

Optimized integration strategies for the PMR-based H₂ production with CO₂ capture process

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ABSTRACT

This work develops process options using a novel protonic membrane reformer (PMR) and liquefaction-based CO₂ capture process for low-carbon hydrogen production from natural gas. Several hybrid concepts of the PMR and liquefaction process are suggested based on the strategies to handle the residual gas from the reformer. The process intensification and optimization results indicate that the hybrid system with a water-gas-shift reactor and off-gas recycling guarantees high H₂ and CO₂ recovery rates for the PMR operating at relatively low H₂ recovery. The hybrid concept also has 74% energy conversion efficiency, which is higher than a conventional steam-methane reforming (SMR)-based H₂ production with chemical absorption CO₂ capture.

Keywords: Hydrogen, Carbon Dioxide Capture, Energy Efficiency, Process Design, Process Intensification, proton conducting membrane.

INTRODUCTION

To achieve low-carbon hydrogen production, a novel protonic membrane reformer (PMR) has been developed that uses electricity to convert natural gas into pure hydrogen while generating a CO₂-rich retentate gas [1,2]. This syngas composition enables efficient low temperature-based carbon capture, achieving high CO₂ capture rates with reduced complexity and cost [3]. Thus, the PMR system produces hydrogen with a low carbon intensity, which can be further reduced with low-carbon electricity.

For process intensification, the integration of the PMR with CO₂ liquefaction offers several potential configurations that optimize energy efficiency and maximize hydrogen and CO₂ recovery. In particular, the hybrid concept allows the PMR to operate at relatively low H₂ recovery rates with less electricity input, guaranteeing high system throughput at a wide range of operating conditions in the reformer. It should be noted that the PMR stacks can achieve very high H₂ recovery rates over 99 % [2], indicating that the PMR-based concepts are not bound to lower recovery scenarios.

This hybrid approach has also been examined in an autothermal reforming (ATR)-based H₂ production

system [4]. Previous studies, however, have only analyzed a single configuration of this hybrid system in detail [5]. Therefore, this study extends earlier work by proposing several hybrid configurations that explore different approaches integrating hydrogen production and CO₂ capture. This comparative analysis aims to identify the optimal configuration that balances energy efficiency, hydrogen and CO₂ recovery, and economic viability, covering a wide operating range of the PMR.

PMR AND HYBRID PROCESS OPTIONS

The focus of this work is on the management of the residual gas from the CO₂ liquefaction process, which has a significant impact on system performance. In particular, (1) the residual gas may contain significant amounts of hydrogen, which directly affects the hydrogen recovery rate of the system, and (2) its flow rate affects both power consumption and capital cost when recycled to the PMR for further hydrogen recovery. Based on the two considerations, four possible hybrid process options are suggested.

Hybrid process without off-gas recycling (Option 1)

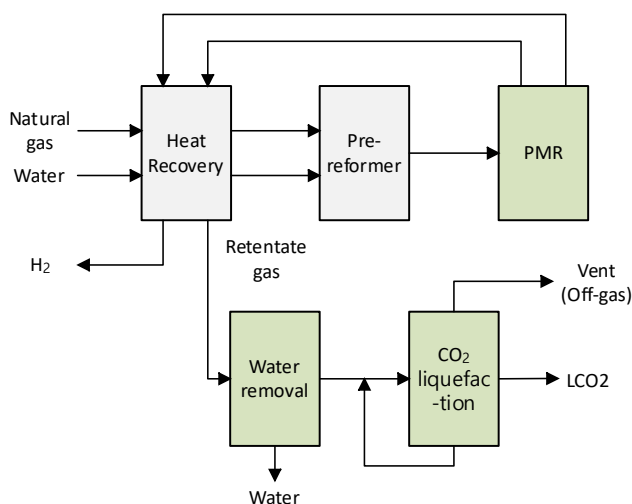


Figure 1. Block diagram of the hybrid process without off-gas recycling (Option 1) (white blocks: process without energy input, green blocks: process with energy input).

A simple cascade of the PMR and liquefaction is a promising option for a low process complexity and easy operation. However, other process steps are required for PMR-based H₂ production, as presented in Figure 1. The first step is heating the two feed streams (natural gas, water) before sending them to a pre-reformer. The heat duty is supplied by the H₂ and retentate gas from the PMR, which has a high temperature. In the pre-reformer, heavier hydrocarbons are converted to methane, which is then fed to the PMR. In the pre-reformer, some CO₂ and H₂ will also already be produced.

The PMR feed stream is further heated by the heat generated from the PMR and supplied to the membrane reformer. The PMR has a net endothermic reaction with steam-methane reforming (SMR) and water-gas-shift (WGS), which is compensated by heat produced during hydrogen separation and compression through the membrane with electricity input. As a result, high-pressure pure H₂ from methane is produced in one step through the PMR while generating a CO₂-rich retentate stream. The internal heat exchange also makes the membrane reformer efficient by eliminating the need for external heating, often regarded as the primary loss point for natural gas-based H₂ production systems. After delivering heat to the heat recovery unit, the retentate stream is dehydrated and condensed through the liquefaction process to capture high-purity CO₂. The impurities in the captured CO₂ are removed via off-gas purging.

Although this configuration efficiently produces hydrogen, the overall hydrogen recovery rate of the hybrid system will be limited by the PMR operation at a relatively low-performance region. This is due to the vent stream, which contains considerable amounts of hydrogen. The hydrogen left in the PMR is sent to the liquefaction process through the retentate gas. Since the H₂ is not

condensed in the CO₂ capture process, it is wasted through the vent gas, resulting in a low system hydrogen recovery rate. In addition, the retentate gas from the PMR contains a relatively high CO fraction, which is difficult to separate from CO₂ while keeping the CO₂ capture rate high in the liquefaction process.

Hybrid process with off-gas recycling (Option 2)

To minimize the H₂ loss of the hybrid system, the off-gas from the liquefaction process can alternatively be recycled to the PMR, as seen in Figure 2. Although recycling will increase the size and capital cost of the system, valuable hydrogen products can be collected from the off-gas, achieving a very high hydrogen recovery rate while maintaining the energy input to the PMR low. However, purging of a part of the recycled off-gas will be required in this configuration to avoid inert gas (such as N₂) accumulation in the hybrid system.

Although the recycled off-gas will improve the system performance with a higher H₂ recovery rate, the retentate gas from the PMR will still contain a considerable amount of CO. Thus, the possible drawbacks of this configuration are (1) the separation of CO in the liquid CO₂ stream will result in a lower CO₂ capture rate, (2) a higher content of impurities in the retentate gas will lead to larger specific power consumption of the CO₂ capture process and thus the hybrid system.

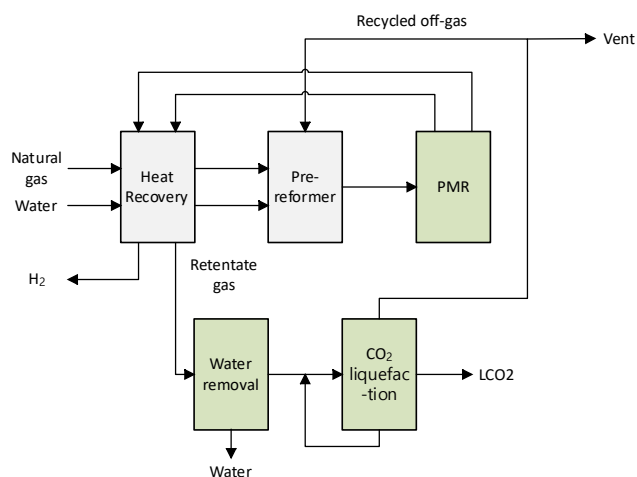


Figure 2. Block diagram of the hybrid process with off-gas recycling (Option 2) (white blocks: process without energy input, green blocks: process with energy input).

Hybrid process with off-gas recycling and extra WGS after liquefaction (Option 3)

To handle the issues of CO, an extra WGS reactor is considered to convert CO to CO₂ in the hybrid system. However, the configuration and the performance of the system will vary depending on the location of the extra WGS reactor.

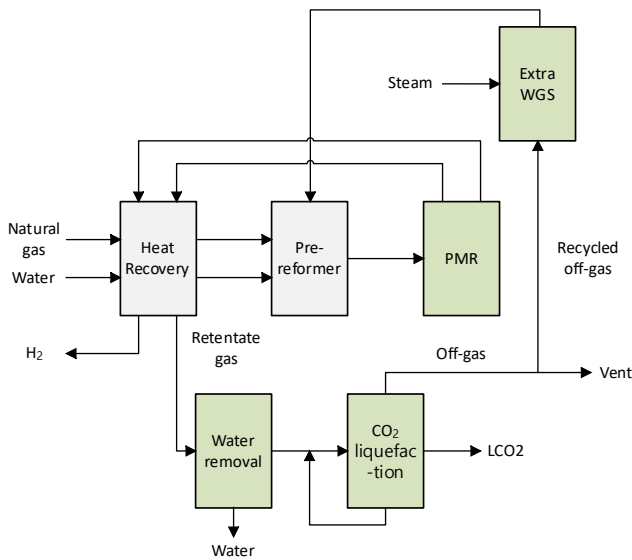


Figure 3. Block diagram of the hybrid process with off-gas recycling and extra WGS after liquefaction (Option 3) (white blocks: process without energy input, green blocks: process with energy input).

Possible locations of the extra WGS reactor are either on the recycled off-gas or the retentate gas. The former configuration is Option 3, where the extra WGS is located before the pre-reformer for the recycled off-gas, as illustrated in Figure 3. In this configuration, the size of the extra WGS is minimized as it is only responsible for the recycled off-gas. This option is considered one of the promising options to be evaluated in detail. However, the extra WGS will not handle the CO in the retentate gas, which is fed to the CO₂ capture part. Thus, this option will also result in poor performance of the liquefaction process and, hence, the hybrid system. In addition, due to the low temperature of the off-gas from the liquefaction process, an extra heat supply will be needed to preheat the recycled stream, thereby reducing the energy efficiency of the hybrid concept.

Hybrid process with off-gas recycling and extra WGS after liquefaction (Option 4)

As shown in Figure 4, another possible hybrid configuration with an extra WGS is to place it on the retentate gas in front of the water removal unit to convert the CO in the feed gas to the liquefaction process. Consequently, almost no CO in the retentate gas is sent to the CO₂ separation process, giving lower specific power consumption and a higher CO₂ capture rate. Another possible advantage is that the vent stream will not require additional equipment to handle the CO. Therefore, this hybrid system will achieve high hydrogen and CO₂ capture rates.

However, the size of the extra WGS reactor will be significantly larger than for Option 3, where the extra WGS is only responsible for the recycled off-gas.

Nevertheless, the high temperature of the retentate gas will not require any additional heat supply system for the reactor, which is essential for Option 3. Thus, an objective comparison of Options 3 and 4 using economic analysis will be necessary to identify the cost-optimal process for the hybrid concept.

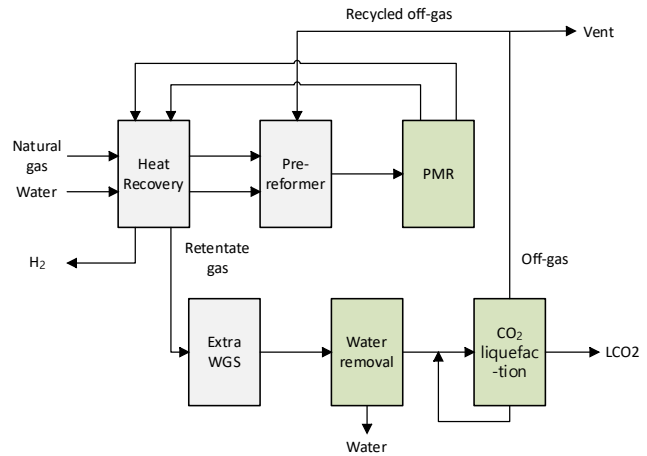


Figure 4. Block diagram of the hybrid process with off-gas recycling and extra WGS after PMR (Option 4) (white blocks: process without energy input, green blocks: process with energy input).

SYSTEM MODELING AND DESIGN BASIS

The hybrid system is modeled using the PMR model in C, which is validated against the data supplied by previous work [1]. The reformer model is integrated with Aspen HYSYS where other process units are modelled to build the hybrid process. This framework uses Matlab to interface the PMR model in C and the HYSYS model. To identify optimal operating conditions for the four different configurations, the hybrid systems are optimized to minimize their specific power consumption (SPC), while the energy conversion efficiency of the system is calculated.

$$SPC_{\text{sys}} = \frac{Power_{\text{net}}}{\dot{m}_{\text{H}_2 \text{ product}}} \quad (1)$$

$$\eta_{\text{energy conversion}} = \frac{LHV_{\text{H}_2 \text{ product}}}{Power_{\text{net}} + LHV_{\text{NG}}} \quad (2)$$

This enables an objective comparison of the different configurations, identifying the most promising option for the hybrid concept. The Particle Swarm Optimization (PSO) algorithm is used for the optimization work as it is a derivative-free approach that can be easily applied to complex or black box models such as this hybrid process.

During the optimization, the system hydrogen recovery rate (HRR) and CO₂ capture rate (CCR) are constrained to be larger than or equal to 95 % and 90 %, respectively. It is worth noting that the operating condition of the PMR is set to give 90% of HRR to identify the benefit of the hybrid concept under a relatively mild operating region for the membrane reformer.

$$HRR_{\text{sys}} = \frac{\dot{n}_{\text{H}_2}}{\dot{n}_{\text{H}_2 \text{ pre-reformer}} + \dot{n}_{\text{H}_2 \text{ PMR}} + \dot{n}_{\text{H}_2 \text{ WGS}}} \quad (3)$$

$$CCR_{\text{sys}} = \frac{\dot{n}_{\text{CO}_2 \text{ Captured}}}{\sum \dot{n}_{\text{C, Natural Gas}}} \quad (4)$$

In addition, the CO₂ loss from the CO₂ capture process is limited to be smaller than or equal to 5 % so that enough CO₂ in the retentate gas is either captured through the liquid CO₂ or recycled via the off-gas. Considering the trade-off between cost and energy efficiency, the minimum approach temperature of heat exchangers is set differently for heat exchangers operating above (20 °C) and below ambient temperature (3 °C).

For the energy-efficient operation of the hybrid concept, the heat generated from the PMR should be matched with the heat required in the heat recovery part to avoid using external heaters. Thus, the system heat balance is constrained to be equal to or larger than zero, which means the system will always have net surplus heat [6].

The thermodynamic performance of the hybrid concept is also affected by the operating conditions of the PMR (temperature, pressure, current density). Yet, their values are fixed in this work for a comparative analysis of different process configurations.

The hybrid system assumes a natural gas feed rate of 3000 kmol/h, with a lower heating value of 50 MJ/kg, to generate around 500 t/d of H₂. CO₂ is specified for delivery at 150 bara with a purity of 99 mol% while maintaining CO levels below 0.5 vol% for pipeline transport [7]. Other key design conditions are listed in Table 1.

Table 1: Design basis for the PMR and the CO₂ capture process [1,5].

Parameters	Unit	Value
PMR SC ratio	-	2.5
PMR temperature	bara	26
PMR pressure	°C	800
PMR current density	A/m ²	7000
PMR retentate pressure	bara	26
PMR retentate temperature	°C	800
Pre-reformer temperature	°C	450
Extra WGS temperature	°C	200
H ₂ product pressure	bara	26
CO ₂ product pressure	bara	150
Compressor efficiency	%	80
Pump efficiency	%	75
Gas expander efficiency	%	85

RESULTS

This section compares the performance of the

hybrid process with that of a conventional H₂ production method with CO₂ capture [8]. The conventional process consists of SMR and WGS reactors, a solvent-based CO₂ capture process, and a pressure swing adsorption H₂ purification step. As seen in Table 2, the hybrid concept gives a higher H₂ and CO₂ recovery rate than the conventional technology.

In addition, the hybrid concept provides a higher energy conversion efficiency than the conventional process, except for Option 1. Another advantage of the hybrid concept is that CO₂ is captured at transport conditions while the conventional system needs purification and compression steps for the captured CO₂, requiring extra power. The simple heat integration performed in the hybrid system also means that a detailed study on the heat integration with the surplus heat from the PMR will further increase the energy conversion efficiency. Thus, the hybrid system will be a less carbon-intensive solution for natural gas-based hydrogen production than the conventional method.

Among the four configurations of the hybrid process, Option 1, which is a simple cascade of the PMR and the liquefaction process, cannot meet the minimum HRR and CCR requirements. In Option 2, both the HRR and CCR can be satisfied by recycling 90 % of the off-gas to the PMR. However, the CO content in the pre-reformer and the retentate gas is too high, which can be an operational burden to the PMR and the CO₂ capture system.

To handle the potential issues with CO, an extra WGS reactor is considered for the recycled off-gas in Option 3. It is observed that the CO in the recycled off-gas is successfully removed. However, a considerable amount of CO generated in the PMR will still exist in the retentate gas, leading to a poor performance of the CO₂ capture process.

In Option 4, an extra WGS reactor is placed after the PMR. The CO in the retentate gas is then removed, and better CO₂ capture performance (SPC and CCR) is achieved. The reduced SPC for the CCS also gives the smallest system SPC compared to other alternatives. Although Option 4 has a slight reduction in system HRR, the lowest system SPC and CO₂ loss will make it the most promising hybrid concept. The detailed process configuration of Option 4 is presented in Figure 5.

CONCLUSION

A hybrid process comprising protonic membrane reformer technology and CO₂ liquefaction is developed in this work for efficient hydrogen production with integrated carbon capture. The hybrid system without recycling the off-gas can have a smaller equipment size and capital cost while having a significant H₂ loss through the off-gas, which is wasted as a vent stream. Therefore, this simple hybrid concept will be practical when the PMR is

Table 2: Performance of the PMR-based hybrid process options and a conventional SMR-based H₂ production with CO₂ capture.

Parameter	SMR with CCS	Option 1	Option 2	Option 3	Option 4
p _{H2} [bara]	22.3	26.0	26.0	26.0	26.0
p _{CO2} [bara]	1.3	150.0	150.0	150.0	150.0
HRR _{sys} [%]	87.0	91.1	99.7	98.9	96.8
CCR _{sys} [%]	90.0	57.8	93.2	92.6	99.1
SPC _{PMR} [MJ/kgH ₂]	-	46.4	42.5	42.6	41.8
SPC _{Liq} [MJ/kgCO ₂]	-	0.5	0.3	0.3	0.3
SPC _{sys} [MJ/kgH ₂]	-	48.2	44.2	44.2	43.9
η _{energy conv} [%]	71.1	64.0	76.4	76.6	74.3

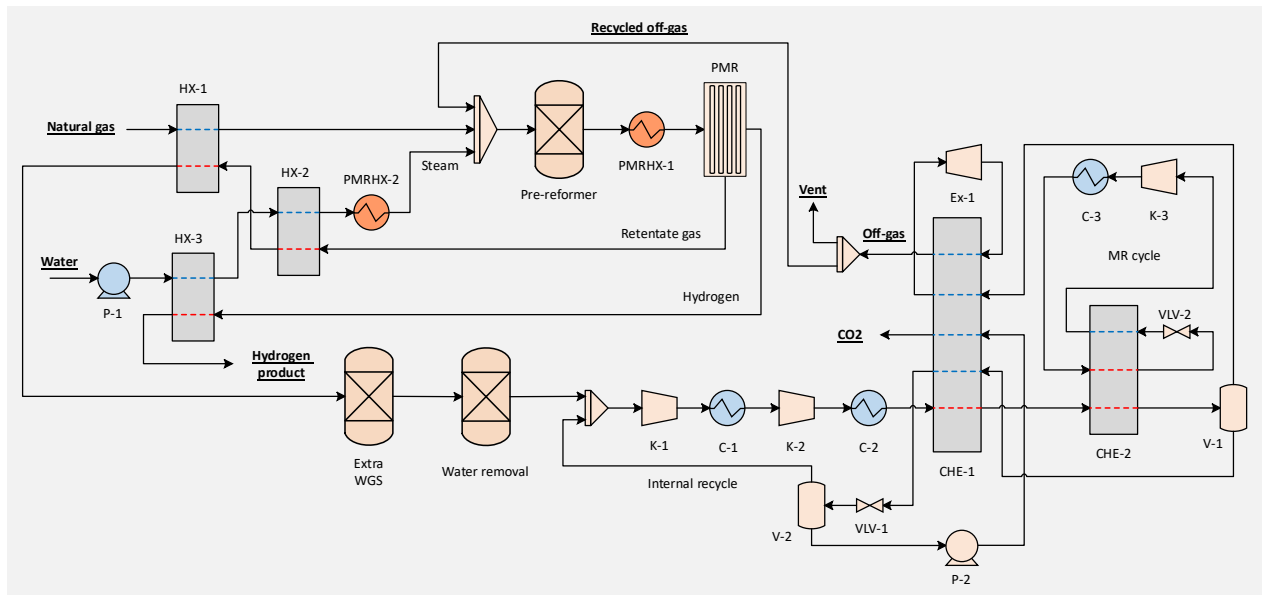


Figure 5: Detailed process flow diagram of hybrid process with off-gas recycling and extra WGS after PMR (Option 4).

in a high-performance operating region where hydrogen recovery is high.

Although the configurations recycling the off-gas will minimize the hydrogen loss, it is found that the CO content in the retentate gas needs to be treated for the downstream carbon capture process. Thus, using a WGS reactor with off-gas recycling is deemed necessary to achieve both high H₂ recovery and carbon capture rates when the PMR is operated at a lower load condition.

In particular, the configuration with the WGS reactor for the retentate gas is the most promising option as it can effectively remove CO in the liquefaction process feed stream, maximizing the carbon capture rate of the system with reduced energy consumption. Therefore, this hybrid concept is considered for further evaluation to explore its potential and role in the hydrogen economy.

Since the PMR-based hybrid utilizes both heat and electricity, their price and CO₂ intensity will be key factors

influencing the techno-economic viability. Therefore, a detailed analysis considering uncertainties in energy prices and CO₂ intensity will be conducted to characterize the economic performance of the hybrid system.

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