GREEN AMMONIA SYNTHESIS IN A MULTI-RES SYSTEM

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ABSTRACT

Green ammonia is a promising hydrogen carrier and an excellent candidate for the decarbonization of the transport sector. Despite the synthesis process (Haber Bosch, HB) being well known and widely applied in conventional natural gas-fed plants, much effort is required for the coupling with Variable Renewable Energy Sources (V-RES). V-RES intermittency does not meet the limited partial load transient capability of the conventional ammonia process unless large electricity and thermal storage are installed. For that, V-RES may be complemented with biomass-based processes, to have multiple sources of hydrogen supply for the constant-load HB synthesis. This study investigates a multi-RES system for green ammonia production, combining solar-powered high-temperature electrolysis and lignocellulosic oxy-steam gasification. The co-existence of the two processes for hydrogen production allows minimum variations of the HB load, backup hydrogen production, improved thermal integration and the reduction of VRES generator size. The proposed system is investigated with a thermochemical 0D modelling approach, and the discussion of simulation results is based on the 3E (energy-economic-environment) indicators set. The Specific Energy consumption falls in the range of 8.76-10.65 MWh/ton$_{NH3}$, the Levelized cost of Ammonia is approximately 970-1230 €/ton$_{NH3}$ based on current costs of technology and raw feeding materials, and the CO_2 reduction ranges from -65% to 100% (totally green ammonia) while the raw water withdrawal index is on average 3.27 ton$_{H2O}$/ton$_{NH3}$.

1 INTRODUCTION

Ammonia is one of the most widely used chemicals in the process industry, and about 70% is used for fertiliser production. In 2020, the ammonia sector required 8.6 EJ (2% of total global energy consumption), associated with noteworthy CO_2 emissions, 5% of the global total *(IED, 2023)*. In the EU's RED II target *(REDII, 2018)*, Renewable Fuels of Non-Biological Origin (RFNBOs), such as ammonia, and e-fuels, play a key role in the decarbonisation of the transport sector, especially for heavy-duty applications *(EEA, 2021) (IMO, 2023*). Ammonia is claimed as an alternative to fossil fuels, due to its high energy density (18.65 MJ/kg.), ease of storage in liquid form and an already established supply chain. Based on this scenario, ammonia production will increase by almost 40% by 2050 *(IEA, Ammonia Technology Roadmap, 2021).* Today, ammonia is produced industrially via the Haber-Bosch (HB) process. Depending on the technology and the primary energy source ammonia is categorized into: *brown ammonia*, synthesised with hydrogen produced from fossil fuels (typically natural gas decomposition via steam reforming - SMR), *blue ammonia*, synthesised with hydrogen produced from fossil fuels with Carbon Capture and Storage (CCS), and *green ammonia*, synthesised with hydrogen produced from renewable sources (RES) *(Rouwenhorst & Reindert, 2020)*. In 2020 72% of ammonia production worldwide relied on steam reforming of natural gas, 26% on coal gasification, about 1% on petroleum products and, only 1% on electrolysis. Despite the current low rate of implementation, the most promising technology for green hydrogen is water electrolysis, coupled to solar or wind energy. In the Net Zero Emissions (NZE) scenario it is estimated that the electrolyzers installed capacity will grow from 690 MW today, to 550 GW by 2030 worldwide *(IEA, Global Hydrogen Review, 2021*). Moreover, there is a growing, interest in biomass to produce H_2-rich syngas through gasification and co-gasification processes *(Ghodke et al., 2023).*

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1.1 Ammonia Synthesis: state of the art

The Haber-Bosch process is based on the fundamental synthesis reaction $3\ H_2 + N_2 \leftrightarrow 2NH_3$, ΔH_0=-91.8 kJ /mol, which is mediated by an iron catalyst, typically between 400-650°C and 100-400 bar. The activity of the iron catalyst may be reduced due to pollutants *(Frattini, et al. 2016) (Yara Italia Spa),* namely H_2S (max 1 ppm_v), H_2O (max 5 ppm_v), CO and CO_2 (max combined 10 ppm_v).

1.1.1 Hydrogen supply from renewable sources: The key point to make ammonia production green stands in hydrogen production. Whilst conventional plant still relies on fossil primary sources (steam methane reforming), the utilization of renewable feedstocks is encouraged. For the so-called green hydrogen, there are two major pathways: *i)* biological hydrogen via thermochemical or biochemical processes, *ii)* electrolytic production using renewable electricity.
Among thermochemical pathways, gasification offers a robust alternative to convert a solid fuel into a gaseous product, called syngas (a mixture of H_2 and CO), in the presence of a gasifying agent (atmospheric air, steam or oxygen) which partially oxidizes biomass. To increase the hydrogen yield of the gasification process, steam and oxygen are preferred. Gasification normally occurs in either fixed bed or fluidized bed reactors between 800-1000 °C *(Song, et al., 2022)*. The syngas produced has an average composition that depends on the feedstock, however typically syngas composition is 30-40% carbon monoxide (CO), 25-35% hydrogen (H_2), 0-5% methane (CH_4), 10-25% carbon dioxide (CO_2), with minor/trace contaminants load (H_2S and tars). Since hydrogen quality is a critical issue for ammonia synthesis, gas post-processing and clean-up before feeding the make-up gas stream to the HB reactor is mandatory. For CO removal, the Water Gas Shift (WGS $CO+H_2O \rightarrow H_2+CO_2$) reaction is used. WGS takes place between 350-450 °C in the presence of a catalyst to promote the conversion of CO into CO_2 and H_2. The removal efficiency reaches about 95% depending on temperature and requires extra water feeding *(Ryu et al, 2010)*. The most common system for CO_2 and H_2S removal is chemical adsorption with amines, with a removal efficiency of up to 95% at around 20-50 °C. Alternatively, hydrogen can be produced by electrolysis using renewable electricity, Among the available technologies, Solid Oxide Electrolysis (SOE) is featured by a higher efficiency range, up to 95-97% depending on the voltage at which the cell operates. SOE operate between 650-850°C and 1-10 bar. This technology requires high thermal energy, so it perfectly integrates with high-temperature processes where a large amount of waste heat is available *(Amores et al, 2021)*.

1.1.2 Nitrogen supply: For nitrogen supply complying with the HB synthesis requirements, the most common technology is the Cryogenic Air Separation Unit (ASU), accounting for over 90% of the world's nitrogen production. The air is cooled until water, CO_2 and oxygen are condensed (-182.9 °C, 1 bar) and progressively removed until a stream of high-purity gaseous nitrogen (99.999%) is obtained. The energy consumption of the technology is around 0.1 kWh/kg_{N2} *(Hamayun et al, 2020)*. Whilst this process shows reasonable specific energy consumption and excellent gas separation performances, partial load and transient operation are critical for severe negative temperature gradients. In the coupling of the ammonia loop with a gasification plant, nitrogen can be supplied as a fraction of syngas, in the event of basic air gasification *(Frattini, et al. 2016)*. If oxygen/steam are the preferred gasification agents to increase the hydrogen yield of the gasifier, the nitrogen sub-flow hardly meets the stoichiometric requirements of the HB process.

1.2 Scope of the research

The objective of this work is to analyse a new system design to produce green ammonia, involving the integration of a multi-RES-fuelled system for hydrogen production. Namely, hydrogen is produced with a combination of solid oxide electrolysis and lignocellulosic biomass gasification. The synergy between the two technologies allows internal re-use of oxygen, a valuable by-product issued from the SOE and recirculated to the fluidized bed gasifier to increase the hydrogen yield. Moreover, the integration of the two technologies allows the downsizing of each unit and improved hydrogen production management to cope with the intermittency of the primary power source (i.e., sun) driving electrolysis. Thermochemical analysis of the plant is performed to analyse the novel system under two implementation scenarios: (*i*) *ON-GRID,* with electricity withdrawal from the national grid whether the auxiliary Photovoltaic generator does not meet the electrical load of the SOE, (*ii*) 100% *OFF-GRID*.

2 METHODOLOGY

2.1 Modelling approach and assumptions

The system flowsheet is modelled and analysed by the commercial software ASPEN Plus V10, under zero-dimensional and steady-state chemical equilibrium assumptions. The thermodynamic properties library used for the calculation is the PENG-ROB set. Any substance that does not belong to default categories is defined as either an *unconventional component* (see Biomass and Ash), or a *conventional solid component* (Char). Therefore, HCOALGEN and DCOALIGT models are used to define the properties of the unconventional components in terms of Proximate Analysis, Ultimate Analysis, and Low Heating Value (LHV) - see Table 1. For all material streams within the system, the MIXCINC flow class is selected. Pressure drops are neglected for a preliminary analysis of the concept proposed.

Table 1: Proximate. Ultimate and LHV analysis of lignocellulosic biomass *(Sarabhorn, et al., 2023)*.

ULTIMATE ANALYSIS %w, dry basis (db)						**PROXIMATE ANALYSIS %w, wet basis (wb)**				**CALORIFIC ANALYSIS**
Ash	**C**	**H**	**N**	**S**	**O**	**Moisture**	**Fixed Carbon**	**Volatile Matter**	**Ash**	**LHV**
2.60%	46.26%	8.12%	0.13%	0.00%	42.89%	5.92%	74.80%	16.83%	2.45%	19.44 MJ/kg$_{db}$

2.2 Flowsheet description

The system flowsheet is arranged into 5 main sub-models. Fig. 1 depicts the main blocks and i/o material streams. The entire flowsheet has the following input material streams: "Biomass" (to the *Gasifier* block), "Water" (to the electrolysis *SOE,* the *Gasifier* and the *Upgrade* blocks), and "Air" (to the *SOE* and Air Separation Unit *ASU* blocks). The flow rate of all input material streams is determined to meet ammonia throughput specifications set for the primary output material stream "Ammonia" (*HB* block). Nonetheless, the system issues oxygen and CO_2 as by-products, and a roster of residues and waste stream materials (ashes, combustion exhaust gases, depleted water, pollutants – grey dashed lines in Fig.1). Electric power input is highlighted for the two utilities with the higher impact, while thermal management is not discussed afterwards (not represented in Fig.1).

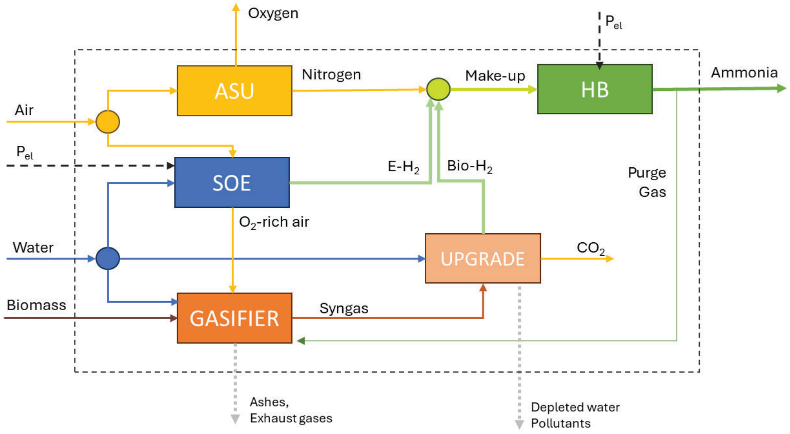

Figure 1: Flowsheet overview and sub-models connection.

In detail, the sub-models are:

- water electrolysis (*SOE* block), modelling an SOE reactor as detailed in the sub-flowsheet shown in Fig.2, referred to a previous model developed and explained by *(Cinti et al, 2016)*. Steam generation is modelled inside this sub-model and achieved with a high rate of internal heat recovery. The outflows are almost pure oxygen and 99.99 % pure hydrogen (*E-H_2*). Water that does not undergo electrolysis in R-1 is condensed in F-1 and recirculated (Fig.2).

- biomass gasification (*Gasifier* block), modelling a fluidized bed gasifier as shown in Fig.3 where the main sections of the gasifier are highlighted (feedstock drying, pyrolysis, gasification). In addition, a post-combustion section using a syngas slip-stream from the gasifier is provided to ensure the auto-thermal condition within the *Gasifier* block and other high-temperature heat sinks within the system.
- syngas upgrading section (*Upgrade* block), modelling the gas post-processing made of WGS, monoethanolamines (MEA) adsorption to remove CO_2, a methanation section to convert the residual CO and CO_2, and a condensation section to remove water - details depicted in Fig.4. This section include a heat recovery steam generator. The main outflow is called *Bio-H_2.*

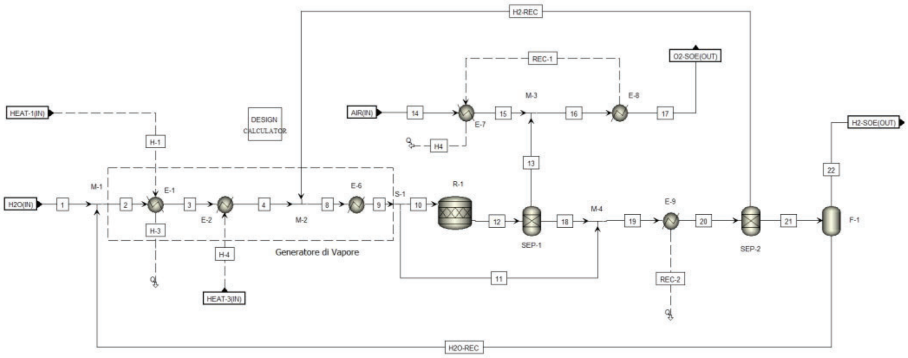

Figure 2: *SOE* block sub-flowsheet.

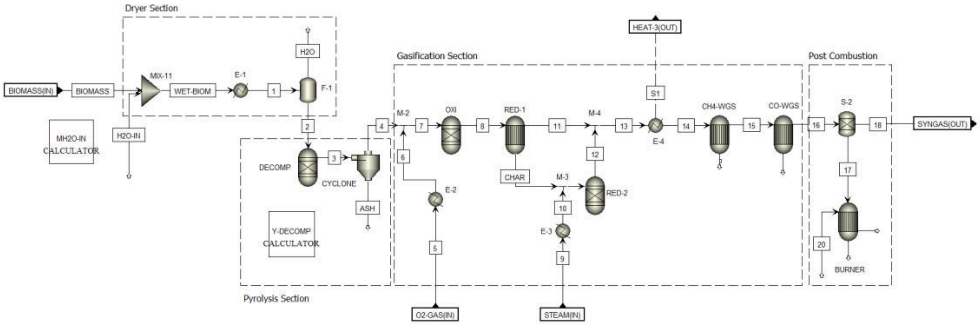

Figure 3: *Gasifier* block sub-flowsheet.

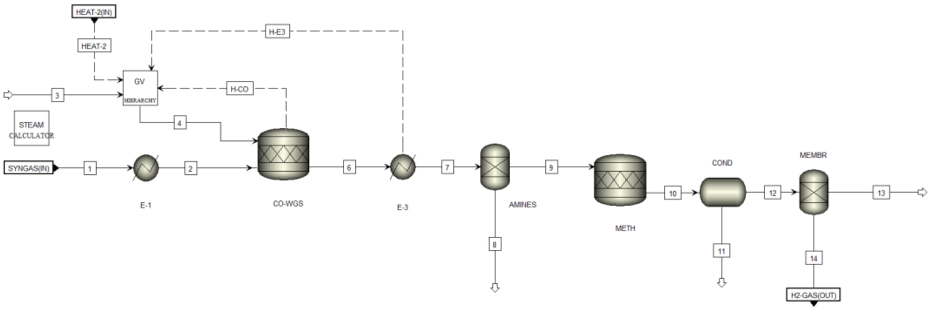

Figure 4: *Upgrade* block sub-flowsheet.

- air separation unit (*ASU* block), modelling a cryogenic process.
- the Haber-Bosch synthesis (*HB* block), based on a simple-loop scheme equipped with a multi-stage inter-cooled compressor as reported in Fig.5. The reference model is inspired by the

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ammonia production plant in Ferrara managed by Yara Spa *(Yara Italia Spa)*. In order to achieve the right stoichiometry at the HB process (H_2:N_2= 3:1), the *O2FEED calculator* adjusts the amount of gasifying agent needed for the gasification (*STEAM* and *O2-GAS*), provided that oxygen is also recovered from the electrolyzer (*O2GAS*, fraction of *O2EL*). Similarly, the calculator block *N2FEED* controls the amount of air to be processed in the *ASU.* The HB products undergo a flash separation to split liquid ammonia from the gas phase, which is partially recirculated back to mid-stage compression. The leftover stream is purged and delivered to the Gasifier afterburner to help the system thermal balance.

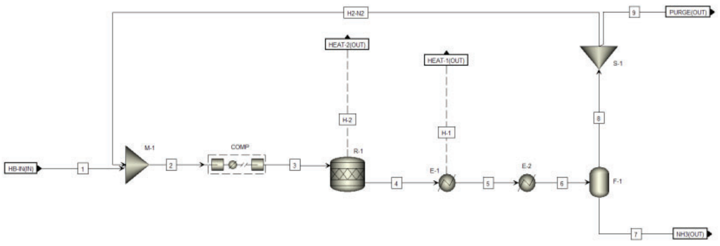

Figure 5: *HB* block sub-flowsheet

2.3 Steady-state set points and design specifications

Table 2 reports the steady-state setpoint for all the fundamental operation units in the flowsheets, namely the *SOE*, the gasifier and the chemical reactor *HB*. Moreover, electrochemical performance related to the *SOE* is set in a dedicated calculator block, to consider the electric energy required for the water splitting - namely, the cell voltage (1.3 V) and the current density (1300 mA/cm^2). These values are based on experimental polarization curves, as in *(Kupecki, et al., 2019)*.

Table 2: Operating conditions for the plant units

Hierarchy	**SOE**				**Gasifier**					**Upgrade**				**HB**			
Block	**S-1**	**R-1**	**SEP-2**	**F-1**	**E-1**	**DECOMP**	**OXI / RED**	**CH4-WGS**	**CO-WGS**	**CO-WGS**	**AMINES**	**METH**	**COND**	**COMP**	**R-1**	**F-1**	**S-1**
Temperature [°C]	-	750	-	30	150	800	850	400	400	350	80	80	20	-	550	-	-
Pressure [bar]	-	1	-	1	1	1	1	1	1	1	1	1	1	250	250	9	-
Slip Fraction [%]	70	-	10	-	-	-	-	-	-	-	99.9	-	-	-	-	-	-
Frac. Conversion [%]	-	-	-	-	-	-	-	-	-	95	-	95	-	-	-	-	-
Purge fraction [%]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4

2.4 Simulation boundaries

The geographical context elected as case-study is the Tuscan coastal area, in the neighbourhood of Livorno, a city with a big port and an already existing industrial area. In this area, the average annual PV production is 1400 kWh/kW$_p$ with a moderate seasonality of the solar irradiation (± 2.2 kWh/d/m^2 regarding a mid-season baseline of 4.98 kWh/d/m^2). The simulations and the system unit sizing are performed concerning the baseline mid-season day. This assumption offers a practical compromise for a preliminary analysis *(Terna, 2023) (PV GIS, 2023)*. Therefore, the combined generation of hydrogen using electrolysis and gasification is based on the average daily solar cycle. The design specifications on ammonia productivity open the scenario to two different cases:

1. *Industrial production, on-grid plant:* ammonia production of 1500 tons/day (Fig.6). The electric load is partly covered by PV and the grid *(Yara Italia Spa)* and the thermal load is

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balanced through the combustion of the purge gas and a slipstream of the producer syngas. The electrolyser works at rated power for 11 h/day (hereinafter referred to as "light hours"), when the PV plant output overcomes the activation threshold (*Baldinelli et al, 2020*). During the leftover time (13 h/day, referred to as "night hours") the electrolyser input power is reduced to the minimum load, namely 40% of rated power (*Basso et al, 2023*). On the other side, the gasifier is operated at full load when the electrolyzer power is modulated, while biomass feeding is regulated during daytime to reach 40% of rated power (*Basu, 2010*).

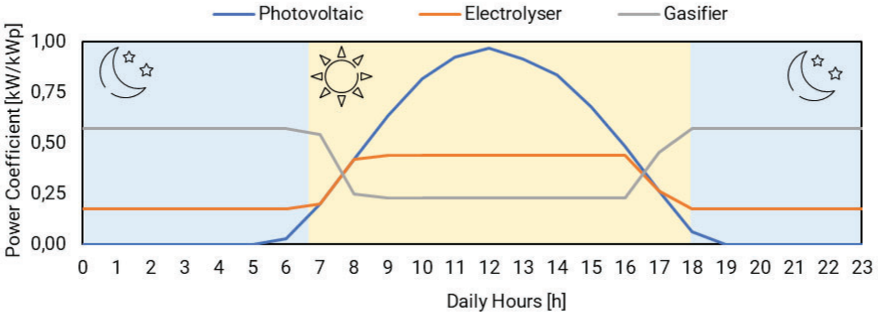

Figure 6: Daily modulation – example from case 1 ("light hours" and "night hours" modes).

2. D*istributed production, off-grid plant;* ammonia production rate equals 56 tons/day. This specification is obtained under the assumption of fuel needs from the maritime transport route "Piombino - Elba Island" *(Traghetti per Elba, 2023) (Elba Report)*[1]. The system is fully independent, the electrical load is covered by the PV and electrical storage (for daytime PV surplus), and the thermal load is balanced by the combustion of the purge gas and a small amount of syngas. The size of the core block is determined considering 100% electric self-sufficiency and 40% modulation threshold for the gasifier and the SOE, as stated in case 1. The electrolyser works at minimum load during night hours, thanks to the electric supply from the battery storage (least round trip efficiency 80%).

2.5 3E Performance indicators

The indices defined to evaluate the quality and performance of the proposed system synthetically cover Energy, Economic and Environmental aspects. They are the specific Energy consumption (SEC, Eq.1), specific CO_2 Emissions (Eq.2)[2], the raw water withdrawal index (Eq.3), and the Levelized Cost of Ammonia[3] (LCOA, Eq.4). The equations are shown below and detailed in the Nomenclature.

$$SEC = \frac{m_{bio} LHV_{bio} + E_{el,in} + Q_{in} + \sum H_{in}}{m_{NH3}} \quad (1)$$

$$\varepsilon_{GHG} = \frac{E_{el,grid} \varepsilon_{g\ mix}}{m_{NH3}} \quad (2)$$

$$w_{H2O} = \frac{\sum m_{H2O,in}}{m_{NH3}} \quad (3)$$

$$LCOA = \frac{\sum_k^n (CAPEX_k + \sum_t^T \frac{OPEX_{t,k}}{(1+r)^t})}{\sum_t^T \frac{m_{NH_3}}{(1+r)^t}} \quad (4)$$

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[1] The average initial consumption of a ferry is estimated around 520 kg/h of Diesel oil while the facility offers up to 70 40-min trip per day. Energy calculation is based on $LHV_{diesel\ oil}$ =43 MJ/kg.

[2] It is assumed that GHG emissions are due to grid electricity $\varepsilon_{g\ mix} = 320 \frac{ton_{CO2}}{GWh}$, Ref: annual report issued by *Ispra, 2021*.

[3] The full LCOA model is not reported in this paper for conciseness reasons. Cost parameters references may be found at *Basso, et al. 2023, Lourinho, et al. 2023, Wang et al., 2023.*

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3 RESULTS

3.1 Sub-processes: main streams properties

The *Gasifier* features a Cold Gas Efficiency of 0.87 and the producer syngas shows an LHV=13.95 MJ/kg, and a composition shown in Table 3 – validated with *(Ghodke et al., 2023)(Song, et al., 2022)*. These results were obtained by setting the Equivalence Ratio ER=0.28 and the Steam-to-Biomass Ratio SBR=0.3 *(Mishra et al, 2023)*. After the *Upgrade* block, water and carbon-containing species are removed to meet HB requirements, hence obtaining a hydrogen concentration >97%$_{mol}$ (Bio-H_2) Finally, clean syngas is mixed with electrolytic hydrogen (E-H_2, purity 99.97%$_{mol}$) and nitrogen (ASU 99.999%$_{mol}$-purity N_2) before the HB process. As Table 3 shows, the composition of the make-up gas mildly varies according to the modulation regime (Fig.6). The product streams are 99.9%$_{mol}$-purity liquid ammonia and a gaseous stream which is split into a recirculation stream and purge gas.

Table 3: Syngas, clean gas, make-up and recycle/purge gas molar composition (mol fractions).

Gas component	Syngas	Bio-H_2	E-H_2	Make-up Gas		Ammonia	Purge (Recycle)
				Light hours	Night hours		
H_2	0.5043	0.9721	0.9999	0.7489	0.7425	0.0003	0.5234
N_2	0.0004	0.0008	-	0.2451	0.2430	<10 ppm$_v$	0.1168
CH_4	0.0002	0.0271	-	0.0060	0.0145	0.0007	0.0702
CO + CO_2	0.4033	10 ppm$_v$	-	< 10 ppm$_v$	< 10 ppm$_v$	< 10 ppm$_v$	< 10 ppm$_v$
H_2O	0.0917	<1 ppm$_v$	< 5 ppm$_v$	< 5 ppm$_v$	< 5 ppm$_v$	< 5 ppm$_v$	< 5 ppm$_v$
NH3	-	-	-	-	-	0.9990	0.2896

3.2 Unit sizing and i/o mass balances

The nameplate sizing for the main parts of the system is reported in Table 4. In case 1, the PV plant is 600 MW, two-fold the SOE (300 MW) and the system utilities calling for power generation beyond the PV capability are fed with grid electricity. The gasifier size is 390 MW. In case 2, the design of the PV is carried out from the daily solar irradiation trend, setting as objective that the energy produced by the PV covers the entire daily electrical load of the system (due to SOE 11 MW at full load, ASU 210 kW and the compression section of the HB 3,85 MW), plus the roundtrip losses arising from the battery storage discharge. This results in a 42-MW PV and a 150 MWh-capacity battery storage (least round trip efficiency 80%). Hydrogen requirements are completed by a 14.3-MW gasifier.

Table 4: Nameplate sizing and annual mass balances of i/o streams in cases 1 and 2.

Subsystems sizing	**CASE 1** 1500 ton$_{NH3}$/day eq. 324 MW$_{th}$				**CASE 2** 56 ton$_{NH3}$/day eq. 12 MW$_{th}$			
Gasifier	390 MW				14.3 MW			
SOE	300 MW				11 MW			
HB compressor	99.75 MW				3.85 MW			
ASU	5.65 MW				210 kW			
Solar PV	600 MW				42 MW + storage 150 MWh			
Input *kton/y*	SOE	Gasifier + Post Comb	ASU	Clean	SOE	Gasifier + Post Comb	ASU	Clean
Water	448	132	-	1211	17	5	-	46
Air	21	1053	658	-	<1	40	25	-
Biomass	-	427	-	-	-	20	-	-
Output *kton/y*	Products	By- Products	Resid.	Waste	Products	By- Products	Resid.	Waste
Ammonia	553	-	-	-	21	-	-	-
Oxygen	-	553	-	-	-	21	-	-
Carbon Dioxide	-	658	-	-	-	25	-	-
Ash	-	-	7	-	-	-	<1	-
Water (depleted)	-	-	1098	-	-	-	41	-
Combustion exhaust	-	-	-	1074	-	-	-	41
Pollutants	-	-	-	7	-	-	-	<1

Considering the operational strategy and power modulation presented before, the annual raw material consumption of the two plant configurations is also shown in Table 4. The oxygen produced by the electrolyser is far more abundant compared to the gasifier requirement in the oxy-steam gasification regime. Therefore, oxygen may be considered a valuable by-product, with an average annual net production ratio of 0.94 ton_{O2}/ton_{NH3}. Alternatively, a different power ratio between the electrolyser and the gasifier could end in the total consumption of the produced oxygen. Similarly, carbon dioxide from the syngas cleaning sections can be recovered as a by-product (1.21 ton_{CO2}/ton_{NH3}), after further upgrading. The residues - material streams with marginal economic value - needing post-treatment before any other re-utilization are depleted water and ashes.

3.3 Thermal integration

The thermal integration between heat sources and sinks follows the same strategy in both cases, yet with the proper scale factor due to the order of magnitude of ammonia throughput. Heat recovery changes according to light hours and night hours operation mode because of different heat capacities ascribed to high-temperature streams and steam demand. To fulfil the heat duty at high temperatures (especially in the gasification section where there are endothermic parts above 800°C), the HB purge gas and a slipstream of the syngas are burnt. The split fraction related to the syngas stream delivered to the afterburner is regulated to satisfy high-temperature heat demand. The theoretical best thermal recovery asset can be visualized thanks to the Grand composite curves in Fig. 7, where the minimum pinch point is imposed equal to 20°C. During light hours, 100% of the heat duty can be satisfied with internal recovery if the purge gas is burnt together with a slipstream of syngas (0.7 kg_{syngas}/kg_{purge}). During night hours, syngas and purge gas are burnt according to the ratio of 1.6 kg_{syngas}/kg_{purge}).

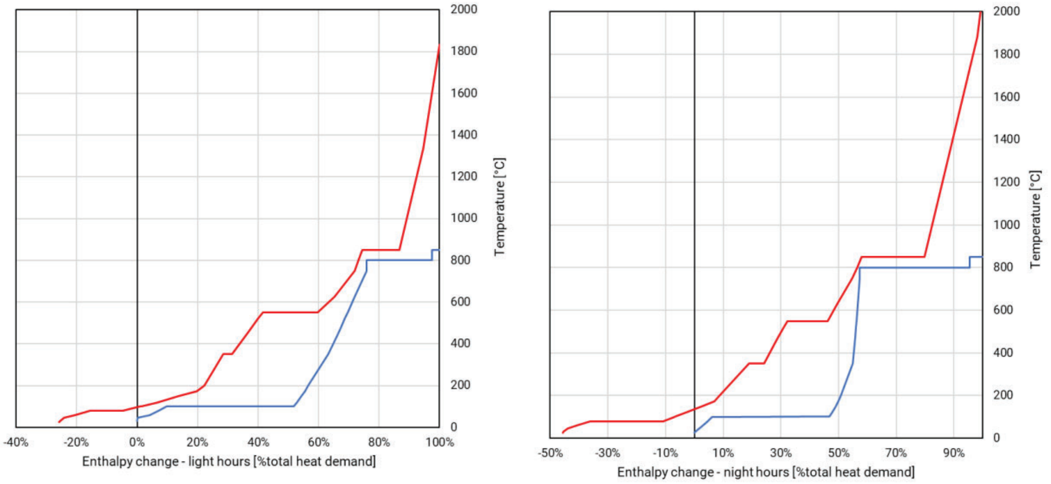

Figure 7: Grand composite curves: *light hours* mode (left) and *night hours* mode (right).

In both cases, the pinch point is in the high-temperature zone, between the biomass reduction step (Cold composite curve) and the cooling of producer syngas/combustion products (hot composite curve). In both cases, the system releases low-temperature heat below 100°C, which is not recoverable in the system according to the configuration adopted. The proportion between heat recovery and net heat availability is highlighted in Fig.7. Extensive results for cases 1 and 2 are reported in Table 5.

Table 5: Heat sources and sinks thermal data (extensive data refer to case 1 sizing)

Heat recovery results	**Light hours**		**Night Hours**	
	CASE 1	**CASE 2**	**CASE 1**	**CASE 2**
Total heat load	292 MW	11.23 MW	378 MW	14.54 MW
Recovery fraction	100%		100%	
Net Heat available at T < 100°C	75 MW	2.52 MW	173 MW	6.64 MW

3.4 3E Performance Indicators assessment

Given the energy and material balances obtained from the model simulation under the case-study assumption, the 3E performance indicators results as reported in Table 6 and subsequently discussed. The results are compared with state-of-art systems documented in the literature *(Cesaro, et al. 2023),* (*Ghavam, et al. 2021), (IEA 2023),* and *(NREL DOE 2023).*

Table 6: 3E results: comparison with SotA systems. Abbreviation: CG=Coal Gasification, BIOG=Biomass Gasification, ELEC=Electrolysis.

3 E performance indicators		**Case**	**Light**	**Night**	**Weighted Average**	**Benchmarking**
Energy	SEC *MWh/ton*$_{NH3}$	1	8.76	9.43	9.12	9.5 brown ammonia (SMR + HB) 11-12 green ammonia (ELEC+ HB)
		2	9.31	11.80	10.65	
Environment	ε_{GHG} *ton*$_{CO2}$*/ton*$_{NH3}$	1	0.44	1.39	0.75	1.8-2.5 brown ammonia (SMR/CG + HB) *negligibile* green ammonia (ELEC + HB)
		2	0	0	0	
	w_{H2O} *ton*$_{H2O}$*/ton*$_{NH3}$	1 and 2	2.63	3.81	3.27	1.59 green ammonia (ELEC+HB) 2.94 brown ammonia (SMR + HB) 5.30 blue ammonia (CG + CCS+ HB) 5.44 blue ammonia (SMR + CCS + HB) 7.35 green ammonia (BIOG + CCS+ HB)
Economic	LCOA *€/ton*$_{NH3}$	1	970-1060			1180-1760 green ammonia (Western Europe VRES) 200-970 SotA brown ammonia plant
		2	1140-1230			

3.4.1 Specific energy consumption: The average SEC between light hours and night hours is 9.12 MWh/ton$_{NH3}$ (case 1) and 10.65 MWh/ton$_{NH3}$ (case 2). Normally, light hours are featured by a lower SEC due to the modulation choice: prevailing electrolysis over gasification ends in a higher efficiency. In the on-grid configuration, the PV plant provides 53% of the electric energy required and during light hours 16% of the PV generation exceeds the system requirements and can be exchanged with the main power grid. In case 2 the PV needs to be over-sized to completely address the electric demand. In this circumstance, SEC increases due to losses in intra-day energy storage (the battery roundtrip losses are ascribed to the energy storage discharge phase, featuring night hours operation). The results obtained show mild enhancement compared to the SotA references reported by (*Ghavam, et al. 2021),(NREL DOE 2023)* and recalled in Table 6. Ammonia produced in case 2 is considered 100% green, in case 1 the final product can be considered 72% green due to electricity withdrawal from the power grid (RES penetration assumed about 40% according to *(Terna, 2023)* data.

3.4.2 Environmental footprint: As far as specific emissions are concerned, in case 1 they are 0.75 ton$_{CO2}$/ton$_{NH3}$ due to energy withdrawal from the grid. This is especially marked in night-hours operation mode. Case 2 yields totally green ammonia: the only CO_2 emissions come from biomass conversion and, for that, are not computed in the indicator. In both cases, the raw water withdrawal index equals 3,27 ton$_{H2O}$/ton$_{NH3}$ (night hours impact more due to the high water requirement allocated to the gasification and upgrading sections). It should be noted that raw water withdrawal entails a share of depleted water due to pollutants removal sections, which is relevant in gasification-based processes as reported in Table 6 (5.30-7.35 ton$_{H2O}$/ton$_{NH3}$). The results obtained by combining water electrolysis and wood gasification are comparable with a standard SMR-based HB process.

3.4.3 Simplified economic analysis: In case 1, the LCOA is sensitive to the market value of electricity and biomass. Fig. 7 shows that the market price of biomass has a mild effect on LCOA. With reference to an electricity value of 0.133 €/kWh (price in November 2023), LCOA varies in the range of 970-1060 €/ton$_{NH3,}$ while considering residual woody biomass available for free and the purchase of woody chips at 100 €/ton$_{wood\ chips}$ respectively. This market condition determines LCOA moderately higher than the actual market of brown ammonia (upper threshold 970 €/ton$_{NH3}$), yet more competitive with green ammonia production referred to the 2021 V-RES Western European countries scenario, whose lower value is 1180 according to (*IEA2023).* For an electricity market price lower than 0.075

€/kWh the results are in the range of commercial production with SMR+HB systems, even in the event of woody biomass purchase. In case 2, the only market variable affecting LCOA is the price of biomass, causing the results to be in the range 1140-1230 €/ton$_{NH3}$, which is fully in agreement with the Green ammonia market reference. LCOA does not suffer from electricity price variations. However, the implementation of the battery storage in case 2 makes the LCOA generally higher compared to case 1. LCOA parity between the grid-connected system (case 1) and the off-grid one (case 2) is achieved for an electricity price of about 0.210-0.220 €/kWh (see red markers in Fig.7).

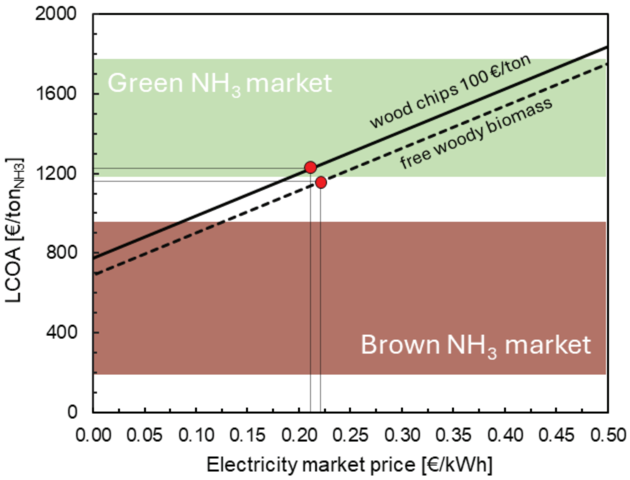

Figure 7: LCOA as a function of grid electricity price and wood biomass price, compared to LCOA reference ranges for brown and green ammonia according to (*IEA 2023*). Legend: red circles mark LCOA parity between case 1 and case 2.

4 CONCLUSIONS

The paper investigates a novel system concept to produce green ammonia, integrating electrolysis and wood biomass gasification for the production of hydrogen required by the Haber Bosch process. Then, the system is simulated in two implementation scenarios, namely an on-grid industrial-size plant and an islanded small-scale facility.

This hybrid RES-based ammonia plant configuration brings good outcomes in terms of specific energy consumption and levelized cost of ammonia. Considering all the operation modes analysed, SEC ranges from 8.76 to 10.65 MWh/ton$_{NH3}$, resulting in an efficiency gain compared to the state-of-the-art. Similarly, the economic analysis with the LCOA index provides an optimistic forecast, scoring a confidence interval of 970-1230 €/ton$_{NH3}$. These results are encouraging, especially since the economic analysis here performed does not allocate CAPEX and OPEX costs on relevant by-products (mainly oxygen and carbon dioxide from CCS). From the point of view of environmental concerns, the islanded mode results in a fully green production, with net-zero CO_2 emissions. Conversely, the on-grid operation exhibits residual GHG emissions, which are due to the primary energy sources mix feeding the reference power grid. However, referring to the Italian energy mix, CO_2 emissions are reduced by 65% compared to an average SMR-HB plant, in agreement with 2030 targets (*MASE, 2023*). The sore point of the analysis stands in water footprint since the flexibility gained thanks to the hybridization of electrolysis and gasification ends in a higher raw water withdrawal.

Most of the key performance indicators show good perspectives, yet the extensive results related to Case 1 pose severe threats to the scalability of the system, due to land use for both the PV plant and biomass collection. Therefore, small-scale systems gain interest also for the feasibility concerns related to land use and viable biomass collection. Moreover, in light of the water-energy nexus concerns, the actual water consumption and depletion need to be addressed to claim the full sustainability of the proposed concept.

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NOMENCLATURE

ASU	Air Separation Unit	OPEX	Operative Expenditure
BIOG	Biomass Gasification	PUN	Unique National Price
CAPEX	Capital Expenditure	RED	Renewable Energy Directive
CCS	Carbon Capture and Storage	(V-)RES	(Variable-)Renewable Energy Sources
CG	Coal Gasification		
ELEC	Electrolysis	RFNBO	Renewable Fuels of Non-Biological Origin
GHG	Green House Gas		
HB	Haber Bosch	SEC	Specific Energy Consumption
LCOA	Levelized Cost of Ammonia	SMR	Steam Methane Reforming
MEA	Monoethanolmines	SOE	Solid Oxide Electrolyzer
NZE	Net Zero Emission	WGS	Water Gas Shift

Subscripts

bio	biomass	n	total number of system components
db	dry basis	p	peak
el	electric	t	t^{th} year of the project
in	input	T	project duration (years)
k	k^{th} plant component	wb	wet basis

Symbols

E	energy	r	discount rate
H	flow enthalpy	$\varepsilon_{g\ mix}$	average equivalent Grid GHG emission
M	mass		
Q	thermal energy	W_{H2O}	water withdrawal index

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