Development of a Small Zero-Loss Hydrogen Liquefaction Plant

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ABSTRACT

A small scale zero-loss hydrogen liquefaction plant including a cryocooler cooled hydrogen liquefier, vacuum jacketed transfer line, and liquid hydrogen (LH_2) storage tank has been developed to demonstrate a zero loss hydrogen liquefaction, transfer, storage and re-condensation for various LH_2 applications. Boil-off gas from the transfer line and storage tank is re-condensed in the liquefier. The liquefier was designed to liquefy hydrogen at 1 L/hr using a single stage Gifford-McMahon cryocooler in a 150 L vacuum and multi-layer insulation (MLI) jacketed tank. A liquid nitrogen precooler, a hydrogen purifier, a heat pipe and two ortho-para hydrogen converters were integrated into the system. LH_2 in the liquefier is transferred to the 5 L storage vessel by using a low loss vacuum-insulated transfer line. Evaporated cold hydrogen gas can be returned to the liquefier and recondensed for future use. The system successfully demonstrated its liquefaction, low loss transfer, storage, and recondensation for various operational modes and applications.

INTRODUCTION

In today's world, we are facing many problems related to energy due to the massive population increase. In addition, there is the more pressing issue of global climate change caused by consumption of traditional non-renewable energy sources such as fossil fuels. These issues have led us to search for alternative renewable energy sources such as solar, wind, ocean-wave, and a variety of others. Storing and distributing the energy collected from these sources is important in making these technologies more viable. Hydrogen can offer one of many solutions for energy storage, distribution and usage.[1-2]

There are several possible methods for storing hydrogen: compression, chemical binding to metal hydride, liquefaction, etc. Of the various storage methods, liquefaction offers low pressure and high energy density per unit mass. In the past, liquid hydrogen (LH_2) was most widely known for its use in the NASA shuttle and rocket programs. Today, there are a variety of applications being developed for its use. The Lawrence Livermore National Laboratory, the BMW, and the Linde Group have developed cryo-compressed hydrogen storage tanks for use in fuel-cell vehicles. Also,

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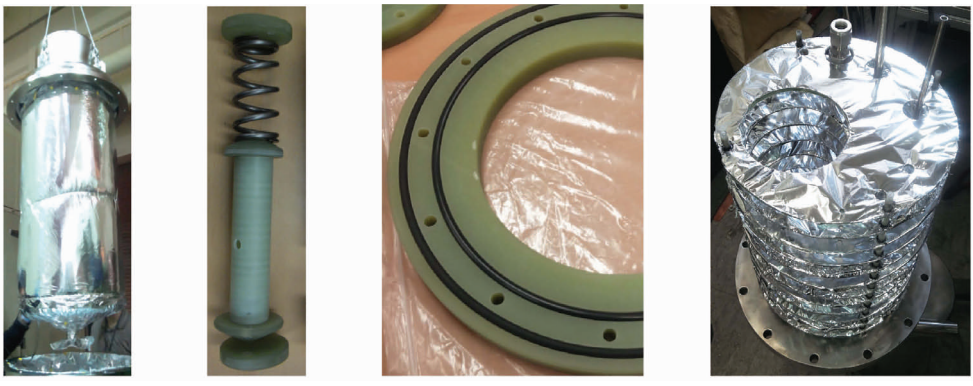


(a) (b) (c) (d)

Figure 1. (a) MLI wrapping of inner tank.(b) G-10 CR MLI wrapped baffle assembly (c) G10-CR machined disk (d) G-10 CR support structure.

LH_2 is being used by Boeing and The Office of Naval Research in aerospace applications to provide extended flight times for unmanned aerial vehicles (UAV).[3-8]

This paper describes the design, fabrication, operation and continuing improvement of Korea Institute of Science and Technology's (KIST) 1 L/hr at 3 bar hydrogen liquefier and separate 5 L storage tank. The two systems with vacuum transfer lines, demonstrated liquefaction, hydrogen transfer and re-liquefaction of hydrogen to create a low loss hydrogen storage system.[9]

SYSTEM DESIGN, FABRICATION AND ASSEMBLY

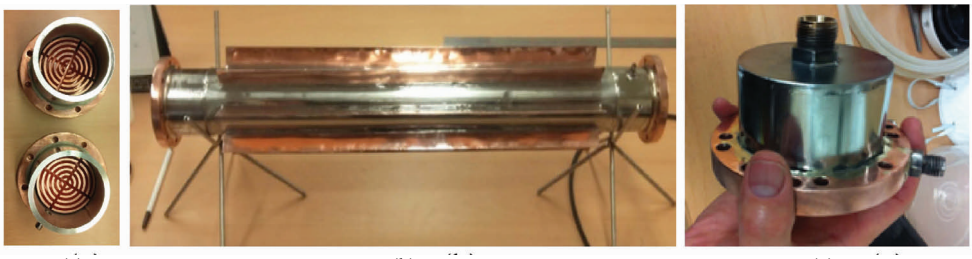
Hydrogen Liquefaction Requirements and Cryocooler Selection

The goal for this project was to design, fabricate and demonstrate a 1 L/hr liquefaction system and store that hydrogen in a zero loss state for later transfer and use. Including the heat of conversion from ortho to para-hydrogen (O-P), approximately 80 W of cooling would be needed to achieve a liquefaction rate of 1 L/hr at 1 bar and 20 K. A market search of available cryocoolers was conducted and Cryomech's AL325, cooling 100 W at 25 K or 70 W at 20 K, was selected to meet the goals of this project. To reach the liquefaction goal of 1 L/hr, the system needed be designed with precooling and take advantage of the cryocooler's higher cooling capacity at higher temperatures. Therefore, the system was designed to handle 3 bar steady state liquefaction.[10-11]

Liquefier Fabrication

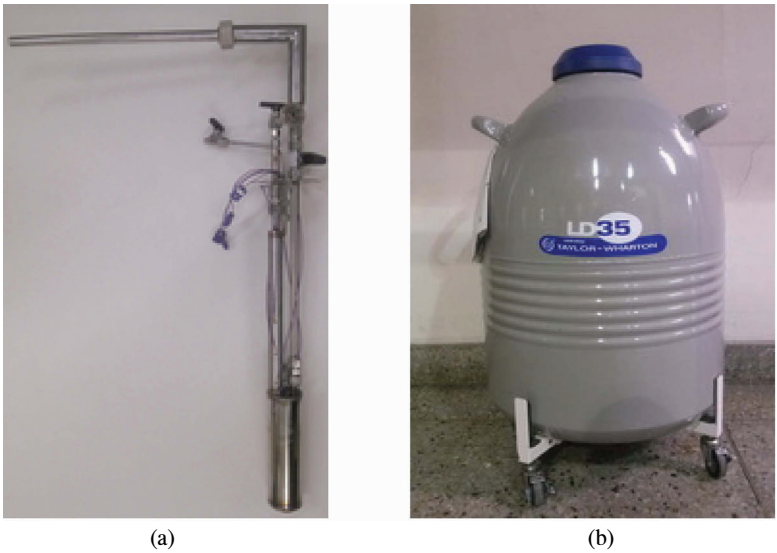
Heat leak into any cryogenic system will cause an increase in temperatures, a reduction in liquefaction capabilities, or an increase in boil-off. To limit convective heat transfer between ambient temperature and the LH_2, a doubled-walled 304 stainless steel (304 SUS) tank design was used to create a vacuum shield. For effective MLI performance, nEXT400D turbo-molecular pump from Edwards was added into the vacuum pumping system. For MLI, the inner tank were covered with 40 layers of Lydall's double sided aluminized Mylar multi-layer insulation (DAM MLI) with CRS-wrap (a micro glass spacer), as shown in Fig. 1(a). G-10 CR was used to create a support structure for the inner tank, Fig. 1(b). This support structure reduced the stress on the neck of the inner tank from its own weight and the weight of the hydrogen inside. Also, a large G-10 CR disk was fabricated to reduce conductive heat transfer between the inner and outer tanks' upper metal flanges, Fig. 1(c). To help reduce convective and radiative heat leaking down the neck of the liquefier, a MLI coated G-10 CR baffle structure was also fabricated, Fig. 1(d). From preliminary loss analyses, 10 W total of heat leak was expected to leak into the vessel.

To increase the heat transfer surface area with AL325 and to quickly transfer heat throughout the tank, a finned hydrogen heat pipe was fabricated and attached to the bottom of the cryocooler



(a) (b) (c)

Figure 2. a) Concentric fin caps after silver brazing and cleaning b) Fully assembled hydrogen heat pipe c) Ortho-Para catalyst packed bed.



(a) (b)

Figure 3. (a) LN_2 precooler with activated charcoal and O-P catalyst (b) a commercial dewar where the precooler was inserted.

cold head. It was made of a 304 SUS pipe and had two oxygen free high conductivity (OFHC) caps with extended concentric fins as shown in Fig. 2(a). The pipe was leak tested with helium to 36 bar.

A packed bed O-P converter was fabricated and mounted to the bottom of the heat pipe, Fig. 2(c). The converter was packed with 30-50 mesh iron(III) oxide. The system was plumbed so that hot hydrogen or precooled hydrogen would enter the system and pass through this catalyst bed. This bed ensured that over 99% of the hydrogen liquefied by the system would be para hydrogen.

Precooler with O-P Converter

An LN_2 precooler with O-P H_2 converter was used in this system to improve liquefaction rates by significantly decreasing the load on the cryocooler. Considering sensible heat of hydrogen at 300K, 77K, and 20K, the use of a precooler can remove 83% of sensible heat. In addition, using an O-P catalyst in the precooler removes the conversion heat at 77K. The precooler was designed as a packed bed heat exchanger with a 35L LN_2 holding capacity dewar as shown in Fig. 3. The bed was made of a 20 cm long 304 SUS pipe filled with 400 cc of 10-18 mesh activated charcoal in the top and 100 cc of the iron oxide O-P catalyst in the bottom. During liquefaction, warm hydrogen gas enters the activated charcoal bed to minimize clogging downstream. Next, the gas is cooled and

(a) (b) (c)

Figure 4. (a) 1 m long G-10 CR twin necks (b) 2 mm copper vapor cooled radiation shield and (c) completed outer assembly.

converted to about 50% para-H_2 in the O-P H_2 converter at 77 K. The conversion heat is completely removed in the LN_2 bath. Then, the gas flows into the liquefier through the vacuum jacketed transfer line.

5 L Storage Vessel

A 5 L tank was also designed, fabricated and tested to demonstrate zero loss transfer and recondensation of the boil-off gas. The initial design target was 0.57L/day (11.5%/day) under liquid hydrogen. The tank was thermally insulated with a copper vapor cooled shield, DAM MLI and 10^{-4} Torr or less high vacuum. To minimize conductive heat transfer to the inner tank, two flanged G10-CR pipes were mounted to the top lid of the outer shell, Fig. 4(a). One pipe was used for filling the tank and the other was used to return cold gas to the liquefier.

Reliquefaction and External Gas Reservoir

With two vacuum-jacketed transfer lines between the liquefier and the storage tank, one can capture and temporarily store the cold boil-off gas from the storage tank during initial cool-down in an external reservoir, then re-liquefy later in the liquefier. In order to demonstrate zero loss LH_2 transfer and zero loss cool down of the storage tank, a 150 L external reservoir was used to capture the evaporated gas during the transfer and initial cool down. The external reservoir is for density difference between GH_2 and LH_2. In this paper, both LH_2 transfer with vent and zero loss transfer tests were performed. The completed system flow diagram is shown in Fig. 5.

EXPERIMENTS

Safety

Safety is a major concern when dealing with hydrogen. To reduce explosive risks and to avoid oxygen deficiency hazards from dealing with cryogenic liquids, these experiments were conducted under a large walk-in fume hood that was in a well-ventilated room. All experiments had check

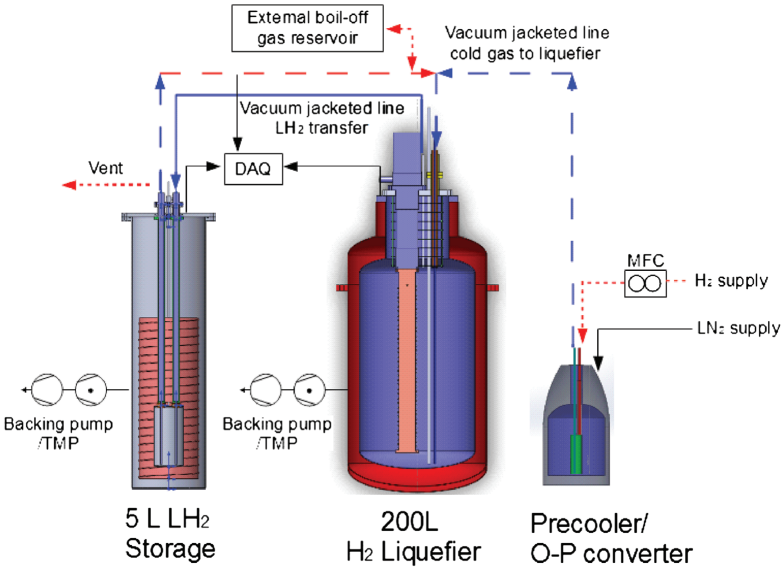


Figure 5. Flow diagram for the systems after fabrication.

valves and rupture disks that would release hydrogen pressure into a large dedicated hydrogen exhaust line. In the unlikely event of major hydrogen leakage into the room, hydrogen sensors in the room would trigger an alarm system in and outside the room. Standard cryogenic safety equipment and practices were used in the operation of these experiments: long-sleeved clothing, cryogenic gloves, etc.

Instrumentation

For safety, operation and data acquisition, a variety of sensors and gauges were incorporated into the system. A temperature rake with four silicon diode (SD) sensors and 1 m capacitance type liquid level sensor from American Magnetics (AMI) were installed in the liquefier for LH_2 level measurement. The lowest diode was placed 1 cm from the bottom of the liquefier corresponding to the bottom of the liquid drain pipe, the four sensors are evenly distributed every 25 cm. Three SD sensors were mounted to the cryocooler cold head, and the top and bottom of the heat pipe. Two E-type thermocouples were installed at the entrance and exit of the transfer line. A temperature rake with four E-type thermocouples was installed in the 5 L tank for LH_2 level measurement. The LN_2 precooler was also outfitted with a four E-type thermocouple temperature rake to indicate LN_2 level. One mass flow controller and one meter were used to measure and control liquefaction rate and evaporation rate of the liquefier and the storage tank. National Instruments (NI) Compact Field Point Module with NI Labview were used to monitor and control the system.

System Preparation

To ensure good vacuum in the systems, a complete helium purge and bake-out was conducted on the liquefier, the 5 L storage tank, the LN_2 precooler/O-P H_2 converter, and transfer lines. The systems were baked out for 3-4 hours at 120°C under 10^{-4} Torr and purged with helium several times. After vacuum bake-out, a no-load test was performed under vacuum. After the cryocooler was turned on, the coldhead reached 12 K in about one hour. Then, the inner tank was charged with 2.5 bar helium for the initial wall cool down. The system was left for one day which allowed the tank wall to cool to approximately 28 K. Next the heat pipe was filled with 66 L of 99.999% warm hydrogen gas. The heat pipe functioned properly showing a temperature difference of less than 1K between the cold head and the bottom of the heat pipe. The liquefier was now prepared for liquefaction.

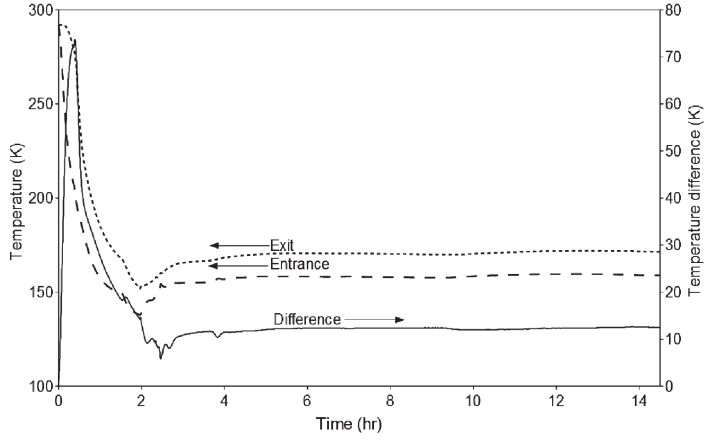


Figure 6a. Temperature profile of transfer line between liquefier and precooler during 1 bar liquefaction (b) temperature profile of transfer line between liquefier and precooler during 2 bar liquefaction

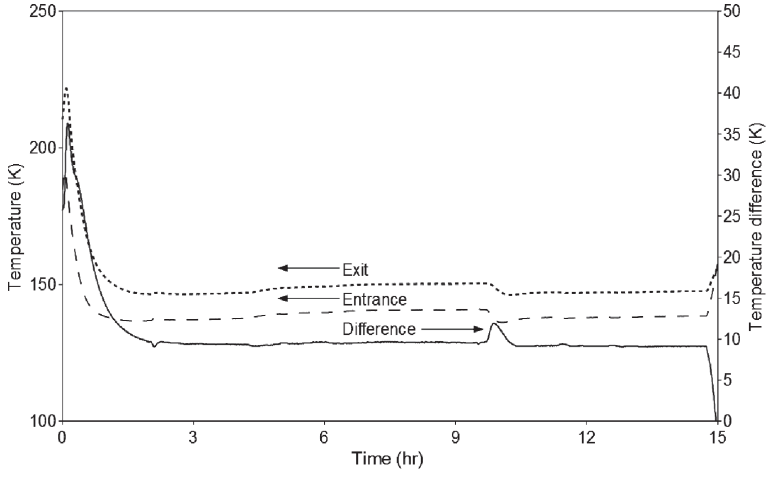


Figure 6b. Temperature profile of transfer line between liquefier and precooler during 2 bar liquefaction

EXPERIMENTS AND DISCUSSION

Liquefaction

After all the preparations were complete, warm hydrogen gas was allowed to flow through the precooler and into the liquefier at a set rate of 15 SLPM. The liquefaction tests were done at 1 and 2 bar, respectively. Figures 6 (a) and (b) show the temperature profiles of the transfer line between the precooler and the liquefier. From the gas flow rate, inlet temperature, exit temperature and hydrogen gas enthalpy difference, the heat leak into the transfer line can be calculated as 1.25 W/m for the 1 bar test, and 1.5 W/m for the 2 bar test due to the difference in the flow rate. For the 2 bar test, lower temperatures were observed due to higher flow rates.

Temperature, pressure and flow profiles for the 1 bar liquefaction are shown in Figures 7(a) and (b). Pressure was allowed to build in the system until the system reached 1 bar, around 1.5 hrs. A PID controller was then enabled to keep a constant pressure by controlling the flow into the system. There was a large swing in the pressure and flow which was undesirable, seen around 2 hrs in Fig. 7(b). The PID was turned off and the flow was controlled manually for the rest of the experiment. The system reached pseudo-steady state liquefaction around 5 hours, which can be

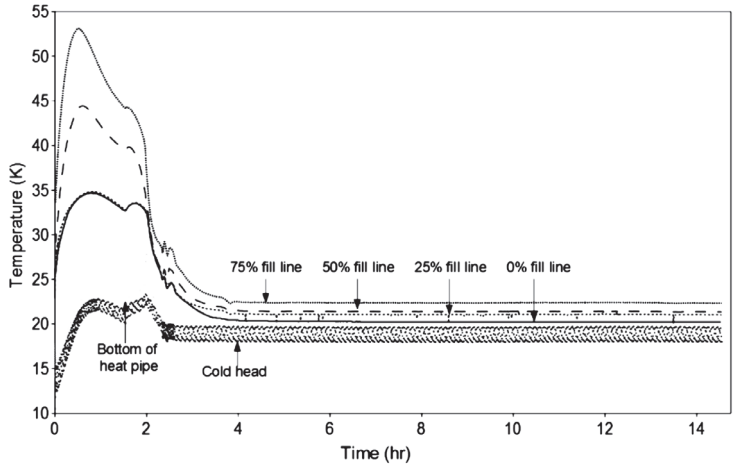


Figure 7a. Pressure and hydrogen gas flow profiles for 1 bar liquefaction

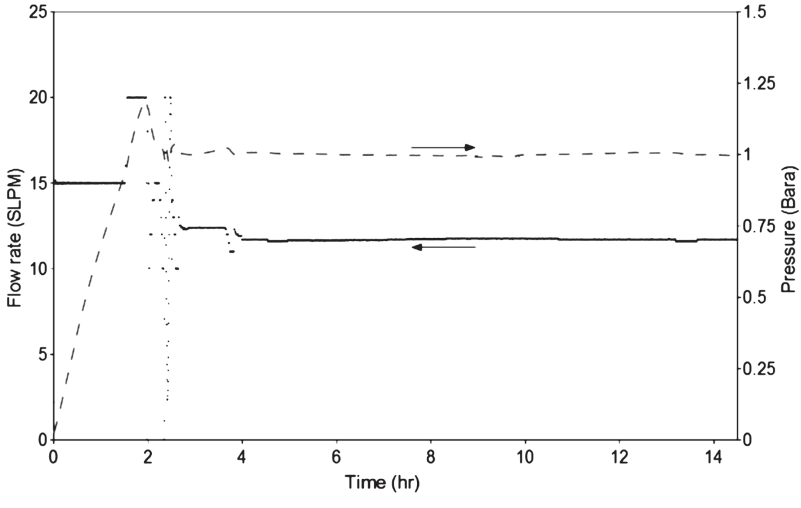


Figure 7b. Temperature profile in the liquefier during 1 bar liquefaction.

seen in the stabilizing temperatures, flow rate, and pressure in the figures. During pseudo-steady state liquefaction, pressure was manually controlled to an average of 1 bar. Average gas flow rate into the system during pseudo-steady state was 11.70 SLPM or liquefaction rate of 0.81 L/hr. Around 7 hours of liquefaction, the lowest silicone diode temperature sensor began reading a constant 20.28 K which is the saturation temperature of liquid hydrogen at 1 bar.

To see the effect of pressure on liquefaction rates, the same experiment was performed at 2 bar. Figures 8a and 8b show the 2 bar liquefaction results. In Figure 7(b), the 0% fill line temperature doesn't peak initially like the other temperature readings and only slowly rises over the next 6 hours. The upper temperature sensors peaked because they were measuring hydrogen gas temperature. This slow rise of temperature confirms the presence of liquid hydrogen around that sensor. Additionally, after 6 hours, the 0% fill line temperature stabilizes at 22.8K, which is the saturation temperature of LH_2 at 2 bar. For this experiment, it was necessary to have the pressure controlled automatically rather than manually. A simple Boolean controller was programed with a high and low flow rate set point to control the pressure. This method of control allowed the system pressure to stabilize around 5 hours. After 6 hours, the temperatures and pressure had stabilized indicating

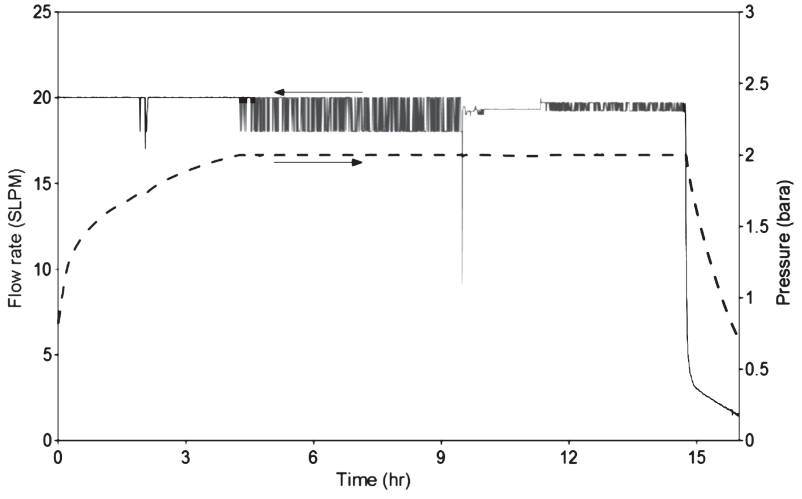


Figure 8a. Pressure and hydrogen gas flow profiles for 2 bar liquefaction

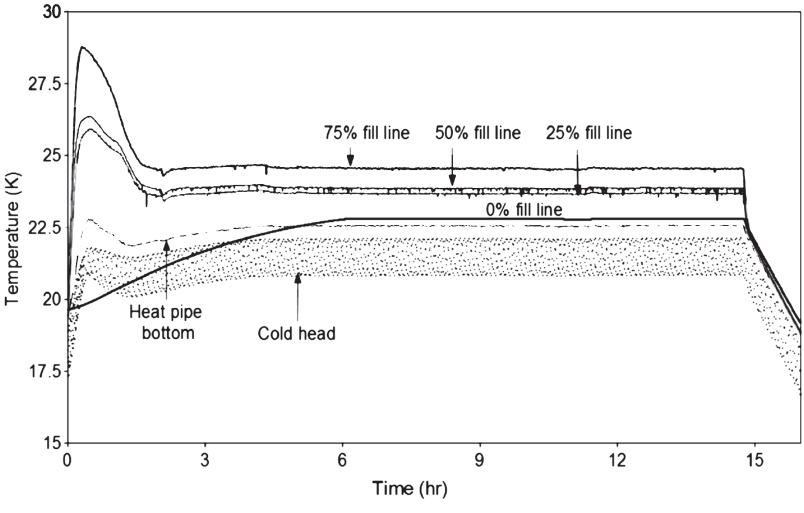


Figure 8b. Temperature profile in the liquefier during 2 bar liquefaction.

the system entered pseudo-steady state liquefaction. Around 12 hours, the Boolean's flow toggle range was decreased to further reduce the small pressure swings that were occurring in the system. For the next 3 hours after reducing the range, the system pressure was controlled to an average of 2 bar. The average flow rate during those hours was 19.45 SLPM or a LH_2 production rate of 1.36L/hr.

After 15 hours of 2 bar liquefaction, the gas feeding stopped. With no gas flowing into the system, the system entered into a sub-atmospheric densification mode, shown in Figs. 8(a) and (b). During sub-atmospheric densification, hydrogen's density increases as temperature and saturation pressure decrease. After consuming six cylinders of hydrogen, there was approximately 42 L of LH_2 in the liquefier.

Reliquefaction

The 42 L of hydrogen in the liquefier was used to demonstrate reliquefaction. First, LH_2 was transferred to the 5L storage tank to demonstrate the reliquefaction of the returned cold hydrogen gas from the storage tank. When the liquefier pressure was at 2 bar, the 5 L tank and two transfer

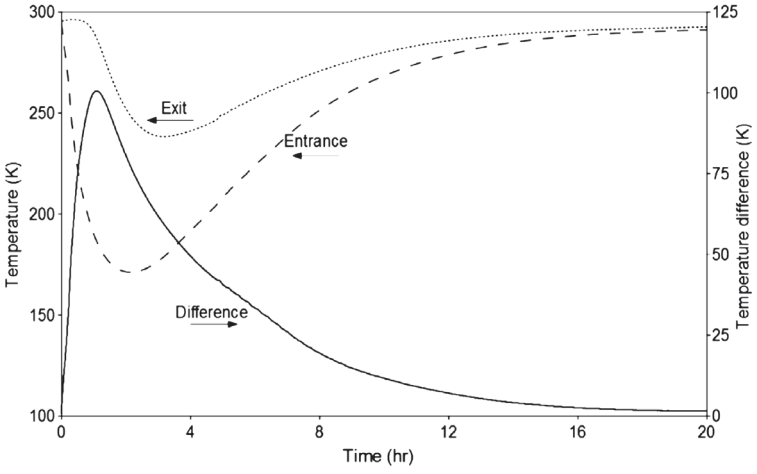


Figure 9. Temperature profile of transfer line during reliquefaction.

lines connecting the liquefier and the 5L tank were evacuated, and the liquid drain valve on the liquefier was opened and LH_2 started flowing in the supply transfer line by pressure difference. This time, the evaporated hydrogen gas was vented to atmosphere until 5 L of LH_2 was stored in the tank. After filling 5 L of hydrogen, the vent valve on the tank and the liquid drain valve on the liquefier were closed, while the cold gas return valves were opened. The pressure in the dewar and the liquefier were equalized to approximately 2 bar. The temperature profile of the cold gas return line during this process is presented in Fig. 9. In this figure, it can be seen that there was a large dip in temperature and then after several hours it starts to rise again. There were several reasons for this. First, the liquefier pressure was dropping due to continuous cryocooler opeation and then enters sub atmospheric densification mode. This mode causes a larger boil-off due to vacuum pressure in the liquefier. Another reason is that the 5 L tank was not fully cooled so there was additional boil off during this time. This high initial boil-off and subsequent drop in flow can also be seen in the next performance experiments, which were able to measure boil-off rate. In Figure 9, the temperature of the transfer line eventually rises back to room temperature. This is the result of the boil-off rate becoming extremely small. The little heat leak that occurs in the bayonets and transfer lines was enough to heat this small volume of gas back to room temperature. With these observations, future reliquefaction experiments will not need to use vacuum transfer line.

Zero Loss Transfer

Another type of LH_2 transfer test was attempted by use of pressure differences between the liquefier and the 5 L storage tank without venting. The pressure of the liquefier was cycled between 1 and 2 bar by turning on/off the cryocooler and zero loss (or, no vent) transfer was attempted by manipulating supply/drain valves with a 150 L external reservoir. Zero loss transfer was conducted after the 5 L dewar had boiled off all the hydrogen from the reliquefaction experiment and warmed to room temperature. To reduce the hydrogen boil-off during transfer, the 5 L tank and the supply transfer line were precooled to 80K, and the 150 L was connected to the vent line of the 5 L tank. Then, all the components except the liquefier were evacuated.

When the liquefier pressure was at 2 bar, the liquid supply valve on the liquefier was opened and LH_2 started flowing to the 5 L tank slowly. However, rapid boiling in the transfer line was observed, and pressure was equalized to 2 bar through the entire system very quickly. The temperature of the transfer line decreased to 50 K. The liquid valve was closed, and the gas return valve was opened. The cryocooler was turned on for an hour to allow the entire pressure to reduce to 1 bar. At 1 bar, the gas return line was closed, the cryocooler was turned off, and warm hydrogen gas was flowed into the liquefier to raise the tank pressure to 2 bar. This took half an hour. This pressure swing cycle lasted about a total of 1.5 hrs. During this pressure swing, the temperature in the trans-

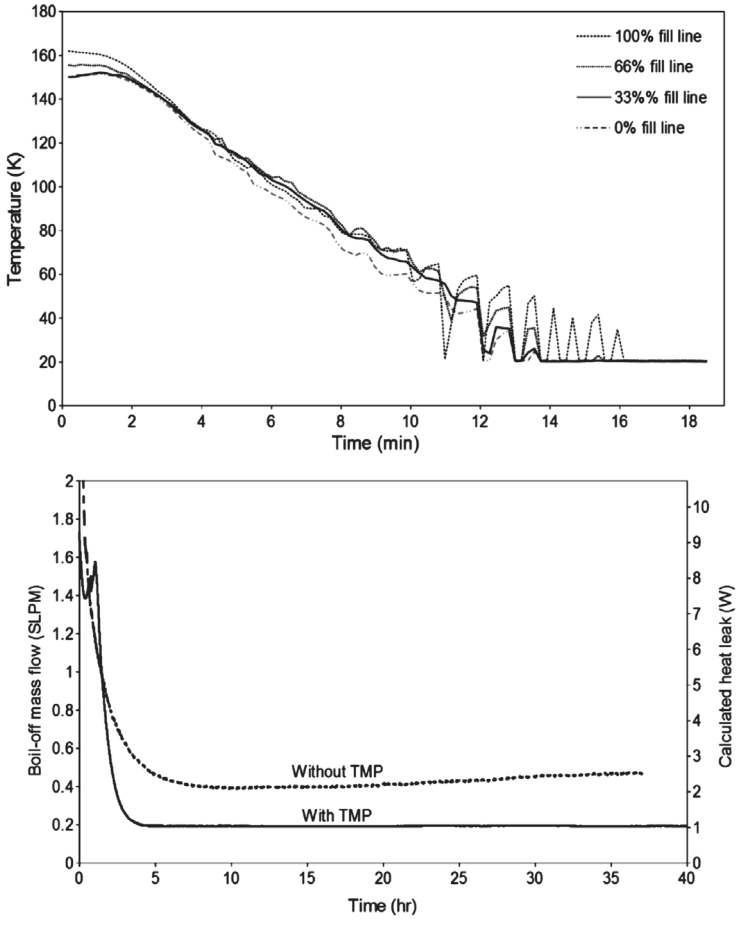


Figure 10. (a) 5 L tank cooldown profile (b) performance test comparison with and without a TMP.

fer line rose substantially—in fact, very close to 100K. Then, the liquid valve was reopened to flow LH_2 into the transfer line and the 5 L storage tank. Another temperature decrease in the transfer line was observed. This cycle was attempted several times, but temperatures in the transfer line didn't reach LH_2 temperatures due to a large heat leak compared to the long pressure swing cycle. Also, the external reservoir volume was too small for this transfer method.

5 L Storage Tank Performance

For the 5 L storage tank boil-off performance measurement, LH_2 was transferred from the liquefier to the storage tank with venting. The cool down profile of the inner 5 L tank is shown in Figures 10a and 10b. The vent line was plumbed into a mass flow meter to measure evaporated gas flow. For the MLI performance comparison, the boil off rates were measured at two different vacuum pressures with and without a TMP. Without a TMP, there was an average of 0.43 SLPM of boil-off for the hydrogen or 15%/day. Also, there is a slight increasing trend in the data. This is likely the result of the radiation shield warming due to less insulation effect at higher pressure. In the test with a TMP, a boil-off rate of 0.19 SLPM was observed or 6.3%/day, which was significantly lower than the expected 11.5%/day. Most of the heat leak through the system is conduction through the G10-CR support pipes. The radiation shield comes in contact with the G10-CR pipes to intercept this heat. When less heat penetrates through the MLI due to improved vacuum level, more heat can be intercepted from the G10-CR support pipes by the radiation shield.

SUMMARY

A hydrogen liquefier, transfer lines, precooler, and 5 L storage vessel have been fabricated and tested. Modifications to the system have maintained liquefaction capabilities of 1.36 L/hr at 2 bar, improved storage and demonstrated reliquefaction. Although zero loss transfer was not able to be demonstrated, future tests will include the use of a dry gas pump or large gas storage bag to capture and return the boil off gas to the liquefier. The system will continue to be upgraded over the course of the project. Current plans include upgrading the precooler to a full purifying-precooling system which will allow for liquefaction of lower purity hydrogen, improve the storage vessel with additional temperature sensors and increasing the size of the inner storage tank to commercial size.

ACKNOWLEDGMENT

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