Techno-environmental assessment of small-scale Haber-Bosch and plasma-assisted ammonia supply chains

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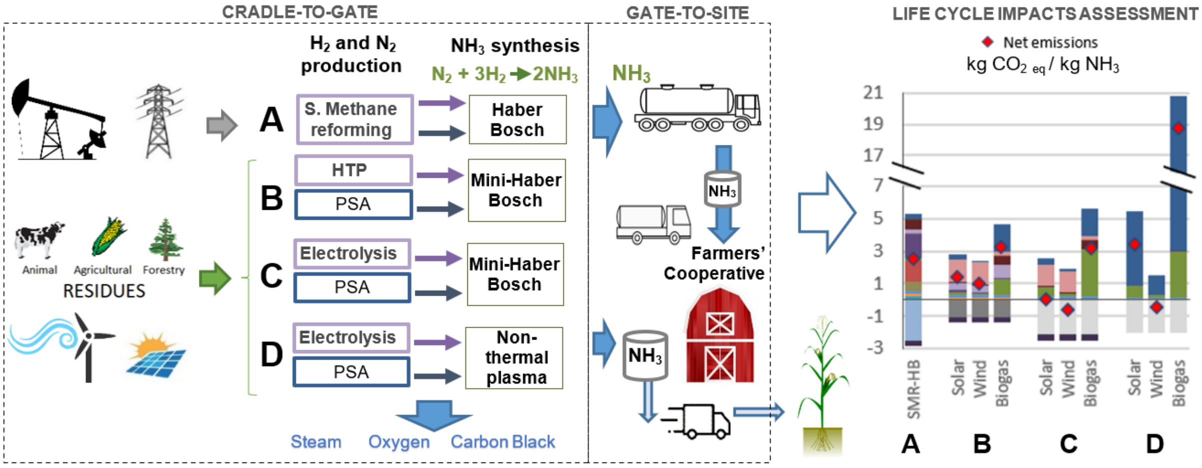
Abstract

Haber-Bosch (HB) process, the main method for ammonia (NH_3) production, contributes to near 2% of the global carbon emissions because the hydrogen input is obtained from fossil sources. NH_3 production is concentrated in a few countries, adding emissions due to global distribution. Distributed plants next to farmers and fed by renewable energy can reduce these impacts, as well as NH_3 storage, shortage risks, and price volatility. Distributed plants cannot reach low NH_3 production costs as centralised plants, but they can be promoted by the environmental benefits of its products lifecycles. Therefore, life cycle assessments of NH_3 production pathways and specific modelling for NH_3 transport in Australia were performed, from cradle-to-site, to identify the influence of storage, transport, and energy sources in their environmental profiles. The carbon footprint of centralised production was up to 2.96 kg.$CO_{2\text{-eq}}$/kg.NH_3, from which 29.3% corresponded to transport. Local production demonstrated substantial avoided transport impacts and that $CO_{2\text{-eq}}$ can reach reductions over 100% when including co-product credits such as oxygen and carbon black. Local plants using electrolysers to supply mini-HB loops obtained rates of 0.12, -0.52, and -1.57 kg.$CO_{2\text{-eq}}$/kg.NH_3 using electricity from solar, wind, and biogas (other than manure) sources, respectively. The alternative using high temperature plasma reactor instead of electrolyser obtained its best rate of -0.65 kg.$CO_{2\text{-eq}}$/kg using biogas different from manure. At farm electrolyser-based plants using novel non-thermal plasma reactors, considering potential energy yields and simplified NH_3 separation technology, could reach a rate of -1.07 kg.$CO_{2\text{-eq}}$/kg.NH_3, using solar energy. Among the assessed pathways, the most notable impact was on freshwater eutrophication in the electrolyser-based plants generating reductions up to 290%, due to oxygen credits. Despite these results, the use of solar energy raises concerns on land use and terrestrial ecotoxicity due to the area needed for solar farms and the manufacture of their components.

Graphical abstract



Keywords: Plasma; LCA; fertilisers; NH_3; distributed production; green hydrogen.

1. Introduction

Ammonia (NH_3) is an indispensable fertiliser feedstock to sustain the global food production. Besides the utilisation in agriculture, NH_3 is also proposed as a form of hydrogen (H_2) storage because it can be stored, transported, and delivered in an easier way than H_2 (Ghavam et al., 2021; Philiber, 2018). Over 90% of NH_3 is produced from H_2 and nitrogen (N_2) through the well-known Haber–Bosch (HB) process (Fúnez-Guerra et al., 2020)), and about 96% of the H_2 is obtained from fossil fuels, mainly natural gas (Parkinson et al., 2018). Extensive efforts have been undertaken for decades to optimize the HB process, but the overall energy consumption of the HB process is still high, around 30 MJ/kg NH_3 in large scale plants (Jennings, 2013). Therefore, this energy intensive process emits about 1.6 kg CO_2/kg NH_3 at factory gate using steam methane reforming (SMR) or twice the emissions using the coal partial oxidation process (Brightling, 2018). In this sense, global NH_3 production contributes to 1.8% of the global carbon emissions (The Royal Society, 2020).

The use of carbon capture and storage (CCS) technologies in large HB plants (known as blue ammonia) has obtained important emission reductions, but there are still concerns about the volatility of natural gas prices (Reed, 2021; Thomas et al., 2021; Woodroof, 2021a, 2021b). For example, the recent rise in natural gas prices in September 2021 forced different NH_3 manufacturers in Europe to reduce or shut down production, generating the increase of NH_3 prices in Western Europe from averages under US$ 300 to peaks of US$ 810 per tonne (t) (Durisin, 2021).

As a result of the high dependence on fossil feedstocks, the global NH_3 production has been concentrated in a few countries where non-expensive natural gas or coal is available. This level of centralisation increases the carbon footprint contribution when delivering the product overseas. In addition, the recent trade disruptions such as the Suez Canal blockage, Covid-related lockdowns, and the containers shortage have increased international shipping costs and times, which arises concerns about the sustainability of global trade. These drawbacks have affected developing countries to a greater extent. In comparison to early 2020 rates, shipping costs in early 2021 from China to South America rose by 443% compared with the 63% increase for the route to the east coast of North America (UNCTAD, 2021). Moreover, the high share of imported fertilisers also affects countries with devalued currencies. For example, in Colombia, the price of fertilisers increased up to 43% in 2021 (DANE, 2021), affecting food prices given that fertilisers participate with over 20% to the total production costs of rice, potato, and maize, or up to 61% for other basic food products (DNP, 2009).

In order to tackle these environmental and supply chain concerns, distributed NH_3 production plants at smaller scales arise as a solution. Despite the higher NH_3 production costs from small-scale plants compared to the costs obtained from centralised large-scale plants (Nghiep Tran et al., 2021), small-scale plants close to farming areas might create socio-economic benefits such as local employment, knowledge transfer, crop intensification by a bespoke fertiliser production, and the deployment of alternative energy technologies in rural areas.

Among the options to replace the conventional SMR-HB process, water electrolysis for H_2 production to feed mini-HB plants have been proposed and tested (Lin et al., 2020; Morgan et al., 2014; Reese et al., 2016). Another alternative for H_2 production is the high thermal plasma (HTP) methane pyrolysis (Monolith Inc, 2020). This HTP process is known as turquoise hydrogen because the reaction occurs using methane and electricity without generating air carbon emissions, only hydrogen and solid carbon black (CB) as a valuable co-product (Long et al., 2021; Sarafraz et al., 2021). Hydrogen produced by water electrolysis can be classified as green hydrogen if the electricity comes from renewable sources (Wang et al., 2018). In this regard, given the lower H_2 demand of distributed plants, fossil energy feedstocks can be replaced by renewable sources such as solar and wind power, or biogas in the case of HTP. Yet, mini-HB plants still need high pressure and heat, about 100–250 bar and 350–550 ◦C (Fertilisers Europe 2000), mainly produced from fossil resources. To avoid these fossil energy inputs, all-electric mini-HB processes have been proposed (Fasihi et al., 2021; Eric R Morgan, 2013).

The above-mentioned plant configurations using water electrolysis and HTP to feed mini-HB plants are being installed at pilot and commercial scales in different continents (Aker Clean Hydrogen, 2021; Austria Energy, 2021; Brown, 2020; CF Industries Holdings, 2021; Eneus Energy, 2021; Gautier et al., 2017; KBR Inc, 2021; Li et al., 2020; Monolith Inc, 2020; Origin Energy Ltd, 2021; Siemens Energy, 2021; Yara, 2021), motivated by the environmental benefits of the use of renewable energy (RE) and the potential use of NH_3 as green H_2 energy carrier (JGC, 2021; Thyssenkrupp AG, 2021).

The analysis of the environmental benefits of green NH_3 production have been focused on carbon emissions from RE-based electrolyser-mini-HB plants. Fasihi et al., (2021) in a tecno-economic analysis found that these plants might be cost-competitive by 2040 if a carbon tax of 75 €/t CO_2 were included. However, they only considered the carbon emissions from the main energy source and assuming zero emissions from RE-based plants. Similarly, zero carbon emissions from RE-based plants were assumed by Cinti et al., (2017) and Fúnez-Guerra et al., (2020), concluding that RE-based plants would completely avoid the emissions of NG-based plants. Other studies have gone further by considering the actual carbon footprint of RE: Smith et al., (2020) estimated emission rates of 0.12 and 0.53 kg CO_2/kg NH_3 for medium and small size wind powered installations, respectively; Bicer et al., (2016) estimated emission rates of 0.38, 0.84, 0.85, and 0.34 kg CO_2/kg NH_3, when supplied by hydropower, nuclear, biomass, and municipal waste, respectively; Chisalita et al., (2020) estimated an emission rate of 0.15 kg CO_2/kg NH_3 when using a mix of RE sources (51.46% wind, 21.39% solar, 18.81% biomass, and 8.34% hydropower); and recently, Liu et al., (2020) and Carlo D'Angelo et al., (2021) estimated carbon emissions rates for several plants configurations by considering different RE sources to feed electrolysers and different energy mixes of grid electricity to feed the rest of the plant components.

Despite the carbon emissions reduction of RE-based mini-HB plants, other alternative NH_3 synthesis processes have been recently proposed to tackle the technical drawbacks of mini-HB plants for the distributed green NH_3 production, such as non-thermal plasma (NTP) reactors. Firstly, The HB process ideally runs continuously (Appl, 2011), requiring hours or even days to reach a steady state process (Muelaner, 2020), which hardly interfaces with the intermittency of wind or sun light. Furthermore, this inflexibility in production requires large storage of NH_3 to respond to changes in demand, as it might not be practical to stop the production when demand is low and start again when demand increases. In contrast, NTP reactors can be started up and shut down quickly due to low thermal inertia, which reduces the idle time and energy costs (Snoeckx and Bogaerts, 2017). However, the current energy efficiency of an NTP-based process is the main constriction for its industrial acceptance (Anastasopoulou et al., 2014). Experiments in dielectric discharge barrier reactors have obtained low energy yields up to 35.7 g

NH_3/kWh (Kim et al., 2017). An analysis of the cradle-to-gate carbon emissions for electrolyser -NTP-assisted plants has shown that this high electricity consumption generates higher carbon emissions than those of the conventional SMR-HB process due to the carbon intensity of the average electricity mix, even using a high share of solar and wind energy (Anastasopoulou et al., 2020b).

In general, literature on distributed NH_3 production suggest that these plants cannot reach the low costs of large centralised SMR-HB plants, being necessary to promote these alternatives by showing their environmental benefits, directly linked to the use of RE, which could be internalised in their economic analyses. To date, studies for green NH_3 pathways have analysed their environmental impacts until the factory gates, omitting the additional impacts reduction in the supply chain due to the lower transport and storage requirements of distributed production. Moreover, these studies have not properly estimated the potential avoided emissions due to the commercialisation of valuable co-products from H_2 production such as pure oxygen and CB.

Transport is usually despised in environmental assessments, such as in the carbon footprint accounting of products and organizations (ISO, 2018; WBCSD, 2013), in which only the emissions from fuels consumption are accounted for. This underestimation of emissions is tackled by the scope of the life cycle assessment (LCA) methodology (ISO, 2006), where emissions from the manufacturing and maintenance of vehicles and infrastructure are also included. However, the specific conditions required for NH_3 transport in tanker vehicles make difficult to incorporate this phase in the LCA of NH_3 pathways. This is because this kind of transport is not characterized in databases for LCA such as Ecoinvent (ETH, 2021), where the transport datasets are applicable for average cargo, considering average freight characteristics, such as load factors, speeds, annually mileage, vehicles lifespan, among others. Since these parameters cannot be modified in LCA software, the use of these datasets would increase the uncertainty in the results. Thus, specific modelling of NH_3 transport must be independently addressed.

In this sense, we aim to analyse the NH_3 life cycle from cradle-to-site in different scenarios to identify the influence of storage and transport in the ammonia supply chain using SMR, HTP, and water electrolysis for H_2 production and HB, mini-HB and NTP for the NH_3 synthesis. For this purpose, we also developed a model for the emissions estimation from the transport of liquid NH_3 by specific tanker trucks. In addition, we incorporate in the LCA the avoided burdens of co-products to analyse the degree to which these credits of distributed plants could promote the adoption of plasma technology. In the remainder of this article, we describe the LCA methodology and its application to four alternatives from conventional to small-scale distributed NH_3 production pathways using different fossil and renewable energy resources in Australia. The results of the critical comparative assessment and the scenario analyses are presented and discussed.

2. Materials and methods

This section is structured based on the four phases described in the standard ISO 14044 (ISO, 2006) for LCA studies. Firstly, the goal and scope of the study are defined. Secondly, for the inventory analysis, data sources for each stage of the NH_3 supply chain (production, storage, and distribution) are identified. Thirdly, the utilised impacts assessment method and tools are described. Finally, how the interpretation of the results was conducted is detailed at the end of this section.

2.1. Goal and scope definition

The aim of this study is to analyse the influence of transport and storage in the NH_3 supply chain and identify the degree to which co-product credits of distributed plants can promote the adoption of plasma technology. For this purpose, this study analyses the energy and material flows based on three key factors: resource supply, NH_3 synthesis method, and location, Fig 1.

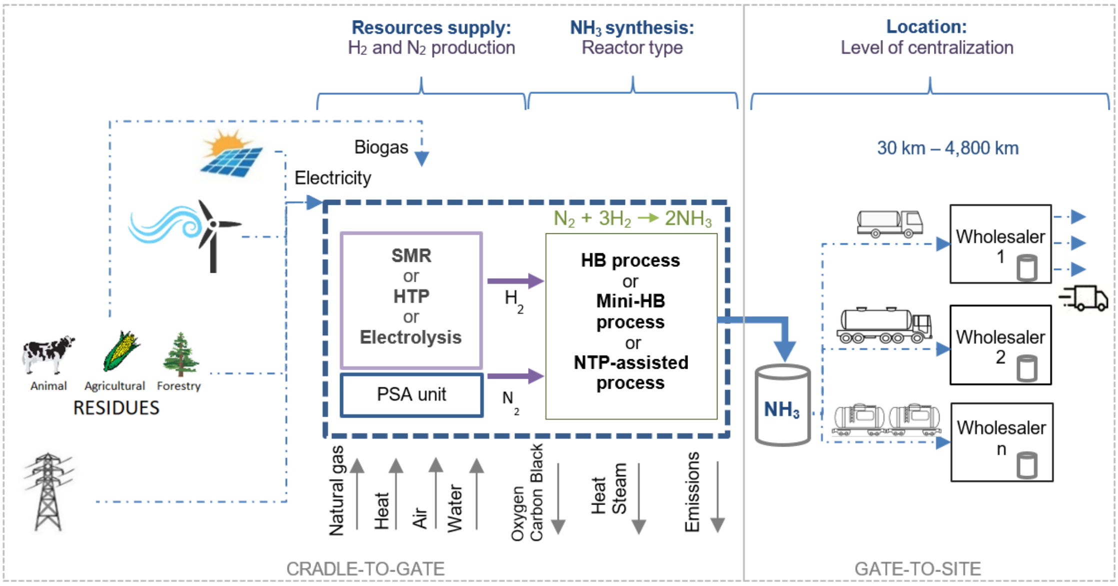


Fig 1. Cradle-to-site systems for different NH_3 production pathways. Note: For the conventional SMR-HB pathway the nitrogen production is incorporated in the SMR process.

Four pathways were analysed in Australia as a case study. The conventional pathway (A) is a centralised large-scale plant, using the HB process fed by SMR to supply NH_3 to customers 4,800 km away, that is, 4,000 km from the plant gate in Perth to regional storage in Queensland, from where NH_3 is distributed to farms up to 800 km away. For alternative B, regional plants, based on mini-HB supplied by HTP, distribute the product around 800 km. For alternative C, local plants to supply the product in the county around 300 km are based on mini-HB supplied by alkaline electrolysers. And for alternative D, small-scale plants located at farmers cooperatives consider NTP reactors supplied by alkaline electrolysers, which are on average 30 km from farms. For the alternative pathways (B, C, and D), the nitrogen production was based on a pressure swing absorption (PSA) unit. Other technologies for N_2 production were not considered because this process consumes little energy compared to that required for H_2 production in this section.

Four scenarios were considered to analyse the environmental impacts of supplying the alternative plants with electricity from the Australian grid, wind energy, solar photovoltaic, and biomass. These energy sources have been selected because electricity costs from wind and solar power have been falling each year, which would open the door to cost-effective green hydrogen production by 2030 from traditionally expensive methods such as water electrolysis (Squadrito et al., 2021). On the other hand, biomass was selected as alternative energy source given that the distributed plants would be in farming areas where biomass and manure waste are available to produce both electricity and biogas.

Two relevant co-products of these novel plants were incorporated in the analysis given their potential demand and market prices, which besides improving the profitability of these plants, they would avoid emissions by reducing the market participation of the equivalent products manufactured by traditionally pollutant methods. One co-product is the solid carbon or mostly commercially named as carbon black generated in the alternative B from the HTP reactor for the H_2 production. CB is increasingly in demand mainly for the manufacturing of tires and industrial rubbers (ChemAnalyst, 2021). The most common production pathway for CB is the oil-furnace or black furnace process in which the partial combustion of heavy hydrocarbons is performed, releasing about 2.4 kg CO_2/kg CB (Athanassiades, 2013; Fan et al., 2020). On the other hand, oxygen has different applications in the steel, mining, paper, glass, and chemical industries, also for drinking water purification and food industry, and specifically, high purity oxygen is used for medical applications. The main pathways for commercial oxygen production are cryogenic air separation and pressure swing adsorption, which can produce oxygen at purities over 99.5% and up to 95%, respectively (Hurskainen, 2017). Medical oxygen would be the most suitable application given that it requires a purity standard of over 99.0%. and alkaline electrolysis systems have reported purity by 99.7% (Zeng and Zhang, 2010). The demand for medical oxygen has recently increased for the treatment of respiratory diseases as a consequence of the Covid-19 pandemic (Squadrito et al., 2021).

The functional unit has been defined as the production of 1 kg of anhydrous NH_3. The system boundaries have been based on the cradle-to-site approach, that is, besides the activities from the extraction of raw materials until the NH_3 leaves the factory gate, these studies also included the transport, intermediate storage, and distribution of NH_3 to final user at farms. Because different pathways produce co-products (i.e., carbon black or oxygen) and by-products (i.e., heat or steam), these credits were incorporated with the approach of the "avoided burden" (Azapagic and Clift, 1999). In this sense, this comparative ex-ante LCA used a cut-off system model based on mass allocation in which the environmental burdens of producing these credits by traditional methods were subtracted from the burdens of the systems under consideration.

2.2. Inventory analysis

For the creation of the energy and materials balances for each stage of the ammonia supply chain for the different pathways, specific modelling and estimations were performed based on literature and the life cycle inventories database Ecoinvent 3.7 (ETH, 2021). The inventories taken from the database were adapted to the specific energy datasets available for Australia. Other details and assumptions are presented in the next sub-sections for each stage of the supply chain.

2.2.1. Ammonia production

This stage represents the inventory analyses for the cradle-to-gate boundary, as part of the whole cradle-to-site systems for each pathway, summarized in Table 1. Given that the proposed NH_3 plants consist of three independent sections (H_2 production, N_2 production, and NH_3 synthesis), changes in energy or materials balances in one section do not affect the performance of the other sections, being possible to analyse different plant configurations considering recent, comprehensive, and diverse data sources. For pathway A, the data were obtained from the existing model in Aspen software for the SMR-HB process (Aspen Plus, 2020). For the HTP process, an electricity consumption of 17.28 kWh/ kg H_2 and a carbon black yield of 3 kg CB/kg H_2 were estimated based on da Costa Labanca (2020). The inputs for alkaline electrolysis were electricity and water with yields of 46 kWh/ kg H_2 and 8.93 kg/kg H_2, respectively, as well other supplies such as potassium hydroxide solution 25% w/w (KOH), steam to pre-heat the systems and nitrogen for cleaning purposes (Koj et al. 2017). The PSA unit for nitrogen production consumed 0.11 kWh/kg N_2, based on E. Morgan et al. (2014). For the NH_3 synthesis, based on an N_2/H_2 molar ratio of 1:3, the data for the mini-HB process were obtained from the plant design in Matzen et al. (2015) and Anastasopoulou et al. (2020a, 2020b) and adapted to the new storage conditions detailed in the next section. The electricity consumption for the NTP reactor was 28.0 kWh/kg NH_3, considering an energy yield of 35.7 g NH_3/kWh at 0.2 mol. % NH_3 (Kim et al., 2017). The low NH_3 concentration of the NTP-assisted reaction implies an additional electricity cost of 28.3 kWh/kg NH_3 for the recycling loop of unconverted N_2 and H_2 (Rouwenhorst and Lefferts, 2020). For the steam flows, as energy carriers in chemical industry, in order to match the water-steam balances, we used mass units (kg) instead of energy units (MJ). Therefore, we utilised the Ecoinvent dataset for steam production in kg, where are included the inputs and emissions generated to produce the energy contained in steam, which corresponds to 2.75 MJ/kg (Althaus et al., 2007).

In the NH_3 synthesis section, it is included the separation process of the final pure anhydrous NH_3 product, in which NH_3 is separated from the unreacted N_2/H_2. However, unlike the HB and mini-HB processes in which the separation is facilitated by the high pressure of the gas stream from the synthesis reactor in a series of flash columns, the NTP-assisted process needs to be separated by absorption at atmospheric conditions with the support of a solvent. The most utilized solvent is water, but due to the difficulties to be separated after the absorption step (Yang et al., 2014), the utilization of an ionic liquid was proposed by Anastasopoulou et al. (2020). However, the use of the ionic liquid requires subsequent heating to 245^oC and a cool down of the stream to recover the ionic liquid, implying additional energy consumptions. To avoid the use of the ionic liquids, we utilized a promising separation method based on zeolites, which allows the NH_3 removal from the reactor at the same temperature of the effluent (100 ^oC) and mild pressures of 10-30 bar, requiring about 2.22 kWh/kg NH_3, including compression and cooling (Rouwenhorst et al., 2020; Rouwenhorst and Lefferts, 2020).

Table 1. Material and energy balances to produce 1 kg of ammonia by the assessed pathways

Material / Energy	Feedstock production	NH_3 synthesis	
Pathway A	**SMR**	**HB**	**Separation**
Natural gas (m^3)	6.27E-01	-	-9.48E-02
Electricity (kWh)	1.15E-01	3.94E-01	2.00E-03
Heat (MJ)	1.69E+01	-	5.10E-02
H2S (kg)	-7.00E-06	-	-
Air (kg)	1.23E+00	-	-
Cooling energy (MJ)	1.03E+01	3.51E+00	3.81E-01
Water (kg)	7.32E+00	9.32E-01	7.00E-03
Steam (kg)	-5.49E+00	-9.32E-01	-7.00E-03
CO_2 (kg)	-1.00E-04	-	-
N_2 (kg)	-9.13E-01	9.13E-01	-
H_2 (kg)	-2.30E-01	2.30E-01	-7.39E-03

NH_3 (kg)	-	-	-1.00E+00

Pathway B	**HTP**	**PSA**	**Mini-HB**	**Separation**
Natural gas (m^3)	1.01E+00	-	-	-
Electricity (kWh)	3.21E+00	9.43E-02	4.89E+00	5.27E-01
Heat (MJ)	-	-	-	1.79E+01
Cooling energy (MJ)	-	7.53E-01	5.44E+00	1.13E+01
Water (kg)	-	-	1.08E+00	7.00E-03
Steam (kg)	-		-1.08E+00	
Air (kg)	-	3.02+00	-	-
Carbon black (kg)	-5.58E-01	-	-	-
N_2 (kg)	-	-8.57E-01	8.57E-01	-1.80E-02
H_2(kg)	-1.86E-01	-	1.86E-01	-5.00E-03
NH_3 (kg)	-	-		-1.00E+00

Pathway C	**Electrolysis**	**PSA**	**Mini-HB**	**Separation**
Electricity (kWh)	9.46E+00	9.43E-02	4.89E+00	6.22E-01
Heat (MJ)				1.79E+01
Cooling energy (MJ)		7.60E-01	5.44E+00	1.00E+01
Water (kg)	1.86E+00		1.08E+00	7.00E-03
Steam (kg)	2.05E-02		-1.08E+00	
Air (kg)		3.02E+00	-	-
O_2 (kg)	-1.49E+00		-	-
KOH (kg)	3.53E-04			
N_2 (kg)	5.39E-05	-8.57E-01	8.57E-01	-1.80E-02
H_2(kg)	-1.86E-01		1.86E-01	-5.00E-03
NH_3 (kg)				-1.00E+00

Pathway D	**Electrolysis**	**PSA**	**NTP**	**Separation**
Electricity (kWh)	9.31E+00	9.39E-02	5.63E+01	2.22E+00
Heat (MJ)				
Cooling energy (MJ)		7.59E-01		
Water (kg)	1.83E+00			
Air (kg)		3.01E+00		
O_2 (kg)	-1.46E+00			
KOH (kg)	3.48E-04			
Steam (kg)	2.01E-02			
N_2 (kg)	5.31E-05	-8.54E-01	8.54E-01	
H_2(kg)	-1.83E-01		1.83E-01	
NH_3 (kg)				-1.00E+00

For cooling requirements, absorption chillers using natural gas were utilized for the large-scale plant since they are among the most used methods due to the access to non-expensive energy feedstock and cogeneration units. Nonetheless, to avoid the use of fossil resources and use renewable electricity, the use of electric chillers in the alternative distributed plants was proposed. Specifically, the inventory dataset was created for water-cooled chiller operated by electric centrifugal compressors with a coefficient of performance (COP) of 6.1, equivalent to a power requirement of 0.58 kW per tonne of refrigeration (Architectural Energy Corporation, 2008). Thus, this electric chiller would consume 0.046 kWh per MJ of cooling energy.

The oxygen generation from electrolysers was assumed 8 kg O_2/kg H_2 (Fuel Cells Etc, 2012; Ottosson, 2021), as considered in other studies to improve the economics of green hydrogen production plants (Nicita et al., 2020; Squadrito et al., 2021) and green ammonia plants (Lin et al., 2020). For the use of O_2 credits, instead of releasing it to the environment, only energy expenses to compress O_2 in cylinders must be added. The electricity needed for compressing this oxygen at 350 bar is about 0.15 kWh/Nm^3 O_2 (Büchi et al., 2014). Impacts related to the manufacturing of cylinders and transport were not considered because the equivalent avoided oxygen produced by the traditional methods that would use similar distributing modes. In this sense, only the burdens generated by the O_2 production with electricity from the Australian grid by the cryogenic air separation method were subtracted from the results for the electrolyser-based evaluated systems.

Regarding the infrastructure, despite the lower complexity of the alternative plants, which would imply lower land use than the required for conventional plants, since no specific data, the average chemical plant from Ecoinvent with a capacity of 50,000 t/year (Althaus et al., 2007) was assumed. The allocation to the functional unit was obtained by considering a 30-year factory lifespan, meaning 6.67 E-10 units per kg of produced NH_3 for all pathways.

2.2.2. Ammonia storage

After the NH_3 separation from the unreacted H_2/N_2, the product is stored in refrigerated tanks or pressurized cylinders at room temperature. The selection of the storage method depended on technical facts related to the plant size and storage capacity needs. For large scale plants, refrigerated storage (-33 ^oC, 1 bar) is preferred because pressurized cylinders (20 ^oC, 10 bar) have maximum capacities of around 270 t (Bartels, 2008). In this sense, given that the typical storage for chemical plants is 30 days of production plus 10% freeboard (Ulrich, 1984; Walas, 1990) and for distributed plants is 15 days of storage (UNIDO/IFDC, 1998), we selected refrigerated storage for the national and regional plants and pressurized storage for the local and at farmers' cooperative plants, Table 2.

Table 2. Storage technology and capacity for each pathway

Pathway	Storage type	Production capacity (t NH_3/day)	Days of storage	Storage capacity (t NH_3)
A	Refrigerated	1,330	30	43,890
B	Refrigerated	107	30	3,531
C	Pressurised	10	15	165
D	Pressurised	1	15	17

Refrigerated tanks require about 64.15 kWh per tonne (NH_3 tank capacity) a year to keep low temperature, considering a boil-off rate of 0.1% per day (Bartels, 2008). This boil-rate is conservative since typical boil-off values are about 0.04% or lower (Morgan, 2013). The electricity to transfer the product to intermediate pressurised storage was thermodynamically estimated at 0.09 kWh/kg $NH_{3,}$ considering a polytropic compression efficiency of 75% (Smith et al., 2020). Material, energy, and land use for the manufacturing of both the refrigerated and pressurised tanks and a 30-year lifespan were considered.

2.2.3. Ammonia distribution

NH_3 is globally transported by pipelines, marine and inland ships, trains, and trucks. The least expensive methods per tonne transported per km (tkm) are pipelines and ships, but they are more suitable for large-scale transport given the required high capital investments (Elishav et al., 2021). Therefore, since in this case study for the centralised NH_3 plant in Western Australia the total production would be distributed to different close and distant regional markets, the use of existent infrastructure such as railways and roads would be more feasible. Rail transport is less expensive than trucking, but trains are only recommended for long distances due to the inflexibility of the limited availability of railways. In this sense, despite the high cost per tkm, the use of trucks is necessary for all the pathways, at least for the last part of the journey to deliver the product to end-users (Elishav et al., 2021).

Due to different kind of vehicles and technologies, to determine the environmental impacts of transport in the NH_3 supply chain, there is the need for specific modelling for this input. An initial screening for the conventional centralised NH_3 production was performed using the global average datasets available in Ecoinvent. The best supply scenario was assumed to be done by diesel-electric train for the 4,000-km journey to the regional storage and by diesel trucks for the 800-km journey to farms. In this scenario, the NH_3 distribution would generate 0.34 kg $CO_{2\ eq}$/kg NH_3, which would represent around 17% to the global warming potential (GWP) of the cradle-to-site analysis, assuming the emission rate of 1.6 kg CO_2/kg NH_3 at factory gate using SMR (Brightling, 2018). Moreover, in the worst supply scenario, using only truck for the 4,800-km journey, the emissions increase to share around 29% of the total GWP of the NH_3 supply chain. For this reason, given the relevant role of transport and to ensure that this input represents the most accurate data, the NH_3 distribution had to be modelled according to the particularities of this transport service in Australia.

The specific modelling for NH_3 distribution was necessary because the available datasets for transport in Ecoinvent did not represent the conditions in which this dangerous liquid is distributed in Australia. Firstly, the Ecoinvent dataset for "*Transport, freight, lorry, unspecified {GLO}"* considers a mix of different sizes of trucks, while for transporting NH_3 we must only consider either a large articulated truck for long distances (>300 km) or a rigid truck for medium and short distances (≤ 300 km). Secondly, the load factors are averages for each truck size (*i.e.*, 53.3% for large articulate truck, 36.7% for medium rigid trucks, etc.), while, for transporting NH_3, the outbound journey is assumed fully loaded, but because of the weight of tank the load capacity decreases to 80% and 70% for articulated and rigid trucks, respectively. Additionally, since for safety issues the trucks cannot transport other products than ammonia, they must return empty. Consequently, the specific load factors would be 40% and 35% for articulated and rigid trucks, respectively. Thirdly, the emissions factors for the different substances were obtained based on standardized European driving cycles tests, which implies average speeds, stops, and journey distances different to real driving conditions in Australia. Finally, Ecoinvent considers a mix of vehicles with Euro III, IV, V, and VI control emissions standards, but, in Australia, a significant part of the trucks have older technologies than Euro III, Table 3.

Table 3. Australian truck fleet by Euro standard technology. Data from: SAFC (2020)

Australian design rule	Euro equivalent	Truck type	
		Rigid	Articulated
None	pre-euro	35.1%	21.4%
ADR 70/00	Euro I	18.5%	18.0%
ADR 80/00	Euro III	21.9%	29.3%
ADR 80/02	Euro IV	15.4%	19.7%
ADR 80/03	Euro V	9.0%	11.5%

These relevant differences between the specific NH_3 transport and the Ecoinvent datasets, besides their effect on the GWP, they would have a greater effect in the environmental impact categories related to human and ecosystems toxicity given that the Euro standards basically ensure fewer emissions of air pollutants such as carbon monoxide (CO), nitrogen oxides (NO_x), volatile organic carbons (VOC), and particulate matter (PM). Moreover, the consideration of the specific Australian fuel composition such as sulphur, carbon, hydrogen, and oxygen content, as well as the volumetric percentage of biodiesel, would let to estimate the CO_2 and SO_2 emissions per transported product per km.

For the above reasons, we proposed a specific transport model by considering, besides the emissions from vehicle operation, the truck manufacturing, fuels production, infrastructure construction, and the end-of-life activities, covering the life cycle of transport services on a systemic approach (Osorio-Tejada et al., 2020). We developed an emissions calculator for the vehicle operation in which besides the fuel combustion, we included the emissions from the operation and maintenance of vehicles and roads and emissions from the abrasion of brakes, tires, and road surface.

The characteristics of the freight service such as truck size, Euro technology, axles number, speed and road slopes were considered for the estimation of CO, NO_x, PM, and VOC emissions based on the Tier 3 emissions factors and coefficients from the EMEP/EEA air pollutant emission inventory guidebook (EEA, 2019) for empty and fully loaded journeys and interpolated to the specific load factors. For other fuel combustion emissions such as N_2O, NH_3, CH_4, PAHs, aldehydes, aromatics, alkanes, alkenes, cycloalkanes, and CO_2, as well as for the tires and brakes abrasion particles, Tier 2 and Tier 1 emissions factors were utilized (EEA, 2019).

The proposed approach was applied for a common west-to-east route through South Australia by the National Highways 94, 1, A1, A32, A71, and A2. Since most of the route was on flat topology, the average slope was almost zero percent (i.e., 0.2%), see Fig A1 in supplementary information SI-1. However, there were sections with particular high slopes and low speeds in mountainous areas and when bypassing urban zones, respectively. Due to these changes in the driving conditions, it was necessary to split into 23 different sections to obtain representative emissions estimates per tkm.

For the fuel production inventory, the origin of the feedstocks to produce the low sulphur diesel B5 (i.e., 10 ppm of sulphur with 5% v/v content of biodiesel) was considered. Regarding truck manufacturing and road construction, as well as for operation, maintenance, and end-of-life activities, the specific inventories were created by considering Australian statistics, based on generic inventories from Ecoinvent (Spielmann et al., 2007). The allocation of the impacts related to the life cycles of vehicle and roads to the specific transport service was performed by the estimation of the total gross tonnes mobilised in Australia each year, by both passenger and freight vehicles, and the total tkm transported by the vehicle in its useful life. For more details of the procedures and obtained inventories, the Excel-based calculator created for articulated trucks is presented in the supplementary information SI-1.

2.3. Impacts assessment

The impacts assessment was focused on a “problem-oriented approach” by evaluating environmental impact categories at a mid-point level (Pérez-Camacho et al., 2018). The impact categories were defined based on the most relevant life-cycle environmental aspects in chemicals production (Maranghi and Brondi, 2020): global warming, terrestrial acidification, terrestrial ecotoxicity, freshwater eutrophication, freshwater ecotoxicity, ozone formation (on human health - HH), ozone formation (on terrestrial ecosystems - TEc), human carcinogenic toxicity, human non-carcinogenic toxicity, and fossil resource scarcity. Additionally, we included the land use impacts given its relevance in agriculture supplies field, adding a total of 11 impact categories. Among the most updated methods, ReCiPe 2016 (Huijbregts et al., 2017) was selected for the impacts assessment because it brings together the defined impact categories for this study and its characterization factors are representative for a global scale (Kobayashi et al., 2022). This impacts assessment was performed using SimaPro 9.2 (PRé Consultants, 2021), considering the ReCiPe hierarchical (100 years) perspective and excluding long-term emissions.

2.4. Interpretation

As a base scenario, midpoint results for pathway A are presented using the average and specific modelled datasets for transport. Then, midpoint results for all production pathways are presented using electricity from the Australian grid. Subsequently, scenarios using solar, wind, and biomass energy for the alternative production pathways are shown. The scenarios using solar and wind energy only replace the grid electricity, while for the scenarios using biomass, we considered one scenario using lignocellulosic biomass for electricity generation and another scenario using a biogas mix (manure (32.7%), biogenic waste (29.9%), sewage sludge (37.1%), and used cooking oil (0.3%) (ETH, 2021)) to produce both electricity and biomethane. Since the pre-treatment of manure generates high greenhouse gases emissions, we added a scenario without using manure. In these renewable energy scenarios, constraints in the availability of feedstocks were not considered.

A sensitivity analysis was performed for pathway D because the assumed energy yield of 35.7 g NH_3/kWh for the NTP-assisted NH_3 synthesis still represents a low energy efficiency compared to HB process. This analysis considered the potential energy consumption of plasma reactors of 4 GJ/t NH_3 based on Rouwenhorst and Lefferts (2020), which translates to a potential energy yield of 900 g NH_3/kWh.

Moreover, since the NH_3 separation step defined for pathway D implies additional electricity consumption and high investment costs, a comparison with a proposed water-based separation method at ambient conditions to obtain as product a solution of NH_3 with water was performed.

3. Results and discussion

3.1. Impacts of storage and transport in the large-scale NH_3 supply chain

To analyse the role of storage and transport in the NH_3 centralised production in Australia, the environmental impacts of pathway A for the best and worst supply scenarios, using the global average and specific modelled datasets for transport, are presented in Fig 2 for the global warming category.

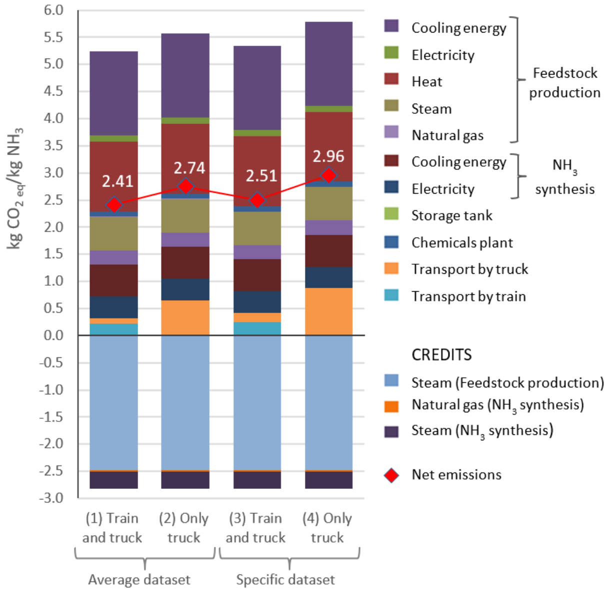


Fig 2. Global warming potential for the conventional (Pathway A) NH_3 production in Australia.
Note: inputs/outputs with contributions lower than 0.5% in all impact categories were excluded from legends. Red symbols and values in white in each column correspond to the net emissions (positive emissions – negative emissions (credits))

According to the results from Fig 2, NH_3 produced in Australia by a centralised SMR-HB plant generates a total of 2.08 kg $CO_{2\ eq}$/kg NH_3 at factory gate due to the higher carbon footprint of the feedstocks and utilities utilized in this country. The intermediate or regional storage tanks for the NH_3 distribution add only 0.01 kg $CO_{2\ eq}$/kg NH_3. On the other hand, transport has important contributions to the climate change impacts. In the best supply scenario, using the average dataset, transport by train and truck adds 0.33 kg $CO_{2\ eq}$/kg NH_3, which represents 13.2 % of total net emissions of 2.41 kg $CO_{2\ eq}$/kg NH_3. In the worst supply scenario, using only truck, the transport emissions increase to share 23.6% of the total net carbon emissions. In the case of using the specific datasets from the transport model detailed in section 2.3.3, the share of transport increases to 16.7% and 29.3% in the best and worst supply scenarios, reaching an emission factor near to 3 kg $CO_{2\ eq}$/kg NH_3. This result means that only the transport of each million-tonne of NH_3 to distant markets in Australia releases up to 867 tonnes of $CO_{2\ eq}$ into the atmosphere.

The carbon emissions increase in the NH_3 supply chain was mainly because of the higher quantity of fuel used per tkm due to the lower load capacity of the specifically modelled trucks, which is staged in more combusted hydrocarbons and released to air in form of CO_2. Specifically, an average articulated truck (>32 t) in Ecoinvent consumes 0,020 kg of low-sulphur diesel per tkm, while our 43.5 t articulated tanker truck consumes 0.031 kg of low-sulphur diesel B5 per tkm. In the case of rigid trucks, the fuel consumption per tkm is 0.037 kg in the Ecoinvent dataset and 0.055 kg in our specific dataset. In addition to the higher fuel consumption, the production of each kg of low-sulphur diesel B5 generates more CO_2 than each kg of global average low-sulphur diesel, with emission factors of 0.75 and 0.64 kg $CO_{2\ eq}$/kg fuel, respectively. These higher emissions are due to the 5% v/v content of vegetable oil methyl ester, which generates significant quantities of $CO_{2\ eq}$ related to the land transformation attributable to the expansion of crops into forests, grasslands, and annual and perennial lands (Moreno Ruiz et al., 2016; Osorio-Tejada et al., 2018). The same issue also affects rail transport because diesel-electric trains in Australia use diesel B5. Thus, the emissions factors per tkm transported by train increased from 0.052 to 0.060 kg $CO_{2\ eq}$, and per tkm transported by truck increased from an average of 0.13 to 0.17 and 0.30 kg $CO_{2\ eq}$ for articulated and rigid trucks in Australia, respectively.

In addition to the effects of load factors and fuel production, the other components of the transport system such as traffic in which other pollutant emissions affect human health and ecosystem, as well as the manufacturing of vehicles and road construction, generate different effects on the other analysed impact categories, as shown in Fig 3.

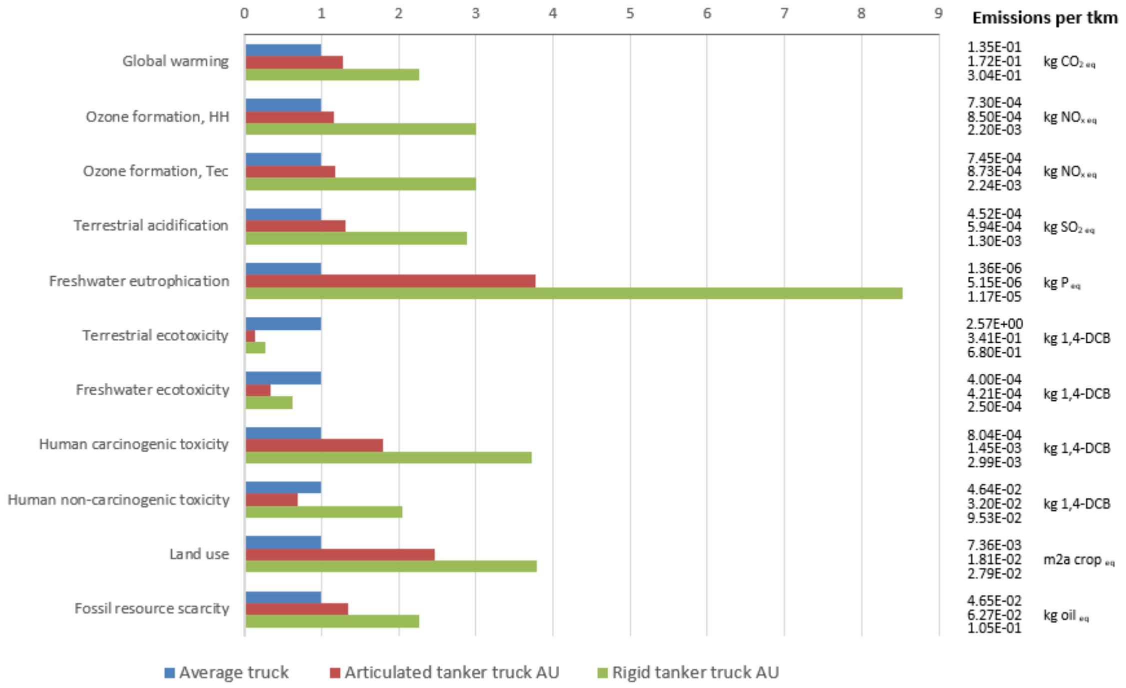


Fig 3. Midpoint results per tkm transported by average truck and specific modelled trucks

Results per transported tkm of anhydrous NH_3 by Average truck were normalized to 1. Then, values in the horizontal axis for the Articulated tanker truck AU and Rigid tanker truck AU correspond to the variation in respect to the Average truck results. AU: Australian vehicle technology mix.

The specific modelled truck transport in Australia shows higher impacts on the ozone formation and terrestrial acidification due to the NO_x and SO_2 emissions from fuel combustion related to older Euro control emission technologies and fuel composition. The main factor in the increase of freshwater eutrophication impacts is the electricity consumption during the maintenance of vehicles and roads. It is because the electricity production in Australia releases more phosphates to water than the global average due to higher usage of hard coal and lignite in power plants. The vehicles maintenance also has important contributions in the fossil fuels scarcity due to the production of truck tyres, as well as in the categories of human carcinogenic and non-carcinogenic toxicity for the use of lead and steel in batteries and other auto parts, respectively. Moreover, impacts on land use are also increased due to the higher allocation of the road construction impacts to each tkm transported per year, as well as due to the cultivation of feedstocks for the biodiesel content.

Despite the specific modelling made to increase the impacts in most of the categories, impacts on terrestrial and freshwater ecotoxicity were reduced. This reduction was because the estimated emissions factor from brake abrasion in the evaluated route in Australia were significantly lower than the Ecoinvent emissions factor, reducing the released particles of cooper from 1.97 to 0.136 kg per tkm. These brake emissions were reduced because the driving mostly took place on straight and uncongested roads at constant speeds around 90 km/h, better conditions for brakes usage than the presented in the European transient cycle tests in which higher shares of urban and medium speeds driving zones are considered.

According to the above, besides the increase in the contribution of transport in the net carbon emissions for the centralised NH_3 production up to 29% (see Fig 2), transport has a different extent of participation in other categories, reaching shares up to 71% on ozone formation and 86% on land use net impacts for the worst supply scenario, as presented in Fig 4.

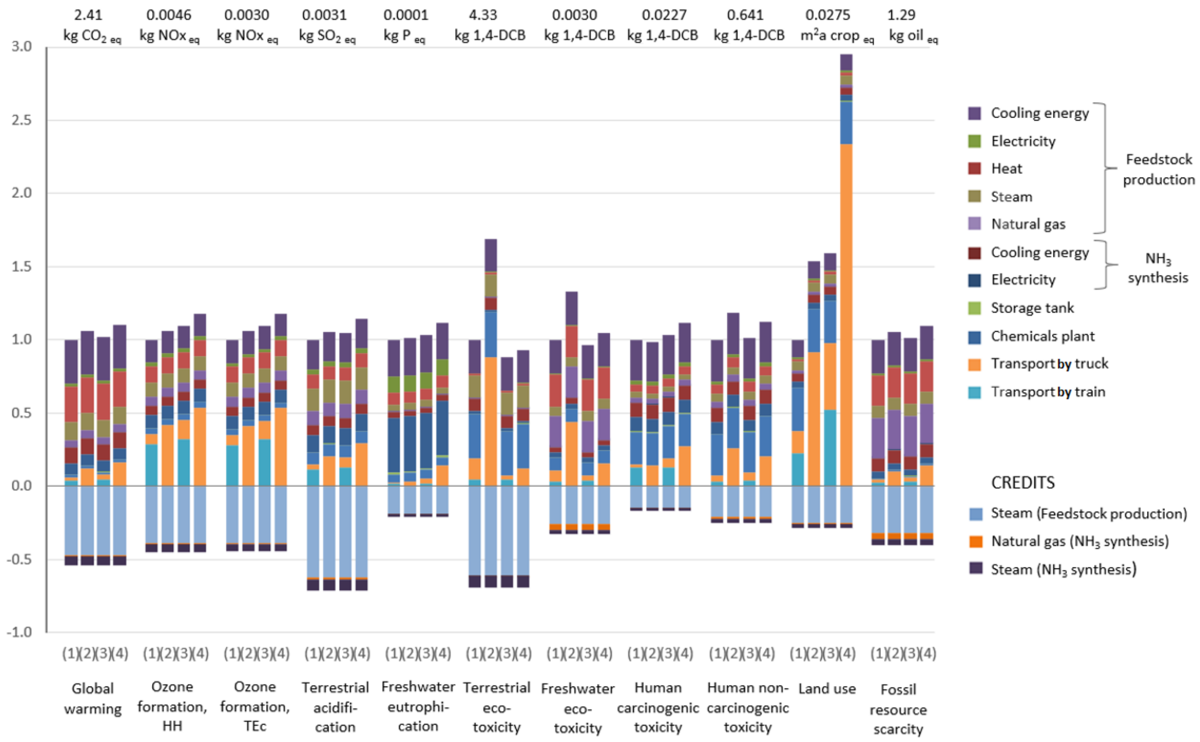


Fig 4. Midpoint results for the conventional (Pathway A) NH_3 production in Australia.
Scenarios: (1) train and truck – average dataset; (2) only truck – average dataset; (3) train and truck – specific dataset; (4) only truck – specific dataset. Notes: inputs/outputs with contributions lower than 0.5% in all impact categories were not included in the chart. Results per kg of anhydrous NH_3 from scenario (1) are showed in the top of the chart, which were normalized to 1 in the vertical axis. Results for scenarios (2), (3) and (4) correspond to the variation in respect to the scenario (1). Note: in scenarios with specific dataset, the "Transport by truck" contribution includes the impacts of transport in rigid truck (300 km) plus the impacts of transport in articulated truck for the rest of the journey (500 km in scenario (3) and 4,500 km in scenario (4)).

Despite the impacts increase in freshwater eutrophication due to the electricity consumption in the transport related activities in scenario (4), the contribution of transport on the net impacts (i.e., 20%) is not as high compared to the contribution of the NH_3 synthesis section (i.e.,54%). The most significant impacts increase due to the specific modelling was on the land use for both rails (i.e., + 157%) and road transport (i.e., + 190%).

In brief, transport in the NH_3 supply chain was demonstrated to have higher environmental impacts than the global average land transport of conventional products. The impact on global warming was evident due to the lower cargo efficiency of tanker trucks and the deforestation caused by the production of the biodiesel fraction in diesel B5. The electricity used for the maintenance of vehicles and roads in Australia made to increase the impacts on freshwater eutrophication due to the use of fossil fuels in the power generation, which also contributes to higher carbon emissions.

3.2. Alternative pathways for distributed NH_3 supply chain

Environmental impacts of alternative pathways for distributed NH_3 production in Australia are compared with the results for the conventional centralised NH_3 production, considering the specific datasets for transport and the best supply scenario for the centralised production (i.e., the results of scenario (3) in Fig 4). As a base scenario, we analysed the results for the plants supplied by electricity from the Australian grid in Fig 5.

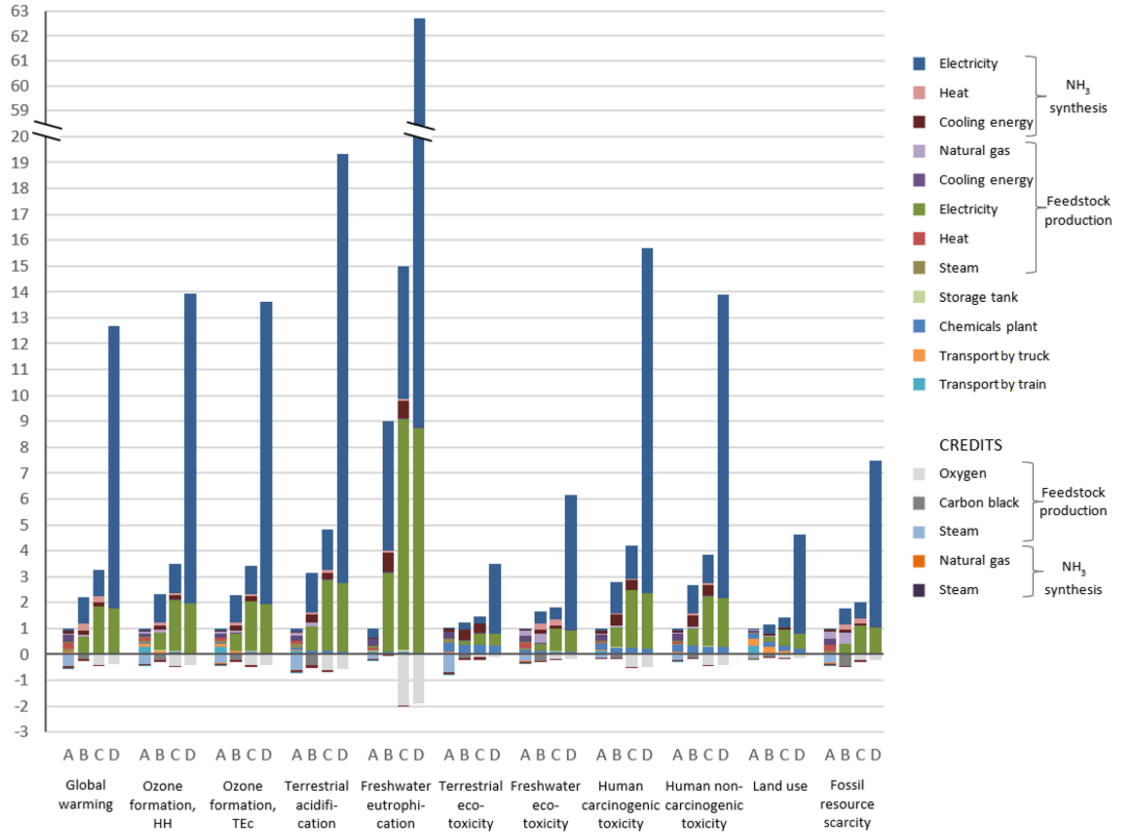
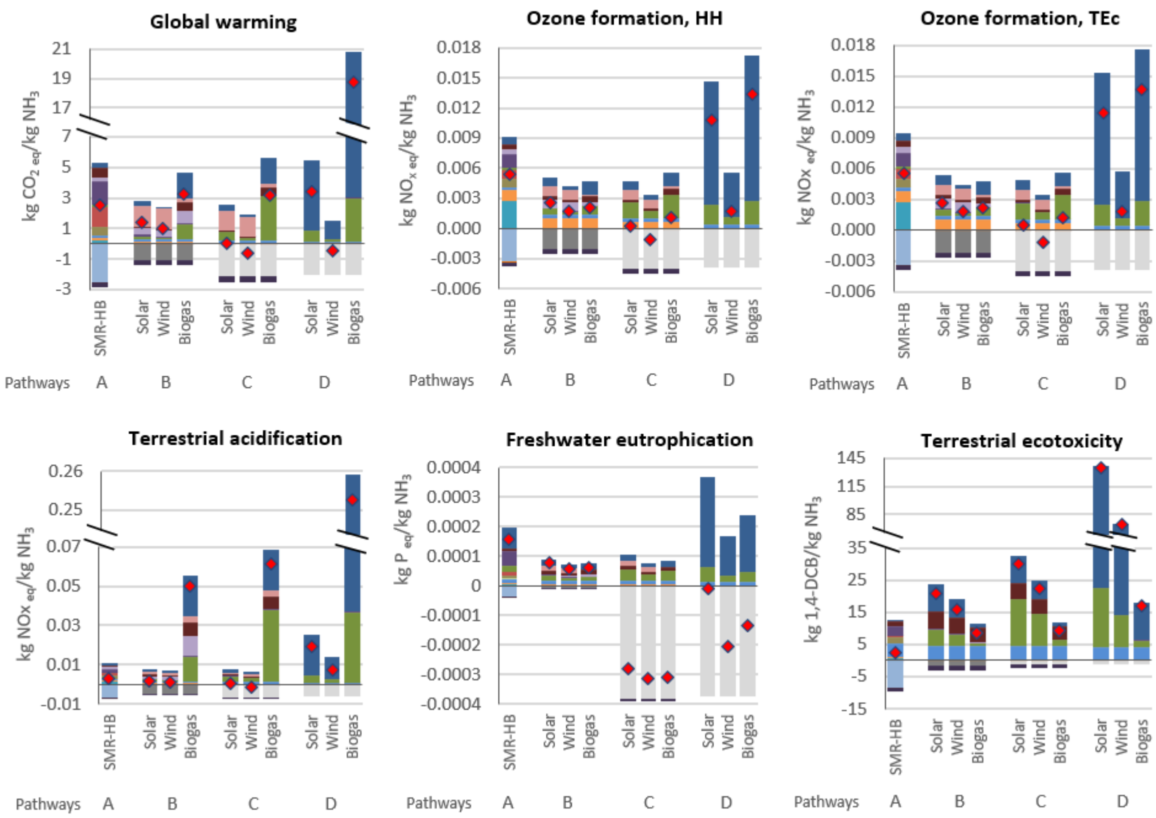


Fig 5. Midpoint results for the conventional and alternative NH_3 production pathways using grid electricity. Pathways: (A) SMR-HB (scenario (3) in Fig 4); (B) HTP-mini-HB; (C) Electrolysis-mini-HB; (D) Electrolysis-NTP. Notes: inputs/outputs with contributions lower than 0.5% in all impact categories were not included in the chart. Transport distances in each pathway: (A) 4,000 by train, 500 km by articulated truck, and 300 km by rigid truck; (B) 500 km by articulated truck and 300 km by rigid truck; (C) 300 km by rigid truck; and (D) 30 km by rigid truck. The results for pathway A were normalized to 1 in the vertical axis, then the results for pathways B, C, and D correspond to the variation in respect to pathway A.

Results in Fig 5 demonstrate that all the proposed alternative plants are less environmentally friendly than the conventional SMR-HB process in Australia if the plants are supplied by grid electricity. For most impact categories, the alternative plants generated more than double the impacts of the SMR-HB plant. The impact on freshwater eutrophication is 60 times greater in the electrolysis-NTP plant. This huge impact is due to the hard coal and lignite power plants, as identified in the previous section, but, in general, the electricity consumption was also the main factor affecting all the environmental impact categories because 87% of the electricity in Australia is produced from fossil sources (Cozzi et al., 2020; ETH, 2021). Specifically, the electricity consumption for the NH_3 synthesis in the NTP-assisted plant was the input with the largest environmental impacts. In this sense, the electrification of industrial processes could only be beneficial if cleaner energy sources in are used to generate electricity.

Since the proposed distributed production plants might be installed in rural areas, away from the national electric grid, it is plausible to evaluate the environmental performance of the plants by assuming the supply from dedicated electricity generation based on renewable resources. We evaluated scenarios using solar and wind energy only to replace grid electricity, and biogas to produce both electricity and biomethane to replace the natural gas inputs, presented in Fig 6.

It is notable that the alternative plants using RE had better environmental performance than the centralised plant in most of the impact categories. The main factors for these benefits are the reduction of transport distances and the electrification of the processes, both factors promoted by the downscaling of plants and relocation close to farming areas. Only in ozone formation categories for regional plants (pathways B), transport still had relevant contributions around 20% due to the NOx emissions from old trucks during the 800-km journeys to farms.



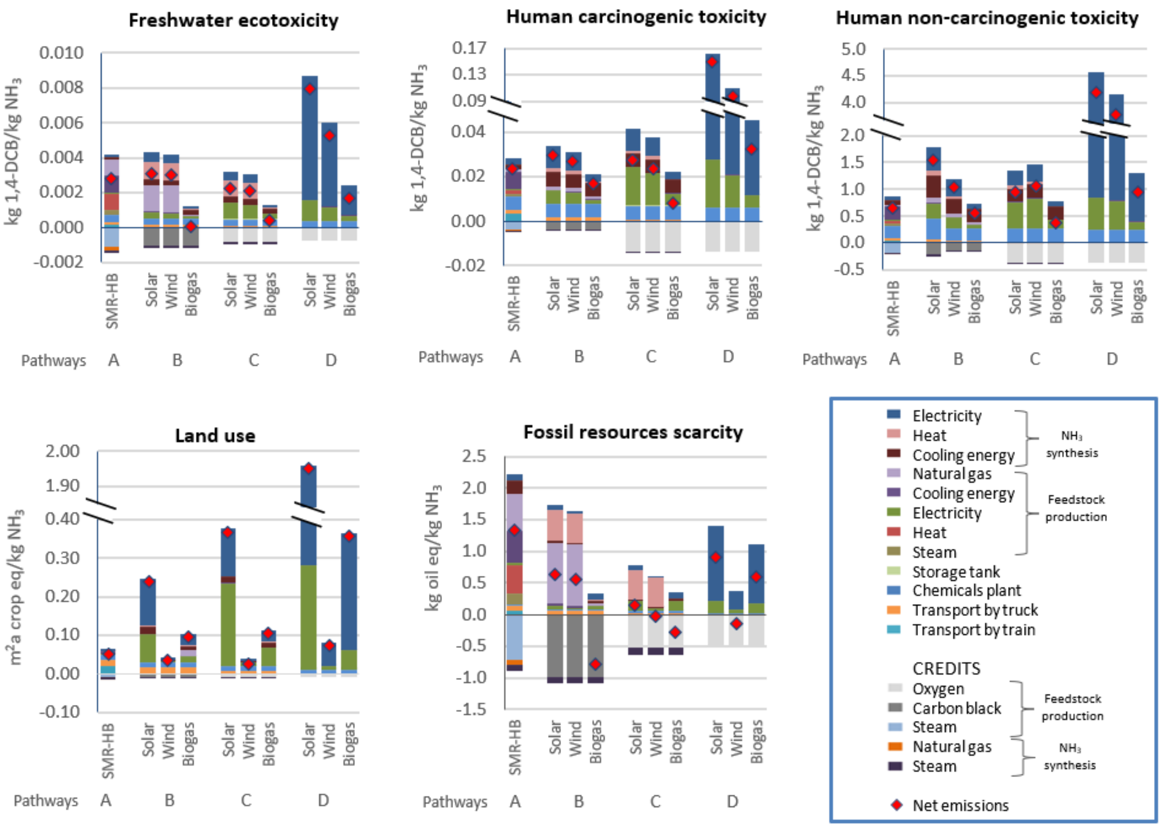


Fig 6. Midpoint results for the alternative NH_3 production pathways supplied different energy sources.
Pathways: (A) SMR-HB (scenario (3) in Fig 4); (B) HTP-mini-HB; (C) Electrolysis-mini-HB; (D) Electrolysis-NTP. Notes: inputs/outputs with contributions lower than 0.5% in all impact categories were not included in the legends box. Transport distances in each pathway: (A) 4,000 by train, 500 km by articulated truck, and 300 km by rigid truck; (B) 500 km by articulated truck and 300 km by rigid truck; (C) 300 km by rigid truck; and (D) 30 km by rigid truck. Biogas sources: manure (32.7%), biogenic waste (29.9%), sewage sludge (37.1%), and used cooking oil (0.3%) (ETH 2021).

The electrification of processes reduced the use of fossil resources for heating and cooling and gave the possibility of using RE, from which wind energy provided the lowest environmental impacts. The environmental performances of the small-scale plants were further improved when including credits because these plants would generate a market reduction for the CB and oxygen produced by grid electricity. For example, on global warming, the total generated burdens in scenarios using wind energy were 2.43, 1.97, and 1.54 kg $CO_{2\,eq}$ /kg NH_3, for pathways B, C, and D, respectively. In addition, if CB and oxygen credits were considered, these plants would further reduce or invert the $CO_{2\,eq}$ emission balance, with net emissions rates of 1.02, -0.52, and -0.52 $CO_{2\,eq}$ /kg NH_3, for pathways B, C, and D, respectively. In scenarios using solar energy, the small-scale plants also obtained positive results, except for the pathway D due to the carbon emissions during the manufacture of photovoltaic modules and other equipment. The obtained net emissions using solar energy were 1.41, 0.12, and 3.40 $CO_{2\,eq}$ /kg NH_3, for pathways B, C, and D, respectively. The NTP-assisted plants supplied by solar energy only had better results than conventional plants in the categories of freshwater eutrophication and fossil resource scarcity.

The most notable impacts reduction has been obtained on freshwater eutrophication in the electrolyser-based plants due to the market reduction for the oxygen produced by fossil-based electricity, generating reductions up to 290% of the quantity emitted by the conventional plant of 1.56E-04 kg P_{eq} /kg NH_3.

It is also notable that the variation in the results in Fig 6 was significantly high when using biogas in impact categories such as global warming and terrestrial acidification, and when using solar energy on terrestrial ecotoxicity, human toxicity, and land use. In these categories, the variation was mainly due to the electricity consumption of the NTP-assisted synthesis section of pathway D. On global warming and terrestrial acidification, electricity production from biogas releases ammonia into the air during the anaerobic digestion of manure. On terrestrial ecotoxicity and human toxicity the high impacts using solar electricity are due to silver, copper and other metal particles released during the manufacturing of photovoltaic modules, inverters, and electric installations. The impact on land use is due to area needed for solar farms. In the impact category of fossil resources scarcity, all alternative plants had better results than the conventional plant, even in pathway B in which natural gas is used for the HTP section due to the benefits of CB credits. Regarding NH_3 storage, the manufacturing and operation of tanks in all the pathways had very low contributions (< 1 %) to the environmental impacts for both analyses using grid (Fig 5) and renewable-based electricity (Fig 6).

To sum up, besides the environmental benefits of the lower transport distances of distributed NH_3, we identified that the main benefit is the electrification of processes, provided that the electricity is produced from RE. Moreover, the incorporation of CB and oxygen credits in the balances would provide significant impacts reductions, as long as these co-products reduce the market to equivalent products made by fossil-based electricity.

3.3. Sensitivity analyses: effect of biomass sources, NTP energy yield, and NH_3 separation technology

In contrast to the use of solar and wind electricity, the estimation of the environmental impacts of the use of biogas presented high uncertainties due to its high variability, which depends on the biomass source, location, technology, and costs (Indrawan et al., 2018; Martín-Hernández et al., 2020; Yang et al., 2020). To obtain precise conclusions for this scenario would be necessary to perform techno-economic analyses for the specific regions to determine the most feasible biomass sources mix, which is beyond the scope of this work. Under the utilized cut-off approach for the impacts assessment, the storage of manure for biogas production by anaerobic digestion was the main emissions generator, while biogas from biogenic waste and sewage sludge are considered burden-free because this biogas is generated as a by-product from essential activities. For this reason, given that in this environmental analysis we found that the 32.7% of manure content in the biomass mix was responsible of the total environmental burdens, we added a scenario without manure. The new biogas consisted of biogenic waste (41%), sewage sludge (47%), and used cooking oil (11%), being the latter the only source with environmental burdens due to the oil collection and processing. In addition, we added a new scenario by assuming the availability of lignocellulosic biomass to produce electricity by a wood chips furnace.

Due to the relevance of the global warming category, as well as the high impacts of biogas production on terrestrial acidification and the importance of land use for the agricultural field, the sensitivity analysis of the effect of new biomass sources are presented in Fig 7 for these impact categories.

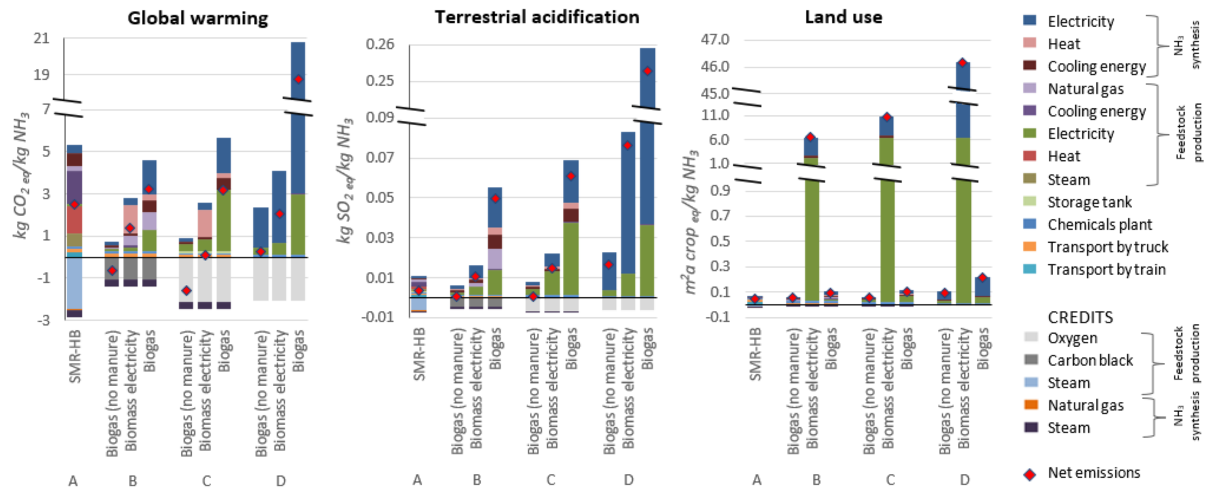


Fig 7. Midpoint results for the conventional and alternative NH_3 production pathways in different biomass scenarios.
Pathways: (A) SMR-HB (scenario (3) in Fig 4); (B) HTP-mini-HB; (C) Electrolysis-mini-HB; (D) Electrolysis-NTP. Notes: inputs/outputs with contributions lower than 0.5% in all impact categories were not included in the chart. The biogas scenarios columns (on the right of each pathway) correspond to the same results in Fig 6.

In the new scenarios in Fig 7, the net emissions affecting global warming in the alternative plants were lower than the conventional pathway for NH_3 production. Especially for pathways B and C in the biogas (no manure) scenario, the net carbon emissions were lower than in the scenario using wind energy with rates of -0.65 and -1.57 kg $CO_{2\ eq}$/kg NH_3 compared to rates of 1.02 and -0.52 kg $CO_{2\ eq}$/kg NH_3 (see Fig 6), respectively.

For the terrestrial acidification category, the new sources of biomass generated significant impacts reductions compared to the impacts of the previous biogas scenario for all the alternative pathways. However, the impacts from the pathway D are still higher than the conventional pathway. The scenario using electricity from biomass still generate high impacts on terrestrial acidification due to the emissions of NOx and NH_3 during the burning of wood chips in furnaces for electricity generation.

In the case of the land use category, removing manure in the biogas mix helped halve the impacts of the previous biogas mix scenario for all alternative plants. Also, the use of biogas without manure in pathway D reduced about 20 times the impact on land use compared to when solar energy was used, but it is still higher than the impact of the conventional pathway, with rates of 0.0966 and 0.0503 m^2a crop $_{eq}$/kg NH_3, respectively. On the other hand, the land use impacts of pathways B and C in this same scenario were similar to the impacts of the conventional plant.

In scenarios in which lignocellulosic biomass supplied the electricity requirements, impacts on land use significantly increased to 6, 11, and 46 m^2a crop $_{eq}$/kg NH_3 for pathways B, C, and D, respectively. This means that for pathway D, impacts on land use increased 650 times compared to the impacts when using wind energy. The significant impact of the electricity generation from wood chips on land use is basically because this biomass was cultivated in sustainable managed forests of birch, pine, spruce, and other plantations dedicated for energy purposes. In this sense, cultivation, transport, and processing of this biomass generate high environmental burdens, different to biomass from forestry waste, which would not add burdens. However, due to the uncertainty of forestry waste availability to supply the high electricity demand, to assume dedicated energy crops is a more conservative scenario.

Using solar energy in pathway D has not obtained good results due to the high electricity consumption of the NTP-assisted NH_3 synthesis section. This section requires further improvements in order to see whether this plant would be environmentally feasible in a country with high solar energy potential. In this sense, a scenario for improved NTP energy yield is proposed based on Rouwenhorst and Lefferts (2020), who envisage that the consumption of the NTP reactor would decrease to 4 MJ/kg NH_3 at 1.0 mol. % NH_3, which in turn this molar concentration would reduce the energy costs for the recycling loop to 1 MJ/kg NH_3. In other words, the NTP section would reach an energy yield of 900 g NH_3/kWh, equivalent to 1.11 kWh/kg NH_3, plus 0.28 kWh/kg NH_3 for recycling and 2.22 kWh/kg NH_3 for separation. It translates to a total energy yield of the section of 277 g NH_3/kWh, which is far over the expectations according to Kim et al. (2016), who stated that the NTP-assisted NH_3 synthesis section might be competitive against the HB process for small-scale production at energy yields between 150 and 200 g NH_3/kWh.

Moreover, the required electricity input to perform the complete NH_3 separation using zeolites in the NTP-assisted plant could be reduced if a separation by absorption in water at ambient conditions was performed to obtain a solution with 28% NH_3. This separation method has been discarded in previous studies due to the difficulties to recover the water, but this NH_3 solution could be useful because it would be directly utilised as fertiliser.

For the comparison of the pathways, despite the obtained product is not pure anhydrous NH_3, the functional unit can still be 1 kg (equivalent) of anhydrous NH_3. This process would also eliminate the need for pressurised storage. However, the transport of the product with only 28% NH_3 content would increase the burdens of transport about 3.57 times per functional unit, requiring the analysis of this decision in a new separation technology scenario. The proposed scenarios are evaluated in Fig 8 based on the results using solar energy for the global warming category.

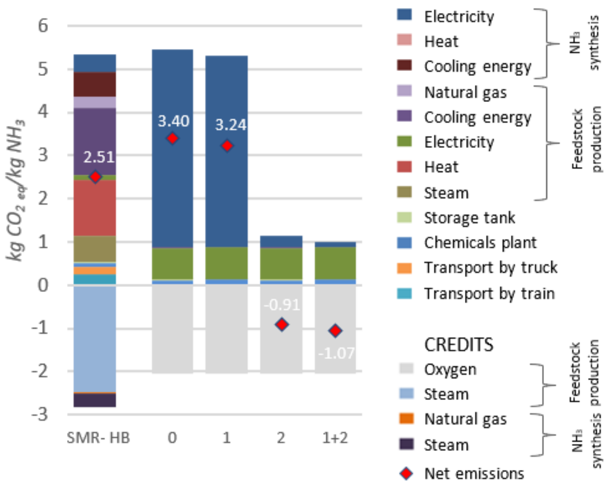


Fig 8. Impacts on global warming for the conventional (SMR-HB) and pathway D (NTP-assisted) NH_3 production in proposed technology improved scenarios.

Pathway D scenarios: 0- Solar energy with NTP 35.7 g NH_3/kWh yield (Fig 6); 1- Solar energy with NTP 37.5 g NH_3/kWh yield and water-based separation; 2- Solar energy with NTP 900 g NH_3/kWh yield; 1+2 - Solar energy with water-based separation plus NTP 900 g NH_3/kWh yield.

For the NTP-assisted plant, in scenario 1, carbon emissions are slightly reduced by 5% due to the water-based separation method. In this scenario, the increase of the transport burden is hardly perceived due to the short distances that the product must be transported from farmer's cooperatives to crops. On the other hand, in scenario 2, the improvement of the energy yield generated the most significant impact reductions about 127%, reaching a rate of -0.91 kg $CO_{2\ eq}$/kg NH_3. In scenario 1+2, an NTP-assisted plant with high energy yield and the water-based separation obtained the best result among all the alternatives using solar energy with a carbon emissions rate of -1.07 kg $CO_{2\ eq}$/kg NH_3.

In short, removing manure of the biomass mixes significantly reduces the environmental impacts in alternative NH_3 pathways. However, when using lignocellulosic biomass, impacts on terrestrial acidification and land use are higher than the impacts of the conventional NH_3 pathway due to NOx and NH_3 emissions and the cultivation of energy crops, respectively. In the scenario of pathway D using water based NH_3 and supplied by solar energy, impacts on global warming are reduced despite the higher need of transport. Moreover, pathway D considering the expected maximum energy yield of NTP reactors would obtain the lowest global warming impact among alternative pathways for NH_3 synthesis.

4. Conclusions

This study has demonstrated that local NH_3 production has a better life-cycle environmental performance than centralised large-scale production in Australia and identified the main polluting factors such as transport, energy sources, and the level of electrification of processes. Among the most relevant findings are:

- Centralised NH_3 production emits up to 2.96 kg $CO_{2\ eq}$/kg NH_3 when supplying distant markets, where up to 0.87 kg $CO_{2\ eq}$ are due to transport. The high carbon emissions rate from transport can be explained by the intrinsic inefficiency of NH_3 logistics due to the empty returns and the out-of-date control emissions technologies in most of the Australian trucks.
- The lower energy demand of local production facilitates the use of renewable energy sources. Distributed production plants using renewable energies in HTP reactors or electrolysers to supply NH_3 synthesis loops could reach $CO_{2\ eq}$ emissions reductions over 100% when including co-product credits, such as oxygen and carbon black. When using solar, wind, or biogas (other than manure) energy sources, the alternative pathways obtained the following emission rates, respectively: for regional HTP-mini-HB plants 1.41, 1.02, or -0.36 kg $CO_{2\ eq}$/kg NH_3; for local electrolyser-mini-HB plants 0.12, -0.52, or -1.57 kg $CO_{2\ eq}$/kg NH_3; and for 'at farm' electrolyser-NTP plants 3.40, -0.52, or 0.27 kg $CO_{2\ eq}$/kg NH_3, under the current energy yield of 35.7 g NH_3/kWh of NTP reactors.
- Among all environmental impact categories, the most notable impacts reduction was on freshwater eutrophication in the electrolyser-based plants due to the market reduction for the oxygen produced from fossil-based electricity, generating reductions up to 290% of the quantity of P_{eq}. Despite these positive results, the use of solar energy obtained concerning results on terrestrial ecotoxicity due to the

manufacturing of facilities components and on land use due to the area needed for mounting solar modules.

- An improved NTP-assisted plant with a water-based NH_3 separation method and an enhanced reaction energy yield, despite the reduced load capacity for the transport of NH_3 solution in water, this plant would obtain its best environmental performance emitting -1.07 kg $CO_{2\ eq}$/kg NH_3, using solar energy, mostly due to the enhanced energy yield. Despite that the water based NH_3 separation method helped to reduce only 5% of the carbon emissions, this method might be less expensive than a separation based on zeolites or metal halides.

In general, this analysis presented technical and environmental benefits for different NH_3 production plant configurations. We identified the relevance of transport and the environmental drawbacks of renewable energy sources such as solar and biomass energy. For this latter energy source, it is still necessary more detailed techno-economic analyses for each region to obtain more accurate environmental impacts results of specific feasible biomass mixes. We also analysed technical considerations for novel NTP-assisted NH_3 production plants. This pathway presents the highest challenges to reach an acceptable energy efficiency to be attractive at commercial scales, which requires further research on plasma-catalytic synthesis of NH_3. Yet, the current low energy efficiency of NTP reactors, compared to its theoretical maximum efficiency, means that this pathway would have the greatest opportunities to replace other alternatives such as mini-HB plants because HB process is already a mature technology, thus, no improvements in the HB energy and conversion efficiencies are expected. Additionally, the high costs of small-scale production could be compensated by the sale of credits, not only green co-products, but also environmental credits such as carbon bonuses. These facts would promote the development of new business models supported by local supply chains optimization to produce self-sustained fertilisers. These prospective results will contribute to the deployment of local green NH_3 production, which would also help to avoid shortage risks and price volatility of imported fertilisers, promoting local employment, knowledge transfer, and the deployment of green energy technologies in rural areas.

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