Supplementary Material

Catalyst-free single-step plasma reforming of CH₄ and CO₂ to higher value oxygenates under ambient conditions

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1. Experimental setup for temperature measurement and optical diagnostics

The optical diagnostics were performed in a darkroom using an intensified charge-coupled device (ICCD) camera and OES to understand the influence of different discharge powers and reaction temperatures on the discharge characteristics. The experimental conditions remained unchanged from the reaction, with a flow rate of 40 mL/min and a CO₂/CH₄ ratio of 1:1. The measurements were taken 1 h after the discharge was ignited. To investigate the uniformity of the plasma discharge, the ICCD images were recorded from two different camera angles, as shown in Figure S1. A mercury pen-ray lamp was used to calibrate the OES.



Figure S1 Schematic diagrams of (a) temperature measurement using a fiber optical thermometer and (b) optical diagnostics using ICCD camera and OES

2. Artificial neural network (ANN) models

ANN is a typical supervised machine learning model¹. An ANN model generally consists of several layers, each of which contains multiple nodes. Each node represents one dimension of input and output data. Each layer is partially or completely connected to the previous and subsequent layers. We used fully connected layers in this work. Assuming that the input of one layer is an n-dim vector, denoted by , the expression for its output can be expressed as follows:

(S1)

Where is the weight for each node and b is the bias. To adapt to a non-linear fitting, the output of each layer is first taken into an activation function, in our case the Sigmoid function (see the expression below), before being connected to the next layer.

In other words, an ANN can be treated as a complex function. The ANN training process ensures that you find the optimum weight and bias values so that the predicted value of a specific input matches the true value with the least amount of error. Back-propagation is the most commonly used algorithm. The gradients and errors are used to update the weight and bias values.

Where denotes the weight correction at the th learning step, denotes the training rate, denotes the total sum squared error of all data in the training set, and is the momentum factor. Furthermore, the Adam algorithm was used to provide a dynamic learning rate for model optimization, which could be useful for the sparse gradients².

A typical single layer ANN model was developed to predict the reaction performance, including the conversion of CO₂ and CH₄, and the selectivity of gaseous and liquid products. Three key process parameters (and three key indicators of plasma reaction) were selected as the input variables, and the reaction performance (more specifically the "conversion & selectivity" and the "energy efficiency") was chosen as the output target. Key process parameters include discharge power, reaction temperature, and residence time, while key

indicators of plasma reaction are mean electron energy (E_e), electron density (n_e), and specific energy input (SEI).



Figure S2 (a) Scheme of the single layer ANN₁ model for process parameters; Comparison of experimental data and predicted results for (b) conversion & selectivity and (c) energy efficiency using the optimized ANN₁.



Figure S3 (a) Scheme of the single-layer ANN₂ model for key discharge indicators of plasma reaction; (b) Comparison between the experimental data and the predicted results for reaction performance using the optimized ANN₂.



3. Energy efficiency

Figure S4 Effect of different process parameters on the energy efficiency for the conversion of CH₄ and CO₂, and the selectivity of H₂ and methanol (MeOH). The default values of

 $\rm CO_2/CH_4$ ratio, discharge power, reaction temperature, and residence time are 1:1, 15 W, 20 $^\circ$ C, and 3.8 s (40 mL/min), respectively.



4. Electrical signals

Figure S5 Applied voltage (a, c) and current (b, d) of the CO₂-CH₄ plasma at different discharge powers (a and b: at 40 mL/min and 20 °C) and reaction temperatures (c and d: at 40 mL/min and 15 W)

5. Plasma characteristics

5.1 Discharge parameters



Figure S6 (a) Equivalent circuit model of a DBD and (b) the corresponding Q-U plots. ^{3–5}

Figure S6b shows the equations for calculating C_{cell} and C_{eff} ^{3–5}. For a fully bridged discharge gap, the dielectric capacitance should be equal to C_{eff} ⁶.

 $C_{\mbox{\tiny gap}}$ is the capacitance of the discharge gap and can be calculated using

(S4)

 $U_{\mbox{\tiny b}}$ is the breakdown voltage that can be calculated using

(S5)

Where U_{min} can be determined in the Lissajous figure (Figure S6b).

5.2 Calculation of mean electric field

The following equation was used to approximate the mean electric field (E):

where d_{gap} is the discharge gap.



Figure S7 Calculated mean electron energy as a function of the reduced electric field (E/N). The range of different reaction temperatures (5 °C – 65 °C) and discharge powers (10 W – 40 W) is also indicated.

5.3 Calculation of mean electron density

The mean electron density (n_e) can be determined by: ^{7,8}

(S7)

Where J is the current density, which is defined as the ratio of the average peak discharge current over three cycles to the surface area of one micro-discharge $(1.05 \times 10^{-6} \text{ m}^2)^9$. E is the average electric field, and μ_e is the electron mobility calculated using BOLSIG+. *e* is the electron charge.

6. Supplemental results of OES

Species	Electron transition	Δν	Wavelength (nm)	Ref.
CO_2^+	$A^2\Pi_u$ - $X^2\Pi_g$		305	10
	2		326	10
			338	10,11
			351	10,11
			368	10,11
CO ₂	${}^{1}B_{2}$ - $X^{1}\Sigma^{+}$		426	10
$\rm CO^+$	$B^{2}\Sigma$ - $X^{2}\Sigma$	4	289	10
СО	$b^{3}\Sigma_{2u}$ - $a^{3}\Pi_{1g}$	0	283	11
	(Third Positive	1	297	11
	System)			
	B^{1} Σ- A^{1} Π	0	451	11,12
	(Angstrom system)	1	483	11,12
		2	519	11,12
		3	560	11,12
		4	608	11,12
CH	$C^2\Sigma^+$ - $X^2\Pi$	0	314	11
		1	316	11
	B^2 Σ- X^2 Π	0	387	11
	$A^2\Delta$ - $X^2\Pi$	0	431	11
C_2	d²П- а³П	1	468	11
	(Swan band)	1	470	11
		1	471	11
		1	474	11
		0	513	11
		0	516	11
OH	$A^2 Σ^+$ - $X^2 Π$		309	13,14
H_{α}	3d-2p		656	11

Table S1 Spectroscopic characteristics of the main species detected in the CO₂-CH₄ plasma.



Figure S8 Emission spectra of the CO₂-CH₄ plasma at different discharge powers (20 °C and 40 mL/min) and reaction temperatures (15 W and 40 mL/min).





Figure S9 Effect of discharge power, reaction temperature and residence time on (a) gas conversion, product selectivity (H₂, CO, C₂, C₃-C₄, methanol (MeOH), ethanol (EtOH), acetic acid (AcA), and acetone (Ace)), and (b) energy efficiency.



8 Relative importance of key discharge indicators on reaction performance

Figure S10 Relative importance of key discharge indicators on reaction performance.

9 Predicted combined effects of process parameters



Figure S11 Predicted combined effects of discharge power, reaction temperature and residence time on the conversion of CH₄ and CO₂, and the selectivity of primary products (H₂, CO, methanol (MeOH) and acetic acid (AcA)) and secondary products (C₂, C₃-C₄, ethanol (EtOH) and acetone (Ace)).



Figure S12 Predicted combined effects of discharge power, reaction temperature and residence time on energy efficiency for the conversion of CO₂ & CH₄ and the production of primary products (H₂, CO, methanol (MeOH) and acetic acid (AcA)) and secondary products (C₂, C₃-C₄, ethanol (EtOH) and acetone (Ace)).

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