



Integrated design for demonstration of efficient liquefaction of hydrogen (IDEALHY)

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Publishable summary

This report documents the work done according to Task 1.1 of IDEALHY, to gain an overview of the technology and the process design for large scale hydrogen liquefaction plants available today. Eight existing hydrogen liquefaction plants are listed with a capacity of 0.5–15 tonnes per day (tpd). Basic parameters, features and flow diagrams are shown in detail for the plants in Ingolstadt (Linde, since shut down) and Leuna (Linde). Plants from Praxair in the US, from Air Products and from Air Liquide with a liquefaction capacity up to 40 tpd are mentioned as well.

As another major part of this deliverable, available plant and cycle considerations from the literature are investigated and analysed. This comprises a Claude cycle option from 2004, a second Claude cycle option from 1997, a Helium Brayton cycle (1997) and a proposed Neon Brayton cycle from 1997 within the framework of the Japanese WE-NET project. Furthermore, cycle concepts from Quack (2001), from Valenti and Macchi (2008), from SINTEF (with mixed refrigerant pre-cooling, 2010), from Baker and Shaner (1978) and from GEECO (2008) are described. The different processes are reviewed and compared. A special complication is given by the fact that different boundary conditions are used in the different layouts (e.g. different feed pressures, different output specifications). This must be taken into account if (for example) efficiencies are compared.

At the end of this chapter a summary is given directly comparing the respective parameters and features of the eleven plants and studies listed above.

In the second part of the deliverable key components of hydrogen liquefaction plants are considered. For the compressors, working parameters and both reciprocating piston and turbo machinery are addressed. For expanders, pressure range, efficiency and known bearing and brake technologies are described. Aluminium plate fin heat exchangers are shown as today's state of the art. Finally, basic features of existing plants are described: cold boxes, cryogenic valves and ortho-para catalyst material.

Key words

Hydrogen liquefaction plants
Cycle analysis comparison
Liquefier plant components

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1. Introduction

Hydrogen is expected to be an important future clean transport fuel. In the absence of a pipeline network, liquid hydrogen is the most effective way to supply larger refuelling stations in the medium term. However, at present hydrogen liquefaction is expensive, energy-intensive and limited in capacity.

The IDEALHY project investigates the different steps in the liquefaction process in detail, using innovations and greater integration in an effort to reduce specific energy consumption by 50 % compared to the state of the art, and simultaneously minimise the total costs (both CAPEX and OPEX). The project brings together world experts to develop a generic process design and plan for a large-scale demonstration of efficient hydrogen liquefaction in the range of up to 200 tonnes per day (tpd). This represents a substantial scale-up compared to existing and proposed plants worldwide.

1.1 Document scope

This document gives an overview of existing hydrogen liquefaction processes in literature and upcoming concepts up to date. It covers theoretical studies as well as existing liquefaction plants. Major differences such as working fluid and pre-cooling options between the cycles are pointed out and discussed.

The principal barriers to a higher energy efficiency are discussed, and cycle components with substantial potential for improvement are pointed out. Each cycle is analysed for its weakest and strongest part concerning the energy efficiency.

Improved energy efficiency is correlated with increased operating costs where relevant. Barriers to better the cost efficiency are also analysed in terms of investment costs. These are estimated from the numbers of components and the complexity of the cycle. The life cycle costs of the different options are not considered.

2. Process overview and comparison

The following sections give an overview of relevant existing and conceptual liquefiers. Where available, a process flow diagram and additional information are included. Very limited public information is available for existing liquefiers, apart from cycles commissioned by Linde, for which reason the latter are presented in greater detail. Regarding conceptual liquefiers, the most relevant publications on large-scale and high-efficiency liquefiers are included.

2.1 Overview of liquefaction processes

The following section gives a summary of relevant hydrogen liquefaction plants built, as well as processes proposed in the scientific literature. In Section 2.2 gives an overview of process parameters for the various cycles reviewed.

2.1.1 Existing plants

Only a small number of existing plants arise available in the literature. Most existing plants today are modified Claude cycles with stepwise ortho-para conversion and additional utility systems. A normal modification is to use a separate closed expander refrigeration cycle, instead of extracting some hydrogen from the feed stream. This is often referred to as a Brayton cycle.

Linde AG

Linde Kryotechnik AG has engineered several small and medium-sized hydrogen liquefaction plants around the world:

- two plants in Japan, each:5 tpd
- Leuna, Germany: 5 tpd
- Kansai, Japan: 10 tpd
- India: 1 tpd
- China: 0.5 tpd
- Ingolstadt, Germany: 4.4 tpd
- Magog, Canada: 15 tpd

Ingolstadt liquefier

The now decommissioned Ingolstadt hydrogen liquefaction plant in Germany had been in operation since 1992 and had a capacity of 4.4 tpd [1][2]. In this plant LN₂ evaporation and heating were utilised for cooling of the hydrogen process stream to about 80 K. A hydrogen Claude cycle generated further refrigeration to approximately 30 K. Three turbines with oil bearings operated between 22 and 3 bar and at rotational speeds of approximately 70 000 rpm. Liquefaction of the process stream was then obtained by a Joule-Thomson expansion, from which the occurring flash gas was recycled, while the saturated liquid phase was stored in a vacuum-insulated tank. Ortho-para conversion was carried out in four stages, two of which were kept isothermal by LN₂ and LH₂ bath Fe(OH)₃ catalytic converters, and the remaining two being adiabatic.

The specific liquefaction energy for the Ingolstadt plant depended on the penalty factored in for LN₂ consumption. Based on the assumption of 0.4 kWh/l LN₂, this calculated to about 13.6 kWh kgLH₂. A process flow diagram of the Ingolstadt liquefier is shown in Figure 1.

Figure not included for copyright reasons.

Figure 1: Process flow diagram of the Linde Ingolstadt liquefier [2].

	Ingolstadt (1992)	Leuna (2007)
Capacity [tpd]	4.4	5
H ₂ feed		
Pressure [bar]	21	24
Temperature [K]	< 308	< 313
LH ₂ product		
Pressure [bar]	1.3	1.3
Temperature [K]	21	21
Para fraction [%]	≥ 95	≥ 95
Isothermal efficiency, main compressors [%]	Unknown	0.65–0.70
Isentropic efficiency, main expanders [%]	Unknown	> 85
Ortho-para conversion	4 stages	Continuous
Specific liquefaction energy [kWh/kg _{LH₂}]	13.6	11.9
Theoretical specific liquefaction energy [kWh/kg _{LH₂}]	2.86	2.81
Exergy efficiency [%]	21.0	23.6

Table 1: Key process parameters for the Ingolstadt and Leuna liquefiers, reproduced from [4].

Praxair

Praxair has four hydrogen liquefaction plants in USA today at scales between 20 and 36 tpd (22–40 short tons per day) [5] with the largest plant as a double-train liquefier. Typical specific energy consumptions are between 12.5 and 15 kWh/kg [6].

Figure 3 shows a Praxair LH₂ process flow diagram. This process includes continuous ortho-para conversion from 80 K. Praxair is a member of the DOE hydrogen program, and claims that the overall energy consumption can be decreased by 2.4 % if continuous conversion is also included in the first heat exchanger [7].

Figure not included for copyright reasons.

Figure 3: Praxair hydrogen liquefaction process [6].

Air Products

Air Products has four hydrogen liquefaction plants in North-America today ranging from 27 to 32 tpd (30–35 short tons per day) [8]. In addition Air Products operate two 6 tpd LH₂ plants, one in the Netherlands and one in the USA.

Air Liquide

Air Liquide has built small and medium size LH₂ plants. Two plants, in France and in Canada, have capacities of about 12 tpd [8] and both are designed using Claude cycles with hydrogen as refrigerant.

2.1.2 Cycles from literature

WE-NET

The Japanese WE-NET project conducted a comprehensive study on large-scale hydrogen liquefaction processes with an envisioned capacity of 300tpd. The following descriptions of process options are found in Matsuda and Nagami [9] and Ohira [10].

H₂ Claude – option 1 (2004)

The process shown in Figure 4 is a combination of hydrogen Claude refrigeration cycle and a closed-loop nitrogen pre-cooling cycle. This process was selected after comparison with other concepts (e.g. the helium, “nelium” and neon Brayton cycles and a mixed

refrigerant cycle) on criteria including efficiency, investment cost, O&M¹ costs, safety etc. All the heat exchangers are aluminium alloy plate-fin type and for the feed hydrogen stream an ortho-para conversion catalyst is used for continuous conversion. The specific energy consumption of the cycle is estimated to be about 8.7kWh/kg.

Figure not included for copyright reasons.

Figure 4: WE-NET hydrogen liquefaction process with H₂ Claude and nitrogen re-liquefaction cycles.

¹ operation and maintenance

H₂ Claude – option 2 (1997)

A structural difference from the 2004 process option is the deployment of an intermediate gas expansion turbine for the hydrogen process stream which induces a temperature drop so that this stream does not require cooling in the temperature interval of the second coldest heat exchanger. The specific energy consumption of this version is estimated to about 8.5kWh/kg.

Figure not included for copyright reasons.

Figure 5: WE-NET hydrogen liquefaction process with nitrogen pre-cooling and H₂ Claude processes.

He Brayton (1997)

This WE-NET liquefier concept assumes nitrogen pre-cooling to around 80K and a reversed Brayton cycle with helium as refrigerant for cryogenic cooling. These processes are combined with a type of hydrogen Joule–Thomson process in which the final cooling step to liquefaction is carried out by throttling back a partial stream of the hydrogen process stream. The specific liquefaction energy is estimated as 8.69kWh/kg.

Figure not included for copyright reasons.

Figure 6: WE-NET hydrogen liquefaction process with nitrogen pre-cooling and He reversed Brayton cycle.

Ne Brayton (1997)

This cycle is structurally similar to the reversed helium Brayton cycle but differs in the number of cryoexpanders and in its parallel configuration. This liquefaction process has an estimated specific energy consumption of 8.59 kWh/kg.

Figure not included for copyright reasons.

Figure 7: WE-NET hydrogen liquefaction process with nitrogen pre-cooling and Ne reversed Brayton cycle.

Quack/TUD (2001)

Quack [11] proposed a process for high-efficiency hydrogen liquefaction employing a three-stage vapour compression propane cycle for pre-cooling and a He/Ne reversed Brayton cycle for cryogenic cooling. As shown in Figure 8 the plant has five compression steps (isentropic efficiency of 85 % for each stage) with water and propane intercoolers before the hydrogen feed enters the propane pre-cooler. The hydrogen enters the helium-neon heat exchangers with a temperature around 220K. Here it is cooled from 220K down to about 25K, the turbine expander inlet temperature. Any hydrogen which is not liquefied when expanding through the turbine is compressed, cooled and throttled back through a Joule-Thomson valve. The ortho-para conversion is assumed to be done continuously by packing catalyst material inside the heat exchangers on the hydrogen side. The LH₂ plant is not mentioned as a near-future concept, but should be a benchmark for future studies on large-scale hydrogen liquefaction. The efficiency of the plant is close to 7 kWh/kg when atmospheric inlet pressure is assumed.

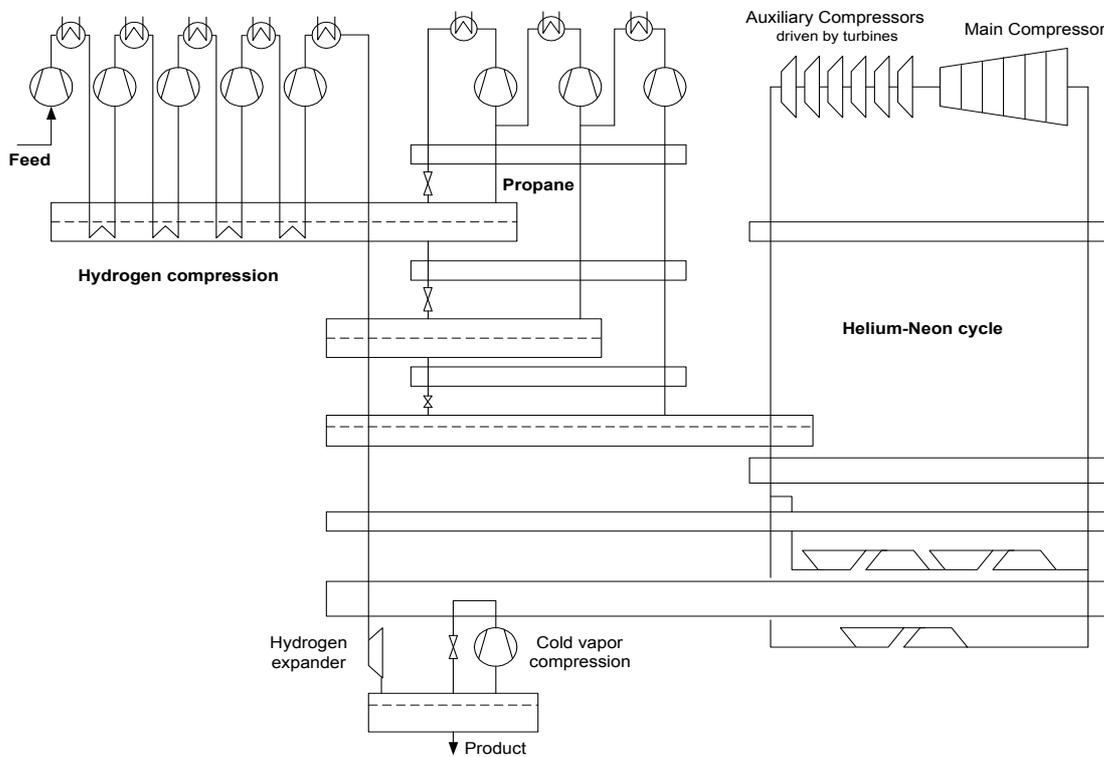


Figure 8: Liquefaction process proposed by Quack with propane pre-cooling and He/Ne reversed Brayton cycle.

Valenti and Macchi (2008)

Valenti and Macchi [12] proposed a large-scale liquefaction process where all cooling duty is provided by a four-stage reversed Brayton cycle using helium as refrigerant. Hydrogen supplied at 60 bar pressure is cooled in four different stages against the reversed Brayton cycle. Four partial flows of helium (expanded in turbines and internally recuperated) generate the requisite cooling across a temperature range of 18.6-296.4 K. Ortho-para conversion is assumed to be continuous and in equilibrium at any temperature. In order to avoid recycling of flash gas and an additional heat exchanger for condensation and sub-cooling of liquefied hydrogen, the final expander transforms the hydrogen stream from the dense phase directly to a sub-cooled state at 1.5 bar and 20 K. The specific liquefaction energy is reported to be 5.04 kWh/kg LH₂. It is claimed that the plant capacity of 860 tpd and the resulting volume flow rates of helium through the compressor train correspond to that of medium-sized axial-flow compressors. Hence a 15-stage compression section with an average stage pressure ratio between 1.2 and 1.3 and polytropic stage efficiency of 92 %, is assumed for the reversed helium Brayton cycle.

Figure not included for copyright reasons.

Figure 9: Liquefaction process by Valenti with reversed helium Brayton cycle.

SINTEF with MR pre-cooling (2010)

In order to investigate the efficiency of mixed refrigerant (MR) pre-cooling for hydrogen liquefaction applications, a MR-modified version of the process proposed by Quack [11] was simulated [4]. Hydrogen feed conditions are specified to 21 bar and 310 K. Pre-cooling of hydrogen to around 80 K is provided by a MR cycle with the refrigerant composition made up by C1–C5, ethylene, nitrogen, neon and R14. Through two phase separators operating at different temperature levels on the high-pressure side, the refrigerants are distributed to fit the temperature and cooling requirements of the hydrogen feed. As the process is derived from the concept by Quack, the cryogenic cooling to 26.5 K before final expansion and liquefaction is provided by a reversed Brayton cycle with the same He/Ne mixture as proposed by Quack. Continuous ortho–para conversion at equilibrium at any temperature is assumed. Based on assumptions considered to be reasonable with respect to other published studies the resulting energy consumption and exergy efficiency were calculated to 6.2–6.5 kWh/kg and 44.5–46.6 %, respectively.

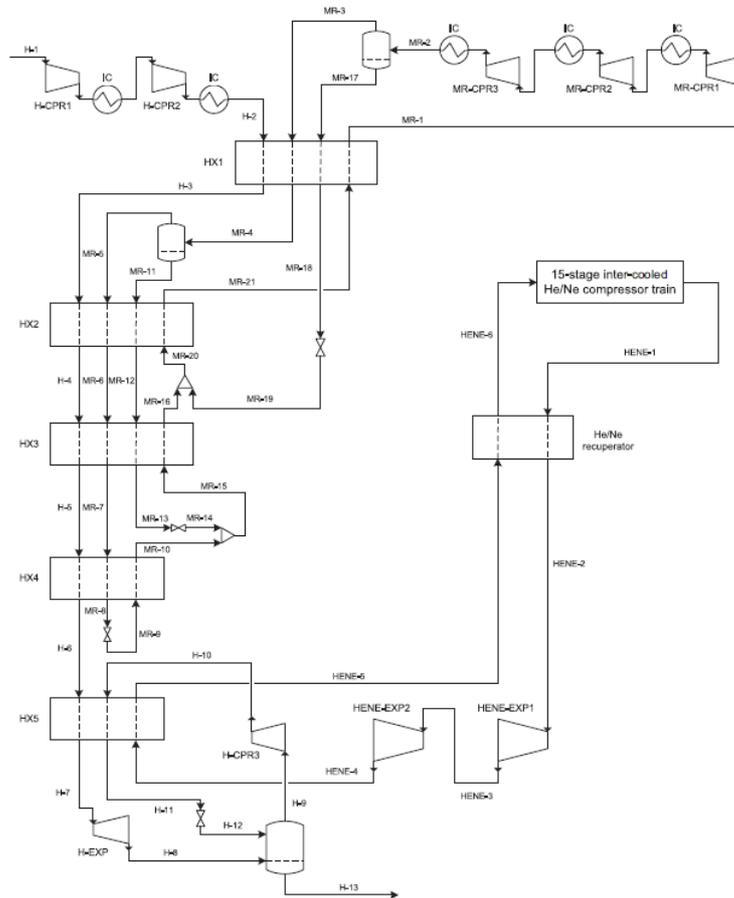


Figure 10: Liquefaction process with MR pre-cooling [4].

Baker and Shaner (1978)

Baker and Shaner [13] presented a study on efficiency and economics of a 250 tpd hydrogen liquefier. The studied cycle is a Claude cycle with nitrogen pre-cooling and hydrogen turbine expansion at two different pressure levels. A dedicated nitrogen re-liquefaction unit is assumed to supply the process with saturated LN₂ and GN₂ for pre-cooling of hydrogen to 80 K. Ortho-para conversion is carried out in two stages: nitrogen- and hydrogen-cooled at 80 K and 20.2 K, respectively. The cycle has an estimated specific energy consumption of about 10.85 kWh/kg LH₂.

Figure not included for copyright reasons.

Figure 11: Liquefaction process by Baker and Shaner with H₂ Claude cycle [13].

Gas Equipment Engineering Corp (GEECO) (2008)

Hydrogen liquefaction processes have been developed by GEECO through the DOE Hydrogen Program [14]. The process version shown in Figure 12 has similarities with the process proposed by Valenti, as only helium is employed as a refrigerant in a multi-stage reversed Brayton cycle, and sub-cooled liquid hydrogen is produced via a final liquid expander with no additional flash gas. In contrast with Valenti's four different helium pressure levels, however, the helium Brayton process by GEECO has only two pressure levels between which all expanders operate. Instead of assuming continuous ortho-para conversion inside heat exchangers, the current process scheme has four additional dedicated helium-cooled catalytic converters, which is likely to be less efficient than the former configuration due to non-equilibrium operation. Liquid hydrogen with 95 % para content is produced at 1 bar with a reported specific energy consumption of 8.73 kWh/kg.

Figure not included for copyright reasons.

Figure 12: Liquefaction process by Shimko with reversed He Brayton cycle [14]

2.2 Comparison of the different processes

For those existing and conceptual liquefiers reviewed in subsections 2.1.1 and 2.1.2 where sufficient quantitative information is available, key process parameters are summarised in Table 2.

For the two plants commissioned by Linde, Ingolstadt and Leuna, the liquefaction capacity is 4–5 tpd, which is at least one order of magnitude below the capacity under consideration in the IDEALHY project. Since these plants have been cost optimised for considerably lower output than the envisioned large-scale plants, the resulting energy consumption (11.9 and 13.6 kWh/kg_{LH2}) is roughly twice the target in this project. When process design is focused on minimising the energy consumption, as is the case in the IDEALHY scenario, several elements can in principle contribute to more efficient processes.

As can be observed, reciprocal, radial and axial compressor types can be found for the various cryogenic refrigeration cycles. The power consumed by compressor trains in liquefiers accounts for by far the largest part of the overall power consumption. Considerations such as stage efficiency, possible pressure ratios per stage for different compressor types, intercooling temperatures and pressure losses etc. are key for determining which compressor can be used, and have a large degree of influence over the resulting power consumption.

Another prerequisite for attaining high efficiency is the recovery of power generated by cryo-expanders. For reversed Brayton processes in particular this is of high importance, and also to a certain extent for Claude processes. In the Ingolstadt and Leuna processes (both Claude cycles) it is not economically feasible to recover the expander shaft power and the energy is therefore dissipated instead. For these types of processes the potential reduction in specific liquefaction energy requirement through power recovery is low, around 0.25 kWh/kg_{LH2}. The estimated power recovery for expanders in the reversed helium Brayton cycle by Valenti, in contrast, accounts for more than 1 kWh/kg_{LH2}.

A common denominator for most of the high-efficiency concepts is high hydrogen pressure. An advantage of this is lower heat duty at very low temperatures for the hydrogen cooling process, as well as a more constant heat capacity and operation further away from the critical point. Among the various liquefaction processes there is a significant variation of hydrogen pressure to which the feed is cooled prior to liquefaction. The optimal combination of hydrogen pressure and temperature before final expansion and liquefaction depends partly on the expansion device used. As an example, if a pure Joule-Thomson (J-T) expansion is assumed, excessive pressure may in some cases cause a lower liquid yield if the hydrogen state reaches the area where the Joule-Thomson coefficient is below zero. For liquefiers like Ingolstadt and Leuna with pure J-T expansions and cooling of hydrogen to 30 K, pressure significantly above 20 bar will therefore not be beneficial and result in a lower liquid yield. If two-phase expanders, liquid expanders or a gas expander in series with J–T can be employed, there are possibilities of increasing the liquid yield and process efficiency by raising the hydrogen pressure. This principle can be observed for some of the high-efficiency concepts, where hydrogen pressures are high: Quack (80 bar); Valenti (60 bar). If 100 % liquid yield is to be obtained via a once-through liquefaction process, the hydrogen must be in saturated or

sub-cooled liquid form after expansion. This is possible for processes according to Valenti and Shimko, where pure helium is used as a refrigerant in the cryogenic cooling stages, enabling cooling of the hydrogen to about 20 K prior to expansion and liquefaction.

As there are large variations in boundary conditions such as hydrogen feed pressure and ambient temperature, as well as for process units such as compressors, expanders and heat exchangers, a direct comparison and ranking of process efficiencies and power consumption figures should be handled with great care. In the study by Berstad et al. [15] the need for equalisation of hydrogen feed pressure for a selection of liquefaction processes was exemplified, as well as the consequences thereof for the energy and efficiency benchmarking.

The liquefaction processes employing reversed Brayton cycles for cryogenic cooling and at the same time assuming high compressor and expander efficiencies (Quack, Valenti, SINTEF MR) appear to show significantly lower energy consumption than other processes. Since these processes have not been compared on an equal footing with respect to assumptions for process parameters, however, a rigorous comparison does not have high value.

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Table 2 Summary of key process parameters.

	Baker & Shaner (1978)	WE-NET H ₂ -Claude (1997)	WE-NET He-Brayton (1997)	WE-NET Ne-Brayton (1997)	Quack (2001)	Valenti & Macchi (2008)
Built / Study	Study	Study	Study	Study	Study	Study
Capacity [tpd]	250	300	300	300	170 / 86	860
H ₂ feed pressure [bar]	1.01	1.06	1.06	1.06	1.0	60
Pre-compression						
Pressure [bar]	41.37	50–50.7	50–50.7	50–50.7	80	—
Compressor type	Piston				Piston	—
Stage pressure ratio					2.4	—
Stage efficiency [%]	79 ^{ab}	80 ^b	80 ^b	80 ^b	85 (i)	—
Pre-cooling	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Propane	—
Cycle type	LN ₂ evap.	LN ₂ @1.2 bar	LN ₂ @1.2 bar	LN ₂ @1.2 bar	Vap. compr.	—
Temperature	80	80	80	80	220	—
LN ₂ energy penalty	—	0.5 kWh/Nm ³	0.5 kWh/Nm ³	0.5 kWh/Nm ³	—	—
GN ₂ energy penalty	—	0.14 kWh/Nm ³	0.14 kWh/Nm ³	0.14 kWh/Nm ³	—	—
Cryogenic cooling	Hydrogen	Hydrogen	Helium	Neon	Helium/Neon	Helium
Cycle type	Claude	Claude	Rev. Brayton	Rev. Brayton	Rev. Brayton	Rev. Brayton
Compressor type	Piston				Turbo	Turbo, axial
Number of compr. Stages	6	2 (not certain)			8 + 6	15
Stage pressure ratio	n/a				< 1.4 & 1.1	1.2–1.3
Compr. stage efficiency [%]	79 ^{ab}	80	80	80	85 (i)	92 (p)
Expander type	Turbo				Turbo	Turbo, axial
Number of expanders	2	2	2	3	6	4
Pressure ratio					2.21, 4.87	
Exp. stage efficiency	79 ^b	85 ^b	85 ^b	85 ^b	90 (i)	88,90,92,93 (p)
Intermediate H ₂ expander						
Outlet pressure [bar]	—	> 13.15	> 13.15	> 13.15	—	—
Efficiency	—	85 ^b	85 ^b	85 ^b	—	—
Pre-liquefaction H ₂ temperature [K]	26				25–26	20.57
Liquefaction expansion device	J–T	J–T	J–T	J–T	Liq. exp.	Liq. exp.
Expander efficiency [%]		—	—	—	85 (i)	85 (p)
Minimum temperature approach [K]	—				2.12 & 1.33	2
LH ₂ product						
Pressure [bar]	9.29	1.06	1.06	1.06	1.0	1.50
Temperature [K]	20.57	20.4–20.5	20.4–20.5	20.4–20.5	20.2	20.0
Para fraction [%]	97	> 95	> 95	> 95	> 99	99.8 ^c
Ortho-para conversion	Isoth.@80K Isoth.@20.2K	Isoth.@80K Continuous	Isoth.@80K Continuous	Isoth.@80K Continuous	Continuous	Continuous
Specific. energy reqt [kWh/kg _{LH2}]	10.85	8.53	8.69	8.58	6.93	5.29 ^d
Theoretical spec. energy reqt [kWh/kg _{LH2}]	3.91	3.92	3.92	3.92	3.94	2.56 ^d
Exergy efficiency [%]	36.0	46.0	45.1	45.7	56.8 (53.8–60.7 in article)	48.3 ^d
Comments		Heat loss and ΔP = 0	Heat loss and ΔP = 0	Heat loss and ΔP = 0		

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	WE-NET H₂-Claude (2004)	SINTEF MR (2010)	Shimko He-Brayton (2008)	Ingolstadt (1992)	Leuna (2007)
Built / Study	Study	Study	Study	Built	Built
Capacity [tpd]	300	86	50	4.4	5
H ₂ feed pressure [bar]	1.01	21	≈ 1	21	24
Pre-compression					
Pressure [bar]	30.4	80	21	—	—
Compressor type	Centrifugal		Piston	—	—
Stage pressure ratio	≥ 1.1	2		—	—
Stage efficiency [%]	80 (i)	85 (i)	80 ^b	—	—
Pre-cooling					
Cycle type	Nitrogen	Mixed refrigerant	—	Nitrogen	Nitrogen
Temperature	LN ₂ @1.2 bar	MR	—	LN ₂ evap.	LN ₂ evap.
LN ₂ energy penalty	80	75	—	80	80
GN ₂ energy penalty	0.5 kWh/Nm ³	—	—	0.4 kWh/l	0.4 kWh/l
Cryogenic cooling	0.137 kWh/Nm ³	—	—	—	—
Hydrogen					
Cycle type	Hydrogen	Helium/Neon	Helium	Hydrogen	Hydrogen
Compressor type	Claude	Rev. Brayton	Rev. Brayton	Claude	Claude
Number of compr. stages	Centrifugal	Turbo	Piston	Piston	Piston
Stage pressure ratio	15 (LP), 25 (HP)	15		2 x 2	2 x 2
Compr. stage efficiency [%]	≥ 1.08–1.12	1.28			2
Expander type	80 (i)	85 (i)	80 ^b	Unknown	65–70 (isoth.)
Number of expanders	Centrifugal	Turbo	Turbo	Turbo	Turbo
Pressure ratio	2	2	4	3	3
Exp. stage efficiency	2.41, 2.76	5.3			
Intermediate H ₂ expander	82 (i)	90 (i)	85 ^b , 83 ^b , 86 ^b , 86 ^b	Unknown	> 85 (i)
Outlet pressure [bar]	—	—	—	—	—
Efficiency	—	—	—	—	—
Pre-liquefaction H₂ temperature [K]					
Liquefaction expansion device	2-stage J–T	Liq. expander	Wet expander	Ejector, J–T	J–T
Expander efficiency [%]	—	85 (i)	90 ^b	—	—
Minimum temperature approach [K]		2	ΔT/T = 0.03		
LH₂ product					
Pressure [bar]	1.06	1	1	1.3	1.3
Temperature [K]	20.4	20.2	20	21	21
Para fraction [%]	> 98	Equilibrium	95	≥ 95	≥ 95
Ortho-para conversion	Continuous	Continuous	4 stages	4 stages	Continuous
Spec. energy [kWh/kg _{LH₂}]	~ 8.72	6.2–6.5	8.73	13.6	11.9
Theoretical spec. energy [kWh/kg _{LH₂}]	~ 3.94	2.90	3.89	2.86	2.81
Exergy efficiency [%]	45.2	44.7–47.1	44.6	21.0	23.6
Comments	Heat loss and ΔP = 0				

^a Weighted average, including those in nitrogen refrigerator; ^b Unknown category; ^c Equilibrium composition assumed; ^d Dead-state temperature modified from 288.15 to 300 K; (i) isentropic; (p) polytropic; (isoth.) isothermal.

3. Components

3.1 Compressors

The plant compression system is a key component for optimization, both for existing H₂ liquefiers and for related scale-up studies. Due to their significant losses compressors contribute substantially to operating expenses (OPEX). Depending on the type of compression, wear on parts such as seals and bearings can also lead to periodic plant shutdowns for overhaul reducing average production rates.

A requirement for higher efficiency also brings a high investment cost (CAPEX – capital expenses). A tailor-made compression system can easily comprise half of all hardware investment costs.

3.1.1 Requirements

Pressure range

Optimized refrigeration cycles all run at low pressures, close to -atmospheric pressure (1.05 bara). Sub-atmospheric pressure in the main cycle is excluded, as this would significantly increase equipment size (such as heat exchangers, compressors, piping etc.) and would render an inward leakage of air (giving an explosive process atmosphere) more likely.

The optimum discharge pressure of the refrigeration recycle compressors is in the range of 20 to 50 bara, depending on the compressor type chosen, the number of expansion stages and the heat exchanger design.

The optimum feed stream pressure will be investigated in this study, and is expected to be in the range of 20 to 80 bara as shown in all available data.

Temperature range

The hydrogen feed will be supplied at ambient temperature.

In the refrigeration cycle the compressor suction temperature is defined by the temperature level of the re-cooling medium which in general is ambient air or water. Nevertheless potential benefits of compression at lower temperatures might be worth investigating.

The discharge temperatures are mainly limited by the type of compressor chosen. At elevated temperatures tolerances become critical for some designs.

Mass flow range

The mass flow required (medium, pressures and temperatures) varies with the chosen process. It can be stated that in general the displacement for a compression stage is in the range of several tens of thousands of m³/hr. Depending on the chosen compressor type, machines may need to be placed in parallel.

Efficiency

The aim of this study – to decrease specific energy consumption for hydrogen liquefaction – requires the highest compressor efficiencies. Screw compressors with an isothermal efficiency of less than 55 % (for helium and hydrogen) as installed in state-of

the-art liquefiers cannot fulfil this requirement despite their very low CAPEX. They will not be considered further in this study.

Availability / maintainability

The minimum mean time between services should be 8,000 hrs. Any shorter period would not be acceptable nowadays for an industrial plant. Longer periods would of course be an advantage for OPEX and are not to be underestimated.

Utilities / impurities

The contribution of utilities to the total energy consumption should be listed, as it can vary depending on the type of compressor. Some utilities can even cause additional operational risks to the hydrogen liquefier. If oil is injected into the compressor, for example, it might enter the process, leading to freeze-out, loss in performance or even damage. The same applies to nitrogen used as a sealing gas.

3.1.2 State of the art

Reciprocating piston

According to the literature[1][3][6], state-of-the-art compressors for mid-range hydrogen liquefiers (3 to 30 tpd) are reciprocating piston compressors. The achievable pressure ratio per stage is limited because the maximum permissible discharge temperature is around 160 °C. A safety margin may apply, depending on the manufacturer's standard. Volumetric efficiencies are around 82 %. An isothermal efficiency per stage of 70 % is a realistic value. Interstage cooling is needed, causing pressure drop in related coolers and resulting in lower system efficiencies.

Piston compressors can be built up to a swept volume of about 120,000 Nm³/h and a power of 33 MW. Installation cost is high (about 800–1,000 €/kW at 1 MW).

Although dry piston compressors for hydrogen can achieve a mean time between services of 8,000 to 16,000 hrs nowadays, frequent maintenance requirements on such machines are still their biggest handicap.

Turbocompressor

Turbocompressors are the most efficient machines for compression on the market. Despite this fact, there is no indication that this kind of machine is used in hydrogen liquefiers to date. The reason for this relates to the properties of hydrogen. It is the lightest gas with the lowest viscosity in the universe. It easily flows back even through smallest clearances. It has a significantly higher sound speed than other gases, causing tremendously high circumferential speed. This makes it very difficult to compress hydrogen in a turbo compressor. Only very small pressure ratios can be achieved in one stage, so that a large number of stages is needed to reach the required pressure ratios. Interstage cooling is here even more necessary, causing pressure drop in related coolers resulting in lower system efficiencies.

Research into the use of turbo compressors for hydrogen is mainly driven by the DOE studies of high pressure hydrogen pipelines. Applying high strength alloys promises to allow pressure ratios of up to 1.25 per stage [16][17].

Despite these hydrogen-specific difficulties, turbocompressors are the choice in studies promising the highest efficiencies for large scale hydrogen liquefiers. To overcome the

difficulties in compressing hydrogen, heavier gases than hydrogen for the pre-cooling and cryogenic refrigeration cycles are chosen.

Turbo compressors are also the biggest machines built to today ranging up to 1,200,000 Nm³/h and a power of 90 MW. The installation cost would be even higher than for reciprocating compressors, at least when used for multistage hydrogen compression. Beside their advantages of high efficiency and size, turbo compressors have very long operating times in between maintenance stops.. Moreover any intervention is then much less intensive then for reciprocating machines.

3.2 Expanders

Expanders are the main source of refrigeration power in cryogenic gas liquefiers. Their efficiency is therefore as crucial as the efficiency of the compression system. Due to their high reliability and low maintenance requirements radial turbo expanders are the only machines left in the industrial market. They can vary in design bearing and brake system design.

3.2.1 Requirements

Pressure range

Turbo-expanders exist for sub-sonic as well as super-sonic operation. Pressure ratios up to 10 are installed. The thrust capacity of the chosen bearing design and the enthalpy difference constrain the possible pressure ratio.

Enthalpy difference

The highest efficiency is achieved by optimising the circumferential speed at the inlet (outer diameter) of the turbine wheel. This optimum speed c_{u_opt} is – independent of the expanded gas – given by the following simple equation:

$$c_{u_opt} = \Delta h^{0.5} \quad (\Delta h \text{ in [J/kg]}) \quad (1)$$

Typical maximum circumferential speeds built in systems to date are less than 400 m/s. This permits a wider range of common materials for the wheels. Maximum speeds of up to 550 m/s are feasible for special high-tensile materials.

Hydrogen itself has a very high heat capacity of ~14 J/g·K, much higher than e.g. nitrogen with ~1 J/g·K. As a result, the optimum circumferential speed is reached at much lower pressure ratios.

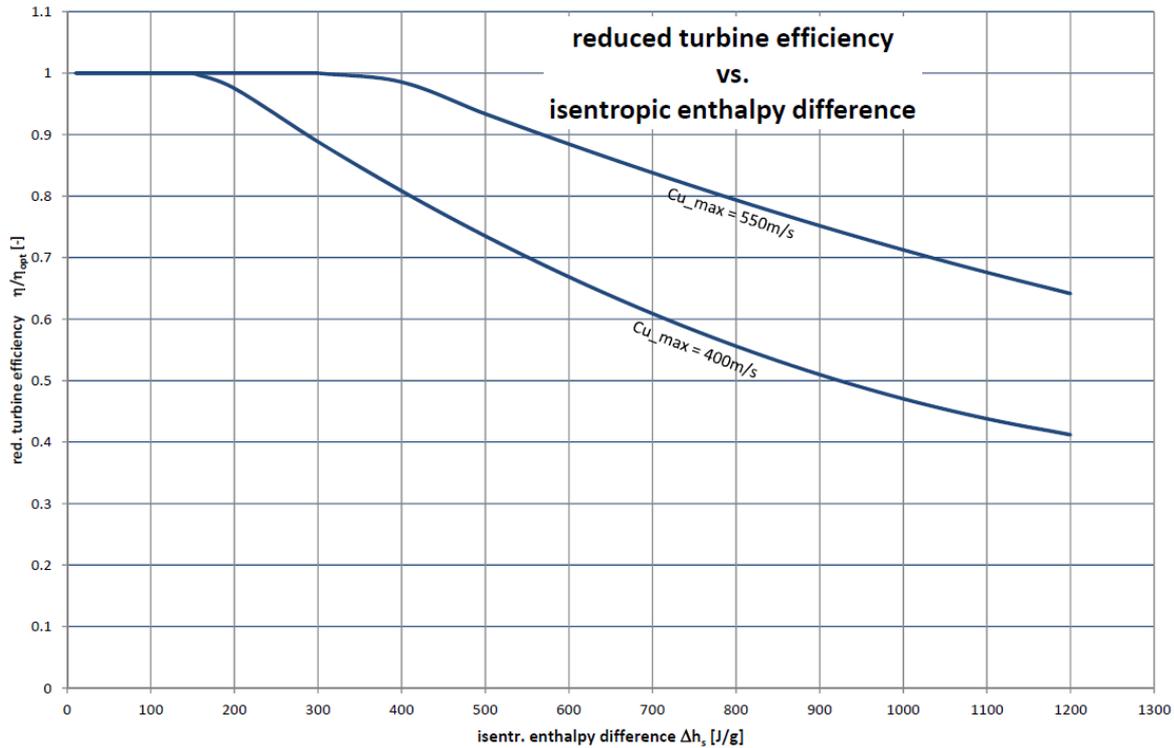


Figure 13: Reduced isentropic efficiency of a gas bearing turbine over the enthalpy difference between the inlet and outlet of the turbine.

Efficiency

The polytropic efficiency of today’s turbo expanders reaches – depending on the machine size – 86 to 90 %. A closer look at the system boundaries is needed when comparing different designs as auxiliary utilities (e.g. for the bearing) may also need power input. The process power extracted by the expanders may be , helping to increase stage efficiency, or simply dissipated..

Availability / maintainability

The availability of existing turbo expanders is very high. Nevertheless there is a difference between bearing designs which are subject to wear and those which are not.

Utilities / impurities

The contribution of utilities to the total energy consumption should be listed, as it can differ depending on the type of expander. Some utilities can even cause additional operational risks to the hydrogen liquefier: e.g. bearing oil might enter the process, leading to freeze out, loss in performance or even damage.

3.2.2 State of the art

The existing turbo expanders mainly differ in design of bearings and energy recovery. Consequently these subsystems shall be discussed next.

Oil bearings

Oil bearings are the oldest design. Besides long time experience they can offer some robustness. However, they need their own continuous oil supply system in order to maintain machine functionality and safety. This means extra oil pumps and other infrastructure to ensure safe machine shutdown in case of any process or utility failure.

This additional power requirement has to be taken into account when defining the stage efficiency. Any additional infrastructure increases CAPEX and OPEX, especially if explosion-proof design requirements apply. The circulating oil also causes significant wear on the components, resulting in the lowest availability of any possible design.

Static gas bearings

Static gas bearings are a younger design but in principle similar to oil bearings; they replace the hydrostatic by a pneumatic cushion. Preferably they run under the same atmosphere as the process gas which eliminates the risk of process contamination. They also need auxiliary bearing gas, which reduces the expander efficiency and causes extra cost and maintenance.

Dynamic gas bearings

Dynamic gas bearings are a recent addition to hydrogen liquefier processes [18], but their very high reliability is well known from cryogenic helium applications. This design needs no any auxiliaries for safe operation and shutdown and therefore can be built in a very compact way. Efficiency is solely driven by fluid-dynamic design and heat transfer into the system. No extra infrastructure is needed in the case of a process or utility failure.

Magnetic bearings

Magnetic bearings permit the high circumferential speeds needed in cryogenic expanders. This design also carries no risk of pollution by other media than the process gas. The controls to ensure safe operation are more sophisticated than for the other design, but progress in electronics has significantly lowered the complexity of thus systems. Despite this, this design is still the most expensive one. In addition any permanent magnet is heavy and subject to hydrogen embrittlement, and would therefore require careful treatment.

Oil brake

The process power can be dissipated in an oil brake. As for the oil bearings, this needs appreciable extra infrastructure and brings the risk of oil leakage into the cryogenic hydrogen process. In case of overload, the oil may even decompose.

Compressor brake

The compressor brake is widely used as it can easily be integrated with the expander shaft. The compression power can either be used simply to dissipate the process power, or to recover it by serving as a compression stage in the refrigeration cycle. If the energy is dissipated, this design allows widest part load operation; conversely, if it is used in a process compressor, operation flexibility is significantly limited.

Generator brake

It is non-trivial to build a generator which can reach the high speeds required, and investment costs are high.. A general rule of thumb is that below 200 kW of process power a generator brake is not economical, although this rule may need revision as the cost of power electronics has decreased significantly in recent years. As for magnetic bearings, any permanent magnet is heavy and subject to hydrogen embrittlement, and thus requires careful handling.

3.3 Heat exchangers

3.3.1 State of the art

The state-of-the-art is represented by vacuum soldered plate fin aluminium heat exchangers. A typical embodiment is visualized in Figure 14. By means of a stack of hermetically brazed layers, high-efficient counter-flow heat exchangers are realised. Main components are aluminium plates, fin plates (usually 4 to 8 mm in thickness), aluminium side bars and headers (for a uniform gas distribution at the inlet and recollection at the outlets). By respective arrangement of stacking orders (layer ABABA... or ABCABCA... respectively) and header connections, mostly two or three stream heat exchangers are built (Figure 15). Large specific exchange surfaces of up to 2 000 m² per m³ are obtained.

This type of heat exchanger can handle design pressures in the range 20 to maximum 100 bar, as discussed in several studies. Maximum dimensions are 8 m x 1.2 m x 2.5 m (length x width x height).

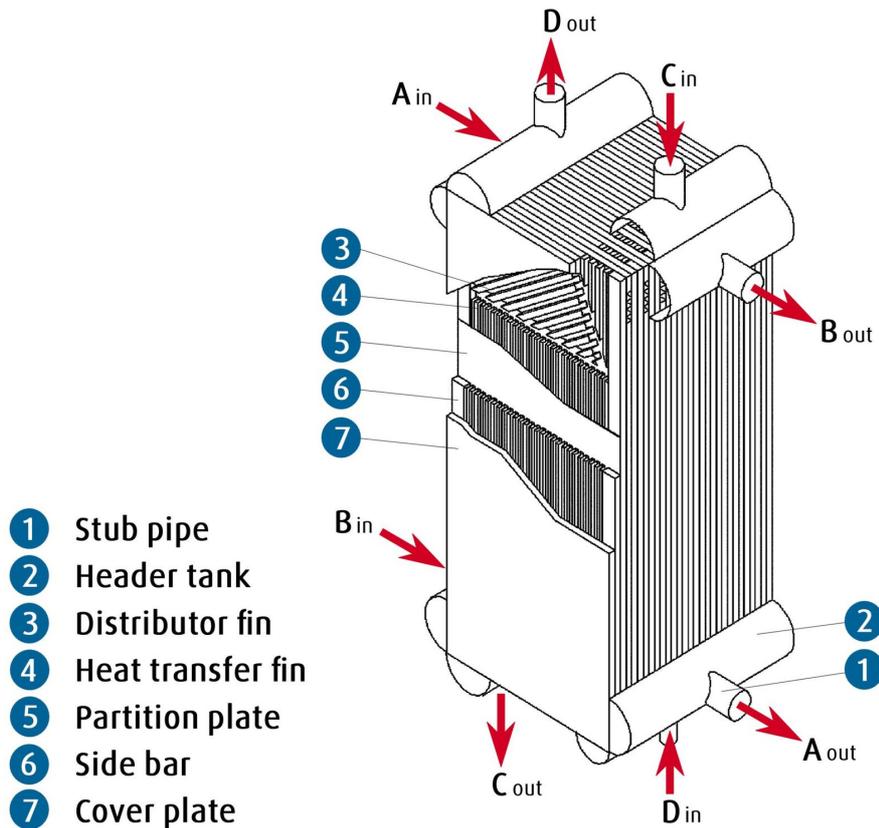


Figure 14: Makeup of a aluminium plate fin heat exchanger used in today's hydrogen liquefiers (Copyright: Linde Group; reproduced by courtesy).



Figure 15: Fabrication of tailor-made aluminium plate fin heat exchanger (Copyright: Linde Group; reproduced by courtesy)..

Soldering is done in vacuum brazing furnaces under carefully controlled conditions, as a clean production environment is essential.

By today's standards, a high degree of performance and heat exchanger efficiency has already been achieved. It seems that there is only minor potential left for further optimization of efficiency and NTU (number of transfer units). Another important parameter is a low pressure drop along the respective heat exchanger channels. Here also only a limited degree of remaining optimization potential remains.

3.3.2 Visible barriers

Some barriers exist to further scaling of heat exchangers towards larger plants.

At present, maximum heat exchanger dimensions are set by the existing brazing furnace chambers at the suppliers. Although the relatively small hydrogen liquefiers in use today do not exploit the full range of heat exchanger sizing, up-scaling of the liquefier capacity by a factor of 5 to 10 will meet limitations in this respect. Special attention has must be paid to the impact of higher process pressures. To withstand higher pressures, fins need to be designed stronger for boosted cycles and they will as a result be efficient. To retain overall heat exchanger efficiency, block dimensions must increase in step with scale-up of the plant..

A possible loophole may exist in a parallel arrangement of several heat exchanger blocks at the same temperature level. This would however lead to higher investment costs and problems with overall space demand inside the cold box . Moreover, such an arrangement would be liable to faulty mass flow distribution between parallel passages, resulting in severe efficiency drops or even malfunction of the whole liquefier plant.

Another alternative might be the direct combination of two maximum -sized standard heat exchanger blocks. There exist already positive experiences with such solutions.



Figure 16: Combination of several aluminium plate fin heat exchanger blocks in parallel arrangement for increased capacity (Copyright: Linde Group; reproduced by courtesy).

3.4 Cold box

3.4.1 Configuration

All the cold components of the liquefier are housed in the cold box container. This comprises:

- Heat exchanger blocks
- Cryogenic valves
- Adsorbers
- Expansion turbines and cold compressors
- Instrumentation
- Internal purifiers and separators (if any)

Most of the space is taken by the heat exchanger blocks, and the required cold box dimensions are mainly governed by these.

Both vertical and horizontal arrangements are in use today. A typical vertical cold box design is shown in Figure 17. All components are fixed at the flat top flange, with no lateral or bottom heat bridges. Due to the small tensile load between cold components and support structure even the remaining material heat bridges to the top can be minimized (low wall thickness etc.).

Turbines, cryogenic valves, instrumentation ports and interconnecting pipework are also located at the top flange. This permits simpler installation, easier opening of the cold box and reasonable access to the interior if needed. For large vertical cold boxes, the outer cold box shell is usually constructed in the form of a number of cylindrical rings. For servicing, these rings and the bottom flange rings can be taken off one by one from the whole cold box. To allow this, the cold box is supported by only its upper part. With a vertical cold box arrangement typically a more compact arrangement of the internal components can be achieved, resulting in smaller overall dimensions. On the other hand an appreciable height is required for the building or shelter.

A horizontal cold box design is commonly used for larger liquefiers operating in regions threatened by earthquake or where limited vertical space is available. The example shown in Figure 18 is from a 5 tpd LH₂ plant. The largest heat exchanger block is also mounted horizontally in this setup alignment. Special care must be taken to avoid gravity-induced mal-distribution within the heat exchanger. As Figure 18 also shows, a horizontal cold box generally gives less dense packing of the components, and thus a larger overall cold box volume. For opening, additional space must be provided along the cold box axis. Turbines, valves and feeds-through are installed at a flat flange section inserted at the top side of the horizontal cold box.

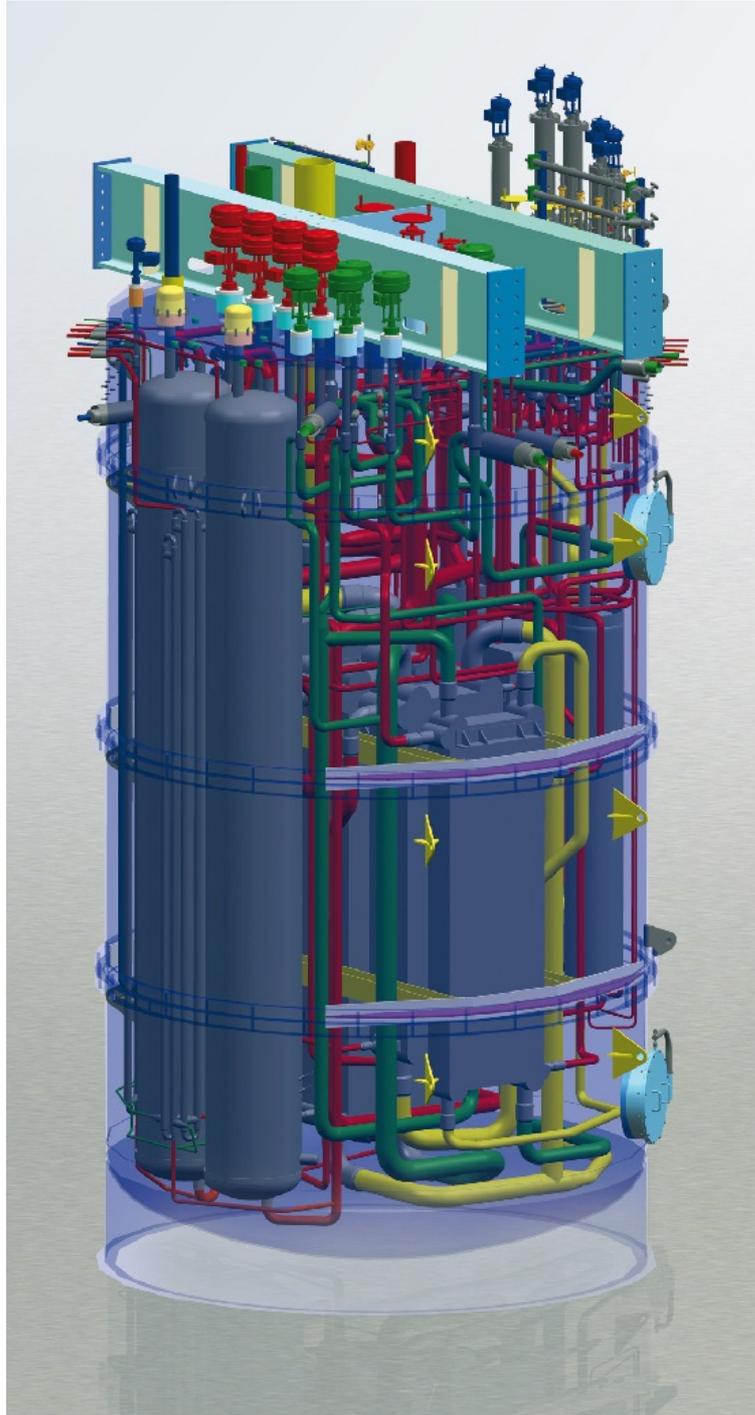


Figure 17: Typical design of the interiors of a helium liquefier coldbox in vertical arrangement (Copyright: Linde Group; reproduced by courtesy).



Figure 18: Typical design of inside of a liquefier coldbox in horizontal arrangement (Copyright: Linde Kryotechnik; reproduced by courtesy).

3.4.2 Special issues

The insulation vacuum is maintained by a standard high-vacuum pump combination. A vacuum level better than 10^{-5} mbar must be obtained. Once the internal components are at operating temperature, the cryo pump effect also supports the perpetuation or even improvement of the vacuum level by freezing out most of the residual gas at cold surfaces. In spite of this, stringent requirements are placed on leak tightness as a result of these vacuum demands; only Helicoflex[®] seals or all-welded joints can be tolerated inside the cold box. For proper sealing of the surfaces of the warm cold box shell segments, a clean environment during installation is essential.

Plant surfaces which are temporarily or frequently below the dew point of the local atmospheric air will be wetted. In some plants the cold box is directly exposed to weather conditions, with no housing or even a shelter. For this reason, all parts of the cold box must be resistant against corrosion. For this reason stainless steel is used for flanges, complete pipework and instrumentation, resulting in significant material costs.

If possible earthquakes are possible at the liquefier site, additional fixing of the cold masses inside the cold box may be necessary. This results in a minor additional heat load and slightly reduced overall efficiency.

3.4.3 Visible barriers

The scale-up of liquefier capacity envisaged brings larger cold box sizes and potential problems.. Preferably the cold box segments should be fabricated at the supplier site with given appropriate facilities. Limits are given thus by feasible transport sizes. Typical restrictions regarding maximum cold box diameter are – within Europe – approx. 4.2 m for road and 5.5 m for waterway transport. With such large cold box diameters, the necessary wall and flange thicknesses also cause high costs and effort. Separate cold boxes both for the cycle components down to 80 K and for those from 80 K down to 20 K have also been used.

Erection of even bigger plants would require pre-fabrication of subsystems in workshops and final assembly at site. The requirements for cleanliness and weld quality for this approach needs to be considered more thoroughly, as such big cryogenic plants have never been built before. Generally the choice of the plant size results in a trade-off between overall efficiency and CAPEX as well as feasibility.

3.5 Cryogenic valves

3.5.1 Cryovalves state of the art

Cryogenic valves are designed to meet the following main requirements:

- Reliable function of opening, closing, controlling behaviour despite of deep-cold valve components, e.g. seat, flow plug and stem
- Minimizing of heat load to the cryogenic medium

Depending on the specific cryogen, there may be several valve solutions for cryogenic requirements. In the first step of the technology overview the market situation is analysed to gather information about concepts for the largest cryogenic valves available.

A number of manufacturers all over the world sell cryogenic valves designed for welding in a vacuum. Figure 19 shows the general construction. Such valves range up to nominal size DN 150 and nominal pressure PN 25 and between 50 and 100 of these are in use in today's hydrogen liquefier plants. However, the biggest nominal sizes that are required therein today, are DN 100 / PN 20.

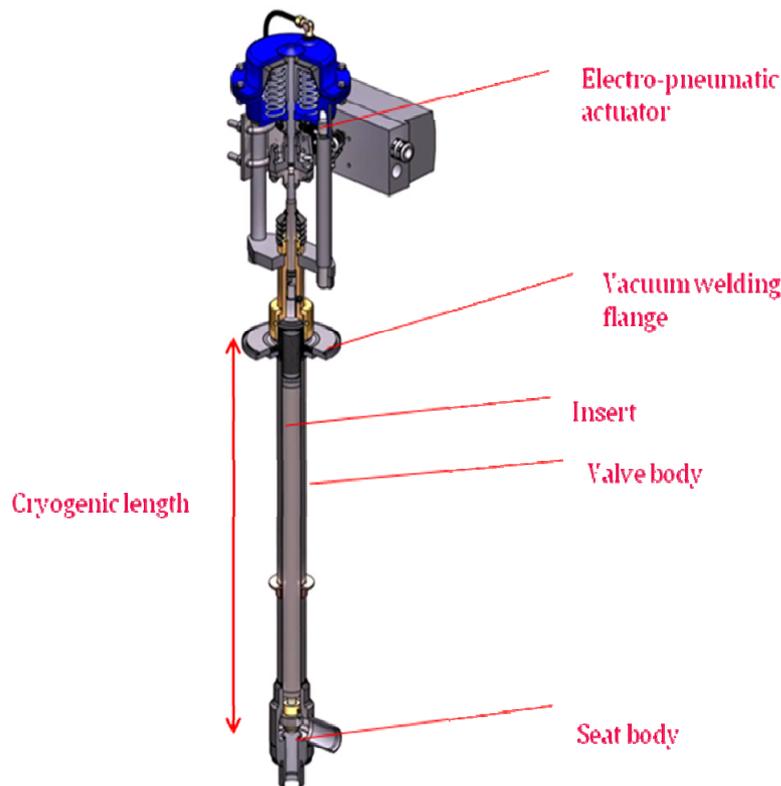


Figure 19: WEKA® cross section through a cryogenic valve.
 (Copyright: WEKA®; reproduced by courtesy).

For much larger sizes butterfly valves, even for cryogenic applications are available today. These valves are specified up to nominal size DN 2000. Figure 20 shows an example of a cryogenic butterfly valve. Although the valve size and therefore the possible flow rates are quite high, that design possesses reduced seat tightness and lower flow control ability. In addition, that design concept does not allow maintenance of the inner valve components (e.g. seat seals) without breaking the vacuum insulation.

Figure not included for copyright reasons.

Figure 20: Velan® cryogenic butterfly valve.

It must be stated that currently no cryogenic valves are available which are suited for the expected specifications in large scale hydrogen liquefiers.

3.5.2 Limitation to scale-up of existing designs: technical barriers

In existing liquefier plants the biggest valves in service are of nominal size DN 100 and K_v values (flow value) of 250. Assuming a maximum scaling factor of 10 for respective lines in future plants, K_v values of up to 2,500 will result. That allows calculation of the depending orifice bore resulting in a diameter of about 300–350 mm.

State of the art valves in industrial application are mostly operated by electro-pneumatic actuators, enabling a safety setting in case of loss of auxiliary energy. The actuator must as a minimum be able to bear the counterforce caused by the average pressure. With the dimensions intended, counterforces of 500 to 800 kN would be caused. Pneumatic actuators are definitely not available in this range; the highest actuating forces from a pneumatic activator range up to only 200 kN (with a weight of 950 kg) Thus either a pressure compensated valve design is needed, or another actuating principle (e.g. a hydraulic actuator) must be developed.

Furthermore there is a trade-off between the wall thicknesses of the pressure-bearing body tubes needed and the requirement for a low-mass design of these parts. Body tubes for DN 300 will need 6–8 mm wall thickness even in higher steel grade 316LN. That would be more than double the wall thickness of valves in present liquefiers.

3.6 Ortho-para catalyst material

Catalyst material to enhance the conversion from ortho- to para-hydrogen during liquefaction is vital for longer storage times. If the ortho-hydrogen is not converted during

liquefaction, a slow self-conversion catalysed by ortho-hydrogen itself will occur. The heat of conversion for this exothermal reaction from normal hydrogen to equilibrium hydrogen at a pressure of 1 bar in the liquid state is about 523 kJ/kg, whereas the enthalpy of evaporation is about 446 kJ/kg. The half-life of this spontaneous reaction is 4.87 d for pure hydrogen. Without conversion, therefore, a huge amount of the liquefied hydrogen will evaporate due to this effect from the liquid storage.

3.6.1 Catalyst material state of the art

A typical catalyst material is the Ionex[®]-Type O-P Catalyst hydrous ferric oxide (Fe₂O₃) which can be purchased from (among others) Molecular Products. The typical price of the material is over US\$100 per kg.

The datasheet for this material advises that the catalyst will achieve 46.5 % or higher conversion to para-hydrogen after 16 hours of re-activation at a temperature of 160°C with dry hydrogen flow, when fed an equilibrium mixture of 75 % ortho- and 25 % para-hydrogen at 1.36 atmospheres and 77 K, and a flow rate of 1200 cc/minute per cc of catalyst (at standard temperature and pressure). More precise performance data can be acquired from the manufacturer. The available data are similar to the data presented in 1957 at the Cryogenic Engineering Conference [19].

The data acquired at that time were taken mainly from liquid cooled converters. In older hydrogen liquefiers adiabatic ortho-para converters were used. This reduces the efficiency of the cycle because more entropy is produced at low temperatures. It is more suitable to use a continuous conversion process, as is the case in more recent designs, but for this purpose there is no precise design data for the catalyst material. It is thus entirely possible that too much catalyst material is currently used, which leads firstly to higher investment costs and secondly to lower cycle efficiency because of additional pressure losses in the feed stream.

The para-hydrogen content at operating plants is measured periodically to ensure the minimum required concentration for long-time storage. Nevertheless there is no data available showing degradation of the catalyst material during a long time of operation.

4. Discussion: Barriers to higher energy and cost efficiency

It is well known that the efficiency of process plants generally increases with plant size. There comes a point, however, where a bigger plant can cause significantly higher costs because fabrication and installation require more complex procedures. The trade-off between plant efficiency and plant size is a complex one and is summarised here..

Linde Kryotechnik estimates the maximum capacity of a hydrogen liquefier built in a workshop to be 50 tpd. The critical unit here is the cryogenic cold box (80 K to 20 K) which beyond this size could not be transported overland as its diameter would exceed road restrictions (~ 4.2 m diameter in Europe). While other plants may be built and erected directly at the production site, the difference for hydrogen liquefaction is that the cleanliness and weldment requirements for the fabrication of a cryogenic coldbox are much more exacting than for most other industrial process plants.

Highly efficient subsystems in a hydrogen liquefier can cost significantly more than only slightly less efficient alternatives. As rule of thumb one can invest €2,000 when reducing power consumption by 1 kW (8,000 h/year operation; €0.05/kWh; amortisation within 5 years). The need for higher efficiency has to be balanced with the investment costs. This also includes the question of the optimum number of compression and expansion stages, and the price of process fluid must also be considered. Neon, for example, is fairly expensive, although the market has excess production capacity, because the processing of neon from an air separation unit requires considerable investment.

It is also important to consider the availability of other process fluids, such as helium. Helium is very scarce, and prices are subject to sudden rises when shortages occur. Can all known and assumed resources cover the demand of a future hydrogen society?

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Annex

Table 3: Succession for impurities (from H2Mobility project)

Contaminant	SAE J 2719 draft	ISO DIS 14687-2 draft	Limit of detection	CUTE design handbook	Ballard specification	Air Liquide N50	Air Products 3.0	Linde 5.0
Hydrogen fuel index	99.99%	99.97%	-	-	-	100.00%	99.90%	100.00%
Total allowable non-H ₂ , non-He	100	300	-	-	-	-	-	-
Water	-	-	-	-	-	-	-	-
- Liquid water	5	5	1	5	0.5	5	5	5
- Water vapour					N/A			
Total hydrocarbons (C1 basis)	2	2	0.05	1	1	0.1	1	0.5
Oxygen	5	5	0.1	5	500	1	5	2
Inerts								
- Helium	TBD	300	10	200	1%	-	-	-
- Nitrogen	TBD	100	0.1			-	-	3
- Argon						-	-	-
Carbon Dioxide	1	1	0.1	2	2	0.1		
Carbon Monoxide	0.2	0.2	0.1					
Total sulphur compounds	0.004	0.004	0.1	1	1	-	-	-
H ₂ S	-	-	0.005	-	<<0.2	-	-	-
Formaldehyde	0.01	0.01	0.06	-	-	-	-	-
Formic Acid	0.2	0.2	0.2	-	-	-	-	-
Ammonia	0.1	0.1	0.1	0.01	0.01	-	-	-
Total halogenated compounds	0.05	0.05	0.005 - 0.05	-	<<1 (Hg, CL2)	-	-	-
Particulate (max. size)	10um	-	0.1	-	-	-	-	-
Particulate concentration	1ug/l	1mg/kg	0.005mg/kg; 1ug/l	-	-	-	-	-

Upper limits in ppm, unless specified otherwise