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

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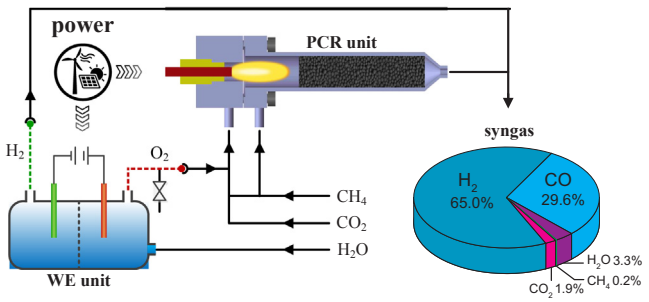
HIGHLIGHTS

- We report a new P2SG approach for CH_4, CO_2 and H_2O 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/Nm^3.
- 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 O_2 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 CH_4, CO_2 and H_2O. 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/Nm^3 at a CH_4 conversion of 99% and a CO_2 conversion of 79% 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/Nm^3. 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 CO_2 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 O_2 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.

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1. Introduction

Synthesis gas (syngas, H_2 + 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 require a 2/1 M ratio of H_2/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 H_2/CO molar ratios of 3 and 1, respectively, which requires additional steps to adjust the H_2/CO ratios to 2. Although oxidative reforming theoretically has a H_2/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 H_2/CO ratio higher than 2 and a considerable amount of CO_2 and H_2O 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 CO_2 and H_2O content of the syngas stream is another important factor relevant to the syngas quality.

Syngas with a H_2/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]:

$$3CH_4 + 2H_2O(g) + CO_2 \rightarrow 4CO + 8H_2 \quad \Delta H^0_{298\,K} = 658.9\,kJ/mol \qquad (R1)$$

However, the BiRfm reaction R(1) consists of two strongly endothermic reactions, and is believed difficult and challenging, and excess steam and CO_2 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 CO_2 and H_2O 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),

$$2H_2O(l) \rightarrow O_2 + 2H_2 \quad \Delta H^0_{298K} = 571.6\,kJ/mol \qquad (R2)$$

$$3CH_4 + O_2 + CO_2 \rightarrow 4CO + 6H_2 \quad \Delta H^0_{298K} = 175.3\,kJ/mol \qquad (R3)$$

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

$$3CH_4 + 2H_2O(l) + CO_2 \rightarrow 4CO + 8H_2 \quad \Delta H^0_{298}K = 747\,kJ/mol \qquad (R4)$$

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 O_2, 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 H_2O is split into pure H_2 and pure O_2, which evolve from the cathode and anode of the WE unit, respectively. Pure O_2 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 H_2 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 CO_2 as a feedstock, which can make an additional important contribution to mitigate the global CO_2 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 $\boldsymbol{F_1}$ 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/CeO_2/Al_2O_3 catalysts (see SI for details), containing Ni of

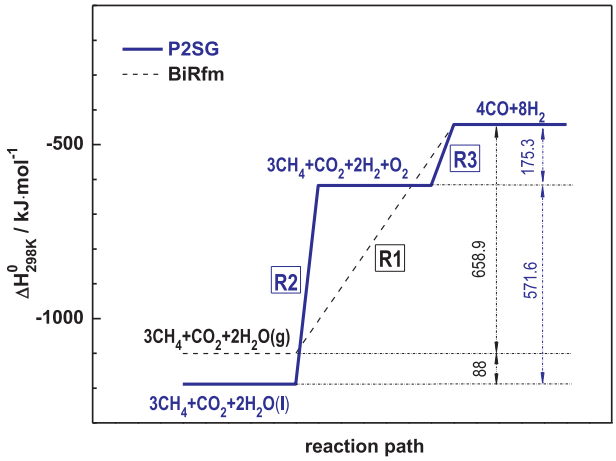

Fig. 1. Standard enthalpy changes of high-quality syngas production from CH_4, H_2O and CO_2 in a 3/2/1 molar ratio, via reactions R(2) and R(3) of the P2SG approach, and via reaction R(1) of the bi-reforming (BiRfm) approach.