

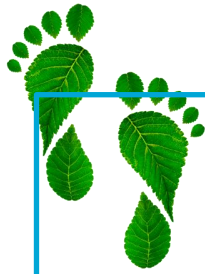
# Energieopslag in brandstoffen: processen en procesintegratie uitdagingen



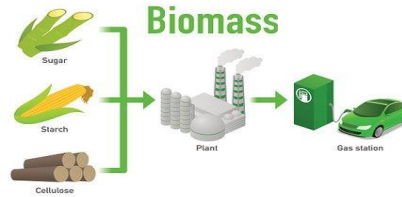
Wiebren de Jong (3mE, Process & Energy)

[wiebren.dejong@tudelft.nl](mailto:wiebren.dejong@tudelft.nl)

# Large Scale Energy Storage section



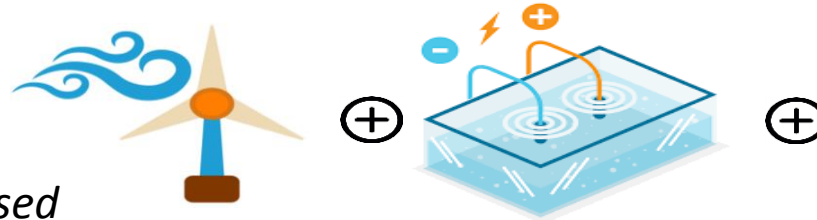
*'Biomass route'*



*Prof. dr. Wiebren de Jong*



*'Indirect route'*

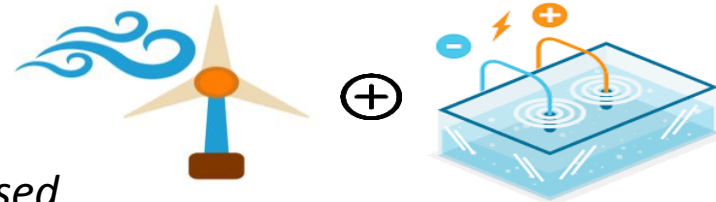


*Dr. Wim Haije*



*Renewable power based*

*'Direct route'*



*Dr. Ruud Kortlever*

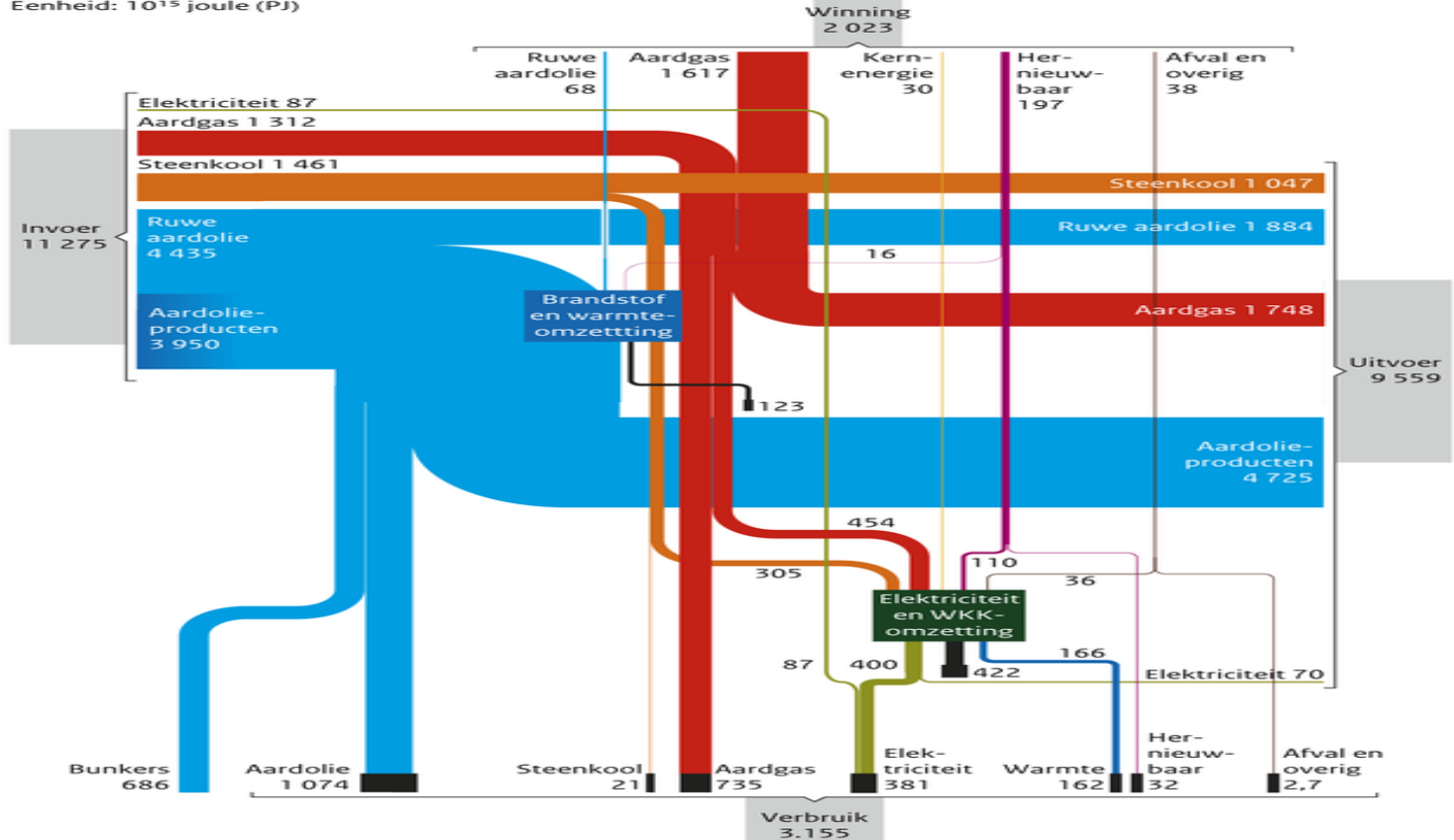


*Renewable power based*



# Dutch energy supply, mainly fossil based

Energiestromen, 2016\*\*  
Eenheid: 10<sup>15</sup> joule (PJ)



N.B. De som van de zwarte blokjes is het totale energieverbruik (finaal verbruik en saldi omzetting). In deze figuur zijn verschillende details verwaarloosd.

Bron: CBS

CBS/feb18  
www.clo.nl/nlo20120



# Wind/solar energy supply is intermittent...



95% of Germany's energy was provided by renewables last Sunday



Portugal just ran for 4 straight days entirely on renewable energy

Awesome!  
PETER OGDENHILL 19 MAY 2016



## Timescales

< ~15-30 min



~12 h



days



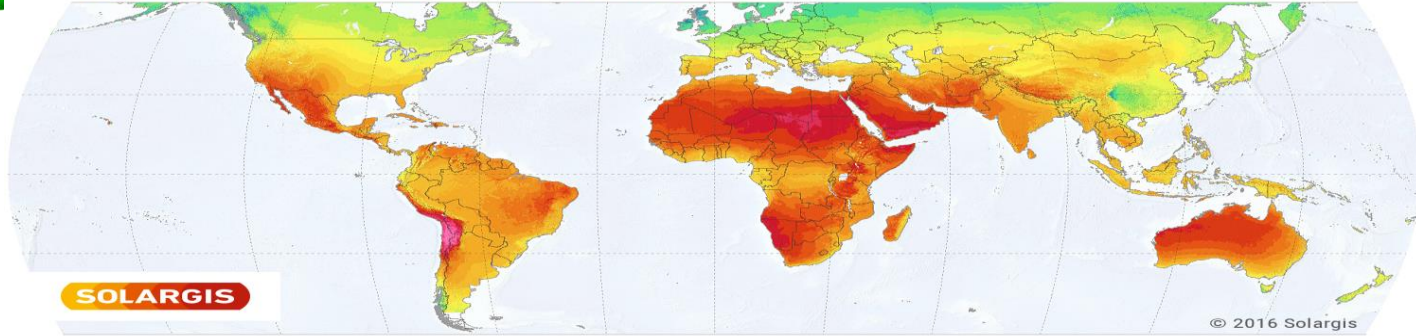
weeks-  
months





# Geographic mismatch demand/supply

GLOBAL HORIZONTAL IRRADIATION



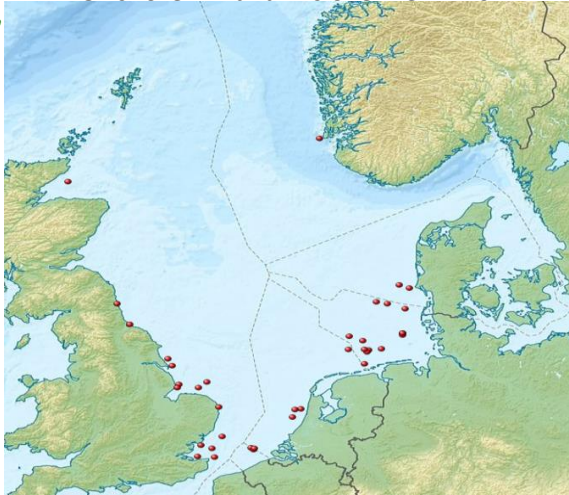
Long-term average of  $\left\{ \begin{array}{l} \text{annual sum} < 800 \quad 1000 \quad 1200 \quad 1400 \quad 1600 \quad 1800 \quad 2000 \quad 2200 \quad 2400 \quad 2600 \quad 2800 \\ \text{daily sum} < 2.0 \quad 2.5 \quad 3.0 \quad 3.5 \quad 4.0 \quad 4.5 \quad 5.0 \quad 5.5 \quad 6.0 \quad 6.5 \quad 7.0 \quad 7.5 > \end{array} \right.$  kWh/m<sup>2</sup>



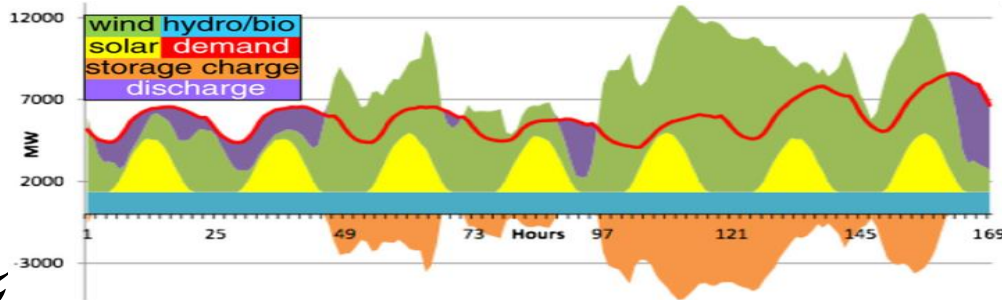
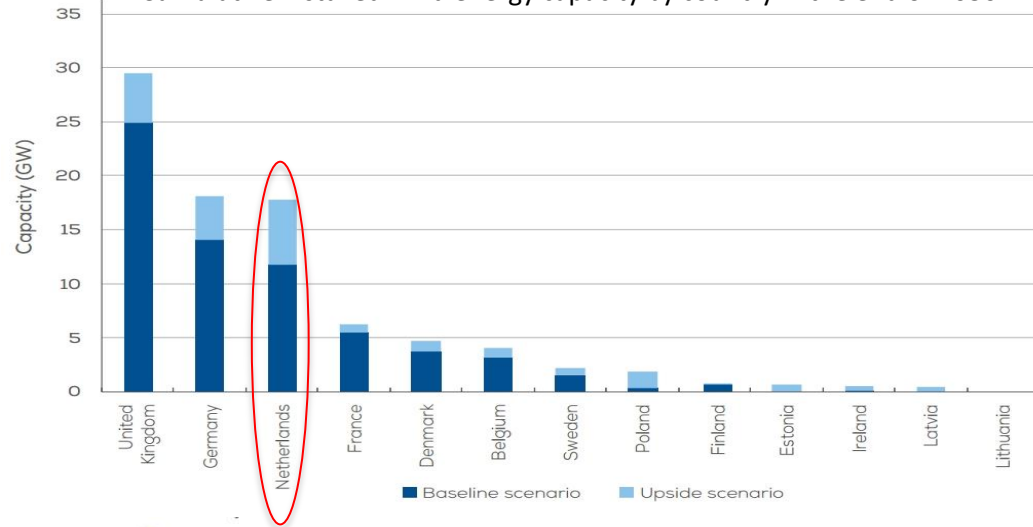


# Need for energy storage, NL context

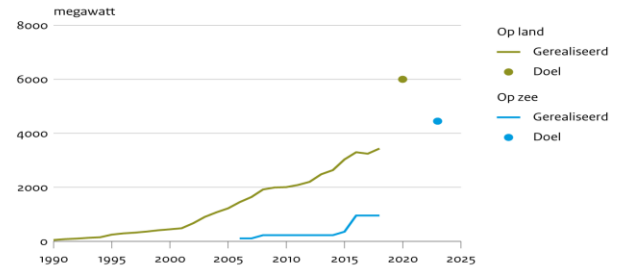
Offshore wind farms overview - 2017



Cumulative installed wind energy capacity by country in the end of 2030



Windvermogen op land en zee

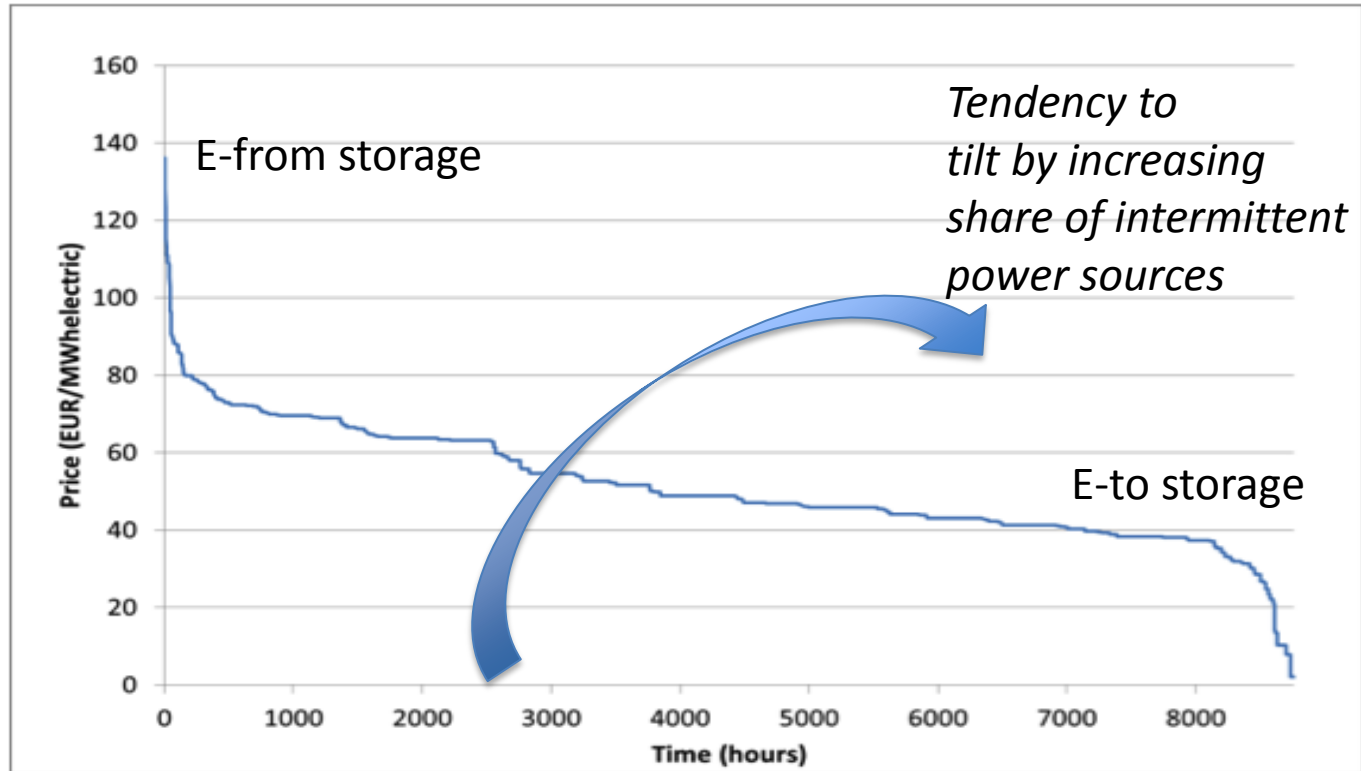


Bron: CBS

CBS/aug19  
www.clo.nl/nl038627

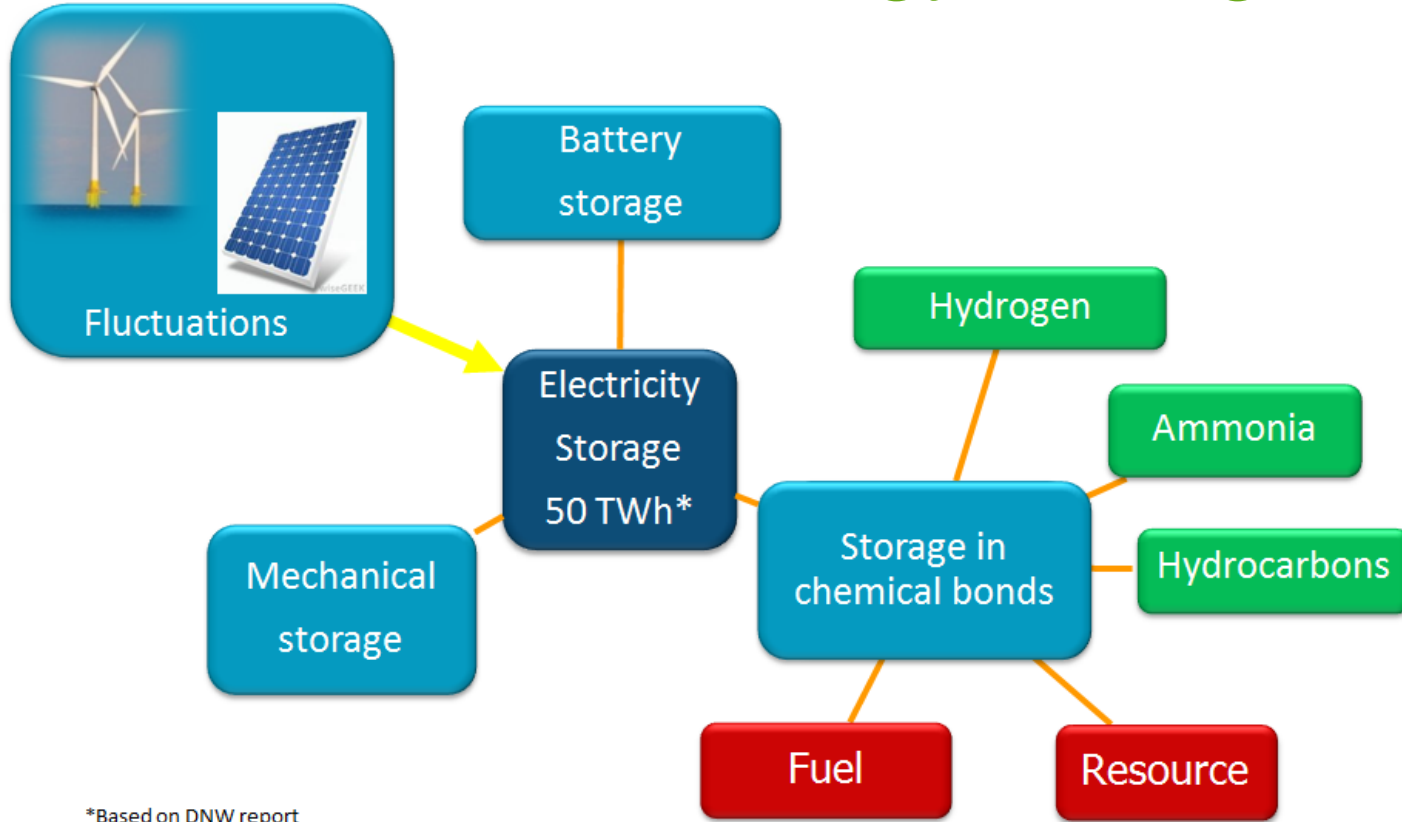


# Possible scenario for power price-duration curve 2030



Source (adapted): <http://www.voltachem.com/news/when-why-power-2-heat>

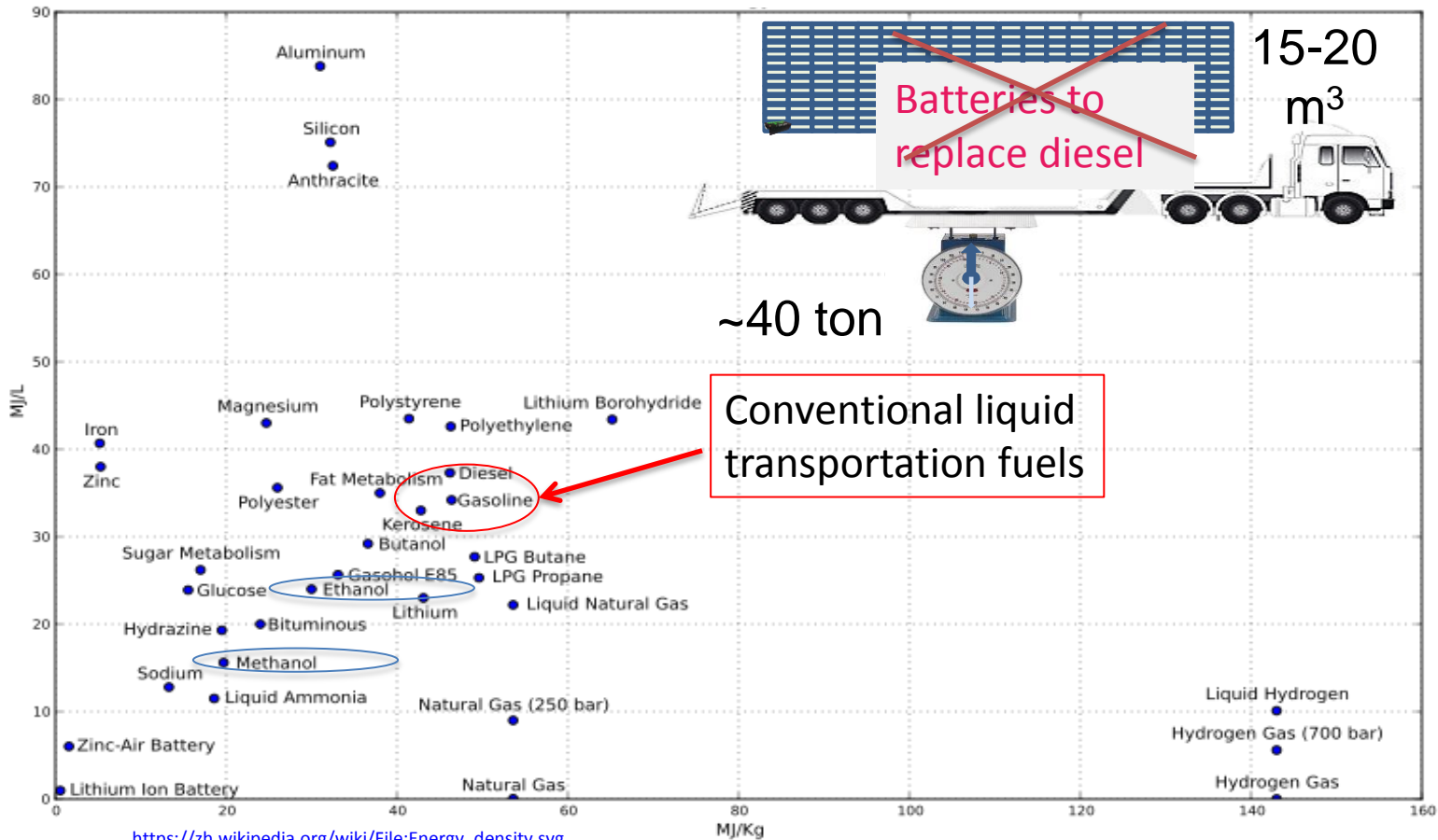
# Modes of energy storage



\*Based on DNW report



# Energy density of several fuels



[https://zh.wikipedia.org/wiki/File:Energy\\_density.svg](https://zh.wikipedia.org/wiki/File:Energy_density.svg)

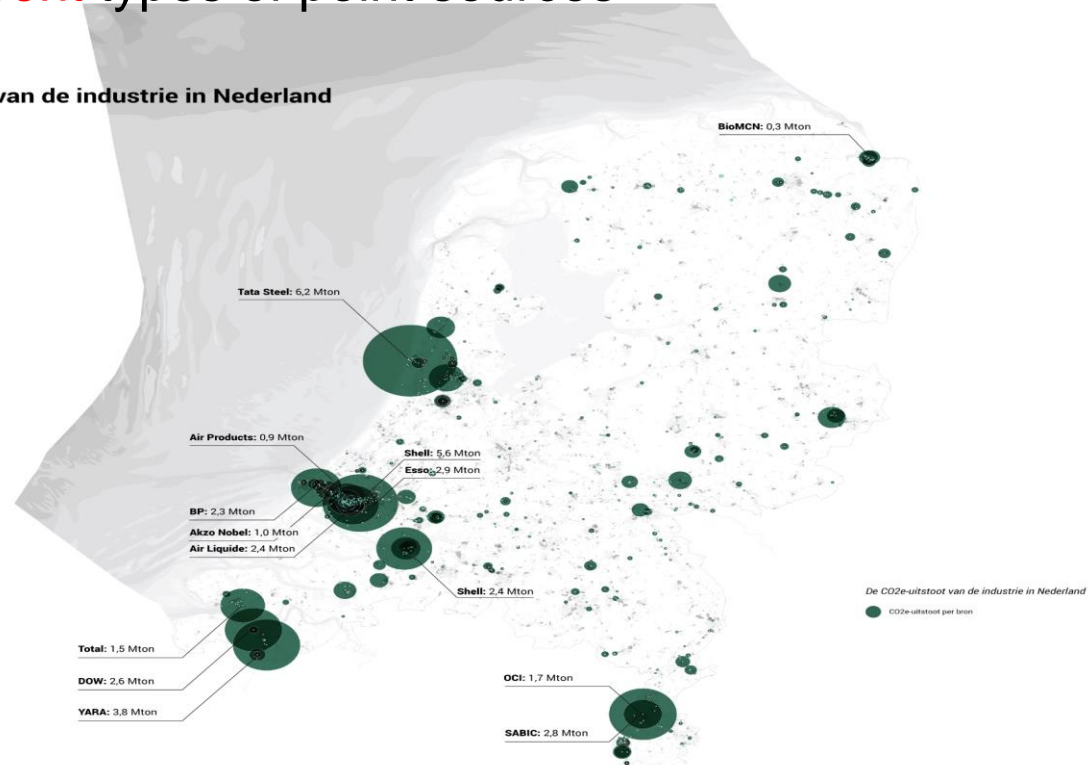
Picture truck, courtesy prof. Philip de Goeij (TU Eindhoven)



# Dutch industry CO<sub>2</sub> reduction

- Reduction by 14.3+5.1 Mton/yr (2030) from 55.1 Mton/yr (2015)
- All **different** types of point sources

CO<sub>2</sub>e-uitstoot van de industrie in Nederland

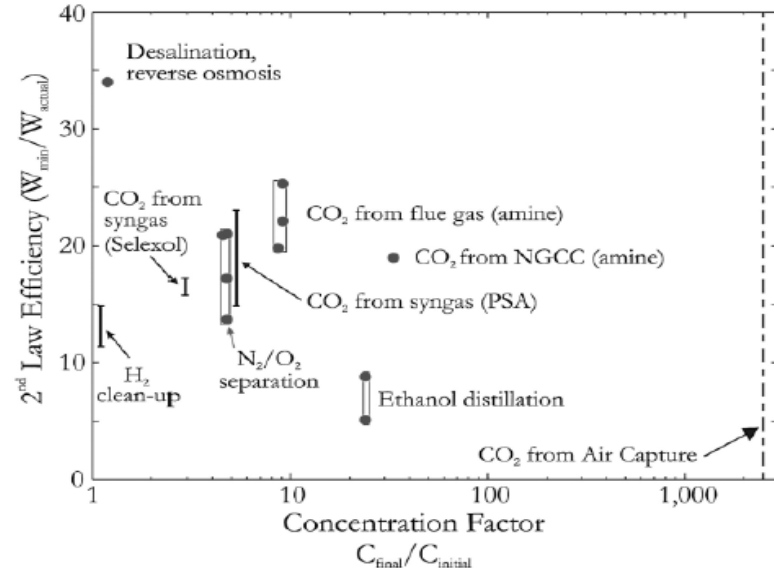
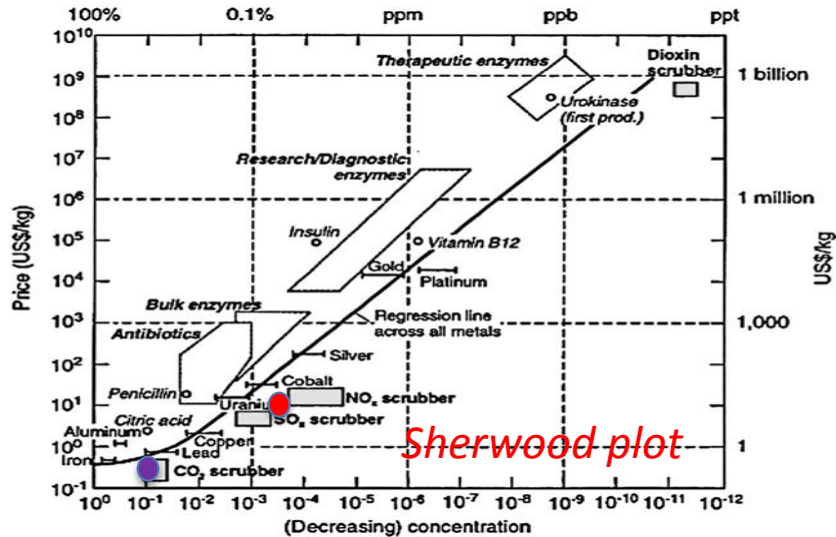




# CO<sub>2</sub> sources

Advantageous to use concentrated CO<sub>2</sub> streams *first*

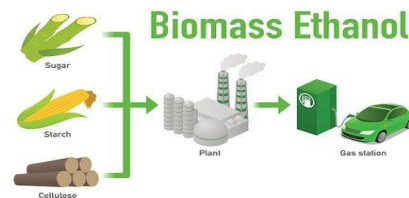
- Minimum work increases when more dilute  $\Delta G^\circ = -RT_o \ln y_{CO_2} \approx 0.5 MJ.kg^{-1}$
- High 2<sup>nd</sup> Law of thermodynamics efficiency
- Costs increase substantially for decreasing concentration



# Scenario's for future production of chemicals and fuels

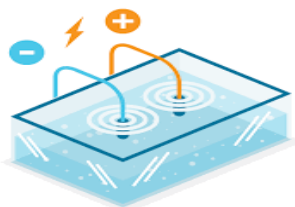


*'Conventional'*



*'Direct route'*

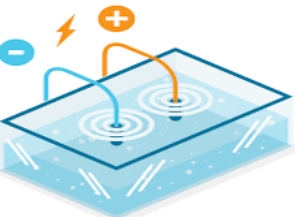
*Renewable power based*



*e-Refinery*

*'Indirect route'*

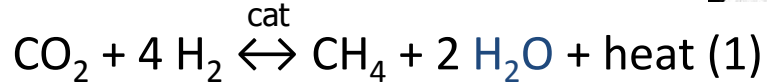
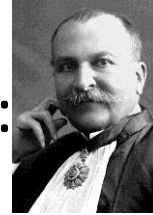
*Renewable power based*



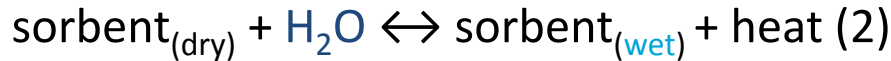


# Indirect power-to-X route to methane

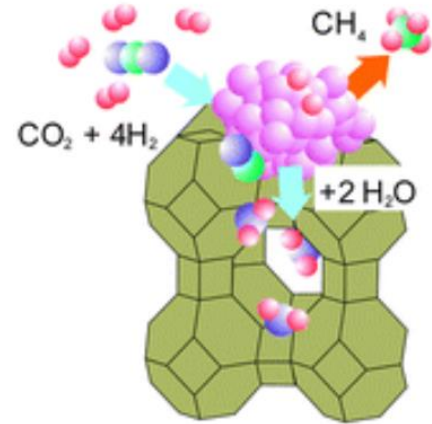
- Sabatier reaction (1902!):



- Shift of the equilibrium by sorption:

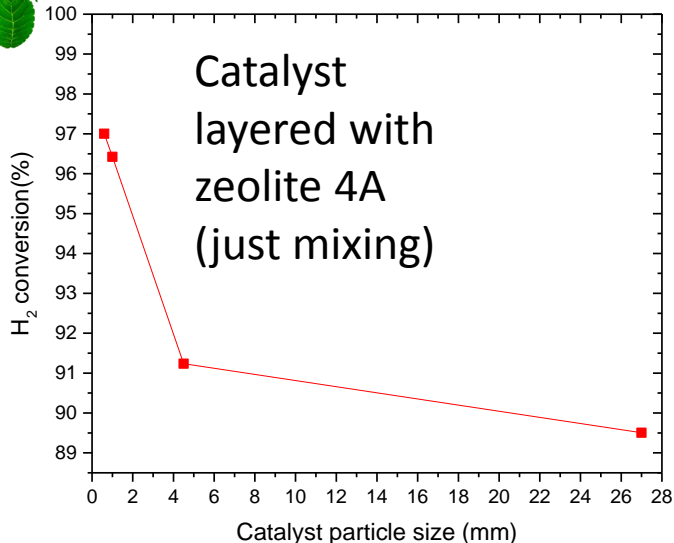
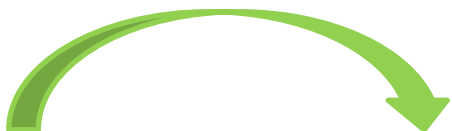
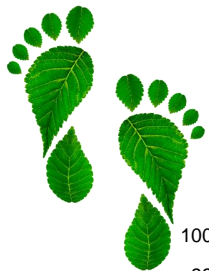


- Dry (=regenerate) sorbent with heat (1)



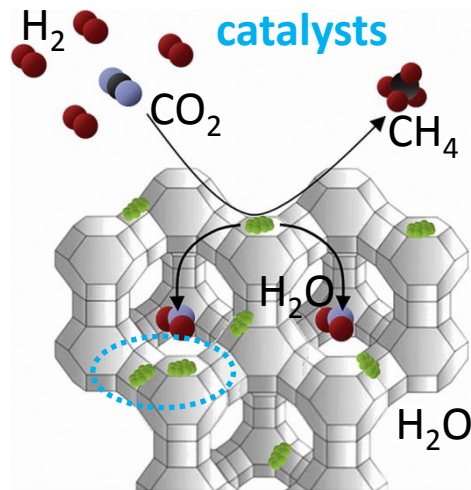
*Sorption-enhanced  
equilibrium*

# Research towards new catalysts

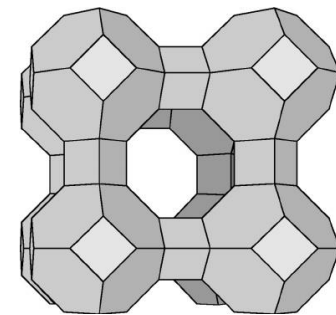


H<sub>2</sub> conversion under the condition of different size catalyst(42g) mixed with zeolite 4A (2.5-5mm, 220 g) at 280 °C, GHSV=2400 h<sup>-1</sup>.

Different precursors to prepare Ni-zeolite catalysts



Zeolite 13X\*

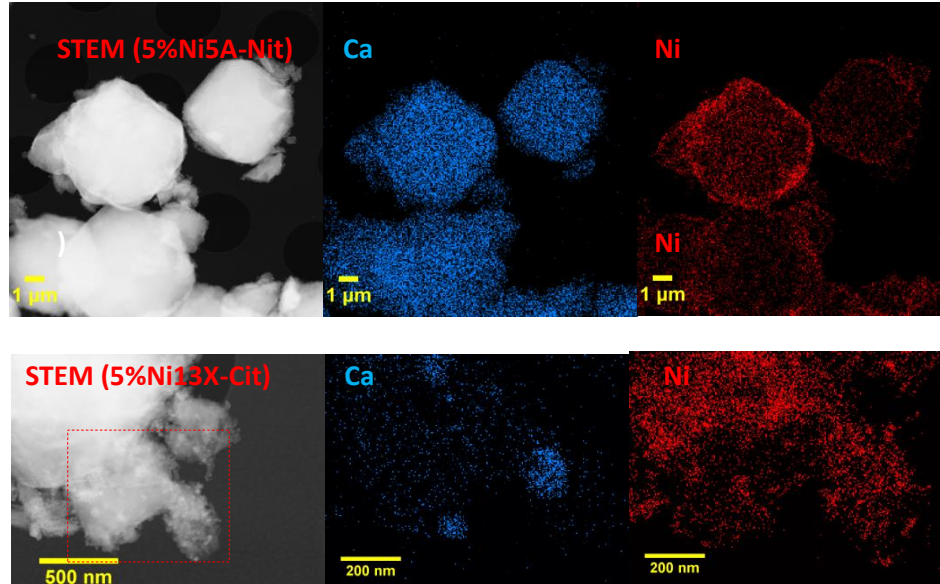


Zeolite 5A

Sorption enhanced CO<sub>2</sub> methanation over a nickel catalyst on zeolite

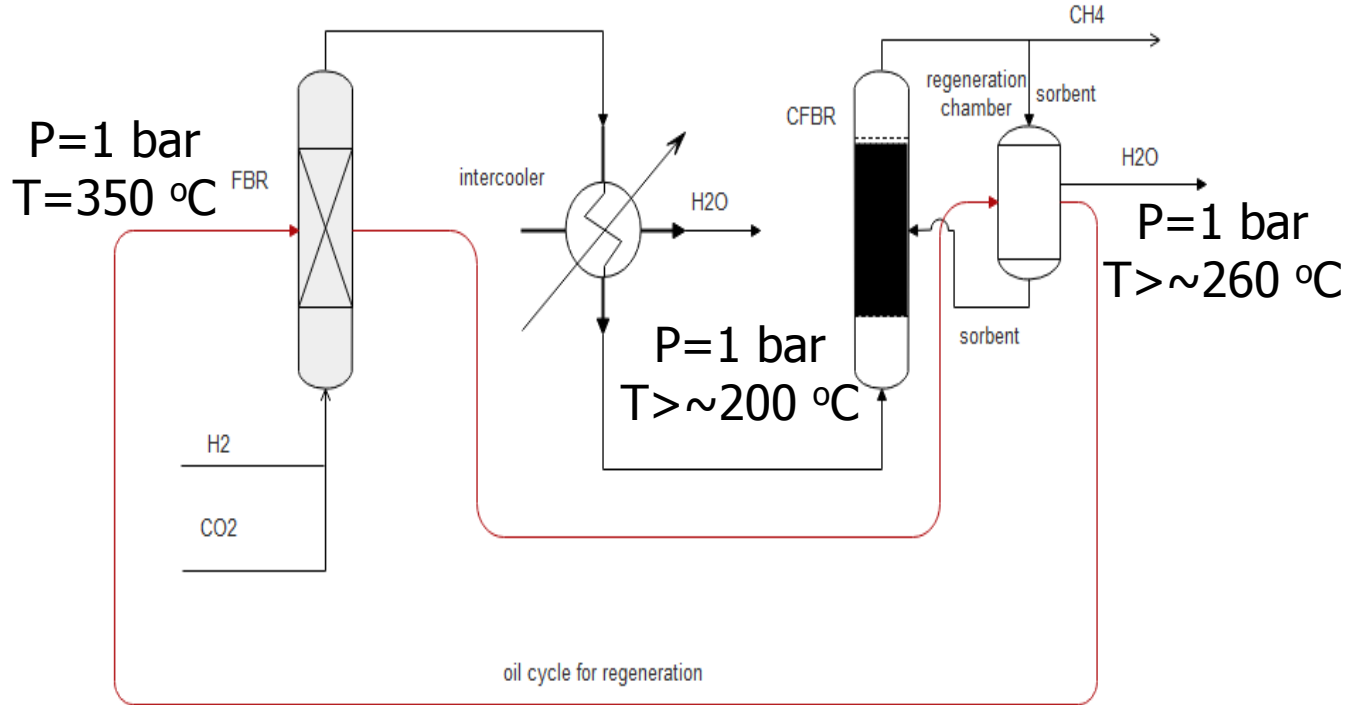


# Material preparation, impact on Ni distribution





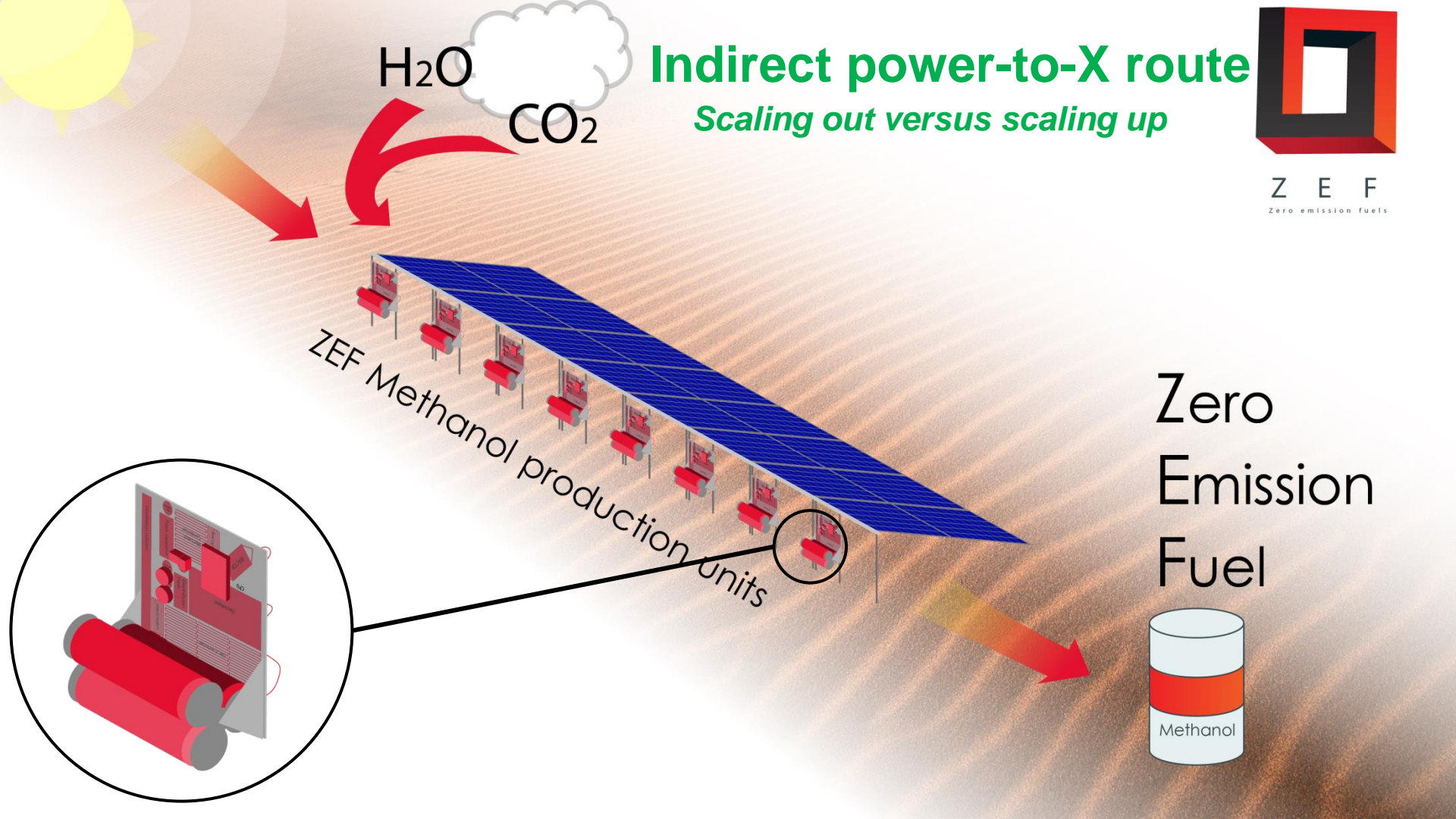
# Towards an Integrated novel process



**Challenge:** Smart reactor system design including **Circulating Fluidized Bed Reactor** with optimal heat integration to regenerate sorbent and to make use of exothermal reaction







# Indirect power-to-X route

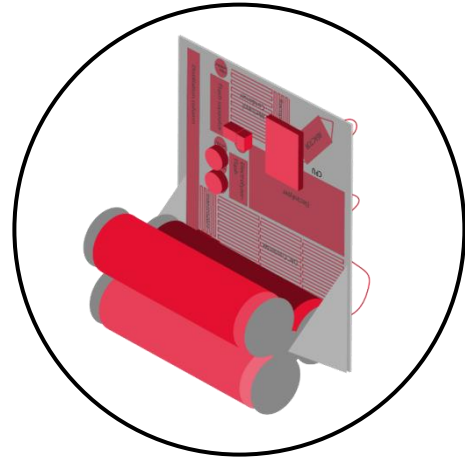
*Scaling out versus scaling up*



Z E F  
Zero emission fuels

ZEF Methanol production units

Zero  
Emission  
Fuel





# Global Methanol production

## Methanol produced from gas (80%)

Production cost: 100–300 €/tonne

10 suppliers @ 50% marketshare

70 large production plants globally

## Methanol produced from coal (17%)

Production cost: 200 – 350 €/tonne

Mainly in China

## Bio Methanol (< 1%)

Production cost: 500 €/tonne

Premium sales price: 700 €/tonne

0.18 million tonnes / year

EU directive incentive: double counting in blending

IHS US GULF AND WESTERN EUROPE METHANOL CONTRACT PRICES AND METHANEX ASIAN POSTED CONTRACT PRICE (APCP) JANUARY 2006 - JANUARY 2017



Grey average: **350 €/tonne**

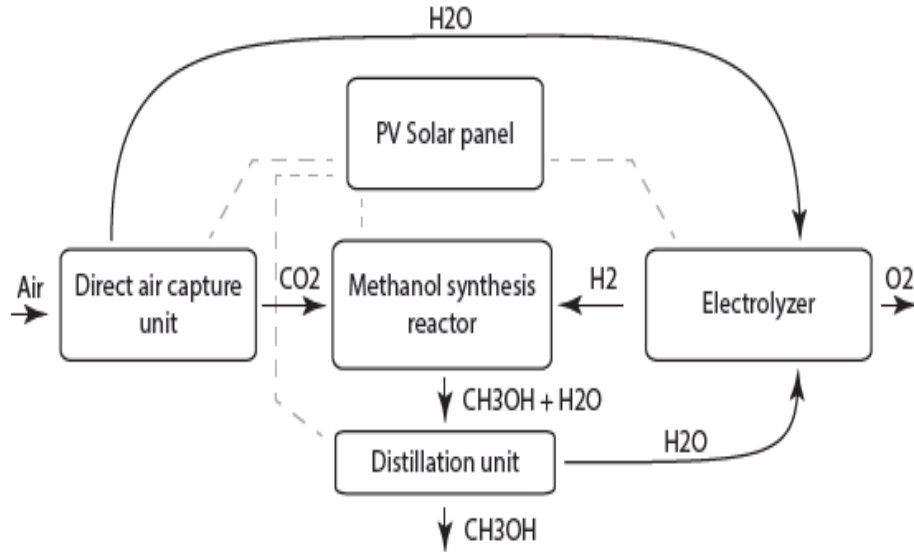
Green premium: **700 €/tonne**





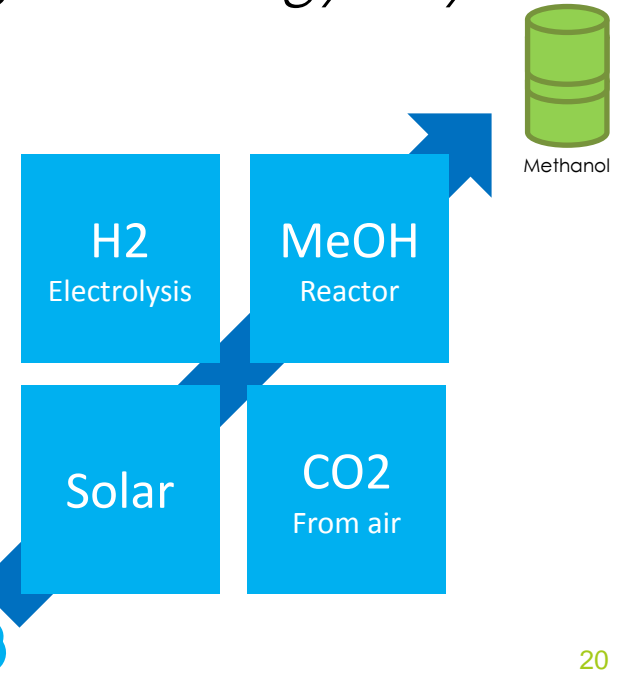
# The ZEF pathway

*“Capture CO<sub>2</sub> from air to produce renewable liquid fuels using solar energy only!”*

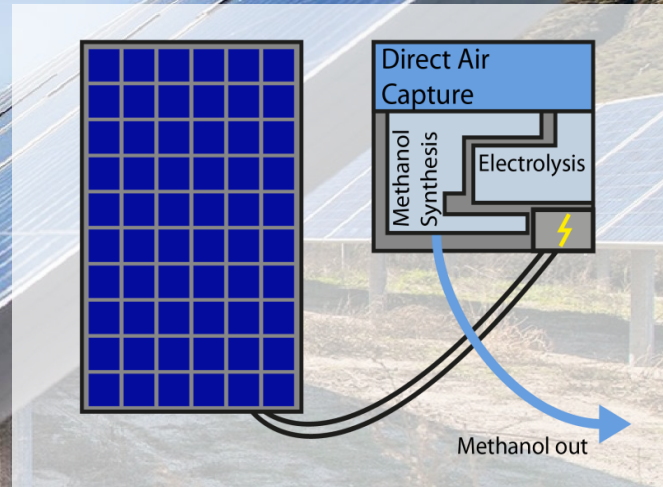


## Symbols:

- System unit
- Material stream
- Energy stream



# ZEF Micro-plant: numbering up



Dynamic operation

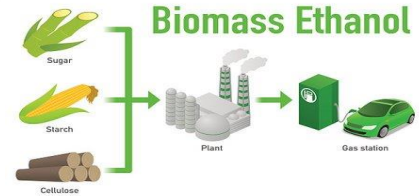
100K Micro-plants  
< 150 Components

Fast(er) realization

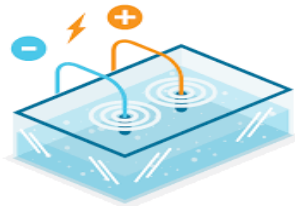


# Scenario's for future production of chemicals and fuels

*'Conventional'*

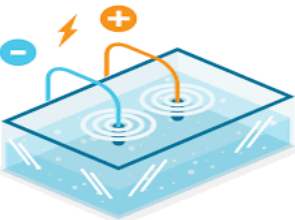


*'Direct route'*



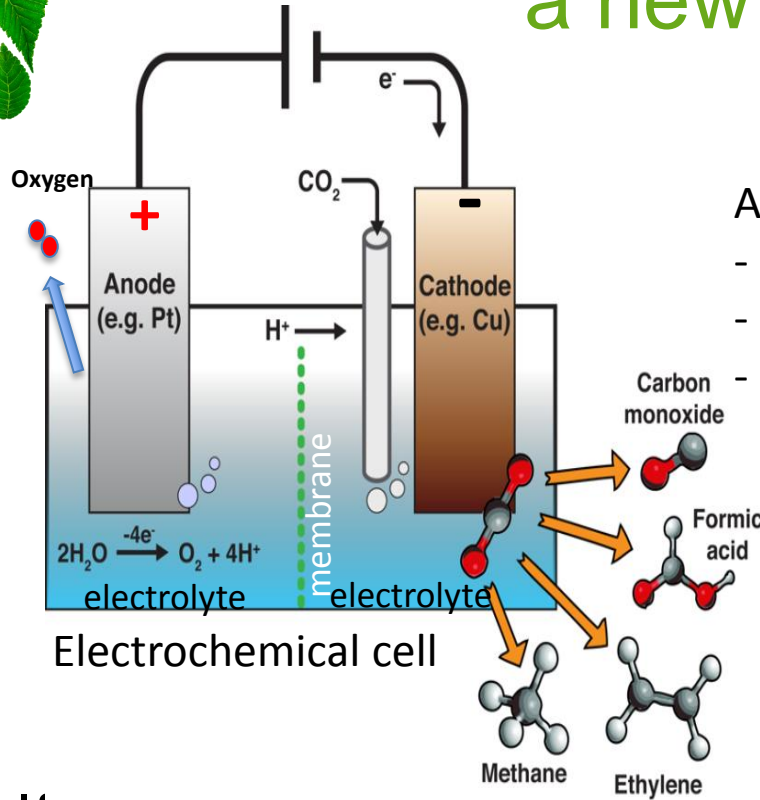
*e-Refinery*

*'Indirect route'*





# Direct electrochemical CO<sub>2</sub> conversion, a new research area



Advantages of using electrochemical conversion:

- Using DC electricity
- Mild process conditions
- Can be carried out relatively selectively

$$\Delta V = \Delta E + \Sigma \eta + IR$$

Equilibrium Potential (thermodynamics)      Overpotentials      Ohmic (resistance) loss

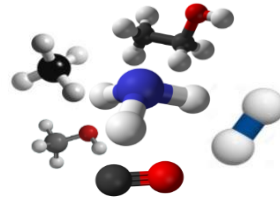
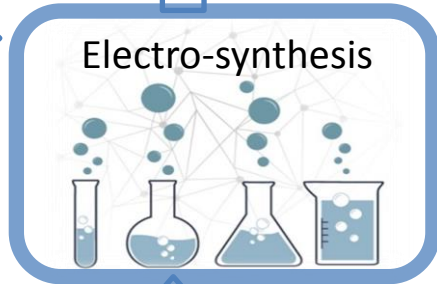
# Delft Initiative: "The e-Refinery"



Water  
Air (CO<sub>2</sub> /N<sub>2</sub>)  
Biomass  
Electricity



Bulk  
chemicals



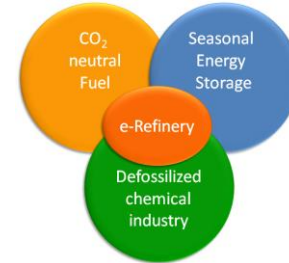
Process



Fuels

Chemicals

Use



CO<sub>2</sub>  
Waste & Emissions



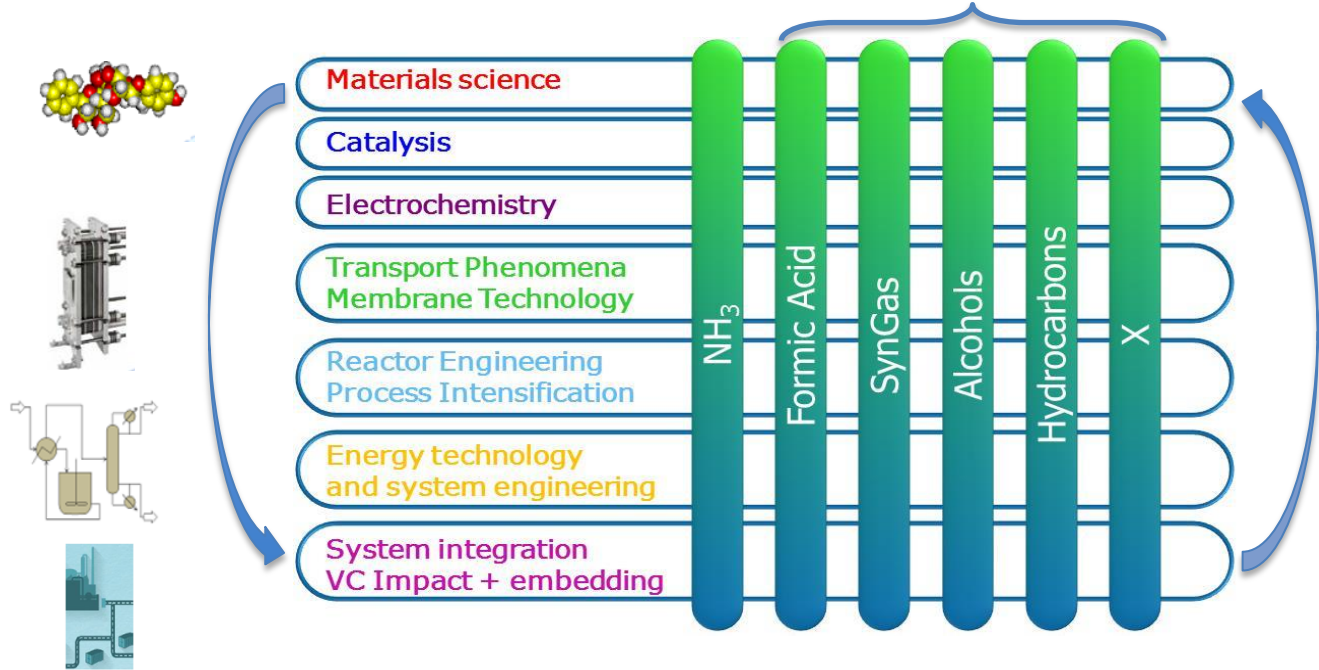




# e-Refinery development at TU Delft

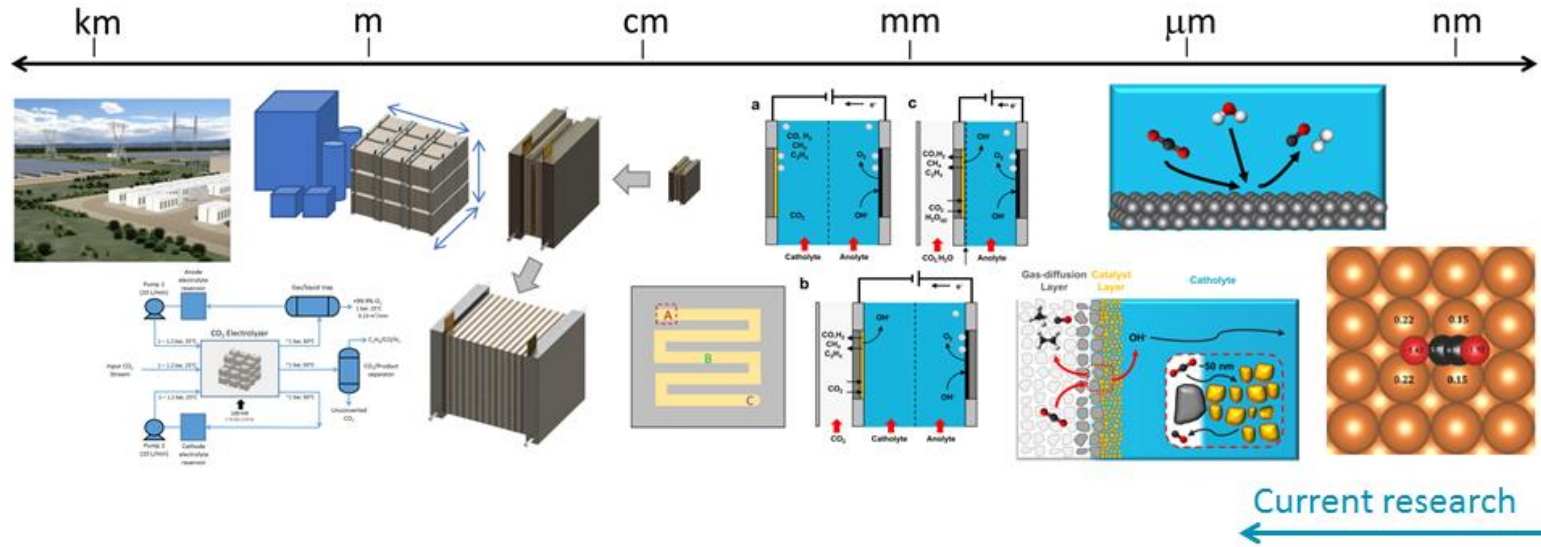
Fuels, bulk chemicals

CO<sub>2</sub> based



**Need for Speed: parallel development together with our industry!**

# Bridging scales



← Large scale research: high current densities using abundant materials

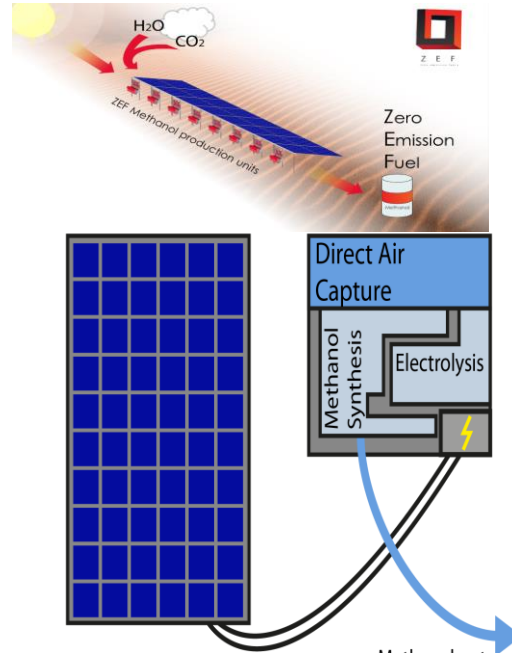




# Bridging TRL levels: idea to pilots



Electrochemical conversion  
Reactor CO<sub>2</sub> to formic acid



System Integration and  
Process Intensification  
3D Printing of Components



Validation



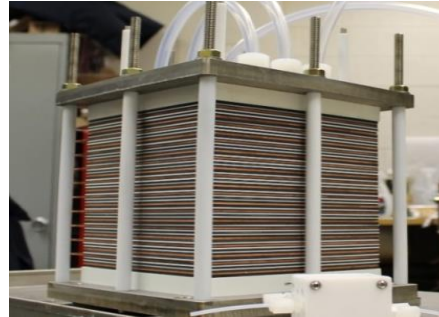
# Ambition: 100 kW electrolyser for ethylene production by 2025

## Operating parameters

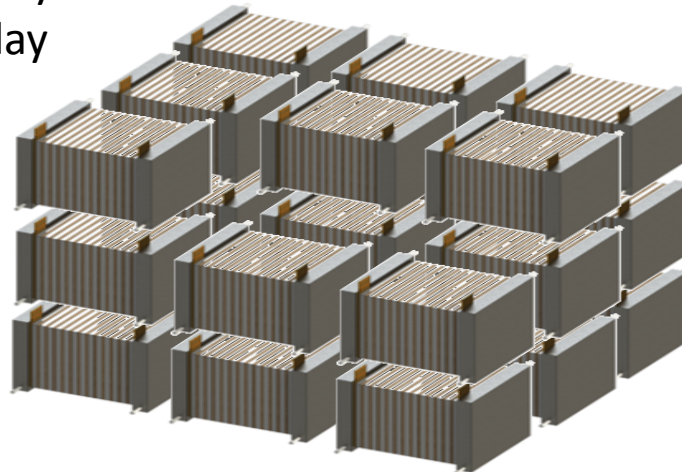
Total amperage:	~31 kA
CO <sub>2</sub> converted:	~143 kg CO <sub>2</sub> /day
C <sub>2</sub> H <sub>4</sub> Produced:	~45 kg C <sub>2</sub> H <sub>4</sub> /day
H <sub>2</sub> O consumption:	~58 kg H <sub>2</sub> O/day
O <sub>2</sub> produced at anode:	~156 kg O <sub>2</sub> /day

## Goals

- Feasibility test
- Find design rules
- Basis for large scale design
- Provide input for LCA



World production  
Ethylene tending to  
~200 Mton/yr  
-> ~**1200 GW<sub>e</sub>** needed



# Further developments



## ‘Indirect route’ of energy storage

- Improving fuel generation selectivity, via material development (catalyst-sorbent)
- Process integration (heat utilization, reaction-regeneration, system dynamics)
- Scale-up (process simulation & valorization, component development and testing)

## ‘Direct route’ of energy storage

- Improving, scale-up and implementing gas diffusion electrodes (increase  $i$ , lower potential)
- Design of better, stable membranes (high recovery of products)
- Design of stable electrodes (high stability in a range of pH values)
- In-situ separation of products (eliminate downstream steps)
- Use of non-aqueous solvents (easier product recovery)
- Optimize gas and liquid flows (increase concentration)
- Paired electrolysis (anode side alternative products, improved economics of overall process)



# Thank you for your attention!

Acknowledgment to current projects at TU Delft:



E2CB NWO Perspectief



Toegepaste en  
Technische Wetenschappen

TKI-Shell 'ToELS' project

