Optimized para fraction of liquid hydrogen for efficient liquefaction and storage

Ho-Myung Chang[1]*, Seong Ho Bang[1], Hyung Jin Kim[2], Jong H. Baik[2] and James E. Fesmire[2]

[1] Hong Ik University, Seoul, 04066, KOREA
[2] GenH2 Corp, Titusville, FL 32780, USA

*E-mail: hmchang@hongik.ac.kr

Abstract. A thermodynamic study is performed to determine the optimal para fraction of liquid hydrogen for efficient liquefaction and storage. Ortho-to-para (OP) conversion is required in liquefaction process to avoid the boil-off loss during liquid storage. In case of short-term storage, however, the liquefaction without conversion could be advantageous, since the natural conversion is a slow process and a liquefier is capable of producing more liquid without catalytic OP conversion. A rigorous cycle analysis is carried out to predict the liquefaction capacity of a small-scale liquefier, where four different levels of para fraction can be obtained by the optional use of staged catalytic conversion. By incorporating a kinetic model for natural OP conversion in a storage tank, it is revealed that there exists an optimal para fraction for efficient liquefaction and storage, depending on the length of storage period. No catalytic conversion is recommended for the storage of 1 day or less, but the full conversion is needed for storage over 5 days.

1. Introduction

Ortho-to-para (OP) conversion is one of the important technical issues in hydrogen liquefaction and liquid storage [1,2]. The equilibrium fraction of para hydrogen is 25% (normal hydrogen) at ambient temperature, but increases continuously to 99.8% as temperature decreases to 20 K. To place the liquid in a storage tank, it is important to achieve the high para fraction in liquefaction process, because any residual ortho hydrogen will lead to boil-off loss of cryogenic liquid due to the conversion heat. In case of short-term storage, however, the high para fraction may not be necessary, since the natural OP conversion is a slow process [2,3]. In some emerging applications (such as the local station for trucks, boats, aircrafts, and heavy machines), the expected storage time between liquefaction and liquid consumption may be relatively short, particularly as the liquid is produced on-site rather than trucked in from a centralized plant [4].

Proper catalysts are employed in most hydrogen liquefiers [2,3] to speed up the conversion and deliver the liquid with a high para fraction. If the catalysts in a liquefier were bypassed, the para fraction (x_p) of exiting liquid would remain nearly at 25%, but the liquefaction capacity would considerably increase by the reduced load of OP conversion. Figure 1 schematically shows a typical liquid inventory in liquid-hydrogen supply system (including liquefier and liquid storage tank) to compare the cases of liquefaction with or without catalytic conversion. It is obvious that "equilibrium" liquid is desirable for a long period of storage, but "normal" liquid could be more advantageous for more liquid supply, if the storage period is short.

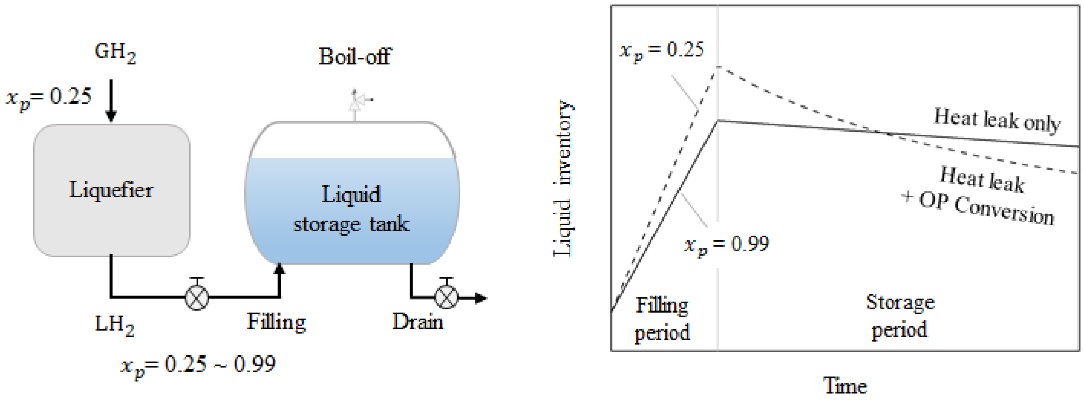

Figure 1. Schematic liquid-hydrogen system (liquefier and liquid storage tank) to illustrate the typical liquid inventory in cases of liquefaction with catalyst (x_p= 0.99) and without catalyst (x_p= 0.25).

This study is proposed to investigate quantitatively how the catalytic OP conversion in liquefier affects the liquefaction capacity and the boil-off loss due to natural conversion in storage tank. A special attention is paid to the existence of optimal para fraction of liquid to maximize the available liquid inventory, depending upon the length of storage time. Towards this goal, a rigorous thermodynamic analysis is performed on selected liquefaction cycles with staged-catalytic conversions and the kinetics of natural conversion in storage tank.

2. Modelling for liquefaction and liquid storage

2.1 Liquefier with optional catalytic OP conversion

For local and small-scale (0.5~1.5 T/day) liquefaction of hydrogen, the helium Brayton cycle has advantages over the standard Claude cycle in safety and easy operation [2,3]. Figure 2 shows two-stage expansion Brayton refrigeration cycle, where two helium turbo-expanders are arranged in series, and no pre-cooling by liquid nitrogen is required. It was reported that the pressure levels and flow rate of helium can be optimized for minimum power consumption [3], and the optimized cycle is plotted on temperature-entropy diagram with exergy expenditure.

The FOM (figure of merit) is a thermodynamic index of liquefaction performance, defined as the ratio of minimum work to actual work for liquefaction [1,3]. 16.5% in FOM is equivalent to 72.7 MJ/kg or 20.2 kWh/kg in specific energy consumption (SEC). The difference between actual and minimum work is the irreversibility or the entropy generation multiplied by the ambient temperature, which can be itemized as the exergy expenditure for each component. The details of optimized conditions for 15 g/s (~1.3 T/day) liquefaction without catalytic conversion are listed in Table 1 with reference to the previous report [3] and under practical design conditions.

Catalysts may be filled in the hydrogen channel of heat exchangers for continuous internal conversion [2]. Alternatively in this system, three external stages of catalyst are added to the hydrogen stream and a bypass valve is installed at each stage for optional use, as shown in Figure 3. The intermediate heat exchanger (HX2) in Figure 2 is divided for the first stage conversion, and a liquid container is added at the cold end for 20 K conversion. It is assumed for simplicity that no OP conversion occurs without catalyst, and the conversion is complete with catalyst or the para fraction reaches its equilibrium value at the exit temperature. This liquefaction system can be operational in four different modes, by the optional use of bypass valves at three stages, as denoted by (a), (b), (c), and (d).

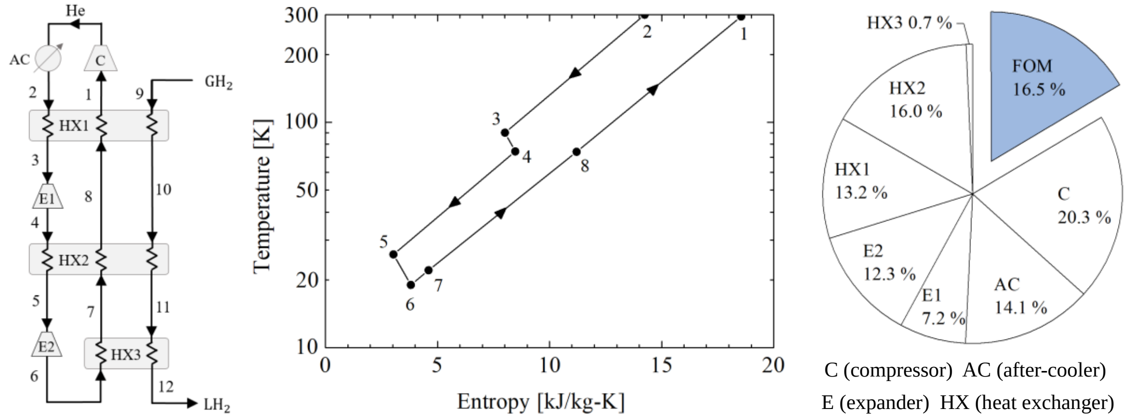

Figure 2. Two-stage expansion helium Brayton refrigeration system for hydrogen liquefaction [3] and an optimized cycle on temperature-entropy (T-s) diagram with exergy expenditure.

Table 1. Details of optimized two-stage expansion Brayton cycle for 15 g/s (1.3 T/day) liquefaction

	Helium								Hydrogen			
	1	2	3	4	5	6	7	8	9	10	11	12
Temp [K]	295.5	300.0	98.4	81.1	25.2	18.4	20.8	80.8	300.0	98.4	25.2	20.9
Press [MPa]	0.12	1.00	0.99	0.49	0.48	0.15	0.14	0.13	0.15	0.14	0.13	0.12
Vapor fraction	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.00
Flow rate [g/s]	596	596	596	596	596	596	596	596	15.0	15.0	15.0	15.0

	Compressors				Expanders			Heat Exchangers		
	C1	C2	C3	C4	E1	E2		HX1	HX2	HX3
Power [kW]	288	293	293	294	54.4	20.5	Min temp app [K]	4.50	1.22	0.31
Efficiency [%]	75.0	75.0	75.0	75.0	72.0	72.0	*UA* [kW/K]	68.0	78.8	6.95

In operation mode (a), the hydrogen stream bypasses all catalytic stages so that the para fraction of delivered liquid remains at 25%. In mode (d), on the contrary, the hydrogen stream pass all catalytic stages so that the para fraction of delivered liquid is 99.8%. Modes (b) and (c) are two intermediate operations by using one or two catalytic stages, resulting in a para fraction of liquid in the range of 50~85% as presented below.

In order to estimate the liquefaction capacity of this specific liquefier in the four different modes of catalytic OP conversion, a few assumptions are made on the performance of key components, including the compressors (C), after-coolers (AC), heat exchanges (HX), and expanders (E). Since C and AC operate at ambient temperature, it is assumed that the flow rate and their inlet/exit conditions are fixed as given values of the optimized cycle, regardless of the operation mode.

For HX's, however, the effectiveness may be slightly affected by the optional conversion, because the hydrogen flow rate is different in each case. It is assumed that the *UA* value of HX (the product of overall heat transfer coefficient between streams and heat exchange area) is fixed, as given in Table 1. In each operation mode, the minimum temperature difference should be calculated by the standard method of HX analysis (LMTD or effectiveness-NTU method) [5], and incorporated into the cycle analysis.

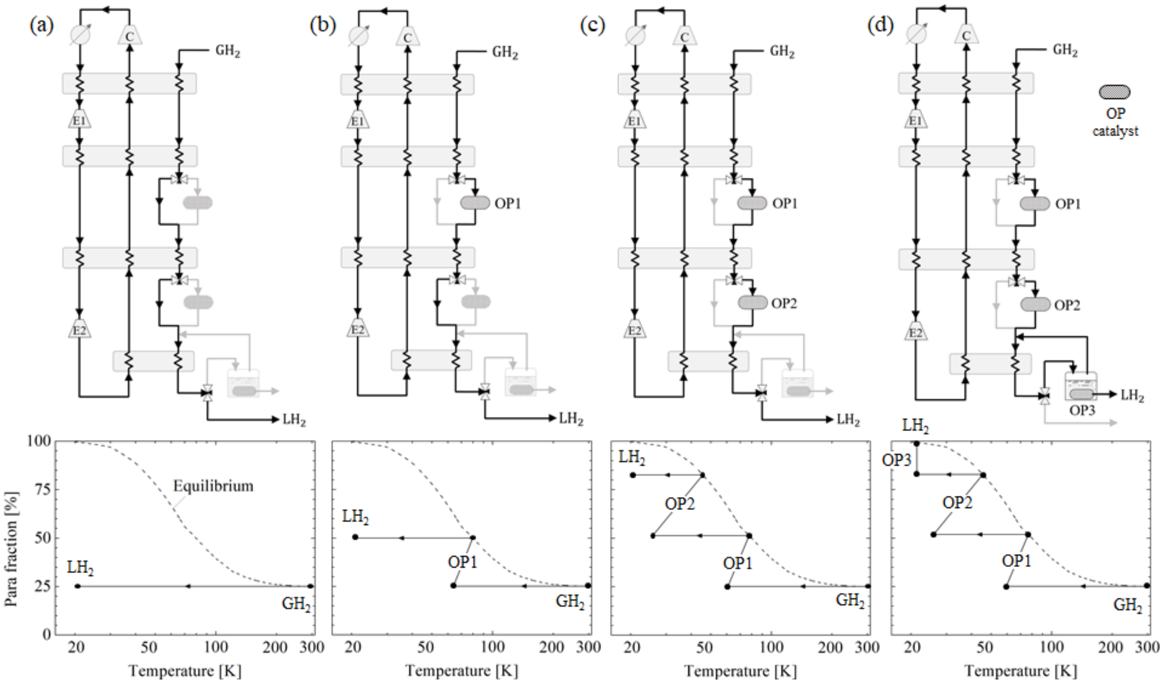

Figure 3. Four optional operation modes by three catalytic OP converters with bypass valves to produce liquid of four different levels of para fraction (a) no converter (b) one converter (c) two converters (d) three converters.

The adiabatic efficiency of expanders (E) may be slightly affected by catalytic conversion as well. It is assumed that the expanders have been designed for the optimized cycle, and helium is considered an ideal gas under the operating conditions. Then the deviation in efficiency for each operation mode can be estimated by the off-design operation model of radial flow-in turbines in terms of the ratio of the rotor tip speed to the spouting velocity [6,7].

A general-purpose process simulator (Aspen HYSYS) is used for the cycle analysis in different operation modes. The standard database (NIST REFPROP) is incorporated into the simulator for the thermodynamic properties of helium and hydrogen.

2.2 Liquid storage with different para fractions

In the absence of catalysts, the natural OP conversion is a second-order reacation [1,2].

$$\frac{dx_p}{dt} = k\left(1-x_p\right)^2 - k'\left(1-x_p\right)x_p \approx k\left(1-x_p\right)^2 \tag{1}$$

where k and k' are the reaction constants of forward and reverse conversion, respectively. Since k (= 0.00114 hr^{-1}) is much greater than k' (by ~500 times) at 20 K, the reverse conversion can be neglected in a liquid storage tank.

The actual storage of liquid hydrogen involves complicated physics. In a constant-pressure tank, the variation of liquid inventory (m) can be approximated by the combined mass and energy balance equations.

$$-\frac{dm}{dt}h_{fg} = \left(\frac{dm}{dt}x_p + m\frac{dx_p}{dt}\right)h_{op} + \dot{Q}_l \tag{2}$$

where h_{fg} and h_{op} are the latent heat of vaporization (= 443 kJ/kg) and the OP conversion heat (the enthalpy differnce between ortho and para hydrogen = 703 kJ/kg), respectively, and $\dot{Q}_l$ is the heat leak from ambient to the tank. It is noted that the decrease of liquid mass is equal to the boil-off loss due to “internal” OP conversion and “external” heat leak. The former is dependent on the para fraction of stored liquid, but the latter is regarded as a constant, regardless of the para fraction. Eq. (1) and (2) are shortly solved for m and x_p as a function of time, when their initial conditions and the external heat leak are given.

3. Results and discussion

For four different modes of catalytic conversion in Figure 3, thermodynamic cycle is simulated with the assumptions and models described in the previous section. It is important to verify the exactness of cycle analysis before proceeding to any quantitative discussion. Even though the full verification may not be presented by space limitation, the basic cycle and overall behaviour may well be confirmed in reference to the results of present authors’ recent publication [3].

From the simulated cycles in modes (a)~(d), the liquefaction capacity and para fraction of liquid are compared as column graphs in Figure 4. In order to examine their correlation, four points are also indicated on the diagram of liquefaction capacity vs. para fraction, and a data-fitted function is plotted as a dashed curve. For convenience, the liquefaction capacity is set at 1 T/day in case of mode (d) with full catalytic conversion. It can be stated that this specific liquefier is capable of delivering approximately 30% more liquid (as normal hydrogen), if there is no catalytic conversion at all. It is noticeable as well that the liquefaction capacity increases almost linearly, as the para fraction decreases. These specific results cannot be generalized to all kinds of liquefiers, but may well be regarded as a first estimate.

Once the liquefaction capacity is obtained for different modes of catalytic conversion, the boil-off loss of resulting liquid can be estimated as a function of time with Eq. (1) and (2). Figure 5 shows the calculated liquid inventory for 30 days in a storage tank, following one day of liquefaction with four different modes of catalytic conversion. The external heat leak is largely dependent on the size, geometry, and insulation design of storage tank [8], and typically given in terms of daily boil-off rate (BOR). In this paper, BOR 0.1%/day and 1%/day are considered as the case of “best-insulated” tank (with the state-of-the-art technology [8]) and “well-insulated” tank,

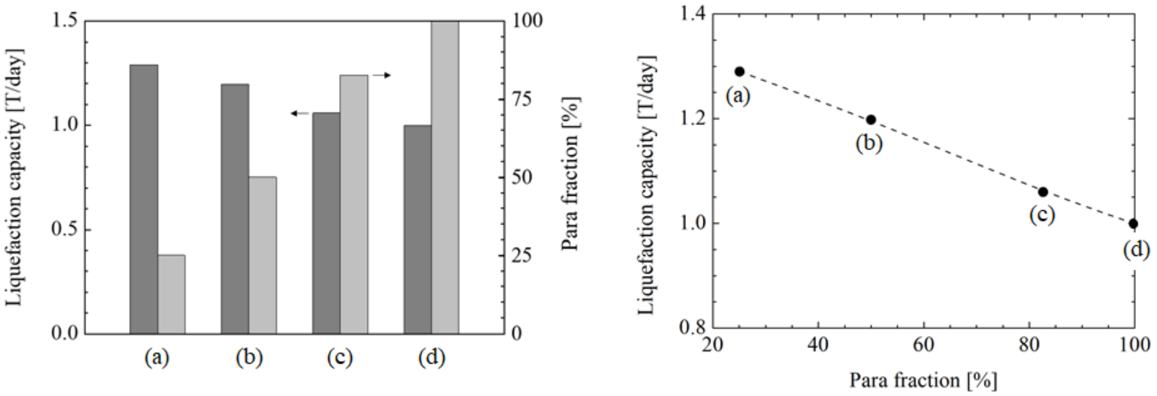

Figure 4. Estimated liquefaction capacity as a function of para fraction of liquid in four operation modes for 1 T/day liquefier with full catalytic conversion.

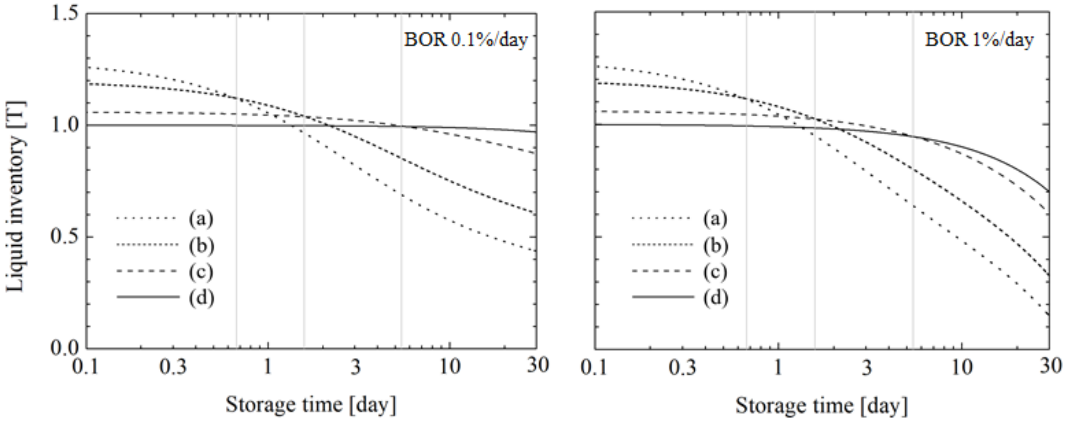

Figure 5. Estimated liquid inventory over a month, following one day of liquefaction with four different modes of catalytic conversion in cases of BOR 0.1%/day and 1%/day)

respectively. It is recalled that the liquid loss is due to the external heat leak only in (d) mode, but the natural OP conversion is added in (a), (b), and (c). With this optional three-stage conversion system, it can be roughly stated that the optimal operation mode is (a) x_p = 25% for storage < 1 day (exactly speaking, < 18 hours), (b) x_p = 50% for storage of 1~2 days, (c) x_p = 80% for storage of 2~5 days, and (d) x_p = 99% for storage > 5 days. It is also interesting to note that the optimal conditions are determined mainly by the storage time, but nearly independent of the BOR rate (i.e. the external heat leak). In practice, the actual schedule of liquid storage and its use could be variable. The decision under the situation depends upon the operational and end-use requirements including an appropriate risk-management program [4].

4. Conclusions

For its energy density, hydrogen is liquefied and stored as liquid for a period of time, and is consumed eventually as gas. The end-use application and operational case governs the need for normal versus para liquid composition. A rigorous thermodynamic study is carried out to verify that there exists an optimum in para fraction of liquid for efficient liquefaction and storage, depending on the length of stored period. The authors agree that there are a number of technical factors which have not been considered in this study, and should be included for better estimation. It can be concluded through this simplified study, however, that no catalytic conversion is recommended for the short storage of 1 day or less, but the full conversion is needed for storage over 5 days. The optional use of staged catalytic conversion in the process of liquefaction enables the liquid storage with optimized para fraction.

References

[1] Barron R F 1985 *Cryogenic Systems* 2nd ed (New York: Oxford University Press)
[2] Saif Z S et al. 2022 *Energy Environ. Sci.* **15** 2690
[3] Chang H M, Ryu K N, Baik J H *Cryogenics* **91** 68–76
[4] Higgins P, Fesmire J, Baik J, Williams M, Earls A 2024 *IOP Conf. Ser.: Mater. Sci. Eng.* **1301** 012060
[5] Barron R F 1999 *Cryogenic Heat Transfer* (Philadelphia: Taylor & Francis)
[6] Dixon S L, Hall C A 2010 *Fluid Mechanics and Thermodynamics of Turbomachinery* (Burlington, MA: Elsevier)
[7] Chang H M, Park C W, Yang H S, Hwang S D 2014 *AIP Conf. Proc.* **1573** 1770-1775
[8] Fesmire J, Swanger A, Jacobson J, Notardonato W 2022 *IOP Conf. Ser.: Mater. Sci. Eng.* **1240** 012088