

Planetary Boundaries Analysis of Low-Carbon Ammonia Production Routes

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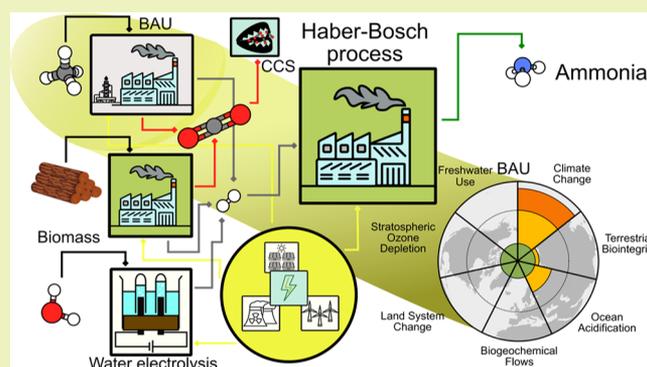
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ABSTRACT: At present, the synthesis of ammonia through the Haber–Bosch (HB) process accounts for 1.2% of the global carbon emissions, representing roughly one-fourth of the global fossil consumption from the chemical industry, which creates a pressing need for alternative low-carbon synthesis routes. Analyzing seven essential planetary boundaries (PBs) for the safe operation of our planet, we find that the standard HB process is unsustainable as it vastly transgresses the climate change PB. In order to identify more responsible strategies from this integrated perspective, we assess the absolute sustainability level of 34 alternative routes where hydrogen (H_2) is supplied by steam methane reforming with carbon capture and storage, biomass gasification, or water electrolysis powered by various energy sources. We found that some of these scenarios could substantially reduce the global impact of fossil HB, yet alleviating the impact on climate change could critically exacerbate the impacts on other Earth-system processes. Furthermore, we identify that reducing the cost of electrolytic H_2 is the main avenue toward the economic appeal of the most sustainable routes. Our work highlights the need to embrace global impacts beyond climate change in the assessment of decarbonization routes of fossil chemicals. This approach enabled us to identify more suitable alternatives and associated challenges toward environmental and economically attractive ammonia synthesis.

KEYWORDS: ammonia synthesis, Haber–Bosch process, LCA, planetary boundaries, renewables, techno-economic analysis



1. INTRODUCTION

Today, ammonia (NH_3) is the world's second largest (on a mass basis) chemical, with more than 170 Mt produced annually.¹ The main application of this chemical is fertilizers (>88%), followed by explosives, plastics, and synthetic fibers.^{1,2} At present, more than 90% of NH_3 global production uses the Haber–Bosch (HB) process.³ More than 50 years ago, NH_3 plants were highly energy-intensive, using approximately 60 GJ t^{-1} NH_3 . However, energy efficiency improvements reduced energy requirements by half.⁴ Despite these significant savings, the HB process still represents 24% of the fossil fuel consumption in the chemical industry due to the hydrogen (H_2) required for NH_3 synthesis.⁵ H_2 is mostly generated via steam methane reforming (SMR), which leads to a carbon footprint of 1.5–1.6 kg CO_{2-eq} kg^{-1} NH_3 , accounting for >1.2% of the global carbon emissions.⁶ This amount is roughly equivalent to the total CO_2 emissions from South Africa in 2017.⁷ There is, therefore, a strong motivation to improve the sustainability level of fossil NH_3 production.

Ongoing research efforts focus on decarbonizing NH_3 production following two main strategies: (i) decarbonizing the electricity mix powering the business-as-usual (BAU)

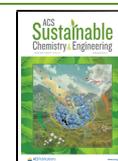
process⁸ and (ii) replacing the fossil SMR H_2 (grey H_2) with greener H_2 sources. The latter technologies rely on electrolytic H_2 powered by renewable energy (green H_2) and H_2 from biomass gasification (BG).^{9–11} The direct electroreduction of elemental nitrogen (N_2) using air as feedstock and water as the proton source is also gaining momentum, yet it is still at a fundamental stage; notably, the lack of reliable benchmark catalysts and the low efficiencies generally reported represent a barrier to overcome.^{12–14}

Quantifying the life cycle impact of these emerging technologies to decarbonize fossil NH_3 is critical to identify the most sustainable ones.¹⁵ Since its emergence, life cycle assessment (LCA) has enabled comprehensive environmental analyses of processes and products, covering activities from raw material extraction to waste management.^{16–19} Several studies

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applied LCA to evaluate NH_3 production technologies, focusing mainly on those coupling carbon capture and storage (CCS) with the BAU process^{20–23} and using H_2 from water electrolysis,^{8,20,24–29} BG,^{23,30} and CuCl cycles^{8,26} to lower the carbon footprint.⁶ In terms of N_2 sources, most of these studies considered cryogenic air separation for N_2 procurement, while some covered pressure swing adsorption (PSA) and membrane separations as well.^{20,23,27,29} LCAs of NH_3 production often focused on analyzing the carbon footprint, while only a few studied other impact categories, for example, human toxicity and abiotic resource depletion^{8,22–26} as well as eutrophication and acidification.^{8,21,22,26} The standard approach was to adopt an attributional cradle-to-gate scope, although consequential LCA was also recently applied.²³ In terms of uncertainties, many works omitted them while some applied Monte Carlo simulation^{8,24,25} or sensitivity analyses to study the most critical uncertain parameters.^{29–31}

The main limitation of standard LCAs, widespread in the assessment of chemicals, is that they allow comparing and ranking alternatives but cannot help determine whether a technology is sustainable in absolute terms. Absolute environmental sustainability assessments (AESAs) emerged recently in the literature³² that consider the Earth's biophysical limits to interpret the LCA results. This approach relates the impact of a system with its maximum allowable impact, which is established by assigning a share of the ecological capacity of the planet to it.

The concept of planetary boundaries (PBs), originally introduced by Rockström et al.³³ and later refined by Steffen et al.,³⁴ provides a comprehensive framework to precisely quantify absolute sustainability. The PBs define a set of critical biophysical limits on key Earth-system processes whose transgression could shift the current state of the planet.^{33,34} These limits jointly identify a safe operating space (SOS) that should be shared among all anthropogenic activities.^{34,35} Recent PB-LCIA methods provided characterization factors to quantify the impact of feedstocks, emissions, and waste on the Earth-system processes linked to the PBs, enabling the AESA of industrial systems. With this spirit, we recently applied the PBs concept in the assessment of CO_2 -based methanol production, and H_2 and bioethanol supply chains.^{36,37} Despite these and other related works, absolute sustainability studies of industrial systems are still in their infancy, particularly concerning chemicals and fuels.

For the first time, we here quantify the absolute sustainability level of low-carbon HB processes in terms of seven PBs focusing mainly on the electricity and H_2 source, namely, considering SMR coupled with CCS, BG, and alkaline electrolysis (AE) and proton exchange membrane (PEM) water electrolysis.

2. METHODS

We assessed three main alternative routes (SMR, water electrolysis, BG) to produce low-carbon NH_3 implementing several configurations, yielding a total of 35 representative scenarios (13 discussed next and the rest available in the Supporting Information). The selection reported here covers multiple scenarios for each different technology for H_2 production, including meaningful combinations of these technologies with different power supplies (see Figure 1 for a general overview). Our analysis combines process simulation, LCA principles, and a recently developed impact assessment model based on the PB concept, as discussed in detail next.

2.1. Process Modeling and Scenarios Definition. We developed a process flowsheet of the HB process in Aspen HYSYS

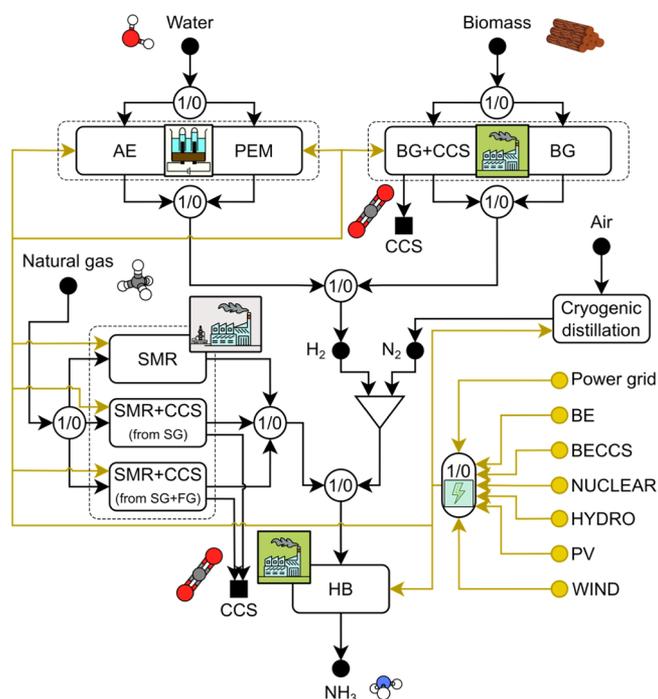


Figure 1. General graphic representation of the technologies included in this study. The acronyms are as follows: HB: Haber–Bosch; BAU: business-as-usual; SMR: steam methane reforming; CCS: carbon capture and storage; SG: syngas; FG: flue gas; AE: alkaline electrolysis; PEM: proton exchange membrane electrolysis; BG: biomass gasification; BE: bioenergy; BECCS: bioenergy with CCS; NUCLEAR: nuclear energy; HYDRO: hydropower; PV: photovoltaic energy; WIND: wind energy. The circle “1/0” stands for a binary switch, which can be activated for any of the input streams and deactivated for every other one, with the only exception of the energy streams (see Section 2.1), where different power sources can be sent to different blocks.

v10 based on the process configuration, operating conditions, and kinetic parameters provided by Araújo and Skogestad.³⁸ The plant was scaled to produce 560 kt yr^{-1} of NH_3 using H_2 and N_2 as reactants, with a final purity above 99.5% on a mass basis. The reactants are fed in stoichiometric proportions, compressed to about 200 bar, and sent to the separation section, consisting of several flash units in series operating at different pressures and temperatures. This configuration improves the process controllability compared to directly sending the feed to the reactor inlet, especially when there are impurities that could damage the catalyst³ (e.g., CO_2 and H_2O). The separation section separates liquid NH_3 from the gaseous unreacted reactants, which are heated up to ~ 230 °C and sent to an interquenched three-bed reactor loaded with the industrial iron-based HB catalyst. The reactor outlet is then cooled down to room temperature and then mixed with the fresh feed before entering the separation section. We provide additional details on the simulation in the Supporting Information. This simulation model was taken as a basis in all scenarios, differing in the H_2 and electricity sources.

As H_2 sources, we consider SMR,³⁹ indirect BG,^{40,41} and electrolytic water splitting.^{42,43} The scenarios discussed herein are assumed to be deployed separately, that is, no integration in terms of material and energy inputs between different scenarios was considered. The electricity of the main process (compressors and pumps of the HB process) is supplied by the current mix, a future mix based on projections, or a dispatchable power source (i.e., nuclear or hydroelectric). Concerning SMR, currently, the conventional and cheapest route toward H_2 ,⁶ we consider SMR without CO_2 capture (BAU), SMR with CCS storing the CO_2 from the generated syngas in a geological reservoir (SMR + CCS_{SG}), and SMR where all CO_2 —from the generated syngas and that produced in the combustion of

natural gas to heat the reformer—undergoes CCS (SMR + CCS_{SG+FG}). Storing the CO₂ present in the syngas only requires additional compressors; however, a capture unit must be deployed to separate the CO₂ in the flue gas of the external furnace. Additional details on these scenarios are provided in the [Supporting Information](#).

BG is regarded as an environmentally promising alternative for electricity and H₂ production.^{4,9,23,30} Coupling BG with CCS allows producing carbon-negative H₂ (on a cradle-to-gate basis).⁴⁴ Accordingly, here, we cover BG⁴⁰ and BG with CCS,⁴¹ scenarios labeled as BG-2018mix and BG + CCS-2018mix, respectively. In particular, among the possible process configurations, the two BG scenarios consider the indirect gasification of biomass with steam fed to the gasifier. In addition to this, these cases assume that the electricity byproduct displaces electricity from the 2018 mix (see Section 3.1 in the [Supporting Information](#)).

Finally, we also consider electrolytic water splitting based on AE⁴² and PEM⁴³ electrolyzers powered by several sources. These sources include the current grid (PEM-2018mix/AE-2018mix), nuclear energy (PEM-NUCLEAR/AE-NUCLEAR), and renewable technologies, that is, photovoltaic (PEM-PV + 2018mix/AE-PV + 2018mix), wind (PEM-WIND + 2018mix/AE-WIND + 2018mix), hydro (PEM-HYDRO/AE-HYDRO), and biomass combustion with or without CCS (PEM-BECCS/AE-BECCS or PEM-BE/AE-BE, respectively). With respect to these last scenarios, we note that using bioenergy to produce H₂ via water splitting is less efficient than directly implementing BG. However, this indirect route was added due to the expected future role of this power source in future sustainable energy scenarios.⁴⁵ In the scenarios based on nondispatchable power sources, that is, wind and photovoltaic, we assume that these technologies supply energy only to the electrolyzer, while the grid covers the auxiliary needs of the HB process (i.e., compressors and pumps). This configuration ensures the full operability of the plant at all times.⁴⁶

We consider additional electricity mixes projected under the sustainable development (2040SD) and stated policy (2040SP) scenarios to cover the electricity requirements of the primary process.⁴⁵ Accordingly, we define the following scenarios: BG without CCS (BG-2040SDmix and BG-2040SPmix) and with CCS (BG + CCS-2040SDmix and BG + CCS-2040SPmix), water electrolysis entirely powered by the mix (PEM-2040SDmix/AE-2040SDmix and PEM-2040SPmix/AE-2040SPmix), water electrolysis powered by wind and where the mix supplies energy to the HB (PEM-WIND + 2040SDmix/AE-WIND + 2040SDmix and PEM-WIND + 2040SPmix/AE-WIND + 2040SPmix), and two analogous scenarios for solar photovoltaic (PEM-PV + 2040SDmix/AE-PV + 2040SDmix and PEM-PV + 2040SPmix/AE-PV + 2040SPmix).

In the three scenarios based on SMR, N₂ is supplied within the air stream.³⁹ In the scenarios not relying on SMR, cryogenic distillation provides high-purity N₂ from the air.⁴⁷ We omitted alternative technologies for air separation, for example, PSA or membranes, because they are either unsuitable for such large capacities or cannot meet the desired purity specifications, respectively.^{6,47}

2.2. Life-Cycle Assessment and Planetary Boundaries Analysis. The environmental assessment follows the LCA guidelines described in the ISO 14040 and 14044 standards.^{48,49} The first LCA phase defines the goal and scope of the study. The goal of the environmental assessment is to quantify the absolute sustainability level of the alternative NH₃ production routes. Hence, we defined the global ammonia production as the functional unit, i.e., 182.4 Mt yr⁻¹; that is, world NH₃ production in 2019.⁵⁰ We adopted a cradle-to-gate scope using an attributional approach, encompassing all upstream activities and omitting further downstream conversion of NH₃ into additional products. In the electrolysis scenarios, we assumed that the oxygen byproduct was vented, as done in previous studies.⁴⁶ Regarding the BG scenario without CCS, we applied an avoided burden approach to deal with the electricity byproduct, which we modeled as an environmental credit.

In the second LCA phase, we modeled the life cycle inventories (LCIs) of the routes by combining the mass and energy flows retrieved from the Aspen-HYSYS simulations (foreground system)

with the data of the background activities available in Ecoinvent v3.5⁵¹ (accessed through SimaPro v9.0).⁵² The LCI of H₂ was obtained by combining data from Ecoinvent and the literature.^{40–43} Additional details about the LCIs and process flowsheet models, with insights on their energy and water requirements, are provided in Sections 2 and 3 in the [Supporting Information](#).

In the third phase of the LCA, we used the characterization factors proposed by Ryberg et al.⁵³ to quantify the impact on the control variables of the PBs introduced by Rockström et al.,³³ who defined 11 control variables, each of them with a corresponding boundary, covering 9 Earth-system processes, namely, climate change, stratospheric ozone depletion, ocean acidification, biogeochemical flows of nitrogen and phosphorus, land system change, freshwater use, biosphere integrity, atmospheric aerosol loading, and introduction of novel entities. We omitted the latter two PBs because they have not been quantified yet. Climate change and biosphere integrity are regarded as core PBs, so they deserve special attention.³⁴ However, a long-lasting transgression of any PB could lead to catastrophic events shifting the current state of the planet. Hence, all PBs together define the SOS for humanity.

To quantify the absolute sustainability performance of each route, we proceeded as follows (see also [Figure S2](#)). We first determined the impact of each scenario on the control variables of the PBs. Considering the set B of PBs *b* and a set S of scenarios *s*, the environmental impact for each scenario *s* (EI_{*b,s*}^{NH₃}) was calculated according to eq 1

$$EI_{b,s}^{NH_3} = \sum_{e \in E} LCI_{e,s} \cdot CF_{b,e} \cdot PV_{NH_3} \quad \forall b \in B, s \in S \quad (1)$$

where LCI_{*e,s*} represents the elementary flow *e* linked to the production of 1 kg of NH₃ in scenario *s*. Note that the values of LCI_{*e,s*} are obtained in the second LCA phase (inventory analysis). Parameter CF_{*b,e*} denotes the characterization factor linked to PB *b* for elementary flow *e*. These characterization factors were taken from Ryberg et al.⁵⁴ for all PBs except for biosphere integrity, for which we used the impact factors developed by Hanafiah et al.⁵⁵ and adapted by Galán-Martin et al.⁵⁶ PV^{NH₃} denotes the production volume of NH₃ in 2019.

With the impact on the control variables, we next computed the level of transgression (LT) attained by each scenario considering the share of the SOS (i.e., ecological budget delimited by the PBs) downscaled to NH₃ production. The SOS, which limits the maximum perturbation that the Earth-system processes can sustain without compromising their long-term stability, is calculated as the difference between the boundary and the natural background level. The SOS should be shared among all anthropogenic activities. A range of sharing principles has been applied in the literature, and the most convenient way to perform this operation is the object of active debate. To allocate part of this budget to NH₃ production, we applied an egalitarian downscaling based on the gross value added (GVA), as shown in eq 2, according to the principle that “it is unjust for individuals to be worse off than others”⁵⁷

$$SOS_b^{NH_3} = SOS_b^{GLO} \cdot \frac{GVA_b^{NH_3}}{GVA_b^{GLO}} \leq SOS_b^{GLO} \cdot \frac{GVA_b^{CHEMS}}{GVA_b^{GLO}} \quad \forall b \in B \quad (2)$$

where SOS_{*b*}^{NH₃} is the SOS downscaled to NH₃ production for PB *b*, SOS_{*b*}^{GLO} is the global SOS for PB *b*, GVA_{*b*}^{NH₃} is the GVA linked to NH₃ production, and GVA_{*b*}^{GLO} is the global GVA of all economic sectors together, estimated here at 70.06 trillion USD in 2017.⁵⁸ Lacking public estimates for GVA^{NH₃}, we generated our main results for the total GVA of the chemical sector (i.e., GVA^{CHEMS} estimated at 5.71 trillion USD⁵⁹), which accounts for the chemical industry's supply chain activities. This simplification overestimates the ecological budget allocated to NH₃ production (i.e., the GVA of the chemical sector is given by all chemicals it produces, not only NH₃) and, therefore, underestimates the LTs of the scenarios. This approach was chosen as the main one presented in this work since it is the most optimistic for the BAU.

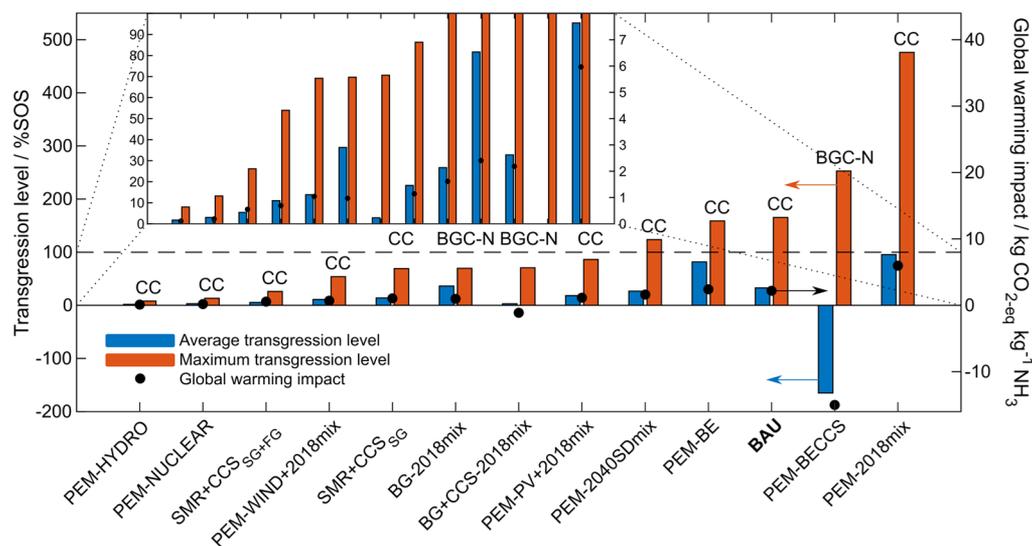


Figure 2. LT considering an egalitarian sharing principle based on the GVA of the chemical industry. The average LT is depicted with blue bars, while the maximum LT is depicted with orange bars (left axis), with the label above each orange bar denoting the PB showing the maximum transgression level (CC: climate change; BGC-N: biogeochemical flows–nitrogen). The scenarios are ordered according to the maximum LT. The black circles represent the global warming impact (GWI, right axis). The cases omitted in this figure are provided in Section 5.1.1 of the [Supporting Information](#) (Figure S3).

Alternatively, we also generated additional results considering a rough estimate for GVA^{NH_3} (eq 3, results reported in Figures S4 and S7 in the [Supporting Information](#))

$$SOS_b^{NH_3'} = SOS_b^{GLO} \cdot \frac{GVA^{CHEMS}}{GVA^{GLO}} \cdot \frac{REV^{NH_3}}{REV^{CHEMS}} \quad \forall b \in B \quad (3)$$

where $SOS_b^{NH_3'}$ is the SOS of the NH_3 industry for PB b according to the alternative downscaling, SOS_b^{GLO} and GVA^{GLO} are defined as in eq 2, GVA^{CHEMS} corresponds to the GVA associated with the chemical industry,⁵⁹ REV^{NH_3} denotes the worldwide gross revenues associated to NH_3 production, and REV^{CHEMS} corresponds to the total revenues of the chemical industry in the world. While REV^{NH_3} was extracted from the calculated production cost of the BAU scenario and the global ammonia production volume, the value for REV^{CHEMS} was assumed equal to 1.10 trillion USD.⁵⁹

Furthermore, alternative results were generated following a nonegalitarian approach (Figures S5 and S8 in the [Supporting Information](#)). Here, the downscaled SOS for each PB ($SOS_b^{NH_3''}$) was calculated as follows (eq 4)

$$SOS_b^{NH_3''} = SOS_b^{GLO} \cdot \frac{EI_{b,BAU}^{NH_3}}{EI_b^{GLO}} \quad \forall b \in B \quad (4)$$

where SOS_b^{GLO} is the global SOS for the specific PB b , while $EI_{b,BAU}^{NH_3}$ is the current global impact on critical Earth-system processes exerted by the BAU NH_3 production and EI_b^{GLO} is the current global anthropogenic impact on the same Earth-system processes. Hence, egalitarian approaches often assign a larger budget to those activities contributing more to the economy. In contrast, nonegalitarian sharing principles allocate larger quotas to those activities currently polluting more, which might be perceived as unfair. Each downscaling principle shows pros and cons, and the final choice should be consistent with the scope of the analysis. We note that ammonia plays a critical role in feeding a growing population, so, arguably, sharing principles leading to larger quotas might be more suitable.

Finally, we compared the environmental impact of NH_3 production ($EI_{b,s}^{NH_3}$) with its share of the SOS to compute the LT in each scenario (i.e., decarbonization route), as shown in eq 5

$$LT_{b,s}^{NH_3} = \frac{EI_{b,s}^{NH_3}}{SOS_b^{NH_3}} \quad \forall b \in B, s \in S \quad (5)$$

where the $LT_{b,s}^{NH_3}$ is given by the environmental impact associated with NH_3 production ($EI_{b,s}^{NH_3}$) divided by the share of the SOS for each PB b allocated to NH_3 production ($SOS_b^{NH_3}$). A value of $LT_{b,s}^{NH_3}$ below 100% implies that the scenario does not exceed the ecological budget assigned to the system and, therefore, could be deemed sustainable for that PB. Conversely, if $LT_{b,s}^{NH_3}$ is greater than 100%, then the scenario is unsustainable for that PB. Exceeding the ecological budget in at least one of the PBs implies that the scenario is unsustainable in absolute terms as transgressing one environmental limit suffices to compromise the resilience of the Earth system. In the assessment of scenarios, we considered both the maximum LT across all PBs as well as the average LT (details in the [Supporting Information](#)). Besides the PB metrics, for comparative purposes, we also quantified the ReCiPe 2016⁶⁰ midpoint indicator “climate change” considering the Hierarchist perspective, often referred to as global warming impact or carbon footprint and expressed in $kg\ CO_{2-eq}$ (Figure 2 as well as Figures S3–S5, and S16 in the [Supporting Information](#)).

Finally, in step four of the LCA methodology, the results are interpreted, and recommendations are made. Here, we analyzed the LTs of the scenarios to identify the main hotspots, compare their absolute sustainability performance, and determine whether they are truly sustainable.

2.3. Economic Assessment. The routes were compared in terms of total production cost, calculated as the summation of the OPEX and CAPEX expenditures. The OPEX term accounts for raw materials, utilities, labor, maintenance, property taxation, insurance, and land rent. The CAPEX term was estimated from the equipment cost, computed from the sizes of the process units provided by Aspen HYSYS, and the correlations and installation factors available in Towler and Sinnott.⁶¹ Finally, the levelized cost of H_2 was calculated with the methodology and the factors provided in the [Supporting Information](#).

3. RESULTS AND DISCUSSION

3.1. Planetary Boundaries Analysis. The AE scenarios^{62,63} are discussed in the [Supporting Information](#) as the PEM technology holds better prospects. Moreover, among the scenarios relying on future mixes, only the most optimistic PEM-2040SD case is reported here, while the others are available in the [Supporting Information](#).

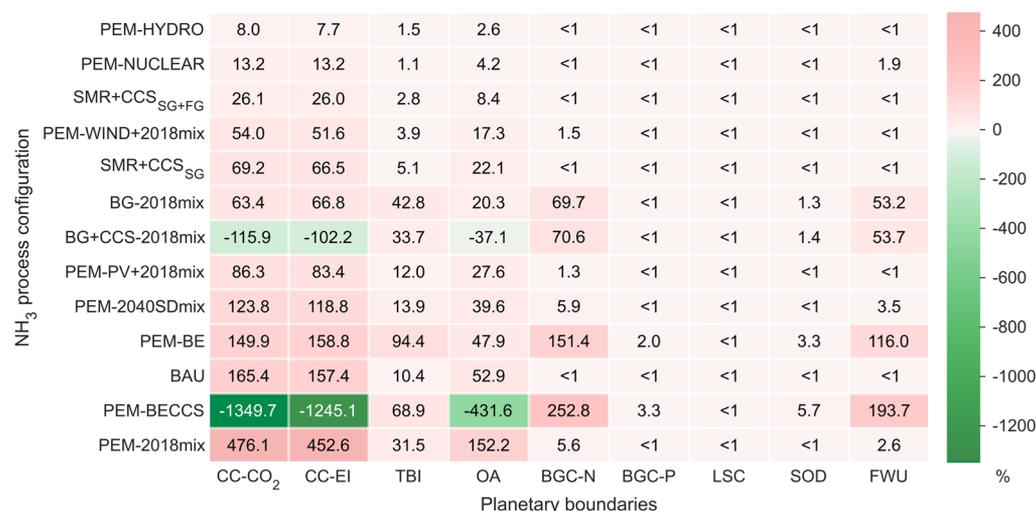


Figure 3. LT in terms of percentage of the SOS assigned to the chemical industry for each of the nine studied control variables. CC-CO₂: climate change—CO₂ concentration; CC-EI: climate change—energy imbalance; TBI: terrestrial biosphere integrity; OA: ocean acidification; BGC-N: biogeochemical flows—nitrogen; BGC-P: biogeochemical flows—phosphorus; LSC: land system change; SOD: stratospheric ozone depletion; FWU: freshwater use. The cases omitted in this figure are provided in Section 5.1.1 of the [Supporting Information](#) (Figure S6).

Figure 2 shows the average LT (across all PBs), the maximum LT, and the global warming impact, where the scenarios are sorted according to the maximum LT. PEM electrolysis powered by hydropower (PEM-HYDRO) emerges as the best route, followed by the same technology powered by nuclear (PEM-NUCLEAR) and then SMR with CCS for both syngas and furnace flue gas (SMR + CCS_{SG+FG}). Five scenarios are unsustainable, including the BAU fossil NH₃ (BAU) and the PEM scenarios powered by biomass (BECCS or BE) or the current or future (decarbonized) mix (2018mix and 2040SDmix, respectively). Indeed, these scenarios exceed the SOS allocated to the whole chemical sector in at least one PB (i.e., climate change for PEM-2040SDmix, PEM-BE, BAU, and PEM-2018mix and the nitrogen flow for PEM-BECCS). Notably, despite its negative carbon footprint, PEM powered by BECCS (PEM-BECCS) is the second-worst scenario in terms of maximum LT (after PEM-2018mix) due to its poor performance in the biogeochemical flow of nitrogen (252.8% of the assigned SOS). BG with or without CCS also shows its highest LT in this Earth-system process, while in the other scenarios, the most critical impact always corresponds to climate change.

In general terms, the carbon footprint (black circles in Figure 2) follows the same pattern as the maximum LT because the largest transgression often corresponds to the climate change PB, strongly linked to carbon emissions. However, this trend does not apply to the biomass routes with CCS, which show very low carbon footprints but a high impact on the nitrogen flow PB (where they perform worse than in climate change). Hence, these scenarios clearly highlight the pitfalls of myopic assessments focused only on carbon emissions. Following this carbon oriented approach, the best scenario would be PEM-BECCS, followed by BG + CCS-2018mix, and then PEM-HYDRO, where the first two show a net-negative carbon balance (−15.00 and −1.12 kg CO_{2-eq} kg NH₃⁻¹, respectively, on a cradle-to-gate basis).

The average LT follows a different pattern, with the best scenario being PEM-BECCS, followed by PEM-HYDRO, and then BG + CCS-2018mix (−165.1, 1.8, and 2.9%, respectively). Focusing on the PEM scenarios, hydropower

shows the lowest positive average LT, followed by nuclear, wind, and solar (1.8, 3.0, 11.0, and 18.2%, respectively). In contrast, bioenergy without CCS shows the second-highest average impact after PEM powered by the current grid mix (81.7 and 95.5%, respectively). Using decarbonized electricity in the PEM-2040SDmix scenario substantially improves the environmental performance (26.7%) but not enough to outperform the SMR + CCS_{SG+FG} (5.4%). H₂ from BG performs worse than the BAU (36.3 vs 32.8%).

Figure 3 displays the LTs attained by the studied scenarios in each Earth-system process. The LT varies substantially across scenarios in the carbon-related PBs, that is, climate change and ocean acidification, from as low as −1350% (PEM-BECCS, climate change—atmospheric CO₂ concentration) to as high as 476% (PEM-2018mix, climate change—atmospheric CO₂ concentration). The BAU, PEM-2018mix, PEM-2040SDmix, and PEM-BE cases transgress the two climate change related control variables, while ocean acidification is only transgressed by the PEM-2018mix scenario.

None of the scenarios transgresses the terrestrial biosphere integrity PB, although those based on biomass lead to large impacts on this Earth-system process (i.e., BG-2018mix, BG + CCS-2018mix, PEM-BE, and PEM-BECCS). This poorer performance is due to their land-use requirements linked to biomass growth, acting as a significant biosphere integrity stressor. These biomass scenarios also perform poorly in the nitrogen flow and freshwater use PBs, with those based on bioenergy with and without CCS transgressing both of them. By contrast, the other scenarios show low LTs in these PBs (<32% in biosphere integrity, <6% in the nitrogen flow, and <4% in freshwater use). All scenarios perform well in the phosphorus flow and land system change PBs (always <4% and in most cases <1%), both connected to agriculture activities.⁶⁴ Likewise, all scenarios show low impacts on the stratospheric ozone depletion PB, with LTs below 6%.

The alternative downscaling based on a rough estimate of the GVA of NH₃ production (Figure S4) would considerably reduce its allowable ecological budget (i.e., from 8.1% of the SOS to 0.2% in the new case); as a result, no single scenario would be environmentally sustainable. However, the relative

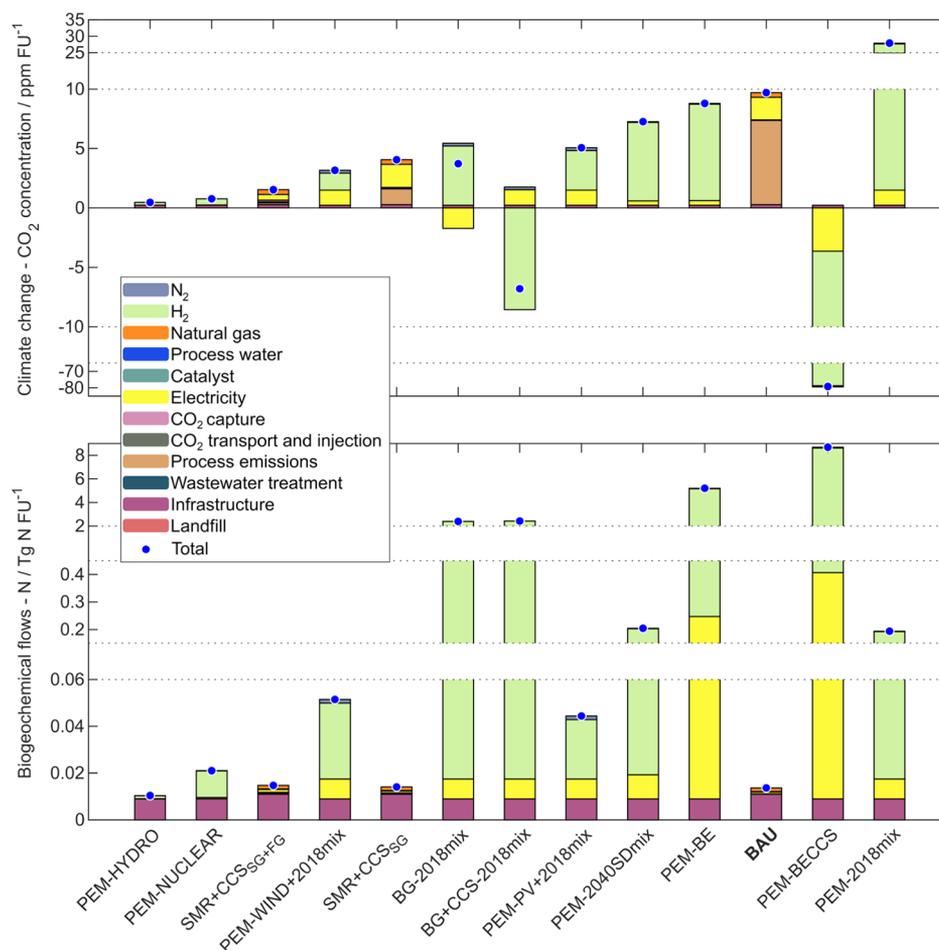


Figure 4. Breakdown of impacts for the control variables climate change—CO₂ concentration (top) and biogeochemical flows—nitrogen (bottom). The total impact is shown in blue circles. The cases omitted in this figure, as well as the PBs not shown here, are provided in Section 5.1.2 of the [Supporting Information](#) (Figures S9–S15). The electrolytic hydrogen accounts for the electricity consumed in the electrolyzer for water splitting. FU stands for functional unit, here selected as global NH₃ production in 2019, that is, 182.4 Mt yr⁻¹.

ranking of all technologies in terms of maximum LT would remain unaltered since the allowable budget would decrease to the same extent across all scenarios. Moreover, this alternative downscaling approach would lead to much larger LTs in all PBs (Figure S7). Here, land system change would be the only PB that is not transgressed across all scenarios, while the others would be transgressed by at least one route. Notably, the climate change PBs would now be transgressed by all scenarios except for those based on biomass.

The nonegalitarian downscaling (Figure S5) would also decrease the share of the SOS assigned to NH₃ production but this time unevenly (e.g., 1.4×10^{-4} % of the SOS in land-system change and 0.9% in climate change, CO₂ concentration). As a result, all scenarios would also exceed at least one PB, with PEM-HYDRO showing the lowest maximum LT (in climate change) and PEM-BECCS the largest transgression (in the nitrogen flow). This downscaling approach shifts the maximum LT category for several scenarios, that is, the worst performance in PEM-NUCLEAR now corresponds to freshwater use (instead of the nitrogen flow) and to the phosphorus flow (instead of the nitrogen PB) for the PEM-2040SDmix and PEM-PV + 2018mix cases. This behavior is due to the very stringent targets on the PBs where the impact of fossil NH₃ is marginal in absolute terms. For example, in the standard egalitarian downscaling, the share of the SOS in freshwater is

8.1% (Figure S8). By contrast, in the nonegalitarian, this value is 1.8×10^{-2} % as NH₃ production contributes marginally to the global freshwater consumption (linked to agriculture activities). In terms of average LT, all scenarios would exceed the SOS except for PEM-HYDRO. Furthermore, all scenarios in the nonegalitarian downscaling case would now transgress the biogeochemical flows, where the global impact of fossil NH₃ (on a cradle-to-gate basis) is negligible, resulting in very stringent quotas.

Figure 4 provides the breakdown of impact in those PBs showing the highest LTs across the scenarios, that is, climate change—atmospheric CO₂ concentration and the nitrogen flow (other breakdowns in Section 5.1.2 in the [Supporting Information](#)). The main contributions to the climate change category in the BAU are linked to the direct CO₂ emissions and the electricity and natural gas inputs (73.0, 19.5, and 4.0% for BAU, 32.7, 47.8, and 9.6% for SMR + CCS_{SG}, and 9.9, 31.4, and 25.3% for SMR + CCS_{SG+FG}, respectively). Hence, capturing the CO₂ emissions from the SMR plant is an effective strategy to reduce the climate change impact.

On the other hand, H₂ is the main contributor to climate change in the PEM scenarios due to the high electricity demand for water splitting (i.e., 45.4 to 94.3% of the total impact), often followed by the electricity needs of the plant (2.0–40.1% share). H₂ is also the main contributor to climate

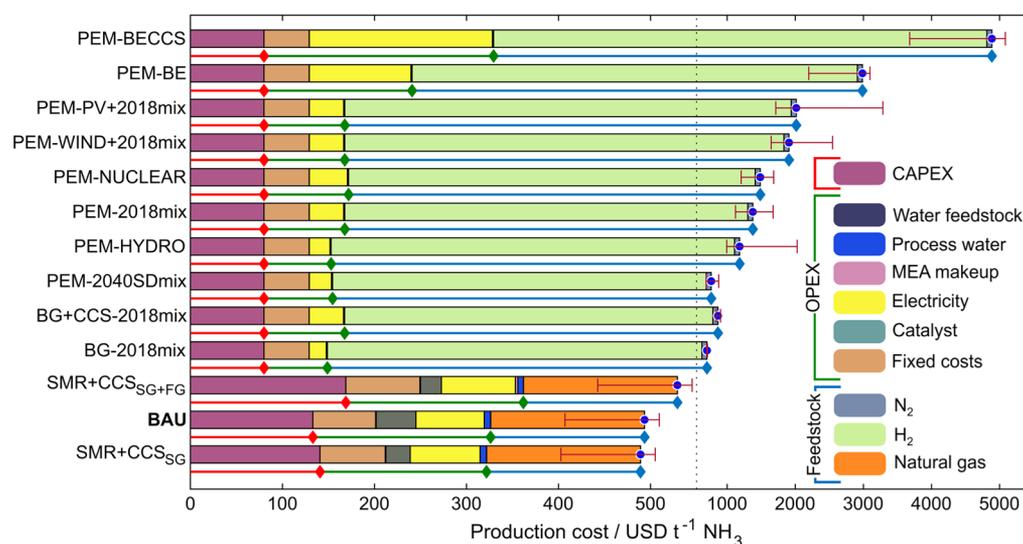


Figure 5. Total production cost breakdown for the selected scenarios. The cases omitted in this figure are provided in Section 5.2 of the [Supporting Information](#) (Figure S17). The uncertainty bars show the best- and worst-case scenario, computed as described in the [Supporting Information](#).

change in the biomass scenarios, two of which show negative impacts on climate change (i.e., PEM-BECCS and BG + CCS-2018mix) due to the negative carbon balance linked to the H₂ source. The BG-2018mix scenario shows a negative contribution from electricity and a positive one from H₂ since electricity coproduction was modeled as an environmental credit. By contrast, the opposite happens in the BG + CCS-2018mix scenario, where the carbon capture unit consumes electricity, leading to a net positive consumption rate.

With regard to the nitrogen flow, H₂ represents, again, the main contribution (share of 94.4 to 99.2% in the biomass scenarios, i.e., BG and PEM powered with electricity from bioenergy with and without CCS), followed by electricity (0.3–4.6% of the total). The high impact of H₂ is here linked to the biomass needed to produce either H₂ or electricity. The biomass source corresponds to a poplar feedstock, with high requirements in terms of fertilizers.

3.2. Economic Assessment. Figure 5 shows the results of the economic analysis. No single scenario would outperform the BAU (increments in production cost in the range 42.4–890.3%). BG-2018mix emerges as the cheapest green H₂ scenario, and PEM-BECCS is the most expensive.

Coupling CCS with the BAU process decreases the costs marginally in the scenario SMR + CCS_{SG} (−0.01%) while increasing it by 7.2% in the SMR + CCS_{SG+FG}. The SMR + CCS_{SG} cost slightly changes (with respect to BAU) due to the trade-off between a higher investment in compressors and lower disposal costs due to lower emissions (30 USD t^{−1} CO₂, [Supporting Information](#) for additional details). Among the PEM electrolysis scenarios, the case powered by the 2040SD mix is the cheapest, that is, 44.4% cheaper than the same technology powered by the current energy mix (PEM-2018mix). The hydropower and PEM-2018mix scenarios follow after the PEM-2040SDmix. The highest production costs correspond to BECCS, where CCS increases the production cost by 63.7% compared to the non-CCS case. The scenarios based on BG with and without CCS are the fourth and sixth most profitable scenarios, with a total increment in the production cost of 42.3% and 75.1% (relative to BAU), respectively.

The main conclusion that can be extracted from Figure 5 is that the largest contributor to the costs of the green H₂ scenarios is H₂ production (i.e., 68.2–91.7% of the total cost). In the PEM and AE scenarios, the H₂ cost is strongly linked to the cost of electricity, which varies with the location of the solar and wind power facility. Here, global average values of 0.0856 and 0.0564 USD kWh^{−1} were assumed for solar and wind, respectively; see Section 4.1 in the [Supporting Information](#) for additional details. According to the observations here reported, considering the future improvements in energy efficiency and the increasing penetration of cheaper renewable power sources, deploying standalone plants relying on H₂ from renewable-powered electrolysis could lead to competitive scenarios with respect to the BAU.

4. CONCLUSIONS

This work assessed, for the first time to the best of the authors' knowledge, the absolute sustainability performance of low-carbon HB ammonia synthesis routes based on BG, water electrolysis, and CCS coupled with the BAU. We quantified the impact of these scenarios on seven Earth-system processes and carried out a techno-economic assessment to shed further light on their feasibility.

We found that the conventional fossil ammonia is unsustainable as it significantly transgresses the climate change PB, while alternative routes could substantially improve the absolute sustainability level of fossil NH₃ to different extents according to the sharing principle. Scenarios based on water electrolysis powered by wind, solar, nuclear, and hydropower and CCS coupled to the BAU are particularly appealing. Among them, ammonia from H₂ produced via PEM electrolysis with hydropower is the most sustainable option, while the same technology powered by the current mix, yet to be decarbonized, is the worst performer. However, the assumption of complete dispatchability of hydropower depends on the specific location. In practice, the large-scale deployment of this technology will be constrained by geographic factors, given the nonuniform distribution of water availability. Scenarios with lower carbon footprints tend to perform better in the studied PBs (in terms of maximum transgression level) because the largest impacts

often occur in the climate change PB (strongly linked to carbon emissions). Biomass scenarios with CCS, however, perform very well in climate change, even attaining carbon-negative footprints, but poorly in other categories, for example, biosphere integrity, nitrogen flow, and freshwater use. This behavior is due to the substantial amounts of land, fertilizers, and water linked to biomass growth. Moreover, N₂ plays a minor role in the PEM- and biomass-based scenarios. Consequently, other technologies for procuring nitrogen, such as air separation through more energy-efficient technologies than cryogenic distillation, might lead to similar results.

Burden-shifting (i.e., exacerbating some impacts when attempting to improve others, e.g., climate change impacts) is negligible in the PEM scenarios not relying on bioenergy. In contrast, BG and PEM electrolysis powered by bioenergy improve climate change at the expense of significantly damaging the biosphere integrity, nitrogen flow, and freshwater use.

The high cost of green H₂ makes environmentally superior strategies such as PEM electrolysis and gasification economically unappealing. Deploying CCS in the BAU process emerges as a cost-effective strategy to reduce the climate change impact of fossil ammonia. However, the limited storage capacity and public acceptance issues represent significant obstacles.

We found that the downscaling approach can critically affect the absolute sustainability of the analyzed routes, to the point that no single scenario might be sustainable for some sharing principles. Hence, cooperation across economic sectors will be needed for operating safely (and collectively) within the SOS. Notably, the excess in impact quota of the ammonia process could be offset by other sectors to sustainably cover the fertilizers' demand needed to feed a growing population. In the climate change PBs, this excess of quota could also be handled by removing carbon from the air via net negative emission technologies and practices, such as direct air capture. In parallel, a distributed scheme based on small- or medium-scale plants also based on low-carbon strategies may exhibit complementary advantages and restrictions, adding a distinct tool toward developing sustainable and profitable fertilizer production. Moreover, preventing the transgression of the PBs strongly linked to agriculture activities may require dietary changes. Notably, the EAT-Lancet Commission already proposed a sustainable diet to preserve planetary health.⁶⁵ Optimizing the nitrogen use efficiency in crop production⁶⁶ and recovering nutrients from organic wastes⁶⁷ could also help to operate within the PBs.

Overall, this work highlights the need to consider absolute environmental sustainability metrics beyond the conventional carbon footprint to evaluate alternative decarbonization routes. For the case of NH₃ production, we show that while some scenarios are superior in absolute sustainability terms, they are not likely to become economically competitive in the short-to-middle term. Therefore, further experimental research and governmental incentives are needed to drive down the production cost of the greener routes, which should be underpinned by environmental studies of the type presented herein.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.1c01915>.

Modeling details for the processes modeled in Aspen HYSYS, life cycle inventories, additional details on the PB methodology, assumptions behind the levelized cost of hydrogen, additional details about CAPEX calculations, additional environmental assessment metrics, and environmental and economic assessment of all scenarios, including those omitted in the main manuscript (PDF)

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Notes

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