INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (XXXX) XXX



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Solid air hydrogen liquefaction, the missing link of the hydrogen economy

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HIGHLIGHTS

 \bullet The energy required to liquefy hydrogen reduces by 25.4% with N_2 and 27.3% with $O_2.$

- \bullet Solid O₂ is a better hydrogen liquefaction energy carrier than solid N₂.
- \bullet Solid N_2 is selected as the energy carrier due to the risk explosion using $O_2.$
- \bullet The solid N_2 occupies 44.5% of the liquid H_2 tank volume.

ARTICLE INFO

Article history: Received 1 February 2023 Received in revised form 24 March 2023 Accepted 25 March 2023 Available online xxx

ABSTRACT

The most challenging aspect of developing a green hydrogen economy is long-distance oceanic transportation. Hydrogen liquefaction is a transportation alternative. However, the cost and energy consumption for liquefaction is currently prohibitively high, creating a major barrier to hydrogen supply chains. This paper proposes using solid nitrogen or oxygen as a medium for recycling cold energy across the hydrogen liquefaction supply chain. When a liquid hydrogen (LH2) carrier reaches its destination, the regasification process of the hydrogen produces solid nitrogen or oxygen. The solid nitrogen or oxygen is then

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https://doi.org/10.1016/j.ijhydene.2023.03.405

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INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (XXXX) XXX

Keywords: Hydrogen Transport Energy carrier Solid air Cryogenic refrigeration Hydrogen economy transported in the LH2 carrier back to the hydrogen liquefaction facility and used to reduce the energy consumption cooling gaseous hydrogen. As a result, the energy required to liquefy hydrogen can be reduced by 25.4% using N₂ and 27.3% using O₂. Solid air hydrogen liquefaction (SAHL) can be the missing link for implementing a global hydrogen economy. © 2023 The Author(s). Published by Elsevier Ltd on behalf of Hydrogen Energy Publications LLC. This is an open access article under the CC BY license (http://creativecommons.org/ licenses/by/4.0/).

Introduction

The world is undergoing an energy transition to reduce CO₂ emissions and mitigate climate change [1]. The most important actions underway are the increase in the role of renewable energies, energy efficiency, the electrification of the transport and heating sectors, and energy storage [2,3]. The hydrogen economy is an essential sustainable alternative that will contribute to decarbonizing the transport and heating sectors and energy storage [4]. The COVID pandemic and the war in Ukraine have further increased the interest of Europe and western countries to invest in the hydrogen economy as an alternative to fossil fuels [5]. Hydrogen significantly reduces geopolitical risks, as it vastly increases the diversity of future energy suppliers [6]. Hydrogen is a particularly interesting alternative to replace natural gas, as it is also a flexible source of electricity, and it can use existing natural gas infrastructure [7].

Hydrogen has a low volumetric energy density and, liquifying it facilitates its long-range transportation. The liquefaction of hydrogen consumes a lot of energy. Existing hydrogen liquefaction plants demand around 13 kWh of electricity per kg of hydrogen. This is around 30% of the energy stored within the hydrogen gas [8]. The theoretical minimum energy consumption for hydrogen liquefaction (298 K-20 K at 1 bar) is 3.7 kWh of electricity per kg of hydrogen, equivalent to 9.3% of the energy stored within hydrogen [8]. New processes under development can reduce energy consumption to 6 kWh of electricity per kg of hydrogen with magnetic refrigeration by reaching efficiencies of 50% of the Carnot cycle [9]. One possible configuration for a magnetic refrigeration system for H₂ liquefaction is the active magnetic regenerator (AMR) system. In this system, the magnetic material is typically a packed bed of particles, which are cycled through a series of magnetic fields to provide the cooling effect. The AMR system has been shown to have high cooling power and efficiency, making it a promising technology for H_2 liquefaction [10]. Another aspect that significantly increases liquefaction efficiency is gains in scale. For example, the increase in hydrogen liquefaction from 100 to 1000 tons per day reduces the liquefaction costs from 2 to 1 USD/kg of H₂ [8].

The use of liquid air has been proposed for different purposed for cold energy recovery [11]. For example, to store electricity with liquid air energy storage (LAES), which consists of storing thermal energy in liquid air and then using it to generate electricity [12]. The use of liquid air has been proposed for cold energy recovery of liquified natural gas (LNG) processes, similar to what is proposed in this paper [13]. Using liquid air for cold energy recovery of LNG is not practical because the liquefaction temperature of LNG is 111 K, which is higher than N_2 (77.5 K) and O_2 (89.7 K). LNG cannot liquefy N_2 and O₂ just by heat transfer. This process requires an additional refrigeration system to liquefy air where the LNG is delivered. The use of liquid air has also been proposed for cold energy recovery in stationary processes that liquify hydrogen for long-term storage of hydrogen as liquid hydrogen [14]. In this case, the liquid hydrogen (20 K) liquify N₂ and O₂ by heat transfer. LNG has also been proposed to be used as cold energy recovery for the liquefaction of H₂ [15,16]. This is not a practical solution because the main objective of the hydrogen economy is to reduce CO₂ emissions, and relying on LNG for the liquefaction of H₂ would not contribute to reducing CO₂ emissions. Taghavi et al. [17] propose an integrated system for hydrogen liquefaction using renewable energy sources. The system combines a combined heat and power system, photovoltaic cells, and liquid air energy recovery to precool hydrogen with cascade refrigeration systems using helium and hydrogen refrigerants for liquefaction. The economic evaluation of the system shows a period of return of 4.249 years, a prime price of 5.432 USD/kg LH2, and an additive value of 1.567 USD/kg LH2.

The proposed solution in this paper was named solid air hydrogen liquefaction (SAHL). The use of solid N₂ or O₂ to recover cold during the regasification of liquid H₂ has not yet been proposed in the literature. We investigate in this paper if using solid N₂ or O₂ instead of liquid air [17] would be a better alternative to recover energy across the hydrogen liquefaction supply chain. This paper is divided into six sections. Section Solid air hydrogen liquefaction presents the proposed SAHL process. Section Methodology presents the methodology applied in the paper. Section Results presents the results. Section Discussions discusses the proposed SAHL processes, and Section Conclusions concludes the paper.

Solid air hydrogen liquefaction

Fig. 1 presents the solid air hydrogen liquefaction process. The main purpose of this process is to store the cold temperatures in the liquid hydrogen delivered in solid N_2 or O_2 and use this cold to reduce the energy consumption in the liquefaction process. SAHL is divided into four main steps: H_2 regasification, solid N_2 or O_2 transportation, H_2 liquefaction and liquid H_2 transportation.

The H_2 regasification step involves extracting the cooling potential from liquid H_2 to solidify N_2 or O_2 as much as possible. This process is divided into several steps: warmer H_2 gas should cool down warmer air, colder H_2 gas should



Fig. 1 – Solid air hydrogen liquefaction process description.



Fig. 2 – (a) Solid N_2 or O_2 production process to produce 99.99% pure hydrogen and (b) hydrogen cooling energy recovery during the H_2 liquefaction process.

liquify N_2 or O_2 , and liquid H_2 should solidify N_2 or O_2 and cool it down to 20 K. To reduce costs and energy losses, we propose that the N_2 or O_2 solidification be performed within the ship's insulated storage tank, as shown in Fig. 2. Liquid N_2 or O_2 is loaded into the cryogenic tank by spraying it close to their fusion temperatures (54 and 63 K, respectively). As soon as the liquid N₂ or O₂ submerges into liquid H₂ at 20 K, the N₂ or O₂ will solidify, accumulate on the bottom of the tank and reduce its temperatures to 20 K, while the H₂ evaporates. The liquid N₂ and O₂ are sprayed into the tank in tiny droplets to



Fig. 3 – Three-phase diagram for N_2 and O_2 [20].

| Table 1 – Partial pressure of N_2 and O_2 at different cryogenic temperatures. | | | |
|--|-----------------------|------------------------|--|
| Temperature (K) | Partial pre | Partial pressure (bar) | |
| | N ₂ | O ₂ | |
| 35 | $3.711 	imes 10^{-7}$ | $9.373 	imes 10^{-8}$ | |
| 40 | $6.939 	imes 10^{-5}$ | 1.526×10^{-6} | |
| 45 | $6.783	imes10^{-4}$ | $3.03 	imes 10^{-5}$ | |
| 50 | 0.004208 | 3.096×10^{-4} | |
| 55 | 0.01875 | 0.00175 | |
| 60 | 0.06518 | 0.0075 | |

0.1786

| Table 2 – Temperature required to achieve different H_2 purity levels with N_2 or O_2 mixtures [19]. | | | | | |
|--|---------------------|----------------------------|--|--|--|
| Purity type | Purity level (%) | Requ tempera the tai | Required temperature in the tank (K) | | |
| | | N ₂ | 0 ₂ | | |
| Pure hydrogen | 99.99 | 52.9 | 61.3 | | |
| High pure hydrogen | 99.999 | 46.2 | 53.1 | | |
| Ultrapure hydrogen | 99.9999 | 40.9 | 47.4 | | |

form light crystallized solid structures (similar to snow) to avoid damaging the cryogenic tank [18]. To minimize the mixture of N₂ and O₂ in the H₂ delivered, the temperature of the cryogenic tank should be as low as possible, as shown in Fig. 3. For example, if liquid N_2 or O_2 enters the tank and solidifies at 63 K or 54 K and the H₂ leaves in equilibrium with the other gases in the tank at 63 K or 54 K, respectively, the partial pressure of N₂ at 63 K would be 0.125 bar and of O₂ at 54 K would be 0.0015 bar. Considering the hydrogen pressure in the cryogenic tank is 1 bar, the N2 and O2 concentrations would be 12.5% of N_2 and 0.15% of O_2 . The concentration of N_2 and O_2 can be significantly reduced if the temperature of the H₂ leaving the tank is lowered. Table 1 presents the partial pressures of N₂ and O₂ at different cryogenic temperatures. The approach to lower the H_2 temperature leaving the tanks consists of creating physical barriers between liquid N₂ and O₂

and the gaseous H₂ stream output from the tank. The purity of the hydrogen depends on its applications. There are three purity levels, pure hydrogen (hydrogen purity \geq 99.999%), high pure hydrogen (hydrogen purity \geq 99.9999%), and ultrapure hydrogen (hydrogen purity \geq 99.9999%) [19]. The temperature required to achieve different H₂ purity levels with N₂ and O₂ mixtures is presented in Table 2.

The solid N₂ or O₂ in Fig. 2 (b) is then transported back to the original location where the liquid H₂ was produced, using the same ship. The H₂ liquefaction process consists of extracting the cooling capacity from solid N₂ or O₂ to cool down the hydrogen gas as much as possible. The hydrogen gas enters the vessel at temperatures ranging from 35 to 65 K, cooling down to 30–60 K. Solid N₂melts at 63 K and solid O₂ melts at 54 K. After it melts, the liquid N₂ or O₂ are removed from the tank to cool down the H₂ outside the ship's tank using heat exchangers. The H₂ will be cooled to around 30 K in this process. A refrigeration system will perform the additional cooling required to liquefy the hydrogen. After the H₂ is liquefied it is added to an empty tank in the same ship. After all the tanks in the ship are filled with H₂, the ship navigates to the H₂ regasification plant.

Methodology

0.02395

Fig. 4 shows the methodological framework used in this article to evaluate the proposed SAHL process. Each stage of the technique is discussed in the subsections below to improve comprehension of the methodology. Step 1 is described in Section 2 (Solid air hydrogen liquefaction) and describes the SAHL process. It describes the H₂ regasification and liquefaction processes, how solid N2 or O2 is loaded and unloaded from the ship, and the approach in which the transportation modes can be integrated to increase the applicability of SAHL. Step 2 is described in Sections 3 (Methodology) and 4 (Results) and consists of estimating the energy conservation of the H₂ liquefaction processes with SAHL. It describes the enthalpy of H₂, N₂ and O₂, the coefficient of performance of SAHL, the volume and mass restrictions of SAHL and estimates the energy conservation with SAHL. Step 3 describes the global potential for SAHL (Section 4). It compares N₂ and O₂ as the cold carrier, compares compressed H₂ and SAHL, and discusses the global role of SAHL in a sustainable future.

The energy conservation estimates for the proposed SAHL process use the enthalpy change of hydrogen, nitrogen, and oxygen. For the sake of simplicity and to have an order of magnitude of the energy conservation, we assume that no heat is lost throughout the whole process and that the heat is completely transferred between the liquid H_2 and the solid N_2 or O_2 , and additional refrigeration is performed with 38% of Carnot efficiency. This heat balance estimates the volume and mass of liquid H_2 and the respective volume and mass of solid N_2 or O_2 produced. The three scenarios analyzed are described in Fig. 5. Scenario 1 consists of liquefying the oxygen, separating the oxygen, and extracting the cold from the oxygen and liquid hydrogen to solidify only nitrogen. Scenario 2 consists of liquefying the oxygen, separating the nitrogen, and

65

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (XXXX) XXX



Fig. 4 - Methodological framework applied to estimate the potential of SAHL.



Fig. 5 - H₂ regasification and air solidification scenarios analyzed in the paper, (a) solid nitrogen and (b) solid oxygen.

extracting the cold from the nitrogen and liquid hydrogen to solidify only oxygen.

The coefficient of performance (COP), assuming Carnot efficiency, is estimated with Equation (1). To estimate the energy conservation with SAHL, we assume an mechanic refrigeration system with an efficiency of 38% of the Carnot efficiency [9].

$$\text{COP} = \frac{T_C}{(T_H - T_C)} \times e \tag{1}$$

Where, COP is the coefficient of performance of the refrigeration system. T_C is the temperature of the cold heat source (i.e., the temperature in the evaporator). T_H is the temperature of the hot heat source, assumed to be 313 K or 40 °C. *e* is the refrigeration system's efficiency, which is assumed to be an mechanic refrigeration, and equal to 38% of the Carnot efficiency.



Fig. 6 – Coefficient of performance of hydrogen with 314 K heat source and varying cold source temperature.

The electricity required to refrigerate H_2 , N_2 or O_2 is presented in Equation 2

$$C = \sum_{Ti}^{Tf} E_T \times COP_T$$
⁽²⁾

Where, C is the electricity required for cooling H_2 , N_2 or O_2 (in kJ/kg) from temperature Ti to Tf. E_T is the enthalpy variation (in kJ/kg) of H_2 , N_2 or O_2 at temperature T (in K). COP_T is the coefficient of performance at temperature T. Ti is the initial temperature of the refrigeration process (in K). Tf is the final temperature of the refrigeration process (in K).

The methodology applied to estimate the energy recovery of SAHL consists of estimating the amount of energy conserved by recycling the cooling energy and dividing it by the total energy required to liquefy H_2 without recycling any cold. This is described in Equation (3). To facilitate the estimation, the methodology only considers the heat that can be extracted directly from the solid N_2 or O_2 to cool down H_2 with heat exchangers. Any additional cooling

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INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (XXXX) XXX



Fig. 7 – (a) enthalpy of oxygen and nitrogen [21], (b) enthalpy of normal hydrogen [22], (c) relative enthalpy of hydrogen, nitrogen and oxygen, (d) electricity consumption for reducing the temperature of H_2 in 5 °C steps from 300 to 20 K, with a 313 K heat source, (e) enthalpy of H_2 , N_2 and O_2 during the H_2 regasification process, (f) enthalpy of H_2 , N_2 and O_2 during the H_2 regasification process, (f) enthalpy of H_2 , N_2 and O_2 during the H_2 regasification process.

potential that could be used with a refrigeration system is not considered.

$$R = 1 - \frac{E_{with SAHL}}{E_{without SAHL}}$$
(3)

 $E_{without SAHL}$ is the electricity demand for liquefying H₂ without SAHL (in kWh/kg of H₂).

Where, R is the percentage of electrical energy consumption reduced with the SAHL process in (%), $E_{with SAHL}$ is the electricity demand for liquefying H₂ with SAHL (in kWh/kg of H₂),

Results

Fig. 6 presents the COP of cryogenic refrigeration processes assuming the heat source with 314 K (40 $^{\circ}$ C). The figure shows

6

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (XXXX) XXX

| Table 3 – Electricity consumption for liquefying H_2 with and without SAHL. | | | |
|---|-----------------------------|-----------------------------|---------------------|
| | H ₂ liquefaction | N ₂ liquefaction | O_2 liquefaction |
| Without SAHL - Regasification | | | |
| Electricity consumption (kWh) | 0 | 0 | 0 |
| Without SAHL – Liquefaction | | | |
| Temperature (K) | 300 (G) - 20 (L) | - | - |
| Relative mass (kg) | 1 | - | - |
| Enthalpy change (kJ) | 1.11 | - | - |
| Average COP | 0.12 | - | - |
| Electricity consumption (kWhe) | 9.29 | 0 | 0 |
| With SAHL - Regasification | | | |
| Temperature (K) | - | 77.5 (G) - 77.5 (L) | 89.7 (G) - 89.7 (L) |
| Relative mass (kg) | - | 6.43 | 6.52 |
| Enthalpy change (kWht) | - | 0.275 | 0.308 |
| COP | - | 0.125 | 0.153 |
| Electricity consumption (kWh) | 0 | 2.20 | 2.02 |
| With SAHL - Liquefaction | | | |
| Temperature range (K) | 20 (G) – 20 (L) | - | - |
| Relative mass (kg) | 1 | - | - |
| Enthalpy change (kWht) | 0.125 | - | - |
| COP | 0.026 | - | - |
| Electricity consumption (kWhe) | 4.73 | 0 | 0 |

the COP with Carnot efficiency, 50%, 30% and 10% of the Carnot efficiency.

Fig. 7 (a) presents the enthalpy of nitrogen and oxygen from 0 to 350 K [21]. The enthalpy difference between solid nitrogen and oxygen at 20 K to gas nitrogen at 300 K is 554.23 and 547.26 kJ/kg, respectively. The latent heat of liquefaction of N₂ is 200 kJ/kg at 77.4 K, and O_2 is 213 kJ/kg at 90 K [21]. N_2 and O_2 also store a significant amount of heat in a solid state due to the latent heat required to change its solid structures. N₂ solidifies at 63.1 K with a latent heat of 25.7 kJ/kg, and changes its solid state from β to α at 35.6 K with 8 kJ/kg [21]. O₂ solidifies at 54.4 K with 13.9 kJ/kg, changes its solid state from γ to β at 43.8 K with 13.9 kJ/kg, then from β to α at 23.6 K with 6.1 kJ/kg [21]. Fig. 7 (b) presents the enthalpy of hydrogen from 14 to 350 K, assuming normal hydrogen at saturation, i.e., where orthohydrogen and parahydrogen molecules are in equilibrium [22]. The enthalpy difference between liquid hydrogen at 20 K and gas hydrogen at 300 K is 4733.78 kJ/kg [22]. The latent heat of liquefaction of H₂ is 448.9 kJ/kg at 20.37 K [22]. With a mass of hydrogen 7.15 and 7.24 times lower than the mass of nitrogen and oxygen, respectively, the relative enthalpy change is presented in Fig. 7 (c).

To estimate the electricity consumption to liquefy H_2 from 300 K to 20 K without SAHL, we combine the COP of the Carnot cycle (Fig. 6), assuming a 38% efficiency (Equation (1))with the enthalpy of hydrogen in Fig. 7 (b), and apply Equation (2). This results in Fig. 7 (d), which shows the electricity demand for refrigeration of H_2 in increments of 5 °C starting from 20 K up to 300 K. The electricity required to lower the temperature of hydrogen from 300 K to 20 K is 33.460 kJ/kg, which is equivalent to 9.29 kWh/kg, where 17.014 kJ/kg is required to cool down hydrogen from 25 K to 20 K. Table 3 compares the electricity consumption for liquefying H_2 with and without SAHL.

To estimate the electricity consumption to liquefy H_2 from 300 K to 20 K with SAHL, we need to take into account the electricity required to liquefy N_2 and O_2 during the regasification process (Fig. 1) and the electricity required to liquefy

Table 4- The volume and mass of liquid $H_2,$ solid $N_2 \mbox{ or } O_2$ in the shipping process.

| | | Proposed | scenario |
|--|----------------|----------------------------|----------------------------|
| | H ₂ | N_2 | O ₂ |
| Trip direction | Outbound | Return | Return |
| Mass carried in the ship (tons) | 6000 | 38,580 | 39,120 |
| Weigh comparison with H ₂ | 1 | 6.43 | 6.52 |
| Density at 1 bar and 20 K (kg/m ³) | 71.27 | 1029.5 [<mark>23</mark>] | 1312.5 [<mark>24</mark>] |
| Volume in the ship (m ³) | 84,187 | 37,475 | 29,806 |
| Share of ship volume (%) | 100 | 44.5 | 35.4 |

the H₂ during the liquefaction process (Fig. 1). To estimate the electricity requirement during the regasification process, we analyze Fig. 7 (e). It compares the relative enthalpy of H₂ (as in Fig. 7 (c)) with 90% of the enthalpy of N₂ and O₂ (as in Fig. 7 (c)). This corresponds to a mass of N₂ of 6.43 kg and O₂ 6.52 kg per kg of H₂. This mass of N₂ and O₂ was selected because it supplies all the energy needed to cool H₂ from 300 K to 21 K (H₂ gas), as shown in Fig. 7 (f). The electricity required during regasification is to supply part of the energy to liquefy N₂ (dark red line in Fig. 7 (e)) and O₂ (light red line in Fig. 7 (e)). This consists of 990 kJ/kg of liquid H₂ to liquefy N₂ (or 0.275 kWht) and 1109 kJ/kg of liquid H₂ to liquefy O₂ (or 0.308 kWht). Assuming a 38% efficiency of the Carnot cycle and liquefaction temperatures of 77.5 for N₂ and 89.7 K for O₂, a hot source temperature of 313 K, and applying Equation (1), the COP for

| Table 5 – Comparison of using solid N_2 or O_2 to liquefy $H_2.$ | | | |
|--|---------------|-------------|--|
| | Solid N_2 | Solid O_2 | |
| Vaporization temperature (K) | -77.5 | -89.7 | |
| Fusion temperature (K) | -62.6 | -53.16 | |
| Volume of solid compared with volume | 44.5 | 35.4 | |
| of liquid H ₂ (%) | | | |
| Safety | Non-explosive | e Explosive | |



Fig. 8 – Possible location for the liquid hydrogen production plant (LH_2PP) in the Northeast region of Brazil, (a) top view, (b) side view. Taken from Ref. [7].

this refrigeration process is 0.125 and 0.153, respectively. Applying Equation (2), this results in electricity consumption of 2.2 kWh for N₂ and 2.02 kWh for O₂. This process does not use 1387 kJ/kg of liquid H₂ with N₂, and 1506 kJ/kg of liquid H₂ with O₂ at a temperature range of 200 K–300 K. This underutilized heat could be used to reduce the electricity consumed to liquefy N₂ and O₂. This is not included in the paper because it would require complex models to estimate its contribution to the reduction electricity consumption.

To estimate the electricity requirement during the liquefaction process, we analyze Fig. 7 (f). It compares the relative enthalpy of H_2 (as in Fig. 7 (c)) with 90% of the enthalpy of N_2 and O_2 (as in Fig. 7 (c)). This supplies all the energy needs to cool H₂ from 300 K to 20 K (H₂ gas), as shown in Fig. 7 (f). Thus, the only electricity required is to supply energy to liquefy H₂ (dark red line in Fig. 7 (f)). This consists of 449 kJ/kg of liquid H₂ to liquefy H₂ (or 0.125 kWht). Assuming a 38% efficiency of the Carnot cycle and liquefaction temperatures of 20 K, hot source temperature of 313 K, and applying Equation (1), the COP for this refrigeration process is 0.026. This results in electricity consumption of 4.73 kWhe. According to Equation (3) and Table 3, the electricity requirements reduction comparing the liquefaction of H₂ with and without SAHL is 25.4% (1-(2.2 + 4.73)/9.29 for N₂ and 27.3% ((1-2.02 + 4.73)/9.29) for O₂. This value could increase if the under-utilized cooling potential in Fig. 7 (e) is utilized to liquefy N2 and O2. These estimates assume no heat loss in the SAHL process and the additional energy required to transport the liquid N_2 or O_2 .

Another important aspect is to analyze the density of the solid N_2 and O_2 to check if the ship could transport the cold temperatures back to the H_2 liquefaction plant. Table 4 presents the volume and mass of liquid H_2 , solid N_2 and O_2 in the ships.

As mentioned, the proposed mass of hydrogen is 6.43 and 6.52 times smaller than the mass of nitrogen and oxygen, respectively. Assuming the outbound ship carries 6000 tons of hydrogen, it will have to carry 38,580 tons of nitrogen, and 39,120 tons of oxygen, respectively. This is equivalent to a volume of 37,475 m³ of nitrogen and 29,806 m³ of oxygen, respectively. As the volume of hydrogen in the ship is 84,187 m³, the share of the volume utilized in the return trip will be 44.5% of nitrogen, and 35.4% of oxygen, respectively. This is convenient because all the cold that could be extracted from the regasification of H₂ can be carried back to the H₂ liquefaction facility. However, the weight of the solid nitrogen and oxygen will be heavier than the hydrogen carried. Thus, the ship must be designed to support the extra weight for the return trip.

Discussions

The equations applied in this paper to estimate the energy recovery from SAHL processes is only an initial estimate and are based on the assuming the overall refrigeration system's efficiency. Applying the same equations, the change in refrigeration efficiency from 38% to 50% of Carnot efficiency does not impact the percentage of energy recovered from the SAHL processes. However, it impacts the absolute energy consumption. To achieve more realistic estimates, the refrigeration system proposed in SAHL should be modeled using specific cryogenic refrigeration software or a general processing simulation software, a detailed analysis should be performed to estimate the energy losses throughout the process, and the additional energy required to transport the solid N_2 or O_2 should be included.

Comparing the use of liquid [17] or solid air to recover energy across the hydrogen liquefaction supply chain, a few important points must be considered. The main advantages of using solid air are: (i) more cooling potential can be transported in the ship, (ii) the amount of cold transported per kg of solid air is higher than for liquid air, (iii) the temperature of solid air can reach 20 K, liquid N₂ is limited to 77.46 K and O₂ 89.7 K, (iv) storing cold at lower temperatures reduce the electricity consumption in the H₂ liquefaction process. The main disadvantages of using solid air are: (i) the need to liquefy N₂ or O₂ in the H₂ regasification plant (i) the high investment costs required to liquefy N₂ or O₂ in the H₂ regasification plant, (ii) the electricity cost in the H₂ liquefaction plant.

For future work, we suggest: (i) the development of a computational fluid dynamics model to better estimate heat transfer phenomena between H_2 , N_2 and O_2 in the cryogen tanks, (ii) a detailed study on the risk of fire and explosion of the use of O_2 to carry the cold temperatures, (iii) an estimate of the heat loss in the SAHL process and N_2 and O_2 boil-off, (iv) additional investigation and relevant studies regarding the characteristics of solid N_2 and O_2 , and their impact on the SAHL process, (v) create a computational model with a process flow diagram of the SAHL process to better estimate the energy savings and cost reductions of the system.

Table 5 compares the advantages and disadvantages of using solid N₂ or O₂ for recycling the cooling energy from H₂ regasification. N₂ is convenient for storing cold due to its lower vaporization temperature compared to O₂. O₂ is better because the fusion temperature is lower than nitrogen's. Another advantage of O₂ is that it occupies a smaller volume in the ship. The biggest disadvantage of O₂ is that it will be a mixture of H₂ in the ship's tank and can result in a large explosion. For this reason, the most interesting alternative is to use solid nitrogen to carry the cold. Another advantage of producing O₂ where the H₂ is delivered is that the O₂ can be used to generate electricity with oxy-combustion at high temperatures, high efficiencies, zero NOx emissions, and facilitate the capture and storage of CO₂. The captured CO₂ could then be used to produce synthetic fuels.

Energy efficiency and storage integration with SAHL

Another strategy to reduce the consumption of energy with the liquefaction of hydrogen is to use seawater at depths of 1000 m, with a temperature of 3-5 °C (which results in a 10 °C is the hot energy source of the refrigeration cycle) [25–28], instead of using the ambient temperature (30–35 °C) in the liquefaction process, as described in Fig. 8 [7]. Applying Equations (1) and (2), the electricity consumption for H₂ liquefaction can be reduced by 12.5% [7].

SAHL can be combined with seasonal hydrogen storage so that the H_2 liquefaction facility and liquid H_2 carrier ship can operate throughout the year. For example, if the demand for hydrogen has a strong seasonal fluctuation, the hydrogen can be transported constantly with SAHL and the hydrogen is stored in salt caverns where there is demand for hydrogen. Alternatives to store electricity seasonally are: seasonal pumped hydropower storage [29–36], compressed air [37] and gravity energy storage [38–40].

Conclusions

The paper has presented a proposal to solidify air in the regasification process of H₂ to recycle the cold temperatures in liquid H₂ and, thus, reduce the energy consumption and costs of H₂ liquefaction. This regenerative solution has shown the potential to reduce the energy required to liquefy H₂ is 25.4% using solid nitrogen and 27.3% using solid oxygen. Solid nitrogen occupies 44.5% of the volume of the liquid H₂. Solid oxygen occupies 35.4%. Future work will be performed to develop a detailed description of the entire process chain to describe in more detail the heat recovered from the SAHL process. We propose not to use solid O₂ in SAHL. This is because we propose that the solidification process happens with the hydrogen entering in direct contact with the liquid H₂ within the ship's tank, which can cause an explosion. For this, the O_2 from air will have to be separated from the N_2 during the H₂ regasification process. SAHL has the potential to become the best alternative to transport hydrogen between continents in the future H₂ economy.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was funded by the project entitled "Desenvolvimento de Roadmap e Projeto Piloto de H_2 do Complexo de Pecém" within the scope of R&D ANEEL program and financed by EDP.

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international journal of hydrogen energy XXX (XXXX) XXX

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