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Phasing out steam methane reformers with water electrolysis in producing renewable hydrogen and ammonia: A case study based on the Spanish energy markets

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HIGHLIGHTS

- Addressing the co-existence of steam methane reformers and electrolysers.
- Novel power dispatch model addressing the flexibility of co-existential pathways.
- PPA availability and pricing and ETS taxation as key enablers of renewable hydrogen.
- Carbon intensity constraints heavily impact the project's sizing and feasibility.
- Techno-environmental study of the carbon intensity of ammonia production.

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ABSTRACT

Deploying renewable hydrogen presents a significant challenge in accessing off-takers who are willing to make long-term investments. To address this challenge, current projects focus on large-scale deployment to replace the demand for non-renewable hydrogen, particularly in ammonia synthesis for fertiliser production plants. The traditional process, involving Steam Methane Reformers (SMR) connected to Haber-Bosch synthesis, could potentially transition towards decarbonisation by gradually integrating water electrolysis. However, the coexistence of these processes poses limitations in accommodating the integration of renewable hydrogen, thereby creating operational challenges for industrial hubs. To tackle this issue, this paper proposes an optimal dispatch model for producing green hydrogen and ammonia while considering the coexistence of different processes. Furthermore, the objective is to analyse external factors that could determine the appropriate regulatory and pricing framework to facilitate the phase-out of SMR in favour of renewable hydrogen production. The paper presents a case study based in Spain, utilising data from 2018, 2022 and 2030 perspectives on the country's renewable resources, gas and electricity wholesale markets, pricing ranges, and regulatory constraints to validate the model. The findings indicate that carbon emissions taxation and the availability and pricing of Power Purchase Agreements (PPAs) will play crucial roles in this transition - the carbon emission price required for total phasing out SMR with water electrolysis would be around 550 EUR/ton CO_2.

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Nomenclature

Acronyms

SMR Steam Methane Reformer
PtA Power-to-Ammonia
PPA Power Purchase Agreement
ETS Emissions Trading Systems
EU European Union
REPowerEU Renewable Power European Union
PtG Power-to-Gas
HB Haber-Bosch
PtX Power-to-X
CCUS Carbon Capture Utilisation and Storage
IRENA International Renewable Energy Agency
LCOA Levelised Cost Of Ammonia
RFNBO Renewable liquid and gaseous Fuels of Non-Biological Origin
PAP Pay As Produced
LCOH Levelised Cost Of Hydrogen
GM Gas Market
EM Electricity Market
OPD Optimal Power Dispatch
MES Multi-Energy Systems
TEA Techno-Economic Assessment
PV-PPA Photovoltaic Power Purchase Agreement
W-PPA Wind Power Purchase Agreement
ELY-AK Electrolysis Plant with Alkaline Technology
ELY-PEM Electrolysis Plant with Proton Exchange Membrane Technology
HS Hydrogen Storage
AS Ammonia Storage
MILP Mixed-Integer Linear Problem
Pyomo Python Optimisation Modelling Objects
PEM Proton Exchange Membrane
RCOA Relative Cost Of Ammonia
NAPC Net Ammonia Production Capacity
OPEX Operational Expenditures
CAPEX Capital Expenditures
ROI Return On Investment
UAE United Arab Emirates
KPI Key Performance Indicator
SOC State of Charge
ELY Electrolyser
PV Photovoltaic Panel
RES Renewable Energy Sources
OMIE Operator del Mercado Ibérico de Energía
REE Red Electrica de España
MIBEL Mercado Iberico de Electricidad
MIBGAS Mercado iberico de Gas
EUA European Union Allowance
EEX European Energy Exchange AG platform
PNIEC Plan Nacional Integrado de Energía y Clima
RED II Renewable Energy Directive II
CertifHy Certification Scheme for Renewable and Low Carbon Hydrogen
BESS Battery Energy Storage Systems

Chemical compounds

H2 Hydrogen
H2O Water
NH3 Ammonia
CO2 Carbon dioxide, also carbon
N2 Nitrogen
CH4 Natural Gas/Methane

Units

(M)W (106) watts [power - energy per unit time] (109) watts [power - energy per unit time]
(G)W ton Metric ton, 1000 kg [unit of mass]
EUR Euros - € [currency]
USD United States Dollar - $ [currency]
AUS Australian Dollar [currency]
(M)Wh (103) watts per hour [unit of energy] (109) watts per hour [unit of energy]
(G)Wh kg Kilogram [unit of mass]
S Second [unit of time]
H 60 s, hour [unit of time]
Y 8760 h, year [unit of time]

Parameters

RCOA Relative Cost Of Ammonia [EUR/ton]
MPL^a Minimum Partial Load [%]
MRU^a Maximum Ramp Up [%]
MRD^a Maximum Ramp Down [%]
CD^a Cooldown [h]
NAPC Net Ammonia Production Capacity [tons/y]
S_k^a Rated capacity [ton, MW]
$E_{k,}^a$ Energy [MWh]
SOC_k^a State Of Charge [%]
γ_v^a Conversion rate into v [MWh/ton, ton/MWh – asset dependant]

Variables

$Cost_t$ Sum of all cost over time [EUR]
$Revenue_t$ Sum of all revenue over time [EUR]
$Vector_t^{c/r}$ Cost or Revenue per vector, including ETS and CO2, over time [EUR]
$Vector_{j,t}^a$ Vector flow per asset over time [ton, MWh]
$E_{j,t}^a$ Energy per time step [MWh]
SOC_t^a State of Charge per time step [%]
a/b_t^a Operational state per time step [binary]
r_t^a Load factor per time step [%]

Indices		J	In, Out, Export (ex), Import (im) [flow direction]
a	EM, GM, PV-PPA, W-PPA, ETS, ELY-AK, ELY-PEM, SMR, HS, HB, AS [asset or process]	K	Nominal, maximum, minimum, rated [specific characterisation parameter]
c/r	Cost, Revenue [EUR - per vector]	V	H2, NH3, Elect, CO2, H2O, CH4 [vector]
t	Time step granularity: t, t-1, y [t -hourly, t-1 previous time step, y - yearly]		

1. Introduction

The European Union's (EU) Green Deal aims to path the way for Europe to become the first carbon-neutral continent by 2050, a target that will rely on large-scale deployment of renewable hydrogen among other sustainable energy solutions [1]. Amid the post-pandemic economy and geopolitical crisis due to the war in Ukraine, the REPowerEU plan announced the target of 20 million tonnes of renewable hydrogen by 2030–50% of which is to be produced locally in Europe and the other 50% imported [2] – reinforcing the key role of hydrogen role towards ensuring the decarbonisation of the and energy security strategy [3]. In this challenging context, the financial viability of new green hydrogen projects is vital. Therefore, primarily, the potential of a renewable hydrogen deployment is intimately linked to the existence of a hydrogen off-taker, such as steel-making and chemical feedstock industries or fertiliser producers [4]. Ammonia is a promising vector for hydrogen shipping and transport and the foundation for all nitrogen-based fertilisers - 85% of its usage [5]. Hydrogen, being a key input in its manufacturing process, accounted for 34% of the total worldwide hydrogen demand in 2018 [6]. Traditionally, ammonia has been largely produced via steam methane reforming followed by a Haber-Bosch process [7], which accounts for 1–2% of worldwide carbon emissions [8]. Consequently, the development of Carbon Capture Utilisation and Storage (CCUS) emerges as an opportunity to reduce the carbon footprint of hydrogen production, not only via a Steam Methane Reformer (SMR) [9,10], but also through other pathways such as biomass gasification [11]. Despite its potential role as a bridging technology [12], CCUS is still facing some fundamental issues preventing its development [13]. The electrification of ammonia production via water electrolysis, the so-called Power-to-Ammonia (PtA), even though energy-intensive, is leading the fertiliser sector to a new era of scientific research and development seeking to downscale and increase the operational robustness of the Haber-Bosch synthesis to couple better with intermittent and distributed renewable energy supply [14–16].

The perspective of easy access to cheap and extensive renewable electricity supply, along with economies of scale, presents a new paradigm for Haber-Bosch synthesis to produce carbon-free ammonia. Thus the need to address the influence of energy markets. The International Renewable Energy Agency (IRENA) compared the cost-competitiveness of renewable ammonia versus fossil-based ammonia in its Innovation Outlook on Renewable Ammonia. The cost of renewable ammonia was calculated at USD 720 USD/ton in 2022, and it is estimated to decrease to 480 USD/ton by 2030 and 310 USD/ton by 2050. The cost of fossil-based ammonia varies in the range of 110–340 USD/ton. Consequently, a CO2 emission tax of at least 150 USD/ton is still necessary for renewable ammonia to become competitive [17]. Meanwhile, SMR with CCUS were proved to increase that cost by 35–150 EUR/ton of H_2 depending on the intensity of the CO_2 sequestration [9]. The scientific literature confirms the tendencies presented by IRENA for both current and prospective production costs. In 2018/2019, the Levelised Cost of Ammonia (LCOA) via water-splitting processes was calculated at 1350 EUR/ton [18]. And, despite promising system efficiency rates above 74%, high electrolyser stack costs and electricity prices above 73 USD/MWh were compromising the economic feasibility of PtA [19]. However, more recent studies confirmed the quick evolution of renewable ammonia. Two case studies in Australia and United Arab Emirates (UAE) showed much more promising LCOA calculations at 750 AUS/ton and 720 USD/ton in 2025, and 650 AUS/ton and 450 USD/ton in 2030, respectively [20,21]. Then, as per gas prices and CO2 emission taxes, a comprehensive study covering hybrid heat and electricity systems in future North European energy scenarios determined that only gas prices above 70 EUR/MWh or CO2 taxes above 200 EUR/tCO2 would make electrolysis and PtA profitable versus SMR around 500 EUR/ton [22]. Renewable ammonia projects' scale and extensive energy consumption require confronting the influence of energy markets and implementing legal frameworks facilitating different Power-to-X (PtX) pathways [23]. The criteria of additionality of the latest delegated act from February 2023 addresses this aspect, preventing extensive consumption from the electricity grid and implementing a hydrogen taxonomy, while strengthening the need for investment in new renewable infrastructure to cover the production of renewable liquid and gaseous fuels of non-biological origin (RFNBOs) through power-purchase agreements (PPA) [24]. Therefore, the consideration of PPAs, which has been noted when addressing the optimisation of renewable ammonia production [21], becomes an unavoidable aspect for any PtA project. However, we need to enlarge the scope from PtA to Power-to-Gas (PtG) in order to find existing research on the effects of PPAs in the production of RFNBOs. In Spain, a case study addressed the techno-economic viability of green hydrogen projects supported by photovoltaic PPAs, showing how the introduction of Pay-as-Produced (PAP) PPA improves the Return On Investment (ROI) rate of the project. A sensitivity analysis was included to link the agreed price of the PPA to the final Levelised Cost Of Hydrogen (LCOH) - a 5 EUR/MWh produced up to 0.13 EUR variation of the LCOH. A similar Italian case study that analysed the production of water electrolysis for mobility purposes, providing a bracket of different PPA prices, was included as part of the sensitivity analysis of 40–100 EUR/MWh [25].

The overview of these case studies, whether PtG or PtA, confirms the inherent need to address the influence of the energy markets. Electricity prices, gas prices, carbon intensity and taxonomy, CO2 taxes, and PPA sizing and prices, which, despite often being addressed separately, are intrinsically related and play a key role in the cost of ammonia production and the project's viability. To date, no existing literature has studied the influence of all these elements in different ammonia production pathways simultaneously. Thus, this paper offers a novel approach to studying the interaction and influence of energy markets in the ammonia production dispatch and cost of PtA projects.

Furthermore, the cost of renewable hydrogen, being the most relevant factor in the long term, represents around 90% of the final cost of renewable ammonia [17], while electricity costs contribute to 50–70% of the final LCOH [26]. Additionally, renewable hydrogen deployment faces strong entry barriers due to substantial initial capital investment linked to the high CAPEX of electrolyser technology [27], and infrastructure costs [28]. Therefore, the phase-out of SMR, with or without CCUS, is expected to occur gradually as existing hydrogen producers and off-takers are the most likely stakeholders to co-invest in decarbonisation alternatives while keeping their existing SMR plants in operation until electrolytic hydrogen becomes a cost-competitive alternative [10,29]. Therefore, SMR and water electrolysis, while often compared in the literature [19,30–33], are likely to coexist for several years. This approach has been addressed when analysing the complementary role of blue and green, or renewable and low-carbon hydrogen [34], or when studying Renewable Energy Sources (RES) research [35], and applied to different levels, such as Multi-Energy Systems [36] or supply chain analysis involving Emission Trading Systems (ETS) [37]. However, there is no prior literature that models the coexistence of SMR and water electrolysis towards ammonia production via Haber-Bosch synthesis. Nonetheless, different methodological approaches applied to the processes involving the modelling of PtA energy systems are found in the literature. Due to the inherent intermittent nature of RES, the consideration of the operational dynamics and flexibility of the whole energy system is of key relevance. On the one side, multiple authors have extensively addressed such aspects in the modelling of PtG systems, where intermediate states of operation and factor load constraints are considered in the power output modelling as a means to represent the metaphysical limitations of the involved electrochemical processes [38,39]. However, on the other side, when focusing on the whole PtA system, thus including the Haber-Bosch (HB) process, the flexibility of the process is commonly addressed at a physical level through chemical and thermodynamical modelling [40–42], but not at an energy system level. Limitations on the load factor have been indicated in the modelling of PtA, such as a minimum partial load of 20% [43] or a 20% ramp-up flexibility and 48 h of cooldown [44]. More recent literature has addressed the limited flexibility and power dispatch of the whole PtA process, without SMR consideration, and its effects on pricing and optimal sizing of the system in the Chinese context [45]. However, several environmental aspects, such as the carbon intensity and footprint of the hydrogen produced, remain unclear. Therefore, a higher level assessment that takes into account all these elements is needed for optimal power dispatches, techno-economic and environmental analysis.

Then, to accurately assess the replacement of existing SMR by electrolysis plants towards the production of renewable hydrogen and ammonia, this paper proposes an Optimal Power Dispatch (OPD) model for PtA and SMR, which optimises the variable cost of producing ammonia for a given energy scenario. To this end, the scientific novelty of the research proposed in this paper can be divided into three levels.

- Address the complexity and intrinsic relationship between Power Purchase Agreements (PPAs), Gas and Electricity Markets (GM, EM) and ETS with hourly granularity as a means to analyse the impact and cost-competitiveness under different energy scenarios.
- Consideration of the coexistence of the different hydrogen production processes - SMR and water electrolysis towards ammonia production via a Haber-Bosch synthesis in an OPD model that includes the flexibility and operational aspect of the different processes involved.
- Then, as a means to jointly assess the previous points, the methodology is applied to the analysis of the potential of Spain for GW-scale deployment of water electrolysis for renewable ammonia production.

The paper is structured in the following manner: firstly, the ‘Introduction’ section provides an overview of the context and current state of the art. Secondly, the ‘Methodology and mathematical formulation of the model’ section explains the algorithm and equations that make up the model. Thirdly, the ‘Case study: The Remote project’ section demonstrates the effectiveness of the model through a real-life application. Fourthly, the ‘Results and Discussion’ section presents the techno-economic outcomes that were achieved by utilising the OPD model in the case study. Lastly, the ‘Conclusions’ section summarises the takeaways and outlines potential avenues for future research.

2. Methodology and mathematical formulation

The present paper aims to show a novel PtA model that allows the OPD for an industrial plant comprising co-existent hydrogen production pathways towards a subsequent ammonia synthesis process. Therefore, this section explains the methodological approach developed. The dispatch is achieved at hourly granularity over a yearly simulation that runs on historical data. Hence the model follows a deterministic approach. In Fig. 1, the model considers all elements, including different energy markets, namely the EM and GM, photovoltaic PPA (PV-PPA) and wind PPA (W-PPA), then carbon emissions taxation are also considered through the ETS, as well as the different assets forming the MES: electrolysis plant with alkaline technology (ELY-AK), electrolysis plant with Proton Exchange Membrane (PEM) technology (ELY-PEM), SMR, hydrogen storage (HS), an HB synthesis plant and ammonia storage (AS). The model has been formulated as a quadratically constrained Mixed-Integer Linear Programming (MILP) by means of the Python framework Pyomo. The optimisation algorithm is solved with Gurobi.

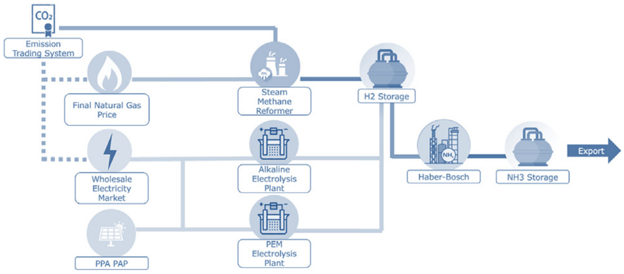

Fig. 1 – Layout of the energy system model. Legend: PPA PAP (Pay As Produced Power Purchase Agreement), H2 (Hydrogen), NH3 (Ammonia), PEM (proton Exchange Membrane.

2.1. *Model definition and data input*

The definition of the model comprises the characterisation of the different assets and processes. The characterisation of the different assets has been achieved with the parametrisation of their sizes, efficiencies, conversion rates, flexibility and operational constraints such as minimum partial loads, ramping-up and down limitations, and cooldown cycles. However, certain general assumptions were made regarding their characterisation. Non-linear or quadratic efficiencies were not considered, and effects from the self-discharge of storage tanks were disregarded. Then, the Net Ammonia Production Capacity (NAPC) target is the main parameter that, while constrained by the energy market final prices, hourly emissions pricing and the PPA capacity, defines the planning and OPD results.

Additionally, the data input for the optimisation of the model includes a significant feed-in of data series conformed by the hourly values over a year concerning the energy and emissions markets: (i) EM final hourly price, (ii) EM hourly injection price, (iii) EM hourly carbon intensity, (iv) GM final hourly price, (v) W-PPA final hourly price, (vi) PV-PPA final hourly price, and (vii) ETS hourly price. Several assumptions apply to the definition of the PPAs. The model considers PPAs from two sources, W-PPA and PV-PPA, which are characterised by different generation profiles and pricing ranges. The financial arrangement, given that the Spanish electricity market is composed of one single market zone, the PPAs are assumed as virtual or off-site, which allows the geographical des-collocation of the RES regarding the plant situation. Then, the PPA profiles are calculated as the sum of the baseload price and the fraction of the EM's final price corresponding to the tolls and taxes. Finally, the PPA is assumed as PAP or "paid as produced", implying that the consumer must consume the gross generation of the PPA at all time periods, which is a common financial agreement to divide the risk of the investment on RES infrastructure between the PPA supplier and the client.

2.2. *The objective function and cost-revenue breakdown*

The objective function of the optimisation problem is the Relative Cost Of Ammonia (RCOA) in Eq. 1 – which is to be minimised over a year-long hourly simulation with 8760 time steps for a given net production capacity. The RCOA is an expression of the variable cost of producing ammonia based on the project's cash flows. It is defined as the yearly variable cost per ton of ammonia, expressed as the sum of the cost ($Cost_t$) subtracting the revenues ($Revenue_t$) and divided by the NAPC. The selection of the RCOA responds to the need for a techno-economic KPI for studying the effects of the environment, defined by the energy markets data input, on the dispatch. It is a simplified representation of the LCOA that does not include the annualisation of CAPEX and OPEX over the lifetime of the project. In an OPD model, the impact of capital expenditures (CAPEX) and operational expenditures (OPEX) of every asset, being constant values, do not affect optimisation and are negligible from the objective function. Furthermore, the rest of the variable costs, such as the replacement cost, were annualised as part of the OPEX and thus also neglected. Therefore, as applied in previous research regarding energy systems operating under dynamic conditions [46], the RCOA is selected as the reference KPI allowing comparative results and discussion.

$$RCOA = \frac{\min\left(\sum_{t=0}^{8759} Cost_{(t)} - Revenue_{(t)}\right)}{NAPC} \tag{1}$$

Furthermore, Eqs. (2) and (3) show cost and revenue breakdown per time step. The cost structure is composed of the total cost of the electricity consumption ($Elect^{Cost}_{(t)}$), the cost of the natural gas ($CH4^{Cost}_{(t)}$), the cost of water consumed ($H2O^{Cost}_{(t)}$) and the cost related to the CO2 emissions ($H2O^{Cost}_{(t)}$). The revenues include the revenue from selling ammonia ($NH3^{Revenue}_{ex,(t)}$), and the revenue resulting from selling the excess of power contracted in the PPA ($Elect^{Revenue}_{ex,(t)}$).

$$Cost_{(t)} = Elect^{Cost}_{im,(t)} + CH4^{Cost}_{(t)} + H2O^{Cost}_{(t)} + ETS^{Cost}_{(t)} \tag{2}$$

$$Revenue_{(t)} = Elect^{Revenue}_{ex,(t)} + NH3^{Revenue}_{ex,(t)} \tag{3}$$

Then, the different elements contributing to calculating the cost - Eqs. (4)–(7), and revenue - Eq. (8), are likewise broken down into the variables and parameters determining their hourly value. (i) The cost of buying electricity ($Elect^{Cost}_{im,(t)}$), is the result of applying the hourly prices of the EM, PV-PPA and W-PPA ($Elect\_price^{a}_{(t)}$) to the respective electric input ($E^{a}_{im,(t)}$), and the regulation of the PAP PPAs managed by decision variable ($b^{PPA}_{(t)}$) further explained in Eq. (10). (ii) The cost of the natural gas consumed in the SMR ($CH4^{Cost}_{(t)}$), it Is calculated based on the hourly GM final price ($CH4\_price^{GM}_{(t)}$) and the consumption in the SMR ($CH4^{SMR}_{in,(t)}$). (iii) The cost of the water ($H2O^{Cost}_{t}$), which is consumed in the electrolysis and the SMR processes ($H2O^{a}_{in,(t)}$) at a fixed price (H2O_price). (iv) The cost of the equivalent CO_2 emissions based on the hourly price of the UAE market ($UAE\_price^{ETS}_{(t)}$) and the emissions resulting from the SMR ($CO2^{SMR}_{out,(t)}$).

$$Elect^{Cost}_{im,t} = b^{PPA}_{(t)}.Elect\_price^{EM}_{(t)}.\ E^{EM}_{im,(t)} + Elect\_price^{PV-PPA}_{(t)}.\ E^{PV-PPA}_{im,(t)} + Elect\_price^{W-PPA}_{(t)}.\ E^{W-PPA}_{im,(t)} \tag{4}$$

$$CH4^{Cost}_{t} = CH4\_price^{GM}_{price,(t)}.CH4^{SMR}_{in,(t)} \quad (5)$$

$$H2O^{Cost}_{t} = H2O\_price.\left(H2O^{ELY-AK}_{in,(t)} + H2O^{ELY-PEM}_{in,(t)} + H2O^{SMR}_{in,(t)}\right) \quad (6)$$

$$ETS^{Cost}_{t} = UAE\_price^{ETS}_{(t)}.CO2^{SMR}_{out,(t)} \quad (7)$$

Then, the revenues are only affected by the exports from the PAP PPA ($Elect^{Revenue}_{ex,(t)}$). Since, the price of ammonia is a fixed parameter ($NH3_{price}$), and the gross generation belongs to the consumer, this energy is either imported and consumed in the modelled energy system or sold to the EM ($E^{a}_{ex,(t)}$) at the given hourly injection price ($Injection\_price^{EM}_{(t)}$). This implies that the revenue can actually take negative values when the injection price is lower than the settled PPA price. Therefore, an important aspect to consider is the regulation of this PPA. Thus, two decision variables are introduced in Eq. (10), to ensure that the PAP constraint correctly applies to the model – either injecting electricity into the grid ($a^{PPA}_{(t)}$) or buying from the EM ($b^{PPA}_{(t)}$), but not both simultaneously.

$$NH3^{Revenue}_{ex,(t)} = NH3_{price}.NAPC \quad (8)$$

$$Elect^{Revenue}_{ex,(t)} = a^{PPA}_{(t)}.\left(\left(Injection_{price_{(t)}}^{EM} - Elect\_price^{PV-PPA}\right)E^{PV-PPA}_{ex,(t)} + \left(Injection_{price_{(t)}}^{EM} - Elect\_price^{W-PPA}\right)E^{W-PPA}_{ex,(t)}\right) \quad (9)$$

$$\left(a^{PPA}_{(t)} + b^{PPA}_{(t)}\right) \leq 1 \quad (10)$$

2.3. Energy balance

The energy balance of the model, expressed in megawatts per hour (MWh), is defined at two different levels. Firstly, Eq. (11) defines the balance of the energy imports ($E^{W/PV-PPA}_{im,(t)}$) and exports ($E^{W/PV-PPA}_{ex,(t)}$) based on the dispatch of the gross generation of the PAP PPA ($E^{W/PV-PPA}_{(t)}$).

$$E^{PV-PPA}_{(t)} + E^{W-PPA}_{(t)} - E^{W-PPA}_{im,(t)} - E^{PV-PPA}_{im,(t)} - a^{PPA}_{(t)}.\left(E^{W-PPA}_{ex,(t)} + E^{PV-PPA}_{ex,(t)}\right) = 0 \quad (11)$$

Then, in Eq. (12), the total PPA imports from Eq. (10) are combined with the energy imported from the EM ($E^{EM}_{im,(t)}$). It includes all the energy input of the different assets and processes - SMR, ELY-AK, ELY-PEM and HB ($E^{a}_{in,(t)}$)

$$b^{PPA}_{(t)}.E^{EM}_{im,(t)} + E^{W-PPA}_{im,(t)} + E^{PV-PPA}_{im,(t)} - E^{SMR}_{in,(t)} - E^{ELY-AK}_{in,(t)} - E^{ELY-PEM}_{in,(t)} - E^{HB}_{in,(t)} = 0 \quad (12)$$

2.4. Carbon emissions and footprint

The calculation of the CO2 emissions ($CO2^{Emissions}_{(t)}$) takes into account the EM hourly carbon intensity ($CO2^{EM}_{(t)}$), and the emissions of the SMR ($CO2^{SMR}_{out,(t)}$). The emissions regarding the involved equipment's lifecycle and the hourly carbon intensity of PPA are neglected, as indicated in Eq. (13).

$$CO2^{Emissions}_{(t)} = CO2^{EM}_{(t)}.\ E^{EM}_{im,(t)} + CO2^{SMR}_{out,(t)} \quad (13)$$

Accordingly, the calculation of the ammonia's hourly CO2 footprint ($NH3^{CO2-footprint}_{(t)}$), in Eq. (14), expresses the hourly value of the KPI as the fraction of the CO2 emissions by the HB hourly output ($H2^{ELY}_{out,(t)}$). Then, the average yearly value is calculated as a fraction of the NAPC in Eq. (15).

$$NH3^{CO2-footprint}_{(t)} = \frac{CO2^{Emissions}_{(t)}}{NH3^{HB}_{out,(t)}} \quad (14)$$

$$NH3^{CO2-footprint} = \frac{\sum_{t=0}^{8760} CO2^{Emissions}_{(t)}}{NAPC} \quad (15)$$

2.5. Operation and flexibility

In Eqs. (16)–(18), applying to all assets, on ($a^{a}_{(t)}$) and off ($b^{a}_{(t)}$) operational states are considered to define the operation of the energy system. Furthermore, the load factor ($r^{a}_{(t)}$) is also introduced as a means to model the flexibility and degree of usage of the different assets. The Minimal Partial Load (MPL^{a}) is applied as a constraint to restrict the lower bound of the load factor:

$$\left(a^{a}_{(t)} + b^{a}_{(t)}\right) = 1 \quad (16)$$

$$r^{a}_{(t)} - a^{a}_{(t)} \leq 0 \quad (17)$$

$$-r^{a}_{(t)} + MPL^{a}.a^{a}_{(t)} \leq 0 \quad (18)$$

Furthermore, applying to the major thermo-chemical processes – SMR and HB, in Eqs. (19) and (20), the load factor's maximum ramping-up (MRU^{a}) and ramping-down (MRD^{a}) conditions are applied to limit the assets' flexibility over time. Similarly, a minimal cooldown time (CD^{a}) is modelled through Eq. (21):

$$r^{a}_{(t)} - r^{a}_{(t-1)} < = MRU^{a}.\ a^{a}_{(t)}.\left(1 - b^{a}_{(t-1)}\right) + MPL^{a}.b^{a}_{(t-1)} \quad (19)$$

$$r^{a}_{(t-1)} - r^{a}_{(t)} = > -MRD^{a}\ .\ a^{a}_{(t)} - MPL^{a}.b^{a}_{(t)} \quad (20)$$

$$b^{a}_{(t)}.\ a^{a}_{(t-1)}\ .\ CD^{a} - \sum_{d=0}^{CD} b^{a}_{(t+d)} \leq 0 \quad (21)$$

2.6. Multi-energy system

The interactions between the different assets and vectors of the energy system represent a complex MES. Therefore, these processes have been modelled through input and output vectors and their respective efficiencies and/or conversion rates.

Eqs. (22)–(26) cover the energy vector modelling of the SMR, an asset produces hydrogen ($H2^{SMR}_{out,(t)}$) and emits carbon dioxide ($CO2^{SMR}_{out,(t)}$) from electricity ($Elect^{SMR}_{in,(t)}$) and natural gas ($CH4^{SMR}_{in,(t)}$). The nominal capacity ($S^{SMR}_{Nominal}$) is defined by the maximum hourly hydrogen output. Thus, the conversion rates of the natural gas (γ^{SMR}_{CH4}), electricity (γ^{SMR}_{Elect}) and CO2 (γ^{SMR}_{CO2}) are referenced to the hydrogen output.

$$H2^{SMR}_{out,(t)} = a^{SMR}_{(t)} \cdot r^{SMR}_{(t)} \cdot S^{SMR}_{Nominal} \tag{22}$$

$$CH4^{SMR}_{in,(t)} = a^{SMR}_{(t)} . H2^{SMR}_{out,(t)} * \gamma^{SMR}_{CH4} \tag{23}$$

$$Elect^{SMR}_{in,(t)} = a^{SMR}_{(t)} . H2^{SMR}_{out,(t)} * \gamma^{SMR}_{Elect} \tag{24}$$

$$H2O^{SMR}_{in,(t)} = a^{SMR}_{(t)} . H2^{SMR}_{out,(t)} * \gamma^{SMR}_{H2O} \tag{25}$$

$$CO2^{SMR}_{out,(t)} = a^{SMR}_{(t)} . H2^{SMR}_{in,(t)} * \gamma^{SMR}_{CO2} \tag{26}$$

Eqs. (27)–(29) aim at modelling the electrolysis process, applying to both assets ELY-AK and ELY-PEM, water molecules ($H2O^{EL}_{in,(t)}$) are split into hydrogen ($H2^{EL}_{out,(t)}$) by the application of an electric current ($Elect^{EL}_{in,(t)}$). The nominal capacity of the electrolyser ($S^{ELY}_{Nominal}$) is expressed as its nominal power consumption. Therefore, conversion rates apply for the processes' hydrogen output (γ^{ELY}_{H2}) and water input (γ^{ELY}_{H2O}).

$$Elect^{ELY}_{in,(t)} = a^{ELY}_{(t)} \cdot r^{ELY}_{(t)} \cdot S^{ELY}_{Nominal} \tag{27}$$

$$H2^{ELY}_{out,(t)} = a^{ELY}_{(t)} \cdot Elect^{ELY}_{in,(t)} * \gamma^{ELY}_{H2} \tag{28}$$

$$H2O^{ELY}_{in,(t)} = a^{EL}_{(t)} . Elect^{ELY}_{in,(t)} * \gamma^{ELY}_{H2O} \tag{29}$$

Eqs. (32)–(32) define the Haber-Bosch process, where ammonia ($NH3^{HB}_{out,(t)}$) is produced from hydrogen ($H2^{HB}_{in,(t)}$) and electricity ($Elect^{HB}_{in,(t)}$). Nitrogen input for the thermochemical process and water consumption for cooling were assumed as negligible regarding their impact on the final RCOA. Furthermore, the nominal capacity of the HB is expressed as the hourly nominal ammonia output ($S^{HB}_{Nominal}$). Hence, the conversion rates for ammonia (γ^{ELY}_{NH3}) and electricity (γ^{ELY}_{Elect}) are applied.

$$NH3^{HB}_{out,(t)} = a^{HB}_{(t)} \cdot r^{HB}_{(t)} \cdot S^{HB}_{Nominal} \tag{30}$$

$$H2^{HB}_{in,(t)} = a^{HB}_{(t)} \cdot NH3^{HB}_{out,(t)} \cdot \gamma^{HB}_{H2} \tag{31}$$

$$Elect^{HB}_{in,(t)} = a^{HB}_{(t)} . NH3^{HB}_{out,(t)} \cdot \gamma^{HB}_{Elect} \tag{32}$$

2.7. *Storage buffer*

The storage buffer differentiates two elements, Hydrogen Storage (HS) and Ammonia Storage (AS), defined by their State Of Charge (SOC). In Eqs. (33) and (34), the SOC of hydrogen storage ($SOC^{HS}_{(t)}$) and ammonia storage ($SOC^{AS}_{(t)}$) are calculated as an expression of the output and input flows from different involved processes in the MES. Then, in Eq. (35), applying both equations, the boundaries on the SOC are defined by the minimum (SOC^{a}_{min}) and maximum (SOC^{a}_{max}) SOC. Finally, in Eq. (35), the sum of ammonia export ($NH3^{AS}_{ex,(t)}$) which is defined in the AMS, is fixed to the yearly NAPC.

$$SOC^{HS}_{(t)} = SOC^{HS}_{(t-1)} + H2^{SMR}_{out,(t)} + H2^{ELY-AK}_{out,(t)} + H2^{ELY-PEM}_{out,(t)} - H2^{HB}_{in,(t)} \tag{33}$$

$$SOC^{AS}_{(t)} = SOC^{AS}_{(t-1)} + NH3^{HB}_{out,(t)} - NH3^{AS}_{ex,(t)} \tag{34}$$

$$SOC^{a}_{min} \le SOC^{a}_{(t)} \le SOC^{a}_{max} \tag{35}$$

$$NAPC = \sum_{t=0}^{8,760} NH3^{AS}_{ex,(t)} \tag{36}$$

3. Case study definition

The case study is based on publicly available information from an existing standard fertiliser plant from the Fertiberia Group. The factory in Palos de la Frontera, Huelva, Spain, mainly produces ammonia and urea, with a yearly NAPC of 400,000 tons [47].

3.1. *Input datasets*

The input for the model is generated from historical datasets collected for the years 2018 and 2022. A third group of synthetic datasets, based on the data profiles from 2018, was recreated to define the 2030 energy scenario.

The selection of the years 2018 and 2022 was not arbitrary. In the Spanish and European contexts, 2018 was selected as a standard year with low electricity and gas prices and low carbon emission taxation. Also, at that stage, there was a relatively lower RES penetration in the Spanish energy mix – 40.46%, and a lower PPA pricing and presence in the market. Then, 2022 was studied as a particularly interesting case with higher electricity and gas prices, which offered a high contrast to 2018's situation. By 2022, RES's penetration had risen to 48.26%. The ETS pricing had increased by roughly 640% compared to 2018. Then 2030 shows the short and mid-term evolution towards the decarbonisation targets of the Paris Agreement [48], which are addressed through the Plan Nacional Integral de Energia y Clima (PNIEC), or National Energy and Climate Strategy [49].

Regarding the data recollection for 2018 and 2022, the final electricity prices were obtained from the publicly available databases of the Spanish market operator (OMIE) [50] and the service operator - Red Electrica de España (REE) [51]. The final price comprised hourly electricity prices, power and access tariffs, taxes and grid services charges. The PAP PPA price baselines for PV and wind were assumed based on prices provided by the Iberian Electricity Market website (MIBEL) [52] and the PPA price index report from LevelTen [53]. Final gas prices were obtained from the Iberian Market Operator's (MIBGAS) database [54]. The hourly carbon intensity of the electricity consumed from the Spanish grid was also considered [55]. ETS prices were extracted from historical data from the European Union Allowance (EUA) market [56].

Then, different assumptions were applied regarding the definition of the inputs for 2030. Average electricity, natural gas, PPA and ETS pricing were defined based on future market values for 2030 provided by the previously mentioned sources and the European Energy Exchange AG platform (EEX) as of May 2023 [57]. Finally, the PNIEC defined the objective of a 72% RES penetration in electric generation by 2030, foreseeing a 64% reduction of emissions between 2015 and 2030. Therefore, the grid carbon intensity reduction was estimated accordingly [49]. Table 1 summarises yearly average values for all the datasets collected for the 3 time horizons, and Fig. 2, shows the resulting synthetic data profiles for the year 2030.

Based on the single electricity Spanish market, which is formed by a single biding zone, a diversified portfolio comprising 2 PV-PPA and 4 W-PPA in different geographical locations was assumed. The European Union's Earth Observation Programme, Copernicus [58], was used to extract the meteorological datasets corresponding to the wind speed and solar irradiation from the year 2018, which applied to the calculation of the RES production profiles used to calculate the PPA profile in all sensitivity cases. The effect of yearly variation of meteorology was neglected in the study. As per the configuration of the PPA, a diversified portfolio comprising 6 different locations with existing RE infrastructure was assumed: 1 GW of W-PPA equally divided between Sil-Ourense, Sasoplano-Huesca, La Victoria-Cadiz and Gecama-Cuenca. 2 GW of PV-PPA equally divided between, Mula-Murcia and Aljarafe- Sevilla. Fig. 3 shows the approximate layout of all the cited sites.

Results are based on the production costs given by the RCOA. Thus, the price for selling ammonia was fixed at 0 EUR/ton. The cost of water was assumed at 2.44 EUR/m^3 [59].

3.2. *Sensitivity analysis*

A sensitivity analysis was conducted as a means to study the technical, economic and environmental implications of the two target technologies for hydrogen production, SMR and water electrolysis, under the various energy scenarios defined - 2018, 2022 and 2030. In the first step, 5 different cases per time horizon were simulated: (a) SMR only with neither water electrolysis technology nor PPA, (b) Co-existence of SMR and ELY without PPA, (c) Co-existence of SMR and ELY with PPA, (d) ELY only without PPA, (e) ELY only with PPA. The average values of the datasets corresponding to different time horizons, 2018, 2022 and 2030, are shown in Table 1.

Then case (c), which defines the co-existence of both technologies under a PPA, is further developed to offer a broader assessment of how the energy system balances both technologies. For that purpose, a second step of the sensitivity analysis is suggested, 7 different hypothetical energy scenarios are simulated under different ETS and GM pricing, as well as ELY and PPA sizing options: (i) a 100% increase in ETS, (ii) a 200% increase in ETS, (iii) a 100% increase in ETS and GM pricing increase up to 2022 values, (iv) a 200% increase in ETS with 50% increase on the PPA size, (v) a 200% increase in ETS and 50% increase on the ELY size, (vi) (vii) a 200% increase in ETS and 50% decrease on the ELY size, and (viii) a 300% increase in ETS. The full overview of all the scenarios is defined in Table 2.

Table 1 – Sensitivity analysis overview: yearly average values per scenario.

Year	Electricity grid final price (€/MWh)	PV- PPA electricity base price (€/MWh)	W- PPA electricity base price (€/MWh)	Natural gas final price (€/MWh)	Grid carbon intensity (tons CO_2/MWh)	ETS (€/ton CO_2)
2018	73.2	28	42	35.97	0.283	13.5
2022	117.32	46	60	131.22	0.178	81.36
2030	60.19	36	50	42.48	0.112	110.43

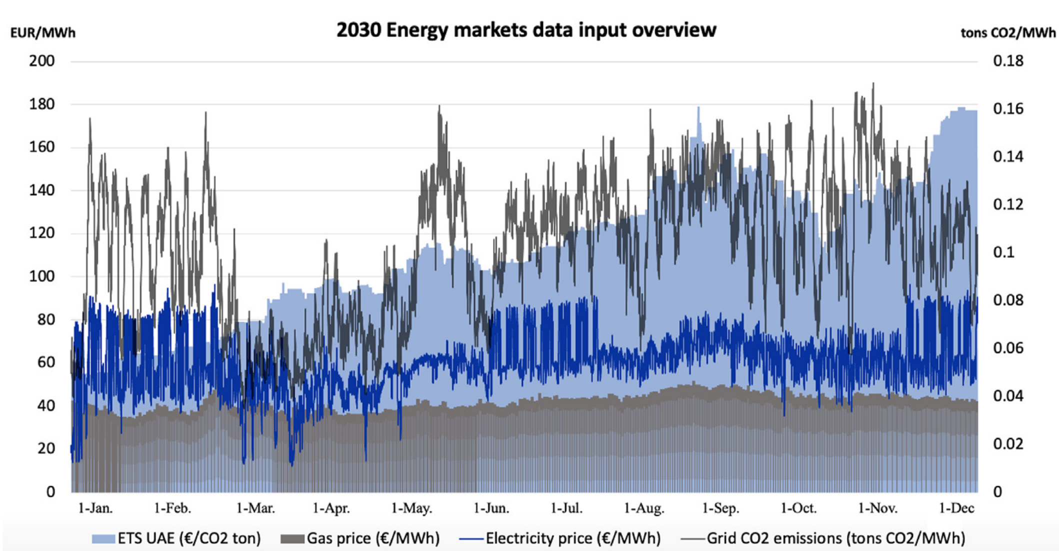

Fig. 2 – Overview of 2030 energy market's data input.

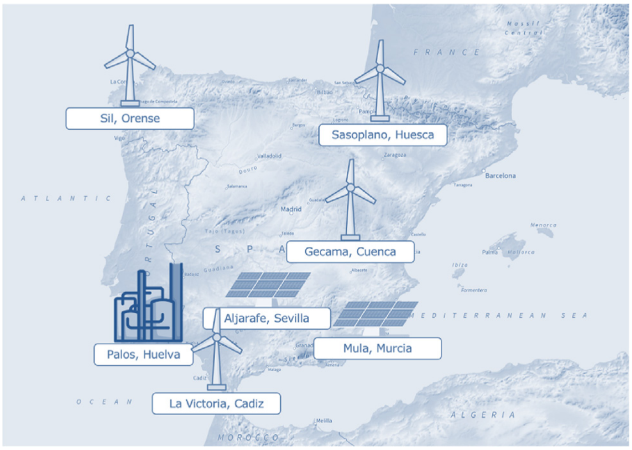

Fig. 3 – Case study layout with the geographical disposition of PPA and plant.

3.3. *Model parameters definition*

The parametrisation of the model for the case study is shown in Table 3.

3.4. *Power-to-gas carbon intensity and taxonomy*

The taxonomy of different regulatory organisms has also been considered as part of the case study. The given reference values for renewable hydrogen have been converted to its ammonia equivalent -multiplying by 0.1778 (HB's conversion rate) - to determine whether it can be considered renewable, non-renewable or low carbon [6].

The different criteria applying shown in Table 4: (i) the EU-ETS Benchmark: 8.85 kg CO_2/kg H_2, which considers the emissions for processes and inputs [60], (ii) the EU Taxonomy threshold for sustainable hydrogen manufacturing: 5.8 kg CO_2/kg H_2 [61], (iii) CertifHy threshold for low carbon hydrogen: 4.4 kg CO^2/kg H_2 [6], (iv) RED II threshold for RFNBO: 3.384 kg CO_2/kg H_2 [62].

4. Results and discussion

This section presents the results and analysis of the OPD application to the case study. In the first step, the techno-economic results achieved by optimising the objective function, RCOA, are compared for the different scenarios defined in the data input and sensitivity cases. Furthermore, the techno-environmental aspect of the ammonia production pathways is addressed as a means to analyse the evolution of the carbon emissions over the different simulated cases.

4.1. *Techno-economic analysis*

The results of the first part of the sensitivity analysis are shown in Fig. 4. In 2018, SMR only defined the reference RCOA at 133 EUR/NH_3 ton. The co-existence of ELY and PPA did not affect the dispatch of the hydrogen production

Table 2 – Sensitivity analysis for 2030c overview.

	Scenario	Electricity grid final price (€/MWh)	ELY size (MW)	PV PPA size (GW)	W PPA size (GW)	PV- PPA electricity base price (€/MWh)	W- PPA electricity base price (€/MWh)	Natural gas final price (€/MWh)	Grid carbon intensity (tons CO_2/MWh)	ETS (€/ton CO_2)
1	2x ETS	60.19	500	2	1	36	50	42.48	0.112	220
2	3x ETS	60.19	500	2	1	36	50	42.48	0.112	330
3	4x ETS	60.19	500	2	1	36	50	42.48	0.112	440
4	3x ETS + 2022 GM	60.19	500	2	1	36	50	131.22	0.112	330
5	3x ETS + 0.9x PPA	60.19	500	2	1	32.4	45	42.48	0.112	330
6	3x ETS + 0.8x PPA	60.19	500	2	1	28.8	40	42.48	0.112	330
7	3x ETS + 1.5x PPA size	60.19	500	3	1.5	36	50	42.48	0.112	330
8	3x ETS + 1.5x ELY size	60.19	750	2	1	36	50	42.48	0.112	330

Table 3 – Model's parametrisation per asset/process.

Asset	Size	Operation and flexibility parameters	Conversion/Efficiency rates (referenced to the asset's output)
PPA	1 + 2 GW	4 × 0.25 GW W-PPA and 2 × 1 GW PV-PPA. Grid access is limited to 1 GW	N.A.
SMR	9.37 tons/h	CD = 30 h, MPL = 30%, MRU/MRD = 10%	$\gamma_{H2O} = 32.2$, $\gamma_{elect} = 1.2$, $\gamma_{CO2} = 9.21$ $\gamma_{CH4} = 3.5$
ELY	500 MW	MPL = 20%	$\gamma_{H2} = 54$, $\gamma_{H2O} = 9$
HS	50 tons	$SOC_{t=0} = 10\%, SOC_{min} = 10\%, SOC_{max} = 100\%$	N.A.
HB	52.5 tons/h	CD = 36 h, MPL = 30%, MRU/MRD = 20%	$\gamma_{H2} = 0.1778$, $\gamma_{elect} = 1.2$
AS	15,000 tons	$SOC_{t=0} = 10\%, SOC_{min} = 10\%, SOC_{max} = 100\%$	N.A.

Table 4 – Overview of EU taxonomies applying to hydrogen's carbon intensity.

	EU-ETS Benchmark	EU Taxonomy	CertifHy	RED II
Hydrogen ($kg\ CO_2/kg\ H_2$)	8.85	5.8	4.4	3.38
Ammonia ($kg\ CO_2/kg\ NH_3$)	1.57	1.03	78	0.6

pathway. SMR + ELY only registered a 0.3% share of hydrogen produced via water electrolysis. At the same time, the addition of the PAP PPA did not affect the dispatch, leading to a negative RCOA value from the exported electricity revenues – the SMR was still more profitable than producing hydrogen via electrolysis. Then, regarding the ELY-only cases, the full grid-connected case provided a cost 450% higher than the SMR, only reduced to 246% higher with the integration of the PPA. The total electrical consumption for the grid-connected ELY-only case was 4320 GWh, which is reduced to 1382 GWh with the integration of the PPA. However, only 57.68% of the total energy produced in the PAP PPA was used in the electrolysis, mostly due to the excess of PV production during the central hours of the day, representing two-thirds of the energy sold to the grid.

In the case of 2022, the higher gas prices highly impacted the RCOA of the SMR, showing a cost increase of 142% for the reference case compared to 2018. The higher energy prices also explain why the combination of SMR and PPA also led to revenues from the electricity exports that totally eclipsed the

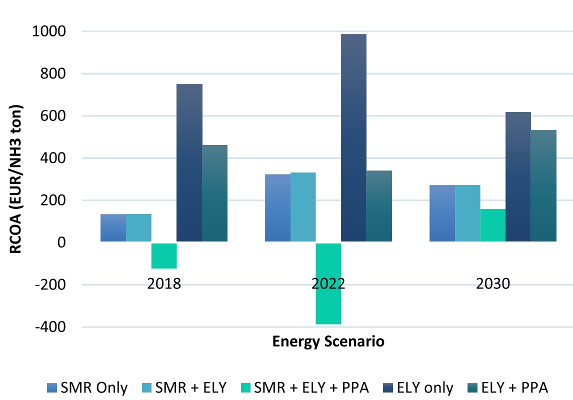

Fig. 4 – RCOA results for 2018, 2022 and 2030. Legend: SMR (Steam Methane Reformer), ELY (Electrolyser), PPA (Power Purchase Agreement), RCOA (Relative Cost Of Ammonia), NH3 (Ammonia).

cost of the SMR, which yet again covered 100% of the hydrogen demand. Then, the grid-connected scenario experienced a 0.31% increase in price compared to 2018, showing that electrolysis-produced hydrogen, although still more expensive, is at least more resilient versus the volatility of the GM experienced in 2022. Therefore, the only real cost reduction versus 2018 was achieved in the ELY + PPA case, which was only 0.5% more costly than the SMR-only option in the same conditions.

The results for 2030's scenario showed a lower discrepancy in the overall RCOA values. Despite the increase in the ETS pricing, the impact of the reduced gas prices kept the SMR-produced hydrogen at a 15% lower cost than the 2022's scenario. The competitiveness of grid-connected was highly increased by benefitting from more stable electricity prices – still more than twice as expensive as SMR. The parity level between the PPA and EM pricing explains the smaller difference between the grid-connected and PPA-connected ELY cases.

This first analysis outlines two important aspects: SMR was found unbeatable under past and business-as-usual future energy and emissions market circumstances. Advantageous PPA financial structures are key to reducing the cost differential between non-renewable and renewable hydrogen/ammonia.

Then, as explained in the Methodology, the second sensitivity analysis focused on the SMR + ELY + PPA case, in which previous results were highly deviated due to the whole demand of hydrogen being covered by the SMR, which simultaneously led to additional revenues coming from the unused PAP PPA. Consequently, the ETS pricing, PPA, and ELY sizing were addressed to identify the external factors leading to increasing the share of renewably-produced hydrogen. The results are shown in Fig. 5.

The gradual increase of the ETS pricing was related to higher RCOA results, as the system quits its reliance on natural gas with higher penetration of RES via PPA and the electricity grid. Starting with the 100% increase in ETS pricing, the ELY increased its share from 0.1% in the base reference case, to 4%. Eventually, this value gets closer to the 531 EUR/ton optimal value for the ELY + PPA case: 459 EUR/ton for the 200% increase and 501 EUR/ton for the 300% increase cases. Showing that the ETS value required for total phasing out SMR with water electrolysis would be around 550 EUR/ton CO_2.

The dispatching results from the last two scenarios showed the impact of sizing the PPA and ELY regarding the RCOA. A bigger ELY and/or PPA sizing reduces the dependency on non-renewable hydrogen and the electric grid, allowing it to produce the same or more hydrogen in fewer hours – when RES are available. However, this incurs higher investment

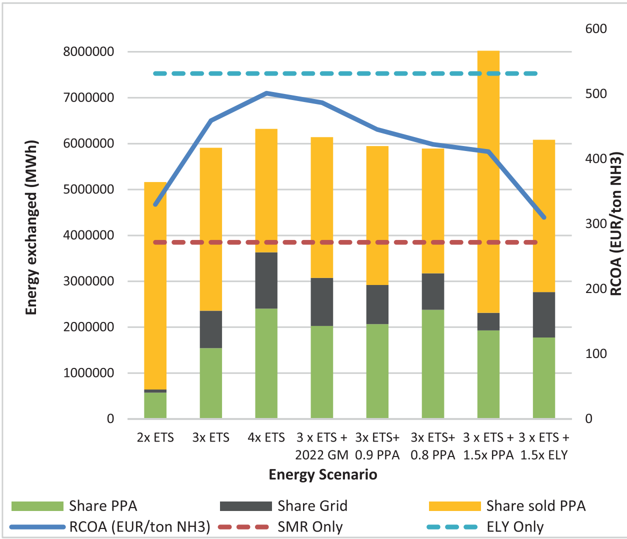

Fig. 5 – RCOA results from the sensitivity analysis on scenario 2030c - SMR + ELY + PPA. Legend: SMR (Steam Methane Reformer), ELY (Electrolyser), PPA (Power Purchase Agreement), RCOA (Relative Cost Of Ammonia), NH3 (Ammonia).

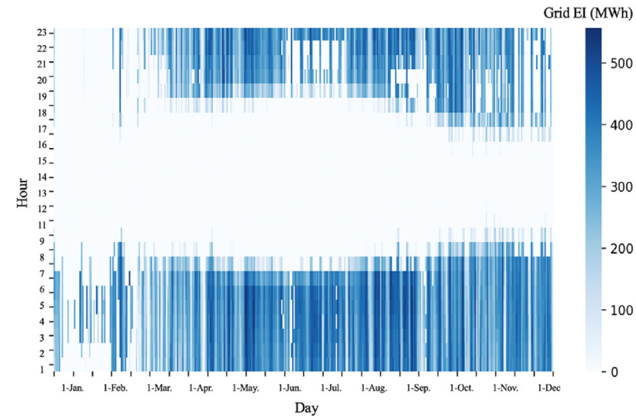

Fig. 7 – Daily variation over a year of the grid Energy Imports in MWh. Legend: EI (Energy Import).

costs that, even though they are not considered in this study, heavily impact the profitability of this kind of project. Particularly interesting is the case of the "1.5xELY" case, which, if compared to its "3x ETS" reference, has a notably higher share of PPA, bringing the RCOA almost down to the SMR-only reference of 271.7 EUR/ton.

Another important result showed that even though electrolytic hydrogen production heavily relied on the PPA's pricing and sizing, grid connection proved important in increasing the plant's load factor during low or non-PPA import hours - shown through the nearly perfect matching in the comparison through Figs. 6 and 7.

4.2. *Techno-environmental assessment*

The ammonia's production carbon intensity results were also analysed for the two sensitivity analyses. The carbon intensity of the ammonia was calculated based on the carbon intensity of the hydrogen consumed during its production. Then, it was compared to various reference values provided by different authorities: EU-ETS benchmark, EU, taxonomy, RED II and CertifHY – which have been converted to the equivalent ammonia footprint as per Table 4.

In Fig. 8, the results of the first sensitivity analysis showed that none of the carbon intensity values obtained for any of the SMR production pathways falls into the category of renewable hydrogen. Meanwhile, the 2018 ELY-only scenario shows how polluting it could be to produce hydrogen directly from the grid if insufficient RES penetration exists. However, grid-connected electrolysis can also become beneficial - higher renewable penetration in the energy mix expected by 2030 could potentially lead to grid-

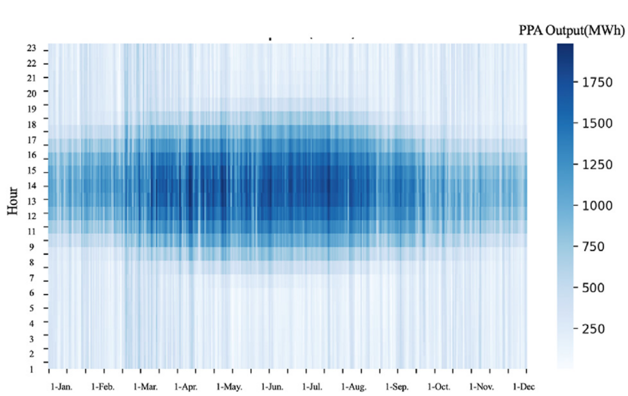

Fig. 6 – Daily variation over a year of the PPA production in MWh. Legend: PPA (Power Purchase Agreement).

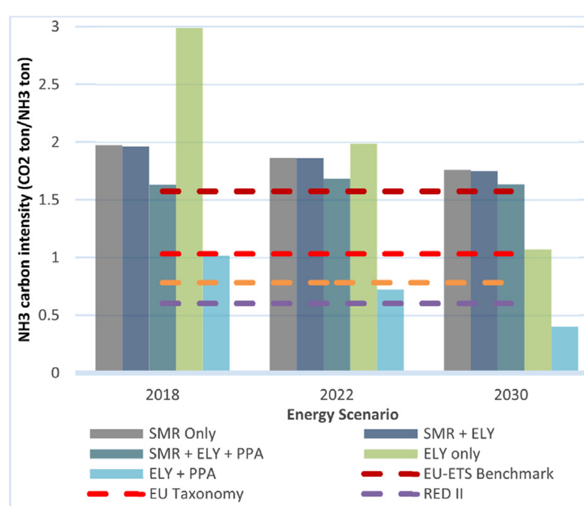

Fig. 8 – RCOA results for 2018, 2022 and 2030. Legend: SMR (Steam Methane Reformer), ELY (Electrolyser), PPA (Power Purchase Agreement), NH3 (Ammonia), CO2 (Carbon Dioxide).

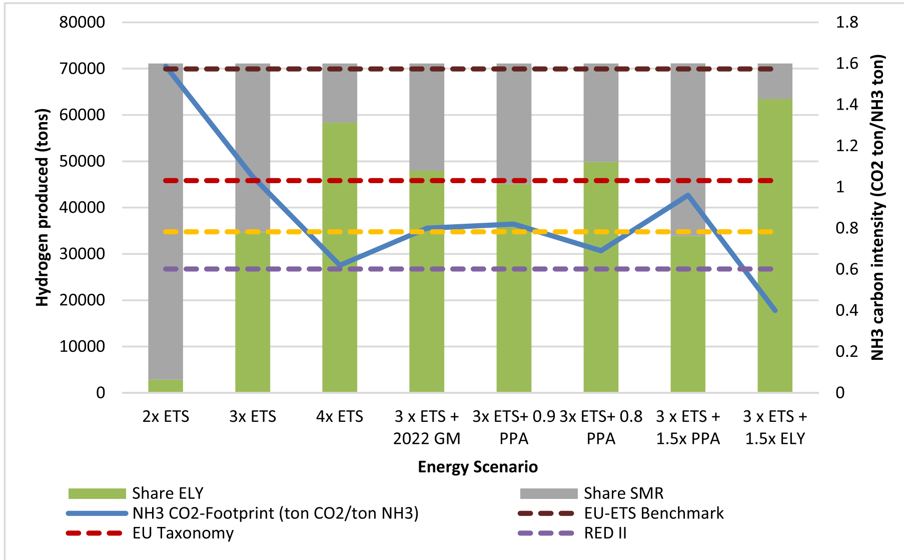

Fig. 9 – RCOA results for 2018, 2022 and 2030. Legend: SMR (Steam Methane Reformer), ELY (Electrolyser), PPA (Power Purchase Agreement), GM (Gas Market), NH3 (Ammonia) CO2 (Carbon Dioxide), EU (European Union), ETS (Emission Trading System), RED II (Renewable Energy Directive). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

only hydrogen being considered renewable within the EU-ETS benchmark. For renewable hydrogen to be considered as so by the most recent and demanding criteria, the RED II, only the ELY + PPA 2030 scenario could fall into such a category – despite grid imports accounting for 33% of the electricity consumed.

The results of the second sensitivity analysis showed the evolution of the ammonia carbon intensity for the different proposed scenarios, in Fig. 9. These results are again compared to the selected taxonomy references, confirming that at least 10% of participation of the ELY is needed to achieve the consideration of green hydrogen in the EU-ETS Benchmark – which nearly happened in the "2x ETS" scenario. Regarding the RED II criteria, the target is only achieved with an increased 300% ETS or with a bigger ELY size, which disincentives the usage of SMR. Additionally, another particularly interesting result came from the PPA pricing variations. A 10% PPA price reduction shown in the scenario "3x ETS +0.9 PPA", which despite showing only a 3% lower RCOA reduction, enabled a 30% higher share of the ELY production, hence, a 22% carbon intensity reduction. The same tendency was confirmed in the "3x ETS +0.8 PPA) scenario, which fell into the CertifHy threshold.

The results showed how renewable hydrogen could only phase out SMR-sourced hydrogen if carbon emissions are heavily linked to cost. Consequently, the higher the share of ELY in the production of hydrogen, the lower the carbon intensity. However, in order to produce enough renewable hydrogen, water electrolysis plants risk needing to oversize their capacity regardless of PPA pricing or the possibility of operation under a grid connection.

In this regard, the importance of traceability on the carbon intensity of the ammonia/hydrogen is key, and the

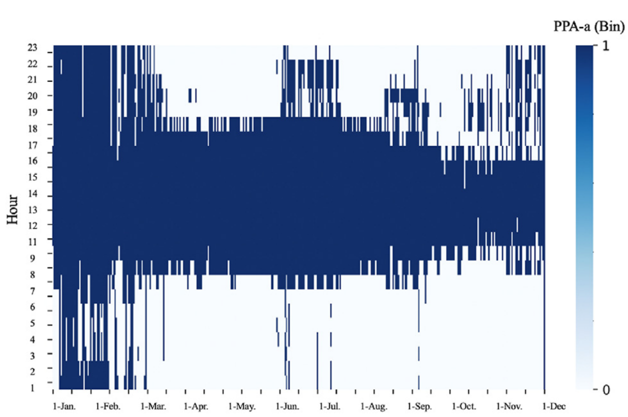

Fig. 10 – Daily variation over a year of the PPA import binary. Legend: PPA (Power Purchase Agreement).

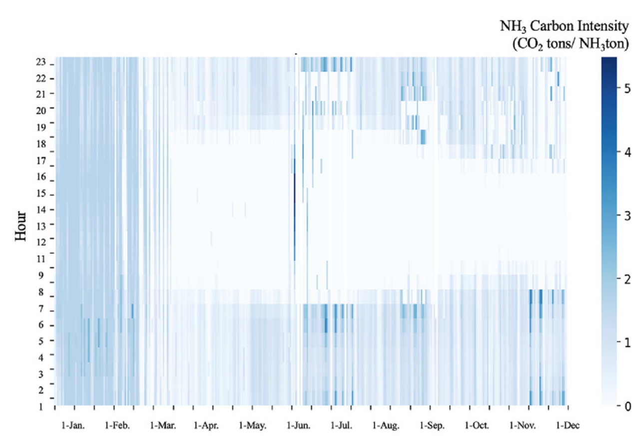

Fig. 11 – Daily variation over a year of the produced ammonia's carbon intensity. Legend: NH3 (Ammonia).

Table 5 – Overview of results for all sensitivity cases.

Energy Scenario	RCOA (EUR/ton NH_3)	Ammonia Carbon intensity (ton CO_2/ton NH_3)	Share ELY (%)	Share SMR (%)
2018a: SMR only	133.14	1.97	0	100
2018b: SMR + ELY	135.8	1.96	0.30	99.70
2018c: SMR + ELY + PPA	−122.9	1.63	0	100
2018d: ELY only	461	1.02	100	0
2018e: ELY + PPA	749	2.99	100	0
2022a: SMR only	322.5	1.86	0	100
2022b: SMR + ELY	331.82	1.86	0.90	99.10
2022c: SMR + ELY + PPA	−387	1.68	0	100
2022d: ELY only	339.88	0.72	100	0
2022e: ELY + PPA	987	1.98	100	0
2030a: SMR only	271.69	1.75	0	100
2030b: SMR + ELY	272.17	1.74	0.90	99.10
2030c: SMR + ELY + PPA	158.53	1.63	0	100
2030d: ELY only	531.35	0.4	100	0
2030e: ELY + PPA	616.88	1.07	100	0
2030c: 2x ETS	330	1.58	3.97	96.03
2030c: 3x ETS	458.79	1.05	48.80	51.20
2030c: 4x ETS	501	0.62	82.04	17.96
2030c: 3 x ETS + 2022 GM	486.59	0.8	67.45	32.55
2030c: 3x ETS+ 0.9 PPA	445.15	0.82	63.40	36.60
2030c: 3x ETS+ 0.8 PPA	422.26	0.69	70.12	29.88
2030c: 3 x ETS + 1.5x PPA	411.07	0.96	47.61	52.39
2030c: 3 x ETS + 1.5x ELY	310	0.4	89.19	10.81

temporal correlation mechanisms have an extremely important impact on the dispatch of the plant. In Figs. 10 and 11, the comparison of the PPA import binary and the hourly carbon intensity of the produced ammonia shows that outside of “PPA hours”, the CO_2 footprint of the ammonia quickly rises above the taxonomy thresholds defined previously. The present paper picked the yearly average for convenience. However, different levels of correlation might apply in the future, such as monthly or even hourly – as defined by the RED II for after 2030 [24].

4.3. *Summary of results*

For clarification, in Table 5, a compilation of the main results comprising RCOA, carbon intensity and dispatch of ELY and SMR, is included for all the scenarios discussed in this paper.

5. Conclusions

The present paper argued the external influence of energy markets, including PPAs and CO_2 emissions taxation mechanisms via the ETS, on the cost-competitiveness of different hydrogen production pathways for ammonia synthesis – SMR and water electrolysis. With that purpose, an OPD model was developed and validated by its application to the case study of a fertiliser plant in the context of the Spanish energy markets and European ETS. The full multi-year techno-economic analysis of the project's viability, comprising CAPEX and OPEX, and life-cycle assessment of the carbon footprint of the equipment were left out of the scope of this paper, and will be focus of future research developments towards the implementation of dynamic modelling. Techniques that take into account the variability of the data input over the assessment year's scope. Nevertheless, the results of the OPD which focused on relative and incremental results that considered the project's cashflows, defined by the RCOA, allowed the comparison of the optimal operation of the energy system under a broad sensitivity analysis that covered more than 20 different energy scenarios. To this end, the co-existence model successfully allowed a flexible and dynamic comparison of the dispatch achieved under the different simulations with the subsequent comparison of KPIs.

Overall, the results showed the key importance of ETS pricing in the penetration of electrolytic hydrogen, especially if the 2030 business-as-usual predictions on electricity, gas and the regulatory framework are to be confirmed. The value of ETS required for water electrolysis to totally phase out SMR was estimated at around 550 EUR/CO_2 ton. Although more expensive, water electrolysis proved to be a more resilient pathway since its price is decoupled from gas market pricing. Ultimately, the consumption of RES in hydrogen production will need regulatory interventions to achieve cost-competitiveness against traditional SMRs. In this regard, even though future trends announced low electricity prices and higher RES penetration in the energy grid, and while the inclusion of the PPA proved to be essential, the grid-connection option must be studied as a possibility to increase the operating hours of the electrolyser over the year. The electricity imported from the grid represented between 25 and 35% of the total electricity input in most of the optimal scenarios studied. Nevertheless, the latest RED II from early 2023, considered a reference for the taxonomy of renewable hydrogen in the techno-environmental assessment, aims to strengthen the conditions for the electric supply of electrolytic hydrogen production. The different criteria applying: additionality (need for PPA), temporal correlation (carbon intensity tracking) and geographical correlation (same biding zone), were addressed in the present study but not explored in-depth. Particularly the effects of hourly correlation, which although assessed were not included as a limiting constraint in the dispatch of the energy system.

Hence, the results showed that Spain does have the RES potential for the development of PtA. However, in order to achieve a cost-effective deployment that does not oversize electrolysis plants or PPA contracts, the regulatory framework must push in the right direction if the cost differential versus traditional SMR needs to be overcome. As stated by multiple literature, and confirmed in this paper, electricity price, or in this case PPA price is the most determinant factor in the final price of the renewable-hydrogen. However, being a PV-predominated country, it is important to remark the need for balanced PPA portfolios that allow for hydrogen production out of the central hours of the day. Similarly, the possibility of integrating Battery Energy Storage Systems (BESS) needs to be considered as a means to cope with the daily variability of RES, avoiding to rely on electricity grid overnight, when its carbon intensity is higher. Accordingly a more complex modelling of the assets regarding self-discharge and non-linear efficiencies will be studied as potential future research line towards the improvement of the model. Finally, we can conclude that considering different energy scenarios, multi-year dynamic trends in the energy markets and the correlation of the carbon intensity traceability will be essential in the optimal sizing of the PtG systems and the PPA structure, which constitutes a critical point for correctly assessing the techno-economic viability of projects.

Declaration of competing interest

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

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REFERENCES

[1] Fuel cells and hydrogen joint undertaking (FCH). Hydrogen Roadmap Europe 2019. https://doi.org/10.2843/249013.

[2] European Commission. REPowerEU: a plan to rapidly reduce dependence on Russian fossil fuels and fast forward the green transition. May, 2022.

[3] European Commission. A hydrogen strategy for a climate neutral Europe #EUGreenDeal. 2020 [Online]. Available: https://ec.europa.eu/commission/presscorner/detail/en/fs_20_1296. [Accessed 14 April 2023].

[4] BloombergNEF. Liebreich: separating hype from hydrogen – Part Two: the demand side. 2020. https://about.bnef.com/blog/liebreich-separating-hype-from-hydrogen-part-two-the-demand-side/. [Accessed 14 April 2023].

[5] International Energy Agency, "Ammonia Technology Roadmap towards more sustainable nitrogen fertiliser production." [Online]. Available: www.iea.org/t&c/.

[6] Clean hydrogen Partnership. Clean hydrogen monitor 2020. 2020.

[7] Liu H. Ammonia synthesis catalyst 100 years: practice, enlightenment and challenge. Cuihua Xuebao/Chinese Journal of Catalysis Oct. 20, 2014;35(10):1619–40. https://doi.org/10.1016/S1872-2067(14)60118-2. Science Press.

[8] Dechany A, Van Geem K, Proost J. Process implications of electrifying ammonia production. In: Current opinion in chemical engineering, vol. 40. Elsevier Ltd; Jun. 01, 2023. https://doi.org/10.1016/j.coche.2023.100915.

[9] Pruvost F, Cloete S, Arnaiz del Pozo C, Zaabout A. Blue, green, and turquoise pathways for minimizing hydrogen production costs from steam methane reforming with CO2 capture. Energy Convers Manag Dec. 2022;274. https://doi.org/10.1016/j.enconman.2022.116458.

[10] Al-Qahtani A, Parkinson B, Hellgardt K, Shah N, Guillen-Gosalbez G. Uncovering the true cost of hydrogen production routes using life cycle monetisation. Appl Energy Jan. 2021;281. https://doi.org/10.1016/j.apenergy.2020.115958.

[11] Rosa L, Mazzotti M. Potential for hydrogen production from sustainable biomass with carbon capture and storage. Renew Sustain Energy Rev Apr. 2022;157. https://doi.org/10.1016/j.rser.2022.112123.

[12] George JF, Müller VP, Winkler J, Ragwitz M. Is blue hydrogen a bridging technology? - the limits of a CO2 price and the role of state-induced price components for green hydrogen production in Germany. Energy Pol Aug. 2022;167. https://doi.org/10.1016/j.enpol.2022.113072.

[13] Liu E, Lu X, Wang D. A systematic review of carbon capture, utilization and storage: status, progress and challenges. Energies Mar. 01, 2023;16(6). https://doi.org/10.3390/en16062865. MDPI.

[14] Spatolisano E, Pellegrini LA. Haber-Bosch process intensification: a first step towards small-scale distributed ammonia production. Chem Eng Res Des Jul. 2023;195:651–61. https://doi.org/10.1016/j.cherd.2023.06.031.

[15] Faria JA. Renaissance of ammonia synthesis for sustainable production of energy and fertilizers. In: Current opinion in green and sustainable chemistry, vol. 29. Elsevier B.V.; Jun. 01, 2021. https://doi.org/10.1016/j.cogsc.2021.100466.

[16] Kyriakou V, Garagounis I, Vourros A, Vasileiou E, Stoukides M. An electrochemical haber-bosch process. Joule Jan. 2020;4(1):142–58. https://doi.org/10.1016/j.joule.2019.10.006.

[17] Blanco H, Jinks B, Bianco E, Sezer U. Innovation Outlook renewable ammonia (IRENA). 2022 [Online]. Available: www.irena.org.

[18] Sánchez A, Martín M. Optimal renewable production of ammonia from water and air. J Clean Prod 2018;178:325–42. https://doi.org/10.1016/j.jclepro.2017.12.279.

[19] Zhang H, Wang L, Van herle J, Maréchal F, Desideri U. Techno-economic comparison of green ammonia production processes. Appl Energy 2020;259(October 2019):114135. https://doi.org/10.1016/j.apenergy.2019.114135.

[20] Osman O, Sgouridis S, Sleptchenko A. Scaling the production of renewable ammonia: a techno-economic optimization applied in regions with high insolation. J Clean Prod 2020;271:121627. https://doi.org/10.1016/j.jclepro.2020.121627.

[21] Wang C, Walsh SDC, Longden T, Palmer G, Lutalo I, Dargaville R. Optimising renewable generation configurations of off-grid green ammonia production systems considering Haber-Bosch flexibility. Energy Convers

Manag Mar. 2023;280:116790. https://doi.org/10.1016/j.enconman.2023.116790.
[22] Ikäheimo J, Kiviluoma J, Weiss R, Holttinen H. Power-to-ammonia in future North European 100 % renewable power and heat system. Int J Hydrogen Energy 2018;43(36):17295–308. https://doi.org/10.1016/j.ijhydene.2018.06.121.
[23] Skov IR, Schneider N. Incentive structures for power-to-X and e-fuel pathways for transport in EU and member states. Energy Pol Sep. 2022;168:113121. https://doi.org/10.1016/j.enpol.2022.113121.
[24] Hydrogen Europe. Impact assessment of the RED II delegated acts on RFNBO and GHG accounting. 2023.
[25] Fragiacomo P, Genovese M. Technical-economic analysis of a hydrogen production facility for power-to-gas and hydrogen mobility under different renewable sources in Southern Italy. Energy Convers Manag 2020;223(August):113332. https://doi.org/10.1016/j.enconman.2020.113332.
[26] IRENA. Green hydrogen cost reduction. 2020 [Online]. Available:/publications/2020/Dec/Green-hydrogen-cost-reduction%0A, https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2020/Dec/IRENA_Green_hydrogen_cost_2020.pdf.
[27] Martinez Alonso A, Costa D, Messagie M, Coosemans T. Techno-economic assessment on hybrid energy storage systems comprising hydrogen and batteries: a case study in Belgium. Int J Hydrogen Energy 2023. https://doi.org/10.1016/j.ijhydene.2023.06.282.
[28] Hazrat MA, Rasul MG, Jahirul MI, Chowdhury AA, Hassan NMS. Techno-economic analysis of recently improved hydrogen production pathway and infrastructure. Energy Rep Dec. 2022;8:836–44. https://doi.org/10.1016/j.egyr.2022.12.148.
[29] Katebah M, Al-Rawashdeh M, Linke P. Analysis of hydrogen production costs in Steam-Methane Reforming considering integration with electrolysis and CO2 capture. Clean Eng Technol Oct. 2022;10. https://doi.org/10.1016/j.clet.2022.100552.
[30] Ji M, Wang J. Review and comparison of various hydrogen production methods based on costs and life cycle impact assessment indicators. Int J Hydrogen Energy Nov. 11, 2021;46(78):38612–35. https://doi.org/10.1016/j.ijhydene.2021.09.142. Elsevier Ltd.
[31] Lim J, Joo C, Lee J, Cho H, Kim J. Novel carbon-neutral hydrogen production process of steam methane reforming integrated with desalination wastewater-based CO2 utilization. Desalination 2023;548(Feb). https://doi.org/10.1016/j.desal.2022.116284.
[32] Dincer I, Acar C. Review and evaluation of hydrogen production methods for better sustainability. Int J Hydrogen Energy Aug. 2014;40(34):11094–111. https://doi.org/10.1016/j.ijhydene.2014.12.035.
[33] Nowicki DA, Agnew GD, Irvine JTS. Green ammonia production via the integration of a solid oxide electrolyser and a Haber-Bosch loop with a series of solid electrolyte oxygen pumps. Energy Convers Manag Mar. 2023;280. https://doi.org/10.1016/j.enconman.2023.116816.
[34] Durakovic G, del Granado PC, Tomasgard A. Are green and blue hydrogen competitive or complementary? Insights from a decarbonized european power system analysis. Energy Nov. 2023:128282. https://doi.org/10.1016/j.energy.2023.128282.
[35] Jurasz J, Canales FA, Kies A, Guezgouz M, Beluco A. A review on the complementarity of renewable energy sources: concept, metrics, application and future research directions. In: Solar energy, vol. 195. Elsevier Ltd; Jan. 01, 2020. p. 703–24. https://doi.org/10.1016/j.solener.2019.11.087.
[36] Guan T, Lin H, Sun Q, Wennersten R. Optimal configuration and operation of multi-energy complementary distributed energy systems. In: Energy procedia. Elsevier Ltd; 2018. p. 77–82. https://doi.org/10.1016/j.egypro.2018.09.062.
[37] Zhao W, Bao X, Yuan G, Wang X, Bao H. The equilibrium model for the coexistence of renewable portfolio standards and emissions trading: the supply chain analysis. Energies Jan. 2019;12(3). https://doi.org/10.3390/en12030439.
[38] Abdelghany MB, Shehzad MF, Liuzza D, Mariani V, Glielmo L. Optimal operations for hydrogen-based energy storage systems in wind farms via model predictive control. Int J Hydrogen Energy 2021;46(57):29297–313. https://doi.org/10.1016/j.ijhydene.2021.01.064.
[39] Martinez Alonso A, Matute G, Yusta JM, Coosemans T. Multi-state optimal power dispatch model for power-to-power systems in off-grid hybrid energy systems: a case study in Spain. Int J Hydrogen Energy Jun. 2023. https://doi.org/10.1016/j.ijhydene.2023.06.019.
[40] Mukelabai MD, Gillard JM, Patchigolla K. A novel integration of a green power-to-ammonia to power system: reversible solid oxide fuel cell for hydrogen and power production coupled with an ammonia synthesis unit. Int J Hydrogen Energy May 2021;46(35):18546–56. https://doi.org/10.1016/J.IJHYDENE.2021.02.218.
[41] Cheema II, Krewer U. Operating envelope of Haber-Bosch process design for power-to-ammonia. RSC Adv 2018;8(61):34926–36. https://doi.org/10.1039/c8ra06821f.
[42] Palys MJ, McCormick A, Cussler EL, Daoutidis P. Modeling and optimal design of absorbent enhanced ammonia synthesis. Processes Jul. 2018;6(7). https://doi.org/10.3390/PR6070091.
[43] Schulte Beerbühl S, Fröhling M, Schultmann F. Combined scheduling and capacity planning of electricity-based ammonia production to integrate renewable energies. Eur J Oper Res Mar. 2015;241(3):851–62. https://doi.org/10.1016/J.EJOR.2014.08.039.
[44] Armijo J, Philibert C. Flexible production of green hydrogen and ammonia from variable solar and wind energy: case study of Chile and Argentina. Int J Hydrogen Energy Jan. 2020;45(3):1541–58. https://doi.org/10.1016/j.ijhydene.2019.11.028.
[45] Yu Z, et al. Optimal sizing and pricing of grid-connected renewable power to ammonia systems considering the limited flexibility of ammonia synthesis. IEEE Trans Power Syst 2023:1–18. https://doi.org/10.1109/TPWRS.2023.3279130.
[46] Matute G, Yusta JM, Beyza J, Correas LC. Multi-state techno-economic model for optimal dispatch of grid connected hydrogen electrolysis systems operating under dynamic conditions. Int J Hydrogen Energy 2021;46(2):1449–60. https://doi.org/10.1016/j.ijhydene.2020.10.019.
[47] Production centres of the grupo Fertiberia." https://www.grupofertiberia.com/en/structure/production-centres/ (accessed May 16, 2023).
[48] Delbeke J, Runge-Metzger A, Slingenberg Y, Werksman J. The paris agreement. Towards a Climate-Neutral Europe: Curbing the Trend 2019:24–45. https://doi.org/10.4324/9789276082569-2.
[49] Plan nacional integrado de Energía y Clima (PNIEC) 2021-2030." https://www.miteco.gob.es/es/prensa/pniec.aspx (accessed May 22, 2023).
[50] OMIE - Spanish Electricity Market Operator, "File access | OMIE." https://www.omie.es/en/file-access-list (accessed May 16, 2023).
[51] Red Eléctrica de España, "REData - todate." https://www.ree.es/en/datos/todate (accessed May 16, 2023).
[52] Omip." https://www.omip.pt/en (accessed May 16, 2023).

[53] LevelTen PPA price index.” https://www.leveltenenergy.com/ppa (accessed May 22, 2023).

[54] MIBGAS - Iberian Gas Market Operator, “MIBGAS daily prices.” https://www.mibgas.es/en/market-results (accessed May 16, 2023).

[55] Electricity Maps | Live 24/7 CO_2 emissions of electricity consumption.” https://app.electricitymaps.com/map (accessed May 22, 2023).

[56] European union allowance (EUA) yearly futures historical prices - investing.com.” https://www.investing.com/commodities/european-union-allowance-eua-year-futures-historical-data (accessed May 16, 2023).

[57] European energy Exchange AG (EEX).” https://www.eex.com/en/(accessed May 22, 2023).

[58] Copernicus. European Union's Earth observation Programme. 2021.

[59] Asociacion Española de Abastecimiento de Aguas y Saneamiento. Precios y costes de los Servicios del Agua en España. 2023. https://www.aeas.es/.

[60] European Commission. Update of benchmark values for the years 2021-2025 of phase 4 of the EU ETS. 2021.

[61] European Commission. Delegated regulation (EU) 2020/852,. 2021.

[62] European Commission. Delegated regulation on Union methodology for RFNBOs. 2023. https://energy.ec.europa.eu/delegated-regulation-union-methodology-rfnbos_en. [Accessed 7 March 2023].