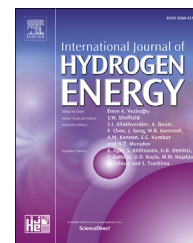




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Roadmap to economically viable hydrogen liquefaction

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ABSTRACT

The distribution of hydrogen in liquid state has several advantages because of its higher volumetric density compared to compressed hydrogen gas. The demand for liquid hydrogen (LH₂), particularly driven by clean fuel cell applications, is expected to rise in the near future. **Large-scale hydrogen liquefaction plants will play a major role within the hydrogen supply chain.** The barriers of built hydrogen liquefiers is the **low exergy efficiency and the high specific liquefaction costs.** Exergy efficiency improvements, however, are limited by economic viability. The focus of this paper is to present a roadmap for the scale-up of hydrogen liquefaction technology, from state-of-the-art plants to newly developed large-scale liquefaction processes. The **work is aimed at reducing the specific liquefaction costs by finding an optimal trade-off between capital costs and operating costs.** To this end, two developed hydrogen liquefaction processes were optimized for **specific energy consumption and specific liquefaction costs,** showing the potential to reduce the specific liquefaction costs by **67% for a 100 tpd LH₂ plant** compared to a conventional **5 tpd LH₂ plant** while achieving a specific energy consumption **between 5.9 and 6.6 kWh per kg LH₂** with technology that is or will be available within 5 years. The **results make liquid hydrogen a viable distribution route for hydrogen for mobility.**

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Introduction

Air pollution and global warming coming along with globalization, a growing world population and its ambition for higher living standard menace the future of mankind. For the last 200 years mobility, heating and power generation relied mainly on combustion of hydrocarbons causing carbon dioxide, soot and other pollutants. Carbon dioxide with more than 80% share is by far the main greenhouse gas (GHG) [1]. Transport, being responsible for one third of total GHG

emission in the US [1] and about 20% in the EU, is the only major sector in the EU where greenhouse gas emissions are still rising [2]. Any technological progress in combustion engines has been outbalanced by an increasing individual mobility and the demand for larger and heavier vehicles. In recent years, focus has therefore been set on individual cars accounting for about 75% of all CO₂ emissions coming from transport [2].

Hydrogen has come into focus as a potential future energy carrier as it reacts in a fuel cell with atmospheric oxygen releasing only electric energy, heat and water. Fuel cells can

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be used for mobility and stationary applications [3]. Several national initiatives, for instance in California, Japan and Germany [3–5], promote and support the installation of hydrogen refilling station (HRS) networks; car industries such as Hyundai and Toyota [5] have started the commercial production of fuel cell electric vehicles (FCEV) running on hydrogen, others such as Honda and Mercedes will follow [5].

These cars are equipped with gas tanks for highly compressed gaseous hydrogen (CGH₂) at 700 bar and near to ambient temperature [6]. Most of the refilling stations also operate on CGH₂ because of its flexible availability and its low distribution costs for small quantities in short range. Individual mobility requires a minimum number of refilling stations even at a small number of FCEVs being operated. A reasonable network density of hydrogen refilling stations (HRS) requires a high investment in infrastructure e.g. for up to 400 HRS to be built in Germany by 2023 [4] with a total estimated investment of approximately €400 million. Starting on a small number of fuel cell cars leads to a very low traffic frequency at the HRS [6], causing significant amortization cost. A focus on vehicles with higher daily consumption would reduce this problem and bring down more quickly the cost in the hydrogen supply chain. Table 1 shows typical consumption rates for different vehicle types assumed in this paper based on [3,5,6], and estimates their resulting number being served by one CGH₂ trailer, one liquid hydrogen (LH₂) trailer, one hydrogen source of 5 tons per day (tpd), for instance [7], and one of 50 tpd.

Buses, trains and maybe ferry services are ideal candidates to establish a low cost hydrogen infrastructure for a hydrogen based green mobility. Due to their all day long operation they require significant amounts of fuel. According to Table 1, each fuel cell bus consumes in average 75 times and each train about 400–600 times of hydrogen compared to a fuel cell car [6], bringing down specific amortization costs for infrastructure to an acceptable level. One or two filling stations can serve all fleet vehicles overnight. The network density is not that of importance, instead these larger HRS can serve as distribution bases for relatively cheap hydrogen to car refilling stations. Production numbers of buses and trains are not so high allowing return on development already at smaller series. And space for fuel storage is also of minor priority.

Other fleets of fuel cell vehicles, such as trucks for retail and logistics, taxi and car sharing can also help to bring up the number of hydrogen consumers, keeping needs on infrastructure low. Ferry services [5] and coastal shipping would even inflate the hydrogen mobility. Assuming the estimate in Table 1, each ship would consume as much hydrogen as five

thousand cars. Ship HRS infrastructure could in turn become the basis for a bus and train network. Although non private traffic contributes only to 25% percent of the total transport emissions, starting in public and logistics transport allows a much faster and economically viable market development in hydrogen mobility.

Distributing and storing the required hydrogen as a cryogenic liquid offers several advantages compared to CGH₂. Because of the significantly higher volumetric density of liquid hydrogen (LH₂), the transportable load per LH₂ trailer is significantly higher than in a CGH₂ trailer [3], bringing down transport cost and trailer frequency at the station. Compared to CGH₂, the delivery of LH₂ becomes increasingly cost-efficient for larger transport volumes and over longer transport distances [3], as required by hydrogen mobility. Further on, the liquid hydrogen comes in guaranteed clean condition as any impurity will be frozen out in the liquefier plant.

The footprint of storage and infrastructure on the filling station is much smaller when compressing the cold hydrogen directly into the vehicles CGH₂ or LH₂ tank. The evaporation rate of the liquid hydrogen is of minor concern as the consumption rate is high enough for a regular operation.

Liquid hydrogen is produced by the cooling, expansion and the liquefaction of an expanded gaseous hydrogen feed gas stream from ambient conditions to a temperature of about 20 K [8]. The principles of hydrogen liquefaction and installed industrial liquefaction processes are described extensively in literature [7–12]. The hydrogen cooling in built industrial hydrogen liquefaction processes is typically performed in two refrigeration steps. For the hydrogen precooling to an intermediate temperature of about 80 K, a liquid nitrogen (LN₂) stream is used. For the cryogenic hydrogen cooling between 80 K and a liquefaction temperature of about 20 K, only helium and hydrogen are available as pure refrigerant fluids for a cryogenic refrigeration cycle [8]. A further challenge of industrial hydrogen liquefiers is the required catalytic ortho-to-para-hydrogen conversion [8,13].

The relatively low exergy efficiency of installed hydrogen liquefaction plants is the main draw back of a LH₂ supply infrastructure. The specific energy consumption SEC of a state-of-the-art 5 tpd LH₂ hydrogen liquefier with LN₂ precooling is about 10 kWh per kg LH₂ [14,15]. The future hydrogen mobility market will ask for large-scale hydrogen liquefaction plants with a significant improvement in exergy efficiency. Therefore, several studies for future large-scale hydrogen liquefaction plants were published since the late 1970s. An encompassing literature review is given in Refs. [16–18]. The majority of these publications focused on

Table 1 – Estimated number of fuel cell powered vehicles based on assumed hydrogen fuel consumption rates.

Vehicle type	Assumed H ₂ consumption (tpd) [3,5,6]	Trailer [3]		Hydrogen source	
		CGH ₂	LH ₂	5 tpd	50 tpd
		1 ton H ₂	3.5 tons H ₂		
Passenger car	0.0004	2500	8750	12,500	125,000
Bus/Truck	0.03	33	117	167	1667
Train	0.25	4	14	20	200
Coastal ship	2	0.5	1.75	2.5	25
Large ship	10	0.1	0.35	0.5	5

developing new process concepts by maximizing the liquefier exergy efficiency through theoretical simulation [15]. The recent IDEALHY study [19], for instance, sets an ambitious benchmark for the specific energy consumption SEC to 6.4 kWh per kg LH₂ by applying a complex and capital intensive hydrogen liquefaction process.

The improvements in the exergy efficiency for novel hydrogen liquefaction processes, however, are limited by economic viability, technological readiness of equipment as well as plant operability and maintainability. A higher specific energy consumption SEC can be compensated by lower capital expenditures and reduced risks [15]. These aspects are often underestimated.

The roadmap proposed in this paper outlines a stepwise implementation of large-scale hydrogen liquefaction technology for a low cost hydrogen supply chain, from installed state-of-the-art liquefier plants towards new large-scale liquefaction processes developed [15,20] and optimized to reduce the specific liquefaction costs SLC, which include plant capital and operating costs.

From current liquefiers to recent studies

The exergy efficiency of the hydrogen liquefaction process must be increased in order to decrease electricity costs, which are part of the plant variable operating costs (OPEX). The liquefier exergy efficiency is defined as the ratio between the specific work for an ideal hydrogen liquefaction process w_{ideal} and the real specific energy consumed by the process w_{real} . It is expressed as exergy efficiency in equation (1):

$$\eta_{ex} = \frac{w_{ideal}}{w_{real}} = \frac{(h_{Product} - h_{Feed}) - T_0 \cdot (s_{Product} - s_{Feed})}{w_{real}} \quad (1)$$

The minimum required theoretical liquefaction work w_{ideal} is equal to the difference in specific exergy between the liquid product state and the inlet feed gas. It is calculated with the specific enthalpy h and the specific entropy s of the feed and the liquid product. The work required for an ideal hydrogen liquefaction process is calculated to 2.7 kWh per kg LH₂ for an inlet hydrogen feed gas pressure of 25 bar, an inlet temperature of 303 K and an inlet *para*-hydrogen fraction of 25%. The liquid hydrogen product is assumed as saturated liquid with a pressure of 2 bar and a final *para*-hydrogen fraction of 98% at the outlet. In this paper, all given pressure values are absolute. The work for an ideal hydrogen liquefaction increases by over 40% to 3.8 kWh per kg LH₂ if the feed is available at ambient pressure.

Current liquefaction technology

Up to now, several industrial scale hydrogen liquefiers were built and operated, particularly in North America, Europe and Japan [16]. The largest trains are reported to be sized in the USA for liquefaction capacities of up to 55 tpd LH₂ [21,22] while more recent liquefiers were designed with a smaller plant capacity close to 5 tpd LH₂ or slightly above [16,22].

The current technology for small to medium scale industrial hydrogen liquefaction is mainly based on the process configurations summarized in Table 2 [8,11]. Hydrogen gas

Table 2 – Typical design of current industrial hydrogen liquefaction plant technology [8,11].

Parameter	Current technology	
	Helium	Hydrogen
Liquefaction capacity, in tpd	<3	2 to 15 or higher
Cryogenic refrigeration cycle	Helium Brayton cycle <25 bar	Hydrogen Claude cycle <25 bar
Precooling	LN ₂ once-through	LN ₂ once-through
Compressor type	Oil flooded screw	Reciprocating piston
Feed gas pressure, in bar	10 to 15	15 to 30

from a production plant e.g. a methane steam reformer or an electrolyzer [3], is fed to the liquefier with a typical feed pressure between 15 bar and 30 bar. Built liquefiers can be categorized into processes based either on a helium Brayton cycle or a hydrogen Claude cycle, just by referring to the type of closed loop cryogenic refrigeration cycle [11,23]. The process is typically chosen in function of plant capacity as well as economic boundary conditions such as plant location and electricity prices. Liquid nitrogen (LN₂) is often used for a precooling of the hydrogen feed gas to approximately 80 K. The benefit of LN₂ precooling is the low capital expenditure compared to a closed cycle, since no additional expander or compressor is required [8,11]. The liquid nitrogen is typically produced in an air separation units (ASU). The required catalytic *ortho*-to *para*-hydrogen conversion [8,13] in modern industrial hydrogen liquefiers is carried out with the catalyst filled inside the plate-fin heat exchangers [24].

These conventional hydrogen liquefaction processes are energy intensive. The availability of performance data of industrial liquefiers is, however, very limited. The specific energy consumption SEC of liquefier trains operated in the USA is stated to range between 12.5 and 15 kWh per kg LH₂ for capacities between 5.4 and 32 tpd LH₂ [25], but no data on boundary conditions or process configuration was given. More process details are available from the Ingolstadt plant [7] and from the Leuna plant [10]. Based on a capacity of 5 tpd LH₂ and process conditions given in Ref. [10], the SEC for the Leuna process was calculated to 11.9 kWh per kg LH₂. This value for the specific energy consumption was often taken as a benchmark for process and cost comparisons without checking for consistency. For example, the value includes the power required to compress the feed from ambient pressure to 24 bar as well as a specific energy consumption of 0.4 kWh per liter LN₂ assumed for the production of liquid nitrogen (LN₂) [10].

Recent conceptual studies

Improved large scale liquefaction plants, designed to produce liquid hydrogen more efficiently and at reduced costs, are predicted to be an opportunity and a challenge to boost the future hydrogen economy. Particularly in the last two decades, a significant number of conceptual studies were conducted and scientific papers were published on the topic of large-scale hydrogen liquefaction processes. An extensive

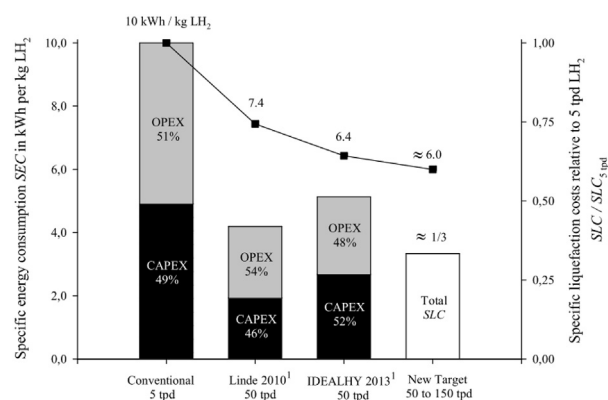
literature review of available conceptual processes is given by the authors in Refs. [16–18].

A selection of large-scale liquefier concepts from literature was given by the author [15]. In 1978, an early study of a 250 tpd LH₂ plant was performed by Ref. [26] for a large-scale hydrogen liquefier with a hydrogen Claude cycle and nitrogen precooling. An economic analysis of three different hydrogen liquefaction systems was presented in Ref. [27]. The Japanese WE-NET project assessed different liquefier process concepts for hydrogen liquefiers and selected a hydrogen Claude cycle with closed loop nitrogen precooling as preferred concept [28]. An innovative process concept was proposed by Ref. [29] for a 170 tpd LH₂ liquefier with a hydrogen feed gas compression to 80 bar and a propane vapor compression refrigerator for precooling. A helium–neon mixture was designed as refrigerant for a cryogenic cycle with turbo compressors with up to 16 compressor stages. A hydrogen cycle precooled by a liquefied natural gas (LNG) stream was investigated in Ref. [30]. The helium–neon cryogenic cycle proposed by Ref. [29] was adopted in a new design by Ref. [17] with a 9-component mixed-refrigerant precooling cycle composed of a blend of nitrogen with hydrocarbons, neon and R14. These conceptual processes were designed with liquefier capacities ranging from 50 tpd LH₂ to as much as 860 tpd LH₂, and indicating exergy efficiencies of up to 50% or higher. However, many studies have focused on maximizing the liquefaction exergy efficiency η_{ex} through theoretical simulations, while neglecting plant total ownership costs, which include both capital expenditure (CAPEX) and operating expenditure (OPEX).

The evaluation and correct interpretation of liquefier designs in terms of costs and efficiencies is complicated if process simulations are not based on identical criteria and boundary conditions. This is well understood in literature [31], but is often not applied in practice e.g. due to missing data. In particular, plant capacity, feed inlet and product conditions have a major impact on the calculated specific work of liquefaction, and hence, also on exergy efficiency. Finally, the quality of assumptions on the technical readiness and performance of key process equipment should not be underestimated e.g. isentropic efficiencies.

Comparison of selected conceptual liquefiers

Based on identical process and cost boundary conditions given in Table 4, two existing 50 tpd LH₂ conceptual liquefiers and one conventional 5 tpd LH₂ design with LN₂ precooling were recalculated with a newly implemented process model which is directly linked to spreadsheets for a detailed cost estimation [14,15]. The IDEALHY project [19] was chosen as a benchmark for exergy efficiency, as well as being the most recent study which included some of the authors and process features of the aforementioned papers [17,29]. The Linde 2010 design [11] was considered as a reference for a technically ready large-scale concept, which focused more on low capital investment and simple improvements to the Leuna process [10,14]. The results for the recalculated processes predicted that the specific energy consumption SEC of the IDEALHY design is about 1 kWh per kg LH₂ lower than the SEC for the Linde 2010 design, as indicated in Fig. 1 [14,15].



¹The process and cost calculation was adapted from the original publication

Fig. 1 – Calculation results for the specific energy consumption SEC and the specific liquefaction costs SLC for the conventional 5 tpd, Linde 2010 50 tpd and IDEALHY 50 tpd LH₂ liquefiers.

In the original publication [19], the specific liquefaction costs SLC for the capital intensive IDEALHY concept were calculated to 1.38 € per kg LH₂ at an electricity price of 0.05 € per kWh_{el}. The SLC estimated in the original publication [19] appear to be slightly underestimated since the total capital investment required for the IDEALHY process was given only as a ball-park figure without a detailed plant capital cost calculation and without considering additional annual operating costs e.g. mixed-refrigerant and helium–neon gas losses.

The specific liquefaction costs SLC of both processes were estimated with the cost model implemented within this research work [14,15,20]. The recalculated SLC for the high-efficient IDEALHY liquefier were higher than the 1.38 € per kg given in Ref. [19], and were approximately 20% higher than the SLC predicted for the less efficient Linde 2010 design [14]. By upscaling production capacity by a factor of 10 with only minor modifications, the Linde 2010 process results in a more than 50% lower SLC compared to a conventional 5 tpd LH₂ liquefier.

New process development

Electricity costs, which are directly linked to the specific energy consumption SEC of the plant, are not the sole cost item within the annual OPEX. Moreover, the results from the previous section have indicated that even for liquefaction capacities of 50 tpd LH₂, the total capital investment is a major item within the liquefier total costs of ownership e.g. about 50% at electricity prices of 0.05 € per kWh_{el}. The development approach outlined in Refs. [14,15,20] therefore focuses on optimizing the specific liquefaction costs SLC rather than only exergy efficiency. To reach the targets in Table 3, new processes were designed [15,20] to liquefy up to 150 tpd LH₂ with technology that is available today or within 5 years.

Process simulation and costs

The hydrogen liquefier model is implemented in the chemical process simulator UniSim Design [32] for process calculations

Table 3 – Research objectives for large-scale hydrogen liquefier [14,15].

Parameter	Target
Technological readiness	Within 5 years
Liquefaction capacity	Up to 150 tpd
Specific energy consumption and Exergy efficiency	Near 6 kWh per kg LH ₂ ≥45%
Specific liquefaction costs	≈ 1/3 of 5 tpd

and parameter optimization [15,20]. The main boundary conditions used as a design basis for the simulation cases are listed in Table 4 [14,15]. The liquefier process simulation model and the assumptions related to the component simulation are described in Ref. [20]. The isentropic efficiencies for the expanders and compressors, for instance, are calculated with equipment size dependent functions which are implemented in the simulation model [20]. The high number of process variables and constraints lead to a complex liquefier model.

The simulator is therefore coupled to an external mathematical optimizer in MATLAB® [33] to manipulate key process variables and solve the liquefier simulation by objective function minimization [15,20]. Either the calculated specific energy consumption SEC or liquefaction costs SLC were used as objective functions. A detailed description of the simulation model as well as the optimization method including constraints and assumptions used for SEC and SLC calculation is given in Ref. [20]. To assess the process economics of new hydrogen liquefier designs, a cost estimation model was developed and directly linked to parameters calculated by the process simulation model. The implemented cost model is based on the method and scope of supply shown in Fig. 2 [14,15,20]. The total capital expenses are calculated with cost-capacity functions that are fitted with available cost data or assumptions from literature. The liquefaction costs

represent the plant total cost of ownership (TCO) and include all yearly operating expenses as well as the annuity deriving from the capital investment. A more detailed description of the cost model is given in Ref. [20].

New hydrogen liquefaction processes

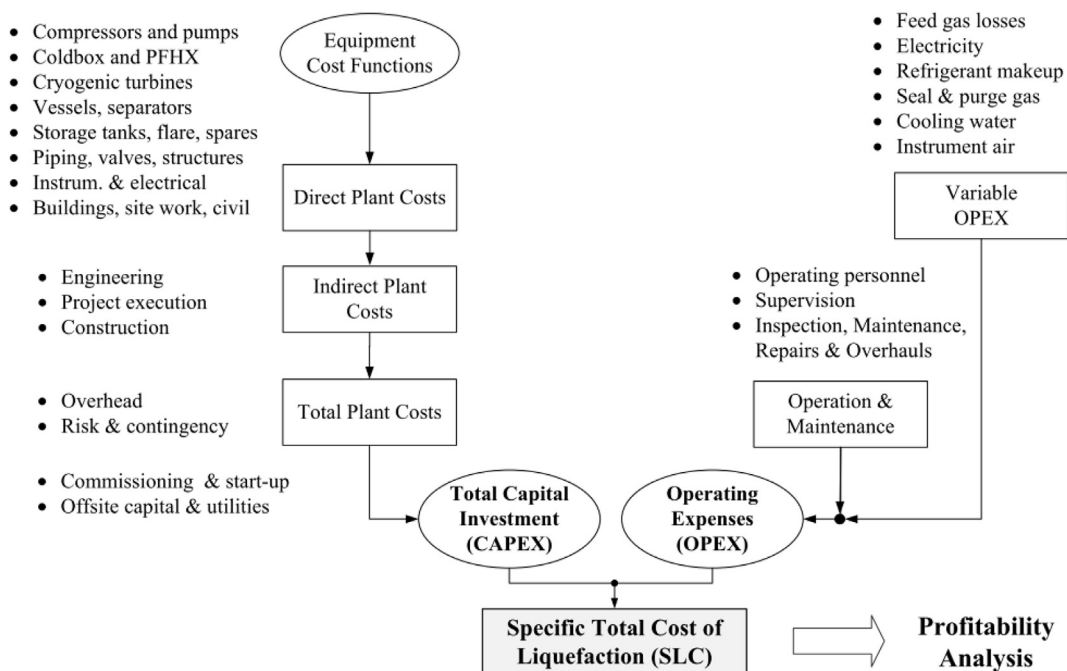
As a result of process-economic analyses of the liquefier subsystems and the total liquefaction process [20], two new large-scale process concepts were developed for hydrogen liquefaction [15,20,34,35].

Concept A: high pressure hydrogen Claude cycle

The cryogenic cycle of Concept A is designed with an optimized high-pressure (HP) hydrogen Claude cycle, using available highly-efficient reciprocating compressors and turbo expanders with the energy recovery option. The major differences to the conventional Claude process are the significantly higher cycle pressure levels and the elevated precooling temperature. For 100 tpd LH₂, the preferred hydrogen precooling is designed with the mixed-refrigerant cycle (MRC) shown in Fig. 3. The MRC is optimized for precooling temperatures between 90 K and 110 K with only four mixture components consisting of nitrogen and hydrocarbons to ensure a simple gas management system [15,20].

Concept B: dual hydrogen–neon cascade cycle

In the second developed process, 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 the final liquefaction of the feed. The hydrogen–neon Brayton is designed to use integrally-g geared turbo compressors available on the market with improved sealing systems to minimize the loss of expensive neon gas [15]. Alternatively,

**Fig. 2 – Schematic procedure for the liquefier cost estimation [15,20].**

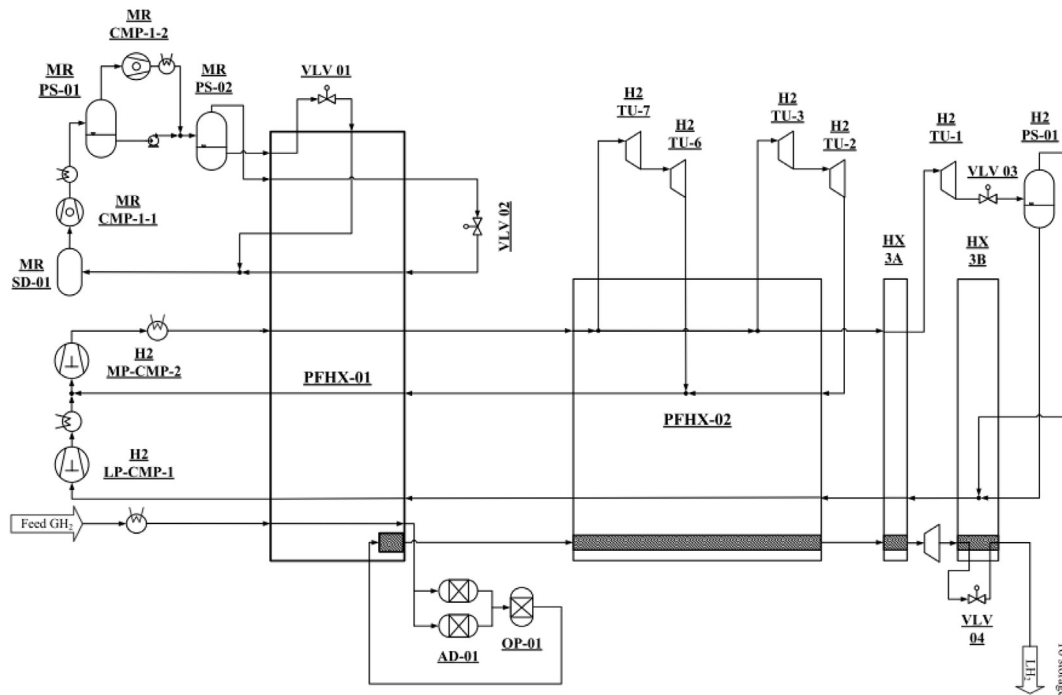


Fig. 3 – Concept A: simplified process flow diagram of HP hydrogen Claude cycle with MRC [20,34].

hermetically sealed compressors can be implemented as in Ref. [19]. The hydrogen Claude system is implemented with reciprocating compressors. As in Concept A, the base 100 tpd LH₂ design is implemented with an optimized MRC precooling. A process flow diagram of Concept B is given in Ref. [20].

Simulation results and discussion

For the presented large scale liquefaction Concepts A and B, parametric optimization studies and sensitivity analyses were performed to select a range of optimal configurations for different boundary conditions, e.g. varying train capacity and electricity prices. The simulation modeling assumptions, the methods and optimization results are described in Refs. [15,20]. Alternative precooling modifications are assessed and optimized in combination with the presented cryogenic cycles [20,34], including conventional LN₂ precooling and different MRC options, as well as N₂ expander cycles and hybrid MR expander cycles. The main optimization results for the Concepts A and B simulated with MRC precooling are shown in Fig. 4. Each design has been optimized with either SEC or SLC as objective function leading to, respectively, energy (EO) or cost optimized (CO) cases [20].

The lowest specific energy consumption for the 100 tpd LH₂ train is achieved by the energy optimized “EO 1/Feed Variable” simulations with a variable feed pressure between 25 bar and 80 bar. For these cases, the optimizer finds the solution with minimized specific energy consumption SEC by increasing the feed pressure variable to the upper limit of 80 bar. At feed pressures above 25 bar, a feed compressor is added as unit operation to the simulation and cost model. The “EO 2/Feed 25 bar” cases are optimized at the fixed feed pressure defined in Table 4 with no feed compressor unit resulting in lower

specific liquefaction costs SLC but slightly higher specific energy consumptions SEC: 6.0 kWh per kg for Concept A (+1.7%) and 6.3 kWh per kg LH₂ for Concept B (+4.2%). In the cost optimized (CO) cases, the optimizer keeps a feed pressure of 25 bar to avoid additional equipment costs as the gain in exergy efficiency of a higher feed pressure is rated as less profitable by the solver at the cost of electricity of 0.05 € per kWh_{el}. This and further cost optimization by the optimizer, e.g. reduction in heat exchanger size, lead to higher SEC compared to the EO cases [15,20].

The results for the calculated specific energy consumption SEC of the new 100 tpd LH₂ processes show that a SEC value below the aimed 6 kWh per kg LH₂ is achieved, resulting in exergy efficiencies of about 45% compared to the exergy efficiency of 27% of current 5 tpd LH₂ liquefiers. The simulated SEC of Concept A can theoretically be decreased below 5.9 kWh per kg LH₂ e.g. by increasing train capacity or including liquid expanders [17] in the MRC. Significant improvements can also be achieved by applying the new optimized cycles to smaller train capacities [20].

For Concept A and Concept B, the optimization results for the specific liquefaction costs (CO) are shown on the right diagram in Fig. 4 and are compared to the conventional non-optimized 5 tpd LH₂ process with hydrogen Claude cycle and liquid nitrogen precooling (LN₂) [15,20]. The optimization of the process variables for Concept A and Concept B was carried out for the liquefaction capacities of 50 tpd and 100 tpd LH₂. The different liquefaction capacities influence the optimization of the process variables. For instance, a higher liquefaction capacity can lead to higher refrigerant mass flows and larger components e.g. compressors, expanders and heat exchangers. This can affect the defined optimization constraints that still need to be satisfied by the optimizer. Also, the

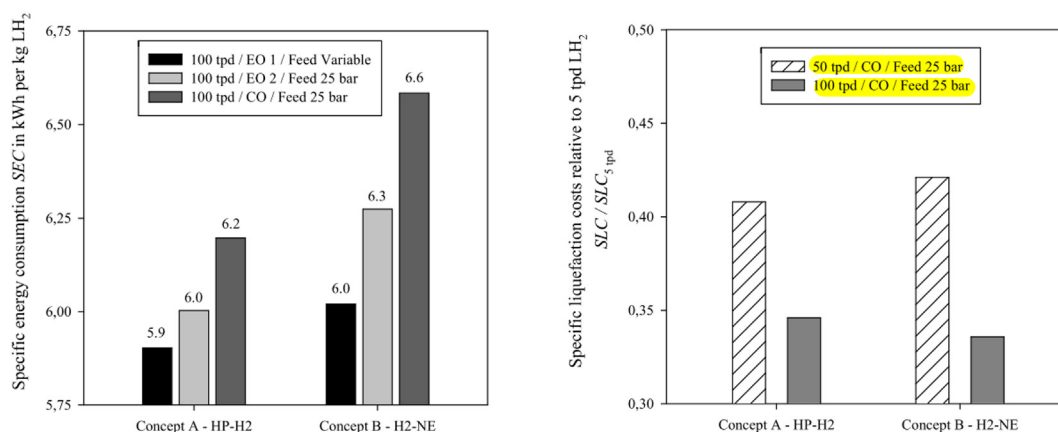


Fig. 4 – Results for Concepts A and B with MRC: specific energy consumption SEC for 100 tpd LH₂ (left) and specific liquefaction costs SLC for 50 tpd and 100 tpd LH₂ (right).

implemented equipment size dependent functions, e.g. for costs or isentropic efficiency, can be influenced by a variation in liquefaction capacity [20]. The results in Fig. 4 indicate a substantial improvement in specific liquefaction costs for both Concept A and Concept B. The predicted costs are reduced by nearly 60% from the 5 tpd LH₂ trains to 50 tpd LH₂, and by about 67% for the 100 tpd LH₂ designs [15,20].

Based on the results from the parametric optimization and sensitivity analyses [15,20], one 100 tpd LH₂ design case of Concept A with the HP hydrogen Claude cycle will be elaborated to a technically ready process with accurate prediction of catalytic ortho-para conversion in plate fin-heat exchangers [36], turbine configuration and optimal dimensioning of key hardware components with manufacturers.

Roadmap to hydrogen liquefaction

To summarize the findings on the new developed large-scale liquefaction processes [15,20] in terms of economic viability, the computed range of industrially viable liquefaction costs is plotted in Fig. 5 as a function of liquefier train capacity and boundary conditions. The total costs are related to current 5 tpd LH₂ liquefiers and are distinguished in technology

available today or within a medium term future. In this work, short to medium term in this paper is defined as a time-frame of up to 5 years in which minor modifications to proven liquefier technology can be industrially qualified and implemented. This corresponds to a Technology Readiness Level (TRL) between 7 and 9 [37]. A long term development is defined in this paper for a technology that requires at least five years or longer before it can be implemented in an industrial plant.

Large hydrogen consumption rates ask for a liquid hydrogen distribution infrastructure. The liquefaction process can be optimized in specific energy consumption SEC as well as in specific liquefaction costs SLC as shown for larger capacities. From well to wheel the target hydrogen costs at the filling station can be lowered to 5 to 7 € per kg H₂ with a liquid hydrogen supply chain compared to 8 to 10 € per kg H₂ with compressed gaseous hydrogen [38]. In order to reach this cost target, liquefier capacities starting from 20 tpd up to 50 tpd LH₂ are already economically viable based on current technology. Further reduction in specific liquefaction costs and larger plant capacities can be achieved by minor changes in existing equipment.

Making use of synergies between other industrial applications and hydrogen liquefiers would further help to bring down the specific cost of hydrogen. The closed precooling cycle could be replaced by the use of inexpensive LN₂ coming directly from a nearby air separation units (ASU) for liquid oxygen (LOX) production. Alternatively, liquefied natural gas (LNG) from a nearby LNG import terminal [30] could offer precooling for “free” to about 130 K instead of today’s inefficient practices for LNG re-vaporization. The compressor system of the main cryogenic refrigeration cycle, working from medium to high pressure, could be deleted if a hydrogen liquefier can be placed near to an industrial hydrogen consumer that requires hydrogen at a lower hydrogen pressure than the hydrogen feed gas pressure from a steam reformer or a high pressure electrolyzer. Instead of dissipating the compression energy, the hydrogen can pass once through the main refrigeration cycle before being routed directly to the hydrogen consumer.

The medium term modifications required for the process equipment in large-scale hydrogen liquefiers, for instance for

Table 4 – Simulation basis of design: main process and cost boundary conditions [15,20].

Parameter	Value
Cost model	
Electricity costs, in € per kWh _{el}	0.05
Plant availability	95%
Plant operation, in years	20
H₂ feed	Gaseous
Feed pressure, in bar	25
Feed temperature, in (K)	303
Para fraction	25%
LH₂ product	Sat. liquid
Prod pressure, in bar	2.0
Product temperature, in (K)	22.8
Product para fraction	≥98%

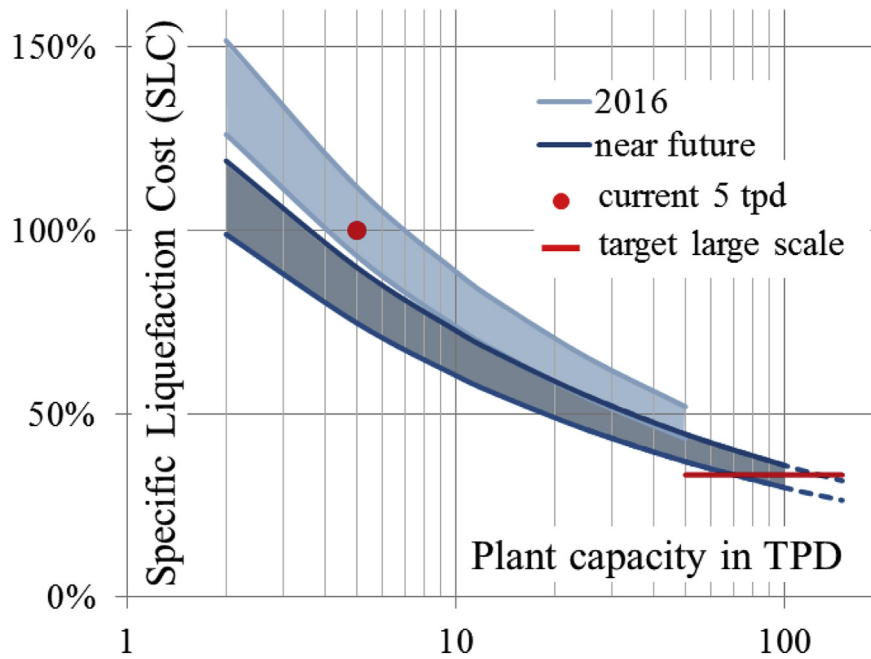


Fig. 5 – Calculated range of specific hydrogen liquefaction costs in function of plant capacity, boundary conditions and technological readiness.

Concept A and B, comprises the frame-size of cryogenic turbo expanders. These need to be matched to the required load capacities as the gas bearing turbines available today for hydrogen and helium [39] are smaller and oil bearing turbines are typically larger in size. Recovering the expansion energy would be beneficial for a higher process exergy efficiency. This is state-of-the-art in larger industrial applications such as air separation units (ASU) or natural gas liquefaction (LNG) plants [40] and would only needed to be downscaled. The developed MRC design for hydrogen precooling must be qualified under the process conditions for the hydrogen liquefier that differ from the conventional MRC application in LNG plants e.g. the lower precooling temperature [15,20].

The process Concept B, in which the hydrogen–neon mixture is proposed as new cycle refrigerant, requires a longer development horizon than process Concept A. Accurate equations of state (EOS) describing the properties of the hydrogen–neon mixture at cryogenic temperatures are not yet available in common fluid property estimation packages [41]. Losses of expensive neon have to be minimized. Hermetically-sealed turbo compressors are available today, but are currently limited in frame-size and in efficiency for light gas application, and would need to be increased.

Conventional non-hermetic turbo machines show high efficiencies but need to guarantee tight shaft sealings.

The herein presented stepwise implementation of large-scale hydrogen liquefaction is summarized in Table 5. Large-scale hydrogen liquefaction with state-of-the-art technology can already today reach hydrogen mobility objectives. In the short to medium term, depending on boundary conditions, a specific energy consumption for hydrogen liquefaction between 5.9 and 6.6 kWh_{el} per kg LH₂ can be achieved with the presented cost-optimized processes [15,20]. Further development in a large-scale hydrogen supply chain should focus on the development of fuel cell buses, trucks, trains and ships as well as on the development of turbo compression for light gases, as only hydrogen and helium or a blend of them eventually with neon are suitable as process gas for the cryogenic cycle needed for hydrogen liquefaction. For very large plants, their compression at ambient temperature still struggles with limitations in skid size for reciprocating compressors or a low stage compression ratio for turbo compressors due to tip speed limitations. In the longer term, high-speed light gas turbo compressors that are under development may be employed for pure hydrogen or helium compression to

Table 5 – Stepwise implementation of large-scale hydrogen liquefaction technology.

Parameter	Future trend		
	Today	Short to medium term	Long term
Train capacity, in tpd	15 to 50	up to 150	≥100
Main cryogenic cycle	Hydrogen claude (Conventional)	HP hydrogen claude (Concept A)	H ₂ or mix with neon (Concept B)
Precooling	N ₂ cycle	MR (or N ₂) cycle	MR cycle
Compressor type	Reciprocating	Reciprocating	Centrifugal

further reduce the specific liquefaction costs and increase the liquefier capacities above 200 tpd LH₂.

Conclusions

The main drawback of today's hydrogen liquefaction plants is the relatively **small train size, with typical capacities of 5 tpd LH₂**. Consequently, **specific liquid hydrogen production costs and specific energy consumption of these liquefiers is relatively high**. The impact of reducing the specific liquefaction costs on the overall hydrogen chain costs is significant. Two new liquefaction processes presented within this research work were therefore optimized in specific liquefaction costs [15,20]. The process Concept A has a high technological readiness and achieves a **specific energy consumption close to 6 kWh per kg LH₂ for 100 tpd LH₂**, with a major **reduction in specific liquefaction costs**. The major improvements compared to conventional liquefiers involve the optimized scaling-up of the liquefaction process and equipment, with a **closed-loop MRC for hydrogen precooling and an optimized hydrogen refrigeration Claude cycle with turbine energy recovery**. For future large-scale hydrogen liquefaction plants requiring even larger liquefaction capacities above 100 tpd LH₂, the process Concept B with two separate cryogenic cycles is proposed. It includes the use of **turbo compressors for the novel hydrogen–neon mixture cycle**. For 100 tpd LH₂, the predicted specific liquefaction costs can be reduced by nearly 67% compared to conventional 5 tpd LH₂ liquefiers. Even for a smaller upscale in capacity from 5 tpd to 50 tpd LH₂, specific liquefaction costs are reduced by approximately 60%.

A cost of hydrogen liquefaction close to or below 1 € per kg LH₂ can be achieved with optimized large-scale liquefiers. For Germany, based on a liquid hydrogen supply chain, a benchmark between approximately **5 and 7 € per kg** was given in Ref. [38] for the **hydrogen price for FCEV refilling**. These targets can be **achieved with large scale liquefier capacities, depending on boundary conditions such as hydrogen feed gas and liquefier electricity costs**.

For a faster launch of economically viable hydrogen mobility focus must now be placed on cost reduction in large-scale hydrogen gas production from renewable energy running in **parallel with strong efforts in establishing larger fleets of commercial vehicles, trains and ships running on fuel cell**.

REFERENCES

- [1] U.S. Environmental Protection Agency. Inventory of US greenhouse gas emissions and sinks: 1990 to 2013. 2015. <http://www.epa.gov/climatechange/Downloads/ghgemissions/US-GHG-Inventory-2015-Main-Text.pdf>.
- [2] European Commission. Road transport: reducing CO₂ emissions from vehicles. http://ec.europa.eu/clima/policies/transport/vehicles/index_en.htm.
- [3] Ball M, Wietschel M. The hydrogen economy: opportunities and challenges. Cambridge University Press; 2009.
- [4] H2 Mobility. H2 mobility. <http://h2-mobility.de/>.
- [5] US Department of Energy. DOE technical targets for hydrogen delivery. Website. 2015.
- [6] H2 Mobility. 70mpa hydrogen refuelling station standardization functional description of station modules. Technical Report V1.1. H2 Mobility; June 2010.
- [7] Bracha M, Lorenz G, Patzelt A, Wanner M. Large-scale hydrogen liquefaction in Germany. *Int J Hydrogen Energy* 1994;19(1):53–9.
- [8] Ohlig K, Decker L. Hydrogen liquefaction. In: Ullmann F, editor. *Ullmann's encyclopedia of industrial chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA; 2013.
- [9] Alekseev Alexander. Hydrogen Liquefaction. Wiley-VCH Verlag GmbH & Co. KGaA; 2016. p. 733–62.
- [10] Bracha M, Decker L. Grosstechnische Wasserstoffverflüssigung in Leuna. In: *Deutsche Kaelte-Klima-Tagung 2008*; 2008.
- [11] Ohlig K, Decker L. The latest developments and outlook for hydrogen liquefaction technology (1573). 2014. p. 1311–7.
- [12] Fukano T, Fitz U, Loehlein K, and Vinage I. Efficiency of hydrogen liquefaction plants. Website.
- [13] Essler J. Physikalische und Technische Aspekte der Ortho-Para-Umwandlung von Wasserstoff. PhD thesis. Technische Universitaet Dresden; 2013.
- [14] Cardella U, Decker L, Klein H. Wirtschaftlich umsetzbare Wasserstoff Grossverflüssiger. In: *Deutsche Kaelte-Klima-Tagung 2015*, vol. AA I; November 2015.
- [15] Cardella U, Decker L, Klein H. Economically viable large-scale hydrogen liquefaction. In: *Materials science and engineering. Proceedings of the 26th international cryogenic engineering conference and international cryogenic materials conference*. Delhi, India: IOP Conference Series; 2016.
- [16] Krasae in S, Stang J, Neksa P. Development of large-scale hydrogen liquefaction processes from 1898 to 2009. *Int J Hydrogen Energy* 2010;35(10):4524–33.
- [17] Berstad D, Stang J, Neksa P. Large-scale hydrogen liquefier utilising mixed-refrigerant pre-cooling. *Int J Hydrogen Energy* 2010;35(10):4512–23.
- [18] IDEALHY Consortium. Report on technology overview and barriers to energy- and cost-efficient large scale hydrogen liquefaction. FCH JU FP7-JTI Proj. Ref. 278177 D1.1. IDEALHY Consortium; 2012.
- [19] IDEALHY Consortium. Hydrogen liquefaction report. FCH JU FP7-JTI Proj. Ref. 278177 D5.22. IDEALHY Consortium; 2013.
- [20] Cardella U, Decker L, Klein H, Fendt J. Process optimization for large-scale hydrogen liquefaction. *Int J Hydrogen Energy* 2016. submitted for publication.
- [21] Gardiner M. Energy requirements for hydrogen gas compression and liquefaction as related to vehicle storage needs. Technical Report Record Number 9013, DOE Hydrogen and Fuel Cells Program. July 2009.
- [22] Shigekiyo H. International workshop on liquefied hydrogen technology. Workshop, Japan Ship Technology Research Association. March 2015.
- [23] Alekseev A. Basics of low-temperature refrigeration. In: *Contribution to the CAS-CERN accelerator school: superconductivity for accelerators*; 2014. p. 29. <http://dx.doi.org/10.5170/CERN-2014-005.111> (arXiv:1501.07392); Erice, Italy, 24 April - 4 May 2013.
- [24] Lipman M, Cheung H, Roberts O. Continuous conversion hydrogen liquefaction 1963;59(8):49–54.
- [25] Drnevich R. Hydrogen delivery-liquefaction and compression, strategic initiatives for hydrogen delivery. Workshop. May 2003.
- [26] Baker C, Shaner R. A study of the efficiency of hydrogen liquefaction 1978;3(3):321–34.
- [27] Syed M, Sherif S, Veziroglu T, Sheffield J. An economical analysis of three hydrogen liquefaction systems. *Int J Hydrogen Energy* 1998;23(7):565–76.
- [28] Ohira K. A summary of liquid hydrogen and cryogenic technologies in japans we-net project. In: *Advances in*

- cryogenic engineering: Transactions of the cryogenic engineering conference CEC, vol. 710. AIP Publishing; 2004. p. 27–34.
- [29] Quack H. Conceptual design of a high efficiency large capacity hydrogen liquefier. In: Advances in cryogenic engineering: proceedings of the cryogenic engineering conference, vol. 613. AIP Publishing; 2002. p. 255–63.
- [30] Kuendig A, Loehlein K, Kramer G, Huijsmans J. Large scale hydrogen liquefaction in combination with LNG re-gasification. In: Proceedings of the 16th world hydrogen energy conference 2006, Lyon, France. Red Hook, NY, USA: Curran Associates, Inc.; 2006. p. 3326–33.
- [31] Berstad D, Stang J, Neksa P. Comparison criteria for large-scale hydrogen liquefaction processes. *Int J hydrogen energy* 2009;34(3):1560–8.
- [32] Honeywell International Inc. UniSim design R440. 2005-2015.
- [33] Fendt J, Klein H, Rehfeld S, Kender R. A hybrid approach to process optimization by coupling matlab with commercial process simulators. In: Presentation at the CAPE forum in Paderborn; 2015.
- [34] Cardella U, Decker L, Klein H, Fendt J. Process optimization for large-scale hydrogen liquefaction. In: Presentation at the 21th world hydrogen energy conference, Zaragoza, Spain; June 2016.
- [35] Cardella U, Decker L, Klein H. Economically viable large-scale hydrogen liquefaction. In: International cryogenic engineering conference and cryogenics materials conference, number 8-O-1A-1, New Delhi, India; March 2016.
- International Cryogenic Engineering Conference and the International Cryogenic Material Conference, <http://icec26-icmc2016.org/downloads/8-O-1A-1.pdf>.
- [36] Cardella U, Donaubaue P, Klein H, Decker L. Katalytische ortho-para Wasserstoff Umwandlung in Plattenwaermetauscher. In: Deutsche Kaelte-Klima-Tagung 2015, vol. AA I; November 2015. Dresden.
- [37] Mankins C. Technology readiness levels: a white paper. Technical report. Office of Space Access and Technology, Advanced Concepts Office, NASA; April 1995.
- [38] Kampitsch M, Gruber T. Liquefied hydrogen in the supply chain for hydrogen based mobility. In: Presentation at the 21st world hydrogen energy conference, Zaragoza, Spain; June 2016.
- [39] Bischoff S, Decker L. First operating results of a dynamic gas bearing turbine in an industrial hydrogen liquefier. In: Transactions of the cryogenic engineering conference CEC: advances in cryogenic engineering, vol. 1218. AIP Publishing; 2010. p. 887–94.
- [40] Cryostar SAS. Turbo-expanders for cold production and energy recovery. <http://www.cryostar.com/pdf/dnl-zone/Cryostar-process-machinery.pdf>.
- [41] Lemmon W, Huber M, McLinden M. NIST standard reference database 23: reference fluid thermodynamic and transport properties-REFPROP, Version 9.1. Gaithersburg, MD: National Institute of Standards and Technology; 2013. Standard Reference Data Program.