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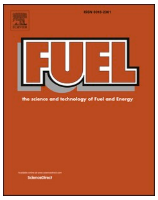

Review article

A Review of Hydrogen Production from Onboard Ammonia Decomposition: Maritime Applications of Concentrated Solar Energy and Boil-Off Gas Recovery

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ABSTRACT

The growing interest in the potential role of hydrogen in reducing CO_2 emissions as an energy carrier has significant implications in the natural gas industry. Hydrogen will eventually replace natural gas as the most widely used cleaner energy carrier. However, due to the challenges of transporting pure hydrogen and its technological immaturity, transporting ammonia would be a practical alternative. Furthermore, unlike hydrogen, ammonia's distribution and transportation system has already been developed widely and is adaptable to several novel and promising purposes. Additionally, it is noted that ammonia commonly acts as a hydrogen carrier, meaning that the end product is likely to be hydrogen. Hence, there is a need to convert ammonia into hydrogen at the destination port or onboard. To date, existing literature primarily focuses on hydrogen production in general. There is a lack of intensive research on hydrogen production from ammonia decomposition, especially considering the boil-off gas recovery on board. Furthermore, there are limited studies on solar integration infrastructure for energy carrier ships due to the conventional utilization on land, in factories, or onshore plants. Therefore, this paper aims to comprehensively review various ammonia decomposition techniques to produce clean hydrogen by recovering the boil-off ammonia while integrating solar energy infrastructures onboard the energy carrier ship for electricity and heat requirements. Four techniques of ammonia decomposition were investigated: thermal decomposition, catalytic membrane reactor, electrochemical decomposition, and ammonia cracker integrated Solid Oxide Fuel Cell. Moreover, parabolic through collectors, linear Fresnel reflectors, solar dishes, and solar towers were examined as potential solar energy technologies for onboard applications. The selection of natural refrigerants and reliquefication methods was also studied based on their limiting and determining factors to define the suitable options for the reliquefication of boil-off gas onboard.

Abbreviations: AC, Alternating Current; ASHRAE, American Society for Heating Refrigerating and Air-Conditioning; ATRM, Autothermal Reforming of Methanol; BC, Brayton Cooling; BOG, Boil Off Gas; BOR, Boil Off Rate; C3MR, Propane pre-cooled Mixed Refrigerant; CCD, Central Composite Design; CDP, Cesium Dihydrogen Phosphate; CFC, Chlorofluorocarbons; CMR, Catalytic Membrane Reactor; CNG, Compressed Natural Gas; CSP, Concentrated Solar Power; DC, Direct Current; DMR, Dual Mixed Refrigerant; DNI, Direct Normal Irradiation; EL, Electrocatalyst Layer; FPSO, Floating Production Storage and Offloading; GHG, Greenhouse Gases; GHI, Global Horizontal Irradiation; GSR, Glycerol Steam Reforming; GWP, Global Warming Potential; HC, Hydrocarbons; HCFC, Hydrochlorofluorocarbons; HFC, Hydrofluorocarbons; HFO, Heavy Fuel Oil; HFO, Hydrofuoroolefin; HTF, Heat Transfer Fluid; HTP, Human Toxicity Potential; ICE, Internal Combustion Engine; LFR, Linear Fresnel Reflector; LNG, Liquefied Natural Gas; LOHC, Liquid Organic Hydrogen Carrier; LPG, Liquefied Petroleum Gas; MCH, Methylcyclohexane; MR, Mixed Refrigerants; MRC, Mixed Refrigerant Cycle; MSHE, Multi-Stream Heat Exchanger; MSR, Methanol Steam Reforming; NG, Natural Gas; NTP, Normal Temperature and Pressure; ODP, Ozone Depletion Potential; ODS, Ozone Depletion Substance; PCEC, Proton Ceramic Electrolytic Cells; PCFC, Proton Ceramic Fuel Cells; PMR, Plasma Membrane Reactor; PRICO, Poly Refrigerant Integral Cycle Operation; PSA, Pressure Swing Adsorption; PSDS, Parabolic Solar Dish Stirling; Pt-Rh, Rhodium-Platinum; PTC, Parabolic Trough Collectors; PV, Photovoltaic; R-SOC, Reversible Solid Oxide Cell; Ru, Ruthenium; SAFC, Solid Alkaline Fuel Cells; SD, Solar Dish; SE, Stirling Engine; SEGS, Solar Electric Generating Systems; SMR, Single Mixed Refrigerant; SOEC, Solid Oxide Electrolytic Cells; SOFC, Solid Oxide Fuel Cells; ST, Solar Tower; TCL, Thermal-cracking Catalyst Layer; TES, Thermal Energy Storage; TSA, Temperature Swing Adsorption; WMR, Warm Mixed Refrigerant.

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1. Introduction

Natural gas has been the most prevalent and dependable form of energy generation for decades. Unlike renewables with intermittent supply, natural gas could provide continuous supply in significant quantities with stable infrastructure, technology, and transportation system. However, while the natural gas industry might seem robust and resilient, it is not close to being and maintaining sustainability. Profile [1] reported that to meet the need for energy, over 36 billion tons of CO_2 are released into the atmosphere annually, that over 90% of these emissions come from fossil fuels and are anticipated to rise much more in the upcoming years. This is where alternative and clean energy carriers come into play, aiming to shift toward a more sustainable present and, thus, the future. One of the most influential and promising clean energy carriers is hydrogen. However, it does not occur in nature in large quantities in its molecular form (it is usually found bonded or in combination with other elements rather than existing as pure molecular hydrogen, such as with oxygen (in water, H_2O) or carbon (in hydrocarbons)). Therefore, this prospective energy carrier must be developed using renewable feedstocks and a sustainable energy source to achieve a negligible or zero carbon footprint and meet a zero-carbon economy's demands. In general, the most common methods of producing hydrogen currently and commercially are via Methanol Steam Reforming (MSR), bio-oil model molecules reforming, Glycerol Steam Reforming (GSR), gasification, Autothermal Reforming of Methanol (ATRM), photocatalytic method, and the electrolysis of water [2]. Apart from water electrolysis, other clean hydrogen productions from renewable sources can be potentially achieved from the decomposition of ammonia (considering the ammonia production itself is via renewable feedstocks) or by employing microorganisms to produce biophotolysis, thermal energy (thermolysis) and photonic energy (photo-electrolysis), as well as biomass [3].

Furthermore, the absence of carbon in hydrogen makes it a "clean alternative" to natural gas; hence during combustion, hydrogen does not create carbon emissions during utilization [4]. Several studies have proven many superiorities of hydrogen as a clean energy substitute. Kalinci et al. [5] claims that hydrogen has the potential to offer cost-effective, dependable, clean solutions with significant social advantages in many applications. According to Singh et al. [6] reports, hydrogen can facilitate the widespread usage and unlimited market potential of renewable energy resources. While Cipriani et al. [7] researched how hydrogen is essential as a supplement to electricity on the end-user (service) side to store intermittent renewable energy, which is a tremendous step towards greening the energy systems. Additionally, in the literature written by Uyar & Beşikci [8], hydrogen is expected to fulfill 18% of global energy demand by 2050, eliminate 6 Gt of CO_2 emissions annually, and provide 30 million new jobs. Similarly, by the year 2050, Mostafaeipour et al. [9] reported that hydrogen could be powered by approximately 400 million vehicles, 15 to 20 million trucks, and about 5 million buses, or roughly 20 to 25 percent of the transportation sector. Moreover, a study by Nakamura et al. [10] anticipated that hydrogen energy systems would function at better efficiency in the future and have significant economic and environmental benefits. Therefore, hydrogen is viewed as the key to sustainable growth and a remedy for the problems caused by global warming, as examined by González et al. [11]. However, technological immaturity and unsettled policy make especially hydrogen transport challenging.

In addition to that, utilizing conventional onboard hydrogen storage technology still faces cost and safety challenges. Hydrogen can be chemically stored as solid hydrides, hydrocarbons, or liquid ammonia to enhance efficiency and reduce losses during transportation and storage [12]. Another hydrogen storage and delivery alternative is Liquid Organic Hydrogen Carrier (LOHC) technology [13]. LOHCs can be transported sufficiently over any distance using the existing liquid fuel transportation technologies (pipelines, shipping vessels, and cargo vehicles) and stored for a long time like traditional liquid fuels. However, most LOHC materials have lower hydrogen content, from around 5% to 10%, compared to ammonia. This means ammonia can store more hydrogen per unit weight, resulting in higher energy density. Moreover, the efficiency of hydrogen release from LOHC materials can be lower than ammonia. The hydrogenation and dehydrogenation reactions in LOHC systems often involve additional energy inputs and require specific operating conditions. This can result in energy losses and reduced overall system efficiency [13]. After all, among these available options, liquefied ammonia is a carbon-free and easily transported hydrogen carrier that enables the cost-effective storage and distribution of significant amounts of renewable energy. As a hydrogen energy carrier, ammonia contains 17.6% hydrogen by weight. It can be transported and stored as a liquid at 20 °C under 8.6 bars [14] and –33 °C under 1 bar [15]. Additionally, liquid ammonia has a higher volumetric hydrogen density than liquid hydrogen itself (i.e., liquid hydrogen has about 70 kg of H_2/m^3 at 20 K, while liquid ammonia has 106 kg of H_2/m^3 at 300 K and 1.0 MPa) [16].

Therefore, these problems can be solved by employing onboard hydrogen production from ammonia rather than hydrogen storage itself; the two prominent techniques to produce hydrogen from ammonia are thermal cracking and electrocatalysis [17]. Ammonia with reliable storage, transportation, and explosion safety characteristics is the future pathway for sustainable hydrogen production. Furthermore, according to Sittichompoo et al. [18] report, employing Ruthenium (Ru) as the catalyst can boost the conversion ratio from ammonia to hydrogen by 50% while utilizing a Rhodium-Platinum (Pt-Rh) catalyst can increase the value to 60%.

1.1. Significance and contribution

The usage of hydrogen in various industries is widespread, and it produces no greenhouse gas byproducts when it is utilized because it only produces water when it is oxidized. More than 90% of all atoms in the universe are made of hydrogen, which is also the lightest (molecular weight: 2.016) and non-toxic [19]. Therefore, it is essential to develop effective and dependable storage and transportation system to address the hydrogen energy markets. Gaseous hydrogen is liquefied by compressing and cooling it to below − 253 °C. Methanol, ammonia (NH_3), and Methylcyclohexane (MCH) are hydrogen carriers that potentially overcome many of the main difficulties with transporting and storing gaseous and liquid hydrogen [20].

Current literature mainly concentrates on hydrogen production from ammonia decomposition on land, factories, and onshore plants [21] rather than on ships during transportation. Therefore, this review paper aims to provide a comprehensive review of the decomposition of ammonia into hydrogen; the final product, and nitrogen; which can be used as refrigerants to treat the reliquefication of Boil Off Gas (BOG) onboard. Several approaches to ammonia decomposition technologies were discussed, emphasizing concentrated solar energy integration. As well as proper treatments of the BOG of ammonia, hydrogen, and nitrogen and their reliquefication techniques were also evaluated with a suitable selection of natural refrigerants.

Ammonia, a promising hydrogen carrier, is a valuable commodity with both direct and indirect uses, as it can be utilized both directly as a carbon-free fuel source and indirectly for the storage and transportation of renewable hydrogen [12]. Therefore, ammonia is the main focus of this paper, and due to its high capacity – it has a higher energy density than methanol, synthesis gas, and other hydrogen-containing materials, at approx. 3000 Wh/kg [22], no CO_x emission – it is advantageous for the separation and purification of hydrogen that no CO_x byproducts are produced during the conversion of ammonia into hydrogen [23], easier to transport – it is easily liquefied at low pressure (3 atm) and low temperature (25 ^{0}C) [24], and high selectivity – since the only byproducts of ammonia decomposition are hydrogen and stoichiometric nitrogen, that outperforms other liquid organic hydrogen carriers [25]. Furthermore, ammonia contains more hydrogen atoms per mole than hydrogen itself; compared to hydrogen cylinders, ammonia storage tanks are far less expensive and more straightforward because it can be stored as a liquid at atmospheric pressure and temperatures that are pretty tolerable (less than 34 °C), and has a greater ignition temperature than hydrogen, which is considerably safer [18]. Additionally, using renewable energy for ammonia production has significant potential to lower overall CO_2 emissions within the NH_3 life cycle, making ammonia utilization even more reasoned and appealing.

One of the current studies and implementation of producing and storing hydrogen onboard is by utilizing seawater, as in October 2019, the electric catamaran Energy Observer is powered exclusively by three sources of renewable energy, such as solar (200 m^2 solar panels on top; soaked up the sunshine from the sky above, and at the bottom; from the reflections of the ocean surface, this charged up a set of Li-ion battery for short term energy storage (100 kWh) during the day), wind (using the ocean wings; automated rotating sail to generate electricity for hydrogen production even when the ship is moving), and hydrogen (fuel cell) produced onboard through seawater electrolysis. This ship has traveled 18,000 nautical miles in the Mediterranean Sea and other oceans, including a 5700-kilometer autonomous journey from Saint-Petersburg to Spitsbergen in the Arctic [26]. Although ammonia has no carbon content and thus no carbon emission, it releases NO_x during combustion (causes damage to the ozone layer); hence the cracking of ammonia could potentially mitigate the release of NO_x and act as a temporary measure until pure hydrogen storage technology advanced [27].

1.2. Scope and objectives

The scope of this review study is summarized as follows:

- Various ammonia decomposition techniques were investigated to determine the one producing the highest and purest hydrogen yield.
- Hydrogen was produced and stored on the same vessels transporting ammonia (although some modification to the ship conditions might be necessary).
- Nitrogen and other cryogenic liquefied gases were studied to determine the suitable choice of refrigerants for the corresponding reliquification process.
- Different types of Concentrated Solar Power (CSP) were examined to determine the appropriate types of solar infrastructure for vessels (e.g., area, height, efficiency, operating temperature).
- Several reliquefication techniques (e.g., Single Mixed Refrigerants (SMR) cycle, Dual Mixed Refrigerants (DMR) cycle, Propane pre-cooled Mixed Refrigerants (C3MR) process, and Brayton Cooling (BC) cycle) were considered to determine the suitable process for onboard BOG treatment.

The general aims and driving forces of this review work are written as follows to address sustainable development goals:

- To produce alternative energy carriers (non-fossil fuel or contains no carbon).
  - o Clean energy carrier, hydrogen, is expected to highly contribute to reducing Greenhouse Gas (GHG) emissions caused by the existing fossil-based fuel systems.
- To utilize the stable and existing transportation systems (with minimal refinement).
  - o Constructing transportation systems, especially for a new and immature energy carrier such as hydrogen, requires high capital investment, new technology, and expertise. Thus, it is more practical to use the existing one that is stable and reliable, i.e., storing hydrogen as ammonia in fleet carriers.
- To use natural refrigerants as heat transfer fluids in the BOG reliquefication processes.
  - o Primarily used and commercialized refrigerants such as Chlorofluorocarbons (CFCs): R-11 and Hydrochlorofluorocarbons (HCFCs): R-22 are artificial refrigerants that cause ozone depletion. Hence, to reduce this damage, natural refrigerants are more appropriate and preferable in terms of sustainability.
- To integrate solar energy infrastructure onboard for fuel, heat, and electricity requirements.
  - o All sources of energy are proposed to be sourced from solar energy to produce clean hydrogen from ammonia.
- To implement suitable reliquefication processes to treat BOG onboard.
  - o Both ammonia and hydrogen (or even nitrogen) stored in storage tanks are in their liquefied state; BOG is expected due to the different temperatures, pressure, or voyage conditions, hence, to reduce any flared gas or loss of materials (gas escaped), it is necessary to treat their BOG properly.

2. Methodology

A comprehensive literature review was conducted to examine the extensive process of production and storage of hydrogen, specifically from ammonia decomposition on fleet carriers, with emphasis on renewable energy integration such as solar power, aiming to reduce the number of emissions released during transportation, as well as treating their BOG to optimize the outcome. The methodology roadmap of this review paper is outlined in Fig. 1 below. First, since ammonia is preferable to hydrogen in terms of storage due to its higher volumetric energy density (12.7 MJ/L, whereas hydrogen is only at 8.5 MJ/L [28], various methods of ammonia decomposition were explored, including the recent studies of Catalytic Membrane Reactor (CMR). Secondly, as the desired final product of ammonia is expected to be hydrogen, the exploration of its production, storage, and utilization was reviewed, including the treatment of its BOG, reliquefication on board, and the regasification process on the destination port when necessary. Thirdly, nitrogen was also produced from hydrogen as the product of ammonia decomposition; it will mainly be used as a natural refrigerant to treat the gasses' BOG during the reliquefication process. Fourthly, different approaches to solar power integration and their feasibility to be adapted onboard were investigated. Fifthly, several reliquefication methods were carefully explored to lessen the number of gases lost/escaped from the storage tanks due to evaporation during voyages. Lastly, several natural refrigerant types were examined to determine the ones that would work best with the proper reliquification techniques.

In addition to these, the articles chosen for this review paper were selected based on inclusion criteria such that only written in the English language, original research articles, review articles, some conference proceedings, and articles that are relevant to the topic of interest, as well as based on exclusion criteria such that only includes articles from the last ten years (2012–2022) although some fundamental knowledge articles dated before 2012 were included, excluding non-peer revied source and grey literature (i.e., policy, government documents, urban plans, newspapers).

Furthermore, these articles were obtained from various reliable search engines and recognized databases such as Science Direct (with additional focus on the journals from Fuel, Fuel Processing Technology, and Energy&Fuel), Springer Link, Wiley Online Library, Taylor & Francis Online, and IOP Science as well as through "citation snowballing" (articles found from the list of related cited articles, additionally from websites, Sciendo, MDPI (Energies, Processes, Membranes), AIP Publishing, Research Gate, the Royal Society of Chemistry, and theses (published online), as it recorded in Table 1.

Additional emphasis is given to Scopus-indexed research papers to enhance the literature quality. Since hydrogen production and storage, ammonia decomposition, and solar energy integration are the main subject of this review; thus, various keywords were used to search the research articles, including "Onboard" AND "energy" AND "storage",

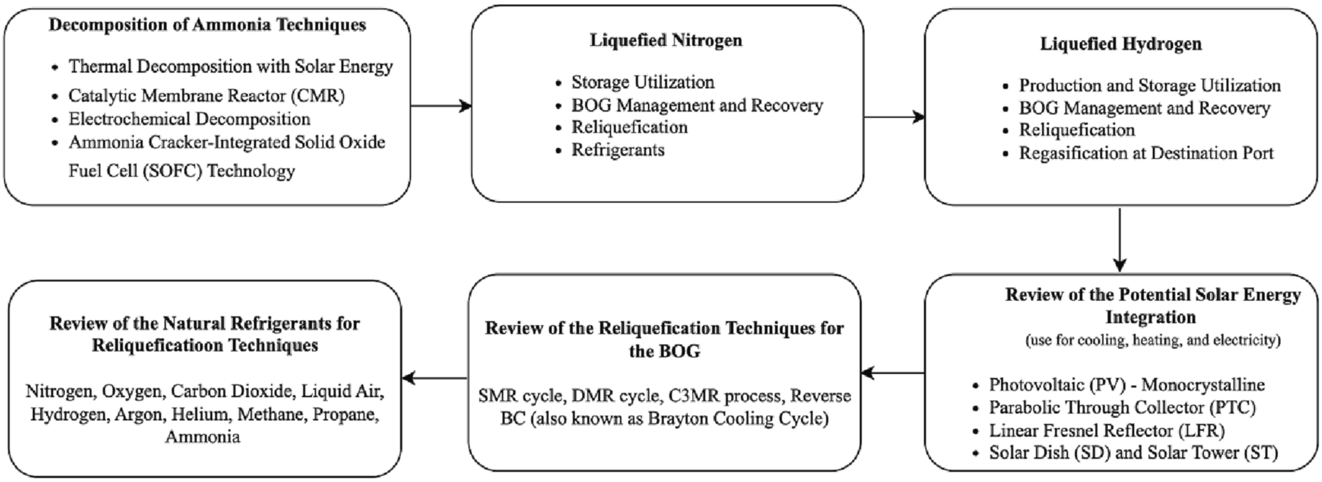


Fig. 1. The methodology followed for the comprehensive literature review.

Table 1
Search results from various search engines and included studies.

Search Engines	Search Results	Selected Paper
Science Direct	162	83
Springer Link	9	3
Wiley Online Library	10	4
Taylor & Francis Online	7	3
IOP Science	8	3
Snowballing (references found from other related papers read)	–	24
Total		**120**

"Hydrogen" AND "storage" AND "onboard", "Hydrogen" AND "fuel" AND "energy" AND "renewable", "Boil-Off-Gas" AND "liquefication", "Natural" AND "refrigerants" AND "liquefaction" AND "nitrogen" OR "hydrogen", "Fuel" AND "processing" AND "ammonia" OR "hydrogen", "Decomposition" AND "ammonia" AND "solar", "Hybrid" AND "energy" AND "onboard", and "Boil-Off-Gas" AND "ammonia" OR "hydrogen". The number of articles published based on these keywords is also recorded in Fig. 2, with "Hydrogen" AND "fuel" AND "energy" AND "renewable", as the most widely used keywords. Whereas the yearly record of the number of articles found and used for this review is shown in Fig. 3, with a maximum number of 28 articles out of a total of 120 articles found in year 2022. All non-open accessed and non-modified figures are obtained with a reuse license from the publisher, and lastly, Mendley software was used to handle all referencing.

3. Critical Discussion and Evaluation

This chapter outlines a more detailed analysis of the topic evaluated in this review paper. Firstly, four types of ammonia decomposition techniques were discussed, namely, thermal decomposition with solar energy (using trough solar collector), CMR, electrochemical decomposition (can be hybrid with thermal to keep operating temperature lower), and ammonia cracker-integrated Solid Oxide Fuel Cell (SOFC) technology. Their operating temperatures, pressures, and ammonia conversion rate to produce high-purity of hydrogen are also outlined.

Secondly, the feasibility of installing solar energy integration on the vessel is evaluated, starting with reviewing various solar energy technologies such as photovoltaic (PV) panels and several CSP types concerning their limiting and determining factors to be feasibly installed onboard. A potential vessel design is also discussed, showing a reasonable modification of the vessels in order to support the integrated systems.

Thirdly, several BOG reliquefication methods, such as SMR, DMR, C3MR, and BC cycle, were outlined due to the BOG effect during voyages. Finally, different types of refrigerants were detailed, including the artificial and natural ones, to determine their superiorities as the cooling source in BOG reliquefication and their impact on the environment,

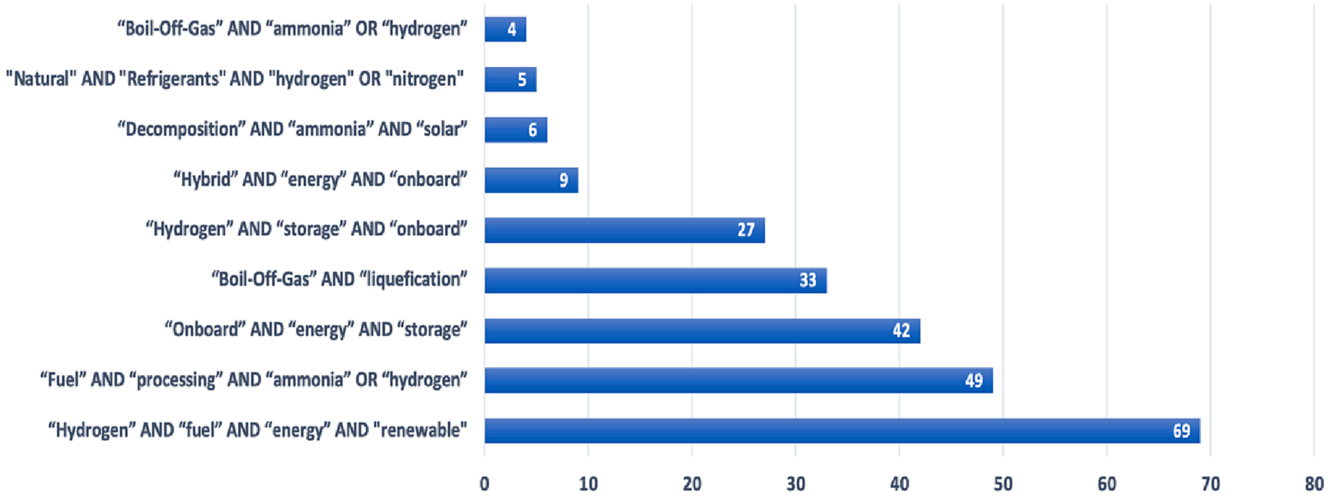


Fig. 2. The number of articles published based on keywords used in Scopus.

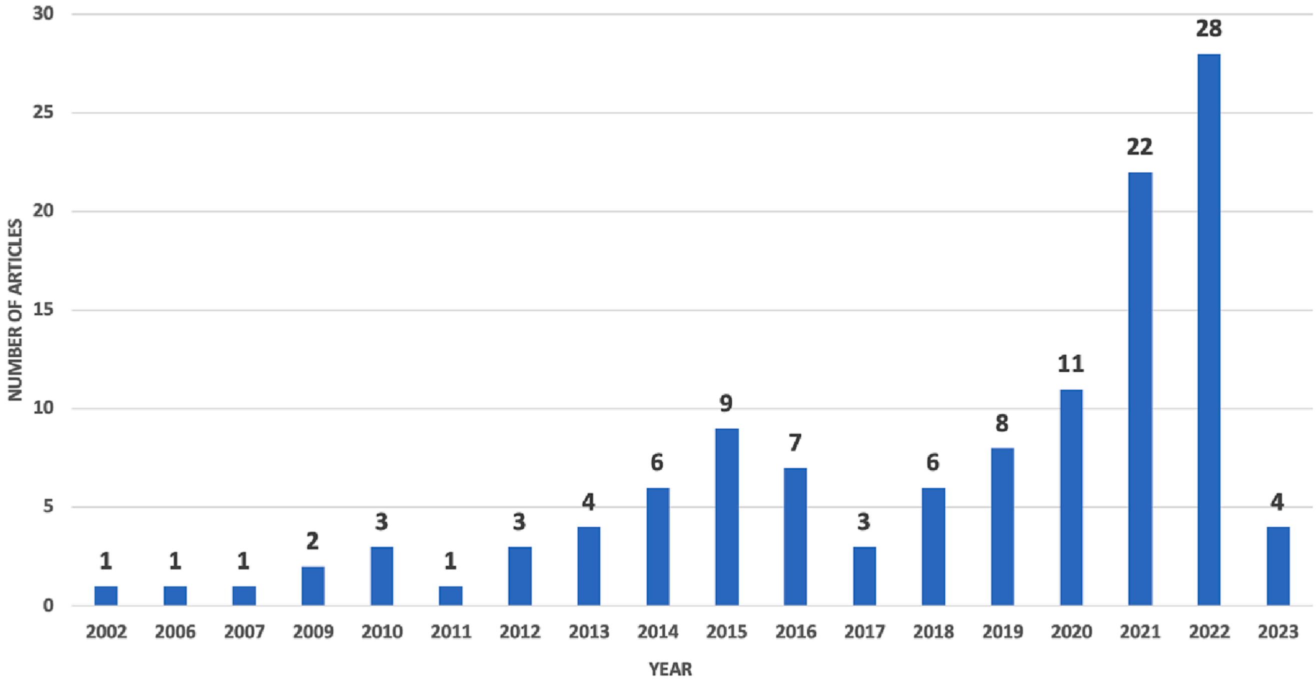


Fig. 3. The number of articles found each year for all the mentioned keywords.

considering their Global Warming Potential in 20 years (GWP20years), Ozone Depletion Potential (ODP), and Human Toxicity Potential (HTP).

3.1. Details of Ammonia Decomposition Techniques

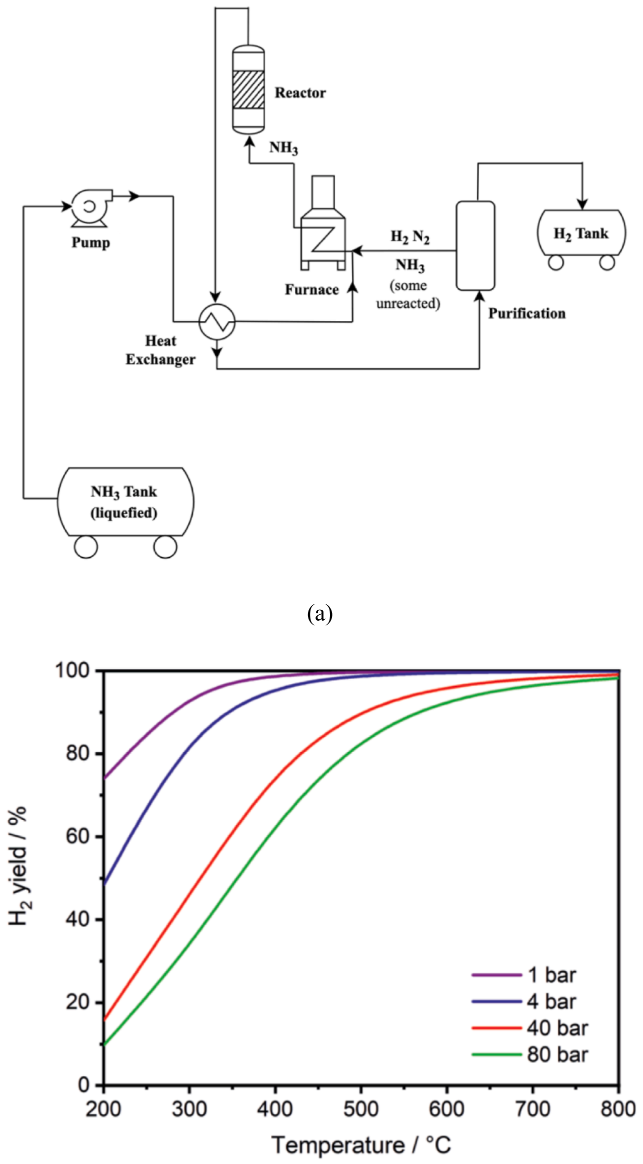
Hydrogen is well known for having a significant part in achieving reliable and effective renewable energy development. Nevertheless, there are many obstacles along the value chain in establishing a sustainable hydrogen economy. Furthermore, a few significant limitations also constrain hydrogen storage and transportation. Hydrogen is frequently liquefied at very low temperatures or stored under high pressure; it has a low energy density (8–10 MJ/m^3) [29]. Additionally, pressurization consumes 10–13% of the hydrogen's net energy, making it an energy-intensive process [30]. Even though hydrogen can be transported as a liquid at 20 K, it continuously boils off (0.2–0.3% daily) [31], and the energy required for liquefaction lowers the net energy content by 30–40% [32]. Moreover, hydrogen's small molecular size and tendency to infiltrate into metals, which results in the fragility or blistering of materials like storage tanks, add additional concern in storing hydrogen [33]. Also, safety measures must be taken when transporting, storing, and utilizing hydrogen due to its flammable range of 4–75% [34].

As a result, producing hydrogen from ammonia is a viable approach. The method for producing hydrogen from ammonia over a catalyst at high temperatures and normal pressures is known as ammonia cracking or decomposition. Thermal reactions of typical ammonia decomposition usually begin at temperatures higher than 773 K (500 °C) without the requirement for a catalyst. In comparison, most catalytic cracking occurs in the presence of a catalyst at temperatures lower than 698 K (425 °C) with a higher efficiency of roughly 98–99% [35]. However, the missing piece in this value chain is the effective way to crack or decompose ammonia to recover high-purity hydrogen. To obtain a high yield of hydrogen (greater than99.9%) and to keep the ammonia content in the produced hydrogen low, a nearly complete conversion of the ammonia is necessary [36]. Since ammonia is highly reactive and corrosive, it could potentially harm the hydrogen's purity during many subsequent processes. Due to thermodynamic constraints, a minimum temperature is always needed to produce practically all hydrogen (greater than99%) during ammonia decomposition, which rises with pressure. The temperature should be kept as low as possible for a technical procedure to minimize the energy required for heating. The endothermic nature of ammonia decomposition makes it particularly necessary for a technical operation to have a steady energy supply for heating.

In this ammonia decomposition/cracking process, as shown in Fig. 4 *(a)*, first, liquefied ammonia is pumped from a storage tank through a heat exchanger to remove waste heat from the hot gases out of the cracking reactor. The gases would then be heated to the temperatures required in a furnace or catalytic combustor. This reaction is endothermic (i.e., it absorbs heat from the surrounding). Catalysts determine the temperature required for efficient cracking. Various types of materials are applicable, such that some employ Nickel (Ni) catalysts with temperatures higher than 1000° C, and others transform well at temperatures ranging from 650° C to 700° C or even as low as 400 °C, as shown in Fig. 4 *(b)*. The flow that emerges from the reaction would be directed to a purification system that was tuned to generate a very pure flow of hydrogen while at the same time maintaining sufficient hydrogen with the nitrogen and unreacted ammonia to provide heat for the endothermic cracking reaction [37].

$$2NH_3 \rightleftharpoons 3H_2 + N_2 \tag{1}$$

The ammonia decomposition reaction shown in Equation (1) is the reverse reaction of ammonia synthesis at equilibrium because their reactions are reversible. In this process, hydrogen and nitrogen were separated in a stoichiometric ratio of 3:1, with a comparatively low enthalpy for a chemical reaction of $\Delta H_0 = 92.44\ kJ\ mol^{-1}$ [36]. Since the reaction is endothermic, increasing the temperature favors ammonia decomposition. Correspondingly, as pressure is increased, the equilibrium conversion of ammonia decreases. Therefore, high temperatures and low pressures are required to achieve a high yield or even a complete conversion of ammonia in the decomposition process. As shown in Fig. 4 *(b)*, at 1 bar (atmospheric pressure), a minimum temperature of about 400 °C is sufficient for a hydrogen output of more than 99%. While Fig. 4 shows the simplified system diagram of ammonia decomposition and the hydrogen yield of different temperatures and pressures, Table 2 outlines detailed and different techniques of ammonia decomposition to produce hydrogen with specific operating parameters. A similar study



(a)

(b)

Fig. 4. (a) Ammonia decomposition system (modified from [37]) and (b) equilibrium yield of hydrogen from ammonia decomposition obtained using Aspen Plus software (reproduced from [36]).

was conducted by Devkota et al. [12] using Aspen Plus V.12 by performing a multi-catalytic packed bed reactor steady-state model, a feed of 4000 kg/hr of pure ammonia at 298 K and 10 bar of pressure was examined. The Peng-Robinson model was used to calculate the components' thermodynamic characteristics. Theoretical modeling and simulations have also been performed. According to this experiment, due to the endothermic process, the combustion of carbon-free ammonia produced the necessary heat energy (an intermediate heating system may accelerate the ammonia decomposition). Approximately 9% of the fresh feed ammonia was required to produce the intended heat energy. There is some unreacted ammonia in the product stream from the decomposition unit. This unreacted ammonia was combined with fresh fuel and air and fed to the furnace through a pre-heater to be separated from the decomposed hydrogen and nitrogen gas combination using a two-bed Temperature Swing Adsorption (TSA) unit. The air–fuel mixture was used to remove the waste heat from the product and flue gas streams. Finally, a four-bed Pressure Swing Adsorption (PSA) unit with

Table 2
Techniques and their related operating Parameters for Ammonia Decomposition.

Techniques	Study	System Description	Operating Parameters
Thermal Decomposition with Solar Energy (using trough solar collector)	[38]	A one-dimensional ammonia decomposition endothermic membrane reactor model uses finite-time thermodynamics based on actual lighting conditions. The reactor has a regenerative preheater and a trough solar collector for heating	Ruthenium-based catalyst Operating temperature 700 K (427 °C) Permeate zone pressure is 0.1–1 bar
	[39]	A system for thermochemical energy storage using high-temperature ammonia was integrated with CSP technologies. As a result, the research prototype was chosen to be a portion of a tubular ammonia reactor heated by semi-perimeter irregular heat flow	Nickel-based catalyst Inlet temperature 100–400 °C Operating pressure 2 MPa
	[40]	A mid and low-temperature solar thermochemical ammonia decomposition for hydrogen generation in membrane reactors was implemented. In a single step, a hydrogen permeation membrane reactor can separate the product and advance the reaction equilibrium for a high conversion rate	Ni/Al_2O_3-based catalyst Reaction temperature 100–300 °C Separation pressure 0.01–0.25 bar
Catalytic Membrane Reactor (CMR)	[41]	Ammonia decomposition and high-purity hydrogen separation were concurrently processed in the same unit, and it demonstrated that high hydrogen separation efficiency is attained at a lower temperature than conventional systems	Ruthenium-based catalyst Temperature 350–450 °C Pressure 1–5 bar
Electrochemical Decomposition	[42]	A hybrid thermal-electrochemical technique to decompose ammonia into high-purity hydrogen at a relatively lower temperature, aiming to simultaneously treat the ammonia impurities in the hydrogen generated by a typical high-temperature thermal decomposition	Cesium-promoted Ruthenium-based catalyst Reaction temperature 250 °C at atmospheric pressure (1 bar)
Ammonia Cracker-Integrated SOFC Technology	[43]	A high-temperature SOFC installed on a cruise ship is suitable for decomposing ammonia into hydrogen before feeding it to the fuel cell. In this case study, the decomposition of ammonia onboard was necessary to use ammonia as a marine fuel	Temperatures between 500 and 800 °C (average 650 °C) $Ni–Pt/Al_2O_3$ catalyst at atmospheric pressure

eight steps (having two pressure equalizations) produced more than 99.99% pure hydrogen.

Other relevant studies have shown hydrogen production from ammonia on a container ship by applying ammonia cracker-integrated SOFC technology [44]. In 2021, the case study of a 16.94 MW SOFC built on a cruise ship showed that the system efficiency of direct ammonia-fed SOFC is lower than that of hydrogen-fed SOFC. Thus, it is necessary to crack ammonia into hydrogen onboard [45].

3.1.1. Thermal Decomposition by Utilizing Solar Energy

Although using hydrogen for energy applications does not release greenhouse gases and it is desirable to produce highly pure hydrogen from ammonia, it is worth noting that both the production of ammonia in the first place and the sustainability of the hydrogen production methods depend on how cleanly they are produced and how much energy is utilized in the process. In this way, the generation of green hydrogen must be maintained by utilizing sustainable energy and renewable resources such as the sun [3]. After all, utilizing the clean energy produced by solar power has been an innovative approach to ammonia decomposition. Xie, Xia, Huang, et al. [46] studied that with the aid of ammonia-based storage systems, solar thermal power generation systems can assist in maintaining 24-hour stability. One of the critical elements of the ammonia-based solar thermal storage system is the ammonia decomposition endothermic reactor that transforms solar energy into chemical energy. In this ammonia decomposition reaction, using hydrogen-permeable membranes enables the produced hydrogen to be purified, shifting the chemical equilibrium in the reaction direction and enhancing the heat absorption rate. To validate that the experiment is more closely related to the actual scenario of the solar thermal power station, the schematic diagram of solar-based ammonia decomposition is shown in Fig. 5 by installing the most popular LS-3 trough-type solar concentrator (reflector type: mirror type 3, with measurement of 12 m for each collector length, 124.457 m for each row length, and 5.774 m for collector aperture width [47]. This concentrates sunlight onto the membrane reactor to produce heat for the ammonia decomposition reaction. This system also has a regenerative preheater that heats the inlet ammonia by employing the reactor output gas. Furthermore, an interpretation was made on the impact of four parameters on the total heat absorption rate, entropy generation rate, and system effectiveness of the membrane reactor. These parameters include the ammonia inlet flow rate, preheated temperature, permeate zone pressure, and ground light intensity.

Likewise, one of the book chapters by Lovegrove & Stein [48] highlighted that producing hydrogen from an ammonia separation using solar energy was experimented. The study showed that a 24 h power generation was achievable by storing the hydrogen produced from decomposing ammonia under the influence of concentrated solar energy (a 20 m^2 dish solar concentrator is exposed to a whole receiver with 20 reactor tubes loaded with iron-based catalyst material).

3.1.2. Catalytic Membrane Reactor

Throughout the globe, CMR is often employed in numerous industry sectors. By employing CMR, waste generation is reduced from the standpoint of a cleaner process, and energy usage is minimized to correspond with the process optimization approach. CMR unites a chemical or biochemical reaction with a membrane separation procedure in a single unit by enhancing the process's conversion and selectivity. The membrane, which can be polymeric or inorganic, depending on how the catalytic process is used, comprises the basis of the CMR. Algieri et al. [49] reviewed the membrane roles in the CMR process, focused on the manufacture and use of inorganic membranes in catalytic membrane reactors, and discussed the use of membrane reactors in various catalytic processes. It was determined from this study that the membrane can serve as a distributor, contractor, and extractor. When it serves as a distributor, and a reactant is delivered to the reaction environment in a controlled manner by restricting the side reactions, removing a reaction product is possible with more excellent conversion due to the capability of overcoming chemical equilibrium restrictions [49]. After all, producing hydrogen in a catalytic membrane reactor involves combining catalytic reactions with selective permeation through a membrane to separate hydrogen from the reaction mixture. It is important to note that the specific details of the catalytic membrane reactor design, operating conditions, and membrane materials can vary depending on the chosen hydrogen production reaction and the specific objectives of the process. Additionally, reactor designs, catalyst formulations, and membrane technologies are essential to enhance catalytic membrane reactors' efficiency, selectivity, and overall performance for hydrogen production.

Ongoing research and development in this field are constantly improving; the definition of a membrane reactor is when a device simultaneously separates and reacts with one or more products by using a selective membrane as the separation component of an integrated reaction/separation system situated in a reactor module. The process reinforcement strategy is applied by membrane reactors, which provide the same performance as the conventional catalytic reactors while operating at more flexible conditions and employing fewer devices to produce a pure product stream of interest while reducing the complexity, production cost, and energy consumption [50]. Research by

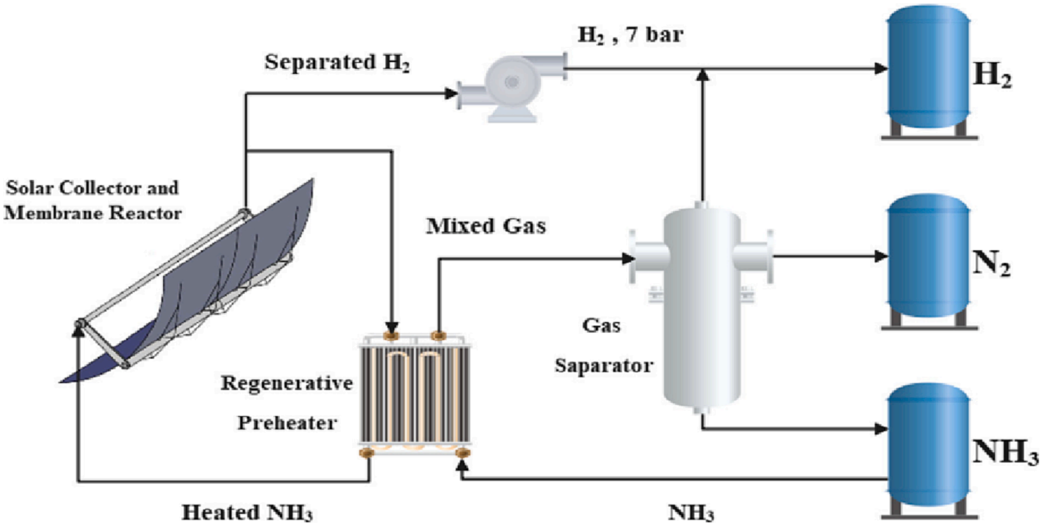


Fig. 5. Schematic diagram of the solar-heated ammonia decomposition endothermic system (reproduced from [38]).

Y. Park et al. [51] develops a steam carrier-adapted composite membrane reactor system to manufacture pure hydrogen (greater than99.99%) from ammonia with high hydrogen yield (greater than 0.35 mol-H_2 $g_{cat}^{-1}h^{-1}$) and ammonia conversion (greater than99%) at a temperature of above 723 K. The membrane reactor is desirable for catalytic reactions involving hydrogen extraction because it improves equilibrium and kinetics while omitting redundant purification stages. This experiment uses a coupled ruthenium on lanthanum-doped alumina catalysts with a specially constructed palladium/tantalum composite metallic membrane to enable stable operation of the membrane system with significant mass transfer improvement. An overview of using CMR to produce high-purity hydrogen on porous ceramic converters was included in the work of Fedotov et al. [52] which discussed the outcomes of the development of membrane-catalytic techniques for getting hydrogen that has been purified to various degrees in order to feed high-, medium-, and low-temperature fuel cells. Porous ceramic catalytic converters were made to conduct this experiment using self-propagating high-temperature synthesis. These converters are appropriate for high-speed procedures that produce synthesis gas with varying carbon monoxide contents (0.08–0.1 vol%) that may be used to fuel various fuel cells. Utilizing a hybrid CMR where the stages of catalytic conversion of organic substrates and selective extraction of ultrapure hydrogen (the hydrogen content was approximately 99.9999 vol %) from the reaction zone were combined. This work led to the development a small-scale electric generator plant prototype that combined a SOFC and a catalytic membrane reactor.

Another recent work on the optimization analysis of hydrogen production by utilizing ammonia was carried out by Ali Rothan et al. [53]. This work examines the ammonia-based hybrid Plasma Membrane Reactor (PMR) with 15 conditions and a catalytic reactor system for hydrogen-generating parameters. As the ammonia entirely decomposes, the volume of the dissolved gas doubles. In that order, the most significant influences on hydrogen yield were ammonia flow rate, electrical voltage, and upstream pressure. The results indicate that ammonia flow rate has a more significant impact on hydrogen yield than voltage and upstream pressure. In contrast, voltage impacts hydrogen yield more than upstream pressure. A unique design for PMR is suggested based on the Central Composite Design (CCD) optimization method to address the gap in this field. In addition, a promising approach for producing hydrogen without carbon emissions from ammonia decomposition in a solar-powered catalytic palladium membrane reactor was studied by B. Wang et al. [40]. This paper examines kinetic and thermodynamic evaluations of solar thermochemical ammonia decomposition at mid- and low temperatures for hydrogen production in membrane reactors. It is noted that in just a single step, a hydrogen permeation membrane reactor can separate the output and enhance the reaction equilibrium for higher conversion efficiency. Analysis revealed how different characteristic parameters, such as reaction temperature (100–300 °C), tube length, and separation pressure (0.01–0.25 bar), affect conversion rate and thermodynamic efficiency. This experiment resulted in a system efficiency of that 86.86% in first-law thermodynamic efficiency, 40.08% in net solar-to-fuel efficiency, and as high as 72.07% in exergy efficiency. Hence, these demonstrate the viability of combining mid/low temperature solar thermal technology with ammonia decomposition for hydrogen generation.

In similar research, Cechetto et al. [41] experimentally conducted ammonia decomposition in a Palladium-based membrane reactor over a Ruthenium-based catalyst, and as a baseline for comparability, the effectiveness of the traditionally packed bed reactor was used. The findings show that incorporating a membrane into a traditional reactor improves its functionality and enables it to accomplish conversion rates higher than thermodynamic equilibrium conversion at reasonably high temperatures. Furthermore, a complete ammonia conversion was accomplished for temperatures higher than 425 °C, and more than 86% of the hydrogen supplied into the system as ammonia was recovered with a purity of 99.998%. Additionally, the studies by Abashar et al. [54] and Abashar [55] achieve an efficient ammonia decomposition in a packed bed membrane reactor utilizing a Ni/Al_2O_3 catalyst at a temperature range of 680–740 K and a pressure of 3.65 MPa. Their findings discovered that the conversion rate achieved by utilizing a reactor with a permeation membrane was 60.48% higher than without it. Rizzuto et al. [56] also modeled a study using a ruthenium-based catalyst in an ammonia decomposition of a palladium membrane reactor, demonstrating that the ammonia conversion was most efficient at 450 °C. It was experimentally obtained that at a reaction pressure of 7 bar, the ammonia flow rate and the temperature did not affect the rate of hydrogen synthesis.

On the contrary, another catalytic ammonia decomposition experiment was carried out by Armenise et al. [57] that shows Ru-based catalysts outperformed Ni-based ones in terms of conversion in the decomposition of pure ammonia. In this evaluation, the Ru-based catalyst made utilizing ruthenium-nitrosyl-nitrate as a precursor had the highest conversion and the lowest apparent activation energy of all the Ru-based catalysts. After the passivation process, this catalyst had an ideal mean particle size and the highest ratio of Ru_0/Ru(total) in the reduced state. Furthermore, since the desired outcome of hydrogen production from carbon-free energy carrier such as ammonia is to reduce COx emission, Armenise et al. [57] also suggests that the energy needed for the synthesis and decomposition processes, as well as the hydrogen production, must be generated using renewable energies for the entire process of storing hydrogen as ammonia to be environmentally viable. On the other hand, a small portion of the energy contained in ammonia might be used to generate the energy required for its decomposition. If a catalyst active at the lowest temperature is utilized, this portion will be reduced to the absolute minimum, and thus, a high-purity hydrogen stream is obtained. Therefore, hydrogen production from ammonia is more economically and sustainably possible due to all these factors compared to other paths.

3.1.3. Electrochemical Decomposition

A study by Pinzón et al. [58] proposed an electrochemical activation of Ruthenium-based catalyst film with alkaline ion (Na + and K +) conductors to produce hydrogen from ammonia decomposition. This experiment was conducted at atmospheric pressure, functioning at temperatures ranging from 220 to 350 °C. Initially, under the open loop condition of the decomposition reaction, the catalytic activity of the ruthenium catalyst film, Ru/Na-βAl_2O_3 electrocatalyst, was examined from 200 to 450 °C. The other electrocatalyst analyzed was Ru/K-βAl_2O_3. The experiment result demonstrates that the reaction with potassium (Ru/K-βAl_2O_3) had the more significant impact of the two alkali ions tested, raising the hydrogen generation rate above 230% at 300 °C under ideal circumstances. In another research done by Lim et al. [42], at a relatively low temperature of 250 °C, a hybrid thermal-electrochemical approach to the ammonia conversion reaction to produce hydrogen was examined. Since a typical ammonia decomposition demands a higher temperature (min 400 °C) to overcome thermodynamic restrictions and kinetic barriers, however, a low temperature should be maintained to maintain a high yield. The electrochemical decomposition of ammonia offers the possibility to produce high-purity hydrogen at near-ambient conditions and with high conversion rates as an alternative to high-temperature thermal decomposition.

As well as aiming to resolve the ammonia contaminants in the hydrogen caused by high-temperature thermal decomposition. Therefore, thermal decomposition is integrated with electrochemical hydrogen removal from the ammonia decomposition reaction zone to solve the thermodynamic restrictions that product accumulation would otherwise create. Fig. 6 shows the overall diagram of the thermal-electrochemical hybrid cell for ammonia-to-hydrogen conversion. The hydrogen oxidation Electrocatalyst Layer (EL), which is next to the Cesium Dihydrogen Phosphate (CDP) electrolyte, is put next to the internal Thermal-cracking Catalyst Layer (TCL). The infrastructure is sandwiched between stainless steel lattice current collectors and

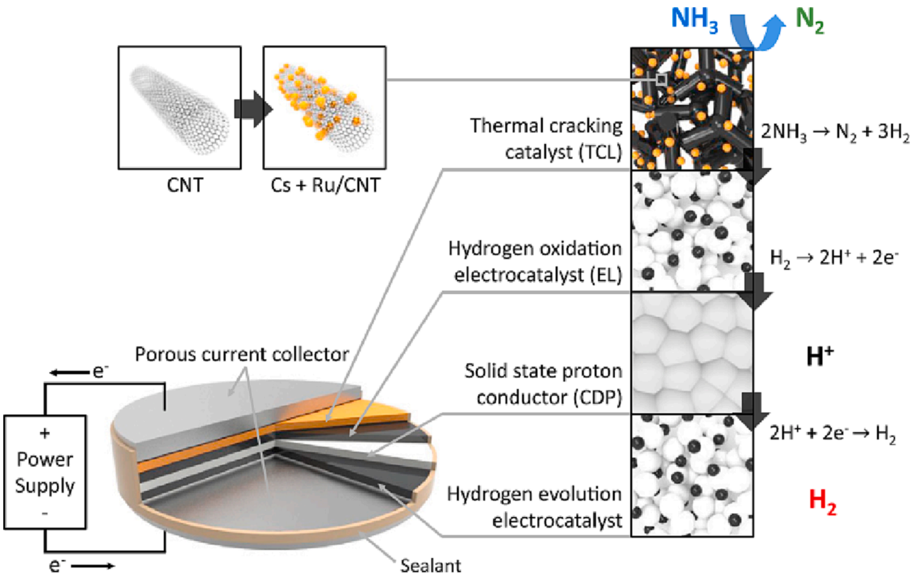


Fig. 6. An overall diagram of the hybrid thermal-electrochemical cell for ammonia-to-hydrogen conversion (reproduced from [42]).

incorporates a hydrogen evolution electrocatalyst layer at the counter electrode. The design is comparable to that used in direct methanol Solid Alkaline Fuel Cells (SAFCs) and similar fuel cells that operate on sophisticated (non-hydrogen) fuels [42].

Although producing carbon-free energy carriers such as hydrogen from ammonia is crucial, ensuring that ammonia production is sustainable is imperative. Therefore, it is worth noting that the overall process of producing green hydrogen from green ammonia requires a reliable renewable energy source, such as solar (CSP), wind, or other renewables, to power the ammonia production steps. This ensures the entire process is free from carbon emissions and contributes to a more sustainable and clean energy transition. B. Wang et al. [59] investigated the Reversible Solid Oxide Cell (R-SOC), a promising technology that offers a potential route to decarbonize several applications dependent on fossil fuels that can be well integrated with the electrochemical synthesis of green ammonia from renewable energy. According to this study, the ammonia production rates for electrochemical ammonia synthesis employing both Solid Oxide Electrolytic Cells (SOEC) and Proton Ceramic Electrolytic Cells (PCEC) can reach 8 to 9 × 10^9 mol $s^{-1}cm^{-2}$ at temperatures as low as 400 °C. The best power density observed for direct ammonia conversion utilizing SOFC and Proton Ceramic Fuel Cells (PCFC) is comparable to that of hydrogen fuel cells, reaching greater than 1.2 W/cm^2.

3.1.4. *Ammonia Cracker-Integrated Solid Oxide Fuel Cell (SOFC) Technology*

MAN Energy Solutions has announced that since 2019, they have been investigating the Internal Combustion Engine (ICE) powered by ammonia. With the help and cooperation of maritime stakeholders, two-stroke ammonia engines are anticipated to be commercially accessible for deep-sea cruising ships by 2024 [44]. Besides, due to its potential and numerous benefits, fuel cell technology such as SOFCs is predicted to be among the effective potential propulsion options in the future. Although SOFCs are a promising technology for power generation, fossil fuels such as natural gas are generally the primary commercialized fuel used for SOFC; thus, generating CO_2 is inevitable. However, it releases lower emissions than the traditional power plant [60]. A study by Wan et al. [24] further enhanced the utilization of ammonia as a hydrogen carrier to generate power through direct feeding to SOFCs. Thus, green electricity can be used for the electrochemical decomposition of ammonia because SOFC is an electrochemical device that converts chemical energy into electrical energy [61]. Literature by Hossein Ali & Shin [43] examined the technological process for ammonia to hydrogen conversion, mainly using a SOFC reactor that produces electricity directly using hydrogen generated from ammonia at temperatures between 500 and 800 °C. However, developing catalysts is necessary to increase conversion rates at low temperatures. Another similar study using SOFC was conducted by Saadabadi et al. [62]; at high temperatures, ammonia as a hydrogen carrier can be decomposed to produce hydrogen. At 405 °C, the endothermic ammonia cracking reaction begins, and at 590 °C, the ammonia is wholly converted. Since the SOFC's typical operating temperature is between 650 and 850 °C; as a result, ammonia cracking becomes feasible to occur inside the SOFC. Nonetheless, commercially viable ammonia-fed SOFCs are still under development, and only in 2020 that a commercial-size SOFC stack with 30 cells that uses ammonia as a fuel is documented by Kishimoto et al. [63]. These SOFCs were recorded to increase the power generation efficiency to 57% and stability for 1000 h operational period, demonstrating the potential of employing ammonia for electrical power generation.

3.1.5. *Utilizing Renewables for Power Production in Ammonia Decomposition Process*

Utilizing CSP for power generation onboard ships is still a relatively nascent and developing idea. While solar power has been widely adopted on land for many years, its integration within the maritime industry is still in its early stages. Several initiatives have been undertaken to incorporate solar power into the propulsion systems of vessels. The installation of solar panels on the ship's deck or superstructure allows for the generation of electricity, which can supplement the power requirements of electric propulsion systems. This approach is primarily being explored in smaller vessels such as ferries and small boats. Furthermore, solar power can be harnessed to provide electricity for auxiliary systems onboard ships, thereby reducing reliance on traditional diesel generators. This includes powering various onboard systems like lighting, communication equipment, refrigeration units, and more. By doing so, it contributes to a decrease in fuel consumption and emissions, particularly during periods of low power demand. The efficiency and efficacy of solar panels and concentrated solar power systems are constantly advancing. Ongoing innovations in solar cell technology, including enhancements in conversion efficiencies and the use of lightweight materials, are making solar power increasingly viable for marine use. These developments hold the potential to drive greater acceptance and implementation of solar power on vessels in the coming years.

However, research on the integration of solar energy with ammonia decomposition is currently limited, necessitating a comprehensive review of this subject. The primary objective of incorporating renewable sources like CSP into the ammonia decomposition process is to reduce or eliminate the reliance on fossil fuels and associated emissions. By integrating renewable energy into ammonia decomposition, the aim is to enable a more sustainable and environmentally friendly production of hydrogen. CSP technology employs mirrors or lenses to concentrate sunlight onto a receiver, converting solar energy into thermal energy. This thermal energy can be utilized to drive various industrial processes, including ammonia decomposition. Nonetheless, the limited number of studies and applications in this area can be attributed to several challenges associated with implementing CSP onboard vessels. These challenges include restricted space availability and the need to ensure structural integrity and stability, making the installation of solar power systems more complex compared to land-based applications. Additionally, the variable nature of solar power, influenced by weather conditions and the vessel's location, presents challenges in terms of power predictability and reliability.

Hence, this research paper delves into comprehensive investigations of the existing state of CSP implementation on vessels. It assesses the viability and practicability of installing four prominent CSP technologies that are well-suited for powering the ammonia decomposition process. The evaluation process, discussed in *Section 4*, employs a ranking system that takes into account essential characteristics of CSP, including its operating temperature compatibility with ammonia decomposition, the space required for onboard vessel application, and the thermal efficiency of each technology in converting thermal energy into electricity.

3.2. Feasibility of Solar Energy Integration

CSP is a desirable replacement for conventional power generation that uses fossil fuels because of the sustainability and cleanliness of solar energy. CSP encompasses four significant types of technology, namely Parabolic Trough Collectors (PTC), Linear Fresnel Reflectors (LFR), Solar Dish (SD), and Solar Towers (ST; also referred to as central receiver), systems as shown in Fig. 7. The two main categories of CSP configurations are the linear focus (PTC and LFR) and the point focus (SD and ST systems), as shown in Fig. 8.

All CSP technologies have a similar fundamental interpretation while having distinct deployment and processes for each. The main elements of CSP are reflectors, receivers, Heat Transfer Fluid (HTF), and an appropriate cooling system [64]. The solar energy from the sun is focused onto a receiver, which then transforms it into heat using heliostats or controlled mirrors. Lenses or mirrors are the standard reflectors that concentrate sunlight into a narrow beam and directing it at the receiver. Steam, the product from heating HTF and circulating it through the receiver, is used to convert mechanical energy to power a turbine to generate electricity. Because thermal energy in CSP systems must be stored before being converted to electricity, Thermal Energy Storage (TES) is necessary. CSP plants use TES devices to store the energy until it is needed, such as when there is limited sunlight. CSP is a versatile renewable energy source because of its capacity for energy storage. Furthermore, a TES subsystem, such as a solar tower, parabolic trough, or dish type, must also be integrated into a solar thermal power plant to provide constant and continuous electricity for an extended period. TES is currently categorized as sensible heat storage, latent heat storage, and thermochemical storage, with minimum volume and highest energy density [66].

Fig. 9 shows the working diagram of an improved solar power plant utilizing CSP to generate heat for electricity production studied by Spelling et al. [67] compared to the traditional molten salt solar plant. It relies upon using a dense particle suspension as the HTF, enabling the receiver to operate at high temperatures (over 650 °C), thus, opening potentials for high-efficiency power-generating cycles applications such as supercritical Rankine cycles. The thermal conversion efficiency is improved by this supercritical Rankine-cycle power block from 39.9% to 45.4%, resulting in a 9.6% decrease in the heliostat field's area. It is noted that a 24.5% increase in the operational temperature range results in a 12.5% increase in storage density and a 22.5% decrease in overall storage capacity. The absence of heat tracing also results in a reduction in parasitic power consumption. Overall, it is expected to reduce by approximately 10.8% in electricity costs due to better cycle efficiency, increased storage density, and decreased parasitic altogether [67].

As shown in Fig. 10, Ammonia-based thermochemical storage used in a CSP system is an excellent alternative among all the materials that are ideal for TES due to several benefits, including abundant resources, a reaction without COx byproducts, a reactor with simple construction, a

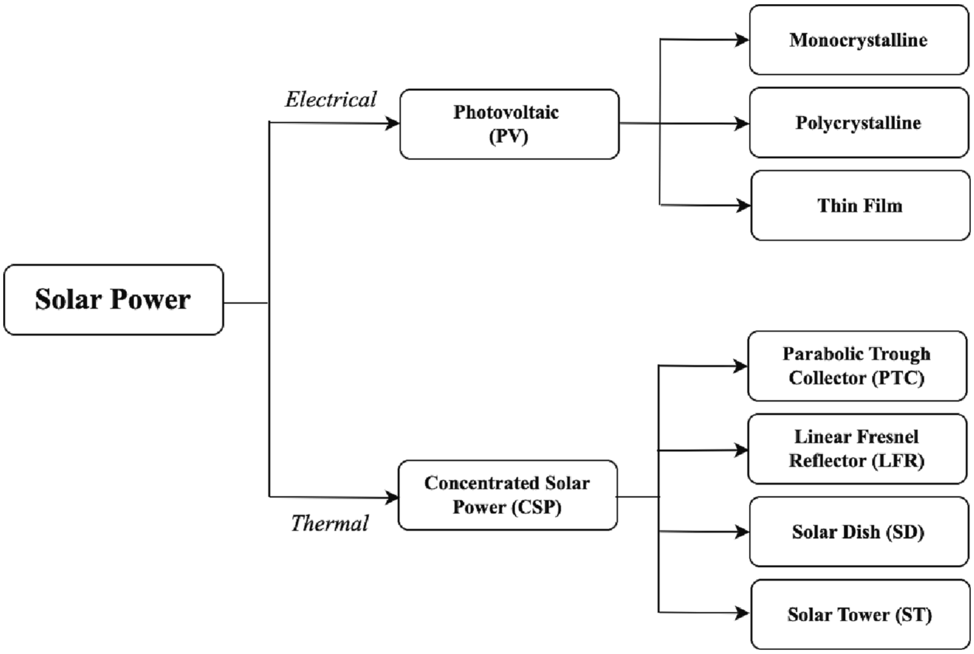


Fig. 7. Leading technologies of solar power integration (modified from [64]).

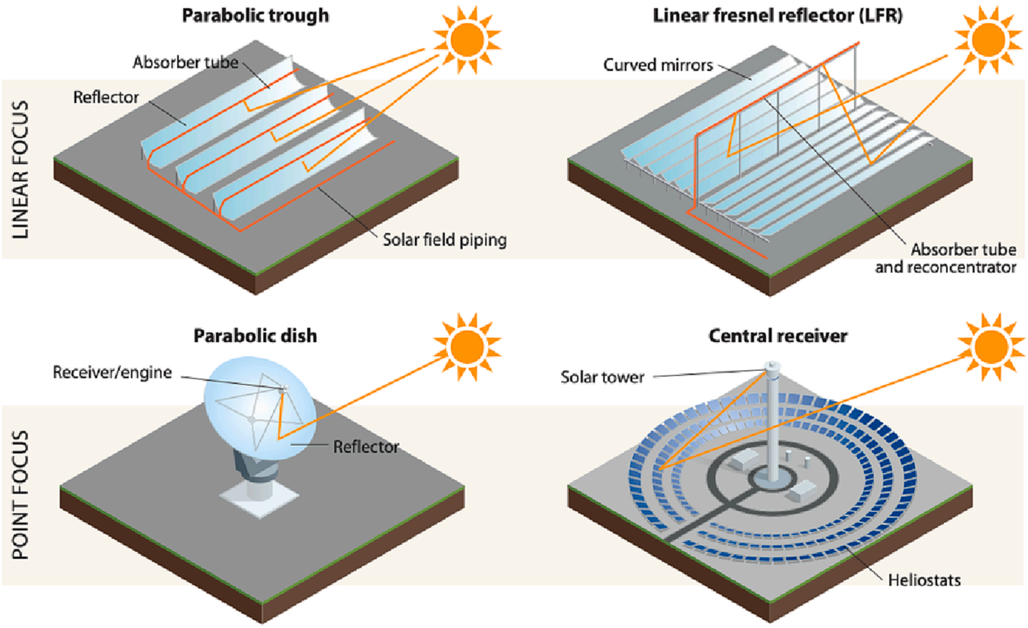


Fig. 8. Four main types of CSP technologies (reproduced from [65]).

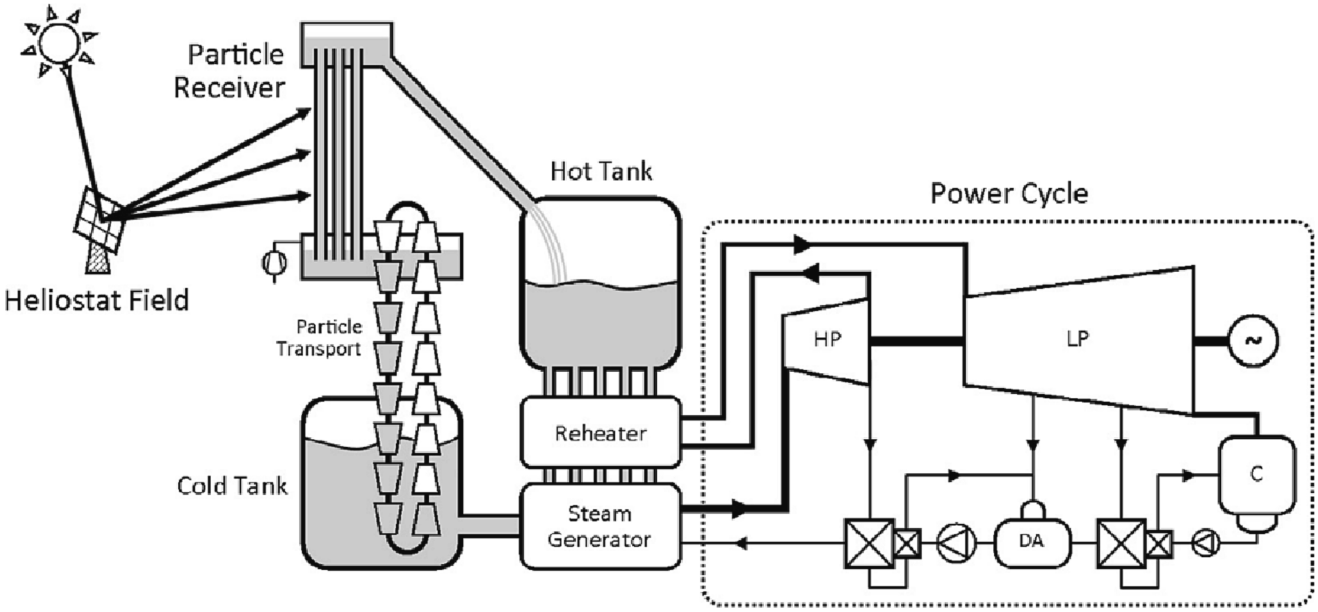


Fig. 9. Schematic diagram of an improved CSP technology to generate electricity from heat (reproduced from [67]).

small storage tank, and the maturity of ammonia synthesis [39]. Besides, an ammonia-based thermochemical storage system can be implemented in a trough and tower system because the reaction catalyst can adapt to various temperatures. It is notably linked that CSP can be used as an electricity generation source during ammonia decomposition (i.e., electrochemical decomposition). In contrast, ammonia can be a dependable energy source (ammonia-based) storage for CSP.

3.2.1. *Photovoltaic (PV) Panels*

In addition to CSP, photovoltaic (PV) panels are the leading solar power technologies. Due to their high-power output and efficiency, monocrystalline solar panels are the most popular and commonly used. They also typically produce more power than other types of panels, not just because they are more efficient (able to achieve efficiencies of above 20%) but also because they are available in higher-wattage modules with a power capability of more than 300 W [68].

PV immediately transforms light into electricity, in contrast to CSP. Instead of reflecting heat, the solar PV cells absorb light, instigating electrons to produce a current. The direct current (DC) is acquired and transformed into an alternating current (AC) delivered across the electrical grid for electricity utilization by inverters. [68] proposed that one of the effective methods to employ solar energy is via photovoltaic technology, by converting direct or indirect sunlight to electricity. That study compared two distinct, commercially available solar modules, monocrystalline and polycrystalline, in the semi-arid region of Iran for a year and monitored their overall performance.

It is concluded that the monocrystalline module performed more effectively in terms of maximum efficiency and overall specific energy yield and is more suitable in this type of climate/location. To evaluate the performance of PV modules, [69] proposed several factors that need

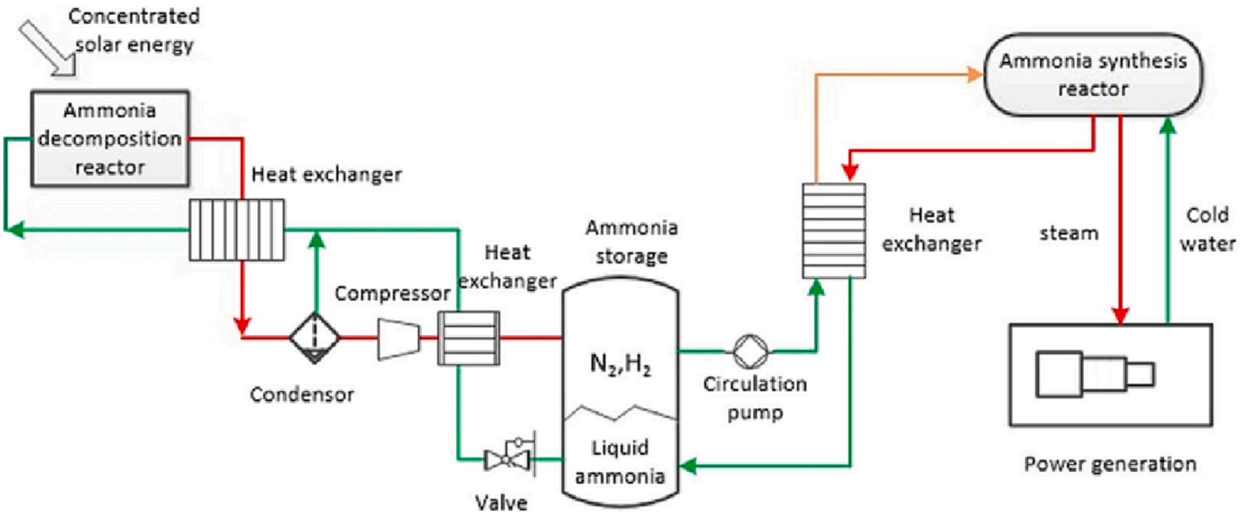


Fig. 10. Ammonia-based storage in CSP system (reproduced with permission from [39]).

Table 3
Comparison between PV and CSP [64].

Feature	PV	CSP
Storage and Intermittency	It immediately produces electricity, thus, is difficult to store, and batteries are not economically viable for large-scale plants. Intermittency is the main downside of PV	By overcoming intermittency and maintaining supply during the night, TES is an appealing characteristic of CSP that makes it dispatchable and increases the penetration of CSP in the energy sectors
Efficiency	10–28% max efficiency and performance degrades over time	41% average efficiency, and efficiency increases with temperature
Capacity factor	10–35%	With TES is 29–33%, while without is 28–29%
Equipment	DC must be converted to AC using inverters	Output is AC if combined with power cycles; thus, no inverter is needed.
Solar irradiance	It uses Global Horizontal Irradiation (GHI) and is capable of functioning in dispersed light	CSP only utilizes Direct Normal Irradiation (DNI), and it fluctuates between 65 and 85% of the total GHI

to be considered, including the type of technology utilized, the light spectrum, solar irradiation, ambient temperature, humidity, and wind. In addition to those factors, it is suggested by [70] that climate and environmental factors also affect the deterioration and aging of solar modules. Other features are listed in Table 3 to compare the differences between PV and CSP.

3.2.2. *Integration of Solar Energy with Ammonia Decomposition and BOG Reliquefication*

An integrated design of utilizing CSP as the renewable solar energy source to supply heat (or electricity) required for the ammonia decomposition process is shown in Fig. 11, as well as combining the BOG reliquefication plants to treat the evaporated gas of ammonia and hydrogen during voyages, with the use of natural refrigerants as the cooling source. It focuses on demonstrating the four potential types of CSP technologies with the proposed four ammonia decomposition methods, interconnects with one of the suggested BOG reliquefication processes, and the use of natural refrigerants. Since the conventional fuel commonly used in maritime transportation is Heavy Fuel Oil (HFO), also known as bunker fuel or marine fuel oil that is heavily polluting the environment, the maritime industry is undergoing a transition to cleaner and more sustainable fuels in response to environmental concerns and stricter emission regulations. This transition includes the adoption of alternative fuels such as hydrogen and ammonia as potential future fuels for maritime transportation. Ultimately, some portion of their BOG can be employed as fuel for the vessels as studied by Zamfirescu & Dincer [71] in terms of economic and technical feasibility to use ammonia and hydrogen as a sustainable fuel alternative as compared with other standard fuels (gasoline, Compressed Natural Gas (CNG), LPG, and methanol).

3.2.3. *Parabolic Trough Collector (PTC) for Ammonia Decomposition Onboard the Vessels*

The actual beginning of the industry of CSP was deployed in California in the 1980 s, with 354 MW-electric (MWe) capacity of 9 separate PTC Solar Electric Generating Systems (SEGS) [72]. Tabassum et al. [64] highlighted the mechanism of PTC that reflectors in the form of parabolically curved troughs direct sunlight onto a receiver pipe. The receiver is situated at the parabola center. Heat is absorbed by an HTF (typically organic oil) that circulates through the absorber tubes and then transmits to a traditional steam generator. PTC has an expected efficiency of 10–16$^{\%}$.

In this system, curved, trough-shaped reflectors concentrate solar radiation, which is then directed onto a receiver pipe. The pipe often stores thermal oil, which is heated and utilized in a steam generator's thermal power block to produce electricity. Fig. 12 demonstrates the integration of PTC into the other blocks, such as ammonia decomposition, BOG reliquefication plants, and the cooling source. The working temperature of PTC should match that of ammonia decomposition's operating temperature for it to be compatible with the integrated system. Since one of the CSP technologies will be installed on the vessels, the height and area of them should be suitable for onboard integration (due to less space, the area should be kept minimal, and the height should not be beyond an international height limit of vessels due to some unmovable bridges along the voyages. For more detailed evaluation will be explained in Section 4).

Similarly, a study conducted by Malik et al. [73] modeled a PTC by employing Stirling Engine (SE), referred to as Parabolic Solar Dish Stirling (PSDS). The system performance and essential technical characteristics of the parabolic dish concentrator, thermal receiver, and SE are demonstrated to identify the best design options for deploying PSDS plants.

3.2.4. *Linear Fresnel Reflector (LFR)*

In this system, multiple numbers of collectors are arranged in rows. Flat on the ground, the mirrors reflect the sun onto the receiver pipe above. LFR can incorporate storage in a power block or generate steam

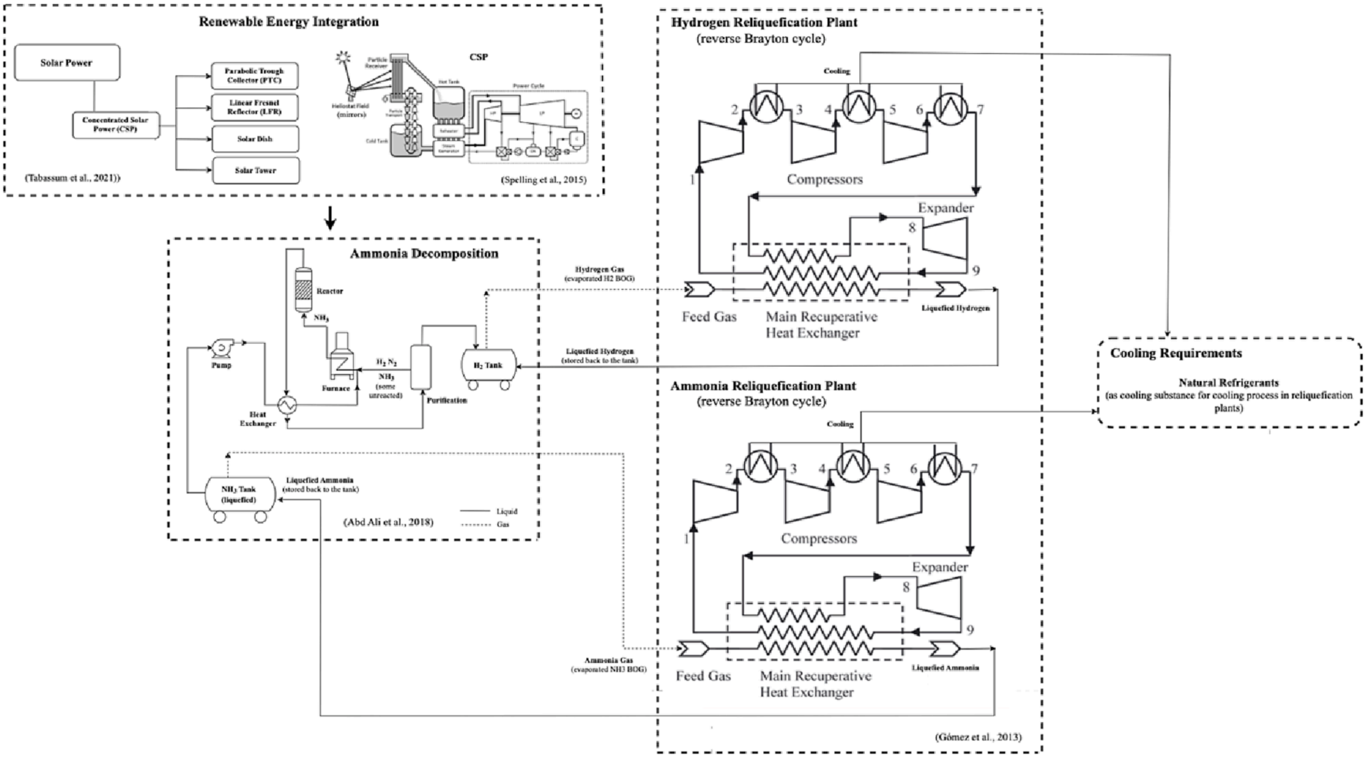


Fig. 11. Process flow diagram of integrating solar energy with ammonia decomposition and BOG reliquefication plants using natural refrigerant.

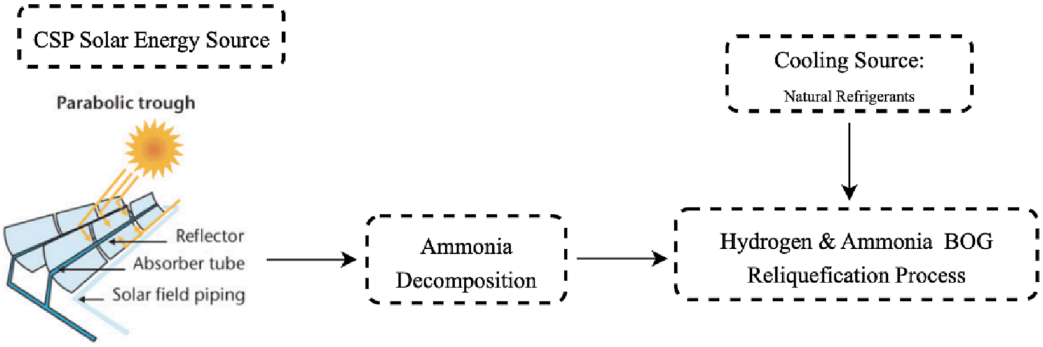


Fig. 12. A fundamental diagram of PTC (modified with permission from [72]).

directly, similar to the mechanism of trough and tower systems. The same paper Tabassum et al. [64] outlines the mechanism of LFR as having a similar operation as PTC. However, the primary distinction is that several mirrors share a single receiver and have shallow curvature or flat mirrors rather than parabolic mirrors. Unlike PTC, the fixed receiver does not need a fluid coupling, making the total system less expensive. Meanwhile, similar to PTC, LFR has a medium to high capacity but slightly lower efficiency, 8–12%, and its integration to the whole building blocks are shown in Fig. 13, interconnected to ammonia decomposition, BOG reliquefication plants, and the cooling source.

In their research, Taramona et al. [74] addressed the primary drawback of the previously proposed hyperbolic secondary reflector in LFR. Developing a new secondary reflector consisting of numerous fixed flat mirrors positioned at the same height is suggested. A Monte-Carlo Ray-Tracing software was used to define the optimal layout of the reflector, and the result showed that it lowered the relative error to at least 15%. Moreover, the concentration ratio was achievable up to 31 with a maximum of 60% optical efficiency. Comparably, to fully utilize renewable resources, Jafari & Ameri [75] integrates PV panels and LFR, which is expected to yield promising results. It uses carbon dioxide as the working fluid to simulate a hybrid PV/LFR energy storage system. The performance of the entire cycle, system, and individual components during four different seasons has been examined based on energy and exergy analysis. The findings showed that the thermal efficiencies for LFR were between 37 and 60%, stationary PV panels have 14–16% efficiency, and rotating PV panels have 18–20%.

3.2.5. *Solar Dish (SD) and Solar Tower (ST)*

Technology for SD comprises a collection of parabolic reflectors, metallic support, and a Stirling engine. A parabolic-structured dish performs as a concentrator to reflect solar radiation onto a receiver affixed to a structure with a tracking system that moves with the sun. A heat (Stirling) engine then produces the heat that has been captured. The device may be suitable for solar reactors because the dish may reach very high temperatures. It has a substantially high heat-to-electricity conversion when integrated with Stirling engines. Stirling solar dish systems have demonstrated impressive results in terms of conversion efficiency; roughly 30% of the sun's rays can be captured and employed to generate electricity [76].

On the other hand, ST devices track the sun using mirrors known

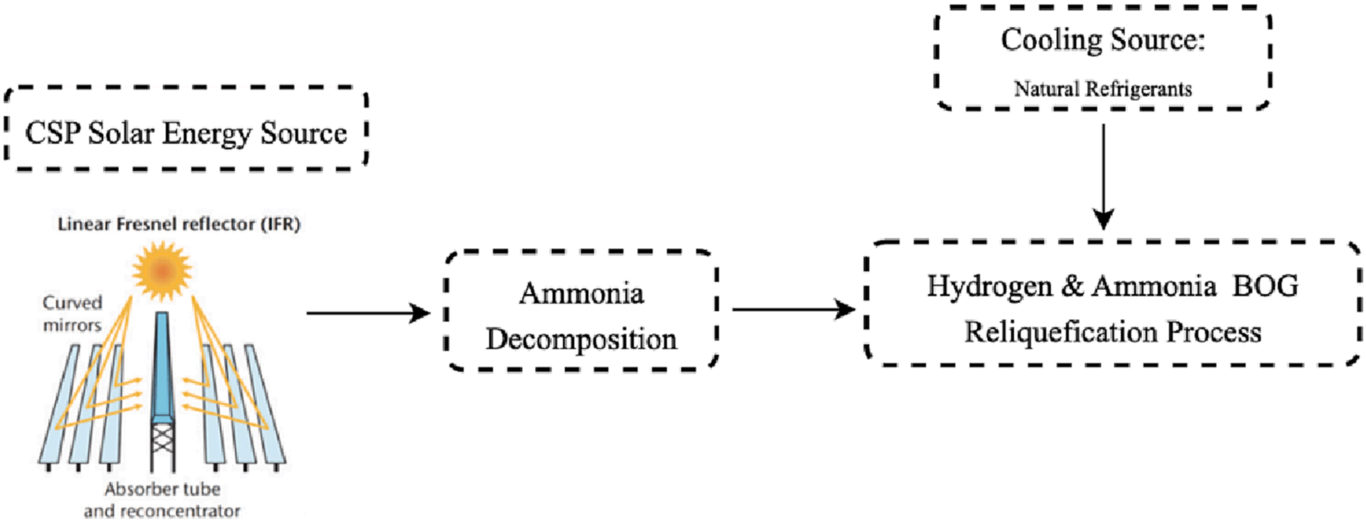


Fig. 13. A fundamental diagram of LFR (modified with permission from [72]).

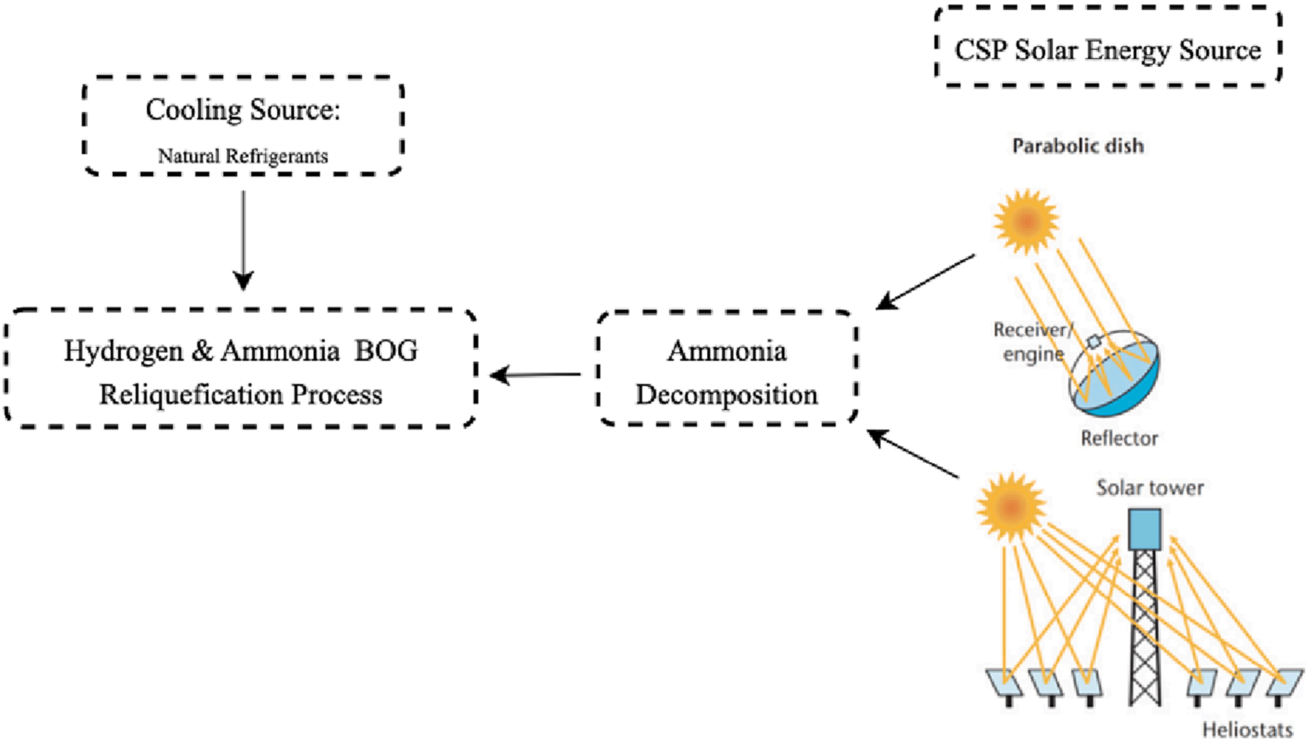


Fig. 14. A fundamental diagram of SD and ST systems (modified with permission from [72]).

as heliostats and direct their energy onto a receiver positioned on a tower. A fluid is heated inside the receiver to produce steam, which powers a turbine generator. Molten salts are frequently used in this heating process. ST requires enormous heliostat fields for a single receiver, though they can harness more than 1,000 suns. Hence, it is more expensive, and this extremely high capital cost has led to modular SD being used in broader applications [72].

In contrast to LFR and PTC, which direct sunlight onto a linear

Table 4
Leading CSP technologies comparison [76].

Parameters	PTC	LFR	SD	ST
Operating Temperature (^{0}C)	290–390	250–390	250–700	250–500
Concentration Ratio	70–80	25–100	1000–3000	300–1000
Tracking System	Single axis	Single axis	Two-axis	Two-axis
Power Cycle	Steam and organic Rankine	Steam and organic Rankine	Steam Rankine, Brayton, and Stirling	Steam Rankine and Brayton
Annual Solar Thermal Efficiency (%)	15	8–10	25–30	20–35
Land Occupancy	Large	Medium	Small	Medium

receiver using line-focus techniques (their lower concentration ratio is the primary constraint), SD and ST have far higher concentration ratios since the system are point-focus, yet accurate tracking system (typically two-axis) is necessary. Their integration with other building blocks of ammonia decomposition, BOG reliquefication plants, and the cooling source is shown in Fig. 14. While the comprehensive analysis of these four leading technologies of CSP is outlined in Table 4.

CSP Technology Adaptability on the Vessels.

Based on a study by Sato & Chung [77], in typical LNG carriers, the lower portion of the spherical tanks beneath the upper deck is supported by a cylindrical hemline structure, while a semispherical cover protects the higher portion above the ship's upper deck. Intricate structures also support the tunnels, piping, and electric cables. Whereas a new modification of the energy carrier vessel is illustrated in Fig. 15, the SAYAENDO uses a continuous cover connected with the ship's primary strength components, housing all tanks "under one roof" while retaining the essential compartment divisions. This increases overall structural strength and enables hull weight reduction. CSP, particularly the solar parabolic dish, with the smallest area requirement and robustness, enables it to be installed practically anywhere and thus can be fitted on the continuous tank cover's flat surface, as shown above.

The new design improves maintainability by eliminating the need for such intricate supporting systems. The continuous cover enhances aerodynamics by significantly reducing headwind force, which acts as a drag on the ship's motor and increases fuel consumption during actual operations at sea. The critical factors of this modification are the

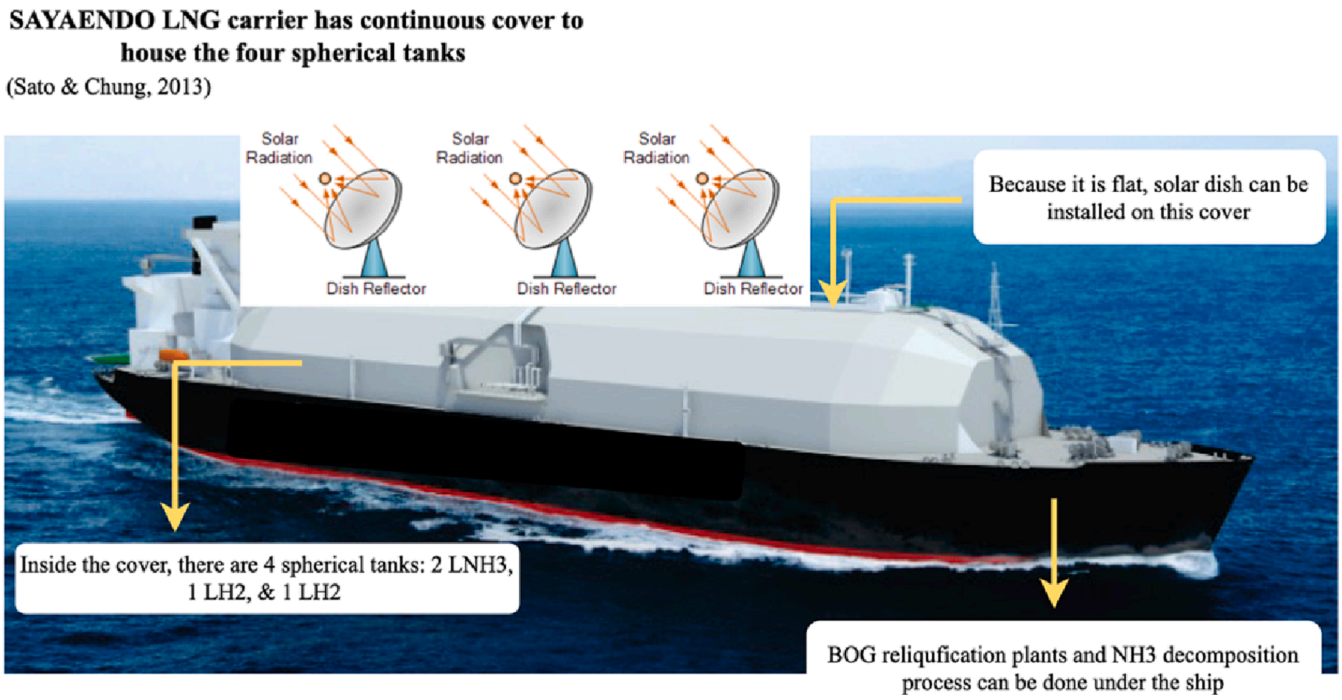


Fig. 15. Ship design of the proposed integrated system (modified from [77]).

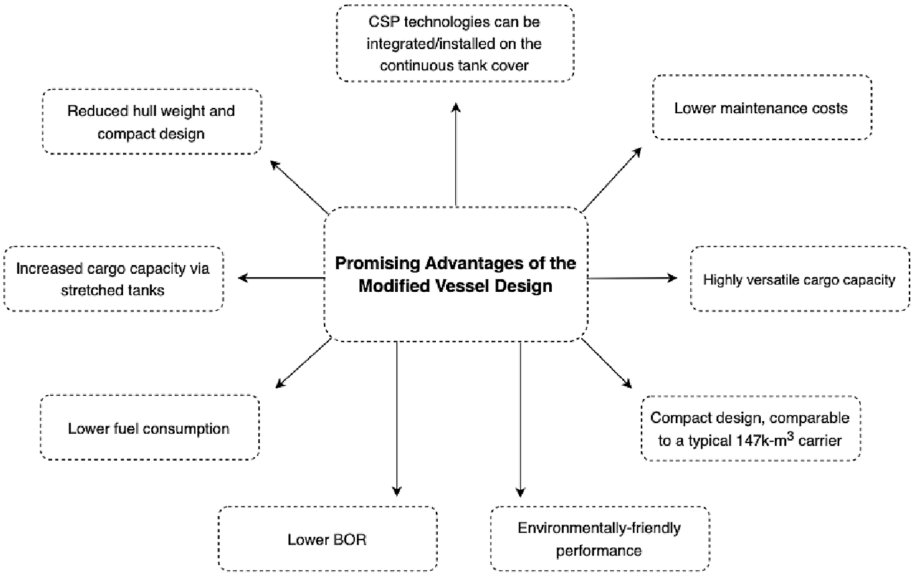


Fig. 16. The promising advantages offered by the modified vessel design (modified from [77]).

structural design and assessment, the aerodynamic assessment with wind-tunnel tests, and the maneuverability simulation and mooring analysis, whereas its superiorities are displayed in Fig. 16 [77].

However, when the chosen CSP technology is placed on the top of the continuous tank, its height should be less than the maximum international limit for ships' height due to the existence of some unmovable bridges along the voyages, or it should have the total height of that Q-Max, the most prominent LNG vessels in the world with a recorded height of 34.7 m [78].

3.2.6. CSP to Power the Reliquefication Process Onboard

Integrating CSP as the primary power source for the vessel's reliquefication process offers potential benefits, including reduced fuel consumption, lower emissions, and enhanced energy efficiency. While CSP has been successfully deployed in various applications, its direct utilization for reliquefication onboard vessels may require further research, development, and customization to suit the energy industry's and vessel operations' specific needs. Therefore, it is essential to note that the reliquefication process typically requires significant power, and the feasibility of using CSP as the primary power source will depend on factors such as the size and efficiency of the CSP system, the vessel's operational profile, available space, and cost considerations. This paper analyzes the four types of well-established reliquefication techniques of the BOG on the storage tanks in terms of their schematic diagram, types of refrigerants as the working fluid, and the potential of integrating them with renewable energy for power generation (if they are both heat (cooling) and electricity-driven, thus any renewables would be suitable, including CSP).

If the power from CSP is insufficient for the energy-intensive reliquefication process, it can contribute to the overall power supply onboard and indirectly support the reliquefication process. That CSP can generate electricity that can be used as an auxiliary power source for various onboard systems, including those supporting the reliquefication process. This can include powering pumps, compressors, cooling systems, and control systems necessary for reliquefication. As well as to incorporate energy storage technologies, such as thermal storage or battery systems, to store excess solar energy. This stored energy can then be used during periods of higher power demand, such as when the reliquefication process requires additional power. Energy storage enhances the reliability and availability of power supply. Therefore, a combination of CSP and other power generation technologies, such as diesel generators (conventional), battery storage, and other combination of renewable energy sources (wind, ocean thermal energy conversion, marine current power, etc.), can be employed as a hybrid power system. In this setup, CSP can provide some of the power needed for the reliquefication process. At the same time, other sources complement the supply during periods of low solar radiation or increased demand.

3.3. Evaluation of BOG Reliquefication Techniques

Unlike conventional Liquefied Natural Gas (LNG) plants on land, the processing requirements for the reliquefication of BOG on board are different. While the most problematic requirement for on-land liquefaction plants is thermodynamic efficiency, there are other more crucial aspects to consider in onboard reliquefied plants. Thus, evaluating and analyzing various essential aspects in determining the most effective reliquefication techniques is necessary. Table 5 outlines several practical reliquefication techniques that can be adopted onboard, detailing the process, refrigerant types, and the potential of renewable energy integration. Most importantly, the factors that should be considered are due to the limited space available onboard; thus, the techniques chosen must be compact and lightweight, also able to provide high availability, reliability, and durability during operation; the sea conditions should not affect the plant operation (it should be stable, less swaying, and sloshing since it increases the generation of BOG in storage tank), low cost, as well as simple to install and maintain [79].

Table 5
Reliquefication techniques for BOG.

Study	Technology	Definition	Refrigerants	Potential Renewable Energy Integration
[80]	Single Mixed Refrigerants (SMR) Cycle	Consists of one cycle of mixed refrigerant either at one or at two different pressure levels to provide refrigeration over the required temperature range	Mixed (artificial) refrigerants from R1 to R13 (as shown in Fig. 19)	It is both heat (cooling) and electricity-driven; thus, any renewables would be suitable
[81,82]	Dual Mixed Refrigerants (DMR) Cycle	Similar to SMR, but uses two mixed refrigerant cycles to improve the efficiency of the liquefaction cycle further	First cycle (warm) refrigerants: ethane and propane (precooling) Second cycle (cold) refrigerants: nitrogen, methane, ethane, and propane	It is both heat (cooling) and electricity-driven; thus, any renewables would be suitable
[83]	Propane Mixed Refrigerant (C3MR) process	Use propane as precooling refrigerant, and this increases energy efficiency and production capacity	Propane is used in pre-cooling and mixed with nitrogen, methane, and ethane in final cooling	It is both heat (cooling) and electricity-driven; thus, any renewables would be suitable
[79,84]	Reverse Brayton Cycle (BC)	It consists of three sections: the nitrogen cooler, a condenser, and a sub-cooler. Three-stage centrifugal compressors with intercooling are used to compress nitrogen to 35 bar	Nitrogen is used as the working fluid; it is cooled before entering an expander. Hence, generating the cold current that flows upstream to the cold box to subcool the main gas stored and the N_2 before expansion	It is both heat (cooling) and electricity-driven; thus, any renewables would be suitable

In addition to its immature technology, building hydrogen-producing units cost very much. Most of the time, it is not suitable for every location due to its complexity and large storage volume for transportation. Hence storing it in a liquefied form could potentially resolve this problem. However, transporting hydrogen over long distances creates another obstacle as it needs a specific storage tank; such that the early design and performance of the liquefied hydrogen tanker that was built exclusively to transport liquid hydrogen should be assessed using tank sizing, ship stability, and ship characteristics [85]. The storage tanks are typically cylindrical shaped containers, as is the most common form of hydrogen tanks [86]. The ships must be suitable to support hydrogen reliquefication onboard, and the fact that it vaporizes quicker than other energy carriers, BOG, mainly due to the difference in temperature of the ambient temperature and the rising temperature inside the hydrogen storage tank [87]. Fig. 17 shows the schematic flow diagram of the first onboard reliquefication plant implemented in an LNG carrier, Jamal, with a cargo capacity of roughly 135.000 m^3 [79].

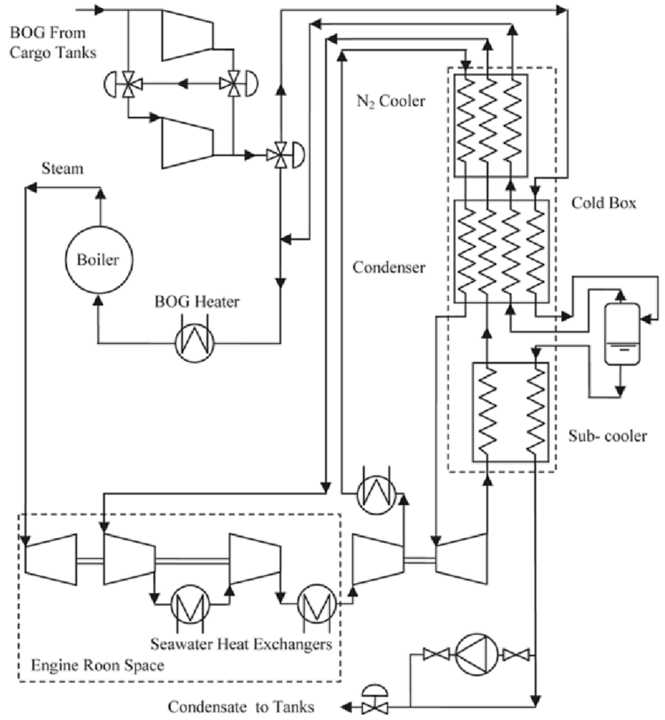


Fig. 17. BOG reliquefication process flow diagram on the first LNG ship - “LNG Jamal” (reproduced from [79]).

As shown in Fig. 18, a revolutionary hybrid system’s process flow diagram produces liquid hydrogen at 22.34 kg/s. It was researched by Jouybari et al. [88] that offers a cutting-edge integrated structure for liquid hydrogen production, which derives from the pre-cooling and liquefaction stages of the compression-ejector unit and six cascade multi-component refrigerant cycles. An analysis of a cryogenic hydrogen production structure comprised of the propane-ethylene compression-ejector refrigeration (pre-cooling section), cascade multi-component refrigerant (liquefication section), and Kalina power generation cycles (to utilize waste heat in the integrated system) is the primary goal of this design. In this process, hydrogen is cooled from 298.1 K to 173.1 K using the compression-ejector refrigeration cycle, and it is liquefied at 17.64 K using the cascade multi-component refrigeration cycle. The Kalina power generation cycle uses the Linde-Hampson cycle’s output heat to recover energy. The performance of conventional refrigeration systems is enhanced by replacing the throttle valve with an ejector [89]. The main benefit of using an ejector is that its nozzle expansion is more effective than the throttle valve expansion. Additionally, the power consumption of the ejector output stream is lowered due to the pressure increase compared to the conventional compression refrigeration cycle [88].

Another aspect to consider the importance of BOG reliquefication onboard is the Boil Off Rate (BOR) parameter. It is typically used to represent the rate of energy carrier evaporation during shipment. The amount of BOG generated overall is affected by storage time, which reduces the amount of energy that can be transported along the supply chain and lowers energy efficiency [90]. For ammonia, the transport phase contributes to the highest BOR, while for hydrogen, the BOR during the loading and unloading process provides the most considerable portion of the total BOR. However, the total BOR of ammonia is 0.047%, which is still significantly less than the BOR of hydrogen (2.401%); each sub-process likewise exhibits this pattern when comparing the BOG of ammonia and hydrogen. The primary factor is that liquefied hydrogen has a far more significant temperature difference from its surroundings than ammonia. This shows that if hydrogen is

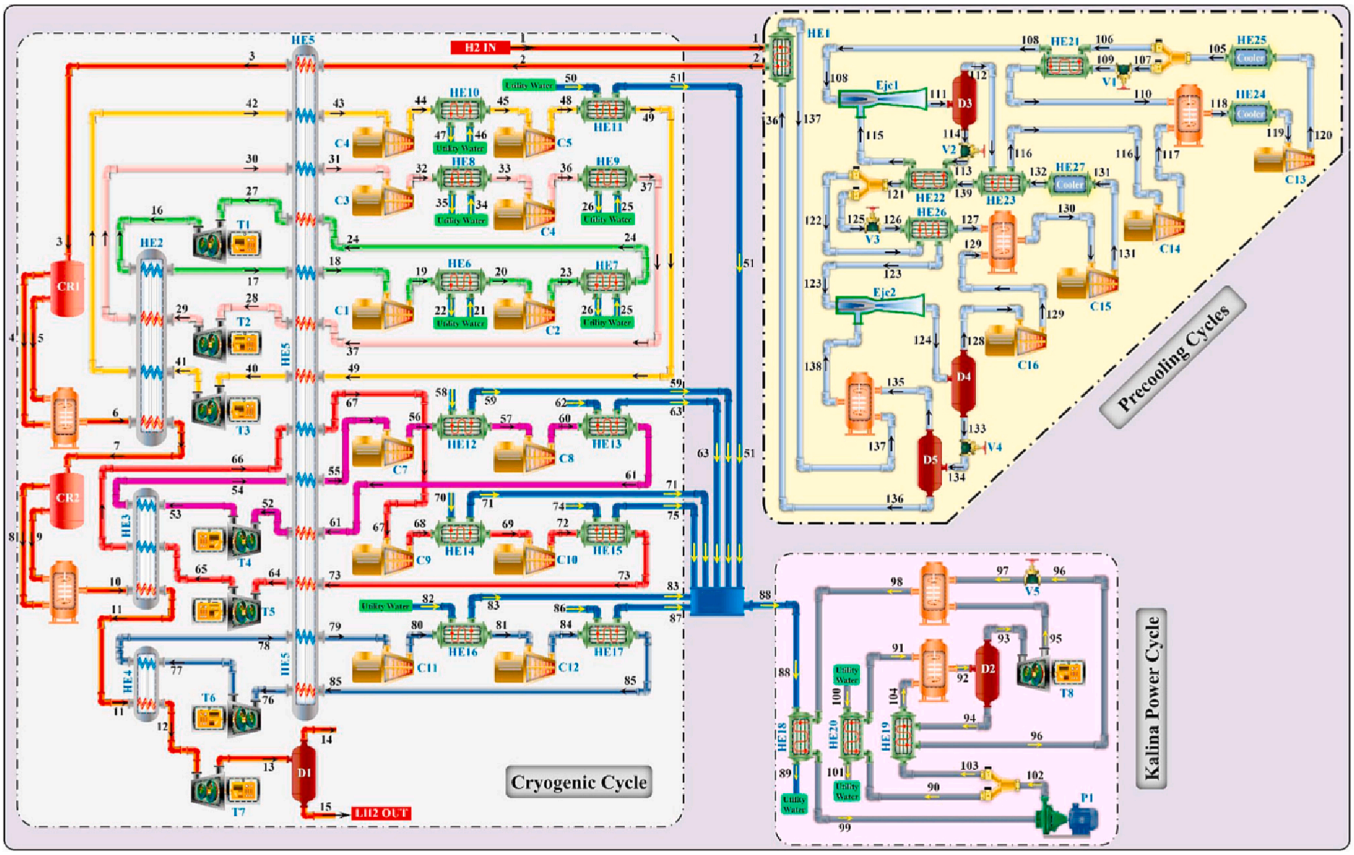


Fig. 18. An innovative hybrid system’s process flow diagram for producing liquid hydrogen (reproduced with permission from [88]).

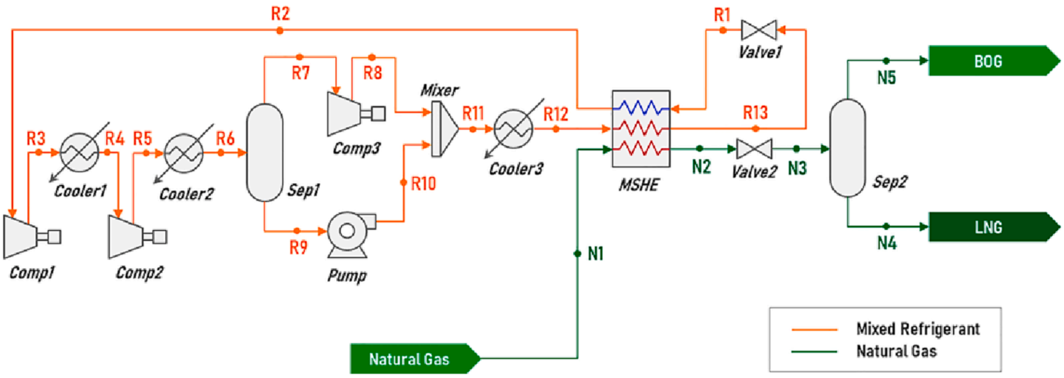


Fig. 19. SMR cycle schematic flow diagram and operating conditions (reproduced with permission from [80]).

stored and transported in liquid form, the problem of BOG creation will be more problematic than ammonia; this is why proper reliquefication treatment of hydrogen BOG is critical.

The BOG reliquification is crucial to supply chain efficiency since its evaporation causes significant energy losses. With an energy efficiency of 89%, roughly 6–9% lower than the other energy carriers, producing large amounts of BOG in the hydrogen supply chain has also become the main barrier to its practical transportation. The energy efficiency of all energy carriers is expected to increase with the utilization of BOG, with hydrogen's efficiency increasing by 4.88% and ammonia's by 0.29% [90]; this reduces the energy efficiency gap between hydrogen and the other energy carriers. The storage and transportation phases are where the increase in energy efficiency is most noticeable. BOG treatment systems will, therefore, become more crucial for energy efficiency as the voyage duration increases.

Those technologies listed in Table 5 are most likely to be used for liquefaction and BOG reliquefication of LNG; however, their operation and mechanism could potentially be adopted to treat other similar gasses, such as ammonia and hydrogen. In their analysis, Remeljej & Hoadley [91] used an SMR, nitrogen, and methane to examine various liquefaction methods for an offshore LNG production plant. The analysis revealed that SMR performed better than other refrigerants. However, due to the denseness of the system, a nitrogen process and open loop cycle employing methane were advised.

3.3.1. *Single Mixed Refrigerants (SMR) Cycle*

The choice of appropriate refrigerants liquefaction procedures dramatically influences the efficiency of the cycle. Soujoudi & Manteufel [92] has been demonstrated that mixed refrigerants have a higher energy efficiency than a single pure refrigerant in a cycle. According to the schematic diagram and operating condition in Fig. 19 provided by J. Park et al. [80], in the SMR liquefaction technique, initially, by employing heat exchange with mixed refrigerant in a Multi-Stream Heat Exchanger (MSHE), the natural gas in stream N1 is cooled to 140 °C. Then through valve 2, the natural gas in stream N2 is expanded, causing it to liquefy because of the Joule-Thomson effect. It is noted that stream N4 recovers the LNG, while stream N5 discharges the BOG, and refrigerant is continuously circulated throughout this operation. In MSHE, heat exchange causes the liquid-state refrigerant in stream R1 to evaporate. The refrigerant is then cooled with seawater from streams R2 through R12 under pressure; stream R13 passes the valve after cooling in the MSHE and is liquefied by the Joule-Thompson effect.

3.3.2. *Dual Mixed Refrigerants (DMR) Cycle*

Among the preferred natural gas refrigerants is DMR. Since it is recognized to be the most efficient of the liquefaction cycles, In one of the investigations by Khan et al. [81] it was determined that the DMR process had 15% more capacity than the C3MR process when comparing the rates of LNG and Liquefied Petroleum Gas (LPG) production. The results show that the DMR process is flexible enough to utilize gas turbines fully. The DMR process, therefore, offers 11% more potential for application than the C3MR technique. Especially in remote and colder areas, using a second refrigerant loop improves the efficiency of LNG production in the DMR process. The turbine operates more effectively and generates more power when it is cold. Additionally, DMR liquefies Natural Gas (NG) more efficiently due to the broader temperature range (from low boiling to high boiling refrigerant in MR). Also, the DMR process can operate with both spiral wound and plate frame exchangers to fully utilize the installed turbine's power. Similarly, a cycle that uses a combination of mixed refrigerants (ethane, propane, butane, and methane) was constructed by Hwang et al. [82] to precool natural gas. This method is being researched for potential use in LNG Floating Production Storage and Offloading (FPSO) because it is known to have the highest efficiency among the liquefaction cycles. The schematic diagram of DMR designed by Khan et al. [81] is shown in Fig. 20 below, consisting of two mixed cycles for refrigerants: the warm (WMR) cycle mainly uses ethane and propane, while propane, ethane, methane, and

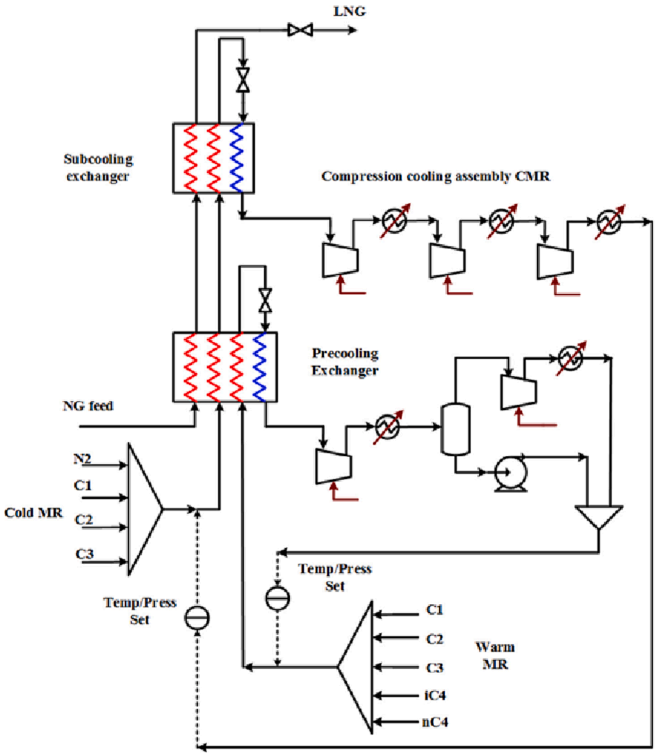


Fig. 20. DMR cycle schematic flow diagram (reproduced with permission from [81]).

nitrogen are used in the cold MR (CMR) cycle.

In most cases of mixed refrigerants used in the DMR reliquefication processes, there are hydrocarbons with non-zero GWP index, such as methane (GWP = 28), ethane (GWP = 6), propane (GWP = 4); thus, there is a need to find environmentally benign and sustainable alternatives of the refrigerant mixtures with a zero GWP index [92]. Primarily due to the ongoing restrictions put in place by the energy and environmental sectors over the past several decades, some of these refrigerants with higher GWP are not known to have a promising future. Ammonia is a well-known, highly efficient refrigerant with zero GWP index utilized as a single/mixed refrigerant for precooling processes.

In a study conducted by Soujoudi & Manteufel [92], the use of a precooling propane cycle was compared to the use of ammonia. It was discovered that using a precooling propane cycle would require 2.3 times the size of a condenser due to a higher heat retransfer coefficient than ammonia, and propane compression power are 15% higher than the required compression power for ammonia. Additionally, in that experiment, the concentration of methane, or other more polluting refrigerants with a relatively high GWPI, is to be reduced by the addition of ammonia to the mixture of refrigerants that increased the cycle efficiency by 4.3% and reduced heat exchanger total energy loss to 47.9. Similarly, Zamfirescu & Dincer [71] have looked into the prospect of utilizing ammonia as a refrigerant, particularly as a cooling agent in fuel for vehicle propulsion. Since ammonia also seems to be a medium for thermo-chemical energy storage, it can be advantageous as a working fluid or refrigerant and in automotive applications as a fuel, hydrogen source, NOx reduction agent, or potential energy storage medium.

3.3.3. *Propane Pre-cooled Mixed Refrigerants (C3MR)*

A study by Primabudi et al. [83] mentioned that the propane pre-cooled mixed refrigerant method, also called C3MR, is currently the foremost natural gas liquefaction process. It is frequently utilized for large-scale plants and created for high-efficiency base-load plants. In comparison to the optimized cascade, C3MR is more economical. In terms of the process, C3MR is similar to that of DRM, besides the fact that all working fluids used by C3MR processes are mixed refrigerants, which results in a more significant inventory for plant operators. Furthermore, a study was conducted to liquefy distinctive offshore-related gases in the South China Sea Q. Y. Li & Ju [93] explored several liquefaction processes such as C3MRC, Mixed Refrigerant Cycle (MRC), and the nitrogen expander cycle. The outcomes showed that the nitrogen expander cycle provides higher benefits for offshore applications than the C3/MRC and MRC processes.

Using Aspen Plus, the process flowsheet of the C3MR liquefaction technique depicted in Fig. 21 was designed and simulated. Propane is utilized as the pre-cooling working fluid in a C3MR process. For liquefying (and sub-cooling) the natural gas, a fluid including natural gas and mixed refrigerant (MR) is used. Processes of liquefaction and precooling are set up on different cycles. Peng-Robinson equation of state was chosen because it offers high calculation performance around critical conditions and is appropriate for non-polar and slightly polar mixtures [83].

3.3.4. *Reverse Brayton Cycle (BC)*

It is also known as Brayton Cooling Cycle when inversed; otherwise, it acts as power generation, similar to the Stirling cycle. Here, the nitrogen is converted back into liquid nitrogen via an economizer, compressor, cooler, and expander for storage and the subsequent heat

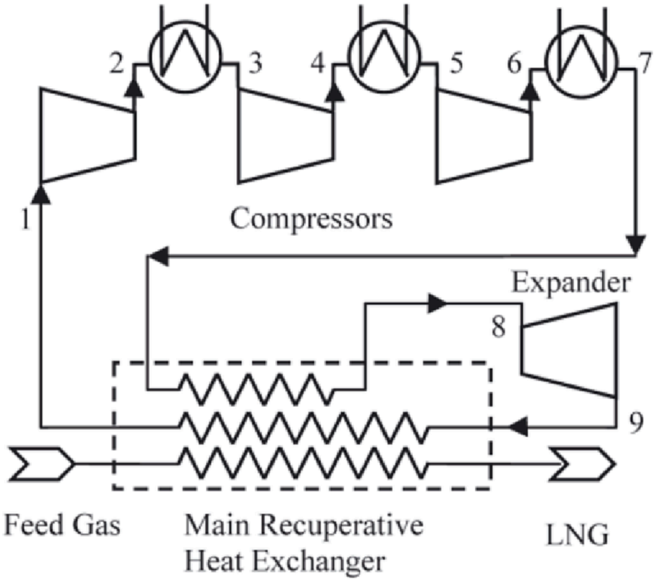


Fig. 22. Reverse Brayton cycle schematic diagram (reproduced from [79]).

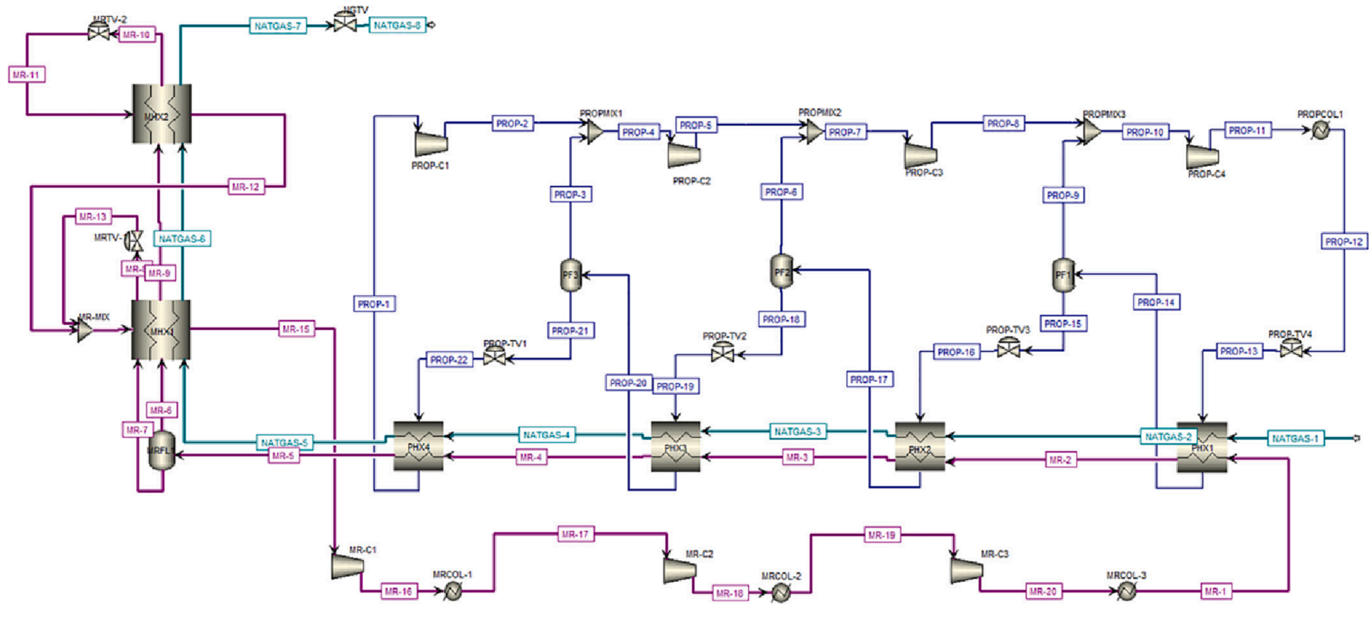


Fig. 21. C3MR process flow diagram (reproduced with permission from [83]).

exchange based on the reverse Brayton nitrogen cycle as researched by Z. Wang et al. [94]. As proposed by Gómez et al. [79] a schematic diagram of reverse BC in Fig. 22 shows the primary equipment required for the operation, including compressors, coolers, expanders, heat exchangers, and economizers. Inert nitrogen is safe and could be obtained on board as a working fluid since it meets all the requirements for the procedure. Making it the most suitable selection, with its boiling point lower than methane. In this process, with intercooling, nitrogen is compressed in stages (stages 1–7). Intercoolers with seawater or an intermediate fluid are required to reduce compression work. The nitrogen is sub-cooled (stages 7–8) by utilizing the same nitrogen in an exchanger following the final cooling in the compression. At this temperature, it expands adiabatically in an expander (stages 8–9), providing the cold current necessary to liquefy the BOG and sub-cool the nitrogen prior to expansion while returning a portion of the power used to compress the nitrogen (roughly 20%).

3.3.5. *Working Fluids Conditions Used in the Reliquefication of Boil-Off Gas*

A working fluid is needed in the reliquefication process of BOG onboard the vessel to facilitate the conversion of the BOG from a gaseous state to a liquid state. The primary purpose of the working fluid is to transfer heat and enable the cooling and condensation of the BOG. The working fluid serves as a heat transfer medium. It absorbs heat from the BOG at a higher temperature and carries it to a cooling system or a heat sink. This heat transfer process reduces the temperature of the BOG, facilitating its condensation. By cooling the BOG, the working fluid helps to remove the thermal energy from the gas, causing it to transition from a gaseous state to a liquid state.

Furthermore, in some reliquefication processes, the working fluid is compressed after it has absorbed heat from the BOG. Compression increases the pressure and temperature of the working fluid, allowing it to release the absorbed heat to a heat sink or a cooling system. The compressed working fluid can then be cooled and condensed to complete the reliquefication process. Therefore, it is essential to utilize a working fluid in the reliquefication process that can effectively transfer heat, lower the temperature of the BOG, and promote its condensation. Since the working fluid acts as an intermediary, absorbing and releasing thermal energy facilitates BOG's conversion into its liquid state for storage and transportation purposes. Refrigerants are commonly used as working fluids in the reliquefication process for both on-land or onboard vessel applications. This is because refrigerants have excellent heat transfer properties; their low boiling point and high heat capacity enable them to extract heat from the BOG effectively, enabling the gas to transition from a gaseous state to a liquid state. Also, they are used in the compression stage of the reliquefication process, where they can be compressed to higher pressures, allowing the condensed BOG to be further compressed and stored as a liquid. The compression process increases the density of the liquid energy carrier, thus, making it easier to store and transport. Refrigerants used can also be artificial or natural refrigerants.

In this paper, natural refrigerants such as nitrogen, hydrogen, or ammonia are the leading interest for sustainability and environmentally benign purposes. This is because they have very low or zero ODP and negligible GWP. Such that they have minimal impact on climate change and do not contribute to the depletion of the ozone layer, making them environmentally friendly alternatives to synthetic refrigerants. They are also generally non-toxic or have low toxicity levels, making them safer for onboard personnel and the environment. Apart from that, natural refrigerants are most likely and widely available and relatively inexpensive compared to some synthetic refrigerants. This availability and cost-effectiveness make them practical options for reliquefication systems onboard vessels. Also, they have favorable thermodynamic properties that contribute to high energy efficiency in the reliquefication process. They provide good heat transfer and cooling capabilities, allowing for effective boil-off gas (BOG) liquefaction with reduced energy consumption. The evaluation of each natural refrigerant for practicality and suitability on their utilization in the BOG reliquefication process is examined in section 4, considering their boiling point temperature, critical temperature, critical pressure, density, GWP index, ODP index, HTP, and flammability for safety consideration.

3.4. *Use of Natural Refrigerants*

In general, there are five primary types of refrigerants [95], namely:

- Halocarbons – a minimum of one of the three halogens: chlorine, fluorine, or bromine, are present. This group's most utilized refrigerants were halocarbons, composed of chlorine, fluorine, and carbon (CFCs). Apart from CFCs, other elements in this family include halons, carbon tetrachlorides, and per-fluorocarbons.
- Hydrocarbons – are primarily consist of carbon and hydrogen-based molecules, such as methane (R50), ethane (R170), propane (R290), butane (R600), isobutane (R600a).
- *Inorganic compounds* – these are categorized as natural refrigerants, which are most suitable for environmentally friendly applications. Ammonia (R717), water (R718), liquid air (R729), carbon dioxide (R744), and sulfur dioxide (R764) are a few examples.
- Azeotropic mixtures – two chemicals with differing characteristics that behave as one substance make up an azeotropic refrigerant mixture. the most widely used azeotropic refrigerant is R-502, which comprises 48.8% R-22 (HCFC) and 51.2% R-115 (CFC).
- Non-azeotropic mixtures – when employed in refrigeration cycles, a non-azeotropic mixture is a fluid made up of numerous components of various volatiles that undergo composition changes during evaporation (boiling) or condensation (e.g., R11 + R12, R12 + R22, R12 + R114).

The evolution of refrigerants throughout the period is shown in Fig. 23, where the refrigerants are described in relation to their subsequent generations from 1 to 5. It was not until the 1970 s that efforts were made to identify how various chemically composed greenhouse gases affected the temperature of the atmosphere and, thus, the Earth's surface. Moreover, refrigerants that can deplete the ozone layer and produce the greenhouse effect were commonly and commercially used in the nineteenth century. Therefore, over the years and through development, the introduction of each new generation of refrigerants has been associated with the effort to reduce CO_2 equivalent emissions into the atmosphere. It can be seen that in the 5th generation, concerning environmental awareness, natural refrigerants are becoming more popular. Consequently, among all these refrigerants, the options of interest to be examined are the inorganic compounds or natural refrigerants due to their low GWP20 years, low ODP, and low HTP (low toxicity and low flammability) values. The environmental impact of the proposed natural refrigerants for reliquefication onboard suitability is assessed using these parameters.

Several studies were also conducted by a competent team of researchers in utilizing natural refrigerants for the liquefaction process. Information was gathered from various sources, including the studies conducted by Shin & Lee [97] that focused on the importance of non-flammable refrigerants used offshore and investigated the liquefaction process using nitrogen as a refrigerant that was used to reliquefy a significantly large LNG plant. Nowadays, various refrigerants have been intensely researched to improve liquefaction effectiveness in an LNG facility. Morosuk et al. [98] recommended improving an MR process by adding a pre-cooler that uses propane as an extra refrigerant for Poly Refrigerant Integral Cycle Operation (PRICO: using a single-mixed refrigerant loop) liquefaction.

Also, Ding et al. [99] performed a pre-cooled propane N_2-CH_4 expansion procedure, and according to their findings, the system performance was halfway between an MR process and a nitrogen expansion technique. For further cooling cycle enhancement, Bi & Ju [100]

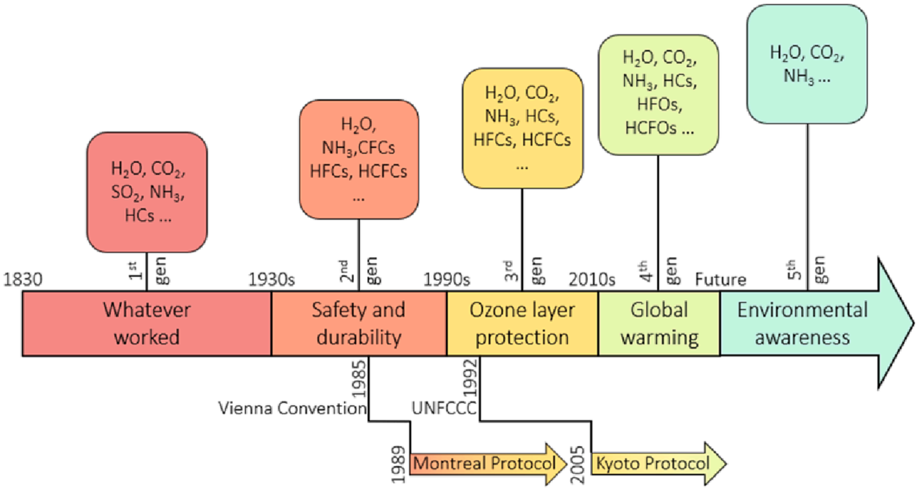


Fig. 23. Historical development of refrigerants (reproduced from [96]).

examined the cycles of cryogenic refrigeration for NG liquefaction processes using Joule-Thomson and Brayton cycles that use pure and mixed refrigerants.

When considering energy consumption efficiency, Hu et al. [101] examines the dual nitrogen expansion natural gas liquefaction process with pre-cooling. Nitrogen was used as the feed gas instead of natural gas, and propane was used as a pre-cooling refrigerant. This liquefaction process is considered the safe, most ecologically sustainable method and appropriate for small-scale plants due to its ease of use, fast startup, and practical maintenance; hence it is suitable to be implemented onboard. However, the main downside is that it consumes a huge amount of energy. On the other hand, J. Park et al. [80] discovered that using liquid air as a cold carrier is more effective than C3MR, widely known as a method that consumes remarkably less energy. Liquid air in the cold composite is a supplementary cooling system, increasing the heat exchange efficiency. Other natural refrigerants are listed in Table 6 with corresponding boiling points and their uses in the reliquefication process (i.e., precooling or primary cooling system).

Ozone Depletion Potential (ODP).

It is noted that rather than using artificial ones, natural refrigerants are used in these reliquefication processes. This is mainly because the most used and commercialized refrigerants are Ozone Depletion Substances (ODSs) which include CFCs, HCFCs, halons, methyl bromide, carbon tetrachloride, and methyl chloroform, that contribute to damaging the ozone layer [95]. Refrigerant chemicals have a lifespan of 70 to 100 years; during this period, they will remain in the atmosphere and continue to deplete ozone until they are naturally decomposed, especially CFCs and HCFCs that contain chlorine. These refrigerants are also generally stable, meaning rain or sunlight does not quickly degrade them. Since the ozone layer is in the stratosphere, this raises the risk that they will reach that layer easily [107]. The Hydrofluorocarbons (HFCs) family of refrigerants are known as artificial refrigerants with an estimated ODP value of 0 since it does not contain chlorine.

All natural or artificial refrigerants have an ODP, a comparative measurement of the substance's impact on the ozone layer's depletion. The gases ' impact on the ozone layer is quantified by comparing them to R-11 (CFC11), equal to 1.0. The highest ODP of all existing refrigerants, starting with CFCs, is 1. Both R-11 and R-12, two CFCs, have an ODP of 1. All of the HCFC (R22: OPD 0.05), HFC (R410a: ODP 0), and newer refrigerants have an ODP of less than 1, which implies it still depletes the ozone layer but considerably less than the CFC) [95]. In other words, the ODP value given to a refrigerant indicates how destructive it is to ozone in the atmosphere, and the greater the value, the more damaging it is. In the case of natural refrigerants, also known as inorganic compound type refrigerants, as listed in Table 6, since they do not contain chlorine or bromine, they do not contribute to destroying the ozone layer. Therefore, natural refrigerants are most predominantly used for sustainability reasons.

Global Warming Potential (GWP).

Another indicator of choosing the most suitable and least harmful refrigerants is to consider their GWP value, a comparative measurement of how much heat is captured in the atmosphere by a particular gas to how much heat is trapped by a comparable mass of carbon dioxide (CO_2: GWP 1) [107]. HFCs are known for not destroying the ozone, but they contribute to global climate change; R410a: ODP 0 but $GWP_{100years}$ 2088, which means it will capture 2088 as much heat as carbon dioxide over 100 years. Because of this, HFCs are gradually eliminated. On the other hand, although natural refrigerant such as propane (family of hydrocarbons (HCs), also has an ODP of 0, it does not necessarily have a GWP value of 0. In fact, propane has a very low $GWP_{20years}$ of 0.072. The least likely to cause global warming are the HCs; they are developed after the CFCs and HCFCs and created as alternatives to HFCs because of their significant potential for global warming. Therefore, the lower the GWP value, the less heat a particular gas is trapped in the atmosphere.

Human Toxicity Potential (HTP).

HTP is equally vital as ODP and GWP when determining suitable refrigerants. It is defined as a quantitative index that indicates the potential damage a particular chemical discharged into the environment could cause, particularly to humans (e.g., through inhalation, ingestion, or eye/skin contact). It is measured using kg 1,4-dichlorobenzene (1,4-DB) equivalent as the reference unit. According to the American Society for Heating, Refrigerating, and Air-Conditioning (ASHRAE), there are two categories of refrigerants depending on their toxicity levels: Class A for low-toxicity and Class B for high-toxicity refrigerants, while three categories for their flammability level: 1 for no flame propagation, 2 for lower flammability, and 3 for higher flammability [108]. As a natural refrigerant with ODP 0, ammonia has a high toxicity rating (B2 refrigerant: high toxicity but lower flammability), so it is not always ideal to use it as a refrigerant for every type of application. It must be appropriately handled before it can be utilized on a large scale. As a result, safety considerations should advance toward developing new standards and scientific/industrial experiments that will assess ammonia's potential, especially in the energy sectors [16]. Meanwhile, propane (A3 refrigerant: low toxicity but higher flammability) has a low toxicity

Table 6
Natural Refrigerants for Reliquefication Techniques.

Study	Refrigerants	Availability	Boiling points	Remarks
[101]	Nitrogen	78.08%	–195.8 °C	Main cooling (& final cooling in C3MR)
[102]	Oxygen	20.95%	–183 °C	Main cooling
[103]	Carbon dioxide	0.04%	–78.46 °C	Use in pre-cooling
[104], [80]	Air (liquid)	A mixture of nitrogen, oxygen, argon, helium, and other gases	−194.35° C (BP between LN2 and LO2)	Main cooling
[105]	Hydrogen	0.1% naturally but can be produced from others (e.g., water, ammonia, biomass)	–253 °C	Main cooling
[100,106]	Helium	0.00052%	–268.9 °C	Main cooling
[83]	Propane	5% in NG	–42 °C	Use in pre-cooling in C3MR and mixed with nitrogen, methane, and ethane in final cooling
[71]	Ammonia	Naturally occurs in soil, air, and water (although its concentration can vary depending on the specific location and ecosystem) and can be synthetically made from hydrogen and nitrogen from any fossil fuel (coal, natural gas, petroleum, naphtha), and can also be produced using any renewable energy source (solar, wind, hydro, geothermal, ocean), heat waste, or electricity (e.g., nuclear), biomass or organic waste (city waste)	–33.34 °C	Used as a refrigerant mixture (often mixed with lighter hydrocarbon methane or ethane) in the precooling cycle for better cycle efficiency and less environmental burden (lower the GWP index)

rating, zero ODP, very low GWP, and is not expensive to produce, and it may be advantageous as an alternative refrigerant. However, due to its high flammability, its applications might be restricted to specific processes of reliquefication.

Criteria for Selecting Appropriate Refrigerants.

There are several factors to consider when choosing an appropriate refrigerant for use in a refrigeration or reliquefication process, and these refrigerants should meet the following requirements: [95].

- Ozone and environmentally friendly.
- Non-flammable and nonexplosive.
- Noncorrosive and nontoxic.
- Nonacidic, nonreactive, and non-depletive.
- Easily detectable due to any leakage.
- Low boiling temperature.
- Lower vaporization pressure than the atmospheric pressure.
- Stable chemically.
- Available commercially and at a low cost.
- Suitable thermal and physical properties (e.g., thermal conductivity).

4. Overall Evaluation and Comparison

Ammonia Decomposition Techniques.

To effectively compare each technology, the evaluation results discussed in the preceding sections are normalized in this section. The normalized values (rank) of the operating temperature (*Equation (2)*) and the ammonia conversion rate (*Equation (3)*) are based on the following equation [109]:

$$\text{Rank}_{\text{temperature}} = \frac{\text{Maximum - Actual}_{\text{temperature}}}{\text{Maximum}} \times 10 \qquad (2)$$

According to this normalized equation, the ranking is between 0 and 10, where 0 indicates the least ideal temperature to decompose ammonia into hydrogen and 10 indicates the ideal case. For example, in this case, it was found that at a relatively low temperature of 250 °C, as shown in Table 7, a hybrid thermal-electrochemical approach to the ammonia conversion reaction to produce hydrogen as researched by Lim et al. [42] then 250 °C is assigned to the ranking of the normalized value of 6.15 as the closest to the ideal “10” since the lower temperature is desirable while maintaining higher hydrogen yield. Calculation example for the operating temperature of 250 °C:.

$$\text{Rank}_{\text{temperature (2500 C)}} = \frac{650\text{ - }250}{650} \times 10 = 6.15$$

The normalized values for the operating temperature of the decomposition are shown in *Equation (2)*. The same equation is also used to assign a higher temperature decomposition (maximum possible temperature within the comparison in Table 7); 650 °C, as researched by [62], is normalized as the rank “0″. It is because decomposing ammonia into hydrogen is endothermic, requiring energy input in the form of heat to proceed). High-temperature reactions require a significant input of energy, usually in the form of heat. The process of decomposing ammonia to hydrogen at extremely high temperatures can be energy-intensive and inefficient. It may lead to substantial energy losses and reduce the overall energy efficiency of the hydrogen production process; this is why it is considered the least ideal in this application.

Similarly, the ammonia conversion rate values are normalized as well; the equation for their ranking is as follows [109]:

$$\text{Rank}_{\text{ammonia conversion rate}} = \frac{\text{Actual}_{\text{ammonia conversion rate}}}{10} \qquad (3)$$

In this case, the highest conversion rate is 99.6%, as studied by Cechetto et al. [41] using catalytic membrane reactor techniques; thus, it is assigned as “9.96”, almost ideal (rank 10), while the lowest conversion rate is 98.4% as examined by Xie, Xia, Kong, et al. [38] by employing solar thermal decomposition (using trough solar collector); is as assigned as “9.84” according to the normalized ranking in *Equation (3)*. While the other two techniques have a 99.9% conversion rate which shows that all four reviewed methods of ammonia decomposition are

Table 7
Comparison of operating temperature and conversion rate of the different types of ammonia decomposition techniques.

Ammonia Decomposition Techniques	Typical Operating Temperature	Typical Ammonia Conversion Rate
Thermal decomposition with solar energy	427 °C	98.4 %
Electrochemical decomposition	250 °C	99 %
Catalytic membrane reactor	450 °C	99.6 %
Ammonia cracker-integrated SOFC technology	650 °C	99 %

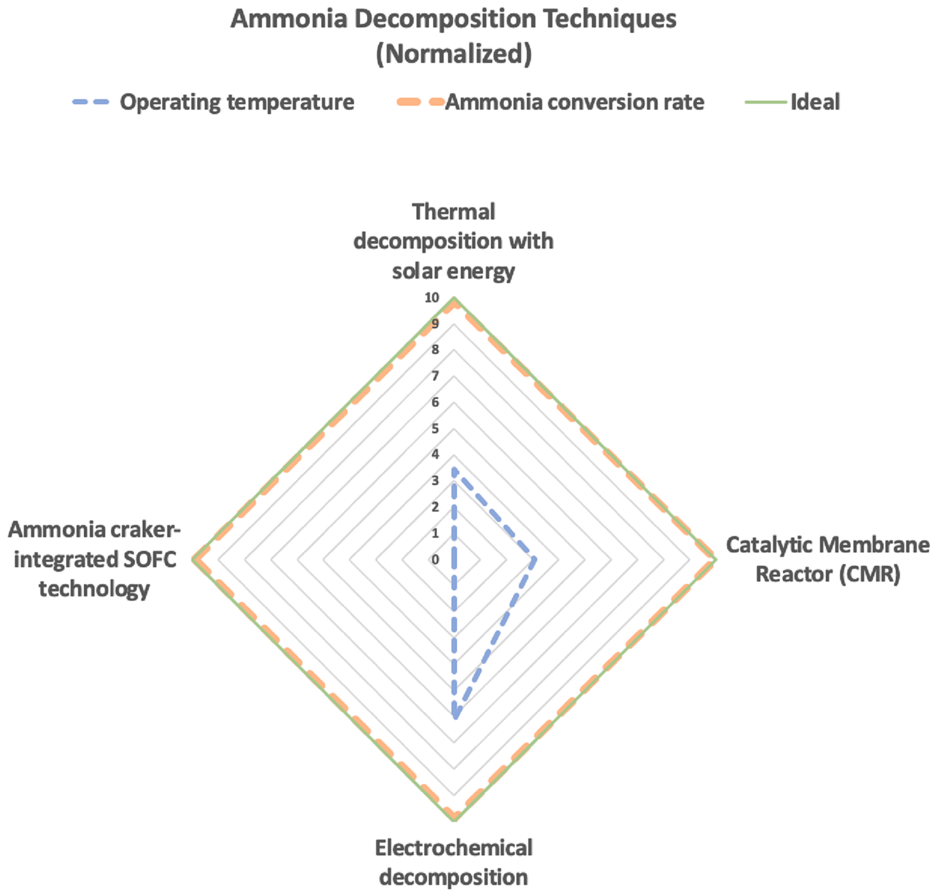


Fig. 24. Physical properties of the proposed ammonia decomposition techniques.

almost ideal, what differentiates them is the limiting and determining factors of the other integrated system (i.e., the temperature compatibility with the solar energy method selection, maximum temperature for onboard operation, etc.).

As shown in Fig. 24 is the comparative diagram of the discussed ammonia decomposition techniques concerning their operating temperature and ammonia conversion rate. According to the study researched by Lim et al. [42], a hybrid thermal-electrochemical approach to the ammonia conversion reaction to produce hydrogen at a relatively low temperature of 250 °C was considered ideal for onboard application, mainly when energy can be limited. Since a typical ammonia decomposition demands a higher temperature (min 400 °C) to overcome thermodynamic restrictions and kinetic barriers, however, a low temperature should be maintained to produce a high yield. The electrochemical decomposition of ammonia offers the possibility to produce high-purity hydrogen at near-ambient conditions and with high conversion rates as an alternative to high-temperature thermal decomposition. As well as aiming to resolve the ammonia contaminants in the hydrogen caused by high-temperature thermal decomposition. Therefore, thermal decomposition is integrated with electrochemical hydrogen removal from the ammonia decomposition reaction zone to solve the thermodynamic restrictions that product accumulation would otherwise create. Therefore, a hybrid thermal-electrochemical decomposition is the most feasible choice, with the help of solar energy generation as a renewable energy source for electricity and heating/cooling purposes.

Concentrated Solar Power Integration.

Using mirrors and tracking technologies to concentrate a vast amount of sunlight into a narrow beam, concentrated solar power facilities convert sunlight into electricity. Solar thermal energy production uses concentrated sunlight to generate heat, which is then used to power a steam turbine, which spins a generator to produce electricity. Water is a working fluid heated by a ray of concentrated sunshine [110]. Therefore, generating steam without burning coal, oil, natural gas, or releasing uranium causes no damage to the ecosystem.

- *Ranking for operating temperature compatibility* (CSP's operating temperature should match that of the ammonia decomposition):
  - o If its operating temperature is compatible with the ammonia decomposition techniques, it is ranked 10; otherwise, 0. According to Table 4 by Allouhi et al. [76], all four CSP technologies have operating temperatures within the range of ammonia decomposition temperature in Table 7. The CSP operating temperature is typically around 400 °C but could be as low as 250 °C, such that PTC (290–390 °C), LFR (250–390 °C), SD (250–700 °C), and ST (250–500 °C) are all ranked 10 (most ideal).
- *Ranking for land occupancy* (smaller land area is desirable since the area on the vessel is limited):
  - o Due to the limited spaces on the vessel, the most ideal CSP technologies to be installed are those with the least area (the smaller the area, the most ideal it is).
  - o A study by Soomro et al. [111] categorized the land occupancy of these four CSP technologies as large (rank 0), medium (rank 5), and small (rank 10), such that PTC (large area needed – rank 0), LFR (medium area – rank 5), SD (small area – rank 10), and ST (medium area – rank 5), therefore the one with the smallest area is considered the most ideal, in this case, the solar dish.
- *Ranking for thermal efficiency*:
  - o Ideally, the thermal efficiency of CSP technologies is between 7% (lowest – rank 0) and 25% (highest – rank 10) [112] and a study by

Allouhi et al. [76] also determined the four CSP technologies' thermal efficiency, such that PTC (15% – rank 4.5), LFR (8% – rank 0.5), SD (25% – rank 10), and ST (20% – rank 7.5) as shown in Fig. 25 and Table 8 for detail calculations.

- The formula used for these normalized values is as follows:

$$\text{Step increment}_{\text{thermal efficiency}} = \frac{\text{Maximum}_{\text{actual}} - \text{Minimum}_{\text{actual}}}{10} \tag{4}$$

From this equation, each step increment is $= \frac{25-7}{10} = 1.8$, therefore:

- Accordingly, the CSP technologies with the highest thermal efficiency are considered the most ideal, resulting in the solar dish with 25% efficiency.

Table 8
Calculation of the step increment for CSP thermal efficiency ranking.

Normalized (rank)	Actual thermal efficiency value	Types of CSP
0	7	**LFR = 8%** (thus in between this value)
1	8.8 (e.g., 7 + step increment)	
2	10.6	
3	12.4	
4	14.2	**PTC = 15%** (thus in between this value)
5	16	
6	17.8	
7	19.6	**ST = 20%** (thus in between this value)
8	21.4	
9	23.2	
10	25	**SD = 25%**

The four most popular types of CSP are compared in terms of their ranking from 0 (least ideal) to 10 (most ideal), as shown in Fig. 25. Therefore, according to their ranking , the solar dish has a broader range of operating temperatures starting from 250 to 700 °C, which is suitable for a typical ammonia decomposition with a higher temperature above 400 °C (i.e., thermal decomposition with solar energy (using trough solar collector), researched by Xie, Xia, Kong, et al. [38]) or lower temperature (i.e., hybrid thermal-electrochemical decomposition, studied by Lim et al. [42]). Regarding land occupancy reviewed by Soomro et al. [111], the solar dish has the lowest area requirement, which is the most suitable option to be integrated into vessels where the area is a limiting factor. It was also quantified by Prado et al. [113] that a steel solar dish measurement could be as small as 68 cm in height and 62 cm in width. At last, the determining factor is the thermal efficiency; among all the other three candidates, the solar dish has the highest thermal efficiency of 25%, whereas, for CSP, the thermal efficiency ranges from 7% to 25% [112].

Compared to other concentrated solar technologies, the parabolic dish concentrator has some strengths, such as continuous exposure to the sun and excellent thermal and optical efficiency [114], as well as other significant promising superiorities, primarily as distributed solar thermal energy sources. The largest energy end-use, accounting for more than 50% of energy consumption, is heat, according to the IEA [115]. Furthermore, in the 70–80% range or more, parabolic dish systems offer significantly greater solar–to–steam conversion efficiency than parabolic trough systems. This is because they always face the sun due to dual-axis tracking (as opposed to a single-axis for trough) and a more effective cavity receiver (compared to an evacuated tube receiver for trough). Additionally, parabolic dish systems can be linked to a roof support column or put on a tower, allowing them to be installed practically anywhere with enough clearance, especially on rocky or steep

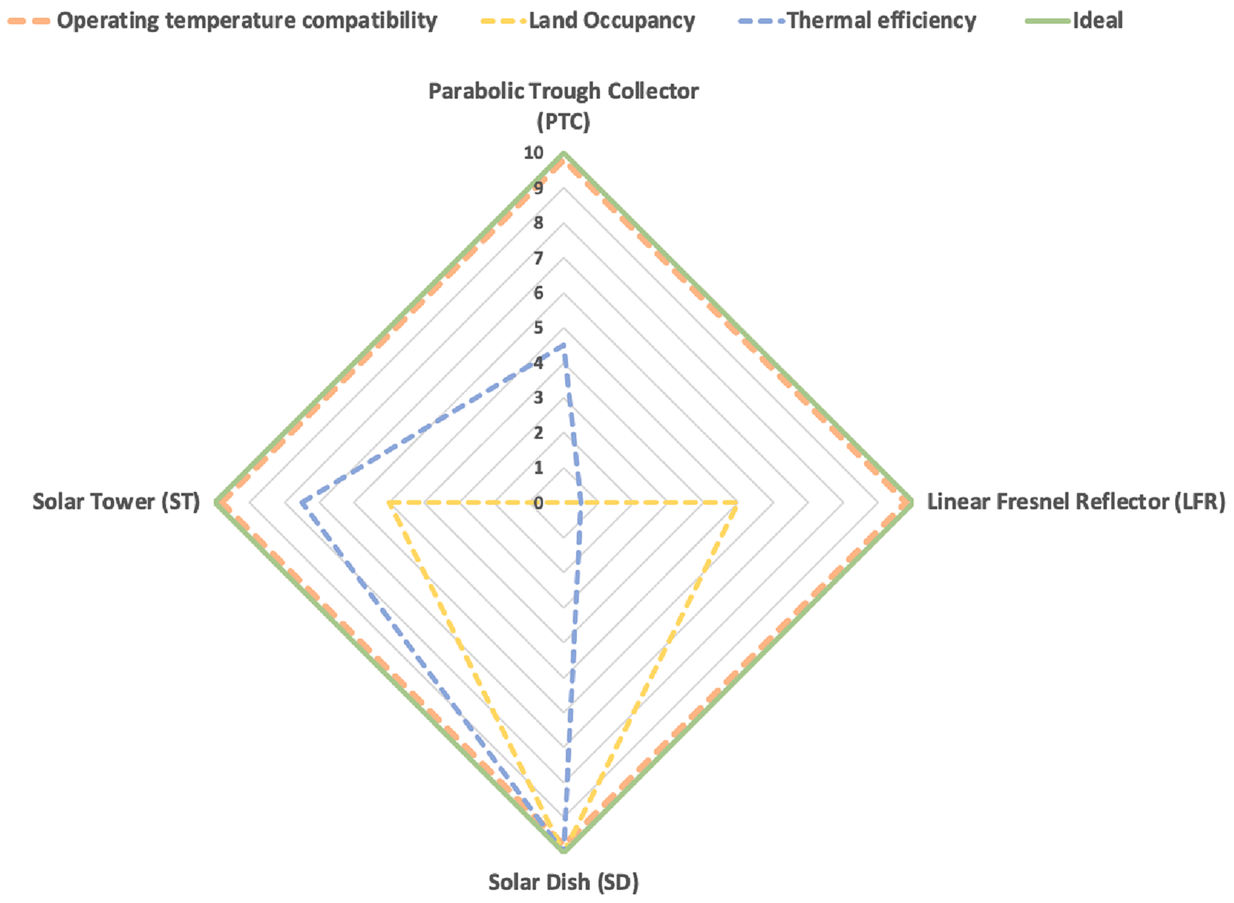


Fig. 25. Comparison of the CSP technologies' properties for onboard suitability.

terrain (dispensing with the expensive rooftop support structure required for parabolic trough or PV panels) [116]. Therefore, compared to parabolic trough systems, parabolic dish systems offer significantly more energy per unit of installed land because of their superior energy conversion capability.

Natural Refrigerants.

Table 9
The actual values of both natural and artificial refrigerants in terms of their GWP and ODP indexes.

Types	Refrigerants	GWP 20-years	ODP
Natural	Nitrogen (R728)	0	0
	Oxygen (R732)	0	0
	Carbon Dioxide (R744)	1	0
	Air (Liquid) (R729)	0	0
	Hydrogen (R702)	0	0
	Helium (R704)	0	0
	Propane (R290)	0.072	0
	Ammonia (R717)	0	0
Artificial	CFC (R11)	4750	1
	HFC (R407C)	4100	0
	HCFC (R22)	5310	0.07
	HFO (R450A)	1600	0

The actual values of both natural and artificial refrigerants are outlined in Table 9. While the evaluated natural refrigerants are contrasted with the other four artificial refrigerant families to compare their effects on the environment, is shown in Fig. 26.

Natural refrigerants have a GWP of less than 1 (CO_2) and ODP of 0 values, while the artificial ones, particularly HCFC (R22), have a 5310 times impact on global warming as CO_2 and CFC (R11) has the highest ODP of 1. While their actual values of GWP20 years and ODP are based on Benhadid-Dib & Benzaoui [117], these refrigerants' GWP and ODP values are normalized in a similar manner as shown in *Equation 4*, as well as a modification from Acar & Dincer [109]:

$$\text{Step increment}_{\text{GWP, ODP}} = \frac{\text{Max value - Min value}}{10} \tag{5}$$

Since the highest value belongs to HCFC (R22) = 5310, it is considered the maximum value and therefore assigned a ranking of "0″ as having the worst environmental impact. In contrast, the actual value of 0 GWP and ODP index is regarded as the ideal case, thus, assigned to a ranking "10". As seen from *Equation 5*, the steps increment for this particular ranking is relatively very high due to the enormous difference between the maximum and minimum values; therefore, a comparative diagram is made to comprehensively show the difference natural refrigerants made compared to the artificial ones as shown in Fig. 26 that all natural refrigerants have values that are very close to the ideal for

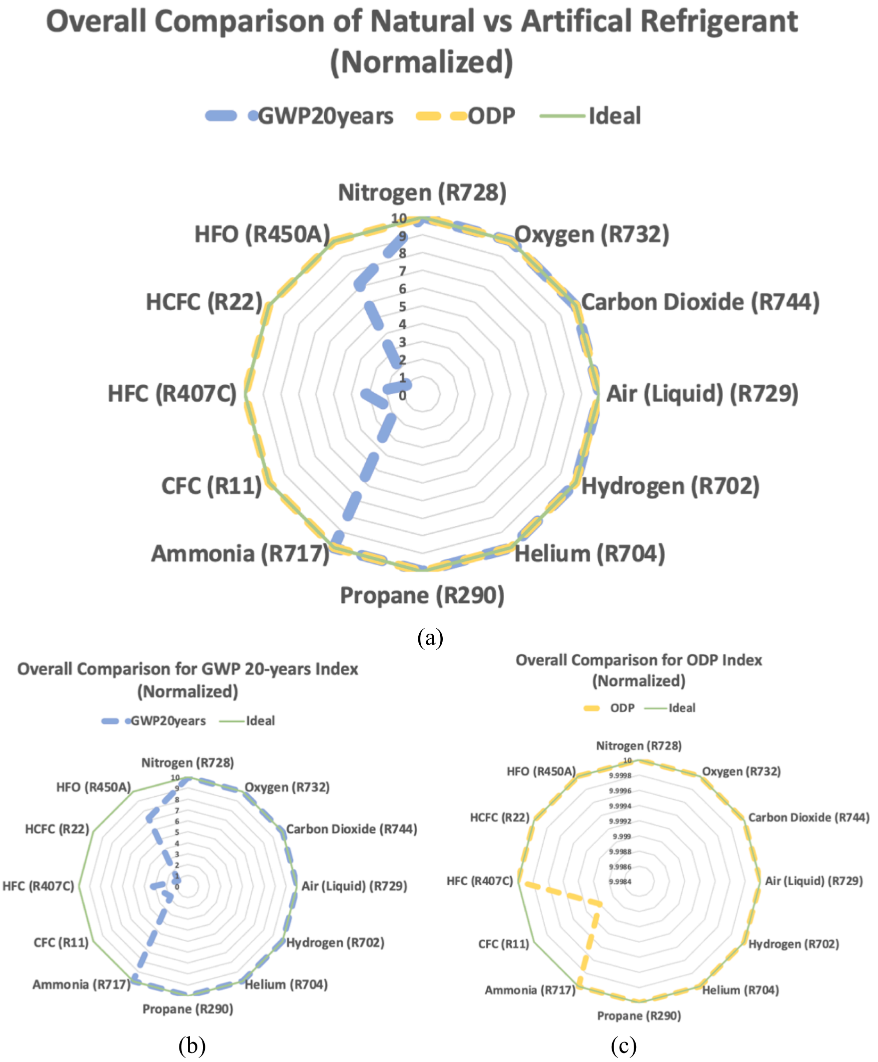


Fig. 26. (a) Ranking of the natural and artificial refrigerants in terms of their GWP20years and ODP values concerning the ideal values, (b) Comparison only for the GWP 20-year index, and (c) Comparison only for the ODP index.

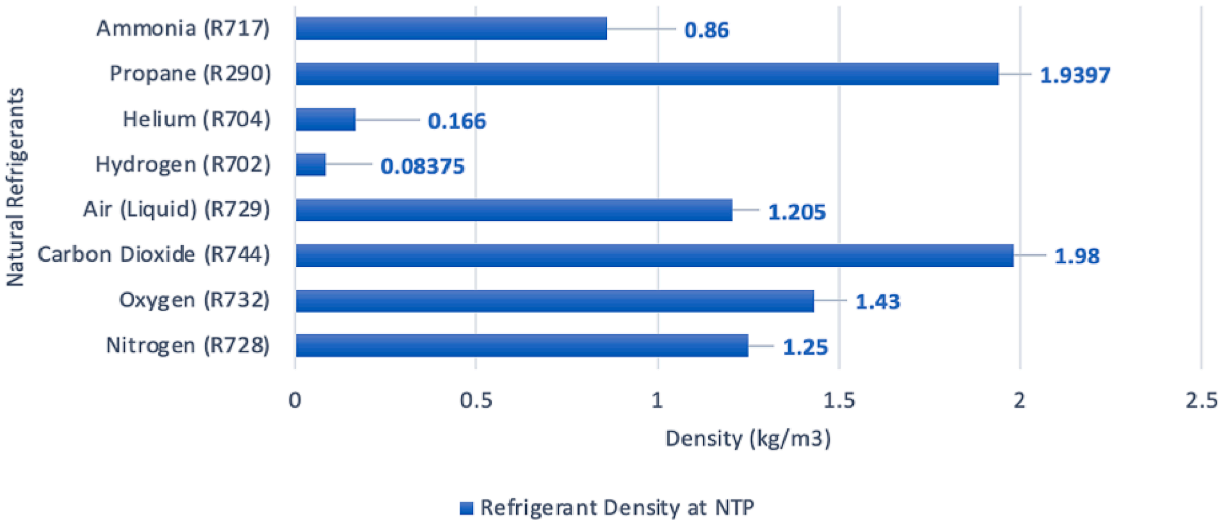


Fig. 27. Comparisons of the natural refrigerants' density at NTP (reproduced from [119]).

both GWP and ODP values. On the other hand, the four artificial ones are far from ideal regarding their GWP20 years impact. For clarity, natural and artificial refrigerants indexes are also shown separately to compare them individually based on the GWP20 years and ODP indexes.

Furthermore, according to the study by Devecioǈlu & Oruç [118], to increase capacity and consume less energy, refrigerants with thermodynamic features such as a high vaporizing temperature (boiling points) and a high gas density should be considered when selecting a refrigerant. High-density refrigerants are necessary because increasing the density of the refrigerant return gas to the compressor will improve system capacity. Thus, it requires a small compressor so that the velocity can be minimally impacted, allowing smaller-diameter condenser tubes to be employed. A comparison of densities for the proposed natural refrigerants is shown in Fig. 27, indicating that carbon dioxide has the highest density at Normal Temperature and Pressure (NTP). In contrast, hydrogen has the lowest density at NTP because hydrogen has the most negligible atomic weight of any element. NTP's standard is based on a room temperature of 20 °C and pressure of 1 atm [119] and is used as a

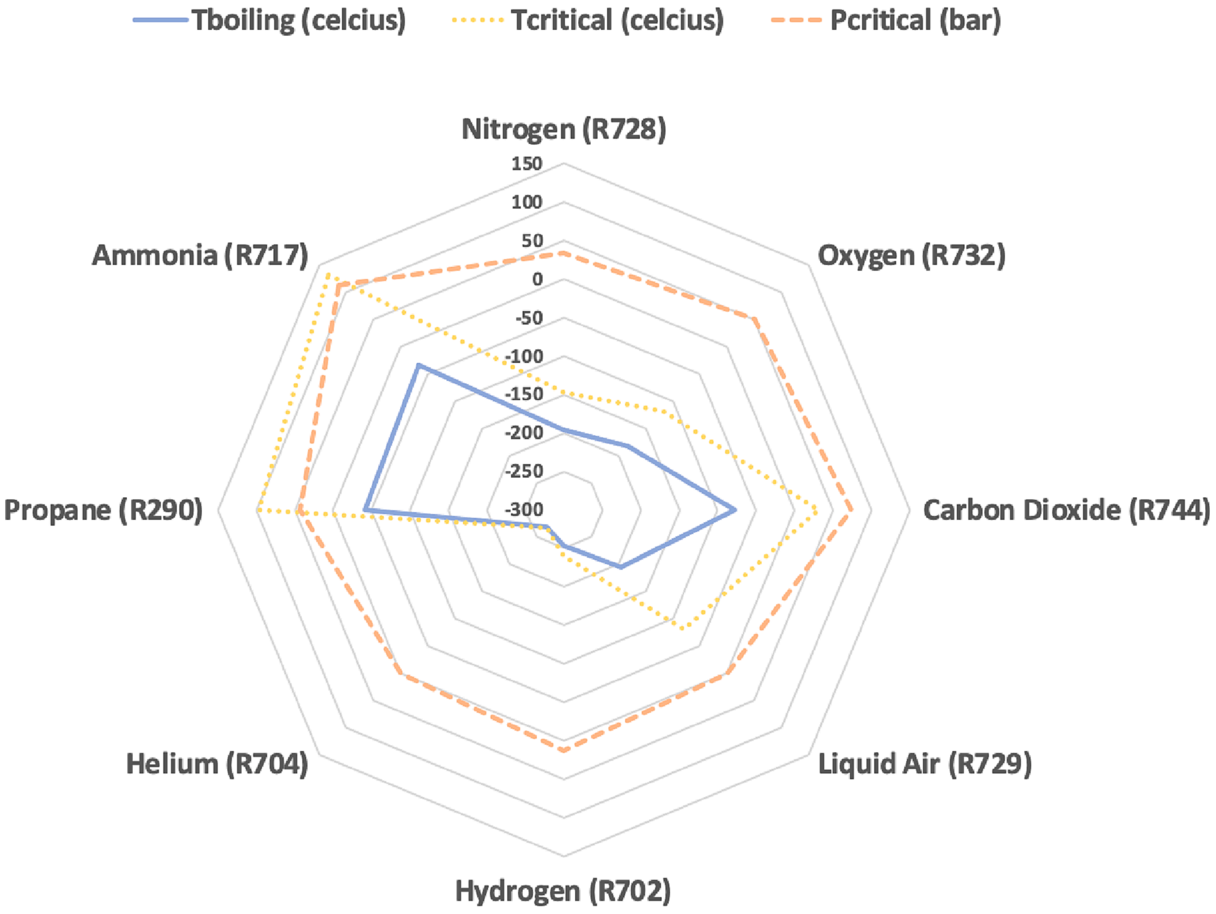


Fig. 28. Comparison of the natural refrigerant physical properties.

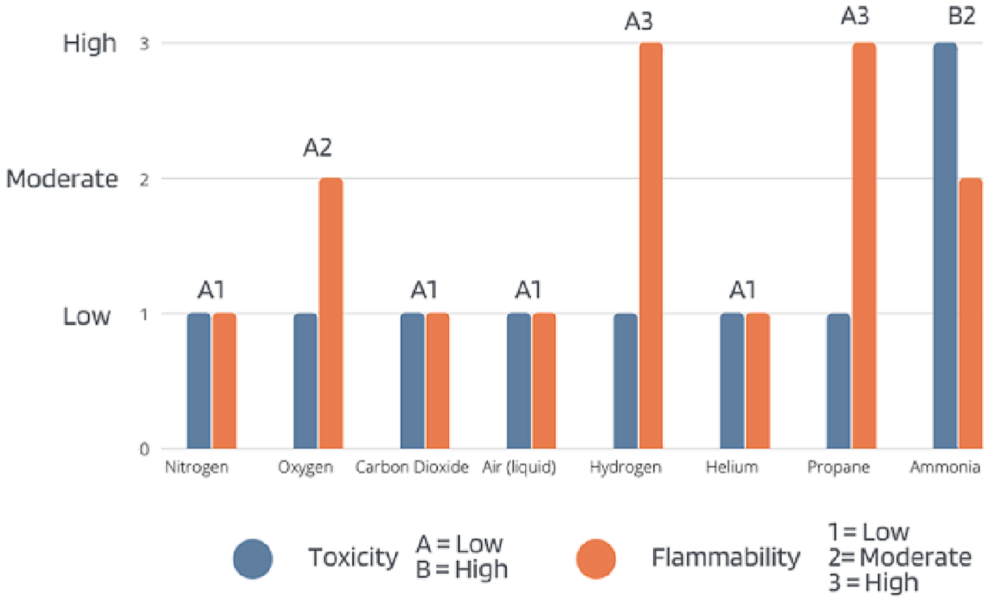


Fig. 29. Comparison of the HTP values for the proposed natural refrigerants.

standardized reference condition to express liquid or gas volumes or densities.

Fig. 28 compares the proposed natural refrigerants' boiling points, critical temperature, and pressure. Selecting refrigerants with low boiling points is essential because refrigerants with low boiling points can be easily transformed into gas when heated. If they have higher boiling points, the compressor must create a substantial amount of vacuum before reducing the pressure enough for vaporization. In the ranking from the lowest to highest according to their boiling points, as shown in Fig. 28, helium ranked the first (lowest boiling point of –268.9 °C), then hydrogen (–253 °C), nitrogen (–195.8 °C), liquid air (−194.35 °C), oxygen (–183 °C), carbon dioxide (–78.46 °C), propane (–42 °C), and lastly ammonia (–33.34 °C). The last three are often used as pre-cooling refrigerants in the reliquefication process due to their higher boiling points, while the first five are usually used in the main cooling.

Due to their environmental advantages (zero ODP and low GWP), natural refrigerants were predicted to replace conventional artificial ones [120]. However, as illustrated in Fig. 29, they present some disadvantages, such as toxicity and flammability. According to the ASHRAE safety class, it can be noticed that some of the proposed gasses are moderately flammable, which can be a limiting factor for some applications. Nonetheless, class A1 (low toxicity and flammability), such as nitrogen, carbon dioxide, liquid air, and helium, could be the safer options.

In summary, after considering several important factors in selecting the most proper refrigerants for suitability of the reliquefication process onboard, such as low boiling point, low GWP, 0 ODP, low toxicity, and low flammability. *Nitrogen*, as the other natural product of ammonia decomposition, is considered the most suitable one due to its lower boiling points (-195.8 °C), 0 GWP20 years, 0 ODP, and type A1 (low toxicity and low flammability), as well as because it is also the most used refrigerant in several reliable reliquefication techniques, such as:

- SMR: used mixed refrigerants; nitrogen is one of them.
- DMR: used mixed refrigerant in the second cycle; nitrogen is one of them (since this is a dual cycle system, the first cycle is usually for precooling, using propane as refrigerant).
- C3MR: used mixed refrigerants in the final cycle; nitrogen is one of them (the first cycle is generally for precooling, using propane as refrigerant).
- Reverse Brayton Cycle: Nitrogen is used as the working fluid; it is cooled before entering an expander.

However, to liquefy the hydrogen gas itself, a gas with a lower boiling point is required, such as utilizing helium as refrigerant, since it has a lower boiling point than hydrogen (–268.9 °C).

5. Conclusions

While hydrogen does not exist abundantly in nature as a single molecule (typically combined with other compounds such as water, methane, etc.), a carbon-free molecule such as ammonia can potentially and effectively serve as a carrier for hydrogen. Ammonia has various advantages as a hydrogen carrier, including high hydrogen density, existing infrastructure, global supply chains, safe handling practices, carbon-free production pathways, flexibility in hydrogen release, and ongoing standardization efforts. These factors contribute to the attractiveness of ammonia as a viable option for hydrogen storage, transport, and utilization. Producing hydrogen from ammonia can be sustainably beneficial, especially when incorporating renewable energy sources for both ammonia production and decomposition, minimizing environmental and safety risks. This review emphasizes the need for sustainable and clean energy sources, mainly in the maritime industry. By leveraging concentrated solar energy, the onboard decomposition of ammonia into nitrogen and hydrogen can be achieved, providing a renewable and efficient pathway for hydrogen production. This approach offers a promising alternative to conventional energy sources, reducing greenhouse gas emissions and promoting a more sustainable maritime sector. Furthermore, the recovery of boil-off gas, an inevitable byproduct typically released during storage or transportation during voyages, presents an opportunity to utilize waste gases. This integration of boil-off gas recovery enhances the efficiency and overall sustainability of the hydrogen production process, minimizing waste and optimizing resource utilization.

In this review paper, several approaches for producing hydrogen from various ammonia decomposition techniques are comprehensively and comparatively compared, treating its BOG by outlining diverse potential reliquefication processes, along with the available mixture of refrigerants, in the presence of utilizing solar power to achieve less CO_x emissions. The methodology for conducting this review was also outlined and supported by reliable sources of relevant studies to validate the objective of filling the research gaps.

The main findings of this study can be summarized as follows:

- Hydrogen is a promising clean energy carrier due to the absence of carbon in hydrogen, making it a “clean alternative” to natural gas.
- The efficiency, total cost, and structural complexity of the hydrogen liquefaction processes have all been optimized in various ways, such as by using the multi-component or multi-staged/cascaded refrigerant cycle.
- Its significant issues include the lack of innovative technology, high economic expenses, limited efficiency, and huge losses.
- Thus, as an alternative, hydrogen will be produced and stored on fleet carriers while transporting ammonia.
- Ammonia’s distribution and transportation system have already been developed on a wide scale and are adaptable to several novel and promising purposes.
- As a hydrogen energy carrier, ammonia.
  - It contains 17.6% hydrogen by weight,
  - Due to its high capacity, it has a higher energy density than methanol, synthesis gas, and other hydrogen-containing materials, at approx. 3000 Wh kg^{-1},
  - No CO_x emission: it is advantageous for the separation and purification of hydrogen that no CO_x byproducts are produced during the conversion of ammonia into hydrogen,
  - Easier to transport; it is easily liquefied at low pressure (3 atm) and low temperature (25 ^{0}C),
  - And high selectivity; since the only byproducts of ammonia decomposition are hydrogen and stoichiometric nitrogen, which outperforms other liquid organic hydrogen carriers.
- The main focus of this paper is the study of various ammonia decomposition techniques to produce clean hydrogen by recovering the boil-off ammonia. A selection of natural refrigerants was studied concerning their limiting and determining factors to determine the suitable choice for the reliquefication of boil-off gas onboard and to examine several BOG recovery treatments on the vessel.
- Among other ammonia decomposition techniques, a hybrid of electrochemical and thermal decomposition was considered the most suitable one, especially in terms of temperature efficiency (relatively lower temperature: 250 °C; less energy required, while able to maintain high yield and complete conversion).
- The BOG reliquefication methods have their winning and losing factors; depending on the ship’s design and conditions, one would be an optimal choice for the other. However, in terms of the flexibility of refrigerants used and the number of reliquefication cycles, DMR was more suitable since the properties of mixed refrigerants provide optimal cooling results, and the use of a second refrigerant loop improves the production efficiency of the reliquefied gas.
- Since nitrogen is the other product of ammonia decomposition, it is considered the most suitable refrigerant due to its lower boiling points (-195.8 °C) and critical temperature (-147 °C), and it is also the most used refrigerant in several reliable reliquefication techniques.
  - Regarding its environmental impacts, nitrogen is a class type A1 (low toxicity and low flammability), with 0 Global Warming Potential and 0 Ozone Depletion Potential.

As future recommendations, it is necessary to establish a sustainable and resilient hydrogen economy that requires addressing hydrogen production, storage, and transportation and incorporating all at once while strengthening strategic policy. Although the future of the hydrogen economy looks promising, the ongoing global focus on decarbonization and the need to increase realization/awareness for sustainable energy solutions position hydrogen as a critical player in the transition towards a greener and more sustainable future is highly essential. And that collaborations among academia, industry, and government institutions are as crucial to ensure the research findings are effectively translated into real-world applications and contribute to the transition toward a clean and sustainable energy future.

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.

Data availability

No data was used for the research described in the article.

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