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The life cycle environmental impacts of a novel sustainable ammonia production process from food waste and brown water

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ABSTRACT

To replace existing high impact ammonia production technologies, a new sustainability-driven waste-based technology producing green ammonia with and without urea was devised using life cycle thinking and sustainable design principles, targeting efficiency, carbon emissions, water, and power use competitiveness. We have used life cycle assessment to determine whether cradle-to-gate, multiple configurations of the core waste-based processes integrating several carbon capture/utilization options can compete environmentally with other available ammonia technologies. Our waste-to-ammonia processes reduce potential impacts from abiotic depletion, human toxicity, and greenhouse gas (GHG) emissions relative to fossil-based and renewable technologies. Among the assessed technologies, coupling dark fermentation with anaerobic digestion and capturing CO_2 for sequestration or later use is most efficient for GHGs, water, and energy, consuming 27% less energy and reducing GHGs by 98% compared to conventional ammonia. Water use is 38% lower than water electrolysis and GHGs are 94% below municipal waste incineration routes per kg NH_3. Additionally, displacing conventional, high impact urea by integrating urea production from process CO_2 decreases life cycle environmental impacts significantly despite increased energy demand. On a fertilizer-N basis, the ammonia + urea configuration without dark fermentation performs best on all categories included. Methane and ammonia leakage cause nearly all life cycle impacts, indicating that failing to prevent leakage undermines the effectiveness of new technologies such as these. Our results show that a green ammonia/ammonia + urea process family as designed here can reduce waste and prevent the release of additional CO_2 from ammonia production while avoiding fossil-based alternatives and decreasing emissions from biogenic waste sources.

1. Introduction

Ammonia (NH_3) is both crucial as a fertilizer in the agricultural industry and has promising prospects as an energy carrier. Consequently, much academic and industrial effort has been put into seeking the most energy efficient, environmentally benign, and economically viable processes for ammonia synthesis. This study adds to the body of work in the area by providing the first Life Cycle Assessment (LCA) of a waste-based sustainable ammonia and urea production process developed using life cycle thinking and sustainable design principles. As described in Ghavam et al. (2021a), the process itself also opens new ground in waste-derived products and technology configuration integrating novel membrane technologies being developed.

As global population grows, nutritional requirements are driving the need for more food production, leading to the demand for more fertilizers, which leads to higher food demands and more food and human waste (HW) generation. According to statistics, the increase in nutrient N demand keeps pace with global population and this trend is projected to continue. Global population is set to increase by about 14% over the course of 6 years; while nitrogen fertilizer demand has increased nearly 6% over the same time period (FAO, 2019).

Bioconversion of wastes such as food waste (FW) and human waste into important chemical compounds such as ammonia and urea offer, to some degree, a new resource recovery alternative for fossil-based chemicals. Excessive accumulation of these waste streams poses a serious threat to GHG reduction. Uncontrolled degradation of organic waste in landfills, if left untreated, results in the discharge of methane (CH_4), a potent GHG, trapping approximately 85 times more heat than CO_2 throughout the first 20 years from when it is discharged (EDF, 2021).

As a result, designing a sustainable waste management process for

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List of abbreviations

AD	Anaerobic Digestion
BW	Brown Water
CapEx	Capital expenditures
CARB	California Air Resource Board
CCS	Carbon Capture and Sequestration
CCU	Carbon Capture and Utilization
CML	Institute of Environmental Sciences, University of Leiden, The Netherlands
DF	Dark Fermentation
DI	Deionized
EMS	Electrochemical Membrane Separation
EPA	Environmental Protection Agency
ESI	Electronic Supplementary Information
FAO	Food and Agriculture Organization
FU	Functional Unit
FW	Food Waste
GHG	Greenhouse Gas
GLO	Global
GWP	Global Warming Potential
GWI	Global Warming Impact
HW	Human Waste
IPCC	Intergovernmental Panel on Climate Change
ITM	Ion Transport Membrane
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCT	Life Cycle Thinking
MFI	Membrane Filtration Index
MSW	Municipal Solid Waste
NG	Natural Gas
NREL	National Renewable Energy Laboratory
PV	Photovoltaic
RoW	Rest-of-the-World
SDP	Sustainable Design Principles
SMR	Steam Methane Reforming
SOFC	Solid Oxide Fuel Cell
SOFEC	Solid Oxide Fuel Electrolysis Cell
SSAS	Solid State Ammonia Synthesis
WECC	Western Electricity Coordinating Council

Nomenclature

TPD	tons per day
CO_2	eq Carbon Dioxide Equivalent

ammonia synthesis and reducing the GHG emissions such as the utilization of Anaerobic Digestion (AD) will be an effective pathway to target the replacement of higher impact, fossil-based chemicals. One of the main advantages of a waste-based process such as the green ammonia production technology developed in this study is the potential to prevent the release of methane from uncontained degradation of waste.

According to the Food and Agriculture Organization (FAO) of the United Nations, the world supply capacity of ammonia was 157,819 thousand tonnes in 2018 and it is expected to reach 163,219 thousand tonnes in 2022 (FAO, 2019). This chemical compound is the second most produced chemical after sulfuric acid (H_2SO_4) and is derived mainly from fossil fuels (Ghavam et al., 2021b). Approximately 89% of the ammonia produced is used as an intermediate chemical for direct production of fertilizers such as urea and only about 11% is traded as ammonia (Jackson et al., 2020). The scale of the ammonia market makes development and deployment of more environmentally sustainable production routes particularly important.

Ammonia production technologies currently in use require either a steady supply of Deionized (DI) water in high volumes to operate, and/or result in high CO_2 emissions (Ghavam et al., 2021b). Globally, more than 90% of ammonia is produced through the Haber-Bosch process (Guerra et al., 2020). The downside of Haber-Bosch technology is the production of high GHG emissions, greater than 2.16 $kgCO_2eq/kg$ ammonia, and high amounts of energy usage surpassing 30×10^9 J/tonne NH_3 mostly due to high operational conditions (Yoo et al., 2013). For the production of 1 t of ammonia through steam methane reforming (SMR) coupled with Haber-Bosch, 0.66 t H_2O is utilized and 9–10 t CO_2eq is produced over its full life cycle (Parkinson et al., 2018). The most extensively adopted technology for sustainable hydrogen (H_2) production required for ammonia synthesis is water electrolysis powered by renewable technologies such as solar and wind. Generally, a water electrolyzer requires a constant supply of pre-treated water with high purity levels for its operation. Approximately 1.6 t H_2O is consumed for producing 1 t of ammonia through water electrolysis (Will and Lukas, 2018).

To replace the existing high impact ammonia production technologies currently in use, a new sustainability-driven waste-based technology was devised using life cycle thinking and sustainable design principles to guide the design. Crucially, meeting the design targets requires the effective management of CO_2. Other performance goals were set for competitiveness on carbon emissions, water and power use. LCA was used as part of the design process, to provide quantitative guidance.

The life cycle thinking and sustainable design principles approach led to development of new technology centred around the use of emerging and novel membranes and utilizing waste resources, thus supporting more efficient resource and space management while enabling the viable utilization of food, human and CO_2 waste streams (Ghavam et al., 2021a). A family of four primary configurations and four CO_2 fates arise from this new technology and the intent of this work is to evaluate these on environmental and productivity/efficiency grounds. An alternative approach to manage CO_2 to meet the design goals would be utilizing the CO_2 that otherwise would be released into the atmosphere during ammonia production to produce urea, a key agricultural nutrient. In addition to its importance in the agricultural industry, urea which is readily produced from ammonia and CO_2 is also used extensively in polymers (CICE, 2017). Demand for approximately 40–60% of food production worldwide is tied to the usage of commercial fertilizers and more than 60% of this amount is attributed to nitrogen-based fertilizers (Roberts, 2009). Data released by Yara indicates that urea makes up most of the nitrogen-based fertilizer market globally (Yara, 2018). Incorporating urea production to consume waste CO_2 utilizes a large share of the end-product ammonia. Significantly, this CO_2 that is used in the urea will be discharged, thus, although the CO_2 in this system is biogenic, it will return to the atmosphere. However, according to the environmental analysis tools (e.g. SimaPro, GaBi) it will do so having displaced fossil CO_2 that would increase the atmospheric CO_2 levels. Thus, incorporating a green urea plant may slow, though not abate the GHG crisis, while getting useful services (in this case, offsetting the production of conventional urea, which uses significant fossil resources and leads to significant life cycle GHGs).

The multiple configurations of the core waste-based processes in this study were linked with several carbon capture/utilization options to create multiple green ammonia and green ammonia + urea production processes, which have been assessed for environmental performance are described in the methodology section.

2. Methodology

2.1. Technology description

In this study, waste is fed into a two-stage Dark Fermentation (DF) coupled with Anaerobic Digestion (AD)/AD-only process, producing biogas. The resulting gas stream is then upgraded to hydrogen by passing through a sequence of process steps comprised of different types of membranes described further in Table A1. The upgraded hydrogen will then react with nitrogen which is the product of the migration of air throughout the membrane, in order to produce ammonia. Simultaneously, the separated CO_2 from the digestion process along with the ammonia can be utilized for urea production.

In this modelled process, two configurations with four possible CO_2 fates are assessed for this green design-based process: Technology-1: Ammonia production through a two-stage DF coupled with AD (DF + AD) and Technology-2: Ammonia production through AD-only. There are four possible CO_2 fates for each process configuration:

- Scenario set-i (the base case): CO_2 is discharged directly into the atmosphere
- Scenario set-ii: (CCU) CO_2 is used for urea production
- Scenario set-iii: (CCS) CO_2 is compressed, liquefied, captured, and injected into the ground
- Scenario set-iv: (CCU) CO_2 is compressed, liquefied, captured, and enters the commodity liquid CO_2 market and likely will return to the atmosphere based on its usage

Depending on the scenario configuration, the process configuration and computational model behaviour changes. Additionally, since electricity is an important contributor to impact, an alternative configuration option where the Solid Oxide Fuel Cell (SOFC) is used was also modelled (assessed in section 3.2.3). The technology and the technology modelling are described in detail in Ghavam et al. (2021a). In general terms, the process configurations are shown in Fig. 1. The elements that differ in each scenario are shown in cream colour and the fixed elements are in white (Fig. 1). We have assessed the impacts from three selected sources of energy, solar, wind, and grid, however, solar is our default primary source, the rationale behind choosing it is discussed in section 2.2.4.1.

The design rationale of the proposed process is discussed in detail in Ghavam et al. (2021a). The waste feedstock in particular provides a wealth of sustainability benefits mainly in avoiding fossil energy sources as well as utilizing the stream through a valorization strategy which prevents the release of carbon emissions as well as recovering useful chemical compounds and nutrients. In place of conventional processing units, we focused on the use of membrane technologies (assessed in Table A1) in order to minimize the physical footprint, water, and chemical usage in our designed process. In addition, the by-products produced through the selected membrane technologies do not need to be upgraded, eliminating associated waste stream or additional process steps for refining (Table A2). Fig. 2 shows all the process configurations, scenarios, and CO_2 fates designed and evaluated here.

In these processes, waste (food waste and brown water (BW)) is fed into a DF + AD, panel (a) or one-stage AD-only, panel (b), producing biogas. Hydrogen is separated from the gas mixture through a series of operating stages (membranes) and reacts with nitrogen derived from the migration of air via a membrane known as Ion Transport Membrane (ITM) (Table A1), for the production of ammonia. The CO_2 recovered together with the ammonia can be utilized for urea production (scenario set-ii). This process is compared to the scenario where the CO_2 is not captured/utilized, as well as to scenarios where the CO_2 is captured, compressed, liquefied, and either injected into the ground (CCS) or assumed to enter the commodity liquid CO_2 market (base CCU) (scenario sets i-iv). Each process configuration is shown as a dotted line in three different colours in Fig. 2a: (1 red dashed box)- with and without DF, (2 orange dashed box)-with and without SOFC, and (3 green dashed box)-with and without urea production process. Fig. 2b shows the production process (AD-only without urea production process and without SOFC) with the three components (DF, SOFC, and urea production process) removed from Fig. 2a.

For scenario set-ii (those producing urea), the effect of allocation is also evaluated, with three alternatives: Mass allocation, avoided product, and the unallocated process on a unit waste processed basis. All mentioned scenarios have three energy supply options comprised of solar (base case), grid, and wind. The afore-mentioned four carbon-fate scenarios and their permutations (72 in total) are then compared with each other and with other ammonia production processes (partial

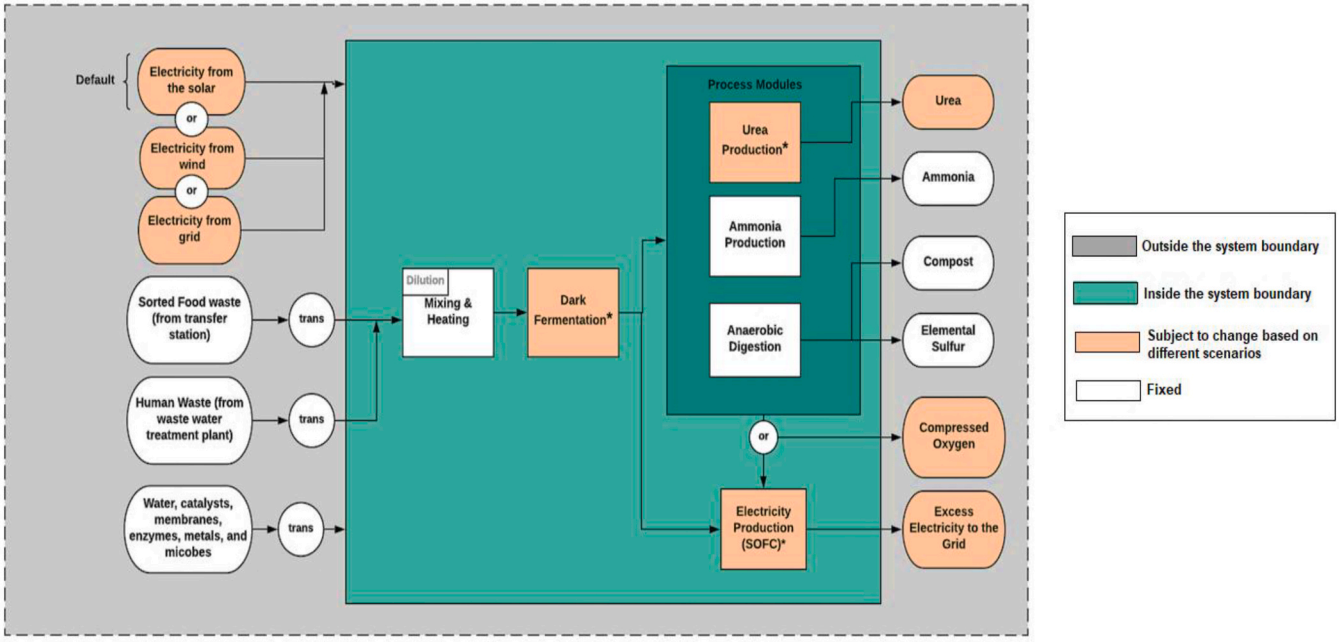

Fig. 1. A schematic of the proposed ammonia production process inside the black box shown in Fig. 3.

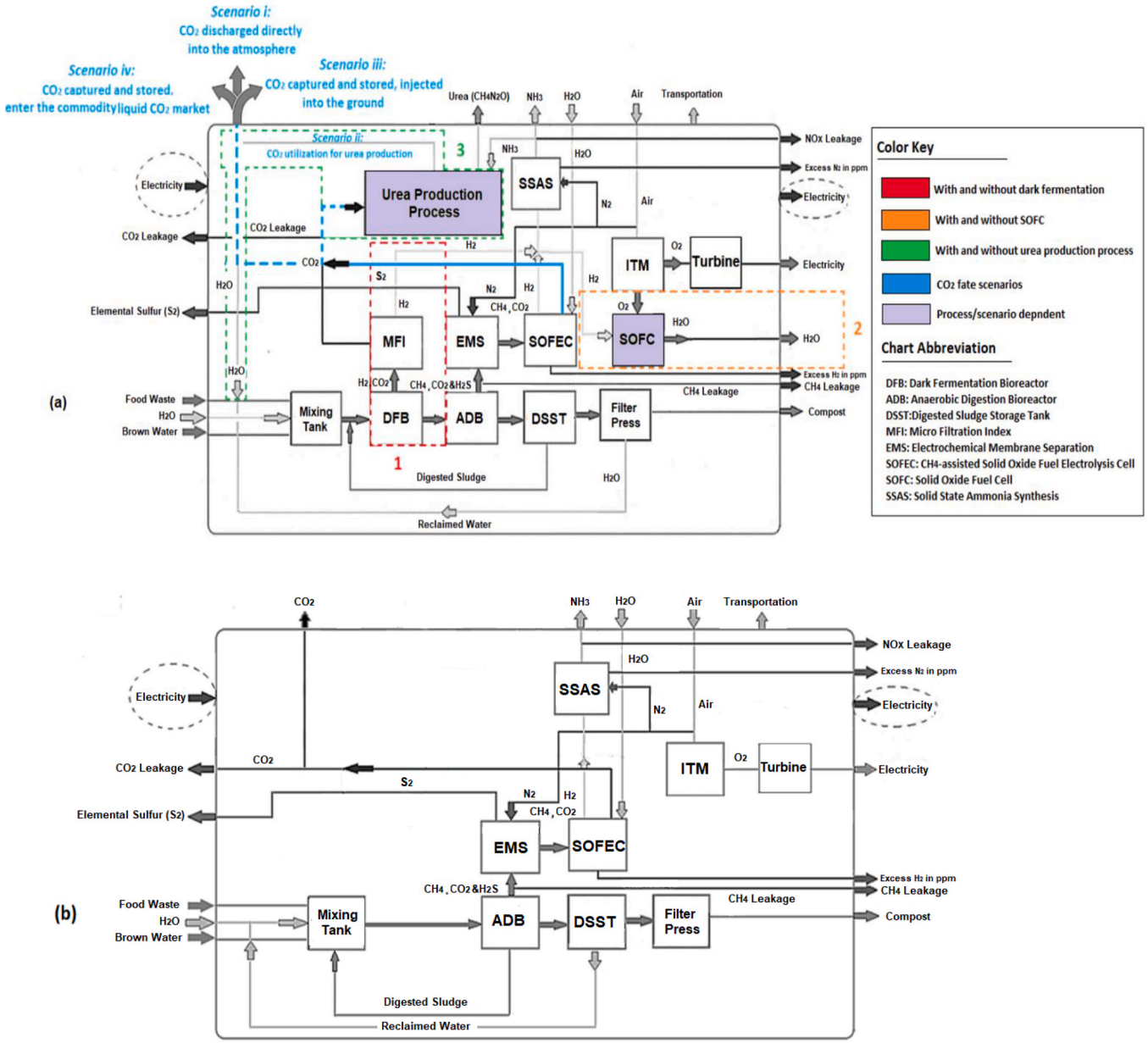

Fig. 2. A schematic of (a) a DF + AD with SOFC (b) AD-only without urea production process and without SOFC.

oxidation, cocamide diethanolamine production, and natural gas steam reforming).

2.2. Life cycle assessment

LCA is a primary technique used to support decision-making for sustainable design in production. This study presents a cradle-to-gate comparative LCA of a waste management facility for ammonia production. This comparative LCA considers relative environmental impacts in the areas of global warming, water scarcity, human health, ecosystems, and resource use, as well as human toxicity, acidification potential, eutrophication, depletion of abiotic resources, ozone depletion, and terrestrial ecotoxicity. For two configurations and four scenarios, Life Cycle inventories (LCIs) were developed based on computational modelling and design decisions. Biogenic CO_2 was used in all calculations (contribution, uncertainty, and sensitivity analyses). The ISO 14040 (ISO, 2006) and ISO 14044 (ISO, 2009) standards offer direction on the LCA framework which is comprised of the following four main stages:

I) Defining the goal and the scope of the LCA
II) Gathering and keeping a list of energy and mass inputs/outputs throughout all relevant life cycle stages
III) Assessing relevant environmental impacts that are related to the life cycle inputs and outputs
IV) Finally, interpreting the results, that will lead to a decision based on the data obtained from previous stage and improving the results

2.2.1. Goal and scope

Goal definition defines the objectives of the study, the intended applications, the target audience, and the key stakeholders. The scope definition, in turn, defines the Functional Unit (FU), system boundaries, impact assessment methods, allocation, and cut-off criteria, Life cycle inventory, assumptions, and limitations.

The goals/objectives of this study are:

I) To determine the environmental impacts of the proposed ammonia production processes and whether they can compete with other existing ammonia production technologies on a full life cycle environmental impact basis.
II) To investigate the use of LCA and life cycle thinking early in the green design process.

The system boundaries of an LCA define what processes are included or excluded in the studied system. The overall scope of this attributional LCA is cradle-to-gate, meaning it includes all stages from raw material extraction through the ammonia production facility, but does not include subsequent "downstream" storage, transportation, distribution, consumption, and end-of-life fate of the product. The system boundary for this study is illustrated in Fig. 3. The processes considered within the system boundaries in this cradle-to-gate LCA are grouped into four stages: (1) Brown water and food waste transportation to the proposed ammonia process site; (2) Ammonia production process; (3) CO_2 handling; and (4) Depending on the source of power (solar, wind, or grid) the extra electricity produced will be sold to the grid. Fig. 1 illustrates the black box shown in Fig. 3.

The primary FU used in this analysis is 1 kg of NH_3. Impacts were also assessed on a urea production basis, in which a FU of 1 kg urea is considered, as well as on the basis of total nutrient N (kg urea-N + kg NH_3–N) (refer to the Electronic Supplementary Information (ESI)).

2.2.2. Impact assessment methods

Life cycle inventory models for ammonia/ammonia + urea production at the defined scale in each scenario were developed and assessed using SimaPro 9.0.0.49 PhD version, developed by PRé Consultants, the Netherlands (Oele et al., 2020). The inventories are detailed in section 2.2.4. Secondary data is drawn from the widely-used ecoinvent library (version 3.6) (Wernet et al., 2016). Comparison processes are drawn from both ecoinvent v3.6 and Agri-footprint v4 (Durlinger et al., 2017). The impact assessment methods used are the Intergovernmental Panel on Climate Change (IPCC) Global Warming Potential (GWP, 100 years) {2013} (IPCC, 2013), ReCiPe 2016 endpoint (H) (Huijbregts et al., 2017), water scarcity (AWARE) (Boulay et al., 2018), and CML 2001 (Guinée et al., 2002). The selected impact categories and corresponding methods and units are shown in Table A3. The CML 2001 and Eco-indicator 99 methods from the superseded impact categories were used for the purpose of comparing with literature data.

The IPCC approach for GHG emissions excludes biogenic CO_2 (Liu et al., 2017). However, more recent studies indicate that the CO_2 emissions from biomass combustion will remain in the atmosphere for years. We have thus assessed the inclusion of biogenic emissions using the GHG Protocol impact assessment method version 1.02, which includes fossil, biogenic, land, uptake, and transformation emissions individually to incorporate biogenic CO_2 (for detailed calculations for each CO_2 fate refer to the ESI) (IPCC, 2008).

2.2.3. Allocation

In cases where a process produces more than one product, allocation of flows and emissions associated with the co-product system is needed. ISO guidance is to avoid allocation where possible by using system expansion where possible/reasonable and to compare to an alternative allocation method where allocation is used. In keeping with the ISO standards, system expansion was used to account for all non-urea co-products throughout. There is a large disparity in production volumes (urea dwarfs the primary ammonia production volume), in cases where the urea co-product comes from the waste CO_2 stream. As for the multi-product systems, those making urea along with ammonia, the impacts were allocated in keeping with ISO 1404416 recommendations (ISO, 2009). This was done through: System expansion with urea as an avoided product for cases where ammonia is the primary focus; and based on mass to allow comparison of the combined system on a nitrogen content basis and the effect of allocation. Since the production volumes of urea are so much higher than that of ammonia in the co-production cases, mass allocation between the two was used for the primary analysis and avoided product considered in the sensitivity analysis. The allocation types used and % table of allocation shares are shown in Table A4.

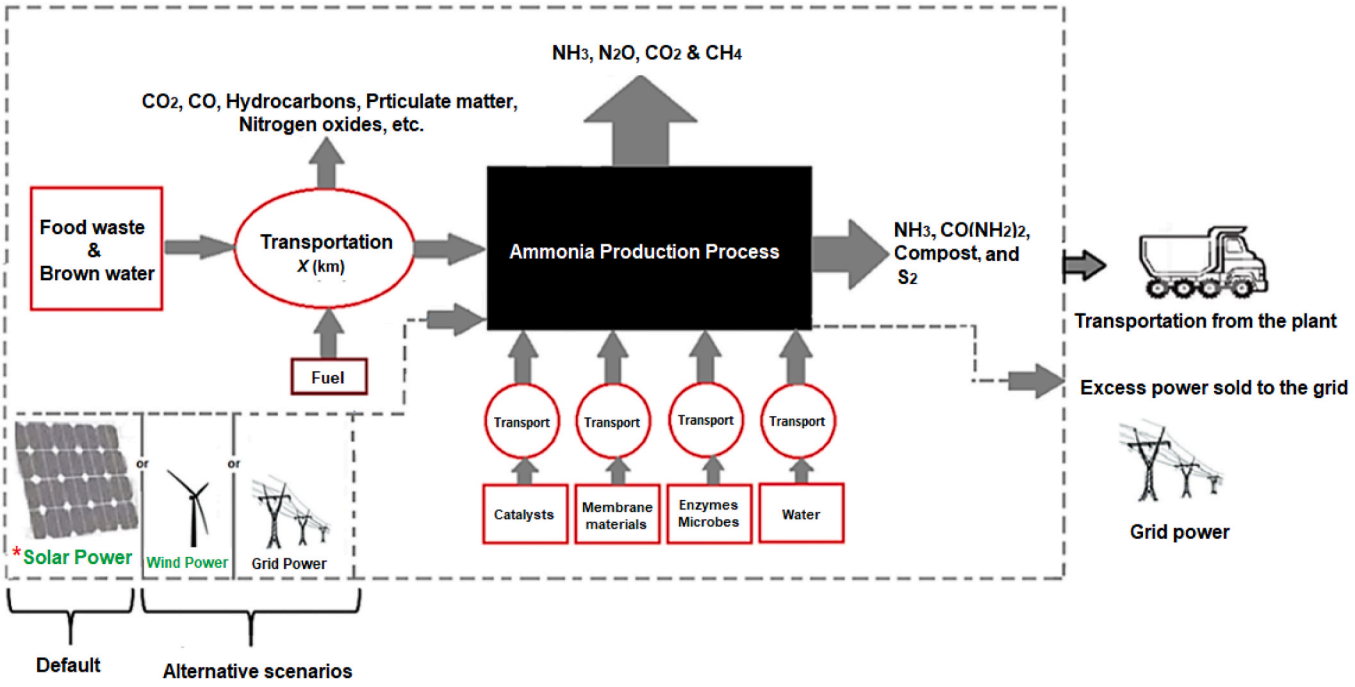

Fig. 3. System boundary for the cradle-to-gate LCA for this study's green ammonia and ammonia + urea production from waste (for a detailed description of the ammonia production process shown in the black box refer to Fig. 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

2.2.4. Life cycle inventory

Process operating parameters and yields are taken from the technology model and simulations for the four scenario sets of technologies and set out in Table 1 derived from Ghavam et al. (2021a). The results presented here (Table 1) are based on the calculations for 20 tons per day (TPD) of input waste (food waste and brown water). This value is calculated to roughly represent the size of a mid-size city such as Bakersfield, California, although other scaling can be evaluated with the implemented model (siting is discussed further in section 2.2.4.1) (Brown, 2018). Leakage, as in other methane and natural gas systems, has a high environmental impact on the process. Therefore, the processes are modelled with and without the impact from leakage, using values from US Environmental Protection Agency (US EPA) and California Air Resources Board (CARB) as shown in Table 1. Membrane components are represented using proxy background data, refer to section 4 in the ESI for further detail. Table 1 also provides the electricity inventory for the studied technologies. The effect of SOFC on energy demand is negligible. The technology configuration with the lowest energy intensity (two-stage) consumes about 41% less energy than water electrolysis coupled with Haber-Bosch and approximately 27% lower energy than SMR coupled with Haber-Bosch per kg NH_3 (Ghavam et al., 2021a).

2.2.4.1. Facility siting. Location will influence both feedstock availability and renewable energy supply options, it is an important factor in sustainable production of chemical compounds such as ammonia for maximizing both productivity and sustainability. As the inputs and outputs for this proposed ammonia production process are food waste and brown water, wastewater treatment and solid waste management facilities are the resources of interest. Based on the inputs and outputs of

Table 1
Material and electricity demand inventory for assessed processes, per tonne of processed input waste.

Process data	Values				Units	Notes
	CCU-Urea		No CCU-Urea			
	AD	DF + AD	AD	DF + AD		
Inputs						
Total waste	1	1	1	1	tonne	
Food waste	*0.5*	*0.5*	*0.5*	*0.5*	*tonne*	*Main Feedstock*
Brown water	0.5	0.5	0.5	0.5	tonne	Main Feedstock
NaOH	0	0.3711	0	0.3711	tonne	Added for pH balance (pH target: 5.5), based on De Gioannis et al. (2013)
Dilution water	0.1411	0.0634	1.25	1.25	tonne	Water used for feedstock dilution
Deionized (DI) water	1.872	1.664	1.872	1.664	tonne	DI water used for SOFEC
Outputs						
Ammonia (default)	0.1739	0.00113	2.343	2.246	tonne	Primary product in default configurations
Ammonia (without SOFC)	0.1913	0.00124	2.360	2.246	tonne	Primary product in process configurations without SOFC
Urea	3.823	3.956	0	0	tonne	Main Product
Compost	0.0077	0.00635	0.0077	0.00635	tonne	By-product
Sulfur	0.0002	0.00018	0.0002	0.00018	tonne	By-product
Direct emissions						
CO_2	0	0	2.807	2.495	tonne	Direct emission from SOFEC, applicable for Base case only
leakage rates						
CH_4	1.5	1.5	1.5	1.5	%	Based on Odeh (2019)
CO_2	1	1	1	1	%	Based on the modifications made on the U.S. EPA, (2021)
NH_3	1	1	1	1	%	Based on the modifications made on the U.S. EPA, (2001)
N_2O	0.5	0.5	0.5	0.5	%	From nitrogen in waste CARB, (2017)
Transport						
FW distance	24.9 ± 10%	24.9 ± 10%	24.9 ± 10%	24.9 ± 10%	km	Distance travelled from collection facility to the plant
BW distance	45.4 ± 10%	45.4 ± 10%	45.4 ± 10%	45.4 ± 10%	km	Distance travelled from collection facility to the plant

Energy demand (kWh)	CCU-Urea		CCU-market		No CCU-Urea (Base Case)		CCS	
	AD	DF + AD	AD	DF + AD	AD	DF + AD	AD	DF + AD
SOFC configurations (default)	9.551	9.385	1.104	0.674	1.054	0.661	1.107	0.675
Configurations without SOFC	9.553	9.385	1.106	0.674	1.056	0.661	1.106	0.675

Labels for configurations included in study	CCU-Urea: AD CCU-Urea: AD no SOFC	CCU-Urea: DF + AD CCU-Urea: DF + AD no SOFC	No-CC: AD No-CC: AD no SOFC CCS: AD CCS: AD no SOFC CCU-market: AD CCU-market: AD no SOFC	No-CC: DF + AD No-CC: DF + AD no SOFC CCS: DF + AD CCS: DF + AD no SOFC CCU-market: DF + AD CCU-market: DF + AD no SOFC	CCU-market is captured CO_2 compressed and assumed to enter the CO_2 market

this proposed ammonia production process, a site suitability analysis is necessary in determining where the proposed facility should be located. Siting was based on analysis of food waste and brown water in central California and overlapped with solar energy availability. Among the three energy supply options (solar, wind, and grid) considered in this analysis, solar power was selected as our base case electricity supply option (based on location assessment method using RETScreen software) (Natural Resources Canada, 2019) and calculations were conducted based on National Renewable Energy Laboratory (NREL)'s PVWatts® Calculator (NREL, 2014). The geographic analysis of these led to the estimation of the distance from waste treatment and waste management facility to the ammonia plant at 24.9 ± 10% (km) and 45.4 ± 10% (km) respectively. +/-10% distance from the waste treatment facility to the proposed ammonia plant has been selected to allow flexibility in placement (refer to section 5 in the ESI).

Calculations are based on the solar panel specifications (solar radiation, efficiency, and Photovoltaic (PV) array size) for the process demand of 17 MW, located in the city of Bakersfield, California, with the latitude and longitude of 35.37, −119.02 respectively, are provided in the ESI. PV array sizes range from under 300 m^2 to over 800 m^2 based on efficiency and solar irradiance. The system is modelled with a PV array size of 4401.705 m^2 for a 570 kW installed capacity using a modified library process for solar electricity. The impact of using wind as the primary electricity source was assessed, as was the impact of using grid electricity, to allow for consideration in situations where this plant is employed in other geographic locations where wind power works effectively (wind speed is in an acceptable range 30–55 mph) (NWW, 2005) and solar radiation is not in an acceptable range (<6 kWh/m^2/day) (U.S. Department of Energy's FEMP, 2017). Table A5 shows the list of library processes used from ecoinvent for conducting the LCA for this study.

2.2.5. Data quality, uncertainty and sensitivity analysis

Table A6 shows the uncertainty characteristics used for various inventory components, based on data quality estimates. For the estimation of default uncertainty distributions and parameters of values from flow data and their related processes, pedigree matrices are used. In the pedigree matrix approach, expert judgement is used to determine the uncertainty factors rather than empirical variability data. For the developmental technologies created here, three different pedigree matrices were used depending on the degree of speculativeness (new, lab, and pre-pilot stage) and/or maturity (more established components). The values for material and energy inputs have a relatively narrow left skewed uncertainty, while output yields of mature technology (e.g., urea production) are less narrow because they reflect the uncertainty in the modelling. Finally, a broader distribution is applied for output yields for technologies under development (e.g., ammonia). Uncertainty for the nitrous oxide (N_2O) leakage rates is treated with a pedigree matrix rather than a uniform distribution like the other leakages because it is a value derived from the modelled quantity where it has a mechanistic process of conversion to N_2O prior to release. The background processes, taken from the ecoinvent library, also use the pedigree approach, with matrices assigned to parameters within each library process. An uncertainty analysis was carried out in order to identify the range of possible values of the impact categories evaluated in this study. Monte Carlo simulations with 3000 steps were run for all of the technologies and scenarios, and their substituent parts, to assess distinguishability of technology scenarios and major contributors to uncertainty for the primary impact assessment methods. In order to confirm convergence, simulations were run with 1,000, 2,000, 4000 and 5000 steps for both two-stage and AD-only for the base case and urea production scenario sets without using SOFC. After an initial series of uncertainty analyses, in which the extremely high responsiveness to leakage overwhelmed all other factors, leakage rates were treated as fixed values in the uncertainty analysis and assessed via sensitivity analysis.

Sensitivity analyses were performed to determine which input variables may substantially change the results of the analysis and consequently, relative ranking. Parameters assessed in the sensitivity analyses include: Leakages (CH_4, CO_2, N_2O, and NH_3), input feedstock, gross energy demand for ammonia and urea production, electricity source and supply from SOFC, injection energy use, ammonia and urea production yields, distance of transportation for both food waste and brown water, dilution water and DI water for CH_4 assisted-SOFEC.

3. Results and discussion

Results in the contribution, comparison, and uncertainty analyses presented below are based on the parameters in Table 1, with a combination of food waste and brown water, using solar power and SOFC, with coproduct credits for sulfur and compost and either mass allocation or avoided product for urea as indicated. Unless otherwise stated, the results shown include leakage.

3.1. Comparative analysis

Figs. 4–6 show the impacts associated with ammonia produced through the waste-based process for different carbon fates. The fate of the waste CO_2 stream is the primary determinant in relative performance for all impact categories. The additional urea product carries a share of the impacts, reducing the burden associated with ammonia – (mass allocation) shown in Figs. 4 and 5. When system expansion is used and the green urea product displaces conventional urea, the decreased ammonia impacts are dramatic. All of the calculations are relative to the FU of the reference product, in this case 1 kg NH_3, therefore, the impact in resources has almost the same trend for CC(u) and base case except for CCS and the urea case. Amongst non-urea cases, CCS has a higher impact for the resources damage which reflects the energy use for injection into the ground (Fig. 5c). For this damage category the results for AD and DF + AD are relatively similar for each carbon fate case.

As can be seen in Figs. 4 and 5, ammonia produced using the AD-only process has higher GHG emissions and impact on ecosystems, human health, and resources compared to the two-stage (DF + AD). Leakage is the largest contributor to different life cycle impacts in the two core technologies (AD-only and DF + AD). This is more evident for GHG emissions compared to the three other damage categories, while the impacts from AD-only and DF + AD are non-negligible in ecosystem and human health impact categories. However, the aggregated damage values show very little difference between the two core technologies. The distinction between AD-only and DF + AD is more visible for GWP.

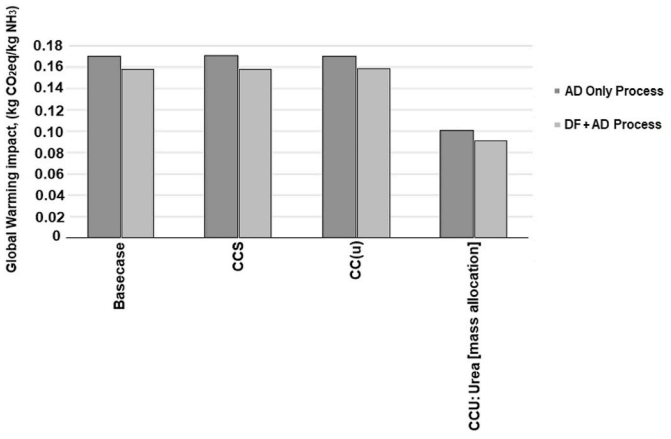

Fig. 4. GHG impacts of waste-to-ammonia and ammonia + urea processes for all CO_2 fates for both AD-only and two-stage (DF + AD technologies) via the default (with SOFC) configurations using mass allocation with leakage impacts included (Impact assessment method: IPCC, 2013 GWP 100a).

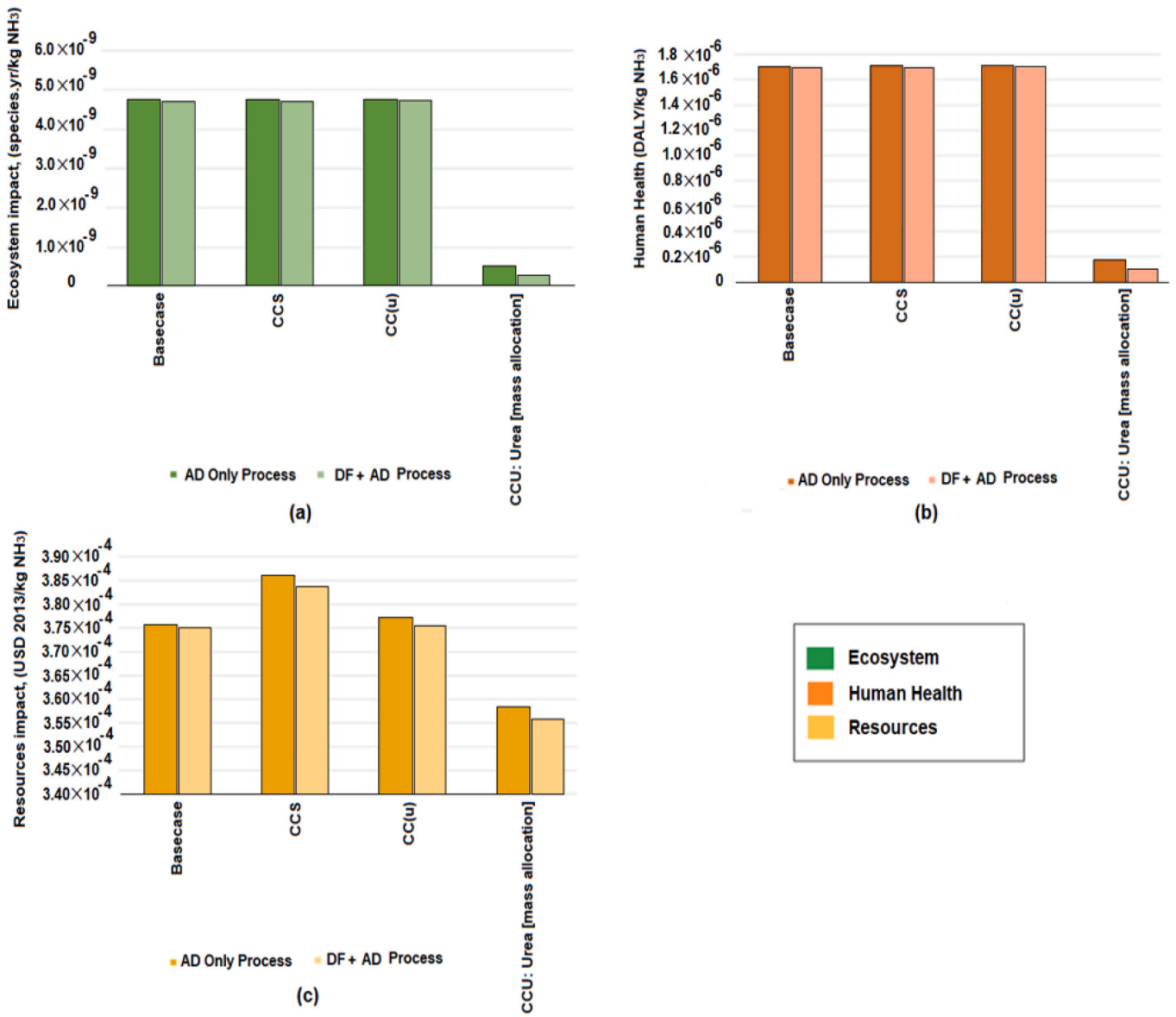

Fig. 5. Damage impacts of waste-to-ammonia and ammonia + urea processes for all CO_2 fates for both AD-only and two-stage (DF + AD technologies) via the default (with SOFC) configurations using mass allocation with leakage impacts included (a) Ecosystem, (b) Human Health, and (c) Resources (Impact assessment method: ReCiPe 2016 endpoint H/A).

Both the AD-only and the two-stage processes result in very similar GHG emissions, ecosystems, and human health impacts in almost all carbon fates, except for the resources damage in which the impact is higher in non-urea cases, specifically for the CCS.

As shown in Fig. 6, the impact of water consumption (dilution and DI water) is higher in AD-only process compared to the DF + AD, this is due to higher water consumption in AD-only compared to the two-stage. As urea is produced, its byproduct water which is reclaimed to be utilized for dilution, reduces the consumption of external sources of water. This will result in lower impact for the scenario set where urea is produced compared to non-urea cases.

3.2. Contribution analysis

The contributions to the life cycle environmental impacts for the production of ammonia/ammonia + urea from the co-digestion of food waste and brown water for all CO_2 fates for both AD-only and two-stage (DF + AD technologies) are shown in Figs. 7–9 and Figs.B1–B4.

The comparison of the results for all proposed green ammonia processes show that leakage is the highest contributor to all impact categories in Figs. 7a and 8a, B2a, and B3c except for the resources damage.

3.2.1. Contribution results for the GHG impacts (GWP_{100})

Leakage is overwhelmingly the largest contributor to GHG impacts (Fig. 7, panel a), once the leakage is removed (Fig. 7, panel b), the second largest contributor to global warming is electricity consumption followed by transportation from waste hub to the ammonia plant. The impact drivers mentioned are assessed in the contribution analysis and tested in the sensitivity analysis. The results point to the significance of electricity in our proposed processes, especially in cases where urea is produced, the electricity dominates the impact in the contribution analysis compared to the non-urea cases.

Despite being a crucial component of the technology, the composition of the membranes has a negligible effect on the impact (Fig.B1), further detail can be found in Appendix B. The results indicate that impacts for our modelled technologies are non-responsive to the production impacts of these membranes and their components (Fig. B1

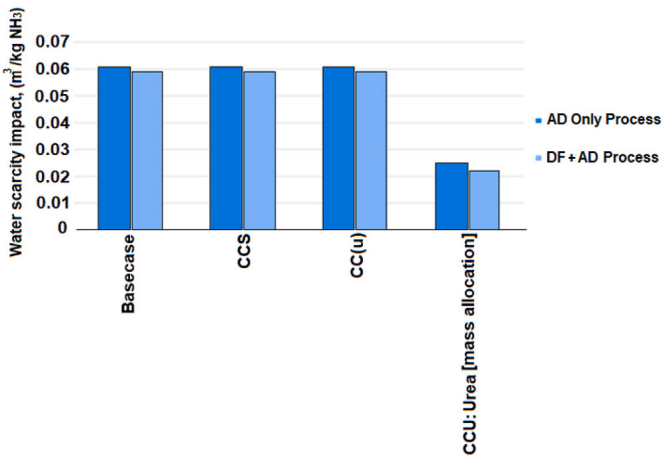

Fig. 6. Water scarcity impacts of waste-to-ammonia and ammonia + urea processes for all CO_2 fates for both AD-only and two-stage (DF + AD technologies) via the default (with SOFC) configurations using mass allocation with leakage impacts included (Impact assessment method: AWARE).

inset), however, their performance with low energy draw directly contributes to the relative benefit of this technology over alternatives.

The membranes make a very small direct contribution to our system impacts (for detailed information refer to section 4 in the ESI). The newness of the membranes utilized in the modelled technology contributes to a high level of speculativeness of the membranes utilized in the studied process. Lifetime, performance, and detailed composition of membranes all have significant uncertainty (section 3.4).

3.2.1.1. Biogenic emissions. As the process feedstocks are derived from plant and animal matter, emissions are biogenic. The GHG emissions also calculated using the GHG Protocol method, which augments the IPCC values with non-zero characterization factors for biogenic carbon, from the production of waste-to-ammonia and ammonia + urea processes for all CO_2 fates. This is for both AD-only and two-stage using mass allocation with and without the contribution from leakage via the default (with SOFC) configuration. Biogenic emissions for non-urea cases under $GWP_{biogenic}$ are significantly higher compared to GWP_{100}, due to increased CO_2 leakage rates. Most importantly, however, CO_2 uptake is not included for the waste feedstock, which is an organic material. Including CO_2 uptake would decrease emissions close to the IPCC values. Since impacts for the modelled systems are almost entirely from leakage, when this factor is removed, the GHG impacts using $GWP_{biogenic}$ are equivalent to GWP_{100}, highlighting the significance of controlling leakage in this study.

3.2.1.2. Avoided product. The ammonia impacts with system expansion used to account for urea production is shown in Fig. 8 (the avoided product for other damage categories can be found in section 6 in the ESI). The magnitude of credit from the avoided production of conventional, fossil-based urea is almost three thousand-fold larger than the ammonia impacts using mass allocation, which emphasizes the importance of offsetting urea production in this system. This holds for both two-stage and AD-only processes and is independent of leakage inclusion. However, the higher urea yield for the two-stage technology results in a larger avoided product credit for that route. The benefit of shifting from conventional fossil-based urea production processes to biogenic routes such as the one presented in this study is dramatic. Since the urea credit overwhelms the contribution from all process categories (feedstock, transportation, electricity, process excluding electricity, leakage, and co-product credits) assessed in this study, the rest of the results are shown for mass allocation.

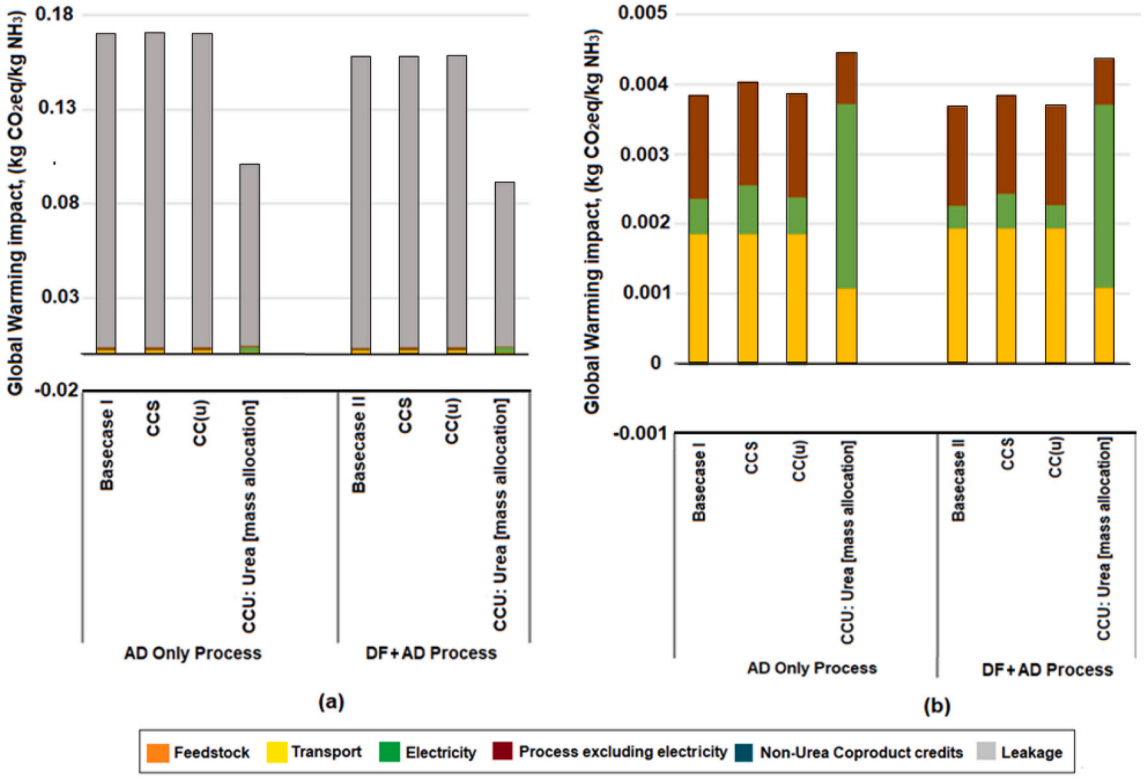

Fig. 7. GHG impacts of waste-to-ammonia and ammonia + urea processes for all CO_2 fates for both AD-only and two-stage (DF + AD technologies) via the default configurations (with solar energy and SOFC) using mass allocation (a) leakage impacts included (b) leakage impacts excluded (Impact assessment method: IPCC, 2013 GWP 100a).

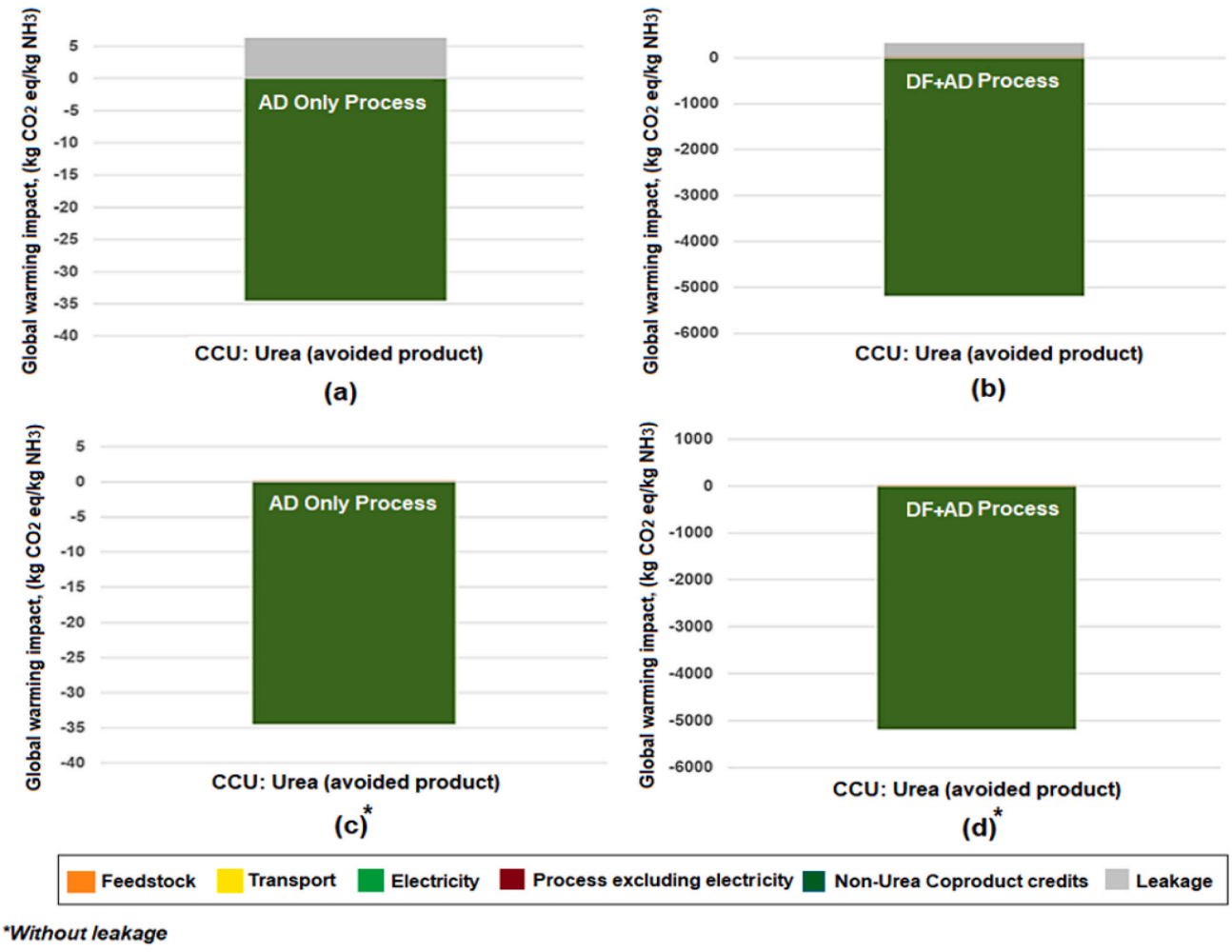

Fig. 8. GHG impacts of waste-to-ammonia and ammonia + urea processes using system expansion and avoided products for urea and other coproducts (a) AD-only process including the impacts from leakage, (b) DF + AD process including the impacts from leakage, (c) AD-only process excluding the contribution from leakage, and (d) DF + AD process excluding the contribution from leakage (Impact assessment method: IPCC, 2013 GWP 100a).

3.2.2. *Contribution results for the non-GHG impacts (damage categories)*

The largest contributors to ecosystem and human health for non-urea cases, after leakage (ammonia followed by CH_4 leakage), are electricity and transportation, respectively. As transportation is the largest contributor to the impact from resources damage and due to urea being the avoided product (along with ammonia as the primary product) for this scenario set, the impact from transportation is smaller, resulting in a lower impact for the resources damage compared to non-urea cases. The two damage categories (ecosystem and human health) have almost the same contribution as the other categories (Fig. B2 and B3). Ammonia is the largest contributor to leakage in non-urea cases followed by CH_4 leakage, while in urea cases, the highest impact comes from CH_4 leakage. However, in the resources damage category, the impact of transportation is the highest due to the use of petroleum followed by electricity in both urea and non-urea cases (Fig.B4).

3.2.3. *Electricity supply scenarios*

Fig. 9 demonstrates the importance of electricity supply to the studied technologies and the effect of changing the source of electricity on the results. This figure shows different configurations in which some of the energy is generated internally based on resource availability within the process, while prioritizing ammonia and urea. It clearly shows that the source of electricity does not have an effect on the non-urea cases compared to the urea production ones.

The effect of changing the primary source of energy for the studied processes from solar to wind on all impact categories (ecosystem, resources, human health, and GWP_{100}) is relatively similar, however, switching from renewable to fossil-based (grid) energy, leads to visible changes in the following impact categories. This especially applies to resources damage followed by GWP impacts for the CCU cases (Fig. 9b). This is due to the fact that urea production processes are energy intensive, in addition, the impact of changing the source of energy, on both human health and ecosystem is relatively similar.

3.3. *Comparison with existing ammonia production technologies*

Our ammonia production processes are intended to be a more environmentally-benign option to conventional technologies. The potential impacts for the proposed processes are thus compared with other renewable options (electrolysis) and to conventional ammonia production routes. This comparison is based on the literature obtained from Bicer et al. (2016) and conventional ammonia production methods using library processes from the ecoinvent 3.6 database, which reflect global averages for those routes. The CML 2001 impact assessment method was used to allow comparison with the literature values, and with other impact assessment methods. The GWP, human toxicities, and abiotic depletions are shown in Fig. 10 (log scale) for the comparison of ammonia production processes. A similar comparison using Eco-indicator 99 impact assessment method (Goedkoop and Spriensma, 2000) can be found in section 8 of ESI and for urea production using

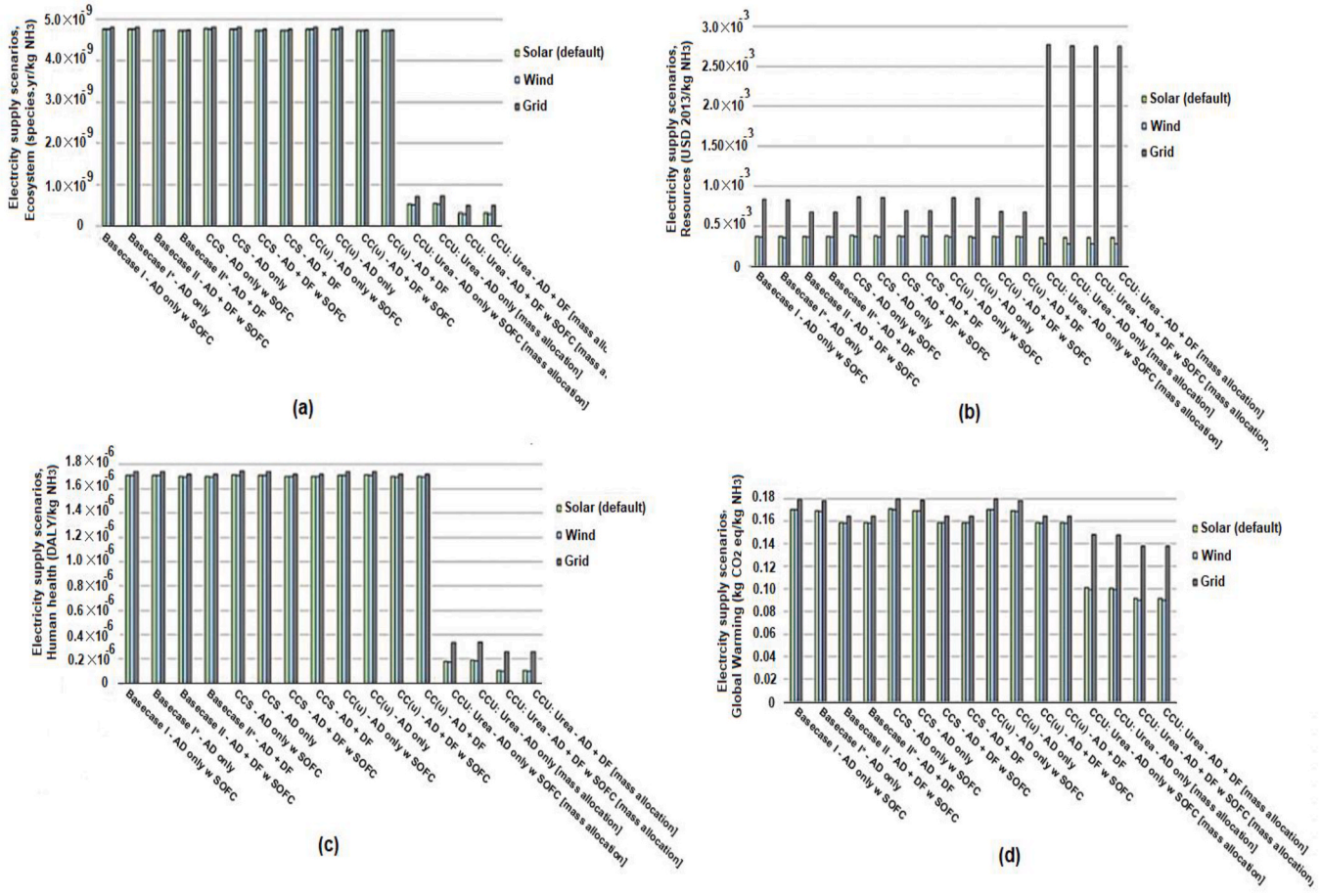

Fig. 9. Electricity supply scenarios of waste-to-ammonia and ammonia + urea processes for all CO_2 fates for both AD-only and two-stage (DF + AD technologies) using mass allocation with leakage impacts included (a) Ecosystem (b) Resources (c) Human health, using ReCiPe 2016 endpoint H/A and (d) GHG emissions, using IPCC 2013 GWP 100a.

IPCC 2013 GWP 100a is detailed in section 9 of ESI. As Fig. 10 shows, abiotic depletion, human toxicity, and global warming impacts for both conventional and electrolysis routes are much higher than for our modelled processes.

The Cocamide diethanolamine route has the highest impact on human toxicity, about 12.65 kg 1,4-DB eq/kg NH_3, due to the dehusking process for coconut and the production process for diethanolamine. This is followed by partial oxidation (due to the use of fossil fuels) and the nuclear power-based high temperature electrolysis method (drivers unspecified in Bicer et al. (2016)). Conversely, for our waste-based processes, human toxicity, and abiotic depletion are driven by solar PV cells, while CH_4 leakage dominates contributions to the GWP.

The decreased solar energy consumption and corresponding decrease in impact from construction of solar PV (Fig. 10a) means that the base case for AD-only process (using SOFC) has the lowest human toxicity impact of 0.0027 kg 1,4-DB eq/kg NH_3.

Amongst our technology configurations, abiotic depletion impacts (Fig. 10a) are lowest for the base case (AD using SOFC) at 2.68E-05 kg Sb eq/kg NH_3, due to low power consumption. The CCU* market case is the next lowest. As can be seen from Fig. 10a, the abiotic depletion impact is the highest for partial oxidation with 0.021 kg Sb eq/kg NH_3, followed by natural gas steam reforming, and nuclear high temperature-based ammonia production processes resulting from petroleum and gas production.

As shown in Fig. 10b, the highest GWP under GWP_{100} is partial oxidation at 2.79 kg CO_2eq/kg NH_3, due to the high impact operation of refining petroleum followed by natural gas reforming (SMR) at 1.74 kg CO_2eq/kg NH_3. In contrast, the CCU for urea production described in this study has a GWP of 0.024 kg CO_2eq/kg NH_3 which is the lowest among all three categories. The dramatic decrease in impact is due to the fact that offsetting high-impact conventional urea production significantly lowers the life cycle GHGs.

The absence of burden on the feedstocks means that the waste-based processes have the lowest GWP impacts: electrolysis with power from municipal solid waste is the lowest impact among the electrolysis routes, and CCU with urea production is the lowest among the low impact waste-to-ammonia technologies modelled here. The lowest GWP amongst the conventional ammonia production process categories is from the bio-based feedstock production process, cocamide diethanolamine, this impact is the result of coconut production.

3.4. Uncertainty analysis

The results of the uncertainty analysis are shown in Fig. 11 (error bars show the 95% confidence interval). Methane leakage is by far the strongest factor which drives the uncertainty analysis, it overwhelms any other contributions to the uncertainty, as the contribution results imply. In order to interrogate the importance of uncertainty for comparing alternatives, leakages have been treated separately via sensitivity analyses. Comparison of the results indicates that, when leakage rates are held fixed, electricity is contributing the most uncertainty to both AD-only and two-stage. The magnitude of uncertainty is consistent across all process types except for urea cases (see Fig. B5 for per tonne of processed waste). In cases where urea is produced, allocation of impacts between ammonia and the dominant urea co-product results in an apparently smaller uncertainty. This is also illustrated in

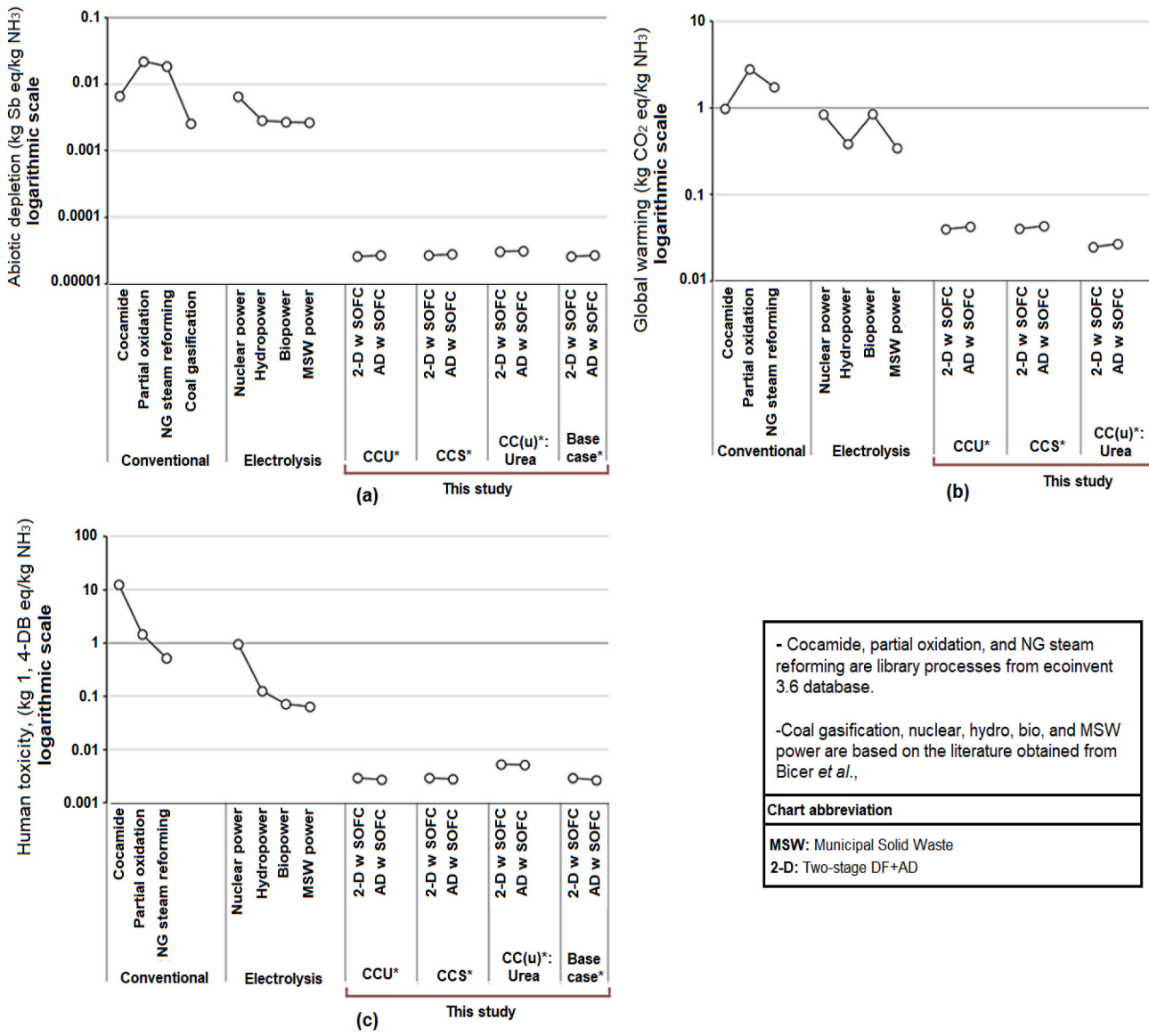

Fig. 10. A comparison of impacts for waste-to-ammonia and ammonia + urea processes (using mass allocation with leakage impacts included) along with conventional, and electrolysis technologies for (a)Abiotic depletion, (b) GHG emissions (GWP_{100}), and (c) Human toxicity, values are shown on a log scale (base case, CCU and CCS routes: this study; electrolysis routes and coal gasification (abiotic depletion only): from Bicer et al. (2016); conventional routes except coal gasification: ecoinvent 3.6 library processes) (Impact assessment method: CML 2001).

Fig. 11c and d, which shows the results of uncertainty analysis using system expansion for the urea coproduct: the uncertainty on the avoided product basis dwarfs that of the non-urea cases. In the urea-production scenario sets, the amount of ammonia produced is small while large amounts of urea are produced. Thus, variation in the urea, results in large changes (e.g., the avoided product credit for urea is magnifying the uncertainty). Uncertainty analysis for green ammonia through AD-only process using IPCC 2013 GWP 100a impact assessment method for mass allocations, avoided product, and per tonne of processed waste (including leakage with fixed rates as mentioned in section 2.2.5) are shown in Fig. 11 and B5. The significant increase of impact in response to switching the primary source of power from renewable (solar) to fossil-based (grid) is shown in the contribution analysis section. However, changing the source of energy from solar to grid (shown in red) does not have a significant effect on the uncertainty analysis, since the uncertainty (in the absence of uncertainty on leakage rates) comes from the speculativeness of the process and not from the energy source (Fig. 11a and b).

The most significant contributors to uncertainty in the tests run for the processes that produce urea are urea product mass, followed by CH_4 leakage, ammonia product yield, electricity, and small amounts from the remainder of the parameters in the entire process. For the scenario where urea is not produced, the most significant contributors to uncertainty in the tests run for the ammonia processes are the CH_4 leakage followed by ammonia and small amounts from the rest of the parameters in the entire process. This was consistent for each of the technologies.

Because of the extremely high responsiveness to leakage, these factors were assessed via sensitivity analysis and were treated as fixed values in the uncertainty analysis. This has the effect of magnifying the apparent uncertainty disproportionately, as no other factor in this study contributes to the impact as much as leakage.

3.5. *Sensitivity analysis of GWP results to changes in feedstock parameters, primary product yields, leakage rates, and electricity demand*

Results of the sensitivity analyses for each impact category indicate that the potential impacts are relatively insensitive to changes in everything except product yields and leakage rates. Potential impacts

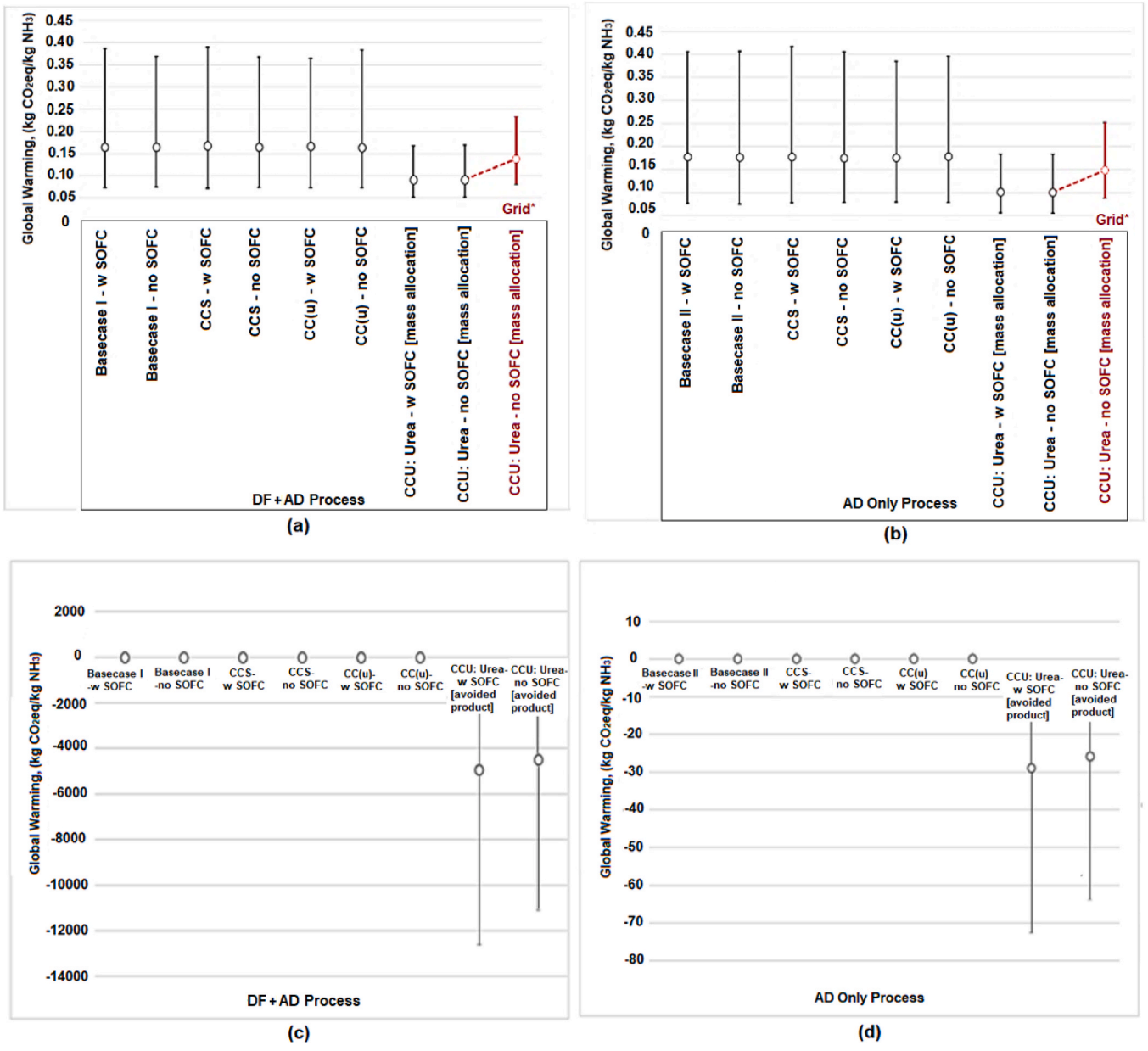

Fig. 11. Uncertainty analysis of waste-to-ammonia and ammonia + urea processes for all CO_2 fates for (a), (c) DF + AD process and (b), (d) AD-only process, with and without SOFC using mass allocation (a, b) and avoided product (c,d) for urea production, leakage impacts included (Impact assessment method: IPCC, 2013 GWP 100a).

respond strongly to changes in leakage assumptions, supporting the significance of these two factors visible in the contribution analysis. Fig. 12 shows the results of the sensitivity analysis for GWP_{100}, other results for water scarcity using AWARE and for damage categories using ReCiPe2016 on key parameters and the factors driving the responses are assessed in section 10 of ESI. Based on the sensitivity analysis (Fig. 12), the GWP is relatively insensitive to most input parameters. It is, however, strongly sensitive to the CH_4 leakage, which can significantly change the results of GHG emissions. The sensitivity analysis was carried out for both SOFC and non-SOFC cases and the results show that the two configurations are almost indistinguishable.

- **Waste flow rate:** Our process is sensitive to flow rate especially for the two-stage, this is followed by brown water distance, food waste distance, and the fraction of FW/BW as shown in Fig. 12a. Increasing the flow rate leads to a small increase in the impact.
- **Transportation distance of food waste and brown water to the plant:** Varying the transportation distance of brown water to the plant has a stronger impact than for food waste. As the ratio of food waste to brown water decreases, more brown water is moved over long distances which is inversely proportional to the mass of brown water.
- **FW/BW ratio:** When the amount of food waste goes up relative to the amount of brown water, more water is consumed which in turn increases the electricity usage for generating water in the system, resulting in a slightly higher impact. Availability of the particular feedstock will vary seasonally, regionally, and can even vary on a day to day basis, factors which need to be considered in deployment and siting decisions and in technology selection based on impact.
- **Product yield:** In cases where urea is not produced, sensitivity to ammonia product yields increases, while in the cases where urea is produced, the sensitivity to urea product yields increases. Despite the CCU cases where the process is sensitive to urea product yields,

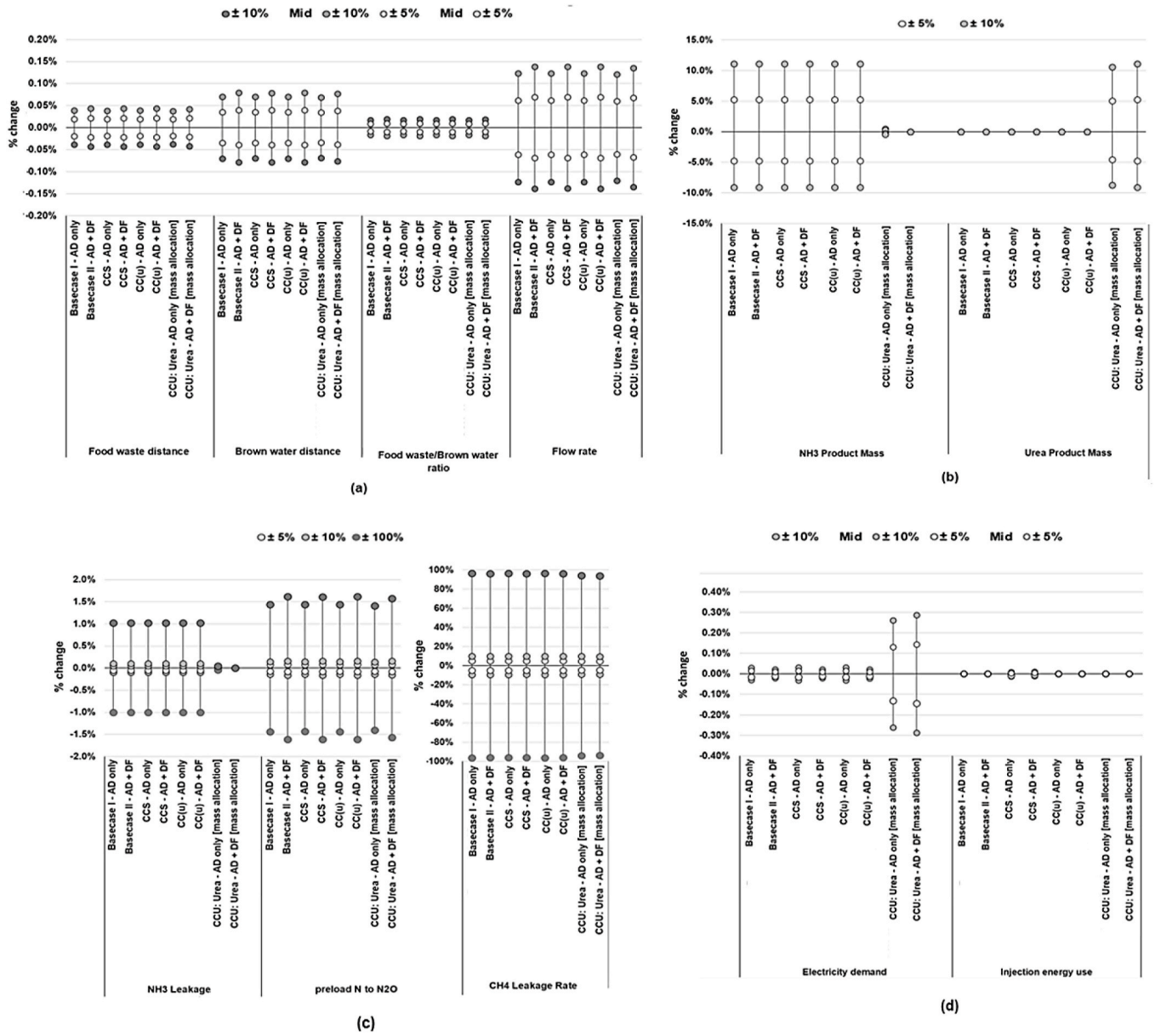

Fig. 12. Sensitivity of GWP results for the production of waste-to-ammonia and ammonia + urea processes for all CO_2 fates for both AD-only and two-stage (DF + AD technologies) via the default (with SOFC) configurations using mass allocation to changes in (a) feedstock parameters, (b) primary product yields, (c) leakage rates, and (d) electricity demand (Impact assessment method: IPCC, 2013 GWP 100a).

especially in the two-stage process. Primary product yields (ammonia/ammonia + urea) are inversely proportional to the environmental impact, as the product yield goes down, the impact goes up (higher yields will result in a lower impact).

- **Leakage rates:** The most significant factor in our sensitivity analysis is CH_4 leakage, showing a nearly linear response for GWP results. In cases where urea is not produced, sensitivity to NH_3 leakage rates are higher compared to where there is urea production, this is due to the consumption of ammonia in urea production cases, as urea carries a share of the burden. On the other hand, the two-stage is more sensitive to N_2O leakage rates despite the AD-only processes. In the assessed model, the only factor that significantly affects climate change is CH_4 leakage.
- **Electricity demand:** Electricity demand has a higher impact compared to the use of injection energy followed by energy derived from the SOFC. Incorporating SOFC increases the CapEx and added process complexity with no tangible environmental benefit, based on the results obtained, making it an unattractive option. In cases where urea is produced sensitivity to electricity demand is higher especially for the two-stage, as urea is carrying a share of the impact. Fig. 12d shows that this process is not sensitive to energy derived from the SOFC. The same applies to the injection energy use except for the CCS cases where CO_2 is injected into the ground. The sensitivity would be far more pronounced if grid electricity was required.

3.6. Interpretation

The results of our LCA indicate that the two-stage process using SOFC is the most efficient for GHG emissions, abiotic depletion, and human toxicity compared to the AD-only process. All process configurations assessed here would result in lower GHG emissions per kg NH_3 and kg urea compared to conventional and renewable technologies. Our non-urea processes generate approximately 90% lower GHG impact for GWP_{100}. In comparison to water electrolysis, a rapidly emerging and potentially sustainable technology, the GHG impact for urea cases under both GWP_{100} and $GWP_{biogenic}$ impact assessment methods are approximately 90% lower.

The integration of novel and emerging membranes is a crucial component of our waste-to-ammonia and urea processes. Their optimal performance with low energy draw directly contributes to the relative benefit of this technology over alternatives and the results indicate that the production impacts of these membranes and their components are insignificant to the total life cycle impacts. The life cycle thinking and sustainable design principles focus, validated by the LCA analyses of 72 configurations, resulted in a unique and flexible process. A major factor enabling this is the integration of these novel and emerging membranes.

Acidification and eco-toxicity in our proposed processes are higher compared to the library processes for conventional ammonia production and the values in the literature. The relatively high leakage assumptions used here for the new technologies result in higher acidification impacts than that found with conventional processes, which may reflect either an underestimate in general leakage or an over-estimate of potential leakage in the proposed processes based on conservative values. The higher ecotoxicity impacts result from the construction of solar cells. However, shifting the energy source for our process from solar to grid will result in a significant increase in global warming impact and all three damage categories. This is a classic example of trade-off and potential burden shifting.

An important implication of our analysis is that controlling/avoiding leakage is an essential element of sustainable, climate safe design. For both two-stage and AD-only cases, impacts are driven primarily by N efficiency (primary product yields) and by leakage of methane (potential GHG emissions) and ammonia (potential human health and ecosystem damages). Emissions from leakage completely dominate the climate impacts of the studied process in every configuration even with conventional (U.S. EPA) assumptions for emissions from methane, natural gas, and waste. Failing to prevent leakage undermines the effectiveness of new technologies such as the one presented in this study, and the fact that highly toxic gases can be contained at scale, suggests that this is not an insurmountable issue. The impact from abiotic depletion, GHG emissions, and human toxicity shows that this process is environmentally viable compared to fossil-based and renewable technologies.

In some instances, the studied green-ammonia technology may not be the optimal technology option because it is based on urban and semi-urban waste and has some constraints on where it can be sited economically, whereas the conventional technologies generally based on natural gas do not have this limitation and are flexible in where they can be deployed. However, this set of technologies assessed in this study competes very well on a life cycle environmental basis and has significant potential for benefits, including avoided emissions.

4. Conclusions

In this work, we have assessed technologies developed based on sustainable design principles to emphasize GHG mitigation (CO_2 utilization) and waste utilization. Our goal has been to determine whether a waste-based process designed first around CO_2 capture can compete with other available ammonia technologies on an environmental impact basis, with or without urea production. The ammonia production technologies are assessed for environmental performance from cradle-to-gate using two configurations, four CO_2 fates, including use for urea production, and several smaller variations, resulting in 72 assessed processes. Both CCS and CCU provide a valuable route to additional valuable products while avoiding direct release of CO_2 emissions, where those products are able to displace their high impact, fossil derived analogues. Much of the success for reducing potential impacts in this study arises from the integration of novel and emerging membranes. This is a direct result of the design principles used where the LCA results validate this.

The process designed here and components utilized in it are in many cases at earlier stages of development, so that the system and, consequently, calculated impacts (even with fixed leakage) show relatively high uncertainty due to the speculativeness and the few contributors to impact. Higher resolution analysis of the various membranes incorporated in this study and their fabrication are important next steps in exploring this technology, as is narrowing practical leakage constraints.

CRediT authorship contribution statement

Seyedehhoma Ghavam: Conceptualization, Methodology, Formal analysis, Software, Validation, Writing – original draft, Writing – review & editing. **Caroline M. Taylor:** Conceptualization, Writing – review & editing. **Peter Styring:** Supervision, Writing – review & editing, Funding acquisition.

Declaration of competing interest

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

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Appendix A

The descriptions, material compositions, and chemical reactions taking place in each of the membranes incorporated in the modelled waste-to-ammonia/ammonia and urea production process are defined in Table A1.

Table A1
Descriptions, material compositions, and chemical reactions used for membranes, electrolyzer, and fuel cell incorporated in the modelled waste-to-ammonia and ammonia + urea production process (adapted from Ghavam et al. (2021a). Key sustainability design decisions are listed in Table A2.

Membrane	Description	Composition	Reactions	References
Electrochemical Membrane Separation (EMS)	Converts H_2S into H_2 and S_2 in the presence of N_2 used as the sweep gas	Cathode: $Gd_2Ti_{2-x}Mo_xO_7$ (x = 0.0–2.0), Electrolyte: $La_{0.7}Sr_{0.3}VO_3$ Anode: NiO	Cathode: $H_2S + 2e^- \rightarrow H_2 + S^{2-}$ Anode: $S^{2-} \rightarrow ½ S + 2e^-$ The overall reaction: $H_2S \rightarrow ½ S_2 + H_2$	Winnick and Liu (2003)
Ion Transport Membrane (ITM)	Solid inorganic oxide ceramic material that transports oxygen ions at high pressures (10–30 bar) and temperatures (800–900 °C)	$SrCo_{0.9}Sc_{0.1}O_{3-\delta}$	Non permeate side: $½ O_2 + 2e^- \rightarrow O^{2-}$ Permeate side: $O^{2-} \rightarrow ½ O_2 + 2e^-$	Sun et al. (2011)
Membrane Filtration Index (MFI)	An electrochemical zeolite-based incorporated into the system for the separation of H_2 from the H_2 and CO_2 gas mixture	Ceramic MFI zeolite membranes	$H_2 + CO_2 \rightarrow CO_2$ (Permeate side) H_2 (Non permeate side (retentate))	Fouladvand (2016)
Solid Oxide Fuel Cell (SOFC)	Electricity generation via electrochemical conversion of fuel gas mainly H_2 at high temperatures of 700–1000 °C	Cathode: $La_{1-x}Sr_xMnO_3$, (LSM) Electrolyte: YSZ Anode: Ni-YSZ composite	Cathode: $½ O_2 + 2e^- \rightarrow O^{2-}$ Anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$ Overall reaction: $½ O_2 + H_2 \rightarrow H_2O$	Jimenez (2013)
CH_4 assisted-Solid Oxide Fuel Assisted Electrolysis Cell (CH_4-assisted SOFEC)	Electrolyzer using CH_4 at the anode to reduce the decomposition potential (voltage) of H_2O resulting in lower energy usage compared to SMR and a higher conversion ratio of electricity for H_2 production	Cathode: LSM- ScSZ Electrolyte: ScSZ Anode support layer: Ni-YSZ composite Anode active layer: Ni-ScSZ composite	Cathode: $H_2O + 2e^- \rightarrow H_2 + O^{2-}$ Anode: $¼ CH_4 + O^{2-} \rightarrow ½H_2O + ¼ CO_2 + 2e^-$ Overall reaction: $½ H_2O + ¼ CH_4 \rightarrow H_2 + ¼ CO_2$	Xu et al. (2016)
Solid State Ammonia Synthesis (SSAS)	Ammonia production via an electrochemical conversion process in a proton-conducting solid electrolyte cell from gaseous H_2 and N_2	Cathode: $SmFe_{0.7}Cu_{0.3-x}Ni_xO_3$ (x = 0–0.3) (SFCN) Electrolyte: Nafion (membrane) Anode: Ni-doped SDC (Ni-SDC) NiO–$Ce_{0.8}Sm_{0.2}O_{2-\delta}$	Cathode: $N_2 + 6H^+ + 6e^- \leftrightarrow 2NH_3$ Anode: $3H_2 \leftrightarrow 6H^+ + 6e^-$ Overall reaction: $N_2 + 3H_2 \leftrightarrow 2NH_3$	Xu et al. (2009)

Table A2
Some of the key sustainability design decisions for this process.

Key elements	Conventional	This study	Benefits over conventional
Feedstock	Natural gas	Food waste and brown water (urban and semi-urban waste streams)	-Avoidance of fossil excavation -Decreased processing/treatment demand -Diversion of emissions from improper handling -Valorization of waste streams -Recovery of key nutrients
Processing units	Reformer, reactor, scrubber, and cryogenic air separation	Bioreactor and membranes	-Small physical footprint -Lower cost (lower amount of water and/or chemical usage) -Produces by-products that can be sold commercially without the need to be upgraded
Hydrogen production	SMR coupled with Haber-Bosch	CH_4 assisted-Solid Oxide Fuel Assisted Electrolysis Cell	-Higher conversion rate -Smaller physical footprint -Decreased energy draw -Lower cost

The selected impact categories, corresponding methods, and units are shown in Table A3. The CML 2001 method from the superseded impact category was used for the purpose of comparing with literature data.

Table A3
The selected impact categories and corresponding methods and units. The allocation types used and % table of allocation shares are shown in Table A4.

Impact Category	Method	Units
Human Health (Damage)	ReCiPe World Endpoint (H)	DALY
Ecosystem (Damage)	ReCiPe World Endpoint (H)	Species.yr
Resources (Damage)	ReCiPe World Endpoint (H)	USD 2013 ($)
GHG emissions/GWP_{100}	IPCC 2013 GWP 100a V1.03	kg CO_2 eq.
GHG emissions/$GWP_{biogenic}$	Greenhouse Gas Protocol V1.02	kg CO_2 eq.
Water foot-print	AWARE (water scarcity)	m^3
	Used for comparison to prior literature	
GHG emissions	CML 2001 (All impacts)	kg CO_2 eq.
Abiotic depletion	CML 2001 (All impacts)	kg Sb eq
Human toxicity	CML 2001 (All impacts)	kg 1,4-DB eq
Human Health	Eco-indicator 99	DALY
Ecosystem Quality	Eco-indicator 99	PDF*m^2yr
Resources	Eco-indicator 99	MJ surplus

Table A4
Allocation types used and % table of allocation shares.

	AD	DF + AD
Urea producing processes		
Allocation Case 1: Mass allocation		
Ammonia	4.72% by mass	0.0312% by mass
Urea	95.3% by mass	99.968% by mass
Allocation Case 2: System expansion		
Ammonia	100%	
Urea	Avoided product	
All processes		
Sulfur (S_2)	Avoided product	Avoided product
Compost	Avoided product	Avoided product
Oxygen (O_2) (l)	Avoided product	Avoided product

Table A5 shows the list of library processes used from ecoinvent for conducting the LCA for this study. The last two items, for solar PV and SOFC were modified to fit this system. For solar, the PV mounting system and panel calculations and for the SOFC, composition materials using proxy background data based on mono-layer calculations were modified.

Table A5
Library processes used for ammonia production model.

Library Process Used (from ecoinvent 3.6)
Electricity, medium voltage {WECC, US only} | electricity voltage transformation from high to medium voltage | Cut-off, U
Electricity, low voltage {RoW}| electricity production, photovoltaic, 3kWp flat-roof installation, single-Si | Cut-off, U
Water, deionized, from tap water, at user {RoW}| production | Cut-off, U
Tap water {GLO}| market group for | Cut-off, U
Sodium hydroxide, without water, in 50% solution state {GLO}| market for | Cut-off, U
Transport, freight, lorry with refrigeration machine, 7.5–16 ton, EURO3, carbon dioxide, liquid refrigerant, cooling {GLO} | Cut-off, U
Urea, as N {RoW}| production | Cut-off, U
Compost {RoW}| treatment of biowaste, industrial composting | Cut-off, U
Sulfur {GLO}| market for | Cut-off, U
Electricity, medium voltage {WECC, US only}| market for | Cut-off, U
Electricity, high voltage {WECC, US only}| electricity production, wind, <1 MW turbine, onshore | Cut-off, U
Lanthanum oxide {GLO}| market for | Cut-off, U
Activated carbon, granular {RoW}| activated carbon production, granular from hard coal | Cut-off, U
Platinum {GLO}| market for | Cut-off, U
*Modified Solar Electricity, low voltage {WECC, US only}| electricity production, photovoltaic, 570kWp open ground installation, multi-Si | Cut-off, U
*New SOFC Modified Heat, future {GLO}| Hydrogen, burned in solid oxide fuel cell, with micro gas turbine, 180kWe, future | Cut-off, U

**Modified.*

Table A6 shows the uncertainty characteristics used for the various inventory components, based on data quality estimates.

Table A6
Data quality characteristics of inventory parameters.

Uncertainty based on Pedigree matrix				Uncertainty based on Distribution
Pedigree matrix	(3,1,1,1,1)	(4,1,1,1,4)	(4,1,1,1,5)	Uniform
SD/2SD	1.11	1.56	2.05	N.A
Inventory components	-Material inputs (waste stream and water) - N_2O leakage rate	- Urea daily output flow rate -Electricity demand -CO_2 emissions -Array incidence	- Daily output flow rate for ammonia and byproducts -Number of membrane cells and tubes	-NH_3 and CO_2 leakage rates -CH_4 leakage rate -Distance travelled from collection facility to the plant

Appendix B

Impact of emerging membranes incorporated in the modelled process

Fig. B1 shows that the membranes make a very small direct contribution to our system impacts (for detailed information refer to section 4 in the ESI). The main determinant of their contribution is their estimated lifetime of 10 years (based on our analogy to other similar materials and other data) (Ramsden, 2013). The effect of time to replacement was assessed via sensitivity analysis. Even if replacement were to be required annually, the membrane production and disposal contribution to impact remains insignificant, even in the absence of leakage.

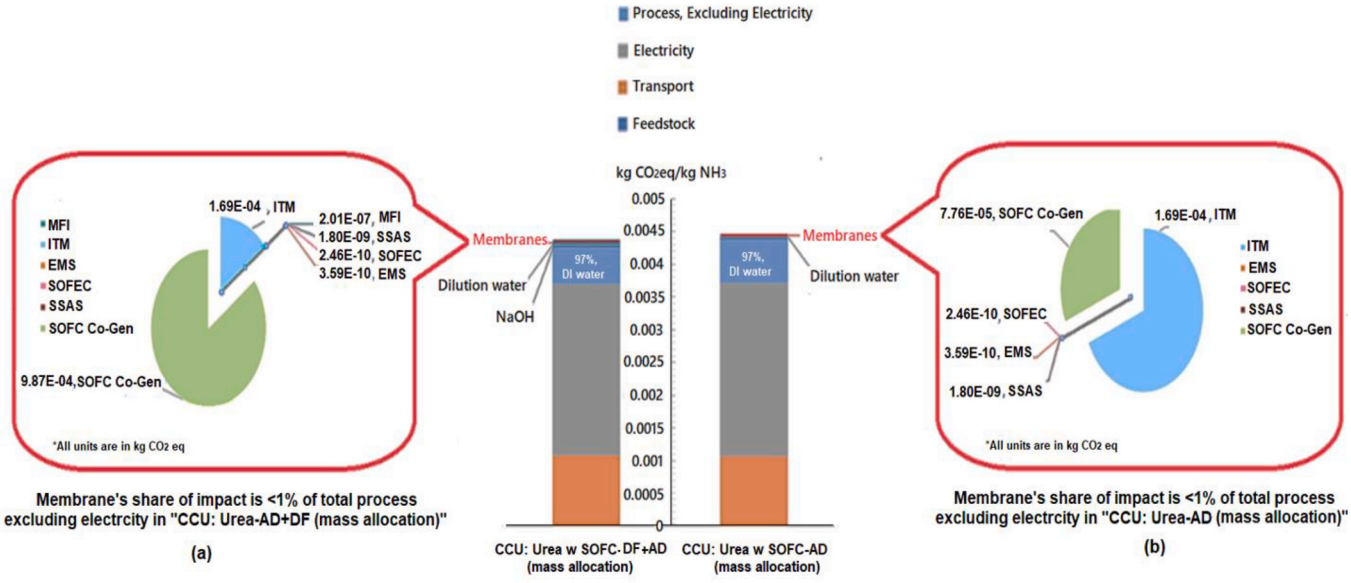

Fig. B1. Each membrane's share of impact for both AD-only and two-stage (DF + AD technologies) using mass allocation for urea case with SOFC and with leakage impacts excluded (a) DF + AD and (b) AD-only process (Impact assessment method: IPCC, 2013 GWP 100a).

Contribution results for the non-GHG impacts

Contribution results for the damage categories

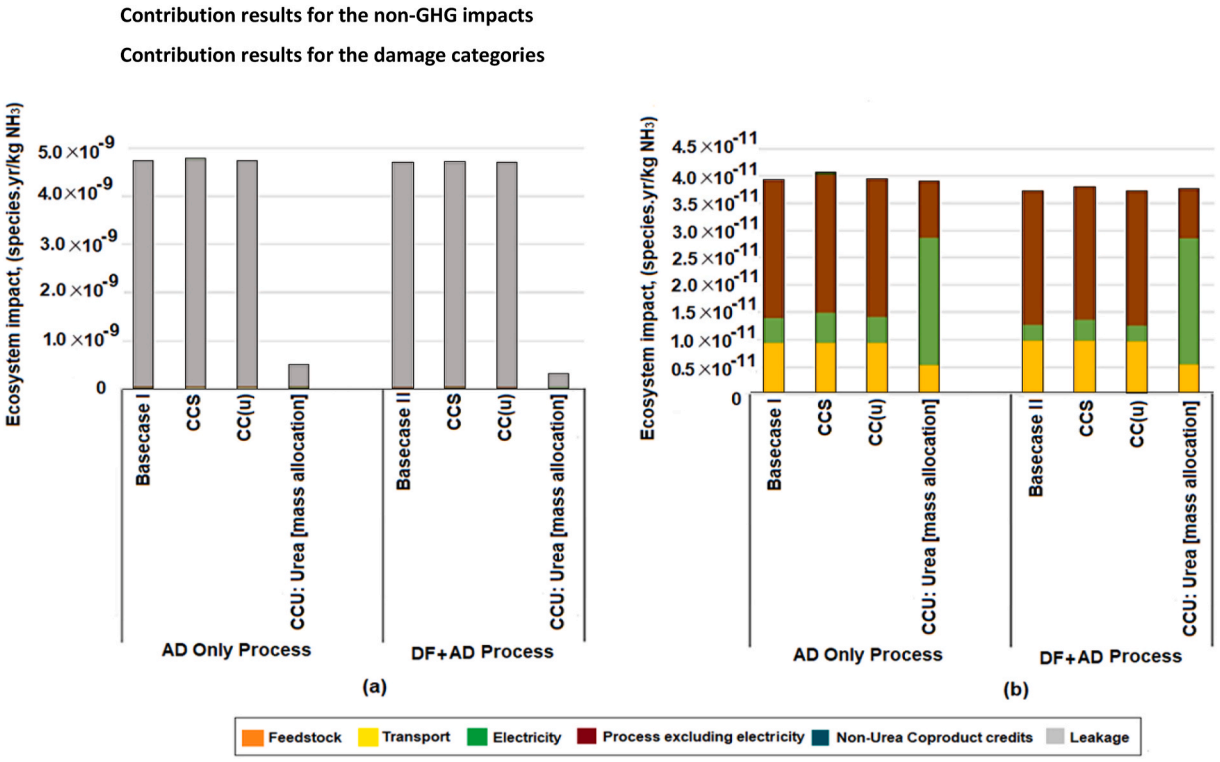

Fig. B2. Ecosystem impacts of waste-to-ammonia and ammonia + urea processes for all CO_2 fates for both AD-only and two-stage (DF + AD technologies) via the default (with SOFC) configurations using mass allocation (a) leakage impacts included (b) leakage impacts excluded (Impact assessment method: ReCiPe 2016 endpoint H/A).

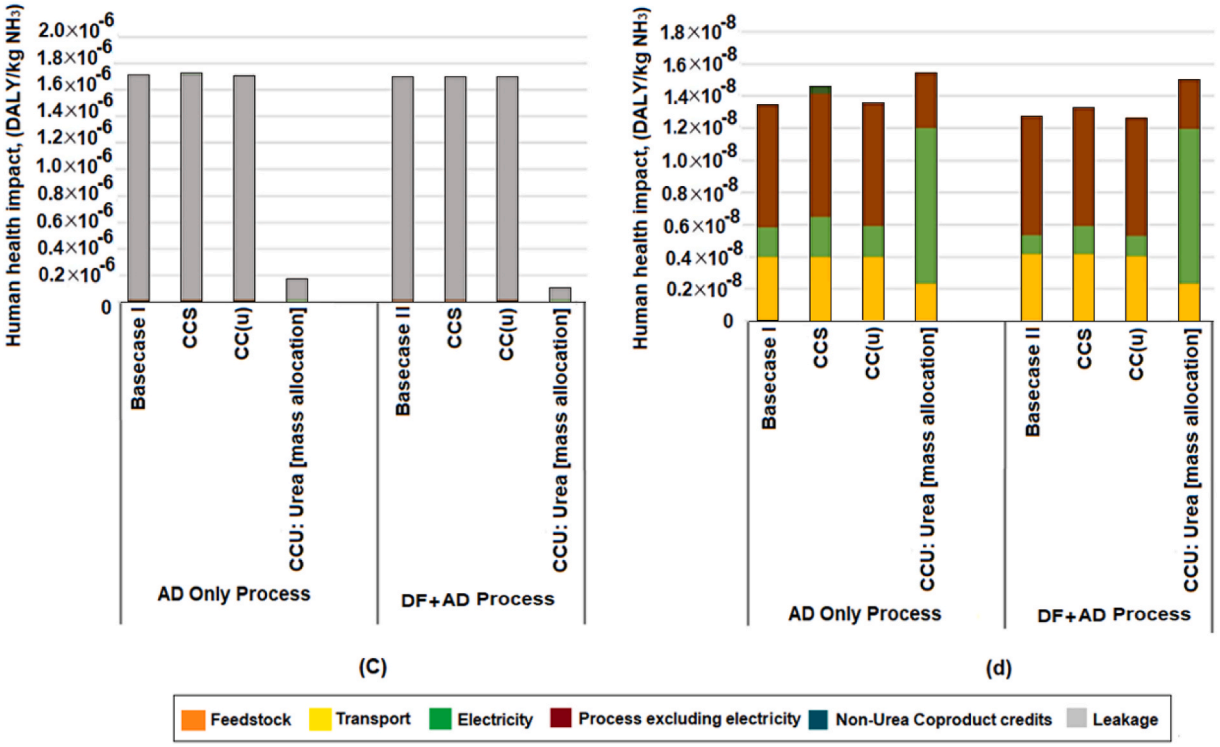

Fig. B3. Human health impacts of waste-to-ammonia and ammonia + urea processes for all CO_2 fates for both AD-only and two-stage (DF + AD technologies) via the default (with SOFC) configurations using mass allocation (c) leakage impacts included (d) leakage impacts excluded (Impact assessment method: ReCiPe 2016 endpoint H/A).

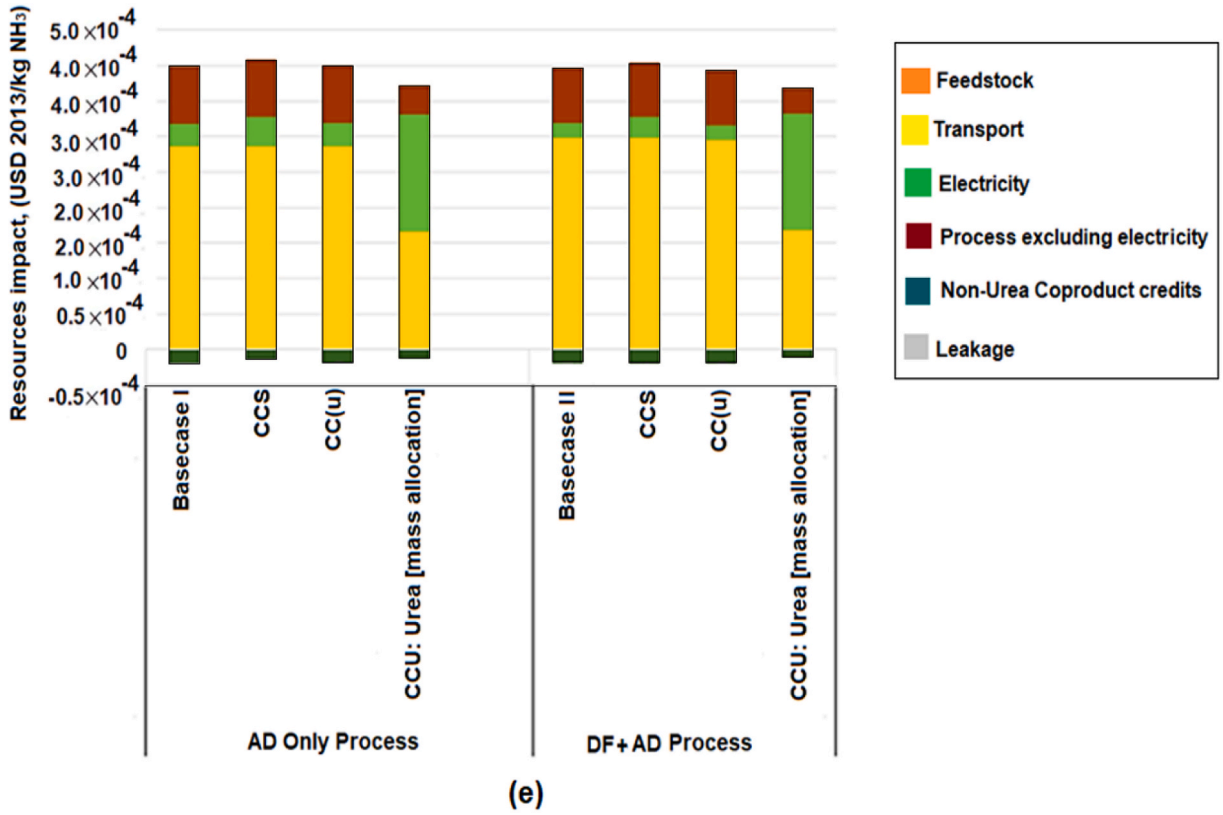

Fig. B4. Resources impacts of waste-to-ammonia and ammonia + urea processes for all CO_2 fates for both AD-only and two-stage (DF + AD technologies) via the default (with SOFC) configurations using mass allocation with leakage impacts included (Impact assessment method: ReCiPe 2016 endpoint H/A).

Uncertainty analysis

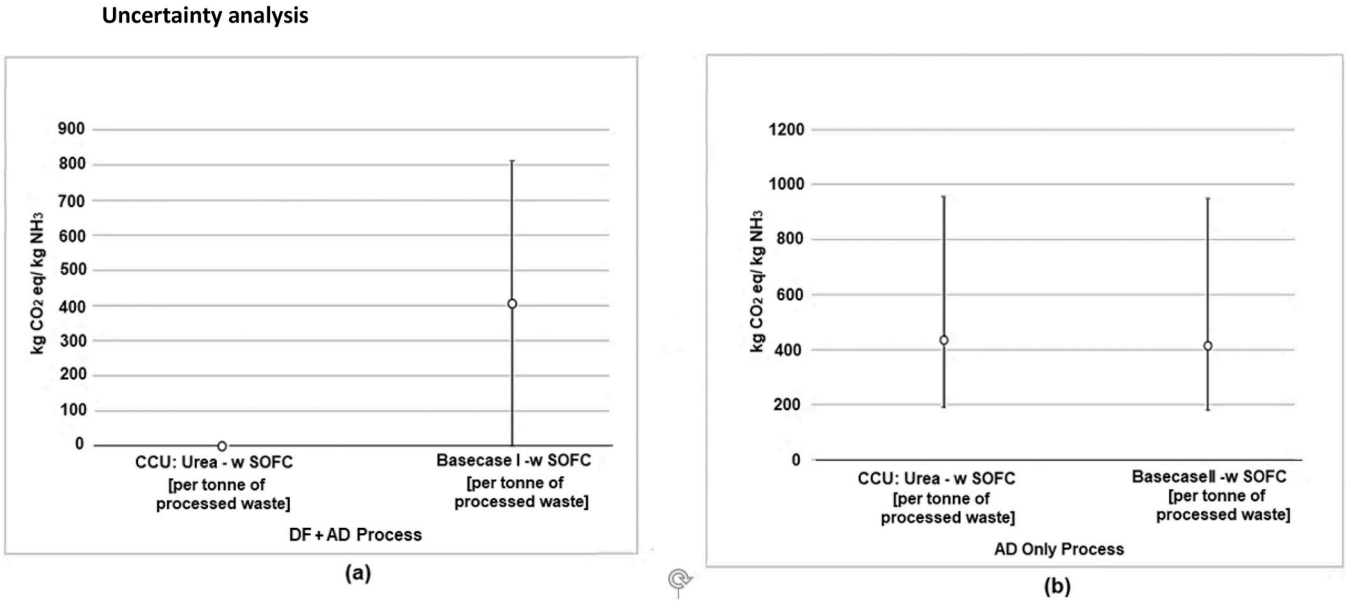

Fig. B5. Uncertainty analysis of waste-to-ammonia and ammonia + urea processes for urea and base case (a) DF + AD process and (b) AD-only process, using per tonne of processed waste (unallocated) for the default (with SOFC), leakage impacts included (Impact assessment method: IPCC, 2013 GWP 100a).

Appendix C. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2021.128776.

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