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Life cycle assessment of clean ammonia synthesis from thermo-catalytic solar cracking of liquefied natural gas

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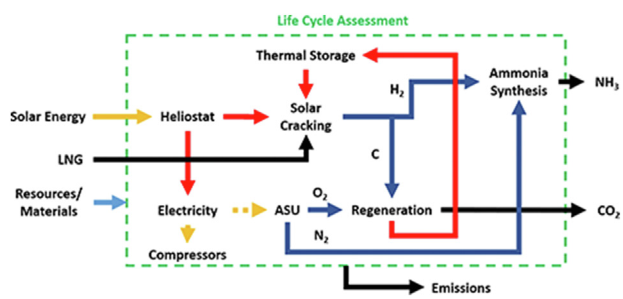
HIGHLIGHTS

- The effect of cracking operating temperature on environmental load was studied.
- At 900 °C, the predicted GWP was approximately 0.616 kg CO_2 (eq.)/kg NH_3.
- The construction phase is shown to be responsible for 6.4% of the GWP.
- The plant emissions are lower than the global average regardless of its lifetime.

GRAPHICAL ABSTRACT



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ABSTRACT

Ammonia is considered a sustainable energy storage medium with zero carbon content. In this work, thermal catalytic cracking of liquefied natural gas (LNG) at elevated temperatures employing concentrated solar tower is considered to produce clean hydrogen (CO_2-free) and studied in terms of life cycle emissions. The generated hydrogen is utilized for clean ammonia synthesis in a Haber-Bosch reactor. The proposed system is initially assessed from a thermodynamic perspective, considering energy and exergy analyses emphasizing optimization of operating conditions. Then, the proposed system's life cycle assessment (LCA) is performed to analyze ammonia synthesis's environmental impacts. The aggregate environmental impact of the proposed system is quantified and compared with conventional production processes. Through the utilization of solar energy resources, ammonia production can be attained, avoiding high harmful emissions. The LCA study is carried out in GaBi software, and the selected impact assessment methodology is ReCiPe. The impact categories studied in this work are global warming potential (GWP), terrestrial acidification, human toxicity, and particulate matter formation potential. Considering 30 years of use phase and allocation, the predicted GWP is approximately 0.616 kg CO_2 (eq.)/kg NH_3, showing the potential to reduce up to 69.2% of the GWP compared to the global average value. Concerning human toxicity and fine particulate matter formation impact

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categories, the system produces about 3.32E-2 kg 1,4-DB (eq.) and 5.96E-4 kg PM2.5 (eq.), respectively, per kg NH_3. The results are further analyzed by dominance, break-even, and variation analyses in detail.

Introduction

Current commercial ammonia production relies on high energy usage and converges into extreme pollutants' emissions [1]. The ammonia synthesis reaction from dinitrogen and dihydrogen is an exothermic reaction that favors low-temperature conditions and high pressures to optimize the ammonia yield. The typical operating conditions for the reaction are a temperature of 400–500 °C and a pressure of 150–300 bar [2,3]. Nitrogen, which comprises 78% of the atmosphere, is separated from the air mixture through a cryogenic separation, an energy-intensive process [4]. On the other side, hydrogen is mainly produced through the reforming process. Carbon-based fuel (i.e., Natural gas, coal, and petroleum) is combusted in the presence or absence of water vapor to produce synthesis gas and hydrogen. A substantial amount of greenhouse gases are emitted in this process. Several studies reported greenhouse gas (GHG) emissions in the ammonia synthesis plant. A compiled list of these studies is provided in Ref. [5]. The values range from 1.25 to 2.16 kg CO_2 (eq.)/kg NH_3, where the global average and European average are estimated to be 2.07 [6] and (1.91 [7] and 1.94 [8]). Other processes such as CO_2 reforming, autothermal reforming, and partial catalytic oxidation exist besides steam reforming.

Several studies focused on the hydrogen supply to ammonia synthesis to reduce ammonia overall impact assessment. Since the steam methane reforming step is the most pollutant, establishing a greener alternative to supply hydrogen significantly reduces of GHG. Chisalita et al. compared several cases of ammonia production using traditional route and green production methods [9]. The work concluded that the lowest Global Warwming Potential (GWP) is achieved throughout coupling of hydrogen production using chemical looping to natural gas ammonia synthesis (0.373 kg CO_2 (eq.)/kg NH_3). The paper underlines the importance of integrating renewable energy sources to reduce electrolysis-based hydrogen production emissions [9]. Production of hydrogen utilizing solar energy and other renewable energy forms can decrease the environmental impact of producing ammonia. Several works studied the replacement of methane reforming with biomass gasification [10–12] and electrolysis powered by wind [13], photovoltaic technology [11], municipal waste, hydropower, and nuclear energy [12]. Biomass gasification has shown the potential to reduce emissions to 65% [10]. Bicer et al. conducted a life cycle assessment (LCA) on the effect of using electrolysis to obtain hydrogen on ammonia production's overall environmental impact [12]. Among the cases studied, a minimum of 0.34 kg CO_2 (eq.)/kg NH_3 can be achieved by implementing municipal waste-based electrolysis [12]. Singh et al. revealed that the GHG could be reduced to 1.28 and 0.378 kg CO_2 (eq.)/kg NH_3 using photovoltaic technology and biomass gasification to derive the electrolysis process, respectively [11]. A value of 0.581 kg CO_2 (eq.)/kg NH_3 has been reported based on an exergy allocation study of thermochemical ammonia production coupled with chemical looping combustion of liquefied natural gas LNG [14].

Concentrating solar thermal energy can be a viable solution to achieve the high temperatures required to crack hydrocarbon. Steinberg [15] concluded that hydrogen production through methane cracking requires the least energy and offers the lowest CO_2 emissions. Under 900 °C and 56.1 atm, the conversion increases with residence time and approaches equilibrium value without catalytic material. Methane decomposition is favored at low pressures, but the reaction rate is favored by high pressure. The methane cracking design can be accomplished in a packed or fluidized bed reactor [16]. Problems associated with methane cracking that have to be resolved before commercialization are carbon management, deactivation, and continuous carbon withdrawal. Other methods developed to make the process continuous and overcome the deactivation problem are molten metal and plasma dissociation [16]. It was argued that burning the accumulated carbon inside the porous structure is the only way to remove carbon, stressing the absence of other viable methods [17].

Dufour et al. used an LCA methodology to study the environmental load associated with methane cracking. The decomposition of methane was considered to occur in the presence and absence of catalytic material compared with conventional steam reforming [18]. The functional unit used was 1 Nm^3 of hydrogen. LCA evaluated the material (raw material) acquisition and manufacturing stages. One of the main conclusions was that the autocatalytic decomposition presented the lowest total impact and CO_2 emissions. Typically, this is a result of lower temperature operations. Catalytic materials reduce the process's intensity (lower temperatures are needed for particular conversion). However, the reactor's conversion did not rely on a thermodynamic or kinetic model to support it.

An LCA was accomplished to quantify the environmental impact of hydrogen production following the thermal cracking liquid metal route [19]. The liquid-metal technology was proposed to eliminate the catalysts requirement. Thus, the cracking is not facilitated by a catalyst and is solely dependent on elevated temperatures. It was determined that a 64% reduction in GWP could be reduced compared to steam reforming. Carbon produced can be used, with 80% efficiency, in a carbon fuel cell to produce electricity. Besides, carbon can be sold and utilized to produce inks, paints, tires, and batteries [20]. Carbon was considered a non-useable co-product (waste). Process data were obtained from experiments, simulations, and assumptions from literature. Bicer and Dincer showed that a 50% reduction in traditional ammonia synthesis could be obtained via the implementation of concentrated sunlight to produce solar hydrogen [21]. The process used solar hydrogen to produce ammonia in an electrochemical cell. Further reduction is feasible as efficiency increases and more efficient materials are introduced.

There are four main methods to concentrate solar energy: solar tower, troughs, Fresnel lens, and parabolic dish. Solar power tower or central receiver systems use a circular field array of adequately large sun-tracking mirrors, named heliostats, which focus sunlight onto a central receiver. A temperature between 800 and 900 °C is achievable. Usually, such systems' production targets the production of a clean and reliable source of electrical power using conventional Rankine or Brayton cycles.

Lechon et al. [22] conducted an LCA-based analysis to determine the environmental impact of electricity produced from a 17 MW solar thermal plant with central tower technology. The system utilized 2750 heliostats, and molten salt was used as a heat transfer fluid. The majority of greenhouse gas emissions were attributed to the operational stage, with 91.6% of the total life cycle. Solar field and storage systems combine for 7% of the life cycle emissions. Thus, global warming emissions are mainly due to the consumption of natural gas and external electricity consumption. Besides GWP, other impact categories considered were ozone layer depletion, abiotic depletion, human toxicity, and marine aquatic eco-toxicity.

Kuenlin et al. carried out a comparative LCA study for four CSP plants; parabolic, central tower, Fresnel, and dish [23]. The LCA modeling was made possible by using data from a plant recently built. The Gemasolar plant, located in Spain, was used to model the solar tower case. The Gemasolar plant is constructed in 210 ha with 2650 heliostats. The capacity factor is 63%, and the annual net output of 110 GWh. A new power plant (Hysol) was analyzed environmentally using LCA [24] for 25 years of lifetime. That study demonstrated the effect of location on performance. The performance of the plant is a function of location due to natural resources and solar energy.

Significance of the study

This study aims to demonstrate the potential of solar cracking of methane, employing a solar tower system, to minimize the environmental load in ammonia production by implementing a cradle-to-gate LCA study. This paper focuses on providing a solution for catalytic deactivation by demonstrating a proper carbon management route. Energy requirements and design parameters for solar collectors have been defined and estimated previously from thermodynamic calculations, thus complementing the energetic perspective [25]. Environmental impacts associated with liquefaction, transportation, and methane cracking to produce ammonia are assessed and quantified under specific impact categories. The study highlights the contribution of solar energy in the overall impact assessment.

The work emphasizes the importance of a decentralized plant capable of powering required electricity from an environmental perspective. Furthermore, the work includes the impact of the cracking unit's operating conditions on the environmental load. Moreover, the results are analyzed by dominance, contribution, break-even, and variation analyses. Finally, the analysis's major results are compared with other renewable-based ammonia production methods.

Material and methods

LCA is considered a powerful tool to quantify elementary inputs and outputs from a specific product system. It allows for meaningful comparisons as it assesses the footprint associated with a particular product. LCA consists of four core phases. First, the goal and scope are clearly defined, then inventory analysis is made, which involves data preparation and calculation procedures. Third, emissions and resource depletion are quantified and grouped in categories in the impact assessment step. The last step involves reporting and further analysis of the result (Result Interpretation). GaBi software [26] is used in the study to model the LCA; most of the material and energy flows are determined from the Ecoinvent database [27].

Goal and scope

In this study, catalytic cracking of methane is accomplished at elevated temperatures employing a solar collector system. A solar field is employed to drive the solar cracking of methane. The deposited carbon on the catalytic material is burned using pure oxygen from an air separation unit (ASU) in a regenerative reactor where carbon dioxide is produced. Carbon dioxide is recycled into the regenerator for temperature moderation. It was shown that the temperature profile of oxy-CO_2 is consistent with air-fired conditions when the molar fraction of CO_2 is set at 66% [28]. The carbon dioxide produced is collected and sent to the urea production reaction through an intermediate compression stage. The regeneration and process reactors act as a separation process in the case of steam reformers.

A descriptive process flow diagram is shown in Fig. 1, and Fig. 2 shows the Rankine cycle used to produce necessary electrical power for the plant. The functional unit is 1 kg of ammonia. System boundaries can be seen in Fig. 3. Life cycle stages that are being considered include; (i) methane extraction, purification, liquefaction, transportation, (ii) manufacturing of solar-based plant (solar tower, reactor, air separation, and others), (iii) maintenance and operational impact (use phase of the LCA). Several impact assessment methods are used here, including but not limited to; GWP, human toxicity, fine particulate matter formation potential, and fossil depletion. In addition, contribution, dominance, and break-even analysis are considered to improve the results of the LCA. Limitations include specific catalyst design and preparation data. The main assumptions are written as follows:

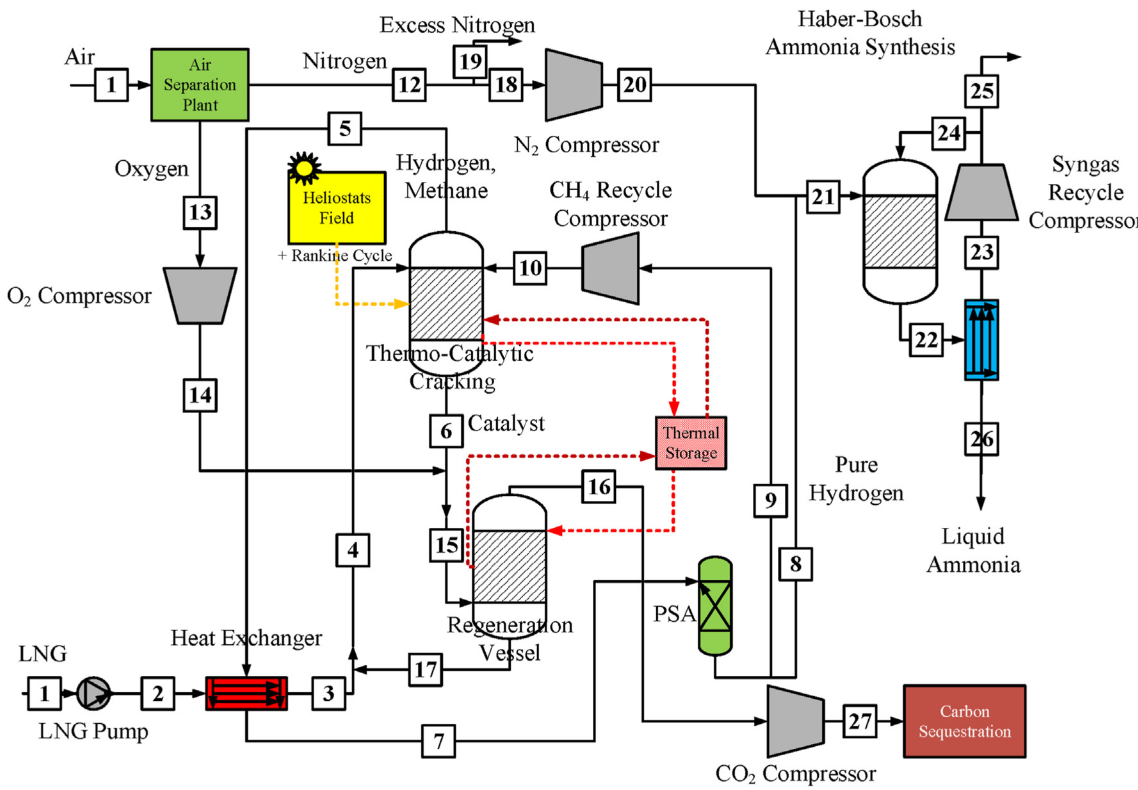

Fig. 1 – Process flow diagram of the thermo-catalytic synthesis of hydrogen. Reprinted from Ref. [25], with permission from Elsevier.

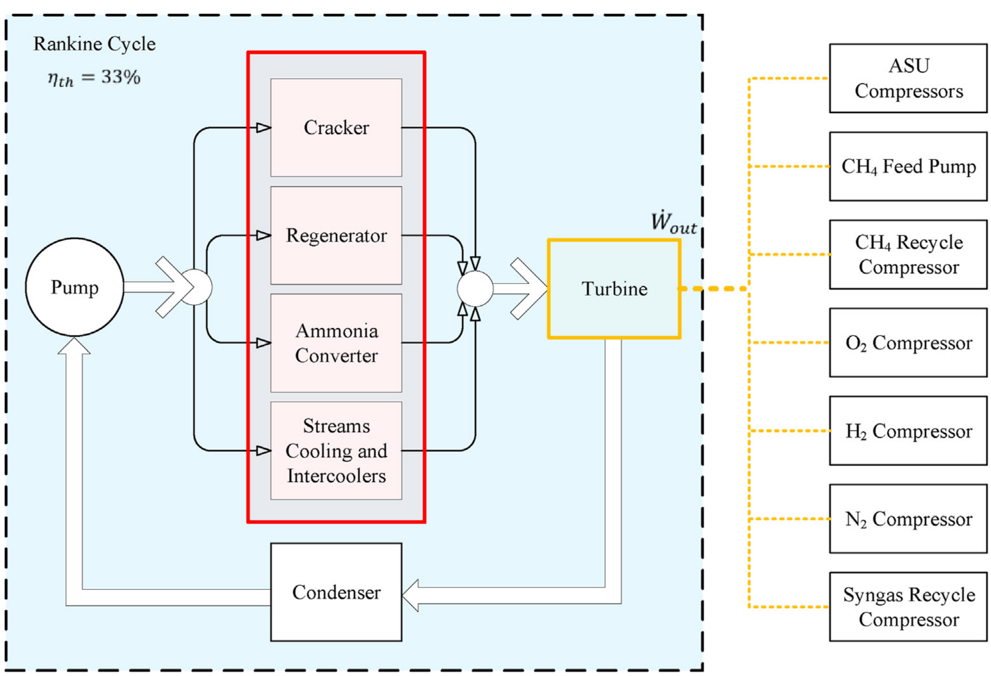

Fig. 2 – Steam Rankine cycle components and interrelations. Reprinted from Ref. [25], with permission from Elsevier.

- Civil work in pipes, storage tanks are not included. Also, fittings, flanges, and safety systems are excluded from the inventory analysis.
- The sizing and materials required are scalable.
- Pumps and compressors' life spans are set at ten years with constant efficiency (isentropic efficiency of 80%) [29], so the number of used rotary equipment is calculated by the lifetime of the chemical plant.

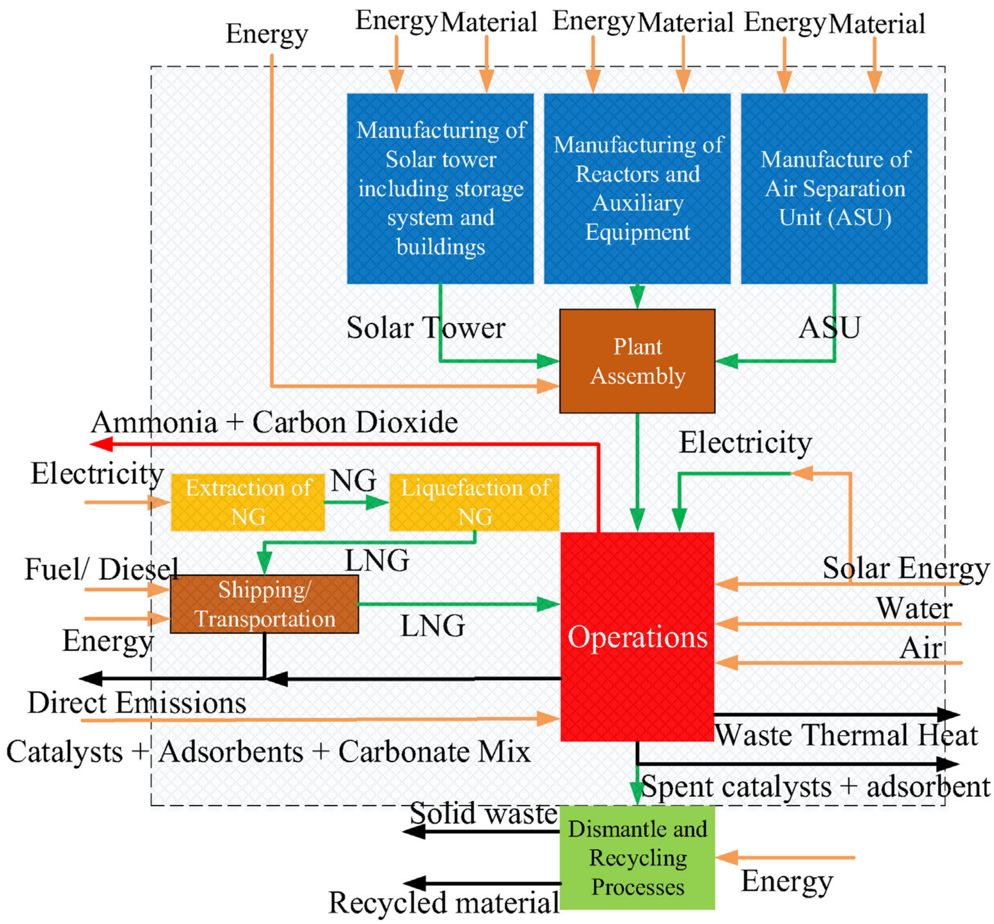

Fig. 3 – The system boundaries for the ammonia synthesis from LNG solar-driven decomposition.

- The plant is initially designed to run for 30 years. Analysis of the plant's lifetime impact on environmental impact is also studied.

Inventory analysis

Kuenlin et al. studied the LCA of three different power plant sizes at (50, 100, 200 MW) utilizing solar tower setup, the extraction and manufacturing, construction, operation and maintenance, and dismantling of the solar tower collector was considered in their study [23]. Direct emissions of some chemicals to the atmosphere were 9.39E-3 and 5.52E-3 kg CO_2/kWh for the 100 and 200 MW plants. Another inventory data set for a solar power plant is the Gemasolar power plant data [23]. Building, insulation materials, urbanization, and electricity network materials are gathered from Viebahn et al. [30]. The amount of steel used in the receiver has been modified from Kuenlin et al. [23].

Process simulators such as Aspen can provide essential information to build and fill required inventory data for LCA studies [31,32]. Commercial databases are utilized to model the upstream processes (electricity and heat supply, material supply, and compressor for the membrane). In allocating environmental load to the products, carbon dioxide produced will be considered useful material, unlike previous LCA studies.

Energy requirement, material elementary input, and output streams have been determined from the thermodynamic study [25,33]. The study involved several assumptions; these include 2% losses in reactors, conversion of ammonia is set at 20%, nitrogen and oxygen streams are pure. The study also showed several parameters' effects, such as irradiance and charge/discharge thermal storage periods. In this study, the irradiance of 600 W/m^2 and the day-night ratio of 1–2 are used. A complete list of used inventory data is available in Table S1 in the supporting information document.

Several assumptions have been taken in the inventory analysis to quantify flows of materials:

- The high pressure (HP) stream is at a pressure of 150 bar, and the steam condensate is fully recycled.
- The pressure swing adsorption (PSA) system was designed to have 10 columns in total, 5 each in parallel adsorption operations. The isotherm of the adsorbent (zeolite 5 A) is given by Ref. [34]. The pressure swing was between the operating pressure of the cracking/regenerator reactions and 2 bar.
- It was assumed that the recovery of hydrogen is complete to simplify the recycling and cracking modeling.
- The parameters used to assess the catalytic material and adsorbent contributions in the LCA study included manufacturing a given amount of these materials. The amount was specified by determining the required amount

with an additional amount to recover the deactivation and attrition losses in the regeneration/reactor system, ammonia converter, and PSA separation system.

- The storage system uses sensible thermal energy storage using a eutectic mixture of Li/K/Na carbonate, and the amount is quantified to allow for continuous operations.
- The catalysts used in the heat-balance reactors are the 7% Ni/Al_2O_3 catalyst selected in this work. The conditions are similar in terms of the reactor configuration adopted and temperature of the regeneration reaction [35].
- The ammonia synthesis converter was designed as steel cylinders of 80–140 cm internal diameter and 10–18 m height.
- The flow of the purge gas is negligible in the assessment. The presence of the purge gas stream has been introduced in the previous thermodynamic system to fulfill the typical ammonia synthesis loop, although the supply of hydrogen is assumed to be free of impurities.
- The parameters used to assess the catalytic material and adsorbent contributions in the LCA study included manufacturing a given amount of these materials. The amount was specified by determining the required amount with an additional amount to recover the deactivation and attrition losses in the regeneration/reactor system, ammonia converter, and PSA separation system.

We assumed that these vessels are cylindrically shaped to estimate the material required in building reactors, gas-gas separators, and gas-liquid separations vessels. The shell thickness is also calculated based on the material of construction and designed pressure. Finally, separators are designed, taking a pre-defined L(H)/D ratio based on the operating pressure. The following equation is used to estimate the total amount of construction material for vessels, reactors, heat exchangers tubes, and separation columns.

$$m = \rho t \pi \left(D_i h + 2\left(\frac{D_i}{2}\right)^2 \right) \quad (1)$$

where

m is the mass of the vessel.

ρ is the density of the material of construction.

t is the shell thickness calculated from equation.

D_i is the inside diameter.

h is the height of the vessel.

For determining the shell thickness, the following equation is used for the estimation. The allowable stress is a function of material, operating pressure, and temperature. The higher the operating temperature, the lower the allowable stress, which increases the manufacturing thickness.

$$t - \alpha = \frac{PD_i}{2\sigma\eta - 1.2P} \quad (2)$$

where

P is the design pressure in MPa.

η is the welding factor.

σ is the allowable stress value in N/mm2.

D_i is the inside diameter in mm.

α is the corrosion allowance in mm.

t is the shell thickness in mm.

The Vapor-Liquid Equilibrium (VLE) separator was designed using the following equation.

$$U_d = SK_d \sqrt{\frac{\rho_L - \rho_V}{\rho_L}} \quad (3)$$

where

S is safety factor = 0.8.

K_d is the demister factor.

The vessel's diameter and length are determined through a pre-defined L(H)/D ratio based on the operating pressure.

Japan, natural gas mixture process was selected from the Gabi database to represent the LNG in the LCA's modeled operational part. Japan imports almost 97.6% of its natural gas need in the form of LNG from various countries. Among these countries there are Australia (23%), Malaysia (18%), and Qatar (16%) [36]. The distance from each major contributor port to Japan was estimated [37]. A normalized weight distance (total amount imported from a country times the distance traveled) is calculated to represent the traveled distance. Japan's natural mixture's average distance is 8657 km (4675 nautical miles), approximately the distance traveled from Ras Laffan in Qatar to LNG terminals in Italy, France and Germany.

The data set spans the whole supply chain of natural gas; this includes exploration, well drilling, production and processing of natural gas, transportation, liquefaction, exportation through LNG vessels, and regasification. Also, losses during the process of transportation are taken care of in the system. As the proposed system includes the regasification process, eliminating the regasification step is necessary to avoid double counting. According to International Gas Union (IGU), the regasification process contributes to 0.2–0.4% of the total LNG cycle emissions [38]. A percentage, which corresponds to an average value of 8.94E-3 kg CO_2/kg LNG, is negligible relative to LNG's liquefaction, extraction, and operational aspects in the LCA study.

In this work, properties of stainless steel of standard "18/8" were used throughout steel usage approximation and modeling, which is the closest to the available "17/7" in the database in terms of chemical composition. Ammonia converter catalyst is approximated using Ferrous oxide "Iron (II) oxide." The cracking unit's catalyst was modeled using Ni and aluminum oxide (alumina). The hydrogen/methane gas-gas separator material used is aluminum silicate (zeolite type A), The associate impact of the blending process of aluminum oxide, sodium silicate, and sodium hydroxide is made.

It is worth mentioning that the oxygen and nitrogen cradle to gate environmental impact used in this work utilizes the country's electricity mix (in this case, Norway). Norway was selected as its electricity mix is dominated by a renewable energy source which is hydropower. The case is most relevant because electricity produced from the regeneration reactor's thermal heat compensates for the energy requirement. Comparison between environmental impacts from several countries is carried out to observe the variations in electricity mix influence and importance of self-sufficient solar energy system in minimizing the environmental impact. The nitrogen and oxygen amounts are used for the synthesis of ammonia is the value used in the LCA study.

Table 1 – List of impact categories considered in this study.

Impact category	Impact indicator
Global warming potential	kg CO_2 (eq.)
Human toxicity	kg 1,4-dichlorobenzene (eq.)
Terrestrial acidification	kg SO_2 (eq.)
Fine particulate matter formation	kg PM2.5 (eq.)
Metal depletion	kg Cu (eq.)
Photochemical ozone formation, human health	kg NO_x (eq.)

Table 2 – List of the investigated temperature and pressure of cracking process.

Temperature (°C)	Pressure (bar)
600	5.55
700	10.10
800	14.65
900	23.75

Impact assessment

The selection of the LCIA method, whether it is ReCiPe or another, supports the selection based on literature [19] or the study's specific application and location. The ReCiPe method is considered the most recent and harmonized indicator approach. It does not include potential impacts from future extractions in the impact assessment calculations. The most relevant and essential impact assessment is the GWP, as this directs the comparison with benchmark processes such as methane steam reforming. Fossil depletion has been included in previous LCA studies, and the importance of this category lies in the continuous methane depletion [19]. Previous LCA studies on hydrocarbon cracking; include ozone layer depletion, acidification, eutrophication, heavy metals, and summer and winter smog. Dufour et al. [18] showed that acidification and heavy metals depletion are significant in methane's thermal and catalytic-based decomposition. Table 1 shows the list of the impact categories assessed with the impact indicator.

Interpretation

Several interpretation techniques are used to report LCA results. Sensitivity analysis is also adapted to detect changes in process modeling data and the plant's lifetime; this mainly focuses on inventory data input from the thermodynamic analysis. The proposed system is then compared comprehensively against conventional hydrogen and ammonia production routes.

To account for uncertainty, we recline on the databases information regarding the completeness of data and percentage supply or production covered. The error bars implemented are directly associated with the coverage of mass/energy balances and environmental relevance. Cut-off rules for each unit process typically cover of at least 95% of mass and energy flows and 98% of environmental relevance. The complied information regarding this matter is presented in Table S1. As the results are associated with the inclusion of data, only a positive error bar is reported.

There are other sources of errors. First, uncertainty is associated with the selection of country-based data. We have demonstrated the importance and uncertainty of LCA with different sources of nitrogen and oxygen in the last discussion of this work. Second, the influence of varying technology in the same country. Third, uncertainty thermodynamic design and parameters. The work shows the effect of changing operating conditions that work as uncertainly in the system's mass and energy balances. Fourth,

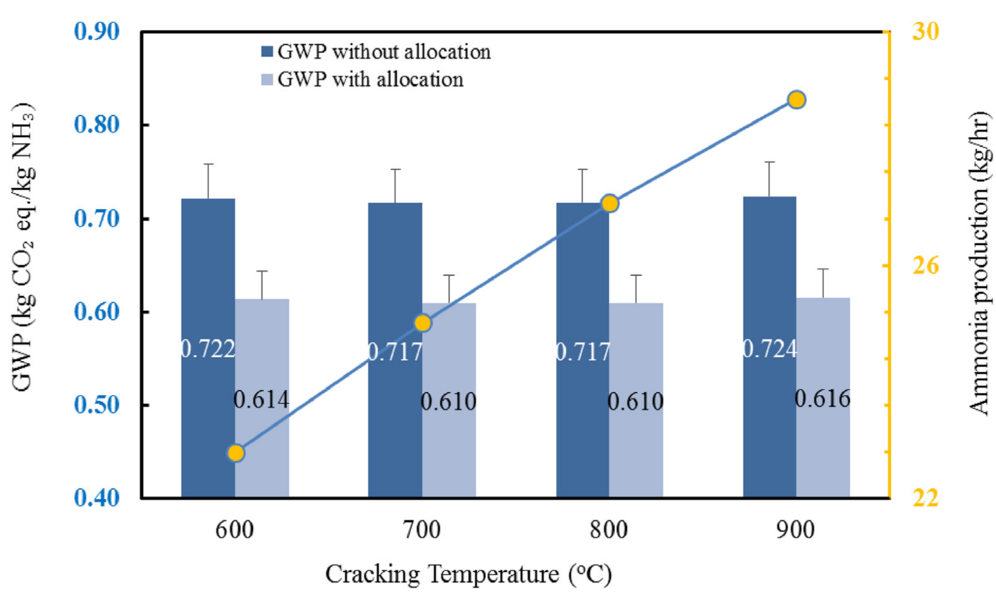

Fig. 4 – Impact of cracking operating conditions on GWP and ammonia production.

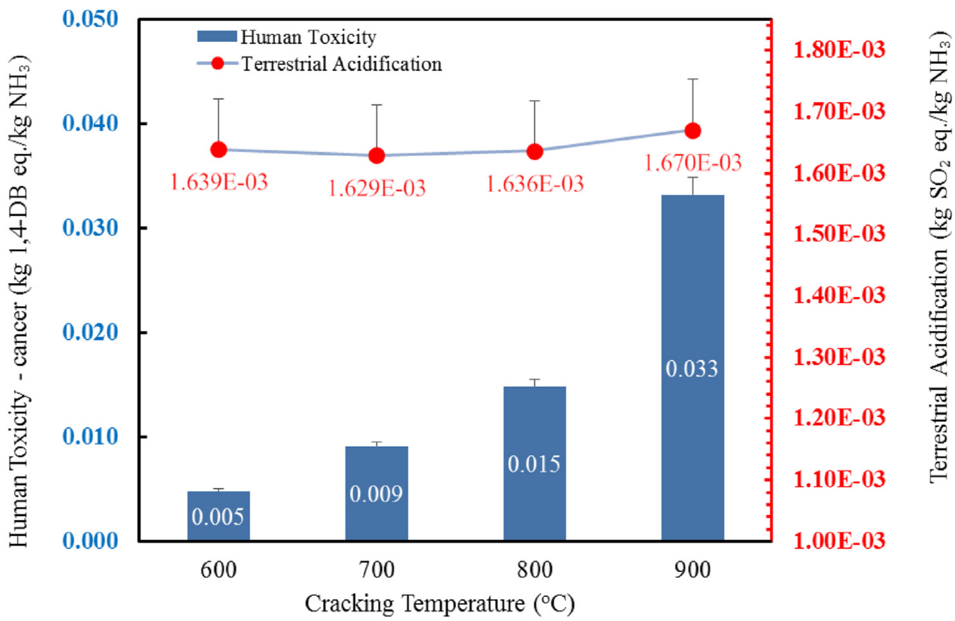

Fig. 5 – Impact of cracking operating conditions on human toxicity and terrestrial acidification.

one would expect increased emissions from the theoretical steady-state operating due to other factors such as leakages, unexpected events, shutdowns, and startup phases of the chemical plant.

Results and discussion

The primary focus will be on the integration of impact assessment at the characterization level. The first significant analysis is the dominance analysis, which demonstrates the most pollutant part of the life cycle and reflects the significance of the solar reactors' construction phase. Sensitivity analysis is also adapted to detect changes in process modeling data; this mainly focuses on inventory data input from the thermodynamic analysis.

Effect of cracking operating conditions on the environmental load

The proposed system is studied at a cracking operating temperature range (600–900 °C). An increment of 100 °C is used, making four process data points. Table 2 lists the operating pressure at the corresponding temperature. Operating pressures as a function of cracking temperature are determined as discussed in previous thermodynamic studies [25,33].

This part of the results intends to demonstrate the impact of altering operating conditions on the overall system environmental impact. The two parameters affect the efficiency of thermal cracking and thus ammonia production. Besides its direct effect on the production of chemicals and power generations, temperature and pressure impact the mass quantity

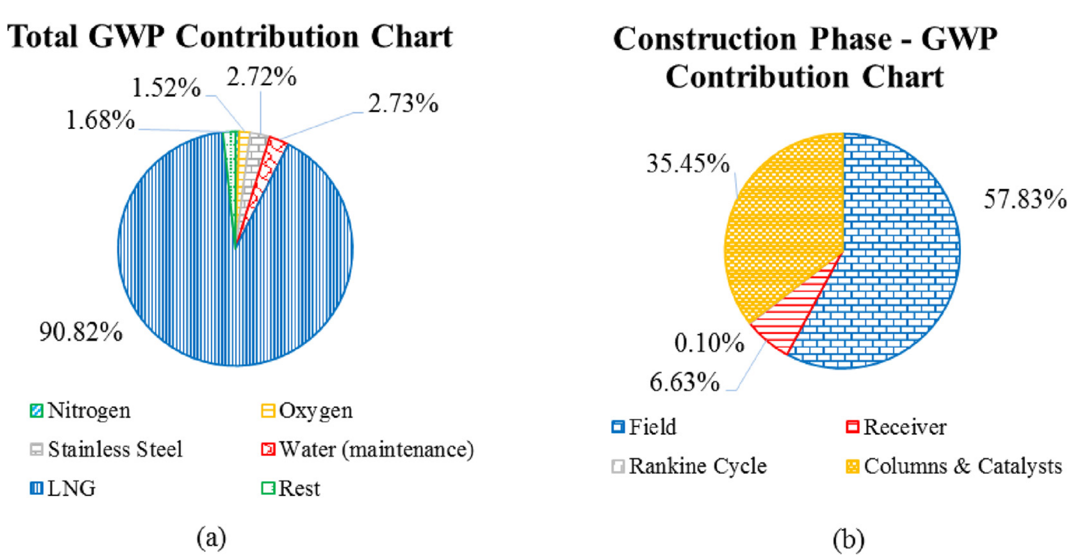

Fig. 6 – Contribution charts of (a) total GWP and (b) construction phase GWP.

of materials needed in the solar cracking unit. Higher temperature requires a material with higher environmental impact (stainless steel vs. carbon steel) but achieves better overall energy efficiency—higher temperature and higher pressure-demand increase of shell thickness, elevating the material requirement. The pressure also affects the amount of adsorbent needed to separate the H_2/CH_4 mixture. The adsorbent reaches a saturation point higher than 25 bar, higher than the figures listed in Table 2. Table S2 provides numerical values of important inventory data affected by the selection of cracking operating temperature.

Fig. 4 depicts the impact of operating conditions on GWP values at an operating interval of 30 years while considering a 70% continuous operation capacity factor. Higher pressure requires a larger thickness of the reactor, and the temperature affects the allowable stress on the material. On the other hand, at a higher temperature (900 °C), methane cracking reaction efficiency is 62%.

The tradeoff between minor quantities of construction and ammonia production is slight, considering the time interval, especially observing GWP, as shown in Fig. 4. The more pronounced impact of operations is revealed in several other impact categories (Fig. 5). It is important to note that the impact is quantified without allocation. An extended allocation can be considered based on the product's economic value. In some cases, 85% of the environmental impact share is allocated to ammonia; the balance is assigned to carbon dioxide. It is essential to highlight that while the system accounts for approximately 0.724 kg CO_2 (eq.)/kg NH_3 without considering the allocation at 900 °C, a 1.94 kg CO_2/kg NH_3 stream is produced. The stream is transported for carbon sequestration or urea synthesis. It can be seen that human toxicity impacts increase up to 2.2 folds from the system operating at 800–900 °C. The operating temperature with the lowest terrestrial acidification impact is 700 °C. Overall, due to the negligible difference between the operating conditions from the GWP environmental perspective, energetic efficiency-driven conditions might be favorable as ammonia production reaches 28.9 kg/hr.

Dominance and sensitivity analyses

The results related to four selected impact categories are reported here. At the operating temperature of 900 °C, optimum pressure is found, and consequently, amounts of oxygen, nitrogen, and LNG are determined. The results, depicted in Fig. 6(a), from LCA modeling, show the contribution of extracting materials and building the solar field, receiver, and operating system.

LNG contributes to around 91% of the total GWP, as shown in Fig. 6(a). The water system used for cleaning and other purposes contributes to more than 2.5%. The major contributor to human toxicity is steel (stainless and reinforcing steel), followed by LNG and circulating pumps. LNG is responsible for more than three-quarters of the particulate matter formation and the dominating stream in the terrestrial acidification impact category. Overall considering 30 years of operations, the chemical plant would result in a 63.8% reduction in GWP (0.724 kg CO_2 (eq.)/kg NH_3) relative to the global average. The particulate matter formation from the construction phase is approximately 4.1E-5 kg PM2.5 (eq.) per kg NH_3. Moreover, human toxicity and particulate matter formation recorded a total of 3.32E-2 kg 1,4-DB (eq.) and 5.96E-4 PM2.5 (eq.), respectively.

The solar field is the main contributor to the construction phase, comprising 58%, 56%, and 95% of the total GWP, particulate matter formation, and human toxicity, respectively. The second-largest contributor to GWP of the construction phase is the combination of materials used to construct columns, reactors, and catalytic materials, as shown in Fig. 6(b).

A sensitivity analysis is conducted to demonstrate the effect of the number of years of activity on the three impact categories. The purpose is to capture and isolate the effect of the construction and extraction phase. As demonstrated by Fig. 7(a), the GWP of the system reduces from 0.860 to 0.714 kg CO_2 (eq.) (approximately 17% reduction), without allocation,

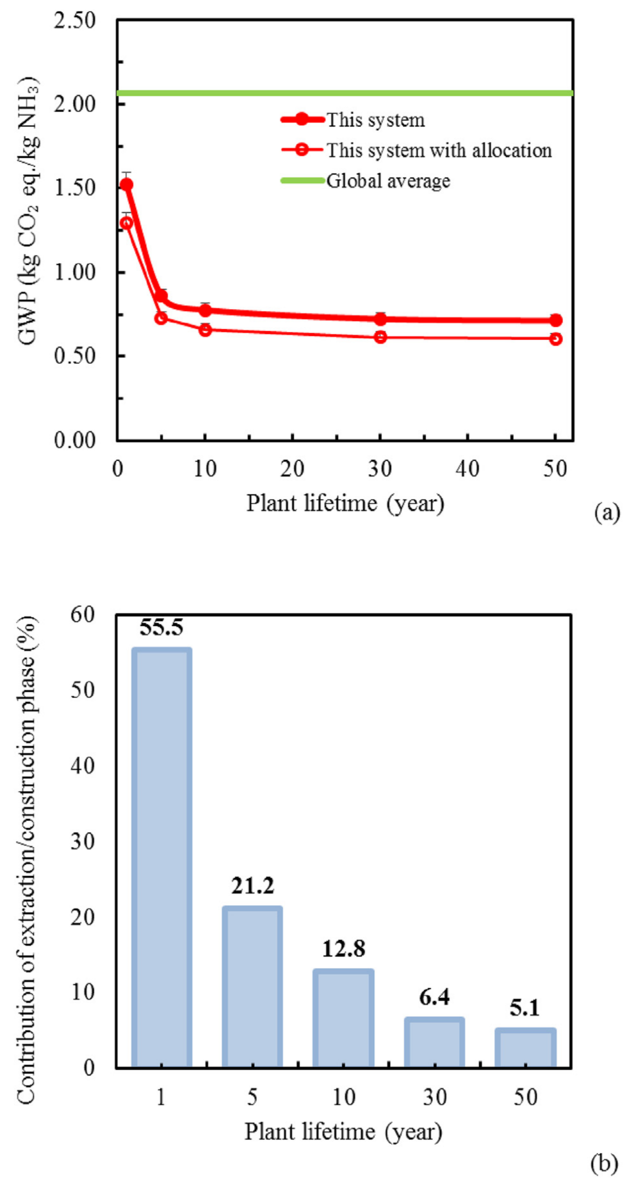

Fig. 7 – The effects of years of operation (lifetime) on (a) the aggregate GWP of the system (b) contribution of extraction and construction phase from the GWP.

moving from 5 to 50 years of operations, respectively. It can be deduced from Fig. 7(a) that the break-even period relative to the global average value is less than a year. A power law can be used to model the reduction of relative impact per operational year, resulting from reducing the contribution of the construction phase, as shown in Fig. 7(b). The figure demonstrates the potential of this system to minimize the environmental impact associated with ammonia production.

The chemical plant was designed initially by implementing heat integration to provide the required electricity for compressors in the system. As aforementioned in the methodology section, ASU based on Norway electricity mix impact was used as it is the closest to the case in hand. In order to present the importance of solar energy as the sole energy provider to the system, a study is carried out by varying the source of nitrogen and oxygen. If the system were to obtain nitrogen and oxygen from an external source, ammonia production would be expected to increase as additional solar energy is available to crack methane. Two impact categories are studied here, GWP and terrestrial acidification. The base scenario is the Norway case with 30 years of operations. Fig. 8 depicts the percentage increase in the environmental impact of the overall system as a result of the electricity mix in several European countries, the United States and EU-28.

From Fig. 8, it can be observed that Norway and France demonstrate the lowest impact among the listed countries. France's electricity mix is substantially contributed by nuclear energy. United States shows the highest increase in terrestrial acidification. In contrast, it shares the highest contribution in the GWP category with Germany, mainly because of the heavy oil and coal contributions in the energy mix. Overall, the GWP without allocation varies between 0.724 (Norway, base case scenario) and 1.038 (Germany) kg CO_2 (eq.)/kg NH_3, respectively. On the other hand, terrestrial acidification has the highest value at 2.71E-3 kg 1,4-DB (eq.).

Accuracy of thermodynamic and kinetic calculations is of great importance as any fluctuation in a component's efficiency would significantly change the environmental load at a lifetime of higher than 10 years. From the results, it can be concluded that the solar tower system will significantly reduce the operational phase's environmental impact through the replacement of fossil fuel in thermal heat production and electricity generation. At the same time, it slightly increases the contribution in loads related to construction and extraction phases. Therefore, the system served to reduce the impact and produce a ready-to-use and potentially sequestrated CO_2 stream.

Comparison with other systems

Although the presented system employs renewable energy sources to satisfy the energetic requirement of the plant, carbon-based fuel is used to generate hydrogen. Thus, the GWP of the system would be expected to exceed other systems which utilize renewable energy coupled with Haber-Bosch [39]. These systems produce hydrogen from municipal waste, biomass, and hydropower to power the water electrolysis unit [12]. Elimination of carbon-based fuel reduces emissions and avoids handling the CO_2 stream since the sequestration step adds complexity and the cost to the ammonia synthesis [40]. The current system isolates and provides concentrated CO_2, which is, on the other hand, useful in industries, such as fertilizers, while using LNG as an energy carrier with an existing supply chain and distribution. It is essential to highlight that this modeling excluded the recycling of materials and recovery of catalysts. Consideration of recovery and recycling would further reduce emissions. In addition, reducing the amount of deionized water in the system can affect the load by employing recycling and efficient reusing techniques.

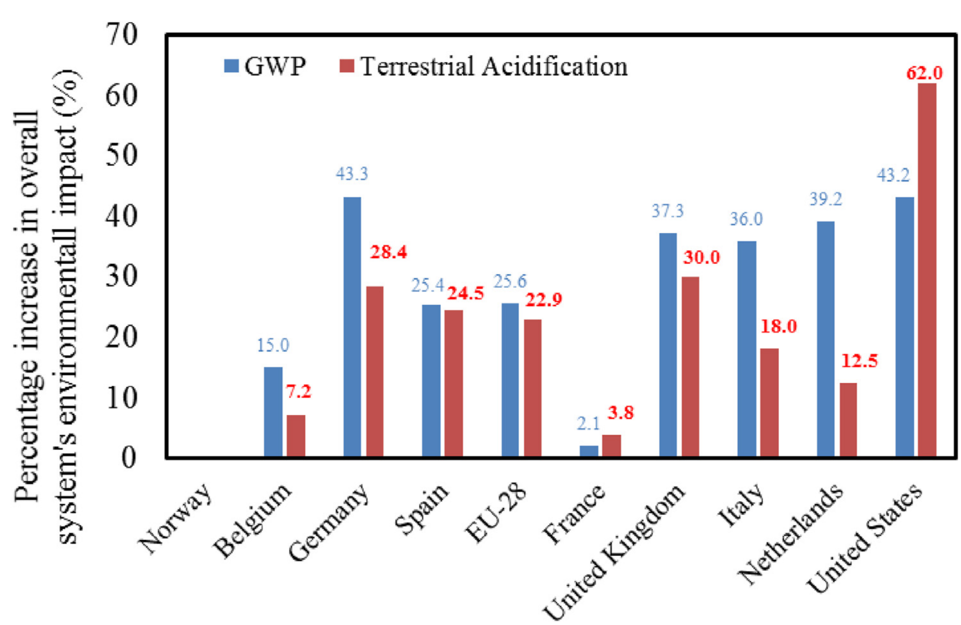

Fig. 8 – The effect of electricity mix used to model ASU in the system's GWP and terrestrial acidification impact categories (Norway is the base case scenario).

From an energetic perspective, LNG has an essential role in heat exchange to cool down thermal cracking effluent before the pressure swing adsorption separation. Replacing LNG by natural gas transmitted via pipeline may present environmental benefits. The use of natural gas through pipelines may present an additional reduction of the overall environmental impact of the system. Focusing on the GWP category, the liquefaction and shipping steps represent 30–40% and 15-20% of the total GHG from LNG's life cycle, respectively. Transporting natural gas through pipeline includes gas transmission, calculated approximately 0.14 kg CO_2 (eq.)/kg NH_3 taking average transportation GHG emission intensity from Di Lullo et al. [41] while considering 3000 km distance. When replacing the liquefaction emissions with the transmission emissions, emissions could be minimized by approximately 18% based on the assumptions of 3000 km. From an environmental perspective, a distance of approximately 7000 km would be considered the break-even point between using LNG and natural gas through pipeline. Moreover, this type of setup can be used at the LNG import terminals where natural gas is by default in liquid form and has to be either converted to gaseous natural gas or other commodities such as ammonia.

Conclusions

The process of clean hydrogen and ammonia production employing solar methane decomposition is assessed from an environmental standpoint using LCA. A cradle-to-grave LCA is carried out to estimate different life cycle stages' environmental load under different operating scenarios. Various impact assessment categories are discussed in this work from local to global scales. The ReCiPe method is selected for the classification and characterization of environmental impact. The GWP of producing 1 kg of ammonia using the proposed system is estimated to be 0.616 kg CO_2 (eq.), considering 30 years of continuous operations and allocation of environmental load. The results demonstrate the potential of the system to cut emissions to more than half its global average. The dominance analysis shows that the operational stage is the most pollutant step in this process, considering the amount required of LNG (source of hydrogen) and energy-intensive ASU.

Supporting information

Detailed lists of the inventory are provided in tables. In addition, tables for cracking operating conditions and duration of operations impact on impact categories besides GWP are listed in the supporting information document.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2021.09.080.

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