CIRCULAR THERMOECONOMICS APPLIED TO A GREEN AMMONIA SYNTHESIS PLANT: FUTURE PRODUCTION SCENARIOS AND ALTERNATIVE BYPRODUCTS

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ABSTRACT

In the current world energetic context, circular thermoeconomics offers a pathway to integrate exergy cost evaluation into a spiral economy. This study focuses on this concept by investigating the case of green ammonia production - an extensively studied and prominent application in recent years. The primary objective of this research is to analyze the exergy costs associated with a green ammonia synthesis plant directly integrated with different green hydrogen electrolysis-renewable energy scenarios for 2025 and 2030. We modeled a steady-state version of this small-scale integrated multi-product chemical plant using Aspen HYSYS V14, whose software integration with MATLAB and TAESLab employed an automatic circular thermoeconomic analysis, emphasizing the methodology of liquid ammonia and waste cost allocation evaluation. Our findings highlight the impact of combining different renewable energy sources (hydro, wind, and solar PV) with different electrolysis technologies (alkaline, PEM, and SOEC) on the exergy costs and specific energy consumption of obtaining liquid ammonia. In 2025, these values fluctuate between 1.806 MW/MW and 9.89 MWh/t and 3.553 MW/MW and 20.45 MWh/t for solid oxide electrolysis + hydro energy and solar photovoltaic + proton-exchange electrolysis scenarios, respectively. Furthermore, our findings project a continuous exergy costs reduction up to 2030, especially for wind and solar photovoltaic energy matrices. An extended discussion about industrial symbiosis possibilities involving alternative byproducts of such plant (Ar, H_2, O_2), water loss reduction and heat-cold integration is presented. Our innovative methodology enhances current small-scale plant projects, emphasizing the imperative to address industrial wastes conscientiously by underscoring that a system's sustainability is reflected in how it manages wastes and allocates their respective costs. The economic attractiveness and environmental significance of its outputs make it particularly relevant for specific regions in Europe and the world.

1 INTRODUCTION

The real importance of the Haber-Bosch process on our society is highlighted by estimations such as nearly 40% of the global human population depended on synthesized ammonia fertilizers to produce food in the world (**Chehade2021**). However, needs such as fast economy decarbonization, increasing global energy demand, the depleting of natural resources (water, air, land, fossil fuels, and minerals), and transition into a more circular economy, are requiring scientific prospects to achieve a more sustainable and homogeneous food sovereignty (**IRENA2023**). In order to address these needs of different origins, this paper presents an initial investigation of the exergy costs associated with a green ammonia synthesis plant under three different electrolysis technologies, alkaline, proton-exchange membrane (PEM), and solid-oxide

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electrolysis cell (SOEC) and three renewable energy sources, hydro, wind, and solar photovoltaic (PV) for 2025 and 2030. These 18 energy scenarios are fundamental to check how renewable these systems can be, and to properly allocate the product (liquid ammonia) and wastes (cooling water, purge stream, heat/cold streams) exergy costs in our designed plant.

Green hydrogen and green ammonia have received huge attention over the last years. The European energy crisis severely changed European Union's plans towards their own renewable energy sovereignty. On one hand, hydrogen gas is a very particular substance whose properties make it very difficult to store (e.g., critical temperature of 33K) for future use. Even though its elevated mass energy density ($142 MJ/kg$) is very attractive, its poor volumetric counterpart ($2.54 kW.h/L$ in liquid state at -252.9K and $1.55 kW.h/L$ in compressed gas state at atmospheric temperature) (**Aziz2020**) further complicates its use as a prevailing energy vector, requiring extra costs of compression and liquefaction to be transported from a production system to a consumption place. Evidently, it is more efficient and cost-effective to consume hydrogen locally by sectors that urge for it, such as the ammonia/fertilizer sector (**Brown2018**). On the other hand, ammonia's properties are more appropriate to be used as an energy vector ($4.32 kW.h/L$, 41% and 64% higher than liquid and compressed gas hydrogen) (**Chehade2021**) and are more interesting for longer storage durations (**Ishaq2024**). Besides, ammonia is also a strong candidate to be adopted as an alternative e-fuel and humanity already has appropriate infrastructure to store and transport it.

One of the key messages of 2024 UN Global Resources outlook is that humanity currently consumes three times more materials than half a century ago (**UN2024**). Under this context, the acceptance of green ammonia plants (GAPs) as a solution for the non-sustainability issue has changed the view of part of the fertilizer sector, whose urgent bottlenecks need to be carefully addressed at this transition period to a renewable energy source matrix (**Ishaq2024**). The agricultural sector is the main water consumer of our society, thus the adoption of more sustainable ammonia production systems will not only occur due to the hard decarbonization need but also to reduce its high water consumption rate. Additionally, gray and blue ammonia production systems are very energy-demanding (natural gas) and account for 2% of the global energy consumption (**Chehade2021**). Consequently, they release around 451 Mt of carbon dioxide per year to produce 157 Mt of ammonia, thus resulting in a yearly average plant emission of $2.87 t_{CO2}/t_{NH_3}$. It is clear that this level of CO2 emissions cannot be acceptable anymore. As an alternative, GAPs also have some primary economical issues that need to be thoroughly addressed to their implementation in our society. Self-sustenance, flexibility, low electric power cost, and minimization of supply chain costs and custom duties are just some of the mandatory factors that need to be accounted for in order to achieve a low CAPEX, OPEX, and economic viability.

The flexibility and optimization of green ammonia synthesis plants have received significant scientific attention recently (**Sekhar2024**). Estimations about ammonia production suggest an increase of 31% up to 2030 (**IEA2019**), and in 2050 we will likely need almost 688 Mt of ammonia to cover our possible demands (e.g., fertilizers production, shipping, hydrogen carrier, power generation) (**IRENA2022**). Under this context, the concept of GAPs visualized so far involve small-scale production plants (10000-15000 ton/y) (**Brown2018**) for local/regional production and operational flexibility for very volatile and dynamic conditions due to intermittent weather behavior (**Sun2024**; **Campion2023**). These plants will likely involve clean, sustainable, and reliable green hydrogen production systems with low CAPEX and minimum CO2 emissions. In parallel, the ammonia industry demand of onsite renewable hydrogen will keep increasing up to 2050 (**IEA2023**) in order to avoid significant transport, energy infrastructure, and storage costs. All these features mentioned diverge from traditional configurations of gray or blue ammonia plants, which were optimized to operate based on the economy of scale. And even though these plants are optimized and very energy efficient, they are not completely adequate for our current needs of small-sized local production plants (**Restelli2024**).

In general, current cost ranges for green hydrogen production depend significantly on the energy matrix and applied technology. Currently, they range from 2.5 to 5.5 $\$/kg$ - values significantly superior than those from gray and blue hydrogen sources (1.5 and 2.0 $\$/kg$, respectively) (**Li2023**). However, it is expected that green hydrogen production costs will drop over the next years due to the renewable

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energy production growth throughout the world. In terms of green ammonia production, current prices are around 720 $\$/t$ for the most adequate renewable energy locations, but projected scenarios for 2030 and 2050 suggest costs around 310-500$\$/t$ (**IRENA2022**; **Ishaq2024**). This point reinforces the need of a continuous investigation on improving these systems in order to speed up their propagation and implementation in adequate regions of the world, thus providing multidisciplinary benefits (e.g., renewable energy, food, material usage, land, water, and economical development) in our pursue to sustainability.

Some examples of theoretical and industrial plant-based data analyses about different green ammonia plant configurations are available on the literature: An optimal operation state was found for an already-operational power-to-ammonia system (**Zhang2020**) with a reported energy efficiency of 74% by an integration with a Rankine cycle to steam production and an optimized heat network. Investigations about local techno-economic, thermoeconomic, and 4E assessments of green hydrogen and ammonia production systems have been gaining highlight recently (**Gado2023**; **Shamsi2024**; **Pagani2024**; **Wu2024**). However, these all focused on higher-scale plants. Alternative studies on small-scale plant applications are also available (**Koschwitz2024**; **Cameli2024**), but we require further investigations due to the increasingly higher (and expected) demand for small-scale plants over the next years around the world.

In order to reinforce the main objective of this paper, some intermediate goals include: highlighting the impact of combining likely 9 different combinations of renewable energy and electrolyzer technology scenarios at 2025 and 2030 on the exergy costs of the GAP product, wastes, and overall performance, and evaluating the exergy cost of byproducts (e.g., argon, heat/cold, water, hydrogen and ammonia recovery) from the purge stream. We discuss a novel view for these plants based on industrial symbiosis and circular economy to better allocate costs by using a software integration between ASPEN HYSYS, MATLAB, and TAESLab. It is expected that both the exergy costs of liquid ammonia under the studied scenarios and presented discussion help elucidate the importance of small-scale plants, where it is a must to emphasize how to allocate waste costs properly in order to enhance the plant ecological footprint, and thus highlight how these can be installed in European abundant renewable energy regions.

2 METHODOLOGY

2.1 Plant features, process flow diagram, and model assumptions

In order to reach our described goals, the first step was to develop a mathematical model that allowed a circular thermoeconomic analysis of a representative green ammonia production process. Figure 1 presents the process flow diagram (PFD) of our steady-state green ammonia production system developed in Aspen HYSYS v14. This plant produces 10239.0 t/year of ammonia, whose inputs are green hydrogen originated from a green hydrogen plant and a nitrogen-argon mixture (1% mol/mol Ar) originated from a cryogenic air separation unit (ASU), and both streams are at a 3:1 hydrogen/nitrogen ratio, 300K and 30bar absolute. There are two compressor stages (COMP1 and COMP2) that increase the main stream pressure to 100bar and 200bar, respectively. The intercooler (HEX1) located between the compressors cools the gaseous mixture down to 350K. The ammonia converter system splits the main stream in half, where stream 9 is preheated before entering the first converter bed (REAC1) at 630K. Then, it is quenched to 597K before the second bed. We assumed a 10-bar pressure drop for each converter. Next, the converter products (stream 13) heats up the first converter inlet to recover some of the heat of reaction originated from the synthesis (HEX2). Water and air coolers bring the gaseous mixture (HEX3 and HEX4) into a two-phase stream at 300K, where most of the ammonia is condensed and separated from the main mixture (SEP) at 30 bar. Then, the vapor separator stream (stream 18) is partially purged (1% of the recycled mass) to avoid argon accumulation and is sent to be recycled and mixed with the main input stream (stream 3). Water enters the plant at 300K and 10bar. The compressor power and heat transfers are available on Tab. 5.

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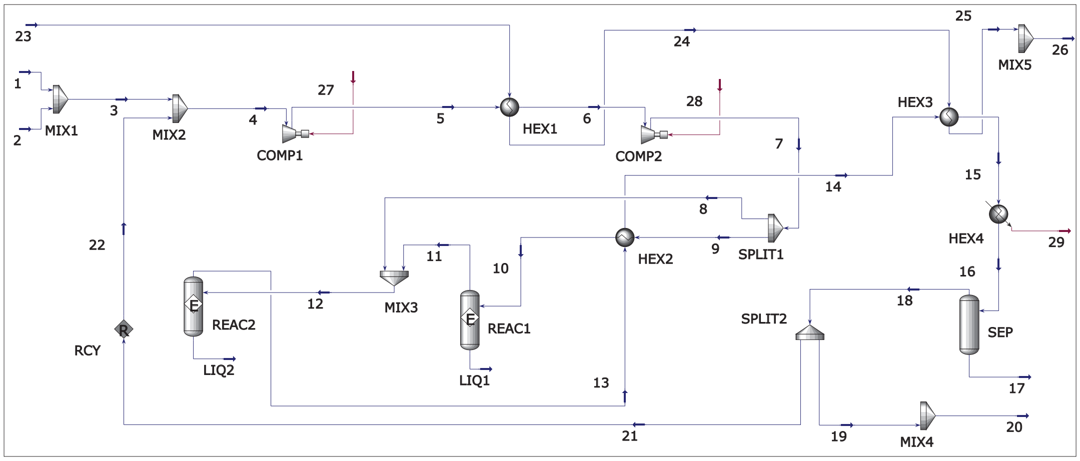

Figure 1: Process flow diagram of the GAP in study (developed in Aspen HYSYS).

2.2 HYSYS modeling, exergy and circular thermoeconomic analyses

The chemical plant model was developed on Aspen HYSYS to evaluate the steady-state mass, chemical species, and energy balances present in all unit operations required to obtain liquid ammonia. Thermodynamic properties, such as enthalpy, entropy, and physical exergy, were evaluated based on Peng-Robinson Equation of State (PR-EoS) available on the software. The chemical exergy contribution was evaluated based on an in-house MATLAB code developed for real gases, by taking into account the activity coefficients and standard-state exergy under reference conditions - 298.15K and 1 atmosphere (**Szargut1988**). Table 1 presents the main thermodynamic properties of all streams involved in the plant as well as their molar composition.

The exergy flow values $\dot{B}$ are the main inputs of TAES (Thermoeconomic Analysis of Energy Systems), a software (**Torres2023**) specialized in circular thermoeconomic analyses built in MATLAB, where our thermoeconomic evaluation took place. The fuel-product definitions adopted to all unit operations are available on Tab. 2, with all expressions used to evaluate the equipment irreversibilities related to our plant.

2.3 Evaluation of renewable energy source exergy costs

In order to proceed with the circular thermoeconomic analysis, we need to discover appropriate values to represent the exergy costs of our plant inputs, that is, streams 1 (hydrogen), 2 (nitrogen + argon), 23 (water), 27, and 28 (compressor electric power). This approach will allow us to evaluate the costs of our main product, stream 17 (liquid ammonia), and our wastes, streams 20, 26, and 29 (purge, water, and heat). The method applied to estimate these costs involves analyzing the origin of each input, as described next:

The first task was to obtain representative efficiency values of the processes required to yield our inputs. In the case of electricity, we adopted only electricity generated by renewable energy sources. We chose hydro, wind, and solar photovoltaic (PV) as representative renewable sources to this work and decided to analyze their costs of production on two future scenarios: 2025 and 2030. For hydrogen, it is also necessary to account for the water electrolysis efficiency (alkaline, PEM, or SOEC), whose estimations for different technologies up to 2050 are available on (**IEA2019**). Then, we combined these parameters into 18 different production scenarios where the exergy costs will be propagated and analyzed together. For nitrogen, we obtained its exergy cost by evaluating it from general cryogenic air separation units (ASUs). We adopted a representative exergy efficiency of 14.7% (**Aneke2015**). Finally, we assumed for this work that the costs of water and air are zero. Table 3 presents the efficiencies of all processes involved in the production of hydrogen and nitrogen, as well as the respective exergy costs for producing electricity

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Table 1: Stream table summarizing the main thermodynamic properties (in order, temperature, pressure, exergy flow, mass flow, enthalpy, entropy, and overall mole fraction) of all streams involved in the plant.

Stream	T [K]	p $[bar]$	$\dot{B}$ $[kW]$	$\dot{m}$ $[\frac{kg}{s}]$	h $[\frac{kJ}{kg}]$	s $[\frac{kJ}{kg.K}]$	x_{H_2} [-]	x_{N_2} [-]	x_{NH_3} [-]	x_{Ar} [-]
1	300.0	30	7236.1	0.060	25.54	47.08	1	0	0	0
2	300.0	30	90.3	0.281	-5.80	4.25	0	9.90E-01	0	1.00E-02
3	299.3	30	7271.2	0.341	-0.30	12.31	7.48E-01	2.49E-01	0	2.52E-03
4	276.2	30	39943.3	1.965	-577.53	10.53	6.38E-01	2.14E-01	1.16E-01	3.25E-02
5	426.0	100	40616.7	1.965	-158.14	10.79	6.38E-01	2.14E-01	1.16E-01	3.25E-02
6	350.0	100	40515.9	1.965	-382.35	10.21	6.38E-01	2.14E-01	1.16E-01	3.25E-02
7	450.4	200	40989.8	1.965	-91.70	10.38	6.38E-01	2.14E-01	1.16E-01	3.25E-02
8	450.4	200	20494.9	0.982	-91.70	10.38	6.38E-01	2.14E-01	1.16E-01	3.25E-02
9	450.4	200	20494.9	0.982	-91.70	10.38	6.38E-01	2.14E-01	1.16E-01	3.25E-02
10	630.0	200	20731.0	0.982	451.12	11.39	6.38E-01	2.14E-01	1.16E-01	3.25E-02
11	745.8	190	20679.3	0.982	451.12	11.57	5.74E-01	1.92E-01	1.99E-01	3.49E-02
12	597.5	190	41103.4	1.965	179.71	11.09	6.07E-01	2.03E-01	1.56E-01	3.36E-02
13	714.4	180	40998.0	1.965	179.71	11.27	5.39E-01	1.81E-01	2.44E-01	3.62E-02
14	622.8	180	40702.9	1.965	-91.70	10.87	5.39E-01	1.81E-01	2.44E-01	3.62E-02
15	350.0	180	40122.3	1.965	-892.56	9.17	5.39E-01	1.81E-01	2.44E-01	3.62E-02
16	300.0	180	40073.6	1.965	-1250.27	8.06	5.39E-01	1.81E-01	2.44E-01	3.62E-02
17	270.4	30	6400.2	0.325	-4035.52	4.31	1.70E-03	4.20E-04	9.96E-01	2.03E-03
18	270.4	30	33025.6	1.640	-698.83	10.12	6.08E-01	2.04E-01	1.48E-01	4.06E-02
19	270.4	30	330.3	0.016	-698.83	10.12	6.08E-01	2.04E-01	1.48E-01	4.06E-02
20	270.4	30	330.3	0.016	-698.83	10.12	6.08E-01	2.04E-01	1.48E-01	4.06E-02
21	270.4	30	32695.3	1.624	-698.83	10.12	6.08E-01	2.04E-01	1.48E-01	4.06E-02
22	270.4	30	32695.3	1.624	-698.83	10.12	6.08E-01	2.04E-01	1.48E-01	4.06E-02

(**Torrubia2024**). This electricity exergy cost is an attempt of representing an annual average energy cost due to the three renewable energy matrices in study:

Table 4 summarizes all exergy costs adopted for our plant: both the exergy cost of green hydrogen and green nitrogen are based on the 18 renewable energy production scenarios previously discussed.

3 RESULTS AND DISCUSSION

3.1 Thermoeconomic costs

The exergy costs of Tab. 4 allowed us to provide realistic physical costs (i.e., based on exergy) to the green ammonia plant (GAP) inputs and evaluate the cost allocation over the plant streams. TAESLab (**Torres2023**) was used to develop all thermoeconomic analyses presented here - all of which were based on the updated theory of exergy cost (**Torres2021**). Exergy analyses of gray ammonia production systems are already well covered by specialized literature with different approaches and configurations (**Penkuhn2017**; **Florez-Orrego2017**); these also extend for green ammonia plants (**Ishaq2020**). Thus, the authors intend with this work to bring a novel view on the exergy costs of such chemical plants, under the aforementioned future renewable energy scenarios.

Table 5 presents the fuel-product exergy values (based on the definitions of Tab. 2) related to each unit operation of the designed plant, as well as their unit exergy cost, irreversibility, and exergy efficiency. The mixing processes did not contribute to exergy destruction, as indicated by their very low unit exergy cost. This analysis assumed that mixing phenomena, such as enthalpy, entropy, volume change of mixture,

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Table 2: Fuel-product equations of all equipment/unit operations in study (where $I = F - P$).

Equipment	Fuel (F)	Product (P)	Type
MIX1	$\dot{B}_1 + \dot{B}_2$	$\dot{B}_3$	Productive
MIX2	$\dot{B}_3 + \dot{B}_{22}$	$\dot{B}_4$	Productive
MIX3	$\dot{B}_8 + \dot{B}_{11}$	$\dot{B}_{12}$	Productive
MIX4	$\dot{B}_{19}$	$\dot{B}_{20}$	Dissipative
MIX5	$\dot{B}_{25}$	$\dot{B}_{26}$	Dissipative
SPLIT1	$\dot{B}_7$	$\dot{B}_8 + \dot{B}_9$	Productive
SPLIT2	$\dot{B}_{18}$	$\dot{B}_{19} + \dot{B}_{21}$	Productive
COMP1	$\dot{B}_{27}$	$\dot{B}_5 - \dot{B}_4$	Productive
COMP2	$\dot{B}_{28}$	$\dot{B}_7 - \dot{B}_6$	Productive
HEX1	$\dot{B}_5 - \dot{B}_6$	$\dot{B}_{24} - \dot{B}_{23}$	Productive
HEX2	$\dot{B}_{13} - \dot{B}_{14}$	$\dot{B}_{10} - \dot{B}_9$	Productive
HEX3	$\dot{B}_{14} - \dot{B}_{15}$	$\dot{B}_{25} - \dot{B}_{24}$	Productive
HEX4	$\dot{B}_{15} - \dot{B}_{16}$	$\dot{B}_{29}$	Dissipative
REAC1	$\dot{B}_{10}$	$\dot{B}_{11}$	Productive
REAC2	$\dot{B}_{12}$	$\dot{B}_{13}$	Productive
SEP	$\dot{B}_{16} - \dot{B}_{17}$	$\dot{B}_{17}$	Productive
RCY	$\dot{B}_{21}$	$\dot{B}_{22}$	Productive

Table 3: Water electrolysis technology and air separation unit (ASU) efficiencies in 2025 and 2030, and estimations on annual average electricity exergy cost produced by different renewable energy sources. Projection data for three different water electrolysis technology (alkaline, PEM, and SOEC) and for the renewable energy sources were obtained from **IEA2019**, whereas an average ASU efficiency was assumed constant for this period and obtained from **Aneke2015**.

Year/source	Water electrolysis + ASU				Renewables [kW/kW]		
	Alkaline	PEM	SOEC	ASU	Hydro	Wind	Photovoltaic (PV)
2025	0.655	0.618	0.790	0.147	1.034	1.164	2.454
2030	0.680	0.655	0.805	0.147	1.035	1.163	1.742

are taken into consideration on HYSYS thermodynamic property evaluation tool. Another aspect is that the compressor exergy efficiencies are similar to the 80% isentropic efficiency. In terms of heating and cooling, the heat transfer units (especially HEX 1) were responsible for the lowest exergy efficiency and thus the highest unit exergy cost (29.3% and $3.41 kW/kW$, respectively) found on the plant simulation. As shown by Tab. 1, HEX1 heat transfer occurred close to the reference temperature for both water and feed streams - factor that was fundamental to the poor unit exergy performance. And as expected, the innate irreversibility of a separation process caused the highest exergy destruction among all productive processes studied here (around $647 kW$), thus collaborating for the increase of the unit exergy cost of our product stream, liquid ammonia ($1.55 kW/kW$ only for the plant operation).

An important factor to clarify is that since the ammonia synthesis was assumed to occur under chemical equilibrium conditions, the reaction irreversibility was affected. However, the intention of this work was not represent this conversion as real as possible, but to evaluate how renewable electricity, green hydrogen and nitrogen exergy costs allocate over this plant unit operations. Therefore, our reactor model did not take into account factors fundamental to represent real ammonia conversion conditions, such as the catalyst efficiency (Iron- or Ruthenium-based catalysts), chemical kinetic model (e.g., Temkin heterogeneous reaction model) catalyst distribution, reactor geometry, adsorption and desorption phenomena, and fluid dynamics, but rather to represent minimum conditions to allocate exergy costs on the ammonia compression, conversion, cooling, and separation processes.

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Table 4: Exergy cost scenarios from different renewable energy sources and water electrolysis technologies. Stream B_1 refers to green hydrogen, B_2 to green nitrogen, B_{23} to water, and $B_{27,28}$ to compressor power. All exergy cost evaluations based on (**Torrubia2024**) and original data from **IEA2019** [Unit: kW/kW].

Scenario	Combination	B_1	B_2	B_{20}	B_{27}, B_{28}
S1	Alkaline + Hydro (2025)	1.580	7.022	0	1.035
S2	Alkaline + Wind (2025)	1.776	7.890	0	1.163
S3	Alkaline + PV (2025)	2.660	11.818	0	1.742
S4	PEM + Hydro (2025)	1.676	7.022	0	1.035
S5	PEM + Wind (2025)	1.883	7.890	0	1.163
S6	PEM + PV (2025)	2.821	11.818	0	1.742
S7	SOEC + Hydro (2025)	1.310	7.022	0	1.035
S8	SOEC + Wind (2025)	1.472	7.890	0	1.163
S9	SOEC + PV (2025)	2.205	11.818	0	1.742
S10	Alkaline + Hydro (2030)	1.521	7.022	0	1.035
S11	Alkaline + Wind (2030)	1.644	7.890	0	1.163
S12	Alkaline + PV (2030)	2.085	11.818	0	1.742
S13	PEM + Hydro(2030)	1.579	7.022	0	1.035
S14	PEM + Wind (2030)	1.707	7.890	0	1.163
S15	PEM + PV (2030)	2.165	11.818	0	1.742
S16	SOEC + Hydro (2030)	1.284	7.022	0	1.035
S17	SOEC + Wind (2030)	1.389	7.890	0	1.163
S18	SOEC + PV (2030)	1.761	11.818	0	1.742

Table 5: Thermoeconomic analysis for the base-case without external exergy costs from the inputs.

Unit Op.	F(kW)	P(kW)	I(kW)	k(J/J)	η (%)
MIX1	7326.49	7271.19	55.30	1.0076	99.25
MIX2	39966.51	39943.28	23.23	1.0006	99.94
MIX3	41174.21	41103.37	70.84	1.0017	99.83
MIX4	330.26	330.26	0.00	1.0000	100.00
MIX5	1702.69	1702.69	0.00	1.0000	100.00
SPLIT1	40989.75	40989.75	0.00	1.0000	100.00
SPLIT2	33025.58	33025.58	0.00	1.0000	100.00
COMP1	823.96	673.38	150.58	1.2236	81.72
COMP2	571.02	473.87	97.15	1.2050	82.99
HEX1	100.77	29.55	71.23	3.4107	29.32
HEX2	295.08	236.17	58.91	1.2494	80.04
HEX3	580.64	413.32	167.31	1.4048	71.18
HEX4	48.63	48.63	0.00	1.0000	100.00
REAC1	20731.04	20679.33	51.71	1.0025	99.75
REAC2	41103.37	40997.98	105.39	1.0026	99.74
SEP1	7048.05	6400.23	647.83	1.1012	90.81
RCY1	32695.32	32695.32	0.00	1.0000	100.00
ENV	9981.29	6400.23	3581.06	1.5595	64.12

In order to compare all 18 renewable energy production scenarios evaluated from IEA projections to 2025 and 2030, Tab. 6 presents the exergy costs and the specific energy/exergy consumption (SEC) for producing liquid ammonia. It is noteworthy how the renewable energy source affects the unit exergy cost (c)

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of obtaining pure ammonia (99.6% from Tab. 1) on 2025: these can be as low as $1.80 MW_{NH_3}/MW_{\text{inputs}}$ or as high as $3.74 MW_{NH_3}/MW_{\text{inputs}}$, as found for scenarios S7 and S6, respectively. This range of values is significantly higher than the one of 2030 (1.78 *versus* $2.89 MW_{NH_3}/MW_{\text{inputs}}$ for S17 and S16), which projects a significant reduction on the costs of renewable energy production and thus on green hydrogen, regardless of the electrolysis technology or source. This finding highlights how strong and viable the combo GAP + hydro + SOEC can be (S7 and S16), where their costs are favorable even for the wind matrix, whose values lie around 2.0 and $1.9 MW_{NH_3}/MW_{\text{inputs}}$, for S8 and 17, respectively. The projected high efficiency of the SOEC technology is based on its favorable thermodynamics and high temperature operation, presenting it as significantly superior to the other two water electrolysis technologies mentioned in this work. Additionally, it does not depend on rare metals usage (**Shiva-Kumar2022**). However, SOEC is still a technology under development with lower stability than alkaline and PEM, which contrasts all good projections on it and thus let SOEC on standby for its usage on more conservative industry applications.

Table 6: Exergy costs (c) and specific energy/exergy consumption (SEC) under 18 different renewable energy production and water electrolysis technologies scenarios. Reference value for SEC: $LHV_{NH_3} = 18577 kJ/kg = 5.1603 MWh/t$ (**Chehade2021**).

Scenario	c [MW/MW]	C [MW]	SEC [MWh/t]
S1	2.111	13.51	11.56
S2	2.372	15.18	12.99
S3	3.553	22.74	19.45
S4	2.220	14.21	12.15
S5	2.494	15.96	13.66
S6	3.736	23.91	20.45
S7	1.806	11.56	9.89
S8	2.029	12.99	11.11
S9	3.040	19.45	16.64
S10	2.044	13.08	11.19
S11	2.210	14.14	12.10
S12	2.803	17.94	15.34
S13	2.109	13.50	11.55
S14	2.281	14.60	12.49
S15	2.893	18.51	15.84
S16	1.777	11.37	9.73
S17	1.921	12.29	10.52
S18	2.436	15.59	13.34

With respect to the other two energy sources, wind presents as the second most cost effective option regarding green ammonia production, with all its exergy cost values lower than $2.5 MW_{NH_3}/MW_{\text{inputs}}$ in 2025 (S2, S5, and S8) and $2.3 MW_{NH_3}/MW_{\text{inputs}}$ in 2030 (S11, S14, and S17). Its specific energy consumption to produce liquid ammonia lies between 11.0 and $13.0 MWh/t_{NH_3}$ on 2025 and will reach almost $10.5 MWh/t_{NH_3}$ in 2030 (S17). These values represent approximately the double of ammonia's lower heating value (LHV_{NH_3}), and are useful as references for future usage of green ammonia as an energy vector or fuel. Another favorable point towards this energy source are that wind regions are more available all around the planet than those with significant hydro potential (currently found in China, Brazil, Canada, etc.), and it is already in use in many countries in Europe and in the world (**Kakoulaki2021**; **IEA2023**; **IRENA2023**). On the other hand, with $3.0 kW_{NH_3}/kW_{\text{inputs}}$ in 2025 (S3, S6, and S9) and $2.4 kW_{NH_3}/kW_{\text{inputs}}$ in 2030 (S12, S15, and S18), solar PV presents the worst exergy costs among all three renewable energy sources, but it is the most available over the world among them. Besides, its cost

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of production and infrastructure is already falling down and projections indicate a continuous decrease up to 2050 (**IEA2019**). Therefore, both wind and solar PV are two options also important to make GAP plants economically and technically viable, especially for regions without elevated hydro potential, such as Spain in Europe, where wind and solar energy production potentials are the most abundant among all EU countries (**Kakoulaki2021**).

In terms of water electrolysis technologies, alkaline is an economic viable option that will likely allow the construction of the first small-scale GAP plants for projects with lower CAPEX capacity, though this choice comes with higher liquid exergy costs than SOEC. PEM presents a fundamental issue of depending on noble metals (Iridium and Platinum) on their electrodes, which might not be favorable in terms of a sustainable application whose exergy costs are similar to alkaline's. Additionally, these two technologies can be complicated to operate together with solar PV systems, whose exergy costs can reach up to $2.9 kW_{NH_3}/kW_{\text{inputs}}$ in 2030. However, for wind matrix applications, these costs will likely be more accessible ($2.5 kW_{NH_3}/kW_{\text{inputs}}$) and thus acceptable for small-scale GAPs. Thus, the idea of hybridizing wind and solar PV energy production sounds more interesting for them, because this approach would allow a more feasible physical cost to yield green ammonia, and provide a more stable renewable energy production, overcoming the issues that single renewable source plants might have during specific periods of the year (**Sarker2023**; **Wu2024**).

3.2 Discussion of future possibilities

It is a known fact that small-scale GAPs can neither compete financially (OPEX) nor technically (i.e., efficiency or size production) with currently gray ammonia plants due to the economy of scale factor (**Chehade2021**). It is thus fundamental to operate them based on the fundamentals of industrial symbiosis and proper waste exergy cost allocation to turn this novel type of chemical plant as economically and technically viable as possible. Therefore, we discuss some intricate aspects of these plants that require proper attention to reach the aforementioned goals of our text.

Novel configurations of green hydrogen plants have been built with hybrid renewable energy sources to obtain a more stable electricity management system in order to be small-cost and simple in operation to be economic viable. The combination of solar PV with wind energy represents a classical hybrid configuration where PV plants can assist on the (more) erratic and volatile behavior of wind plants, whereas their higher efficiency can make up the low efficiency of PV plants (**Sarker2023**; **Wu2024**). This robust hybrid renewable energy plant would be capable of feeding water electrolyzers at off-grid conditions most of the time, whereas outside these moments, on-grid certified renewable electricity could be used to keep the plant CO2-neutral and fully operational - a mandatory feature to reduce the 830 Mt CO2 per year to obtain hydrogen (2% of global emissions). This nonrenewable energy aspect should also be accounted for on the exergy costs, since only by doing this we will be able to properly evaluate how sustainable GAPs with hybrid renewable sources can actually be under operation.

An important aspect connected to the industrial symbiosis of our plant is proper usage of the purge stream. Stream 20 is composed by almost 61% hydrogen, 20% nitrogen, 15% ammonia, and 4% argon (Tab. 1) and is required to avoid argon accumulation on the recycled stream and thus on the reactor. Even though purges are fundamental for this type of plant, it is evident for us that in a world where natural resources are continuously wasted, each of the gas components have their technical value and importance. Hydrogen and ammonia are obviously the first and most interesting options plant to be recovered, especially when they already are at viable molar fractions to be recovered from. Additionally, we would like to shed a light on argon. A traditional argon production pathway is via ASU systems, but these struggle with the low argon's molar fraction in air (around $0.9\% mol/mol$), the low difference of oxygen and argon boiling points (3K difference), as well as that argon separation is a very energy demanding process. Therefore, why not take advantage of such an argon-rich stream to separate and obtain it as a byproduct? In our work, the purge stream exergy cost based on all 18 scenarios ranged around 1.61 to 3.39 $kW_{\text{purge}}/kW_{\text{inputs}}$, which is already advantageous in comparison to regular ASUs and would present a significantly lower specific energy consumption to obtain it than $19.5 KWh/kg$ (**Aneke2015**), as

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reported on the literature. Also, we would not have to deal with the oxygen boiling point issue anymore. There are reports that support a minimum specific energy consumption of $1.18kWh/Nm^3$ (**Zhao2011**) of purge streams from gray ammonia plants. In addition, alternatives for this issue such as new cryogenic ASU configurations for obtaining noble gases (**Saedi2022**) or pressure swing adsorption (PSA) systems (**Banaszkiewicz2018**) are already available, so we can stop treating a purge stream as a full waste, but rather as an interesting byproduct whose exergy cost was already covered.

Another byproduct of GAPs is the oxygen gas. This substance is obtained from water electrolysis and ASUs, is very important for medical applications, and can be used to feed nitrogen-free combustion systems to avoid NO_x formation. Metallurgy is an example of a industrial sector that, in opposition to the ammonia one, demands oxygen and obtains nitrogen as a byproduct/waste. An industrial symbiosis between these sectors would greatly benefit both of them by sharing a green hydrogen production system, an energy storage unit (batteries and hydrogen), and the nitrogen and oxygen streams from the ASUs. These aspects enhance their ecological footprint and reduce their exergy costs by allocating the economical and physical/exergy costs between both plants in a fully-based renewable energy plant.

Lastly, fundamental technical aspects internal to GAPs such as heat/cooling integration between small-scale green hydrogen and green ammonia plants are important to their OPEX and ecological footprint (**Shamsi2024**; **Ishaq2024**; **Ishaq2020**). In our case, these would involve material/energy integration between GAP, green hydrogen, and ASU plants, and the inclusion of renewable energy production fluctuation over the year. The possibility of industrial symbiosis via byproducts for self-usage or other industries, such as cooling and hot water, steam production (stream 26), hydrogen, oxygen, and argon recovery, would enhance the plant overall efficiency and reduce their exergy costs. SOEC systems could also be thermally integrated with subsequent chemical plant production systems (**Shiva-Kumar2022**). On the other hand, the inclusion of water (essential especially for dry regions) and air costs, need for hydrogen storage due to renewable energy production intermittence, and infrastructure (i.e., materials, time of operation, and thermodynamic rarity), and nonrenewable energy fraction costs will likely bring the exergy cost to a value closer to real operation, thus these aspects would allow us to discover how sustainable our GAP can operate and how it can collaborate in a circular/spiral economy that the world needs so much.

4 CONCLUSIONS

We developed a circular thermoeconomy analysis of a small-scale green ammonia plant whose input exergy costs were based on future projections of renewable energy production and efficiency for 2025 and 2030. Projections of three water electrolysis technology efficiencies, ASU efficiency, and hydro, wind, and solar PV electricity exergy costs provided conditions to estimate the exergy costs of green hydrogen, green nitrogen, and electricity - inputs of our green ammonia plant example that allowed us to evaluate the exergy cost of liquid ammonia and some byproducts.

Results obtained via TAESLab software showed 18 different scenarios of liquid ammonia production, where the most interesting and attractive involved SOEC and hydro in 2030 with an exergy cost of 1.78 or $9.73MWh/t_{NH_3}$. Solar PV scenarios presented the highest exergy costs regardless of the energy matrix due to its current high exergy cost ($2.43MW/MW_{NH_3}$ or $13.34MWh/t_{NH_3}$ in 2030), whereas wind presents as a very flexible alternative in terms of exergy costs for all three water electrolysis technologies to be adopted in most places in the world ($1.92MW/MW_{NH_3}$ or $10.52MWh/t_{NH_3}$ in 2030). Alkaline water electrolysis exergy costs appear to be viable in terms of immediate implementation due to its commercial availability and to not be dependent on critical raw materials usage, such as PEMs are.

The simulated green ammonia plant yielded high-purity liquid ammonia with an exergy efficiency of 63% (or $1.55kW/kW$ only for the plant operation) and with potential to be more efficient and economically attractive with proper attention to its byproducts (e.g., purge stream, with argon production, hydrogen, and ammonia recovery), material/energy integration between the its components not outside the presented analysis.

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Fundamental aspects to complement the plant operation in terms of industrial symbiosis were discussed as well, with highlight to the need of hybridization of renewable energy production. Even though GAPs cannot directly compete with the costs of traditional gray ammonia plants, there is a foreseeable market in which these type of plants can operate distributed on regions all around the world for local or regional ammonia production for fertilizers of energy storage.

Future works will involve focus on approaching higher degrees of complexity to fully evaluate how sustainable this type of plant can actually be. A full plant representation under transient conditions with hybrid renewable energy systems, energy storage via batteries and hydrogen, production and storage, electricity curtailment is on the scope of this research. Also, purge optimization with alternative ASU systems to reduce nitrogen exergy cost (novel cryogenic, PSA and membrane adsorption systems) and a further future representation up to 2050 are also in sight in order to pursue our goal of evaluating how sustainable these plants can be based on the concept of industrial symbiosis.

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