Economically viable large-scale hydrogen liquefaction

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Abstract. The liquid hydrogen demand, particularly driven by clean energy applications, will rise in the near future. As industrial large scale liquefiers will play a major role within the hydrogen supply chain, production capacity will have to increase by a multiple of today’s typical sizes. The main goal is to reduce the total cost of ownership for these plants by increasing energy efficiency with innovative and simple process designs, optimized in capital expenditure. New concepts must ensure a manageable plant complexity and flexible operability. In the phase of process development and selection, a dimensioning of key equipment for large scale liquefiers, such as turbines and compressors as well as heat exchangers, must be performed iteratively to ensure technological feasibility and maturity. Further critical aspects related to hydrogen liquefaction, e.g. fluid properties, ortho-para hydrogen conversion, and coldbox configuration, must be analysed in detail. This paper provides an overview on the approach, challenges and preliminary results in the development of efficient as well as economically viable concepts for large-scale hydrogen liquefaction.

1. Introduction

The investment in the global hydrogen infrastructure for clean energy has lately seen a significant acceleration. Liquefying hydrogen is a way to efficiently transport hydrogen over long distances. It can be particularly cost effective for volumes required by the potential fuel cell vehicle market [1]. Liquid hydrogen (LH\textsubscript{2}) production capacities exceeding conventional 5 to 10 tons per day (tpd) plants may soon be required. Besides challenges in the upscaling, a substantial reduction in specific hydrogen liquefaction costs, \textper kg LH\textsubscript{2}, is required to advance the whole hydrogen value chain. These total ownership costs include plant capital (CAPEX) and operational (OPEX) expenditures.

To reduce specific OPEX, energy efficiency can be increased. The liquefier exergy efficiency is expressed ‘in equation (1)’ as the ratio between specific ideal work of liquefaction \(w_{\text{ideal}}\) and the real energy demand \(w_{\text{real}}\). The ideal work is calculated by applying the First and Second Law of Thermodynamics. The difference in specific exergy \(e\) between LH\textsubscript{2} product and the inlet feed represents the minimum theoretical work required, with specific enthalpy \(h\) and entropy \(s\):

\[
\eta_{\text{ex}} = \frac{w_{\text{ideal}}}{w_{\text{real}}} = \frac{(e_{\text{Product}}-e_{\text{Feed}})}{w_{\text{real}}} = \frac{(h_{\text{Product}}-h_{\text{Feed}}) - T_{0} (s_{\text{Product}}-s_{\text{Feed}})}{w_{\text{real}}} \tag{1}
\]

Electricity costs, however, represent only a portion of total costs. Capital costs are still a major item, even for liquefaction capacities above 50 tpd. In practice, lower plant energy efficiencies can thus be compensated by a simple design with low technical risks, improved operability and maintainability. In process development, these factors are often underestimated.

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This paper outlines a new process development approach for large scale liquefiers up to 150 tpd LH₂. Along with a technically ready plant scale up, the main goal is a reduction in total costs to approximately one third of current 5 tpd liquefiers. This, while coming close to an energy demand \( w_{\text{real}} \) of 6 kWh per kg LH₂ (45% efficiency). Promising process configurations developed within this research undertaking are presented and preliminary results are compared to prior conceptual designs.

2. Prior art

2.1. State-of-the-art plants
A tentative list of known commercial hydrogen liquefiers is given by [3], with reported capacities up to nearly 35 tpd. Liquefiers in operation today can be categorized, by referring to the cold cycle type, into reversed helium Brayton and hydrogen Claude cycles. The former are typically employed for smaller liquefaction capacities due to lower investment costs related to the use of standardized helium screw compressors [4]. Larger liquefiers, up to 15 TPD, or higher, are normally designed with a hydrogen Claude cycle. These are characterized by the use of more expensive reciprocating piston compressors, but savings in OPEX due to a higher energy efficiency and lower refrigerant costs. Once-through liquid nitrogen (\( \text{LN}_2 \)) evaporation at 80 K is used for precooling in both configurations.

Figure 1. State-of-the-art hydrogen Claude cycle with \( \text{LN}_2 \) precooling [3]

‘Figure 1’ illustrates a process flow diagram for a conventional hydrogen Claude cycle similar to the 5 tpd Leuna plant which went on-stream in 2007 [5]. It includes three hydrogen turbines in series, operating at moderate pressures. Oil bearing or high-speed gas bearing turbines are employed [6]. Ortho to para conversion is performed continuously with catalyst filled in plate-fin heat exchangers (PFHX) passages as the feed is cooled and liquefied [7]. The energy demand for an improved 5 tpd liquefier was calculated to 10 kWh per kg LH₂ with 27% efficiency. This figure, however, includes a value of 0.40 kWh/\( \text{LN}_2 \) for the energy required to produce \( \text{LN}_2 \) from a common air separation unit.

2.2. Conceptual liquefiers
A significant number of papers on large scale liquefier concepts has been published in the last two decades. An overview of conceptual designs from literature is given in [3] and [12]. These concepts are designed for capacities ranging from 50 tpd to as much as 860 tpd LH₂. Several, however, have focused only on theoretical efficiency optimization rather than on total costs, operability and technical readiness. A relevant selection of industrially feasible conceptual designs is given hereinafter.
A hydrogen Claude cycle with nitrogen precooling was chosen within the WE-NET project [8] and preferred over helium and neon Brayton options. Quack [9] designed a 170 tpd propane precooled liquefier with 80 bara feed compression and a helium-neon mixture reversed Brayton cycle with 16 compressor stages. Kuendig et al. [10] studied a LNG precooled hydrogen cycle. Berstad et al. [11] adopted the design from [9] introducing a nine component mixed-refrigerant cycle (MRC) with hydrocarbons, nitrogen, neon and R14. The Linde 2010 design [4] focuses on simple improvements to the Leuna process. LN₂ precooling is replaced by chillers and a nitrogen expander cycle. The EU funded IDEALHY project [12] developed a design that included several features proposed in [9] and [11] e.g. 80 bara feed, helium-neon Brayton and MRC precooling above 130 K.

![Figure 2: Liquefaction energy demand and costs of conventional and conceptual liquefiers](image)

Linde 2010 and IDEALHY are evaluated as reference processes in a previous paper [2]. Calculated results for energy demand and costs are compared in ‘Figure 2’ to the 5 tpd liquefier and new targets. The IDEALHY design shows significant improvements in efficiency. The predicted liquefaction costs for the capital intensive IDEALHY are, however, about 20% higher compared to the simple Linde 2010 design. The total cost difference is considerable over a plant lifetime.

### 3. Process development

Further process optimization is required to reach defined targets for specific energy demand and costs. The new development approach considers the factors summarized ‘in Figure 3’. Initially, equipment limitations and technological readiness are assessed. Then, process and cost boundary conditions are defined as design basis. Main assumptions are listed ‘in Table 2’. An extensive total plant cost and profitability model has been developed and validated specifically for hydrogen liquefiers. It is based on equipment cost-capacity functions derived from available cost data or adapted from literature [13].

#### Table 1. Design basis: main liquefier process and cost boundary conditions.

| Process boundary conditions          | Cost model assumptions | Cost model assumptions |
|-------------------------------------|------------------------|------------------------|
| Feed temperature (K) / Para fraction| 303.15 / 25%           | Electricity costs (€ per kWh,el) 0.05 |
| Feed pressure (bara)                | 25                     | Plant availability (-) 95% |
| Product temperature (K) / Para fraction | 22.8 / ≥ 98%          | Cost of capital (-) Ψ 4% |
| Product pressure (bara)             | 2.0 (sat.)             | Depreciation (years) 20 |

*Proprietary data.
A schematic procedure of the implemented cost estimation model is shown in Figure 4 [2]. The cost functions are dependent on simultaneously calculated process parameters. Resulting capital investment and operating costs are used to calculate specific liquefaction costs and profitability indicators. In the development phase, process-economic analyses of precooling and cryogenic cycle subsystems are performed. The impact of different configurations on the integrated plant design is assessed based on efficiency, total costs and technical readiness. As a result, two new developed concepts are identified as particularly promising for large scale hydrogen liquefiers.

3.1. Process concept A: HP Hydrogen Claude with MRC

Pure hydrogen is, as a refrigerant, available on-site, inexpensive and has superior heat transfer properties compared to helium and neon. The new cryogenic cycle is designed with an optimized Claude cycle with pure hydrogen. A simplified process flow diagram is shown in Figure 5.

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**Figure 3.** Process development approach.  
**Figure 4.** Procedure for liquefier cost estimation

**Figure 5.** Concept A: High-Pressure hydrogen Claude with low-temperature MRC
Fundamental differences to conventional plants are higher expansion/compression pressure ratios and higher pressure levels in the hydrogen cycle. The design is optimized for available reciprocating compressors with volumetric flows feasible up to at least 150 tpd LH₂. In the longer term, also turbo compressors may be employed. Additional expanders are added and can be equipped with energy recovery via turbo generators for increased efficiencies.

Alternative precooling options besides LN₂ have been assessed, including nitrogen-expander, MRC and hybrid MR-expander cycles. The precooling temperature choice is crucial in liquefier design. Precooling temperatures below 80 K can be reached with pure nitrogen. MRC in LNG plants typically operate above 120 K. MRC configurations similar to classical small-scale LNG processes, such as PRICO® or LIMUM®, are chosen as preferred precooling solution. Herein designed MRC are operated for hydrogen liquefaction precooling temperatures below 110 K, and thus significantly lower than in LNG applications. To keep simple make up systems, MRC compositions are optimized for up to four components consisting of nitrogen and hydrocarbons. Due to the potential risk of freezing of high boiling components, minimum MRC operation temperature is limited to about 90 K or slightly below.

3.2. Process concept B: Dual cold cycle with MRC

The second developed process adds more new features to conventional hydrogen liquefaction, as illustrated in ‘Figure 6’. Precooling is performed with MRC. The cryogenic cycle is separated into two cascade cooling cycles: a reversed Brayton cycle with a hydrogen-neon mixture and a pure hydrogen Claude cycle for final feed cooling and liquefaction. Hydrogen is kept as principal cold cycle coolant.

The neon fraction increases the molecular weight of the mixture enabling ambient temperature compression in conventional turbo compressors with maximum 6 or 8 stages. Additionally, fewer expander stages are required compared to the pure hydrogen cycle and energy recovery can be implemented more easily. Due to the extremely high neon costs, continuous losses during operation have to be minimized. A hydrogen-neon mixture allows the use of advanced but conventional turbo compressor sealing systems. Compared to helium-neon mixtures, potential refrigerant makeup costs can thus be kept economic even without the use of capital expensive hermetically-sealed compressors.
4. Liquefier process simulation
For process calculation and optimization, the hydrogen liquefier model is implemented in the chemical engineering software UniSim Design® [14]. The model is built in relevant process modules with subflowsheets: compression, precooling, cryogenic cooling and liquefaction. Implemented within simulator spreadsheets, the developed cost model and equipment predesign tools are linked to calculated process parameters. Machine type and frame-size dependent isentropic efficiency functions are defined. Pressure drops are assumed for each fluid stream based on experience.

4.1. Fluid property model
The liquefier model is able to perform accurate process design calculations based on chosen fluid property methods. MRC mixture properties for hydrocarbons and nitrogen are calculated using the Peng-Robinson (PR) equation of state (EOS) and compared to the GERG-2008 model in [14]. NIST REFPROP [15] thermophysical property methods are employed for pure helium and neon as well as the isomeric forms of hydrogen. The latter are based on Leachman et al [16]. The hydrogen-neon mixture is operated in the gas phase. The used simulator does not provide binary interaction parameters for hydrogen-neon systems. Therefore, experimental binary vapor-liquid-equilibrium data of hydrogen-neon by [17][18] were used to fit PR and Soave-Redlich-Kwong (SRK) interaction parameters in [14]. Results were compared to a proprietary model and performed satisfactorily.

4.2. Optimization
The high number of process variables and constraints lead to a complex liquefier model. In order to evaluate new designs, the process simulator is coupled to an external mathematical optimizer developed by Fendt et al. [19] in MATLAB®. The optimization problem involves an objective function \( f(x) \) minimization, with respect to constraints \( g(x) \), by manipulating a vector \( x \) of variables, limited by lower and upper bounds. Energy demand and costs calculated from the simulation model are used as objective optimization functions. Process conditions are linked to the optimizer as variables or constraints. The main optimization variables are refrigerant compositions, pressure as well as temperature levels and differences. Constraints include PFHX temperature differences as well as equipment limitations. The optimizer converges reliably for 16 variables while satisfying constraints.

4.3. Simulation results
In this section, preliminary optimization results for liquefier concepts A and B are presented. For the 100 tpd concept A, the influence on energy demand of MRC precooling temperature before JT expansion is shown in Figure 7 with energy as objective function. The optimized mixed-refrigerant compositions of up to four components include nitrogen and hydrocarbons. The freezing point depression is considered in the low-temperature MRC design while keeping an adequate distance.

![Figure 7. Impact of MRC precooling temperature before JT expansion on concept A.](image-url)
Simulation cases 90 K and 110 K resulted in a negative impact on the hydrogen cold cycle and total plant efficiency. The predicted variation in liquefier energy demand is small between simulation points 95 K and 105 K. Thus, an optimal precooling temperature in this range is chosen.

Calculated energy demand for 100 tpd LH\(_2\) concepts A and B is shown ‘in Figure 8’ for energy (EO) and cost (CO) optimized cases. Concept B is simulated with a conservative hydrogen-neon mixture of 50 mol. %. The composition is undergoing optimization as higher hydrogen fractions are feasible with conventional turbo compressors and lead to higher energy efficiencies. With energy as objective function, consumptions below the aimed 6.0 kWh per kg\(LH_2\) are predicted. Energy recovery via turbo generators is included for larger cryogenic expanders. The efficiency optimized design reaches the defined upper constraints for heat exchanger sizes and feed compression (80 bara). The cost optimized simulation finds an optimum between CAPEX and OPEX, manipulating particularly cost triggering process variables such as \(UA\). The calculated feed pressure level, for instance, is kept to 25 bara by the optimizer, thus eliminating the feed compressor. This commonly leads to reduced plant efficiencies. Simulation results for total cost optimization are shown ‘in Figure 9’ for 50 tpd and 100 tpd LH\(_2\). A stronger negative impact on efficiency was estimated for concept B due to the neon fraction. Calculations show a substantial improvement in liquefaction costs with the new designs. Economy of scale effects are stronger in concept B, mainly driven by turbo compressor and refrigerant make up costs, yielding lower liquefaction costs for 100 tpd. Concept A has also been simulated with LN\(_2\) once-through precooling, assuming a medium LN\(_2\) price for northern Europe. Higher total costs are predicted compared to the MRC simulation option. LN\(_2\) precooling can, however, become competitive under certain favourable boundary conditions.

![Figure 8](image8.png) **Figure 8.** Predicted 100 tpd LH\(_2\) energy demand for concepts A and B with MRC precooling.

![Figure 9](image9.png) **Figure 9.** Predicted 50 tpd and 100 tpd LH\(_2\) total liquefaction costs for concepts A and B.

5. Conclusion

Preliminary results for two newly developed large scale process concepts show that a major reduction in total liquefaction costs can be achieved while energy efficiency can be improved substantially with low technical risk. An evaluation of concepts A and B with MRC precooling is summarized ‘in Table 2’ based on preliminary simulation results presented in this work. An energy consumption of 6 kWh per kg\(LH_2\) with exergy efficiency of 45% can be achieved, but is limited by total cost optimization. Predicted total liquefaction costs for 100 tpd can be reduced to nearly 1/3 of the costs estimated for conventional 5 tpd liquefiers. For a final evaluation of the concepts, a further process and equipment optimization is being carried out to iteratively improve the detail of the design. A multi-objective energy and cost optimization is planned along with sensitivity analysis e.g. with electricity costs. A stepwise implementation of the finally selected design will be outlined.
Table 2. Preliminary comparison of concepts A and B with state-of-the-art. (+) Strength (-) Weakness.

| Parameter         | Conventional Claude | Concept A: HP H2 | Concept B: Dual Cycle |
|-------------------|---------------------|-----------------|----------------------|
| Capacity          | 2 to 15 tpd         | 25 to 150 tpd\(^a\) | 25 to 150 tpd\(^b\) |
| Precooling        | LN\(_2\)            | MRC             | MRC                  |
|                   | + Efficiency        | + Efficiency    | + Efficiency         |
|                   | - Additional equipment | - Additional equipment | H2-Ne Mix & H2     |
| Cold Cycle        | H2 Claude           | + Technical readiness | + Machine count      |
|                   |                      | - No. Compressors | - Neon costs         |
| Energy Efficiency | 10 kWh per kg\(_{LH2}\) | ++              | ++ Total specific costs |
| CAPEX & OPEX      | + Low CAPEX         | ++ Total specific costs | ++ Total specific costs |

\(^a\)Based on economic equipment plant up and down scaling estimation.

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