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Plasma-based conversion of CO_2 and CH_4 into syngas: A dive into the effect of adding water

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A R T I C L E I N F O	A B S T R A C T
Keywords: Plasma Bi-reforming of methane Atmospheric pressure glow discharge Hydrogen-rich syngas	Plasma technology can play a vital role in the electrification and decarbonization of chemical processes. In this work, we carried out the bi-reforming of methane (BRM), producing syngas out of H ₂ O vapor and the greenhouse gases CO ₂ and CH ₄ , in an atmospheric pressure glow discharge reactor. Compared to dry reforming of methane (DRM), the addition of H ₂ O helps in counteracting soot formation, and thus avoids severe destabilization of the generated plasma. A mixture of 14–41-45 vol% (CO ₂ -CH ₄ -H ₂ O) leads to the overall best results in terms of stable plasma and performance metrics. We obtained a CO ₂ and CH ₄ conversion of 49 % and 74 %, respectively, at a SEI of 210 kJ/mol. The energy cost is 390 kJ/mol converted reactants, which is below the target defined for plasma-based syngas production to be competitive with other technologies. Moreover, we reached CO and H ₂ yields of

59 % and 49 %, and a syngas ratio (SR) of 2, which is ideal for further methanol synthesis.

1. Introduction

To reduce CO₂ emissions originating from human activity, several avenues for CO₂ capture have been established over the last decades. However, capture and storage alone still represents a significant and costly endeavor for industry. Carbon capture and utilization (CCU) technologies try to close the carbon loop, while also providing an economic opportunity, by direct utilization of CO₂ in a number of applications (e.g. as an ingredient of foaming agents, fire extinguishers, soft drinks, etc.) or by transforming the captured CO₂ into valuable chemicals or high energy density fuels [1-3].

A CO₂ conversion technology that has received increasing interest in the last decades is plasma technology [4,5]. Plasma is an ionized gas that consists of many reactive species, such as radicals, free electrons, ions, atoms and molecules, in ground and excited states. Even at ambient conditions, it provides a suitable environment for the conversion of highly stable molecules (like CO₂) into value-added chemicals. Compared to a traditional reactor where the process is driven by thermal catalysis, plasma reactor technology has several advantages: [4,6,7] (i) it operates on electricity, (ii) unlike thermal catalysis with relatively high inertia, temperatures of 2000–3000 K are reached nearly immediately upon ignition and (iii) it can be operated at atmospheric pressure without the need of high pressure equipment and associated energy costs. This makes plasma technology ideal to be coupled to a renewable energy network, which provides a fluctuating energy profile [4,5]. Overall, a high flexibility and modularity are considered as the main advantages of plasma technology for chemical production [7].

Plasma technology has already been applied to several CO_2 conversion processes over the past few years [4,5], including pure CO_2 splitting [8–17], dry reforming of methane (DRM) [18–31] and CO_2 hydrogenation [32–35]. Specifically, DRM has shown to be promising due to (i) the combined conversion of CO_2 and CH_4 , the two main greenhouse gases [26], (ii) the ability to use a biogas mixture (originating from e.g. agricultural waste) as feedstock [28,31,36], and (iii) the possibility to produce high-value chemicals and/or fuels – either as liquid products directly [24,29], or as syngas [18–29,36], which is further processed into other valuable products in a later stage.

One of the more valuable chemicals that can be produced from syngas is methanol, which is both a liquid fuel and a hydrogen carrier, and many other chemicals and products can be derived from it [37]. However, to produce methanol from syngas, a H₂/CO ratio of 2 is typically required [38]. To achieve this ratio through DRM, the CH₄/CO₂ ratio in the feed gas must be well above 1 [26]. Unfortunately, this typically leads to extensive soot formation [26,30], creating an unstable plasma, and lowering the performance of the highly endothermic DRM.

In order to overcome this issue, an additional reactant can be added, which is more effective than CO_2 in preventing extensive soot formation. Adding O_2 is possible – leading to oxidative CO_2 reforming of methane

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Received 23 March 2024; Received in revised form 17 May 2024; Accepted 25 June 2024 Available online 15 July 2024 0016-2361/© 2024 Elsevier Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies. (OCRM), which has syngas as main product [39], or in some cases produce oxygenates as well [29]. In fact, a small fraction of O_2 is usually also present in raw biogas mixtures [36]. However, in our earlier studies, also performed in an atmospheric pressure glow discharge (APGD), the highest syngas ratio (SR, i.e. H₂/CO ratio) without extensive carbon deposition was at best around the same level as the one obtained without additional O_2 [39]. Another possibility is the addition of H₂O, promoting the steam reforming of methane (SRM, CH₄ conversion with H₂O) which, combined with CO₂, leads to the so-called bireforming of methane (BRM):

$$CO_{2(g)} + 2 H_2O_{(l)} + 3 CH_{4(g)} \rightleftharpoons 4 CO_{(g)} + 8 H_{2(g)}$$

In literature, BRM is already described extensively by means of thermal catalysis [36,40–43], but also for various plasma types, such as a microwave (MW) [44–46], dielectric barrier discharge (DBD) [47] or gliding arc (GA) [48,49] reactor, and clearly holds promise. On one hand, H_2O addition can efficiently prevent soot formation [36,44,45,47–51]. On the other hand, H_2O acts as an additional source for H_2 , next to CH₄, so it is easier to obtain a SR close to 2 [36,46,48,49,52]. This means that, when coupled to a methanol synthesis reactor further downstream, plasma-based BRM can produce methanol, in contrast to plasma-based DRM or OCRM, where an additional external supply of H_2 (from e.g. H_2O electrolysis) would be required [53]. In addition, some amount of H_2O is also present in certain raw biogas mixtures [36].

To our knowledge, plasma-based BRM has not yet been studied in an APGD reactor. In previous work, we concluded that a confined APGD is a promising type of plasma reactor for CO_2 splitting [17], DRM [26] and OCRM [39], considering the high conversions that can be obtained, while keeping a rather low energy cost (EC). However, at the optimal conditions for DRM and OCRM, the SR was so far limited to ca. 0.7, and further increasing the input fraction of CH₄ yielded too much soot, negatively affecting the plasma stability. In the present work, we therefore investigate the performance of BRM, in an upgraded version of the APGD, specifically focusing on reactant conversion, syngas yield, SR, EC and energy efficiency (EE), as well as comparison with the state-of-the-art.

2. Methods

2.1. Experimental setup

An overview of the experimental setup is presented in Fig. 1. CH₄ and CO2 (both 99.9 vol%) were purchased from Air Liquide, and the flow rates of both gases are regulated through Bronkhorst thermal mass flow controllers. Both gases are mixed with de-ionized water before entering the reactor. The H₂O container is heated by a silicon oil bath positioned over a hotplate stirrer (IKA RCT basic). The exact flow rate of H₂O vapor (and hence its input fraction) is regulated through keeping the oil bath at a specific temperature. The calculations for the flow rates of H₂O vapor (in mol/min) are provided in the SI (section S1). For each selected oil bath and H₂O vapor temperature, the stainless steel gas line between the H₂O container and the reactor inlet is heated up to a temperature approx. 10 °C higher than the oil bath temperature to avoid condensation of H₂O and to allow the introduction of a homogeneous CO₂-CH₄-H₂O gas mixture into the plasma. This is also why we refer to the H₂O input as "vapor", and not as "steam": no heterogeneous H₂O droplets enter the plasma reactor. The output gas mixture is led into a cold trap and carbon filter before entering a heated sample gas line, connected to an Agilent two-channel 990 MicroGC, which is used for analysis of the dry gas mixture.

A current-controlled high voltage DC Technix power supply unit (PSU), capable of supplying max. 20 kV and 150 mA (=3 kW), is used to deliver power to the plasma. In order to limit and stabilize the current, ballast resistors (with a net resistance of 100 kOhm) are put between the PSU and the cathode pin in the plasma reactor. The power deposited in the plasma is derived by subtracting the power lost through the ballast resistors from the power delivered by the PSU [17,26,39]. The glow discharge plasma is ignited between the stainless steel cathode pin and anode plate, connected to the grounded reactor body, which is schematically and photographically presented in Fig. 2.

The reactor used in this study is an upgraded version of the reactor previously described by Wanten et al. [26] and Maerivoet et al. [39] While the concept of the design itself is not significantly altered, there is an important change that can improve the reactor performance. Indeed, the stainless steel cathode pin is now connected to a remotely controlled stepper motor, allowing the cathode to be moved in the axial direction closer to or further away from the anode plate, even while the plasma is already ignited. As a consequence, plasma ignition can take place very easily at reduced inter-electrode distances, and subsequently the



Fig. 1. Overview of the experimental setup. Gas lines are represented by blue (around room temperature) and red (heated) arrows, thick black lines represent HV and ground cables. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. Schematic (left + middle) and photographic (right) representation of the APGD plasma reactor used in this study. Important reactor parts are indicated.

electrodes can be moved further apart, to obtain a longer (desired) discharge length (and higher plasma power). Ultimately, this eliminates the need to have a separate ignition sequence.

2.2. Experimental procedure and performance metrics

We kept the total input flow rate constant at 3 Ls/min (using the Bronkhorst definition for standard conditions, i.e., 1 atm and 20 °C) and the plasma power at 300 W. Initially the plasma is ignited for pure CO_2 and the oil bath surrounding the H₂O container is set to a temperature corresponding to a specific H₂O vapor flow rate (75, 85 and 95 °C – the relationship between temperature and H₂O vapor flow rate is derived and presented in the SI, section S1). Once this temperature is reached, CH₄ is added. At this point, the CO₂ and CH₄ flow rates are arranged through separate MFCs to obtain various CO₂/CH₄ ratios (13:7, 1:1, 7:13 and 1:3). This leads to 12 different mixtures, presented in Table 1. For each stable condition (the stability of the mixtures will be further elaborated in section 3.1), four GC samples are taken, with the first sample taken 2–3 min after the input mixture, power and flow rate are set, and further after 3.5 min runtime between each sample. For each GC sample, we recorded the voltage, current and oil bath temperature. This procedure is repeated three times in total for each condition, and the results presented in section 3 are the weighted averages for each condition.

The formulas to calculate the performance metrics are presented in Table 2. The input molar flow rates \dot{n}^{in} are controlled through the MFC's for CO₂ and CH₄ and the oil bath temperature for H₂O. The output molar flow rates \dot{n}^{out} are derived through the molar fractions associated to each species measured through the GC samples on one hand, and the total output molar flow rate on the other hand. The latter can be derived from the carbon balance, and this approach was validated by comparison with measurements done with a soap film flow meter. More information on the derivation of the output molar flow rates of all species can be found in the SI (section S2).

The input power $\ensuremath{P_{input}}$ is derived through the following equations:

$$\begin{split} P_{input} &= P_{plasma} + P_{H_2O \ evap.} \\ P_{plasma} &= I \cdot V_{PSU} - R_{resistor} \cdot I^2 \\ P_{H_2O \ evap.} &= \frac{\dot{n}_{H_2O}^{input} \cdot HHV_{H_2O_{(g)}}}{60 \ s \ min^{-1}} \end{split}$$

The plasma power P_{plasma} (W) is derived through the applied current I (A), the voltage provided by the power supply unit V_{PSU} (V), and the resistance of the ballast resistor $R_{resistor}$ (Ω). Since H_2O is introduced in the reactor as H_2O vapor, we also include $P_{H_2O \text{ evap}}$. (W), i.e. the minimum power required to fully evaporate H_2O to afford the desired input flow rate of H_2O ($n_{H_2O}^{in}$). HHV_{$H_2O_{(g)}$} stands for the higher heating value of H_2O vapor, or also the latent heat of vaporization, equal to 44.2 kJ/mol [54].

3. Results & discussion

3.1. Soot formation & plasma stability

As mentioned in the introduction, soot formation can have a significant effect on the plasma stability and overall performance. To demonstrate this, we show the plasma power as function of time for a 55–45 CO_2 -CH₄ input mixture, without any additional H₂O as a reactant, and for a 32–32-36 CO_2 -CH₄-H₂O input mixture in Fig. 3.

For a 55–45 CO_2 -CH₄ input mixture, after approximately 5 min, the plasma drops to almost one third of its initial value. The reason for this behavior is the effect that the soot formation has on the plasma voltage, and consequently the plasma power. Specifically, because soot particles are conductive, their formation and accumulation between the two electrodes leads to a decrease in voltage, thus decreasing the power deposited in the plasma. Since this leads to a lower temperature, at which soot formation is favored [36], this negative effect will only

Table 1

Overview of 12 different mixtures tested experimentally, obtained through combining four different CO₂:CH₄ ratios and three different H₂O temperatures.

		CO2:CH4 ratio										
		65:35 (1.86)	50:50 (1.00)	35:65 (0.54)	25:75 (0.33)							
		CO ₂ -CH ₄ -H ₂ O mixture (vol%)										
Liquid H ₂ O	75	47-25-28	36-36-28	25-47-28	18-54-28							
temperature	85	42-22-36	32-32-36	22-42-36	16-48-36							
(°C)	95	36-19-45	27.5-27.5-45	19-36-45	14-41-45							

Table 2

Description of performance metrics used to analyze the experimental data, incl. associated symbol, unit and formula. The molar flow rates $\dot{n}_{i/j}^{i, out}$ are expressed in mmol/min, the input power P_{input} is expressed in W. In the formula to calculate the yield of product j, μ_i^a and μ_j^a are the stoichiometric coefficients of atom a in molecule i and j, respectively. The higher heating values HHVs for all reactants and products are expressed in kJ/mol and are taken from literature [54].

Performance metric	Symbol or abbreviation	Unit	Formula
Conversion of reactant i	Xi	%	$\frac{\dot{n}_{i}^{converted}}{\dot{n}_{i}^{in}} \cdot 100 \%$
Conversion rate of reactant i	$\dot{n}_i^{converted}$	mmol/min	h _i in - h _i out
Production rate of product j	$\dot{n}_{i}^{produced}$	mmol/min	n _j ^{out}
Yield of product j	Ya	%	$\frac{\mu_{j}^{a}\cdot\dot{n}_{j}^{produced}}{\sum_{i}(\mu_{i}^{a}\cdot\dot{n}_{i}^{in})}\cdot100~\%$
Syngas ratio (H₂:CO)	SR	-	$\frac{\dot{n}_{H_2}^{produced}}{\dot{n}_{CO}^{produced}}$
Conversion-based energy cost	ΕC _χ	kJ/mol	$\frac{P_{input} \cdot 60 \ s \ min^{-1}}{\sum_{i} \dot{n}_{i}^{converted}}$
Syngas-based energy cost	EC _{SG}	kJ/mol	$\frac{P_{input} \cdot 60 \ s \ min^{-1}}{\dot{n}_{H_2}^{produced} + \dot{n}_{CO}^{produced}}$
Energy efficiency	EE	%	$\frac{\sum_{j} (\dot{n}_{j}^{\text{produced}} \cdot \text{HHV}_{j}) \cdot 100 \%}{(P_{\text{input}} \cdot 60 \text{ s min}^{-1}) + \sum_{i} (\dot{n}_{i}^{\text{converted}} \cdot \text{HHV}_{i})}$



Fig. 3. Plasma power as a function of time for a 55–45 CO_2 -CH₄ input mixture, where the effect of soot formation on the plasma power is clearly visible and for a 32–32-36 CO_2 -CH₄-H₂O input mixture, where no significant soot formation and a stable plasma power is observed. Total input flow rate and initial plasma power are 3 Ls/min and 300 W, respectively.

enforce itself. The slight fluctuations observed afterwards are likely due to growing soot clusters, which at some point break into smaller particles, temporarily increasing the voltage, after which the process repeats itself [39]. In Fig. 4 we present a picture of the reactor's glass tube after this measurement, where the glass wall of the side after the anode is covered with soot. Illustratively, at the same (initial) conditions for a 32-32-36 CO₂-CH₄-H₂O mixture, no significant soot formation was observed. In this case, the plasma power remains very stable around the



Fig. 4. Picture of APGD reactor's glass tube after the measurement, with a $55-45 \text{ CO}_2$ -CH₄ input mixture at 3 Ls/min and 300 W. The glass wall at the side after the anode, where the gas exits the plasma, is covered with soot.

initial value of 300 W.

This significant change in plasma power will affect the performance metrics severely. The CO₂, CH₄ and H₂O conversion, as well as the CO and H₂ yield, are presented as a function of time for a 32-32-36 CO₂-CH₄-H₂O input mixture in Fig. 5a, and for a 55-45 CO₂-CH₄ mixture in Fig. 5b. The total input flow rate and (initial) plasma power are 3 Ls/min and 300 W, respectively. The GC measurements with water started three minutes after the oil bath temperature, power and flow rate were set, as described in section 2.2. The GC measurements without water started as soon as the plasma was ignited.

Fig. 5a shows a constant conversion and yield over the entire duration of the experiment. In Fig. 5b, we see that the initial conversion and yields are approximately at the same level as for the condition with H₂O added, but they decay rapidly over time. Because a drop in plasma power also leads to a drop in temperature, the performance of this highly endothermic reaction process will decrease as well. Note that this confirms the observations in our previous work with the same APGD reactor, where we were unable to obtain a stable plasma for DRM with CH₄ fractions above 35 vol% [26]. When adding a small fraction of O₂ to the input mixture, the feasible CH₄ fraction could be increased, leading to a stable plasma at 42.5 vol% CH₄, but at 49 vol% CH₄ the negative



Fig. 5. CO_2 , CH_4 and H_2O conversion (%) and CO and H_2 yield (%) as a function of time for (a) a 32–32-36 CO_2 - CH_4 - H_2O input mixture and (b) a 55–45 CO_2 - CH_4 input mixture. Both measurements are done at a total input flow rate of 3 Ls/min and an initial plasma power of 300 W.

effects were again too significant [39]. Therefore, when studying different CO_2 -CH₄-H₂O mixtures, we should not only focus on conversion or SR, but also on soot formation (and plasma stability).

In section 2.1, we briefly explained how our improved reactor design (with adjustable cathode–anode distance) yields better control over the plasma power. Interestingly, within the range of tested conditions, slightly changing the inter-electrode distance and current such that the plasma power remains equal did indeed not change any of the performance metrics, i.e. the effect of the deposited power was dominant over other variables, such as the effect of the residence time through the discharge length. More details on this aspect can be found in the SI (section S3). Specifically to the present experiments, this also aids us in counteracting the negative effect of soot formation on the plasma power. Nevertheless, when the rate of soot formation was too high, we observed a clear instability similar to what is shown in Fig. 3 and Fig. 5, which could not be avoided.

For this reason, we categorized the 12 different mixtures presented in Table 1 into three groups based on their stability, and we indicated them through a color code in Table 3. A green color represents mixtures where no significant soot formation was observed. When only a very small fraction of soot (i.e. < 1 mg after 15 min) was collected afterwards with a negligible effect on the plasma power, the mixtures are indicated in orange. Mixtures where the rate of soot formation was too high to achieve stable performance, are indicated in red. Consequently, for the gas mixtures in red color, no reproducible experimental results could be obtained.

Table 3 clearly indicates that at the conditions under study, a CH_4 fraction above ca. 42 vol% (i.e. upper right corner of Table 3) is accompanied with extensive soot formation. This confirms earlier observations for DRM [26] and OCRM [39]. However, also the specific energy input (SEI, i.e. power divided by total input flow rate) has an influence. Specifically, we also tested the 14–41–45 (CO₂-CH₄-H₂O) mixture at the bottom right corner with the same total input flow rate (3 Ls/min) but a higher plasma power (400 W instead of 300 W). At these conditions, the plasma was significantly more stable. We hypothesize that a higher SEI leads to more reactive oxidative species available to remove the deposited carbon, due to a higher CO_2 and H_2O conversion. The latter is indeed the case, as will be discussed in section 3.4.

At the same CH₄ input fraction, we also observed a difference in stability depending on the CO₂:H₂O ratio. For example, two mixtures in Table 3 have 36 vol% CH₄, yet the mixture with only 19 vol% CO₂ and 45 vol% H₂O was visibly more stable (no soot observed at reactor walls, stable plasma power), while combined with 36 vol% CO₂ and only 28 vol% H₂O, soot formation (and its effect on the plasma power) was visible. This confirms earlier findings in literature regarding the effectiveness of H₂O to counteract soot formation [36,44,45,55]. Essentially, when H₂O is present as reactant, the concentration of OH radicals is increased. Though there still seems to be debate regarding the exact mechanism, the general agreement in literature is that the OH radicals efficiently intervene in the soot nucleation step, and thus prevent the growth of polycyclic aromatic hydrocarbons (PAH) into soot particles [51,56]. Hence, this is highly beneficial compared to DRM (at CH₄ fractions > 35 vol%), where only in specific cases (e.g. below atmospheric pressure and reverse vortex flow dynamics) soot formation can be inhibited [30].

3.2. Effect of H_2O input fraction

In section 3.1, we showed that adding H₂O to a CO₂-CH₄ mixture improves the overall plasma stability. In this section, we present the effect of H₂O addition on the other performance metrics. Specifically, we compare 28, 36 and 45 vol% H₂O addition, at a 1:1 CO₂:CH₄ ratio (corresponding to the BRM mixtures of the second column in Table 3). The reactant conversions and product yields are presented in Fig. 6 (a), along with the conversion and production rates (b), at three different H₂O input fractions. EC, EE and SR as a function of H₂O input fraction are presented in Fig. 7.

Increasing the H₂O input fraction has no significant effect on the CH₄ and H₂O conversion (Fig. 6a). It remains relatively constant at approx. 66 % and 9 %, respectively. The CO₂ conversion only slightly decreases, from ca. 46 % to 41 %. However, the conversion rate (in mmol/min, Fig. 6b) decreases for both CO₂ and CH₄, due to the lower flow rate of these components in the feed gas. Specifically, the CH₄ conversion rate drops from ca. 29 to 22 mmol/min (24 % decrease). The H₂ production rate also decreases, but not as much: it drops from 52 to 45 mmol/min (13 % decrease). This could mean that simply more H₂ is formed directly from H₂O plasmolysis. However, the CO₂ conversion rate drops from 21

Table 3

Overview of different mixtures tested experimentally. Mixtures indicated in green had a stable plasma power and no soot was observed, mixtures indicated in orange required a few slight changes to the inter-electrode distance to maintain a constant plasma power, and only < 1 mg soot was collected afterwards. Mixtures indicated in red had too extensive soot formation to achieve reliable results.

		CO2-CH4 ratio										
		65:35 (1.86)	50:50 (1.00)	35:65 (0.54)	25:75 (0.33)							
			nixture (vol%)									
Liquid H ₂ O	75	47-25-28	36-36-28	25-47-28	18-54-28							
temperature	ature 85	42-22-36	32-32-36	22-42-36	16-48-36							
(°C)	95	36-19-45	27.5-27.5-45	19-36-45	14-41-45							



Fig. 6. (a) Conversion and yields (%), and (b) conversion and production rates (mmol/min) of the reactants and products, respectively, as a function of the H_2O input fraction (vol%) at a 1:1 CO₂:CH₄ ratio. C_xH_y stands for the combined yields and production rates of the small hydrocarbons detected, consisting of (in decreasing order) C₂H₂, C₂H₄, C₂H₆ and C₃H₈ (i.e. n-propane). The error bars are obtained through linear error propagation, based on the standard deviation of the measured values. In some cases they are too small to be visible.



Fig. 7. (a) Energy cost (expressed in kJ/mol converted gas, EC_{χ} , and in kJ/mol syngas formed, EC_{SG}), and (b) energy efficiency (%, left axis) and syngas ratio (right axis) as a function of H₂O input fraction (vol%) at a 1:1 CO₂:CH₄ ratio. The error bars are obtained through linear error propagation, based on the standard deviation of the measured values. In some cases they are too small to be visible.

to 14 mmol/min (33 % decrease) – more than the drop in CH_4 conversion rate, suggesting that a reaction leading to CO_2 formation may be occurring. Taken together, this suggests that the water–gas shift (WGS) reaction could be taking place, which leads both to re-conversion of CO (which drops from 45 to 34 mmol/min, or 24 % decrease) back into CO_2 and formation of extra H_2 . While a detailed chemical pathway analysis would be required to fully unravel to what extent this reaction takes place, other references also report the WGS as a common side-reaction of the BRM [41,46,48].

Since adding H₂O negatively affects both conversion and production rates overall, the EC rises upon H₂O addition, i.e. from 370 kJ/mol to 490 kJ/mol (for 28 and 45 vol% H₂O); cf. Fig. 4a. In their 2017 review paper, Snoeckx and Bogaerts proposed a value of 4.27 eV/(molecule converted) (i.e., 412 kJ/mol) as a target for plasma technology to be competitive with other existing/emerging technologies producing syngas [4]. However, this target was defined for plasma-based DRM. To allow a more fair comparison between BRM and DRM (as done in section 3.4 below), we also plot the EC expressed in kJ/mol syngas (i.e. 1 mol of CO and H₂ combined, with the SR at the associated condition) produced in Fig. 7a, as this is the product shared between both reactions. This value is significantly lower than the target mentioned above, and also than the EC expressed per mol converted reactant, because the number of moles expands during reaction, but the observed trend remains the same.

The EE is also negatively affected upon H_2O addition, with a drop of 7 %, from 67 % to 60 % (Fig. 7b). On the other hand, the SR rises from ca. 1.15 to 1.33. This is not a consequence of more H_2 produced, but due to a more substantial drop in CO production rate. However, a ratio of about 1.3 is still far away from the targeted ratio of 2.

Overall, the performance metrics show a negative trend when adding H_2O , so the benefit is limited to plasma stabilization at conditions when otherwise too much soot is produced, i.e. higher CH_4 input fractions, as explained in section 3.1. In literature, an increase in the H_2O input fraction or flow rate also does not prove to be beneficial. An overall negative or negligible effect on the conversion is observed by Hrycak et al. [45], Alawi et al. [46], Wang et al. [48] and Xia et al. [49], as well as a decreasing CO yield. The H_2 yield is sometimes reported to increase, in contrast to our work, though the amount of H_2 produced is often seen

relative only towards the CH₄ input, neglecting the H₂ that comes from H₂O [46,49]. The same references all report an increasing SR as well, which is the only positive effect we observed with our data. Most importantly, Hrycak et al. [44] conclude that an increased H₂O input fraction does not lead to an increased H₂ production rate, CH₄ conversion and EC, but that it does allow the use of higher CH₄ input fractions through the suppression of soot formation. Based on the BRM reaction equation (see Introduction), CH₄ should indeed be further increased, to e.g. afford a SR closer to 2. Hence, adding H₂O might still become beneficial when simultaneously the CH₄ input fraction is increased and thus, the following section is dedicated to results obtained with the highest H₂O content (45 vol%) and an increasing CH₄ fraction.

3.3. Effect of CO₂:CH₄ ratio

In Fig. 8 and Fig. 9, we plot the same performance metrics as in section 3.2, but comparing four different CO_2 :CH₄ ratios at constant H₂O input fraction (45 vol%, corresponding to the last row in Table 3).

Changing the CO₂:CH₄ input ratio towards higher CH₄ amounts is clearly beneficial for the overall conversion rate, which rises with 20.4 mmol/min. Also the H₂O conversion changes drastically, starting with a negative conversion of -6% (meaning additional H₂O is formed - the reaction between CH₄ and CO₂ often leads to H₂O as a by-product [26,57–59]) at 1.86 CO₂:CH₄ ratio, up to a conversion of 32 % at 0.33 CO₂:CH₄ ratio, reaching the same level of conversion as CO₂. At the same time, the CO_2 and CH_4 conversion are both reduced, but as the CH_4 fraction increases from 19 to 41 vol%, its conversion rate rises significantly by 13.2 mmol/min. Due to the lower bond energy of a C-H bond (i.e., 413 kJ/mol, compared to a C = O or O-H bond, i.e., 799 kJ/mol and 467 kJ/mol, respectively), CH₄ always has the highest conversion. The reason for the significant drop in CO₂ conversion rate is because its input fraction is the lowest at the 0.33 CO₂:CH₄ ratio, while simultaneously H₂O makes up 45 vol% of the input mixture (vs 14 vol% of CO₂). Hence, SRM is heavily promoted over DRM in this overall BRM process, and/or the WGS reaction could again take place, explaining the lower CO₂ and higher H₂O conversion.

In terms of yields and production rates, there is a visible decrease for CO and increase for H_2 . This is explained by the higher conversion rate of CH_4 and H_2O and the lower CO_2 conversion rate. As a consequence, the SR rises up to 2.03 (cf. Fig. 6b), more than twice compared to the

value at 1.86 CO₂:CH₄ input ratio, and reaching the desired target for further downstream production of value-added oxygenates, e.g. methanol. Note that also the C_XH_Y yield and production rate increases at higher CH₄, which is also logical, although not exceeding 7 % and 2.6 mmol/min, respectively.

The EC is substantially reduced as well. At 0.33 CO_2 :CH₄ input ratio, the EC per mol of converted reactants equals 380 kJ/mol, which is 320 kJ/mol lower than at 1.86 CO₂:CH₄ input ratio. Moreover, it drops below the EC target of 412 kJ/mol [4]. We observe the same trend for the EC expressed per mol syngas, though its drop (approx. 75 kJ/mol) is less spectacular. The EE improves as well, up to 63 % at 0.33 CO₂:CH₄ input ratio.

Our observations in terms of trends are generally in agreement with literature. Hrycak et al. [44] also reported an improved H₂ production rate and EC at a higher CH₄ input fraction. Wang et al. [48] and Xia et al. [49] reported a lower CH₄ conversion and a higher SR, as in our work. A difference with our work is that they reported a higher CO₂ conversion at a lower CO₂:CH₄ input ratio. However, the large H₂O input fraction in our conditions can be the cause of this different trend, as e.g. Wang et al. [48] did not apply an input fraction above 27 %, and H₂O can compete with CO₂ as explained above.

It is clear that changing the CO₂:CH₄ ratio towards higher CH₄ amounts is beneficial. In fact, the best results are reached for almost all performance metrics (except CO₂ conversion) at the highest CH₄ fraction, and the most important targets (i.e., SR of 2 and EC below 412 kJ/mol) are achieved. The ideal stoichiometric BRM reaction (cf. Introduction) dictates a 1–3-2 CO₂-CH₄-H₂O mixture as input, while our best results are obtained for this 1–2.9–3.2 ratio. However, a drop in H₂O content from 45 to 33 vol% (as dictated by the optimal stoichiometry), compromises the plasma stability due to too extensive soot formation (see Table 3: conditions in red).

3.4. Effect of SEI and comparison with state-of-the-art

As mentioned in section 3.1, the plasma stability improved upon increasing SEI. The same applies to (most of) the other performance metrics. Table 4 indeed demonstrates that a higher SEI (due to a higher power of 400 W instead of 300 W, at the same total input flow rate of 3 Ls/min) greatly improves the conversions and product yields, while the SR, EC and EE are only slightly worse. However, a SR of 1.94 is still at a



Fig. 8. (a) Conversion and yield (%), and (b) conversion and production rate (mmol/min) of the reactants and products, respectively, as a function of the $CO_2:CH_4$ input ratio at a 45 vol% H_2O input fraction. C_xH_Y stands for the combined yields and production rates of the small hydrocarbons detected, consisting of (in decreasing order) C_2H_2 , C_2H_4 , C_2H_6 and C_3H_8 (i.e. n-propane). The error bars are obtained through linear error propagation, based on the standard deviation of the measured values. In some cases they are too small to be visible.



Fig. 9. (a) Energy cost (expressed in kJ/mol converted gas, EC_{χ} , and in kJ/mol syngas formed, EC_{SG}), and (b) energy efficiency (%, left axis) and syngas ratio (right axis) as a function of CO_2 : CH_4 input ratio at a 45 vol% H_2O input fraction. The error bars are obtained through linear error propagation, based on the standard deviation of the measured values. In some cases they are too small to be visible.

Table 4

Comparison of our work (at two different SEI values) with literature, both in the same APGD reactor but without H₂O addition (no BRM) [26,39], and for BRM in other reactors [44,46,48,49], for conversion χ (%), product yield Y (%), SR, syngas production rate $n_{syngas}^{produced}$ (mmol/min), EC (kJ/mol) and EE (%). Values with '*' were not explicitly reported in the cited references, but could be derived from other reported values in the paper. Values with '**' were explicitly reported, but are recalculated to allow comparison with our data (based on the formulas presented in Table 2). Values that were not reported and could not be derived through other data, are indicated with '/'. Parameters that are not applicable are indicated in grey.

		SEI	Input fraction (vol%)				χ (%)			Y (%)		CD	n produced	ed EC (kJ/mol)		EE		
		(kJ/mol)	CO2	CH₄	H ₂ O	02	N ₂	CO2	CH₄	H ₂ O	Total	со	H ₂	JK	(mmol/min)	Conv.	Syngas	(%)
BRM, DRM and OCRM in APGD	This work	160	14	41	45			32.1	59.6	32	43	45.3	39	2.03	93.9	380	220	63
	210 Inis work	210	14	41	45			49.0	73.9	40	54	59.2	49	1.94	119.1	390	220	62
	Wanten et al. [26]	190	65	35				53.9	72.4		61.1	57.3	52	0.64	42.4	320	200	69
	Maerivoet et al. [39]	127	42.5	42.5		15		49.5	74.4		66.7	58.6	46.5	0.78	39.3	190	143	70
BRM in other reactors	Hrycak et	95*	27.3*	27.3*	45.3*			63*	74.3	-47*	17*	41*	35*	1.56*	2326	565*	145*	56*
	al. [44]	54*	15.4*	46.2*	38.4*			48*	48.9	-51*	12*	16*	21*	2.80*	2682	445*	168*	42*
	Alawi et al. [46]	280*	10.7*	5.3*	43.3*		40.7*	19.2	82.7	1	1	9.04	14**	5.23	13.5	1	3107*	1
	Wang et al. [48]	75*	40	40	20			22.5	15	1	1	11*	3*	0.35	36.6	1	635*	29*
	Xia et al. [49]	200**	16*	47*	37*			47.5	52.5	1	1	18*	26*	3	10.7	1	447*	1

sufficiently high level for further methanol synthesis.

These general trends are in line with available literature in many plasma reactors for both DRM and BRM [4,26,44–46,52]: higher conversions and yields, but at the cost of a higher EC and lower EE. It should be noted that we also tested a power of 500 W (and thus an even higher SEI of 240 kJ/mol), but the reactor showed signs of overheating, hence we did not further investigate this higher power and SEI. In addition, when further increasing the SEI, different ways to limit the energy losses should be considered as well. A possible route for this is placing a heat exchanger in the plasma afterglow, that can transfer a fraction of the heat lost to the input gas stream, and pre-heat the input gas mixture. Another method to limit the energy losses is placing a catalyst bed at a short distance after the plasma, where the residual (downstream) heat from the plasma is used to activate the catalyst and consequently further increase the conversion and energy efficiency [53,60–62]. The potential of both approaches is the topic of future works.

Table 4 also contains literature values, including (i) obtained in the same reactor type (i.e. APGD), for DRM [26] and OCRM [39], and (ii) BRM experiments in other reactor types, i.e., a microwave [44,46] and gliding arc [48,49] reactor. In our earlier work [26], we used an APGD for DRM at similar SEI as in this work. Noticeably, the CH₄ conversion

and CO and H_2 yields are almost equal. The somewhat higher CO_2 and total conversion than for BRM is due to the H_2O addition, reducing the CO_2 conversion, as observed in section 3.2 and 3.3. This also explains the better EC expressed per mol converted for DRM. However, the EC expressed per mol syngas formed is only slightly better for DRM. This indicates that the lower conversion is compensated by a larger selectivity towards syngas with BRM. The most substantial difference lies with the SR, which is more than three times higher for BRM than for DRM. Since our work aims at producing syngas for further methanol synthesis, this is a crucial advantage of BRM over DRM.

We also recently tested OCRM in an APGD reactor [39]. Though the SEI used in these experiments was lower than used for BRM in this work, the conversions and product yields are very much in line (and the total conversion was even higher, due to the more difficult conversion of H_2O , which is absent in OCRM). Consequently, the EC is approx. 200 kJ/mol lower for OCRM. This can be explained by the effect of adding O_2 on the chemistry. While DRM and BRM are clear endothermic reactions, adding O_2 promotes the (partial) oxidation of CH₄, which is an exothermic reaction. As a consequence, the overall reaction enthalpy for OCRM is lower than for DRM or BRM, hence, a much lower SEI can give the same level of conversion and syngas yield. However, in case of OCRM, the SR

barely differs from the one obtained by DRM, again demonstrating the advantage of BRM. Note that also the syngas production rate for BRM is higher than for DRM and OCRM, mainly because of the larger total input flow rate in our work (3 Ls/min instead of 1 Ls/min).

BRM has also been investigated recently in other plasma reactors. Hrycak et al. [44] described BRM in a MW plasma, operating at a plasma power of 6.5 kW and flow rates of 50–100 L/min. Due to this large flow rate, the syngas production rate is much higher than in our experiments, but simultaneously, the SEI is much lower. Still, at a SEI of 95 kJ/mol, they reported a CH₄ conversion of 74.3 %, comparable to our data, with a SR of 1.5 - 2.8. However, based on their data and assuming that H₂O was the only significant component missing to obtain a perfect mass balance, they had a significant H₂O production instead of conversion. In fact, these data imply that the presence of H₂O merely suppressed the soot formation. The latter was also observed at an even lower SEI, for a mixture comparable to our best BRM mixture. In section 3.3, we also observed a negative H₂O conversion for one condition, and in general, the H₂O conversion was the lowest of all reactants. This indicates that at even lower SEI, the H₂O conversion drops the most, and can become negative (i.e., net H₂O production). Taking this negative conversion into account, the EC expressed per mol converted is of course very high for their conditions (cf. Table 4) and much higher than in our experiments. Yet, when expressing the EC per mol syngas formed, its value is lower than our results. This can also be explained by the net H₂O formation, which is an exothermic process, hence increasing the temperature of the mixture, similar to the effect we observed for O₂ addition in OCRM [39].

Alawi et al. [46] used a significantly higher SEI than in our work. Furthermore, while their H₂O input fraction was similar to ours, a large fraction of N₂ was also added. As explained in previous work, the addition of N₂ takes up a large fraction of the supplied energy to reach an excited state, without any additional conversion [63]. As a result, their syngas-based EC was extremely high, even in the order of MJ/mol syngas. The CO₂ conversion and syngas yield were also significantly lower than in our work, despite the much higher SEI. Only the CH₄ conversion exceeds ours, which may be explained by the higher SEI, but also due to its low input fraction and the fact that it is the easiest reactant to convert. This also explains why the authors reached a high SR (even of 5.23).

Wang et al. [48] used a gliding arc reactor, generating a CO_2 -H₂O plasma with CH₄ injected in the afterglow, and at much lower SEI than in our work, hence their results are quite different from ours. In fact, they even obtained a lower CH₄ conversion than CO_2 conversion, attributed to their specific setup, where CH₄ is only injected in the afterglow. This further results in low product yields, a low SR, a very high syngas-based EC and low EE. It should however be mentioned that they focused on the production of liquid by-products, rather than on obtaining a high SR.

Finally, Xia et al. [49] described BRM in a GA reactor, with a similar SEI and input mixture as in our work. Their CO_2 conversion was similar as ours, yet their CH_4 conversion was more than 20 % lower, and also the syngas yield was a factor 2–3 lower, with the lowest syngas production rate in Table 4. They reported a higher C_2H_2 than CO selectivity, obviously different from our work. However, exact comparison is difficult, due to the different reactor types. They used a classical GA, and such design suffers from a large fraction of gas not being treated by the plasma [4]. This could perhaps explain the difference with our APGD reactor, where the confinement of the gas prevents this issue [17].

Overall, our obtained conversions, syngas yield, SR, EC and EE are among the best values reported in literature thus far for plasma-based BRM. Furthermore, BRM exhibits similar performance in terms of conversion, yield and EC as DRM and OCRM (in the same reactor setup), while the SR is significantly improved up to the desired level of 2, required for further methanol synthesis.

4. Conclusions

We demonstrated that BRM in an APGD reactor is beneficial on several fronts. First, compared to DRM, the addition of H_2O helps in counteracting soot formation, and thus in creating more stable plasma conditions. A mixture of 14–41-45 vol% (CO₂-CH₄-H₂O) leads to the overall best results in terms of stable plasma and performance metrics. Specifically, at a SEI of 210 kJ/mol, we obtained a CO₂ and CH₄ conversion of 49 % and 74 %, respectively, at an EC of 390 kJ/mol converted reactants, which is below the target defined for plasma-based syngas production to be competitive with other technologies. Moreover, we reached CO and H₂ yields of 59 % and 49 %, and a SR of 2, which is ideal for further methanol synthesis.

Our results for BRM in an APGD, in terms of conversion and syngas yield, are in line with our previous results for DRM and OCRM in an APGD, while the EC is slightly higher than for OCRM, which could benefit from the presence of O_2 as reactant. However, BRM scores substantially better in terms of SR, because our obtained value of 2 is three times higher than the values obtained for DRM and OCRM. We also compared our results to other works that investigated plasma-based BRM, and we obtain conversions and syngas yields that are among the best reported, at an EC that is lower than most of the values reported in literature, while reaching a SR ideal for further methanol synthesis.

In their perspective paper, Mallapragada et al. [7] identified the low technology readiness (TLR) level as the main disadvantage of plasma technology, to be implemented in industrial chemical processes. Indeed, while our work shows a lot of promise, further research is obviously required to e.g. upscale this process, implement heat recovery, and couple the plasma conversion to a methanol synthesis reactor based on the plasma-produced syngas. With these extra steps, we expect plasma technology to be able to contribute to the electrification and decarbonization of the chemical industry.

CRediT authorship contribution statement

Bart Wanten: Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Conceptualization. **Yury Gorbanev:** Writing – review & editing, Methodology, Conceptualization. **Annemie Bogaerts:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2024.132355.

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