

# Appendix

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## Decarbonization of the German chemical industry in light of the Paris Agreement

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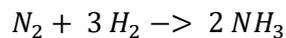
*\*Within each excel file, an explanation of the appendix is given.*

## Appendix A: Description of production pathways

### Ammonia

Ammonia (NH<sub>3</sub>) is the product with the highest production volume, the highest total emissions and the highest energy consumption globally (IEA et al., 2013). Ammonia is a relevant product in Germany as well, with a high demand of 3 Mt per year and intensive use for fertilization in agriculture.

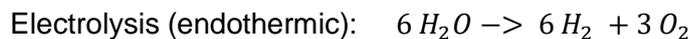
The production of ammonia consists of two steps, first the production of hydrogen and second, the so-called Haber-Bosch synthesis, where hydrogen reacts with atmospheric nitrogen (N<sub>2</sub>) to ammonia as described in the flow diagram in Fig. A1.



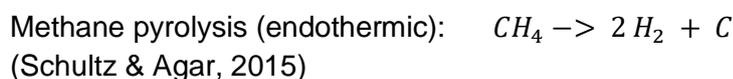
The status-quo technology for hydrogen production is steam reforming where natural gas is used as a feedstock and as a fuel to heat the reaction in the primary reformer. After the steam reforming, a water gas shift is used to convert the flue gas to hydrogen and CO<sub>2</sub>. Nitrogen is supplied via a combustion of natural gas in a secondary reformer and together with hydrogen, ammonia is synthesized in the Haber-Bosch process.

The process step of hydrogen production is with respect to energy demand and emissions the relevant one. Thus, two alternatives have been identified.

Firstly, electrolysis is a process to create hydrogen from water (H<sub>2</sub>O). In an electrolyzer under pressure and under voltage, water reacts endothermically to hydrogen and oxygen (O<sub>2</sub>). For powering this process, the electricity demand is high despite different types of electrolyzers.



Secondly, methane pyrolysis represents a low-carbon alternative for hydrogen production for the ammonia production pathway. This process requires methane (CH<sub>4</sub>) as a feedstock and can be powered either via a methane surplus or via electricity which is preferred to reduce the related emissions. This process is also heated and conducted under pressure causing a high energy demand.



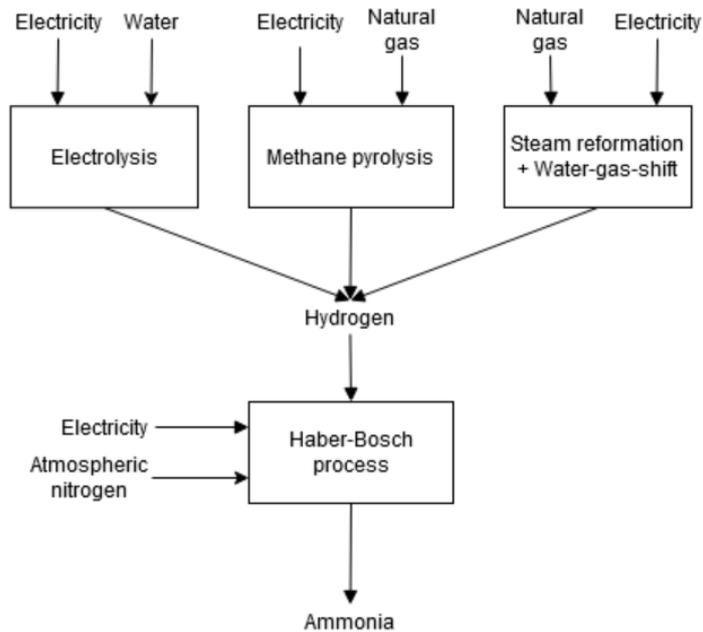


Fig. A1. Flow diagram of production pathways of ammonia

## Urea

Urea is a chemical that is based on ammonia and is likewise used in agriculture. For its production, ammonia is synthesized with  $\text{CO}_2$  via ammonia carbamate ( $[\text{H}_2\text{NCOO}]\text{NH}_4$ ) in a two-step process. In practice the ammonia and urea ( $\text{H}_2\text{NCONH}_2$ ) production are highly integrated as can be seen in Fig. A2. The different production pathways only differ in their hydrogen production, as for the ammonia production, the status quo is the natural gas-based steam reforming and the two low-carbon alternatives are electrolyzers and methane pyrolysis. The urea production process is one of the processes where  $\text{CO}_2$  is used as an input.

1. Step Ammonia carbamate production:  $2 \text{NH}_3 + \text{CO}_2 \rightarrow [\text{H}_2\text{NCOO}]\text{NH}_4$
2. Step Urea synthesis:  $[\text{H}_2\text{NCOO}]\text{NH}_4 \rightarrow \text{H}_2\text{NCONH}_2 + \text{H}_2\text{O}$

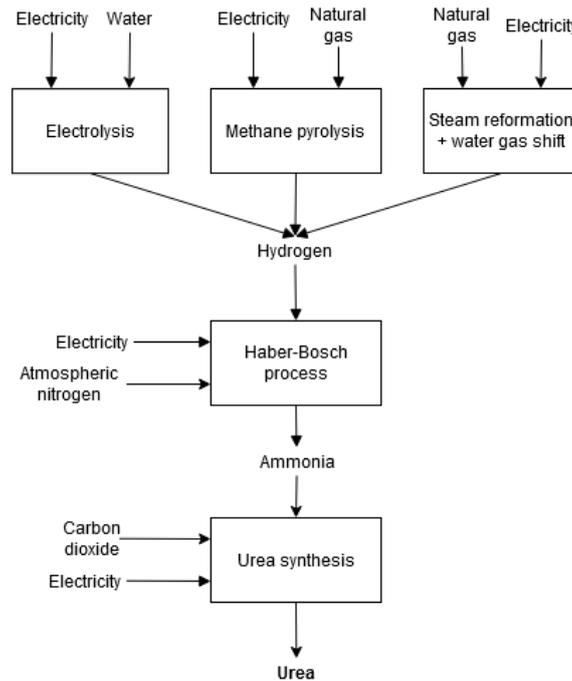


Fig. A2. Flow diagram of production pathways of urea

### Chlorine

Chlorine is produced by the electrolysis of sodium chloride as seen in Fig. A3. The difference between the pathways is through which type of electrolysis cell the chlorine is produced. There are mainly three types of electrolysis cell: membrane, diaphragma, and amalgam. The membrane cell shows the highest efficiency among the three options, with electricity demand of 2.8 MWh/t Chlorine. Currently, mercury cell plants are at a trend of phasing out, with most plants for chlorine production newly built or transformed into membrane cells.

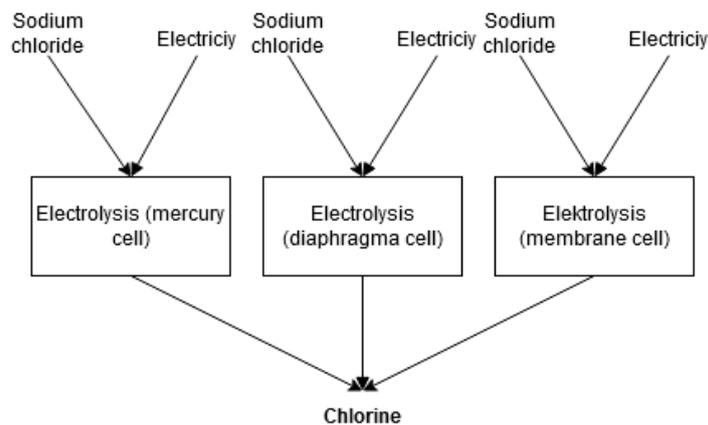
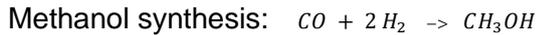


Fig. A3. Flow diagram of production pathways of chlorine

## Methanol

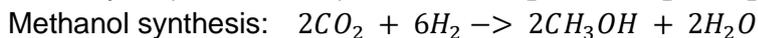
Methanol ( $\text{CH}_3\text{OH}$ ) is a chemical product group with one of the largest product volumes in the world. It can also serve as a basis for the production of other product groups, such as HVC via the methanol-to-olefins (MTO) or methanol-to-aromatics (MTA) process.

The conventional way of methanol production consists of steam reforming of natural gas, which produces syngas that is put into methanol synthesis. Syngas is a mixture of carbon monoxide (CO),  $\text{CO}_2$ , and hydrogen. A visual description of the pathway can be found in Fig. A4. The methanol synthesis can be described in a chemical formula as below:



Alternatively, methanol can be produced with syngas that is generated with hydrogen produced via low carbon technologies such as water electrolysis and methane pyrolysis. The produced hydrogen goes through a hydrogenation process which adds  $\text{CO}_2$  as a carbon source to form methanol.

Methanol production from electrolysis and methanol synthesis can be described in the chemical formula as below (DECHEMA, 2017):



Another way of low-carbon methanol production pathway is biomass gasification. In this pathway, first pretreated biomass is put into a gasifier to produce hydrogen, carbon monoxide, and methane. Later these outputs go through a water-gas shift process to balance the carbon monoxide and hydrogen ratio for methanol synthesis.

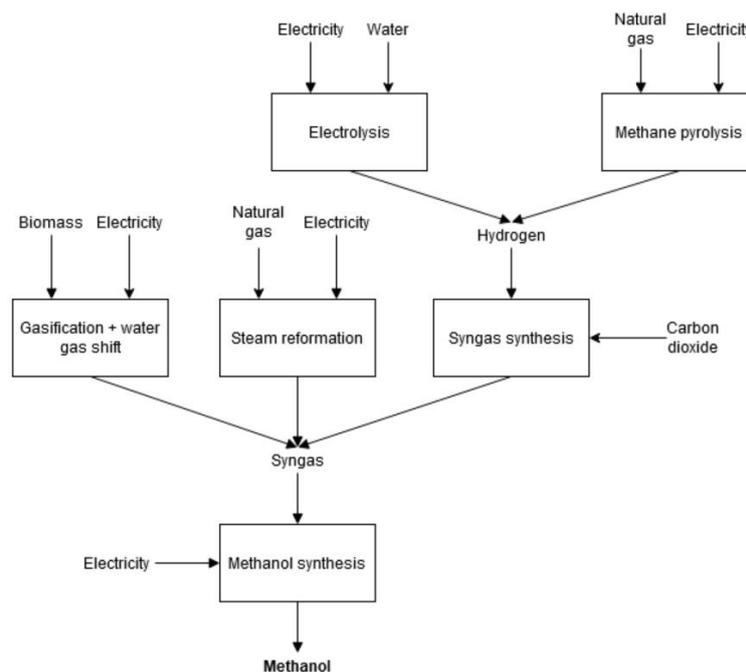


Fig. A4. Flow diagram of production pathways of methanol

## High Value Chemicals (HVC)

HVC is a group of chemical products including ethylene, propylene, benzene, toluene, and mixed xylenes. Among these, ethylene and propylene are commonly grouped as 'olefins,' while benzene, toluene, and mixed xylenes are grouped as BTX.

The production pathways of HVC are manifold depending on the intermediate chemicals in use and production processes. In a simple manner, the pathways can be explained based on three aspects: 1) methanol-based production pathway 2) different types of cracking 3) different ways of naphtha production. Details of production pathways are visualized in Fig. A6.

### Methanol based pathway

One alternative way of HVC production is using methanol as a basis. In this production pathway, methanol produced via hydrogen from water electrolysis goes through the MTO or MTA process. In the MTO/MTA process, methanol is put into a reactor powered by natural gas, and can be transformed into a targeted product depending on the type of catalyst (DECHEMA, 2017).

### Types of steam cracking

Other than methanol-based production pathways, HVC is in general produced by the cracking of naphtha. Thermal steam cracking of naphtha has been a conventional way of cracking. In a typical naphtha steam cracker, a part of naphtha put into the cracking process is used as a fuel to heat the furnace of the process as depicted in Fig. A5 (Ren et al., 2006). As an alternative technology to the thermal cracking process, electrical steam cracking powered by electricity is in development. Here, instead of burning by-products, electricity is used to provide the heat required for the process, hence process emissions are significantly reduced.

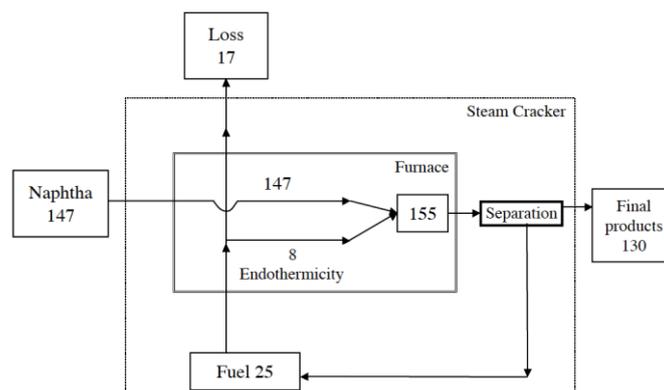


Fig. A5. Energy flow in a typical naphtha steam cracker (all values in GJ/t ethylene) from Ren et al. (2006)

### Ways of (synthetic) naphtha production

Steam crackers can be fed with different feedstocks such as ethane, however, in Europe and Germany, naphtha is the predominant feedstock (DECHEMA, 2017). How the naphtha for steam cracking was produced can be the other way of distinguishing HVC production

pathways. The study focuses on three ways of naphtha production, via crude oil refining, plastic waste pyrolysis, and Fischer-Tropsch process with hydrogen from electrolysis.

In the crude oil refining, which is a conventional way of naphtha generation, naphtha is gained by the distillation of oil powered by electricity and steam.

An alternative way of synthetic naphtha production is plastic waste pyrolysis. In this process, plastic waste is decomposed via thermal energy generated by natural gas and electricity to produce naphtha. The process has advantages in that it has lower emissions than incineration, and that it enables circular economy by contributing to the circular loop of plastic recycling (Qureshi et al., 2020).

Lastly, a Fischer-Tropsch can be used to produce synthetic fuels from the syngas. Electrolysis of hydrogen and biomass gasification can be used as low-carbon technologies to produce syngas that are fed into Fischer-Tropsch process. With the Fischer-Tropsch process naphtha is produced, which is put into a cracking process to turn it into HVC.

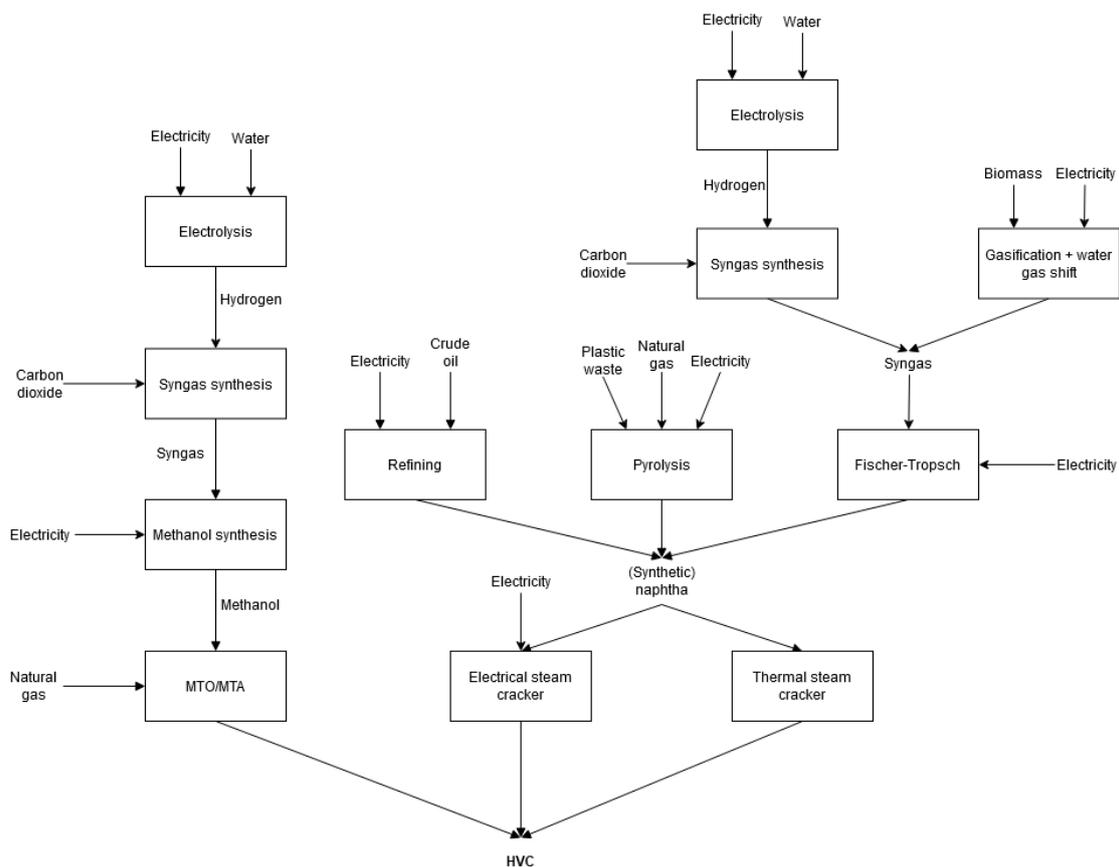


Fig. A6. Flow diagram of production pathways of HVC

**Appendix B: Technology table with data sources (Excel)**

**Appendix C: Market entry year of production technologies (Excel)**

## Appendix D: Description of constraints

There are multiple sets of constraints which are applied in a specific order, which is summarized in the table below.

The first set of constraints is implemented at the start of the optimization process and applies to all products. So for all products, the production pathways should together add up to 100% in each timestep (T). Then the technologies which are not available at a specific T should have a share of 0%. The years in which technologies become available are derived from the literature or estimated using TRL values, as discussed previously in the Technological Scope section. In order to avoid shares jumping from low to high values and to ensure market stability, the shares of production pathways can either increase or decrease over time. The conventional technologies are typically replaced by cleaner technologies, which require stable investments. Only a 5% deviation is possible, since some technologies may function as intermediate technologies that aid later developing technologies.

After running the optimization for the first time, a second set of constraints is added based on the results. Where new technologies are introduced, the market shares are constrained for the first two timesteps after the technology becomes available. An educated guess is that a new technology should not exceed 7.5 in the first timestep (T1) and 40% in the next 5 years (T2) after market introduction. Furthermore, where a technology is phased out, the speed at which this occurs is constrained. The last non-zero value is constrained to a maximum of 40% to avoid a sudden phase out.

The optimization is run a second time, after which a third set of constraints is applied. A correction is applied to the newly introduced technologies where the shares were optimized to  $T1 = 0$  and  $T2 = 40$ . For these cases, T1 is set to a minimum of 5%. Based on the report by Dechema and Futurecamp (2019), additional constraints are applied to the products chlorine and HVC. First, information on the phasing out of certain technologies has been included. Second, the initial shares of chlorine have been made more realistic by using given values. And finally, the dominance of methane pyrolysis is found to be unrealistic and is therefore constrained not to be dominating.

Table D1. List of constraints

Constraint	Product	Set	Sign	Value (%)
Balance of production pathways for each T	All	First	=	100
Unavailable technology at T	All	First	=	0
Only increase or decrease, 5% deviation possible	All	First	>=	-5
Newly introduced technology, T1	All	Second	<=	7.5
Newly introduced technology, T1 + T2	All	Second	<=	40
Phase-out	All	Second	<=	40
Newly introduced technology, T1	All	Third	>=	5
Initial shares in 2020	Chlorine	Third	=	various
Phase-out mercury cell in 2025	Chlorine	Third	=	0
Phase-out thermal crackers in 2045	HVC	Third	=	0
Methane pyrolysis not dominant	HVC	Third	<=	50

## Appendix E: Technology share table

Table E1. [RS] Share of production pathways for each product group

Product group	Production pathway	2020	2025	2030	2035	2040	2045	2050
Ammonia	H2 from steam reforming	100%	100%	100%	100%	98%	83%	40%
	H2 from electrolysis	0%	0%	0%	0%	3%	15%	40%
	H2 from methane pyrolysis	0%	0%	0%	0%	0%	3%	20%
Urea	H2 from steam reforming	100%	100%	100%	100%	98%	83%	40%
	H2 from electrolysis	0%	0%	0%	0%	3%	15%	40%
	H2 from methane pyrolysis	0%	0%	0%	0%	0%	3%	20%
Chlorine	Mercury cell	5%	5%	5%	5%	5%	5%	5%
	Diaphragma cell	23%	23%	23%	23%	23%	23%	23%
	Membrane cell	71%	71%	71%	71%	71%	71%	71%
Methanol	Steam reforming	100%	100%	100%	98%	84%	62%	50%
	Biomass gasification	0%	0%	0%	2%	12%	15%	15%
	H2 from electrolysis	0%	0%	0%	0%	3%	13%	25%
	H2 from methane pyrolysis	0%	0%	0%	0%	2%	10%	10%
HVC	Methanol-to HVC (with H2 from electrolyser)	0%	0%	0%	0%	1%	4%	7%
	Crude oil-based naphtha in thermal cracker	100%	99%	92%	87%	82%	61%	41%
	Crude oil-based naphtha in electrical cracker	0%	0%	0%	0%	2%	13%	19%
	Plastic waste pyrolysis in thermal cracker	0%	0%	2%	3%	5%	6%	5%
	Plastic waste pyrolysis in electrical cracker	0%	0%	0%	0%	0%	1%	2%
	Fischer-Tropsch from gasified biomass in thermal cracker	0%	1%	6%	10%	10%	8%	7%
	Fischer-Tropsch from gasified biomass in electrical cracker	0%	0%	0%	0%	0%	2%	3%
	Fischer-Tropsch from H2 from electrolysis in thermal cracker	0%	0%	0%	0%	0%	5%	10%
	Fischer-Tropsch from H2 from electrolysis in electrical cracker	0%	0%	0%	0%	0%	1%	5%

Table E2. [NS] Technology share of production pathways for each product group

Product group	Production pathway	2020	2025	2030	2035	2040	2045	2050
Ammonia	H2 from steam reforming	100%	100%	95%	65%	25%	0%	0%
	H2 from electrolysis	0%	0%	5%	35%	68%	68%	73%
	H2 from methane pyrolysis	0%	0%	0%	0%	8%	33%	28%
Urea	H2 from steam reforming	100%	100%	95%	65%	25%	0%	0%
	H2 from electrolysis	0%	0%	5%	35%	68%	68%	63%
	H2 from methane pyrolysis	0%	0%	0%	0%	8%	33%	38%
Chlorine	Mercury cell	5%	0%	0%	0%	0%	0%	0%
	Diaphragma cell	23%	0%	0%	0%	0%	0%	0%
	Membrane cell	71%	100%	100%	100%	100%	100%	100%
Methanol	Steam reforming	100%	95%	48%	8%	0%	0%	0%
	Biomass gasification	0%	5%	35%	68%	63%	58%	53%
	H2 from electrolysis	0%	0%	10%	5%	23%	33%	43%
	H2 from methane pyrolysis	0%	0%	8%	20%	15%	10%	5%
HVC	Methanol-to HVC (with H2 from electrolyser)	0%	0%	0%	0%	0%	0%	0%
	Crude oil-based naphtha in thermal cracker	100%	100%	88%	70%	58%	18%	0%
	Crude oil-based naphtha in electrical cracker	0%	0%	0%	0%	8%	5%	0%
	Plastic waste pyrolysis in thermal cracker	0%	0%	8%	15%	10%	5%	0%
	Plastic waste pyrolysis in electrical cracker	0%	0%	0%	0%	8%	33%	28%
	Fischer-Tropsch from gasified biomass in thermal cracker	0%	0%	5%	15%	10%	5%	0%
	Fischer-Tropsch from gasified biomass in electrical cracker	0%	0%	0%	0%	8%	30%	25%
	Fischer-Tropsch from H2 from electrolysis in thermal cracker	0%	0%	0%	0%	0%	0%	0%
	Fischer-Tropsch from H2 from electrolysis in electrical cracker	0%	0%	0%	0%	0%	5%	48%

Table E3. [NS] Technology share of production pathways for each product group for sensitivity analysis with maximum emission factors for electricity

Product group	Production pathway	2020	2025	2030	2035	2040	2045	2050
Ammonia	H2 from steam reforming	100%	100%	95%	65%	25%	0%	0%
	H2 from electrolysis	0%	0%	5%	35%	70%	65%	60%
	H2 from methane pyrolysis	0%	0%	0%	0%	5%	35%	40%
Urea	H2 from steam reforming	100%	100%	95%	65%	25%	0%	0%
	H2 from electrolysis	0%	0%	5%	35%	70%	65%	60%
	H2 from methane pyrolysis	0%	0%	0%	0%	5%	35%	40%
Chlorine	Mercury cell	5%	0%	0%	0%	0%	0%	0%
	Diaphragma cell	23%	0%	0%	0%	0%	0%	0%
	Membrane cell	71%	100%	100%	100%	100%	100%	100%
Methanol	Steam reforming	100%	95%	53%	13%	0%	0%	0%
	Biomass gasification	0%	5%	35%	68%	85%	80%	75%
	H2 from electrolysis	0%	0%	5%	0%	0%	10%	20%
	H2 from methane pyrolysis	0%	0%	8%	20%	15%	10%	5%
HVC	Methanol-to HVC (with H2 from electrolyser)	0%	0%	0%	0%	0%	0%	0%
	Crude oil-based naphtha in thermal cracker	100%	100%	93%	85%	58%	18%	0%
	Crude oil-based naphtha in electrical cracker	0%	0%	0%	0%	8%	8%	3%
	Plastic waste pyrolysis in thermal cracker	0%	0%	8%	15%	10%	5%	0%
	Plastic waste pyrolysis in electrical cracker	0%	0%	0%	0%	8%	33%	50%
	Fischer-Tropsch from gasified biomass in thermal cracker	0%	0%	0%	0%	10%	5%	0%
	Fischer-Tropsch from gasified biomass in electrical cracker	0%	0%	0%	0%	8%	33%	48%
	Fischer-Tropsch from H2 from electrolysis in thermal cracker	0%	0%	0%	0%	0%	0%	0%
Fischer-Tropsch from H2 from electrolysis in electrical cracker	0%	0%	0%	0%	0%	0%	0%	

Table E4. [NS] Technology share of production pathways for each product group for sensitivity analysis with 100:0 allocation of CCU

Product group	Production pathway	2020	2025	2030	2035	2040	2045	2050
Ammonia	H2 from steam reforming	100%	100%	95%	65%	25%	0%	0%
	H2 from electrolysis	0%	0%	5%	35%	68%	68%	73%
	H2 from methane pyrolysis	0%	0%	0%	0%	8%	33%	28%
Urea	H2 from steam reforming	100%	100%	95%	65%	25%	0%	0%
	H2 from electrolysis	0%	0%	5%	35%	68%	68%	73%
	H2 from methane pyrolysis	0%	0%	0%	0%	8%	33%	28%
Chlorine	Mercury cell	5%	0%	0%	0%	0%	0%	0%
	Diaphragma cell	23%	0%	0%	0%	0%	0%	0%
	Membrane cell	71%	100%	100%	100%	100%	100%	100%
Methanol	Steam reforming	100%	88%	40%	0%	0%	0%	0%
	Biomass gasification	0%	8%	18%	13%	8%	3%	0%
	H2 from electrolysis	0%	5%	35%	68%	78%	88%	95%
	H2 from methane pyrolysis	0%	0%	8%	20%	15%	10%	5%
HVC	Methanol-to-HVC (with H2 from electrolyser)	0%	0%	0%	0%	0%	5%	0%
	Crude oil-based naphtha in thermal cracker	100%	100%	88%	70%	53%	30%	0%
	Crude oil-based naphtha in electrical cracker	0%	0%	0%	0%	8%	5%	0%
	Plastic waste pyrolysis in thermal cracker	0%	0%	8%	15%	10%	5%	0%
	Plastic waste pyrolysis in electrical cracker	0%	0%	0%	0%	8%	5%	0%
	Fischer-Tropsch from gasified biomass in thermal cracker	0%	0%	5%	15%	10%	5%	0%
	Fischer-Tropsch from gasified biomass in electrical cracker	0%	0%	0%	0%	8%	5%	0%
	Fischer-Tropsch from H2 from electrolysis in thermal cracker	0%	0%	0%	0%	0%	5%	0%
Fischer-Tropsch from H2 from electrolysis in electrical cracker	0%	0%	0%	0%	5%	35%	100%	

## Appendix F: Emission factors

Table F1. Emission factors used to calculate the energy-related emissions (for electricity the lower emission factors and the higher emissions factors used in the sensitivity analysis are given)

	2020	2025	2030	2035	2040	2045	2050
Hard coal (t CO <sub>2</sub> /t)	0.34	0.34	0.34	0.34	0.34	0.34	0.34
Lignite (t CO <sub>2</sub> /t)	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Oil (t CO <sub>2</sub> /t)	0.26	0.26	0.26	0.26	0.26	0.26	0.26
Oil products (t CO <sub>2</sub> /t)	0.27	0.27	0.27	0.27	0.27	0.27	0.27
Natural gas (t CO <sub>2</sub> /t)	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Biomass (t CO <sub>2</sub> /t)	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Solarthermal heat (t CO <sub>2</sub> /t)	0	0	0	0	0	0	0
Geothermal heat (t CO <sub>2</sub> /t)	0	0	0	0	0	0	0
Public district heat (t CO <sub>2</sub> /t)	0.28	0.28	0.28	0.28	0.28	0.28	0.28
Heat pump (t CO <sub>2</sub> /t)	0.28	0.28	0.28	0.28	0.28	0.28	0.28
Electricity (t CO <sub>2</sub> /t) (lower)	0.45	0.41	0.28	0.17	0.08	0.04	0
Electricity (t CO <sub>2</sub> /t) (higher, used for sensitivity analysis)	0.45	0.44	0.35	0.27	0.2	0.15	0.12

## Appendix G: Calculation model [Default] (Excel)

## Appendix H: Calculation model [100:0 allocation of CCU emissions] (Excel)