

CRYOGENIC CO₂ CONDENSATION AND MEMBRANE SEPARATION OF SYNGAS FOR LARGE-SCALE LH₂ PRODUCTION

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ABSTRACT

Liquid hydrogen (LH₂) has the potential to become a global energy commodity analogous to liquefied natural gas (LNG) in the future. This will require LH₂ production capacities of similar scale as for large-scale LNG plants. Natural gas is an attractive energy source for production of carbon-neutral LH₂. This production will require efficient CO₂ capture and storage (CCS) combined with hydrogen purification. This work presents an advanced technology combination for large-scale hydrogen production with CCS intended for subsequent liquefaction and ship transport. Pure hydrogen for liquefaction is produced by exposing shifted syngas to a palladium membrane unit. The CO₂-rich retentate is dehydrated and separated in a cryogenic condensation unit. The decarbonised, hydrogen-rich top gas from the cryogenic unit can be partly recycled to the membrane unit to increase the hydrogen recovery ratio and CO₂ capture ratio. This paper investigates the influence of central process design parameters on important process performance indicators such as hydrogen recovery ratio and CO₂ capture ratio.

Keywords: Low-temperature; cryogenic; CO₂ capture; Pd membrane; hydrogen production; liquid hydrogen.

1. INTRODUCTION

Liquid hydrogen (LH₂) has the potential to become a global energy commodity analogous to liquefied natural gas (LNG), shipped worldwide in large cryogenic-liquid carriers. An important advantage with LH₂ compared to LNG is that hydrogen produced from steam reforming with CCS is a clean energy carrier. In order to achieve LH₂ production in volumes of similar scale as for LNG, hydrogen production plants with capacity of hundreds, or even thousands, of tons per day are required, corresponding to an energy conversion rate in the magnitude of several hundred megawatts, possibly well above one gigawatt. In addition to brown coal resources in Australia (Kamiya et al., 2015) Norway is also an attractive option in this respect. In the long term, surplus renewable power in Norway may become a potent energy source for hydrogen production of the above-mentioned magnitude. Currently, natural gas is the primary energy source readily available in the required scale. The production of carbon-neutral LH₂ from natural gas requires efficient CCS combined with hydrogen purification in order to minimise emissions and at the same time maximise conversion efficiency.

This work presents an advanced technology combination for large-scale hydrogen production with CCS. The hydrogen is intended for subsequent liquefaction and ship transport to end users, but the concept is applicable to any hydrogen use and a large range of output rates. Syngas is first separated by a metallic membrane with high-purity hydrogen as permeate, which is highly beneficial for subsequent hydrogen liquefaction due to the high purity specifications. The retentate, which consists of enriched CO₂ mixed with residual non-permeated hydrogen and other volatile components, is dehydrated and separated in a low-temperature/cryogenic condensation unit. The CO₂ condensation unit offers flexibility with respect to transport mode, as the CO₂ product stream can be either pressurised by liquid pumping to a high-pressure pipeline transport state, or extracted as liquid CO₂ for ship transport. The gaseous, hydrogen-rich product from the CO₂ condensation unit can be partly recycled to the membrane unit to maximise the hydrogen recovery ratio. The co-location of cryogenic CO₂ separation and hydrogen liquefaction units can provide further synergies such as common centralised chilling and pre-cooling utilities.

2. METHODOLOGY

2.1. The overall process design

The overall technology combination for combined hydrogen and CO₂ separation is shown in Figure 1. Shifted syngas, containing mainly hydrogen, CO₂ and water enters tubular palladium (Pd) membrane units, through which a high fraction of the feed hydrogen permeates. The selective permeation of hydrogen increases the concentration of CO₂ on the retentate side considerably, and the concentration is further increased by subsequent water knockout and dehydration. The resulting CO₂ concentration is typically in the range of 60–80 %, which is a very favourable concentration range for low-temperature/cryogenic bulk separation of CO₂ in the liquid phase.

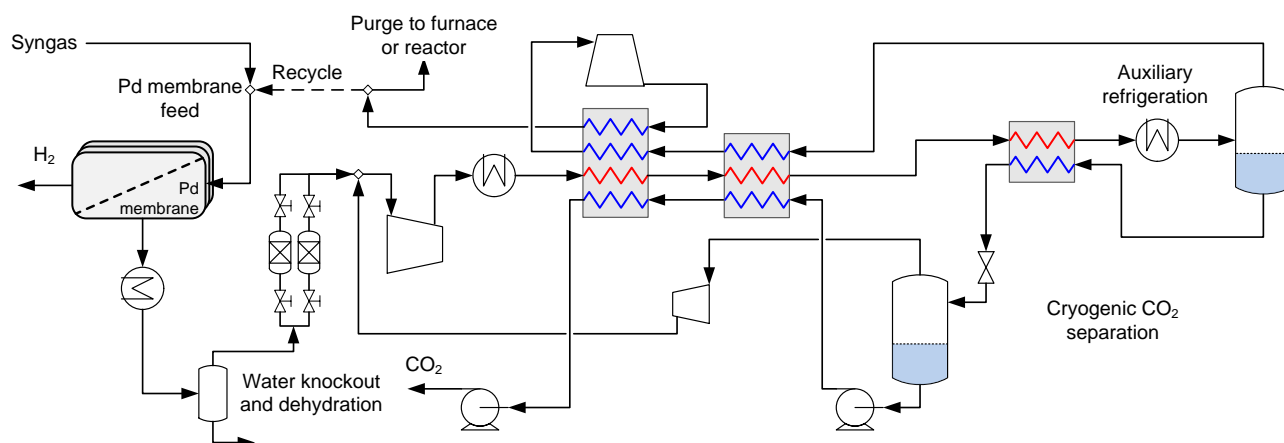


Figure 1: Overall system layout of H₂ purification by Pd membrane separation and cryogenic CO₂ capture.

Upon water removal, the CO₂-rich stream may be compressed to a higher pressure. The feed CO₂ concentration and pressure as well as the CO₂ capture ratio (CCR) target determine whether, or to what extent, compression is needed. After dehydration and optional compression, the stream enters the coldbox and is cooled to separation temperature in a heat exchanger network. Refrigeration is provided by counter-current heat exchange against cold product streams and by auxiliary refrigeration. After the final refrigeration stage, the temperature is typically 219 K and the feed gas is partially condensed. Liquid CO₂ is separated in two stages, the first of which is bulk separation. The second separation occurs at similar temperature, but at a considerably lower pressure of around 0.7 MPa, which results in increased CO₂ purity and recovery of otherwise lost combustible components such as hydrogen, methane and CO. The liquid CO₂ is pressurised to 11 MPa in two pumping stages prior to and after heating. The top gas from the first separation stage is also heated against the feed stream. Depending on the required outlet pressure for this waste product stream, the pressure-based energy can be partially recovered by expanding the top gas stream, as indicated in Figure 1. The top gas is purged to a furnace and/or reforming reactor, but can also be partially recycled to the Pd membrane unit if higher hydrogen recovery ratio (HRR) and CCR is desired. Recycling will require increased membrane area, and becomes thus subject to a trade-off between investment and energy cost.

2.2. Palladium membrane model for hydrogen separation

Crucial process units for realising the advanced technology combination displayed in Figure 1, are membrane modules for separation and purification of hydrogen. Only high-purity hydrogen can be used in conventional hydrogen liquefaction processes. Pd membranes are principally well suited for separating out high-purity hydrogen. This means that bulk separation and purification of hydrogen can be achieved in a single processing step, instead of using for instance an additional multi-stage pressure-swing adsorption (PSA) unit for hydrogen purification before the liquefier. In this work, a detailed mathematical model has been used to describe the membrane module, which has a tubular geometry as displayed in Figure 2. Differential equations were solved, representing the steady-state mass, energy and momentum balances for the permeate/sweep gas (flows in the centre tube) and the feed mixture (flows in the annular section) along the membrane unit. Ideal gas law was used to describe the thermodynamic properties of the gas mixtures. For

all simulations, it was assumed that the membrane unit has perfect thermal insulation from the ambient. Since a large number of pipes will be stacked inside a larger shell in an actual full-scale layout, the adiabatic assumption is reasonable for the current simulations. The local flux along the membrane module, from the feed to the sweep section is a function of the temperature, T , the thickness of the membrane, d , and the partial pressures of hydrogen, $p_{H_2, \text{sweep}}$ and $p_{H_2, \text{feed}}$, as following:

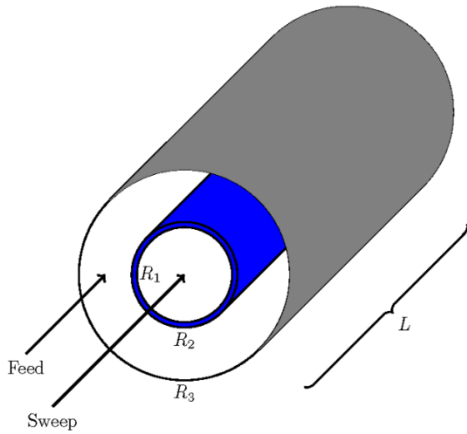


Figure 2: Illustration of the tubular membrane module geometry

$$J_{H_2} = \frac{Q_0}{d} \exp\left(\frac{E_p}{RT}\right) \left(\sqrt{p_{H_2, \text{feed}}} - \sqrt{p_{H_2, \text{sweep}}}\right), \quad \text{Eq. (1)}$$

where Q_0 and E_p are parameters, and R is the universal gas constant. No sweep gas apart from a minor recycle stream of pure hydrogen is assumed to flow on the permeate side of the membrane units. The pressure is assumed to be maintained at a constant value of 110 kPa in order to maximise the hydrogen partial pressure difference and thus flux through the membrane unit, but at the same time keep the permeate pressure above

ambient pressure. Co-current flow was assumed for all simulations, as shown in Figure 2. Maximum HRR is achieved when the driving force for the hydrogen flux becomes zero, that is, when the hydrogen partial pressure is equal on both sides of the membrane. Given a constant pressure of 110 kPa maintained on the permeate side and correspondingly 2.5 MPa on the feed side, the partial pressure is equalised when the retentate-side hydrogen fraction becomes 0.044.

2.3. Low-temperature/cryogenic simulation model for CO₂ separation

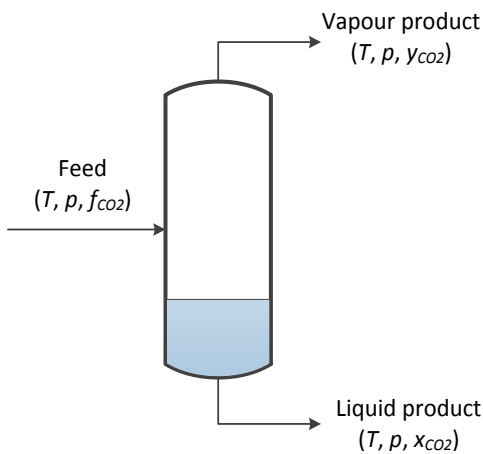


Figure 3: Phase separation of syngas

For gas mixtures with a relatively high CO₂ concentration, the latter component can be separated efficiently from the more volatile gas components by cooling the gas mixture under pressure. Figure 3 illustrates such a vapour–liquid separation process. This type of CO₂ capture process becomes increasingly efficient with respect to CCR and energy requirement at medium to high CO₂ concentrations in the feed (f_{CO_2}). Above a certain threshold, it is superior to physical and chemical solvents for bulk separation of CO₂. This is also the case for the conditions of the retentate gas from a Pd membrane unit. Below the CO₂ dew point temperature at the given pressure, the gas mixture will partially condense and form a CO₂-rich liquid phase with CO₂ concentration x_{CO_2} . The partially decarbonised vapour product from the separation contains the main portion of volatile components, with CO₂ concentration y_{CO_2} . The maximum obtainable yield of the CO₂ condensation process is governed by

the vapour–liquid equilibrium conditions for the given gas mixture. The obtainable CO₂ capture ratio for equilibrium conditions in the binary CO₂/H₂ system is given by Eq. (2), where f_{CO_2} is CO₂ fraction in the feed stream to the cryogenic CO₂ separation unit.

$$CCR = \frac{x_{CO_2}(f_{CO_2} - y_{CO_2})}{f_{CO_2}(x_{CO_2} - y_{CO_2})} \quad \text{Eq. (2)}$$

Experimental vapour–liquid equilibrium (VLE) data for the binary CO₂/H₂ system is available in the literature. Tsang and Street (1981) published VLE measurements for the CO₂/H₂ system for temperatures between 220 K and 290 K, and for pressures up to 172 MPa. Fandiño et al. (2015) published VLE for the respective CO₂/H₂ and CO₂/N₂ systems for temperatures between 218.15 K and 303.15 K and pressures up to 15 MPa.

To ensure that results from the process simulations in this work adhere to those of experimental measurements, the Peng–Robinson (PR) equation of state (EOS) was equipped with interaction parameters for CO₂/H₂ and CO₂/N₂, as recommended by Fandiño et al. (2015). Figure 4 shows a comparison of predictions by PR EOS and experimental results published by Fandiño et al. (2015). The comparison shows that the experimental results are reproduced accurately, particularly for the 218.15 K isotherm, which is the most important isotherm for the cryogenic CO₂ capture unit in the present work. The simulation results underestimate the liquid-phase CO₂ fraction at very high pressure levels (above roughly 6 MPa), but these conditions are not of direct relevance for the process design in the present work. For the same pressure range, a certain underestimation of the vapour-phase CO₂ fraction can be observed for the 258.15 K and 243.15 K isotherms, but these points are also of lesser relevance for the process designs in consideration.

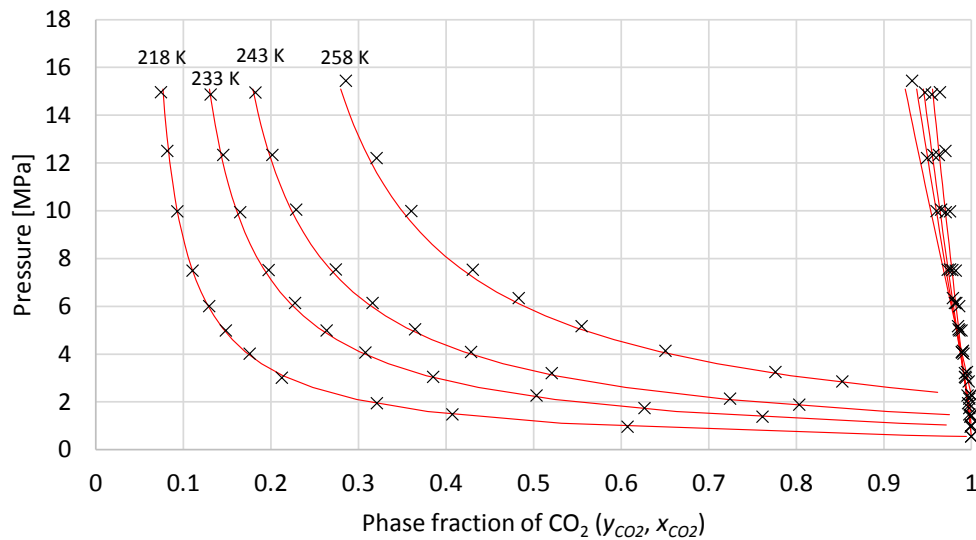


Figure 4: Validation of VLE data for the binary CO₂/H₂ system. Cross markers are experimental results published by Fandiño et al. (2015). Red solid lines are results obtained from computer simulations using Peng–Robinson EOS with modified CO₂/H₂ interaction parameters as recommended by Fandiño et al. (2015). Curves on the left represent y_{CO_2} for four different isotherms while corresponding values for x_{CO_2} are on the right.

3. RESULTS AND DISCUSSION

3.1. Results for hydrogen recovery ratio and CO₂ capture ratio

All system simulations were performed using the shifted syngas feed stream shown in Table 1, and is assumed to be a typical product stream from an adiabatic, low-temperature water-gas shift reactor. Since both separation processes have very high selectivity with respect to hydrogen and CO₂, very high purity of both product streams can be achieved together with high values for HRR and CCR.

Table 1. Syngas feed stream.

T	p	Mol flow	Mass Flow	Composition (mol fraction)					
				CH ₄	N ₂	CO ₂	H ₂	H ₂ O	CO
536	2.5	4.460	52.46	0.0193	0.0016	0.1663	0.6665	0.1354	0.0109

For the syngas in Table 1, the minimum theoretical retentate hydrogen fraction is 0.044 as mentioned in section 2.2. This fraction is achieved when the membrane module is sufficiently long. To illustrate this, Figure 5 shows the simulated hydrogen concentration profile for a membrane with the geometry [$R_1 = 0.035$ m, $R_2 = 0.038$ m, $R_3 = 0.048$ m, $L = 16$ m] and a syngas feed flowrate of 0.633 mol \times s⁻¹, which gives a superficial gas velocity of about 0.6 m \times s⁻¹ at the feed-side inlet.

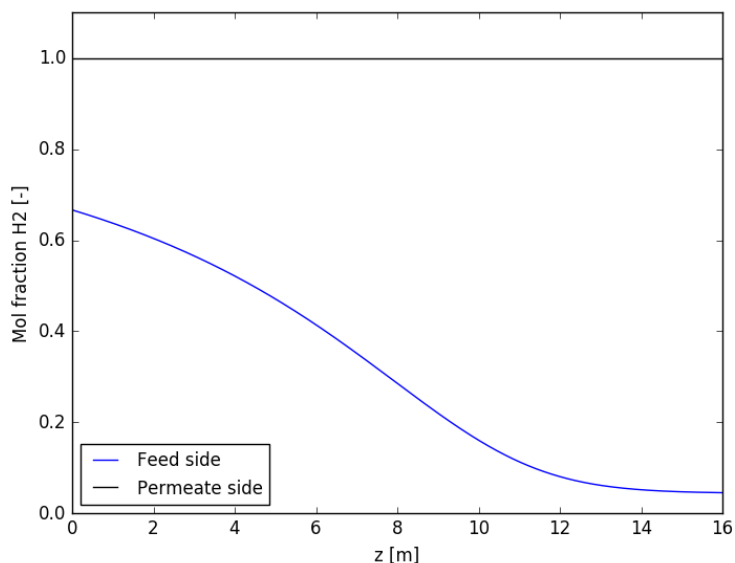


Figure 5: Example of hydrogen concentration profiles in the membrane, as a function of spatial distance, z

therefore generally reduce the hydrogen concentration and partial pressure of the Pd membrane feed. The combination of reduced hydrogen partial pressure and increased volumetric throughput will require increased membrane length or area to achieve a given retentate hydrogen concentration.

Another parametric variation made in the present study is the separation pressure in the cryogenic CO₂ capture unit. The separation temperature was kept constant at 219.15 K and 218.15 K in the primary and secondary separator, respectively. The separation pressure can be used to increase the overall CCR of the system considerably. Higher CCR will in turn increase the hydrogen concentration in the top gas, which can

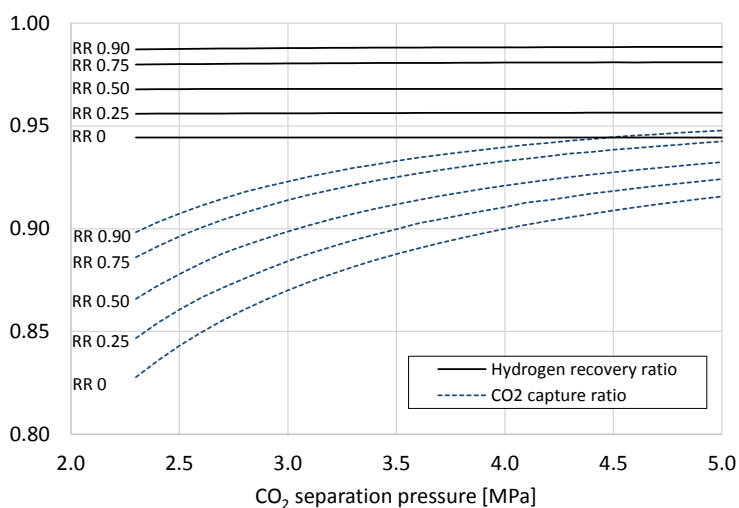


Figure 6: Results for HRR and CCR for variations in separation pressure and recycle ratio. A constant hydrogen concentration of 0.10 is assumed for the retentate stream

be partially recycled to the Pd membrane unit. Results for HRR and CCR are shown in Figure 6, from which a strong correlation between CO₂ separation pressure and CCR can be observed. With no top gas recirculation (RR = 0), the estimated CCR is approximately 83 % for 2.3 MPa separation pressure, and can be increased e.g. to 90 % by raising the separation pressure to around 4 MPa. Increasing RR will also give higher CCR. The separation pressure does not have a strong influence on the HRR, which is mostly affected by the RR. For the case with no top gas recirculation to the membrane (RR = 0), the HRR is 94.4 % for any separation pressure level. Raising the RR from zero to 0.25 while keeping the permeate hydrogen concentration constant, increases the HRR to 95.6 % with 2.3 MPa separation pressure.

Another free variable in the process design is the recycle ratio (RR) of hydrogen-rich top gas from the cryogenic CO₂ capture unit. The optimal degree of top-gas recirculation will depend on the trade-off between positive and negative consequences thereof. The positive effect of recirculation is increased HRR since otherwise purged hydrogen can be partly recovered as a valuable product. This must be weighed against negative effects: the top gas will have a lower hydrogen concentration than the syngas feed, and recirculation will

partially reduce the hydrogen concentration and partial pressure of the Pd membrane feed. The combination of reduced hydrogen partial pressure and increased volumetric throughput will require increased membrane length or area to achieve a given retentate hydrogen concentration.

3.2. Energy results

One simulation case was designed in more detail to provide a typical value for energy requirement. The illustrative case was specified to have 90 % CCR at RR = 0, i.e. no recirculation of decarbonised top gas back to the membrane unit. The design is otherwise as illustrated in Figure 1. Rather conservative values were chosen for most parameters influencing the energy requirement: the syngas compressor and top gas

expander were both assumed to have isentropic efficiencies of 85 %; the expander shaft power was assumed to be recovered with 98 % efficiency; the total pressure drop for the water knock-out and dehydration units was assumed to be around 200 kPa; the pressure drop per heat exchanger channel was set to 50 kPa; the efficiency of the small recycle compressor and the liquid CO₂ pumps in the cryogenic process was set to 80 % and 75 %, respectively; the minimum temperature approach used in the internal heat recovery heat exchangers was 3 K; the coefficient of performance (COP) for the auxiliary refrigeration cooling the feed to 219.15 K was set to 1.5.

The power requirement on a specific basis, i.e. scaled by the captured CO₂ flowrate, is summarised in Table 2. The net specific power requirement for the illustrative case, however not optimised, is 279 kJ×kg_{CO₂}⁻¹. Cooling water pumping has not been included, but will give only a very minor addition to the overall power requirement. Since the specific power requirement is very low in the context of CO₂ capture and compression, the technology concept presented in this paper has a very high potential with respect to overall energy efficiency, and can be further improved through optimisation.

Table 2. Energy results for illustrative case with 94.4 % hydrogen recovery and 90.0 % CO₂ capture ratio.

	Retentate compression	Auxiliary refrigeration	Recycle compression	CO ₂ pumping	Expander recovery	Net power requirement
Spec. power (kJ×kg _{CO₂} ⁻¹)	75.8	174	24.6	13.6	9.6	279

4. CONCLUSIONS

An advanced and novel process concept for hydrogen separation and CO₂ capture from syngas is presented. Hydrogen is separated selectively by a palladium membrane and the retentate is cooled, partially condensed and phase-separated in a low-temperature/cryogenic CO₂ capture unit. The system can be designed to give a very high hydrogen recovery ratio, well above 90 %, which is very favourable for maximising the hydrogen output. A high CO₂ capture ratio can be achieved by either increasing the separation pressure, or by recycling parts of the top gas product from the cryogenic CO₂ separation unit back to the membrane unit.

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NOMENCLATURE

d	Membrane thickness (m)	E_p	Parameter in Eq. 1 (J×mol ⁻¹)
f_i	Fraction of component i in gas feed	p	pressure (MPa)
p_i	Partial pressure of component i (MPa)	Q_0	Parameter in Eq. 1 (mol×m ⁻¹ ×s ⁻¹)
R_n	Radius of layer n (m)	R	molar gas constant (8.314472 J×mol ⁻¹ ×K ⁻¹)
T	temperature (K)	x_i	Fraction of component i in liquid phase
y_i	Fraction of component i in vapour phase	z, L	Length (m)

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