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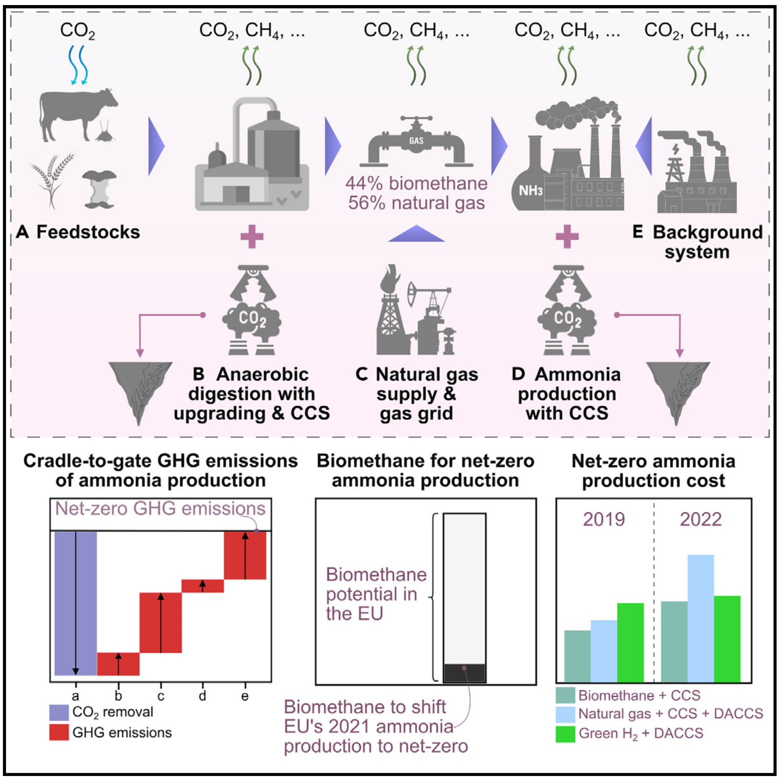
Graphical abstract



Highlights

- Biomethane-based ammonia production with CCS can achieve negative GHG emissions
- Using a biomethane blend of 44% and CCS enables net-zero ammonia production in the EU
- Shifting EU ammonia production to net zero requires just 11.7% of its biomethane potential
- Biomethane with CCS is at least 16% cheaper than other net-zero alternatives

Authors

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In brief

Ammonia manufacturers aim to reduce greenhouse gas (GHG) emissions, but economically viable pathways to net zero, using domestic feedstocks without major infrastructure changes, are limited. Here, we show that partially replacing natural gas with biomethane, combined with carbon capture and storage (CCS), can achieve net-zero ammonia production in the EU. This approach, requiring an average biomethane blend of 44%, would use only 11.7% of the EU's sustainable biomethane potential and proves more cost-effective than other net-zero options.

Istrate et al., 2024, One Earth 7, 2235–2249
December 20, 2024
https://doi.org/10.1016/j.oneear.2024.11.005

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One-tenth of the EU's sustainable biomethane coupled with carbon capture and storage can enable net-zero ammonia production

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https://doi.org/10.1016/j.oneear.2024.11.005

SCIENCE FOR SOCIETY Ammonia serves as the building block for a wide range of products, including synthetic nitrogen fertilizers. However, its production via the Haber-Bosch process relies heavily on fossil fuels (e.g., natural gas), making ammonia a large source of greenhouse gas (GHG) emissions. Among many mitigation options, sustainable biomethane, which is derived from biomass that does not compete with food production for land and is compatible with existing ammonia facilities, is gaining momentum. With its plan to expand biomethane production and its role as a large ammonia producer, the EU has a unique opportunity to use biomethane as a pathway toward net-zero ammonia. However, the feasibility of this route in the EU context remains unclear. Here we demonstrate that, using only a small fraction of the sustainable biomethane potential, the EU can cost-effectively shift to net-zero ammonia production by partially replacing natural gas with biomethane combined with carbon capture and storage. A full replacement of natural gas has the potential for negative GHG emissions in ammonia production. Our findings underscore the need for policymakers and stakeholders to give greater consideration and enhance ammonia industry's access to sustainable biomethane.

SUMMARY

Ammonia is a vital industrial chemical, but its production is greenhouse gas (GHG) emissions intensive. Prevailing mitigation options, such as electrification of heating, carbon capture and storage (CCS), and green hydrogen, face challenges related to limited mitigation potential, switch to new infrastructure, and likely high costs. Sustainable biomethane, derived from biomass that does not compete with food production for land and can leverage existing ammonia facilities, emerges as a promising option. However, whether and how biomethane can catalyze net-zero ammonia production remains underexplored. Here, using life-cycle assessment, we show that the European Union (EU)'s ammonia production can achieve cradle-to-gate net-zero GHG emission using, on average, a blend of natural gas (56%) and biomethane (44%) combined with CCS. This strategy would require only 11.7% of the EU's sustainable biomethane potential and is at least 16% cheaper than the green hydrogen option. Moreover, cradle-to-gate negative GHG emissions can be attained by completely switching to biomethane coupled with CCS, but the natural gas-biomethane blend strategy provides a sensible starting point.

INTRODUCTION

Ammonia is the basis of synthetic nitrogen fertilizers that boost agricultural productivity and ensure global food security.[1] About 70% of the 185 Mt of ammonia produced annually worldwide is used for urea and other fertilizers, which feed approximately 50% of the global population.[2,3] Ammonia is predominantly synthesized from nitrogen and H_2 in the Haber-Bosch process, which is energy intensive and fossil fuel dependent.[4] Notably, H_2 is mostly generated on site by natural-gas-based steam reforming or coal gasification (70% and 26% of global production, respectively),[3] making ammonia responsible for 20% and 5% of industrial natural gas and coal demand, respectively, and for over 1.2% of anthropogenic greenhouse gas (GHG) emissions.[5]

Current GHG emissions from ammonia production are not compatible with limiting global warming to well below 2 °C above pre-industrial levels.[6,7] Ammonia manufacturers are committed to reducing GHG emissions, aspiring to achieve even net-zero emissions. However, prevailing mitigation options such as electrification of heating in the steam reforming process and carbon capture and storage (CCS) have demostrated limited effectiveness.[8–11] Therefore, there is a strong motivation to shift toward renewable feedstocks that can be sourced locally with lower emissions.[12,13] One promising low-carbon alternative is running the Haber-Bosch process with green H_2 sourced from water electrolysis powered by wind or solar energy.[3,11] While the economic barrier to producing green H_2 is decreasing due to reduced renewable energy costs and increased natural gas prices,[14,15] the deployment of renewable power capacity remains a critical bottleneck.[16] Previous studies suggest that a chemical industry largely based on green H_2 could potentially exceed the projected renewable power generation.[17,18] Moreover, achieving net-zero through water electrolysis would still require offsetting the life-cycle GHG emissions of the required infrastructure (e.g., emissions associated with the manufacturing of wind turbines), potentially through energy-intensive and costly direct air carbon capture and storage (DACCS).[2,3]

Biomethane, a near-pure CH_4 gas produced from biomass, emerges as a promising avenue for ammonia manufacturers to achieve net-zero or even negative GHG emissions by utilizing a locally sourced renewable feedstock within the conventional steam reforming and Haber-Bosch processes. Biomethane relies on well-established technologies, such as anaerobic digestion for biogas production (a mixture of 50–70 vol % CH_4 and CO_2) followed by upgrading, where CO_2 is removed through standard processes like water scrubbing or pressure swing adsorption (PSA).[19,20] Because this renewable gas meets the same specifications as natural gas (e.g., >95 vol % CH_4 content), it can be injected into the gas grid and used as a direct substitute with minimal changes to existing infrastructure.[21] However, unlike natural gas, the carbon present in biogas and biomethane is of biogenic origin, derived from CO_2 previously taken up from the atmosphere during biomass growth through photosynthesis. Thus, the permanent storage of the CO_2 removed during the upgrading process holds the potential for net removal of CO_2 from the atmosphere.[22,23] The utilization of biomethane for ammonia opens new avenues for capturing and storing biogenic carbon, considering the substantial CO_2 generated in steam-reforming-based ammonia production. In this context, biomethane not only serves as a substitute for natural gas but also emerges as an appealing option for carbon dioxide removal (CDR), playing a pivotal role in achieving climate targets.[24] Despite this potential, the use of biomethane in ammonia production remains largely unexplored, hindered by a lack of studies quantifying its GHG emissions mitigation potential in specific applications and shedding light on the associated environmental and economic implications.

Although a number of life-cycle assessment (LCA) studies have addressed the environmental impacts of biomethane, those specifically focusing on its use in ammonia production remain scarce and limited in scope (a review of previous works is provided in the section "experimental procedures"). Previous studies either neglected CCS,[25] thus missing the potential for CDR, or focused on emerging technologies rather than leveraging existing infrastructure.[26] Antonini et al.[27] revealed the potential for achieving negative GHG emissions in hydrogen production through steam reforming of biomethane when combined with CCS. However, this study did not explore ammonia production and omitted the opportunity for CO_2 capture from biogas upgrading. Another limitation of prior LCAs is their focus on specific facilities[25,28] or regions (e.g., California).[26,27] This narrow scope fails to account for regional variations, including available feedstock types and electricity mixes, which can influence the mitigation potential. Consequently, the limited existing knowledge makes it hard for ammonia manufacturers to determine the feasibility of switching to biomethane coupled with CCS as a mitigation option in their respective locations. Addressing this gap requires a more comprehensive LCA encompassing various CCS deployment scenarios (i.e., partial vs. full CCS deployment) and quantifying impacts across countries with ammonia production infrastructure.

Additional considerations critical to the successful adoption of biomethane with CCS include addressing supply constraints, economic viability, and potential burden shifting to other impacts. A notable concern revolves around the availability of biomass feedstocks for large-scale biomethane production,[29] with global projections indicating that biomethane may only be able to substitute about 29% of the demand for natural gas.[30] This indicates that a complete switch to biomethane could be challenging. Alternatively, ammonia manufacturers might consider incorporating a blend of natural gas and biomethane alongside the deployment of CCS. The pivotal question lies in whether this blending strategy could effectively achieve net-zero life-cycle GHG emissions. Consequently, determining the required share of biomethane across locations and assessing the broad environmental and economic implications of such a net-zero scenario become essential. Prior techno-economic analysis (TEA) studies consistently emphasized the key role of policy incentives in rendering biomethane economically appealing (see the literature review within the section "experimental procedures"). However, recent market analyses suggest that, amid the escalating energy prices in Europe, biomethane could emerge as a cost-effective alternative to natural gas.[31] Moreover, previous economic analyses have not compared net-zero ammonia production scenarios, which would likely require expensive offsetting of residual GHG emissions (in contrast to the use of biomethane coupled with CCS as feedstock). Similarly, the potential burden shifting (i.e., collateral damage caused when attempting to combat climate change) of such net-zero scenarios remains largely unexplored.

Here, we explore the potential of sustainable biomethane—produced from feedstocks that do not compete for land with food production—coupled with CCS to mitigate GHG emissions in ammonia production within Europe (Figure 1). We apply LCA to quantify the carbon footprint of ammonia production on a country level, considering various CCS deployment scenarios and regional specificities. We further determine the natural gas-biomethane blend ratio required to achieve net-zero GHG emissions in each country and compare the impact on 15 indicators and production costs of this blending strategy with two

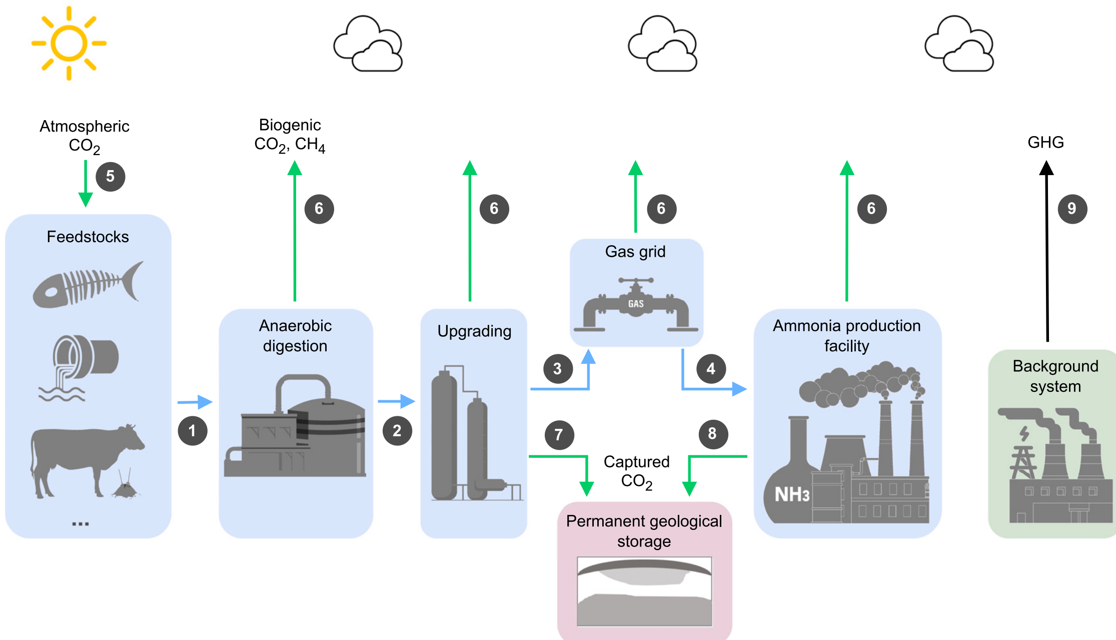

Figure 1. Overview of ammonia production from biomethane coupled with CCS and the associated carbon flows

Biodegradable feedstocks undergo anaerobic digestion (1) to produce biogas (2), which is subsequently upgraded to biomethane. The biomethane is injected into the gas grid (3) and used at the ammonia production facility as a direct substitute for natural gas (4). The carbon content of the biodegradable feedstocks comes from the CO_2 previously taken up from the atmosphere via photosynthesis during biomass growth (5). Emissions of biogenic CO_2 and CH_4 occur at every production stage (6), either as fugitive emissions (at anaerobic digestion, upgrading, and gas grid) or as direct emissions due to biogas or biomethane combustion (at anaerobic digestion and ammonia production facility). CO_2 is captured at the biogas-to-biomethane upgrading (7) and at the ammonia production facility (8), and it is compressed and permanently stored in underground geological formations. Flow (8) includes two streams, namely the capture of the CO_2 removed from the syngas stream after the water gas shift reactor plus the capture of the CO_2 in the flue gas resulting from the combustion of methane in the steam reforming process. Moreover, GHG emissions are associated with the background system (9) (e.g., electricity generation). Overall negative GHG emissions can be achieved if (5) is higher than the sum of (6) and (9).

alternative net-zero scenarios: one based on natural gas and the other on green H_2, both with residual emissions offset by DACCS. Findings show that using biomethane with CCS enables cradle-to-gate negative GHG emissions in ammonia production across all the studied European countries, ranging from −0.23 to −2.04 kg CO_2-eq kg^{-1} ammonia. The biomethane ratio required to achieve net-zero GHG emissions ranges from 14% to 87% by volume across countries, with an average of 44%. The European Union (EU) would require only 11.7% of its sustainable biomethane potential to make ammonia production levels (as of 2021) net zero. We also show that this approach would represent a cheaper net-zero alternative, as it does not require offsetting residual emissions while avoiding the use of expensive electrolytic hydrogen. Additionally, readily available options exist to mitigate the burden-shifting risks associated with the large-scale deployment of biomethane. A blend of natural gas and biomethane, coupled with the deployment of CCS, is a feasible strategy that should be regarded as a complementary mitigation option for the ammonia industry.

RESULTS

Carbon footprint of ammonia production

We start by assessing the carbon footprint of alternative ammonia production scenarios in Europe, comparing the Haber-Bosch process fed with natural gas, green H_2, and biomethane (a detailed description of the scenarios assessed is provided in the section "experimental procedures" and Table S1). The average carbon footprint of ammonia production from natural gas is 2.7 kg CO_2-eq kg ammonia^{-1} (Figure 2). About 53% of the impact is due to the direct emission of the concentrated stream of CO_2 from syngas generated from natural gas via steam reforming. Another 28% is due to the flue gas generated by burning natural gas for heating the reformer. Thus, capturing and storing the CO_2 from both the syngas and flue gas streams can reduce the carbon footprint to 0.92 kg CO_2-eq kg^{-1}. Alternatively, running the Haber-Bosch process with green H_2 obtained from water electrolysis powered by wind would reduce GHG emissions even further to 0.28 kg CO_2-eq kg^{-1}, with 56% of the impact coming from H_2 production.

Despite the important mitigation potential, neither CCS nor green H_2 can achieve ammonia production with net-zero GHG emissions. Conversely, biomethane could enable even negative emissions (on a cradle-to-gate basis) provided that CCS is systematically deployed. The average carbon footprint of ammonia production in the biomethane scenario without CCS is 1.81 kg CO_2-eq kg^{-1}, equivalent to a 33% reduction over the natural-gas scenario. Notably, biomethane coupled with CCS at the ammonia production facility (capturing and storing the CO_2

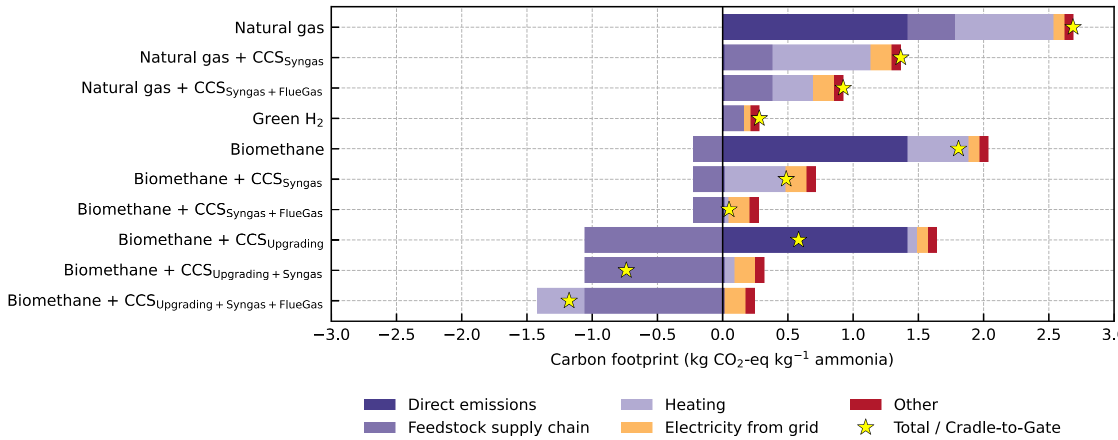

Figure 2. Carbon footprint of ammonia production in Europe using natural gas, green H_2, and biomethane

Green H_2 is obtained from water electrolysis powered by on-shore wind turbines. Biomethane is obtained by upgrading the biogas from anaerobic digestion. In the scenarios with CCS, CO_2 is captured from three sources: biogas-to-biomethane upgrading ($CCS_{Upgrading}$), syngas (CCS_{Syngas}), and the flue gas generated by burning natural gas for heating the reformer ($CCS_{FlueGas}$). Description of the scenarios can be found in the section "experimental procedures" and Table S1. Negative values indicate a net removal of CO_2 from the atmosphere due to the capture and storage of CO_2 previously taken up via photosynthesis during biomass growth. "Direct emissions" refers to emissions from steam reforming and/or Haber-Bosch processes; "feedstock supply chain" to the production and supply of natural gas, green H_2, or biomethane; "heating" to the natural gas or biomethane combusted to provide heat to the reformer; and "electricity" to the overall electricity consumed by the process. "Other" includes the remaining contributions (e.g., infrastructure, water supply, or CO_2 transport and storage).

from syngas and flue gas, i.e., stream 8 as in Figure 1) would achieve near net-zero emissions (0.05 kg CO_2-eq kg^{-1}), while CCS at both biogas-to-biomethane upgrading and ammonia facility (i.e., streams 7 and 8 as in Figure 1) would achieve a large negative carbon footprint; −0.74 kg CO_2-eq kg^{-1} if capturing CO_2 from upgrading and syngas and −1.18 kg CO_2-eq kg^{-1} if also capturing CO_2 from flue gas.

The negative emissions indicate that the captured CO_2 largely offsets the climate impacts associated with methane leakage and other emissions throughout the biomethane supply chain. This remains valid up to a 1.84- to 2.32-fold increase in methane leakage rates (see Figure S1). For example, the methane leakage rate of anaerobic digestion would need to increase from the assumed 3.2% (average value from the literature) to 5.86%–7.42% for ammonia to become net zero, which align with the upper bound values reported in the literature.[32–35] These findings highlight the importance of reducing methane losses in the biomethane supply chain.

GHG emissions associated with biomethane production and supply are largely influenced by local conditions. To further explore such regional variability, we calculated the country-specific carbon footprint of ammonia production from biomethane for EU countries (excluding Cyprus, Malta, and Luxemburg due to data availability and their relatively minor biomethane potential) plus Norway, Switzerland, and the United Kingdom. Our analysis considers factors such as the available types of biodegradable feedstocks in each country or the respective national electricity mix (Figure 3). Notably, we find that all countries could produce ammonia with negative GHG emissions under a full CCS deployment (i.e., streams 7 and 8 in Figure 1), with the impact ranging from −0.23 kg CO_2-eq kg^{-1} in Poland to −2.04 kg CO_2-eq kg^{-1} in Sweden. Germany, the major ammonia producer in the EU in 2021,[36] would exhibit a carbon footprint of −1.06 kg CO_2-eq kg^{-1}. Other ammonia producers—Croatia, France, Lithuania, Romania, Slovakia, and Spain—show similar carbon footprints (i.e., between −1.07 and −1.55 kg CO_2-eq kg^{-1}). Some countries provide the required conditions to achieve negative emissions even under a partial CCS deployment. For example, Sweden and Finland could already produce ammonia with negative emissions if CO_2 is captured either from syngas or from biogas-to-biomethane upgrading. Furthermore, 13 out of the 27 studied countries would only require CCS at the ammonia production facility.

Our results clearly show the huge potential of biomethane as a GHG emissions mitigation strategy in ammonia production. It is important to acknowledge, however, that the application of ammonia to soil as a fertilizer or its utilization as shipping fuel introduces additional emissions of N_2O, with large implications for achieving negative GHG emissions on a cradle-to-grave basis (see Figure S2). Since effectively reducing these emissions without eliminating the use of fertilizers seems challenging,[3] it is crucial to clarify that the claim of negative or net-zero emissions is valid exclusively on a cradle-to-gate basis.

Blending strategy for net-zero ammonia production

Currently, the EU produces around 3 billion cubic meters (bcm) year^{-1} of biomethane,[29] with the European Commission's REPowerEU plan targeting 35 bcm year^{-1} by 2030.[37] The sustainable potential of biomethane by anaerobic digestion in the EU is estimated at 38 bcm year^{-1} in 2030.[29] The EU's ammonia production has shown stability over time,[36] with the exception of 2022 when more than half of Europe's ammonia production capacity was shut down due to surging energy prices following the Russian invasion of Ukraine.[38] Therefore, for our analysis, we consider the EU's ammonia production levels as of 2021, totaling 11.3 Mt year^{-1}.[36] To produce this volume of ammonia from biomethane, approximately 10 bcm year^{-1} of biomethane would be needed, equivalent to 26.7% of the total sustainable potential (see Table S2). The demand for biomethane in ammonia production would vary significantly among countries, with Germany

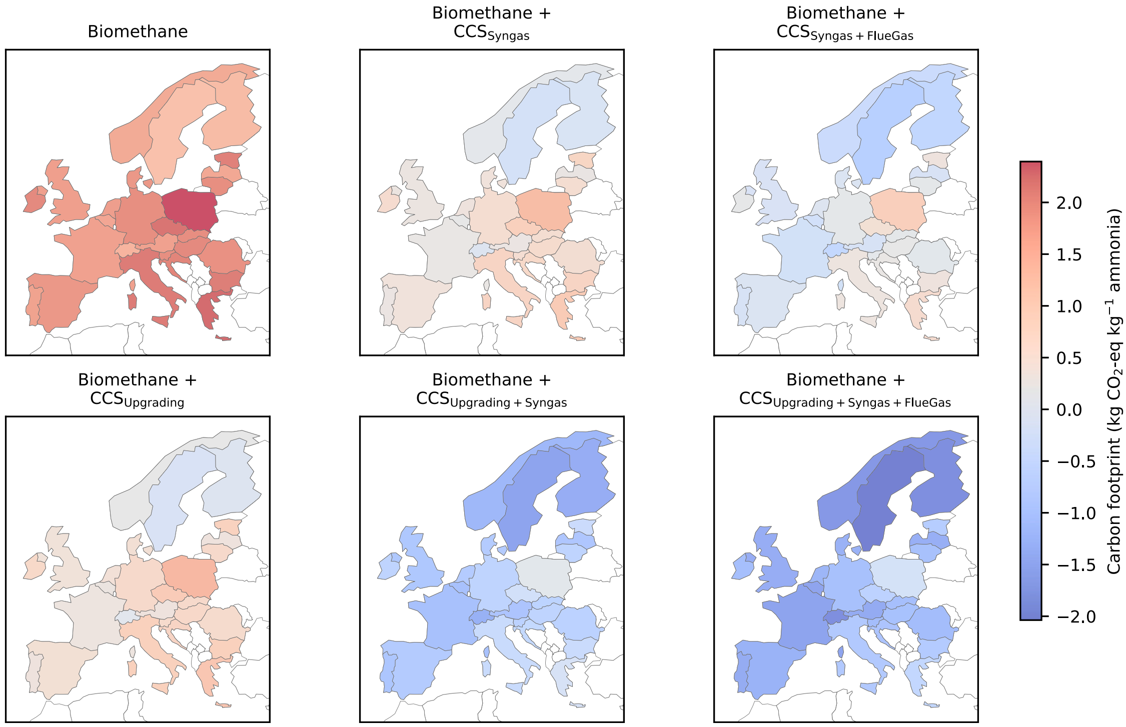

Figure 3. Country-specific carbon footprint of ammonia production using biomethane in Europe

Biomethane is obtained by upgrading the biogas from anaerobic digestion. In the scenarios with CCS, CO_2 is captured from three sources: biogas-to-biomethane upgrading (CCS$_{Upgrading}$), syngas (CCS$_{Syngas}$), and the flue gas generated by burning natural gas for heating the reformer (CCS$_{FlueGas}$). Description of the scenarios can be found in the section "experimental procedures" and Table S1. Negative values indicate a net removal of CO_2 from the atmosphere due to the capture and storage of CO_2 previously taken up via photosynthesis during biomass growth. All the studied countries could produce ammonia with negative GHG emissions under a full CCS implementation (i.e., scenario Biomethane + CCS$_{Upgrading + Syngas + FlueGas}$).

requiring 26.5% of their sustainable biomethane potential, Poland requiring 60.7%, France 7.7%, Romania 17.5%, Spain 7.1%, and Lithuania, Slovakia, and Croatia >100%. The switch from natural gas to biomethane with full CCS implementation would result in cradle-to-gate net-negative emissions of −13.3 Mt CO_2-eq year^{-1}, compared with 30.3 Mt CO_2-eq year^{-1} under the current scenario (see Table S3).

The total sustainable biomethane potential appears to be sufficient to sustain the current ammonia production levels, although countries like Lithuania or Slovakia will not be able to completely switch to biomethane. Moreover, the exploitation of this potential entails serious technical and socio-economic challenges[39,40] and the competition with other uses (e.g., transport) should not be disregarded. While the optimal use of biomethane lies beyond the scope of our study, here we explore the minimum volume of biomethane required to achieve net-zero GHG emissions in ammonia production. More specifically, we propose a natural gas-biomethane blending strategy under which the negative emissions of biomethane (with CCS) compensate the residual emissions from using a share of natural gas. We find that, under the full CCS deployment scenario, the required average biomethane blend ratio would be 44% by volume, ranging from 14.4% in Norway to 86.5% in Poland (Figure 4). Other producers could achieve net-zero ammonia at biomethane blend ratios of 48.2% in Germany, 34.2% in France, 42.7% in Romania, 43.5% in Spain, 48.3% in Lithuania, 53.7% in Slovakia, and 50.2% in Croatia. Notably, the EU would require 4.5 bcm year^{-1} of biomethane to attain the ammonia production levels as of 2021 at net-zero GHG emissions. This figure is similar to the current biomethane production level (3 bcm year^{-1}), while representing only 11.7% of the sustainable biomethane potential (Table S4).

Environmental impacts of net-zero ammonia production

We next compare the environmental implications in 15 impact categories of producing net-zero ammonia using natural gas with CCS (Net-zero blue scenario), green H_2 (Net-zero green scenario), and a natural gas-biomethane blend with an average biomethane content of 44% by volume and CCS (Net-zero biomethane scenario). In the Net-zero blue and Net-zero green scenarios, residual GHG emissions are offset via DACCS.[41] We consider the amount of CO_2 that needs to be removed from the atmosphere to achieve overall net-zero GHG emissions, i.e., to offset both emissions from ammonia production and from deploying the DACCS system (considering a low-temperature DAC technology based on solid sorbents).[42] Consequently, the Net-zero blue scenario requires removing from the atmosphere 1.69 kg CO_2 kg ammonia^{-1}, while the Net-zero green scenario requires removing 0.51 kg CO_2 kg ammonia^{-1}.

We find that none of the three net-zero scenarios perform best in all of the 15 impact categories (Figure 5). In other words, due to inherent trade-offs between categories, there is no absolute winner when looking at the whole spectrum of impacts. The Net-zero biomethane scenario has the highest impact in

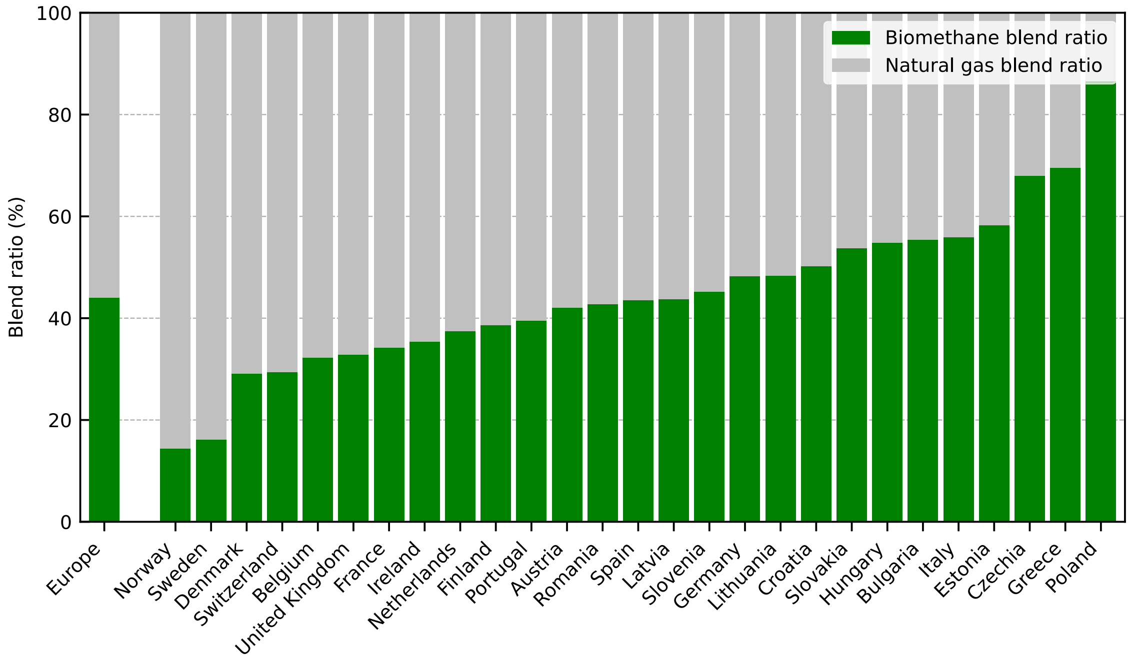

Figure 4. Natural gas-biomethane blending strategy to attain net-zero GHG emissions in ammonia production under a full CCS deployment
CO_2 is captured and stored from three sources: biogas-to-biomethane upgrading, syngas, and the flue gas generated by burning natural gas/biomethane for heating the reformer. On average, net-zero GHG emissions are achieved at a biomethane blend ratio of 44%, ranging from 13.5% in Norway to 83.2% in Poland. The results for the other scenarios with partial CCS deployment can be found in Figures S3–S6.

six categories, namely acidification, marine eutrophication, terrestrial eutrophication, photochemical oxidant formation, particulate matter formation, and land use. The use of biomethane contributes more than 60% to the impact in these categories. More specifically, biogas-to-biomethane upgrading via chemical scrubbing is largely responsible for the impact in acidification, terrestrial eutrophication, photochemical oxidant formation, and particulate matter formation. This technology separates the CO_2 present in the biogas through chemical absorption using mono-ethanolamine (MEA), whose degradation releases ammonia and acetaldehyde, which contribute significantly to the aforementioned impact categories. In this study, we assumed an upgrading technologies mix composed by water scrubbing (32% of the mix), chemical scrubbing (31%), membranes (24%), and PSA (13%), based on current market shares.[43] A sensitivity analysis reveals that a switch toward water scrubbing, membranes, or PSA could reduce these impacts below the Net-zero blue scenario (see Figures S7 and S8). Moreover, the higher impact in marine eutrophication in the Net-zero biomethane scenario is primarily caused by nitrate emissions from the use of nitrogen fertilizers for sequential cropping (representing about 22.6% of the biogas market in this study), while the higher land use is mainly due to the land requirements for the construction of the anaerobic digestion facilities.

Compared with the Net-zero blue scenario, the natural gas-biomethane blending strategy is advantageous in several impact categories, including freshwater eutrophication, ozone depletion, ecotoxicity, non-carcinogenic human toxicity, ionizing radiation, non-renewable energy resources depletion, mineral and metals resources depletion, and water use. However, the Net-zero green scenario performs similarly to or better than the blending strategy across all the impact categories but mineral and metal resources depletion. Finally, it is important to note that the robustness of the impact assessment methods varies across categories. The highest uncertainties are associated with ecotoxicity, human toxicity, resources depletion, land use, and water use. For these categories, the underlying impact assessment methods are recommended but either need further improvements or should be applied with caution (see Table S2 for an overview of impact assessment methods and their robustness).

Economic implications of net-zero ammonia production

We next assess the ammonia production cost in each net-zero scenario for two reference years: (1) 2019, just before the sharp increase in prices caused by the COVID-19 pandemic, skyrocketing inflation, and the Russian invasion of Ukraine[15]; and (2) 2022, considering the surge in energy prices experienced in Europe (details on the economic assessment are provided in the section "experimental procedures"). For the reference year 2019, the Net-zero biomethane scenario shows the lowest production cost at 0.65 USD kg ammonia^{-1}, compared with 1.00 and 1.61 USD kg^{-1} in the Net-zero blue and Net-zero green scenarios, respectively (Figure 6). Here, we consider a natural gas price of 16 USD MWh^{-1}, corresponding to the average spot price in Europe in 2019.[44] While the biomethane price is significantly higher (ranging from 59 to 106 USD MWh^{-1}, with an average of 83 USD MWh^{-1}),[43] it arises as a cheaper alternative for net-zero ammonia production since it does not require offsetting residual GHG emissions via DACCS. Even under the highest biomethane price and the most optimistic DACCS cost, the production cost in the Net-zero biomethane scenario would be 16%

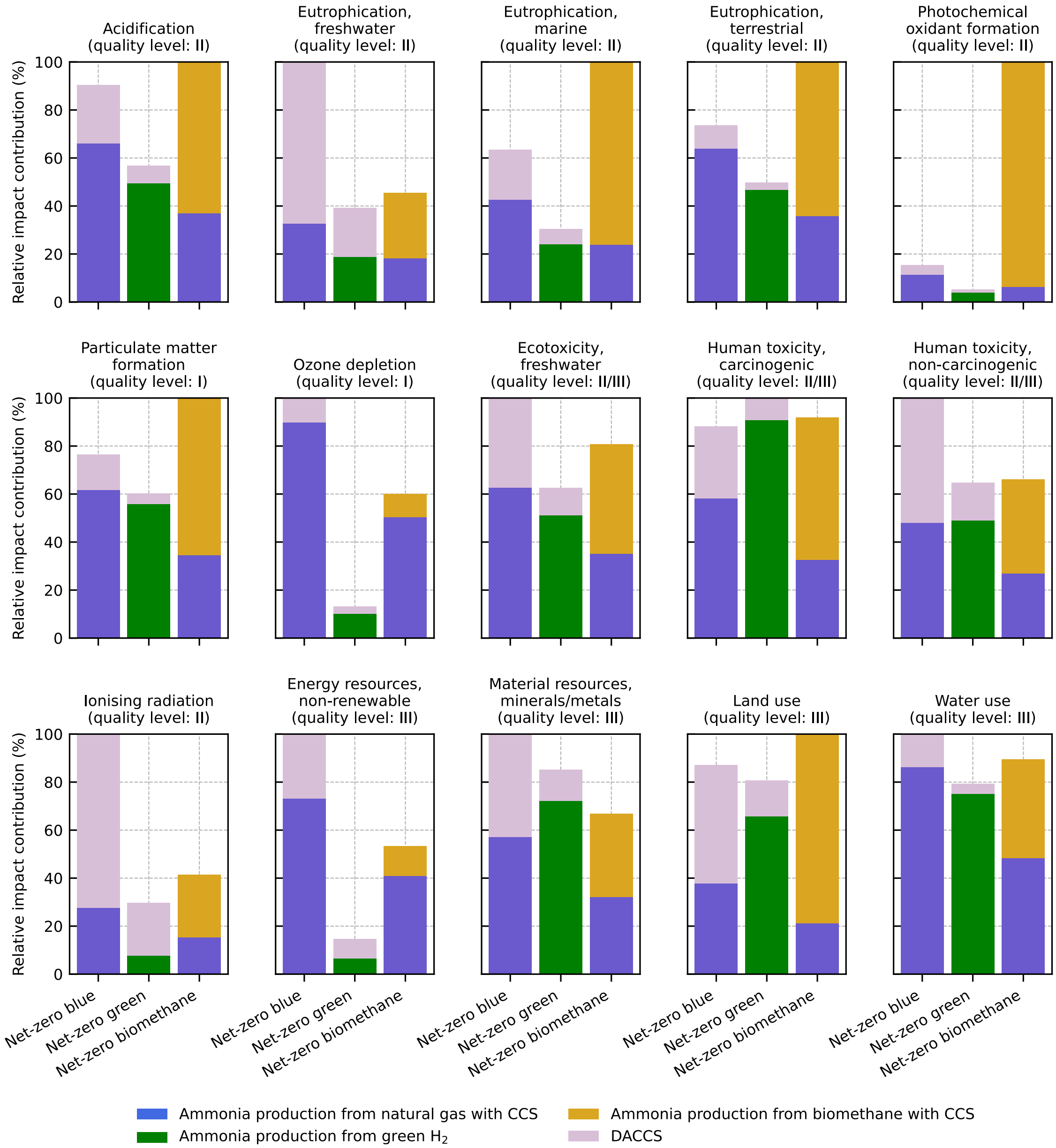

Figure 5. Life-cycle environmental impacts of ammonia production under three net-zero GHG emissions scenarios in Europe

Net-zero blue: ammonia production from natural gas with CCS plus residual emissions offset by DACCS. Net-zero green: ammonia production from green H_2 obtained from water electrolysis powered by on-shore wind turbines plus residual emissions offset by DACCS. Net-zero biomethane: ammonia production from a natural gas-biomethane blend with an average biomethane content of 44% and CCS. Results are normalized considering the maximum impact across the three options in each category. Each impact category shows the quality level as recommended by the European Commission's Joint Research Centre (further details on the impact categories and impact assessment methods and their robustness can be found in Table S5).

lower than in the net-zero blue scenario (0.75 and 0.88 USD MWh^{-1}, respectively). Finally, producing net-zero ammonia based on green H_2 is the most expensive scenario due to the cost-intensive water electrolysis step, accounting for 75% of the production cost.

Natural gas spot prices in Europe have experienced a steady increase since 2020, reaching an average of 134 USD MWh^{-1} in 2022[44] with large implications for the economic competitiveness of the chemical industry.[15] In comparison to 2019, the production cost of net-zero ammonia in 2022 is 3.3 times higher in the net-zero blue scenario and 2.6 times higher in the Net-zero biomethane scenario. Conversely, the Net-zero green scenario is less vulnerable to natural gas price volatility since the major cost contributor is H_2 production via wind power. Overall, the natural gas-biomethane blending scenario remains the most favorable, with a production cost of 1.66 USD kg^{-1}, in contrast to 1.86 USD kg^{-1} in the net-zero green scenario and 3.28 USD kg^{-1} in the net-zero blue scenario.

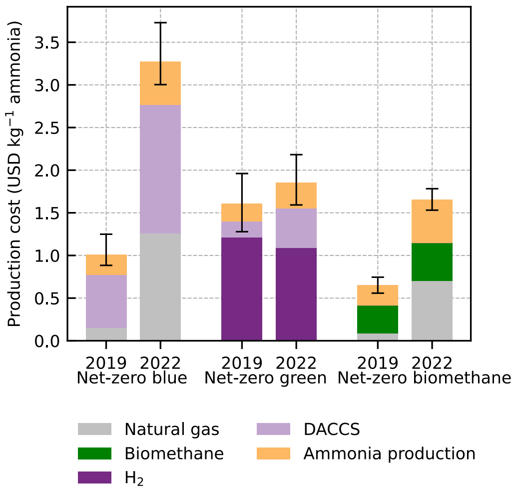

Figure 6. Production cost of ammonia under three net-zero GHG emissions scenarios in Europe

Net-zero blue: ammonia production from natural gas with CCS plus residual emissions offset by DACCS. Net-zero green: ammonia production from green H_2 obtained from water electrolysis powered by on-shore wind turbines plus residual emissions offset by DACCS. Net-zero biomethane: ammonia production from a natural gas-biomethane blend with an average biomethane content of 44% and CCS. Costs are provided for two reference years: (1) 2019 just before the sharp increase in prices caused by the COVID-19 pandemic, skyrocketing inflation, and the Russian invasion of Ukraine; and (2) 2022, considering the drastic increase in energy prices experienced in Europe. The stacked bars provide the cost breakdown into feedstock and fuel (i.e., natural gas, biomethane, or H_2), DACCS, and ammonia production (including capital, fixed, and utilities costs). Error bars show the minimum and maximum cost estimates based on the range of costs for biomethane, H_2, and DACCS found in the literature (see section "experimental procedures").

DISCUSSION

Substantially reducing GHG emissions from ammonia production is imperative for transitioning the chemical industry to net-zero[16] and has large implications for achieving more sustainable food and energy systems.[5,6] Our analysis demonstrates that European ammonia production can achieve cradle-to-gate negative GHG emissions (i.e., a net removal of CO_2 from the atmosphere) by switching to biomethane coupled with CCS. This is possible across all studied European countries, including those with heavily fossil fuel-reliant energy systems, provided that CCS is fully deployed at both the biomethane and ammonia production sites. We further show that achieving net-zero GHG emissions is feasible with a natural gas-biomethane blend with an average of 44% biomethane by volume, ranging from 14% to 87% depending on the country.

The natural gas-biomethane blending strategy offers several advantages over other net-zero alternatives. Biomethane has essentially the same composition as natural gas, enabling the continued use of existing ammonia production facilities. This prevents the costly standing of these assets and avoids the substantial initial investment required for alternatives like green H_2. While previous studies suggested that biomethane lacks economic appeal without policy incentives,[30,45,46] our findings indicate that a natural gas-biomethane blend and CCS can yield net-zero ammonia at a reduced cost. This superiority lies on the capacity to achieve net-zero without relying on offsetting mechanisms. As shown in our analysis, the costs associated with offsetting residual GHG emissions through DACCS substantially increase production costs in natural gas- and green H_2-based net-zero scenarios. Moreover, during the peak natural gas prices experienced by Europe in 2022, the price of biomethane was comparable to that of natural gas, with the advantage of being less prone to fluctuations since it relies on local resources. Looking into the future, as decarbonization becomes a key factor in policymaking, more stringent carbon taxes and incentives by governments will further enhance the appeal of biomethane. For example, the European Commission's REPowerEU plan envisions financing support for innovative technologies for the upgrading of biogas to biomethane and its subsequent injection into the gas grid.[37] Moreover, shifting to biomethane in ammonia production, a key chemical to feed future generations, will help cope with the future likely volatility of natural gas prices linked to geopolitical conflicts.

Ammonia manufacturers would have to compete with other industries to secure a stable supply of biomethane. Thanks to its versatility, biogas has various other potential applications beyond its upgrading to biomethane, including electricity generation and heating. Additionally, biomethane could substitute natural gas in various other industrial applications such as high temperature heating or could be used as a transport fuel. However, ammonia production might arguably be one of the most efficient ways of harnessing the climate change mitigation potential of biomethane coupled with CCS. Ammonia stands out as particularly appealing since it is carbon free, allowing for the capture and permanent storage of most of the biogenic carbon content in the original feedstock. Capturing the high-purity CO_2 stream separated from the syngas at ammonia production incurs lower costs compared to capturing CO_2 from more diluted streams, like the flue gas generated by combusting biogas/biomethane for electricity generation or heating.[47] Using biomethane as a transport fuel would not enable the capture of the CO_2 from combustion, thereby overlooking its full CDR potential. Moreover, certain alternative uses may be limited by infrastructure availability, as, for example, the large-scale deployment of biomethane as transport fuel is hindered by the scarce refueling infrastructure.[48]

Notwithstanding these evident benefits, the proposed solution is not without its challenges. Limited availability of resources (e.g., biowaste) or the potential impact of climate change on biomass productivity have been acknowledged as limitations to the large-scale deployment of biomethane.[39,40,49] Consequently, achieving the share of biomethane in the gas grid required for net-zero ammonia (e.g., 44% on average) appears to be highly ambitious. For example, the International Energy Agency forecasts a 2.5%–10% share of biomethane in the European gas grid by 2040.[21] A more realistic approach would entail the use of guarantee of origin (GO) certificates, which enable biomethane producers to market biomethane as a renewable gas and allow ammonia manufacturers to claim the use of biomethane in their facilities. For example, the chemical company BASF has been employing biomethane in one of its existing methanol production facilities in Germany.[50] Here, the biomethane share is certified according to the REDcert standard, which is recognized under the Renewable Energy Directive.

The BASF methanol facility reports that approximately 15% of their annual production is derived from biomethane.[50] However, this performance must be contextualized within the early stages of the biomethane market's development, where only about 9% of EU-produced biogas is upgraded to biomethane.[51] The imminent expansion of the EU biomethane market, propelled by the REPowerEU plan,[37] alongside the maturation of GO registries across Europe, is anticipated to markedly improve accessibility to biomethane.[52]

At the European level, the overall biomethane potential does not appear to be a critical bottleneck. Converting the EU's ammonia production levels to net zero through a natural gas-biomethane blend and CCS would require only 11.7% of the overall sustainable biomethane potential or 13% of the EU's biomethane target by 2030. However, regional aspects should be carefully considered. Germany could transition to net-zero ammonia with just 12% of its national sustainable biomethane potential. In contrast, other major producers like Poland and Croatia would need more than 50%, while Lithuania and Slovakia would require more than 80%. It seems highly unlikely that these countries could exploit such a high percentage of their potential exclusively for ammonia production. Instead, the ammonia industry in Poland, Croatia, Lithuania, and Slovakia could rely on cross-border trade of biomethane. This would be facilitated by the European Renewable Gas Registry (ERGaR), which enables the transfer of ownership of biomethane certificates between established national GO registries within Europe. Potential biomethane suppliers may include France, Spain, and Italy, which have a large biomethane potential but low or non-existent ammonia production capacities. While these countries could allocate their biomethane production to other national applications, it could be argued that a European common goal toward climate neutrality should involve prioritizing applications where biomethane can have the highest benefits. Although our study already underscores ammonia's standout potential, achieving this vision requires future research to systematically compare all potential applications across European countries to determine an optimal biomethane network that maximizes contributions to European climate goals.

Further development and establishment of CO_2 storage sites in Europe, along with a European CO_2 transportation network and appropriate regulatory frameworks and social acceptance, are essential to unlocking the CDR potential of biomethane.[53] Currently, there are only 10 CO_2 geological storage sites in use or planned in Europe, with all but one located in northern Europe.[22] Although none of the ammonia-producing countries have CO_2 storage sites within their territories, Germany and Poland offer favorable conditions due to their proximity to storage projects in the North Sea. However, challenges arise from the fact that biomethane production is typically distributed across small-scale plants spread throughout the national territory. For example, in 2021, Germany had 238 biomethane plants, with many more planned for the next decade.[54] Developing the pipeline infrastructure to connect these small CO_2 sources with storage sites is therefore essential. Moreover, future developments of GO certificates should consider including specification regarding the deployment of CCS.

It is equally imperative not to overlook the potential for burden shifting. Our findings revealed that transitioning from natural gas to biomethane in ammonia production could exacerbate the impact on acidification, marine and terrestrial eutrophication, photochemical oxidant formation, particulate matter formation, and land use. All these are critical impacts intricately connected to various planetary boundaries, including biodiversity integrity (acidification, eutrophication, photochemical oxidant formation, and land use), nutrient cycles (acidification and eutrophication), and land-system change (land use).[55,56] The increase in impacts associated with ammonia emissions—comprising acidification, terrestrial eutrophication, photochemical oxidant formation, and particulate matter formation—could be curtailed by avoiding chemical scrubbing for biogas-to-biomethane upgrading (see Figures S7 and S8). Moreover, impacts on marine eutrophication could be minimized by reducing the use of sequential cropping in favor of waste and residual feedstocks that do not necessitate fertilizers, thereby avoiding nitrate emissions. Therefore, readily available options exist to mitigate the burden-shifting risks associated with the large-scale deployment of biomethane. Future research can focus on assessing whether the adoption of mitigation options could facilitate a transition to biomethane that improves all environmental aspects. Moreover, future work could further address the fundamental question of whether ammonia production from biomethane could operate within the assigned safe operating space defined by the planetary boundaries.

We should remark that we do not advocate for expanding the conventional steam reforming and Haber-Bosch infrastructure, as new fossil fuels-related infrastructure may hinder the transition toward renewable energies due to its long lifetime.[57] Therefore, we only considered the use of biomethane as a substitute for natural gas in existing infrastructure. For the same reason, we do not advocate for a complete shift away from other ammonia production options, such as green H_2 or novel approaches such as the ammonia leaf technology.[58,59] The transition toward more sustainable ammonia production (and all chemicals in general) calls for a portfolio of alternatives optimized considering regional advantages.[18] Within this context, we argue that a natural gas-biomethane blend along with CCS is a sensible starting point that deserves further consideration by the industry. The use of biomethane as a renewable carbon source could also have implications for future research directions on alkane functionalization (C–H activation) through the biomethane platform. These strategies could benefit from the low cost of biomethane and the avoidance of expensive electrolytic hydrogen when relying on captured CO_2 as a source of renewable carbon. To make this approach successful, it is crucial to establish regulatory frameworks that grant chemical companies access to biomethane with assurance of its origin, including whether CCS has been implemented at the biomethane facility.

EXPERIMENTAL PROCEDURES

A review of previous works

Here, we provide a review of previous research on the economic and environmental performance of mitigation options for ammonia production. A number of studies have applied LCA and TEA to compare blue ammonia (i.e., based on natural gas coupled with CCS) with green ammonia (i.e., based on green H_2).[60,61] Another common goal has been to assess alternative pathways for sourcing H_2, including H_2 from water electrolysis or biomass gasification,[62–64] various water electrolysis technologies,[60,65] and different electricity sources for water electrolysis (e.g., solar photovoltaics, wind power, hydropower, and nuclear energy).[60,66,67] These previous studies generally concur that green H_2, reliant on low-carbon electricity sources, can be the best option for reducing GHG emissions. However, they also underscore potential bottlenecks associated with higher production costs[60] and burden shifting to other environmental impacts (e.g., increased use of mineral and metal resources, water, and land) linked to electrolytic H_2.[61] These limitations have motivated research on more innovative ammonia production pathways, such as decentralized electrocatalytic ammonia synthesis,[58] electrochemical ammonia production,[68] thermal decomposition of methane,[69] and bio-oil reforming or partial oxidation.[70] These studies showcase the potential economic and environmental benefits of these innovative concepts, which, however, still remain far from large-scale deployment.

Conversely, LCA and TEA studies specifically investigating the utilization of biomethane for ammonia production are scarce. Most of previous LCAs on biomethane have focused on its production[71–73] and/or use as a fuel in road[74–76] and maritime[77,78] transportation. A few LCAs have explored the integration of biomethane production and CCS. For example, Varling et al.[79] considered the permanent storage or utilization of the CO_2 removed during the upgrading process, while Styles et al.[74] focused on the combustion of biomethane for electricity generation equipped with CCS. Some LCAs have assessed the application of biomethane in specific chemical products like hydrogen,[27] methanol,[25,80] and dimethyl ether.[25] To the best of our knowledge, only two LCAs have explored the use of biomethane for ammonia production. Moghaddam et al.[25] conducted an LCA considering an existing biomethane production plant in Sweden utilizing maize as feedstock. They reported a 30% reduction in the life-cycle GHG emissions of ammonia by replacing natural gas with biomethane (without CCS). This study also assessed two additional impacts, finding that, while biomethane could reduce acidification, it results in a notable increase in eutrophication. Ghavam et al.[26] presented an LCA of ammonia production from biogas coupled with CCUS utilizing food waste and wastewater from a mid-size city in California. This study focuses on an emerging technology configuration based on an electrochemical membrane separation for H_2 production followed by electrochemical conversion of ammonia. The results indicate that the proposed approach may lead to lower GHG emissions compared to conventional steam reforming and Haber-Bosch process without CCUS.

Moreover, Antonini et al.[27] assessed the European average life-cycle environmental impacts of hydrogen production using biomethane in the conventional steam reforming and autothermal reforming processes. This study accounted for the adoption of CCS in the reforming process, investigating both pre-combustion CO_2 capture and a novel vacuum PSA. The study offers valuable insights by showcasing the potential for achieving net negative GHG emissions in hydrogen production, the key step preceding ammonia production. Moreover, it highlights the potential for burden shifting, as biomethane coupled with CCS leads to increased impacts across various other categories, including acidification, human toxicity, respiratory effects, and land use. Likewise, Mersch et al.[28] presented the carbon intensity of hydrogen production from biomethane coupled with CCS for a case study in Texas, United States. This study suggests that a share of 10%–20% of biomethane achieves hydrogen with net-zero emissions. However, the authors extend this assumption to suggest net-zero ammonia production without quantifying the impacts through an LCA.

The bulk of prior TEA studies concerning biomethane have focused on determining its economic viability in comparison with natural gas, often pointing to the necessity for policy incentives like feed-in tariffs and power purchase agreements.[45,46] For example, Wong et al.[45] found that the current climate policy in California is already enough to incentivize the production of biomethane coupled with CCS. Notably, Mersch et al.[28] conducted a TEA specifically on ammonia production from biomethane coupled with CCS, focusing on a case study in the United States. Their findings indicate that the inclusion of production tax credits for clean hydrogen production is likely to make this route economically competitive with the conventional natural-gas-based route. However, this study failed to include the offsetting of residual GHG emissions, which is imperative to achieve net zero in the natural-gas-based route.

Ammonia production scenarios

We evaluated 10 ammonia production scenarios by assessing three production routes (natural-gas- and biomethane-based steam reforming and water electrolysis) while also considering CO_2 capture and storage from various sources (see Table S1). In all the scenarios, ammonia is synthetized from nitrogen and H_2 over an iron-based catalyst in the Haber-Bosch process, which operates at high temperatures (400°C–500°C) and pressures above 100 bar.[4]

In the Natural gas scenario, H_2 is obtained from natural-gas-based steam reforming, internal heat demand is covered by a furnace burning natural gas, and CO_2 is vented. Two variants of this scenario were assessed. In the first variant, the concentrated stream of CO_2 removed from the syngas after the water gas shift reactor is compressed and stored (Natural gas + CCS_{Syngas} scenario). In the second variant, the CO_2 from both the syngas generated from natural gas and the flue gas stream resulting from the combustion of natural gas in the steam reforming process is compressed and stored (Natural gas + $CCS_{Syngas + FlueGas}$ scenario). The CO_2 in the flue gas is captured through chemical absorption using MEA, which is the most mature CO_2 capture technology with a technology readiness level (TRL) of 9.[81] Essentially, a lean solvent stream of 10% vol. MEA is sent to an absorption column, where approximately 99.7% of the input CO_2 is absorbed and separated in the liquid stream. The concentrated solvent from the absorption column is directed to a regeneration column with a reboiler, allowing for the recovery of lean solvent that is subsequently recycled to the absorption column. In all the scenarios with CCS, the captured CO_2 is compressed to 110 bar and transported by pipeline over 200 km to a geological storage site, where it is injected at 1,000 m depth.[82]

The Green H_2 scenario represents a low-carbon alternative in which the H_2 required for the Haber-Bosch process is obtained from proton exchange membrane (PEM) water electrolysis. The electricity demand of the electrolyzer is satisfied by on-shore wind power, while the grid supplies the auxiliary electricity (e.g., to run compressors and pumps).[60] Moreover, in this scenario, the high-purity N_2 is obtained through cryogenic distillation.

In the Biomethane scenario, biomethane is used as a direct substitute for natural gas in the steam reforming process and the furnace. Biomethane is obtained by upgrading the biogas generated via anaerobic digestion of biodegradable feedstocks. We focus on anaerobic digestion since it is a well-established technology with a TRL of 9, whereas gasification and power-to-gas concepts are much less mature and have very limited market implementation. Only biomass feedstocks that do not compete for land with food or feed production were considered, namely biowaste (food and green waste), industrial wastewater, sewage sludge, animal manure, agricultural residues, and sequential crops (i.e., the cultivation of a second crop before or after the main crop on the same land).[29] Regarding biogas-to-biomethane upgrading, we considered the four most relevant technologies, all with a TRL of 9: water scrubbing, chemical scrubbing, membranes, and PSA.[43] Water scrubbing separates the CO_2 from biogas through dissolution in water in an absorption column under high pressure. The CO_2 is then released from the water in the desorption column. Chemical scrubbing entails the chemical absorption of CO_2 using MEA, as previously described. In the membranes technology, most of the CH_4 contained in the biogas is retained in the membrane, while CO_2 permeates through. In the PSA, biogas undergoes compression and is directed to an adsorption column that retains CO_2. Subsequently, this CO_2 is desorbed by releasing pressure.

We further assess five scenarios of biomethane-based ammonia production by considering CCS. The first two scenarios involve the capture and storage of CO_2 from syngas (Biomethane + CCS_{Syngas} scenario) and CO_2 from both syngas and flue gas (Biomethane + $CCS_{Syngas + FlueGas}$ scenario) implemented at the ammonia production facility. The process for capturing and storing the CO_2 from syngas and flue gas is the same as in the scenarios with natural gas. The third scenario focuses on capturing and storing CO_2 specifically from biogas-to-biomethane upgrading (Biomethane + $CCS_{Upgrading}$ scenario). Given that upgrading biogas to biomethane inherently involves removing the CO_2, integrating CCS is relatively straightforward, requiring only the compression of this concentrated CO_2 stream and subsequent transportation via pipelines for underground injection. The fourth scenario combines the capture and storage of CO_2 from both syngas and upgrading (Biomethane + $CCS_{Upgrading + Syngas}$ scenario), while the fifth scenario describes the implementation of CCS at the three emission sources (Biomethane + $CCS_{Upgrading + Syngas + FlueGas}$ scenario). The same assumptions regarding compression, transportation, and injection as in the scenarios with natural gas apply to the scenarios with biomethane.

We also assessed three net-zero ammonia production scenarios. In the Net-zero blue scenario, ammonia is produced as in the Natural gas + $CCS_{Syngas\ +\ FlueGas}$ scenario, i.e., from natural-gas-based steam reforming while considering CCS. Here, residual GHG emissions to achieve overall net-zero emissions are offset via DACCS as described in the main text. Similarly, in the Net-zero green scenario, ammonia is produced as in the Green H_2 scenario with residual GHG emissions offset via DACCS. Finally, in the Net-zero biomethane scenario, ammonia is produced from a natural gas-biomethane blend with an average biomethane content of 37.1% and full CCS deployment. Here, the negative emissions from biomethane compensate for the residual emissions resulting from the use of a share of natural gas.

LCA

Goal and scope definition

We performed an attributional LCA following ISO standards[83,84] to assess the environmental impacts of alternative ammonia production scenarios. The specific goals are 2-fold: (1) to determine whether biomethane coupled with CCS can enable net-zero or negative GHG emissions in ammonia production and (2) to compare the life-cycle impacts of net-zero ammonia production scenarios based on natural gas, green H_2, and biomethane. The LCA uses the most recent available life-cycle inventory (LCI) data and focuses on the European context (we quantified European average as well as country-specific impacts). We considered mainly well-established technologies based on average market data. The functional unit has been defined as producing 1 kg of anhydrous ammonia. We adopt cradle-to-gate system boundaries, including all the relevant processes in ammonia production, from raw materials extraction and processing to synthesis and CO_2 storage (see Figure S9). The required infrastructure (e.g., construction of anaerobic digestion plants) as well as the disposal of waste generated throughout the supply chain (e.g., waste from infrastructure construction) have been considered. Conversely, the use and end of life of ammonia have been omitted since the focus is on its production, and these further stages would remain unaffected in the alternative scenarios. LCI modeling and LCA calculations were performed with Brightway2, a Python-based open-source LCA software.[85] All LCI dataset are made available in a format that can be directly imported into Brightway2.

Inventory analysis

The inventory analysis phase involves the compilation of the inputs and outputs (i.e., raw materials, energy, emissions, etc.) associated with the functional unit, differentiating between the foreground and background systems. The foreground system comprises those processes that are directly affected by the assessed decisions.[86] In our study, foreground system comprises feedstock collection and transport; biogas production by anaerobic digestion; biogas-to-biomethane upgrading; ammonia production (including H_2 production via steam methane reforming [SMR] or water electrolysis, the Haber-Bosch process, and on-site heat production); CO_2 capture from point sources and atmosphere; and CO_2 compression, transport, and permanent storage. We compiled the LCIs for these processes from the literature and our own calculations, as described below. The background system comprises those processes that are outside the direct influence of the assessed system (e.g., raw materials extraction and processing and power generation).[86] These LCIs were obtained from the ecoinvent database v3.9.1, cutoff system model.[87] In the following, we describe the modeling of foreground processes inventories.

Anaerobic digestion is what is known as a multifunctional process as, in addition to the waste treatment service, it co-produces biogas and digestate (the latter can be used as a fertilizer under certain circumstances). This multifunctionality issue needs to be addressed as in this study we are interested only in the environmental impacts of the biogas. To ensure consistency, we followed the allocation approach adopted in the cutoff system model of the ecoinvent database. Accordingly, the biogas produced via anaerobic digestion of biowaste, industrial wastewater, and sewage sludge is considered as a by-product of the main activity (waste treatment) and hence free of burdens (i.e., the environmental impacts are fully allocated to the waste treatment function). In contrast, biogas production is considered to be the single purpose of the anaerobic digestion of animal manure, agricultural residues, and sequential crops. Consequently, the environmental impacts of collecting and treating these feedstocks are fully allocated to the biogas.

The approach employed for allocating the environmental impacts of anaerobic digestion may cause a violation of the carbon balance as in some cases the CO_2 uptake from the atmosphere via photosynthesis during biomass growth is not allocated to the biogas. As here we aim to determine whether biomethane with CCS can enable ammonia production with net-zero GHG emissions, the carbon balance needs to be adjusted accordingly. Following the same approach as in Antonini et al.,[27] we calculated the amount of CO_2 taken up from air based on the carbon atoms present in the biogas (assuming that biogas is 57% methane and 43% CO_2 by volume)[29] and added this flow to the LCI of biogas production. For example, the LCI for biogas production from biowaste includes 1.98 kg of CO_2 from the atmosphere per m^3 of biogas.

To model the LCI for biogas production via anaerobic digestion of animal manure, agricultural residues, and sequential crops, we assumed that 3.2% of the biogas volume is leaked,[32] 10% is flared due to storage limitations and/or low methane flux,[46] 10.1% is combusted to cover internal heat demand, and the remaining 76.7% is upgraded to biomethane. Hence, 1.23 m^3 of biogas needs to be produced in order to supply 1 m^3. This efficiency and the physicochemical properties of the feedstock determine the input mass of feedstock, which was estimated to be 3.76, 9.75, and 25.60 kg wet feedstock m^{-3} of biogas for agricultural residues, sequential crops, and animal manure, respectively. Electricity consumption ranges from 0.13 kWh m^{-3} of biogas for animal manure to 0.17 kWh m^{-3} of biogas for agricultural residues and sequential crops.[88] The average European biogas production mix consists of 34% biogas from animal manure, 26% from agricultural residues, 23% from sequential crops, 10% from industrial wastewater, 5% from biowaste, and 2% from sewage sludge.[29]

For biogas-to-biomethane upgrading, we considered a mix of the four most relevant technologies according to their European market shares: water scrubbing (32% of the market), chemical scrubbing (31%), membranes (24%), and PSA (13%).[43] We assumed a biomethane purity of 97% for water scrubbing, 99% for chemical scrubbing, 97% for membranes, and 96% for PSA.[89] Methane leakage rates range from 0.10% by volume for chemical scrubbing to 1% for membranes, 2% for water scrubbing, and 3% for PSA.[89] Based on these parameters, we estimated the volume of biogas required per m^3 of biomethane as follows: 1.74 m^3 of biogas for water scrubbing, chemical scrubbing, and PSA, and 1.72 m^3 of biogas for membranes. Electricity consumption for upgrading and compression to 24 bar (to meet the natural gas grid requirements) is 0.55, 0.34, 0.55, and 0.51 kWh m^{-3} of biomethane for water scrubbing, chemical scrubbing, membranes, and PSA, respectively.[89] Chemical scrubbing also consumes 3.44 MJ of heat m^{-3} of biomethane as well as other chemicals such as MEA. Moreover, water scrubbing requires 0.17 kg water m^{-3} of biomethane.[89]

The LCI for ammonia production via natural gas- or biomethane-based steam reforming has been adapted from the ecoinvent database. The process consumes about 0.90 m^3 of natural gas or biomethane per kg of ammonia, including both feedstock and fuel. The LCI for the supply of high-pressure natural gas is from the ecoinvent database. Methane leakage from natural gas or biomethane distribution has been considered equal to the average losses in the European high-pressure natural gas networks based on the ecoinvent database (i.e., 1% by volume).[87] Ammonia production from H_2 obtained by water electrolysis is mainly based on data from D'Angelo et al.,[60] complemented with data from the ecoinvent database and Bareiß et al.[90]

As for CCS, LCIs were obtained from Volkart et al.[82] for CO_2 capture through chemical absorption and from Antonini et al.[27] for CO_2 transportation to the geological storage site where it is injected. Furthermore, the LCI for the DAC system is from Terlouw et al.[42] The low-temperature DAC technology considered here consumes about 1.13 kWh electricity kg^{-1} CO_2 removed from the atmosphere.

In addition to the European average, we have created country-specific LCIs for ammonia production from biomethane. The biogas production mixes for European countries were derived from the types of biodegradable feedstocks available in each country, as reported in Alberici et al.[29] (country-specific shares are provided in the supplementary dataset). Beyond changing the biogas production mix, we relinked the country-specific LCIs to the background LCI datasets for the same location, whenever possible. Based on available LCIs within the ecoinvent database, this relinking primarily applied to the electricity mix, waste treatment, and industrial heat production. All other background LCIs as well as the performance of processes along the biomethane supply chain (e.g., methane leakage rates) remain unaltered due to the lack of country-specific data. The potential implications of this assumption have been thoroughly assessed through sensitivity analysis (refer to the "interpretation" section below).

Impact assessment

We computed the carbon footprint using the global warming potentials (GWPs) according to the Intergovernmental Panel on Climate Change (IPCC) Sixth Assessment Report (AR6)[91] as implemented in the ecoinvent database. The default implementation of the IPCC method assigns a GWP of zero to both CO_2 taken up from air and biogenic CO_2 emissions, under the assumption that these flows offset each other. However, this approach does not allow for a correct carbon balance in systems with biogenic CO_2 capture and permanent storage.[27,92] Hence, we used a modified version of the IPCC method that assigns a GWP of −1 to CO_2 taken up from air and a GWP of 1 to biogenic CO_2 emissions. This approach would result in negative CO_2 emissions when the amount of biogenic CO_2 emitted is lower than the amount of CO_2 that was previously removed from the atmosphere. Moreover, given that biogenic and fossil CO_2 are treated equally (i.e., with a GWP of +1), we assigned the same GWP to both fossil and biogenic CH_4 as suggested by Muñoz and Schmidt.[93] Finally, in order to evaluate potential trade-offs, we also assessed the other 15 impact categories included in the Environmental Footprint (EF) v3.1 methods recommended by the European Commission's Joint Research Centre.[94] Further details on the impact categories and impact assessment methods and their robustness can be found in Table S5. Note that our study does not involve impacts due to land-use changes since we consider only biomass feedstocks that do not compete for land with food or feed production.

Interpretation

The interpretation is the last phase of an LCA and involves a critical analysis of the results and overall conclusions alongside a thorough discussion of underlying assumptions. We performed a perturbation analysis to identify the most sensitive LCI flows concerning the carbon footprint of ammonia production from biomethane coupled with CCS. For each LCI flow within the foreground system, we systematically varied it one at a time by ±20% around its default value, while keeping the other flows constant at their default values. A sensitivity ratio was then computed as the ratio between the relative change in the carbon footprint and the relative change in the specific LCI flow value.[95] We found that the LCI flows exerting the largest variation in the carbon footprint include (1) the amount of CO_2 uptake from air during biomass growth, (2) biogas consumption in biogas-to-biomethane upgrading, (3) electricity consumption in ammonia production, (4) biomethane consumption in ammonia production, and (5) methane leakage from anaerobic digestion and upgrading (see Figure S10). LCI flows (1) and (2) depend on the type of feedstock, while LCI flow (3) is strongly linked to the electricity mix. These flows were addressed in the country-specific analysis, revealing their variability across countries as a significant factor in shaping the carbon footprint of ammonia production from biomethane. Despite this, overall net-negative emissions were achieved across all countries (see Figure 3). In the case of flow (4), we performed an additional sensitivity analysis on the choice of the biogas-to-biomethane upgrading technology, finding minor implications for the carbon footprint but potential significance in other impact categories (see Figures S7 and S8). Lastly, for the methane leakage rates, our sensitivity analysis unveiled the potential to undermine achieving negative or net-zero emissions via biomethane, but this would require a twice increase in leakage rates (see Figure S1). Additional discussion on the main LCA methodological limitations and assumptions can be found in Note S1 of the supplemental information, complementing the sensitivity analyses presented above.

Economic assessment

We estimated the unitary ammonia production cost in each net-zero scenario from the respective capital and operating expenditures (CAPEX and OPEX, respectively). The CAPEX accounts for the necessary infrastructure and the associated costs of purchased equipment, while the OPEX accounts for fixed OPEX (e.g., labor, maintenance, overhead expenses, and interests) and variable OPEX (e.g., energy and raw materials consumption).

The CAPEX for the ammonia production facility is taken from D'Angelo et al.[60] Thus, the CAPEX was assumed to be equal to 0.13 USD_{2019} kg^{-1} ammonia in the net-zero blue and net-zero biomethane scenarios and 0.08 USD_{2019} kg^{-1} in the net-zero green scenario. These costs were taken for the reference year 2019 and updated for inflation using the Chemical Engineering Plant Cost Index (CEPCI) for the year 2022. The levelized cost of the hydrogen used in the net-zero green scenario (i.e., hydrogen from PEM water electrolysis powered by on-shore wind) was assumed to be equal to 6.88 USD kg^{-1} in 2019 (with a minimum and maximum of 5.23–8.48 USD kg^{-1}) and 6.21 USD kg^{-1} in 2022 (with a minimum and maximum of 5.19–7.29 USD kg^{-1}).[15] Moreover, the cost of the DACCS system, excluding electricity expenses, was assumed to be equal to 281 USD t^{-1} captured CO_2 (with a minimum and maximum of 220–405 USD t^{-1} captured CO_2) based on Sendi et al.[96] We further estimated the total cost of DACCS in Europe in 2019 and 2022 by applying an electricity consumption of 2.2 MWh t^{-1} captured CO_2[96] and the annual average electricity prices in Europe for these years (see below).

For the fixed OPEX, we assumed 0.07 USD_{2019} kg^{-1} ammonia in the Net-zero blue and Net-zero biomethane scenarios and 0.05 USD_{2019} kg^{-1} in the Net-zero green scenario, based on D'Angelo et al.[60] The variable OPEX was estimated from the mass and energy balances, as derived from the respective inventories and the average prices of commodities and utilities in 2019 and 2022. We considered the average natural gas spot prices and electricity prices in Europe for 2019 and 2022 based on the Dutch Title Transfer Facility (TTF) index[44] and EMBER European power price tracker,[97] respectively. For biomethane, we considered an average price of 83 USD MWh^{-1}, with a minimum and maximum value of 59 and 106 USD MWh^{-1}.[43] Moreover, a price of 90 USD t^{-1} has been considered for the high-purity nitrogen obtained through cryogenic distillation.[98] Further discussion on the assumptions for the economic assessment is included in Note S1 of the supplemental information.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Gonzalo Guillén-Gosálbez (gonzalo.guillen.gosalbez@chem.ethz.ch).

Materials availability

This study did not generate new unique materials.

Data and code availability

All the data used in this study can be found from the references mentioned in the section "experimental procedures." The dataset generated in this study and the Python code needed to reproduce the results presented in the manuscript are available online at https://doi.org/10.5281/zenodo.13900680.

ACKNOWLEDGMENTS

This publication was created as part of NCCR Catalysis (grant number 180544), a National Centre of Competence in Research funded by the Swiss National Science Foundation.

AUTHOR CONTRIBUTIONS

Conceptualization, R.I. and G.G.-G.; methodology, R.I., A.N., and G.G.-G.; investigation, R.I. and A.N.; writing – original draft, R.I., A.N., and G.G.-G.; writing – review & editing, R.I., A.N., J.P.-R., and G.G.-G.; funding acquisition, J.P.-R. and G.G.-G.; visualization, R.I.; supervision, G.G.-G.

DECLARATION OF INTERESTS

The authors declare no competing interests.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.oneear.2024.11.005.

Received: October 3, 2023
Revised: December 21, 2023
Accepted: November 13, 2024
Published: December 9, 2024

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