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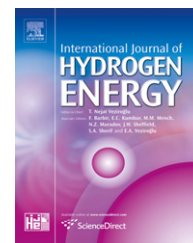
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Review

Development of large-scale hydrogen liquefaction processes from 1898 to 2009

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ABSTRACT

This paper presents a review of the development of large-scale hydrogen liquefaction processes throughout the world from 1898 to 2009. First, there is a concise literature review including numerous past, present, and future designs given such as the first hydrogen liquefaction device, long time ago simple theoretical processes, today's actual plants with efficiencies 20–30%, a list of the capacity and location of every hydrogen liquefaction plant in the world, and some modern more efficient proposed conceptual plants with efficiencies 40–50%. After that, further information about the development and improvement potential of future large-scale liquid hydrogen liquefaction plants is given. It is found that every current plant is based on the pre-cooled Claude system, which is still the same as was 50 years ago with little improvement. Methods to resolve the challenges of the future plants include proposing completely new configurations and efficient systems coupled with improved efficiencies of the main system components such as compressors, expanders, and heat exchangers. Finally, a summary and comparison of the process efficiencies are described, including a newly proposed Multi-component Refrigerant (MR) system being developed by NTNU and SINTEF Energy Research AS.

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1. Introduction

As hydrogen has shown promise as an important energy source for use in future transportation vehicles, several hydrogen research activities have been conducted since 1980 and especially since 2000. One of the challenges in creating a hydrogen economy is the low efficiency of the current hydrogen liquefaction plant cycles. Since 2000, there have been several papers that have proposed conceptual plants with efficiencies up to 40–

50% [1–7]. This paper chronicles the development of systems from 1898 to 2009 and gives a comparison of several cycle efficiencies for the future hydrogen plant developer. Hydrogen was first liquefied in 1898 by a small device [8]. Some years later, a pre-cooled Linde–Hampson system was used as the first simple laboratory system to liquefy hydrogen. Around 1900, more efficient laboratory systems were invented including the Claude, pre-cooled Claude, and helium-refrigerated systems, arranged in order of increasing efficiency [9]. Next, in 1957, the

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first few large hydrogen plants were built in the USA for the growing petrochemical and aerospace industries and were based on the pre-cooled Claude cycle with more complicated systems that used liquid nitrogen as a pre-coolant to cool hydrogen gas down to -193°C and hydrogen refrigeration systems to further cool feed hydrogen gas to -253°C on a large scale. Up to the present, almost all the large-scale plants in use across the world today still employ nearly the same cycle as the first few plants built in the US and have exergy efficiencies of just 20–30%. This can be seen in the Ingolstadt plant installed in Germany in 1991 [10]. Today, the most technologically advanced plants available in the literature are located in Leuna, Germany, and near Tokyo, Japan, which were commissioned in 2008; however, only a slight improvement of efficiency was realized. Thus, there is potential for improvement.

2. Simple hydrogen liquefaction processes

Barron [9] illustrated the fundamental principles and how these simple processes work very well.

2.1. The first hydrogen liquefaction system

In 1885, Michael Faraday published a paper regarding gas liquefaction. At that time, his method was able to achieve refrigeration temperatures down to -110°C using baths of ether and solid carbon dioxide. Gases with boiling points below that temperature, including hydrogen, were called “permanent gases” [11]. For the first time, the liquefaction of hydrogen was achieved by Sir James Dewar in 1898 [8]. This process utilized carbolic acid and liquid air for pre-cooling compressed hydrogen at 180bars. The system was similar to the one that Linde used for the liquefaction of air.

2.2. Theoretical liquefaction systems for hydrogen

In 1895, Carl von Linde and William Hampson invented a simple liquefaction cycle to liquefy air. This cycle is called the ‘Linde–Hampson cycle’. However, according to what was explained by Barron [9], the systems that cannot be used to liquefy hydrogen are the Linde–Hampson, Linde dual-pressure, Cascade, and Heylandt systems. A liquid nitrogen, pre-cooled Linde–Hampson system can be used to liquefy hydrogen. This cycle is shown schematically by Barron [9].

2.3. Theoretical Claude system for hydrogen

In addition to liquefying air, the Claude cycle invented by Georges Claude in 1902 can also be used to liquefy hydrogen [9]. This cycle was a development some years after the first Linde–Hampson cycle. There was an expansion engine in the Claude cycle, which produced a temperature much lower than the temperature generated by isenthalpic expansion as proposed by Linde.

2.4. Theoretical pre-cooled Claude system for hydrogen

The performance is somewhat improved if a pre-cooling bath of liquid nitrogen is used with the Claude system.

Timmerhaus and Flynn [12] explained that if liquid nitrogen is used for pre-cooling, one could achieve an exergy efficiency 50–70% higher than a pre-cooled Linde–Hampson cycle. Nandi and Saragni [13] made a comparison of the two cycles and found that the typical Figure of Merit (FOM) for the pre-cooled Linde–Hampson cycle was lower than the standard pre-cooled Claude. The Claude cycle, as explained by Nandi et al. [13], is the basis for most other conventional liquefaction cycles. An example of a modified pre-cooled Claude cycle in use today is the hydrogen liquefaction plant in Ingolstadt near Munich, Germany, as shown in Fig. 2, which has been in operation since 1992 [10].

2.5. Helium-refrigerated hydrogen liquefaction system

A secondary helium-gas refrigerator can also be used to liquefy hydrogen, as shown in Nandi and Sarangi [13] and Barron [9], but this system has never been used in any actual large-scale plants.

3. Current plants

Table 1 shows a list of all of the hydrogen liquefaction plants in use around the world. In 1960, the first few liquid hydrogen plants were built to support the Apollo program. In the beginning of the 1960s there was a demand for US space programs. The capacity installed up to 1965 was capable of supplying the demand of NASA and others until 1977. In this period, no additional plants were built, not least because of the reduction of NASA’s space activities. Since 1977, this time was mainly caused by the steadily increasing commercial demand for liquid hydrogen. Today, there are more than 9 hydrogen liquefaction plants in the US with production rates of 5–34 tons per day (TPD), 4 plants in Europe with capacities of 5–10 TPD, and 11 plants in Asia with capacities of 0.3–11.3 TPD. Air Products supplies the largest quantity of liquid hydrogen in North America, followed by Praxair. Today, liquid hydrogen is used to reduce the cost of hydrogen distribution [14]; however, the current worldwide liquid hydrogen (LH_2) production capacity exceeds the market demand. Liquid hydrogen demand and production today is the largest in North America, which constitutes 84% of the world production. Of the total production in the US, 33.5% is used in the petroleum industry, 18.6% is for government aerospace, and the rest is for other industries. Only 0.1% is used for fuel cells today [15].

3.1. Large-scale plants: Praxair, Air Products, and Air Liquide

Praxair has five hydrogen liquefaction plants in the US today with production rates between 6 and 35 TPD LH_2 . Typical specific power consumptions are between 12.5 and 15 kW h/ kg_{LH_2} [14]. Fig. 1 shows a Praxair LH_2 process flow sheet. It looks like the pre-cooled Claude cycle, but is more complicated for the large-scale system. There are three heat exchangers. The first heat exchanger is cooled by nitrogen gas (GN_2) and an external refrigeration system. The second heat exchanger is cooled by liquid nitrogen (LN_2) and some of the H_2 feed. The third is cooled by a hydrogen refrigeration system

Table 1 – Commercial hydrogen liquefaction plants worldwide.

Continent/Country	Location	Operated by	Capacity (TPD)	Commissioned in	Still in operation
<i>America</i>					
Canada	Sarnia	Air Products	30	1982	Yes
Canada	Montreal	Air Liquide	10	1986	Yes
		Canada Inc.			
Canada	Becancour	Air Liquide	12	1988	Yes
Canada	Magog, Quebec	BOC	15	1989	Yes
Canada	Montreal	BOC	14	1990	Yes
French Guyane	Kourou	Air Liquide	5	1990	Yes
USA	Painsville	Air Products	3 ^a	1957	No
USA	West Palm Beach	Air Products	3.2 ^a	1957	No
USA	West Palm Beach	Air Products	27 ^a	1959	No
USA	Mississippi	Air Products	32.7 ^a	1960	No
USA	Ontario	Praxair	20	1962	Yes
USA	Sacramento	Union Carbide, Linde Div.	54 ^a	1964	No
USA	New Orleans	Air Products	34	1977	Yes
USA	New Orleans	Air Products	34	1978	Yes
USA	Niagara Falls	Praxair	18	1981	Yes
USA	Sacramento	Air Products	6	1986	Yes
USA	Niagara Falls	Praxair	18	1989	Yes
USA	Pace	Air Products	30	1994	Yes
USA	McIntosh	Praxair	24	1995	Yes
USA	East Chicago, IN	Praxair	30	1997	Yes
Subtotal			300		
<i>Europe</i>					
France	Lille	Air Liquide	10	1987	Yes
Germany	Ingolstadt	Linde	4.4	1991	Yes
Germany	Leuna	Linde	5	2008	Yes
Netherlands	Rosenburg	Air Products	5	1987	Yes
Subtotal			24.4		
<i>Asia</i>					
China	Beijing	CALT	0.6	1995	Yes
India	Mahendragiri	ISRO	0.3	1992	Yes
India	India	Asiatic Oxygen	1.2	–	Yes
India	Saggonda	Andhra Sugars	1.2	2004	Yes
Japan	Amagasaki	Iwatani	1.2 ^a	1978	No
Japan	Tashiro	MHI	0.6 ^a	1984	No
Japan	Akita Prefecture	Tashiro	0.7	1985	Yes
Japan	Oita	Pacific Hydrogen	1.4	1986	Yes
Japan	Tane-Ga-Shima	Japan Liquid Hydrogen	1.4	1986	Yes
Japan	Minamitane	Japan Liquid Hydrogen	2.2	1987	Yes
Japan	Kimitsu	Air Products	0.3	2003	Yes
Japan	Osaka	Iwatani (Hydro Edge)	11.3	2006	Yes
Japan	Tokyo	Iwatani, built by Linde	10	2008	Yes
Subtotal			30.6		
Worldwide			355		

a Not included in the subtotal of the capacity for the year 2009.

that uses some of the feed to expand through turbines and the Joule–Thomson (J–T) valve. The system is unique. Air Products has four hydrogen liquefaction plants capable of producing between 30 and 35 TPD LH₂ in use in North America today. In addition, they have two 5 TPD LH₂ plants: one in Holland and the other one in the USA. However, there is no literature about Air Product's technology. Air Liquide has a plant in France and one in Canada, and both have capacities of about 10 TPD. Both of these plants make use of the Claude cycle with hydrogen used as the cycle fluid; however, there are no papers about Air Liquide's cycle. The best plant in the USA requires about 10 kW h/kg_{LH₂} [14]. The LH₂ production capacity is still greater

than the demand. It seems that every large-scale LH₂ plant has the cycle of LN₂ as a pre-cooling process to cool hydrogen gas from 25 °C to –193 °C and a hydrogen refrigeration system to further cool hydrogen gas to –253 °C.

3.2. Linde large-scale N₂ pre-cooled Claude plant in Ingolstadt

This plant used to be the largest German hydrogen liquefier. The cycle is illustrated in Bracha et al. [10]. Feed hydrogen gas obtained from an air separation plant is generated from a steam reforming process using natural gas. Fig. 2 shows the

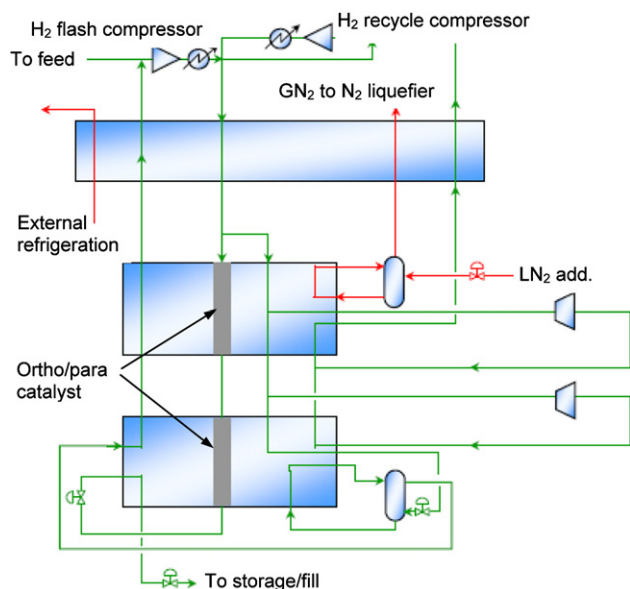


Fig. 1 – Praxair hydrogen liquefaction process (adapted from [14]).

actual liquefier in the plant. The big, vertical tank nearby on the left is the LN_2 tank that the nitrogen liquefaction system uses to liquefy nitrogen to pre-cool hydrogen inside the LH_2 liquefier. All of the compressors are kept inside the machinery building on the right. The leftmost tank is the LH_2 storage tank where liquefied hydrogen is kept for delivery. The tank is vacuum insulated. Fig. 3(a) is for the other side. To minimize the delivery cost, the hydrogen is delivered in liquid form by truck. Fig. 3(b) demonstrates how LH_2 is loaded from the storage tank to the trailer.

3.3. The new Linde large-scale plant system in Leuna

Linde opened a second, 20 million Euro hydrogen liquefaction plant in September 2007 in Leuna, as depicted in Figs. 5 and 6. It is currently the newest and largest H_2 liquefier plant in Germany. The system with a new cycle as depicted in Fig. 4 is similar to the existing plant in Ingolstadt depicted in Fig. 2, but

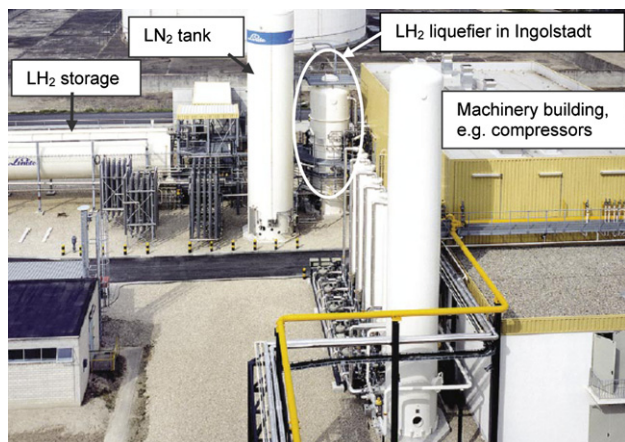


Fig. 2 – The location of Linde LH_2 in Ingolstadt.

is more efficient. There is an important difference in the turbine arrangement between the plants in Leuna and Ingolstadt in that the plant in Leuna receives a single feed GH_2 stream from an air separation plant. There is no recycled hydrogen, and the ortho-para (o-p) conversions are put inside heat exchangers.

4. Conceptual plants

From year 2000 to 2009, some researchers have proposed new improved processes with exergy efficiencies between 40 and 50%. The details are given below.

4.1. Large-scale H_2 liquefaction in combination with liquefied natural gas (LNG) pre-cooling system

Kuendig et al. [1] conducted a study regarding the integration of a pre-cooling LNG system to a new one like the Leuna N_2 pre-cooled Claude system. The study concluded that using LNG for pre-cooling in the hydrogen liquefaction process would be extremely useful to decrease the power input and the overall liquefier construction cost because the source would be free. Compared to a conventional liquefaction process, such as the one at Leuna using liquid nitrogen for pre-cooling but with compression at ambient temperature, the reduction would be from 10 to 4 $\text{kW h/kg}_{\text{LH}_2}$ [16]. However, this process could only be used for hydrogen gas made from LNG, and the plant would have to be located near a seaport.

4.2. Nitrogen pre-cooled Claude by Matsuda and Nagami [2]

The World Energy Network (WE-NET) project [17] has suggested building large-scale hydrogen liquefaction plants with liquefaction capacities of 300 TPD. The plant is based on a Claude cycle with nitrogen pre-cooling [2]. It appears that WE-NET's cycle is similar to the plant in Ingolstadt in that the nitrogen cycle is used to pre-cool hydrogen from 25 to -193°C . Then, the hydrogen cycle is used to cool from -193°C down to -253°C ; however, WE-NET's cycle is more complicated and is specifically designed for greater capacity. There is a large N_2 liquefaction system to reliquify GN_2 for the pre-cooling process.

4.3. Conceptual plant by Quack [3]

Quack [3] has made a conceptual design of a high-efficiency, large-capacity liquefier for hydrogen. However, internal process simulation tests run in a commercial software package; SimSci/PROII by NTNU-SINTEF indicated that it was not able to explicitly determine whether it has a high-efficiency or not because the configuration of the proposed propane refrigeration is impossible for low power consumption. The software was checked for its reliability and accuracy of process simulation. Also, the proposed helium-neon refrigeration system consumes more power due to the fact that helium-neon mixture has inferior refrigerant heat transfer properties compared with hydrogen, which is commonly found in use today in actual hydrogen liquefaction plants.

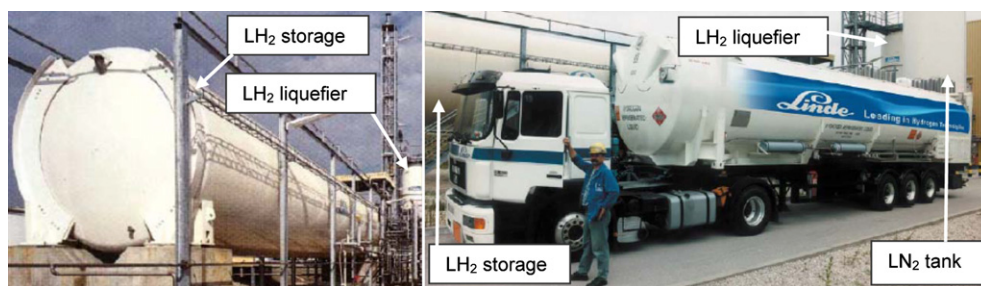


Fig. 3 – (a) Liquid hydrogen storage tank of Linde AG in Ingolstadt, (b) articulated train with semi-trailer equipped for liquid hydrogen.

4.4. Conceptual plant with helium refrigeration cycle by Kuzmenko et al. [4]

Before this, Beljakov et al. [18] successfully created a reliable, high-efficiency, low-capacity hydrogen liquefier with a helium refrigeration cycle. Later on, engineer Kuzmenko et al. [4] at Open Joint-Stock Company used this concept to design a liquefier. He made a conceptual study of building a medium-capacity hydrogen liquefier with a helium refrigeration cycle; however, it only produced a slight improvement from the Ingolstadt plant's efficiency.

4.5. MR refrigeration by Stang et al. [5]

A hydrogen liquefaction prototype laboratory unit was developed by NTNU-SINTEF. The process was based on using an MR process for pre-cooling, as shown in the figure of Stang et al. [5]. The rig is under experiment by the author of this paper. With the

initial test, the hydrogen gas could be cooled by the MR refrigeration system from an ambient temperature of 25 °C down to near −193 °C with the highest efficiency. Detailed experimental results will be reported by the author in a future paper.

4.6. Helium refrigeration cycle by Shimko and Gardiner [6]

This is the design and construction of an estimated \$2.6 million small-scale pilot plant (20 kg/h) that will be used for hardware demonstration (will be finished in 2011) and as a model for scaling to an estimated \$39 million larger plant (50 TPD) [6]. Simulations were performed using EXCEL and REFPROP. Nevertheless, the efficiency is still lower than the proposed NTNU-SINTEF system. Moreover, helium is not suitable (hydrogen has better heat transfer properties) for cooling GH_2 from -193 to -253 °C. If used, every component such as compressors, expanders, and heat exchangers will have to be bigger.

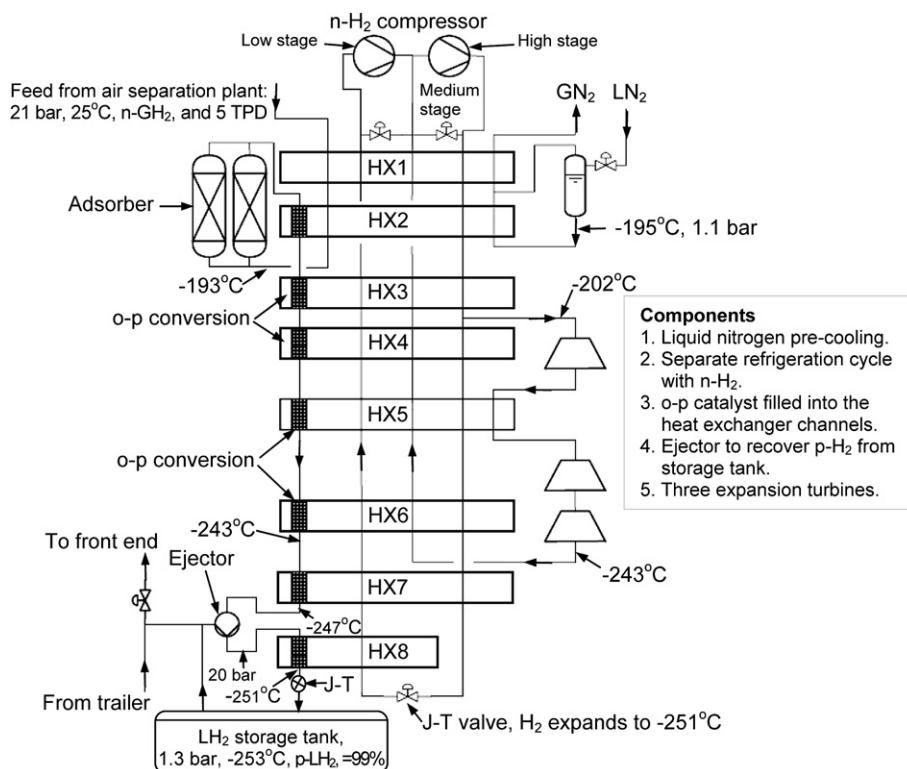


Fig. 4 – Process flow sheet of hydrogen liquefaction plant in Leuna [1].

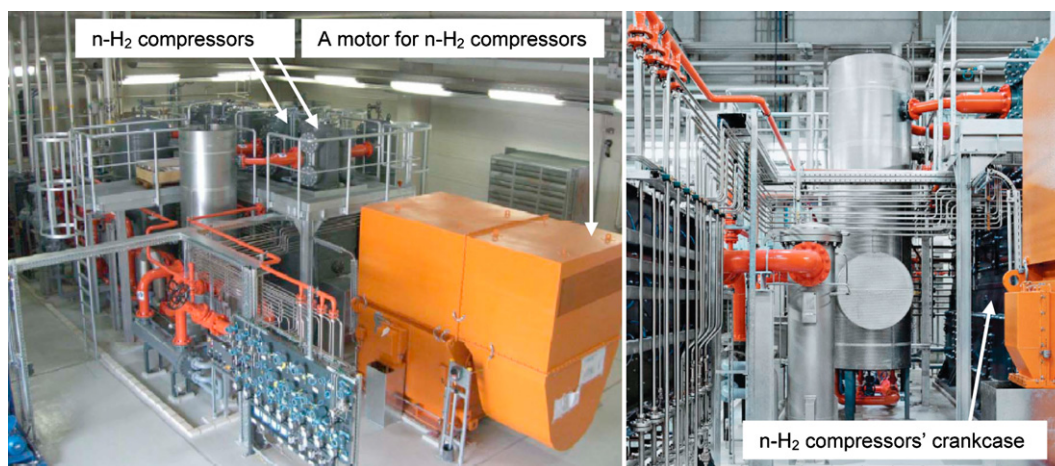


Fig. 5 – Piston compressors of hydrogen liquefaction plant in Leuna (adapted from Finanzberichte.Linde.com, 2008).

4.7. Helium Joule–Brayton cascade system by Valenti [7]

Valenti [7] proposed an innovative, high-efficiency, large-scale hydrogen liquefier that utilizes four cascaded helium Joule–Brayton cycles. However, helium is not suitable for cooling GH_2 from 25 to -193°C and from -193 to -253°C due to its inferior heat transfer properties compared to hydrogen. Moreover, the cycle's configuration itself to cool GH_2 from 25°C to near -193°C makes it impossible to have low exergy efficiency as reported. Also, internal simulation tests run in PROII by NTNU-SINTEF indicated that the system is not guaranteed to have a high-efficiency.

5. Development potential of large-scale LH_2 plants

A potential efficiency increase in future hydrogen liquefaction plants can be realized by the following means:

- Replacement of the J–T valve at the liquefaction stage by an expansion turbine. An increase in the number and quality of expansion turbines can minimize exergy losses.
- Reduction of the circulating mass flow or using a single H_2 feed stream as used by the Leuna plant, Quack [3], and Valenti [7]. By doing this, the last heat exchanger must be designed to cool the hydrogen to the lowest possible temperature, e.g. near -253°C , so there is no vapor fraction after the expansion at the last J–T valve. A small ejector is recommended to recover p- GH_2 from the storage tank, the same as the plant in Leuna.
- Operating with a refrigerant mixture for pre-cooling hydrogen gas from 25 to -193°C . This way, pre-cooled hydrogen gas and cold Multi-component Refrigerant (MR) streams get closer. This new system is currently being studied at NTNU-SINTEF [5], and the results will be published soon.
- Another major factor influencing liquefier efficiency is the feed gas input pressure. One alternative is to raise the hydrogen output pressure of the preceding hydrogen production plant, e.g. a high-pressure electrolysis process or

a steam reforming plant. A good example is the 21 bar feed n-H_2 at the LH_2 plants in Ingolstadt and Leuna. The higher the feed pressure, the greater the liquefier's efficiency. The minimum liquefaction work is in conjunction with feed pressure. The minimum feed pressure must not be below 15 bars because there could be hydrogen condensation during the cooling process. If it is below 15 bars, more energy is needed in liquefaction, and there will be more exergy loss.

- Most of the exergy losses in the hydrogen liquefaction processes are dissipated through compressors. Therefore, it is recommended for manufacturers to design new high-efficiency compressors and expanders and design all compressors in a way such that the suction temperatures are reduced as done by Quack [3]. Also, it is recommended to ventilate heat from the compressors as much as possible during the compression process to reduce the exergy loss.
- Use aluminum plate-fin heat exchangers with maximum effectiveness to reduce the exergy losses.
- If possible, construct plants near seaports for delivering LNG to be used in the pre-cooling process. This will help significantly reduce the plant size and energy consumption as recommended by Kramer et al. [16] and Keundig et al. [1].
- A cost overview for the specific investment costs of conventional liquefaction plants. When designing a large-scale plant, the cost must be compared with other existing plants. Inflation should be accounted for in current and old plants. Companies who can offer cheap, large-scale hydrogen liquefaction plants are Linde, Air Products, and Praxair. Praxair has the largest hydrogen plant in the USA with the lowest investment cost.
- Krewitt and Schmid [19] say that costs for liquefaction are driven primarily by capital costs (today: 63%), then energy costs (29%), and finally, O&M [14]. Energy costs on the other hand are strong functions of the liquefier efficiency and are less dependent on the production rate. In small plants, energy and non-energy costs are comparable. In large-scale plants, the energy costs become more important. Krewitt and Schmid [19] also derived the following equation for the specific investment costs: Specific investment cost for liquefier ($\text{€}2000/\text{kg/h}$) = $828\,313 \times (\text{production capacity, kg/h})^{-0.48}$.

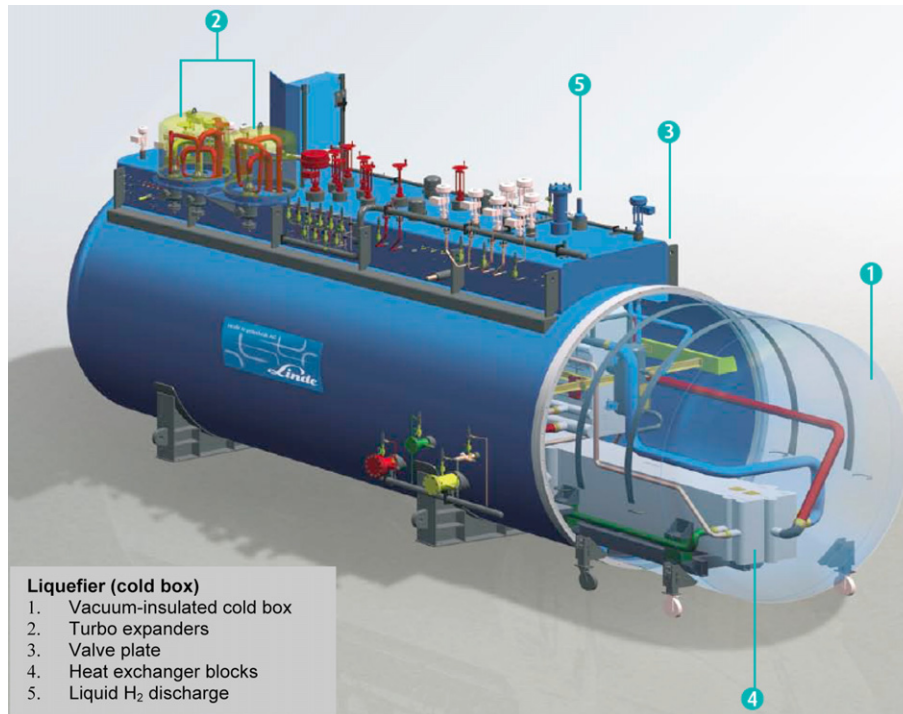


Fig. 6 – A Linde hydrogen (cold box) liquefier in Leuna (adapted from Linde-kryotechnik.ch, 2008).

- A method to decrease capital costs is to build plants on a larger scale and use the effect of building multiple plants of the same design. The following challenges for more cost effective LH₂ production systems are [14] system modularization for traditional sized units, large-scale equipment, higher efficiency compressors and expanders, more efficient refrigeration, and lower cost high-efficiency insulation.

The conclusions are the following:

- The problem with the current liquefaction systems is their high-energy consumption. Every large-scale hydrogen liquefaction plant is based on the pre-cooled Claude system, which is still the same as 50 years ago with little improvement. If it is possible to reduce from today's energy usage of 10 kW h/kg_{LH2} to around 5 kW h/kg_{LH2} which will reduce electrical power consumption of the plant to be half in the future, all of the compressors and motors in the plant, which constitute the most expensive components, could be reduced by 50%, which will also lead to cheaper plants.
- Methods to resolve the challenges include proposing completely new configurations and efficient systems coupled with improved efficiencies of the main system components such as compressors, expanders, and heat exchangers.
- The development trend is that a lot of people have tried to propose new better systems [1–7], but they are still neither more efficient nor realistic. Furthermore, compressor and expander manufacturers must invent more efficient machines.

6. Summary and comparison of hydrogen liquefaction process efficiencies

Table 2 gives the summary and comparison. Feed hydrogen flow is normal hydrogen at 1 atm, 25 °C. $FOM \times 100\% = (\text{Ideal liquefaction power} / \text{Actual system liquefaction power}) \times 100\%$ or Exergy efficiency. The efficiencies of systems 3, 5, and 6 are from Nandi and Sarangi [13]; the same systems have different energy consumptions and exergy efficiencies because it depends on the assumptions of the efficiencies of compressors and expanders used in the systems. When making a comparison between several different cycles and liquefiers, Berstad et al.'s [20] comparison method is recommended. This method, which is a direct comparison of liquefiers based on the overall exergy efficiency and specific power consumption, favors those with a higher portion of pre-compression. The feed stream was assumed and calculated at 21 bars and 25 °C before going into any cycle/liquefier, which is identical to the Ingolstadt plant. Every system is directly compared with the Ingolstadt plant at a modified feed stream pressure of 21 bars. The energy consumptions and exergy efficiencies of the Ingolstadt, WE-NET, and Quack systems as shown in Table 2 were calculated by Berstad et al. [20].

The compression power reductions of the third, fourth, fifth, and sixth hydrogen liquefaction systems in Table 2 are 0.9167, 0.9167, 0.2313, and 0.1026 kW h/kg_{LH2}, respectively. These are from the ideal H₂ feed exergy reduction of 0.55, 0.55, 0.1388, and 0.0616 kW h/kg_{LH2}, respectively. Make-up gas is reversibly and isothermally (ideally) compressed from the feed at 21 bars and 25 °C to each cycle's high side. This was all calculated assuming a compression exergy efficiency of 60%.

Table 2 – Summary and comparison of hydrogen liquefaction process efficiencies.

System with modified feed state: normal hydrogen @21 bars, 25 °C	Original energy consumption (kW h/kg _{LH2})	Modified energy consumption (kW h/kg _{LH2})	Modified exergy efficiency (%)
1. The thermodynamically ideal liquefaction system Feed: 21 bars, 25 °C, n-GH ₂ Output: 1 bar, –253 °C, n-LH ₂ Output: 1 bars, –253 °C, 99.8% p-LH ₂	– –	2.178 2.890	100 100
2. Theoretical simple Linde–Hampson system [8]. *Cannot liquefy hydrogen	–	–	–
3. Theoretical pre-cooled Linde–Hampson [8,13]. Output: 1 bar, –253 °C, n-LH ₂	64.5–71.7	63.6–70.8	3.0–3.4
4. Theoretical Claude system [8,13]. Output: 1 bar, –253 °C, n-LH ₂	Less than the pre-cooled Claude		
5. Theoretical pre-cooled Claude system [8,13]. Output: 1 bar, –253 °C, n-LH ₂	24.8–35.0	24.6–34.8	6.2–8.8
6. Theoretical helium-refrigerated system [8,13]. Output: 1 bar, –253 °C, n-LH ₂	29.3–49.5	29.2–49.4	4.4–7.4
7. Large-scale Praxair plant system [14]. Output: ≈1 bar, –253 °C, 95% p-LH ₂	≈12–15		19–24
8. Large-scale Air Products plant system [14]. Output: ≈1 bar, –253 °C, 95% p-LH ₂			
9. Large-scale Air Linde plant system [14]. Output: ≈1 bar, –253 °C, 95% p-LH ₂			
10. Large-scale plant, Claude system in Ingolstadt on stream in 1994 by Bracha et al. [10]. Output: 1.3 bars, –253 °C, 95% p-LH ₂	13.58		21.0
11. WE-NET: Nitrogen pre-cooled large-scale Claude plant by Matsuda and Nagami [2] Output: 1.3 bars, –253 °C, 95% p-LH ₂ 1) Hydrogen Claude 2) Helium Brayton 3) Basic neon 4) Neon with cold pump	≈8.5	N/A 7.0	N/A 41.3
12. Large-scale conceptual plant by Quack [3] Output: 1 bar, –253 °C, 99.8% p-LH ₂ 1) Without pressure drop in calculation 2) With pressure drop in calculation	7.0 ≈7.3	5.49 N/A	52.6 N/A
13. Four helium Joule–Brayton cascade cycle by Valenti [7]. Output: 1.5 bars, –253 °C, 99.8% p-LH ₂	5.04	5.76	50.2

For cycles 7–9, the hydrogen feed pressure was 21 bars, the same as Ingolstadt's. Thus the energy consumption was the same. With Valenti's system, GH₂ compression must be made from 21 bar supply feed to 60 bars; therefore, there is an increased consumption of 0.72 kW h/kg_{LH2} with an assumed 60% exergy efficiency from the ideal H₂ feed exergy increase of 0.43 kW h/kg_{LH2}. Finally, all of the system exergy efficiencies were calculated by comparing with an ideal energy consumption of 2.89 kW h/kg_{LH2}; however, systems 3–6 were calculated using an ideal energy consumption of 2.178 kW h/kg_{LH2}.

Fig. 7 contains the information shown in Table 2. From the data, the theoretical pre-cooled Linde–Hampson system was the first imaginary system invented a long time ago, and its exergy efficiency is the lowest. After that, the second was the theoretical helium-refrigerated system, which is followed by the theoretical pre-cooled Claude system. All have a very low yield: e.g. 10% after expansion. The theoretical systems mentioned have never been used to liquefy hydrogen on a large-scale production. They were just small-scale laboratory systems. Next, Ingolstadt and Praxair brought this

concept to invent real plants. Today, actual large-scale hydrogen liquefaction plants, e.g. Praxair, Air Products, and Air Liquids plants in the USA, energy consumptions are reported to be between 12 and 15 kW h/kg_{LH2} [14]. Baker and Shaner's [21] was the first conceptual plant, and it had the lowest efficiency. The conceptual large-scale systems proposed by Matsuda and Nagami [2], Quack [3], and Valenti [7] were designed later. Recently, the efficiency of the Leuna plant (with energy consumption less than 13.58 kW h/kg_{LH2}) is a little better than Ingolstadt is assumed here. Quack's process reports the best cycle exergy efficiency at 5.76 kW h/kg_{LH2}. The best plant in the USA today is reported to require 10 kW h/kg_{LH2} [14], but it is not known where. A simulated 50 TPD large-scale Shimko plant, which is a helium refrigeration system with a hydrogen feed at 21 bars, is reported at 8.7 kW h/kg_{LH2}. The proposed large-scale MR system is 5.35 kW h/kg_{LH2} as depicted. The ideal theoretical minimum value is 2.89 kW h/kg_{LH2}. For the process with LNG for pre-cooling studied by Kuendig et al. [1], the power consumption is reported by Kramer et al. [16] to be 4 kW h/kg_{LH2}. Thus, the overall

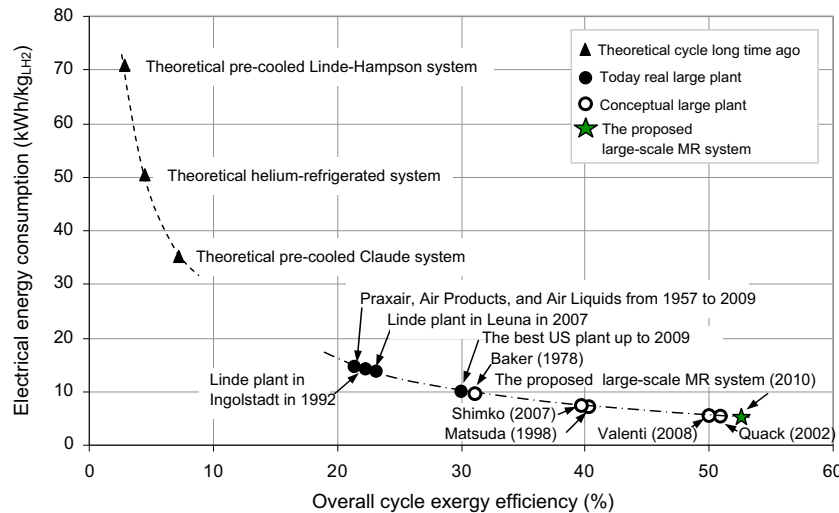


Fig. 7 – Comparison of hydrogen liquefaction process efficiencies by assuming that all processes are with uniform feed pressure equal to that of Ingolstadt plant at 21 bars.

efficiency, compared with the ideal process, is $[(2.89 \text{ kW h/kg}_{\text{LH}_2}) / (4 \text{ kW h/kg}_{\text{LH}_2})] \times 100 = 72\%$, which is the highest with respect to all current systems. However, this is not shown in Fig. 7 because the process is cooled by free LNG, not by the system itself. Completely new approaches for low temperature refrigeration are magnetic refrigerators and acoustic refrigerators. Magneto caloric cooling may reduce liquefaction energy to $5.0 \text{ kW h/kg}_{\text{LH}_2}$ [22]; however, this may only be for small-scale to medium-scale plants. All of the literature related to magnetic cooling has been reorted on small-scale hydrogen plants. Nobody thinks such a system is realistic in large-scale systems.

7. Conclusion

Today large hydrogen liquefaction plants have exergy efficiencies of just 20–30%; thus, there is potential for improvement. From 1998 to 2008, some conceptual plants have been proposed with reported efficiencies of 40–50%. Finally, in the year 2010, NTNU and SINTEF Energy Research AS will propose a new MR system with an efficiency greater than 50%. Details of the proposed system will be reported in upcoming papers.

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