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LNG Cold Energy Recovery for Hydrogen Production Combining Multiple Technologies in Synergy

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As a result of the rising global reliance on fossil fuels, freshwater scarcity and environmental problems are getting worse. The process of regasifying liquified natural gas (LNG) releases cold energy, which is often wasted, causes issues for the environment, and increases energy system inefficiencies. This project aims to enhance the sustainability of LNG regasification plants by effectively harnessing this cold energy. The research proposes using this cold energy in four main areas: seawater desalination, hydrogen production, power generation, and carbon dioxide liquefaction. The study explores creating a process that combines Steam Methane Reforming (SMR) with carbon capture and solar-powered water electrolysis, using the organic Rankine cycle for energy recovery and implementing a hybrid desalination process. The majority (82.9 %) of the input liquefied natural gas (LNG) is directed to the natural gas distribution pipeline, the primary function of the regasification facility. For every twelve kilograms of LNG processed, approximately one kilogram of valuable hydrogen is produced. While this hydrogen stream may appear insignificant relative to the complexity of the proposed process from an environmental perspective, it is crucial to acknowledge the low molecular weight of hydrogen. This characteristic implies that a captured and liquefied carbon dioxide (CO_2) stream, roughly half the weight of the input LNG, is also collected. This approach enhances environmental sustainability by collecting captured CO_2 and energy efficiency, laying the groundwork for future advances in LNG cold energy usage.

1. Introduction

Population, urbanization, and industrial growth are all contributing to an increase in global energy consumption and freshwater scarcity. However, using fossil fuels to supply this demand has highlighted serious environmental issues. As a result, it has become critical to explore cleaner and more sustainable energy sources to counteract these negative consequences.

LNG is transported by ship to receiving terminals (Shakrina et al, 2021). At the terminal, LNG is regasified by heating to convert it back to gas. This regasification releases stored cold energy to the seawater (Lim et al, 2020). Advanced techniques are being explored to utilize this cold energy, such as power generation, air separation, seawater desalination, CO_2 capture via cryogenics, and hydrogen production. This study complements the review from Wang et al (2023) but focusing on hydrogen production as a final goal instead of air separation. Hydrogen is crucial for decarbonizing sectors like transportation and industry. Efficient large-scale hydrogen production methods, including renewable sources (Hai et al., 2024) and traditional reforming systems (Zhang et al., 2023), are needed. Freshwater production technologies like reverse osmosis and multi-effect distillation are energy-intensive, making freeze desalination using LNG's cold energy an attractive alternative (Wang and Chung, 2012).

Literature studies proposing different alternatives for LNG cold energy recovery are reviewed. In this study instead of considering them as alternatives, all of them are combined in a single process to operate in synergy. The mass balance and energy consumption of each process are provided by the studies cited in this work. In this way the only required streams are LNG and seawater and the output streams are the natural gas (main product), hydrogen (worth byproduct), brine and captured CO_2 (avoiding the emission of this greenhouse gas).

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2. Methodology

Six steps are followed. First, an exhaustive literature review and comparison of LNG cold energy applications is carried out, with an emphasis on water, hydrogen, and energy generation. Two hydrogen generation methods, steam methane reforming with carbon capture and water electrolysis utilizing a proton exchange membrane, are chosen for their energy efficiency and compatibility with the Sustainable Development Goals. Third, the system critical components and operations are described. This included mapping interrelationships, and material flows. This stage provided the groundwork for identifying areas for improvement, maximizing resources, and exploring prospective innovations. Fourth, all process flows, and global energy requirements are documented but their results are not verified, being considered feasible and reliable from economic and practical feasibility viewpoint. A process block diagram is created to illustrate these flows, which are complemented with diagrams for each subprocess to help in understanding system dynamics and interconnections. Fifth, global mass balances are estimated in Microsoft Excel, and energy calculations are done using the Aspen Plus® simulation program to ensure coherent and consistent findings. An economic feasibility analysis comparing the price of LNG and hydrogen was then performed to estimate the output-input balance, as well as assess the proposed system's economic advantages and practical feasibility. Finally, and sixth, based on the system analysis, recommendations for increasing system performance were developed.

3. Results

An innovative integrated system that maximizes efficiency and reduces energy waste in a variety of industrial operations by utilizing LNG cold energy is shown in Figure 1. The process that is presented is the product of combining multiple processes that have been documented in the literature; it has been designed such that all their connections match together and work together effectively.

This integrated system is an innovation in the field of LNG cold energy use, as it was not reported in the literature before, unlike the separate research that has been previously detailed. To improve the system's energy efficiency, additional units that are not covered in the literature have been incorporated into these processes. Such as oxycombustion, this unit generates the heat required for methane reforming. In this process, natural gas (NG) and O_2 produced by water electrolysis are burned to produce CO_2 and thermal energy, the heat exchange system receives the CO_2 that is produced to liquify it.

This strategy supports sustainability initiatives by reducing CO_2 emissions. The mass and energy flows presented in the diagram reflect a detailed analysis, ensuring efficient and balanced operation. With the objective to achieving optimal system performance, these balances are obtained and adjusted employing information from the literature, combining several technologies and techniques.

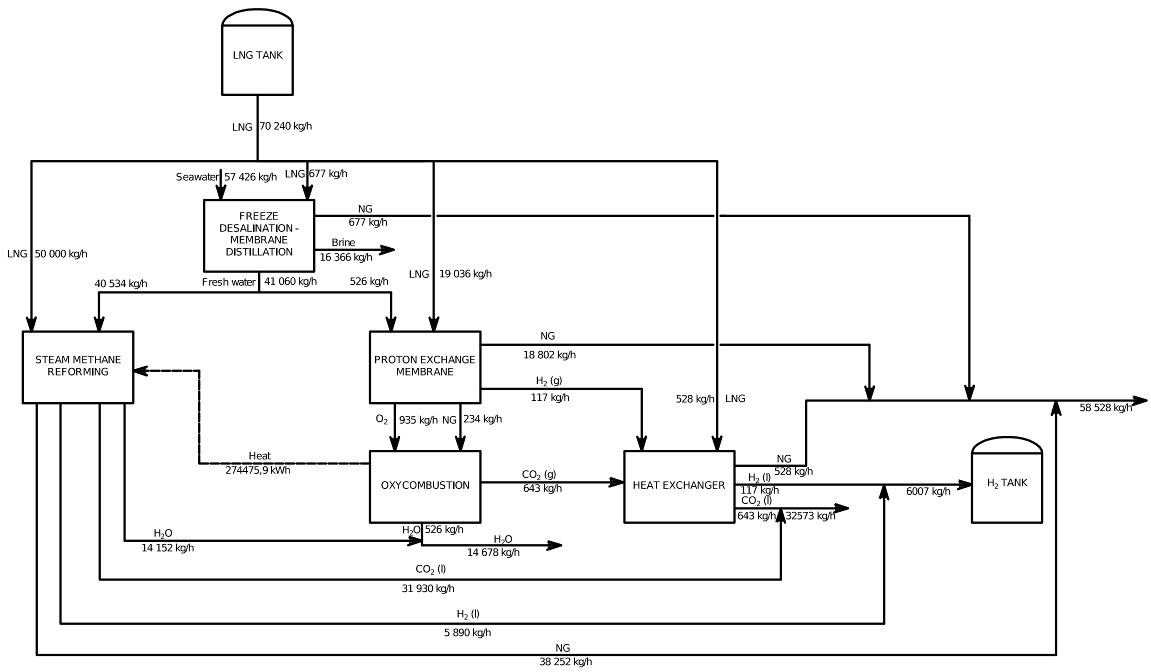

Figure 1: Block diagram of the general process

The process is designed to optimize efficiency and the production of desired products, adhering to quality and sustainability standards. After being carefully adjusted and checked to satisfy the specifications and operating parameters of the process, the mass balances are carried out using data from the literature. With this strategy, all material flows are guaranteed to be appropriately balanced and the process runs as efficiently as possible because the design is based in reliable and tested data. The general mass balance is shown in Table 1.
Once the data from Table 1 is analysed, it becomes evident that a significant amount of the LNG input (82.9 %) is going to the natural gas distribution pipeline. Moreover, a great amount of LNG has been used for the pre-cooling and liquefaction of CO_2 and hydrogen. The processes of steam methane reforming and oxycombustion generate a significant amount of clean water, which may be utilized in other processes that require water, such as electrolysis or steam methane reforming. The data from the steam methane reforming unit is based on the work of Zhang et al. (2023); Wang and Chung (2012) for the desalination process; and Hai et al. (2024) for the electrolysis of water.
Figure 2 illustrates a highly effective seawater desalination and purification process that uses a variety of advanced technologies to produce fresh water while reducing salty waste. Since freeze desalination has low efficiency, the resulting brine undergoes membrane distillation to obtain higher purity water and increase the overall desalination system's performance. This process, which includes crystallization, ice and brine separation, ice washing and melting, and membrane distillation, is very efficient and employs the latest technologies to generate high-quality pure water while reducing waste and optimizing energy consumption. The incorporation of the LNG vaporizer further highlights the system's adaptability, since it allows for the use of various energy sources. The location of degasification terminals at the seaside has promoted the research on seawater desalinization (Ong and Chen, 2018).

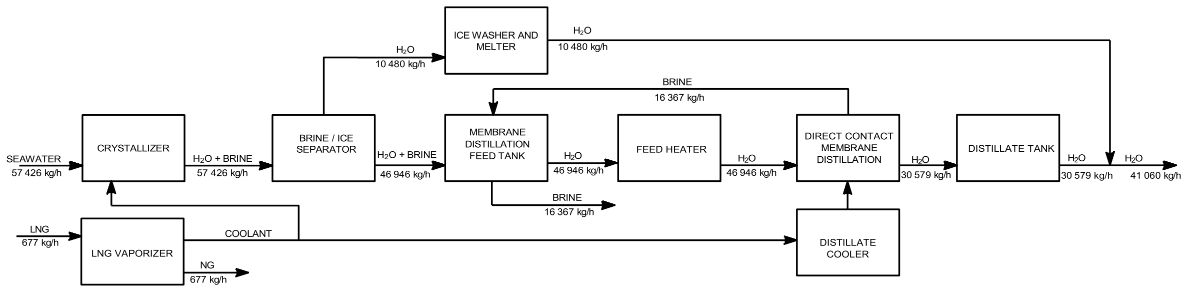

Figure 2: Block diagram of the freeze desalination-membrane distillation process

The mass balance demonstrates (Table 1) the system's high yield (71.5 %) and the lower quantity of LNG required to operate the system, exhibiting its high energy efficiency. Additionally, the output water from the freeze desalination has a salinity of 0.146 g/L (the water entering had a salinity of 3.5 g/L) , and the water that leaves the membrane distillation has a salinity of 0.062 g/L, which leads to the system's salinity of 0.086 g/L, meeting the World Health Organization's (WHO) criteria for salinity in potable water, which is 0.500 g/L. Adding the second stage, the membrane distillation shows a great increase in the efficiency of the system, while the freeze desalination obtains water with sufficient purity. This step reduces the salinity to half, increasing the amount of water obtained by 292 %.
This system integrates two processes for hydrogen production: steam methane reforming, which converts natural gas and steam into H_2 and CO_2, and proton exchange membrane water electrolysis, which produces H_2 and O_2 by decomposing H_2O molecules. It is innovative to merge these two processes into a single system. Combining various processes into a single system provides benefits in terms of efficiency, economics, and sustainability by utilizing technological synergies and maximizing resource use. Figure 3 shows an integrated industrial process that combines green H_2 production with natural gas combustion, energy recovery, and cooling for domestic use, optimizing resource utilization, increasing energy efficiency, and reducing waste, all of which contribute to sustainable industrial operation. LNG also precools the generated hydrogen before liquefaction. Pre-cooling part of H_2 improves the energy efficiency of liquefaction; the results showed that using LNG could reduce the energy consumption of the process by 11 % (Zhang et al., 2024).
The data demonstrates the great quantity of LNG required in relation to the amount of the desired product, hydrogen. It is shown in Table 1. Because of the high quantity of energy required, all the energy created in the solar collectors and organic Rankine cycle is directed to feed the proton exchange membrane. This also demonstrates the implementation of actions to increase energy efficiency and the search for alternatives to purchasing external electricity. Although the process scheme producing green H_2 proposed by Hai et al (2024) has been implemented in this study there are also interesting previous studies about. Yu et al (2019) investigated the suitable working fluid for the Rankine organic cycle using LNG to produce electricity and later they proposed

to combine it with a multiple effect desalination to produce also water (Alirahmi et al, 2022). The reaction produces oxygen, which is consumed in the next unit. When the LNG cold energy is split, one portion feeding the proton exchange membrane and the other goes to the cooling unit for domestic use, lowering the temperature of the hydrogen produced. Specifically, 269 kWh of energy are used for residential purposes, whereas 14,439 kWh are dedicated to powering the electrolysis process.

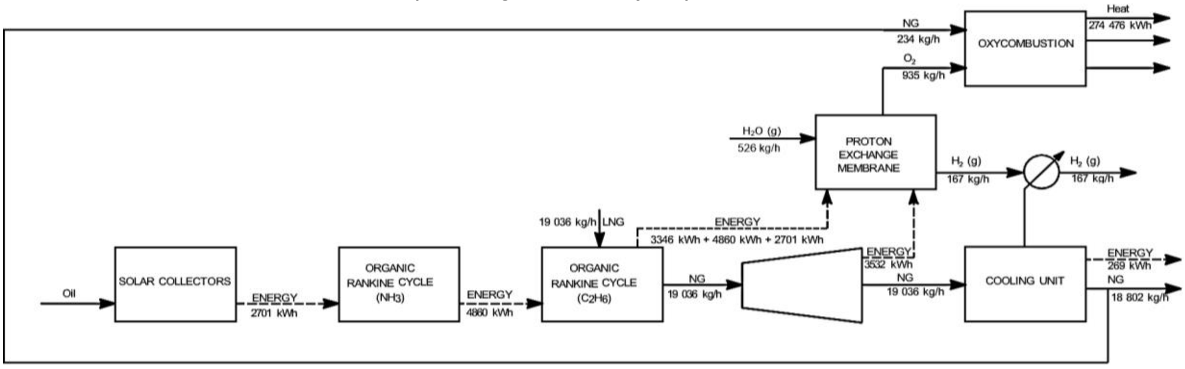

Figure 3: Block diagram of the water electrolysis process with the power generation system and oxycombustion

The mass fluxes in the oxycombustion process are displayed in Table 1; the heat and mass flows produced for SMR have been simulated using a Gibbs reactor in the Aspen Plus software. The entire O_2 produced by the electrolysis is used in this process with natural gas from proton exchange membrane. Figure 4 depicts the hydrogen production process, it begins with the use of LNG to pre-cool hydrogen, reducing the energy needed for liquefaction. Part of the LNG, after its cold energy is used, is directed to the distribution network, while the rest enters the production system.

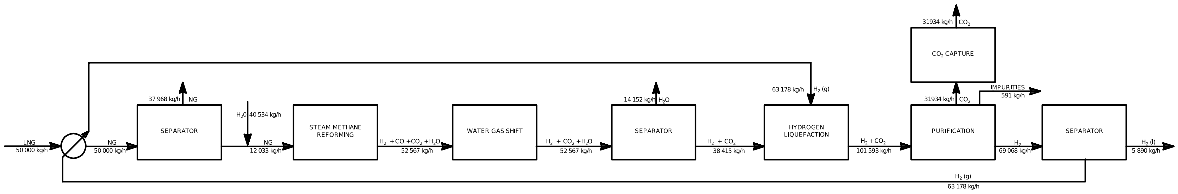

Figure 4: *Block diagram of the steam methane reforming process*

Table 1: Overall and process sections mass balances

	Compounds	LNG/NG	H_2	H_2O	CO_2	Others
Overall	Inputs (kg/h)	70,240		57,426		
	Outputs (kg/h)	58,259	6,007	14,678	32,573	
Freeze desalination-membrane distillation	Inputs (kg/h)	677		57,426		
	Outputs (kg/h)	677		41,060		16,367 Brine
Electrolysis of water	Inputs (kg/h)	19,036		526		935 O_2
	Outputs (kg/h)	18,802	117			
Oxycombustion	Inputs (kg/h)	234				
	Outputs (kg/h)	935		526	643	
Steam methane reforming	Inputs (kg/h)	50,000		40,534		
	Outputs (kg/h)	38,252	5,890	14,152	31,934	591 impurities

In the steam methane reformer, NG and water vapor react to produce H_2, CO, and CO_2. This gas mixture then undergoes a water-gas shift process, converting CO and H_2O vapor into more CO_2 and H_2, optimizing H_2 production and reducing CO levels. The mixture is then cooled and liquefied through a three-stage expansion refrigeration system. After liquefaction, CO_2 and other impurities are removed from the liquid hydrogen. The hydrogen is separated into gas and liquid phases, with the gaseous hydrogen recirculated to improve efficiency and purity. The process concludes with the capture and liquefaction of carbon dioxide, producing high-quality hydrogen while efficiently managing the carbon dioxide.

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According to Table 2 the mass balance, only 23.5 % of the LNG is consumed directly in the process, with the remainder being used mostly to cool and liquefy hydrogen and carbon dioxide. Liquifying these is more suitable for storage than in gas phase.
Oxycombustion provides the heat necessary for steam methane reforming (274,475.9 kWh), removing the requirement for additional energy inputs and considerably improving process sustainability. Furthermore, the process produces a significant volume of clean water, which may be utilized in other processes that require water, such as electrolysis or recirculated to the reactor.
The combined benefit of hydrogen synthesis and water creation emphasizes the system's efficiency and environmental benefits. Impurities such as 307 kg/h of carbon monoxide and 284 kg/h of methane are also removed from the system during hydrogen purification. These byproducts have the potential to be used, e.g. as combustible, increasing the overall efficiency and sustainability of the operation. This complete method maximizes the usage of LNG while also reducing waste and improving resource use.

4. Discussion

The addition of a desalination system to the process supplies the water required for both steam methane reforming and proton exchange membrane. The system makes use of the cold energy of LNG, reducing the requirement for additional energy input and avoiding the extraction of fresh water. This is especially advantageous in the current water scarcity situation. Moreover, there is a net output of pure water; it would also be beneficial to recirculate this water to the system, using this water in the process.
Steam methane reforming generates hydrogen and CO_2 through the methane reaction. Although this method produces CO_2, it is possible to reduce emissions by utilizing monoethanolamine absorption columns for carbon capture and storage. This method captures CO_2 before it is released into the atmosphere, considerably lowering the environmental impact of the operation. Green hydrogen is produced through electrolysis, which involves the decomposition of water using electrical energy. In this situation, LNG is not consumed in the process. However, when natural gas is supplied to the grid and consumed, it produces diffuse CO_2 emissions that are difficult to manage, resulting in increased atmospheric pollution. As a result, while the hydrogen produced is deemed "green," the indirect emissions from the process should be considered.
The CO_2 emission factor for natural gas is 0.181 kg/kWh (Colakoglu and Durmayaz, 2021). This value is critical for determining the CO_2 emissions connected with this process, with a higher heating value (HHV) of 15.4 kWh/kg, implanting this combined system will diffuse CO_2 emissions decrease a 17 %.
The two processes differ greatly in terms of hydrogen production and energy requirements. At first glance, the method of creating "blue" hydrogen by steam methane reforming appears to be more cost-effective and energy efficient. Nonetheless, both strategies have been incorporated into the proposal. Although proton exchange membrane takes more energy, it is generated by solar collectors and the LNG cold energy using an organic Rankine cycles, removing the need to purchase energy and enhancing the project profitability. Furthermore, the oxygen produced in the proton exchange membrane process is used to generate the necessary heat for steam methane reforming.

Table 2: Production and energy comparison between SMR and PEM

Method	Production ($kg\ H_2/kg\ LNG$)	Energy consumption ($kWh/kg\ H_2$)
SMR	0.49	46.6
PEM	0.06	123.4

In terms of total profitability, considering only the price of the raw material (methane at 154 $/t) and the main output (hydrogen at 1,500 $/t) (2024, a profit of 7,165 $/h is obtained. Resulting in an increase of 488 % if the system is not implemented. The collected CO_2 can be employed in a variety of commercial processes, including methanol and urea manufacturing, or stored in geological formations. These applications not only lower CO_2 emissions, but they also add value to the process. The systems can be further optimized, for instance using two organic Rankine cycles instead of one enhances the process energy efficiency.

5. Conclusions

A sustainable process that harnesses the cold energy inherent in liquefied natural gas is proposed, based on extensive bibliographic research. The suggested process for producing water and hydrogen utilizing steam methane reforming and proton exchange membrane makes use of LNG cold energy, with each subprocess exhibiting its own benefits. Through steam methane reforming, robust hydrogen production and effective control of CO_2 emissions are achieved using carbon capture technologies. On the other hand, despite facing problems such as poor H_2 output and high energy consumption, proton exchange membrane makes a substantial contribution to green hydrogen generation. It also contributes to the process's energy efficiency by delivering oxygen, useful for an oxycombustion. Synergies across many subprocesses provides a novel efficient overall process. The utilization of desalination systems and the increase in energy efficiency through the use of organic Rankine cycle are critical measures for optimizing the whole process and lowering environmental impact. Furthermore, the hydrogen produced has a much higher value than the methane and CO_2 emissions are avoided. This makes the overall process more sustainable and economically feasible than considering individually the different alternatives to use the cold energy. This study not only develops a sustainable process, but it also recognized prospects for future expansion and ongoing improvement, establishing the process as a vital contributor to a more sustainable and resilient future.

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