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Harnessing Liquid Air Cold Energy for Performance Enhancement of Hydrogen Liquefaction Process

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ABSTRACT

As an energy vector, hydrogen faces bulk storage and transportation challenges due to its low volumetric energy density. Following the footsteps of liquefied natural gas, hydrogen is also liquefied prior to transportation. Liquid nitrogen is usually used as the refrigerant in the precooling cycle; however, alternate candidates are also being studied. Liquid air, which is already drawing attention as a standalone cryogenic energy storage system, is one such candidate as enormous cold energy is available in its regasification phase or the discharge half-cycle. In the present study, liquid air is considered the refrigerant stream in the precooling section of the hydrogen liquefaction process. A well-known commercial simulator Aspen HYSYS® v12.1 is used for this unique concept's design and performance analysis. Composite curves analysis is performed to analyze the proposed integrated scheme's performance graphically. The specific energy consumption of 8.52 kWh/kg LH_2 has been obtained in the unoptimized base case.

Keywords: hydrogen liquefaction, hydrogen economy, ortho-para conversion; hydrogen energy network, energy storage system; liquid air energy system

NOMENCLATURE

Abbreviations	
CHX	Cryogenic Heat Exchanger
ESS	Energy Storage System
LA	Liquid Air
LAES	Liquid Air Energy System
CNESA	China Energy Storage Alliance
SEC	Specific Energy Consumption
MR	Mixed Refrigerant
CMR	Cooling Mixed Refrigerant
LMR	Liquefaction Mixed Refrigerant
MITA	Minimum Internal Temperature Approach

1. INTRODUCTION

The world energy demand and consumption have been continually increasing over the years. The energy supply and demand balance is expected to restore from 2021 onwards after getting affected by the covid-19 pandemic [1]. However, renewables have shown the highest growth rate in primary energy in these trying times, i.e., 41% [2]. The projected share of renewables in the global electricity supply is within the range of 70–85% by 2050 [3]. To materialize these projections and expectations regarding the global warming pathway of 1.5 °C above the preindustrial levels, it is essential to overcome the challenges associated with renewables, challenges like long distances between production and consumption sites, weather, and climate-dependent daily and seasonal fluctuations, and efficiency. An energy storage system (ESS) is considered a solution against the changeability and controllability of output power from renewables [4]. According to the CNESA [5] statistics report for 2020, the global operational ESSs capacity has increased by 3.4% compared to 2019 to a total capacity of 191.1 GW.

Depending on the end usage, objectives, and operational issues, different ESS technologies have been proposed. They may be classified as mechanical, chemical, electrochemical, electrical, and thermal systems, each with distinct characteristics. Cryogenic

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energy storage is a relatively new system, and since air or liquid nitrogen is the most considered option, it is generally referred to as the liquid air energy storage system (LAES). However, liquid hydrogen is also considered an important choice among cryogens. Each of these is briefly discussed in the following lines

1.1 Liquid air energy storage system

LAES is a promising candidate because of its high volumetric specific energy, making it suitable for large-scale energy storage [6]. During the off-peak times, the air is liquefied using the available grid electricity and cryogenically stored at atmospheric pressure (charging half cycle). During peak times, LA is boiled off using ambient heat, and the resultant high-pressure gas is used to generate electricity by driving a turbine (discharging half cycle) [7]. The air is compressed to 120 bar with interstage cooling in a typical configuration based on the Hampson-Linde cycle. The cold box reduces air temperature to -180 °C, followed by Joule Thompson's expansion to 1.5 bar. At the discharge end, LA relinquishes its cold energy to liquid propane (operating between -185 to -60 °C) and methanol (operating between -60 to 25 °C) before entering the combustion chamber followed by turbogenerator to produce power. These intermediary fluids help liquefy the air during the charging phase and improve the thermal efficiency of the overall process. In certain other configurations, thermal oils have been used instead of combustion chambers to evaporate and superheat the air [8].

The hybrid configuration of LAES includes integration with other heat/cold sink processes to improve the thermal and round-trip efficiencies. In this regard, the organic Rankine cycle has been the choice of many studies, whether alone [9] or in combination with the vapor compression refrigeration cycle [10] and absorption chiller system [11].

1.2 Liquid hydrogen (LH_2)

Hydrogen is another candidate for large-scale application and can be stored for a long duration. Hydrogen possesses the highest energy density of all fuels, making it an excellent choice for energy storage and grid balancer. Ever since the success of liquefied natural gas at a commercial scale, there has been a great interest in liquid hydrogen as a transportation media and an alternate energy storage system. The bottleneck, however, lies in the extremely low temperature required to liquefy hydrogen, i.e., ~-252 °C. Commercially, liquid nitrogen is used to cool gaseous hydrogen from 25 °C to -190 °C, and for further cooling and liquefaction, expanders and liquid hydrogen are used [12].

The liquefaction process requires a tremendous amount of energy, and if hydrogen itself were to provide this energy, it would consume 25-35% of the initial quantity of hydrogen. Latest hydrogen liquefaction plants have Specific Energy Consumption (SEC) in the range of 12-15 kWh/kg LH_2, while their exergy efficiencies lie within 20-30%. Theoretically, for a feed at 25 bar, the minimum work required is ~2.7 kWh/kg LH_2 [13]. In recent years, various conceptual designs have been proposed with SEC as low as 5-7 kWh/kg LH_2 and exergy efficiencies higher than 50%. To minimize the energy consumption by sharing the load on different liquefaction sections and reduce the cost of the overall process, process integration with absorption-precooling cycles [14], geothermal energy [15,16], solar energy [17], LNG regasification [18] have been studied.

Usually, hydrogen liquefaction plants are installed near cryogenic air separation plants to benefit from liquid nitrogen. In the present study, a unique integral concept is proposed whereby the cold energy of LA at the discharging half-cycle be used in the precooling section of hydrogen liquefaction. The proposed process is rigorously evaluated using the established thermodynamic techniques such as composite curves and SEC.

2. HYDROGEN LIQUEFACTION PROCESS

Hydrogen liquefaction is highly energy-intensive due to its low boiling point, second only to helium. In the commercial process, the temperature is reduced in three stages; first at -193 °C, second at -243° C, and the last is at the boiling point of hydrogen (~-252 °C). For the first stage, liquid nitrogen (b.p. -195.8 °C) is used, whereas liquid hydrogen is used for the later stages. Apart from the simple temperature drop, hydrogen liquefaction is characterized by the exothermic interconversion of its spin isomers. At 25 °C, molecular hydrogen consists of 75% ortho-hydrogen (o-H_2), with nuclei spin in the same direction, and 25% para-hydrogen (p-H_2), with nuclei spin in the opposite direction; commonly referred to as the normal hydrogen. The orientation of nuclei spin results in slightly different properties. The equilibrium between the two states is temperature-dependent and shifts towards 100% p- H_2 as the temperature decreases to 0 *K* [19,20]. Energy is, therefore, released when o-H_2 is converted to p-H_2; this is analogous to the latent heat of vaporization [21]. This equilibrium shift is of paramount importance from the liquid hydrogen storage point of view.

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3. PROPOSED PROCESS

The proposed process revolves around the concept of utilizing the available cold energy at the discharge half-cycle of LA at the precooling stage of hydrogen liquefaction. LA is pumped to a higher pressure of 35 bar during the discharge cycle since it is more economical to raise the pressure in the liquid phase. Instead of relinquishing its cold energy to intermediary fluids (as in the conventional schemes), LA is passed through the first of the three cryogenic heat exchangers (CHXs). The air in gaseous form (at 15 °C) is then passed through the combustion chamber to increase its temperature to 1300 °C before generating electricity through the expansion turbine.

Hydrogen, because of this heat integration, is reduced to -179 °C. Another point worth mentioning is the use of MR-based two refrigeration cycles working in a cascade scheme, as shown in Fig. 1. The two cycles are named after their duty as cooling MR (CMR) and liquefaction (LMR). These MRs consist of hydrocarbons and pure gases like N_2, H_2, and He in a unique composition.

The slow nature of o-H_2 conversion to p-H_2 is facilitated by catalyst placed inside the CHXs on the hydrogen side. Equilibrium reactors follow the three CHXs to achieve the p-H_2 concentration higher than 99%. H_2 gas, which enters the plant at 25 °C and 21 bar, is reduced to liquid state at -251.8 °C and 1.3 bar, which are the standard storage conditions for hydrogen.

4. SIMULATION METHODOLOGY

The entire process was simulated in Aspen HYSYS® v 12.1 as it provides an extensive database of thermodynamic properties at varying operating conditions. With the latest version, Aspen supports spin isomers of hydrogen and perfect property estimation using RefProp as the property package. The same has been employed in this study. Ortho-Para conversion is assumed to follow the equilibrium behavior. Adiabatic efficiencies of pumps, compressors, and expanders were assumed to be 80%. Minimum approach temperature (MITA) for CHXs has been maintained between 1–2 °C. Table 1 presents the composition and operating conditions of LA and gaseous hydrogen.

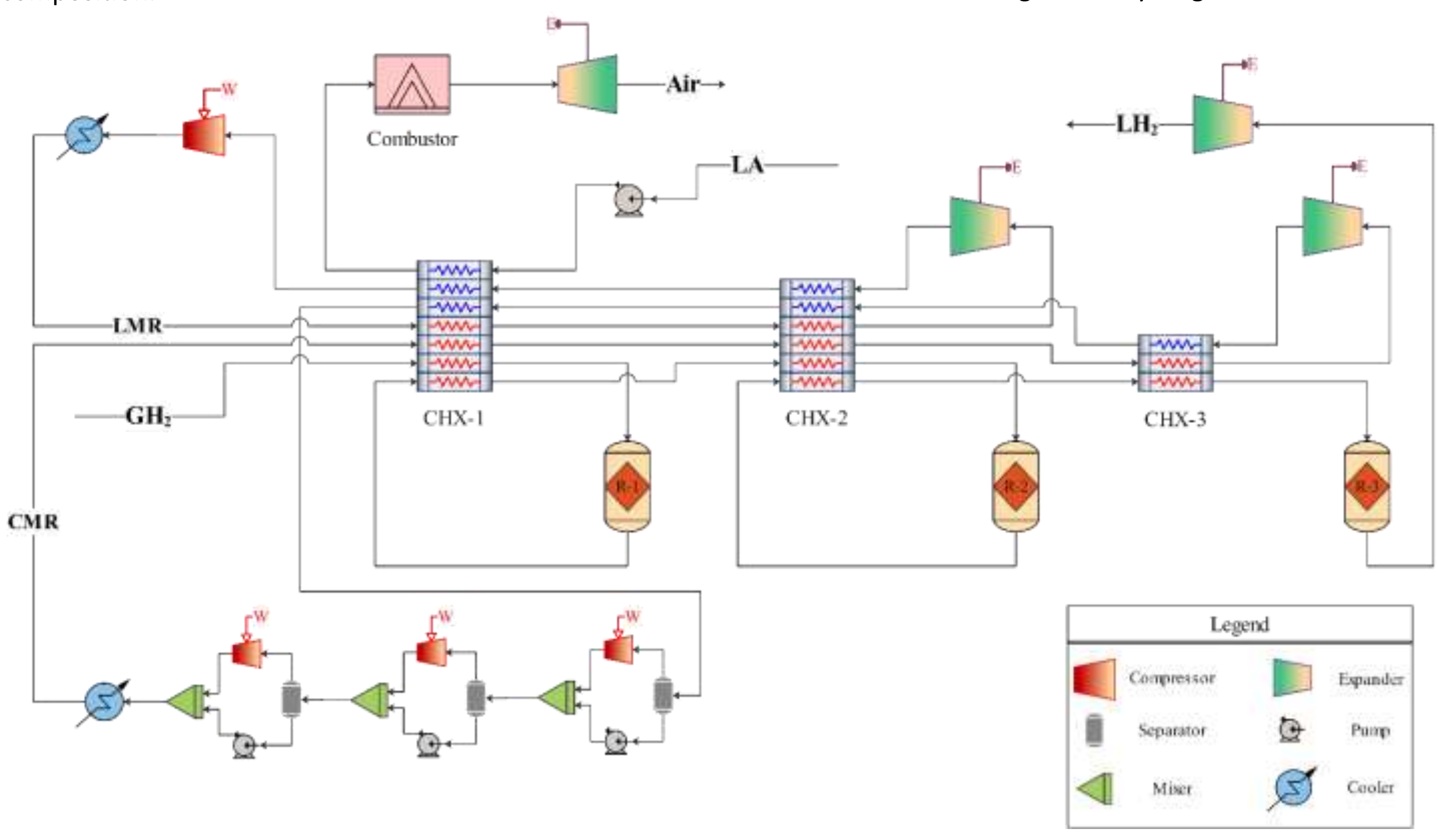

Fig. 1 *Process flowsheet of the proposed hydrogen liquefaction process integrated with LAES*

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5. RESULTS AND DISCUSSION

In this section, some of the important simulation results of the unoptimized study are presented. The itemized energy consumption of the integrated process is presented in Table 2. The highest power required is for the LMR cycle, followed by the CMR. The high concentration of the lightest gas, H_2, in the LMR is the reason for higher energy consumption.

Table 1 Feed composition

Gaseous Hydrogen	
Temperature, *°C*	25.0
Pressure, bar	21.0
Mass Flowrate, *kg/s*	31.71
o-Hydrogen	0.74925
p-Hydrogen	0.25075
Liquid Air	
Temperature, *°C*	−190.7
Pressure, *bar*	35.0
Mass Flowrate, *kg/s*	810
Nitrogen (mass fract.)	0.767
Oxygen (mass fract.)	0.233

Instead of the Joule-Thomson expansion valves, expansion turbines generate electricity while simultaneously reducing pressure. LA turbine leads the way in the power generation section and helps reduce the SEC. SEC is considered an important benchmark to gauge the performance of any process. The commercial processes of hydrogen liquefaction work at SEC of 12-15 kWh/kg LH_2. However, the proposed process boasts an SEC value of 8.52 kWh/kg LH_2, 43% less than commercial processes. Additionally, it is worth highlighting that these figures are unoptimized and can be further reduced once the entire process is rigorously improved.

Table 2 Energy requirement of the proposed process

CMR cycle pumping and compression power (*kW*)	2.949×10^5
LMR cycle compression power (*kW*)	1.348×10^6
LA pumping power (*kW*)	4.237×10^3
CMR and LMR cycles expanders output power (*kW*)	1.516×10^4
LH_2 expander output power (*kW*)	5.863×10^2
LA expander output power (*kW*)	6.459×10^5
Net power, *kW*	9.736×10^5
Specific energy consumption (SEC), kWh/kg_{LH_2}	8.53

The composite curves analysis is a conventional method to analyze the performance of CHXs. Overlapping of hot and cold composite curves indicates the heat exchanger's high efficiency, as shown in Fig. 2(a) & (b) for CHX-1 and CHX-2. A minimum approach temperature of 1-2 °C was maintained. The horizontal part of the cold composite curve in Fig. 2(c) shows the boiling of the refrigerant stream. It is known that the boil-up can absorb more heat per mass flow rate due to the latent heat of the phase change. This results in lower flow rates and less energy consumption.

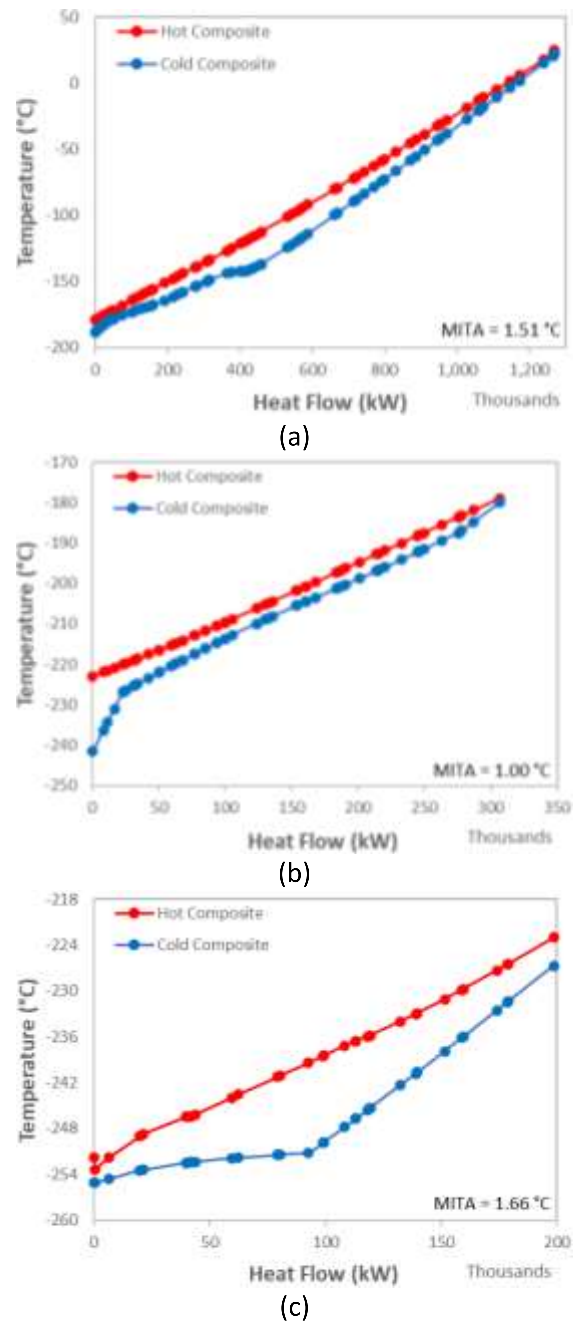

Fig. 2 Composite curves analysis for the multi-stream exchangers (a) CHX-1, (b) CHX-2, and (c) CHX-3

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6. CONCLUSIONS

A unique and efficient integral process for large-scale hydrogen liquefaction is proposed in the present study. The cold energy from the discharge half-cycle of LAES is utilized in the precooling section of the complex and energy-intensive hydrogen liquefaction process. In the unoptimized version presented here, an excellent SEC of 8.52 kWh/kg LH_2 has been achieved with a high p-H_2 concentration >99.5%. Considering the simplicity of the process and effective use of LA cold energy, the proposed process shows potential for commercialization in the near future.

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