



Ignition of CO₂ methanation using DBD-plasma catalysis in an adiabatic reactor

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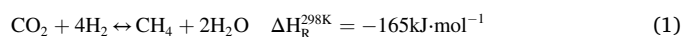
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ABSTRACT

In this work, a novel strategy of the use of dielectric barrier discharge (DBD) plasma-catalysis for exothermic reactions is presented. DBD-plasma is used as reaction ignitor, rather than the classical approach of continuous operation, by taking advantage of the synergy between catalytic plasma activation from room temperature and a self-sustained exothermic reaction. CO₂ methanation reaction was performed in a thermal insulated reactor using an active nickel-based catalyst loaded in two catalytic bed sections, with electrodes implemented solely in the first section. DBD plasma was employed to activate the reaction from cold conditions with the subsequent increase in reactor temperature and, finally, reaction was self-sustained by thermal-catalysis. The experimental results pointed out the sensitive dependence of the reactor temperature on the gas flow rate during the plasma operation. Low-energy conditions were found in which the reaction could operate in autothermal mode, after plasma shut-off. Power and start-up time were optimized, obtaining a considerable low start-up time from cold conditions (25 °C) of only 3 min. Besides, the autothermal operation mode was maintained for 8 h without any energy input. This proof-of-concept work demonstrates that plasma can be implemented as initial power ignition in exothermic reactions using proper reactor design and conditions, and then, the reactor can operate in autothermal mode.

1. Introduction

The conversion of CO₂ to high value-added chemical and fuels have been extensively investigated over the last years, aimed at offering low-carbon products to society. The combination of CO₂ with H₂ can generate CH₄, an interesting energy storage vector within the Power-to-Gas strategy [1,2]. CO₂ methanation (Eq. (1)), also known as Sabatier process, is a highly exothermic reaction (-165 kJ·mol⁻¹) industrially performed by thermal-catalysis in a range of temperatures between 300 and 500 °C. Due to the high exothermicity, heat management is essential to control catalyst bed temperature and several reactor configurations are proposed in the literature [1–5]. Among them, current commercial technologies consist of multi-tubular or structured catalytic reactors, including boiling water, air, oil or salt cooling systems.



In recent years, the use of plasma technologies has gained interest as an alternative to conventional thermal-catalysis [6,7]. Non-thermal

plasma (NTP) and warm plasmas technologies offer new opportunities for CO₂ conversion. In NTP, generated electrons acquire high energy in the range of 1–10 eV, while heavy molecules and atoms remain at low temperature. The collision between the electron and the gas molecules generates several reactive species that can trigger different chemical reactions at low temperatures (25 – 250 °C) [8]. In warm plasma, energy is also transferred to the heavy particles, achieving a higher gas temperature (700 – 3000 °C). In addition, the characteristics of a high vibrational excitation in warm plasma make it attractive for some chemical reactions, such as the direct transformation of CO₂ to CO [7,9].

For the catalytic hydrogenation of CO₂ to CH₄, NTP has been extensively studied during the last ten years [10–12], being DBD the most used for CO₂ methanation. The selection of DBD over other technologies stands out for its feasibility to combine plasma with a catalyst (so-called plasma-catalysis) and the availability to work at atmospheric pressure. In fact, the use of catalyst is mandatory in plasma methanation to boost conversion and selectivity to the desired product [13,14]. Analogous to thermal-catalysis, Ni-based catalyst presents an excellent

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cost-benefit balance when compared with noble metals [10].

In the literature, most studies were carried out by applying a continuous plasma without any external heating, achieving conversion between 70 and 80% and CH_4 selectivity from 95 to 99% [13,15–17]. In these conditions, the reactor temperature increased by the combination of heat losses from the plasma and the heat released by the exothermic methanation reaction. After start-up, the registered temperature ranged from 100 °C to 200 °C [16–18], a considerably lower temperature compared with thermal methanation (<300 °C). All these works inferred that methanation takes place at a lower temperature due to the activation of plasma compared with thermal methanation. In recent studies, the threshold temperature of the CO_2 methanation reaction in plasma was found to be as low as 116 °C [19].

Our group has developed an alternative approach in order to increase the energy efficiency of the plasma methanation process [20]. The reaction was carried out in adiabatic conditions by thermally insulating the reactor. In that setup, higher temperatures were obtained (200–400 °C), facilitating the synergy between plasma and thermal catalysis, which allows the reduction of the required applied power. The reactor temperature was highly dependent on the gas flow rate as the exothermicity of the reaction was the main source of heat. In a parallel work, we have demonstrated that thermal-catalysis can be self-sustained with a proper heat-management strategy based on free convection [21].

In this work, we have studied the use of plasma in a hybrid DBD-thermo-catalytic reactor, with the aim to ignite the reaction efficiently without preheating the gases. This novel strategy is based on using the DBD-plasma as ignitor to initiate the chemical reaction in adiabatic conditions and take advantage of the heat released due to the exothermic methanation reaction to warm up the subsequent sections of the reactor up to a temperature where the catalyst is thermally active. After ignition, plasma was turned off and self-sustained thermal conditions were attained as the reaction was maintained by the heat released. In this way, the use of DBD-plasma as reaction ignitor opens the path to electrify chemical reactions while minimizing the start-up time to avoid the classical reactor warm-up under standby conditions.

2. Materials and methods

2.1. Catalyst synthesis

Ni-CeO_2 was used as an active methanation catalyst, prepared by wet impregnation method on commercial $\gamma\text{-Al}_2\text{O}_3$ microspheres (Saint-Gobain NorPro, $d = 400\text{--}500\ \mu\text{m}$). A composition of 15 wt% Ni and 30 wt% Ce was selected as shows high performance toward CO_2 methanation [13].

In a typical synthesis, the $\gamma\text{-Al}_2\text{O}_3$ support was dried at 150 °C overnight. The Ni/Ce precursor solution was prepared, containing Ni

nitrate (98% Alfa Aesar), Ce nitrate (99% Fluka) and water with a $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of 3. The $\gamma\text{-Al}_2\text{O}_3$ support was mixed with the precursor solution in a rotatory vacuum evaporator at 25 rpm and 25 °C for 1 h and slowly evaporated at 25 rpm, 80 °C and 0.8 bar for 6 h. Finally, the impregnated alumina was dried at 105 °C overnight and further calcinated at 450 °C for 30 min with a $1\ \text{°C}\cdot\text{min}^{-1}$ ramp.

Before the methanation experiments, catalyst was ex-situ reduced at 450 °C for 3 h under 5% $\text{H}_2\text{-Ar}$ atmosphere ($150\ \text{mL}\cdot\text{min}^{-1}$).

2.2. Reactor setup and experimental procedure

The reaction was studied in a hybrid DBD-thermo-catalytic reactor. The hybrid reactor consisted in a coaxial DBD plasma reactor divided in two main sections (Fig. 1). The plasma was only generated in the first section [13,20], while the catalyst was placed in both sections (two catalyst beds). All the reactor was thermally insulated with insulation spheres (Liapor, expanded clay). Additional photos and scheme of the reactor setup are provided in the Supporting info (Fig. S1 and S2).

The DBD reactor consisted of two concentric quartz tubes for the implementation of the electrodes. The external tube had an inner diameter (ID) of 18 mm and with 1 mm of thickness, while the internal tube had an outer diameter (OD) of 14 mm and a thickness of 1 mm. The electrodes for the plasma generation were implemented in the first section (1st zone – plasma, Fig. 1). The electrodes were made with two stainless steel meshes with 10 mm of length. The plasma was generated with a power supply (PVM500), applying an AC voltage ($4\text{--}9\ \text{V}_{\text{pk}}$ and 52 kHz) between the two electrodes. The plasma discharge was monitored with an oscilloscope (PicoScope 5444A), and the power was measured with the Lissajous method using a monitoring capacitor.

The catalyst was immobilized with glass wool in the space between the two quartz tubes. A total amount of 0.9 g of catalyst was placed in the reactor. The catalyst was divided into two beds (Fig. 1). The first 0.3 g were placed in the zone where the plasma was generated (first catalyst bed). The remained 0.6 g were placed just after, in the second catalyst bed, only separated by a small quantity of quartz wool from the first bed (<2mm). The separation between catalytic beds ensured that the latest section was not activated by plasma.

Two thermocouples were used to monitor the temperature in the different regions. Temperature in the first section (plasma) was measured by a thermocouple (1.5 mm probe diameter) in contact with the external electrode (T1). At steady-state conditions, the temperature at the external electrode is close to the temperature in the catalyst bed [19], with a difference of <10 °C. Temperature in the second section (thermal) was measured inside the reactor at the end of the catalyst bed (T2) with a thinner thermocouple (0.5 mm probe diameter), providing a faster response.

The methanation reaction was performed with a stoichiometric

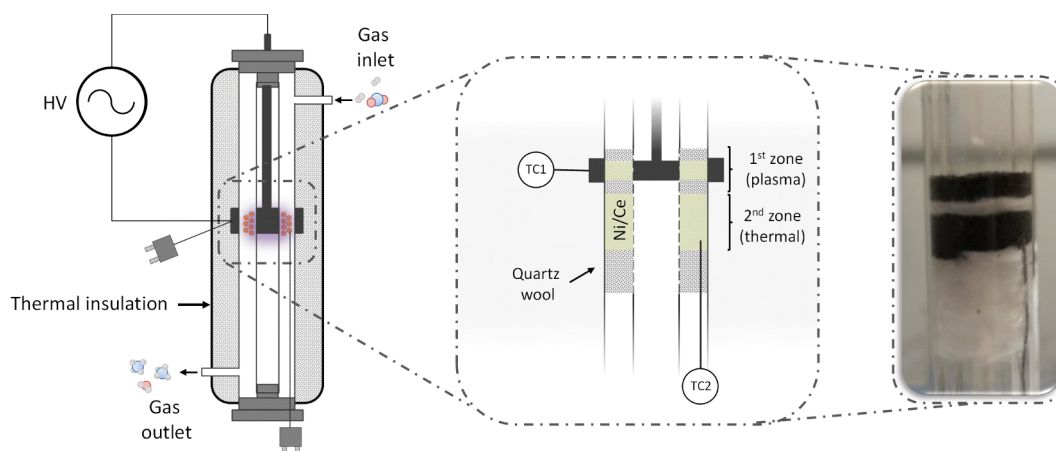


Fig. 1. Hybrid DBD-thermo-catalytic reactor used in plasma ignition experiments.

mixture of $\text{CO}_2/\text{H}_2 = 1:4$ at different gas flow rates, from 200 to 800 $\text{mL}\cdot\text{min}^{-1}$. After water condensation, the dry gas flow was measured using a volumetric flow meter (ADM1000, Agilent) and the products generated were analysed by a micro gas chromatograph (Varian 490 microGC) equipped with one PoraPLOT Q and two Molsieve 5A columns, with Ar and He carrier gases. The oven temperatures were set to 70 °C and 60 °C, for the two Molsieve 5A and the PoraPLOT Q respectively. The microGC was calibrated with several gas cylinders to quantify H_2 , CO_2 , CO, CH_4 and C_2 hydrocarbons. Only CO and CH_4 were detected as reaction products, together with condensed water. Condensate was analysed by GC-FID to check that no other liquid product was produced.

CO_2 conversion (X_{CO_2}), CH_4 selectivity (S_{CH_4}) and CH_4 yield (Y_{CH_4}) were calculated using the following equations:

$$X_{\text{CO}_2} = \frac{n_{\text{CO}_2\text{in}} - n_{\text{CO}_2\text{out}}}{n_{\text{CO}_2\text{in}}} \cdot 100 = \frac{Q_{\text{in}} \cdot [\text{CO}_2]_{\text{in}} - Q_{\text{out}} \cdot [\text{CO}_2]_{\text{out}}}{Q_{\text{in}} \cdot [\text{CO}_2]_{\text{in}}} \cdot 100 \quad (2)$$

$$S_{\text{CH}_4} = \frac{n_{\text{CH}_4\text{out}}}{n_{\text{CH}_4\text{out}} + n_{\text{COout}}} \cdot 100 = \frac{[\text{CH}_4]_{\text{out}}}{[\text{CH}_4]_{\text{out}} + [\text{CO}]_{\text{out}}} \cdot 100 \quad (3)$$

$$Y_{\text{CH}_4} = X_{\text{CO}_2} \cdot S_{\text{CH}_4} \quad (4)$$

where n_z is the number of mols for a given z gas, $[z]$ is the gas concentration and Q is the gas flow.

The energy cost (EC) was defined as the energy supplied to the system per one mole of CH_4 generated:

$$\text{EC}(\text{kJ}\cdot\text{mol}^{-1}) = \frac{P(\text{kW})}{Q_{\text{out}}(\text{L}\cdot\text{s}^{-1}) \cdot [\text{CH}_4]_{\text{out}}} \cdot 24.5(\text{L}\cdot\text{mol}^{-1}) \quad (5)$$

where P is the plasma applied power measured by the Lissajous method [22,23] and Q is the outlet flow.

The energy efficiency was defined as the ratio between the outlet energy after reaction and the energy input (Eq. (6)). The energy input was calculated considering the low heating value (LHV) of the converted hydrogen (242 $\text{kJ}\cdot\text{mol}^{-1}$) and the energy cost (EC). The outlet energy was calculated using LHV of methane (801 $\text{kJ}\cdot\text{mol}^{-1}$), without considering the unreacted hydrogen.

$$\eta(\%) = \frac{E_{\text{out}}(\text{kJ})}{E_{\text{in}}(\text{kJ})} = \frac{\text{LHV}_{\text{CH}_4}(\text{kJ}\cdot\text{mol}^{-1}) \cdot n_{\text{CH}_4}}{\text{LHV}_{\text{H}_2}(\text{kJ}\cdot\text{mol}^{-1}) \cdot n_{\text{H}_2\text{conv}} + \text{EC}(\text{kJ}\cdot\text{mol}^{-1}) \cdot n_{\text{CH}_4}} \quad (6)$$

A theoretical maximum efficiency of 83 % can be obtained when the energy cost is reduced to zero ($\text{EC} = 0$).

3. Results

3.1. Plasma ignition

The hybrid DBD-thermal-catalysis reactor was evaluated in the CO_2 methanation reaction by applying different plasma power over time at the DBD plasma ignition section. Gases were introduced to the reactor at room temperature, being the electrical plasma activation and the heat released from the methanation reaction the sole energy inputs.

The experiments were carried out in three consecutive stages at different plasma power inputs, as seen in Fig. 2. First, plasma power was increased gradually in sequential steps. Second, the plasma power was decreased step-by-step. Third, in the last stage, the plasma was switched off. These three stages are marked as 1, 2 and 3. Fig. 2a shows the temperature profile versus time during the experiment, being T1 the temperature in the plasma activated zone and T2 the temperature in the second catalyst bed section. In Fig. 2b, the obtained CO_2 conversion is represented for the same experiment, performed with a low gas flow of 200 $\text{mL}\cdot\text{min}^{-1}$ of CO_2/H_2 , corresponding to a GHSV of 13,333 $\text{mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$.

As it can be seen, during the first stage, methanation reaction started at 7 W (Fig. 2a) and at the temperature of 170 °C (Fig. 2b). Immediately

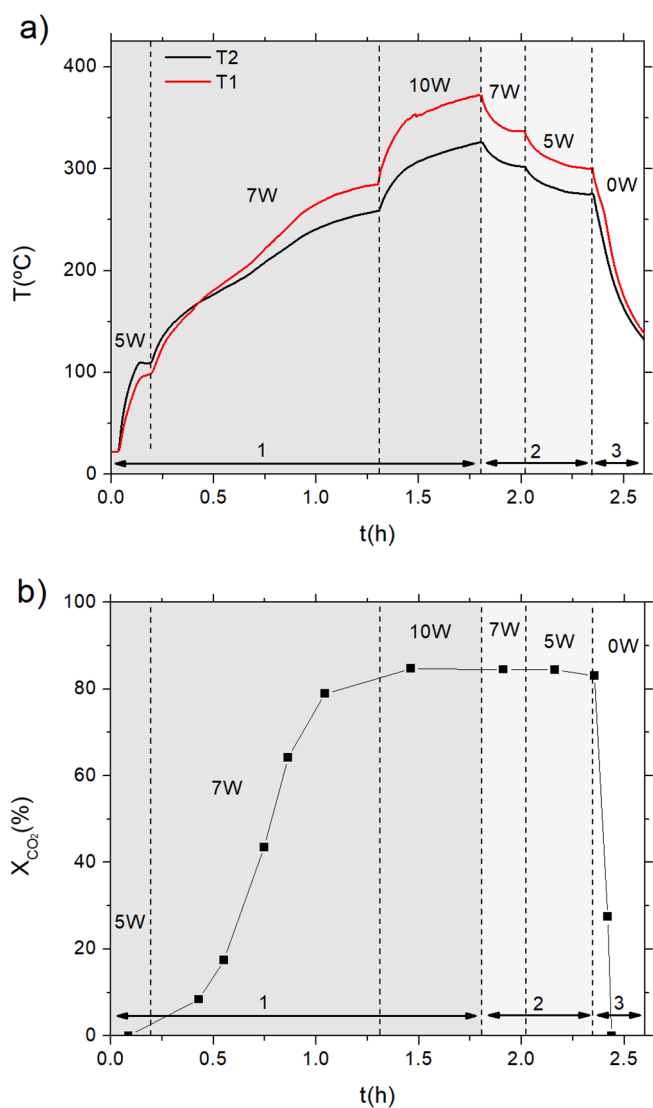


Fig. 2. Plasma ignition experiments at a GHSV of 13,333 $\text{mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. (a) Reactor temperature in the two sections of the reactor: plasma catalytic (T1) and catalytic bed (T2). (b) CO_2 conversion values. Applied plasma power is indicated in the figure.

after, the temperature drastically increased due to the heat released by the methanation reaction, reaching a temperature of 285 °C with a CO_2 conversion of 78% and 99% selectivity to methane. Temperature in the plasma zone (T1) was higher than at the end of the second bed (T2) since heat was produced mainly in the first part of the reaction due to the plasma discharges and the heat released by the reaction. Only during the first minutes of the reaction (5 W), T1 was lower than T2, which was caused by the thermocouple position outside the reactor. Hence, T1 required more time to thermalize and exhibited a slower response than T2 thermocouple. Power was further increased up to 10 W to obtain higher reactor temperature, where the catalyst could be more active by thermal-catalytic routes (350–400 °C). At this power, the temperature reached 360 °C at 10 W while conversion slightly increased to 84 %. The temperature measured at the end of the second bed (T2) was always lower than in the plasma zone, indicating a temperature gradient of 30–40 °C in the reactor. Therefore, a temperature gradient from 370 °C to 325 °C was obtained along the length of the catalyst bed. At these temperatures, the catalyst could be active by thermal route (Fig.S3) in the first and second catalyst bed.

In the second stage, power was reduced in steps; from 10 to 7 W and from 7 to 5 W. Consequently, temperature decreased to 335 °C at 7 W

and 300 °C at 5 W, while conversion and selectivity were practically unchanged. Compared with only thermal activation, higher conversion was obtained at 300 °C (Fig. S3) due to the synergy of plasma and thermal catalysis [20].

In the last stage, the power was completely stopped, conversion and temperature started to drop until the reaction was extinguished entirely. Therefore, the heat released by the methanation reaction was not sufficient to maintain the reaction at $13,333 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$.

In summary, experimental results inferred that DBD plasma section was capable to initiate the chemical reaction and to increase the temperature of the reactor. Plasma started the reaction at a temperature around 170 °C due to the formation of reactive species, mainly excited species (electronic and vibrational), radicals (H, CHO, C, etc.), ions (CO_2^+ , etc.) and other subproducts as CO (from CO_2 electron impact dissociation) [24]. As observed in previous studies, without the use of catalyst, the principal product was CO with a conversion of around 5–10%, while a major reactive species partially reacts back to CO_2 . The combination of catalyst and plasma boost the conversion and the selectivity to the desired product (CH_4). The reactive species generated by the plasma lower the energy barrier allowing it to ignite the reaction at a lower temperature.

After plasma ignition, the temperature was significantly increased due to the heat released by the methanation reaction. Furthermore, under the conditions achieved, the catalyst was active in the second section of the reactor, as heat released by the methanation reaction increased temperature above 300 °C. The activation of the second section increased the conversion up to 84 %, higher values than the obtained in experiments performed with a single plasma section (obtaining values 75–80 % see Figure S7). Although all the catalyst was active, more reaction heat was generated in the initial part of the reactor, as larger conversion occurred in the first bed. A decreasing temperature gradient was always observed along the reactor, indicating that some of the generated heat was lost despite the thermal insulation. Thus, temperatures were always lower at the second catalyst bed.

The synergies between the different reactor zones were successfully validated. The reaction can be ignited only using the first part of the reactor, increasing reactor temperature and activating the second catalyst bed, which boosts conversion values. However, the reaction stopped as soon as the plasma was shut-off as the heat released by the reaction was not enough to self-sustain the system, suggesting that, at those conditions, plasma power could be reduced but not avoided.

The plasma ignition experiments showed that during plasma operation, the benefits were the reduction of the power after the activation of the thermal bed and the synergy between plasma and thermal activation. In the best conditions, the energy consumption was reduced by 30% compared to solely plasma-catalysis (from 7 W to 5 W) with an energy cost of $219 \text{ kJ}\cdot\text{mol}_{\text{CH}_4}^{-1}$, which corresponds to an energy efficiency of 68%.

3.2. Reaching autothermal operation

In view of the previous results, higher amount of heat is required to self-sustain the reaction without external power. For a gas flow of $600 \text{ mL}\cdot\text{min}^{-1}$ (GHSV of $40,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) results followed a similar initial trend, the reaction started at 7 W with temperature close to 170 °C (Fig. 3a and Fig. 3b). However, as the reaction took place, the temperature rose to 450 °C, with a notable difference of almost 200 °C more than the results obtained at $200 \text{ mL}\cdot\text{min}^{-1}$. A direct relation of temperature with the total gas flow was observed, as the heat released by the methanation increased proportionally to the gas flow. The results are in agreement with the previous publications in thermal CO_2 methanation [25] and CO_2 plasma methanation [19], where higher reactor temperatures are obtained at higher gas flow. In this case, a temperature gradient from 450 °C to 330 °C was achieved along the reactor (T1 and T2). Regarding the activity values, 76% of conversion and 99% of selectivity were obtained.

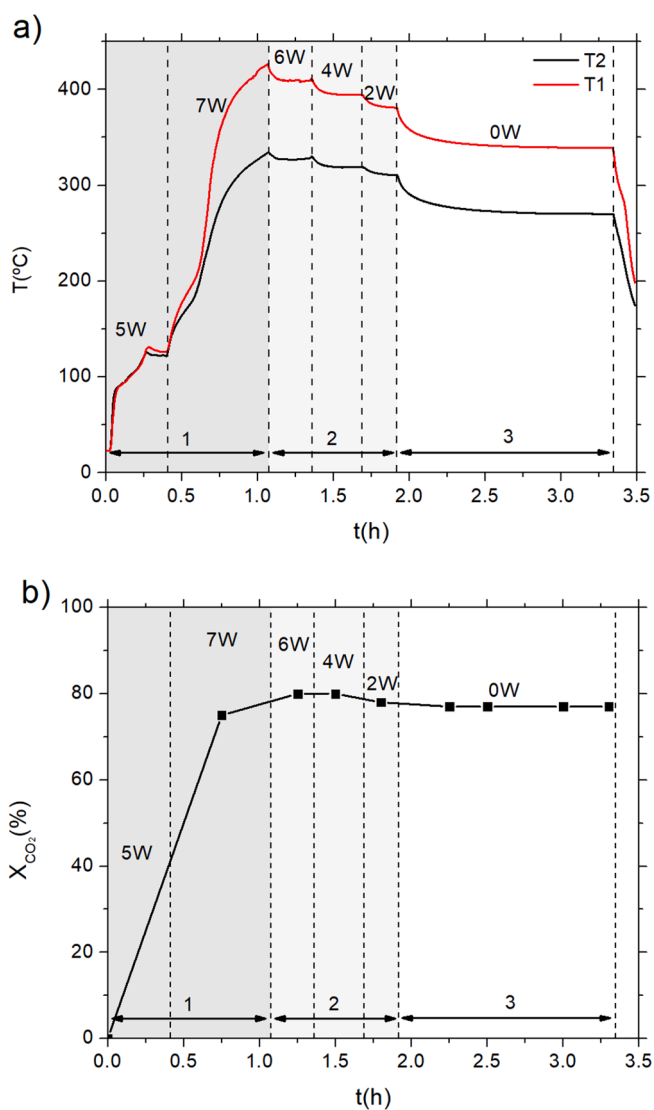


Fig. 3. Plasma ignition experiments at GHSV at $40,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. (a) Reactor temperature in the two sections of the reactor: plasma catalytic (T1) and catalytic bed (T2) (b) CO_2 conversion values. Applied plasma power is indicated in the figure.

In the second stage, temperatures started to decrease when the power was reduced due to less heat was generated by the plasma. For 6 W, 4 W and 2 W, stable conditions with 79–78% of conversion and temperature higher than 350 °C were obtained. Finally, the applied plasma power was completely stopped and the temperature was stabilized at 337 °C with 77% of conversion and 99% of selectivity. The reactor temperature was maintained between 337 and 270 °C along the reactor (T1 and T2). Remarkably, self-sustained conditions were obtained for more than 1 h without any external energy input since the heat generated by the reaction was enough to keep the reactor temperature. Therefore, the concept of using DBD plasma as reactor ignitor was experimentally validated at those specific conditions of gas flow rate. From these experiments, it is inferred that the amount of gas flow rate, and therefore the amount of heat released, should be adjusted to balance heat losses in the present device.

After one hour, the reaction was intentionally stopped decreasing the gas flow from 600 to $200 \text{ mL}\cdot\text{min}^{-1}$, resulting in the reactor cool down. The temperature was dropped by the lower amount of heat released and, consequently, the conversion stopped in line with the previous experiment. The employed cool-down procedure also demonstrated that a

minimum flow of CO_2/H_2 is needed to work in autothermal conditions.

The limitation of the gas flow to obtain autothermal methanation was further confirmed by a complementary experiment performed with a gas flow of $400 \text{ mL}\cdot\text{min}^{-1}$ (Fig. S5). Self-sustained conditions were not obtained in this case after the plasma was shut-down. Therefore, using a $600 \text{ mL}\cdot\text{min}^{-1}$ flow seems to be adequate to reach the self-sustained condition in our reactor. On the other hand, working at even higher flow ($900 \text{ mL}\cdot\text{min}^{-1}$; $60,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) autothermal condition was achieved (Fig. S6). However higher temperatures were obtained (390°C) without reaching stable values, since after 1 h the reactor was warming up at a rate of $0.3^\circ\text{C}\cdot\text{min}^{-1}$. Under these conditions, a cooling element will be needed to achieve a continuous operation, which is out of the scope of this work. In view of these results, autothermal conditions are highly dependent on the gas flow, with a specific minimum flow. The gas flow increases the only source of heat to the system (reaction). The ratio between the heat source (reaction) and heat losses (gas heating and reactor heat losses) needs to be adjusted to obtain the optimum temperature range to perform the reaction (Table S2).

Therefore, it has been demonstrated that the reactor temperature and conversion can be adjusted by varying the total inlet gas flow in autothermal conditions.

The stability of autothermal methanation after plasma ignition was validated with a long-time experiment. Fig. 4 shows the temperature obtained during the experiment. The reaction was ignited at 10 W of applied plasma power until reaching 450°C and just after the plasma was turned off (t_1). The autothermal condition was achieved for almost 8 h of continuous operation. The conversions were stable during the self-sustained operation with CO_2 conversion values near 76–77% and a selectivity of 99%. In autothermal conditions, the energy efficiency reached the maximum value of 83%, as the energy cost was reduced to zero. After 8 h, the reaction was intentionally stopped by decreasing the CO_2/H_2 flow (t_{off}). This proof-of-concept experiment demonstrated the feasibility of continuous autothermal operation after the plasma ignition.

3.3. Fast and efficient operation

In the previous section, plasma has been presented as an ignitor, demonstrating the possibility to obtain self-sustained methanation in autothermal conditions. The use of plasma as an ignitor could be an efficient process if start-up time and power are low enough. In this section, the optimization of energy consumption and start-up time is presented. The experiments were done at the optimum GHSV of $40,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$.

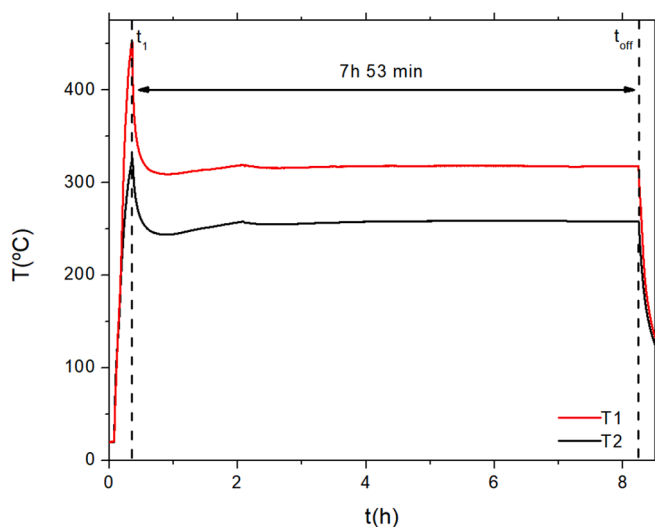


Fig. 4. Autothermal experiments at GHSV of $40,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ during ~ 8 h, from t_1 to t_{off} (cool-down).

$\text{mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which was needed to work under autothermal conditions. The following experiments were done in one step ignition at constant power during the minimum time required to activate the reaction and reach temperature to assure that the reaction was self-sustained. Thus, 450°C was set as a target to ensure that reaction could be continued by thermal-catalysis and to avoid thermal degradation of the catalyst (limiting higher temperatures above 450°C).

Fig. 5 shows the results obtained applying 7 W, 10 W and 15 W. The results were similar to those of the previous section, starting conversion at a temperature below 200°C . For the lowest power (7 W), it took almost more than 20 min (t_0) to obtain higher conversions (t_0 , $X_{\text{CO}_2} \sim 70\%$). In addition, the higher temperature required to maintain the autothermal conditions were not reached in <40 min (t_1). At this time, plasma was shut-off (t_1) and autothermal conditions were achieved. The experiment was finished at t_{off} by decreasing the inlet flow (in a similar way to the previous section).

In the case of 10 W, start-up time was reduced to 7.9 min and the power was stopped after 17 min. More importantly, the total energy required to activate the reaction was substantially reduced from 17.8 to 10.4 kJ, as less time was needed. Thus, a significant reduction in the start-up time and total energy was obtained by increasing the power supplied. Following the same procedure as the 7 W ignition, the experiment was finished manually at t_{off} by decreasing the inlet flow.

On the other hand, higher power was counterproductive to obtain

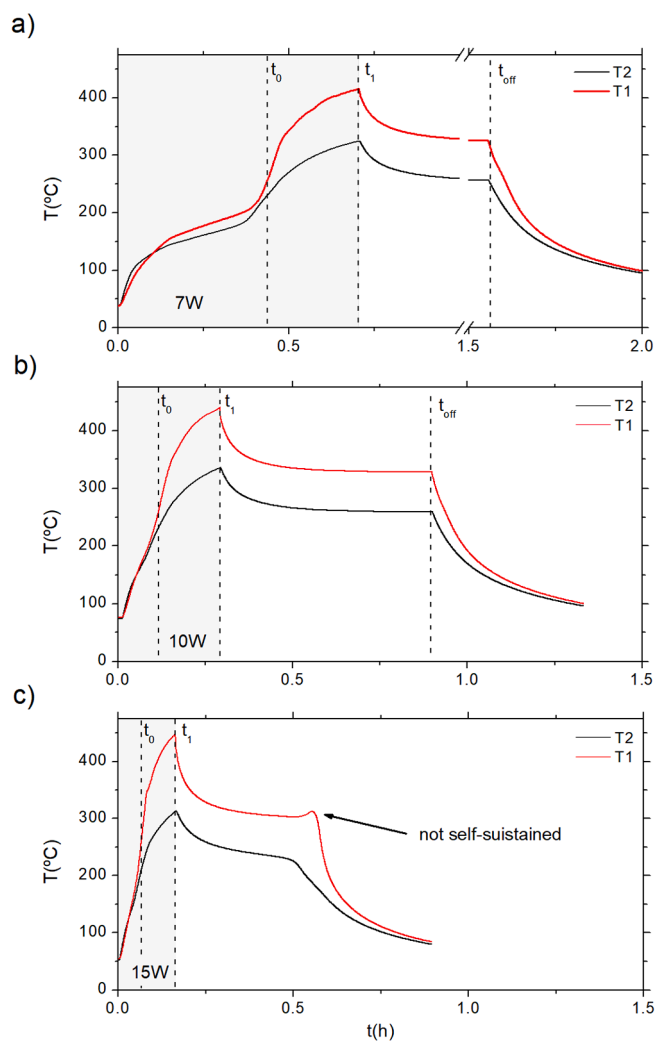


Fig. 5. Experiments done at GHSV of $40,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for three different applied power. a) 7 W b) 10 W c) 15 W. t_0 is the start-up time ($X \sim 70\%$), t_1 is the plasma shut-off time and t_{off} are the cool-down time.

self-sustained conditions in one activation step. For 15 W, autothermal conditions were initially achieved for 20 min after plasma shut-off. However, conditions were not stable; the temperature decreased continuously, and the reaction was no longer self-sustained after 20 min. At this point, it was observed a drastic drop in temperature as conversion dropped. Therefore, the results indicate that the reaction heat could not maintain the reactor temperature. The negative feedback between temperature and conversion caused the reaction to shut down (as the temperature decreases, the conversion also drops, decreasing the released heat and, consequently, the temperature further decreases).

The temperature along the reactor, start-up time, plasma-off time and energy consumption for the three experiments are summarized in Table 1. A proportional decrease of t_0 , t_1 , E as a function of the applied power can be clearly observed. In addition, the difference of temperature along the reactor (ΔT) increased for a higher power. In fact, ΔT would be directly related to the limitation to achieve autothermal conditions at higher power (15 W).

At the highest applied power, the overall reactor temperature was not sufficiently high when the power was stopped. This can be clearly observed in the second catalyst bed temperature (T2), where the values were lower than in the other cases. Just before the plasma was shut-off ($t \sim t_1$), the reactor was hotter in the plasma zone but colder in the rest of the reactor zones (compared with the other cases, 7 W and 10 W). After plasma shut-off ($t > t_1$), temperature decreased faster as heat was dissipated faster to the colder zones. The final temperature (at $t \sim 30$ min) was not sufficient to self-sustain the reaction.

This can be clearly seen at the temperature achieved during self-sustained conditions, just previous to the stop of the reaction (t_{off}). The temperature was considerably lower for 15 W compared to 10 and 7 W (302 vs 328–325 °C). Therefore, temperature was not enough to self-sustain the reaction during autothermal conditions at 15 W.

The limitation seems to be the reactor thermal inertia, as temperature at plasma zone increased too quickly, but the overall reactor was colder. Consequently, the heat was dissipated to the rest of the reactor, decreasing the overall temperature during the autothermal operation.

Despite the results obtained and considering that the reactor inertia seems to be the limitation to obtain self-sustained conditions, a different approach can be applied to use higher power and decrease the start-up time. In this sense, we proposed to add a second step with a lower power after the first plasma ignition to maintain a higher temperature. In this way, the first ignition step would be done at higher power to obtain faster start-up time, while a second plasma activation step would be done at lower power with the objective to ensure that temperature along the reactor was high enough to maintain the reaction.

2-steps experiments were done at 15 W and 20 W (Fig. S8 and Fig. S9). The best results, in terms of start-up time and energy, were obtained for 20 W with a second step applying 5 W for 8.5 min (Fig. 6). A start-up time of only 3 min from cold conditions (25 °C) was obtained with a total energy consumption of 9.5 kJ (2.6 Wh).

Finally, after plasma ignition experiments, catalysts were characterized by XRD and N_2 physisorption in order to study the possible structure modification during ignition experiment. The used catalyst was compared with the fresh catalyst (Fig.S10 and Table S1). Few differences were found with the fresh catalyst, indicating that fast plasma ignition

Table 1
Summary of results of experiments done at different power.

P (W)	Start-up t_0 (min)	Plasma-off t_1 (min)	T1 (°C) at t_1	T2 (°C) at t_1	ΔT at t_1	T1 (°C) at t_{off}	T2 (°C) at t_{off}	E (kJ)
7	26.5	42.3	415	325	90	325	256	17.8
10	6.7	17.4	438	335	103	328	259	10.4
15	3.9	9.8	447	312	135	302*	225*	8.8

*For 15 W experiments, T1 and T2 were measured at $t \sim 30$ min since the reaction was not self-sustained.

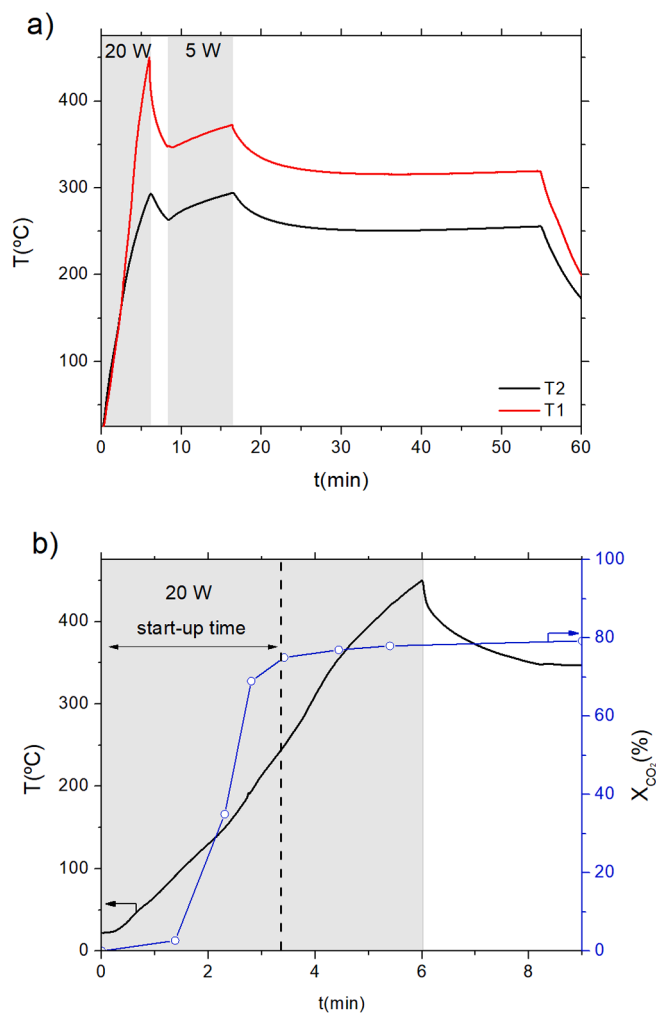


Fig. 6. Experiments done at GHSV of $40,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ applying 20 W and second step of 5 W (a) Temperature vs time (b) Temperature and conversion vs time during the start-up.

can slightly modify the catalyst. This can be caused by the plasma modification of the catalyst and the temperature gradient during plasma ignition. Although, no difference in the activity was observed.

3.4. Discussion

The presented hybrid plasma-thermo catalytic reactor allowed to ignite the reaction at lower temperature (170 °C) due to the plasma activation of CO_2/H_2 into energetically reactive species. After plasma ignition, the temperature increased due to the heat released by the methanation reaction. The adiabatic configuration allowed to reach temperatures where the catalyst can be activated by thermal-catalysis. Thus, a second catalyst bed was activated, increasing the reactor performance. In the right conditions, reactions were self-sustained in autothermal operation after the plasma was shut-off.

The start-up time and energy consumption during plasma ignition have been optimized. Our results show extremely short times (3 min) compared with thermal reactors, which usually have higher start-up times when the reaction starts from cold conditions (30 min) [25]. Although most studies typically reported start-up time from warm or hot standby conditions, where reactors are kept at moderate temperatures (e.g. 250 °C). Faster times in the range of 3 to 30 min have been reported for start-up from warm conditions [3,25,26]. In comparison, plasma ignition showed a similar start-up time, but with the difference that no warm conditions or hot standby were required, simplifying the reactor

engineering and energy consumption during standby.

On the other hand, the time obtained was sufficient to integrate with the other sub-systems of PtG, as electrolyzers. For example, commercial alkaline electrolyzers have a similar start-up time near 1–2 min. For other types of electrolyzers, such as polymer electrolyte membrane (PEM), faster start-up times in the range of second are reported [27], also leaving space for improvement of start-up in methanation units. The reduction in the start-up time is also important to decrease the hydrogen consumption during start-up, as generally, hydrogen is fed into the reactor to avoid carbon deposition during start-up and shut-down cycles [28].

In summary, by igniting the reaction with plasma, an extremely short start-up time was achieved facilitating the flexibility of this technology when coupled to a renewable energy source, reducing the inertia of thermal catalysis. Two main advantages arise from plasma ignition methanation. On the one hand, the low activation temperature in plasma-catalysis (<200 °C) reduces the time to start the reaction. On the other hand, plasma heats the reactor up to 100 – 200 °C (without reaction). As part of the heat is produced directly in the gas by the plasma, the temperature can be increased faster and more efficiently than using external heaters. The presented methodology could also be applied to other exothermic reactions that are capable of operating under auto-thermal conditions.

Although the results show an interesting approach to combine plasma and thermal reactors, further research is necessary to obtain the required quality of the synthetic natural gas that could be injected into the gas grid (PtG tech.). The main limitation would be the low content of hydrogen allowed to be injected into the gas grid. The use of plasma as an ignitor or the entire combination of plasma and thermal reactor could help to achieve the requirements. In this regard and inspired in thermal reactor, work at higher pressure could increase the CH₄ yield. Recently, the effect of pressure in plasma methanation reaction was reported, where the slight increase in pressure did not negatively affect the plasma activation and higher conversion was obtained [29]. Exploring the limit of pressure in DBD are recommended. On the other hand, increasing the total conversion by combining reactors in series seems to be mandatory for plasma-catalysis, following a similar approach to thermal methanation [30]. The effect of the different gas composition, as CH₄, should be investigated in conventional plasma assisted and plasma ignition configuration. Once the required composition is obtained, the scale-up should not be an impediment, it could be implemented with multiple unit cells, in a multi-tubular configuration.

4. Conclusions

A new methodology of plasma CO₂ methanation was presented where plasma was used to ignite the reaction. Under this condition, a minimum GHSV of 40,000 mL·g⁻¹·h⁻¹ was found to be necessary in order to obtain autothermal condition after plasma ignition. In auto-thermal operation, the reaction continued without any energy input (neither plasma nor external heating), only self-sustained by the own heat generated by the methanation reaction. Autothermal condition was demonstrated with a long-time experiment in which a stable performance was achieved for more than 8 h. Finally, the ignition procedure was optimized in order to reduce the total energy and obtain the faster start-up possible in our system. In the best conditions, the total energy consumption was 10.4 kJ to ignite the reaction in one step-ignition and reach autothermal conditions. Regarding start-up times, the faster ignition was achieved in two steps ignition with a remarkably fast time of only 3 min, starting from cold condition (25 °C), and with an energy consumption of only 9.5 kJ. Thus, plasma ignition has been demonstrated to be an interesting option with faster start-up time and low energy consumption. In this regard, the main advantages to using plasma as ignition are: 1) the reduction of the threshold temperature in plasma methanation 2) faster heating as heat is generated inside the reactor due to plasma power losses and heat released by the reaction.

That permits to reduce start-up time from cold conditions up to 3 min which is a key factor when coupling a chemical reaction with electrical energy from intermittent renewable sources.

The concept herein demonstrated could be applied to other exothermic reaction, using plasma as an ignitor of reactions that could be self-sustained. On the other side, this methodology could be integrated into thermal reactor, accelerating the starting reaction by plasma that continues in thermal catalysis or in a plasma-assisted thermal catalytic reactor. The result of the work could help to move towards reactor electrification, improving the versatility and control of the reaction.

CRediT authorship contribution statement

Martí Biset-Peiró: Investigation, Visualization, Writing – original draft. **Jordi Guilera:** Conceptualization, Writing – review & editing. **Teresa Andreu:** Conceptualization, Supervision, Writing – review & editing, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2021.133638>.

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