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NOVEMBER 2019

# TECHNICAL APPENDIX

PART 2 - SUSTAINABLE AMMONIA PRODUCTION



SOLAR ENERGY FOR A CIRCULAR ECONOMY



# SUNRISE

**Solar Energy for a Circular Economy**

## **Technological Roadmap**

*Technical Appendix*

*Part 2 - Sustainable Ammonia Production*

**November 2019**

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**Sustainable hydrogen production**

Conventional process data

SUNRISE technologies

- Large-Scale hydrogen production using PEM electrolysis
- Hydrogen production using photoelectrochemical cell devices
- Hydrogen via buried-junction photoelectrochemical cells
- Hydrogen production by photosynthetic microorganisms
- Hydrogen photoproduction by biomolecular technologies
- Baggies with particulate systems

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**Sustainable carbon-based chemicals and (jet)fuels**

SUNRISE technologies

Dark electrochemical reduction of CO<sub>2</sub> to C<sub>1</sub>/C<sub>2</sub>/C<sub>3</sub> products

Electrochemical production of hydrocarbon fuels

Thermochemical production of hydrocarbons and jet fuels

Biocatalytic production of chemicals by microorganisms

Carbon-based fuel production by biomolecular approaches

**Sustainable Carbon Capture**

Amine-based Carbon Capture

Polymeric membranes based carbon capture

Low Temperature Direct Air Capture

High Temperature Direct Air Capture

**SUNRISE key enablers**

Computational materials modelling: from novel materials to solar fuel devices

Development of new methods and software tools for early quantitative sustainability

assessment of emerging SUNRISE technologies: bridging environmental, economic and social impacts

Redesigning photosynthesis for the biocatalytic production of chemicals and fuels

Synthetic Biology

Bottom-up chemical engineering of bioinspired artificial photosynthesis reactor materials and cascades

Upscaling artificial photosynthesis systems for a sustainable larger scale production of energy carriers

Oxygen evolution (Water oxidation)

# Definitions

**Energy:** specific energy consumption (**SEC**) in GJ/t is the amount of energy that an average plant requires to produce a specific product. It includes net electricity and fuel consumption to provide heat, hence processes generating electricity or supplying excess steam are accounted for in the SEC. The **total energy demand** in addition to the SEC contributions also includes the energy required to produce the feedstock used in the process and the energy content of the feedstock which is built in the product.

**Carbon footprint:** Emissions during synthesis of the target product comprise energy related emissions (i.e. heat and electricity) and process related emissions (e.g. CO<sub>2</sub> generated in ammonia synthesis), i.e. **cradle to gate** contributions (Production of methanol from hydrogen and CO<sub>2</sub> includes the supply of electricity for electrolysis of water to produce hydrogen, the electrolysis process itself, capture and supply of CO<sub>2</sub> and subsequent methanol synthesis).

## Technology Readiness Level (TRL):

TRL	Milestones		TRL		
	Common to all sectors	RE alt. fuels		Common to all sectors	RE alt. fuels
1	Identification of new concept, applications and barriers	New concept identified, benefits and technological gaps identified	6	Technology pilot demonstrated in relevant environment, manufacturing strategy defined	Pilot scale prototype fine-tuned in field
2	Definition of application, consideration of interfaces and commercial offer	Definition of the proof of concept, first indications of fuel properties	7	Pilot demonstrated in operational environment, manufacturing approach demonstrated	Fuel qualification completed
3	Proof of concept prototype ready: concept is laboratory tested	Proof of concept verified through simulation	8	Technology in its final form, low-rate production	System certified for market application, compliance with legal obligations
4	Integrated small-scale prototype with auxiliary systems laboratory validated	Fuel/process tested and validated at laboratory scale (small-scale prototype/simulation model)	9	System fully operational and ready for commercialization	New technology fully operational and market available, full-rate production ready
5	Large-scale prototype completed with auxiliaries, refined commercial assessment	Large-scale prototype realized			

TRL: based on *Technology Readiness Level: Guidance Principles for Renewable Energy technologies*, DG RTD 2017;

# Sustainable ammonia production

## Conventional process data

<p><b>Conventional fossil-based process</b></p>	<p>Ammonia is currently mainly produced by Haber-Bosch synthesis. For this <math>H_2</math> and <math>N_2</math> are reacted at high temperature <math>T</math> and pressure <math>p</math>. The <math>H_2</math> is produced from fossil fuels and this process releases about 3% of the world's <math>CO_2</math> emissions. Ammonia production requires today 1-2% of the global energy production. 80% of the produced ammonia goes to fertilizer production.</p> <p>As of today (2019) the technology consists of the following elements:</p> <ul style="list-style-type: none"> <li>- <b>Desulfurization</b> to remove sulfur compounds and hydrogen sulfide</li> <li>- <b>Reforming</b> to achieve correct H/N ratio through primary and secondary reforming</li> <li>- <b>Water-gas shift</b> process for CO conversion</li> <li>- <b><math>CO_2</math> and CO removal</b> through chemical absorption and methanation processes</li> <li>- Multi-stage compression</li> <li>- Ammonia synthesis and refrigeration</li> <li>- All these steps are based on steady operation and at a typical production scale of 1500 to 3000 metric tons per day.</li> </ul> <p>It is envisioned to transition the technology to a renewable energy based approach including the main elements:</p> <ul style="list-style-type: none"> <li>- Renewable electricity generation, and incorporation of renewable electricity in the ammonia production steps</li> <li>- Water electrolysis for hydrogen production, nitrogen separation from air, and ammonia synthesis adapted to intermittent / variable load operation</li> <li>- Ammonia synthesis at lower temperature and pressure than 2019 state of the art</li> <li>- Non-precious material ammonia synthesis catalyst</li> </ul>
<p>Global annual production volume</p>	<p>180 Million tons of ammonia per year, about 50% from natural gas reforming and 50% from coal gasification (Mission possible report ,Nov 2018, by Energy Transition Commission)</p>

Total energy demand [GJ/t]	mean value: 28 GJ/ton About 33.6 for natural gas based plants About 46.2 for coal based plants State of the art factory; mean value = 36GJ/t (values from IFA benchmarking 2014 reported in: <a href="https://ammoniaindustry.com/ammonia-technology-portfolio-optimize-for-energy-efficiency-and-carbon-efficiency/">https://ammoniaindustry.com/ammonia-technology-portfolio-optimize-for-energy-efficiency-and-carbon-efficiency/</a> )
Energy feedstock [GJ/t]	22.1 GJ/ton_NH3
Fuel demand [GJ/t]	7.2-9.0 GJ/ton_NH3 Natural gas; 2% of total energy demand worldwide
Steam balance [GJ/t]	Included in the figures above, plants are self-sufficient for steam and electric power
Electricity [GJ/t]	Included in the figures above, plants are self-sufficient for steam and electric power
Air supply unit	Either not present (in natural gas based plants) or with energy input already included in the figures above.
Compressors	Air, synthesis gas (N2/H2) and ammonia compressors are present in all state of the art ammonia production plants, their energy input already included in the figures above
CO2 emissions [tCO2 eq/t] (cradle-to-gate, including feedstock production)	0.5 GT/year or 1.6-2.7 t CO2 per 1t NH3 (2.5t CO2/t NH3 average emission for gas and coal based), 1.5% Current technology: 300 Million tons of CO2 per year; production of 1 ton NH3 produces 1.9 tons CO2
Water consumption per t product	>6.5 t/t for gas based process, including the loss of the evaporative cooling towers Process water only consumption is 1.5 t/t
Current TRL	9
Current cost per t product	300-350 Eur per ton NH3 (Power-to-Ammonia Report 2017) Witte, J. Power to Ammonia, Institute for Sustainable Process Technology: Amersfoort, The Netherlands, 14 Feb 2017, 2017.  100 to 300 \$/t depending on the location, and cost of feedstock at the location
DOI References	<a href="http://www2.eng.ox.ac.uk/systemseng/publications/Ammonia-based_ESS.pdf">http://www2.eng.ox.ac.uk/systemseng/publications/Ammonia-based_ESS.pdf</a>

## Biomass-based process

Biomass-based process	Biomass gasification for H2 production and HB process
Global annual production volume	Today the ammonia production from biomass gasification is negligible
Energy demand [GJ/t]	28 GJ/t as average expected figure including the equivalent consumption for feedstock and for additional thermal energy input, excluding electricity
Feedstock demand [GJ/t]	Included in figure above
CO2 emissions [tCO2 eq/t] (cradle-to-gate, including feedstock production)	About 3 ton of CO2 per ton of biomass is the average expected emission figure for ammonia production via this route
Water consumption per t product	
Electricity needs [MWh/t]	About 70 MWh/t ammonia are needed to power the plant
Current TRL	
Current cost per t product	
DOI References	P. Gilbert, P. Thornley, "Energy and carbon balance of ammonia production from biomass gasification," Bio-ten, Birmingham, 2010.



# SUNRISE technologies

## Renewable Haber-Bosch process

Technology	Combining Haber-Bosch with PV-produced hydrogen and nitrogen from solar																																																				
Targeted product	<table border="1" style="width:100%; border-collapse: collapse;"> <tr> <td style="width:10%;">H<sub>2</sub></td> <td style="width:10%;">NH<sub>3</sub></td> <td style="width:10%;">CH<sub>3</sub>OH</td> <td style="width:10%;">EtOH</td> <td style="width:10%;">CH<sub>4</sub></td> <td style="width:10%;">Jet fuel</td> <td style="width:10%;">CO<sub>2</sub></td> <td colspan="2" style="width:20%;">Other</td> </tr> <tr> <td></td> <td style="text-align:center;">x</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> </table>								H <sub>2</sub>	NH <sub>3</sub>	CH <sub>3</sub> OH	EtOH	CH <sub>4</sub>	Jet fuel	CO <sub>2</sub>	Other			x																																		
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	x																																																				
Nature of active material	x Solid-state Inorganic	Molecular			Biomolecular			Biological (living cells)																																													
Sunrise approach	x PV-powered electrocatalysis	Photoelectrochemical direct conversion			biological and biohybrid direct conversion			Key enabler*																																													
<b>Contribution to SUNRISE goals (what?)</b>	<table border="1" style="width:100%; border-collapse: collapse;"> <tr> <td style="width:5%;"></td> <td colspan="8">Sustainable low-carbon production of <u>carbon-based fuels</u> with high efficiency and competitive costs</td> </tr> <tr> <td></td> <td colspan="8">Sustainable low-carbon production of carbon-based <u>commodity chemicals</u> with high efficiency and competitive costs</td> </tr> <tr> <td style="text-align:center;">x</td> <td colspan="8">Sustainable low-carbon production of <u>ammonia</u> with high efficiency and competitive costs</td> </tr> <tr> <td></td> <td colspan="8">Sustainable low-carbon production of <u>hydrogen</u> with high efficiency and competitive costs</td> </tr> <tr> <td></td> <td colspan="8"><u>CO<sub>2</sub></u> as a valuable product</td> </tr> </table>									Sustainable low-carbon production of <u>carbon-based fuels</u> with high efficiency and competitive costs									Sustainable low-carbon production of carbon-based <u>commodity chemicals</u> with high efficiency and competitive costs								x	Sustainable low-carbon production of <u>ammonia</u> with high efficiency and competitive costs									Sustainable low-carbon production of <u>hydrogen</u> with high efficiency and competitive costs									<u>CO<sub>2</sub></u> as a valuable product							
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Envisaged																																																					

production system	Decentralized, local production at small scale (households, niche applications)		
	x	Large-scale production using existing centralized infrastructure	
	x	Large-scale production necessitating new centralized infrastructure (PV and CSP fields)	
Rough timeline (when?)	Short term (2020-25)	Medium term (2025-30)	Long term (2030-50)
	TRL° 5-6	TRL° 7	TRL° 9
Who are the main actors? Who has to be involved?	<p>Ammonia fertilizer produced in Norway by YARA (not a SUNRISE supporter) using hydropower electrolysis H<sub>2</sub> is sufficient for fully satisfying the European fertilizer demand.</p> <p>CASALE SA in Lugano (SUNRISE supporter) is a high (p,T) ammonia technology company.</p> <p>Thyssenkrupp in Dortmund, Germany is plant manufacturer and general contractor of large fertilizer plants.</p> <p>Haldor Topsøes (SUNRISE supporter) is producing HB catalysts.</p> <p>Siemens is working with Oxford University to combine Solar and wind H<sub>2</sub> with HB technology</p>		

\* key enabler: fundamental for diverse technological approaches ° TRL: see Annex

Please indicate who gave concrete input; this is **optional**, but allows us to quantify the reach of the proposed technological solution.

<b>Contributors</b>	CASALE SA, Lugano: Michal Bialkowski, Pierdomenico Biasi, Raffaele Ostuni SABIC, Riyadh, Saudi; Hicham Idriss (also Univ. College London); UHC-PV-Electrolysis Empa; Artur Braun, Rita Toth Vincent Artero, Matthieu Koepf, CEA Martin Roeb, DLR Laurent Baraton, Nouaamane Kezibri, ENGIE
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## 1. Short description of the proposed technological solution

<b>Main technological elements, working principle (max. 5 lines, for scientists not expert in the</b>	Renewable Haber-Bosch process (HBP) will implement solar or wind-powered water electrolyzers in the process to provide fully decarbonized hydrogen to HB reactors. Air separation by renewable
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field)	electricity or heat needs to be further developed and established. Green ammonia production will be achieved when all the energy needs for the entire process will be solely covered by renewables.
<b>Why is this technology not commercially available right now? (major challenges)</b>	<p>Renewable hydrogen production is not economically competitive at the moment.</p> <p>Renewable nitrogen production is still under technical development but has potential to become competitive.</p> <p>In solar HBP, hydrogen production will account for 83% to 92% of the total energy needs of the process.</p> <p>Haber-Bosch synthesis needs constant operation while renewable energy sources are intermittent, which makes temporary H<sub>2</sub> storage necessary.</p> <p>In the current HBP demonstrators, only a fraction (~10%) of the H<sub>2</sub> needed is renewable. O<sub>2</sub> removal from air is achieved by CH<sub>4</sub> combustion ahead of the gas reforming process. The resulting heat is used in the process.</p> <p>Small-scale (1 t/day), distributed, cost-effective, capable of load following ammonia systems (including hydrogen generation, ammonia separation and ammonia storage) are under development (USA).</p>
<b>What does it take to make it happen? (in short)</b>	<p>Improving solar-powered water electrolysis for H<sub>2</sub> production (related to H<sub>2</sub> task) and developing solar-powered air separation for N<sub>2</sub> production (O<sub>2</sub> removal from air). A solution is being developed that consists in producing excess H<sub>2</sub> that can then be recycled at the anode of a fuel-cell that will consume O<sub>2</sub> from air at the cathode. Electricity and heat are generated by this fuel cell so that the process is not very energy intensive.</p> <p><a href="https://ammoniaindustry.com/haldor-topsoes-solid-oxide-electrolyzer/">https://ammoniaindustry.com/haldor-topsoes-solid-oxide-electrolyzer/</a> ; <a href="https://nh3fuelassociation.org/wp-content/uploads/2018/12/0915-Haldor-Topsoe-Roadmap-AIChE-2018.pdf">https://nh3fuelassociation.org/wp-content/uploads/2018/12/0915-Haldor-Topsoe-Roadmap-AIChE-2018.pdf</a>)</p> <p>Solving the storage of H<sub>2</sub> and N<sub>2</sub> at the Haber-Bosch synthesis site.</p> <p>Adapt the ammonia synthesis process for intermittent operation.</p> <p>Develop new ammonia synthesis catalyst able to work at lower temperature and pressure, possibly O<sub>2</sub> tolerant.</p>
<b>What is the benefit for society? (in short)</b>	<p>-“The renewable sources with their improved efficiency can reduce the overall environmental footprint and can replace the current fossil fuel based centralized ammonia production facilities.”</p> <p>-<i>Dincer, Vezina, et al: Comparative Life Cycle Assessment of Various</i></p>

	<p><i>Ammonia Production Methods, July 2016</i>. The evolutionary approach of transitioning the current fossil-based ammonia production will allow to maintain the existing infrastructure, to keep the existing jobs, and to keep the cost of fertilizer at acceptable value</p> <p>- Solar powered water electrolysis+HB can offer a cost-competitive strategy to store H<sub>2</sub> and ship it on long distances thus enabling the deployment of carbon-free H<sub>2</sub>-based economical schemes on a global scale</p> <p>(<a href="https://arena.gov.au/assets/2018/08/opportunities-for-australia-from-hydrogen-exports.pdf">https://arena.gov.au/assets/2018/08/opportunities-for-australia-from-hydrogen-exports.pdf</a>, chapter 4.3 for cost analysis).</p>
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## 2. Existing R&I projects

Existing national/EU project	Final objective	TRL	Run-time	Funding Instrument
SOC4NH3-project, Haldor Topsoe	Solid oxide electrolyzer directly produces H <sub>2</sub> -N <sub>2</sub> mixture which is used for Haber-Bosch synthesis; (no additional air separation unit required)	6	2025	Danish Energy Agency
SESAM	Solar air separation for N <sub>2</sub> production: Prototype demonstration in mini-plant scale	3-4	Nov/2019 – Oct/2022	EFRE-NRW (DLR + YARA + ThyssenKrupp)
YARA project ( Australia)	Provide green Hydrogen (PV + electrolysis 50-60 MW) for ammonia production in Australia.	9	2021	ENGIE + YARA

SIEMENS project with Oxford University	Provide insights into the business case for ammonia as an energy storage vector; Planed wind powered pilot production plant with prod capacity of 30 kg(NH <sub>3</sub> )/day	6-7	Operational since June 2018	SIEMENS+ Innovate UK
FREA pilot demonstrator Fukushima, Japan	Catalyst development for optimized operation of synthesis loop. Low pressure electrolysis integration		Operational since April 2018	Fukushima Renewable Energy Institute – AIST

DÜSOL	Solar air separation for N <sub>2</sub> production: proof of feasibility in the lab	2-3	Until Nov 2019	EFRE-NRW (DLR)
ThyssenKrupp (Port Lincoln plant / Australia)	Green hydrogen production demonstration plant (15 MW electrolyzer; 20 MW PV) + green ammonia production (50 mtd)	6-7	From 2020	ThyssenKrupp + H2U
Starfire Energy in collaboration with Colorado School of Mines	Development of a rapid ramp ammonia synthesis demonstrator for low pressure operation (below 12.5 bar). Catalyst development for flexible operation. The aim is to reach a 50 t/day system		Started in 2015	

### 3. State-of-the-Art: where are we now?

<b>Technological solution to be developed in SUNRISE</b>	<b>Using electrolysis to produce hydrogen for ammonia production through Haber-Bosch process. In the short term, we will simply compress and store solar H<sub>2</sub>; In the long term, we should develop alternative catalysts able to work at low pressure and temperature (better conversion yield expected) without requiring a major modification of the plants and processes for air separation based on solar electricity and heat</b>
TRL	3
Cost	
Energetic conversion yield	25% (solar-to-hydrogen efficiency)
Stability	Long term
Product separation yield	
Total energy demand [GJ/t]	43-45
Electricity needs [GJ/t]	43-45 (incl. ca. 39 GJ/t for electrolysis)
Energy demand utilities [GJ/t]	Included in the above figures (ca 5 GJ/t for compressors; ca 1 GJ/t for Air Separation Unit)
Steam balance [GJ/t]	
CO2 emissions [tCO2 eq/t]	0.240 to 0.313 t <sub>CO2</sub> /t <sub>NH3</sub> (Assuming total electricity needs 12 – 12.5

(cradle-to-gate, including feedstock production)	MWh/t and CO <sub>2</sub> emissions for the total life cycle of PV of ca 20 – 25 g <sub>CO2</sub> /kWh)
Water consumption	For hydrogen production (it is H <sub>2</sub> O/H <sub>2</sub> ) which is 1/9 : so 1.7 tH <sub>2</sub> O/tNH <sub>3</sub>
Air supply unit	Yes, account for 1% of the overall energy consumption.
Compressors	Expensive (CAPEX) and <1% of total energy required (coming out at 30 bars from the electrolyzer or the photoreactor, this allows for two-step compression (30 to 70 and 70 to 140 atm.). An alternative way would be to find alternative HB catalysts working at 20-35 atm.
DOI References	<a href="https://cefic.org/app/uploads/2019/01/Low-carbon-energy-and-feed-stock-for-the-chemical-industry-DECHEMA_Report-energy_climate.pdf">https://cefic.org/app/uploads/2019/01/Low-carbon-energy-and-feed-stock-for-the-chemical-industry-DECHEMA_Report-energy_climate.pdf</a> <a href="https://www.nature.com/articles/ncomms13728">https://www.nature.com/articles/ncomms13728</a> <a href="https://doi.org/10.1063/1.4985090">https://doi.org/10.1063/1.4985090</a>

#### 4. Available techno-economical analysis:

<b>DOI Reference &amp; Summary</b>	<a href="https://www.ispt.eu/media/Final-report-P2A-def.pdf">https://www.ispt.eu/media/Final-report-P2A-def.pdf</a>
	Witte, J. <i>Power to Ammonia - Feasibility study for the value chains and business cases to produce CO2-free ammonia suitable for various market applications</i> ; Institute for Sustainable Process Technology: Amersfoort, The Netherlands, 14 Feb 2017.  Key findings: "We have concluded that CO2 neutral NH3 produced in an electrochemical way from sustainable electricity will be a feasible alternative for NH3 produced from natural gas in the longer term. Comparing the processes for electrochemical production of NH3 resulted the following ranking in decreasing order of efficiency; Solid Oxide Electrolytic Cell (SOEC), Low Temperature Solid State Ammonia Synthesis (LT SSAS), Battolyser, Proton Exchange Membrane (PEM) and High Temperature SSAS (HT SSAS)."
<b>DOI Reference &amp; Summary</b>	Philibert, C. (2017). Producing ammonia and fertilizers: new opportunities from renewables (International Energy Agency).
	"Ammonia production in large-scale plants based on electrolysis of water can compete with ammonia production based on natural gas, in areas with world-best combined solar and wind resources.'
<b>DOI</b>	DOI: 10.1016/j.chempr.2017.10.016

<b>Reference &amp; Summary</b>	<p>"As the cost of RE rapidly decreases, ammonia holds great potential (given its favorable technical and chemical characteristics) at least as a partial substitute for fossil fuels as a seasonal electrical storage method. This offers exciting potential for using ammonia to store energy with better energy density factors than liquid hydrogen. An established logistics chain for worldwide trading and transportation of ammonia already exists. Compressed ammonia is a current solution for ammonia storage and transportation, but for longer-term applications (given that ammonia is toxic and corrosive), new storage and transport systems for decarbonized commodities and energy vectors should be continually developed.</p>
<b>DOI Reference &amp; Summary</b>	<p><a href="http://www2.eng.ox.ac.uk/systemseng/publications/Ammonia-based_ESS.pdf">http://www2.eng.ox.ac.uk/systemseng/publications/Ammonia-based_ESS.pdf</a></p> <p>This report addresses the techno-economics of an ammonia-based energy storage system (ESS) integrated with renewable electricity generation on an island system (a power network which is not connected to the grid). The ammonia-assisted renewable energy system satisfies specific power (and possibly ammonia) demands. The key observations and conclusions derived from the literature review, model-based assessment and market analysis include:</p> <ul style="list-style-type: none"> <li>- Electrolysis and the conversion of stored ammonia to power account for most of the energy losses and for the largest percentage of capital and operating costs of the ESS. Improvement of current technologies or adoption of more advanced ones in the future can have a large impact in making an NH<sub>3</sub>-based ESS economically attractive.</li> <li>- Levelized cost of ammonia (LCOA) via water electrolysis was estimated, using conservative assumptions, to be between 1.5 and 3 times more expensive than that of ammonia produced via natural gas steam reforming.</li> <li>- There is significant potential for ammonia to bypass electrical grid construction in the exploitation of stranded renewable energy resources. There may also be a market for an NH<sub>3</sub>-based ESS in 'islanded' locations which simultaneously require both energy storage and anhydrous ammonia fertilizer and where simplicity is valued.</li> </ul>

## 5. Deliverables, milestones

Define a set of deliverables that provide a series of stepping-stones from the current state to the future application/vision. Define the associated time dimension.

<b>Define time: short-/medium-/long-term, x years</b>	By 2025
<b>Deliverable, milestone</b>	Modification of a large scale, fossil-based ammonia production unit achieving a reduction of specific CO <sub>2</sub> emissions down to 1 ton per ton ammonia
<b>Solved Challenges / Lifted barrier (in bullet points)</b>	<ul style="list-style-type: none"> <li>• Reduction of carbon dioxide emissions for ammonia production through incorporation of 40-50% of renewable H<sub>2</sub></li> </ul>

	<ul style="list-style-type: none"> <li>• Valorization of green electricity</li> <li>• Valorization of oxygen byproduct in reforming process</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	<ul style="list-style-type: none"> <li>• Partial/complete electrification of the ammonia process</li> <li>• Water electrolysis integration</li> <li>• Development of air separation unit</li> <li>• Renewable energy intermittent behavior requiring a buffer storage of hydrogen and oxygen</li> </ul>
TRL	7-8
Stability	Depending on the electrolysis technology, a partial integration of green hydrogen to a conventional Haber-Bosch process shouldn't affect overall stability. As this intermediate hybrid solution relies on substituting part of the feedstock (coal or natural gas) with renewable hydrogen. Although this would certainly require a buffer storage capacity to deal with the intermittent hydrogen production.
Energetic conversion efficiency	For a substitution of 18% of natural gas by electrolysis H <sub>2</sub> around 1.2 MWh of electricity is consumed to produce one metric ton of ammonia.
Scale	Large scale, 1000-2000 MTD
DOI Reference	<a href="https://nh3fuelassociation.org/wp-content/uploads/2018/12/0915-Haldor-Topsoe-Roadmap-AIChE-2018.pdf">https://nh3fuelassociation.org/wp-content/uploads/2018/12/0915-Haldor-Topsoe-Roadmap-AIChE-2018.pdf</a>

<b>Define time: short-/medium-/long-term, x years</b>	by 2030-2035
<b>Deliverable, milestone</b>	Modification of a large scale, fossil-based ammonia production unit to demonstrate near-zero CO <sub>2</sub> emission ammonia production
<b>Solved Challenges / Lifted barriers</b> (in bullet points)	<ul style="list-style-type: none"> <li>• Reduction of carbon dioxide emissions for ammonia production through incorporation of 100% of renewable H<sub>2</sub>.</li> <li>• Valorization of excess green electricity production</li> <li>• Valorization of oxygen byproduct in reforming process</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	<ul style="list-style-type: none"> <li>• Green electricity at a cost of less than 0.1€/kWh for more than 6000 hours per year</li> <li>• Local storage of H<sub>2</sub></li> <li>• Electrification of the ammonia process</li> <li>• Air separation run completely on solar energy supply</li> <li>• Water electrolysis integration</li> <li>• adaptation to fluctuation of renewable energy supply</li> </ul>



TRL	7-8
Stability	Without improving the conventional Haber-Bosch loop, introducing a large amount of green hydrogen could significantly impact system stability. Load charge variation should be addressed by combining different solutions such as lower operating conditions, dynamic control of recycled flow rate, more efficient ammonia separation.
Energetic conversion efficiency	
Scale	Large scale, 1000-2000 MTD
DOI Reference	

<b>Define time: short-/medium-/long-term, x years</b>	By 2035-2040
<b>Deliverable, milestone</b>	Demonstration of small-scale, flexible near-zero CO <sub>2</sub> emission ammonia production using only solar hydrogen
<b>Solved Challenges / Lifted barriers</b> (in bullet points)	<ul style="list-style-type: none"> <li>• 100% renewable H<sub>2</sub></li> <li>• zero carbon dioxide emissions for ammonia production</li> <li>• Increased overall efficiency due to reduced operating conditions</li> <li>• Flexible operation of Haber-Bosch synthesis loop</li> <li>• Air separation run completely on solar energy supply</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	<ul style="list-style-type: none"> <li>• Enhanced ammonia separation process through absorption/desorption instead of conventional low temperature condensation</li> <li>• Solve load change variation through increased flexibility</li> </ul>
TRL	5
Stability	
Energetic conversion efficiency	
Scale	1 ton H <sub>2</sub> /day
DOI Reference	For hydrogen production at about 20% STH one needs 2km <sup>2</sup> for the production of 50 tons of H <sub>2</sub> (11 hours from the sun and 13 hours from an electricity grid). Idriss et al. SABIC-TechnoEconomy Report, Dec. 2018 (Classified).

## [Link to TRL level](#)

### **At TRL 5-6:**

Production volume	<b>20-30 kg/day</b>
Light harvesting area needed per t/product	
Political/societal barriers to be overcome	
Market barriers to be overcome	

### **At TRL 7-8:**

Production volume	<b>200-300 kg/day</b>
Light harvesting area needed per t/product	
Political/societal barriers to be overcome	
Market barriers to be overcome	

### **At TRL 9:**

Production volume	<b>1000-2000 MTD</b>
Light harvesting area needed per t/product	
Political/societal barriers to be overcome for market introduction	
Market barriers to be overcome	

## **6. [Opportunity criteria](#)**

What are the criteria that make this technology an opportunity when ready?  
 Score the potential opportunity from 0 (very low) to 12 (very high).  
 Each contributor provides an individual score (we average afterwards).

Opportunity criteria	Individual Score
Environmental regulations	12
Excess or high deployment of renewable electricity	12
Need for energy storage	8
Demand for decarbonized ammonia	12
Ammonia as an energy carrier	10

### 7. Feasibility criteria

What factors determine the feasibility of the final application?  
 Score the potential feasibility from 0 (very low) to 12 (very high).  
 Each contributor provides an individual score (we average afterwards).

Feasibility criteria	Individual Score
The cost of hydrogen	8

### 8. Key learning points

From the exploration of the selected topic, what are the key learning points?  
 (Resources, enablers, barriers, decision points, knowledge gaps, risks)

<b>Decision points</b>	Cost premium needed to produce green NH <sub>3</sub> ; possibility to decentralize production to avoid transport; emergence of a market for NH <sub>3</sub> as an H <sub>2</sub> storage mean
<b>Knowledge gaps</b>	Ammonia synthesis that follows renewable energy intermittency; low temperature and pressure ammonia catalyst; small scale ammonia reactors

	for 4.0 manufacturing
<b>Risks</b>	<p>Decentralization implies that small ammonia factories could be operated closer to residential areas.</p> <p>If H<sub>2</sub> comes from water electrolysis, water demand becomes very high and will compete with other industries. Maybe easier to achieve with small scale decentralized plants able to use atmospheric water (hybridization with air conditioning systems).</p>

### **Resources**

Critical, rare elements	Current HB processes are using Ru and Fe catalysts. Mo and Co are proposed as plausible alternatives.
Non-fluctuating energy sources	
Hydrogen storage	Will be required for fully renewable HB processes except if new catalysts are found
CO2 storage	
Water purification	Marginal for the production – based on cost. Purification of seawater would imply an additional cost of <1% for renewable ammonia. Use of atmospheric water vapor is possible for electrolysis (hybridization with air conditioning systems is also an option).
CO2 from the atmosphere	
Concentrated, pure CO2	
Specific, new infrastructures	PV and CSP fields; wind turbines; integration of storage to mitigate fluctuations
Low-cost, low-carbon electricity	to drive electrolyzers
Renewable energy	Wind, solar
Renewable heat	
Critical, rare elements	Current HB processes are using Ru and Fe catalysts. Mo and Co are proposed as plausible alternatives.


### **Breakthroughs in key enabling disciplines**

Scale-Up	Renewable H <sub>2</sub> production
System integration	
Novel reactor designs	
Novel catalyst materials: earth-abundant, non-toxic, efficient, stable	Haber-Bosch catalyst working at low pressure and temperature and tolerant to fluctuation
Novel absorber materials: earth-abundant, non-toxic, efficient, stable	
Standardized life-cycle assessment methodologies	
Further developments in quantitative sustainability analysis	
Strain robustness	
Genomic stability	
Preservation (culture collection)	

### **Political/societal/market barriers**

EU-wide, homogeneous regulatory frameworks	Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry, Booklet No. 1 of 8: PRODUCTION OF AMMONIA, 2000, EFMA, European Fertilizer Manufacturers' Association  Ammonia accepted as energy carrier but at "0" carbon emission
Adaptation/ novel regulations (e.g. genetics, use of waste CO <sub>2</sub> , ..)	

EU/national regulations for the deployment of the technology/product	Need to decarbonize industries; approval of using ammonia as an energy carrier; cross country trading of hydrogen;
EU/national incentives for the deployment of the technology/product	Carbon tax and incentives for energy storage (in chemicals);
Fast idea protection (patenting, etc.)	
Large capital investment for market introduction	
Standardization of efficiencies, etc.	
Societal acceptance	General problem with ammonia as a toxic and combustible chemical. Frequent ammonia accidents worldwide. Not specific to novel ammonia synthesis routes. Sissell, K., Mexico - 1,000 evacuated in Pemex ammonia release. Chemical Week 1998, 160 (12), 13. However, as ammonia smells, leaks are easily detected. Need for ammonia fertilizer is warranted by food production. But: more than 50% of produced ammonia fertilizer is supposedly wasted to water. The Nitrogen cycle is the most unbalanced one and is a major ecological concern.
Political security	NH <sub>3</sub> can be seen as a H <sub>2</sub> carrier, therefore enhancing the possibility to store renewable energies. Can secure european energy supply.
EU supply chain	

### **Funding/research frameworks**

International collaboration	
Funding schemes for demonstrators, pilots, etc.	
Large-scale EU research initiatives	Circular Agronomics 7 Mio Euro <a href="https://cordis.europa.eu/project/rcn/214742/factsheet/en">https://cordis.europa.eu/project/rcn/214742/factsheet/en</a>
	N2 as Chemical Feedstock – Synthetic Nitrogen Fixation beyond Haber-Bosch, 2 Mio Eur ERC Grant <a href="https://cordis.europa.eu/project/rcn/197090/factsheet/en">https://cordis.europa.eu/project/rcn/197090/factsheet/en</a>

## Electrochemical Ammonia Synthesis

Technology	Electrochemical Ammonia Synthesis										
Targeted product	H <sub>2</sub>	NH <sub>3</sub>	CH <sub>3</sub> OH	EtOH	CH <sub>4</sub>	Jet fuel	CO <sub>2</sub>	Other			
		x									
Nature of active material	X	Solid-state Inorganic		X	Molecular		x	Biomolecular		Biological (living cells)	
Sunrise approach	X	PV-powered electrocatalysis		Photoelectrochemical direct conversion		biological and biohybrid direct conversion		Key enabler*, Other			
<b>Contribution to SUNRISE goals (what?)</b>	Sustainable low-carbon production of <u>carbon-based fuels</u> with high efficiency and competitive costs										
	Sustainable low-carbon production of carbon-based <u>commodity chemicals</u> with high efficiency and competitive costs										
	X	Sustainable low-carbon production of <u>ammonia</u> with high efficiency and competitive costs									
	Sustainable low-carbon production of <u>hydrogen</u> with high efficiency and competitive costs										
	<u>CO<sub>2</sub></u> as a valuable product										
Sustainability criteria	Carbon capture from the atmosphere										
	X	Exclusive use of abundantly available, non-toxic and non-critical elements									
	X	Sunlight as the primary energy source									
	X	Low resource consumption									
	X	Solar to products yields tenfold to hundredfold higher than current biomass practice									
Envisaged production system	Decentralized, local production at small scale (households, niche applications)										
	Large-scale production using existing centralized infrastructure										
	Large-scale production necessitating new infrastructure										

<b>Rough timeline (when?)</b>	Short term (2020-25)	Medium term (2025–30)	Long term (2030–50)	
	TRL°4	TRL°5	TRL°6-7	
<b>Who are the main actors? Who has to be involved?</b>	European public research institutions (Fr: CEA, CNRS universities; Sweden : Uppsala and Umea, Italy) up to TRL4 European public institution / private R&D actors from TRL5 on			

\* key enabler: fundamental for diverse technological approaches ° TRL: see Annex

Please indicate who gave concrete input; this is **optional**, but allows us to quantify the reach of the proposed technological solution.

<b>Contributors</b>	Matthieu Koepe (CEA), Thomas Wagberg and Johannes Messinger (University Uppsala), Artur Braun (EMPA), Antonin Vlcek (Heyrovsky Institute)
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## 1. Short description of the proposed technological solution

<b>Main technological elements, working principle (max. 5 lines, for scientists not expert in the field)</b>	Electrochemical cells based on proton-coupled N <sub>2</sub> reduction (nitrogen reduction reaction = NRR) with cathode electrocatalysts (these electrocatalysts can be solid-state materials, nitrogenases or molecular mimics of their active sites). These cathodes can either be coupled to water oxidation in a PV-powered electrolyzer or to the oxidation of solar hydrogen with slight bias (0.2-0.4 V). The devices can work either at ambient or high temperature with protonic or metal-oxide membranes)
<b>Why is this technology not commercially available right now? (major challenges)</b>	Poor efficiency of cathode NRR electrocatalysts  Poor selectivity of cathode NRR electrocatalysts  Difficulty in employing proper controls, standards, and experimental methods to definitively show that ammonia is truly synthesized by N <sub>2</sub> reduction as opposed to emerging from contamination or other sources.
<b>What does it take to make it happen? (in short)</b>	Discovery/development of new nitrogen reduction electrocatalysts (computationally guided approaches would be an asset)  Engineering of the catalyst-gas-electrolyte interface to improve selectivity of existing (and new) catalysts (NRR vs. HER)



	For energy-carrier applications: low cost NH <sub>3</sub> recovery strategy from aqueous based liquid electrolytes / development of non-aqueous electrolytes (membranes) for electrocatalytic systems
<b>What is the benefit for society? (in short)</b>	<ul style="list-style-type: none"> <li>• Reduction of the overall environmental footprint of the current fossil fuel based centralized ammonia production facilities.</li> <li>• Providing an alternative mean to store hydrogen i.e. clean energy.</li> <li>• Enabling autonomous on-site fertilizer production units for precision farming &gt; reduction of global nitrogen cycle imbalance</li> </ul>

## 2. Existing R&I projects

Existing national/EU project	Final objective	TRL	Run-time	Funding Instrument
Sweden Univ Uppsala and Umea	Build lab electrolyzer for NRR coupled with OER	4	2019-2025	national
CEA	Develop novel NRR electrocatalysts	4	2018-2021	CEA

## 3. State-of-the-Art: where are we now?

<b>Technological solution to be developed in SUNRISE</b>	<b>Electrocatalytic nitrogen reduction</b> : A recent paper by Jaramillo questions all the data on N <sub>2</sub> RR electrocatalysts described so far
TRL	1
Cost	n/a
Energetic conversion yield	0.008 (solvation effects ignored –total energy content NH/total input)
Stability	24h
Product separation yield	n/a
Total energy demand [GJ/t]	~10 (Solvation in aqueous media ignored. If needed NH <sub>3</sub> recovery will increase the total energy demand)

Electricity needs [GJ/t]	~10
Energy demand utilities [GJ/t]	
Steam balance [GJ/t]	n/a
CO2 emissions [tCO2 eq/t] (cradle-to-gate, including feedstock production)	n/a
Water consumption	Not evaluated
Air separation unit	Yes (use of pure N2)
Compressors	
DOI References	<a href="https://doi.org/10.1002/adma.201803498">https://doi.org/10.1002/adma.201803498</a>  <a href="https://doi.org/10.1038/s41586-019-1260-x">https://doi.org/10.1038/s41586-019-1260-x</a>

<b>DOI Reference</b>	<p>For environmental issues: 10.1126/science.aav8215</p> <p>For electrochemical ammonia synthesis:  10.1126/science.aav.3506  10.1016/j.joule.2017.07.008  <a href="https://doi.org/10.1016/j.ijhydene.2013.09.054">https://doi.org/10.1016/j.ijhydene.2013.09.054</a></p>
<b>Summary</b>	<pre> graph TD     Root[Electrolytic Ammonia Synthesis] --&gt; L1[Liquid Electrolyte]     Root --&gt; L2[Molten Salts]     Root --&gt; L3[Composite Membrane]     Root --&gt; L4[Solid State Electrolyte]          L1 --&gt; L1_1[Organic solvents - LiClO4 in tetrahydrofuran (Room Temperature)]     L1 --&gt; L1_2[Ionic Liquids - LiClO4 in IL (Room Temperature)]     L1 --&gt; L1_3[Aqueous solutions - Li2SO4 in 0.03M H2SO4, LiClO4 in 0.03M H2SO4 (Room Temperature)]          L2 --&gt; L2_1["(Li, K, Cs) Cl Eutectic with Li3N (300-500°C)"]          L3 --&gt; L3_1["(Na, K, Li) carbonate and LiAlO2 (400-450°C)"]     L3 --&gt; L3_2["-YDC-Ca3(PO4)2-K3PO4 (650°C)"]          L4 --&gt; L4_1[Proton Conducting Membranes - Nafion (RT - 80°C)]     L4 --&gt; L4_2[Oxygen ion conducting ceramic membranes - 8 mol% Y2O3 - ZrO2 (650°C)]     L4 --&gt; L4_3[Proton conducting ceramic membranes - Yb2O3 doped SrCeO3, Sm2O3 doped BaCeO3, Gd2O3 doped CeO2 (600-750°C)]          style Root fill:#003366,color:#fff     style L1 fill:#ffff00     style L2 fill:#90ee90     style L3 fill:#ffff00     style L4 fill:#ffcc99     style L1_1 fill:#ffff00     style L1_2 fill:#ffff00     style L1_3 fill:#ffff00     style L2_1 fill:#90ee90     style L3_1 fill:#ffff00     style L3_2 fill:#ffff00     style L4_1 fill:#ffcc99     style L4_2 fill:#ffcc99     style L4_3 fill:#ffcc99 </pre>

	Solid state electrolyte membranes are reported to be the most promising; they allow an easy separation of the hydrogen feed from the ammonia product. However, none of these technologies is ready for commercial production.
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#### 4. Available techno-economical analysis:

<b>DOI Reference</b>	
<b>Summary</b>	

#### 5. Deliverables, milestones

Define a set of deliverables that provide a series of stepping stones from the current state to the future application/vision. Define the associated time dimension.

<b>Define time: short</b>	2020-2025
<b>Deliverable, milestone</b>	Active electrocatalysts for N2 reduction
<b>Solved Challenges / Lifted barrier</b> (in bullet points)	<ul style="list-style-type: none"> <li>• establish robust benchmarking of NRR electrocatalysts</li> <li>• identify active classe(s) of NRR electrocatalyst(s)a preferably derived from non-noble elements</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	<p>Requires robust testing protocol to avoid false positives.</p> <p>Needs to reach significant NH3 production rates (1-2 orders of magnitude higher than today; target 100 mmol NH3/h/gcat)</p> <p>Possibly needs computer guided material design for faster breakthroughs</p>
TRL	4
Stability	>1day
Energetic conversion efficiency	>0.01
Scale	Lab scale
DOI Reference	

<b>Define time: medium</b>	2025-2030
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<b>Deliverable, milestone</b>	Proof of principle lab scale electrolyzer
<b>Solved Challenges / Lifted barriers</b> (in bullet points)	<ul style="list-style-type: none"> <li>● integration of NRR electrocatalysts in functional cathode</li> <li>● coupling NRR / OER ( oxygen evolution reaction) in AEM or PEM device</li> <li>● NH3 recovery</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	<p>Optimization of the catalyst formulation for integration into PEM devices</p> <p>Identification of most relevant OER anode material</p> <p>Identification of the appropriate electrolyte composition (pH, additives...).</p> <p>Development of NH3 recovery strategies for aqueous electrolytes</p>
TRL	5
Stability	weeks
Energetic conversion efficiency	0.1 (before products separation)
DOI Reference	

<b>Define time: medium</b>	2025-2030
<b>Deliverable, milestone</b>	Proof of principle lab scale electrolyzer with solar H2 as input
<b>Solved Challenges / Lifted barriers</b> (in bullet points)	<ul style="list-style-type: none"> <li>● integration of NRR electrocatalysts in functional cathode</li> <li>● coupling NRR / HOR (hydrogen oxidation reaction) in AEM or PEM device</li> <li>● NH3 recovery</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	<p>Optimization of the catalyst formulation for integration into PEM devices</p> <p>Identification of most relevant HOR anode material</p> <p>Identification of the appropriate electrolyte composition (pH, additives...).</p> <p>Development of NH3 recovery strategies for aqueous electrolytes;</p> <p>Consider reinjecting H2 produced at the cathode towards the anode?</p>
TRL	5

<b>Stability</b>	weeks
<b>Energetic conversion efficiency</b>	0.1 (before products separation)
<b>DOI Reference</b>	

<b>Define time: long-term</b>	2030-2050
<b>Deliverable, milestone</b>	Functional small-scale autonomous PV-driven electrolyzer (either using H <sub>2</sub> O or H <sub>2</sub> as anode substrate)
<b>Solved Challenges / Lifted barriers</b> (in bullet points)	<ul style="list-style-type: none"> <li>• Devices stable and functional for &gt;1 year</li> <li>• Implementation of a strategy for NH<sub>3</sub> capture, concentration and storage</li> </ul> <p>In aqueous conditions</p> <ul style="list-style-type: none"> <li>• devices incorporating H<sub>2</sub> management –or–</li> <li>• strategy to avoid HER</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	<p>Optimization of all parts of the PEM device (catalyst formulation, nature of the electrode material, integration of the components in a compact PEM device, working electrolyte)</p> <p>Integration of PV</p>
TRL	6-7
Stability	1 year
Energetic conversion efficiency	>0.1 from sunlight
DOI Reference	

### [Link to TRL level](#)

#### At TRL 5-6:

Production volume	
Light harvesting area needed per t/product	
Political/societal barriers to be overcome	

Market barriers to be overcome	
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**At TRL 7-8:**

Production volume	
Light harvesting area needed per t/product	
Political/societal barriers to be overcome	
Market barriers to be overcome	

**At TRL 9:**

Production volume	
Light harvesting area needed per t/product	
Political/societal barriers to be overcome for market introduction	
Market barriers to be overcome	

**6. Opportunity criteria**

What are the criteria that make this technology an opportunity when ready?

Score the potential opportunity from 0 (very low) to 12 (very high).

Each contributor provides an individual score (we average afterwards).

<b>Opportunity criteria</b>	<b>Individual Score</b>
Low-cost, low maintenance, scalable production units	9
Reduced environmental impact	12
Opening new markets (NH3 energy carrier)	8
Compatibility with intermittent (stop and go)	10

production	
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## 7. Feasibility criteria

What factors determine the feasibility of the final application?

Score the potential feasibility from 0 (very low) to 12 (very high).

Each contributor provides an individual score (we average afterwards).

Feasibility criteria	Individual Score
Sustained/increasing need for NH <sub>3</sub>	12
Development of a robust enabling technology (low temperature NRR PEM device)	8
Reaching significant NH <sub>3</sub> production rate and NH <sub>3</sub> selectivity	6
Development of noble-metal free catalysts for both NRR and OER	8

## 8. Key learning points

From the exploration of the selected topic, what are the key learning points?

(Resources, enablers, barriers, decision points, knowledge gaps, risks)

<b>Decision points</b>	<p>Evaluation of the benefits of the technology vs. alternatives (PEM vs. electrified thermal HBP using solar H<sub>2</sub>)</p> <p>Evaluation of the market opportunity for non-centralized small production units</p> <p>Concurrent development of technologies based on NH<sub>3</sub> as energy carrier</p>
<b>Knowledge gaps</b>	<p>Catalyst material for NRR to be found/confirmed independently</p> <p>Operating conditions (fully aqueous or not)</p>
<b>Risks</b>	<p>Poorly cost-competitive technology</p> <p>Side product (H<sub>2</sub>) management may be an issue for large scale systems</p>

## **Resources**

<b>Suggestion</b>	<b>Please detail</b>
Critical, rare elements	Ideally not required in the final devices; initial design should not be restricted to noble-metal free system
Non-fluctuating energy sources	PEM device ideally compatible with fluctuating energy sources
Hydrogen storage	H <sub>2</sub> separation and storage may be a major secondary point to consider for aqueous electrolyzer (may be reinjected at the anode?)
CO <sub>2</sub> storage	n/a
Water purification	Extant required to be deified (depends on the active materials tolerance)
CO <sub>2</sub> from the atmosphere	n/a
Concentrated, pure CO <sub>2</sub>	n/a
Specific, new infrastructures	
Low-cost, low-carbon electricity	n/a
Renewable energy	PV
Renewable heat	n/a

## **Breakthroughs in key enabling disciplines**

Scale-Up	required
System integration	required
Novel reactor designs	To be defined
Novel catalyst materials: earth-abundant, non-toxic, efficient, stable	required



Novel absorber materials: earth-abundant, non-toxic, efficient, stable	Would be beneficial
Standardized life-cycle assessment methodologies	required
Further developments in quantitative sustainability analysis	Would be beneficial
Strain robustness	n/a
Genomic stability	n/a
Preservation (culture collection)	n/a

### **Political/societal/market barriers**

EU-wide, homogeneous regulatory frameworks	
Adaptation/ novel regulations (e.g. genetics, use of waste CO <sub>2</sub> , ..)	
EU/national regulations for the deployment of the technology/product	
EU/national incentives for the deployment of the technology/product	
Fast idea protection (patenting, etc.)	
Large capital investment for market introduction	
Standardization of efficiencies, etc.	

Societal acceptance	
Political security	
EU supply chain	

**Funding/research frameworks**

International collaboration	
Funding schemes for demonstrators, pilots, etc.	
Large-scale EU research initiatives	

## Direct photoelectrocatalytic ammonia synthesis

Technology	Direct photoelectrocatalytic ammonia synthesis									
Targeted product	H <sub>2</sub>	NH <sub>3</sub>	CH <sub>3</sub> OH	EtOH	CH <sub>4</sub>	Jet fuel	CO <sub>2</sub>	Other		
		x								
Nature of active material	X	Solid-state Inorganic		X	Molecular		x	Biomolecular		Biological (living cells)
Sunrise approach		PV-powered electrocatalysis		X	Photoelectrochemical direct conversion			biological and biohybrid direct conversion		Key enabler*, Other
<b>Contribution to SUNRISE goals (what?)</b>		Sustainable low-carbon production of <u>carbon-based fuels</u> with high efficiency and competitive costs								
		Sustainable low-carbon production of carbon-based <u>commodity chemicals</u> with high efficiency and competitive costs								
	X	Sustainable low-carbon production of <u>ammonia</u> with high efficiency and competitive costs								
		Sustainable low-carbon production of <u>hydrogen</u> with high efficiency and competitive costs								
		<u>CO<sub>2</sub></u> as a valuable product								
Sustainability criteria		Carbon capture from the atmosphere								
	X	Exclusive use of abundantly available, non-toxic and non-critical elements								
	X	Sunlight as the primary energy source								
	X	Low resource consumption								
	X	Solar to products yields tenfold to hundredfold higher than current biomass practice								
Envisaged production system	X	Decentralized, local production at small scale (households, niche applications)								
		Large-scale production using existing centralized infrastructure								
		Large-scale production necessitating new infrastructure								

<b>Rough timeline (when?)</b>	Short term (2020-25)		Medium term (2025–30)		Long term (2030–50)	
	TRL°3		TRL°4		TRL°5-7	
<b>Who are the main actors? Who has to be involved?</b>						

\* key enabler: fundamental for diverse technological approaches ° TRL: see Annex

Please indicate who gave concrete input; this is **optional**, but allows us to quantify the reach of the proposed technological solution.

<b>Contributors</b>	Matthieu Koepf (CEA), Vincent Artero (CEA), Artur Braun (EMPA), Antonin Vlcek (Heyrovsky Institute)
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### 1. Short description of the proposed technological solution

<b>Main technological elements, working principle (max. 5 lines, for scientists not expert in the field)</b>	<p>Photo(electro)catalysts should be developed to use sunlight to convert N<sub>2</sub> into ammonia. Electrons and protons required for this process can come from water or solar H<sub>2</sub>.</p> <p>These photoelectrocatalysts can either exploit light-driven electron transfer processes (in this case, this is a mere combination of the knowledge gained in the electrochemical NRR taskforce + the monolithic device taskforce for H<sub>2</sub> production) or use in addition light to split the strong N≡N bond (proper photocatalytic activation).</p> <p>These photocathodes will either be coupled to water oxidation in a PV-powered electrolyzer or to the oxidation of solar hydrogen with slight bias (0.2-0.4 V).</p> <p>The devices can work either at ambient or high temperature with protonic or metal-oxide membranes)</p> <p>Alternatively, baggies systems can be envisioned where the photocatalysts for NRR will be coupled with photocatalysts for water oxidation</p>
<b>Why is this technology not commercially available right now? (major challenges)</b>	<p>Poor efficiency of cathode NRR electrocatalysts</p> <p>Poor efficiency of cathode NRR photoelectrocatalysts</p>

	<p>Poor selectivity of cathode NRR electrocatalysts          Poor efficiency of cathode NRR photoelectrocatalysts</p> <p>Difficulty in employing proper controls, standards, and experimental methods to definitively show that ammonia is truly synthesized by N<sub>2</sub> reduction as opposed to emerging from contamination or other sources.</p>
<b>What does it take to make it happen? (in short)</b>	<p>Discovery/development of new nitrogen reduction photocatalysts</p> <p>Engineering of photoelectrodes incorporating these electrocatalysts or photocatalysts</p> <p>In addition to breakthroughs indicated in the electrocatalytic N<sub>2</sub> fixation document and on the Monolithic devices for H<sub>2</sub> evolution document</p>
<b>What is the benefit for society? (in short)</b>	<ul style="list-style-type: none"> <li>• Reduction of the overall environmental footprint of the current fossil fuel based centralized ammonia production facilities.</li> <li>• Providing an alternative mean to store hydrogen i.e. clean energy.</li> <li>• Enabling autonomous on-site fertilizer production units for precision farming &gt; reduction of global nitrogen cycle imbalance</li> </ul>

## 2. [Existing R&I projects](#)

Existing national/EU project	Final objective	TRL	Run-time	Funding Instrument

## 3. [State-of-the-Art: where are we now?](#)

<b>Technological solution to be developed in SUNRISE</b>	<b>Photocatalytic and photoelectrocatalytic nitrogen reduction</b> : A recent paper by Jaramillo questions all the data on N <sub>2</sub> RR
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	electrocatalysts described so far: photoproduction of ammonia has been reviewed by Saboo and Quadrelli (10.1016:B978-0-444-64127-4.00003-3)
TRL	2
Cost	n/a
Energetic conversion yield	
Stability	
Product separation yield	
Electricity needs [GJ/t]	
Energy demand utilities [GJ/t]	
Steam balance [GJ/t]	
CO2 emissions [tCO2 eq/t] (cradle-to-gate, including feedstock production)	
Water consumption	
Air separation unit	Yes (use of pure N2)
Compressors	
DOI References	Quadrelli (10.1016:B978-0-444-64127-4.00003-3)

#### 4. [Available techno-economical analysis:](#)

<b>DOI Reference</b>	
<b>Summary</b>	

#### 5. [Deliverables, milestones](#)

Define a set of deliverables that provide a series of stepping stones from the current state to the future application/vision. Define the associated time dimension.

<b>Define time: short</b>	2020-2025
<b>Deliverable, milestone</b>	Active photo(electro)catalysts for N2 reduction
<b>Solved Challenges / Lifted barrier</b> (in bullet points)	<ul style="list-style-type: none"> <li>• establish robust benchmarking of NRR photo(electro)catalysts</li> <li>• identify active classe(s) of NRR photo(electro)catalyst(s)a preferably derived from non-noble elements (</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	<p>Requires robust testing protocol to avoid false positives.</p> <p>Needs to reach significant NH3 production rates (1-2 orders of magnitude higher than today.</p> <p>Possibly needs computer guided material design for faster breakthroughs</p>
TRL	3
Stability	>1day
Energetic conversion efficiency	>0.01
Scale	Lab scale
DOI Reference	

<b>Define time: medium</b>	2025-2030
<b>Deliverable, milestone</b>	Proof of principle lab scale monolithic device
<b>Solved Challenges / Lifted barriers</b> (in bullet points)	<ul style="list-style-type: none"> <li>• integration of NRR electrocatalysts in functional photocathode</li> <li>• integration of NRR photoelectrocatalysts in functional photocathode</li> <li>• coupling NRR / OER (oxygen evolution reaction) in AEM or PEM photoelectrochemical device</li> <li>• NH3 recovery</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	<p>Optimization of the electrocatalyst/photoelectrocatalysts formulation for integration into photoelectrochemical devices</p> <p>Exploit knowledge from electrocatalytic Nitrogen fixation and Photoelectrochemical H2 production task forces</p> <p>Identification of the appropriate electrolyte composition (pH, additives...).</p>

	Development of NH3 recovery strategies for aqueous electrolytes
TRL	5
Stability	weeks
Energetic conversion efficiency	0.1 (before products separation)
DOI Reference	

<b>Define time: medium</b>	2025-2030
<b>Deliverable, milestone</b>	Proof of principle lab scale monolithic device
<b>Solved Challenges / Lifted barriers</b> (in bullet points)	<ul style="list-style-type: none"> <li>• integration of NRR electrocatalysts in functional photocathode</li> <li>• integration of NRR photoelectrocatalysts in functional photocathode</li> <li>• coupling NRR / HOR( Hydrogen oxidation reaction) in AEM or PEM photoelectrochemical device</li> <li>• NH3 recovery</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	<p>Optimization of the electrocatalyst/photoelectrocatalysts formulation for integration into photoelectrochemical devices</p> <p>Exploit knowledge from electrocatalytic Nitrogen fixation and Photoelectrochemical H2 production task forces</p> <p>Identification of the appropriate electrolyte composition (pH, additives...).</p> <p>Development of NH3 recovery strategies for aqueous electrolytes</p>
TRL	5
Stability	weeks
Energetic conversion efficiency	0.1 (before products separation)
DOI Reference	

<b>Define time: medium</b>	2025-2030
<b>Deliverable, milestone</b>	Proof of principle lab scale baggie system for NRR
<b>Solved Challenges / Lifted barriers</b> (in bullet points)	<ul style="list-style-type: none"> <li>• integration of NRR electrocatalysts/photoelectrocatalysts in functional materials coupling light capture, NRR / OER( Oxygen evolution reaction) when suspended in water</li> <li>• NH3 recovery</li> </ul>



<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	Optimization of the photocatalysts formulation  Identification of the appropriate suspension composition (pH, additives...)  Development of NH3 recovery strategies for aqueous electrolytes
TRL	5
Stability	weeks
Energetic conversion efficiency	0.1 (before products separation)
DOI Reference	

<b>Define time: long-term</b>	2030-2050
<b>Deliverable, milestone</b>	Functional small-scale autonomous monolithic device (either using H2O or H2 as anode substrate)
<b>Solved Challenges / Lifted barriers</b> (in bullet points)	<ul style="list-style-type: none"> <li>• Devices stable and functional for &gt;1 year</li> <li>• Implementation of a strategy for NH3 capture, concentration and storage</li> </ul> In aqueous conditions <ul style="list-style-type: none"> <li>• devices incorporating H2 management –or-</li> <li>• strategy to avoid HER</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	Optimization of all parts of the monolithic device (photo(electro) catalyst formulation, nature of the photoelectrode material, integration of the components in a compact monolithic device, working electrolyte)
TRL	6-7
Stability	1 year
Energetic conversion efficiency	>0.1 from sunlight
DOI Reference	

<b>Define time: long-term</b>	2030-2050
<b>Deliverable, milestone</b>	Functional small-scale autonomous baggie device (using H2O as electron and proton source)
<b>Solved Challenges / Lifted barriers</b>	<ul style="list-style-type: none"> <li>• Devices stable and functional for &gt;1 year</li> </ul>

(in bullet points)	<ul style="list-style-type: none"> <li>Implementation of a strategy for NH<sub>3</sub> capture, concentration and storage</li> </ul> <p>In aqueous conditions</p> <ul style="list-style-type: none"> <li>devices incorporating H<sub>2</sub> management –or–</li> <li>strategy to avoid HER</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	Optimization of all parts of the baggie system (photocatalysts formulation, chemostatic conditions); safety issues in case of H <sub>2</sub> production
TRL	6-7
Stability	1 year
Energetic conversion efficiency	>0.1 from sunlight
DOI Reference	

### [Link to TRL level](#)

#### **At TRL 5-6:**

Production volume	
Light harvesting area needed per t/product	
Political/societal barriers to be overcome	
Market barriers to be overcome	

#### **At TRL 7-8:**

Production volume	
Light harvesting area needed per t/product	
Political/societal barriers to be overcome	
Market barriers to be overcome	

**At TRL 9:**

Production volume	
Light harvesting area needed per t/product	
Political/societal barriers to be overcome for market introduction	
Market barriers to be overcome	

**6. Opportunity criteria**

What are the criteria that make this technology an opportunity when ready?

Score the potential opportunity from 0 (very low) to 12 (very high).

Each contributor provides an individual score (we average afterwards).

<b>Opportunity criteria</b>	<b>Individual Score</b>
Low-cost, low maintenance, scalable production units	9
Reduced environmental impact	12
Opening new markets (NH3 energy carrier)	8
Compatibility with intermittent (stop and go) production	10

**7. Feasibility criteria**

What factors determine the feasibility of the final application?

Score the potential feasibility from 0 (very low) to 12 (very high).

Each contributor provides an individual score (we average afterwards).

<b>Feasibility criteria</b>	<b>Individual Score</b>
Sustained/increasing need for NH3	12
Development of a robust enabling technology (low temperature NRR PEM device)	8

Reaching significant NH <sub>3</sub> production rate and NH <sub>3</sub> selectivity	6
Development of noble-metal free catalysts for both NRR and OER	8

## 8. Key learning points

From the exploration of the selected topic, what are the key learning points?  
(Resources, enablers, barriers, decision points, knowledge gaps, risks)

<b>Decision points</b>	<p>Evaluation of the benefits of the technology vs alternatives (PEM vs electrified thermal HBP using solar H<sub>2</sub>)</p> <p>Evaluation of the market opportunity for non-centralized small production units</p> <p>Concurrent development of technologies based on NH<sub>3</sub> as energy carrier</p>
<b>Knowledge gaps</b>	<p>Catalyst material for NRR to be found/confirmed independently</p> <p>Operating conditions (fully aqueous or not)</p>
<b>Risks</b>	<p>Poorly cost-competitive technology</p> <p>Side product (H<sub>2</sub>) management may be an issue for large scale systems</p>

## Resources

<b>Suggestion</b>	<b>Please detail</b>
Critical, rare elements	Ideally not required in the final devices; initial design should not be restricted to noble-metal free system
Non-fluctuating energy sources	Monolithic and baggie device ideally compatible with fluctuating energy sources
Hydrogen storage	H <sub>2</sub> separation and storage may be a major secondary point to consider for aqueous systems; mixtures of H <sub>2</sub> and O <sub>2</sub> may explode depending on H <sub>2</sub> content ( 4-96% ) ;membrane separation?
CO <sub>2</sub> storage	n/a
Water purification	Extant required to be deified (depends on the active materials)

	tolerance)
CO2 from the atmosphere	n/a
Concentrated, pure CO2	n/a
Specific, new infrastructures	
Low-cost, low-carbon electricity	n/a
Renewable energy	sunlight
Renewable heat	n/a

### **Breakthroughs in key enabling disciplines**

Scale-Up	required
System integration	required
Novel reactor designs	To be defined
Novel catalyst materials: earth-abundant, non-toxic, efficient, stable	required
Novel absorber materials: earth-abundant, non-toxic, efficient, stable	Would be beneficial
Standardized life-cycle assessment methodologies	required
Further developments in quantitative sustainability analysis	Would be beneficial
Strain robustness	n/a
Genomic stability	n/a

Preservation (culture collection)	n/a

**Political/societal/market barriers**

EU-wide, homogeneous regulatory frameworks	
Adaptation/ novel regulations (e.g. genetics, use of waste CO2, ..)	
EU/national regulations for the deployment of the technology/product	
EU/national incentives for the deployment of the technology/product	
Fast idea protection (patenting, etc.)	
Large capital investment for market introduction	
Standardization of efficiencies, etc.	
Societal acceptance	
Political security	
EU supply chain	

**Funding/research frameworks**

International collaboration	
Funding schemes for demonstrators, pilots, etc.	

Large-scale EU research initiatives	

## Ammonium production by photosynthetic microorganisms

Technology	Ammonium bio-photoproduction by photosynthetic microorganisms																																																													
Targeted product	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 10%;">H<sub>2</sub></td> <td style="width: 10%;">NH<sub>3</sub></td> <td style="width: 10%;">CH<sub>3</sub>OH</td> <td style="width: 10%;">EtOH</td> <td style="width: 10%;">CH<sub>4</sub></td> <td style="width: 10%;">Jet fuel</td> <td style="width: 10%;">CO<sub>2</sub></td> <td colspan="2" style="width: 20%;">Other</td> </tr> <tr> <td></td> <td style="text-align: center;">x</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td colspan="2"></td> </tr> </table>								H <sub>2</sub>	NH <sub>3</sub>	CH <sub>3</sub> OH	EtOH	CH <sub>4</sub>	Jet fuel	CO <sub>2</sub>	Other			x																																											
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	x																																																													
Nature of active material	Solid-state Inorganic		Molecular			Biomolecular		X	Biological (living cells)																																																					
Sunrise approach	PV-powered electrocatalysts		Photoelectrochemical direct conversion		X	Biological and biohybrid direct conversion		Key enabler*, Other																																																						
Device category	Electrolyzer		Photo(bio)electrolyzer		X	Photo(bio)reactor		fermentors, thermocatalytic reactors																																																						
<b>Contribution to SUNRISE goals (what?)</b>	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 5%;"></td> <td colspan="8">Sustainable low-carbon production of <u>carbon-based fuels</u> with high efficiency and competitive costs</td> </tr> <tr> <td></td> <td colspan="8">Sustainable low-carbon production of carbon-based <u>commodity chemicals</u> with high efficiency and competitive costs</td> </tr> <tr> <td style="text-align: center;">x</td> <td colspan="8">Sustainable low-carbon production of <u>ammonia</u> with high efficiency and competitive costs</td> </tr> <tr> <td></td> <td colspan="8">Sustainable low-carbon production of <u>hydrogen</u> with high efficiency and competitive costs</td> </tr> <tr> <td></td> <td colspan="8"><u>CO<sub>2</sub></u> as a valuable feedstock</td> </tr> <tr> <td></td> <td colspan="8">Sustainable <u>building materials</u>, mineralization, long-lasting C-based materials</td> </tr> </table>									Sustainable low-carbon production of <u>carbon-based fuels</u> with high efficiency and competitive costs									Sustainable low-carbon production of carbon-based <u>commodity chemicals</u> with high efficiency and competitive costs								x	Sustainable low-carbon production of <u>ammonia</u> with high efficiency and competitive costs									Sustainable low-carbon production of <u>hydrogen</u> with high efficiency and competitive costs									<u>CO<sub>2</sub></u> as a valuable feedstock									Sustainable <u>building materials</u> , mineralization, long-lasting C-based materials							
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Sustainability criteria	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 5%; text-align: center;">x</td> <td colspan="8">Carbon capture from the atmosphere</td> </tr> <tr> <td style="text-align: center;">x</td> <td colspan="8">Carbon capture from point sources/ flue gas</td> </tr> <tr> <td style="text-align: center;">x</td> <td colspan="8">Exclusive use of abundantly available, non-toxic and non-critical elements</td> </tr> <tr> <td style="text-align: center;">x</td> <td colspan="8">Sunlight as the primary energy source</td> </tr> <tr> <td style="text-align: center;">x</td> <td colspan="8">Low resource consumption</td> </tr> <tr> <td style="text-align: center;">x</td> <td colspan="8">Solar to products yields tenfold to hundredfold higher than current biomass practice</td> </tr> </table>								x	Carbon capture from the atmosphere								x	Carbon capture from point sources/ flue gas								x	Exclusive use of abundantly available, non-toxic and non-critical elements								x	Sunlight as the primary energy source								x	Low resource consumption								x	Solar to products yields tenfold to hundredfold higher than current biomass practice							
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Envisaged production system	<input checked="" type="checkbox"/>	Decentralized, local production at small scale (households, niche applications)		
	<input type="checkbox"/>	Large-scale production using existing centralized infrastructure		
	<input type="checkbox"/>	Large-scale production necessitating new centralized infrastructure		
Rough timeline (when?)	Short term (2020-25)		Medium term (2025–30)	Long term (2030–50)
	TRL°2-3	TRL°4-5	TRL°5-8	
Who are the main actors? Who has to be involved?	University of Nantes, France University of Turku, Finland Hydroponic industries Aquaculture E.g. H2WIN in Nivelles (SUNRISE Supporter)			

\* key enabler: fundamental for diverse technological approaches ° TRL: see Annex

Please indicate who gave concrete input; this is **optional**, but allows us to quantify the reach of the proposed technological solution.

<b>Contributors</b>	Jack Legrand (Nantes), Dominique Grizeau (Nantes), Yagut Allahverdiyeva-Rinne (Turku), Juliette Jouhet (Grenoble), Joanna Kargul (Warsaw), Artur Braun and Rita Toth (Empa)
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## 1. Short description of the proposed technological solution

<b>Main technological elements, working principle (max. 5 lines)</b>	Some photoautotrophic cyanobacteria use photosynthetically produced ATP as an energy source to break the strong triple bond of atmospheric N <sub>2</sub> via the O <sub>2</sub> sensitive nitrogenase enzyme. This process differs from the Haber-Bosch process, which is extremely demanding in energy (high temperature and pressure) and resources (purified N <sub>2</sub> and H <sub>2</sub> ). In N <sub>2</sub> -fixing cyanobacteria the ammonium production in light is catalysed in specialized cells, the heterocysts (or trichomes), which are microoxic cells (or niches). These cells enable the functioning of the O <sub>2</sub> -sensitive nitrogenase under ambient air. The proposed technology will include: (i) newly engineered cyanobacterial strains acting as N <sub>2</sub> -fixing cell factories: producing and secreting NH <sub>3</sub> and (ii) thin-layer artificial heterocysts bofilm functioning as a long-term N <sub>2</sub> -fixing biocatalysts.
<b>Why is this technology not commercially available right</b>	In cyanobacteria glutamine synthetase (GS) is expressed along with nitrogenase and initiates assimilation of ammonium. Therefore

<b>now? What are the major challenges?</b>	engineering novel strains with decreased ammonium assimilation capacity is needed (Bui et al. 2014). The maturity and efficiency of the technology is not yet sufficient. The investigations are only made at the lab scale. Algae cultivation is not cost-competitive.
<b>What does it take to make it happen? (in short)</b>	Construction of special photobioreactors (see enabler). A need for screening and/or engineering new strains with enhanced N <sub>2</sub> fixing and ammonium production capacity. Investigation at pilot scale will be necessary to evaluate the real potential and bottlenecks of large scale ammonium production. Developing culture condition optimised for the long-term stability of the cells (biocatalysts).
<b>What is the benefit for society? (in short)</b>	Clean and sustainable bioproduction of ammonium from solar energy by photosynthetic microorganisms. The process also contributes to CO <sub>2</sub> sequestration. Such ammonium bioproduction will be compatible with organic farming by developing integrated crop/algae co-culturing in a close nutrient recirculation loop.

## 2. Existing R&I projects

Existing national/EU project	Final objective	TRL	Run-time	Funding Instrument

## 3. State-of-the-Art: where are we now?

<b>Technological solution to be developed in SUNRISE</b>	Development of pilot photobioreactor to evaluate the real potential of the biological production of ammonia. A part of the combined nitrogen excreted in the culture medium is shown to be stripped through the aeration of the cultures as NH <sub>3</sub> . The NH <sub>4</sub> <sup>+</sup> /NH <sub>3</sub> production is shown to be affected by parameters such as temperature, irradiance, gas flow rate and MSX concentrations.
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	Kinetics study reveals that the dissolved $\text{NH}_4^+/\text{NH}_3$ as well as the gaseous $\text{NH}_3$ productions are correlated to pH variations production; a pulse regulation of pH is used to increase the $\text{NH}_3$ production. All these parameters have to be deeply investigated to increase the ammonia production. Without optimisation of the process in a lab photobioreactor, 40 mg $\text{NH}_3/\text{m}^2/\text{day}$ with a mutant of Anabaena (about 10 ten times more than in nature: 1kg/ha/year).
TRL	2-4
Cost	
Energetic conversion yield	
Stability	
Product separation yield	
Total energy demand [GJ/t]	
Electricity needs [GJ/t]	
Energy demand utilities [GJ/t]	
Steam balance [GJ/t]	
CO2 emissions [tCO2 eq/t] (cradle-to-gate, including feedstock production)	
Water consumption	
Air separation unit	
Compressors	
DOI References	

#### 4. Available techno-economical analysis:

<b>DOI Reference</b>	
<b>Summary</b>	

## 5. Deliverables, milestones

Define a set of deliverables that provide a series of stepping stones from the current state to the future application/vision. Define the associated time dimension.

<b>Define time: short-term, 5 years</b>	
<b>Deliverable, milestone</b>	<ul style="list-style-type: none"> <li>- Identification of efficient N<sub>2</sub>-fixing cyanobacteria</li> <li>- Revealing electron-transfer network in the model heterocysts cyanobacteria</li> <li>- Modelling of electron-transfer network in heterocysts</li> <li>- Delivering highly active artificial heterocysts biofilms</li> <li>- Construction new strains (including strains with modified glutamine synthesis) with enhanced ammonium production and secretion</li> <li>- Effect of culture conditions on ammonium production</li> <li>- Identification robust strains in pH and pO<sub>2</sub> variations</li> </ul>
<b>Solved Challenges / Lifted barrier</b> (in bullet points)	<ul style="list-style-type: none"> <li>● Efficient N<sub>2</sub>-fixation and ammonia excretion</li> <li>● Effect of the culture parameters on ammonia production</li> <li>● Conception of an optimal photobioreactor</li> <li>● Conception of a controlled NH<sub>3</sub> delivery system for optimal doses, without risk of reaching inhibitory dose</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	Construction of new strains, Optimisation of the strains and culture conditions.
TRL	2-3
Stability	A robust strain already isolated 6 years ago
Energetic conversion efficiency	No need of energy, except for the agitation, compression and temperature control of the culture media
Scale	Lab
DOI Reference	<a href="https://doi.org/10.1016/j.bej.2014.06.016">10.1016/j.bej.2014.06.016</a>

<b>Define time: medium-term, 5-10 years</b>	
<b>Deliverable, milestone</b>	Study of the effect of day-light conditions on ammonia

	production. Validation of the efficiency of a photobioreactor equipped with an original stripping device to transfer ammonia through gas phase from diazotrophic cyanobacterial culture to microalgae cultures and hydroponic cultivations. Design of a pilot solar photobioreactor for ammonia production.
<b>Solved Challenges / Lifted barriers</b> (in bullet points)	<ul style="list-style-type: none"> <li>• Effect of day-light conditions on ammonia productivity</li> <li>• Control of the ammonia stripping and delivery to the cultures</li> <li>• Conception of an adapted photobioreactor for mass production of ammonia</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	Control of the metabolism of the cyanobacteria in real (solar) culture conditions. Scale-up of the lab scale photobioreactor.
TRL	4-5
Stability	
Scale	Lab scale to pilot scale
Energetic conversion efficiency	No need of energy, except for the agitation, compression and temperature control of the culture media
DOI Reference	

<b>Define time: long-term, 10-20 years</b>	
<b>Deliverable, milestone</b>	Experimentation in a pilot scale photobioreactor. Mass and energetic balance. Economic study. Modelling and development of control tools. Scale-up modelling
<b>Solved Challenges / Lifted barriers</b> (in bullet points)	Long-term experiments in order to have real figures for making the different balances. Predicted models for ammonia production, including life cycle analysis coupled with process simulation
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	Long-term experiments at pilot scale in order to have real figures for making the different balances.
TRL	5-8
Stability	Pilot scale – preindustrial pilot

Scale	No need of energy, except for the agitation, compression and temperature control of the culture media
Energetic conversion efficiency	
DOI Reference	

**[Link to TRL level](#)**

**At TRL 5-6:**

Production volume	~40 m <sup>3</sup> NH <sub>3</sub> liq/year
Light harvesting area needed per t/product	~300-500 m <sup>2</sup>
Political/societal barriers to be overcome	none
Market barriers to be overcome	

**At TRL 7-8:**

Production volume	~400 m <sup>3</sup> NH <sub>3</sub> liq/year
Light harvesting area needed per t/product	~3000-5000 m <sup>2</sup>
Political/societal barriers to be overcome	None
Market barriers to be overcome	

**At TRL 9:**

Production volume	~40000 m <sup>3</sup> NH <sub>3</sub> liq/year
Light harvesting area needed per t/product	~3-5 ha
Political/societal barriers to be overcome for market introduction	None

Market barriers to be overcome	
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## 6. Opportunity criteria

What are the criteria that make this technology an opportunity when ready?

Score the potential opportunity from 0 (very low) to 12 (very high).

Each contributor provides an individual score (we average afterwards).

Opportunity criteria	Individual Score
<i>In situ</i> transfer to soilless horticulture (hydroponic greenhouses)	12
<i>In situ</i> coupling to microalgae cultures	10
Space application; micro-ecological life support	5

## 7. Feasibility criteria

What factors determine the feasibility of the final application?

Score the potential feasibility from 0 (very low) to 12 (very high).

Each contributor provides an individual score (we average afterwards).

Feasibility criteria	Individual Score
Energy efficiency	12
Conversion efficiency	10
Separation process	12

## 8. Key learning points

From the exploration of the selected topic, what are the key learning points?

(Resources, enablers, barriers, decision points, knowledge gaps, risks)

<b>Decision points</b>	The number of new selected natural and mutant strains, specially from extremes environments, with high efficiency and robustness
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<b>Knowledge gaps</b>	The chemical mediators which mimics exchange between cyanobacteria and hosts in symbiotic relationships
<b>Risks</b>	

### **Resources**

<b>Suggestion</b>	<b>Please detail</b>
Critical, rare elements	
Non-fluctuating energy sources	
Hydrogen storage	
CO2 storage	
Water purification	
CO2 from the atmosphere	Needed for the reactor start-up; algae cultivation, no need for pH regulation
Concentrated, pure CO2	
Specific, new infrastructures	Photobioreactor equipped with a stripping system
Low-cost, low-carbon electricity	
Renewable energy	Solar processes
Renewable heat	

### **Breakthroughs in key enabling disciplines**

Scale-Up	
System integration	
Novel reactor designs	Photobioreactor equipped with an efficient stripping system and a



	controlled delivery
Novel catalyst materials: earth-abundant, non-toxic, efficient, stable	
Novel absorber materials: earth-abundant, non-toxic, efficient, stable	Only if NH3 would stocked
Standardized life-cycle assessment methodologies	
Further developments in quantitative sustainability analysis	
Strain robustness	yes
Genomic stability	yes
Preservation (culture collection)	yes

**Political/societal/market barriers**

EU-wide, homogeneous regulatory frameworks	
Adaptation/ novel regulations (e.g. genetics, use of waste CO2, ..)	Use of natural strains and of selected strains through evolutionary engineering by (semi)-continuous cultures without introducing foreign genes
EU/national regulations for the deployment of the technology/product	
EU/national incentives for the deployment of the technology/product	
Fast idea protection (patenting, etc.)	

Large capital investment for market introduction	
Standardization of efficiencies, etc.	
Societal acceptance	
Political security	
EU supply chain	

**Funding/research frameworks**

International collaboration	
Funding schemes for demonstrators, pilots, etc.	
Large-scale EU research initiatives	

## Plasma-assisted ammonia synthesis

Technology (how?)								
Targeted product	H <sub>2</sub>	NH <sub>3</sub>	CH <sub>3</sub> OH	EtOH	CH <sub>4</sub>	Jet fuel	CO <sub>2</sub>	Other
		x						
Nature of active material	Solid-state Inorganic		Molecular			Biomolecular		Biological (living cells)
Sunrise approach	PV-powered electrocatalysis		Photoelectrochemical direct conversion			biological and biohybrid direct conversion		Key enabler*, Other
Device category	Electrolyzer		Photo(bio)electrolyzer			Photo(bio)reactor		fermentors, thermocatalytic reactors
Contribution to SUNRISE goals (what?)	Sustainable low-carbon production of <u>carbon-based fuels</u> with high efficiency and competitive costs							
	Sustainable low-carbon production of carbon-based <u>commodity chemicals</u> with high efficiency and competitive costs							
	x	Sustainable low-carbon production of <u>ammonia</u> with high efficiency and competitive costs						
	Sustainable low-carbon production of <u>hydrogen</u> with high efficiency and competitive costs							
	<u>CO<sub>2</sub></u> as a valuable feedstock							
	Sustainable <u>building materials</u> , mineralization, long-lasting C-based materials							
Sustainability criteria	Carbon capture from the atmosphere							
	Carbon capture from point sources/ flue gas							
	Exclusive use of abundantly available, non-toxic and non-critical elements							
	Sunlight as the primary energy source							
	Low resource consumption							
	Solar to products yields tenfold to hundredfold higher than current biomass practice							

Envisaged production system	Decentralized, local production at small scale (households, niche applications)			
	Large-scale production using existing centralized infrastructure			
	Large-scale production necessitating new centralized infrastructure			
Rough timeline (when?)	Short term (2020-25)	Medium term (2025–30)		Long term (2030–50)
	TRL°	4	7	9
Who are the main actors? Who has to be involved?	Chemical Synthesis Industry Industrial Partners for plasma devices and ceramic membranes.			

\* key enabler: fundamental for diverse technological approaches ° TRL: see Annex

Please indicate who gave concrete input; this is **optional**, but allows us to quantify the reach of the proposed technological solution.

<b>Contributors</b>	Matthias Walker (University of Stuttgart), Jakob Barz (Fraunhofer IGB)
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## 1. Short description of the proposed technological solution

<b>Main technological elements, working principle (max. 5 lines, for scientists not expert in the field)</b>	Plasma-catalytic cells use electricity to directly convert N <sub>2</sub> and water (either vapor or liquid) or N <sub>2</sub> and H <sub>2</sub> ammonia in one step. A strong electric field generates a plasma of energetic electrons. Via electron-molecule collisions, these electrons can then dissociate molecules into atoms or create vibrationally excited molecules with higher reactivity. As a consequence, the requirement on catalysis is lowered.
<b>Why is this technology not commercially available right now? (major challenges)</b>	-Many approaches available, but no systematic data basis. -Lab processes, not verified to be long-term operable or up-scalable. -It is not yet shown which process can provide good energy efficiency on a large technical scale. -Separation efficiency of products to be optimized.
<b>What does it take to make it happen? (in short)</b>	New plasma sources allowing for all ranges of temperatures and process pressures, and the optional combination with catalysts will allow several regimes to be tested and to identify efficient processes

	which can be operated 24/7. Early involvement of industry for technical-scale prototype testing. Research approaches can partially be based on other conversion research.
<b>What is the benefit for society? (in short)</b>	<ul style="list-style-type: none"> <li>The renewable sources with their improved efficiency can reduce the overall environmental footprint and can replace the current fossil fuel based centralized ammonia production facilities.</li> </ul> <p>Since ammonia has high energy content and is easy to transport, it has huge potential as a mean to store hydrogen i.e. clean energy. This approach of nitrogen fixation favors decentral production of fertilizers.</p>

## 2. Existing R&I projects

Existing national/EU project	Final objective	TRL	Run-time	Funding Instrument

## 3. State-of-the-Art: where are we now?

Technological solution to be developed in SUNRISE	
TRL	2/3
Cost	n/a
Energetic conversion yield	The best system so far is 14 times less efficient than conventional HB
Stability	n/a
Product separation yield	n/a
Total energy demand [GJ/t]	est. 100-120 GJ/t

Electricity needs [GJ/t]	est. 100-120 GJ/t
Energy demand utilities [GJ/t]	Technology bases on “working on demand”
Steam balance [GJ/t]	n/a
CO2 emissions [tCO2 eq/t] (cradle-to-gate, including feedstock production)	approx. 0
Water consumption	<ul style="list-style-type: none"> <li>- <math>2 N_2 + 6 H_2O \rightarrow 4 NH_3 + 3 O_2</math></li> <li>- Similar to HB process if H2 is used as an intermediate</li> </ul>
Air separation unit	
Compressors	
DOI References	<p>Without catalyst: e.g. DOI: 10.1126/sciadv.aat5778; DOI: 10.1039/C6GC01560C;</p> <p>With Catalyst:  <a href="https://doi.org/10.1038/s41929-018-0045-1">10.1038/s41929-018-0045-1</a>  10.1002/ppap.201600157</p> <p>Review: DOI: 10.1002/cssc.201901211</p>

#### 4. **Available techno-economical analysis:**

<b>DOI Reference</b>	
<b>Summary</b>	

#### 5. **Deliverables, milestones**

Define a set of deliverables that provide a series of stepping stones from the current state to the future application/vision. Define the associated time dimension.

<b>Define time: short-term, 1-3 years</b>	
<b>Deliverable, milestone</b>	Operating plasma systems on lab-scale with standardized measurement technique to achieve comparable yield data
<b>Solved Challenges / Lifted barrier</b> (in bullet points)	<ul style="list-style-type: none"> <li>● Establish appropriate measurement system</li> <li>● Realize at least 4 different set up at different partners</li> </ul>

<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	<ul style="list-style-type: none"> <li>• Development of a plasma-based process for producing NH<sub>3</sub> from N<sub>2</sub> and H<sub>2</sub>O, which operates in a wide range of input parameters at almost maintenance-free condition with a high tolerance against contaminations.</li> <li>• Combined operation of a plasma process with integrated conventional catalysts.</li> </ul>
TRL	4
Stability	4h
Energetic conversion efficiency	
Scale	lab
DOI Reference	

<b>Define time: medium-term, 4-6 years</b>	
<b>Deliverable, milestone</b>	Technical scale prototype
<b>Solved Challenges / Lifted barriers</b> (in bullet points)	<ul style="list-style-type: none"> <li>• Devices that are operating at least 24 h continuously</li> <li>• Professional user interface</li> <li>• Easy and low-cost maintenance</li> <li>• Long-term stability, easy maintenance, user friendly and safe</li> </ul>
<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	Optimization of materials (electrodes) used. Same for the choice of catalysts and for materials used for product separation
TRL	5
Stability	>24 hrs
Energetic conversion efficiency	
DOI Reference	

<b>Define time: long-term, 7-10 years</b>	
<b>Deliverable, milestone</b>	Operating industrial-scale plasma pilot plant in real grid connection
<b>Solved Challenges / Lifted barriers</b> (in bullet points)	<ul style="list-style-type: none"> <li>• Scale-up to high power (100 kW) of the plasma source.</li> </ul>

<b>What was necessary to solve the challenge? Did it depend on advances in other fields?</b>	• Plasma sources working with high powers up to 100 kW
TRL	6
Stability	>5d without short maintenance
Energetic conversion efficiency	50%
DOI Reference	

### Link to TRL level

#### At TRL 5-6:

Production volume	As demanded
Light harvesting area needed per t/product Based on one year on STC: 25 °C, 1000 W/m <sup>2</sup> , AM 1.5, $\eta_{PV} = 0.2$ , Germany 1.000 kWh·a <sup>-1</sup> ·5 <sup>-1</sup> ·m <sup>-2</sup>	≈ 293 m <sup>2</sup>
Political/societal barriers to be overcome	None
Market barriers to be overcome	Product costs

#### At TRL 7-8:

Production volume	As demanded
Light harvesting area needed per t/product Based on one year on STC: 25 °C, 1000 W/m <sup>2</sup> , AM 1.5, $\eta_{PV} = 0.2$ , Germany 1.000 kWh·a <sup>-1</sup> ·5 <sup>-1</sup> ·m <sup>-2</sup>	≈ 251 m <sup>2</sup>
Political/societal barriers to be overcome	None
Market barriers to be overcome	Product costs

#### At TRL 9:



Production volume	As demanded
Light harvesting area needed per t/product Based on one year on STC: 25 °C, 1000 W/m <sup>2</sup> , AM 1.5, $\eta_{PV} = 0.2$ , Germany 1.000 kWh·a <sup>-1</sup> ·5 <sup>-1</sup> ·m <sup>-2</sup>	≈ 234 m <sup>2</sup>
Political/societal barriers to be overcome for market introduction	None
Market barriers to be overcome	Product costs

## 6. Opportunity criteria

What are the criteria that make this technology an opportunity when ready?

Score the potential opportunity from 0 (very low) to 12 (very high).

Each contributor provides an individual score (we average afterwards).

Opportunity criteria	Individual Score
<b>Controllability</b> in time, power and output	12
<b>Scalability</b> from local small to centralized industrial size	10
<b>Tolerance</b> against impurities	10
<b>Low maintenance</b>	9

## 7. Feasibility criteria

What factors determine the feasibility of the final application?

Score the potential feasibility from 0 (very low) to 12 (very high).

Each contributor provides an individual score (we average afterwards).

Feasibility criteria	Individual Score
Energy efficiency	10
Conversion efficiency	8
Separation process	10

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## 8. **Key learning points**

From the exploration of the selected topic, what are the key learning points?  
(Resources, enablers, barriers, decision points, knowledge gaps, risks)

<b>Decision points</b>	<ul style="list-style-type: none"> <li>• Gas/water vapor management</li> <li>• Separation process</li> </ul>
<b>Knowledge gaps</b>	<ul style="list-style-type: none"> <li>• Modelling of the plasma process</li> </ul>
<b>Risks</b>	<ul style="list-style-type: none"> <li>• Insufficient efficiency for plasma and membrane process and therefore high costs</li> </ul>

## **Resources**

<b>Suggestion</b>	<b>Please detail</b>
Critical, rare elements	None
Non-fluctuating energy sources	Process controllable to fluctuating energies, like PV and wind supply. "working on demand"
Hydrogen storage	None
Nitrogen supply	Air fractionation
Water purification	Not known yet
Specific, new infrastructures	Not necessarily
Low-cost, low-carbon electricity	Preferred
Renewable energy	Yes, of course
Renewable heat	Not known yet

## **Breakthroughs in key enabling disciplines**

Scale-Up	
System integration	Interface compatibility to supply chain and to subsequent technologies

Novel reactor designs	Combination of N <sub>2</sub> plasma/ water vapor reactor
Microwave technology	Novel high power ultra-pulsed microwave generators
Separation technique	Not known yet

**Political/societal/market barriers**

EU-wide, homogeneous regulatory frameworks	
Adaptation/ novel regulations (e.g. genetics, use of waste CO <sub>2</sub> , ..)	
EU/national regulations for the deployment of the technology/product	
EU/national incentives for the deployment of the technology/product	
Fast idea protection (patenting, etc.)	
Large capital investment for market introduction	
Standardization of efficiencies, etc.	
Societal acceptance	
Political security	
EU supply chain	

**Funding/research frameworks**

International collaboration	
Funding schemes for demonstrators, pilots, etc.	

Large-scale EU research initiatives	