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Search for the Best Processes to Liquefy Hydrogen in Very Large Plants

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ABSTRACT

The goal of the IDEALHY project is to identify processes and components, which allow liquefying hydrogen with a power consumption much lower than with plants built so far. This requires comparing different possible processes concerning power efficiency, investment cost and compactness. The power consumption of a process depends on a number of boundary conditions. Without a clear overall definition of these boundary conditions, all statements and comparisons on the overall power consumption are questionable. So in the first step of the project the participants agreed on common boundary conditions.

Then it turned out, that the choice of the high pressure of the feed hydrogen influences strongly the rest of the liquefaction process, especially the region below 80 K. For this region there is an option between helium, hydrogen and neon as refrigerants and their mixtures. For the final choice of the working fluid and the process one has to identify the maximum possible circumferential speed of turbo compressors.

1. INTRODUCTION

The goal of the IDEALHY project is to identify the best processes for the liquefaction of hydrogen in very large plants, e.g. 50 t/d and larger. The first task was to check in literature for processes, which have been proposed in the past. A comparison of the collected cycles turned out to be difficult, because each author had selected different boundary conditions and component efficiencies. So the second task was to agree on a list of boundary conditions and component efficiencies, with which the most promising cycles were recalculated. Now a comparison was possible. Such a comparison leads to guidelines how to find an optimum processes.

2. CHOSEN BOUNDARY CONDITIONS

Table 1. Chosen boundary conditions.

Feed	Pressure	20 bar
	Temperature	293 K
	para-content	25 %
	Purity	pure hydrogen
Product	Pressure	2 bar
	Temperature	22.8 K (saturated)
	para-content	98 %
	Purity	pure hydrogen
Cooling water	Temperature	293 K
	Temperature rise	10 K
Heat leak	Process	none
	Storage	none
LN2 precooling	A closed cycle nitrogen plant has to be calculated	

We are aware that the choices of a certain feed pressure of a certain product pressure have a quite a large influence on the power consumption. So after the comparison of the cycles with a set of preliminary values the influence of other pressures has to be evaluated.

It is expected, that the feed hydrogen will contain some impurities in the 100 ppm by volume range. These impurities will be removed by adsorption at the 80 K temperature level. We have estimated, that the refrigeration needed for the hydrogen loss and for the re-cooling of the adsorbers after the regeneration process is negligible compared to the overall power needs of the liquefaction.

3. PRELIMINARY ASSUMPTIONS FOR EFFICIENCIES OF COMPONENTS

Table 2. Selected efficiencies of components

Heat exchange	Cooling water pinch point temperature difference	5 K
	i.e. outlet temperature from inter- and after-coolers of compressors	298 K
	Condensing temperature of refrigerants like propane	303 K
	Sub-cooling of condensate to	298 K
	Whole cryogenic train	NTU < 120
	Pinch point at warm end	3 K
	Pinch point at 80 K level	1 K
	Pinch point at cold end	0.3 K
Pressure drop	Inter- and after-cooler	0.2 bar
Cryogenic part	above 20 bar	2 %
	medium pressure (4 bar)	5 %
	low pressure	20 %
	Linear interpolation between the pressure levels	
Compressor, isentropic efficiency	Piston and turbo-compressor	85 % per stage
	Turbine brake compressor	80 %
	Cold compressor	70 %
Expander, isentropic efficiency	Expansion turbines below 120 kJ/kg enthalpy drop	90 %
	Wet expander	85 %
Ortho-para conversion	Temperature delay	2 K

These choices of boundary conditions and component efficiencies allow to re-calculate cycles on the same basis and to compare them.

4. PROCEDURE FOR THE SEARCH OF THE BEST PROCESSES [1]

The best process from a thermodynamic - i.e. a power consumption – point of view would be a reversible process. On paper there exist many reversible processes. One of them is sketched in Figure 1a. The background is a temperature-entropy diagram. At the top there is the ambient temperature and at the bottom the vapour dome is indicated with the saturated liquid on the left corner. The feed hydrogen is compressed at ambient temperature in many stages with inter-cooling in an ideal isothermal compression. This results in reduction of the entropy to a value, which corresponds to the entropy of the saturated liquid. Then the compressed gas undergoes an isentropic expansion with work recovery until the saturated liquid state is reached.

This simple process can not be realized, because there are no compressors and expanders for the required high pressure and it is difficult to include an ortho-para conversion in the isentropic expansion.

But it should be noted, that the process shown in Figure 1a does not contain any cryogenic heat transfer. So there is no potential for thermodynamic losses due to heat transfer. One search procedure could be to modify this process in the direction to implement realistic hardware while trying to minimize the amount of cryogenic heat transfer.

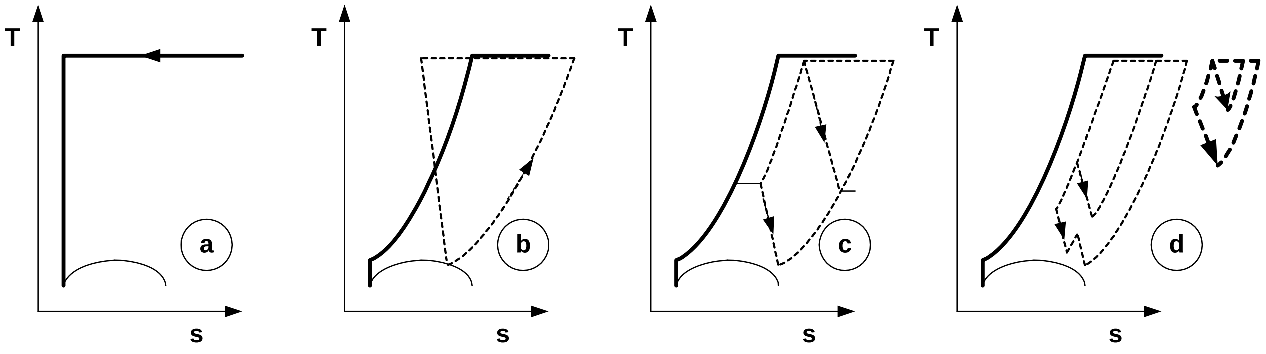

Figure 1. Steps from the ideal to a real process to liquefy hydrogen

In the next step, which is sketched in Figure 1b, the feed hydrogen is compressed only to the maximum pressure, which is compatible with currently existing compressors, heat exchangers and wet expanders, e.g. 80 bar. Then the hydrogen is cooled in a heat exchanger, in which the catalyst for the ortho-para conversion is integrated. At very low temperature the hydrogen is expanded in a “wet expander” with saturated liquid at the outlet.

The needed refrigeration for the cooling is provided by a closed cycle refrigerator, which is shown with dotted lines in Figure 1b. The cycle of this refrigerator includes an isothermal compression at ambient temperature, a work extracting expansion, which is as isentropic as technically possible, and a warm-up of the refrigerant in heat exchange with the hydrogen.

Again the maximum pressure, which can be handled in such refrigeration cycles is limited by today’s technology. Therefore one has to stage several such cycles “above each other” as shown in Figure 1c. This arrangement is called a cascade. The cascade has the intended effect that the maximum pressure is reduced, but it also has the detrimental effect, that additional heat transfer is needed.

There is one additional effect, which complicates the refrigeration cycle: The needed cooling of the hydrogen is not constant over the temperature range. Figure 2 shows the specific heat of equilibrium hydrogen at 20 and 80 bar as a function of temperature with a 2 K deviation from the thermodynamic equilibrium as well as the para content.

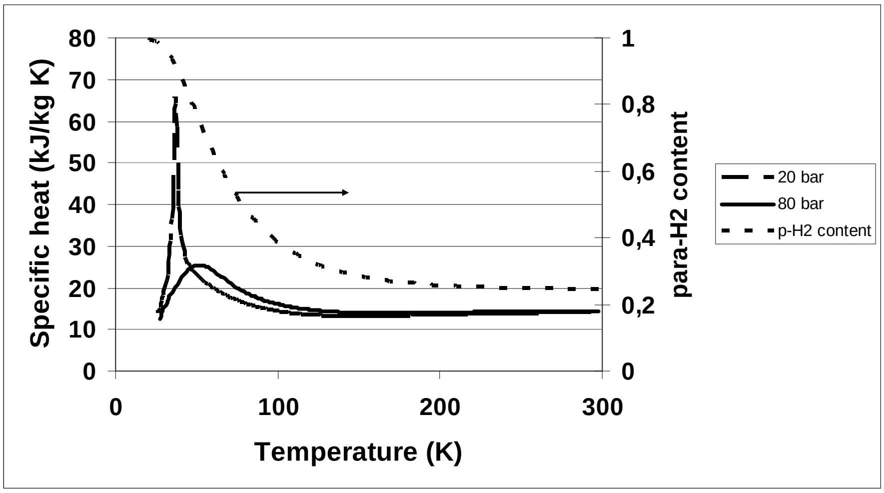

Figure 2. Specific heat of e-H2 at 20 and 80 bar and para content as function of the temperature

The specific heat of hydrogen at ambient temperature corresponds to the value for a two-atomic ideal gas. With falling temperature, the specific heat is first declining, because the rotational degrees of freedom have reached there lowest possible state. Hydrogen behaves then more and more like a one-atomic molecule. But below about 120 K the specific heat rises again due to two influences, the starting ortho-para conversion and the real-gas effects. The values of the specific heat rises to a maximum value, which is more pronounced at 20 bar than at 80 bar. Then the specific heat drops to the value of the liquid hydrogen.

A preferable refrigeration process must be designed such that the refrigeration power is produced just at, or only a little below the temperature where it is needed for cooling.
One example for a refrigeration process, which produces peak cooling in the 40 to 70 K region, is shown in Figure 1d. In this temperature range the expanders are partially overlapping in temperature.

5. CHOICE OF PRESSURES FOR BRAYTON REFRIGERATION CYCLES

The Brayton cycle consists of a compression at ambient temperature, a counter-current heat exchanger and one or more work extracting expanders. In principle one is free to choose the working fluid and the high and the low pressure. But there are a number of limitations, which have to be taken into account:

- Concerning the working fluid there is the choice between N_2, Ne, H_2, He or mixtures of these gases; but with N_2 and Ne one has to make sure that no liquid is generated at the outlet of the expander [2].
- From the heat transfer aspect, i.e. best heat transfer coefficients at a minimum pressure drop, one would prefer H_2 and He over Ne and N_2.
- Concerning turbo compressor, i.e. highest pressure ratio for a given circumferential speed of the impeller, one would prefer N_2 and Ne over He and H_2.
- Some materials of bearings and motors may not be compatible with hydrogen due to hydrogen embrittlement.
- To reduce heat transfer losses, one would prefer high pressure ratios with the smallest mass flow rates.
- To obtain the optimum working conditions for turbo compressors one would prefer low pressure ratios.
- The higher the low pressure of the cycle, the more compact are the heat exchangers.
- The higher the high pressure of the cycle, the closer one gets to the maximum allowed pressure of the heat exchangers.

From this list it is obvious, that it will not be possible to come up with one single “best” process. The choice of working fluid and operating pressures is always a compromise between conflicting requirements.

6. EXAMPLE OF A NEW PROCESS: IDEALHY TUD 5

For the cycle described in the following a number of choices have been made:

- Compression of the hydrogen feed in a two-stage piston compressor to 80 bar
- Continuous ortho-para conversion in the heat exchangers below 150 K
- Wet expander replacing the JT-valve
- The flash gas from the wet expander outlet is warmed up to ambient temperature and used for the regeneration of the upstream hydrogen purification
- Below 90 K a modified Brayton process with four expanders, which operate partially in series and partially in parallel. The working fluid can be either H_2 or He or a mixture of one of theses two gases with neon with a maximum neon content of 30 %
- Some temperature overlap in expansions in the temperature region between 70 and 40 K to cover the specific heat peak of the hydrogen
- Above 90 K a modified Brayton process with nitrogen as working fluid and again four expanders, which operate partially in series and partially in parallel.
- There are two cryogenic cold boxes: The upper one is perlite insulated, whereas in the lower one vacuum is used for insulation.
- A small part of the coldest nitrogen is used for the precooling of two helium heat exchangers, which are also located in the perlite box.
- The main power input occurs in the main nitrogen and helium turbo compressors. Both have the feature that a part of the return stream enters at elevated pressure. This has the effect, that the volumetric flow rate of the lower stages of the compressors are decreased, whereas the flows in the higher stages are increased compared to a system, where the full flow is compressed over the full pressure ratio.
- All eight expanders are directly coupled with one stage “brake” compressors, which take over part of the compression at ambient temperature.

- Expanders are partially arranged in parallel, whereas all brake compressors are arranged in series. This has the effect that the enthalpy increase in the compressors is only about half the enthalpy drop in the expanders. It is assumed that this arrangement gives the best operating conditions for both, expanders and compressors.

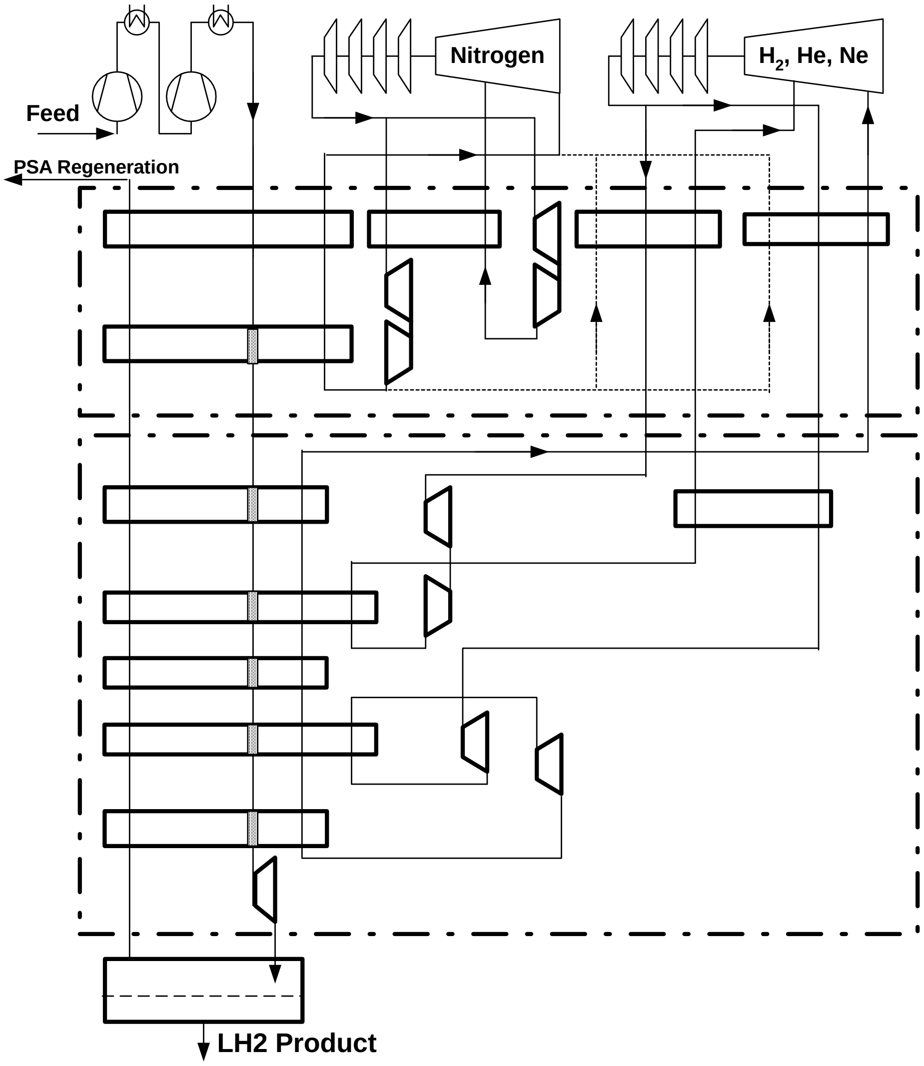

Figure 3. Flow diagram of the process IDEALHY TUD 5

It is not yet clear, whether the refrigerant in the low temperature cooling loop will be pure helium or a mixture of helium and neon. This depends on the available technology for the main turbo compressor. Pure helium requires very high circumferential speeds of the compressor blades. The addition of the neon would make this task easier. On the other hand pure helium would provide better heat transfer characteristics than a helium-neon mixture, i.e. lower pressure drop and better heat transfer coefficient.

The power consumption for the liquefaction depends on one hand on the boundary conditions (like the pressure and purity of the feed and the desired pressure of the product) and on the other hand on the efficiency of heat exchangers, expanders and compressors. This evaluation needs a number of iteration loops together with manufacturers of such equipment. This is presently under way.

Of course the process shown in Figure 3 is not unique. It could be of advantage to replace the nitrogen cycle – totally or partially – by a mixed-refrigerant throttle cycle [3].

7. CONCLUSIONS

When trying to find the optimum process for the liquefaction of hydrogen in large plants one recognizes, that the thermodynamic optimum leads to requirements, which surpass the present capabilities of state of the art machinery and heat exchangers. Thermodynamic aspects would e.g. lead to processes with a high pressure ratio. On the other hand, to obtain high pressure ratios for the light gases such as H2 and He the turbo compressors have to be operated at very high circumferential speed, limited by the strength of the used material.

Pushing machinery to its limits incorporates higher operational risks. So the process development procedure is to go to the limit on paper, and for the realization then go one step backwards towards higher operational reliability. It is clear that this approach requires an iterative procedure, which is still under way.

8. REFERENCES

[1] Berstad D. et al., *Design Principles for High Efficiency Liquefaction Processes*, World Hydrogen Energy Conference 2012, Toronto, June 2012

[2] Quack H.: *Die Schluesselrolle der Kryotechnik in der Wasserstoff-Energiewirtschaft*, Wiss. Zeitschrift der TU Dresden, 50 (2001) Heft 5/6 S. 112 – 117

[3] Walnum H. T. et al., *Mixed Refrigerants for High Efficiency Pre-cooling,* World Hydrogen Energy Conference 2012, Toronto, June 2012