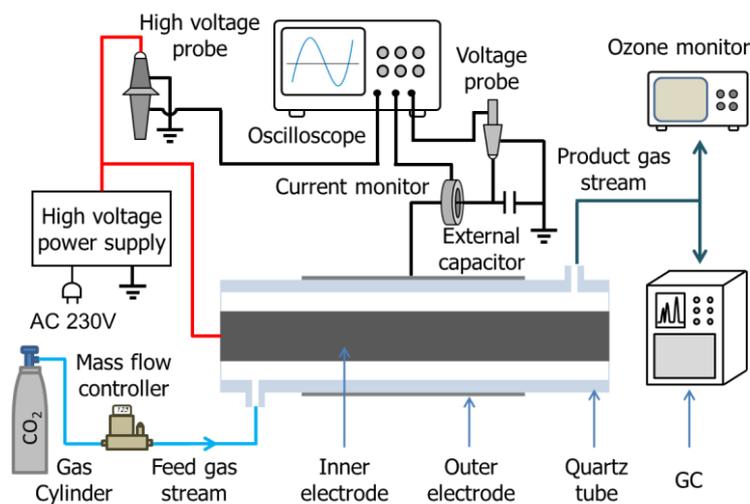
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174 **2. Experimental**

175 **2.1 Experimental setup**

176 The experiment was carried out in a coaxial DBD reactor, as shown in Figure 1. An
177 aluminium foil wrapped around the outside of a quartz tube, with an external diameter of 22
178 mm and an inner diameter of 19 mm, acted as a ground electrode. A stainless steel rod with an
179 outer diameter of 14 mm was placed in the centre of the quartz tube and used as a high
180 voltage electrode. The length of the discharge region could be varied from 90 to 150 mm with
181 a discharge gap fixed at 2.5 mm. Pure CO₂ was used as the feed gas with a gas flow rate of
182 15-45 ml·min⁻¹. The DBD reactor was supplied by a high voltage AC power supply with a
183 peak-to-peak voltage of 10 kV and a frequency of 50 Hz. The applied voltage was measured

184 by a high voltage probe (Testec, HVP-15HF), whilst the current was recorded by a current
 185 monitor (Bergoz CT-E0.5). The voltage across the external capacitor (0.47 μF) was measured
 186 to determine the charge passing through the DBD. All the electrical signals were sampled by a
 187 four-channel digital oscilloscope (TDS2014). The $Q-U$ Lissajous method was used to
 188 calculate the discharge power (P) of the DBD reactor. A homemade online power
 189 measurement system was used to monitor and control the discharge power in real time.



190
 191 *Figure 1.* Schematic diagram of the experimental setup.

193 2.2 Product Analysis

194 The reactant and gas products were analyzed by a gas chromatograph (Shimadzu GC-2014)
 195 equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD).
 196 The concentration of ozone was measured by an ozone monitor (2B, Model 106-M). However,
 197 no ozone was detected in the effluent in this study. Each measurement was repeated three
 198 times and had a high reproducibility with a measurement error of less than 5%. The
 199 conversion of CO_2 (C), the selectivity towards CO (S) and the carbon balance (B) are defined
 200 as follows:

$$201 \quad C_{\text{CO}_2} (\%) = \frac{\text{CO}_2 \text{ converted } (\text{mol} \cdot \text{s}^{-1})}{\text{CO}_2 \text{ introduced } (\text{mol} \cdot \text{s}^{-1})} \times 100 \quad (2)$$

$$S_{\text{CO}} (\%) = \frac{\text{CO produced (mol} \cdot \text{s}^{-1})}{\text{CO}_2 \text{ converted (mol} \cdot \text{s}^{-1})} \times 100 \quad (3)$$

$$B_{\text{Carbon}} (\%) = \frac{[\text{CO}_2]_{\text{out}} + [\text{CO}]_{\text{out}}}{[\text{CO}_2]_{\text{in}}} \times 100 \quad (4)$$

The energy efficiency (E) and the specific energy density (SED) are determined from

$$E (\text{mmol} \cdot \text{J}^{-1}) = \frac{\text{CO}_2 \text{ converted (mol} \cdot \text{s}^{-1})}{\text{Discharge power (kW)}} \quad (5)$$

$$E (\%) = \frac{\text{CO}_2 \text{ converted (mol} \cdot \text{s}^{-1}) \cdot \Delta H (\text{kJ} \cdot \text{mol}^{-1})}{\text{Discharge power (kW)}} \times 100 \quad (6)$$

$$\text{SED} (\text{kJ} \cdot \text{l}^{-1}) = \frac{\text{Discharge power (W)}}{\text{CO}_2 \text{ flow rate (ml} \cdot \text{s}^{-1})} \quad (7)$$

where ΔH is the reaction enthalpy for CO_2 decomposition (shown in Equation 1).

209

2.3 Surface response method

In this study, a three-factor, three-level Box-Behnken design is used to investigate the effects of each independent factor and the interactions of these factors on the reaction performance of the plasma CO_2 conversion process. Based on the results from our previous works and other papers,^[9, 40] discharge power (X_1), feed flow rate (X_2), and discharge length (X_3) have been identified as the three most important independent parameters affecting plasma CO_2 conversion and thus are chosen as the inputs for the design, while CO_2 conversion (Y_1) and the energy efficiency of the process (Y_2) are identified as the responses. Each independent process parameter contains three different levels, which are coded as -1 (low), 0 (centre) and $+1$ (high), as shown in Table 1.

220

221 *Table 1.* Levels and ranges of independent input variables in the Box-Behnken design

Independent variables	Symbols	Level and range
-----------------------	---------	-----------------

		Low (-1)	Centre (0)	High (+1)
Discharge power (W)	X_1	8	14	20
Feed flow rate (ml·min ⁻¹)	X_2	15	30	45
Discharge length (mm)	X_3	90	120	150

222

223 In the BBD design, a regression model is developed to describe the relationship between a
 224 set of the input plasma process parameters and each response. The regression model can be
 225 defined as:

$$226 \quad Y = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_{ii}^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} X_i X_j \quad (8)$$

227 where Y is the response, β_0 is a constant coefficient, β_i and β_{ii} are linear and quadratic
 228 coefficients for the terms X_i and X_{ii} , respectively. β_{ij} are the coefficients which represent the
 229 interactions of X_i and X_j . This model can be used to predict the reaction performance under
 230 different process conditions.

231 The analysis of variance (ANOVA) is used to evaluate the adequacy and fitness of the
 232 models. The statistical significance of the models and each term in the models can be
 233 identified by the F -test and adequacy measures such as the coefficient of determination R^2 ,
 234 adjusted R^2 and predicted R^2 . The difference between the predicted R^2 and adjusted R^2 should
 235 be within 0.2 for a well-developed model.^[35]

236

237 3. Results and Discussion

238 In this experiment, CO and O₂ are the two gas products from plasma conversion of pure CO₂.
 239 No ozone was detected in the effluent and no carbon deposition was observed in the plasma
 240 reaction, which results in a high carbon balance (97.5%-98.2%). The selectivity of CO was
 241 within the range of 91.5%-96.1%, while the molar ratio of CO/O₂ was around 2:1. Therefore,
 242 this paper is mainly focused on the investigation of the effect of different processing

243 parameters on CO₂ conversion and energy efficiency and the optimization of these parameters
 244 to provide valuable information for the development of a cost-effective plasma process for
 245 CO₂ conversion.

246

247 3.1 DoE analysis

248 In this study, the total number of the experimental samples required for the BBD design is 18,
 249 including five replicated experimental runs using the processing parameters at the centre
 250 points (Table 2). This number is less than that required for a full factorial design ($3^3=27$).
 251 Quadratic models are designed to describe the relationships between the key input process
 252 parameters (factors) and the output reaction performance (i.e., CO₂ conversion and energy
 253 efficiency), as shown in Equation 9 and 10.

254

255 *Table 2.* Actual response of CO₂ conversion and energy efficiency at experimental design
 256 points

Exp. order	Independent input variables (X)			Response (Y)	
	X ₁ : discharge power (W)	X ₂ : feed flow rate (ml min ⁻¹)	X ₃ : discharge length (mm)	Y ₁ : CO ₂ conversion (%)	Y ₂ : Energy efficiency (mmol kJ ⁻¹)
1	14	30	120	13.0	0.208
2 ^{a)}	14	30	120	12.9	0.205
3	14	15	150	17.3	0.138
4	8	45	120	6.3	0.261
5	8	30	90	5.3	0.147
6 ^{b)}	14	30	120	13.2	0.210
7	20	30	90	13.5	0.150
8	8	30	150	10.5	0.293
9	14	45	150	13.0	0.310
10	20	15	120	16.1	0.090

11	20	30	150	17.3	0.193
12	20	45	120	12.5	0.209
13 ^{c)}	14	30	120	12.8	0.204
14	14	45	90	7.2	0.171
15 ^{d)}	14	30	120	12.2	0.194
16	14	15	90	12.1	0.100
17 ^{e)}	14	30	120	11.9	0.190
18	8	15	120	10.4	0.144

257 a)-e) Replicated experimental runs (Run order: 2, 6, 13, 15 and 17).

Y_1 : CO₂ conversion (%)

$$\begin{aligned}
258 \quad &= -8.846 + 1.584 \times X_1 - 0.125 \times X_2 + 0.092 \times X_3 + 1.575 \times 10^{-3} \times X_1 X_2 \\
&- 2.078 \times 10^{-3} \times X_1 X_3 + 3.778 \times 10^{-4} \times X_2 X_3 - 0.029 \times X_1^2 - 1.398 \times 10^{-3} \times X_2^2 \\
&+ 3.625 \times 10^{-5} \times X_3^2
\end{aligned} \quad (9)$$

Y_2 : Energy efficiency (mmol · kJ⁻¹)

$$\begin{aligned}
259 \quad &= -0.207 + 0.017 \times X_1 + 2.758 \times 10^{-3} \times X_2 + 2.156 \times 10^{-3} \times X_3 \\
&+ 5.556 \times 10^{-6} \times X_1 X_2 - 1.431 \times 10^{-4} \times X_1 X_3 + 5.611 \times 10^{-5} \times X_2 X_3 \\
&- 1.366 \times 10^{-4} \times X_1^2 - 9.296 \times 10^{-5} \times X_2^2 - 1.296 \times 10^{-6} \times X_3^2
\end{aligned} \quad (10)$$

260 The ANOVA analysis is performed to determine the significance and adequacy of the
261 regression models (Table 3 and 4). The *F*-value for the regression model of CO₂ conversion
262 and energy efficiency is 50.65 and 145.08, respectively, both of which are higher than the
263 critical value (3.39 in our case),^[35] which suggests that both models are statistically significant
264 and represent the correlation between the input process parameters and the performance of the
265 plasma process. This can also be evidenced by a good agreement (*R*² close to 1) between the
266 experimental data and the simulated values from the regression models, as shown in Figure 2.
267 In addition, for both CO₂ conversion and energy efficiency, the values of the predicted *R*² are
268 in agreement with those of the adjusted *R*² (the difference between the predicted *R*² and
269 adjusted *R*² is less than 0.2 for each response), which also demonstrates the stability and

270 validity of the models. These results show that both regression models are statistically
 271 significant and adequate for the prediction and optimization of the plasma CO₂ conversion
 272 process.

273

274 *Table 3. Results of ANOVA for the quadratic model of the conversion rate of CO₂*

Model terms	Sum of square	DF ^{a)}	Mean square	F-value	p-value (Prob>F)
Model	182.41	9	20.27	50.65	<0.001
X ₁	90.51	1	90.51	226.20	<0.001
X ₂	35.98	1	35.98	89.93	<0.001
X ₃	49.50	1	49.50	123.71	<0.001
X ₁ X ₂	0.080	1	0.080	0.20	0.6659
X ₁ X ₃	0.56	1	0.56	1.10	0.2710
X ₂ X ₃	0.12	1	0.12	0.29	0.6056
X ₁ ²	4.86	1	4.86	12.15	0.0082
X ₂ ²	0.43	1	0.43	1.08	0.3292
X ₃ ²	4.645E-3	1	4.645E-3	0.012	0.9169
Residual	3.20	8	0.40		
Total	185.61	17			

R²: 0.9828; adjusted R²: 0.9634; predicted R²: 0.9215

a) degree of freedom.

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276

277 *Table 4. Results of ANOVA for the quadratic model of the energy efficiency*

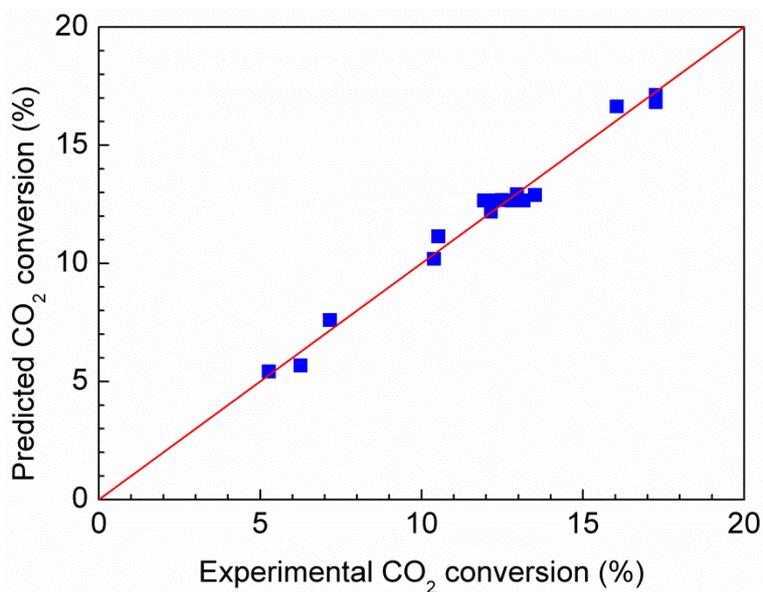
Model terms	Sum of square	DF ^{a)}	Mean square	F-value	p-value (Prob>F)
Model	0.058	9	6.439E-3	145.08	<0.001

X_1	5.151E-003	1	5.151E-3	116.05	<0.001
X_2	0.029	1	0.029	646.16	<0.001
X_3	0.017	1	0.017	377.25	<0.001
X_1X_2	1.000E-6	1	1.000E-6	0.023	0.8844
X_1X_3	2.652E-3	1	2.652E-3	59.75	<0.001
X_2X_3	2.550E-3	1	2.550E-3	57.46	<0.001
X_1^2	1.055E-4	1	1.055E-4	2.38	0.1617
X_2^2	1.909E-3	1	1.909E-3	43.01	0.0002
X_3^2	5.939E-6	1	5.939E-6	0.13	0.7240
Residual	3.551E-4	8	4.439E-5		
Total	0.058	17			

R^2 : 0.9939; adjusted R^2 : 0.9871; predicted R^2 : 0.9827

a) degree of freedom.

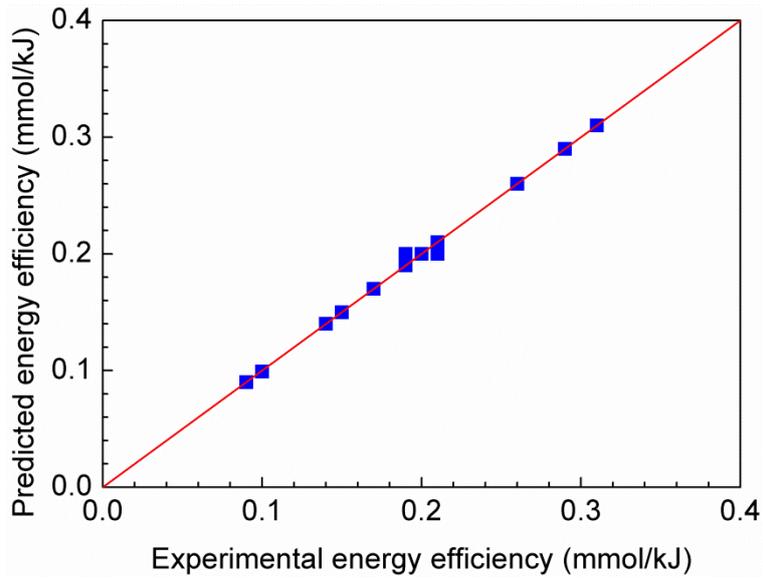
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(a)



(b)

Figure 2. Comparison of experimental and predicted results (a): CO₂ conversion; (b) energy efficiency.

3.2 Effect of plasma process parameters on CO₂ conversion

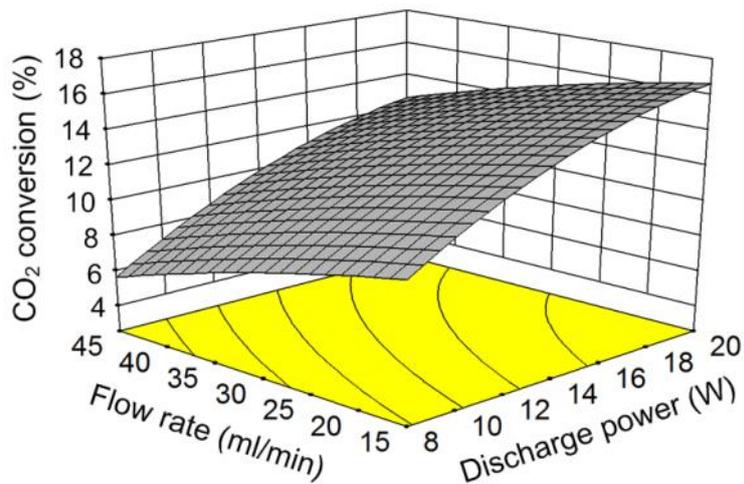
If the *p*-value of a term (individual factor X_i or interaction of two factors X_iX_j) is below the critical value of 0.05 (level of significance), the corresponding term is considered to have a significant impact on the process performance. In the plasma CO₂ conversion, X_1 , X_2 , X_3 , and X_1^2 are identified as the significant terms, while the terms X_1X_2 , X_1X_3 , X_2X_3 , X_2^2 , and X_3^2 play a weak role in the reaction, which suggests that the individual plasma process factor is considered to be more important than the interactions between different factors in terms of CO₂ conversion. The relative importance of a term is determined by its *F*-value. The discharge power has the most significant impact on CO₂ conversion compared to the other factors due to its highest *F*-value of 226.20 (shown in Table 3).

The effects of different process parameters and their interactions on CO₂ conversion are presented in the form of a three dimensional response surface and projected contour derived from the regression equation (Equation 9), as shown in Figure 3-5. If there is no or weak interaction between two process parameters, the fitted response surface will be a plane (i.e.

300 contour lines will be straight). In contrast, if two different process parameters strongly interact,
301 the contour lines will be curved rather than straight, while the contour produced by a second-
302 order model will be elliptical. This phenomenon can also be reflected from the gradient of the
303 response (e.g. CO₂ conversion and energy efficiency) with respect to one of these process
304 parameters. If two process parameters have a significant interaction effect, the gradient of the
305 response to one process parameter can be significantly different when changing the other
306 parameter.

307 Figure 3 shows the effects of the discharge power and reactant flow rate on CO₂ conversion
308 at a discharge length of 120 mm. A maximum CO₂ conversion of 16.1% is achieved at the
309 highest discharge power (20 W) and lowest CO₂ flow rate (15 ml·min⁻¹). The conversion of
310 CO₂ increases with the increase of the discharge power from 8 W to 20 W, regardless of the
311 changes in gas flow rate, which can be reflected by a nearly constant gradient of CO₂
312 conversion with respect to the discharge power (0.48% W⁻¹ at the gas flow rate of 15 ml·min⁻¹
313 and 0.52% W⁻¹ at the flow rate of 45 ml·min⁻¹), as plotted in Fig. 3(b). This suggests that the
314 effect of the interaction between the discharge power and CO₂ flow rate on CO₂ conversion is
315 insignificant. This can also be confirmed by the high *p*-value (0.6659) of the term X_1X_2 .

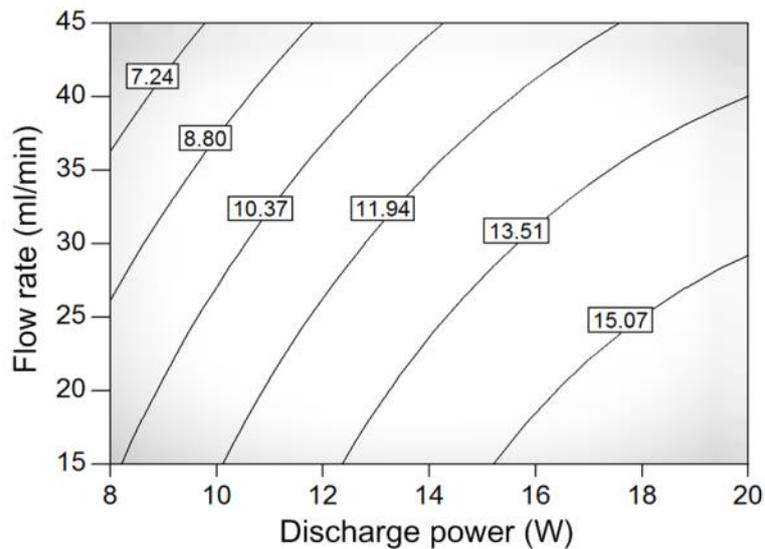
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(a)



(b)

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321 *Figure 3.* Effect of discharge power, feed flow rate and their interaction on CO₂ conversion at
 322 a discharge length of 120 mm (a) 3D surface plot; (b) projected contour plot.

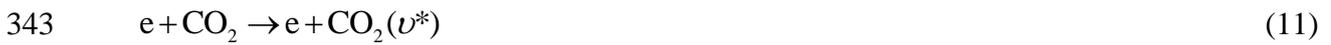
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In this study, the CO₂ DBD can be characterized as a typical filamentary discharge. The
 325 discharge power is changed by adjusting the applied voltage at a fixed frequency. Increasing
 326 the discharge power by only changing the applied voltage does not change the average
 327 electric field of the plasma since the gas voltage and breakdown voltage of the CO₂ DBD is
 328 almost constant (calculated from the Lissajous figure ^[7]), with the increase of the discharge
 329 power. This also means that the average electron energy in the CO₂ discharge does not change
 330 when changing the discharge power at a constant frequency, which can be shown from
 331 Einstein's equation.^[41] In contrast, we find that the number of microdischarges and the current
 332 intensity in the CO₂ DBD increase with the increase of the discharge power or applied voltage,
 333 which can be observed from the increased number and amplitude of the current pulses in the
 334 electrical signals. Dong et al also reported that the number of filaments per unit dielectric
 335 surface in a DBD reactor increases with the increase of the applied voltage.^[42] The increased
 336 number of microdischarges in the CO₂ DBD suggests the formation of more reaction channels

337 and electrons in the plasma, both of which contribute to the enhancement of the reaction
338 performance (e.g. CO₂ conversion) when increasing the discharge power of the CO₂ DBD.

339 It was reported that CO₂ dissociation by electron impact vibrational excitation (Equation 13
340 and 14) is the most effective pathway for CO₂ conversion in non-thermal plasmas and that up
341 to 97% of the plasma energy can be transferred from electrons to vibrational excitation of CO₂
342 at an electron temperature of 1-2 eV, or a reduced electric field (E/N) of 20-40 Td.^[43]



345 Here ν^* is the vibrational excited state. However, Aerts et al developed a chemical kinetics
346 model to understand the plasma chemistry and role of electron vibrational excitation in the
347 CO₂ conversion in a DBD reactor with an average electron temperature (2-3 eV). Their results
348 showed that the majority (94%) of the CO₂ conversion occurs by reactions (e.g. electron
349 impact dissociation shown in Equation 15) with ground state CO₂ and only 6% by reactions
350 with vibrational excited CO₂ as a considerable fraction of the excited states will eventually
351 de-excite to the ground state of CO₂.^[44]



353 The electron impact dissociation of CO₂ will most likely result in CO in its ground state
354 (¹Σ) and O atoms in both the ground state (³P) and metastable state (¹D). However, CO could
355 also be formed in excited states as CO bands are observed in the emission spectra of the CO₂
356 DBD.^[45] The O atoms can react with CO₂ to form CO and O₂ (Equation 16). Oxygen can also
357 be formed from the three-body recombination of atomic oxygen (Equation 17).

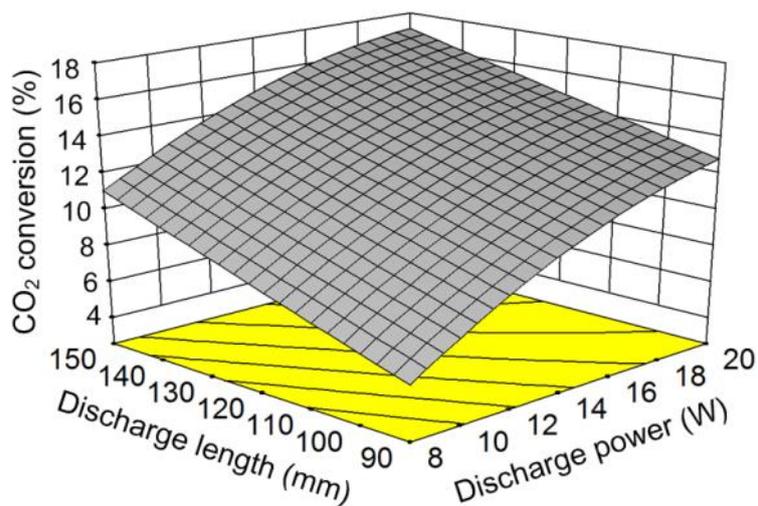


360 Increasing the CO₂ flow rate significantly decreases the conversion of CO₂ due to the
361 decrease of the residence time of CO₂ in the discharge zone. In this study, the residence time

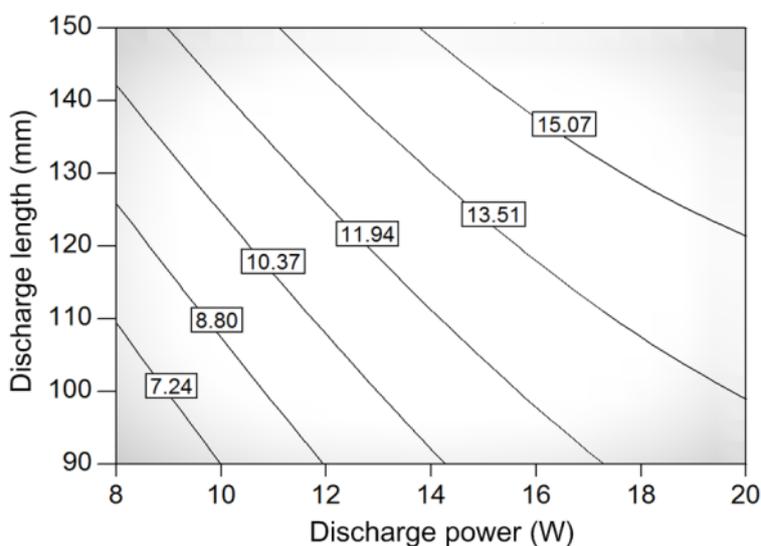
362 is decreased by 66.67% from 62.2 s to 20.7 s when the feed flow rate increases from 15
363 ml·min⁻¹ to 45 ml·min⁻¹ at a discharge length of 120 mm. Significantly decreasing the
364 residence time of CO₂ in the discharge zone results in a reduced chance for CO₂ molecules to
365 react with energetic electrons and reactive species (e.g. O).

366 Figure 4 shows the combined effect of the discharge power and discharge length on CO₂
367 conversion. The maximum CO₂ conversion of 17.3% is achieved at the highest discharge
368 power of 20 W with the discharge length of 150 mm. The discharge length also plays an
369 important role in CO₂ conversion. Increasing the discharge length of the DBD reactor
370 significantly enhances the conversion of CO₂, regardless of the discharge power. This is
371 different to previous results where the variation of discharge length (from 90 mm to 150 mm)
372 only slightly changed the CO₂ conversion in a packed bed DBD reactor.^[10] The effect of the
373 discharge length on CO₂ conversion is the result of the two competing effects. In this study,
374 increasing the discharge length from 90 mm to 150 mm leads to the increase of the residence
375 time of CO₂ molecules by 67% (from 23.3 s to 38.9 s) in the discharge region at a constant
376 flow rate of 30 ml·min⁻¹, which contributes to the enhancement of CO₂ conversion. On the
377 other hand, a longer discharge length lowers the power density due to the increase of the
378 discharge volume, which results in the decrease of the conversion of CO₂. These results
379 suggest that the change in residence time has a more significant impact on the conversion of
380 CO₂ in our DBD reactor compared to the effects from the reduced power density. In addition,
381 we find the conversion of CO₂ is increased to 18.3% when further increasing the discharge
382 length from 150 mm to 180 mm (outside the range of this design). The interaction of the
383 discharge power and discharge length on the plasma process is considered as insignificant
384 since the contour lines are almost straight. This can also be confirmed by the *p*-value (> 0.05),
385 as listed in Table 3.

386



(a)



(b)

387

388

389

390

391 *Figure 4.* Effect of discharge power, discharge length and their interaction on CO₂ conversion

392 at a flow rate of 30 ml·min⁻¹ (a) 3D surface plot; (b) projected contour plot.

393

394 The effects of the discharge length, feed flow rate and their interaction on the conversion of

395 CO₂ are plotted in Figure 5. Similarly, we find the fitted response surface is in the shape of a

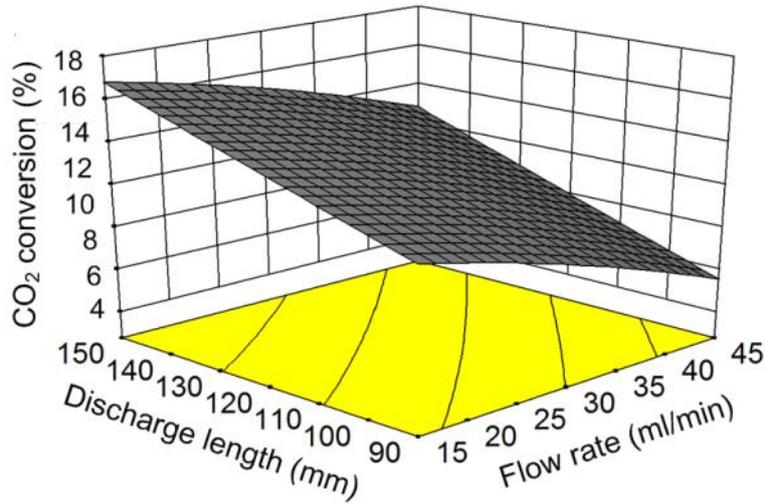
396 plane and the contour lines are almost straight. This can also be reflected by a weak variation

397 in the gradient of CO₂ conversion with respect to either the discharge length or the gas flow

398 rate (see Figure 5). The *p*-value of the term related to the interaction of these two parameters is

399 much higher than the critical value (0.05). These results clearly show that the interaction of
400 the discharge length and gas flow rate on CO₂ conversion is insignificant.

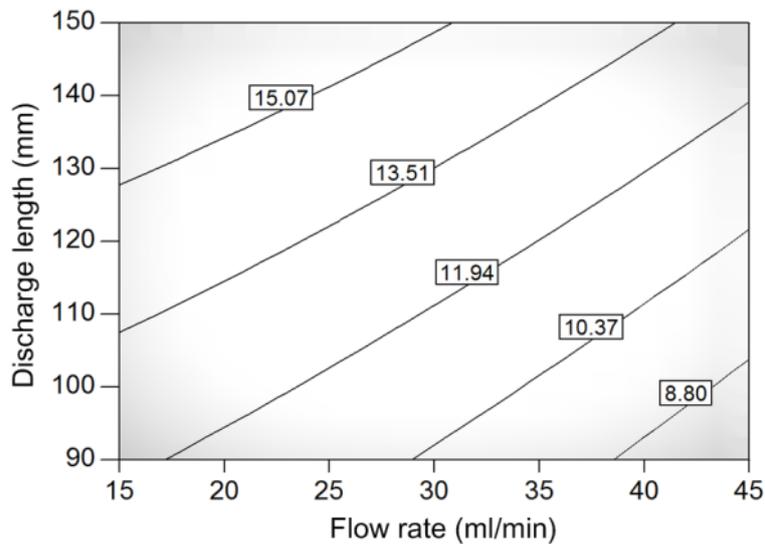
401



402

403

(a)



404

405

(b)

406 *Figure 5.* Effect of CO₂ flow rate, discharge length and their interactions on CO₂ conversion

407 at a discharge power of 14 W (a) 3D surface plot; (b) projected contour plot.

408

409 3.3 Effect of process parameters on energy efficiency

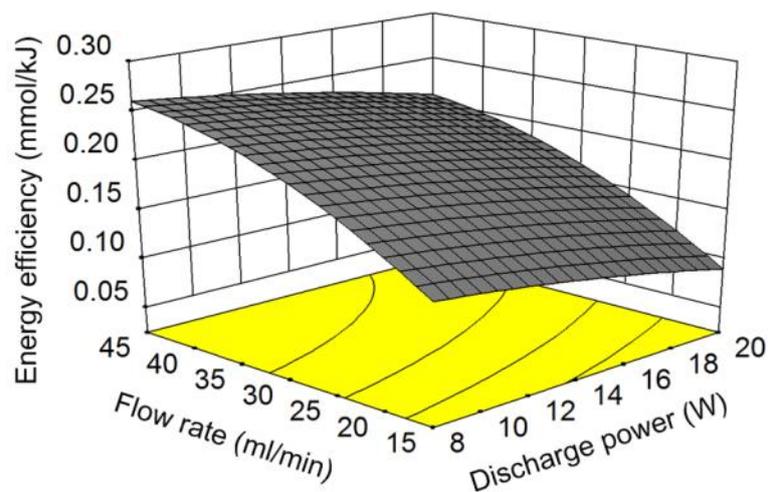
410 The ANOVA results show the effect of the individual process parameters and their

411 interactions on the energy efficiency of the plasma reaction (see Table 4). The terms X_1 , X_2 , X_3 ,

412 X_1X_3 , X_2X_3 , and X_2^2 are identified as the significant factors as their p -values are below the
413 critical value of 0.05. The CO_2 flow rate is found to be the most important factor affecting the
414 energy efficiency of the plasma process with the highest F -value of 646.16.

415 Figure 6 shows the combined effects of the discharge power and CO_2 feed flow rate on the
416 energy efficiency of the plasma process at a constant discharge length of 120 mm. The
417 maximum energy efficiency of $0.261 \text{ mmol}\cdot\text{kJ}^{-1}$ is obtained at the lowest discharge power of 8
418 W and highest feed flow rate of $45 \text{ ml}\cdot\text{min}^{-1}$. A similar phenomenon was also reported in
419 previous studies, where the highest energy efficiency for the reforming of methane or pure
420 CO_2 decomposition was obtained at lower plasma power and higher reactant flow using either
421 DBD or gliding arc.^[27, 31, 40, 45-48] The effect of the discharge power on the energy efficiency
422 shows a similar evolution behaviour when changing the CO_2 flow rate, while the gradient of
423 the energy efficiency with respect to the discharge power is almost constant regardless of the
424 CO_2 flow rate. This suggests the interaction between these two process parameters is very
425 weak in terms of the energy efficiency of the plasma process.

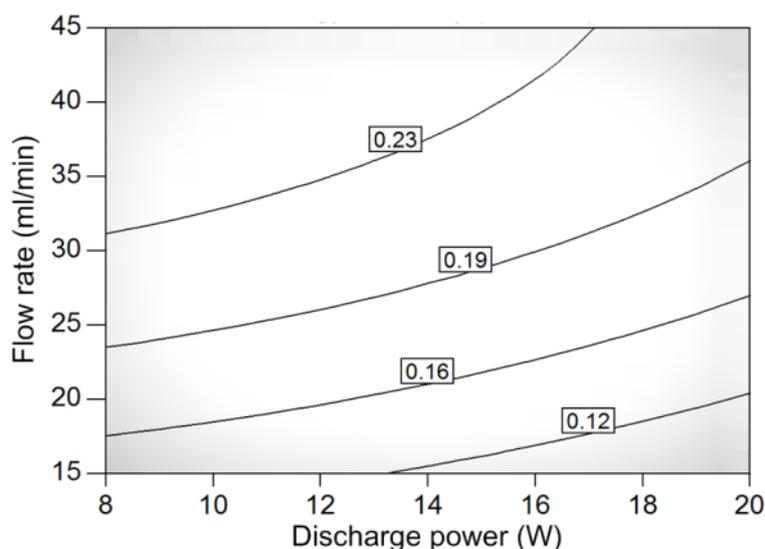
426



427

428

(a)



(b)

429

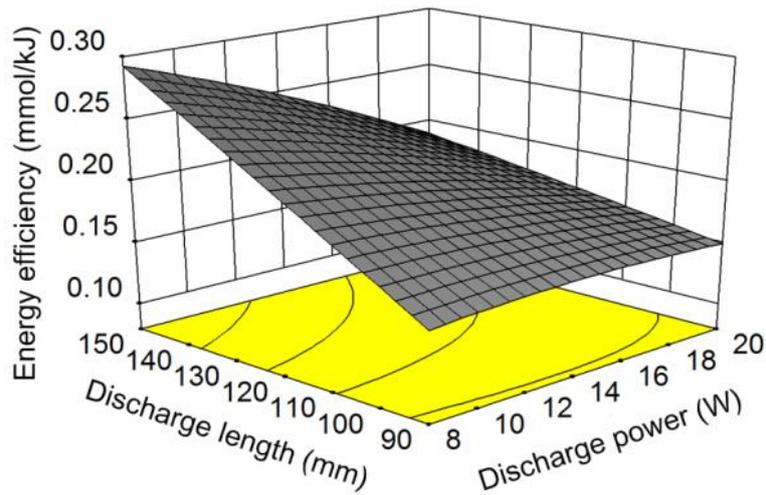
430

431 *Figure 6.* Effect of discharge power, flow rate and their interaction on the energy efficiency at
 432 a discharge length of 120 mm (a) 3D surface plot; (b) projected contour plot.

433

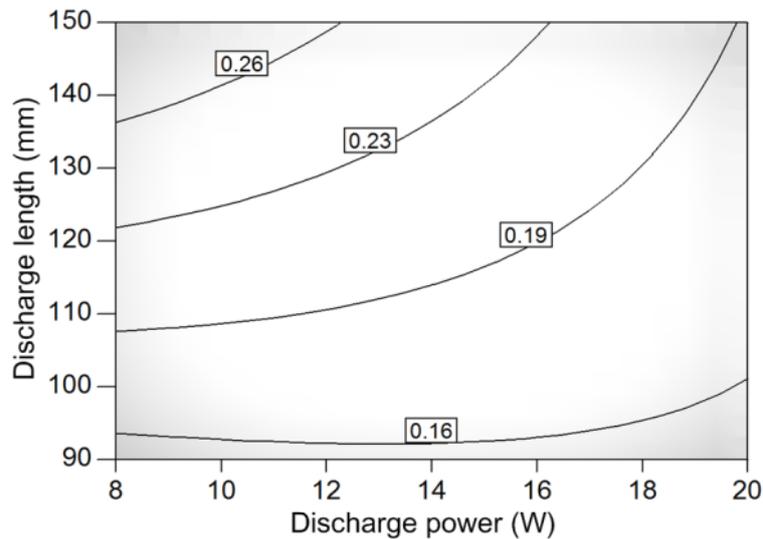
434 The interaction of the discharge power and discharge length on the energy efficiency of the
 435 plasma CO₂ conversion process is presented in Figure 7. At a constant discharge power and
 436 total gas flow rate, increasing the discharge length enhances the conversion of CO₂ due to the
 437 increase of the residence time of CO₂ in the plasma zone (Figure 4), which contributes to the
 438 enhancement of the energy efficiency of the plasma process. The maximum energy efficiency
 439 of the plasma process is achieved at the largest discharge length (150 mm) and lowest
 440 discharge power (8 W). At the discharge length of 150 mm, the energy efficiency of the
 441 process decreases from 0.293 to 0.193 mmol·kJ⁻¹ when the discharge power increases from 8
 442 to 20 W, while the energy efficiency is almost constant with the change of the discharge
 443 power at the short discharge length of 90 mm. Similarly, the gradient of the energy efficiency
 444 with respect to the discharge length is much higher at a low discharge power (e.g. 8 W)
 445 compared to that at a high plasma power (e.g. 20 W). These phenomena demonstrate that
 446 there is a significant interaction between the effect of discharge power and discharge length
 447 on the energy efficiency of the process, which can also be confirmed by the presence of

448 contour lines in Figure 7(b). Table 4 also shows that the p -value of the term X_1X_3 (< 0.001) is
449 much lower than the level of significance (0.05). Furthermore, the energy efficiency of the
450 plasma process is increased to $0.146 \text{ mmol}\cdot\text{kJ}^{-1}$ when further increasing the discharge length
451 to 180 mm (outside the range of this design).
452



453
454

(a)



455
456

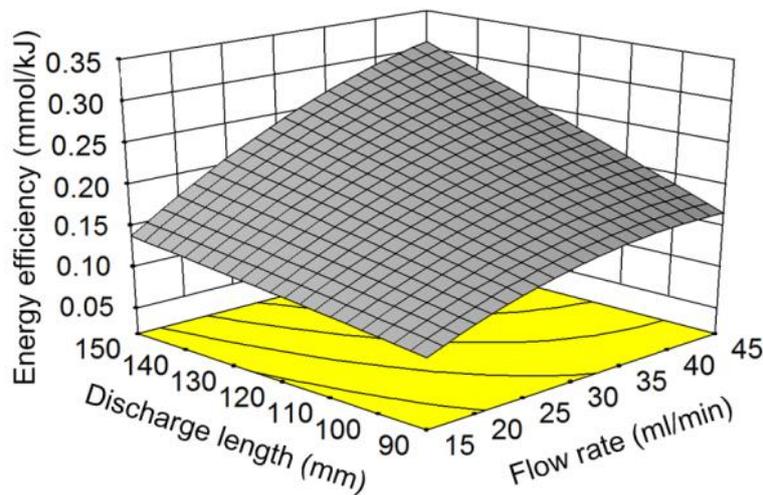
(b)

457 *Figure 7.* Effect of discharge power, discharge length and their interaction on the energy
458 efficiency at a flow rate of $30 \text{ ml}\cdot\text{min}^{-1}$ (a) 3D surface plot; (b) projected contour plot.

459

460 Figure 8 shows the combined effects of the gas flow rate and discharge length on the
 461 energy efficiency in the plasma CO₂ conversion process. At the shortest discharge length of
 462 90 mm, the energy efficiency of the plasma process increases from 0.1 to 0.171 mmol·kJ⁻¹
 463 when the gas flow rate rises from 15 to 35 ml min⁻¹, whereas the energy efficiency is
 464 enhanced by over 120% (from 0.138 to 0.310 mmol·kJ⁻¹) with the increase of the gas flow rate
 465 at the longest discharge length of 150 mm. This means that the gradient of the energy
 466 efficiency with respect to the gas flow rate depends on the discharge length, as plotted in Fig.
 467 8(b). In addition, the energy efficiency decreases significantly when the discharge length
 468 changes from 150 mm to 90 mm at the highest CO₂ flow rate of 45 ml·min⁻¹. In contrast, the
 469 energy efficiency is almost independent of the discharge length at the lowest flow rate of 15
 470 ml·min⁻¹. These results indicate there is a significant interaction between the effect of
 471 discharge length and gas flow rate on the energy efficiency of the plasma process, which can
 472 also be confirmed by the low *p*-value (<0.001) of the term *X*₂*X*₃ and contour plot.

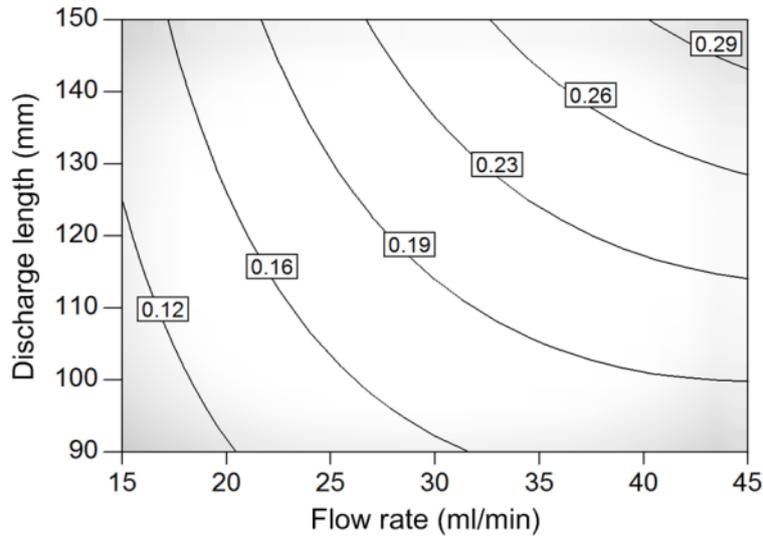
473



474

475

(a)



(b)

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477

478 *Figure 8.* Effect of flow rate, discharge length and their interaction on the energy efficiency at
 479 a discharge power of 14 W (a) 3D surface plot; (b) projected contour plot.

480

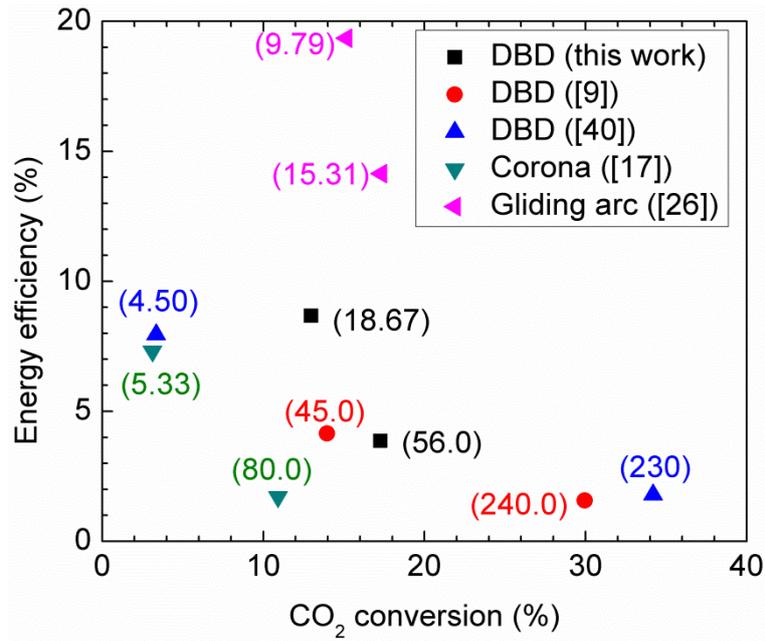
481 3.4 Process optimization

482 We find that CO₂ conversion and energy efficiency of the plasma process cannot reach the
 483 maximum values simultaneously under the same plasma operating conditions. Increasing the
 484 discharge length increases both CO₂ conversion and energy efficiency. However, increasing
 485 the discharge power and CO₂ flow rate has an opposite effect on CO₂ conversion and energy
 486 efficiency.^[40, 49] For example, higher discharge power results in higher CO₂ conversion but
 487 lowers the energy efficiency of the process at a fixed CO₂ flow rate, whereas higher reactant
 488 flow leads to higher energy efficiency of the plasma process but significantly decreases the
 489 conversion of CO₂.

490 Figure 9 summarizes the CO₂ conversion and energy efficiency of the plasma processing of
 491 pure CO₂ using different atmospheric pressure plasma sources. Xu et al. reported a maximum
 492 CO₂ conversion of 10.9% in a DC corona discharge reactor at a discharge power of 40 W and
 493 a CO₂ flow rate of 30 ml·min⁻¹, corresponding to the energy efficiency of 1.68%.^[18] They
 494 claimed that the highest energy efficiency of 7.28% can be achieved at the expense of very

495 low CO₂ conversion (3.1%).^[18] Paulussen et al. investigated the effect of a wide range of
496 operating parameters (e.g. frequency, discharge power, CO₂ flow rate and inlet gas
497 temperature) on the conversion of CO₂ in a coaxial DBD reactor.^[9] They found that the
498 maximum CO₂ conversion of 30 % can be obtained at the lowest CO₂ flow rate of 50 ml·min⁻¹
499 and the highest input power of 200 W. However, the maximum energy efficiency of the
500 plasma process (4.14 %) was not achieved at the same operating conditions, but at the highest
501 CO₂ flow rate of 200 ml·min⁻¹.^[9] Similarly, Aerts et al. investigated the effect of reactor
502 configurations (e.g., dielectric materials, discharge gap) and operating parameters (e.g.,
503 frequency, electrical power and gas flow rate) on the CO₂ decomposition in a DBD reactor.^[40]
504 The maximum CO₂ conversion of 34.2% was obtained at an electrical power of 40 W and a
505 gas flow rate of 10 ml·min⁻¹, while the maximum energy efficiency (9.25%) was achieved at a
506 lower electrical power (17 W) and a higher gas flow rate (100 ml·min⁻¹).^[40] Gliding arc
507 discharge has also been used for CO₂ conversion and offers a high flexibility to work in a
508 relatively high reactant gas flow rate and at elevated power levels.^[27, 47] A maximum energy
509 efficiency of 19.35% was obtained at a flow rate of 0.86 l·min⁻¹, which corresponds to a
510 relatively low CO₂ conversion (15.16%) compared to the maximum CO₂ conversion of 17.3%
511 obtained in their work.^[27]

512



513

514 *Figure 9.* Comparison of CO₂ conversion and energy efficiency in different plasma systems

515 (the number in the brackets is the specific energy density (SED), unit: kJ·L⁻¹)

516

517 Therefore, a balance between CO₂ conversion and energy efficiency is significantly
 518 important for the development of an efficient plasma process for CO₂ conversion. The overall
 519 performance of the plasma conversion of CO₂ strongly depends on a wide range of plasma
 520 operating conditions. It is essential and indispensable to optimise the plasma CO₂ conversion
 521 process with multiple inputs and multiple responses. In this study, the aim of the process
 522 optimization is to find a combination of the plasma processing parameters (different factors)
 523 that maximize the CO₂ conversion and energy efficiency of the plasma process (different
 524 responses) simultaneously. A global desirability function (*D*) has been introduced as a key
 525 parameter to identify the optimal processing parameters and performance in the plasma
 526 conversion of CO₂. This function can be calculated from the product of the individual
 527 desirability function (*d_i*) for each response, as shown in the following Equation:^[50, 51]

528
$$D = (d_1 \times d_2 \times \dots \times d_n)^{\frac{1}{n}} = \left(\prod_{i=1}^n d_i \right)^{\frac{1}{n}} \quad (16)$$

529 where n is the number of the response in the experiment ($n = 2$ in this work) and d_i is in the
 530 range between 0 (least desirable) and 1 (most desirable). The optimal process and processing
 531 parameters can be achieved when the highest value for D is found.

532 Table 5 shows the different obtained values of global desirability of the plasma process in
 533 the process optimization. The optimal process performance - CO₂ conversion (14.2%) and
 534 energy efficiency (0.285 mmol·kJ⁻¹, corresponding to 8.0%) for the plasma CO₂ conversion -
 535 is achieved at a discharge power of 15.8 W, a feed flow rate of 41.9 ml·min⁻¹ and a discharge
 536 length of 150 mm as the highest global desirability of 0.816 is obtained. To validate this
 537 predicted result, five additional experimental runs are carried out using the optimal process
 538 parameters. The results show a fairly good agreement between the experimental results and
 539 predicted one with a relative error of less than 5% for both CO₂ conversion and energy
 540 efficiency. These reproducible results confirm that DoE can be used to optimize the plasma-
 541 assisted CO₂ decomposition process.

542

543 *Table 5. Process optimization for plasma CO₂ conversion by RSM*

Condition	Discharge power (W)	Feed flow rate (ml·min ⁻¹)	Discharge length (mm)	CO ₂ conversion (%)	Energy efficiency (mmol·kJ ⁻¹)	Global desirability
1	15.8	41.9	150.0	14.3	0.285	0.816
2	16.2	41.4	150.0	14.5	0.280	0.815
3	15.2	39.5	150.0	14.4	0.282	0.814
4	14.7	41.8	150.0	13.8	0.294	0.813
5	15.3	38.2	150.0	14.7	0.275	0.811

544

545 **4. Conclusion**

546 In this study, the effects of the key plasma process parameters (discharge power, feed flow
 547 rate and discharge length) and their interactions on plasma conversion of CO₂ in a coaxial

548 DBD reactor has been investigated through the response surface methodology based on multi-
549 objective optimization. Regression models have been developed to describe the relationships
550 between the plasma process parameters and reaction performance. The significance and
551 adequacy of the models for each response (CO₂ conversion and energy efficiency) have been
552 verified by the analysis of variance. The results show that the conversion of CO₂ increases
553 with increasing discharge power and discharge length, but decreases with the increase of feed
554 flow rate. At a discharge length of 120 mm, the maximum CO₂ conversion of 16.1% is
555 achieved at the highest discharge power of 20 W and lowest CO₂ flow rate of 15 ml·min⁻¹.
556 The discharge power is found to be the most important parameter driving the conversion of
557 CO₂, followed by the discharge length and CO₂ flow rate, while the feed flow rate has the
558 most significant effect on the energy efficiency of the process. Increasing the discharge power
559 by changing the applied voltage at a fixed frequency increases the number of microdischarges
560 and average electron density in the CO₂ DBD, both of which contribute to the enhancement of
561 the process performance (e.g. CO₂ conversion). The interactions of different plasma process
562 parameters have a very weak effect on CO₂ conversion. In contrast, there are significant
563 interactions of the discharge length with either discharge power or gas flow rate on the energy
564 efficiency of the plasma process. The optimal CO₂ conversion (14.3%) and energy efficiency
565 (7.98%) for the plasma CO₂ conversion process is achieved at a discharge power of 15.8 W, a
566 feed flow rate of 41.9 ml·min⁻¹ and a discharge length of 150 mm, to balance the conversion
567 of CO₂ and energy efficiency of the plasma process. The reproducible experimental results
568 under the theoretical optimal conditions have demonstrated the capability and reliability of the
569 DoE to get a better understanding of the role of the different process parameters and their
570 interactions in the plasma CO₂ conversion reaction for process optimization.

571

572 **Acknowledgements:** Support of this work by the UK EPSRC Grand Challenge CO₂Chem
573 Network and Foundation of Key Laboratory of Thermo-Fluid Science and Engineering (Xi'an

574 Jiaotong University), Ministry of Education (China) is gratefully acknowledged. D. H. Mei
575 acknowledges the PhD fellowship co-funded by the Doctoral Training Programme (DTP) of
576 the University of Liverpool and the Chinese Scholarship Council (CSC).

577 Received: ((will be filled in by the editorial staff)); Revised: ((will be filled in by the editorial
578 staff)); Published online: ((please add journal code and manuscript number, e.g., DOI:
579 10.1002/ppap.201100001))

580

581 **Keywords:** CO₂ conversion; design of experiments; dielectric barrier discharge; non-thermal
582 plasma; process optimization
583

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Optimization of CO₂ conversion in a cylindrical dielectric barrier discharge reactor using design of experiments

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Design of Experiments has been used to optimize the plasma conversion of CO₂ into CO and oxygen in a dielectric barrier discharge reactor. The importance of different independent process parameters, especially the interactions of these parameters on the plasma conversion of CO₂ has been investigated.

