On the design of an efficient hydrogen liquefaction process

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ABSTRACT:
A first model for a hydrogen liquefaction prototype laboratory unit has been developed. The process is based on using a mixed component refrigerant (MCR) process for pre-cooling. The process also includes an implementation of ortho para conversion. By simulations it has been shown that this process have potential to improve the exergy efficiency for the liquefaction process and thereby also the energy requirements for hydrogen liquefaction. One of the key points in the design work has been to find a refrigerant that is sufficiently wide-boiling and at the same time not freezing at the low temperature end. The goal has been to reach sub-cooling to below 75 K without freezing out any component of the MCR.

KEYWORDS: Hydrogen liquefaction, Multi component refrigerant

Introduction

Hydrogen is regarded as a promising candidate to replace petroleum products in tomorrow’s transportation infrastructure. However, the low density of the hydrogen gas results in large vehicle storage tanks for compressed hydrogen (CH2) gas, if common storage tank pressures are assumed. In this picture, liquefying hydrogen offers several advantages. The density of LH2 of only 0.07 kg/liter does not seem to be particularly high, but because of the high energy density, the result is rather good compared to other solutions for hydrogen storage. If the hydrogen society should be more than a political vision it is necessary to develop more efficient technology for transport and storage of hydrogen.

The major obstacle towards a solution with liquefied hydrogen (LH2), however, is that hydrogen at ambient pressures remains in the gas phase until cooled down to approximately -253 °C. Cooling to such temperatures is an energy intensive process, associated with energy losses. Large liquefaction plants can reduce the losses to a minimum, but for smaller production facilities, reducing the equipment costs becomes more important than minimizing the energy losses. The proposed process has potential to both increase the efficiency and decrease the number of components in the process.

In a scenario with centralized hydrogen production with carbon capture and sequestration from natural gas liquefied hydrogen may be a good alternative for transport from production to end use. With liquid hydrogen available near the end user it will be possible to use the hydrogen in liquid state with very small expenses. Liquid hydrogen could also be an advantage in connection with storage in porous media.

In this chain the liquefaction process will also benefit from the high pressure outlet from the reformer which will decrease the energy consumption for liquefaction. This advantage is omitted in many well to wheel analysis.

This paper describes a liquefaction process that has potential for a considerable reduction in the energy consumption for liquefaction of hydrogen.

Ortho para conversion

Hydrogen exists under two different forms: the ortho state (both nuclear spins are in the opposite direction) and para state (spins in same direction) as shown in Figure 1.
These two states have different energy levels (higher energy for the ortho form) so that the content of each species at equilibrium is temperature dependent. "Normal" hydrogen, which corresponds to the equilibrium mixture at room temperature, is 25% para and 75% ortho hydrogen. At 21 K normal boiling point of hydrogen the para content is almost 100%.

The spontaneous conversion is a very slow reaction in liquid phase, inexistent in the gaseous phase. However, in 24 h, 18% of the liquid will evaporate if the liquefied hydrogen is normal hydrogen. Thus it is important to convert this hydrogen into pure para to avoid boil off losses during the storage time. A rapid cooling and liquefaction of normal hydrogen will still consist of approximately the same amount of ortho-hydrogen as before the operation started, due to the slow ortho/para conversion. Catalysts and magnetic fields can increase the conversion rate considerably. Example of catalysts are hydroxides of Fe(III), Co(III), Ni(II), Cr(III), Mn(IV) or active charcoal /1/. However, due to price, performance and other criteria either iron-oxide or nickel-silica catalysts are used in most liquefaction systems /2/.

Practically, there are three main types of converters:

1. Adiabatic converter: Reactor with a simple bed of catalyst. As no heat is exchanged, the stream temperature will increase. Low cost for each bed but many beds required.
2. Isothermal converter: Reactor with bed of catalyst in a boiling refrigerant (usually liquid nitrogen or hydrogen) that keeps the temperature constant. This is more efficient but the capital cost is higher.
3. Heat exchanger/converter: Heat exchanger fitted with catalyst (inside tubes). Both sensible and conversion heat are removed. Capital cost are higher but this solution minimizes the power cost for removing the heat of conversion. It is difficult to change of the catalyst in this solution so it has to be reactivated in place.

The ideal solution is a continuous conversion. Indeed, at every temperature, the hydrogen mixture is at equilibrium and the conversion release as little heat as possible. Of course continuous conversion is very difficult to realize, but can be approximated. The first solution would be to use heat exchangers with an
integrated catalyst and the second one to use many converters. Apparently a choice must be done, between efficiency and investment cost.

**General liquefaction processes**

There are several ways of producing liquefied hydrogen (LH2). Table 1 seeks to categorize the most common and the most promising cryogenic processes for hydrogen liquefaction.

<table>
<thead>
<tr>
<th>Thermodynamic gas cycles</th>
<th>Magnetic systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recuperative</td>
<td>Regenerative</td>
</tr>
<tr>
<td>Brayton Cycle</td>
<td>Stirling</td>
</tr>
<tr>
<td>Claude Cycle</td>
<td>Gifford-McMahon</td>
</tr>
<tr>
<td>Collins Cycle</td>
<td>Vuilleumier</td>
</tr>
<tr>
<td></td>
<td>Pulse Tube</td>
</tr>
<tr>
<td>AMR</td>
<td>Magnetic wheel</td>
</tr>
</tbody>
</table>

Table 1 Common liquefaction processes /3/

The most common processes are based on thermodynamic gas cycles with compression, heat exchange, and gas expansion as major characteristics. These processes will be referred to as gas compression cycles. Gas compression cycles seem to be the most realistic processes for producing LH2 in considerable quanta in the near future.

It is common to classify the cryogenic systems according to what sort of heat exchangers that are used. Normally, the systems are built on the basis of either recuperative or regenerative heat exchange. The large industrial hydrogen liquefiers are usually of recuperative type, whilst smaller low-temperature refrigerators tend to be of regenerative types.

WE-NET /4/ has made a study of different the liquefaction processes and compared them to the Hydrogen Claude Cycle (using hydrogen in the recycling line) and the Helium Brayton Cycle. Neither hydrogen nor helium was found to be suited for compression because of their low molecular weight. In particular, considerably more compression stages would be required in the case of a centrifugal compressor. Because of this, an examination of several liquefaction processes that use gases of high molecular weight in the recycling line was performed.

<table>
<thead>
<tr>
<th>Process</th>
<th>Hydrogen Claude</th>
<th>Helium Brayton</th>
<th>Basic Neon Brayton</th>
<th>Neon with Cold Pump</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressor Total Power[MW]</td>
<td>74.95</td>
<td>85.20</td>
<td>82.97</td>
<td>79.10</td>
</tr>
<tr>
<td>Input power by Nitrogen[MW]</td>
<td>35.07</td>
<td>28.05</td>
<td>28.36</td>
<td>29.82</td>
</tr>
<tr>
<td>Recovered Generated Power[MW]</td>
<td>3.40</td>
<td>4.63</td>
<td>3.93</td>
<td>3.70</td>
</tr>
<tr>
<td>Total Power[MW]</td>
<td>106.6</td>
<td>108.6</td>
<td>107.2</td>
<td>105.2</td>
</tr>
<tr>
<td>Minimum Work[MW]</td>
<td>49.5</td>
<td>49.5</td>
<td>49.5</td>
<td>49.5</td>
</tr>
<tr>
<td>Process Efficiency[%]</td>
<td>46.4</td>
<td>45.6</td>
<td>46.2</td>
<td>47.1</td>
</tr>
</tbody>
</table>

Table 2 Process calculation results /4/

Prof. Dr. H. Quack at TU Dresden has proposed a hydrogen liquefier with very high efficiency /5/. Here, one important theoretical tool is the exergy analysis of the single process step as well as the overall cycle. This is needed for the choice of the optimum hydrogen feed pressure as well as for the handling of the ortho para conversion. Modern helium liquefiers are being built with up to 10 expansion turbines placed strategically in the cycle to obtain overall optimum efficiency. Here it is proposed to do the same for a hydrogen liquefier and to choose a helium-neon mixture as refrigerant, which allows the use of the best available compression system. The preliminary design of the plant showed that an exergy efficiency of the total plant of the order of 60 % was feasible. This gives an overall power requirement of 7 kWh/kg with a pressure of the feed at 0.1 MPa. These values for the power consumption have been recommended as benchmarks for future studies on large scale hydrogen liquefaction.

The process is arbitrarily divided in the following steps:

- Isothermal compression of the feed at ambient temperature
- Isobaric cooling from 300 to 80 K Pre-cooling
- Isobaric cooling from 80 to 30 K
- Isobaric cooling from 30 to 20.3 K and isothermal expansion.
In a process with multi component refrigerant it would be preferable to extend the pre cooling step further down.

**Multi component refrigerant MCR**

SINTEF Energy Research has suggested to use a multi-component refrigerant cycle for pre-cooling in the process. Multi-component refrigerants are used in plants for liquefaction of natural gas, and NTNU and SINTEF have worked with systems and processes of this type for many years.

The use of a multi-component refrigerant cycle for pre-cooling in a hydrogen liquefaction process could lead to improved efficiency and reduced capital costs. The most important factor in the success of the cycle is its high efficiency, and consequently low power consumption, without the complexity of the cascade cycle. Multi-component refrigerant process allow a better temperature adjustment between the pre-cooling circuit and the hydrogen circuit and the possibility to extend the pre-cooling process further down in temperature.

The Linde hydrogen liquefaction plant in Ingolstadt – Germany /6/ was selected as the most appropriate reference process for comparison with respect to the pre-cooling cycle. In view of the increasing demand for liquid hydrogen on the European market, the Industrial Gases Division of Linde AG invested in a pure hydrogen production facility with a capacity of 4.4 tons/day. It has been in operation since 1992. It is presently the largest hydrogen liquefaction facility in Germany. This process has a substantial lower efficiency than the process proposed by Prof Quack /5/

The flow sheet simulator PRO/II has been used to model and simulate the Ingolstadt process. The results have been compared with the results reported in the literature. It should be mentioned that some specific data for the selected processes were missing and therefore had to be estimated. The flow rate of the recycled hydrogen has been adjusted to give satisfactory minimum internal temperature approach (MITA) values for the heat exchangers.

Simulation of the Ingolstadt process with PRO II /7/ gives the following results:

<table>
<thead>
<tr>
<th></th>
<th>Temp[K]</th>
<th>P [Mpa]</th>
<th>Para cont. [%]</th>
<th>Energy [kWh/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingolstadt /6/</td>
<td>21</td>
<td>0.13</td>
<td>95</td>
<td>13.58</td>
</tr>
<tr>
<td>Ingolstadt PRO II</td>
<td>21.26</td>
<td>0.13</td>
<td>99.6</td>
<td>13.51</td>
</tr>
<tr>
<td>Ingolstadt MCR</td>
<td>21.26</td>
<td>0.13</td>
<td>99.6</td>
<td>11.54</td>
</tr>
</tbody>
</table>

**Table 3 Simulation of the Ingolstadt process**

The results show quite good correspondence between the reported data for Ingolstadt /6/ and the simulated values. It also demonstrates that using multi component refrigerant for the pre-cooling process has a potential to improve the pre-cooling process, and thereby also the total efficiency of the plant.
The proposed LH2 laboratory plant is shown in Figure 3.

The main purpose of building the laboratory plant is to gain experience with hydrogen and hydrogen liquefaction related issues. Further, it will be used to investigate some specific issues. One of them is the MCR pre-cooling process, where one of the goals is to come as low as possible in temperature of the pre-cooled hydrogen. The pre-cooling is defined as cooling down to a temperature around the normal boiling point of nitrogen by using the MCR circuit.

Some modifications have been made on the hydrogen part of the plant. The hydrogen pressure is not higher than 2.1 MPa, since a small size high pressure hydrogen compressor was too costly. This resulted in the need of a liquid helium circuit in the low temperature part of the plant. In this way, it is possible to reach a temperature at this pressure which without would only be possible if an expander was included. The helium circuit may also cover some of the heat losses that will have a relatively large influence in plant of this size.

In the laboratory plant the final cooling down to 22 K is done by Joule-Thomson throttling of the hydrogen flow. In a large scale plant this is supposed to be done with expanders. An expander for the size of the laboratory plant will not be economic feasible.

The ortho para conversion is done in two steps at 150 and 75K. Ideally a two stage conversion should take place at lower temperatures. With continuous conversion in the heat exchanger this will be the case for the pre-cooling. For the last step from 75K down to 20.3K with expander it would be preferable to a two-stage expansion with ortho-para conversion at 40 K.
Conclusion

The simulation results show that hydrogen liquefaction can be done more efficient and with lower investment cost compared with industrial plants in operation today. It has also potential to improve the operation and reduce the investment of a hypothetical best available technology plant.

One of the key points in the design work has been to find a refrigerant that is sufficiently wide-boiling and at the same time not freezing at the low temperature end of a pre cooling unit. We have found a mixture that theoretically can go down below 75 K without freezing in any component of the MCR circuit. Experimental verification will be performed in a laboratory hydrogen liquefaction unit.

The energy efficiency of a laboratory system may obviously not give similar energy efficiency as that of a large scale plant. However, the possibility to run the process and gain experience from the laboratory plant will give an excellent starting point for design, modeling and simulations of a larger scale industrial plant.

References


/2/ Neeraas, B. O., et al., Hydrogen liquefaction - process simulation studies, SINTEF Energy Research, technical report TR A5536, 2001


/7/ PRO/II v. 7.1, steady state process simulation program by Simsci, Inc., 1994-2005