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Comparative Techno-Economic Assessment of Hybrid-Green Ammonia Layouts for Available-to-Date Decarbonization of the Fertilizer Industry

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ABSTRACT

Industrial ammonia synthesis remains a high-impact decarbonization target due to the combined effect of large production volumes and reliance on CO_2-intensive fossil-based hydrogen. Replacing it partially with renewable-based (green) electrolytic hydrogen can minimize direct emissions; however, the intermittency of solar and wind complicates retrofit strategies for existing continuous plants. This paper addresses a techno-economic study centered on a retrofit-oriented hybrid concept: a conventional natural-gas ammonia plant is operated within a pre-defined "hybridization envelope", where part of the process hydrogen is supplied by a renewable Power-to-Hydrogen subsystem. A steady-state process model (gray/blue baselines) is coupled with an hourly energy dispatch and a sizing optimization of solar/wind park, electrolyzer, battery, and hydrogen storage. A case study based on 2024 California data for renewables and carbon pricing illustrates how hybridization can reduce carbon intensity while ensuring all process constraints are met, and how the optimal renewable mix trades off between overbuild and storage. Results highlight the role of solar-wind complementarity in lowering the levelized cost of hydrogen and, consequently, the levelized cost of ammonia, while leaving a clear pathway for combining hybrid-green operation with carbon capture (hybrid-blue-green) as a transitional strategy.

Keywords: Green ammonia, Electrolysis, Hydrogen storage, Energy storage, Retrofit, Power-to-Hydrogen

INTRODUCTION

Ammonia is central to the global fertilizer value chain and is increasingly considered as an energy carrier for hard-to-abate sectors. However, the scientific community consistently identifies ammonia synthesis as a priority petrochemical process for decarbonization, alongside steam cracking and methanol [1, 2]. Conventional ("gray") ammonia production relies on natural gas reforming to supply hydrogen and on high-pressure synthesis loops that operate most efficiently in continuous mode. As a result, deep decarbonization of existing ammonia plants faces a dual challenge: (i) abating CO_2 emissions from hydrogen production and process energy, and (ii) integrating low- or zero-carbon energy vectors without destabilizing plant operation.

Green ammonia pathways typically assume renewable power fully supplies hydrogen via water electrolysis. While conceptually straightforward, the intermittency of solar and wind imposes operational and economic penalties unless extensive flexibility (grid exchange, mass and energy storage, electricity curtailment) is provided [3, 4]. Conversely, blue ammonia combines natural-gas-based hydrogen with carbon capture and storage (CCS). Blue routes can achieve meaningful emission cuts but remain vulnerable to concerns about upstream methane leakage and the associated costs of capture/transport/storage [5, 6]. Hybrid-green pathways, where a fraction of the process hydrogen is supplied by renewable electricity and the rest of the plant remains fossil-fed, can provide a pragmatic bridge, especially for retrofits [7, 8]. The hybrid approach aims to decouple "how much" renewable energy is used from "how the synthesis loop operates", by enforcing an operating envelope compatible with safe and efficient plant behavior.

Therefore, this work details the hybrid-green retrofit

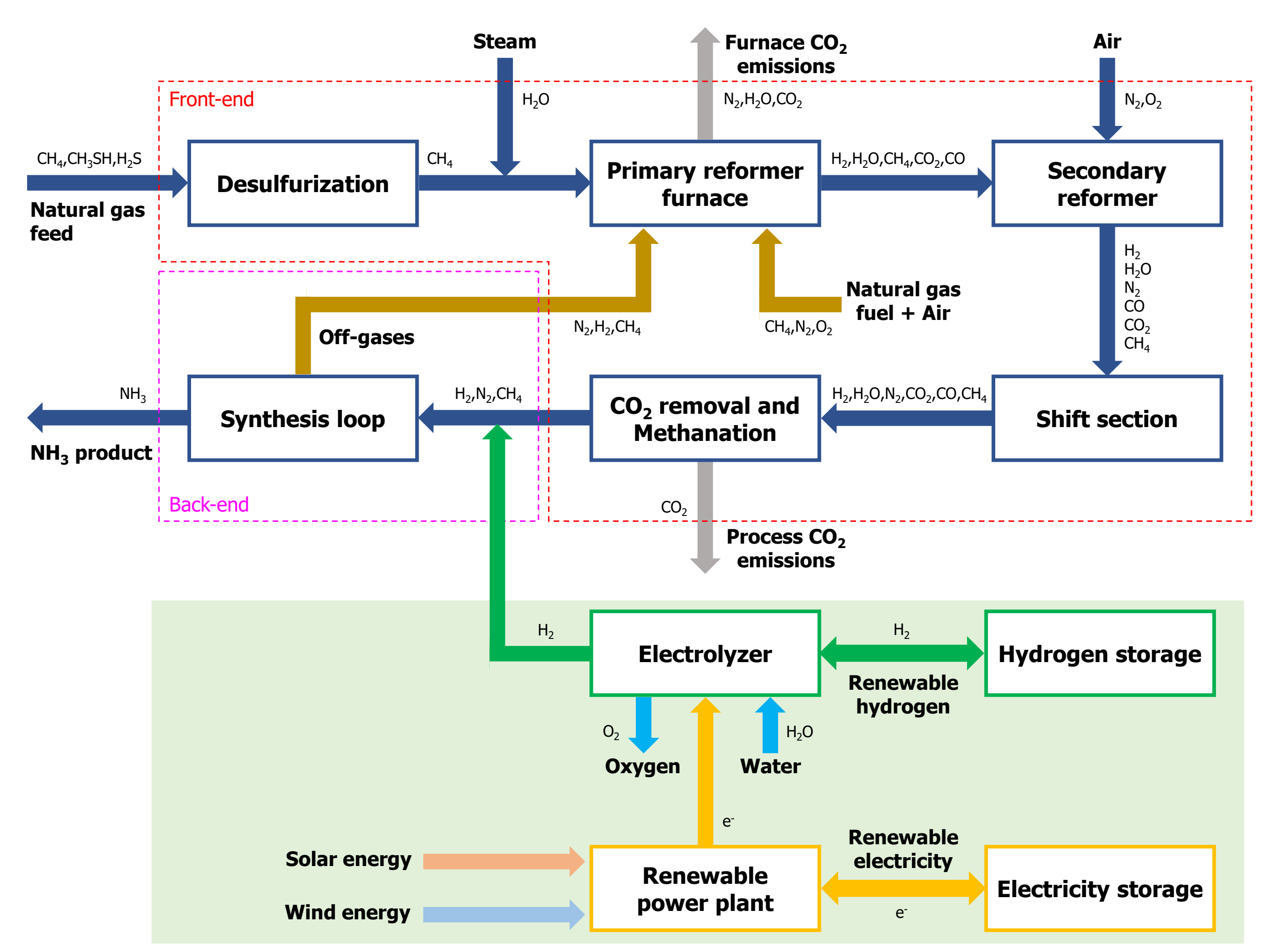

Figure 1. Block flow diagram of the hybrid-green retrofit for an ammonia plant. The green rectangle encloses the additional units introduced by the hybrid concept.

concept for existing ammonia plants and also provides a quantitative assessment of its techno-economic and environmental performance in the 2024 California context. Specifically, the analysis refers to published best-available-technology baselines for ammonia synthesis and recent cost data for renewables, electrolysis, and mass/energy storage. Furthermore, it expands an optimization-based sizing methodology for Power-to-Hydrogen (PtH) assets previously developed by the Authors [8].

HYBRID-GREEN RETROFIT CONCEPT AND OPERATING ENVELOPE

The hybrid concept retrofits a conventional ammonia plant by adding a PtH subsystem (renewable electricity, electrolyzer, battery, H_2 storage) that can displace a fraction of the fossil-based hydrogen produced by the reformer (see **Figure 1**). To keep downstream units and the synthesis loop close to design conditions, we investigate the hybridization factor as the fraction of the plant's hydrogen demand supplied by the PtH system on average.

Rather than allowing arbitrary turndown, the retrofit is constrained to an "operating envelope" expressed by (i) minimum acceptable "throughput" (*i.e.*, the mass flow passing through the primary reformer), and (ii) maximum acceptable changes of key state variables (*i.e.*, the operating temperature in the secondary reformer and the fuel gas mass flow to the primary reformer furnace). This envelope is designed to mimic the practical constraints that arise from catalyst stability, heat-integration requirements, and process units' operating ranges [8].

More specifically, we have the following KPIs:

A. The throughput must always be above 80% of the primary reformer's nominal capacity.
B. The operating temperature in the secondary reformer must not exceed design values by more than 100°C.
C. The fuel gas mass flow to the primary reformer furnace must never drop to zero.

Accordingly, a 0–20% range of allowable hybridization factors was identified (as shown in **Table 1**).

Table 1: Evolution of the 3 KPIs (see the previous list) with increasing hybridization factor [8]. Values highlighted in red exceed operational constraints.

Case	Hybrid. factor	KPI A	KPI B	KPI C
Gray (baseline)	0%	100%	±0°C	100%
Hybrid-green (mild)	10%	89.3%	+47°C	92.3%
Hybrid-green (heavy)	20%	78.8%	+109°C	82.8%

MODELING AND OPTIMIZATION FRAMEWORK

Our assessment links a steady-state process model of the ammonia plant with an hourly electricity-to-hydrogen dispatch model and a capacity-sizing optimization. The goal is to quantify the cost and emissions impact of hybridization at the plant level, while explicitly representing the variability of renewable generation and market electricity prices.

Baseline process models (gray and blue)

A conventional natural-gas ammonia plant is simulated in UniSim® Design R500, following a typical flowsheet: desulfurization, primary and secondary reforming, shift conversion, CO_2 removal, methanation, compression, and ammonia synthesis with recycle and purge (*i.e.*, the Haber-Bosch process). Property methods rely on the Soave-Redlich-Kwong equation of state, consistent with high-pressure systems. Baseline performance and operating ranges are cross-checked against industrial manuals and engineering references.

For the blue baseline, building on the gray ammonia model, CO_2 capture is implemented on both the high-purity process stream (*i.e.*, the emissions from CO_2 removal) and flue gas streams (*i.e.*, the emissions generated by the combustion of fuel gas in the primary reformer furnace), using cost and performance assumptions aligned with public techno-economic studies for industrial capture [9, 10] (see **Table 2**). As our assessment is restricted to the production site battery limits following a gate-to-gate approach, the present analysis excludes both CO_2 transportation and storage.

Power-to-Hydrogen subsystem

The PtH subsystem includes: (i) a renewable generation (solar and/or wind) power plant, (ii) an alkaline electrolyzer, (iii) a lithium-ion battery for short-term smoothing, and (iv) a pressurized hydrogen storage system for multi-hour to multi-day balancing. Component costs follow recent public reports and vendor data for low-temperature electrolysis as well as electricity and hydrogen storage technologies (see **Table 2**). Moreover, the design and flexible operating schedule of batteries and hydrogen tanks are supported by frameworks developed by the Authors for Power-to-X applications [11, 12].

Table 2: The complete set of input values and cost assumptions for the present techno-economic assessment.

RENEWABLE ENERGY DATASET		
Location	California	[-]
Year	2024	[-]
Solar capacity factor	29.67%	[-]
Wind capacity factor	30.68%	[-]
Time discretization	1	[h]
TECHNO-ECONOMIC DATA		
Interest rate	5%	[-]
Solar (Photovoltaics)		
Lifetime	25	[y]
CAPEX	1058	[USD/kW]
OPEX	1.7%	[CAPEX/y]
Wind (Onshore)		
Lifetime	25	[y]
CAPEX	1568	[USD/kW]
OPEX	2%	[CAPEX/y]
Electrolyzer (Alkaline)		
Lifetime	10	[y]
CAPEX	700	[USD/kW]
OPEX	2%	[CAPEX/y]
Electrical efficiency	51.7	[kWh/kg_{H_2}]
Maximum load flexibility	100%	[-]
Minimum load flexibility	5%	[-]
Battery (Lithium-ion)		
Lifetime	10	[y]
CAPEX	234	[USD/kW]
OPEX	2%	[CAPEX/y]
Hydrogen storage (Tanks @ 200 bar)		
Lifetime	20	[y]
CAPEX	1898	[USD/kg_{H_2}]
OPEX	1%	[CAPEX/y]
Ammonia synthesis loop (Haber-Bosch process)		
Target green H_2 feed	1.74	[t_{H_2}/h]
Minimum green H_2 feed	0	[t_{H_2}/h]
Maximum green H_2 feed	3.55	[t_{H_2}/h]
Maximum green H_2 ramp	100%	[load/h]
Carbon capture and compression system		
Process CO_2 emissions	1.17	[t_{CO_2}/t_{NH_3}]
Furnace CO_2 emissions	0.467	[t_{CO_2}/t_{NH_3}]
Furnace CO_2 capture costs	60	[USD/t_{CO_2}]
Total CO_2 compression costs	15	[USD/t_{CO_2}]
California market scenario		
Natural gas price (2024 avg)	37.48	[USD/MWh]
Carbon tax (2024 avg)	38.59	[USD/t_{CO_2}]

Electricity market and policy context

Hourly renewable profiles for 2024 are sourced from the California Independent System Operator (CAISO), representing a high-renewables grid with pronounced diurnal and seasonal patterns [13]. Policy signals are modeled through a carbon price consistent with California's cap-and-trade mechanism [14]. Natural gas prices are based on industrial price indicators referring to industrial delivery rates for large-scale chemical facilities in California [15]. These cost assumptions are detailed in **Table 2**.

Optimization problem

Decision variables are the installed capacities of the solar and wind farm, and the objective is to minimize the levelized cost of hydrogen (LCOH) produced by the PtH plant while meeting the hybridization target and respecting the retrofit envelope constraints.

The LCOH is computed by **Eq. (1)** from annualized CAPEX and OPEX contributions of the PtH subsystem (*i.e.*, solar plant, wind plant, electrolyzer, battery, and hydrogen storage; hereafter denoted by S, W, E, B, and H).

$$LCOH = \frac{\sum_{j=S,W,E,B,H}\left(\frac{CAPEX_j}{\sum_{y=1}^{NY_j}(1+ir)^{-y}}+OPEX_j\right)}{8760\,[\mathrm{h/y}]\cdot \dot{m}_{H_2}^{target}} \quad (1)$$

Optimization proceeds through a systematic evaluation of 1681 solar-wind installed capacity combinations (0–400 MW range, at 10 MW resolution) using MATLAB R2024a, followed by an estimation of the required electricity and hydrogen storage capacities according to the frameworks established by Isella and Manca [11, 12].

RESULTS AND DISCUSSION

Optimal renewable and PtH sizing

The sizing optimization reveals a clear benefit of combining solar and wind. Solar-only systems require larger batteries and hydrogen storage to bridge diurnal variability, while wind-only systems reduce storage needs but still show considerable electrolysis capacities and power generation costs. Lastly, the mixed solar-and-wind case leverages complementarity, reducing both overbuild and storage requirements, which translates into a lower LCOH (see **Table 3**).

Table 3: Optimal installed capacities and resulting LCOH for solar, wind, and solar-wind PtH configurations.

	Solar	**Wind**	**Solar-Wind**
Solar [MW]	330	0	110
Wind [MW]	0	310	210
Electrolyzer [MW]	243.20	147.55	129.88
Battery [MW]	216.45	16.82	8.47
H_2 storage [t_{H_2}]	19.52	2.16	2.95
LCOH [USD/kg_{H_2}]	3.75	3.25	2.94

Ammonia production costs

Figure 2 shows the ensuing levelized cost of ammonia (LCOA) for gray, blue, and hybrid pathways, including hybrid-green and "hybrid-blue-green" (*i.e.*, hybrid-green plus carbon capture). The gray baseline reflects fuel and feedstock costs plus the carbon price burden. The blue pathway benefits from captured process CO_2 but includes carbon capture costs. Hybrid-green pathways show higher LCOA in this scenario, primarily because renewable hydrogen remains costlier than reforming-based hydrogen under 2024 assumptions, despite rapidly declining renewable generation costs.

Numerically, the LCOA values (in USD/t_{NH_3}) resulting from this case study are: gray 373.44, blue 364.51, hybrid-green (solar-only) 415.04, hybrid-green (wind-only) 404.50, hybrid-green (solar-wind) 398.03, and hybrid-blue-green (solar-wind) 395.27. Such results emphasize that, in a high-gas-price moderate-carbon-price context, blue ammonia can be competitive with gray while still reducing direct emissions. On the other hand, hybrid-green becomes more competitive as renewable electricity and electrolysis costs fall further or carbon prices rise.

The cost breakdown provided helps interpret which components dominate the incremental cost of hybridization. In the hybrid-green cases, noteworthy contributors are renewable CAPEX and electrolyzer CAPEX, followed by storage (electricity and hydrogen) to buffer variability. In the hybrid-blue-green case, the addition of CCS introduces capture costs but reduces carbon liabilities and can improve competitiveness depending on policy and CO_2 storage or utilization availability.

Emissions performance and CCS leverage

The operating envelope enables decarbonization progress without forcing deep turndown of the synthesis loop. In the study, increasing the hybridization factor from 0 to 10% and 20% reduces the plant-level CO_2 intensity from 1.64 to 1.48 and 1.31 t_{CO_2}/t_{NH_3}, respectively. The reduction is driven by the partial displacement of reformer-derived hydrogen by renewable electricity-derived hydrogen.

A key insight is that hybridization and CCS are not mutually exclusive. Hybrid-blue-green combines renewable hydrogen displacement with CO_2 capture on remaining fossil-derived streams. This stacking can reduce residual emissions beyond what either measure achieves alone while maintaining high utilization of existing assets. Such combinations align with CCS roadmaps for industrial decarbonization, where early deployment targets high-concentration CO_2 sources and leverages existing infrastructure.

At the same time, the environmental narrative of blue pathways depends on upstream methane emissions and on the overall capture rate achieved at the plant level. Recent debate emphasizes that "how green" blue

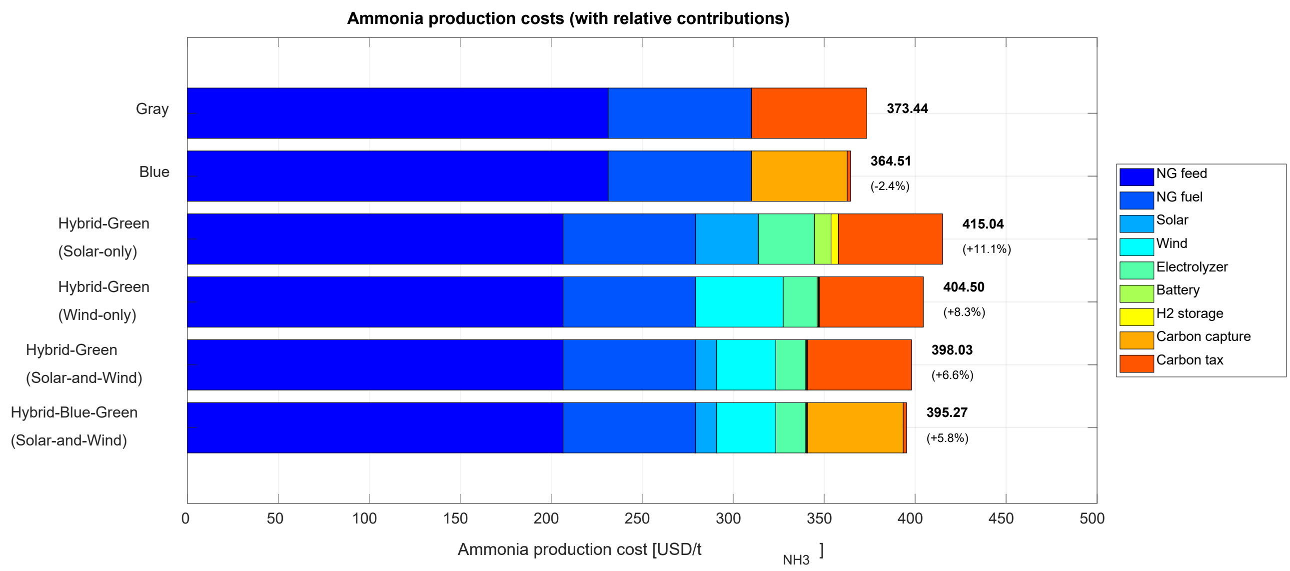

Figure 2. Ammonia production costs and relative contributions for the six assessed configurations. Percentages in parentheses next to the bars indicate the relative difference from the gray ammonia baseline. (NG=Natural Gas)

hydrogen and blue ammonia are depends critically on leakage rates and on capture scope [5]. For this reason, hybridization can be viewed as a hedge: increasing renewable substitution reduces exposure to upstream gas supply emissions even if CCS deployment faces constraints.

Operational insights for retrofit deployment

From an operational perspective, the hybrid retrofit can be implemented with minimal disruption if the PtH subsystem is treated as an auxiliary unit that delivers hydrogen at a suitable mass flow. The process integration challenge is to ensure that hydrogen displacement does not violate reformer heat-balance constraints or alter the synthesis loop's inert levels and purge management. Both scientific literature and industrial practice suggest that maintaining stable inlet compositions and temperature profiles is crucial to reliable operation.

Storage plays a key role: it buffers variability so that the plant receives a smoother electricity and hydrogen supply that is also compliant with the operating requirements of the electrolyzer and the Haber-Bosch process. Battery storage is most valuable for short-term smoothing, whereas hydrogen storage provides longer balancing. In this respect, recent design criteria for flexible electricity and hydrogen storage in PtX systems were applied to select storage capacity without overinvesting in rarely used inventory [11, 12].

The optimal sizing results show that solar-only operation requires significantly larger battery and hydrogen storage capacities than wind-only or mixed operation. This indicates that, for retrofit cases with limited space or where minimizing additional equipment is essential, the availability of a diversified renewable portfolio (either on-site or via PPAs) can be as important as absolute generation cost.

CONCLUSIONS

A hybrid-green retrofit concept can meaningfully reduce ammonia plant CO_2 intensity (about 20% decrease) while preserving continuous operation through an explicit operating envelope. When PtH assets are optimally sized, solar-wind complementarity cuts storage capacities and delivers the lowest LCOH among the tested cases. In the California 2024 scenario, hybrid-green remains more expensive than blue ammonia; however, the gap narrows with lower electrolyzer costs and higher carbon prices. Hybrid-blue-green offers an attractive transitional option by stacking renewable displacement and CCS.

From a deployment viewpoint, our framework supports retrofit screening by quantifying (i) the additional equipment required for a given hybridization target, (ii) the cost drivers that dominate incremental LCOA, and (iii) the emission reductions achievable without major process redesign. The same methodology can be extended to other regions by updating market prices, carbon policies, and technology costs.

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REFERENCES

1. The Royal Society. Ammonia: Zero-Carbon Fertiliser, Fuel and Energy Store. The Royal Society (2020).
2. Isella A, Manca D. GHG emissions by (petro)chemical processes and decarbonization priorities—a review. Energies 15:7560 (2022). https://doi.org/10.3390/en15207560
3. Armijo J, Philibert C. Flexible production of green hydrogen and ammonia from variable solar and wind energy: case study of chile and argentina. International Journal of Hydrogen Energy 45:1541-1558 (2020). https://doi.org/10.1016/j.ijhydene.2019.11.028
4. Isella A, Manca D. Integrating economic, environmental, and social sustainability in power-to-ammonia plants: a multi-objective optimization methodology. Computers & Chemical Engineering 198:109082 (2025). https://doi.org/10.1016/j.compchemeng.2025.109082
5. Howarth RW, Jacobson MZ. How green is blue hydrogen?. Energy Science & Engineering 9:1676-1687 (2021). https://doi.org/10.1002/ese3.956
6. Smith E, Morris J, Kheshgi H, Teletzke G, Herzog H, Paltsev S. The cost of CO2 transport and storage in global integrated assessment modeling. International Journal of Greenhouse Gas Control 109:103367 (2021). https://doi.org/10.1016/j.ijggc.2021.103367
7. Isella A, Lista A, Colombo G, Ostuni R, Manca D. Gray and hybrid green ammonia price sensitivity to market fluctuations: the Russia-Ukraine war case. In: Computer Aided Chemical Engineering. Ed: Kokossis AC, Georgiadis MC, Pistikopoulos E. Elsevier (2023) https://doi.org/10.1016/B978-0-443-15274-0.50364-4
8. Isella A, Ostuni R, Manca D. Towards the decarbonization of ammonia synthesis – a techno-economic assessment of hybrid-green process alternatives. Chemical Engineering Journal 486:150132 (2024). https://doi.org/10.1016/j.cej.2024.150132
9. Cornils B. Haldor topsøe low?energy ammonia process. Catalysis from A to Z : (2020). https://doi.org/10.1002/9783527809080.cataz07654
10. Global CCS Institute. Advancements in CCS Technologies and Costs. Global CCS Institute (2025).
11. Isella A, Manca D. A framework for the design of battery energy storage systems in power-to-x processes. Journal of Energy Storage 123:116744 (2025). https://doi.org/10.1016/j.est.2025.116744
12. Isella A, Manca D. A general criterion for the design and operation of flexible hydrogen storage in power-to-x processes. International Journal of Hydrogen Energy 99:649-660 (2025). https://doi.org/10.1016/j.ijhydene.2024.12.228
13. California Independent System Operator (CAISO). http://www.caiso.com
14. World Bank Group. https://carbonpricingdashboard.worldbank.org/compliance/price
15. U.S. Energy Information Administration (EIA). https://www.eia.gov/dnav/ng/ng_pri_sum_a_EPG0_PIN_DMcf_a.htm

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