Novel power-to-syngas concept for plasma catalytic reforming coupled with water electrolysis

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HIGHLIGHTS

• We report a new P2SG approach for CH4, CO2 and H2O conversions to high-quality syngas.
• The PCR unit features high energy efficiency and avoids catalyst sintering and coking.
• We achieve an overall energy efficiency of 79% and an energy cost of 1.8 kWh/Nm3.
• The high-quality syngas features a concentration of 94.6% and an ideal component.
• We combine this PCR unit with a WE unit for pure O2 supply.

GRAPHICAL ABSTRACT

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ABSTRACT

We propose a novel Power to Synthesis Gas (P2SG) approach, composed of two high-efficiency and renewable electricity-driven units, i.e., plasma catalytic reforming (PCR) and water electrolysis (WE), to produce high-quality syngas from CH4, CO2 and H2O. As WE technology is already commercial, we mainly focus on the PCR unit, consisting of gliding arc plasma and Ni-based catalyst, for oxidative dry reforming of methane. An energy efficiency of 78.9% and energy cost of 1.0 kWh/Nm3 at a CH4 conversion of 99% and a CO2 conversion of 99% are obtained. Considering an energy efficiency of 80% for WE, the P2SG system yields an overall energy efficiency of 79.3% and energy cost of 1.8 kWh/Nm3. High-quality syngas is produced without the need for post-treatment units, featuring the ideal stoichiometric number of 2, with concentration of 94.6 vol%, and a desired CO2 fraction of 1.9 vol% for methanol synthesis. The PCR unit has the advantage of fast response to adapting to fluctuation of renewable electricity, avoiding local hot spots in the catalyst bed and coking, in contrast to conventional catalytic processes. Moreover, pure O2 from the WE unit is directly utilized by the PCR unit for oxidative dry reforming of methane, and thus, no air separation unit, like in conventional processes, is required. This work demonstrates the viability of the P2SG approach for large-scale energy storage of renewable electricity via electricity-to-fuel conversion.
1. Introduction

Synthesis gas (syngas, H2 + CO) is a crucial chemical feedstock for producing synthetic fuels and bulk chemicals via the Fischer-Tropsch (F-T) synthesis process [1,2] and methanol synthesis process [3], which requires a 2/1 M ratio of H2/CO. Methane is the preferred and main source for syngas generation, due to its plentiful supply (such as natural gas, shale gas and biogas) and its highest H/C atomic ratio. Three kinds of reforming reactions are generally used for syngas production from methane: steam reforming, carbon dioxide (dry) reforming and oxidative reforming (partial oxidation) [3–5].

Among the three reforming reactions, steam reforming and dry reforming have H2/CO molar ratios of 3 and 1, respectively, which requires additional steps to adjust the H2/CO ratios to 2. Although oxidative reforming theoretically has a H2/CO ratio of 2, there exist technical issues of local hot spots, catalyst sintering and safety concerns in the catalytic process, besides expensive operating cost to obtain pure oxygen from air separation. Autothermal reforming (ATR), combining oxidative and steam reforming, normally produces a H2/CO ratio higher than 2 and a considerable amount of CO2 and H2O in the product stream, which reduces the syngas purity, final product yield and total efficiency in the subsequent synthesis processes [3,4,6]. Indeed, the CO2 and H2O content of the syngas stream is another important factor relevant to the syngas quality.

Syngas with a H2/CO ratio of 2 can be directly produced from the combination of steam and dry reforming of methane (called bi-reforming, abbreviated as BiRfm) [3,4]:

\[
{3}{CH}_4 + 2{H}_2{O}(g) \rightarrow 4{CO} + 8{H}_2 \quad \Delta H_{298K}^0 = 658.9 \text{kJ/mol} \quad (R1)
\]

However, the BiRfm reaction R(1) consists of two strongly endothermic reactions, and is believed difficult and challenging, and excess steam and CO2 are required to obtain higher methane conversion and to prevent carbon deposition on the catalysts [3,4,7,8]. This inevitably leads to increasing the CO2 and H2O content in the syngas stream and thus it reduces the quality of the syngas stream.

To solve the above-mentioned problem of BiRfm, in this paper we propose a novel combination of water splitting (R2) and oxidative dry reforming of methane (R3),

\[
{2}{H}_2{O}(l) \rightarrow {O}_2 + 2{H}_2 \quad \Delta H_{298K}^0 = 571.6 \text{kJ/mol} \quad (R2)
\]

\[
{3}{CH}_4 + {O}_2 + {CO}_2 \rightarrow 4{CO} + 6{H}_2 \quad \Delta H_{298K}^0 = 175.3 \text{kJ/mol} \quad (R3)
\]

The combination of reactions R(2) and R(3) gives a total reaction, R4,

\[
{3}{CH}_4 + 2{H}_2{O}(l) + {CO}_2 \rightarrow 4{CO} + 8{H}_2 \quad \Delta H_{298K}^0 = 747 \text{kJ/mol} \quad (R4)
\]

Hence, it is reaction R(1) plus a phase transfer process of water vaporization. As shown in Fig. 1, the standard enthalpy changes are 572 and 175 kJ/mol for reactions R(2) and R(3), respectively [9]. Thus, in terms of enthalpy change, reaction R(2) accounts for the majority of the total reaction R(4) (747 kJ/mol). It is clear that reaction R(2) can be conducted easily and efficiently via water electrolysis (WE) [10]. A typical commercial electrolyzer has an efficiency of 80% and a higher efficiency can be obtained with elevated water temperature or steam [11,12].

Moreover, pure O2, as the side product of reaction R(2), which evolves from the anode of the electrolyzer since the electrode compartments are separated, can be directly utilized by reaction R(3) without the need for separation. Hence, an air separation unit to obtain pure oxygen, as in conventional processes, is not needed.

In reaction R(3), the combination of exothermic partial oxidation and endothermic dry reforming makes it weakly endothermic (175 kJ/mol). However, the conventional catalytic process bears a drawback of local hot spots, because the exothermic oxidation reaction proceeds rapidly in oxidizing atmosphere (near the catalyst-bed inlet), which results in catalyst sintering and subsequent deactivation [13,14]. Ni-based catalysts are commonly employed and their deactivation is caused by the changes in valence state of the Ni active phase and carbon deposition, besides the above-mentioned sintering. To avoid these issues, we employ here plasma catalytic reforming (PCR) [15–20] for R3, where oxidative reforming occurs in the plasma zone with complete consumption of oxygen.

The two units of WE (for R2) and PCR (for R3), each of which can be driven by renewable electricity, are combined to produce high-quality syngas for subsequent downstream synthetic fuel production, so the overall concept is named power-to-syngas, P2SG. Fig. 2 shows a schematic diagram of the P2SG approach. A detailed diagram of the PCR unit is presented in the Methods section. H2O is split into pure H2 and pure O2, which evolve from the cathode and anode of the WE unit, respectively. Pure O2 is utilized by reaction R(3) in the PCR unit, and thus, no air separation unit, normally required for reaction R(3), is needed here. In addition, pure H2 is supplied to the product gas of reaction R(3), hence to achieve high-quality syngas. The P2SG strategy is an attractive route to convert renewable, fluctuating electricity into chemical energy, stored on a large scale in synthetic fuels, due to its advantages of fast response and instant adjustability, especially for the PCR unit [20], in contrast to conventional catalytic processes. Meanwhile, this strategy recycles the most serious greenhouse gas CO2 as a feedstock, which can make an additional important contribution to mitigate the global CO2 emission.

2. Experimental

For the P2SG approach, a new PCR reactor for oxidative dry reforming of methane is specially designed. A schematic diagram of the PCR reactor is shown in Fig. 3. A stainless-steel cylinder with inner diameter of 20 mm and length of 24 cm is grounded. The high-voltage electrode is electrically insulated by ceramic and located at the axis of the cylinder. A 5 kHz alternating current (AC) high-voltage power source is connected to the high-voltage electrode, to generate a gliding arc discharge (plasma zone in Fig. 3) at atmospheric pressure. The inlet gas flow F1 is tangential, creating a vortex flow in the plasma. The input plasma power is measured by a watt-meter installed at the transformer primary side of the power source.

The Ni/CoO/Al2O3 catalysts (see SI for details), containing Ni of
11 wt% and Ce of 8 wt%, are packed in the post-plasma zone, at a distance varying between 4.0 and 10.5 cm between plasma and catalyst. A home-made heater with a height of 20 cm, wrapped by ceramic fiber cotton on the outside of the heater for heat insulation, is employed for additional heating of the catalyst bed, needed due to the addition of F2 after the plasma. The axial distributions of the catalyst bed (TCB) and reactor wall (TRW) temperatures are measured by two movable thermocouples. The temperature of the heater, TH, is controlled by the third thermocouple, fixed at the half-height of the heater. The power consumed by the heater is measured by a PowerBay (Shenzhen Northmeter Co., China) and time-averaged over five hours.

To avoid coke formation and achieve complete O2 consumption in the plasma, we use two separate inlet flows: the inlet flow F1 (3.0 SLM) with CH4/CO2/O2 molar ratio of 3/2/2 is introduced before the plasma, while F2 (1.3 or 0.9 SLM) with pure CH4 is introduced after the plasma. The CH4/CO2/O2 molar ratios in the total flow F1 (4.3 or 3.9 SLM), i.e., F1 + F2) are 3/1/1 (stoichiometric ratio of R3) or 2.5/1/1 (slight shortage of CH4). The gas flow rates are controlled by mass flow controllers (Beijing Sevenstar Electronics Co., China). The specific energy input (SEI) in the plasma is calculated by the plasma input power divided by the flow rate F1. The gas hourly space velocity (GHSV) of the catalyst is obtained by the total flow rate F1 divided by the catalyst weight.

The thermodynamic-equilibrium (TE) conversions and concentrations as a function of the end temperature of the catalyst bed are calculated by the HSC Chemistry software (v7.0) using the Gibbs free energy minimization method; see more details in the SI.

Two gas chromatographs (Agilent 1790T and Agilent 6890N) are employed for on-line analysis of the gaseous products using an internal standard method, which was described previously [21,22]. N2 and He are used as internal standard gases for quantification of O2, CH4, CO2, CO and C2 hydrocarbons, and for quantification of H2, respectively. The internal standard gases are mixed with the product stream at the outlet of the PCR reactor, they pass through a cold trap and are analyzed on-line by the two gas chromatographs. The definitions of conversion, carbon-based (C-based) selectivity and hydrogen-based (H-based) selectivity are listed below.

For the PCR unit, the reactant conversions, XR (R = CH4, O2, and CO2), are defined as

\[
X_R(\%) = \frac{F_R^{\text{in}} - F_R^{\text{PCR}}}{F_R^{\text{in}}} \times 100
\]

where \(F_R^{\text{in}}\) and \(F_R^{\text{PCR}}\) are the inlet and PCR outlet flow rate of the reactant, respectively. \(F_R^{\text{PCR}}\) is obtained by the flow rate of the internal standard N2 (Fr) and the concentration ratio of the reactant to N2 in

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Fig. 2. Schematic diagram of power to high-quality syngas via the new P2SG approach, which consists of a PCR unit and a WE unit, both driven by renewable electricity.

Fig. 3. Schematic diagram of the plasma catalytic reactor. The numbers 1, 2, 3, 4, 5, 6, 7, 8, represent the high-voltage electrode, ceramic insulator, plasma zone, catalyst bed zone, heater, two movable thermocouples for recording the temperature of the catalyst bed and the reactor wall (6 for TCB and 7 for TRW), and a static thermocouple (8 for TH) located at the half-height of the heater. The inlet gas flows F1 and F2 are fed into the reactor before and after the plasma, respectively.

Fig. 4. (a) O2, CH4 and CO2 conversions, CO, H2 and H2O selectivities and (b) syngas concentration and H2/CO ratio in the plasma, at a flow rate of 3.0 SLM with CH4/CO2/O2 ratio of 3/2/2 and a SEI of 27 kJ/mol. Inset: plasma images in front view, at exposure times of 1 ms and 10 ms, showing the rotation of the arc.
the PCR outlet gas (C_{CO}^{PCR}/C_{N_2}),

\[ F_{CO}^{PCR} = F_{N_2} \frac{C_{CO}^{PCR}}{C_{N_2}} \]  

Likewise, the flow rates of CO (F_{CO}), C_2 (F_{C_2}^{PCR}) and H_2 (F_{H_2}^{PCR}) products are obtained by Eqs. E(3)-E(5), respectively

\[ F_{CO}^{PCR} = F_{N_2} \frac{C_{CO}^{PCR}}{C_{N_2}} \]  

\[ F_{C_2}^{PCR} = F_{N_2} \frac{C_{C_2}^{PCR}}{C_{N_2}} \]  

\[ F_{H_2}^{PCR} = F_{N_2} \frac{C_{H_2}^{PCR}}{C_{N_2}} \]  

where \( C_{CO}^{PCR} \) and \( C_{C_2}^{PCR} \) are the concentration ratios of CO and C_2 to \( N_2 \), respectively; \( F_{H_2} \) is the flow rate of the internal standard He and \( C_{H_2}^{PCR}/C_{N_2} \) is the concentration ratio of H_2 to He. We can now define the C-based selectivities of CO (S_{CO}) and C_2 (S_{C_2}), and the H-based selectivities of H_2 (S_{H_2}) and H_2O (S_{H_2}O):

\[ S_{CO} = \frac{F_{CO}^{PCR}}{F_{CH_4} \times X_{CH_4} + F_{CO_2} \times X_{CO_2}} \times 100\% \]  

\[ S_{C_2} = \frac{2F_{C_2}^{PCR}}{F_{CH_4} \times X_{CH_4} + F_{CO_2} \times X_{CO_2}} \times 100\% \]  

\[ S_{H_2} = \frac{F_{H_2}^{PCR}}{2F_{CH_4} \times X_{CH_4}} \times 100\% \]  

\[ S_{H_2}O = \frac{F_{H_2O}^{PCR}}{2F_{CH_4} \times X_{CH_4}} \times 100\% \]  

where \( F_{CO_2}^{PCR} \) denotes the flow rate of H_2O produced, which can be calculated by equation E10, assuming an oxygen balance of 100%.

\[ F_{H_2O}^{PCR} = 2 \left( F_{CO_2} \times X_{CO_2} + F_{O_2} \times X_{O_2} \right) - F_{CO}^{PCR} \]  

\[ E(10) \]

3. Results

In the present work, reaction R(3) in the PCR unit is crucial to the P2SG approach, and thus we focus here on this reaction. Reaction R(2), occurring in the WE unit, is included in the Discussion section below. For the PCR unit, we first demonstrate the essential contribution of the gliding arc plasma in the oxidative dry reforming reaction.

3.1. Crucial role of the plasma

A flow of CH_4/CO_2/O_2 with molar ratio of 3/2/2 and flow rate of 3.0 SLM in vortex flow is introduced into the plasma at a specific energy input (SEI) of 27 kJ/mol. The arc, as shown in the inset of Fig. 4, is pushed and elongated by the vortex flow to rotate and glide with high velocity, which provides a highly active plasma region. As shown in Fig. S1, optical emission spectra of OH (A-X), CH (A-X), C_2 (A-X), CO (B-A), H_2O, H_3 and O (3p-3s, 777 nm) are observed from the plasma in the wavelength range of 300–800 nm. The local (arc channel) gas temperature in the plasma cannot be measured directly, but can be estimated by the CO (B-A) rotational temperature of 2500 K (Fig. S2). The plasma has a high electron density of \( 2.7 \times 10^{14} \text{ cm}^{-3} \) (Fig. S3), and in combination with the high gas temperature of 2500 K in the arc channel (Fig. S2), it features high reaction rates. Therefore, O_2 is completely consumed in the plasma, which is indeed highly desired, to avoid catalyst sintering and deactivation in the subsequent catalytic stage (cf. previous section), and 64.8% of CH_4 is converted (Fig. 4a). The CO_2 conversion of \( -3.9\% \) means that there is no net conversion for CO_2, because it is counteracted by complete oxidation of CH_4 producing some CO_2. From CH_4, 42.6% of the H atoms are converted to H_2, 2.9% to C_2 hydrocarbons and 55.0% to H_2O. The CO selectivity is 91.6% and a small amount of C_2 hydrocarbons is formed with 6.3% selectivity. A syngas concentration of 38.7 vol% and H_2/CO ratio of 1.0 are obtained (Fig. 4b). The carbon balance is 97.9%, being close to 100%. Based upon the results of the conversions (64.8% of CH_4, 100% of O_2 and -3.9% of CO_2) and selectivities (42.6% of H_2 and 55.0% of H_2O), we can conclude that CH_4 is mainly converted in the plasma via reaction R(5) and R(6) with an approximately equivalent reaction rate,

\[ \text{CH}_4 + 1/2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \]  

(R5)

\[ \text{CH}_4 + \text{O} \rightarrow \text{CO} + 2\text{H}_2\text{O} \]  

(R6)

The gliding arc plasma is integrated in the PCR unit (see Fig. 3 and Experimental), and accounts already for a significant fraction of the CH_4 conversion, as well as an excellent energy efficiency, due to the non-equilibrium character of the plasma [20], besides complete O_2 consumption to avoid local hot spots and catalyst sintering, as mentioned above. Unless otherwise specified, the PCR unit is conducted at a total flow rate \( F_t \) of 4.3 SLM CH_4/CO_2/O_2 with molar ratio of 3/1/1. More specifically, besides introducing 3.0 SLM flow rate into the plasma (\( F_t \)), 1.3 SLM \( F_s \) of pure CH_4 is added after the plasma to obtain the CH_4/CO_2/O_2 ratio of 3/1/1 in \( F_t \), as this can avoid cokeing issues in the plasma. Furthermore, 41.0 g Ni/CoO/Al_2O_3 catalyst is placed after the active plasma region, with an additional heater. Indeed, the heating by the plasma is not sufficient due to the addition of CH_4 after the plasma (see Fig. 3 in Experimental).

As we reach an O_2 conversion of 100% for all PCR conditions investigated, in the following text we will only focus on the CH_4 and CO_2 conversions, selectivities, syngas concentration and H_2/CO ratio, as well as on the energy cost and energy efficiency of the process. We will also compare with the obtained conversions and syngas concentrations by thermodynamic equilibrium (TE) calculations, as explained in the SI (Fig. S4).

3.2. Effect of the catalyst bed temperature

Fig. 5 shows the axial temperature profiles of the catalyst bed, \( T_{CB} \), for different temperatures of the heater, i.e., \( T_h \) of 1123, 1073, 1023, and 973 K, at a gas hourly space velocity (GHSV) of 6300 mL·g^{-1}·h^{-1}. Interestingly, the first 2 cm of the catalyst bed are characterized by a remarkable drop in \( T_{CB} \) at each \( T_h \), with an almost identical curve independent of \( T_h \). The remarkable drop in \( T_{CB} \) can be ascribed to the fact that large amounts of CH_4 are rapidly converted by the strongly
endothermic reforming reaction, due to substantial heat and active species derived from the plasma. Specifically, $T_{\text{cb}}$ drops from 1143 to 1163 K at the beginning to $\sim$1013 K (with a slope of $\sim$140 K/cm) within the first 1 cm, and to $\sim$663 K (at a slope of $\sim$50 K/cm) within the next 1 cm. After a further (minor) drop, it starts (slightly) rising again and approaches the temperature of the reactor wall ($T_{\text{rw}}$) at the end of the catalyst bed, as shown in Fig. S5.

Due to a great difference in temperature along the catalyst bed, we decided to use the end temperature of the catalyst bed (end $T_{\text{cb}}$) for the thermodynamic equilibrium ($T_{\text{eq}}$) calculations (see S1). Consistent with the TE calculations, we also adopt the end $T_{\text{cb}}$ for the experimental results versus temperature. The end $T_{\text{cb}}$ rises slightly more than linearly upon increasing the heater temperature ($T_H$) from 973 to 1123 K, as shown in Fig. 5. It is slightly lower than $T_H$ at e.g. 95.5% to 92.1% and 85.1%, respectively, upon rising end $T_{\text{cb}}$ from 948 to 1126 K; see Fig. 7a.

Note that the conversion in the first 2 cm of the catalyst bed, characterized by the fastest drop in $T_{\text{cb}}$, is mainly due to the heat and active species provided by the plasma, while further downstream, the additional catalyst bed heating accounts for the further catalytic conversion. The conversion of CH$_4$ is higher than CO$_2$, which is mainly ascribed to the side reaction of methane combustion [23]. Furthermore, it is consistent with other papers for plasma-based CO$_2$ and CH$_4$ conversion [24], and can be explained by model calculations [25,26] because of the easier dissociation of CH$_4$ compared to CO$_2$.

Fig. 7b shows that the H$_2$ selectivity increases slightly from 90.1% to 95.1%, while the H$_2$O selectivity decreases accordingly from 10.5% to 4.1%, and the CO selectivity remains constant at nearly 100%. In addition, the H$_2$/CO ratio also remains 1.5 (Fig. 7c), identical to the stoichiometric ratio in reaction R(3), while the syngas concentration increases remarkably from 76.5 vol% to 95.5 vol%. Finally, when comparing with the TE calculations (see details in S1), it is clear that the experimental CH$_4$ conversion in Fig. 7a and the syngas concentration in Fig. 7c are very close to the TE values, while the CO$_2$ conversion is slightly lower; see Fig. 7a.

### 3.3. Effect of gas hourly space velocity (GHSV)

At $T_H$ of 1123 K (end $T_{\text{cb}}$ of 1126 K), the conversions of CH$_4$ (92.1%) and CO$_2$ (85.1%) are very high, so changing the GHSV will not have great effect on these conversions anymore. Therefore, we selected $T_H$ at 1073 K to show the effect of GHSV on conversion, selectivity, syngas concentration and H$_2$/CO ratio; see Fig. 8. The GHSV is calculated as the total gas flow rate divided by the catalyst weight, so we have varied the amount of catalyst in Fig. 8 (from 41.0 g to 10.0 g), at a fixed total gas flow rate of 4.3 SLM. The effect on the end $T_{\text{cb}}$ is also plotted (Fig. 8a).

The $T_{\text{cb}}$ drops with the same slope in the first 2 cm of the catalyst bed at various GHSV, as shown in Fig. S6. The starting $T_{\text{cb}}$ at a GHSV of 6300 mL·g$^{-1}$·h$^{-1}$ is higher than at a GHSV of 25700 mL·g$^{-1}$·h$^{-1}$ (i.e., 1155 K vs 1101 K), which is caused by a shorter distance between the plasma and the catalyst for the lower GHSV (corresponding to a larger amount of catalyst). Indeed, the distance between the plasma and the catalyst bed is 4.0 cm for the first case, and 10.5 cm for the latter case.

With a drop in GHSV from 25,700 to 6300 mL·g$^{-1}$·h$^{-1}$, the end $T_{\text{cb}}$ rises from 945 to 1059 K (see Fig. 8a and S6). As a result, the CH$_4$ and CO$_2$ conversions increase remarkably from 63.5% and 39.6% to 85.2% and 76.4%, respectively (Fig. 8a). Moreover, the H$_2$ selectivity increases from 87.5% to 95.2%, while the H$_2$O selectivity decreases accordingly, and the CO selectivity remains constant at approximately 100% (Fig. 8b). Furthermore, the H$_2$/CO ratio keeps constant at around 1.5, and a remarkable increase in syngas concentration from 70.9 vol% to 89.7 vol% is observed (Fig. 8c). In general, the CH$_4$ conversion and syngas concentration are again closer to the TE values than the CO$_2$ conversion (cf. Fig. 8a and c), which is consistent with the results in Fig. 7a and c.

### 3.4. Effect of CH$_4$/CO$_2$/O$_2$ ratio

It is worth noting that, for a conventional gas to liquid fuel system, the cost of reforming and post-treatment to produce sufficiently pure syngas accounts for above 50% of the total process cost [6,27]. Indeed, the post-treatment incorporates a costly unit of water gas shift (WGS) [28,29] reaction to adjust the H$_2$/CO ratio and an additional unit for separation of CH$_4$ and the excessive CO$_2$, to attain the needs for the downstream synthesis of fuels. Moreover, a certain amount of CO$_2$ (~2 vol%) needs to remain in the syngas for the downstream synthesis processes [30,31]. Therefore, we should target these two aspects, i.e., a further improvement of the CH$_4$ conversion to ~100% and a remaining fraction of the appropriate amount of CO$_2$ (~2 vol%) in high-quality syngas. Hence, we will now investigate whether we can achieve this by tuning the CH$_4$/CO$_2$/O$_2$ ratio from 3/1/1 (stoichiometric ratio; cf. reaction R(3) above) down to 2.5/1/1 (slight shortage of CH$_4$).

Fig. 9 shows the effect of CH$_4$/CO$_2$/O$_2$ molar ratio on the conversions, selectivities, syngas concentration and H$_2$/CO ratio, by means of a variation in $F_H$, and thus in $F_{P}$ (keeping the same $F_{P}$ of 3.0 SLM). The influence on the temperature profiles of the catalyst bed and reactor wall is presented in Fig. S7. Tuning the CH$_4$/CO$_2$/O$_2$ ratio down to 2.5/1/1 from the stoichiometric ratio 3/1/1 (of reaction R(3)), we can achieve a CH$_4$ conversion of 99.2%, thus nearly reaching 99.4% of the TE conversion (see Fig. 9a). This is because the CH$_4$ fraction is below stoichiometric and because of the slightly lower GHSV and thus slightly higher end $T_{\text{cb}}$ (1153 K vs 1123 K; cf. Fig. S7). The CO$_2$ conversion slightly decreases to 79.4%, but also approaches the thermodynamic equilibrium conversion of 81.1%. The CO selectivity is nearly 100%, like before. The H$_2$ selectivity slightly decreases to 93.1%, with a slight increase in H$_2$O selectivity to 7.2% (Fig. 9b). The syngas concentration remains at around 93 vol%, and the H$_2$/CO ratio slightly decreases from 1.5 to 1.4 (Fig. 9c). As shown in Fig. S7, the temperature profiles of the reactor wall ($T_{\text{rw}}$) are very similar at CH$_4$/CO$_2$/O$_2$ molar ratios of 3/1/1 and 2.5/1/1, while the $T_{\text{cb}}$ profile is slightly higher in the second half of the catalyst bed in case of CH$_4$/CO$_2$/O$_2$ molar ratio of 2.5/1/1, because of less remaining (unreacted) CH$_4$.

### 3.5. Stability test and carbon balance

Fig. S8 shows the stability of the conversions, syngas concentration and H$_2$/CO ratio, by plotting these values as a function of time-on-stream (TOS), i.e., operation time, for 5 h, at $T_H$ of 1123 K, GHSV of 5700 mL·g$^{-1}$·h$^{-1}$ and CH$_4$/CO$_2$/O$_2$ molar ratio of 2.5/1/1 (0.9 SLM $F_H$ and 3.9 SLM $F_P$). The CH$_4$ and CO$_2$ conversions stay constant at 99% and 79%, respectively, for a TOS of 5 h. The same applies for the flow...
rate of the PCR outlet gas (F_{\text{PCR}}^{\text{out}}), the syngas concentration and the H\textsubscript{2}/CO ratio, which remain constant at 7.2 SLM, 93 vol% and 1.4, respectively.

Interestingly, in contrast to the severe issue of coke formation by the conventional catalytic approach of BiRfm [3,4], in our experiments coking is almost absent (see SI: Fig. S9) and accounts for only 0.08% of the total carbon input, as calculated from Fig. S10 and summarized in Table S1 of the SI. This value is negligible and much less than the 0.5% carbon deposition of shale gas to syngas conversion by the chemical looping approach [6]. This tiny amount of coke formation on the used catalyst (0.08% of the total carbon input) is in quite good accordance with the carbon balance between the inlet gas and outlet gas (40.2 mol vs 39.7 mol; cf. Table S1).

The almost absent coking in the P2SG approach can be attributed to two reasons: (1) a significant fraction of the CH\textsubscript{4} is converted in the plasma and thus the CH\textsubscript{4} concentration introduced into the catalyst bed is relatively low; (2) substantial active species derived from the plasma prevent the side reaction of coke formation on the catalysts. Hence, coke formation will not be a problem for the P2SG approach, which assures continuous running of the process to achieve high-quality syngas. In a chemical looping process, to suppress coke formation, a small amount of O\textsubscript{2} is co-fed with CH\textsubscript{4}/CO\textsubscript{2}/O\textsubscript{2} ratio of 1/1/0.2, and thus the H\textsubscript{2}/CO ratio (\sim 1) is relatively low [32].

4. Discussion

So far, we have evaluated the PCR unit in terms of the added value of plasma (Figs. 4 and S1–S3), and the effect of catalyst bed temperature (Figs. 5–7 and S5), GH\textsubscript{SV} (Fig. 9 and S6), and CH\textsubscript{4}/CO\textsubscript{2}/O\textsubscript{2} molar ratio (Fig. 9 and S7) on the CH\textsubscript{4} and CO\textsubscript{2} conversion, product selectivities, syngas ratio and concentration, as well as on the stability and carbon balance (Figs. S8–S10, Table S1). Coupled with a WE unit, the PCR unit forms the novel P2SG system. Hence, we will now discuss the energy efficiency, energy cost, and syngas quality, for the separate PCR unit and for the entire P2SG system.

For the PCR unit, the CH\textsubscript{4} and CO\textsubscript{2} conversions are 99% and 79%, constant in time for at least 5 h (cf. stability test in Fig. S8), at an optimal CH\textsubscript{4}/CO\textsubscript{2}/O\textsubscript{2} ratio of 2.5/1.1. The outlet gas of the PCR unit has a syngas ratio and concentration, as well as on the stability and carbon balance (Table S1). Coupled with a WE unit, the PCR unit forms the novel P2SG system. Hence, we will now discuss the energy efficiency, energy cost, and syngas quality, for the separate PCR unit and for the entire P2SG system.

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Table 1
Flow rate and concentrations of the various products in the outlet gas, and the resulting \((H_2-CO_2)/(CO + CO_2)\) molar ratio (i.e., SN of syngas), as well as the input power, energy efficiency and energy cost, for the separate PCR and WE units, and the entire P2SG system. The results of the PCR unit are obtained at the same conditions as in Fig. S8. For the WE unit, the power and the energy cost are calculated with the assumption of an energy efficiency of 80%, and 2.1 SLM \(H_2\) production rate, as required for the ideal SN value of 2 (see text).

<table>
<thead>
<tr>
<th>unit</th>
<th>power/W</th>
<th>flow rate of outlet gas/SLM</th>
<th>concentration in outlet gas/vol.%</th>
<th>((H_2-CO_2)/(CO + CO_2))</th>
<th>energy efficiency</th>
<th>energy cost/kWh/Nm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCR</td>
<td>397(^a)</td>
<td>7.2</td>
<td>54.8</td>
<td>38.3</td>
<td>2.4</td>
<td>0.2</td>
</tr>
<tr>
<td>WE</td>
<td>560</td>
<td>2.1</td>
<td></td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P2SG</td>
<td>957</td>
<td>9.3</td>
<td>65.0</td>
<td>29.6</td>
<td>1.9</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\(^a\) sum of input power for plasma and heater.

The presence of a low \(CO_2\) concentration in syngas may promote the synthesis rate for the downstream fuel production [30,31]. For instance, a \(CO_2\) concentration of \(-2\) vol\%, as promoter for methanol synthesis [31], must be present in practice to achieve a high \(CO\) conversion into methanol. Hence, for methanol synthesis the ideal syngas stoichiometry is not a molar ratio \(H_2/CO\) of 2, but a molar ratio \((H_2-\ CO_2)/(CO + \ CO_2)\) of 2, also called the stoichiometric number (SN) of syngas [27]. The reverse water gas shift (RWGS) reaction explains why \(CO_2\) appears in the SN. In the absence of \(CO_2\), the SN is simplified as the molar ratio of \(H_2/CO\).

The PCR unit in our study produces syngas with a SN of 1.3 (Table 1), which is less than the ideal value of 2. However, through \(H_2\) addition from the WE unit, the ideal SN value of 2 can easily be reached in the P2SG system, as shown below and in Table 1.

Indeed, for the WE unit, the required \(H_2\) flow rate, \(F_{H_2}^{WE}\) to reach this ideal SN value of 2 is calculated in equation E13,

\[
F_{H_2}^{WE} = \frac{F_{out}^{PCR} \times (2C_{CO}^{PCR} + 3C_{CO_2}^{PCR} - C_{H_2}^{PCR})}{\eta_{H_2}^{PCR}} \tag{E13}
\]

In this way, the required \(H_2\) flow rate of the WE unit (cathode side) is calculated to be 2.1 SLM, yielding an oxygen flow rate of 1.05 SLM (at the anode side), of which 0.9 SLM \(O_2\) is fed in the PCR unit and the rest may be vented.

For the P2SG system, the mixture of 7.2 SLM outlet gas of the PCR unit and 2.1 SLM \(H_2\) of the WE unit yields high-quality syngas of 9.3 SLM with the ideal SN of 2 (see Table 1). Furthermore, the syngas concentration (i.e., sum of \(H_2\) and \(CO\) concentrations) increases from 93.1 vol\% in the PCR unit, to 94.6 vol\% in the P2SG system, and the \(CO_2\) concentration of the P2SG system reaches a favorable 1.9 vol\%, 93.1 vol\% in the PCR unit, to 94.6 vol\% in the P2SG system, and the gas of the PCR unit. Assuming an energy efficiency of 80%, \(CO_2\)/(\(CO + CO_2\)) of 2, also called the stoichiometric number (SN) of syngas [27]. The reverse water gas shift (RWGS) reaction explains why \(CO_2\) appears in the SN. In the absence of \(CO_2\), the SN is simplified as the molar ratio of \(H_2/CO\).

As mentioned above, the required \(H_2\) flow rate of 2.1 SLM is obtained from liquid water via the WE unit, and it is mixed with the outlet gas of the PCR unit. Assuming an energy efficiency of the WE unit, \(\eta_{WE}\) of 80% [11,12], the input power, \(P^{WE}\) and the energy cost of the WE unit, \(E^{WE}\) are calculated according to equations E14 and E15,

\[
P^{WE} = \frac{P^{HE} - HHV_{H_2}}{\eta_{H_2}^{WE}} \tag{E14}
\]

\[
E^{WE} = \frac{P^{WE}}{\eta_{WE}} \tag{E15}
\]

where \(HHV_{H_2}\) denotes the higher heating value of \(H_2\). The obtained values for the input power and energy cost of the WE unit are also listed in Table 1.

Finally, the energy efficiency, \(\eta^{P2SG}\) and energy cost, \(E^{P2SG}\) of the entire P2SG system are calculated according to equations E16, E17,

\[
\eta^{P2SG} = \frac{P^{P2SG} \times (C_{H_2}^{P2SG} - LHV_{H_2} + P_{CO_2}^{P2SG} - HHV_{CO_2})}{P^{PCR} + P^{WE} + P_{CH_4}^{XCH_4} \times LHV_{CH_4}} \times 100\% \tag{E16}
\]

\[
E^{P2SG} = \frac{P^{P2SG}}{P_{out}^{P2SG} \times (C_{H_2}^{P2SG} + C_{CO_2}^{P2SG})} \tag{E17}
\]
synthesis. Therefore, the P2SG approach does not require expensive post-treatment, which distinguishes it from conventional syngas production processes. This work demonstrates the viability of the P2SG approach for large-scale energy storage of renewable electricity via electricity-to-fuel conversion. Indeed, there is no solid evidence yet that the combination with WE unit will effectively work, but this will be studied in the near future.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/jcej.2018.07.111.

References