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Towards the decarbonization of ammonia synthesis – A techno-economic assessment of hybrid-green process alternatives

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ABSTRACT

This paper analyzes the retrofitting of a conventional, "gray" ammonia plant for its partial decarbonization. Specifically, the retrofitting involves the hybridization of the process by providing a certain amount of green hydrogen (*i.e.* by water electrolysis) for the ammonia synthesis to reduce the demand for the original gray hydrogen route (*i.e.* by fossil-based steam reforming) and consequently reduce CO_2 emissions. As such green hydrogen is produced through an electrolyzer that consumes renewable electric energy, two design configurations are considered: (*Option I*) the supply of clean electricity from renewable sources; (*Option II*) the generation of clean electricity by an in-house photovoltaic power plant. Once having analyzed the advantages and limitations of the hybrid plant layouts, the ammonia production costs achieved by the three simulated plants (*i.e.* the reference "gray" plant and the two hybrid alternatives) are estimated by considering the United States (USA) and European Union (EU) market quotations in 2022 and previsions for 2030 and 2050. The main outcomes are that (i) hybrid-green ammonia proves to be a feasible, environmentally friendly retrofitting option for the ammonia production industry, showing production costs that are no more than 36 % higher than gray ammonia; and (ii) *Option I* achieves better cost-effectiveness than *Option II* in the USA, while the opposite happens in the EU. Specifically, the resulting 10 %-green-on-average hybrid-green ammonia production costs range between +0.3 % (*EU-2022*) and +30.8 % (*USA-2022*) for *Option I*, and between −1.3 % (*EU-2022*) and +35.3 % (*USA-2022*) for *Option II*, compared to the reference gray ammonia plant. (iii) Lastly, the projected (*i.e.* in 2030 and 2050) CO_2 avoidance costs associated with hybrid-green ammonia configurations exceed 400 USD/t_{CO2} in the USA and 500 USD/t_{CO2} in the EU.

1. Introduction

Decarbonization of ammonia production is a drive that today rises more urgently than ever. In terms of environmental sustainability, ammonia is by far the most carbon-intensive chemical commodity. Specifically, ammonia synthesis was responsible for the generation of approximately 440 Mt/y of CO_2-equivalent emissions in 2020 [1], which accounted for almost 1 % of global greenhouse gas (GHG) anthropogenic emissions of that year [2]. The link between GHG emissions and ammonia stems primarily from the hydrogen feedstock to the ammonia synthesis, which is still about 98 % derived from fossil fuels: natural gas, 72 %; coal, 22 %; and crude oil, 4 % [3]. These can be defined as the "process emissions", representing about 70 % of the CO_2 emissions of a conventional ammonia plant. The remaining ca. 30 % is associated with the "energy emissions", *i.e.* the ones related to generating the heat and compression required for the process [4]. Back to the process emissions, it stands clear that the main road to achieving full carbon neutrality in ammonia production is to decouple the whole synthesis route from fossil feedstocks. This is the basic idea behind the "green ammonia" technologies, aiming to retrofit and finally replace the "gray", fossil-based hydrogen feedstock with a "green", water-based one thanks to renewable-energy-powered electrolyzers. This challenging decarbonization strategy is supposed to represent the endgame of future ammonia production since it stands as the only zero-emissions technology expected to be economically practicable and technologically established within the next decade [5]. Anyway, until such zero-emissions technologies become commercially ready for large-scale production in the following decades, an available-to-date alternative such as hybrid-green ammonia is an appealing production pathway.

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Notation

AEL	Alkaline Electrolyzer
AEM	Anion Exchange Membrane Electrolyzer
BESS	Battery Energy Storage System
CCUS	Carbon Capture, Utilization, and Storage
CF	Capacity Factor
CW	Cooling Water
$deCO_2$	Overall decarbonization extent
DC	Direct Current
DMW	Demineralized Water
DR1	Throughput decrease in the primary reformer
EL	Electrolyzer
EU	European Union
G2GHR	Green-to-gray hydrogen ratio
NG	Natural gas
O&M	Operation & Maintenance
PEM	Proton Exchange Membrane Electrolyzer
PPA	Power Purchase Agreement
PV	Photovoltaic
SOE	Solid Oxide Electrolyzer
ST	Hydrogen storage
USA	United States of America
VALCOE	Value-Adjusted Levelized Cost of Electricity

Specifically, "hybrid-green ammonia" consists of retrofitting an existing conventional, gray ammonia plant by adding a parallel line to produce water-based, green hydrogen. By doing so, a certain amount of the hydrogen needed as a reactant in the Haber-Bosch section (*i.e.* the one where hydrogen reacts with nitrogen to produce ammonia) of the hybridized ammonia plant is completely carbon–neutral, resulting in lower CO_2 emissions. In this regard, partial decarbonization of large gray plants can make a great impact (fitting currently available renewable and electrolyzers capacities) and allows valorizing of existing expensive assets.

The primary rationale of this paper is to perform a techno-economic assessment of a hybrid-green ammonia plant to analyze its economic feasibility and determine the best operating conditions. Indeed, to our knowledge, no articles have been published yet on this novel technique which might gain increasing importance in the next years as the decarbonization pathway becomes widespread.

2. Gray ammonia plant and hybridization challenges

2.1. The route to hybridization

Before starting with the techno-economic assessment of the hybrid-green ammonia plant, a conventional, natural gas-based 2000 t_{NH3}/d ammonia plant was simulated in UniSim® Design R491 as a reference point (Fig. 1 shows its block flow diagram). This allowed us to correctly estimate the amount of CO_2 emissions generated by the classic gray configuration.

At this point, the hybrid retrofitting of such a plant (to partially abate the CO_2 emissions without affecting its production capacity) would simply consist of placing a renewable-energy-powered electrolyzer side by side with the conventional "Front-end" section (*i.e.* the reforming, shift, and syngas purification units), right before the Haber-Bosch process (*aka* the "Synthesis loop", or "Synloop", that is the main section of the so-called "Back-end"). Indeed, being the electrolyzer a unit aimed at producing green hydrogen by renewable electric energy sources, such a process solution allows for a strong decrease in the amount of gray hydrogen. Indeed, gray hydrogen consumes fossil fuels twice (i) as a feedstock for its synthesis by steam reforming (*i.e.* the natural gas feedstock headed to the reformers) and (ii) as a utility for the thermal energy supply (*i.e.* the fuel gas headed to the burners of the primary reformer furnace). Consequently, a gray ammonia plant involves both process- and energy-related CO_2 emissions which can be lessened by suitable green retrofitting.

Nonetheless, one of the main efforts for the best design of such a process is the choice of the optimal decarbonization extent of the hybrid plant or, in other words, how much green hydrogen should be fed to the Haber-Bosch section instead of gray hydrogen. It should be kept in mind that such a key variable is tied to some issues:

1. Availability of renewable power.
2. Operating conditions variation from the nominal ones (*i.e.* those of the gray plant):
   a. The process flow entering the primary reformer (in jargon, the "throughput").
   b. The operating temperature within the secondary reformer.
   c. The amount of fuel gas fed to the burners of the primary reformer furnace.

The following paragraphs analyze the sense behind these constraints for accuracy.

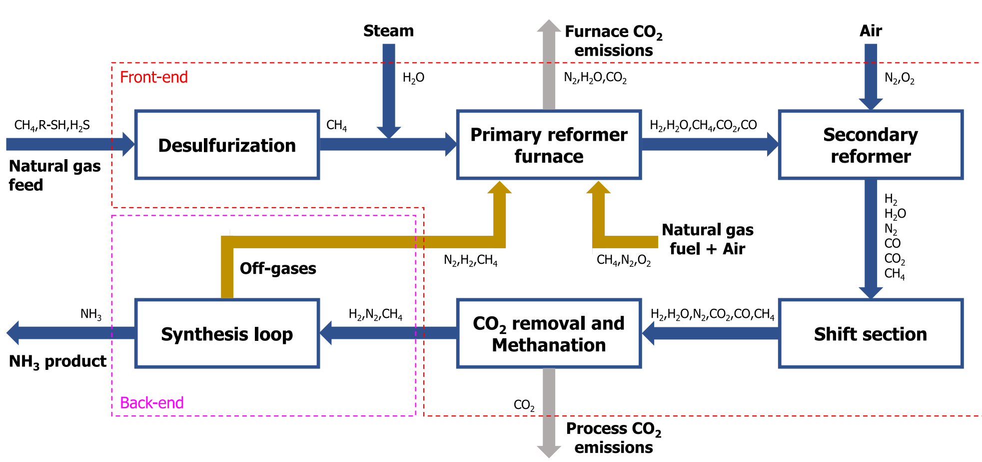

Fig. 1. Block flow diagram of the reference conventional, natural gas-based (gray) ammonia plant (2000 t_{NH3}/d capacity).

2.2. Hybridization constraints on the availability of renewable power

Starting from the first point of the list above, the electrolyzer should be fed with electrical energy by renewables, to ensure a truly green contribution. This means that the whole green section merged with the original plant is strongly subjected to the fluctuating trends of renewable energy profiles. Indeed, renewable energy production is inherently characterized by the irregular availability of energy sources (*e.g.*, sunlight and/or wind in the case of solar and/or wind farms). This means that, in a certain way, the electrolyzer will simply transform such intermittent renewable energy profiles into correspondingly intermittent green hydrogen flows. It follows that the target green hydrogen productivity (or, correspondingly, the target decarbonization extent) should be considered as an average of the fluctuations that span from a minimum of zero (when no clean electricity is available) to a maximum, which is strictly related to the capacity factor of the renewable power plant (that provides the peak electric power made available to the final user) as well as few essential design considerations (that were already mentioned in the previous list and will be discussed in depth in the following). Therefore, a storage system is mandatory to mitigate such fluctuations' impact on the rest of the retrofitted plant. This system can be either a hydrogen storage section downstream of the electrolyzer or a battery energy storage system (BESS) amidst the renewable power plant and the electrolyzer.

2.3. Hybridization constraints on the operating conditions of the plant

Regarding the second point of the aforementioned list (*i.e.* operating conditions as close as possible to the nominal ones), it is quite reasonable that the partial replacement of gray, fossil-based, hydrogen with green, water-based, hydrogen has several effects on the retrofitted plant, especially if one considers that it was originally designed to be fed with natural gas only. The first obvious effect of hybridization is that the lower demand for gray hydrogen (being partially replaced by the green hydrogen from the electrolyzer) calls for a lower amount of natural gas as feedstock. While this undoubtedly grants lower CO_2 emissions, the main drawback is the drop in mass flowrates circulating across the front-end section, specifically in the primary reformer (see point 2a of Paragraph 2.1). Indeed, a conventional steam reformer cannot operate properly when the throughput decreases too much below the design capacity (our assumption was to set the lower bound to 80 % of the nominal capacity [6]). Moreover, such drops in the material flowrates of the "gray route" might also affect the secondary reformer, specifically its operating temperature (see point 2b). Indeed, since the inlet air flowrate must be kept constant to meet the nitrogen demand of the plant and guarantee the stoichiometric hydrogen-to-nitrogen ratio for the ammonia converter, the oxygen-to-carbon molar ratio at the secondary reformer inlet increases promptly and the temperature of the reactor does the same. Such temperature rise must be as limited as possible (our assumption was to consider $+100$ °C as the maximum allowed temperature increase within the reactor) to prevent the overheating of the secondary reformer and the downstream process boiler. Finally, the amount of fuel gas fed to the furnace burners (see point 2c) represents a process variable that should not vary significantly from the original operating conditions. However, in this specific case, this is not a substantial risk for the hybrid plant: indeed, as the secondary reformer tends to reach higher temperatures, the equilibrium of the endothermic steam reforming reaction is further shifted forward, which decreases the presence of methane in the outlet products. Consequently, the inert content in the ammonia synthesis loop is expected to drop and, as a result, the methane content in the off-gases to be burnt in the furnace is lower when compared to the original gray operating conditions, making still compulsory (although necessarily smaller than in the gray plant) the demand for fuel gas. It is also worth bearing in mind that this last issue, *i.e.* the drop in the inert gases headed to the Haber-Bosch section, turns out to be beneficial to the economy of the process as it reduces the compression costs and improves the reaction thermodynamics and kinetics in the ammonia converters.

3. Process simulation of the hybrid plant

As shown in Fig. 2, the retrofitted ammonia plant calls for a parallel line of hydrogen production using a renewable-energy-powered electrolyzer which should be connected to an electrical power supply (*e.g.*, the electrical network or a dedicated power plant) and followed by a hydrogen storage system (indeed, this design option was preferred to the BESS solution due to its lower cost and higher technology readiness level).

As previously discussed, one of the main efforts for the best design of such a plant is the choice of the optimal decarbonization extent of the hybrid plant, *i.e.* the amount of green hydrogen injected into the Haber-Bosch section instead of gray hydrogen. In this regard, simulating the hybrid plant with increasing contributions of green hydrogen, a nearly identity relation among the ratio of green hydrogen over the total hydrogen entering the synthesis loop (the "green-to-gray hydrogen ratio", G2GHR), the percentage of overall (*i.e.* both process and furnace emissions) decarbonization extent of the hybrid plant ($deCO_2$), and the percentage of throughput decrease in the primary reformer (DR1) arises (see Fig. 3).

Panels A and B of Fig. 3 show how $deCO_2$ cannot exceed a certain value to not overtake the operating boundaries discussed in Paragraph 2.3. Specifically, $deCO_2$ should be lower than 20 % at the highest to not deplete the primary reformer throughput by more than 20 % (following the nearly identity relation shown in Panel A of Fig. 3) and not exceed the maximum allowable temperature rise at the secondary reformer (Panel B of Fig. 3). On the contrary, the constraint on the fuel gas flow does not limit the investigated range, as this is due to the nature of the retrofitting itself. Considering the fluctuating renewable energy trends (as discussed in Paragraph 2.2), a reasonable average $deCO_2$ value of 10 % is assumed in this work, which indeed falls exactly in the middle of the 0 % to 20 % allowable range (*i.e.* from the case of no green power/hydrogen availability to the case of maximum green hydrogen input acceptable into the Haber-Bosch section). Specifically, Table 1 reports the main process variables of such three key plant configurations, *i.e.* the hybrid plant performances assessed at the lower (0 %), average (10 %), and upper (20 %) values of $deCO_2$.

Section 4 assesses the proper design of the electrolyzer, the renewable power plant, and the hydrogen storage to continuously guarantee the requirements of the average configuration.

4. Techno-economic assessment of the retrofitting

4.1. CapEx and OpEx estimation of the electrolyzer

Disregarding for the moment the installed capacity of the electrolyzer (as it will be discussed in Paragraph 4.4), the following data and conservative hypotheses were considered for its techno-economic assessment:

- An alkaline electrolyzer was examined. Different electrolyzer technologies are commercially available: alkaline (AEL) and proton exchange membrane (PEM) electrolyzers are the most widespread. More recently, solid oxide (SOE) and anion exchange membrane (AEM) electrolyzers have been developed, but both are still far from reaching market availability [7]. Here, an AEL was preferred to a PEM since the former is still maintaining a market-leading position in the sector (particularly, due to its long tradition) and because, despite its higher inertia due to the greater liquid hold-up, it shows sufficiently higher flexibility for its integration into ammonia plants. Indeed, an AEL-type electrolyzer is much more flexible than the ammonia plant in terms of load ramps and turndown ratio. Specifically, the electrolyzer is here assumed to show a perfectly flexible

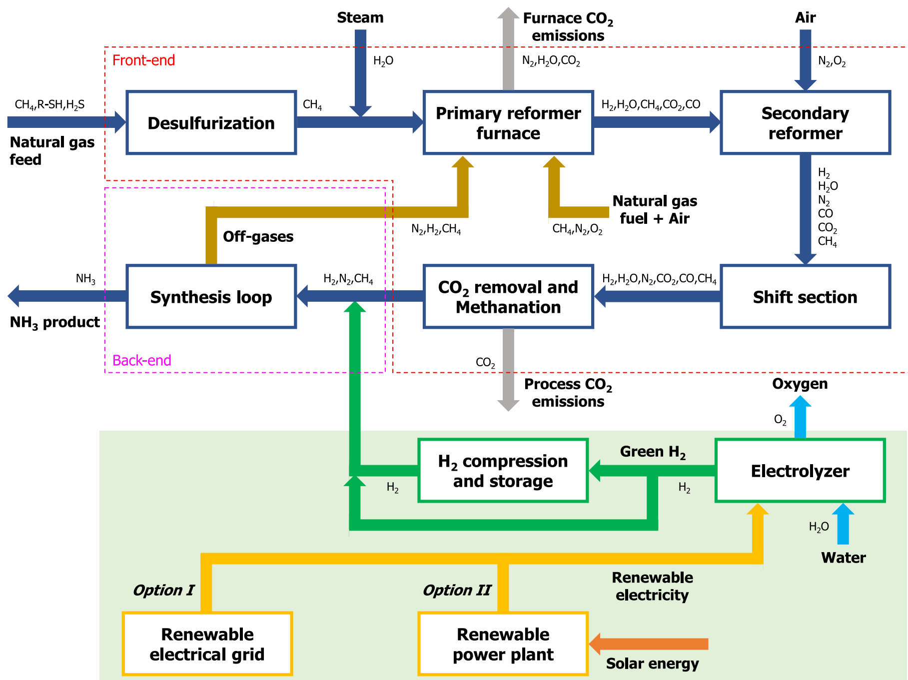

Fig. 2. Hybrid-green ammonia plant (2000 t_{NH3}/d capacity) as simulated and assessed in this work. The green rectangle contains all the additional units (whose operation is "green") introduced by the process retrofit. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

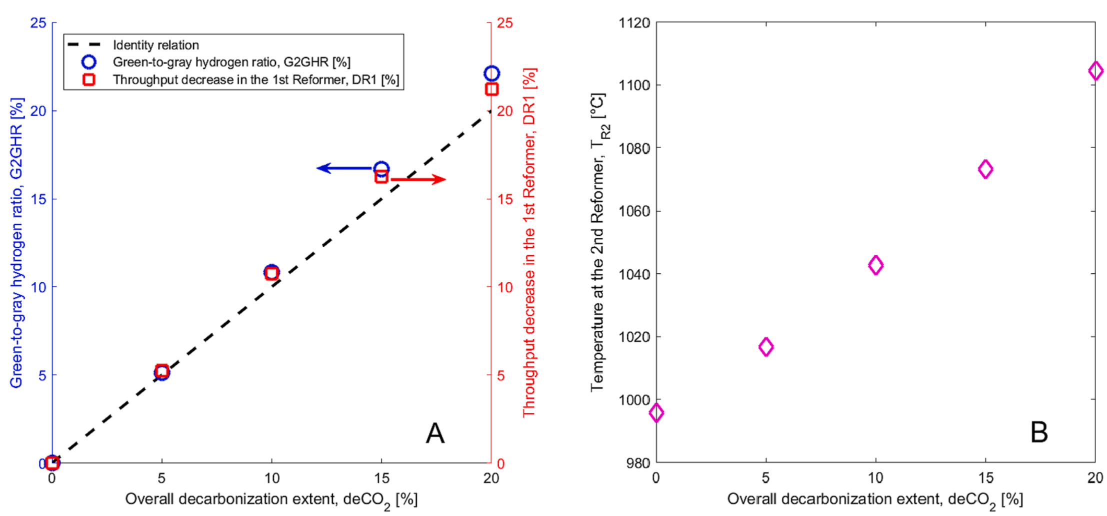

Fig. 3. The effect of increasing the $deCO_2$ extent on the constraints of the hybrid plant. Panel A, the nearly identity relation with G2GHR and DR1. Panel B, the rise in operating temperature within the secondary reformer.

behavior, as characteristic AEL maximal ramping rates of ± 20 %/s are sufficiently rapid to match solar energy variations in renewable power production [8]. Moreover, although achieving a higher current density, a greater operating range, and a higher hydrogen purity, PEM electrolyzers are nevertheless more expensive and less durable. That said, the performances of the AEL unit are inferred from Nel Hydrogen [9], a global company that provides solutions for producing, storing, and distributing hydrogen from renewable energy sources. Specifically, the electrolyzer shows a nominal electricity consumption of 4.5 kWh/Nm^3_{H2}, water consumption of 0.9 kg_{H2O}/Nm^3_{H2}, and a hydrogen outlet temperature and pressure of 35 °C and 30 bar, respectively [10]. Coupling such operating data with the process simulation results, it turns out that the electric demand of the electrolyzer can be as high as 177 MW_e (*upper bound*), with an *average* value of 87 MW_e. Analogously, the demineralized water demand can be as high as 35.5 t/h (*upper bound*), with an *average* value of 17.4 t/h. Note that the *average* configuration values do not correspond exactly to half of the maximum values due to the aforementioned nearly identity relation among the different $deCO_2$ configurations.

- The electrolyzer has a lifetime of 10 years and its CapEx amounts to 700 USD/kW_e [11]. This value includes the engineering, housing, and balance-of-plant components such as the compression and the water and hydrogen purification units. Such a reference value relies on the pronounced economy of scale which affects AEL modules with an installed power capacity exceeding 100 MW_e.

Table 1
Main operating conditions of the investigated hybrid-green ammonia plant. Each column refers to a different plant configuration and reports the actual process variable values on the left, while their ratio to the corresponding *lower bound* (*i.e.* the reference plant) ones on the right (in italics).

Process variable [unit]		Lower bound ($deCO_2 = 0$ %)		Average ($deCO_2 = 10$ %)		Upper bound ($deCO_2 = 20$ %)	
Green hydrogen to the synloop	[t/h]	0		1.74		3.55	
Primary reformer throughput	[t/h]	163	*100 %*	146	*89.3 %*	129	*78.8 %*
Natural gas feed to the front-end	[t/h]	38.0	*100 %*	33.9	*89.3 %*	29.9	*78.8 %*
Natural gas fuel to the furnace	[t/h]	12.9	*100 %*	11.9	*92.3 %*	10.7	*82.8 %*
Furnace CO_2 emissions	[t/h]	38.9	*100 %*	34.8	*89.5 %*	30.7	*78.8 %*
	[t_{CO2}/t_{NH3}]	0.467		0.418		0.368	
Process CO_2 emissions	[t/h]	97.4	*100 %*	87.9	*90.3 %*	78.1	*80.1 %*
	[t_{CO2}/t_{NH3}]	1.17		1.06		0.937	
Total CO_2 emissions	[t/h]	136.3	*100 %*	122.7	*90.0 %*	108.8	*79.8 %*
	[t_{CO2}/t_{NH3}]	1.64		1.48		1.31	

4.2. CapEx and OpEx estimation of the renewable electric power input

This paper investigates two renewable electrical energy sourcing alternatives:

I. Buy electricity from a certified renewable power provider, which delivers it through the grid with a Power Purchase Agreement (PPA) (*Option I* as in Fig. 2).
II. Produce electricity on-site from a photovoltaic (PV) power plant (*Option II* as in Fig. 2).

Both cases show different pros and cons. *Option I* allows the plant to receive a continuous electrical energy input that does not call for any “intermittency-mitigating” features such as supplementary hydrogen storage. Its main drawback, however, is the dependency on the renewable electricity market, which is subjected to strong fluctuations [4] and thus can suddenly impose very expensive costs. *Option II* allows the plant to be self-sufficient from an electric energy point of view (*i.e.* all the renewable electrical energy needed for the process is produced on-site by a photovoltaic solar park and is not purchased from external sources). However, it takes over all the aforementioned problems of hydrogen generation from renewables (first of all, the intermittency issues) and, obviously, the investment and operating expenditures (and the required space) for both the power station and the hydrogen storage.

Regarding *Option I*, the economic assessment of the electric power term simply necessitates as input the market price of clean electricity: *e.g.*, 71.65 EUR/MWh in Europe, January 2023 [12].

Conversely, here follow the data and hypotheses assumed for the design of the PV power plant, as required by *Option II* (disregarding, for now, its installed capacity, as it will be discussed in Paragraph 4.4):

- The power station has a lifetime of 20 years. This is a conservative hypothesis since the estimated operational lifespan of a present-day photovoltaic module exceeds 30 years [13]. Moreover, since both the PV panels and the electrolyzer deal with direct current (DC), no solar inverters are required. Instead, DC/DC converters only are needed for voltage conditioning [14].
- The CapEx and OpEx techno-economic assumptions related to the PV power plant modules and units come from IRENA [15] and are reported in Table 2.

Table 2
Techno-economic assumptions for the photovoltaic power station [15]. O&M = Operation & Maintenance.

PV solar renewable power: utility-scale, ground-mounted, single-axis tracking panels (USA, 2022)		
Total installed costs	[USD_{2022}/kW_e]	1119
Modules (Hardware Costs)	[USD_{2022}/kW_e]	403.4
Inverters (Hardware Costs)	[USD_{2022}/kW_e]	75.4
Racking and Mounting (Hardware Costs)	[USD_{2022}/kW_e]	84.6
Cabling/Wiring (Hardware Costs)	[USD_{2022}/kW_e]	75.4
Grid Connection (Hardware Costs)	[USD_{2022}/kW_e]	64.4
Safety and Security (Hardware Costs)	[USD_{2022}/kW_e]	25.8
Monitoring and Control (Hardware Costs)	[USD_{2022}/kW_e]	12.9
Mechanical Installation (Installation Costs)	[USD_{2022}/kW_e]	161.9
Electrical Installation (Installation Costs)	[USD_{2022}/kW_e]	23.9
Inspection (Installation Costs)	[USD_{2022}/kW_e]	5.5
Margin (Soft Costs)	[USD_{2022}/kW_e]	115.9
Financing Costs (Soft Costs)	[USD_{2022}/kW_e]	14.7
System Design (Soft Costs)	[USD_{2022}/kW_e]	27.6
Permitting (Soft Costs)	[USD_{2022}/kW_e]	5.5
Incentive application (Soft Costs)	[USD_{2022}/kW_e]	17.6
Customer acquisition (Soft Costs)	[USD_{2022}/kW_e]	4.5
Total O&M costs	[$USD_{2022}/kW_e/y$]	9.1

4.3. CapEx and OpEx estimation of the hydrogen storage

As discussed in the previous paragraph, *Option II* calls for hydrogen storage after the electrolyzer to deal with the intermittency and seasonality of the solar power input and to avoid inlet green hydrogen amounts above the $deCO_2 = 20$ % threshold.

The data and hypotheses assumed for the hydrogen storage section are as follows:

- The hydrogen storage system has a lifetime of 10 years and mainly consists of a compressor and multiple Type I pressurized tanks (*i.e.* hydrogen storage vessels commonly used for standard stationary applications [16]) operating at 200 bar.
- The CapEx and OpEx techno-economic assumptions related to the hydrogen storage section come from the Danish Energy Agency [17] and are reported in Table 3.

4.4. Photovoltaic power plant, electrolyzer, and hydrogen storage sizing

Option I, since it benefits from continuous renewable electric power input, simply calls for an electrolyzer capacity equal to the upper bound plant electricity demand (*i.e.* $deCO_2 = 20$ %: 177 MW_e). Conversely, *Option II* calls for an optimization procedure to select the most convenient size of the photovoltaic power plant, the electrolyzer, and the hydrogen storage.

Different photovoltaic installed capacities are investigated and, for

Table 3
Techno-economic assumptions for the hydrogen storage system [17]. A conversion factor of 0.95 EUR/USD (2022 annual average) [18] has been used. O&M = Operation & Maintenance.

Pressurized hydrogen gas storage system (Compressor & Type I tanks @ 200 bar)		
Gravimetric energy density	[kWh/kg]	33.3
Specific investment	[$MUSD_{2022}/MWh$]	0.060
Compressor component	[$MUSD_{2022}/MWh$]	0.032
Type I tanks component	[$MUSD_{2022}/MWh$]	0.019
Installation, equipment, manhours	[$MUSD_{2022}/MWh$]	0.009
Fixed O&M	[$USD_{2022}/MW/y$]	630

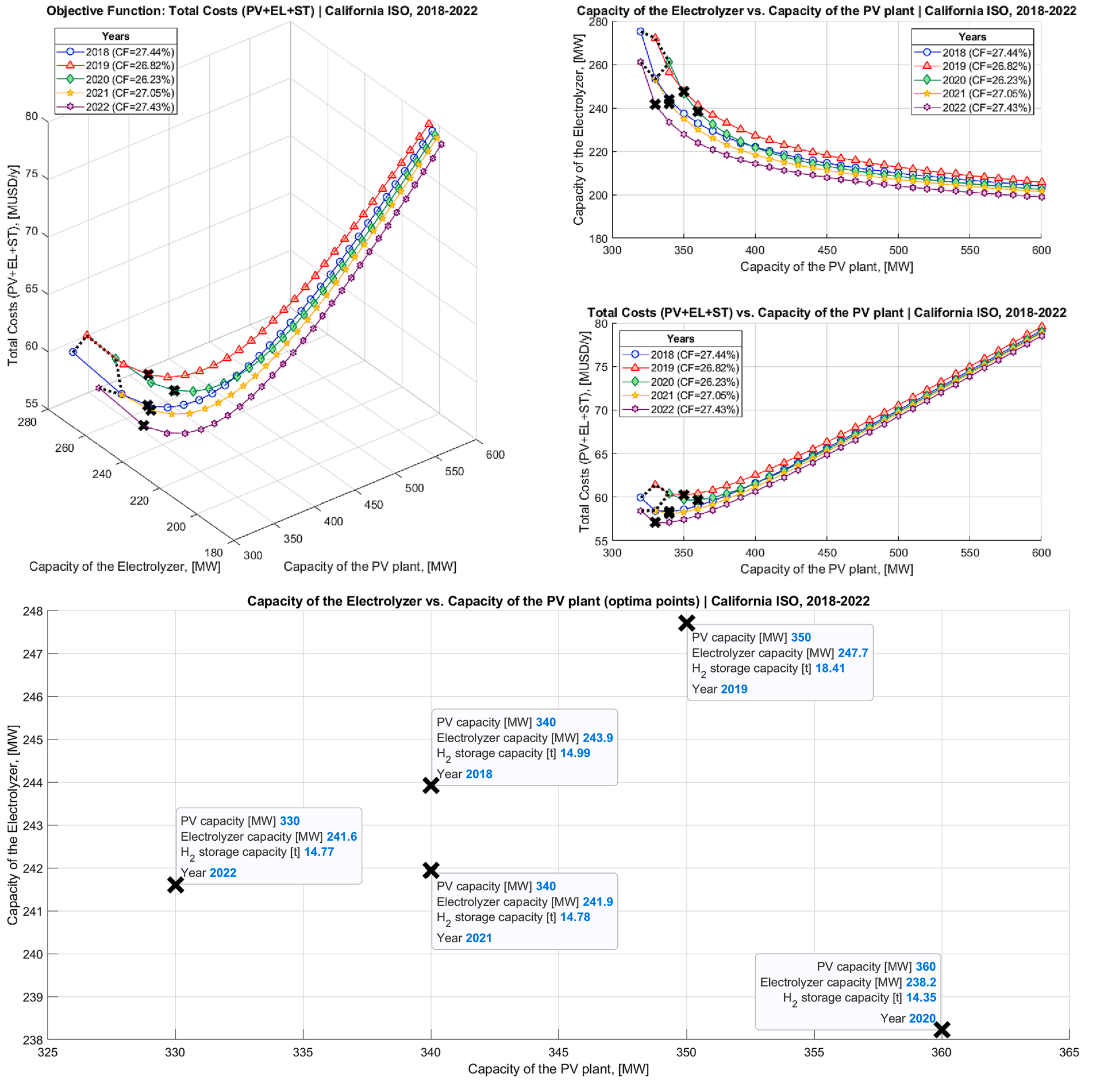

Fig. 4. Objective Function (see Equation (1)) for the optimal sizing of both the photovoltaic power plant and the electrolyzer, based on Californian solar profiles [20] for the 2018–2022 quinquennium (the average yearly capacity factors appear in the legend). Please note that each curve presents a PV plant capacity that ranges from an upper limit equal to 600 MW_e to a lower limit (*i.e.* the minimum value below which not enough renewable power is produced) which depends on the yearly solar profile analyzed (black dotted line). The black bold crosses represent the minima points, *i.e.* the economically optimal configurations for each year.

each of them, the corresponding electrolyzer installed capacity must guarantee an average power input equal to 87 MW_e (*i.e.* $deCO_2 = 10$ % target). Finally, by analyzing the hydrogen flow originating from the electrolyzer, the hydrogen storage size follows. In this regard, we consider a "flexible" hydrogen delivery, *i.e.* showing a hydrogen outlet flow that varies in time, depending on the instantaneous hydrogen inlet flow and hold-up conditions, since a variable hydrogen outlet mass flow guarantees a smaller (and cheaper) design. Alternatively, one might consider a "rigid" hydrogen delivery, *i.e.* showing a constant outlet flowrate corresponding to the hydrogen consumption by the ammonia synthesis loop at target operating conditions (*i.e.* $deCO_2 = 10$ %: 1.74 t_{H2}/h) of the hybrid plant, regardless of the unsteady inlet contribution equal to the production rate profiles of the electrolyzer. Such a configuration is indeed way easier to design, but requires much higher storage volumes, as it does not adapt to the seasonal behavior of renewable energy generation [8].

Accordingly, the whole problem can be summarized by the following optimization procedure:

$$\begin{cases} \underset{P_{PV}^{inst},P_{EL}^{inst}}{\text{minimize}}\Phi_{obj} = \left(CapEx_y + OpEx\right)_{PV} + \left(CapEx_y + OpEx\right)_{EL} + \left(CapEx_y + OpEx\right)_{ST} \\ \qquad s.t. \int_0^{t_{tot}} \min\left(P_{PV}(t), P_{EL}^{inst}\right)dt = P_{EL}^{10\%}\cdot t_{tot} \\ \qquad \int_0^{t_{tot}} \dot{m}_{H_2}^{ST,out}(t)dt = \dot{m}_{H_2}^{10\%}\cdot t_{tot} \end{cases} \tag{1}$$

Where P_{PV}^{inst} and P_{EL}^{inst} are the installed capacities of the PV plant and the electrolyzer, respectively; $\left(CapEx_y + OpEx\right)_{PV}$, $\left(CapEx_y + OpEx\right)_{EL}$, and $\left(CapEx_y + OpEx\right)_{ST}$ are the sum of the annualized capital expenditures and the annual operative expenditures of the PV plant, the electrolyzer, and the hydrogen storage, respectively; t_{tot} is the total timespan considered (a 1-year time frame was assumed in this work); $P_{PV}(t)$ is the instantaneous renewable power produced by the photovoltaic power plant (which depends on the total installed capacity of the PV plant itself); $P_{EL}^{10\%}$ is the renewable power that the electrolyzer needs to produce $\dot{m}_{H_2}^{10\%}$, *i.e.* the green hydrogen mass flow that should enter the ammonia synthesis loop to reach a deCO$_2$ value equal to 10 % (namely, 1.74 t_{H2}/h); and $\dot{m}_{H_2}^{ST,out}(t)$ is the instantaneous green hydrogen mass flow withdrawn from the hydrogen storage. Note that the annualized CapEx (since they must add to the annual OpEx) have been evaluated by the following formula [19]:

$$CapEx_y = \frac{CapEx}{\sum_{j=1}^{N}(1+r)^{-j}} \tag{2}$$

Where N is the lifespan (in years) and r is the discount rate. This work adopts a 5 % discount rate [16].

Then, we referred to a few Californian solar profiles (for a total of five years, 2018–2022, to provide more robustness to the assessment) and minimized the total costs for each PV, electrolyzer, and hydrogen storage configuration (see Fig. 4).

Fig. 5 provides information regarding how total costs are split between the PV plant, the electrolyzer, and the hydrogen storage (in 2019).

The consistent renewable energy management of the optimal configuration is even more visible in Fig. 6 (which shows the most conservative scenario: *i.e.* the 2019 results, as they provide the highest total costs).

Indeed, the optimal configuration depicted in Fig. 6 guarantees an average renewable power input equal to 87 MW$_e$ (*i.e.* an average deCO$_2$ value equal to 10 % throughout the entire operating time) and it accounts just a 7.05 % of wasted (*i.e.* overproduced) energy as against the total amount produced by the photovoltaic plant. However, the main drawback of such a configuration is that the electrolyzer, being oversized compared to the deCO$_2$ = 20 % boundary (*i.e.* 177 MW$_e$), reaches instantaneous deCO$_2$ values as high as 30.9 %. Indeed, considering the electrolyzer specifications listed in Paragraph 4.1, an electric power input of 248 MW$_e$ (*i.e.* the optimal installed capacity of the electrolyzer as for 2019) corresponds to a green hydrogen production rate of 4.95 t_{H2}/h. For this reason, an upper limit for the deCO$_2$ = 20 % boundary has been specified regarding the hydrogen mass flow withdrawn from the storage and headed to the ammonia synthesis loop (which must be less than or equal to 3.55 t_{H2}/h, as reported in Table 1). The hydrogen storage size is evaluated according to [8], *i.e.* computing the minimal required storage size (ST_0) as:

$$ST_0 = \max(\boldsymbol{ST}) - \min(\boldsymbol{ST}) \tag{3}$$

Where $\boldsymbol{ST}$ is the vector containing all the hourly hydrogen hold-up values within the storage system (ST_i) throughout the year (*i.e.* $i = 1$, …, 8760). Specifically, the variation of the hydrogen storage level is computed as:

$$ST_i - ST_{i-1} = \left(\dot{m}_{H_2,i}^{ST,in} - \dot{m}_{H_2,i}^{ST,out}\right)\cdot\Delta t \tag{4}$$

Where $\dot{m}_{H_2,i}^{ST,in}$ and $\dot{m}_{H_2,i}^{ST,out}$ are the hydrogen mass flows that are entering and exiting, respectively, the storage system at each hour step (Δt). In this regard, it is worth noting that not all the hydrogen produced by the electrolyzer enters the storage: indeed, its input just consists of the excess amount that cannot be directly fed to the ammonia synthesis loop to satisfy the operating boundaries. Specifically, this applies also to the

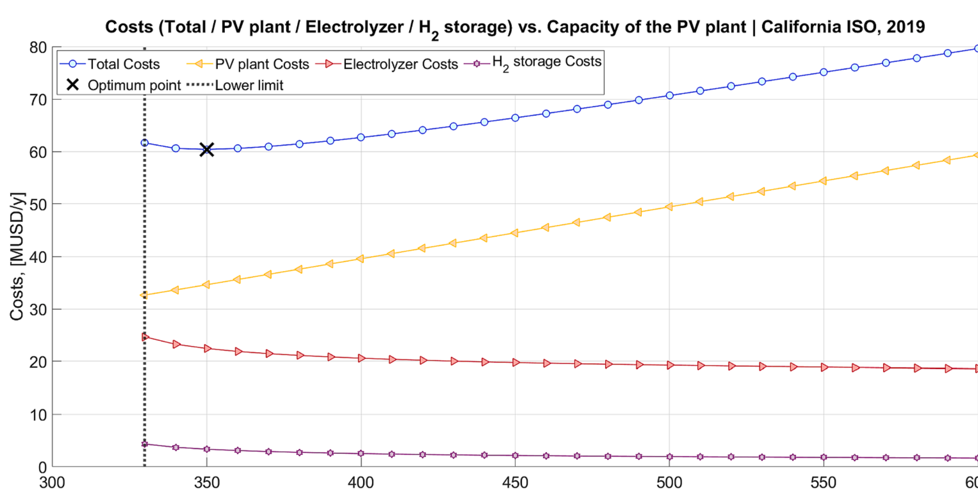

Fig. 5. Focus on the Total Costs profile for 2019, showing the contribution of PV plant, Electrolyzer, and Hydrogen storage expenditures. The black dotted vertical line represents the lower limit for the PV plant installed capacity, while the black cross is the minimum, *aka* optimum, point (*i.e.* 60.4 MUSD/y).

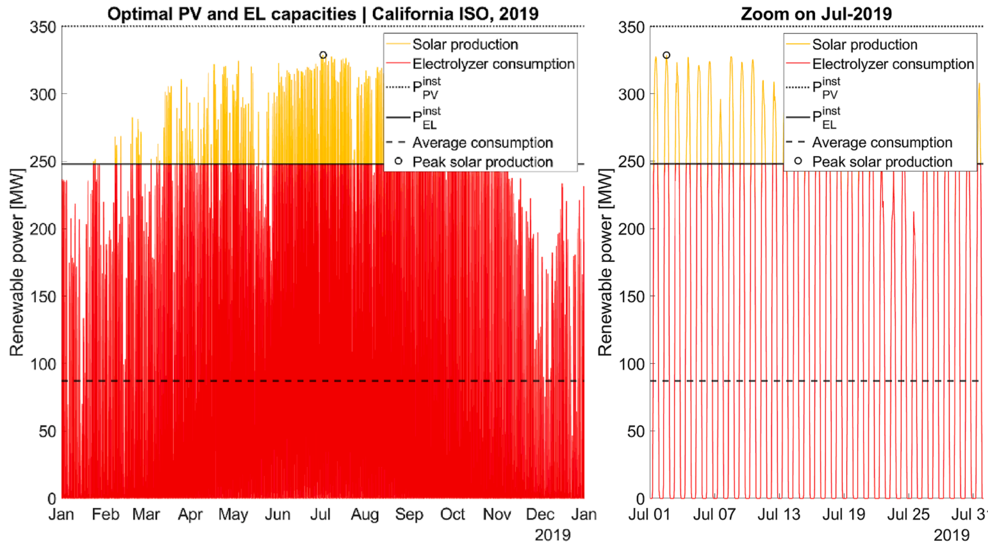

Fig. 6. Optimal photovoltaic plant and electrolyzer sizing. PV plant capacity of 350 MW_e and electrolyzer installed capacity of 248 MW_e, considering Californian solar profiles in 2019 [20]. Left panel, over the entire 2019 year. Right panel, zoom over July 2019 only.

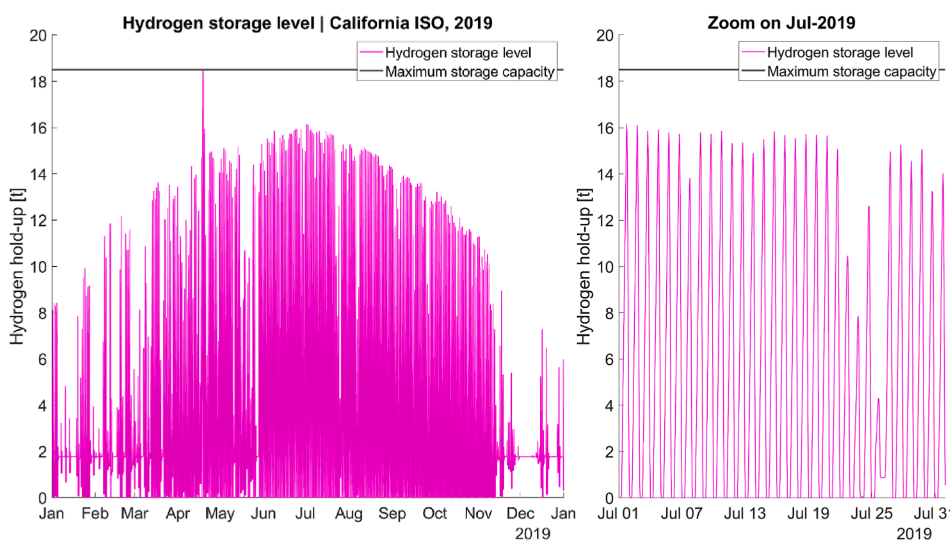

Fig. 7. Green hydrogen storage hold-up corresponding to the renewable energy and electrolyzer profiles reported in Fig. 6. The left panel shows the entire 2019-year profile, while the right panel focuses on July 2019 only. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

hydrogen compression section, which processes just the hydrogen flows fed to the storage. Finally, Fig. 7 shows the total hydrogen storage capacity (*i.e.* 18.5 t_{H2}, note that "Rigid" storage would have required a capacity of 1863 t_{H2}) and hold-up variation that guarantee an average $deCO_2 = 10\ \%$ green hydrogen supply over an entire year while dealing with such a constraint. No specific ramping rates were considered for the green hydrogen load variation entering the Haber-Bosch process, as the gray hydrogen coming from the front-end, which represents the large majority of the overall hydrogen feed (since constantly operating at $G2GHR \leq 20\ \%$), easily succeeds in counteracting and mitigating such fluctuations with sufficient promptness.

For the sake of our techno-economic analysis, precisely the results for 2019 (*i.e.* the year scoring the highest – and then the most conservative – PV plant, electrolyzer, and hydrogen storage capacities of the last five years) were considered as the optimal photovoltaic power station, electrolyzer and hydrogen storage sizes for the *Option II* hybrid configuration. Namely:

- PV plant with an installed capacity of 350 MW_e.
- Electrolyzer with an installed capacity of 248 MW_e.
- Hydrogen storage with a capacity of 18.5 t_{H2}.

On the other hand, an electrolyzer of 177 MW_e was considered for the *Option I* configuration, which does not feature any hydrogen storage

Table 4
United States (USA) and European Union (EU) reference market values as of 2022, 2030, and 2050. Natural gas, renewable electricity prices (VALCOE), and EU carbon prices (according to the Stated Policies Scenario, STEPS) from [18]; USA (California) carbon prices from [24].

Reference market values	2022		2030		2050	
	USA	*EU*	*USA*	*EU*	*USA*	*EU*
Carbon price [USD_{2022}/t_{CO2}]	30	80	55	120	130	135
Natural gas [USD_{2022}/MBtu]	5.1	32.3	4.0	6.9	4.3	7.1
Renewable electricity [USD_{2022}/MWh]	55	80	55	85	60	90

as the renewable electric energy is provided by the grid and constantly ensures the target (*i.e.* $deCO_2 = 10\ \%$) green hydrogen feed to the ammonia synthesis loop.

5. Ammonia production cost assessment

The ammonia production costs of the reference and hybrid (both *Option I* and *II*) plants were estimated. Some further details of the investigated plants are here reported:

- The production facilities operate 8000 h/y.
- The costs for cooling (CW) and demineralized (DMW) water are 0.06 USD/m^3 [21] and 0.78 USD/m^3 [22], respectively.
- The profits from the medium-pressure steam surplus, generated on-site by recovering waste heat from the process streams, are estimated by considering the equivalent amount of natural gas that would be used to produce it in an auxiliary boiler [23]. Precisely, starting from water at 35 °C and 40 bar we have a steam energy export of 0.13 MWh/t_{NH3}, regardless of the process alternative.

The ammonia production costs following the three investigated plant configurations (*i.e.* gray ammonia plant, *aka Reference*; hybrid-green ammonia plant with certified renewable electric power delivered through the grid with a PPA, *aka Option I*; and hybrid-green ammonia plant with electric power from a renewable on-site PV power plant, *aka Option II*) were estimated by considering representative values of the United States and European market quotations in 2022, 2030, and 2050 (see Table 4).

Fig. 8 shows the results of the ammonia production cost assessment for each plant configuration while Fig. 9 reports all the terms that concur in determining such final costs. It is worth noting that in the present assessment, only one negative contribution (*i.e.* a revenue) appears which specifically corresponds to the income by selling the medium-pressure steam surplus (that depends on the natural gas price).

Except for the *EU-2022* scenario, Fig. 8 shows that the hybrid layout always calls for higher prices than the conventional plant. Fig. 9 highlights that the additional expenses associated with the retrofitting exceed significantly the savings resulting from lower natural gas demand (feedstock and fuel) and carbon tax. The exception for the 2022 European market scenario occurs since at that time natural gas prices recorded unprecedented extremely high values in the EU (with a peak quotation of 339.2 EUR/MWh in August 2022) and, although it steadily declined in the following months, it was still sold at 47.84 EUR/MWh in March 2023, which is almost seven times higher than the March 2020 price [25]. As a consequence, such a trend heavily influenced the ammonia price also. Indeed, while the average gray ammonia market price was as low as 300 USD/t_{NH3} in 2020, it exceeded 1600 USD/t_{NH3} in 2022 [26]. In addition, concerning the market fluctuations of natural gas prices, it is worth remarking that plants producing tradeable and storable commodities like ammonia and fertilizers generally shut down when the fossil feedstock becomes too expensive. Hence, even when such a green retrofit is implemented, times of very high fuel prices might still call for a plant shutdown. Nonetheless, in this case, instead of leaving the photovoltaic power station, the electrolyzer, and the hydrogen storage system unused (as it would lead to very high economic inefficiencies), in principle the renewable hydrogen generation section might be kept functioning (*e.g.*, to harvest and sell green hydrogen to the energy market or other final users). Focusing just on the two hybrid configurations, the most competitive one is *Option I* in the USA and *Option II* in the EU. Such an outcome is mainly due to the different electricity market values in those two areas (see Table 4): indeed, as the prices of renewable electric energy turn to be very expensive in the EU, European scenarios discourage sourcing it from the grid and favor self-sufficiency instead. In this regard, production of renewable energy on-site as opposed to its purchase might turn out to be ever more appealing in the future thanks to three key trends: (i) as for natural gas, power purchase agreements (PPA) aimed at renewable power sourcing from the grid strongly depend on market volatility [12]. Indeed, at least in Europe, PPA prices recently followed quite similar trends to those of natural gas and crude oil, being strongly affected by the outburst of the Russia-Ukraine hostilities in February 2022 [4]. (ii) Renewable power generation technologies have shown monotonically decreasing costs (in terms of both CapEx and OpEx) in the last decades. Indeed, concerning the PV power station of *Option II*, it is worth noting that the global weighted-average levelized cost of electricity from utility-scale PV plants dropped by 82 % in the last decade, from around 378 USD/MWh in 2010 to 68 USD/MWh in 2019 [27]. (iii) The continuously increasing service lifespan (and, consequently, longer depreciation times) of the renewable power generation infrastructures strongly mitigates the weight of CapEx contributions on the *Option II* final ammonia cost. By entering a decarbonized economy, PV power plants also represent valid investments for a possible switch to completely green ammonia synthesis or to produce power from renewables even when the production facility would end its lifetime (*e.g.*, for urban use in nearby residential areas). Finally, to quantify the appeal of the hybrid green retrofitting strategy, the CO_2 avoidance cost of both hybrid configurations was evaluated for each assessed market scenario (see Table 5). Precisely, the CO_2 avoidance cost is the extent of carbon tax at which the cost of the

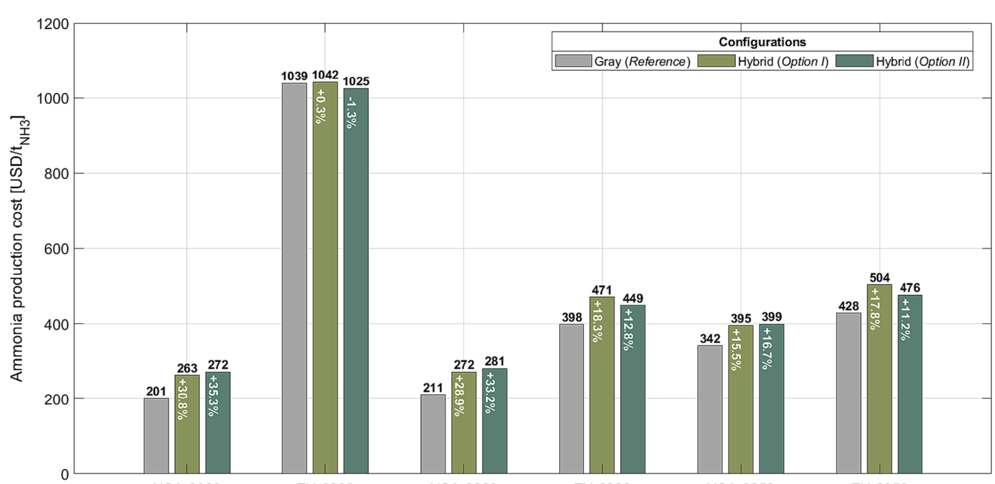

Fig. 8. Ammonia production cost estimations for the three investigated configurations (*i.e. Reference*, *Option I*, and *Option II*) as of 2022, 2030, and 2050 in the United States and the European Union. The percentage values inside the bars refer to the percentage difference between the hybrid and gray ammonia costs.

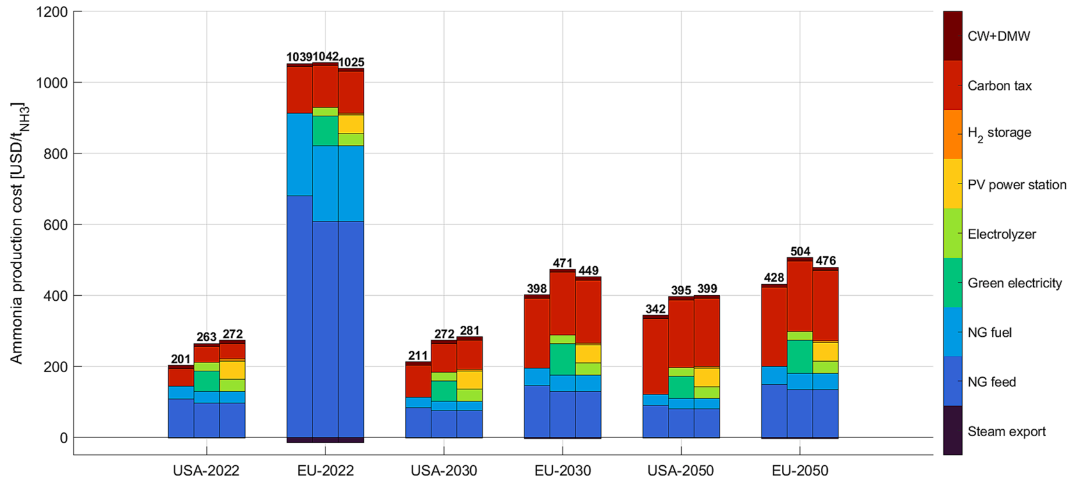

Fig. 9. Relative importance of each contribution to the ammonia production costs by the three investigated configurations (*i.e. Reference*, *Option I*, and *Option II*) for the same scenarios reported in Fig. 8. The discount associated to the medium-pressure steam export revenues on the final ammonia cost is reported as a negative contribution.

Table 5
CO_2 avoidance cost of both hybrid layouts for each assessed market scenario.

CO_2 avoidance cost [USD_{2022}/t_{CO2}]	2022		2030		2050	
	USA	*EU*	*USA*	*EU*	*USA*	*EU*
Hybrid (Option I)	395	98	412	549	441	580
Hybrid (Option II)	450	1	468	423	464	417

product of interest is the same either by producing it from the conventional, carbon-intensive route (but paying the carbon tax) or from a plant including carbon mitigation (thus avoiding most of the carbon tax) [28].

Except for the *EU-2022* scenario (which is not fully representative due to the exceptionally high natural gas prices recorded in Europe right after the outbreak of the Russia-Ukraine war), all the estimated CO_2 avoidance costs are very high. Especially considering that conventional carbon capture, utilization, and storage (CCUS) technologies range today between 15 and 25 USD/t_{CO2} for industrial processes generating highly concentrated CO_2 streams [29]. As a result, although carbon prices of 200 USD/t_{CO2} or higher might even become standard by the end of this decade [30] or a few years later [31] (for instance, EU ETS carbon permits are showing a rapidly increasing overall trend), heavy carbon taxation seems an insufficient instrument for making hybrid-green ammonia economically attractive, especially when compared with the so-called “blue” ammonia (*i.e.* gray ammonia with CCUS). Indeed, implementing carbon removal would avoid over 70 % of the CO_2 emissions (*i.e.* the *Process CO_2 emissions* in Table 1) as against the sole 10 % for the hybrid-green alternative. However, it must be also pointed out that, although the capture of process emissions from the manufacturing sector is well established, the development and scaling of a commercial CO_2 transport and storage infrastructure still faces many obstacles. Indeed, while studies confirm the world showing ample carbon storage capacity, in the form of salt caverns and depleted oil and gas fields, few sites have been settled for actual use [32]. Lastly, blue ammonia synthesis also means still relying on fossil fuels heavily, instead of replacing them as in hybrid-green (partially) and green (totally) ammonia synthesis.

6. Conclusions

Hybrid-green ammonia proved to be an available-to-date retrofitting strategy to reach partial decarbonization in the ammonia production industry. However, while the environmental sustainability of hybrid plants has been verified, their economic sustainability is currently less appealing compared to other carbon-mitigating routes (*e.g.*, gray ammonia with CCUS, *aka* blue ammonia). Indeed, disregarding the 2022 results (unusually encouraging due to the exceptional geopolitical circumstances occurred in that year), the CO_2 avoidance costs associated with hybrid-green ammonia plants (operating at $deCO_2 = 20$ % at maximum) generally exceed 400 USD/t_{CO2} in the USA and 500 USD/t_{CO2} in the EU. Alternatively, CCUS costs are currently an order of magnitude lower, ensuring CO_2 abatement potentials above 70 %. Regarding the production costs achieved by the two investigated hybrid configurations, *Option I* showed percentage differences ranging from +0.3 % (*EU-2022*) to +30.8 % (*USA-2022*) compared to the *Reference* case (gray ammonia) over the assessed scenarios. Conversely, *Option II* resulted in ammonia production costs ranging from −1.3 % (*EU-2022*) to +35.3 % (*USA-2022*), compared to the *Reference* case. Specifically, *Option I* resulted in the most competitive configuration in the USA, as electricity sourcing from American renewable electric grids is at present less expensive than directly generating it on-site (due to still quite high CapEx associated to the photovoltaic station). On the other hand, high renewable electricity prices in Europe lead *Option II* to stand as the most competitive configuration in the EU. Few additional remarks follow: first, in many geographical areas, the only way to provide renewable power is by considering an on-site production as seen in *Option II* (mainly because the concept, and the infrastructures, of a renewable electrical grid still needs to evolve in the next years and decades and may be unavailable at present time, especially for big consumers). Second, the quite optimistic results shown by both *Option I* and *Option II* should encourage governments to invest into the creation and diffusion of renewable energy generation infrastructures and truly renewable electric grids to facilitate the access of the chemical industry and the manufacturing sector to renewable energy and – concerning the grids – to better mitigate the problems associated to intermittent power availability. Third, as a final consideration, by entering a progressively decarbonized economy, the hybrid-green ammonia route might become increasingly competitive: indeed, this already happened in 2022 due to the exceptional rise in natural gas prices [4] and may occur again in the future if proper decarbonization policies are adopted.

CRediT authorship contribution statement

Andrea Isella: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Data curation, Conceptualization. **Raffaele Ostuni:** Writing – original draft, Formal analysis, Conceptualization. **Davide Manca:** Writing – review &

editing, Writing – original draft, Validation, Supervision, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2024.150132.

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