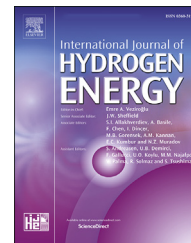


Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

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

Julian David Hunt<sup>a,\*</sup>, Pedro Marin Montanari<sup>b</sup>, Diego Nieto Hummes<sup>b</sup>,  
Masoud Taghavi<sup>c,d</sup>, Behanm Zakeri<sup>a</sup>, Oldrich Joel Romero<sup>e</sup>, Wenji Zhou<sup>f</sup>,  
Marcos Aurélio Vasconcelos de Freitas<sup>g</sup>, Nivalde José de Castro<sup>g</sup>,  
Paulo Smith Schneider<sup>b</sup>, Yoshihide Wada<sup>h,a</sup>

<sup>a</sup> International Institute of Applied Systems Analysis (IIASA), Austria

<sup>b</sup> Federal University of Rio Grande do Sul, Brazil

<sup>c</sup> School of Chemical Engineering and Materials Science, Chung-Ang University, 84, Heukseok-ro, Dongjak-gu, Seoul, 06974, Republic of Korea

<sup>d</sup> Department of Mechanical Engineering, Technical and Vocational University (TVU), Tehran, Iran

<sup>e</sup> Federal University of Espírito Santo, Brazil

<sup>f</sup> Renmin University, China

<sup>g</sup> Federal University of Rio de Janeiro, Brazil

<sup>h</sup> Center for Desert Agriculture, King Abdullah University of Science and Technology, East Thuwal 23955-6900, Saudi Arabia

## HIGHLIGHTS

- The energy required to liquefy hydrogen reduces by 25.4% with N<sub>2</sub> and 27.3% with O<sub>2</sub>.
- Solid O<sub>2</sub> is a better hydrogen liquefaction energy carrier than solid N<sub>2</sub>.
- Solid N<sub>2</sub> is selected as the energy carrier due to the risk explosion using O<sub>2</sub>.
- The solid N<sub>2</sub> occupies 44.5% of the liquid H<sub>2</sub> tank volume.

## ARTICLE INFO

### Article history:

Received 1 February 2023

Received in revised form

24 March 2023

Accepted 25 March 2023

Available online 27 April 2023

## 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 (LH<sub>2</sub>) carrier reaches its destination, the regasification process of the hydrogen produces solid nitrogen or oxygen. The solid nitrogen or oxygen is then

\* Corresponding author.

E-mail address: [hunt@iiasa.ac.at](mailto:hunt@iiasa.ac.at) (J.D. Hunt).

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

0360-3199/© 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/>).

**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 N<sub>2</sub> and 27.3% using O<sub>2</sub>. 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 CO<sub>2</sub> 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, liquefying 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 H<sub>2</sub> 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<sub>2</sub> 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 H<sub>2</sub> [8].

The use of liquid air has been proposed for different purposes 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 liquefied 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<sub>2</sub> (77.5 K) and O<sub>2</sub> (89.7 K). LNG cannot liquefy N<sub>2</sub> and O<sub>2</sub> 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 liquefy hydrogen for long-term storage of hydrogen as liquid hydrogen [14]. In this case, the liquid hydrogen (20 K) liquefy N<sub>2</sub> and O<sub>2</sub> by heat transfer. LNG has also been proposed to be used as cold energy recovery for the liquefaction of H<sub>2</sub> [15,16]. This is not a practical solution because the main objective of the hydrogen economy is to reduce CO<sub>2</sub> emissions, and relying on LNG for the liquefaction of H<sub>2</sub> would not contribute to reducing CO<sub>2</sub> 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 LH<sub>2</sub>, and an additive value of 1.567 USD/kg LH<sub>2</sub>.

The proposed solution in this paper was named solid air hydrogen liquefaction (SAHL). The use of solid N<sub>2</sub> or O<sub>2</sub> to recover cold during the regasification of liquid H<sub>2</sub> has not yet been proposed in the literature. We investigate in this paper if using solid N<sub>2</sub> or O<sub>2</sub> 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<sub>2</sub> or O<sub>2</sub> and use this cold to reduce the energy consumption in the liquefaction process. SAHL is divided into four main steps: H<sub>2</sub> regasification, solid N<sub>2</sub> or O<sub>2</sub> transportation, H<sub>2</sub> liquefaction and liquid H<sub>2</sub> transportation.

The H<sub>2</sub> regasification step involves extracting the cooling potential from liquid H<sub>2</sub> to solidify N<sub>2</sub> or O<sub>2</sub> as much as possible. This process is divided into several steps: warmer H<sub>2</sub> gas should cool down warmer air, colder H<sub>2</sub> gas should

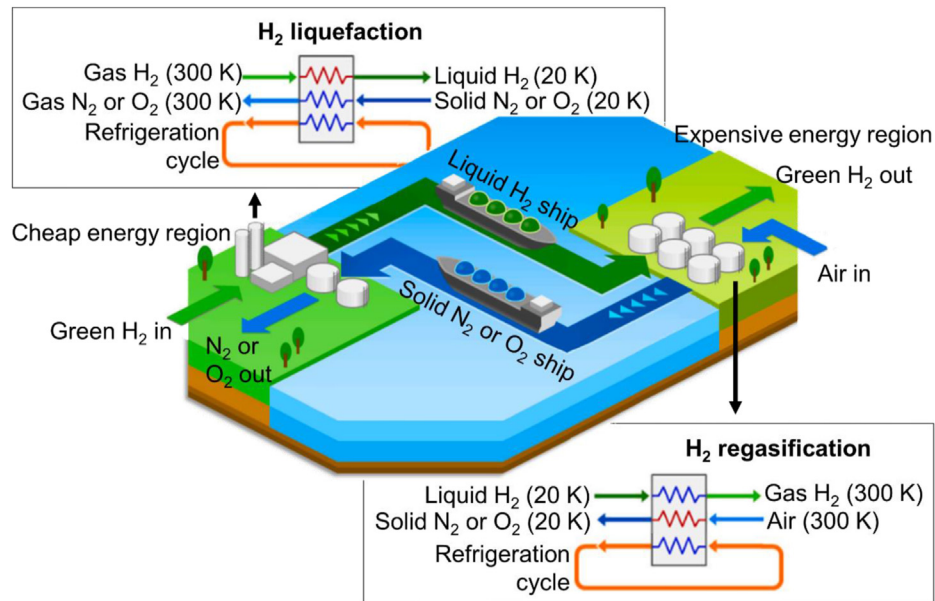


Fig. 1 – Solid air hydrogen liquefaction process description.

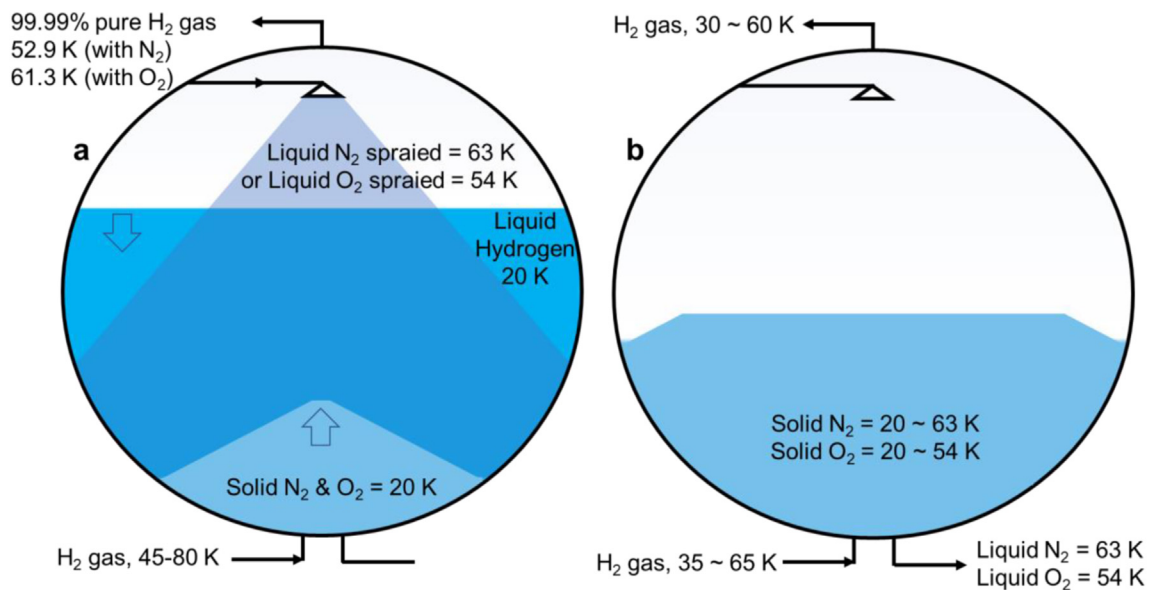


Fig. 2 – (a) Solid  $N_2$  or  $O_2$  production process to produce 99.99% pure hydrogen and (b) hydrogen cooling energy recovery during the  $H_2$  liquefaction process.

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  $N_2$  or  $O_2$  submerges into liquid  $H_2$  at 20 K, the  $N_2$  or  $O_2$  will solidify, accumulate on the bottom of the tank and reduce its temperatures to 20 K, while the  $H_2$  evaporates. The liquid  $N_2$  and  $O_2$  are sprayed into the tank in tiny droplets to

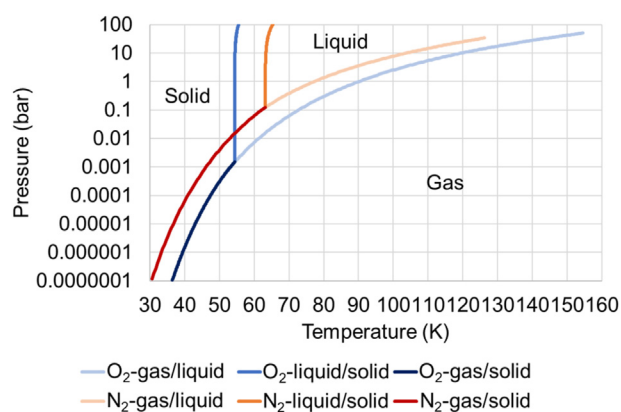


Fig. 3 – Three-phase diagram for N<sub>2</sub> and O<sub>2</sub> [20].

Table 1 – Partial pressure of N<sub>2</sub> and O<sub>2</sub> at different cryogenic temperatures.

Temperature (K)	Partial pressure (bar)	
	N <sub>2</sub>	O <sub>2</sub>
35	$3.711 \times 10^{-7}$	$9.373 \times 10^{-8}$
40	$6.939 \times 10^{-5}$	$1.526 \times 10^{-6}$
45	$6.783 \times 10^{-4}$	$3.03 \times 10^{-5}$
50	0.004208	$3.096 \times 10^{-4}$
55	0.01875	0.00175
60	0.06518	0.0075
65	0.1786	0.02395

Table 2 – Temperature required to achieve different H<sub>2</sub> purity levels with N<sub>2</sub> or O<sub>2</sub> mixtures [19].

Purity type	Purity level (%)	Required temperature in the tank (K)	
		N <sub>2</sub>	O <sub>2</sub>
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 N<sub>2</sub> and O<sub>2</sub> in the H<sub>2</sub> delivered, the temperature of the cryogenic tank should be as low as possible, as shown in Fig. 3. For example, if liquid N<sub>2</sub> or O<sub>2</sub> enters the tank and solidifies at 63 K or 54 K and the H<sub>2</sub> leaves in equilibrium with the other gases in the tank at 63 K or 54 K, respectively, the partial pressure of N<sub>2</sub> at 63 K would be 0.125 bar and of O<sub>2</sub> at 54 K would be 0.0015 bar. Considering the hydrogen pressure in the cryogenic tank is 1 bar, the N<sub>2</sub> and O<sub>2</sub> concentrations would be 12.5% of N<sub>2</sub> and 0.15% of O<sub>2</sub>. The concentration of N<sub>2</sub> and O<sub>2</sub> can be significantly reduced if the temperature of the H<sub>2</sub> leaving the tank is lowered. Table 1 presents the partial pressures of N<sub>2</sub> and O<sub>2</sub> at different cryogenic temperatures. The approach to lower the H<sub>2</sub> temperature leaving the tanks consists of creating physical barriers between liquid N<sub>2</sub> and O<sub>2</sub>

and the gaseous H<sub>2</sub> stream output from the tank. The purity of the hydrogen depends on its applications. There are three purity levels, pure hydrogen (hydrogen purity  $\geq 99.99\%$ ), high pure hydrogen (hydrogen purity  $\geq 99.999\%$ ), and ultrapure hydrogen (hydrogen purity  $\geq 99.9999\%$ ) [19]. The temperature required to achieve different H<sub>2</sub> purity levels with N<sub>2</sub> and O<sub>2</sub> mixtures is presented in Table 2.

The solid N<sub>2</sub> or O<sub>2</sub> in Fig. 2 (b) is then transported back to the original location where the liquid H<sub>2</sub> was produced, using the same ship. The H<sub>2</sub> liquefaction process consists of extracting the cooling capacity from solid N<sub>2</sub> or O<sub>2</sub> 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 N<sub>2</sub> melts at 63 K and solid O<sub>2</sub> melts at 54 K. After it melts, the liquid N<sub>2</sub> or O<sub>2</sub> are removed from the tank to cool down the H<sub>2</sub> outside the ship's tank using heat exchangers. The H<sub>2</sub> 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 H<sub>2</sub> is liquefied it is added to an empty tank in the same ship. After all the tanks in the ship are filled with H<sub>2</sub>, the ship navigates to the H<sub>2</sub> regasification plant.

## Methodology

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 H<sub>2</sub> regasification and liquefaction processes, how solid N<sub>2</sub> or O<sub>2</sub> 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 H<sub>2</sub> liquefaction processes with SAHL. It describes the enthalpy of H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>, 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 N<sub>2</sub> and O<sub>2</sub> as the cold carrier, compares compressed H<sub>2</sub> 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<sub>2</sub> and the solid N<sub>2</sub> or O<sub>2</sub>, and additional refrigeration is performed with 38% of Carnot efficiency. This heat balance estimates the volume and mass of liquid H<sub>2</sub> and the respective volume and mass of solid N<sub>2</sub> or O<sub>2</sub> 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

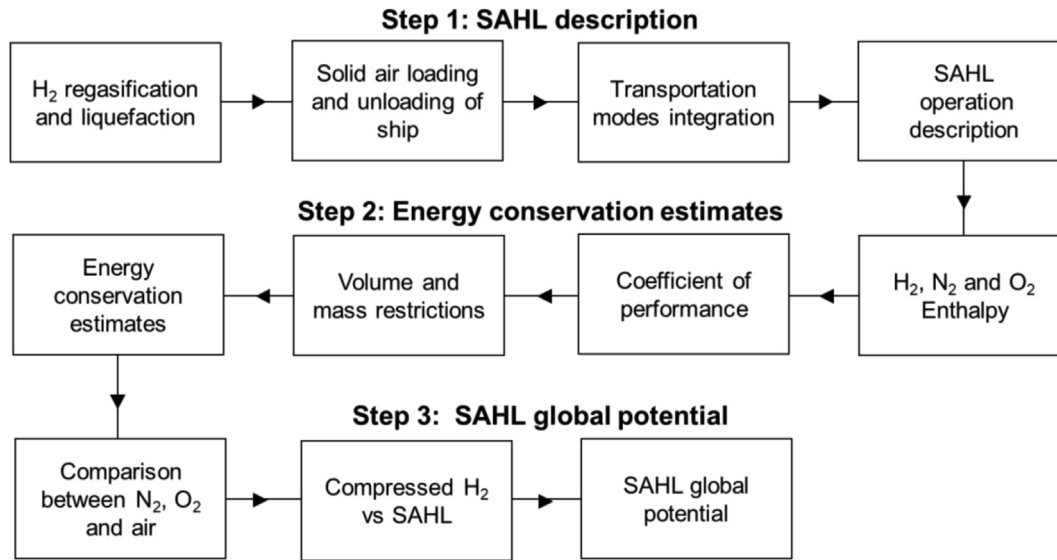


Fig. 4 – Methodological framework applied to estimate the potential of SAHL.

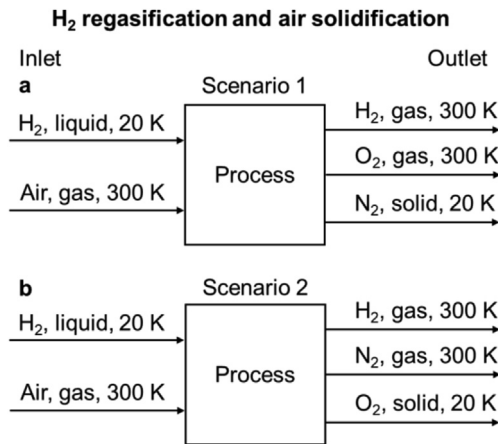


Fig. 5 – H<sub>2</sub> regasification and air solidification scenarios analyzed in the paper, (a) solid nitrogen and (b) solid oxygen.

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 a mechanical refrigeration system with an efficiency of 38% of the Carnot efficiency [9].

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

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 mechanical refrigeration, and equal to 38% of the Carnot efficiency.

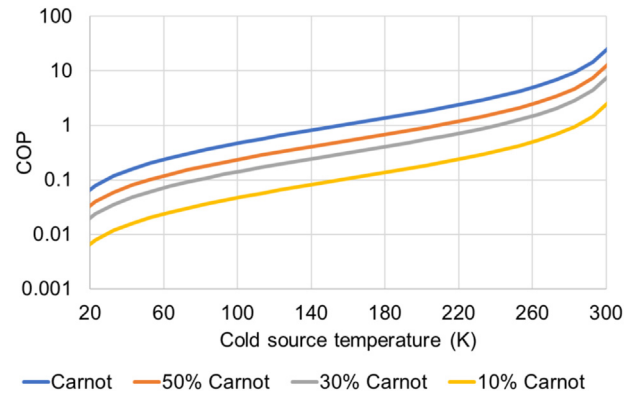


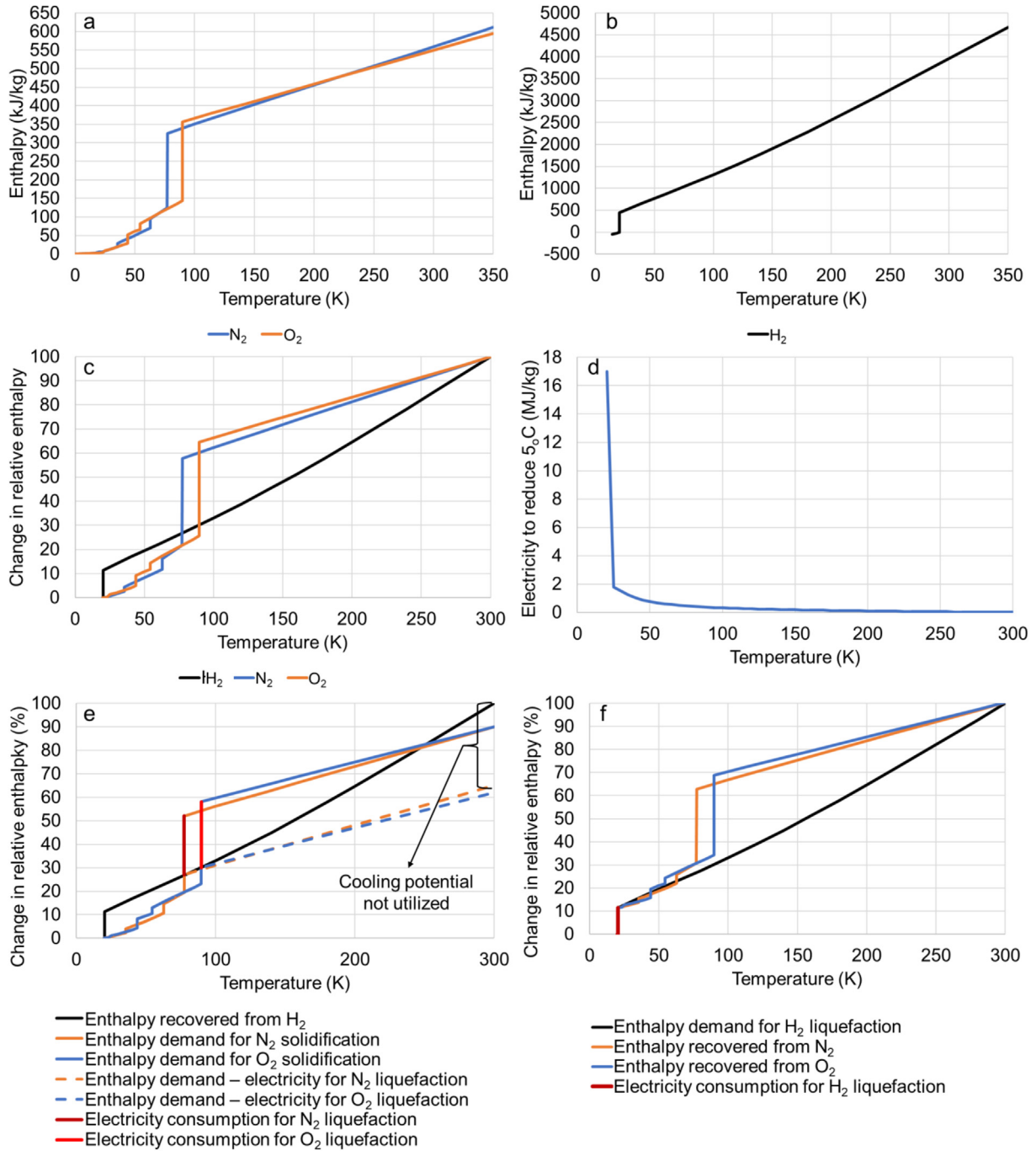
Fig. 6 – Coefficient of performance of hydrogen with 314 K heat source and varying cold source temperature.

The electricity required to refrigerate H<sub>2</sub>, N<sub>2</sub> or O<sub>2</sub> is presented in Equation 2

$$C = \sum_{T_i}^{T_f} E_T \times \text{COP}_T \quad (2)$$

Where,  $C$  is the electricity required for cooling H<sub>2</sub>, N<sub>2</sub> or O<sub>2</sub> (in kJ/kg) from temperature  $T_i$  to  $T_f$ .  $E_T$  is the enthalpy variation (in kJ/kg) of H<sub>2</sub>, N<sub>2</sub> or O<sub>2</sub> at temperature  $T$  (in K).  $\text{COP}_T$  is the coefficient of performance at temperature  $T$ .  $T_i$  is the initial temperature of the refrigeration process (in K).  $T_f$  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<sub>2</sub> 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<sub>2</sub> or O<sub>2</sub> to cool down H<sub>2</sub> with heat exchangers. Any additional cooling



**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<sub>2</sub> in 5 °C steps from 300 to 20 K, with a 313 K heat source, (e) enthalpy of H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> during the H<sub>2</sub> regasification process, (f) enthalpy of H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> during the H<sub>2</sub> liquefaction process.

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

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

Where, R is the percentage of electrical energy consumption reduced with the SAHL process in (%),  $E_{\text{with SAHL}}$  is the electricity demand for liquefying H<sub>2</sub> with SAHL (in kWh/kg of H<sub>2</sub>),

$E_{\text{without SAHL}}$  is the electricity demand for liquefying H<sub>2</sub> without SAHL (in kWh/kg of H<sub>2</sub>).

## Results

Fig. 6 presents the COP of cryogenic refrigeration processes assuming the heat source with 314 K (40 °C). The figure shows

**Table 3 – Electricity consumption for liquefying H<sub>2</sub> with and without SAHL.**

	H <sub>2</sub> liquefaction	N <sub>2</sub> liquefaction	O <sub>2</sub> 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 (kWh)	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 (kWh)	–	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 (kWh)	0.125	–	–
COP	0.026	–	–
Electricity consumption (kWh)	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 N<sub>2</sub> is 200 kJ/kg at 77.4 K, and O<sub>2</sub> is 213 kJ/kg at 90 K [21]. N<sub>2</sub> and O<sub>2</sub> also store a significant amount of heat in a solid state due to the latent heat required to change its solid structures. N<sub>2</sub> 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]. O<sub>2</sub> 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 H<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> with and without SAHL.

To estimate the electricity consumption to liquefy H<sub>2</sub> from 300 K to 20 K with SAHL, we need to take into account the electricity required to liquefy N<sub>2</sub> and O<sub>2</sub> during the regasification process (Fig. 1) and the electricity required to liquefy

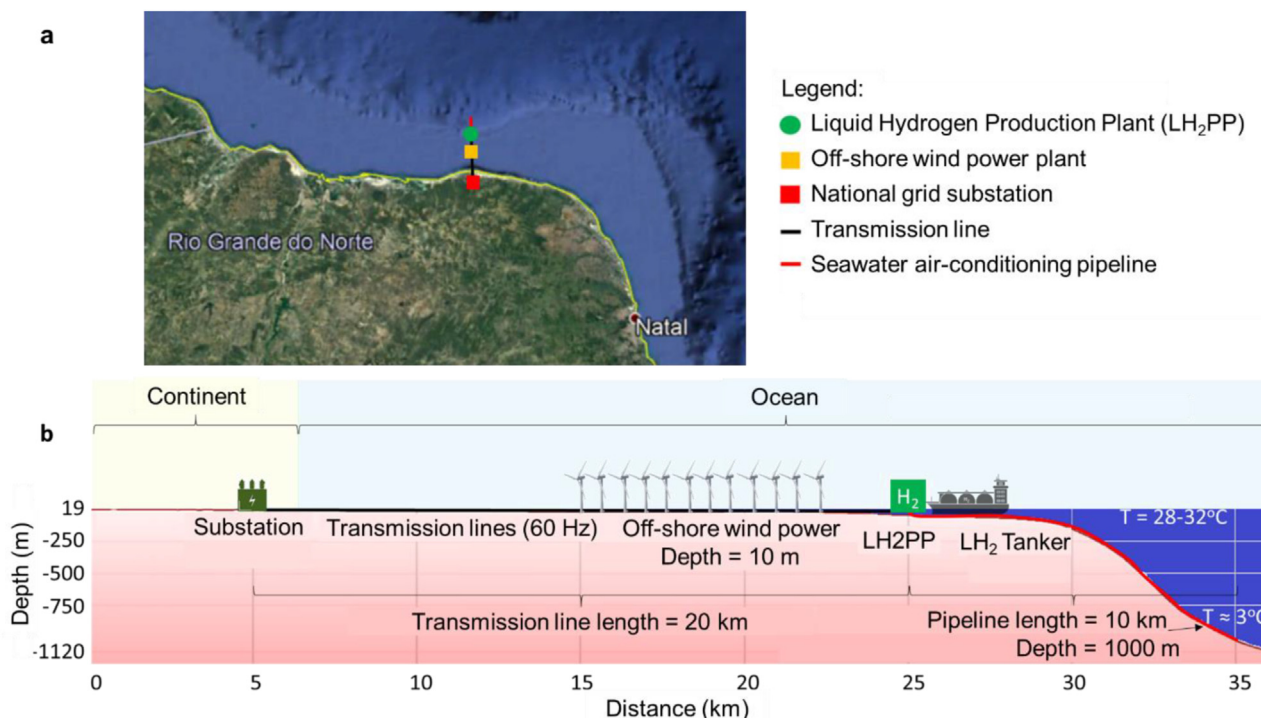
**Table 4 – The volume and mass of liquid H<sub>2</sub>, solid N<sub>2</sub> or O<sub>2</sub> in the shipping process.**

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

the H<sub>2</sub> 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 H<sub>2</sub> (as in Fig. 7 (c)) with 90% of the enthalpy of N<sub>2</sub> and O<sub>2</sub> (as in Fig. 7 (c)). This corresponds to a mass of N<sub>2</sub> of 6.43 kg and O<sub>2</sub> 6.52 kg per kg of H<sub>2</sub>. This mass of N<sub>2</sub> and O<sub>2</sub> was selected because it supplies all the energy needed to cool H<sub>2</sub> from 300 K to 21 K (H<sub>2</sub> gas), as shown in Fig. 7 (f). The electricity required during regasification is to supply part of the energy to liquefy N<sub>2</sub> (dark red line in Fig. 7 (e)) and O<sub>2</sub> (light red line in Fig. 7 (e)). This consists of 990 kJ/kg of liquid H<sub>2</sub> to liquefy N<sub>2</sub> (or 0.275 kWh) and 1109 kJ/kg of liquid H<sub>2</sub> to liquefy O<sub>2</sub> (or 0.308 kWh). Assuming a 38% efficiency of the Carnot cycle and liquefaction temperatures of 77.5 for N<sub>2</sub> and 89.7 K for O<sub>2</sub>, a hot source temperature of 313 K, and applying Equation (1), the COP for

**Table 5 – Comparison of using solid N<sub>2</sub> or O<sub>2</sub> to liquefy H<sub>2</sub>.**

	Solid N <sub>2</sub>	Solid O <sub>2</sub>
Vaporization temperature (K)	–77.5	–89.7
Fusion temperature (K)	–62.6	–53.16
Volume of solid compared with volume of liquid H <sub>2</sub> (%)	44.5	35.4
Safety	Non-explosive	Explosive



**Fig. 8 – Possible location for the liquid hydrogen production plant (LH<sub>2</sub>PP) 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 N<sub>2</sub> and 2.02 kWh for O<sub>2</sub>. This process does not use 1387 kJ/kg of liquid H<sub>2</sub> with N<sub>2</sub>, and 1506 kJ/kg of liquid H<sub>2</sub> with O<sub>2</sub> at a temperature range of 200 K–300 K. This under-utilized heat could be used to reduce the electricity consumed to liquefy N<sub>2</sub> and O<sub>2</sub>. 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<sub>2</sub> (as in Fig. 7 (c)) with 90% of the enthalpy of N<sub>2</sub> and O<sub>2</sub> (as in Fig. 7 (c)). This supplies all the energy needs to cool H<sub>2</sub> from 300 K to 20 K (H<sub>2</sub> gas), as shown in Fig. 7 (f). Thus, the only electricity required is to supply energy to liquefy H<sub>2</sub> (dark red line in Fig. 7 (f)). This consists of 449 kJ/kg of liquid H<sub>2</sub> to liquefy H<sub>2</sub> (or 0.125 kWh). 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 kWh. According to Equation (3) and Table 3, the electricity requirements reduction comparing the liquefaction of H<sub>2</sub> with and without SAHL is 25.4%  $(1 - (2.2 + 4.73)/9.29)$  for N<sub>2</sub> and 27.3%  $((1 - 2.02 + 4.73)/9.29)$  for O<sub>2</sub>. This value could increase if the under-utilized cooling potential in Fig. 7 (e) is utilized to liquefy N<sub>2</sub> and O<sub>2</sub>. These estimates assume no heat loss in the SAHL process and the additional energy required to transport the liquid N<sub>2</sub> or O<sub>2</sub>.

Another important aspect is to analyze the density of the solid N<sub>2</sub> and O<sub>2</sub> to check if the ship could transport the cold temperatures back to the H<sub>2</sub> liquefaction plant. Table 4 presents the volume and mass of liquid H<sub>2</sub>, solid N<sub>2</sub> and O<sub>2</sub> 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 m<sup>3</sup> of nitrogen and 29,806 m<sup>3</sup> of oxygen, respectively. As the volume of hydrogen in the ship is 84,187 m<sup>3</sup>, 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 H<sub>2</sub> can be carried back to the H<sub>2</sub> 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<sub>2</sub> or O<sub>2</sub> 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 N<sub>2</sub> is limited to 77.46 K and O<sub>2</sub> 89.7 K, (iv) storing cold at lower temperatures reduce the electricity consumption in the H<sub>2</sub> liquefaction process. The main disadvantages of using solid air are: (i) the need to liquefy N<sub>2</sub> or O<sub>2</sub> in the H<sub>2</sub> regasification plant (ii) the high investment costs required to liquefy N<sub>2</sub> or O<sub>2</sub> in the H<sub>2</sub> regasification plant, (iii) the electricity cost in the H<sub>2</sub> regasification plant is generally higher than the H<sub>2</sub> liquefaction plant.

For future work, we suggest: (i) the development of a computational fluid dynamics model to better estimate heat transfer phenomena between H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> in the cryogen tanks, (ii) a detailed study on the risk of fire and explosion of the use of O<sub>2</sub> to carry the cold temperatures, (iii) an estimate of the heat loss in the SAHL process and N<sub>2</sub> and O<sub>2</sub> boil-off, (iv) additional investigation and relevant studies regarding the characteristics of solid N<sub>2</sub> and O<sub>2</sub>, 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 N<sub>2</sub> or O<sub>2</sub> for recycling the cooling energy from H<sub>2</sub> regasification. N<sub>2</sub> is convenient for storing cold due to its lower vaporization temperature compared to O<sub>2</sub>. O<sub>2</sub> is better because the fusion temperature is lower than nitrogen's. Another advantage of O<sub>2</sub> is that it occupies a smaller volume in the ship. The biggest disadvantage of O<sub>2</sub> is that it will be a mixture of H<sub>2</sub> 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 O<sub>2</sub> where the H<sub>2</sub> is delivered is that the O<sub>2</sub> can be used to generate electricity with oxy-combustion at high temperatures, high efficiencies, zero NO<sub>x</sub> emissions, and facilitate the capture and storage of CO<sub>2</sub>. The captured CO<sub>2</sub> 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 H<sub>2</sub> liquefaction can be reduced by 12.5% [7].

SAHL can be combined with seasonal hydrogen storage so that the H<sub>2</sub> liquefaction facility and liquid H<sub>2</sub> 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 H<sub>2</sub> to recycle the cold temperatures in liquid H<sub>2</sub> and, thus, reduce the energy consumption and costs of H<sub>2</sub> liquefaction. This regenerative solution has shown the potential to reduce the energy required to liquefy H<sub>2</sub> is 25.4% using solid nitrogen and 27.3% using solid oxygen. Solid nitrogen occupies 44.5% of the volume of the liquid H<sub>2</sub>. 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 O<sub>2</sub> in SAHL. This is because we propose that the solidification process happens with the hydrogen entering in direct contact with the liquid H<sub>2</sub> within the ship's tank, which can cause an explosion. For this, the O<sub>2</sub> from air will have to be separated from the N<sub>2</sub> during the H<sub>2</sub> regasification process. SAHL has the potential to become the best alternative to transport hydrogen between continents in the future H<sub>2</sub> 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<sub>2</sub> do Complexo de Pecém” within the scope of R&D ANEEL program and financed by EDP.

## REFERENCES

- [1] Li K, Tan X, Yan Y, Jiang D, Qi S. Directing energy transition toward decarbonization: the China story. *Energy* 2022; 261:124934. <https://doi.org/10.1016/j.energy.2022.124934>.
- [2] Sorknæs P, Johannsen RM, Korberg AD, Nielsen TB, Petersen UR, Mathiesen BV. Electrification of the industrial sector in 100% renewable energy scenarios. *Energy* 2022;254:124339. <https://doi.org/10.1016/j.energy.2022.124339>.
- [3] Bellocchi S, Manno M, Noussan M, Prina MG, Vellini M. Electrification of transport and residential heating sectors in support of renewable penetration: scenarios for the Italian energy system. *Energy* 2020;196:117062. <https://doi.org/10.1016/j.energy.2020.117062>.
- [4] Nastasi B, Lo Basso G. Hydrogen to link heat and electricity in the transition towards future Smart Energy Systems. *Energy* 2016;110:5–22. <https://doi.org/10.1016/j.energy.2016.03.097>.
- [5] Zakeri B, Paulavets K, Barreto-Gomez L, Echeverri LG, Pachauri S, Boza-Kiss B, et al. Pandemic, war, and global energy transitions. *Energies* 2022;15. <https://doi.org/10.3390/en15176114>.
- [6] Van de Graaf T, Overland I, Scholten D, Westphal K. The new oil? The geopolitics and international governance of

- hydrogen. *Energy Res Social Sci* 2020;70:101667. <https://doi.org/10.1016/j.erss.2020.101667>.
- [7] Hunt JD, Nascimento A, Nascimento N, Vieira L, Romero O. Possible pathways for oil and gas companies in a sustainable future: from the perspective of a hydrogen economy. *Renew Sustain Energy Rev* 2022;160:112291. <https://doi.org/10.1016/j.rser.2022.112291>.
- [8] Ghafri S, Munro S, Cardella U, Funke T, Notardonato W, Trusler J, et al. Hydrogen liquefaction: a review of the fundamental physics, engineering practice and future opportunities. *Energy Environ Sci* 2022;15. <https://doi.org/10.1039/D2EE00099G>.
- [9] Aziz M. Liquid hydrogen: a review on liquefaction, storage, transportation, and safety. *Energies* 2021;14. <https://doi.org/10.3390/en14185917>.
- [10] Kamran MS, Ahmad HO, Wang HS. Review on the developments of active magnetic regenerator refrigerators – evaluated by performance. *Renew Sustain Energy Rev* 2020;133:110247. <https://doi.org/10.1016/j.rser.2020.110247>.
- [11] Qi M, Park J, Lee I, Moon I. Liquid air as an emerging energy vector towards carbon neutrality: a multi-scale systems perspective. *Renew Sustain Energy Rev* 2022;159:112201. <https://doi.org/10.1016/j.rser.2022.112201>.
- [12] Borri E, Tafone A, Romagnoli A, Comodi G. A review on liquid air energy storage: history, state of the art and recent developments. *Renew Sustain Energy Rev* 2021;137:110572. <https://doi.org/10.1016/j.rser.2020.110572>.
- [13] Park J, You F, Mun H, Lee I. Liquefied natural gas supply chain using liquid air as a cold carrier: novel method for energy recovery. *Energy Convers Manag* 2021;227:113611. <https://doi.org/10.1016/j.enconman.2020.113611>.
- [14] Taghavi M, Salarian H, Ghorbani B. Thermodynamic and exergy evaluation of a novel integrated hydrogen liquefaction structure using liquid air cold energy recovery, solid oxide fuel cell and photovoltaic panels. *J Clean Prod* 2021;320:128821. <https://doi.org/10.1016/j.jclepro.2021.128821>.
- [15] Noh W, Park S, Kim J, Lee I. Comparative design, thermodynamic and techno-economic analysis of utilizing liquefied natural gas cold energy for hydrogen liquefaction processes. *Int J Energy Res* 2022;46:12926–47. <https://doi.org/10.1002/er.8064>.
- [16] Cho S, Park J, Noh W, Lee I, Moon I. Developed hydrogen liquefaction process using liquefied natural gas cold energy: design, energy optimization, and techno-economic feasibility. *Int J Energy Res* 2021;45:14745–60. <https://doi.org/10.1002/er.6751>.
- [17] Taghavi M, Salarian H, Ghorbani B. Economic evaluation of a hybrid hydrogen liquefaction system utilizing liquid air cold recovery and renewable energies. *Renew Energy Res Appl* 2023;4:125–43. <https://doi.org/10.22044/rera.2022.11899.1122>.
- [18] Yamashita Y, Kato M, Arakawa M. Experimental study on the rheological properties of polycrystalline solid nitrogen and methane: implications for tectonic processes on Triton. *Icarus* 2010;207:972–7. <https://doi.org/10.1016/j.icarus.2009.11.032>.
- [19] Yang Y, Wang G, Zhang L, Zhang S, Lin L. Comparison of hydrogen specification in national standards for China. *E3S Web Conf* 2019;118:3042. <https://doi.org/10.1051/e3sconf/201911803042>.
- [20] Air Liquide. Air liquide gas encyclopedia. *Air Liquide* 2023. <https://encyclopedia.airliquide.com/>. (accessed on: 10/01/2023)
- [21] Marquet P. On the computation of moist-air specific thermal enthalpy: moist-air Specific Thermal Enthalpy. *Q J R Meteorol Soc* 2015;141. <https://doi.org/10.1002/qj.2335>.
- [22] Leachman J, Jacobsen R, Penoncello S, Lemmon E. Fundamental equations of state for parahydrogen, normal hydrogen, and orthohydrogen. *J Phys Chem Ref Data - J PHYS CHEM REF DATA* 2009;38. <https://doi.org/10.1063/1.3160306>.
- [23] Satorre MA, Domingo M, Luna R, Santonja C. *Density of methane and nitrogen at different temperatures*. Springer; 2004.
- [24] Roder HM. The molar volume (density) of solid oxygen in equilibrium with vapor. *J Phys Chem Ref Data* 1978;7:949–58.
- [25] Hunt JD, Weber N de AB, Zakeri B, Diaby AT, Byrne P, Filho WL, et al. Deep seawater cooling and desalination: combining seawater air conditioning and desalination. *Sustain Cities Soc* 2021;74. <https://doi.org/10.1016/j.scs.2021.103257>.
- [26] Hunt JD, Zakeri B, Nascimento A, Garnier B, Pereira MG, Bellezoni RA, et al. High velocity seawater air-conditioning with thermal energy storage and its operation with intermittent renewable energies. *Energy Effic* 2020. <https://doi.org/10.1007/s12053-020-09905-0>.
- [27] Hunt JD, Byers E, Sánchez AS. Technical potential and cost estimates for seawater air conditioning. *Energy* 2019; 166:979–88. <https://doi.org/10.1016/j.energy.2018.10.146>.
- [28] Hunt JD, Nascimento A, Zakeri B, Barbosa PSF, Costalonga L. Seawater air-conditioning and ammonia district cooling: a solution for warm coastal regions. *Energy* 2022;254:124359. <https://doi.org/10.1016/j.energy.2022.124359>.
- [29] Hunt JD, Zakeri B, Nascimento A, Brandão R. 3 - pumped hydro storage (PHS). In: Letcher TMBT-SE. Second E. Elsevier; 2022. p. 37–65. <https://doi.org/10.1016/B978-0-12-824510-1.00008-8>.
- [30] Hunt JD, Falchetta G, Parkinson S, Vinca A, Zakeri B, Byers E, et al. Hydropower and seasonal pumped hydropower storage in the Indus basin: pros and cons. *J Energy Storage* 2021;41:102916. <https://doi.org/10.1016/j.est.2021.102916>.
- [31] Zakeri B, Hunt JD, Laldjebaev M, Krey V, Vinca A, Parkinson S, et al. Role of energy storage in energy and water security in Central Asia. *J Energy Storage* 2022;50:104587. <https://doi.org/10.1016/j.est.2022.104587>.
- [32] Hunt JD, Freitas MAV, Pereira Junior AO. A review of seasonal pumped-storage combined with dams in cascade in Brazil. *Renew Sustain Energy Rev* 2017;70. <https://doi.org/10.1016/j.rser.2016.11.255>.
- [33] Hunt JD, Byers E, Riahi K, Langan S. Comparison between seasonal pumped-storage and conventional reservoir dams from the water, energy and land nexus perspective. *Energy Convers Manag* 2018;166:385–401.
- [34] Hunt JD, Byers E, Wada Y, Parkinson S, Gernaat D, Langan S, et al. Global resource potential of seasonal pumped-storage for energy and water storage. *Nat Commun* 2020;11:947.
- [35] Hunt JD, Freitas MAV, Junior AOP. Enhanced-Pumped-Storage: combining pumped-storage in a yearly storage cycle with dams in cascade in Brazil. *Energy* 2014. <https://doi.org/10.1016/j.energy.2014.10.038>.
- [36] Hunt JD, Zakeri B, Lopes R, Barbosa P, Nascimento A, Castro N, et al. Existing and new arrangements of pumped-hydro storage plants. *Renew Sustain Energy Rev* 2020;129:109914.
- [37] Hunt JD, Zakeri B, Nascimento A, de Jesus Pacheco DA, Patro ER, Đurin B, et al. Isothermal deep ocean compressed air energy storage: An affordable solution for seasonal energy storage. *Energies* 2023;16(7):3118. <https://doi.org/10.3390/en16073118>.

- [38] Hunt JD, Zakeri B, Falchetta G, Nascimento A, Wada Y, Riahi K. Mountain Gravity Energy Storage: a new solution for closing the gap between existing short- and long-term storage technologies. *Energy* 2020;190:116419. <https://doi.org/10.1016/j.energy.2019.116419>.
- [39] Hunt JD, Jurasz J, Zakeri B, Nascimento A, Cross S, Caten CS, et al. Electric truck hydropower, a flexible solution to hydropower in mountainous regions. *Energy* 2022;248:123495. <https://doi.org/10.1016/j.energy.2022.123495>.
- [40] Hunt JD, Zakeri B, Jurasz J, Tong W, Dąbek PB, Brandão R, et al. Underground gravity energy storage: A solution for long-term energy storage. *Energies* 2023;16:825. <https://doi.org/10.3390/en16020825>.