

Perspective Europe 2030

Technology options for CO₂- emission reduction of hydrogen feedstock in ammonia production



IMPRINT

IMPRINT

Authors

Florian Ausfelder Eghe Oze Herrmann Luisa Fernanda López González

Editor DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V

Responsible for content under the terms of press legislations

DECHEMA e.V. Dr. Florian Ausfelder Theodor-Heuss-Allee 25 60486 Frankfurt am Main Germany

Email: florian.ausfelder@dechema.de

Publication date: January 2022

ISBN: 978-3-89746-237-3



DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V. Theodor-Heuss Allee 25 60486 Frankfurt am Main Germany Phone: +49 (0)69 7564-0 Fax: +49 (0)69 7564-117 E-Mail: info@dechema.de



Study commissioned by Fertilizers Europe Fertilizers Europe asbl Avenue des Nerviens 9-31 1040 Brussels Belgium

Table of content

Introduction	11
1.1 Description of the Fertilizer Industry in Europe	11
1.2 Greenhouse gas emissions reductions in the fertilizer industry	12
Current ammonia production technology	13
2.1 Hydrogen production processes	13
2.2 Haber-Bosch process	14
2.3 Downstream products	14
2.3.1 Urea	14
2.3.2 Nitric acid	15
Technology options	16
3.1 Grey hydrogen	16
3.1.1 Implementing BAT for old and new SMR plants in fertilizer production	16
3.2 Blue hydrogen	17
3.3 Green and yellow hydrogen	18
3.3.1 Water electrolysis	18
3.3.3 Yellow hydrogen	19
3.4 Turquoise hydrogen	21
3.5 Alternative hydrogen sources	22
Methodology	24
4.1 Energy and feedstock demand	24
4.2 GHG emissions	24
4.3 Costs	24
4.4 Regions	25
4.5 Abatement potential	26
4.5.1 Base case scenario	26
4.5.2 Dest case scenario	2/
Evaluation of technology options vs. status quo	28
5.1 Emissions	28
5.2 Energy	29
5.3 Costs	31
5.4 Sensitivity analysis	32
5.5 CO_2 -reduction potential in the ammonia production in 2030	33
5.6 Total abatement potential of the European fertilizer industry in 2030	36
Conclusions	38
Annexes	39
Literature	42
	Introduction 1.1 Description of the Fertilizer Industry in Europe 1.2 Greenhouse gas emissions reductions in the fertilizer industry Current ammonia production technology 2.1 Hydrogen production processes 2.2 Haber-Bosch process 2.3 Downstream products 2.3.1 Urea 2.3.2 Nitric acid Technology options 3.1 Grey hydrogen 3.1.1 Unplementing BAT for old and new SMR plants in fertilizer production 3.2.3 Cereen hydrogen 3.3.1 Water electrolysis 3.3.2 Green nydrogen 3.3.3 Vellow hydrogen 3.3.3 Vellow hydrogen 3.3.3 Vellow hydrogen 3.4 Turquoise hydrogen 3.5 Alternative hydrogen sources Methodology 4.1 Energy and feedstock demand 4.2 GHG emissions 4.3 Costs 4.4 Regions 4.5 Abatement potential 4.5.1 Base case scenario 4.5.2 Best case scenario 4.5.2 Energy 5.3 Costs 5.4 Sensitivity analysis 5.5 Co ₂ -reduction potential in the ammonia production in 2030 5.6 Total abatement potential of the European fertilizer industry in 2030

LIST OF FIGURES

List of Figures

Figure 1.1	Production costs per tonne ammonia of different technologies vs emission savings for the best-case	
	scenario in 2030. Corresponding applicable production capacity is indicated on the bars	4
Figure 1.1	Location and production capacity of ammonia plants in the European Union and Norway	7
Figure 3.1	Conventional ammonia production process (grey hydrogen)	13
Figure 3.2	Conventional ammonia production process with Carbon Capture and Storage (blue hydrogen)	15
Figure 3.3	Electrolyser on-site with air separation unit (green hydrogen)	18
Figure 3.4	Electrolyser off-site with air separation unit (green hydrogen)	19
Figure 3.5	Electrolyser On-site using grid electricity with air separation unit (yellow hydrogen)	19
Figure 3.6	Methane pyrolysis (turquoise hydrogen)	20
Figure 4.1	Decision tree for allocating ammonia plants in different regions to their respective production technologies in the base and best-case scenario for 2030.	28
Figure 5.1	Specific CO_2 emissions of ammonia production (scope 1 + 2) for complete implementation of different process options	30
Figure 5.2	Rate of CO_2 emissions from yellow ammonia to grey ammonia depending on electricity emission factor	31
Figure 5.3	Energy demand of different technologies in 2030 in MWh _{el} for electricity and MWh _{th} for natural gas. * Electricity demand in dashed lines is linked to the production of hydrogen off-site	33
Figure 5.4	Infrastructural changes needed for each technology, relative to grey conventional.	34
Figure 5.5	Specific production costs of ammonia, non-depreciated, full implementation of technologies.	
	*Costs from grey conventional, BAT and blue technologies are depreciated	35
Figure 5.6	Sensitivity analysis of the specific production costs in 2030. *depreciated	36
Figure 5.7	Production costs vs. relative CO_2 -emission savings of different technologies in 2030 compared to grey conventional. *Yellow technology emits more CO_2 than grey conventional	38
Figure 5.8	Cost variation of different technologies in 2030 compared to grey conventional (extrapolated to 2030)	38
Figure 5.9	Emissions savings vs. specific production costs for the base case scenario	41
Figure 5.10	Emissions savings vs. specific production costs for the best-case scenario	41
List of Tab	iles	
Table 4.1	OPEX parameters for the different technologies	25
Table 4.2	Summary of base case and best-case scenarios for nitrate plants	29
Table 4.3	Summary of base case and best-case scenarios for urea plants	29
Table 5.1	CO ₂ avoidance costs of different technologies in 2030 compared to grey conventional. Green (on-site) is represented for region 1.	39
Table 7.1	General costs parameters	44
Table 7.2	Defined average European energy system	44
Table 7.3	Contribution of renewable source in the four defined regions	44
Table 7.4	Average LCOE of the four regions	45
Table 7.5	Cost of renewable electricity in the defined regions	45
Table 7.6	Parameters for electrolysis	46
Table 7.7	Feedstock and energy demand for ammonia production in an "average European ammonia plant" from different technology options	46
Table 7.8	Cost parameters for ammonia production from different technology options.	46

Abbreviations

AC	Avoidance costs
AN	Ammonium Nitrate
ATR	Auto Thermal Reactor
ASU	Air Separation Unit
BAT	Best Available Technique
CAN	Calcium Ammonium Nitrate
CAPEX	Capital Expenditure
CAT	Production costs of alternative technology
CCS	Carbon Capture and Storage
CCU	Carbon Capture and Use
ССТ	Production costs of conventional technology
CMS	Carbon Molecular Sieve
DAC	Direct Air Capture
EAT	CO ₂ emissions of alternative technology
ECT	CO ₂ emissions of conventional technology
EU ETS	European Emission Trading System
EUA	European Union Allowances
GHG	Greenhouse Gas
HTS	High Temperature Shift
LCOE	Levelized Cost of Electricity
LHV	Low Heating Value
LTS	Low Temperature Shift
LPG	Liquified Petroleum Gas
NPK	Nitrogen, Phosphate and Potash Fertilizer
OPEX	Operating Expenditure
PEM	Proton Exchange Membrane
РОХ	Partial Oxidation
PPA	Power Purchase Agreement
PSA	Pressure Swing Absorption
PV	Photovoltaic
SOEC	Solid Oxide Electrolyser Cell
SMR	Steam Methane Reformer
UAN	Urea Ammonium Nitrate

Chemical Symbols

Carbon
Methane
Carbon monoxide
Carbon dioxide
Hydrogen
Water
Nitrogen
Nitric oxide
Dinitrogen monoxide (nitrous oxide)
Nitric dioxide
Ammonia
Ammonium carbamate
Oxides of nitrogen
Nitric acid
Oxygen

Units of Measurement

bar	Unit of pressure, 1 bar = 100,000 Pa
barg	bar pressure above atmosphere
e-	electron
g _{CO2} /kWh	gram CO ₂ per kilowatt hour
GJ	Giga Joule
GJ/tNH ₃	Giga Joules per tonne ammonia
g _{CO2} /kWh	Gram carbon dioxide per kilowatt hour
OH-	Hydroxide ion
kg	Kilogram
kgh ⁻¹	Kilograms per hour
Kt	Kilotonne
kWh	Kilowatt hour (1,000 kWh = 3.6 GJ)
L	Liter (volume)
m	Meter
LHV	Lower Heating Value
Mt/a	Metric tonne per annum
m ³	Cubic Meter (volume)
Nm ³	Normal cubic meter (gas volume)
ppm	Parts per million
ppmv	Parts per million by volume
t	Tonnes (Metric Tons)
TWh	Terawatt-hours (1 TWh = 1 billion kWh)
t _{CO2} /MWh	Tonne carbon dioxide per megawatt hour
€/t _{NH3}	Euro per tonne ammonia
€/t _{CO2}	Euro per tonne carbon dioxide

AUTHORS



Dr. Florian Ausfelder studied chemistry at the Technical University in Karlsruhe and the University of Edinburgh. He obtained his PhD in Physical Chemistry from the University of Edinburgh. He worked as a postdoc at Stanford University in California and with a Marie-Curie Fellowship to the Universidad Complutense de Madrid in Spain. He joined DECHEMA in 2007 and has been in charge of several national and international research projects as well as DECHEMA's energy working groups.

He currently heads the DECHEMA subdivision on energy and climate. He is the co-author of several studies, including on CO_2 utilization, GHG reduction potentials in the chemical industry and recently, the technology study "Low carbon energy and feedstock for the European chemical industry", Roadmap Chemie 2050 (in German), studies on flexibility in the primary industry sector, infrastructure requirements as well as Power-to-X processes (in German).



Eghe Oze Herrmann obtained her bachelor's degree in Chemical Engineering from the University of Port Harcourt in Nigeria and later, a master's degree in Chemical and Energy Engineering from Otto von Guericke Universität, Magdeburg in Germany. She worked as a Process Design and Project Engineer in Oil & Gas, as well as the biogas industry.

She joined DECHEMA e.V. in 2021 and currently works as a Technical Scientific Project Coordinator, in international and national projects, promoting the sustainable use of energy and the mitigation of greenhouse-gases through adoption of Power–to-X technologies in the Energy, Chemical and Petrochemical industry.



Luisa Fernanda López González studied Chemical Engineering at the National University of Colombia and completed a master's degree in Chemical Engineering – Sustainable Chemical Technologies at the Friedrich-Alexander-University Erlangen-Nuremberg. Besides the sustainability component, the main focus of her studies was reaction and process engineering.

She works as scientific project coordinator at the DECHEMA e.V. in Frankfurt am Main since July 2019, where she mainly works on technical aspects like potential analysis and possibilities of reducing CO_2 -emissions in the chemical industry through Power-to-X technologies. In addition, she supports the coordination of projects related to PtX and synthetic fuels.



Executive Summary

Ammonia is a focal point for the development of the hydrogen economy. As the main intermediate product used in fertilizer production, ammonia is also the main building block for mineral fertilizers. Nevertheless, the European fertilizer industry emits considerable amounts of CO_2 and remains an energy and emission intensive industry. However, it has seen a significant decline over time in CO_2 emissions due to improved energy efficiency and even more though in N₂O-emissions through implementation of abatement technologies. Still, ammonia production remains responsible for around 440 Mt/a of global GHG emissions [1].

Scope of Study

With the overarching goal of achieving greenhouse gas neutrality in Europe by 2050, different options for implementation of new technologies with a focus on the timeframe up to 2030 are compared to the existing conventional ammonia production process and evaluated based on their corresponding emissions reductions, energy demand, raw material input, as well as specific ammonia production cost.

The variety of energy consumptions or age structure of European ammonia plants or the large variations of boundary conditions in different European locations were not considered. Instead, an "Average European Ammonia Plant" was used as reference and benchmarked with the new technologies with the boundaries of the ammonia production process as system boundaries. Different process and cost parameters were evaluated to cover relevant and realistic aspects of the fertilizer production process.

The scope of the study includes the CO₂ abatement potential in an average European ammonia plant with an overview on the energy and economic implications of the use of various hydrogen production technologies. Although it addresses Haber-Bosch (ammonia synthesis), urea, and nitric acid, it does not analyse the technology options for reducing emissions in these processes.

EXECUTIVE SUMMARY

This document lays out a basis for the evaluation of the different technology options for hydrogen production, used as feedstock for ammonia, against conventional production and to map potential pathways for the industry's future development.

The timeframe of this study focuses on developments achievable until 2030, with an outlook towards 2050.

Evaluated Technologies

Ammonia is currently produced from nitrogen and hydrogen obtained mainly by steam reforming natural gas via the Haber-Bosch process.

As the leading technology for hydrogen production, Steam Methane Reforming process (SMR), still produces large amounts of emissions despite available improved efficiency options that could reduce CO₂ emissions after the implementation of Best Available Technologies (BAT).

The technology used to produce hydrogen for ammonia synthesis more sustainable, could play an important role in decarbonizing the fertilizer industry. To this end, alternative technologies for hydrogen production are evaluated with a focus on their CO₂ emissions, energy demand as well as production cost.

The pathways for production of hydrogen and subsequently of ammonia, evaluated in this study are shown in the Table below. For simplicity of description, ammonia is designated a colour corresponding to the colour of its hydrogen feedstock, e.g., "blue ammonia" refers to ammonia produced from blue hydrogen.

Key findings and recommendations

To identify opportunities, results from this study regarding reduction of energy consumption, emission reduction potential, specific production costs¹, and avoidance costs were compared.

Opportunities in 2030:

Hydrogen produced via SMR, designated as **grey hydrogen**, presents specific production costs of around $330 \\lefter{specific}$ production costs of around $330 \\lefter{specific}$ in 2020 and 450 $\\lefter{specific}$ the residual plants which implement BAT can reduce energy consumption by 7% and emissions by 8% in 2030. New grey ammonia plants which are BAT-compliant, can also save up to 20% CO₂ emissions in 2030. However, the residual amount of unsaved CO₂ is still emitted into the atmosphere over the life cycle of the new plant. Since the final goal is to achieve emission neutrality in 2050, further investment in improving conventional SMR units is unlikely to take place.

By producing **blue hydrogen** through capturing and storing the emitted CO₂ from the SMR process, CO₂ emissions are reduced compared to grey hydrogen. The main drawback of this option is the difficulty to capture CO₂-emissions arising from the combustion of natural gas used as

Grey hydrogen:	From conventional production process (SMR) using natural gas, i.e., the currently pre- vailing method, which has unavoidable process emissions that cannot continue if 2050 net zero emission target is to be met.
Green hydrogen:	From electrolysis using exclusively renewable electricity for its production. This could be produced on-site or delivered through pipeline. Green hydrogen is the least GHG emitting process, but due to increased green electricity demand, faces challenges from high costs and insufficient access to renewable energy.
Yellow hydrogen:	From electrolysis using the current available electricity mix of the grid. The attractiven- ess of this method is directly linked to emission intensity of the electricity grid.
Blue hydrogen:	From conventional production process (SMR) using natural gas combined with Carbon Capture and Storage (CCS). This method is hampered by availability of adequate storage locations and potentially, cost.
Turquoise hydrogen:	From methane pyrolysis. This method is currently least developed. It has the benefit of having no direct emissions but leads to increased natural gas consumption.

1 Avoidance costs are defined further below in the study and are defined as; the costs differences of the respective technology compared with the conventional technology per tonne of CO_2 avoided (\leq /t_{CO_2}).

fuel, as they are hard to separate due to their low concentration. Ammonia produced entirely from blue hydrogen, has up to 60% CO₂-emission savings compared to conventional grey ammonia in 2030. Its production costs are 450 \in/t_{NH_3} , reaching the same cost level as conventional ammonia the same year. This means that the costs of implementing CCS would be compensated by the CO₂ price that should be paid, if the CO₂ was released to the atmosphere. To fulfill higher CO₂-savings, the fuel for SMR could be replaced by a low carbon fuel (bio- or synthetic fuel). An additional complexity is caused by the limited availability of CCS sites, which depend on accessibility and transport options to the relevant geological formations. The production of blue hydrogen is a suitable option for ammonia production, as separation of CO_2 emissions from the SMR process is already mature and currently implemented in conventional ammonia plants.

A technology option which allows to replace natural gas as feedstock for hydrogen production is electrolysis of water. Water is split into hydrogen and oxygen by applying electricity. The applicability of this method will require a massive increase in electricity consumption by the ammonia industry, compared to current consumption.

Yellow hydrogen is produced by utilizing grid electricity to power electrolysis; hence, its costs and emissions are set by the electricity mix of the host country. In 2030, with the assumptions made for an average electricity grid in Europe, production costs of yellow ammonia $(1,290 \notin I_{NH3})$ are 2.8 times higher than those of conventional grey ammonia. It also emits 39% more CO₂, owing to a large share of fossil fuel in the electricity grid. These results are dependent on the local emission factor of electricity, which shows significant divergence in different regions within the EU [2]. The use of grid electricity for ammonia production only leads to lower emissions, where the emission factor of electricity is lower than 150 g_{CO2}/kWh . With higher emission factors, total emissions from yelow ammonia are higher than those from grey ammonia.

Green hydrogen is produced by exclusively using renewable electricity in electrolysis. It requires a massive increase in generation of green electricity, which is currently not available in sufficient amount for the ammonia industry. To synthetize ammonia, green hydrogen can be produced on-site with renewable electricity or transported to site via pipeline (off-site). For this purpose, the EU countries were categorized into four regions: Southern, Western, Northern and Central Europe, which present different costs for renewable electricity. Specific production costs of green hydrogen produced on-site amount to $760 \notin /t_{NH_3}$ in Northern Europe, $1,350 \notin /t_{NH_3}$ in Western Europe, $1,200 \notin /t_{NH_3}$ in Central Europe \notin /t_{NH_3} and $830 \notin /t_{NH_3}$ in Southern Europe in 2030. 70% CO₂ emission savings in 2030 could be obtained by the exclusive use of green hydrogen in ammonia production. Avoidance costs for 2030 vary from $270 \notin /t_{CO_2}$ to $650 \notin /t_{CO_2}$ for the on-site option and amount to $790 \notin /t_{CO_2}$ for the off-site option. To be economically viable and competitive, efforts should be driven to reduce green electricity price.

Natural gas converted to **turquoise hydrogen** via methane pyrolysis, produces solid carbon rather than gaseous CO_2 as byproduct. Hence, carbon or carbon compounds are stored as solid material instead of being emitted to the atmosphere. Turquoise ammonia if developed, may have the potential of saving up to 56% CO_2 in 2030, with specific production costs of 710 \leq/t_{NH_3} . Its avoidance costs would be 240 \leq/t_{CO_2} in the same year. Other emissions arise from the use of grid electricity. Although this technology shows a significant potential to reduce CO_2 emissions, it is still in development and must be scaledup in order to be considered as an option in 2030.

These evaluated parameters, coupled with the need for low-carbon technology adaptation, present blue hydrogen as a suitable transitional solution for ammonia production until 2030. This allows to reduce emissions partially, while technologies like green or turquoise become economically competitive and/or technological mature. Nevertheless, to implement CCS, the infrastructure for CO₂ transport and storage must be available. It was assumed that blue hydrogen production will take place only near storage facilities and in countries with a positive political view on it. For locations with poor CO₂-storage options, a gradual change from grey to green or yellow hydrogen can be considered, replacing first a low amount of grey hydrogen, e.g., 10%. This is of course highly dependent on the availability of green and low-emission-yellow electricity.

Total abatement potential

To calculate the total abatement potential in the ammonia production in Europe until 2030, two scenarios were defined. The **base case scenario** shows a realistic opportunity for 2030 to reduce emissions in each production plant, based on an assessment of the availability of CCS facilities, the availability and use of renewable energy and reduced grid electricity emissions.

EXECUTIVE SUMMARY

The more optimistic **best-case scenario** assumes that more plants will produce blue and yellow ammonia. In addition, in 2030 it assumes 4% of total considered plant capacity to produce 100% green ammonia and 3% to produce turquoise ammonia. As seen in the figure below, most emissions savings for this scenario are achieved with blue hydrogen, which represents a suitable transition technology to reduce emissions in ammonia production with relatively low costs. Avoided emissions from green, yellow and turquoise technologies are also significant. Efforts to reduce costs of green hydrogen, decarbonize the electricity grid and further develop turquoise hydrogen should be made, to exploit their emission reduction potential for production of ammonia.

Total CO_2 abatement potential during the ammonia production process for Europe in 2030 varies between 13% for base-case and 19% for the best-case scenario.

Opportunities in 2050:

To achieve the European Union's ambition of reaching climate-neutrality by 2050, indirect emissions stemming from grid electricity, would completely reduce scope 2 emissions for yellow, green, blue and turquoise technology options until 2050. This leads to CO_2 savings of 100%² for all technologies except for SMR technologies, due to its combustion emissions arising from natural gas as fuel. Avoidance costs of all technology options will also decrease until 2050.

Turquoise technology, although not mature, and most likely not fully available in 2030, may offer an interesting option for decarbonizing the ammonia industry in the long term. Also, green hydrogen will have an essential role to play for the production of zero carbon ammonia in the long term.



Figure E.1 Production costs per ton ammonia of different technologies vs emission savings for the best-case scenario in 2030. Corresponding applicable production capacity is indicated on the bars

² Production emissions (scope 1 and 2).

1 Introduction

1.1 Description of the Fertilizer Industry in Europe

Plants need nutrients to grow and the latter's availability is directly correlated to yield. As nutrients are removed from the soil by harvesting, there is a need to replenish them which is where fertilizers play a major role. Their use in agriculture has enabled the human population not only to expand, but to produce large amounts of food, enough to feed around half of the world's population. With a predicted increase of global population in the coming years and no prospect of increased arable lands, they will remain critical.

The fertilizer industry can be considered as one of the oldest, large-scale chemical industries. Its roots lie in the development of the Haber-Bosch technology, which enables nitrogen, one of the essential nutrients for crops, to be captured from air. This nitrogen is chemically combined with hydrogen to produce ammonia, the main building block of most fertilizers. At present, the hydrogen supply mainly comes from natural gas and a wide array of fertilizers can then be produced with ammonia, nitric acid, mined phosphorus, calcium nitrate, and potassium inputs. These mineral fertilizers enable half of the global

Due to its critical role in the production of food, ammonia has often been treated as a strategic asset. As a result, the European fertilizer industry has more than 120 production sites scattered throughout majority of European Countries. It employs 74,000 people (including supply chain) and has a turnover of \leq 9.5 BN. The EU imported 3,253 kt and exported 114 kt of ammonia in 2019 [6].

For Europe to become green in industry and agriculture, it needs an efficient and innovative European fertilizer industry, identifying short-, mid- and long-term priorities to advance the transition towards the low-carbon fertilizers.

Finally, while it may be old, the EU fertilizer industry has made significant improvements in the energy efficiency of ammonia production and has greatly reduced N_2O emissions associated with nitric acid production. With these improvements in mind, it will tackle the enormous challenge of reaching carbon neutrality by 2050.

Ammonia production sites in the European Union and Norway are shown in Figure 1.1.

population to be fed. A small fraction of ammonia is used for the manufacture of organic chemical feedstocks for the plastics industry; polyamides, caprolactam, and others, and for the production of explosives (hydrazine, nitriles, etc).

Current developments seen along the ammonia value chain also include small-scale decentralized technology [3], the use of ammonia as potential maritime transport fuel [4] and its use for co-firing in coalfired power plants [5]. Although these efforts might in the future also lead to reduction of greenhouse gas emissions, they are beyond the scope of this study.



Figure 1.1 Location and production capacity of ammonia plants in the European Union and Norway

1 INTRODUCTION

1.2 Greenhouse gas emissions reductions in the fertilizer industry

As of 2020, the European fertilizer industry is responsible for 35 Mt of greenhouse gas emissions, with ammonia production being the dominant emitter with around 30 Mt.³

Combustion of fossil-based energy sources and their use as feedstock in the fertilizers industry, results in the emission of greenhouse gases along the fertilizer production value chain. Pre-eminent of these gases are CO_2 and CH_4 emitted from feedstock mining (natural gas), fossil-based electricity or heat consumption, the steam reforming process and finally, N_2O and CO_2 emitted during agricultural application of fertilizer products.

Ammonia production: On average, 1.9 tonnes⁴ of CO_2 are released on-site to the environment during the production of one ton of ammonia in a conventional method (direct emissions)⁵. The use of external (grid) electricity causes additional CO_2 emissions off-site (indirect emissions)⁵. Consequently, total CO_2 emissions linked to ammonia production depend on electricity used and on heat integration of the site. To reduce or even eliminate these emissions, several technologies can be adapted in the production of fertilizers.

Urea production: most gaseous emissions (nitrogen, oxygen, carbon dioxide, hydrogen, water vapour and inert gases) are released to the atmosphere during the production of urea. CO_2 produced during the steam reforming of methane subsequently reacts with ammonia to form urea. This CO_2 is however released after agricultural field application, therefore its use in urea production is not treated as CCU.

Nitric acid production: Nitrous oxide (N_2O) is formed as an undesirable by-product of the NH₃ oxidation reaction in the nitric acid production process. As its solubility in nitric acid is very low, N_2O , depending on the removal method, is either reduced directly in the oxidation reactor or removed through catalyst units, after the absorption column of the plant and before the tail gas stack. Additionally, not all of the NO and NO_2 is converted to nitric acid and is also emitted if not treated accordingly.

The system boundaries for the current study are the boundaries of the ammonia production process, as it is responsible for most emissions. Within the scope of this study only CO_2 emissions are accounted for and are categorized as follows.

Scope 1 emissions – are generated within process boundaries, they are thus a direct consequence of the production process and include:

- » CO₂ emissions stemming from burning fossil fuels on-site.
- » CO₂ emissions from steam reforming process, even if they are used to produce urea⁶.

Scope 2 emissions are generated outside process boundaries and include: emissions from fossil-based external heat and electricity supply.

Emissions caused by upstream processes (natural gas exploration or transport) as well as emissions from agricultural use or further chemical transformation, except for highly integrated ammonia plants are not within the scope of this study. On-site urea production may limit the amount of feasible absolute decarbonization at a specific site, due to the necessity to provide a CO_2 feed.

³ Provided by Fertilizers Europe

⁴ Provided by Fertilizers Europe

⁵ Ammonia production process is a net exporter of steam, which if integrated in another process could provide process heat and substitute/reduce the use of gas in conventional gas boiler, hence reducing corresponding emissions.

⁶ While the emissions of CO₂ from the decomposition of urea as fertilizer occur on the field, i.e. in the agricultural use of fertilizers, these emissions are still allocated to the original ammonia production in the EU ETS.

2 Current ammonia production technology

Ammonia, a basic chemical product, is produced from nitrogen and hydrogen in the Haber-Bosch process. Nitrogen, in its molecular form, is a readily available substance as it is the main component of atmospheric air. Hydrogen, on the other hand, must first be synthetized starting from other substances like hydrocarbons or water.

Hydrogen, the desired product of the steam reforming process, may be produced from natural gas by three different chemical processes: Steam Methane Reforming (SMR), Partial Oxidation (POX) and Auto-thermal Reforming (ATR).

2.1 Hydrogen production processes

Steam Methane Reforming, as the main process of natural gas conversion into grey hydrogen, is currently the most efficient and economically available technology for hydrogen production. Heavy oil and coal can also be used as feedstocks for the production of ammonia, this requires however, higher energy consumption as well as higher investment and production costs at European economic conditions [7]. Most European ammonia plants currently use natural gas as feedstock.

The SMR process is the most widespread technology at large scale because of its favourable economics and the large number of units currently in operation. It involves the use of heat and steam for the conversion of natural gas to grey H_2 and a substantial amount of CO_2 .

In this process, pre-treated natural gas is fed with steam to a primary reformer, producing synthesis gas (Equation 2.1) with the required heat for the (endothermic) reaction being produced by burning part of the natural gas input.

In the secondary reformer, air is added to the process in order to convert the residual methane and at the same time to introduce to the process the nitrogen required for the synthesis of ammonia [8] by removing the oxygen.

The synthesis gas (CO and H_2) feeds a high temperature shift reactor (HTS) and subsequently a low temperature shift reactor (LTS), where most of the carbon monoxide is converted in the water gas shift reaction, to CO₂ and H₂ (Equation 2.2). The product is purified by removing CO₂ through one of several methods: chemical absorption, physical absorption, or pressure swing adsorption (PSA).

$CH_4 + H_2 0 \rightleftharpoons CO + 3H_2$	Equation 2.1
$CO + H_2O \rightleftharpoons CO_2 + H_2$	Equation 2.2

Hard-to-capture CO_2 emissions from the reformer unit in the SMR process usually contribute the most to GHG emissions, followed by CO_2 from the combustion of fuel for steam generation [9].

Partial Oxidation is a noncatalytic process, in which methane or biogas (or other feedstocks like LPG, naphtha, asphalt, residual oil, petrol coke, or coal) are gasified in the presence of pure oxygen. The first reaction is the reforming reaction (see Equation 2.3 to Equation 2.5), and the second reaction is the water gas shift reaction (see Equation 2.6). The feedstock is fed into the POX reactor where the carbon in the feedstock reacts with oxygen in an exothermic reaction) at temperatures and pressures of about 1200–1500°C and 3 – 8 MPa respectively, producing carbon monoxide (CO). Since there is a lack of oxygen, the reaction does not complete to form carbon dioxide (CO₂). Subsequently, the CO reacts with steam and is converted into H₂ and CO₂.

The H_2/CO ratio ranges between 1.6 and 1.8 and in comparison with natural gas steam reforming, more CO is produced.

The gaseous mixture formed through partial oxidation contains CO, CO_2 , H_2O , H_2 , CH_4 , hydrogen sulfide (H_2S), and carbon oxysulfide (COS) [10].

Steam reaction:

$CH_4 + O_2 \longrightarrow CO + 2H_2$	Equation 2.3
$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$	Equation 2.4
$CH_4 + H_2O \longrightarrow CO + 3H_2$	Equation 2.5

Water gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + 2H_2$$
 Equation 2.6

Auto-thermal Reforming is a combination of both steam reforming (endothermic) and POX (exothermic) reactions [10]. The feedstock for the ATR process can be

natural gas, refinery waste gas, pre-reformed gas, Fischer-Tropsch residual gas, liquefied petroleum gas (LPG) or naphtha [11].

The first reaction is the partial oxidation reaction (see Equation 2.7 2.3), the second reaction is the water gas shift reaction (see Equation 2.62.4) followed by the steam reforming equation 2.5. For this process, preheated and pre-reformed feed gas (natural gas) is fed into the ATR reactor at 30 to 100 bar. It is then reacted with oxygen (partial oxidation) and steam to produce synthesis gas. The gas mixture is passed within the same reactor, over a catalytic bed (nickel catalyst) to achieve a higher hydrogen-rich synthesis gas with an H₂/CO effluent, typical in a ratio of 3:1 to 5:1 [12].

 $4CH_4 + O_2 + 2H_2O \rightarrow 10H_2 + 4CO$ Equation 2.7

The synthesis gas can be used as a feedstock for various synthesis processes, primarily methanol and Fischer-Tropsch synthesis or separated into pure hydrogen, carbon monoxide and carbon dioxide.

2.2 Haber-Bosch process

More than 90% of the world's ammonia production currently applies the Haber-Bosch process [13]. Here, hydrogen and nitrogen react in an exothermic reaction, over an iron catalyst to produce ammonia (see Equation 2.8). The hydrogen required for the process can be obtained from SMR (see section 2.1) but also from alternative processes (see chapter 3). Nitrogen for the reaction, is already part of the synthesis gas in the secondary reformer of the conventional process. In situations where hydrogen is not produced via SMR, an ASU is required to provide the required nitrogen from the air.

In the Haber-Bosch synthesis, nitrogen and hydrogen are compressed to pressures between 120 - 220 bar and sent to an iron oxide catalytic reactor operating at temperatures of 400 - 450°C. The product: gaseous ammonia, is cooled and liquefied at temperatures of -10°C to $-25^{\circ}C$ [13].

 $N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H_0 = -46 \ kJ/mol$ Equation 2.8

The liquefied ammonia acts as feedstock to produce intermediate products like nitric acid (HNO_3) , and downstream products like nitrogen fertilizers (such as ammonium nitrate, urea, UAN, or CAN) and NPK (nitrogen, phosphorous and potassium) fertilizers [7]. With a focus on decarbonizing the fertilizer industry, alternative sources of H_2 are needed for the Haber-Bosch process are evaluated: electrolysis of water (yellow and green hydrogen), SMR process in combination with CCS (blue hydrogen) and methane pyrolysis (turquoise hydrogen).

2.3 Downstream products

While the purpose of this study is to explore the decarbonization of hydrogen production in an ammonia plant, for the sake of completeness we present here two distinct downstream products of the ammonia industry due to their impact on technology choices and emissions.

One is urea, which is produced by directing CO_2 , captured during the SMR process, back to ammonia to produce urea. Urea is relevant because it requires a steady stream of CO_2 , which limits the decarbonization efforts of the relevant ammonia plant.

The second one is nitric acid, which is an intermediate product of ammonia needed for more sophisticated nitrogen fertilizers, such as ammonium nitrates. Nitric acid is relevant, as its production leads to emissions of other GHG, such as: N_2O .

2.3.1 Urea

 CO_2 from the SMR of a nearby ammonia plant is usually used on-site to produce urea and the reaction of ammonia and gaseous carbon dioxide takes place (see Equation 2.9) in a synthesis reactor, operating at relatively high pressures (150 bar) and elevated temperatures (180-210°C) to produce ammonium carbamate. This intermediate product reacts further to urea and water (as shown in Equation 2.10). The product mixture, consisting of ammonium carbamate and urea, is stripped of ammonia with the resultant solution, fed through several decomposers operating at reduced pressures [14]. The urea solution is concentrated by evaporation or crystallization and the crystals melted or granulated to yield pure urea in the form of pills or granules [14].

$2NH_3 + CO_2 \rightleftharpoons [NH_2COO] [NH_4]$	Equation 2.9
$[NH_2COO] [NH_4] \longrightarrow H_2O + (NH_2)_2CO$	Equation 2.10

As a result of the reaction's reversibility, unconverted carbamate is decomposed back to ammonia and carbon dioxide and recycled to the reactor.

 $\rm CO_2$ used as feedstock for urea production is included in emission scope 1.

2.3.2 Nitric acid

Nitric acid, the main feedstock for fertilizer production, is one of the largest sources of N_2O emissions in the European chemical industry.

For its production, compressed, filtered, and preheated air at about 200°C is mixed with ammonia in a chamber, to produce a mixture containing 8-10% ammonia by volume. The ammonia-air mixture is passed through a catalytic reactor, and produces at around 900°C, a gas mixture of nitric oxide, water, oxygen, and nitrogen according to Equation 2.11 [15] with further oxidation of nitric oxide yielding nitrogen dioxide (Equation 2.12).

The nitrogen dioxide is then fed to an absorption tower; where it is absorbed in water, generating a solution of 55 to 60 weight % of nitric acid with NO as a by-product according to Equation 2.13. Some applications require azeotropic nitric acid (68%) which can be reached with further process steps. To increase the concentration of nitric acid to a maximum, it is fed to a distillation column, retrieving a nitric acid stream with concentrations up to 95-98%[15].

$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$	Equation 2.11
$2NO + O_2 \longrightarrow 2NO_2$	Equation 2.12
$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$	Equation 2.13

Depending on combustion conditions, catalyst composition, catalyst state, and burner design, several intermediate reactions may result in the formation of N_2O (a strong GHG). N_2O can however be catalytically or thermally decomposed to avoid emitting it into the atmosphere. as described in Equation 2.14 to Equation 2.16.

$NH_3 + O_2 \longrightarrow 0.5N_2O + 1.5H_2O$	Equation 2.14
$NH_3 + 4NO \longrightarrow 2.5N_2O + 1.5H_2O$	Equation 2.15
$NH_3 + NO + 0.75O_2 \longrightarrow N_2O + 1.5H_2O$	Equation 2.16

3 Technology options

For ammonia synthesis, a stoichiometric amount of hydrogen to nitrogen in a ratio of 3:1 is needed. Through several technologies, hydrogen can be produced from renewable or fossil sources and is assigned the colour schemes as shown in the executive summary.

3.1 Grey hydrogen

Natural gas is catalytically converted by steam reforming into a mixture of carbon monoxide and hydrogen (synthesis gas). The hydrogen, referred to as grey, acts as feedstock for the Haber-Bosch process.

Figure 3.1 represents schematically the production chain of fertilizer from grey hydrogen production to urea and nitric acid.

The main CO_2 emissions of this process are originated in the SMR (scope 1), which uses natural gas as feedstock (process emissions) and as fuel (combustion emissions), as well as in the electricity generation (scope 2). The emissions from the combustion of natural gas (i.e. gas used as fuel) are more diluted and difficult to separate and are therefore usually released into the atmosphere. CO_2 emissions from SMR (process emissions) can be separated and used for other purposes, for example to feed the urea production. These emissions are nevertheless included in the scope 1, as they are released into the atmosphere after field application.

3.1.1 Implementing BAT for old and new SMR plants in fertilizer production

BAT, also known as Best Available Practice, are recommended guidelines, techniques, and limits, set to monitor key plant performance parameters. Environmental performance of production sites can be improved through a combination of recycling or re-routing mass streams, efficiently sharing equipment, increasing heat integration, reducing waste volumes and loads, applying advanced process control systems and implementing effective maintenance practices. By setting energy consumption and emission level limits of process parameters, process plant owners and operators can evaluate and improve the performance of their production plant.

In 2010, average energy demand for existing ammonia plants was 35 GJ/t_{\rm NH_3} [16]. The BAT recommends process,



Figure 3.1 Conventional ammonia production process (grey hydrogen)

energy, equipment, and material modifications for the entire fertilizer production chain and suggests improvements of techniques and methodologies in conventional fertilizer production for optimal plant design, construction, installation, operation, and maintenance, with a priorization on a high level of environmental protection. Specific energy consumption can be reduced to 32 GJ/t NH_3 by applying BAT measures to existing operating plants.

Energy consumption for new ammonia plants is expected to be as low as 28 GJ/ t_{NH_3} by 2020, 27 GJ / tNH_3 by 2030 and 26 GJ / tNH_3 by 2050 and can be achieved when production processes are highly integrated with other industrial processes or heat recovery systems [16].

GHG emissions can be reduced by applying BAT for the SMR process, e.g. by lowering steam to carbon ratios, shifting duties from the primary to secondary reformer, improving synthesis loop efficiencies, the use of burners with low NO_x -emissions and non-iron based ammonia synthesis catalyst [7].

BAT measures applied to nitric acid plants removes N_2O from the process gas stream between the outlet of the ammonia oxidation and the inlet of the absorption tower (built-in) or reduces N_2O after the absorption process (end-of-pipe).

The EU27 countries emitted approximately 7.86 kg_{N20}/ t_{HNO3} in 2005 and 2.9 kg_{N20}/ t_{HNO3} in 2010 [17]. By 2020, all plants were expected to have installed catalytic or thermal abatement technologies with an average emission level of 0.7 kg N₂O per tonne of nitric acid, decreasing further to an average of 0.4 kg in 2030 and 0.3 kg in 2050 [16].

For urea production, unutilized CO₂ can be captured. By doing so, flue gas and reaction emissions are also decreased.

3.2 Blue hydrogen

Blue hydrogen replicates the process of grey hydrogen, with a difference in the application of Carbon Capture and Storage (CCS) (see Figure 3.2). Compared to grey hydrogen, the emitted CO_2 , once captured during the steam reforming process, is compressed into a liquid, transported by pipeline, ship, or road tanker and stored underground.

Usually, due to cost and complexity, only CO_2 process emissions from the SMR are separated. Combustion emissions are approximately up to one third of total SMR emissions and are still emitted to the atmosphere as they are difficult to capture, due to low concentrations of CO_2 in the flue gas. One option to compensate these emissions is the use of low emission fuels rather than



Figure 3.2 Conventional ammonia production process eith Carbon Capture and Storage (blue hydrogen)

natural gas. In cases where it is still desired to produce urea from blue hydrogen, an external CO_2 source must be introduced into the process and the pathway to nitric acid would be a more attractive option.

The main barriers to the development of CCS technology, next to political and societal acceptance, are both economic and technical, as its attractiveness depends on associated costs of development, technological innovation and economies of scale. An additional issue is availability and proximity of adequate storage space.

3.3 Green and yellow hydrogen

Green and yellow hydrogen are produced in an electrolysis process, described in the next section with the only difference being the source of electricity. While green hydrogen is produced exclusively from renewable energy sources like wind or PV, yellow hydrogen proceeds from grid electricity which is not necessarily green, due to the contribution of fossil fuels to the electricity mix.

Unlike the SMR process, which takes nitrogen from the air and can accommodate the presence of other atmospheric gases (oxygen, argon, etc.), the production of ammonia from green or yellow hydrogen requires pure nitrogen, which must be additionally separated from the atmospheric air (see information box on the air separation unit).

3.3.1 Water electrolysis

In water electrolysis, electricity is used to electrochemically split water mainly into hydrogen (H_2) and oxygen (O_2) . An electrolyser is made up of two electrodes (anode and cathode), a membrane and a solution (electrolyte). There are three main types of electrolytic processes to split water: Proton Exchange Membrane (PEM), Alkaline Electrolysis and high temperature Solid Oxide Electrolyser SOEC.

Alkaline electrolysers are the most technologically mature system and in installations up to 165 MW in operation. PEM electrolysers are catching up and installed units reach tens of MW load. SOEC is the least mature technology, with small systems becoming commercial [18].

In **Proton Exchange Membrane** electrolysis, water dissociates at the anode, into oxygen and positively charged hydrogen ions (protons). As electrons from electricity flow through an external circuit, hydrogen ions selectively move through the membrane, to the cathode of the PEM; combining with electrons to produce hydrogen gas. The hydrogen is treated, stored and ready for use as feedstock in the Haber-Bosch process.

Anode:

$$H_2 O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$
 Equation 3.1

Cathode:

$$2H^+ + 2e^- \rightarrow H_2$$
 Equation 3.2

Global reaction:

$$H_2O + electricity \rightarrow H_2 + \frac{1}{2}O_2$$
 Equation 3.3

Alkaline electrolysis operates via transport of hydroxide ions (OH⁻) through the electrolyte. As water dissociates into hydrogen and hydroxide ions in the cathode, the hydroxide ions migrate from the cathode to the anode, with hydrogen generated on the cathode side.

Technology	ALK	PEM	SOEC
Maturity	Commercialized	Commercialized	Research & Development
Installed Capacity range as of 2020 in Europe (kW) [19]	50-5000	100-6000	150
Average Electricity Input (kWhel/kgH ₂) in by 2030 [20]	51	47	41
Investment Costs EUR/kW[20] [21]	800-1500	900-1850	2200 – 6500
Average output H_2 pressure [bar] [21]	10	35	10
Average Operating Temperature (°C) [20]	60-80	50-70	700-800
Electrical Efficiency (LHV, %) [20]	65-68%	57-64%	72-88%
$Max H_2$ production rate ($Nm_3//h$) [21]	10	5	5

~	. 1			
(:	atk	ററ	d	٠.
C (μu	10	uu	- •

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	Equation 3.4

Anode:

 $20H^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$ Equation 3.5

Global reaction:

 $H_2O + electricity \rightarrow H_2 + \frac{1}{2}O_2$ Equation 3.6

In **solid oxide electrolysis** (SOEC), electricity splits water at the cathode into hydrogen and oxygen at temperatures of 700°C to 1000°C. The oxygen ions are transferred through a solid ionic membrane where it combines with electrons, forming oxygen molecules.

Cathode:

$H_2O + 2 e^- \longrightarrow H_2 + O^{2-}$	Equation 3.7
Anode:	
$20^{2-} \rightarrow 0_2 + 4e^{-}$	Equation 3.8
Net reaction:	
$2H_2O \longrightarrow 2H_2 + O_2$	Equation 3.9

3.3.2 Green hydrogen

To produce green hydrogen, 100% renewable (wind, solar, hydro, geothermal, biomass, etc) electricity is used to power the electrolyser.

This replacement of hydrogen from SMR with green hydrogen, has the advantage of not emitting CO_2 nor other GHGs. There are no direct (scope 1) emissions (since water H2O, not methane CH4, is used as source for hydrogen) and given the use of green electricity, there are also no indirect (scope 2) emissions.

Two scenarios for green hydrogen were examined: green hydrogen produced on-site and green hydrogen supplied to the ammonia production site via pipeline. If the green hydrogen is produced on-site, green electricity in sufficient quantities and water are required as shown in Figure 3.3. For this purpose, a decentralized renewable electricity production plant can be connected directly to site, with the disadvantage of low full load hours per year, a discontinuous production, and the need for an electricity storage system. The second possibility is a PPA contract with continuous supply of green electricity⁷ if the regulatory regime allows this and treats such



Figure 3.3 Electrolyser on-site with air separation unit (green hydrogen)

⁷ Within the system boundaries of an ammonia plant, green electricity supply can be ensured via Power Purchase Agreements (PPAs). Within the system boundaries of the overall electric grid, net reductions of CO₂-emissions only occur, if additional renewable electricity is used. Otherwise, renewable electricity is just shifted from one (average) consumer to another.



Figure 3.4 Electrolyser off-site with air separation unit (green hydrogen)



Figure 3.5 Electrolyser on-site using grid electricity with air separation unit (yellow hydrogen)

hydrogen as equally green compared to green hydrogen produced with green electricity generated on-site.

With ammonia being a commodity chemical produced in large quantities (on average 400,000 t/a in Europe) per plant, the second option seems to be the most appropriate for the process.

Due to the disparate cost of producing renewable electricity in various countries, this study categorized the EU into four regions (see section 4.4), to obtain a better representation of their levelized cost of electricity (LCOE). For sake of simplicity, these were designated as region 1 (Southern Europe), region 2 (Western Europe), region 3 (Northern Europe) and region 4 (Central Europe).

For green hydrogen **off-site**, the hydrogen for the reaction with nitrogen, is continuously fed to the production site via pipeline as shown in Figure 3.4.

3.3.3 Yellow hydrogen

Yellow hydrogen (see Figure 3.5), like green hydrogen, is produced through the process of electrolysis, with the electricity obtained from the grid, which may have been partially or completely generated from fossil-based sources, depending on the energy mix of the host country, as at the time of deployment. Indirect emissions and the price of electricity will therefore depend on the given country of production.

As both green and yellow hydrogen do not have any process CO_2 -emissions, the CO_2 required for the urea production should eventually be obtained from another source.

3.4 Turquoise hydrogen

Turquoise hydrogen could be produced through a stillto-be-finalized technology called methane pyrolysis. It would consist of thermally splitting methane into its elements, namely solid carbon and gaseous hydrogen as shown in Equation 3.10. The C-H bonds are cracked at temperatures between 700-1800^oC, splitting methane into hydrogen and carbon in a reactor. Unreacted CH_4 is separated from H_2 , and recirculated to the reactor while other hydrocarbons present are similarly cracked [22].

$$CH_{4(g)} \rightarrow C_{(s)} + 2H_{2(g)}$$
 Equation 3.10

Similar to the other technology options, production of turquoise hydrogen does not have process emissions which could be used in the urea production. For subsequent urea production from the synthetized ammonia, another source of CO_2 is required.



Figure 3.6 Methane pyrolysis (turquoise hydrogen)

Info box – Air Separation

Air comprises by volume of 78.08% nitrogen, 20.95% oxygen, 0.93% argon: and a small amount of neon, helium, krypton, and xenon [23]. An air separation unit extracts the nitrogen needed to react with hydrogen for ammonia synthesis.

Three main methods separate nitrogen from air: cryogenic distillation, pressure swing absorption (PSA), and membrane separation.

The **cryogenic air separation** process is the most applied air separation technique in medium to large scale gas production plants. Here, incoming air is filtered, compressed and cooled and impurities like water and CO_2 are removed [24].

The purified air passes through a heat exchanger which brings the air feed to cryogenic temperature of approximately -185° C, and is then sent to one or two distillation columns to separate air components (gaseous nitrogen, oxygen, and liquid argon) according to their different boiling temperatures [25]. Pure N₂ gas is collected at the top of the column and stored with purities of nitrogen typically very high.

In the **Pressure Swing Adsorption** (PSA), dried, cleaned, and compressed air is sent into adsorber towers filled with a carbon molecular sieve (CMS).

During pressurization of the CMS bed, oxygen is preferentially absorbed on the surface of the carbon pellets at high pressure, while nitrogen is retained in the feed gas flow. The nitrogen separation process is stopped before the CMS comes to the adsorption capacity limit and the feed air supply is switched over to the second adsorber tower. Nitrogen can be obtained with a purity of up to 99,995% vol. [26].

The saturated CMS in the first vessel is regenerated by lowering the pressure and removing adsorbed gas from the CMS through a vent line to the atmosphere. A control valve is set to alternate adsorption and desorption between the two CMS towers, resulting in a continuous nitrogen generation.

The membrane in the **Membrane Separation** process, consisting of hollow polymer fibres, produces nitrogen from the air fed into it. As oxygen, water vapor and carbon dioxide cross rapidly through the membrane walls and are vented as waste gas to the environment, they leave behind nitrogen which can be concentrated and stored as product. The dry gas with up to 99.5% vol nitrogen is then sent into the tanks[26].

3.5 Alternative hydrogen sources

Biomass

Biomass as a renewable energy resource with varied compositions, may originate from forest and agricultural waste, municipal solid waste, livestock waste, energy crops etc. Hydrogen may be obtained from biomass thermochemically or biochemically.

Thermochemical processes:

Thermochemically, hydrogen is produced through gasification, pyrolysis or combustion. Gasification is the incomplete combustion or partial oxidation of carbonaceous material into carbon monoxide, hydrogen, and carbon dioxide (as displayed in Equation 3.11) at a controlled amount of oxygen or steam. Due to the varying chemical composition of biomass, the hydrogen content in its resulting synthesis gas can vary widely from 3% -45% depending on the feedstock and processes used [27].

Biomass + $aH_2O \rightarrow xCO + yH_2 + zCO_2$ Equation 3.11

The theoretical efficiency of the biomass gasification process depends on temperature, pressure, amount of steam and amount of oxygen used.

Fluidized bed gasifiers⁸ using catalysts operate at temperatures greater than 650° C while fixed bed reactors operate in the range between $600-800^{\circ}$ C.

⁸ In fluidized-bed gasifiers, the catalyst flows freely with suspend biomass or feedstock particles in an oxygen-rich gas. Thus, the bed acts as a fluid within the gasifier, promoting efficient mixing of biomass particles, to achieve high conversion rates of feedstock. Fixed bed reactors have fixed catalytic beds which progressively deactivates as biomass reacts to form products. Reaction continues until blockage or deactivation of catalyst pores, necessitating catalyst regeneration or replacement.[28]

Pyrolysis is the decomposition of a solid fuel by heat (at 450° C) in the absence of an oxidizing medium, as shown in Equation 3.12.

While slow pyrolysis takes several hours to complete and results in biochar as the main product, fast pyrolysis which is widely applied, yields up to 60% bio-oil and takes seconds to complete. In addition, it gives 20% biochar and 20% synthesis gas (H_2 , CO, CH₄, C₂H₂, C₄H₄) and liquids [29].

 $Biomass \rightarrow Bio \ oil + Char + xH_2 + yCO + zCH_4$

Equation 3.12

Liquid fractions or bio-oils through subsequent reforming, are most promising for hydrogen production (see Equation 3.13).

Bio oil + $aH_2O \rightarrow xCO + yH_2$ Equation 3.13

Besides the low hydrogen content in biomass and low conversion yields, production from biomass is still an immature technology. Complex processing, production and transport costs of hydrogen even with reasonable energy efficiencies, cannot economically compete with natural gas reforming.

Combining hydrogen production from biomass with CCS could, however, be an option to create so-called "negative emissions", which may have a role to play in the future.⁹

Biochemical processes:

Hydrogen can also be synthetized from biogas instead of natural gas, which is produced from the anaerobic digestion of energy-rich organic biomass. Typical biogas contains mostly of methane and carbon dioxide with little amounts of water vapor, hydrogen sulphide, oxygen, nitrogen, ammonia, hydrogen and trace gases [31]. The amount of methane produced from biogas depends on the energy content of the decomposed raw material. Firstly, biogas is converted to biomethane at natural gas quality, and subsequently undergoes the SMR process to obtain hydrogen. Methane consists of about 25% hydrogen in mass. Hence, the production of hydrogen from biogas depends on the methane content in biogas, the purity of methane after biogas processing, and its conversion efficiency to hydrogen [32].

Another approach to hydrogen production from biogas is the use of a catalytic membrane reactor. Although still in its testing phase, the reactor integrates hydrogen production and separation in a single step, leading to over 70% reaction conversion at 500-550°C.[33].

⁹ The total CO₂ present in a biomass processing plant could include CO₂ emissions from the conversion of biomass in a large-scale facility, as well as the CO₂ absorbed by the biomass during growth. Hence, the application of CCS technology in a biomass plant captures and stores the CO₂ produced during conversion and that taken up from the atmosphere (negative emissions), provided the biomass is sustainably grown and harvested.[30]

4 Methodology

This study evaluates the different ammonia production pathways as well as the potential of CO_2 abatement for the fertilizer industry in Europe. The study was carried out on a regional and territorial basis for an **"average European ammonia plant"**, which was assumed to have a capacity of 500,000 t_{NH3} per year, defined prices for grid electricity, natural gas and CO_2 (see values in Annex 1) and a defined emission factor for grid electricity. Additionally, collected data were aggregated with several assumptions.

The methodologies used to calculate energy and feedstock demand, emissions and costs are presented in the following sections.

4.1 Energy and Feedstock demand

Electricity and natural gas demand for grey, blue and turquoise technologies were assumed constant over time. For yellow and green on-site ammonia options, the electricity demand for electrolysis decreases over time, due to an increase in the electrolysis efficiency from 66% in 2020 to 76% (LHV) in 2050. Electricity demand for utilities like pumps and compressors was assumed to be covered with grid electricity for all technologies and was considered constant until 2050.

Energy and feedstock demand parameters for all technologies are shown in Annex 2, Table 7.7.

4.2 GHG Emissions

CO₂ emissions were separated into two scopes:

Scope 1 emissions are only present in grey and blue ammonia technologies due to the use of natural gas for the SMR on the production site. These emissions remain constant over time, as the demand of natural gas is not subject to any variation. For calculation purposes, an emission factor of 0.2012 t_{CO_2} /MWh for natural gas¹⁰ was assumed.

Scope 2 emissions are indirectly linked to ammonia production using grid electricity. The emission factor of electricity depends on the energy mix used in its generation and the location of the plant. For this study, average European values were assumed: 375 g_{CO_2} /kWh, 250 g_{CO_2} /kWh, 125 g_{CO_2} /kWh and o g_{CO_2} /kWh for 2020, 2030, 2040 and 2050, respectively. To calculate emissions from electricity of a specific ammonia plant, local emission intensity of the electricity grid was used.

4.3 Costs

Costs for all plants were divided in Capital Expenditures (CAPEX) and Operational Expenditures (OPEX).

For CAPEX, only investment costs for the ammonia production plants were taken into account. Conventional grey and blue plants were assumed to have no capital cost, since they already exist and are operational.¹¹ CAPEX of yellow and green ammonia (on-site) was split into investment costs for the electrolysis and Haber-Bosch process.¹² CAPEX of turquoise ammonia includes investment costs for both methane pyrolysis and the Haber-Bosch plant. The assumed values for these costs are shown in Annex 2, Table 7.6 and Table 7.8.

To estimate the annual payments required to pay back the investment costs in a period of n years and with an interest rate i, Equation 4.1 was used, with n and i equal to 20 years and 8%, respectively.

Annuity =
$$CAPEX \times \left[\frac{i}{1 - (1 + i)^{-n}}\right]$$
 Equation 4.1

OPEX encompasses all costs required for plant operation, including feedstocks, fuels, maintenance costs, etc. These parameters are listed in Table 4.1 for each technology with some relevant comments. Price assumptions for each parameter are listed in Annex 2, Table 7.8. Prices for grid electricity and natural gas were assumed constant over time, to enable the sensitivity of

¹⁰ Based on an assumed average value of 57 $t_{\rm CO_2}/TJ$ [34].

¹¹ Slightly higher costs for blue ammonia vs. grey ammonia resulting from additional CCS infrastructure cost have been ignored.

¹² Existing plants can only partially be adjusted to operate with an external hydrogen source, since hydrogen generation and the Haber-Bosch process are currently highly integrated.

	Grey	Yellow	Green (on-site)	Green (off-site)	Turquoise	Blue
Electricity	Grid	Grid for electrolysis and other processes	Green for electrolysis and grid for other processes	Grid	Grid	Grid
Natural gas	As feedstock and fuel	-	-	-	As feedstock	As feedstock and fuel
Water	For SMR	For electrolysis	For electrolysis	-	-	For SMR
Air separation	-	For nitrogen production	For nitrogen production	For nitrogen production	For nitrogen production	-
Green hydrogen	-	-	_	For Haber- Bosch process	-	-
Hydrogen transport	-	-	-	Green hydrogen via pipeline	-	-
CO ₂ (scope 1)	ETS from natural gas as feedstock and fuel	-	_	-	-	ETS from natural gas as fuel
CCS	_	-	_	-	_	CO2 (from natural gas as feedstock) transport and storage
Maintenance	4,7% of CAPEX	4,7% of CAPEX	4,7% of CAPEX	4,7% of CAPEX	4,7% of CAPEX	4,7% of CAPEX

 Table 4.1 OPEX parameters for the different technologies

total cost to other parameters. A European average was hypothesized for parameters dependent on plant location, like electricity and natural gas prices. Hence, it was necessary to carry out a sensitivity analysis (section 5.4), varying one parameter at a time, while holding others constant, and analysing the change in total costs.

Specific production costs were estimated afterwards. Non-depreciated costs result from the sum of CAPEX and OPEX, while depreciated costs are only represented by OPEX.

Avoidance costs were defined and estimated as shown in Equation 4.2 and represent the costs of saving one mass unit of CO_2 :

$$AC = \frac{C_{AT} - C_{CT}}{E_{CT} - E_{AT}}$$

Equation 4.2

AC: Avoidance costs $[\notin/t_{CO_2}]$

 C_{AT} : Production costs of alternative technology [€/ t_{NH_3}] C_{CT} : Production costs of conventional technology [€/ t_{NH_3}] E_{CT} : CO₂ emissions of conventional technology [t_{CO_2}/t_{NH_3}] E_{AT} : CO₂ emissions of alternative technology [t_{CO_2}/t_{NH_3}]

4.4 Regions

For the calculations of green ammonia costs, the European Union and Norway were divided in four regions. For sake of simplicity, these were designated as region 1 (Southern Europe), region 2 (Western Europe), region 3 (Northern Europe) and region 4 (Central Europe).

4 METHODOLOGY

Evaluated representative countries for each region are Italy, Spain and France for region 1; Austria, Belgium, Germany and Netherlands for region 2; Norway¹³ as region 3, and Croatia, Hungary and Slovakia representing region 4.

For the estimation of electricity prices for regions 2 and 4, the LCOE for the technologies present in the respective regions and their energy contribution, were used to calculate the weighted-average costs for 2020. These 2020 costs were multiplied by a factor of 1.5 to obtain a final price of electricity. For region 1, prices for 2020 until 2030 were taken from [35]. As region 4 is just represented by Norway, electricity prices for 2020 were taken from [36]. For all regions, these prices were subsequently extrapolated until 2050. The parameters and final prices used in this study are shown in Annex 1, Table 7.3 to Table 7.5.

These four regions were only used for the calculation of ammonia costs from on-site green hydrogen.

4.5 Abatement potential

To calculate the total abatement potential of ammonia production in 2030, a base-case and a best-case scenar-io were developed.

The decision tree in Figure 4.1 is a general representation of the approach used on all individual ammonia production plants included in this study and was the base for building the base and best-case scenarios for 2030.

4.5.1 Base case scenario

Downstream nitrates production:

As 100% green and 100% yellow technologies will not be economically feasible and turquoise hydrogen, probably still at its infant stages until 2030, these options were not considered for the base case scenario.

The first considered feasible option for 2030 is blue hy-

drogen, due to its relatively high emissions savings and comparatively lower costs to other technologies. Blue hydrogen is a feasible option in the ammonia industry, since the separation of CO₂ from the SMR is an existing state of the art technology. There are two existing commercialized offshore CCS facilities operated in Norway: Snøhvit CO₂ and Sleipner CO₂ storage, and additional facilities under planning in Norway and the Netherlands, which should be operational in 2024 [37]. Plants located nearby or having access to a port in the western or northern coast of Europe, are accordingly expected to have access to this technology by 2030, with exception of plants which produce urea (see explanation below). In addition to the above-mentioned considerations for the adaptation of CCS technology, general local acceptance and support of this



Figure 4.1: Decision tree for allocating ammonia plants in different regions to their respective production technologies in the base and best-case scenario for 2030.

¹³ Norway is included in this report although not a member if the European Union.

technology by the government were also factored in. Under these assumptions, blue ammonia could be applied to 22% of the total capacity of ammonia plants (for nitrates) in the European Union.

A combination of 10% yellow and 90% grey hydrogen was considered for ammonia plants in countries with expected grid electricity emissions lower than 150 g_{CO2} / kWh by 2030. It was assumed that current emission factors will reduce by 33% in each country until 2030, resulting in the application of this technology, for 28% of total ammonia production capacity (for nitrates).

Another 37% of the total ammonia plants capacity (for nitrates) will presumably produce 90% grey and 10% green hydrogen, owing to their renewable electricity generation potential by 2030, while the remaining plants (13%) would continue to use grey conventional SMR process till 2030.

Downstream urea production:

Being the subsequent process of approximately one third of all ammonia plant capacities, urea plants utilize CO_2 from the SMR as feedstock. To secure feedstock supply, it was assumed that the possibility of partially reducing emissions for these plants, will be through a combined technology of 10% green and 90% grey hydrogen¹⁴. For the base-case scenario, 59% of all urea plants will implement 10% green and 90% grey technology while the remaining 41% will remain as grey plants by 2030.

4.5.2 Best case scenario

Downstream nitrates production:

The proportion of plants producing blue hydrogen was increased to 29%, assuming some additional plants will have the capacity to transport CO_2 to the storage facilities. It was also assumed that one plant will produce 100% green and another 100% turquoise ammonia (4% and 3% of total capacity respectively). The proportion of plants applying 10% yellow ammonia was not changed and plants producing 10% green ammonia were reduced to 33%, because of one plant shifting to produce 100% green ammonia.

Downstream urea production:

For the best-case scenario, 81% of all urea plants were assumed to adopt 10% green and 90% grey technologies while 19% will continue to run their plants based on grey technologies. This was evaluated based on the possible availability of renewable energy in those countries by 2030.

The described distribution for both scenarios is summarized in Table 4.2 and Table 4.3.

Technology	Requirements	% Base case	% Best case
Grey conventional	All production plants, which do not fulfill the requirements for other technology options	13%	3%
Blue	Access to a CCS facility via port or land and societal acceptance	22%	29%
Turquoise	Rapid technological development required	0%	3%
Yellow	Not considered for 2030 because of high costs and grid emissions	0%	0%
90% grey, 10% yellow	Production sites with grid emission factor lower than 150 g/kWh	28%	28%
Green	Low specific price of green hydrogen and access to hydrogen pipeline	٥%	4%
90% grey, 10% green	Low specific price of green electricity	37%	33%

 Table 4.2 Summary of base case and best-case scenarios for nitrate plants

Table 4.3 Summary of base case and best-case scenarios for urea plants

Technology	Requirements	% Base case	% Best case
Grey conventional	All production plants, which do not fulfill the requirements for other technology options	41%	19%
90% grey, 10% green	Low specific price of green electricity	59%	81%

14 If all ammonia would be used to subsequently produce urea, the amount of CO₂ produced in the steam reforming would not suffice. However, in general, only a part of the overall ammonia production is used as urea feedstock, allowing for a small abatement due to alternative hydrogen generation.

5 EVALUATION OF TECHNOLOGY OPTIONS VS. STATUS QUO

5 Evaluation of technology options vs. status quo

The production of ammonia from different hydrogen sources in relation to energy consumption, emissions, feedstock demand and costs, were studied and compared with the objective of assessing options, for a cost effective and sustainable transformation to H_2 as a feedstock. All calculations are based on the values and assumptions summarized in Annex 1 and Annex 2.

For simplicity of description, ammonia is designated a colour corresponding to the colour of its hydrogen feedstock, e.g., "blue ammonia" refers to ammonia produced from blue hydrogen, as described in the previous chapter.

5.1 Emissions

Emissions from ammonia production originate mainly in hydrogen production from feedstock conversion and energy consumption (combusted fuel and purchased electricity). Figure 5.1 represents specific CO_2 emissions (scope 1 and 2) from ammonia production based on applied technology. Production of ammonia for the "average European ammonia plant" from conventional **grey hydrogen** in 2020 emits approximately 2.0 t_{CO2}/t_{NH3} , with contributions of 58% and 31% from the processing of natural gas as feed-stock and fuel (scope 1) and 11% from the use of electricity (scope 2). Emissions from the European electricity grid gradually reduce until 2050 and therefore, emissions from conventional ammonia decrease slightly until this year. Although the application of BAT to an existing or a new SMR plant could reduce emissions to 1.8 or 1.6 t_{CO2}/t_{NH3} respectively, this technology does not develop a zero emissions pathway until 2050, due to continuing direct process emissions. Hence the unlikelihood of further investments in this technology.

Yellow ammonia generates 4.2 t_{CO_2}/t_{NH_3} (scope 2) in 2020, more than double the CO₂ emissions from conventional SMR process, due to the high specific emission factor of average electricity from the power grid. This value gradually declines until it reaches approximately equal tonnes of CO₂ as grey ammonia in 2037 and be-



Figure 5.1 Specific CO_2 emissions of ammonia production (scope 1 + 2) for complete implementation of different process options

comes emission free in 2050, if decarbonization of the European electricity grid is achieved in this year.

However, emissions from yellow ammonia are strongly dependent on the emission factor of grid electricity. To calculate the maximal tolerable emission factor for grid electricity, CO₂ emissions from yellow and grey ammonia were plotted, depending on the specific electricity emission factor. The results are shown in Figure 5.2. A specific emission factor of about 150 g_{CO2} /kWh in the electric grid reaches parity of yellow with grey ammonia production. In order to achieve CO₂ savings with yellow ammonia, the emission factor of the grid electricity must be lower than 150 g_{CO_2}/kWh . The considerable differences in the grid electricity mix and hence in indirect emissions in European countries will have a decisive impact on attractiveness of yellow hydrogen for different installations, depending on their location. For example, in 2019, the carbon intensities in France and Poland were 56 $g_{CO_2}/$ kWh and 751 g_{CO2}/kWh, respectively [2]. The assumption of the average European CO₂ emission intensity of electricity is found in Annex 1, Table 7.2.

Ammonia from on-site and off-site **green hydrogen** utilizes the available electricity from the grid for all process equipment like pumps and compressors and, therefore, emissions up to 0.9 t_{CO_2}/t_{NH_3} were generated in 2020 and steadily fall to zero by 2050.

The use of grid electricity (scope 2) emits approximately 1.3 t_{CO2}/t_{NH3} in **turquoise ammonia**, as it is the only process emission source for this technology. Turquoise ammonia is expected to become emission free in 2050, when the emission factor of grid electricity becomes zero. In comparison, 0.9 t_{CO2}/t_{NH3} are released by blue ammonia production in 2020, from both grid electricity use and energy consumption through natural gas combustion in the SMR.

In summary, from 2020 – 2050, all studied technologies for ammonia production are observed to emit less tonnes of CO_2 per tonne of NH_3 compared to their current rates, but only green, turquoise and yellow could reach emission neutrality in 2050.

5.2 Energy

Electric and thermal energy consumptions of the various evaluated technologies were calculated, with results for 2030 shown in Figure 5.3. Energy consumption of the conventional **grey ammonia** was considered constant over time, and consumption of natural gas as feedstock



Figure 5.2 Rate of CO₂ emissions from yellow ammonia to grey ammonia depending on electricity emission factor

5 EVALUATION OF TECHNOLOGY OPTIONS VS. STATUS QUO



Figure 5.3 Energy demand of different technologies in 2030 in MWhel for electricity and MWhth for natural gas. * Electricity demand in dashed lines is linked to the production of hydrogen off-site

(5.8 MWh/ $t_{\text{NH}3}$) remained the same for all three SMR technologies (conventional and BAT compliant old and new plants). Fuel consumption of natural gas amounts to approximately 3.1 MWh/ t_{NH3} for conventional plants. There was a decrease in the consumption of natural gas as fuel (up to 13% and 39%) and of electricity (up to 45% and 91%), after BAT recommendations were applied to old and new SMR-based plants, respectively.

On-site green ammonia and yellow ammonia require equal amounts of electricity (10,9 $MWh_{el}/t_{\rm NH3}$ in 2030, out of which 8,5 $MWh_{el}/t_{\rm NH_3}$ are due to the electrolytic



Figure 5.4 Infrastructural changes needed for each technology, relative to grey conventional

hydrogen generation), with the only distinction: their source of electricity. An ammonia plant with capacity of 500,000 t/a and operating continuously for 8,760 hours per year, would require an electrolyser unit with a power of 480 MW to replace the demand for grey hydrogen with green hydrogen. Therefore, there would be the need for significant infrastructure development, which is beyond the scope of the study.

Ammonia production from purchased pipeline-transported green hydrogen, requires only 20% of the electricity demanded by yellow and green on-site-produced hydrogen. This is because the electrolysis process does not take place in the production site. A drawback of this option is the dependance on a continuous supply of green hydrogen to the production site, which would require additional infrastructure costs to address the risk of supply disruptions.

Natural gas consumption as feedstock and fuel, and electricity demand of **blue ammonia** plants are roughly the same as that for grey conventional plants.¹⁵

Turquoise ammonia plants demand double as much natural gas (feedstock) than conventional technologies, since one mole of methane produces only two moles of hydrogen (Equation 3.10) in contrast to the four moles of hydrogen produced in the SMR (Equation 2.1 and Equation 2.2). This could lead to higher emissions from transport of natural gas, which are not within the scope of the study.

Main infrastructural changes needed for the implementation of the different technologies are shown in Figure 5.4. On the main Y axis (left), pipeline capacities are displayed. Transportation of green hydrogen to an ammonia plant, would require a pipeline with a volumetric flow, 2.7 times higher than that of a conventional natural gas pipeline to maintain the same energy flow. Additionally, an ASU is needed to obtain nitrogen for the reaction. Blue hydrogen on the other hand, requires an additional pipeline for CO₂, with a relative volumetric flow of 0.82 compared to the pipeline of natural gas. On the secondary Y axis (right), electricity loads of all the technologies are plotted (yellow bars). Continuous and fluctuating (4000 h) hydrogen production via electrolysis (on-site) would require an electric power, 18 and 39 times higher than electricity consumed by conventional grey process respectively. This demands the installation of an electric connection capable of transmitting such amounts of energy. Furthermore,

the required electricity to fulfill this demand should be available for the plant to maintain its operation.

5.3 Costs

The specific production costs of ammonia from different technologies are displayed in Figure 5.5. Energy (electricity and natural gas demand), equipment, infrastructure, feedstock and subsequent maintenance costs were used to estimate production, operation, and specific production costs.

Due to an exclusion of CAPEX for existing plants (grey conventional SMR plants and blue ammonia plants), the depreciated costs of these plants are compared to the non-depreciated costs of every other technology. This comparison reflects the economic reality faced by an ammonia producer, who has to make the according investment decision.

The production costs of 1 tonne of **grey ammonia** in 2020, via conventional SMR, old BAT-compliant SMR and new SMR plants were estimated as $330 \notin$ (depreciated), $310 \notin$ (additional CAPEX for improvement non-depreciated) and $350 \notin$ (non-depreciated) respectively, with a cost surge in 2050 more than doubling the specific production costs, due to a rising CO₂ price.

Production costs of **yellow ammonia** in 2020 were calculated as 1,250 \leq/t_{NH_3} (non-depreciated). Electricity price had the greatest contribution on the total costs and varies from country to country. These costs (yellow line) increase slightly initially, due to a rising CO₂ price. After 2035, the influence of declining CO₂ grid emissions is more dominant and accompanied by a drop in total costs to 900 \leq/t_{NH_3} in 2050. Implementation of this technology depends on availability of cheap grid electricity with relative low emissions.

Production cost of **green ammonia** varies largely with the location of the plant, as this determines the availability of green energy and electricity price. Non-depreciated costs of off-site green-ammonia, transported via pipe-lines, amounted to $1,700 \notin /t_{NH_3}$ in 2020 and consequent-ly drops to $1,220 \notin /t_{NH_3}$ in 2050, as a result of reducing green hydrogen price. However, it is expected that green hydrogen will be available at lower costs in some sweet spot countries. In 2020, non-depreciated costs for on-site green ammonia, varied from 930 \notin /t_{NH_3} in region 3

15 A blue ammonia plant will have a slightly higher electricity demand due to the need for compressor to pump CO₂ through the pipelines to storage.

5 EVALUATION OF TECHNOLOGY OPTIONS VS. STATUS QUO



Figure 5.5 Specific production costs of ammonia, non-depreciated, full implementation of technologies. *Costs from grey conventional, BAT and blue technologies are depreciated

to 2,170 \leq/t_{NH_3} in region 1 (see section 3.3.2) and plummets to 511 \leq/t_{NH_3} and 513 \leq/t_{NH_3} respectively in 2050. Under these conditions, ammonia from green hydrogen becomes competitive with conventional ammonia after 2040 for regions 1 and 3 and after 2049 for region 4. It is therefore important to take actions to further reduce renewable electricity prices.

Blue ammonia had an average specific production cost of $400 \notin /t_{NH_3}$ (depreciated) in 2020, slightly higher than those from grey hydrogen (which includes CO_2 costs for ETS), due to CO_2 transport and storage costs. These production costs increase over time. After 2030, ammonia production from blue hydrogen becomes attractive as costs drop below ammonia from conventional SMR technology, which suffers more from rising CO_2 prices.

Finally, non-depreciated costs for **turquoise ammonia** were estimated as $6_{30} \notin /t_{NH_3}$ in 2050 and will be competitive with conventional technologies. Costs for turquoise ammonia for all other years are hypothetical and depend on the availability and maturity of this technology. Turquoise hydrogen technology is still in research and development and must be scaled up to provide the required volumes for ammonia production.

5.4 Sensitivity analysis

This study presents results made with certain internal assumptions and uncertainties. Therefore, a sensitivity analysis of different varying parameters on the specific production costs in 2030 were carried out. The results are shown in Figure 5.6.

Most parameters were varied by \pm 50% and their influence on the final specific production costs analysed. An exception to this is the electric efficiency varied at \pm 10%, due to technical limitations.

Production costs of **grey ammonia** are highly sensitive to natural gas and CO_2 prices. A 50% variation of these parameters affects the total production costs by 18% and 22% respectively.

Grid electricity price had the largest influence on production cost of **yellow ammonia**, resulting in a 29% change of the specific costs, while other studied factors, like CO₂ price, CAPEX, and efficiency of electrolysis, had comparatively less influence.

5 EVALUATION OF TECHNOLOGY OPTIONS VS. STATUS QUO



Figure 5.6 Sensitivity analysis of the specific production costs in 2030. *depreciated

As expected, the principal parameters affecting the production costs of **green ammonia** are the price of green electricity (on-site) and green hydrogen (off-site), which variation causes a change of 33% and 35% on production costs, respectively.

Natural gas and CCS prices had a strong influence on the production of **blue ammonia**, with changes of 18% and 13% in the specific costs observed.

Grid electricity and natural gas prices showed a substantial influence on the final cost of **turquoise hydrogen** production, causing a change of 17% and 15%.

5.5 CO₂-reduction potential in the ammonia production in 2030

The production costs vs. the relative CO_2 savings of different technologies compared to conventional grey ammonia are displayed in Figure 5.7. The sizes of the bubbles are scaled to the CO_2 -reduction potentials of each technology, which represents a theoretical maximum and do not take costs into account. A theoretical technology, which saves 100% CO_2 -emissions compared to grey conventional is shown in the graph with a blue line as a reference.

Yellow ammonia, the only technology without CO_2 savings in 2030, and consequently on the left side of the diagram, presents an average specific grid-electricity emission of approximately 250 g_{CO_2} /kWh (see Annex 1, Table 7.2) in Europe. This technology shows 39% increased emissions over conventional SMR production in 2030. Nevertheless, these emissions are strongly dependent on the local emission factor of electricity grid and subsequently, on the production site. This technology may be adapted in countries with low electricity emission factor and serve as a transitional technology to green ammonia until a complete decarbonization of the electricity grid happens in the EU.

Old and **new BAT** compliant SMR plants add up to 8% to 20% emission savings, respectively.

 CO_2 savings of up to 60% and 70% can be achieved in 2030 with **blue** and **green** technology options, while savings from **turquoise ammonia** are 56%. Remaining emissions from these processes come from grid electricity use and additionally from natural gas combustion for production of ammonia from blue hydrogen. An alternative could be the replacement of natural gas with biogas or other CO_2 neutral/low fuels. The highest relative CO₂ savings (1.4 t_{CO2}/t_{NH3}) are achieved by producing green ammonia, but this technology also present relative high production costs in 2030. Blue ammonia saves 1.2 t_{CO2}/t_{NH3} at lower production costs.

Variations in specific production costs compared to conventional grey ammonia are shown in Figure 5.8, where contributions of CAPEX (grey area) and OPEX (blue area) to total cost are observed. Besides previously described options, three additional scenarios were studied with combinations of 90% grey and 10% yellow, 90% grey and 10% green (off-site) and 90% grey and 10% green electricity (on-site) technologies. Given the drastic increase in electricity demand by electrolysis (see Figure 5.4) and the general lack of sufficient amount of green electricity in the EU, this represents a more realistic approach for existing production plants, allowing gradual transitioning into low carbon productions.

Since **blue ammonia** is an adaptation of existing conventional SMR plants, their investment costs (CAPEX) are minimal and ignored. OPEX of blue ammonia reach the same value of those of grey ammonia in 2030, being economically competitive. **BAT-compliant old plants** require a relatively low CAPEX and 9% lower OPEX due to lower



Figure 5.7 Production costs vs. relative CO₂-emission savings of different technologies in 2030 compared to grey conventional. *Yellow technology emits more CO₂ than grey conventional

fuel demand and reduced CO_2 -cost than conventional plants, resulting in 6% lower specific production costs.

The OPEX costs of a **new grey plant** show a reduction of 22% compared to conventional grey plants, due to its reduced energy consumption. Nevertheless, this option has an increase of 22% in production costs due to the necessary investment costs, resulting in a net zero increase of specific production costs compared to grey conventional. Implementing any of the options using electrolysis (yellow or green ammonia), leads to additional specific cost of 185% to 239%, respectively. These high values emanate from the required high volumes of electricity and related high investments costs for these new technologies. Alternatively, total specific costs of producing **turquoise ammonia** increases by 57%.

Based on results described above, CO_2 -avoidance costs, defined as cost difference over CO_2 difference (see section 4.3), of the different technology options with respect to conventional technology were calculated and are shown in Table 5.1.

Avoidance costs for old BAT **grey plants** are negative (-180 \leq/t_{CO_2}) in comparison to conventional SMR plants, due to lower total costs. BAT new plants present avoid-

ance costs of 5 \leq/t_{CO2} in 2030 and these become negative in 2050.

A negative value is shown for **yellow ammonia** in 2030, as it emits considerably more amounts of CO_2 than the conventional technology since the grid is not yet fully decarbonized. This results in a negative denominator in Equation 4.2. For this reason, its avoidance costs cannot be directly compared to the avoidance cost of other technologies. However, avoidance costs for yellow ammonia become positive in 2050 from the use of zero-emission grid electricity, since they provide real emission savings.

Avoidance costs for **blue ammonia** production in 2030 amount to $0 \notin /t_{CO_2}$, because its production costs equal those of conventional grey ammonia in this year. They consist of the difference of CCS costs and avoided emission costs for emissions allowances (EUA) for captured carbon.

The avoidance costs of **green ammonia** vary between $220 \notin /t_{CO_2}$ and $650 \notin /t_{CO_2}$ in 2030, depending on the region in which the plant is located. These costs are still considerably high, as processes and components still operate on carbon intensive grid electricity.



Figure 5.8 Cost variation of different technologies in 2030 compared to grey conventional (extrapolated to 2030

5 EVALUATION OF TECHNOLOGY OPTIONS VS. STATUS QUO

Avoidance costs of turquoise ammonia amount to $240 \notin t_{CO2}$ in 2030, due to high energy demand.

A high CO_2 price in 2050 resulted in a significant increase in production costs of conventional grey ammonia. Additionally, OPEX costs decrease until 2050 for blue, yellow, green and turquoise technologies in accordance to falling grid and green electricity prices. These two factors lead to a reduced avoidance cost for these technologies in 2050. of o.8 Mt_{CO2}/a by applying it to a capacity of 5.8 Mt_{NH3}/a . Finally, 10% yellow and 90% grey, with specific production costs of 537 ϵ/t_{NH3} , saves o.2 Mt_{CO2}/a if implemented to a capacity of 2.5 Mt_{NH3}/a . In this scenario, a total of 147 kt of hydrogen are produced on-site through electrolysis. For this, 2,100 GWh of grid (yellow) and 5,000 GWh of green electricity would be consumed in the production sites yearly for the electrolytic processes alone (which are applied to about 6% of the total capacity according to this scenario). This can be compared to 8,000 GWh

Table 5.1CO2 avoidance costs of different technologies in 2030 compared to
grey conventional. Green (on-site) is represented for region 1. 16

Technology Options	CO ₂ Avoidance costs				
	2030	2050			
Grey BAT	-180 €	-450 €			
Grey new plant	5€	-140 €			
Blue	0€	-200€			
Turquoise	240€	-90 €			
Yellow	-1,090 € ¹⁷	60€			
90% grey, 10% yellow	-1,090 €	60€			
Green (pipeline)	790 €	240€			
Green (onsite)	220€-650€	-160 € - 22 €			
90% grey, 10% green (pipeline)	790€	240€			
90% grey, 10% green (onsite)	220€-650€	-160 € - 22 €			

of electricity consumption currently needed in all plants evaluated in this study using the conventional process. There is no off-site supply of green hydrogen considered in this scenario.

A similar graph is shown for the **bestcase scenario** in Figure 5.10. The total abatement potential was calculated as **19%**. Emission savings of blue ammonia are higher (3.0 Mt_{CO2}/a), due to a higher capacity converted to blue technology. The plant producing turquoise ammonia with a capacity of 0.3 Mt_{NH3}/a, could save 0.3 Mt-_{CO2}/a with production costs of 710 \leq / t_{NH3}. Savings from 10% green option are also slightly higher, as 81% of all urea plants were assumed to operate with this technology. Comparatively, a green ammonia plant with a capac-

5.6 Total abatement potential of the European fertilizer industry in 2030

The total abatement potential of ammonia plants for the **base case scenario** is estimated as **13%** with the assumptions described in section 4.5. Figure 5.9 displays the potential CO₂ emission savings for each technology and their specific production costs. With the assumptions made, the implementation of blue ammonia for a total capacity of 1.9 Mt_{NH3}/a, could save approximately 2.3 Mt_{CO2}/a at specific production costs of 453 \leq /t_{NH3}. The option of 10% green and 90% grey presents specific production costs of 517 \leq /t_{NH3} and has a saving potential ity of 0.4 Mt_{NH_3}/a would present savings of 0.5 Mt_{CO_2}/a with specific productions costs of 1,540 \leq/t_{NH_3} . In this scenario, a total of 159 kt of hydrogen are produced onsite with 2,100 GWh of grid (yellow) and 5,500 GWh of green electricity, which would be yearly needed only for the electrolytic processes. Additionally, 63 kt of green hydrogen should be yearly transported to the site via pipeline.

In both scenarios, electricity demand would increase exponentially compared to today's consumption. Therefore, the implementation of yellow and green technologies is strongly dependent on the availability of grid and renewable electricity in these plants.

¹⁶ In relation to the avoidance costs equation (see Equation 4.2), a negative value arises from either lower costs or higher emissions of each technology compared to conventional SMR. Similarly, very high positive or negative values are undesirable because they originate from either a low value for avoided emissions or high costs associated with the technology.

¹⁷ Negative value due to higher emissions than the conventional plant.



Figure 5.9 Emissions savings vs. specific production costs for the base case scenario



Figure 5.10 Emissions savings vs. specific production costs for the best-case scenario

6 Conclusions

Today's production of nitrogen fertilizers uses ammonia as the main building block. To achieve a considerable reduction of CO₂-emissions in the fertilizers industry, emissions from ammonia production process must be substantially reduced. SMR, the most emission-intensive process in ammonia production, is currently applied, due to its high efficiency and low costs.

Opportunities in 2030:

Current production of **grey ammonia** presents specific high CO_2 -emissions from natural gas utilization as feedstock and fuel. Existing and new ammonia plants implementing BAT can reduce energy consumptions and emissions by 8% and 20% in 2030, respectively. However, further investments in BAT technologies are not expected, as the implementation of only process optimization could be a step in 2030 but is insufficient to achieve the set climate goals by 2050 due to continuing unavoidable direct process emissions.

Blue ammonia has up to 60% CO₂-emission savings compared to conventional grey ammonia in 2030. Its production costs are $450 \notin /t_{NH3}$ the same year. Blue hydrogen plays a role as a suitable transitional solution for ammonia production, until turquoise or green ammonia can be produced at large scale. To implement this technology, proximity of storage locations is preferred, or at least the infrastructure to transport CO₂ to the storage facility should be available, as well as socio-political acceptance for this technology, so that not all production plants in Europe will have the opportunity to use it.

With assumptions made for an average electricity grid in Europe, **yellow ammonia** plants cost 2.8 times more than conventional ammonia plants and emit 39% more CO_2 in 2030. These results are strongly dependent on the location of the plant and the emission factor of electricity. Hence the development of yellow ammonia plants becomes feasible at sites with electricity emission factors lower than 150 g_{CO2}/kWh.

To synthetize **green ammonia**, green hydrogen can be produced either on-site with renewable electricity or transported to site via pipeline (off-site). 70% CO₂ emission savings in 2030 is obtainable by the exclusive use of green hydrogen in ammonia production. Production costs for the same year were estimated to vary between $750 \notin /t_{NH3}$ and $1,540 \notin /t_{NH3}$. However, currently, there

are insufficient amounts of renewable energy to satisfy the overall demand for green hydrogen in the ammonia industry. Additionally, infrastructure adjustments are needed to either transport green hydrogen to the plant or to produce it on-site.

Finally, **turquoise ammonia**, although still having emissions through the use of grid electricity, has the potential of theoretically saving up to 56% CO₂ with production costs of $710 \notin /t_{NH_3}$ in 2030. Despite its significant CO₂ emissions reduction potential, implementation at large scale remains uncertain by 2030, as it is still in early stages of development.

Since manufacturing urea utilizes part of the CO_2 emitted from grey hydrogen, the implementation of blue, yellow, green and turquoise hydrogen technologies leads to a shortage in this important feedstock. For small scale processes, CO_2 from the atmosphere via DAC can be used. Industrial sources can also be an option, but this is still controversial.

With the assumptions made for the base and best-case scenarios, the total abatement potential for ammonia production in 2030 varies between 13% and 19%.

Opportunities in 2050:

Remaining emissions stemming from grid electricity for the turquoise, yellow, green and blue technology options can be completely reduced until 2050, if the grid electricity is successfully decarbonized until then. This could lead to CO_2 savings of 100% for ammonia produced from turquoise, yellow or green hydrogen. Production costs of all technology options will also decrease until 2050.

Turquoise technology although not feasible in short term (2030) offers an interesting option for decarbonizing the ammonia industry in long term. Also, green hydrogen, either produced on-site or transported through pipe-lines, will be essential to produce zero carbon ammonia.

7 Annexes Annex 1 Definition of average European energy system

Table 7.1 General costs parameters	Table 7.1	General	costs	parameters
------------------------------------	-----------	---------	-------	------------

	Unit	Value	Comment
Depreciation Period	а	20	
ROI	%	8%	
Maintenance and replacement-ratio	%	4.7%	of CAPEX

Table 7.2 Defined average European energy system

	Unit	2020	2030	2040	2050
Electricity price (grid)	€/MWh	70	70	70	70
Electricity price region 1 (green)	€/MWh	144	35	26	17
Electricity price region 2 (green)	€/MWh	99	83	66	50
Electricity price region 3 (green)	€/MWh	34	28	23	17
Electricity price region 4 (green)	€/MWh	83	69	55	41
Natural gas price	€/MWh	19	19	19	19
CO ₂ price	€/t _{CO2}	35	100	200	300
Green Hydrogen price	€/t _{H2}	7,000	6,000	5,333	4,667
Specific emissions electricity	g _{CO2} /kWh	376	251	125	0

To calculate the electricity price, four regions were defined:

- » Region 1 representing southern Europe, based on Italy, Spain and France.
- » Region 2 Western Europe, based on Austria, Belgium, Germany, Netherlands.
- » Region 3 northern Europe, based on Norway.
- » Region 4 central Europe, based on Hungary, Croatia, Slovakia.

Then, the average contribution of renewable energy for region 2 and 4 was defined based on [38] and is shown in Table 7.3. It was assumed, that this contribution remains constant over time until 2050.

Table 7.3 Contribution of renewable source in the four defined regions

	PV	Wind	Hydro	Biomass
Region 2 (western Europe)	20%	49%	24%	7%
Region 4 (central Europe)	15,7%	4,6%	59,8%	20%

Simultaneously, the average LCOE for each energy source depending on the region was calculated based on data from [39] and is summarized in Table 7.4. The LCOE for biomass in region 2 was assumed, because there was not data available for biomass in the corresponding countries.

7 ANNEXES

Table 7.4 Average LCOE of the four regions

	Unit	PV	Wind off-shore	Hydro	Biomass
Region 2 (western Europe)	€/MWh	76	63	32	128
Region 4 (central Europe)	€/MWh	91	79	77	162

Finally, a weighted-average cost was calculated for 2020 for each region based on Table 7.3 and Table 7.4. These 2020 costs were multiplied by a factor of 1.5 to obtain a final price of electricity.

Renewable electricity prices for 2020 for regions 1 and 3 were taken from [35] and [36].

Costs for all regions were subsequently linearly extrapolated with assumed decrease of 50% until 2050.

Table 7.5 Cost of renewable electricity in the defined regions

	Unit	2020	2030	2040	2050
Region 1 (southern Europe)	€/MWh	144	35	26	17
Region 2 (western Europe)	€/MWh	99	83	66	50
Region 3 (northern Europe)	€/MWh	34	28	23	17
Region 4 (central Europe)	€/MWh	83	69	55	41

Finally, a weighted-average cost was calculated for 2020 for each region based on Table 7.3 and Table 7.4. These 2020 costs were multiplied by a factor of 1.5 to obtain a final price of electricity.

Renewable electricity prices for 2020 for regions 1 and 3 were taken from [35] and [36].

Costs for all regions were subsequently linearly extrapolated with assumed decrease of 50% until 2050.

Annex 2 Process specific parameters

Table 7.6 Parameters for electrolysis

		2020	2030	2040	2050
CAPEX	€/kW	1,400	1,100	800	750
Efficiency (LHV)	%	66%	69%	73%	76%

Table 7.7 Feedstock and energy demand for ammonia production in an "average European ammonia plant" from different technology options

	Unit	Grey hydrogen (conventional)	Grey hydrogen (old BAT)	Grey hydrogen (new plant)	Yellow hydrogen	Green hydrogen	Turquoise hydrogen	Blue hydrogen
Full Load Hours	h	8,760	8,760	8,760	8,760	4,000 (on-site) 8,760 (off-site)	8,760	8,760
Electricity demand (other)	MWh/ t _{NH3}	0.61	0.33	0.06	2.32	2.32	3.41	0.61
Natural Gas, Feed	GJ/t _{NH3}	21	21	21	0	0	42	21
Natural Gas, Fuel	$GJ/t_{\rm NH_3}$	11.20	9.80	6.80	0	0	0	11.20
Total energy demand	GJ/t _{NH3}	34.4	32.0	28.0	8.4	8.4	54.3	34.4
Water demand	t/t _{NH3}	2.00	2.00	2.00	1.59	1.59	0	2.00

Table 7.8 Cost parameters for ammonia production from different technology options.

	Unit	Grey hydrogen (conventional)	Grey hydrogen (BAT)	Grey hydrogen (new plant)	Yellow hydrogen	Green hydrogen	Turquoise hydrogen	Blue hydrogen
CAPEX ammonia plant	€/t _{NH3}	1,000	1,000	1,000	500	500	1,000	1,000
CAPEX BAT	€/t _{NH3}	-	150	_	_	_	-	-
Maintenance ammonia plant	€/t _{NH3}	47	47	47	24	24	47	47
CAPEX air separation	€/t _{NH3}	-	_	_	90	90	90	-
Maintenance air separation	€/t _{NH3}	-	_	_	4	4	4	-
Water cost	€/t _{H20}	1	1	1	1	1	-	1
Transport cost hydrogen	€/t _{H2}	-	-	-	-	300	-	_
CCS cost 2020	€/t _{CO2}	_	_	_	_	_	-	100

LITERATURE

Literature

- INTERNATIONAL ENERGY AGENCY, "The Future of Petrochemicals Towards more sustainable plastics and fertilisers." [Online]. Available: https://www.connaissancedesenergies.org/sites/default/files/pdf-actualites/the_future_of_petrochemicals.pdf
- [2] European Environment Agency (EEA), "Greenhouse gas emission intensity of electricity generation in Europe," Jun. 2021. https://www.eea.europa.eu/data-and-maps/indicators/overview-of-the-electricity-production-3/assessment-1 (accessed Oct. 06, 2021).
- [3] CHEManager International, "New Ammonia Synthesis Technology A Process Based on an Electride Catalyst Enables Small-scale Ammonia Production." Mar. 2020. [Online].
 Available: https://tsubame-bhb.co.jp/assets/uploads/2021/03/CHEManager-International_0121_-40-41.pdf
- J. Fahnestock, K. Søgaard, E. Lawson, and H. Kilemo, "NoGAPS: Nordic Green Ammonia Powered Ship," Nordic Innovation, Project Report, 2021. Accessed: Nov. 07, 2021. [Online]. Available: http://norden.diva-portal.org/smash/get/diva2:1560108/FULLTEXT02.pdf
- [5] M. Stocks, R. Fazeli, L. Hughes, and F. J. Beck, "Global emissions implications from co-burning ammonia in coal fired power stations: an analysis of the Japan-Australia supply chain," *The Australian National University*, p. 30, Nov. 2020.
- [6] EUROSTAT, "International trade in goods detailed data," *EU trade since 1988 by HS2,4,6 and CN8*, Mar. 19, 2021. https://ec.europa.eu/eurostat/web/international-trade-in-goods/data/database (accessed Nov. 22, 2021).
- [7] Fertilizers Europe, "Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry," 2000. [Online]. Available: https://www.fertilizerseurope.com/wp-content/uploads/2019/08/Booklet_1_final.pdf
- [8] European Commission, "Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers," Aug. 2007. Accessed: May 26, 2021. [Online].
 Available: https://eippcb.jrc.ec.europa.eu/reference/large-volume-inorganic-chemicals-ammonia-acids-and-fertilisers
- [9] National Energy Technology Laboratory, "Cradle-to-Gate Life Cycle Analysis Model for Alternative Sources of Carbon Dioxide." Sep. 30, 2013.
- [10] C. M. Kalamaras and A. M. Efstathiou, "Hydrogen Production Technologies: Current State and Future Developments", Conference Papers in Energy, vol. 2013, pp. 1–9, Jun. 2013, doi: 10.1155/2013/690627.
- [11] Air Liquide, "Autotherme Reformierung Synthesegaserzeugung Katalytische Synthesegaserzeugung über partielle Oxidation mit anschließender Reformierung des gasförmigen Einsatzstoffes." https://www.engineering-airliquide.com/de/autotherme-reformierung-synthesegaserzeugung
- [12] Global Syngas Technologies Council (GSTC), "Auto-Thermal Reforming." https://globalsyngas.org/syngas-technology/syngas-production/auto-thermal-reforming/
- [13] Bartels, Jeffrey Ralph, "A feasibility study of implementing an Ammonia Economy," Graduate Theses and Dissertations, 2008.
 [Online]. Available: https://lib.dr.iastate.edu/etd/11132
- [14] Independent Commodity Intelligence Service, "Urea Production and Manufacturing Process," Apr. 28, 2010. https://www.icis.com/explore/resources/news/2007/11/07/9076560/urea-production-and-manufacturing-process/ #:~:text=Urea%20was%20first%20produced%20industrially,is%20then%20dehydrated%20to%20urea
- [15] "Nitric Acid Manufacture: Informative Report No. 5," *Journal of the Air Pollution Control Association*, vol. 14, no. 3, pp. 91–93, Mar. 1964, doi: 10.1080/00022470.1964.10468252.
- [16] Ecofys, Cefic, "Unlocking a competitive, low carbon and energy efficient future," Apr. 2013. Accessed: May 31, 2021. [Online]. Available: https://cefic.org/app/uploads/2019/01/Energy-Roadmap-The-Report-European-chemistry-for-growth_BRO-CHURE-Energy.pdf
- [17] Entec UK Limited, "Support for the Development and Adoption of Monitoring and Reporting Guidelines and Harmonised Benchmarks for N₂O Activities for Unilateral Inclusion in the EU ETS for 2008-12," Feb. 2008.
- [18] International Energy Agency (IEA), "The Future of Hydrogen. Seizing today's opportunities," Jun. 2019. [Online]. Available: https://iea.blob.core.windows.net/assets/9e3a3493-b9a6-4b7d-b499-7ca48e357561/The_Future_of_Hydrogen.pdf
- [19] C. Wulf, P. Zapp, and A. Schreiber, "Review of Power-to-X Demonstration Projects in Europe," Front. Energy Res., vol. 8, p. 191, Sep. 2020, doi: 10.3389/fenrg.2020.00191.
- [20] Luca Bertuccioli, Alvin Chan, David Hart, Franz Lehner, Ben Madden, and Eleanor Standen, "Development of Water Electrolysis in the European Union."

- [21] Michael Alkämper, Sebastian Stypka, Bernd Oberschachtsiek, Angelika Heinzel, "Operating results of PEMEL, AEL and SOEC systems," Zentrum für Brennstoffzellentechnik GmbH (ZBT). [Online].
 Available: https://gsm450601838.files.wordpress.com/2019/07/g0310-paper.pdf
- [22] L. Weger, A. Abánades, and T. Butler, "Methane cracking as a bridge technology to the hydrogen economy," *International Journal of Hydrogen Energy*, vol. 42, no. 1, pp. 720–731, Jan. 2017, doi: 10.1016/j.ijhydene.2016.11.029.
- [23] Linde, "Air separation plants. History and technological progress in the course of time," 2019. [Online]. Available: www.linde-engineering.com/en/images/Air-separation-plants-history-and-technological-progress-2019_tcm19-457349.pdf
- [24] Yan, Liwei; Yu, Yunsong; Li, Yun; and Zhang, Zaoxiao, "Energy Saving Opportunities in an Air Separation Process. International Refrigeration and Air Conditioning Conference," 2010. [Online]. Available: http://docs.lib.purdue.edu/iracc/1131
- [25] Universal Industrial Gases, Inc, "Overview of Cryogenic Air Separation and Liquefier Systems," 2019 2003. http://www.uigi.com/cryodist.html
- [26] SK Engineering, "PSA Nitrogen and Oxygen Generation," 2016. http://www.sk-engineering-consulting.com/node/120
- [27] Suresh P. Babu, "Thermal Gasification of Biomass." 2002. [Online].Available: https://www.ieabioenergy.com/wp-content/uploads/2013/10/18_AR1999Task2ocolour.pdf
- [28] Mckinsey, "Fluidized bed," Energy Insights. https://www.mckinseyenergyinsights.com/resources/refinery-reference-desk/fluidized-bed/
- [29] Salman Zafar, "Biomass Pyrolysis Process," Nov. 11, 202AD. https://www.bioenergyconsult.com/tag/flash-pyrolysis/
- [30] Bert Metz, Ogunlade Davidson, Heleen de Coninck, and Manuela Loos, Leo Meyer, "Carbon dioxide Capture and Storage." Intergovernmental Panel on Climate Change. [Online]. Available: https://www.ipcc.ch/site/assets/uploads/2018/03/srccs_wholereport-1.pdf
- [31] Fachagentur Nachwachsende Rohstoffe e. V. (FNR), "BASISDATEN BIOENERGIE DEUTSCHLAND 2018," 2018. [Online]. Available: http://www.fnr.de/fileadmin/allgemein/pdf/broschueren/Broschuere_Basisdaten_Bioenergie_2018_web.pdf
- [32] G. Saur and A. Milbrandt, "Renewable Hydrogen Potential from Biogas in the United States," National Renewable Energy Laboratory, NREL/TP-5400-60283, Jul. 2014.
- [33] BIONICO, "Biogas membrane reformer for decentralized hydrogen production," *FCH-02.2-2014 Decentralized hydrogen production from clean CO2-containing biogas*, [Online]. Available: http://www.bionicoproject.eu/
- [34] UMWELTBUNDESAMT, "Carbon Dioxide Emissions for the German Atmospheric Emission Reporting 1990 2014." https://www. umweltbundesamt.de/sites/default/files/medien/376/dokumente/kohlendioxid-emissionsfaktoren_fuer_die_deutsche_berichterstattung_atmosphaerischer_emissionen_energie-_und_industrieprozesse.xlsx
- [35] OMIP, "OMIPData Market results," 2021 2019. https://www.omip.pt/en/dados-mercado?date=2021-10-18&product=EL&zone=ES&instrument=FTK (accessed Oct. 18, 2021).
- [36] Federal Ministry for Economic Affairs and Energy (BMWi), "Energy Data: Complete Edition." https://www.bmwi.de/Redaktion/EN/Artikel/Energy/energy-data.html (accessed Oct. 19, 2021).
- [37] Global CCS Institute, "CO2RE CCS Facilities Database," 2018. https://co2re.co/FacilityData (accessed Jul. 02, 2021).
- [38] EUROSTAT, "Complete energy balances," Jun. o6, 2021. https://appsso.eurostat.ec.europa.eu/nui/show.do?dataset=nrg_bal_c&lang=en (accessed Jun. 22, 2021).
- [39] International Energy Agency (IEA), "Levelised Cost of Electricity Calculator," 2020. https://www.iea.org/articles/levelised-cost-of-electricity-calculator (accessed Jun. 25, 2021).

DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V. Theodor-Heuss-Allee 25 60486 Frankfurt am Main Germany

 Phone:
 +49 (0)69 7564-0

 Fax:
 +49 (0)69 7564-117

 E-Mail:
 info@dechema.de