Analysis of a Supercritical Hydrogen Liquefaction Cycle

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ABSTRACT

A supercritical hydrogen liquefaction cycle is proposed and analyzed numerically. If hydrogen is to be used as an energy carrier, the efficiency of liquefaction will become increasingly important. By examining some difficulties of commonly used industrial liquefaction cycles, several changes are suggested and a readily scalable, supercritical, helium-cooled hydrogen liquefaction cycle is proposed. An overlap in flow paths of the two coldest stages allowed the heat exchanger losses to be minimized and the use of a single-phase liquid expander eliminates the pressure reduction losses associated with a Joule-Thomson valve. A computational model of the cycle was developed to investigate the effects of altering component efficiencies and various system parameters on the cycle efficiency. Furthermore, a heat exchanger simulation was developed to verify the feasibility and to estimate the approximate size of the heat exchangers in the cycle simulation.

For a large, 50-ton-per-day plant with reasonable estimates of achievable component efficiencies, the proposed cycle offers a modest improvement in efficiency over the current state of the art. In comparison to the 30-40% Second Law efficiencies of today's most advanced industrial plants, efficiencies of 39-44% are predicted for the proposed cycle, depending on the heat exchange area employed.

INTRODUCTION

Given the scale of current hydrogen liquefaction and likely future expansion, improvements in efficiency have the potential to effect large energy and economic savings. Clearly, current liquefaction cycles can be improved by developing more efficient components; however, it is not obvious that these cycles take full advantage of available technology. The objectives of this work are to examine the currently available liquefaction cycle technology, to explore the potential energy savings of new and more efficient cycle configurations, and to propose a new liquefaction cycle that offers increased efficiency without the need for extensive component development.

Motivation

Hydrogen is useful in many industries. It is used as a chemical feedstock in the petroleum and petrochemical industries, as well as for the hydrogenation of oils and fats and the production of fertilizer. Its ability to scavenge oxygen is used to advantage in metallurgical processes. Hydrogen

is used as a fuel in the space industry because of its high energy per unit mass. Over the last decade there has been persistent interest in hydrogen as an automotive fuel because it has zero point-of-use greenhouse gas emission, high combustion efficiency, compatibility with efficient fuel cells, improved safety compared to other fuels, and the ability to be generated from domestic energy sources. The need for large quantities of hydrogen will increase dramatically if even a minute portion of the vehicles in the United States begin to use hydrogen fuel.²

Except for extremely large amounts of hydrogen, where pipelines sometimes become cost competitive, the most economical transportation method for centrally produced hydrogen is via liquid hydrogen tanker trucks.³ Additionally, centralized hydrogen production is more cost and energy efficient than distributed production. Gas liquefaction plants tend to be more efficient as their size increases,⁴ and the lifetime cost of a large hydrogen liquefaction plant will be dominated by the cost of the input power.⁵ Thus, improvement in the efficiency of hydrogen liquefaction plants has the potential to save significant amounts of energy and money.

Hydrogen Liquefaction Challenges

Hydrogen has several features that make efficient liquefaction difficult. Turboexpanders are commonly used in large-scale cryogenic liquefaction plants; however, McIntosh identified hydrogen turboexpanders as one of the most challenging aspects of liquefaction. Hydrogen's low molecular weight and high speed of sound necessitate very high rotor peripheral speeds. Material properties restrict this speed and limit each stage to a low pressure ratio. Additional considerations of using turbomachinery with hydrogen include the difficulty of forming reliable seals and hydrogen's propensity to cause material embrittlement.

Purification requirements for hydrogen liquefiers are stringent, especially in systems that recirculate much of the hydrogen as a working fluid. Contaminants other than helium in the feedstock freeze in the system, which can clog a J-T valve or damage an expander. Systems with a J-T valve expanding to a two-phase state often recirculate a substantial portion of the hydrogen working fluid, and oxygen buildup in the lower temperature regions of the system must be safeguarded against. McIntosh identifies "explosion proof requirements on equipment and facility design" as an important consideration in liquefier design. Indeed, using hydrogen as the working fluid results in more hydrogen-filled components, connection points, and plumbing, introducing a greater number of potentially dangerous leak sites.

Additionally, hydrogen's properties present thermodynamic challenges. The specific heat of hydrogen varies substantially with temperature near the critical point. The ortho-para transition, which must be catalyzed to avoid excessive boiloff losses during storage, constitutes a significant amount of the energy that must be removed from the product. The temperature dependent ortho-para equilibrium requires that heat loads on par with the latent heat at 1 bar be removed at low temperatures in the system, so the operating temperatures of catalyst beds in the cycle must be chosen judiciously.

Clearly, hydrogen liquefaction presents many challenges to a cycle designer. Practical challenges arise from hydrogen's flammability, resistance to being contained by seals, and tendency to cause embrittlement in common materials. Hydrogen's low molecular weight and resultant high speed of sound cause turbine expanders to be less effective. Thorough purification of the feedstock must also be performed to avoid freezing of gaseous impurities and the potential hazard due to accumulated oxygen. Finally, the strongly temperature-dependent heat load, due to changes in the specific heat near the critical point and due to the energy released by the ortho-para conversion, cause entropy-generating heat exchanger imbalances in the cycle and demand careful selection of system operating temperatures and flow rates.

PROPOSED CYCLE

Two plant sizes were considered in this study: a pilot plant, which is a 500 kg/day liquefaction plant, and a large plant, which is 50,000 kg/day. Since testing of the large plant would require an enormous capital investment, it was a priority to make the pilot plant very similar in configuration to the large plant so that validation tests could apply to both designs.

Using a high-pressure product stream was desired due to the availability of high pressure hydrogen from various generation sources. In particular, many water electrolyzers used to generate hydrogen operate at high pressure; by coupling this to the liquefier, the need for a separate product stream compressor would be eliminated. The plant would be able to take advantage of the relatively efficient compression process associated with an electrolyzer rather than having to use a reciprocating machine.

In addition to eliminating the product stream compression, a high-pressure inlet state reduces the severe or infinite peaks in specific heat that occur near or below the critical temperature. The heat capacity of equilibrium hydrogen – that is, hydrogen at the equilibrium parahydrogen concentration for each temperature – for pressures at and above the critical pressure is shown in Fig. 1. It is clear that as the pressure approaches the critical pressure the heat capacity diverges at a temperature of 33 K. At pressures below the critical pressure the heat capacity of all isobars diverge when the fluid undergoes the vapor to liquid transition. In many liquefaction cycles the wildly varying heat capacity makes the heat load of the product stream very difficult to match and can lead to unnecessary heat exchanger losses, which suggests that cooling the hydrogen supercritically can lead to improved cycle efficiency.

Using helium as the working fluid makes some of the hydrogen liquefaction challenges more surmountable. First, helium turboexpanders, which are commonly used in helium liquefaction cycles, operate more effectively than hydrogen turboexpanders. The speed of sound in helium is lower than in hydrogen because of helium's greater molecular weight. Second, material degradation of components does not occur due to exposure to helium as it can with hydrogen. In addition, helium remains gaseous in the required operating temperatures of the cycle. The combination of a supercritical hydrogen product stream and an all-gaseous helium working fluid eliminates difficulties associated with multi-phase expansion. Finally, helium is inert, providing inherent safety in the event of a leak to the environment of the hydrogen stream.

A system that addresses the problems discussed above can be seen in Fig. 2. In this configuration, hydrogen passes through a series of heat exchangers until it reaches a temperature slightly above the storage temperature of 20 K. At this state, all of the hydrogen is a subcooled liquid. The final reduction in temperature and pressure prior to entering the storage tank is accomplished with a single-phase liquid expander, which will be discussed in more detail below. The heat removed

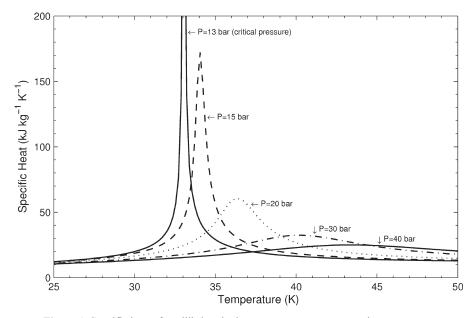


Figure 1. Specific heat of equilibrium hydrogen vs. temperature at various pressures.

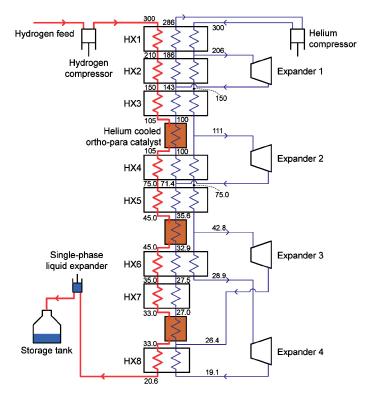


Figure 2. Schematic of the proposed system. Indicated temperatures are in K.

from the hydrogen goes into a refrigeration loop – a helium cycle. The helium cycle cools a hydrogen stream that is maintained at a supercritical pressure. In this way, the divergent behavior of the hydrogen heat capacity in the two phase region is avoided and is replaced by the relatively benign thermal behavior of the supercritical stream. This allows the temperatures and the capacity flow rates in the helium streams to be better matched to the temperatures and capacity flow rates of the hydrogen stream in the low-temperature heat exchangers, reducing the losses in the cycle.

Maintaining a supercritical hydrogen stream eliminates the need for a J-T valve and circumvents the challenges associated with two-phase operation. Rather than undergoing a distinct phase change like subcritical hydrogen, the supercritical hydrogen stream gradually increases in density until it reaches the liquid density. At the bottom of the system, the hydrogen stream is a high-pressure liquid. The single-phase liquid expander extracts a small amount of work from the liquid and reduces its pressure to atmospheric for storage. Essentially, the single-phase liquid expander behaves in the opposite manner of a pump. An improvement in the cycle efficiency results from the reduction of generated entropy at one of the lowest temperatures in the system where it is most costly. Indeed, liquid or two-phase expanders have been employed in similar cryogenic applications; the helium liquefier in the MIT Cryogenic Engineering Laboratory has been using a wet expander that operates at about 90% adiabatic efficiency for nearly 40 years. Its design and construction is discussed in further detail by Johnson et al. In Fig. 2, the temperature of the hydrogen stream as it exits heat exchanger 8 is slightly above the normal boiling point. The single-phase liquid expander operating at 90% efficiency reduces the temperature to the normal boiling point before the stream enters the storage tank.

Three stages of ortho-para conversion can be seen in Fig. 2. Ideally, the ortho-para catalyst would be incorporated into the hydrogen passages in each heat exchanger so that the conversion would occur continuously as the hydrogen is cooled. Continuous conversion catalysis could be incorporated into the cycle by modifying the hydrogen stream heat exchanger passages to include

ortho-para catalyst, in a fashion similar to that employed by Lipman et al.8 The efficiency of the pilot plant could be increased by about 1 point by incorporating continuous conversion.² However, to keep ease of construction a high priority it was assumed that the first iteration of the system would employ conventional, staged catalysis. The low-pressure helium stream provides cooling to the catalyst bed to maintain the bed at near-isothermal conditions.

The spans of the two lowest-temperature expanders overlap. This configuration provides additional cooling in the critical temperature region where the specific heat of the hydrogen peaks. In addition, the overlapping configuration helps to match the substantial heat load due to the orthopara conversion in the low-temperature catalyst bed. The numerical model confirmed that this improvement in the capacity flow rate matching between the hydrogen stream and the helium cooling streams results in improved efficiency compared to a uniformly staged Collins cycle design.

NUMERICAL MODEL

A numerical model was developed to solve the thermodynamic states of the system and evaluate the system's performance. The model was also used to optimize the system's operating conditions, estimate the required heat exchanger sizes to achieve these conditions, and determine the sensitivity of the system efficiency to various parameters.

Thermodynamic States

The system modeled consisted of a hydrogen product stream cooled by a Collins-type helium cycle as described above. As can be seen in Fig. 2, the helium is compressed and the high-pressure stream enters the first stage, which consists of heat exchanger 1 (HX1), HX 2, and expander 1. The cool, low-pressure helium stream cools both the hydrogen and the high-pressure helium stream. The capacity rates of the high-pressure helium and low-pressure helium streams approximately balance each other in heat exchanger 1. Addition of the hydrogen stream causes the downward flow in the heat exchanger to have a larger net capacity flow rate, which results in the tendency of temperatures of the streams to pinch at the top. After HX1, a fraction of the high-pressure helium is diverted into expander 1 so that heat exchanger 2 has a larger net capacity flow rate in the upward direction and pinches at the bottom. In a balanced-flow heat exchanger, a low stream-to-stream temperature difference can be maintained, which results in less entropy generation. It is impossible to balance the flows with the addition of the hydrogen stream, but the balanced-flow scenario may be approximated by allowing the stream temperatures to diverge in one HX and then converge in the next HX by altering the relative flow rates of the two helium streams. High-pressure helium diverted into an expander rejoins the low-pressure stream after work is extracted and its temperature is reduced. The unavoidable heat exchanger imbalance losses can be minimized by choosing appropriate flow rates in each expander. Addition of more expanders also helps to reduce this loss.

Some assumptions were necessary to completely solve the system. A set of temperatures was assumed for the hydrogen stream. The hydrogen stream temperatures, after the system was solved, were changed until a maximum efficiency was approached. It was assumed for simplicity that the temperature of the high-pressure helium stream would be the same as the temperature of the hydrogen stream at each stage point (that is, where the temperature profiles of the high-pressure helium and low-pressure helium pinch). These points can be seen in Fig. 2.

According to the work of Minta,⁹ for a given liquefier design the total heat exchange area is most effectively distributed when the value of $\Delta T/T$ is given a constant value at all stage points. $\Delta T/T$ is defined as

 $\frac{\Delta T}{T} = \frac{T_{\text{hydrogen}} - T_{\text{helium,LP}}}{T_{\text{helium,LP}}} \tag{1}$

where the $T_{\rm hydrogen}$ and $T_{\rm helium,LP}$ are the temperatures of the hydrogen stream and the low-pressure helium stream, respectively. The $\Delta T/T$ constraint was not strictly enforced at each stage point, but a constraint was imposed to prevent $\Delta T/T$ from becoming less than a specified value. When the system efficiency was maximized, the actual $\Delta T/T$ values tended to push this constraint to its limit at each stage point as expected. This constraint limits the total heat exchange area in the simulation by

setting the pinch point temperature differences in the system. In the absence of this constraint, the stream-to-stream temperature differences would be driven to zero during the system optimization, making the efficiency greater but implying infinite heat exchange area.

In the catalyst beds it was assumed that the low-pressure helium cooling stream maintained the temperature of the hydrogen stream at a constant value. The change in enthalpy of the hydrogen in a catalyst bed occurred solely because of the change in the parahydrogen concentration. The heat given off by the ortho-para conversion was taken up by the low-pressure helium stream. This isothermal catalyst bed behavior has been approximated in experiments. For example, Hutchinson maintained small catalyst beds at nearly constant temperature to determine ortho-para conversion rates for hydrous ferric oxide catalyst material. ¹⁰ In the simulations in the present work, it was also assumed that the catalyst beds were large enough to allow the hydrogen to reach the equilibrium parahydrogen concentration at the catalyst bed temperature.

Assumptions about the cycle components were required to obtain a solution that is representative of a physically realizable system. The expanders were assumed to have a fixed adiabatic efficiency. After several communications with a potential expander manufacturer and supplier, the expected efficiency for each expander in both the pilot and large plant was estimated and incorporated into the model. This manufacturer suggested that the highest- temperature expander in the large plant be split into two expanders in series. In this configuration it can be shown that the effective adiabatic efficiency of the two-expander ensemble is greater than the reported efficiency of either by itself. The efficiencies the manufacturer reported were for helium expanders operating at a discharge pressure of 2.5 bar and a pressure ratio of 6. These pressures were not changed in the simulations, because deviation from these pressures would cast doubt on the legitimacy of the expander efficiency estimates. A summary of the expander efficiencies incorporated into the simulation can be seen in Table 1. The expanders in the large plant are more efficient, resulting in considerably higher system efficiency. Also, the helium compressor in the large plant was assumed to consist of a multitude of intercooled compression stages to give a high isothermal efficiency.

In addition to the expanders, efficiency estimates were needed for the compressors. Based on discussions with a manufacturer of air separation units and water electrolyzers as well as the aforementioned expander company, and on typical reciprocating compressor efficiencies reported in literature, ^{11,12,13} isothermal efficiencies were assumed for the helium compressors in the pilot and large plants. Due to sparse literature about hydrogen compressors Conservative isothermal efficiencies of 60% were assumed for the hydrogen compressors. The compressor efficiencies for the pilot and large plants are summarized in Table 1.

	Pilot Plant	Large Plant
Expander 1 Adiabatic Efficiency	0.60	0.85 ^a
Expander 2 Adiabatic Efficiency	0.70	0.83
Expander 3 Adiabatic Efficiency	0.75	0.86
Expander 4 Adiabatic Efficiency	0.65	0.86
He Compressor Isothermal Efficiency	0.65	0.80
H ₂ Compressor Isothermal Efficiency	0.60	0.60
Liquid Expander Adiabatic Efficiency	0.90	0.90
$\Delta T/T$	0.05	0.05
Hydrogen Pressure (bar)	21	21
Ambient Temperature (K)	300	300
Ambient Pressure (bar)	1	1
H ₂ Product Temperature (K)	20	20
H ₂ Product Pressure (bar)	1	1
H ₂ Product Parahydrogen Mass Fraction	0.95	0.95
System Second Law Efficiency	0.184	0.391

Table 1. Summary of base configuration parameters

 $[^]a$ effective efficiency of two-stage expander combination. Individual expander efficiencies were $\eta_{1A}\!\!=\!\!0.82$ and $\eta_{1B}\!\!=\!\!0.83$.

The states in the system were determined as follows. The temperatures of the hydrogen stream were assumed, and the temperatures of the high-pressure helium stream were set equal to the hydrogen temperatures at each of the five stage points in the system. The parahydrogen concentration was set to the equilibrium value for the local temperature at the outlet of each catalyst bed and this concentration was maintained in the hydrogen stream until reaching the outlet of the next catalyst bed. Next, the total mass flow rate through the compressor and the fraction diverted into each of the first three expanders was guessed. With these flow rates, the states in the system were determined by solving a system of equations representing energy conservation in each component. The Second Law of Thermodynamics was then used to evaluate the system and verify that each component operates with a positive rate of entropy generation. Furthermore, constraints on the temperatures were imposed to ensure that Second-Law-violating scenarios were not considered. The guess values were iterated by an optimization routine in MATLAB until the system efficiency was maximized.

The fluid properties were determined using NIST REFPROP 8.0. Portions of the system, especially the hydrogen stream, operate near the critical region where simple constitutive equations like those of an ideal gas would result in unacceptable errors. After ensuring consistency in the reference states of the normal hydrogen and parahydrogen properties, ideal gas mixing equations were used to determine the properties of the hydrogen mixture at arbitrary parahydrogen concentration. This is discussed in further detail by Staats². These mixing rules can be used for the supercritical hydrogen in the system because the *P-v-T* behavior of normal and parahydrogen are virtually identical.¹⁴

Initial simulations of smaller but analogous systems with fewer stages determined the value of additional stages. These simulations, however, did not have an overlap in the bottom stages. The adiabatic efficiencies of each expander and the isothermal efficiency of the compressor were assumed to be 80% and 65%, respectively, and the $\Delta T/T$ value at each stage was restricted to 5%. The temperature of the thermal reservoir into which the compressors reject heat was assumed to be the ambient temperature of 300 K. The Second Law efficiency was defined as

$$\eta_{\text{system}} = \frac{W_{\text{liquefaction,ideal}}}{W_{\text{net,system}}} = \frac{\left| \dot{m}_{\text{hydrogen}} \left[\left(h_{\text{final}} - h_{\text{initial}} \right) - T_{\text{amb}} \left(s_{\text{final}} - s_{\text{initial}} \right) \right]_{\text{hydrogen}}}{\dot{W}_{\text{comp,helium}} + \dot{W}_{\text{comp,hydrogen}} - \sum_{i=1}^{4} \dot{W}_{\text{expander}(i)}}$$
(2)

where $W_{\rm net,system}$ is the net work input to the system, $W_{\rm liquefaction,ideal}$ is the ideal work of liquefaction, $\dot{m}_{hydrogen}$ is the mass flow rate of the hydrogen, \dot{W}_{comp} is the power input of the hydrogen or helium compressor, $\dot{W}_{expander(i)}$ is the power output of expander i, h is the specific enthalpy, $T_{\rm amb}$ is the ambient temperature and s is the specific entropy. The final state is hydrogen at 20 K, 1 bar and 95% parahydrogen and the initial state is at 300 K, 1 bar and 25% parahydrogen. The 95% parahydrogen concentration of the final state is a typical target value for liquefaction plants. The Gare must be taken in comparing Second Law efficiencies reported in different sources since the choice of reference states has a significant effect, and sometimes does not include the ortho-para conversion. Table 2 shows the overall efficiencies of two-, three- and four-stage cycles. Increasing the number of stages from two to three results in a large efficiency increase of 0.167, while increasing from three to four yields a less pronounced gain of only 0.026. From this trend it is expected that adding another stage in a cycle would not be worth the considerable associated increase in capital cost.

Sensitivity Analysis

The systems specified in Table 1 represent the base configurations of the pilot and large plants. These systems were solved using the numerical solving routine described above; their efficiencies are listed in the bottom row of Table 1. The temperatures of the pilot plant base configuration are shown in Fig. 2.

After the establishment of the base configuration operating point and efficiency, the efficiency of each component was varied to determine its impact on that of the cycle. Relative to the base configuration, the change in cycle efficiency is plotted versus the change in component efficiency for the pilot plant in Fig. 3a. The component efficiencies were varied independently, so combined effects are not reflected; however, the slope of the line corresponding to a component gives a good

Number of Stages	Second Law Efficiency
2	0.163
3	0.330
4	0.356

Table 2. Summary of base configuration parameters

idea of the magnitude of the system's response. Fig. 3a suggests that the most significant component efficiencies are those of the helium compressor and expander 3. Some of the inefficiency of the helium compressor can be compensated for by increasing the size of the heat exchangers in the system. Fig. 3b shows the improvement of the overall cycle efficiency associated with improvements in the helium compressor efficiency and the $\Delta T/T$ parameter, which is a representation of the total heat exchange area of the system. A reasonable conclusion from Fig. 3b is that finding an efficient helium compressor should be a very high priority in the system development process.

A heat exchanger model that accounts for local variation in fluid properties was used to confirm the validity of the thermodynamic states in the system. In addition, it was used to estimate the total heat transfer conductance UA_{total} to give a more direct estimate of the required heat exchange area compared to the $\Delta T/T$ parameter. Fig. 4 shows the effect on the system efficiency of increasing UA_{total}. In Fig. 4, UA_{total} is made dimensionless by dividing by the capacity flow rate of the hydrogen entering the system to give the total number of transfer units: $NTU_{total} = \frac{UA_{total}}{\left(\dot{m}c_p\right)_{hydrogen,in}}$

$$NTU_{\text{total}} = \frac{UA_{\text{total}}}{\left(\dot{m}c_p\right)_{\text{hydrogen,in}}}$$
(3)

Fig. 4 shows that the efficiencies of both the pilot and large plants are significantly improved by marginal increases in the total heat exchange area up to a point of diminishing returns. It is desirable to design the system to operate in the flat portion of the curve because small uncertainties in the overall heat transfer coefficient U do not affect the system efficiency strongly in this regime. In this case, both the pilot and large plant base configurations would experience relatively inexpensive increases in system efficiency by adding heat exchange area.

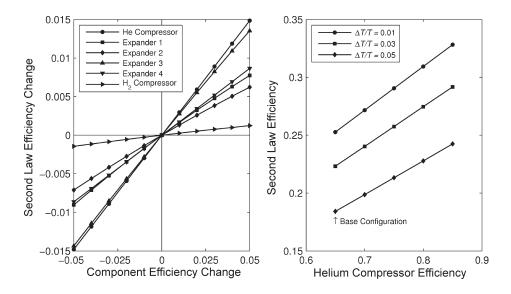


Figure 3. (a) Change in pilot plant system efficiency vs. change in component efficiency. All of the points coincide at the center which represents the base configuration. The parameters were varied one at a time. (b) The effect of helium compressor efficiency on the system efficiency for various values of the $\Delta T/T$ parameter.

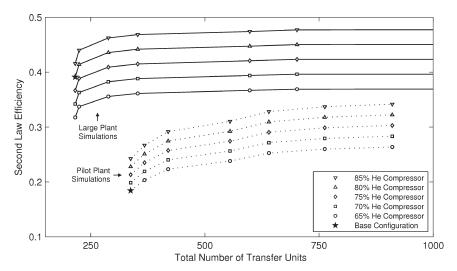


Figure 4. The effect of increasing the total heat exchange area on the second law efficiency of the system for various helium compressor isothermal efficiencies.

SUMMARY

The proposed cycle offers several advantages over a conventional Claude-cycle-based hydrogen liquefaction system. These benefits include: (1) a simple, full-yield hydrogen stream; (2) minimal hydrogen sealing and no hydrogen turbomachinery; (3) a supercritical hydrogen stream with well-balanced heat exchangers and no distinct phase change; (4) efficient pressure reduction using a single-phase wet expander; (5) a working fluid that is safe and chemically inert, and for which efficient cryogenic expanders are readily procurable; (6) overlapping low-temperature expanders that accommodate the large heat load imposed by the hydrogen stream near the critical point; (7) a design that can be upgraded with the addition of integrated ortho-para catalyst in the hydrogen stream of the heat exchangers; (8) a scalable architecture that facilitates the construction of a smaller pilot plant before the full industrial-scale plant; and finally (9) the ability to interface with high-pressure water electrolyzers to eliminate the need for additional compression of the hydrogen stream.

Simulations of the proposed cycle yielded encouraging results. A base configuration was created for both the pilot and large plant based on an assessment of reasonable component efficiencies. Various parameters such as hydrogen pressure, total number of transfer units (a function of $\Delta T/T$), and individual component efficiencies, were changed and the simulations rerun at these new operating points. The cycle efficiency was sensitive to the helium compressor efficiency and, for the pilot plant, the efficiency of expander 3. Depending on the operating point, changes in the total number of transfer units had either a strong or weak effect on the cycle efficiency.

The efficiency of the large plant appears to meet or exceed that of a current industrial-scale hydrogen liquefaction plant. The most efficient liquefaction plants have Second Law efficiencies of 30-40%. 4.12 For the base configuration of the proposed large plant, the Second Law efficiency was calculated to be 39%, and could possibly be made as high as 44% with increases in heat exchange area. For the pilot plant with less efficient components the efficiency ranged between about 18 and 25%. If the hydrogen liquefaction industry grows, the improvements offered by the large plant could result in great energy savings and appreciably reduced operating expenses, thereby improving the utility of liquid hydrogen as an energy carrier.

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REFERENCES

- 1. Ramachandran, R. and Menon, R.K., "An Overview of Industrial Uses of Hydrogen," *International Journal of Hydrogen Energy*, vol. 23 (1998), pp. 593-598.
- Staats, W.L., "Analysis of a Supercritical Hydrogen Liquefaction Cycle," M.S. Thesis, Massachusetts Institute of Technology, Cambridge, MA (2008).
- Amos, W.A., "Costs of Storing and Transporting Hydrogen," National Renewable Energy Laboratory, Golden, CO, NREL/TP-570-25106 (1998).
- 4. Strobridge, T.R., "Cryogenic Refrigerators an Updated Survey," Cryogenics Division, National Bureau of Standards, Boulder, CO, Technical Note 655 (1974).
- 5. Quack, H., "Conceptual Design of a High Efficiency Large Capacity Hydrogen Liquefier," *Adv. in Cryogenic Engineering*, Vol. 47B, Amer. Institute of Physics, Melville, NY (2002), pp. 255-263.
- 6. McIntosh, G.E., "Hydrogen Liquefiers Since 1950," *Adv. in Cryogenic Engineering*, Vol. 49B, Amer. Institute of Physics, Melville, NY (2004), pp. 9-15.
- Johnson, R.W., Collins, S.C. and Smith, Jr., J.L., "Hydraulically Operated Two-Phase Helium Expansion Engine," *Adv. in Cryogenic Engineering*, Vol. 16, Plenum Publishing Corp., New York (1971), pp. 171-177.
- 8. Lipman, M.S., Cheung, H. and Roberts, O.P., "Continuous Conversion Hydrogen Liquefaction," *Chemical Engineering Progress*, vol. 59, no. 8 (1963), pp. 49-54.
- Minta, M. "Analytical and Experimental Studies of an Optimum Helium Liquefaction Cycle," Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA (1984).
- Hutchinson, H.L., "A Kinetics Study of the Para-ortho Shift of Hydrogen," M.S. Thesis, University of Colorado, Boulder, CO (1964).
- 11. Baker, C.R. and Shaner, R.L., "A Study of the Efficiency of Hydrogen Liquefaction," *International Journal of Hydrogen Energy*, vol. 3 (1978), pp. 321-334.
- 12. Voth, R.O. and Parrish, W.R., "Studies of Hydrogen Liquefier Efficiency and the Recovery of the Liquefaction Energy", National Bureau of Standards, Boulder, CO, NBSIR 77-862 (1977).
- 13. Barron, R.F., Cryogenic Systems, 2nd ed., Oxford, New York (1985).
- Hust, J.G. and Stewart, R.B., "A Compilation of the Property Difference of Ortho and Para Hydrogen or Mixtures of Ortho and Para Hydrogen," National Bureau of Standards, Boulder, CO, NBS Report 8812 (1965).
- 15. Gross, R., Otto, W. Patzelt, A. and Wanner, M. "Liquid Hydrogen for Europe the Linde Plant at Ingolstadt," *Reports on Science and Technology*, vol. 54 (1994), pp. 37-43.