

Design of a novel hybrid process for membrane assisted clean hydrogen production with CO₂ capture through liquefaction

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Abstract

This work introduces a novel hybrid concept to produce H₂ from natural gas by using the protonic membrane reformer (PMR) with liquefaction based CO₂ capture system. For process intensification, recycling of the off-gas from the capture process and a water gas shift reactor for the retentate gas from the PMR are applied to the hybrid configuration. The suggested concept achieves around 99 % of system H₂ and CO₂ recovery rates even when the PMR is operated at relatively low hydrogen recovery, resulting in energy efficient H₂ production with a low carbon intensity.

Keywords: Low emission hydrogen production, proton conducting membrane, membrane reactor, CO₂ capture, hybrid process.

1. Background

Hydrogen is a clean fuel and is thus expected to play an important role in a future decarbonized energy scenario. Currently, 48 % of the world's hydrogen is produced by steam reforming (Voldsund et al., 2016), where natural gas and steam react to form hydrogen rich syngas. The focus on low-carbon hydrogen production from natural gas has been predominantly on CO₂ separation technologies. However, CO₂ separation does not contribute significantly to the energy penalty of the process (Voldsund et al., 2016). The largest losses are in the reforming of natural gas to hydrogen and subsequent separation to produce high purity hydrogen. The key focus area for cost-efficient low emission hydrogen production is an intensified process for hydrogen production and separation from natural gas with suitable CO₂ separation technology. Here we investigate an innovative hybrid technology for H₂ production with CO₂ capture combining H₂ production from natural gas by a protonic membrane reformer (PMR) technology with subsequent CO₂ separation by liquefaction in a novel integrated process. The technology enables a high carbon capture rate with high purity CO₂ and H₂ and a hydrogen cost comparable to conventional technologies without CO₂ capture.

The PMR technology produces high-purity hydrogen from steam methane reforming (SMR) in a single-stage electrochemical membrane reactor process with near-zero

energy loss (Malerød-Fjeld et al., 2017). The tubular membrane reformer comprises a BaZrO₃-based proton-conducting electrolyte deposited as a dense film on a porous Ni composite electrode with a dual function as a reforming catalyst. Methane is steam-reformed to CO and H₂ over Ni particles inside the ceramic tube. Hydrogen is electrochemically transported as protons to the outer side, and CO is thereby converted to CO₂ as the water gas shift (WGS) equilibrium is shifted due to the extraction of H₂. The hydrogen produced is of high purity and electrochemically compressed in situ. The H₂ recovery in the PMR is proportional to the electricity input (Malerød-Fjeld et al., 2017). At high hydrogen recovery, the outlet composition is mainly CO₂ and steam. The retentate gas from the PMR has a relatively high fraction of CO₂, which makes CO₂ separation by liquefaction the most competitive technology for this application (Berstad et al., 2013). Liquefaction based CO₂ capture technologies have also been well tested for a wide range of syngas compositions with hydrogen (Kim et al., 2020).

Thus, in this work, different process configurations are developed in an analytical manner to combine the two technologies. One of the process concepts considers the appropriate placement of recycle streams to improve overall H₂ and CO₂ recovery when the PMR is operated at low H₂ recovery of around 90 % (for example reduced current density) for less energy intensive unit operation. Such operating conditions are also expected to lower stress on the material leading to prolonged life. Detailed process models of the different unit operations including the protonic membrane reactor are included in the hybrid system to analyse the different process options.

2. Hybrid process concepts

High recovery rates of H₂ and CO₂ are required on the plant level to achieve energy efficient low carbon hydrogen production for the PMR based system. This requires the development of optimal integration between the PMR and CO₂ liquefaction processes where additional process steps are considered. Figure 1 shows one of the process concepts for the PMR based hydrogen production with carbon capture. In this configuration, natural gas and water are heated by the hot temperature H₂ product and the retentate gas from the PMR. The mixture of natural gas and steam is then sent to a pre-reformer to convert heavier hydrocarbons in natural gas to hydrogen, CO, and CO₂ to supply a pre-reformed feed to the PMR. The pre-reformer outlet stream is set to have a fixed steam carbon ratio.

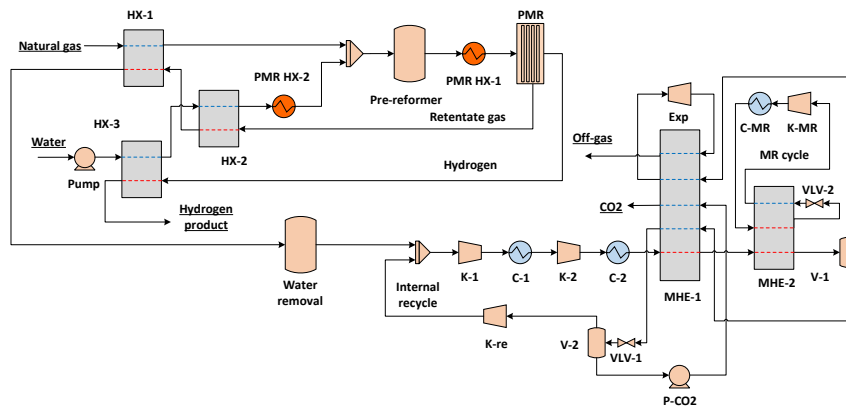


Figure 1. Process flow diagram of the simplified hybrid system for clean hydrogen production.

The temperature of the PMR feed is further increased to the operating temperature of the PMR by using the heat produced from the PMR, which is assumed to be operated isothermally. Then, the compressed pure hydrogen and the retentate gas are produced from the PMR. The SMR and WGS in the PMR result in a net endothermic reaction. However, the heat requirement can be covered by the heat generated by electricity used for the separation and compression of H₂ in the membrane, which is also enough to increase the temperature of the feed streams via PMR HX-1 and 2. The remaining PMR heat after the heat integration could be further used to produce steam.

The retentate gas from the heat recovery unit is fed to the CO₂ liquefaction process, after dehydration, to capture high purity liquid CO₂ while removing impurities in the liquid product through off-gas venting. In the CO₂ capture process (CCP), the dehydrated retentate gas is compressed before being liquefied by a hydrocarbon based mixed refrigerant (CH₄, C₂H₆, C₃H₈, and C₄H₁₀). The cold energy of the incondensable gas (off-gas) from the liquefier (MHE-2) is then used to pre-cool the compressed retentate gas. The off-gas from the pre-cooler is further utilized to supply the cold duty of heat exchanger MHE-1 by depressurizing it via a turbo expander. The liquid CO₂ product from the liquefier is also sent to the pre-cooler to cover the cold duty after being pressurized to the transport pressure. The off-gas leaving the CO₂ capture process could be vented or used as fuel to produce steam in the system.

Hydrogen production of this configuration is, however, dependent on the performance of the PMR as it is the only place where H₂ is extracted. If the hydrogen recovery rate (HRR) of the PMR is low with reduced electric power input, a considerable amount of H₂ left in the PMR is sent to the liquefaction process through the retentate gas. Since the hydrogen is not condensed in the CCP, it is lost through the off-gas, resulting in a low system HRR. Thus, when the PMR is operated at lower hydrogen recovery, the system HRR is also reduced, showing limited flexibility of the process. Another issue of the simplified concept with the PMR operating at low hydrogen recovery is the relatively high CO fraction in the retentate gas that causes poor performance of the CO₂ liquefaction system. The high fraction of CO in the feed to the CCP results in a deeper purification of the liquid CO₂ to achieve high purity. For the purification of the liquid CO₂, a larger amount of off-gas is produced, containing traces of CO₂, hence reducing the system carbon capture rate (CCR). The large flow rate of the off-gas stream will also require an extra facility to treat the CO and H₂ mixture. The high CO fraction, and thus a lower CO₂ fraction in the retentate gas, also means larger power consumption for the liquefaction process where the energy efficiency of the system is proportional to the CO₂ purity of feed gas (Kim et al., 2020).

To maintain H₂ production performance high at a low HRR of the PMR, the off-gas from the liquefaction system can be recycled (see Figure 2). This recycle allows collecting the valuable H₂ in the off-gas through the PMR, achieving a high system HRR. However, some off-gas venting will still be required to avoid N₂ accumulation in the system, which is assumed to be 10 % in this work. The off-gas recycle, however, will not reduce the CO fraction in the retentate gas, resulting in poor carbon capture performance of the hybrid concept. The improvement of the CCP can be achieved by a WGS reactor for the retentate gas as illustrated in Figure 2. The WGS reactor will convert the CO in the retentate gas to CO₂ and H₂, giving a low CO content and simultaneously increasing CO₂ content in the feed to the liquefaction process. Thus, this configuration can achieve high HRR and CCR while producing liquid CO₂ with negligible impurities even when the PMR is operate at low hydrogen recovery.

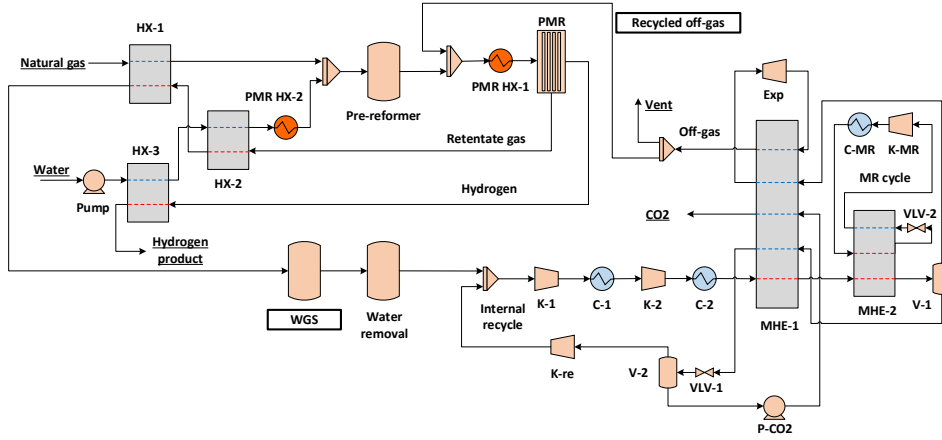


Figure 2. Process flow diagram of the modified hybrid system with off-gas recycle and a WGS reactor for the PMR operating at a low H_2 recovery (See text boxes for the modifications).

3. Modelling approach and design basis

In order to simulate the hybrid system, the PMR is modelled in C to represent the data from Malerød-Fjeld et al. (2017) and connected to Aspen HYSYS where all the other process units are built. In this work, the two process concepts neither include a vent gas utilization nor a steam cycle for the PMR surplus heat left after the heat integration. The PMR operating conditions that give 91 % of HRR are selected for the comparison of the two hybrid configurations assuming the membrane reformer is operated at relatively low H_2 recovery. However, it is worth mentioning that the PMR operating conditions such as temperature and current density will certainly impact process performance. While this has been analysed as part of this work, is not included in the paper. The hybrid system is assumed to have a natural gas feed rate of 3,000 kmol/h (lower heating value of 50 MJ/kg) to produce about 500 t/d hydrogen. CO_2 is assumed to be delivered at 150 bar with 99 mol% purity while allowing CO level lower than 0.5 vol%, assuming pipeline transport (Harkin et al., 2017). Other design conditions are listed in Table 1.

Table 1. Design basis for the PMR and the CO_2 capture process.

Parameters	Unit	Value
PMR feed steam to carbon ratio	-	2.5
PMR operating pressure	bar	26
PMR operating temperature	$^{\circ}C$	800
PMR current density	A/m^2	7000
PMR H_2 product and retentate pressure	bar	26
PMR H_2 product and retentate temperature	$^{\circ}C$	800
Pre-reformer inlet temperature	$^{\circ}C$	450
WGS reactor inlet temperature	$^{\circ}C$	200
ΔT_{min} for gas/gas heat exchanger	$^{\circ}C$	30
ΔT_{min} for gas/liquid heat exchanger	$^{\circ}C$	20
ΔT_{min} for low temperature heat exchanger	$^{\circ}C$	3
Isentropic efficiency of compressor	%	80
Isentropic efficiency of gas expander	%	85
Isentropic efficiency of pump	%	75

4. Key performance indicators (KPIs)

Various key performance indicators are selected to evaluate the thermodynamic performance of the hybrid systems, such as specific power consumption (SPC) of the PMR, the CO₂ capture process, and the overall system. The SPC of the PMR is based on the electricity input to the PMR per unit mass of hydrogen produced. The SPC of the CCP is the net power consumption in the CCP per unit mass of CO₂ captured. The SPC of the hybrid system is estimated by the total net power consumption per unit mass of H₂ produced. The CCR of the CCP is the molar flow rate of the CO₂ captured per unit molar flow rate of CO₂ in the retentate gas. The system CCR is defined as the molar flow rate of CO₂ captured divided by the total molar flow rate of carbon in natural gas. Other KPIs such as hydrogen recovery rate (HRR) are as follows (it is worth mentioning that CH₄ conversion of the PMR is always kept high in this work):

$$HRR_{\text{PMR}} = \frac{\dot{n}_{\text{H}_2, \text{product}}}{\dot{n}_{\text{H}_2, \text{PMR feed}} + \dot{n}_{\text{H}_2, \text{generated in PMR}}} \quad (1)$$

$$HRR_{\text{sys}} = \frac{\dot{n}_{\text{H}_2, \text{product}}}{\dot{n}_{\text{H}_2, \text{produced in pre-ref}} + \dot{n}_{\text{H}_2, \text{produced in PMR}} + \dot{n}_{\text{H}_2, \text{produced in WGS}}} \quad (2)$$

5. Results and discussion

The simulation results in Table 2 indicate that compared to the simplified hybrid concept, the process with off-gas recycle and a WGS reactor has a larger H₂ production capacity and a lower system SPC. Besides, the configuration with the off-gas recycle gives very high system HRR and CCR at around 99 %, verifying that this concept can produce H₂ with a low carbon intensity even when the PMR operating conditions are set for a relatively low HRR (91 %). As presented in Table 2, due to the recycle of the H₂ rich off-gas, the HRR and the hydrogen production rate of the PMR are improved compared to the simplified hybrid system. The recycled stream also makes the PMR feed richer in hydrogen, and it is advantageous to extract and compress H₂ in the membrane reformer, reducing its SPC. Besides, the WGS reactor effectively shifts CO to CO₂ in the retentate gas, increasing the CO₂ content of the feed to the liquefaction process and the efficiency of the CO₂ capture system (higher CCR and lower SPC).

The simplified hybrid concept has a low system carbon capture rate although the process has a similar CCR in the CCP compared to the hybrid process with off-gas recycle. This is because only a part of the natural gas supplied to the system is shifted to CO₂ in the PMR while the rest becomes CO, which is not captured through the liquefaction process. Thus, significant amounts of carbon are lost through the CO rich off-gas from the CO₂ capture process. However, the hybrid concept with off-gas recycle has a WGS reactor where almost all CO in the retentate gas is shifted to CO₂, thus allowing the liquefaction system to reduce the carbon loss via the vented off-gas.

It is worth noting that the heat from the PMR is more effectively utilized in the hybrid concept with off-gas recycle as it has a smaller amount of heat left from the PMR compared to the simplified hybrid system. Although the remaining of the PMR surplus heat is assumed to be used to produce electricity and supplied to the hybrid concepts with a 50 % conversion rate, the configuration with off-gas recycle will still have a lower system SPC (43.0 MJ/kg H₂) compared to the simplified scheme (45.6 MJ/kg H₂).

Table 2. Performance of the two hybrid concepts for clean hydrogen production with the PMR.

Parameter	Unit	Simplified hybrid	Modified hybrid
PMR H ₂ production	t/d	475	560
PMR heat leftover	MW	29.38	13.00
SPC_{PMR}	MJ/kg H ₂	46.39	42.19
HRR_{PMR}	%	91.06	93.99
$x_{CO_2,CCP\ feed}$	(dry basis)	0.53	0.65
$x_{CO,CCP\ feed}$	(dry basis)	0.22	0.01
Captured CO ₂	t/d	1965	3374
SPC_{CCP}	MJ/kg CO ₂	0.45	0.30
CCR_{CCP}	%	83.44	89.27
HRR_{sys}	%	91.06	98.75
CCR_{sys}	%	57.80	99.30
SPC_{sys}	MJ/kg H ₂	48.26	43.99

6. Conclusions

In this work, a novel hybrid concept is developed to produce H₂ from natural gas using an innovative proton membrane reformer followed by a liquefaction based CO₂ capture system. The hybrid concept with off-gas recycle and a WGS reactor effectively recovers H₂ produced in the PMR while capturing almost all CO₂ from the process even when the PMR is operated at relatively low H₂ recovery with less energy input. Thus, this hybrid scheme will be a promising option for H₂ production with a low carbon intensity. This process design can be further improved by optimal heat integration with the PMR surplus heat and the utilization of the vent stream as fuel.

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