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Principles for the liquefaction of hydrogen with emphasis on precooling processes

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ABSTRACT

This paper elaborates a concept for designing efficient large scale hydrogen liquefaction plants, based on dividing the process into 4 independent stages and finding the optimum solution for each stage. The main focus is put on the precooling stage. Not because of its power consumption, but because it is the stage with the most degrees of freedom in design. Several processes have been discussed, mentioning some of the main advantages and disadvantages. One of the main challenges in efficient hydrogen liquefaction is light gas compression. This is unavoidable, since only light gases can provide cooling at the required temperature levels, but should be minimized by using heavier fluids where possible. Due to the higher exergy efficiency of compression compared to refrigeration, the hydrogen feed pressure should be as high as possible, as long as the pressure reduction in the liquefaction stage is performed by expansion machines instead of throttling.

1. INTRODUCTION

Hydrogen is considered to play an important role as an energy carrier in the future and could become an alternative to fuel, especially for the fossil fuel dependent passenger cars and utility vehicles [1]. Hence for the distribution of hydrogen and usage in the transport sector its energy density plays a considerable role. Even though hydrogen has a comparably high heating value its density is very low, which results in a rather low energy density compared to other fossil fuels. At its compressed state at 200 bar and 15 °C, hydrogen has an approximately 17 times lower energy density than liquid gasoline. Yet, the energy density can be increased significantly by liquefying hydrogen, which results in an approximately 5 times higher energy density at its liquid state than at its compressed state at 200 bar and 15 °C [2].

However, the liquefaction of hydrogen has its price, since hydrogen has the second lowest boiling point of all substances, with a boiling temperature of 20 K at atmospheric pressure. Only helium has a lower boiling point. On the other hand liquefied hydrogen provides advantages in efficient transport from the liquefaction site to a filling station. In addition it provides the flexibility of being provided either in liquid form or if needed vaporized and in compressed state. Here, a rather efficient pump could be applied for achieving the desired high pressure instead of a compressor. A study showing the competitiveness of liquefied hydrogen compared to distribution chain with compressed gas is show by Kramer [3].

Yet for hydrogen being able to play a major role in the transport sector a significant amount of liquid hydrogen must be available at a relatively competitive price. So far only a handful of liquefaction plants exist in Europe and Asia with a liquefaction capacity of 10.5 tons/day at the highest [4]. Hydrogen liquefaction plants with a capacity of up to 36 tons/day exist in the USA only [5]. Hydrogen liquefaction plants with higher capacity exist so far only on paper.

As a part of the EU-funded IDEALHY project a large scale liquefaction plant will be developed with a goal of reducing the required energy demand for liquefaction significantly compared to state of the art plants. Here the new process will make use of economy of scale as a capacity of 50 to 100 tons/day represents a scale-up of approximately 20 times to the most plants, which are in operation world wide. In addition, state-of the-art components and technologies will be applied.

However, before developing a new process the theoretical energy demand for the liquefaction process is investigated. For conduction this in a transparent approach, the liquefaction process is divided into several stages, such as: Hydrogen compression, pre-cooling, cryo-cooling and liquefaction. Each stage is individually discussed in a generic manner for illustrating the theoretical energy requirements and challenges.

Emphasis in this paper is placed on the pre-cooling stage of the liquefaction, which cools the hydrogen from ambient temperature to approximately 80 K. This stage represents a lot of variation possibilities as a number of different solutions may be applied. Furthermore, experience is drawn from large scale natural gas liquefaction plants which are commercially in operation all over the world and present a mature technology.

2. EVALUATION CONCEPT

The concept of dividing the liquefaction of hydrogen into several stages has been presented in earlier publications [6]. These stages are:

- Precompression (at ambient conditions)
- Precooling (ambient to about 80 K)
- Cryo-cooling (80 K to 30 K)
- Liquefaction (30 K to LH_2 at 1 atm)

Figure 1 shows where these stages are located in a generic process flow diagram (PFD) for a hydrogen liquefaction plant.

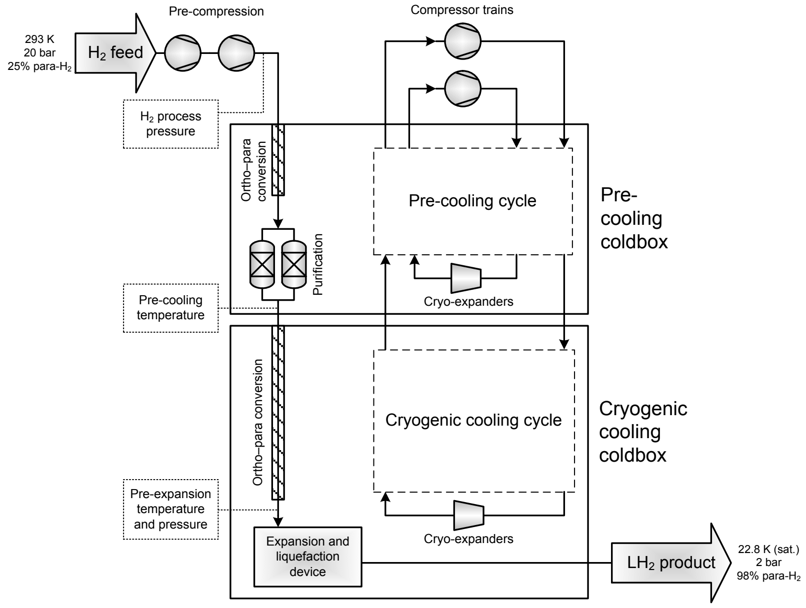

Figure 1: Generic PFD of hydrogen liquefaction

To be able to evaluate the different liquefaction stages separately, one has to assume that they are not influenced by each other. This is definitely not true for the precompression, as it heavily influences the cooling curve for hydrogen in the cryo-cooling and liquefaction stages. Figure 2 shows the distribution of the exergy requirement for each of the four liquefaction stages depending on the precompression outlet pressure. The total exergy requirement is 2.93 kWh/kg liquid product. It is assumed a feed pressure of 20 bar, which is typical from pressure swing absorption. If the inlet feed had atmospheric pressure, this would require 35 % higher exergy input due to increased compressor work.

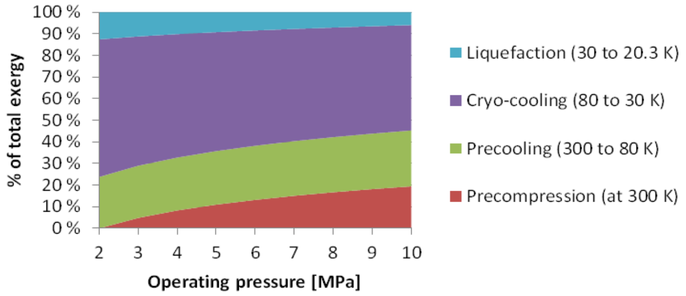

Figure 2: Distribution of exergy requirement for each liquefaction stage

The precooling is almost independent of the precompression outlet pressure. However, the influence of the choice of processes for the cryo-cooling and liquefaction stages on the precooling cycle must be investigated. One could however argue that refrigerants used in the low temperature stages (typically hydrogen or helium) are operating close to ideal gas in the precooling temperature range, which means that the enthalpy is a function of temperature only. The cooling curve for the refrigerant will therefore be independent of the pressure and the precooling duty of the refrigerant will therefore be cancelled out by the return flow.

Based on this, the precooling processes studied in this paper will be studied independent from the other liquefaction stages.

3. DISCUSSION OF THE PROCESS STAGES

3.1. Precompression

As discussed above, the precompression has a big influence on the low temperature part of the liquefaction process Figure 5. By compressing the feed to a higher pressure, part of the cooling demand can be supplied at a higher temperature, which reduces the necessary refrigeration work. The cost for this is then a higher compression work at ambient temperature.

Since one in general is able to compress at a higher efficiency than cooling the gas, one should compress to as high pressure as possible. However, for this to be true, the pressure reduction equipment in the liquefaction stage (see Section 3.4) has to be efficient (using an expander instead of a throttling valve). Yet the maximum pressure is normally limited by the heat exchangers.

The compression of hydrogen (with a molecular weight of 2 kg/kMol) is traditionally performed with piston or screw compressors. When moving towards larger scale liquefaction plants, turbo machinery might become more attractive, due to potentially higher efficiency and availability. Turbo compressors are however limited in pressure ratio per stage (due to the low molecular weight). With state of the art materials, the maximum pressure ratio for hydrogen is about 1.2 for Hydrogen [7]. This means that compression from atmospheric to 80 bar would require at least 24 stages. However, if the feed pressure is 20 bar (typical for pressure swing absorption purification) compression to 80 bar would require only 8 stages.

3.2. Precooling

All existing large scale hydrogen liquefiers utilise liquid nitrogen from an associated nitrogen/air liquefaction plant. For future very large scale plants this would not be the most likely option, since using pure liquid nitrogen for cooling down to 80 K is also fundamentally inefficient, due to the large temperature differences at low temperatures. The minimum exergy needed for production of liquid nitrogen is twice that needed for cooling of the hydrogen feed to 80 K. If one assumes an exergy efficiency of about 50 % for the liquid nitrogen process, the total exergy efficiency is 25 %.

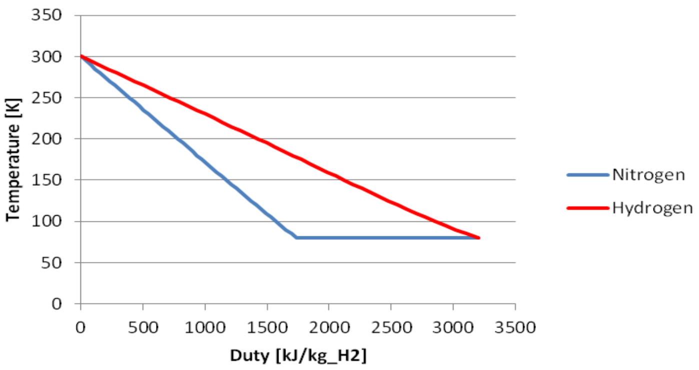

Figure 3: Temperature profile for precooling with liquid nitrogen

In the following section different solutions for precooling will be discussed.

Closed nitrogen loop

The most straight forward solution would be to integrate the nitrogen liquefaction cycle as a closed refrigeration loop, into the hydrogen liquefaction cycle. Compared to the utilization of liquefied nitrogen from a standalone plant, this gives the possibility of improved integration and temperature matches in the heat exchangers. This is done by shifting most of the liquid nitrogen production to cold gaseous nitrogen. In this way, the flat line in Figure 3 is shortened and the two lines will be more parallel, meaning better temperature adaptation and reduced losses. To further improve the efficiency, the liquid and gaseous nitrogen can be produced at multiple temperature levels.

Helium/Hydrogen Brayton

Since reversed Brayton or Claude cycles are necessary for the cryo-cooling stages, it might seem reasonable to add high temperature expansion stages to provide cooling in the precooling temperature range. However, as discussed in the precompression stage, compression of helium and hydrogen is generally much more complicated and power consuming than higher molecular weight gases.

As for compression, expansion is limited in pressure ratio. This is often stated in maximum enthalpy drop per stage, depending on maximum tip speed. This results in a vast number of compressor and expansion stages being necessary in the precooling refrigeration stages. This is exemplified by Valenti [8], utilizing 15 compressor stages and 7 expansion stages for cooling from ambient conditions to 90 K.

Mixed refrigerant systems

Mixed refrigerant (MR) concepts are common within the liquefied natural gas (LNG). Mixing refrigerants enables gliding temperatures during condensation and evaporation of the refrigerant (in contrast to the constant temperature phase change of single component refrigerants). By optimizing the refrigerant mixtures, one can adopt the evaporation curve to the cooling process to minimize the temperature differences and thereby the exergy losses. During the last decades several more or less complex and high efficiency processes have been developed to minimize the power consumption in LNG production.

The simplest MR process is the single stage process often referred to as the PRICO process [9].This process is commonly used for small scale LNG plants. However, due to the long temperature span of the hydrogen precooling (300 K to about 80 K) it will not be suitable, both because it is difficult to find a mixture with such long gliding evaporation temperature and because one would risk freeze-out of the least volatile fluids.

Berstad et al. [10] proposed a MR precooling cycle utilizing the Kleemenko auto-cascade principle. This concept enables removal of the heaviest components at a higher temperature level, and thereby automatically adjusting the mixed refrigerant to the temperature level and reducing the risk of freeze-out. Some of the challenges with such a process relates to optimizing and controlling the mixed refrigerant composition throughout the process.

A different approach would be to combine the MR concept with the cascade concept. Examples of this exist in the LNG industry [11, 12].

A possible layout of a mixed refrigerant cascade process for hydrogen precooling is shown in Figure 4. The upper MR cycle operates at normal natural gas liquefaction temperatures (300 K – 120 K), and the second cools the hydrogen down to about 80 K.

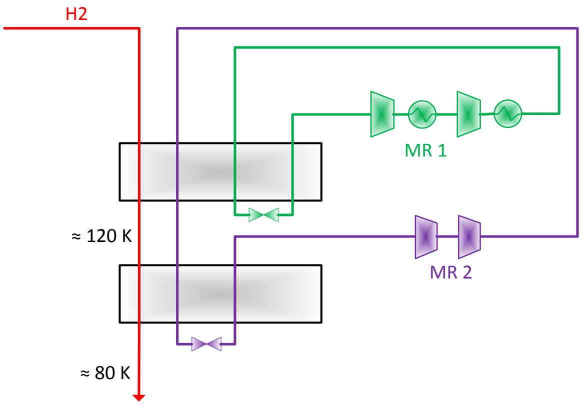

Figure 4: Layout of mixed refrigerant cascade system

Compared to a closed nitrogen system, a MR system usually needs larger heat exchanger surfaces, since the high internal heat exchange results in a lower relative refrigeration capacity (kW refrigeration power per kW transferred in the heat exchanger). This could partially or fully be compensated by the higher heat transfer coefficient of boiling or condensing fluids.

An important aspect is that compared to gas based cooling systems (nitrogen, hydrogen or helium), the number of compressor and expansion stages are drastically reduced. In Figure 4, throttling valves are utilized instead of expanders. This is partially because expanders for two-phase hydrocarbon mixtures are not commonly applied, but also because increase in efficiency by applying expanders is minor compared to Brayton or Claude cycles. This simplifies the system, since one does not need to handle power recovery through generators or coupling with compressors. Some savings are however possible, and Berstad et al. [10] showed a potential for 15 % reduction in MR compression work when replacing the JT-valves with expanders (without power recovery).

3.3. Cryo-cooling

For the cryo-cooling the possible processes are much more limited. The most common solution in state-of-the-art liquefaction plants are Hydrogen-Claude cycles [13]. Another possibility would be to use purely reversed Brayton cycles with Helium (possibly also with Hydrogen, but one is limited in minimum temperature).

As mentioned above, the main issue with using these light gasses for refrigeration is the compression. Quack [6] suggested to deal with this by adding neon to the refrigerant to increase the molecular weight. This reduces the compression problem, but on the other hand, it limits the minimum cooling temperature due to the triple point of neon at 24.6 K. The prediction of the behaviour of such mixtures is also difficult due to limited research within this field.

Another issue with utilizing neon, and possibly also helium, is that it is a very expensive gas, which requires a hermetic system to minimize leakage losses. This is possible with helium-neon systems, but difficult with Hydrogen, since the magnetic bearings are heavily subject to Hydrogen embrittlement.

The main challenge for the cryo-cooling cycle is to deal with the highly variable heat capacity of hydrogen around the critical point (Figure 5), which makes the temperature fit in the heat exchangers challenging. This is partially helped by increasing the pressure of the hydrogen feed (increasing the pre-compression), as this "flattens" the cooling demand at each temperature level. The variable cooling demand needs to be handled by adjusting the refrigeration power, e.g. by utilizing overlapping expander stages [14]. Another concept that was proposed by Valenti [8] is to fully separate the helium Brayton stages and do internal recuperation.

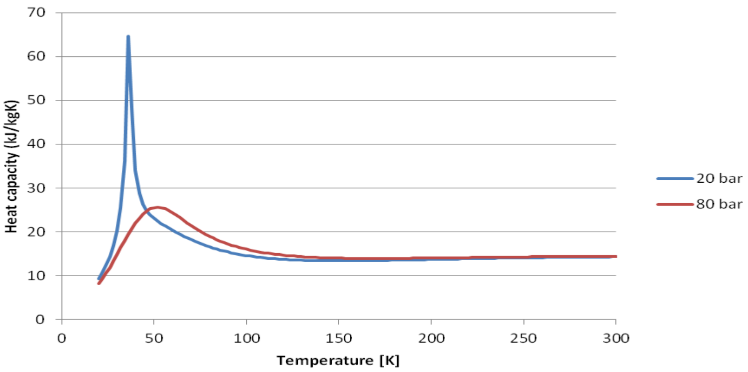

Figure 5: Heat capacity of equilibrium hydrogen at 20 and 80 bar.

3.4. Liquefaction

The main process decision for the liquefaction stage is if the process should be a "once-through" concept or with flash gas recycling. The most common industrial solution is to throttle the hydrogen into the two-phase region and then adding a liquefaction stage at storage pressure [5, 13]. Recent proposals for large scale liquefaction plants suggest to subcool the hydrogen to temperatures that assure only liquid at the outlet of the expansion [8, 14].

Figure 6 shows the vapour fraction after expansion depending on inlet temperature and pressure and expansion equipment (an isentropic efficiency of 0.9 is used for the expander). This shows the importance of utilizing expansion machines instead of isenthalpic throttling, especially when increasing the pre-compression pressure.

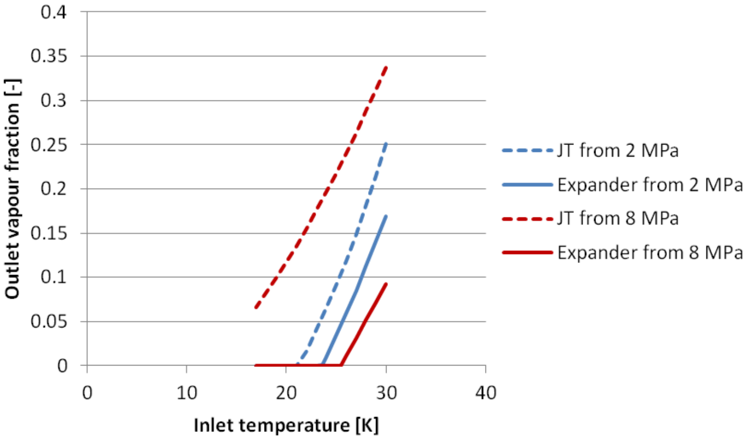

Figure 6: Vapour fraction from expansion of the hydrogen feed.

Another parameter to consider when choosing the liquefaction stage concept is the para-content. Often a very high para content (>98 %) is required in the product. This constrains the highest allowable cooling temperature. The equilibrium temperature for 98 % is about 28 K [15]. However one is probably not able to achieve fully equilibrium composition with continuous conversion, so with a 2K conversion delay one has to cool the hydrogen to at least 26 K.

4. CONCLUSIONS

This paper elaborates a method for designing an efficient large scale hydrogen liquefaction plant. The principal is to divide the process into 4 more or less independent stages, and find the optimum solution for each stage.

The main focus is put on the precooling stage. Not because it is the most power consuming stage, but because it is the stage with the most degrees of freedom in design. The standard concept of liquid nitrogen cooling is highly inefficient, and other concepts are needed for large scale applications. The two most promising concepts are integration of a nitrogen Claude cycle and a mixed refrigerants concept. Both systems have advantages and disadvantages that have to be further elaborated.

One of the main challenges in efficient hydrogen liquefaction is light gas compression. This is unavoidable, since only light gases can provide cooling at the required temperature levels, but should be minimized by using heavier fluids where it is possible.

Due to the higher exergy efficiency of compression compared to refrigeration, the pressure of the hydrogen feed should be as high as possible, as long as the pressure reduction in the liquefaction stage is performed by expansion machines instead of throttling valves. A higher pressure also beneficial for the cryo-cooling stages, since it reduces the peak in heat capacity above the critical point and makes it easier to achieve a good temperature fit in the heat exchangers.

5. ACKNOWLEDGEMENT

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6. REFERENCES

1. GermanHy, *Studie zur Frage "Woher kommt der Wasserstoff in Deutschland bis 2050?* 2009, Im Auftrag des Bundesministerium für Verkehr, Bau und Stadtentwicklung.
2. *Hydrogen Fuel Cell Engines and Related Technologies Course Manual, Module 1: Hydrogen Properties*. 2001, College of the Desert.
3. Kramer, G.J., J.P.P. Huijsmanns, and D.M. Austen, *Clean and green hydrogen*, in *16th World hydrogen energy conference*. 2006: Lyon.
4. Verfondern, K., *Safety Considerations on Liquid Hydrogen*. Vol. 10. 2008: Jülich Forschungszentrum. 167.
5. Drnevich, R., *Hydrogen Delivery - Liquefaction & Compression*, in *Praxair, Strategic Initiatives for Hydrogen Delivery Workshop*. 2003.
6. Quack, H. *Conceptual design of a high efficiency large capacity hydrogen liquefier*. in *ADVANCES IN CRYOGENIC ENGINEERING: Proceedings of the Cryogenic Engineering Conference - CEC*. 2002. Madison, Wisconsin (USA): AIP.
7. Di Bella, F., P.E. Osborne, and C. Osborne. *Development of a Centrifugal Hydrogen Pipeline Gas Compresso*. in *Hydrogen Production and Delivery*. 2011: DOE Hydrogen Program.
8. Valenti, G.G., *Proposal of an innovative, high-efficiency, large-scale hydrogen liquefier.* International Journal of Hydrogen Energy, 2008. **33**(12): p. 3116-3121.
9. Maher, J.B. and J.W. Sudduth, *Method and apparatus for liquefying gases U.S. Patent 3,914,949.* 1975.
10. Berstad, D.O., J.H. Stang, and P. Nekså, *Large-scale hydrogen liquefier utilising mixed-refrigerant pre-cooling.* International Journal of Hydrogen Energy, 2010. **35**(10): p. 4512-4523.
11. Nibbelke, R., S. Kauffman, and B. Pek, *Double mixed refrigerant LNG process provides viable alternative for tropical conditions.* Oil&Gas Journal, 07/08/2002.
12. Linde AG, *LNG Technology*, in *Brochure from LINDE available from: http://www.linde-engineering.co.id/en/images/LNG_1_1_e_10_150dpi34-4577.pdf*. 2010.
13. Bracha, M. and L. Decker, *Grosstechnische Wasserstoffverflüssigung in Leuna*, in *Deutsche Kälte-Klima-Tagung*. 2008.

14. Shimko, M., *III.7 Innovative Hydrogen Liquefaction Cycle*, in *FY 2008 Annual Progress Report, DOE Hydrogen Program*. 2008, DOE.

15. McCarty, R.D., J. Hord, and H.M. Roder, *Selected properties of hydrogen (Engineering Design Data)*. 1981.