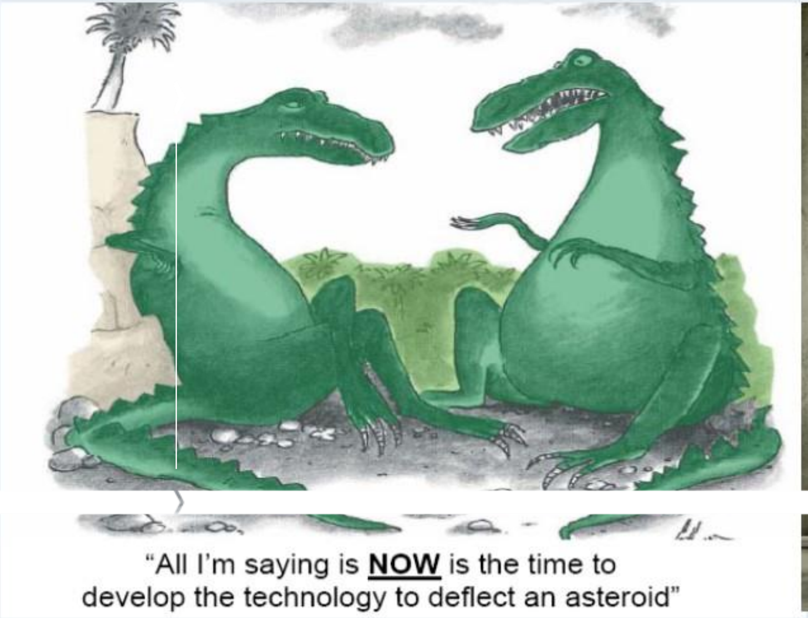
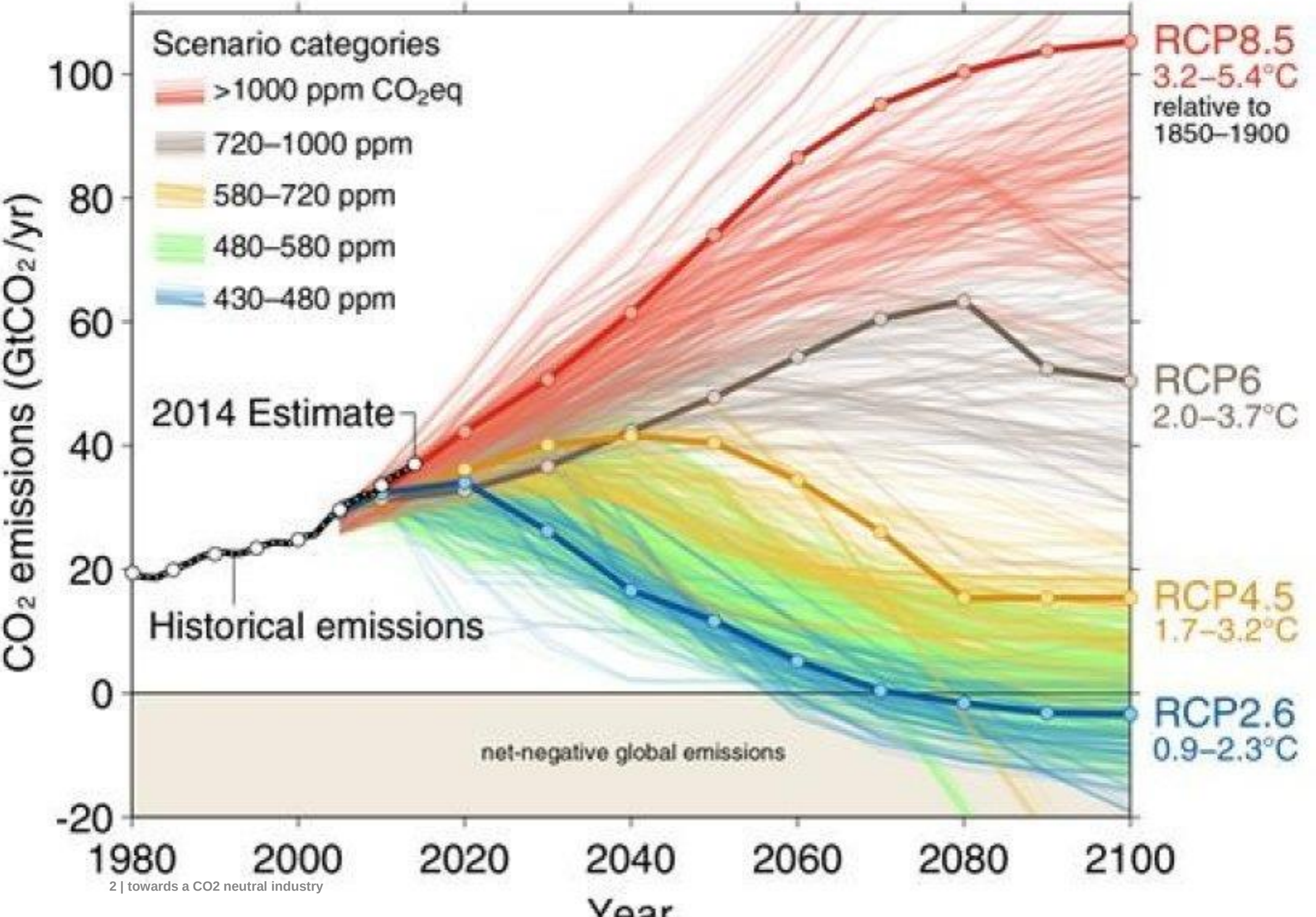
CO2 capture



Prof. Dr. Earl Goetheer



TNO innovation for life

The Rodney & Otamatea Times

WAITEMATA & KAIPARA GAZETTE.

PRICE—10s per annum in advance

WARKWORTH, WEDNESDAY, AUGUST 14, 1912.

3d per Copy.

Science Notes and News.

COAL CONSUMPTION AFFECTING CLIMATE.

The furnaces of the world are now burning about 2,000,000,000 tons of coal a year. When this is burned, uniting with oxygen, it adds about 7,000,000,000 tons of carbon dioxide to the atmosphere yearly. This tends to make the air a more effective blanket for the earth and to raise its temperature. The effect may be considerable in a few centuries.

1912 !!

POPULAR MECHANICS 341

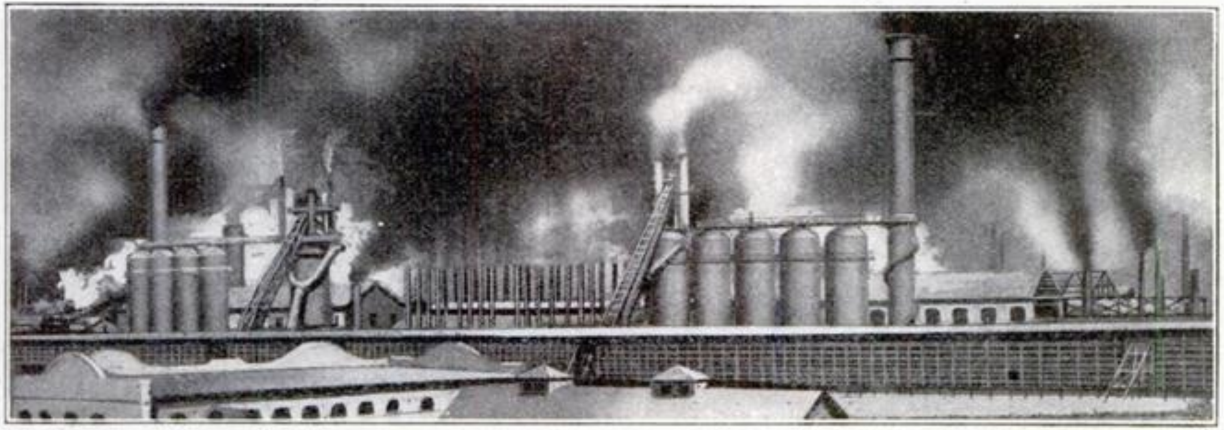


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ILLUSTRATION AND CAPTION ON COAL AND CLIMATE CHANGE FROM MARCH 1912 POPULAR MECHANICS.

NIEUWE APELDOORNSCHE COURANT VAN VRIJDAG 8 JANUARI 1932.

Koude en beschaving.

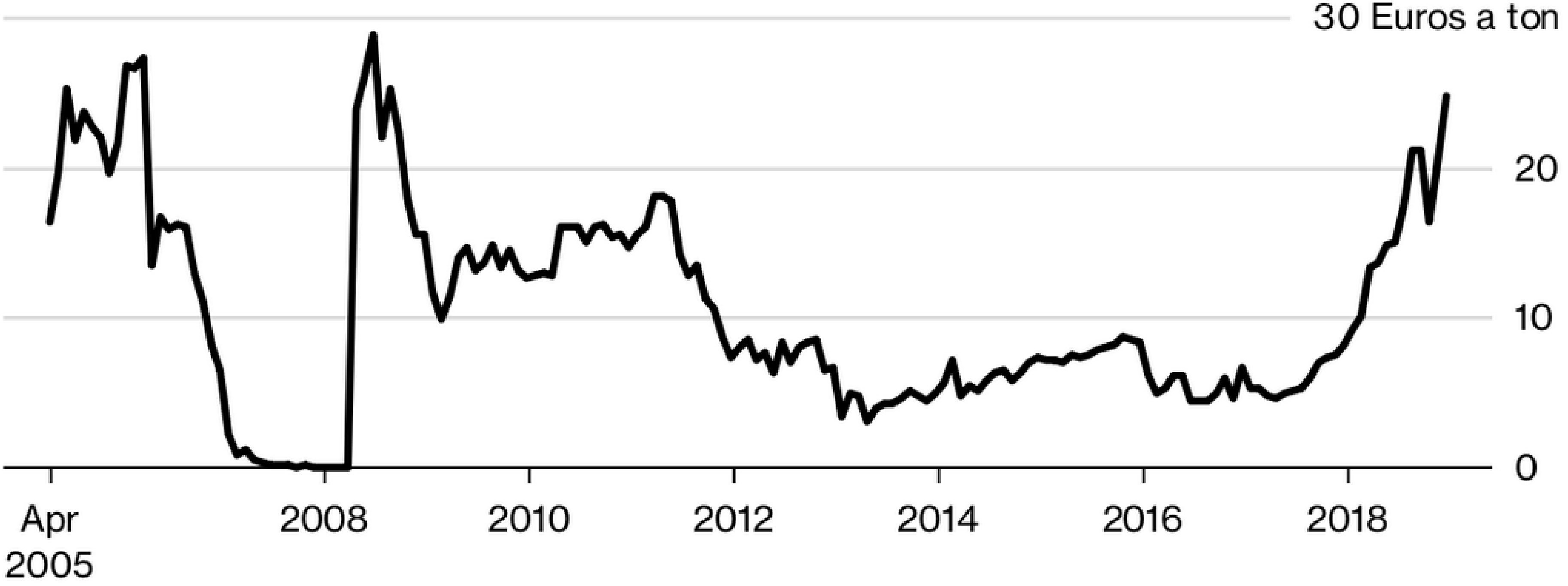
Londen, 5 Jan....... Dr. Robert Innes, een bekend Engelsch astronoom en meteoroloog, heeft in een zitting van de British Astronomical Associaton verklaard dat het klimaat v... de wereld geleidelijk warmer wordt en da... oorzaak daarvan te zoeken is in de toen... de beschaving!

Het klimaat, verklaarde dr. Innes, ...t af van den toestand van de atmosp... Kool-dioxide in de lucht heeft hetze... ffect als een deken — het maakt het we... armer. De bezigheden van den beschaafden mensch — het verbruik van steenkolen en benzine bijvoorbeeld — veroorzaken kool-dioxide. Indien deze theorie juist is, dan beteekent dit, dat wij geen ouderwetsche strenge winters meer krijgen en dat de zomers geleidelijk warmer worden.

‘’Human activity, by using coal and gasoline, is creating carbon dioxide. In case this theory (greenhouse effect) is correct, this means that we are not going to have strong winters anymore and that summers will gradually get warmer’’.

Carbon Since the Creation

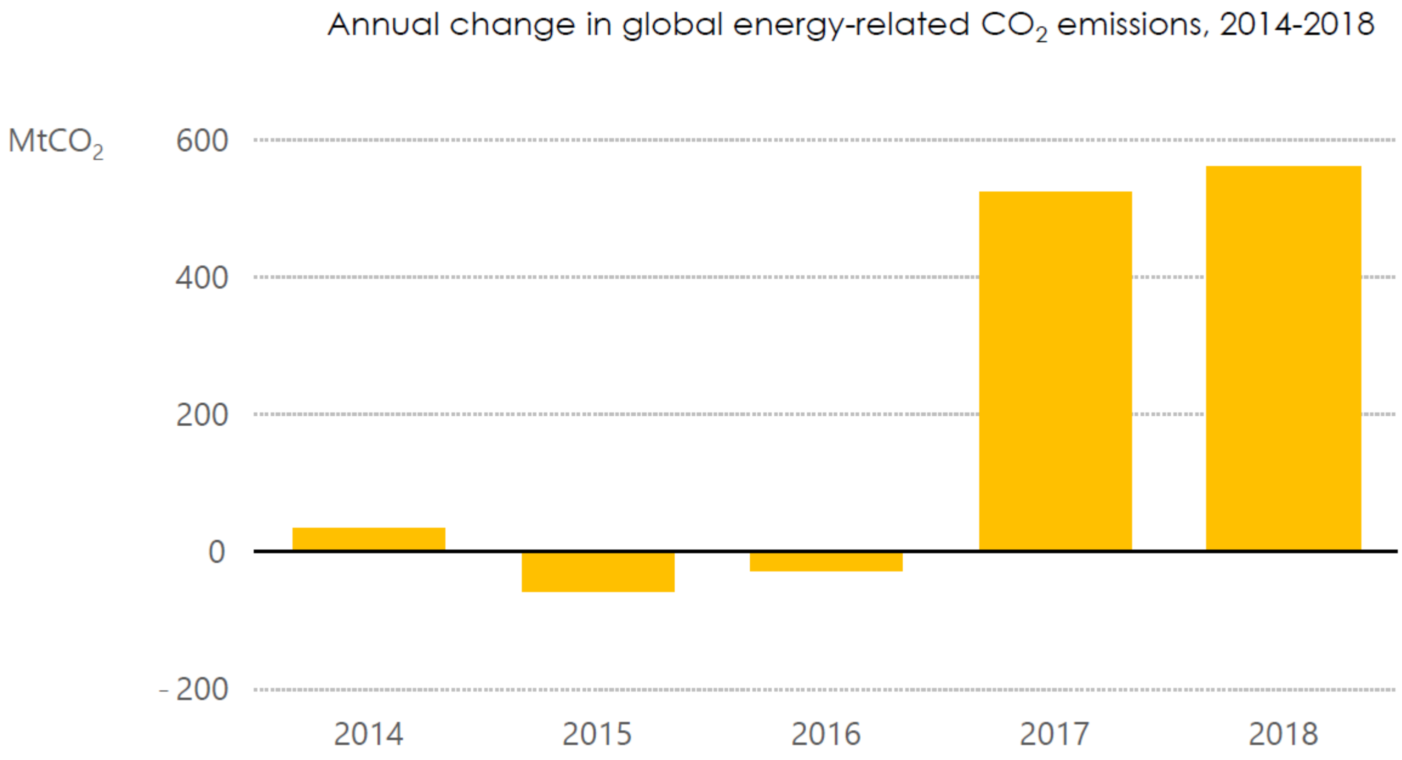
After years in the doldrums, the EU ETS roared back to life in 2018



Source: ICE

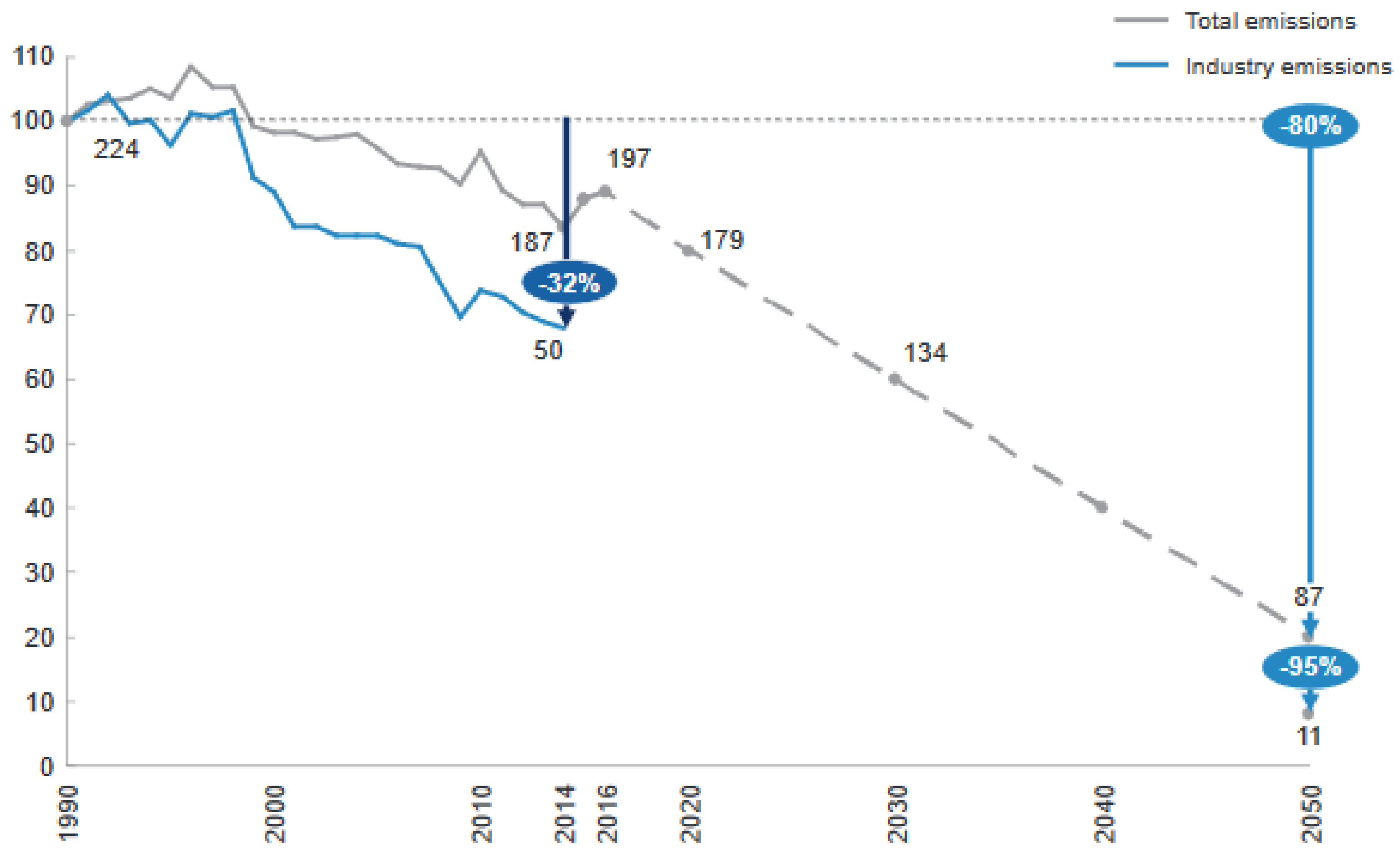
Bloomberg

Energy-related CO_2 emissions hit a record high…



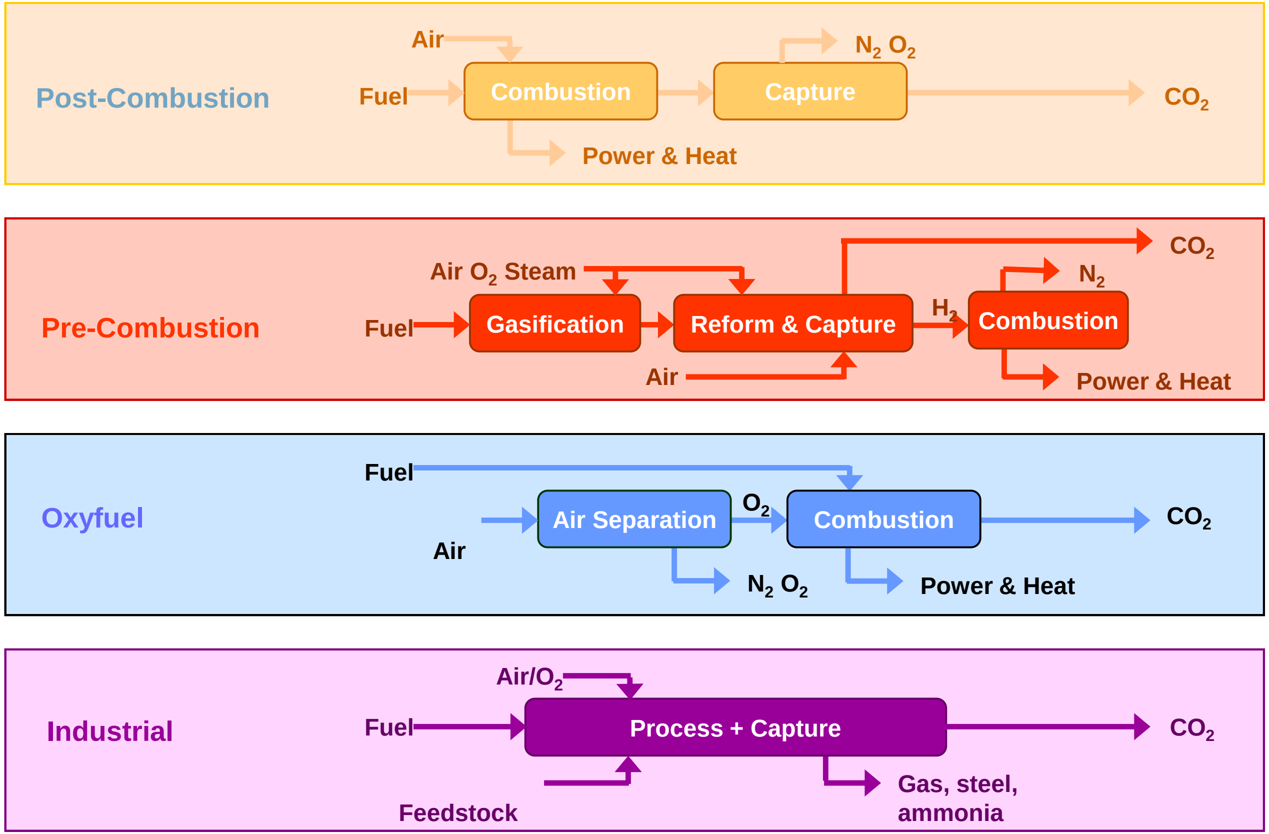
Higher demand for fossil fuels drove up global CO_2 emissions for a second year after a brief hiatus. Increases in efficiency, renewables, coal-to-gas switching and nuclear avoided 640 Mt of CO_2 emissions.

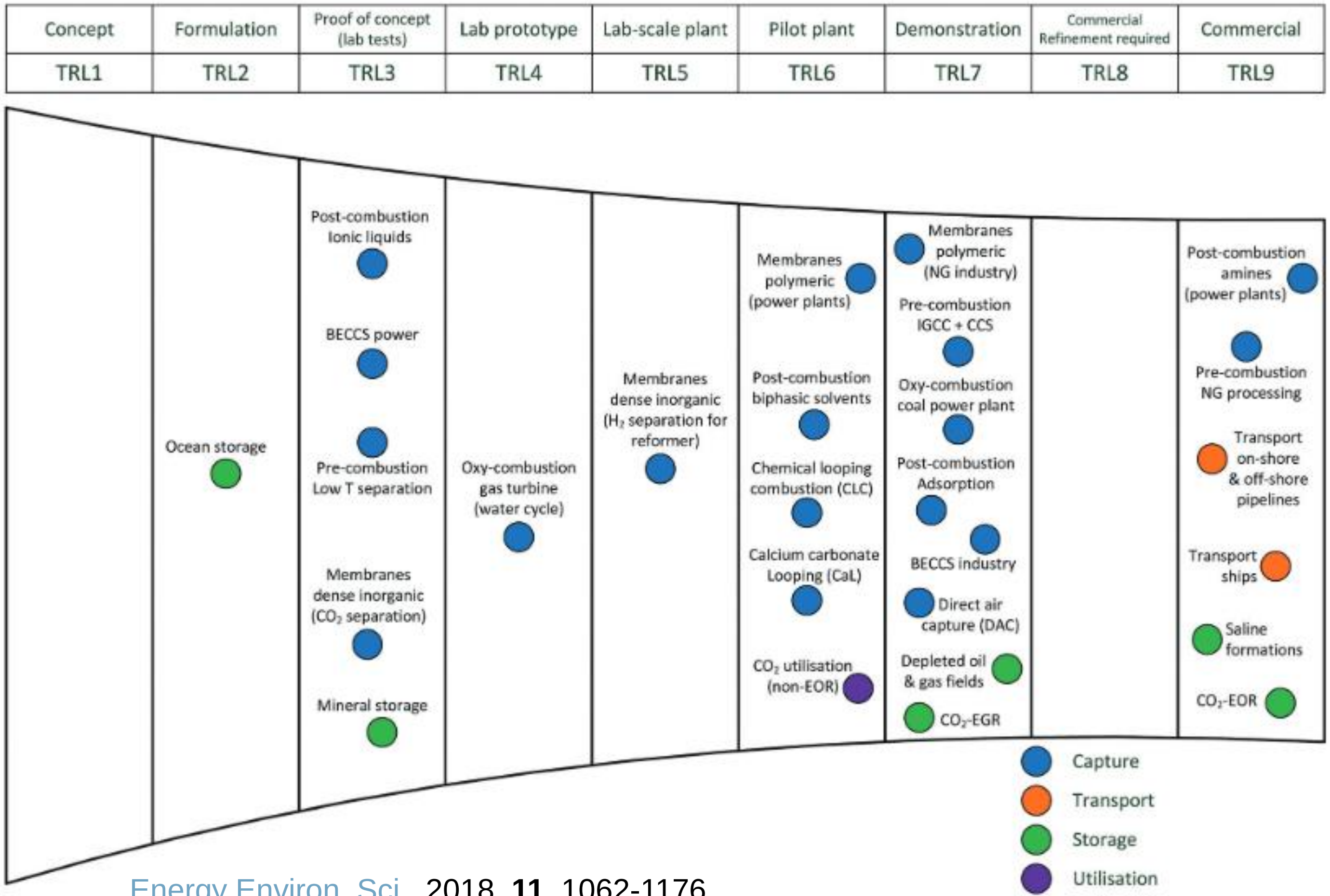
CO_2 equivalent emission, % change as of 1990



SOURCE: CBS, National Inventory Report (1990-2014)

MAIN CO2 CAPTURE TECHNIQUES





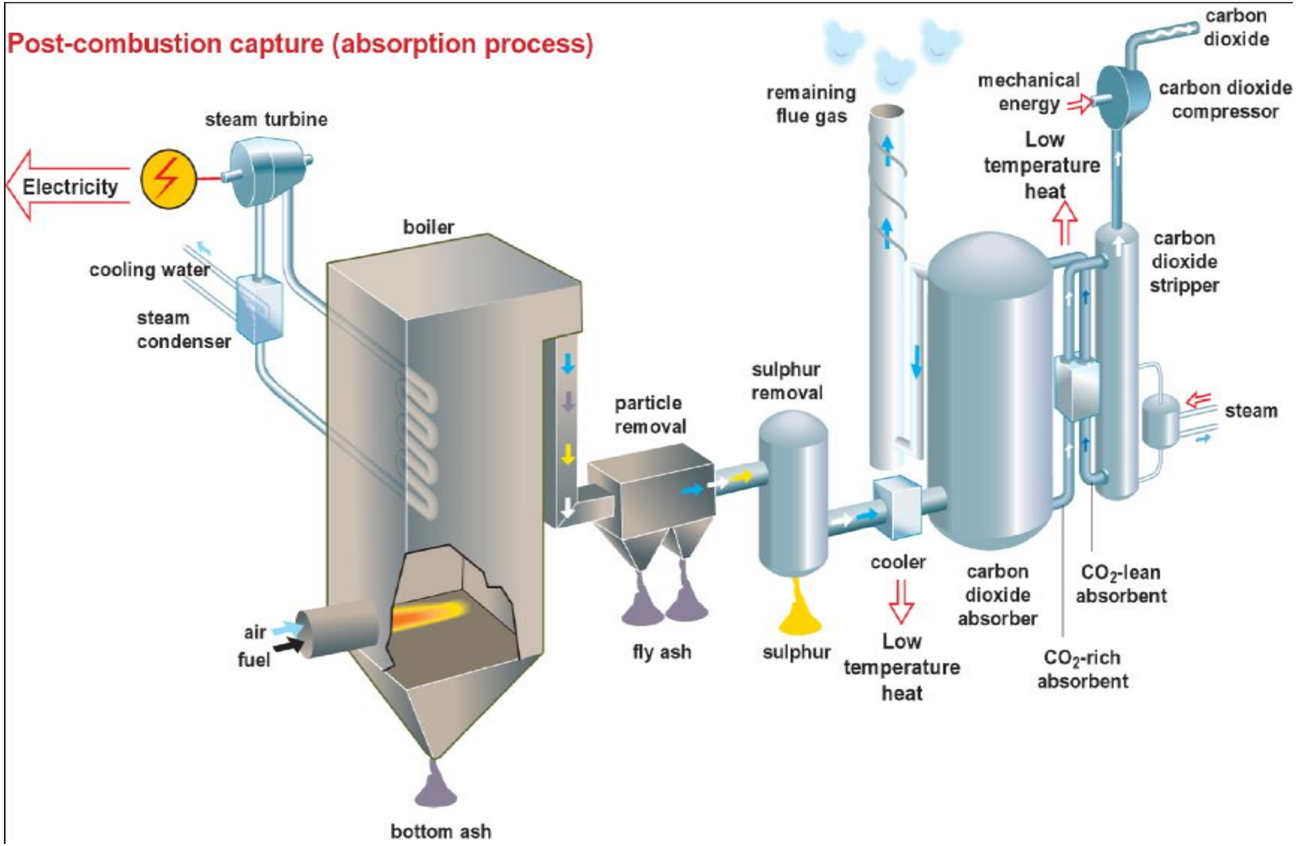
Energy Environ. Sci., 2018, **11**, 1062-1176

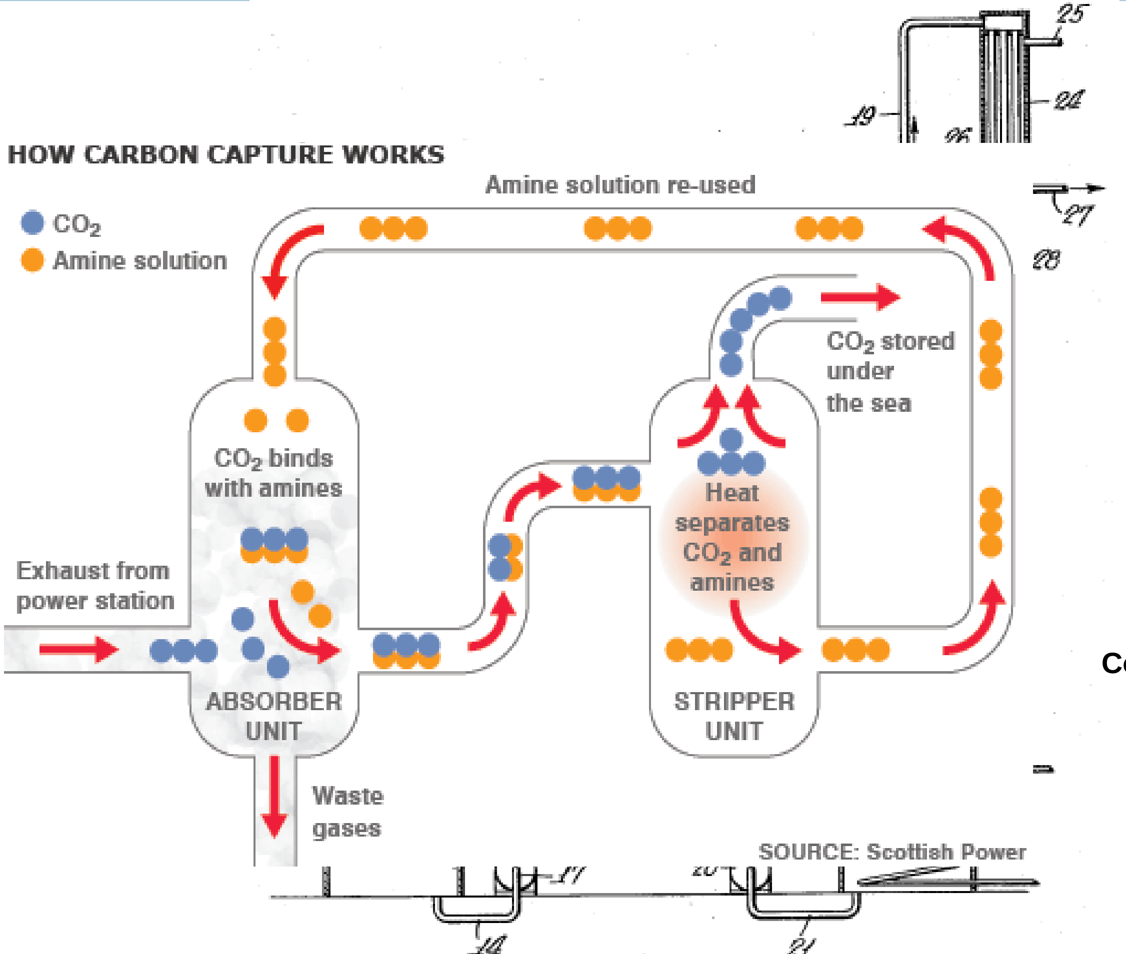
CO_2 CAPTURE ROUTES: CLASSIFICATION

- Post-combustion capture: separation CO_2-N_2
- Pre-combustion capture: separation CO_2-H_2
- Oxyfuel combustion (Denitrogenation): separation O_2-N_2

	Post-comb. (flue gas)	Pre-comb. (shifted syngas)	Oxyfuel comb. (exhaust)
p (bar)	~1 bar	10-80	~1 bar
[CO_2] (%)	3-15%	20-40%	75-95%

POST COMBUSTION CAPTURE

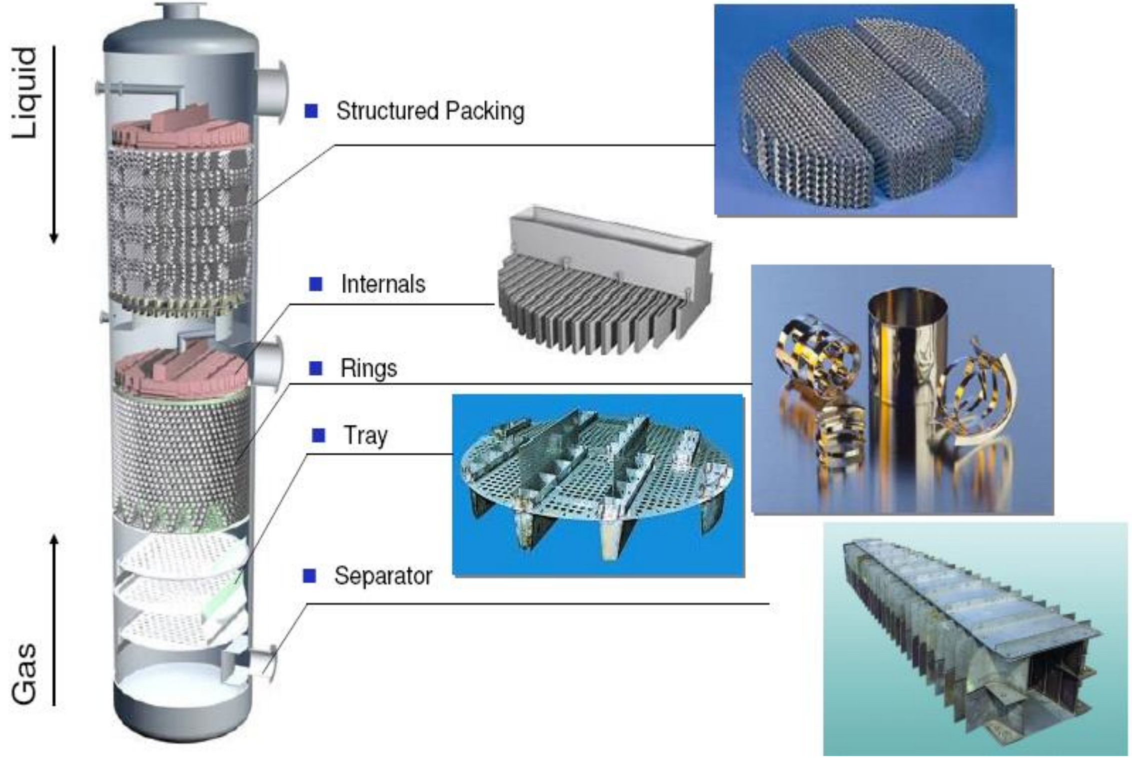




Key-numbers:
Penalty points: ~11%
Extraction of steam: >60%
Electricity compressors: >30%
Electricity blowers: >5%

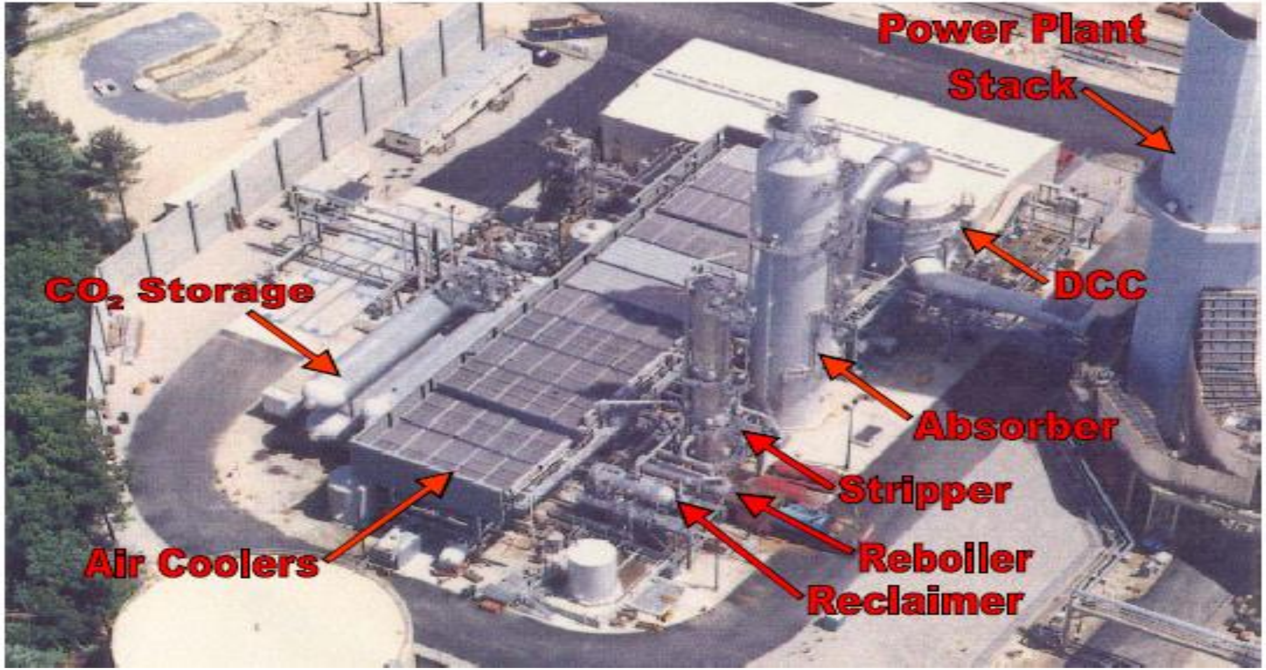
Cost of electricity increases by 60-80%

Mass transfer equipment

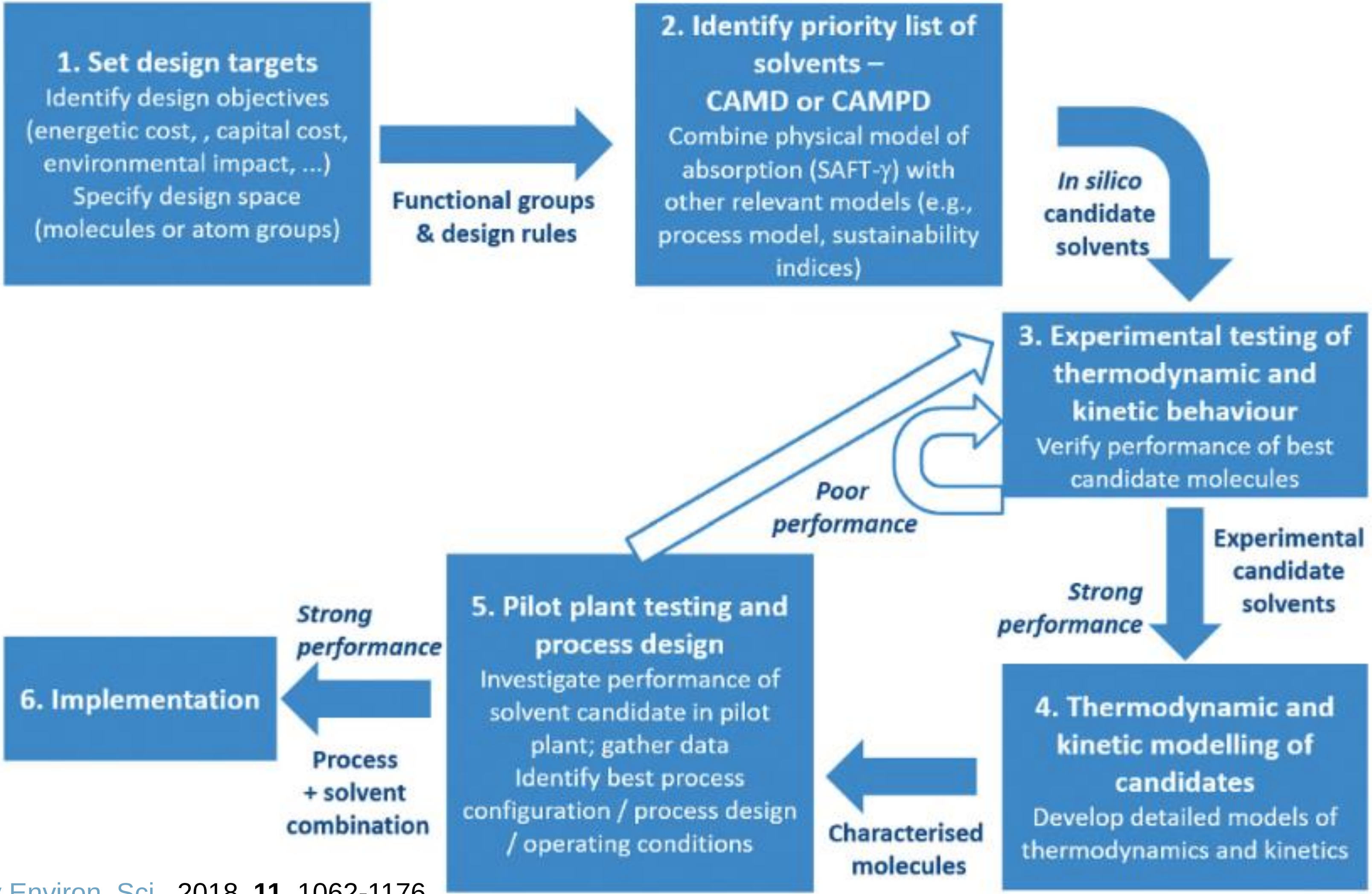


ROAD: MPP3

BELLINGHAM ECONAMINE FGSM AERIAL VIEW



The plant design was based on
air cooling only, hence the large bank of air coolers.



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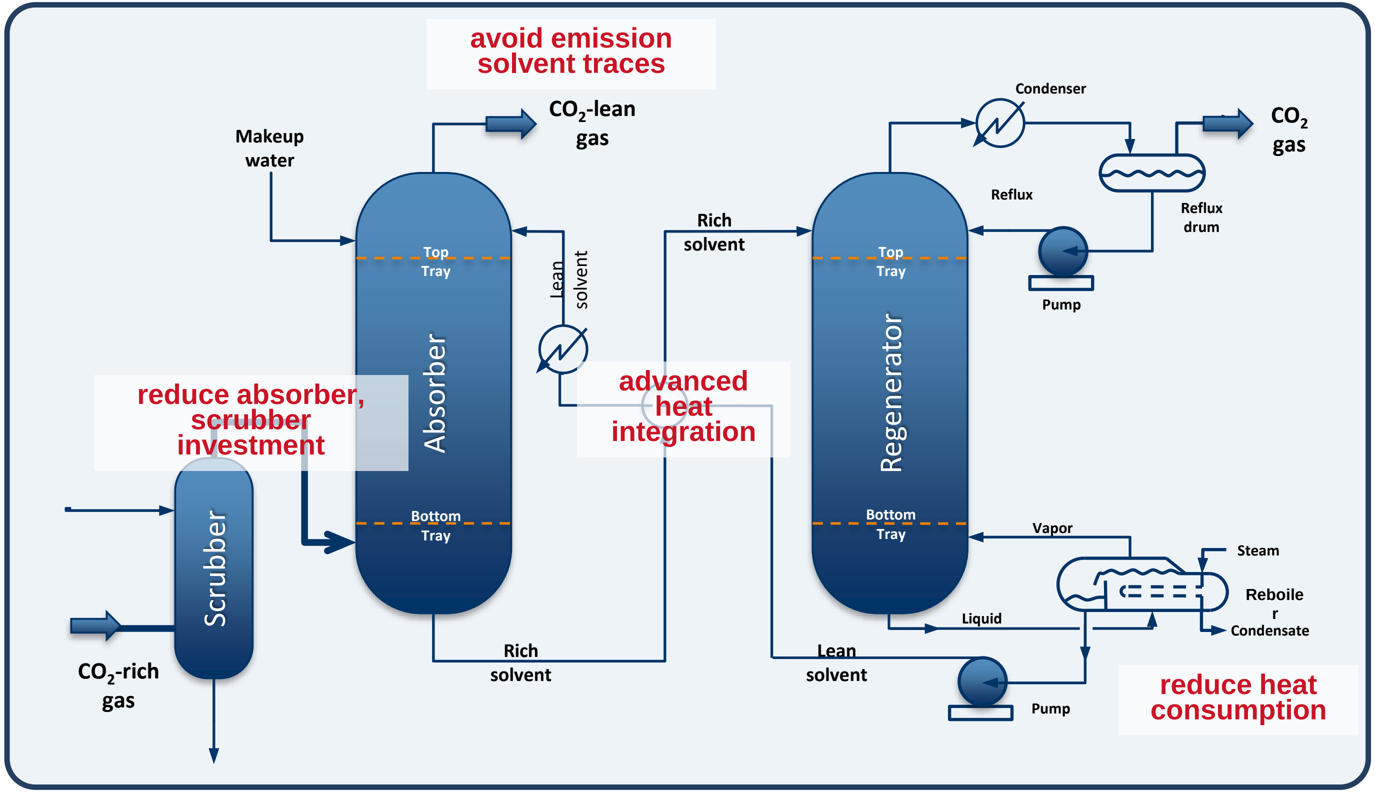
Challenges Post-combustion Capture



Solvent	Reboiler duty (GJ per t_{CO_2})	Ref.
30 wt% MEA	3.6–4.0	Cousins *et al.*,[181] Kwak *et al.*,[182] Mangalapally and Hasse,[183] Stec *et al.*[184]
40 wt% MEA	3.1–3.3	Lemaire *et al.*[205]
40 wt% (8 molal) piperazine (PZ)	2.9	Cousins *et al.*[196]
Cansolv	2.3	Singh and Stéphenne[13]
32 wt% EDA	3.2–3.8	Mangalapally and Hasse,[185] Rabensteiner *et al.*[204]
28 wt% AMP + 17 wt% PZ	3.0–3.2	Mangalapally and Hasse,[185] Rabensteiner *et al.*[186]
MEA + MDEA (variable mix ratio)	2.0–3.7	Idem *et al.*,[227] Sakwattanapong *et al.*[231]
Aqueous ammonia (NH_3)	2.0–2.9*	Darde *et al.*,[232] Dave *et al.*,[233] Yang *et al.*[234]
Aqueous potassium carbonate (K_2CO_3)	2.0–2.5	Anderson *et al.*,[235,236] Smith *et al.*[237]
Amino acids	2.4–3.4*	Sanchez-Fernandez *et al.*[238,239]
DEEA + MAPA	2.1–2.4	Raynal *et al.*,[240] Liebenthal *et al.*[241]
DMCA + MCA + AMP	2.5 (not including extraction)	Zhang[242]

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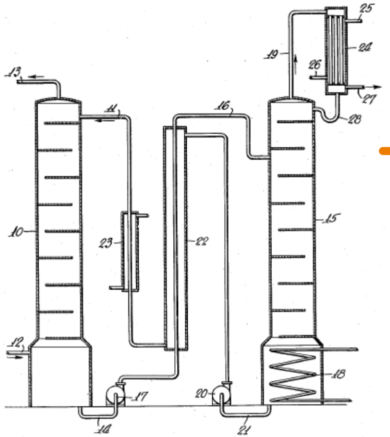
Process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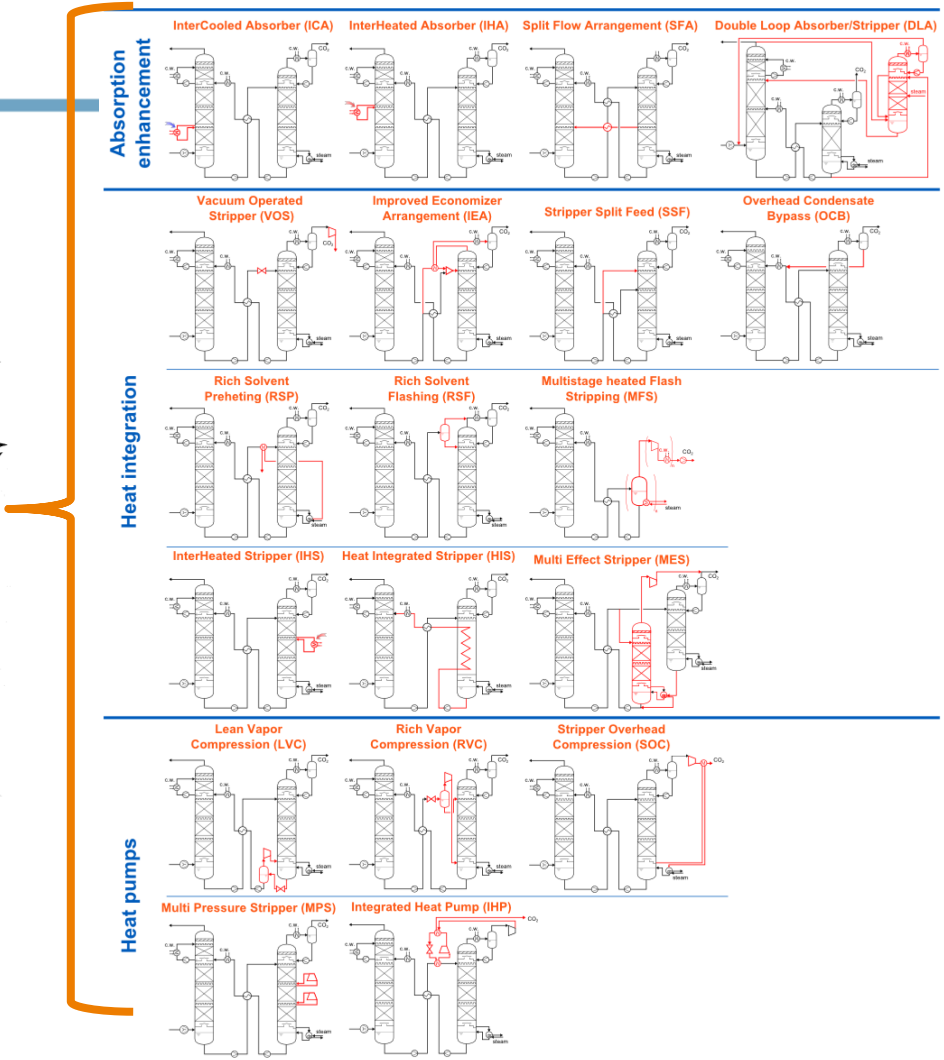
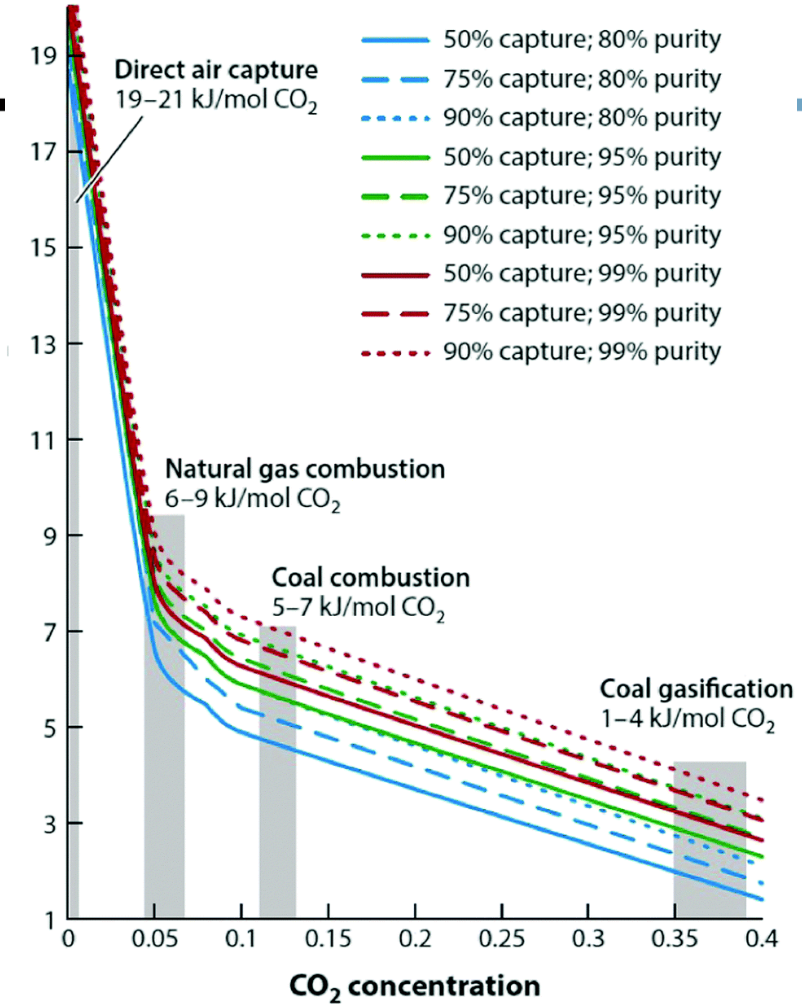
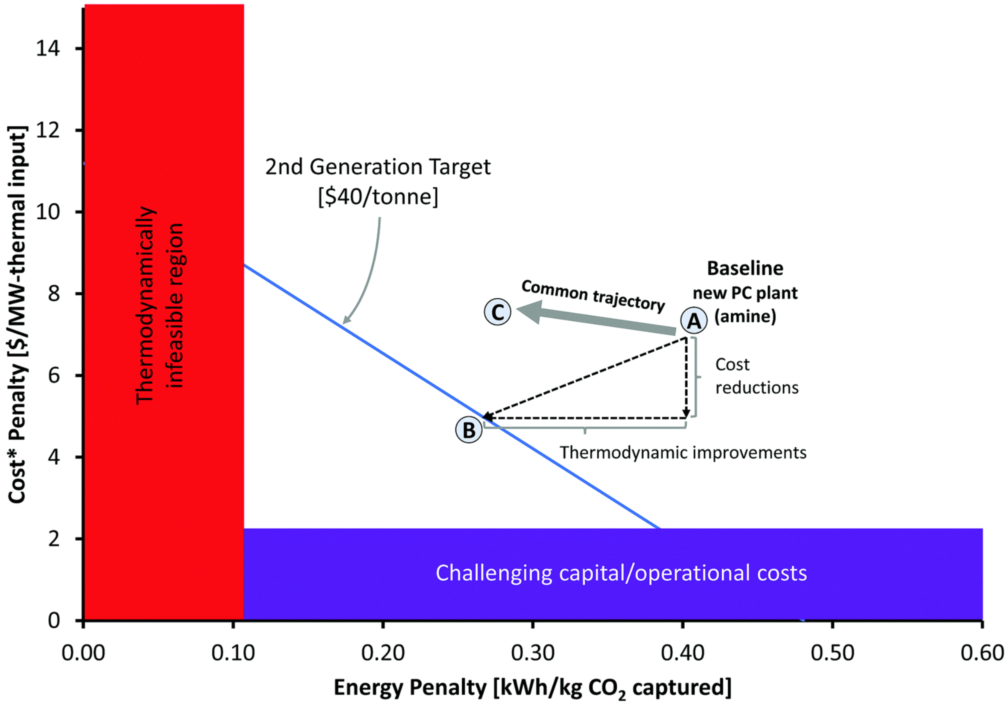
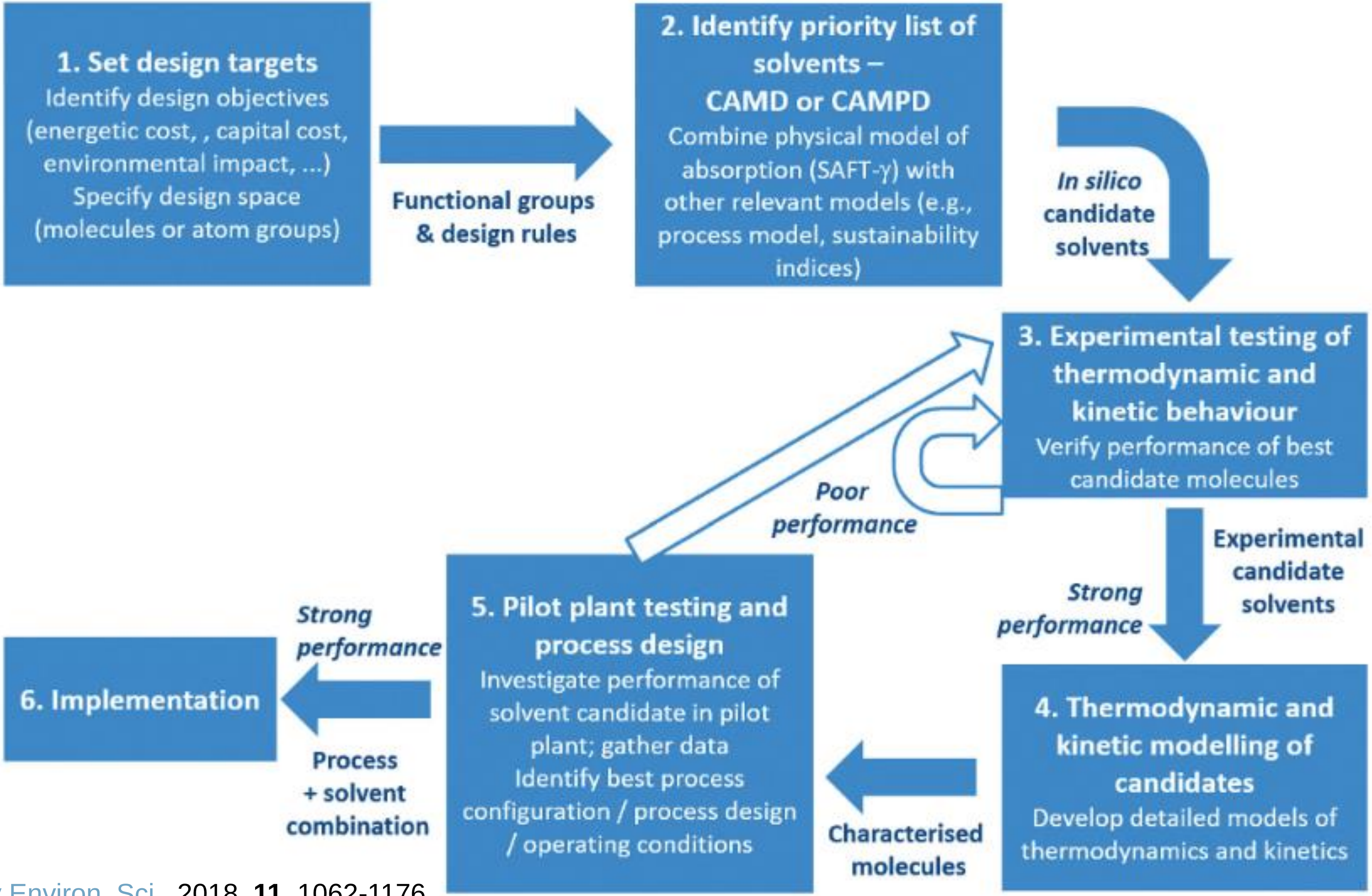

Absorption enhancement
InterCooled Absorber (ICA)
InterHeated Absorber (IHA)
Split Flow Arrangement (SFA)
Double Loop Absorber/Stripper (DLA)
Heat integration
Vacuum Operated Stripper (VOS)
Improved Economizer Arrangement (IEA)
Stripper Split Feed (SSF)
Overhead Condensate Bypass (OCB)
Rich Solvent Preheting (RSP)
Rich Solvent Flashing (RSF)
Multistage heated Flash Stripping (MFS)
InterHeated Stripper (IHS)
Heat Integrated Stripper (HIS)
Multi Effect Stripper (MES)
Heat pumps
Lean Vapor Compression (LVC)
Rich Vapor Compression (RVC)
Stripper Overhead Compression (SOC)
Multi Pressure Stripper (MPS)
Integrated Heat Pump (IHP)





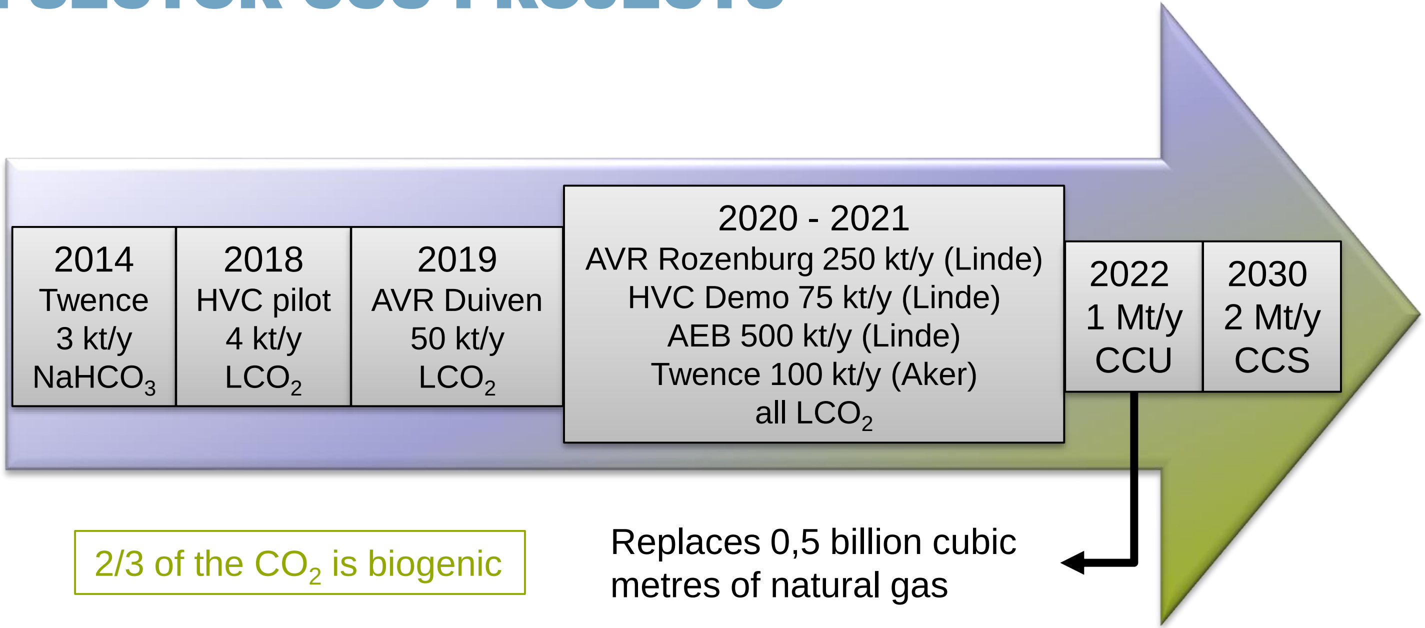
* Also includes O&M

 Energy Environ. Sci., 2018, **11**, 1062-1176



21 Energy Environ. Sci., 2018, **11**, 1062-1176

WTE SECTOR CCU PROJECTS



2/3 of the CO_2 is biogenic

de Volkskrant

REPORTAGE BROEIKAS ALS MESTSTOF

Afgevangen CO2, waar laat je het? Tuinders, is het antwoord van AVR

Als eerste afvalenergiecentrale van Nederland gaat AVR grootschalig CO_2 afvangen. Tuinders zullen dit broeikasgas als meststof gebruiken. Het is een stap in de ontwikkeling van koolstof... belangrijke pijler van het ... regeerakkoord.

Niels Waarlo 30 mei 2018, 0:01

de Gelderlander

Regio Algemeen

Arnhem e.o. Nijmegen e.o. Achterhoek Betuwe

CO2 uit rookpluimen AVR gaat naar glastuinbouw

DUIVEN - AVR in Duiven gaat koolstofdioxide, CO2, uit de grote rookpluimen halen. Het bedrijf haalt al energie en warmte uit afval. Maar het broeikasgas dat bij de verbranding van restafval vrij komt, gaat nog steeds de lucht in.

Suzanne Huibers 01-06-18, 06:58

TNO innovation for life

TECHNIEK MAAKT JE WERELD

DE INGENIEUR

Kunstma... intellige...

Home Dossiers Agenda Engineering Works Vacatures Tijdschrift

Zoek...

AFVALENERGIECENTRALE IN DUIVEN GAAT CO2 AFVANGEN

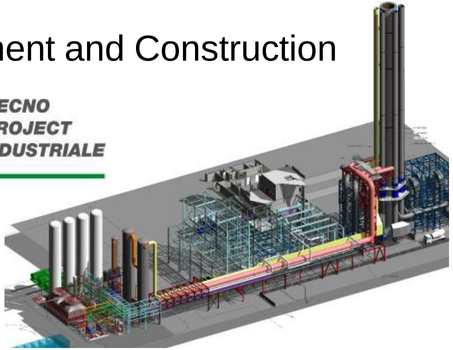
30 MEI 2018

AVR DUIVEN

AVR.

Engineering, Procurement and Construction

TECNO PROJECT INDUSTRIALE
SIAD Group



Solvent:
30wt%
MEA
(flexible)

Distribution of liquid CO_2 to greenhouses

Air Liquide
creative oxygen


AVR.


ABC

TWENCE

Existing 4 kt/y CO_2 capture unit

Solvent: flexible

Basic engineering ready 100 kt/y

Twence®

TWENCE | DUURZAAMHEID | ENERGIE | PROJECTEN | WERKEN BIJ | INFO & CONTACT | NL

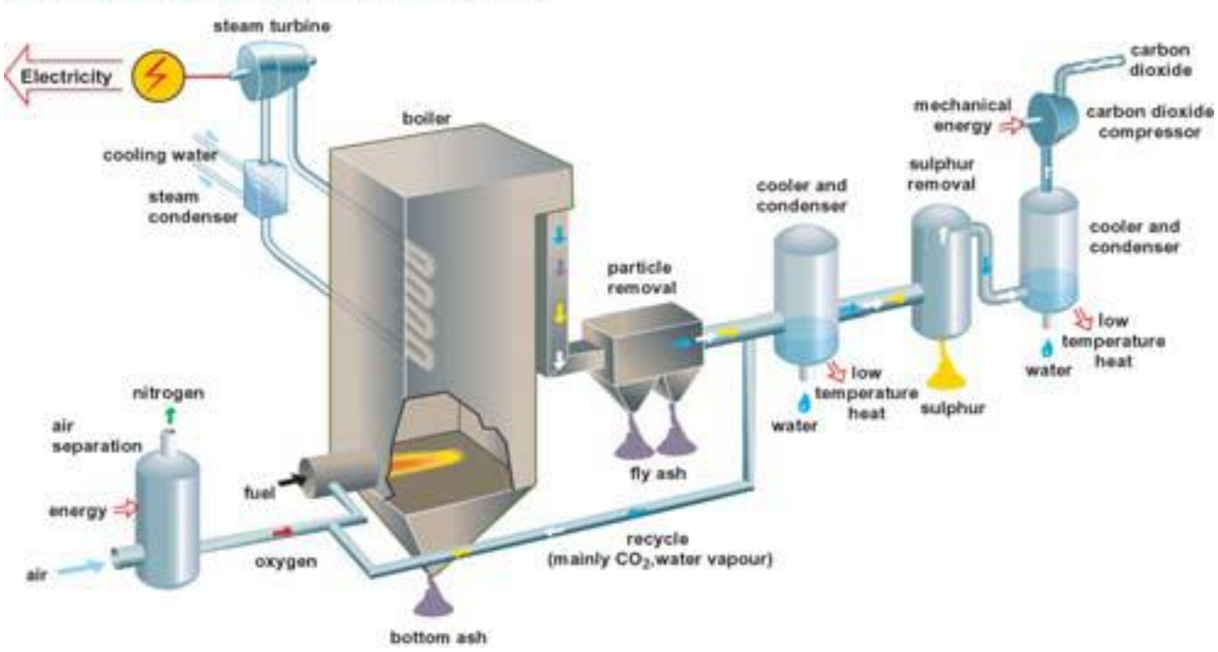
Aker Solutions levert installatie voor afvangen en vervloeien CO2

12-apr-2019

Twence wil uit de rookgassen van de afvalenergiecentrale (AEC) grootschalig CO2 afvangen en geschikt maken voor nuttig gebruik. Deze CO2 wordt dan niet meer direct uitgestoten, maar hergebruikt. In dit innovatieve en omvangrijke project heeft het Noorse Aker Solutions de aanbesteding gewonnen voor het leveren van de installatie voor het afvangen en vervloeien van de CO2. De contracten hiervoor zijn recent getekend.

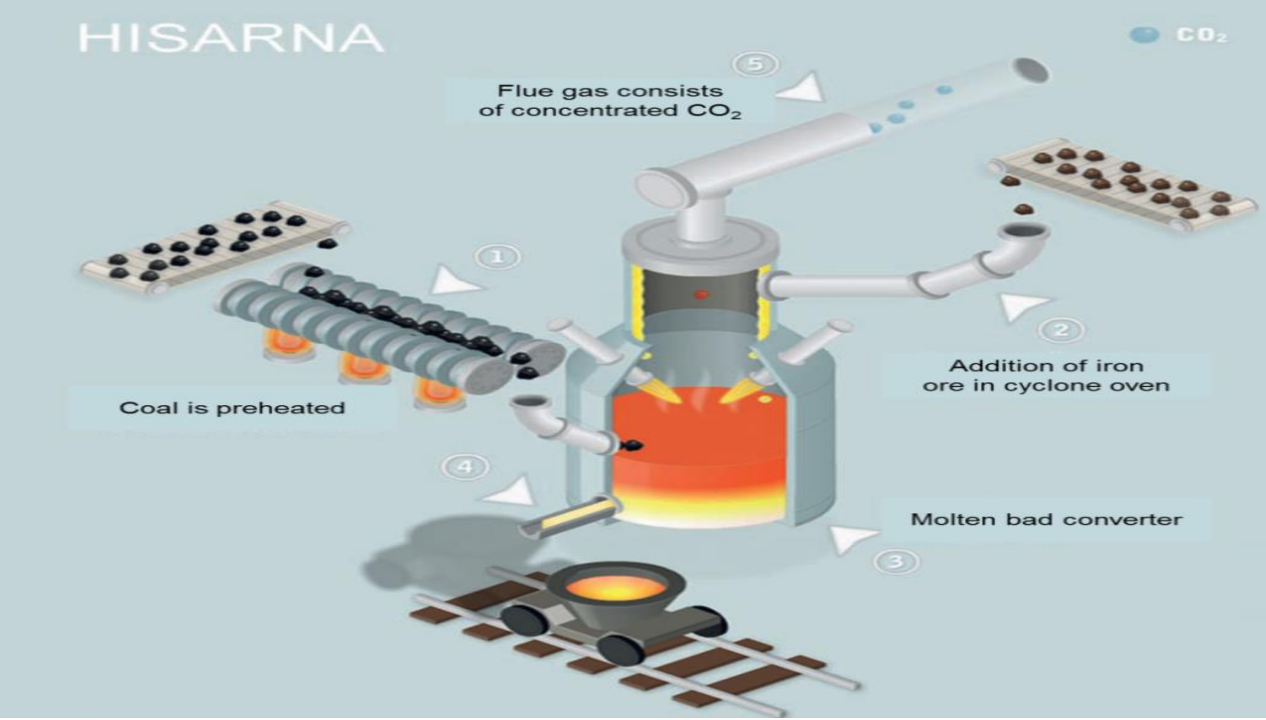
Aker proprietary solvent

OXYFUEL


steam turbine
Electricity
boiler
cooling water
steam condenser
carbon dioxide
mechanical energy
carbon dioxide compressor
sulphur removal
cooler and condenser
cooler and condenser
particle removal
low temperature heat
water
low temperature heat
water
sulphur
fly ash
nitrogen
air separation
energy
fuel
air
oxygen
recycle (mainly CO_2, water vapour)
bottom ash

HISARNA

HIsarna concept is based on a smelting iron reduction process



3. HIsarna technology

Benefits of the HIsarna process

Environmental:

- 20 % reduction of CO_2 per ton steel product
- Well suited for CO_2 storage (nitrogen free off gas)
- 80 % reduction with CO_2 storage
- Substantial reduction of other emissions (dust, NOx, SOx, CO)

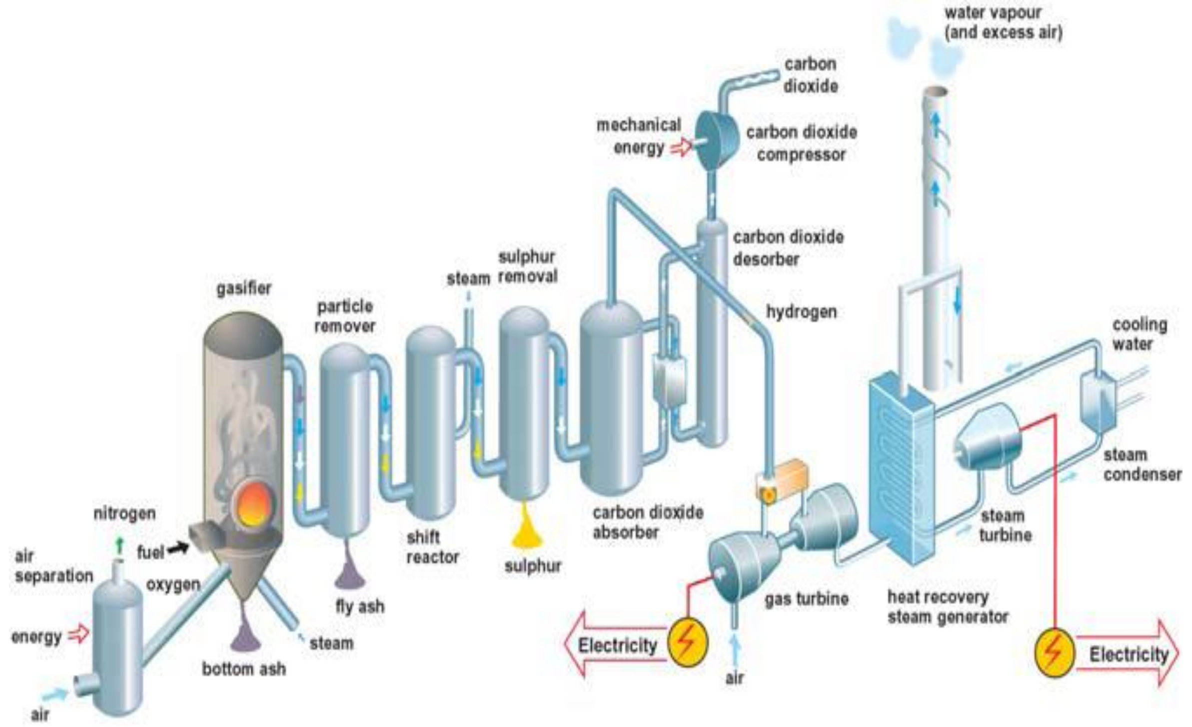
Economical:

- Low cost raw material
- Reduced CAPEX

PILOT HISARNA

PRECOMBUSTION



H-vision

Blue hydrogen for
a green future

The H-vision project

Goal

- Large-scale production of blue hydrogen to achieve a step change in emissions in the Rotterdam port area to help realise climate goals

Approach

- Sixteen parties from the Rotterdam port area are working together to investigate the feasability of the production and application of blue hydrogen in the industry
- Positive outcomes of a pilot will result in a substantial project for large scale supply of blue hydrogen before 2030
- The sixteen participants represent the full hydrogen chain: from production to end-users

Potential CO_2-reduction

- 2 million tons in 2025, ascending to 6 million tons per year in 2030

GREY, BLUE AND GREEN

Grey hydrogen	Blue hydrogen	Green hydrogen
Divide natural gas into CO_2 and hydrogen	Divide natural gas into CO_2 and hydrogen Residual gasses also in H-vision scope	Convert water into hydrogen by electrolysis powered by wind and sun
CO_2 emitted in the atmosphere	*CO_2 stored or re-used*	*No CO_2 emitted*
	Link H-vision with Porthos project for storage under the sea	

H-VISION SIGNIFICANCE

- Increase of grey hydrogen leads to incease of green house gasses
- Green hydrogen is climate neutral. To generate the required amounts of green hydrogen, more green electricity is needed than will become available in the coming decades
- Large scale blue hydrogen usable before 2030
- Substantial impact on the carbon budget
  - Like in a bathtub, the atmosphere will be filled with green house gasses
  - IPCC recent climate report: within the current trend, if we want to remain within the 2°C goal the world only has 25 years of carbon budget left

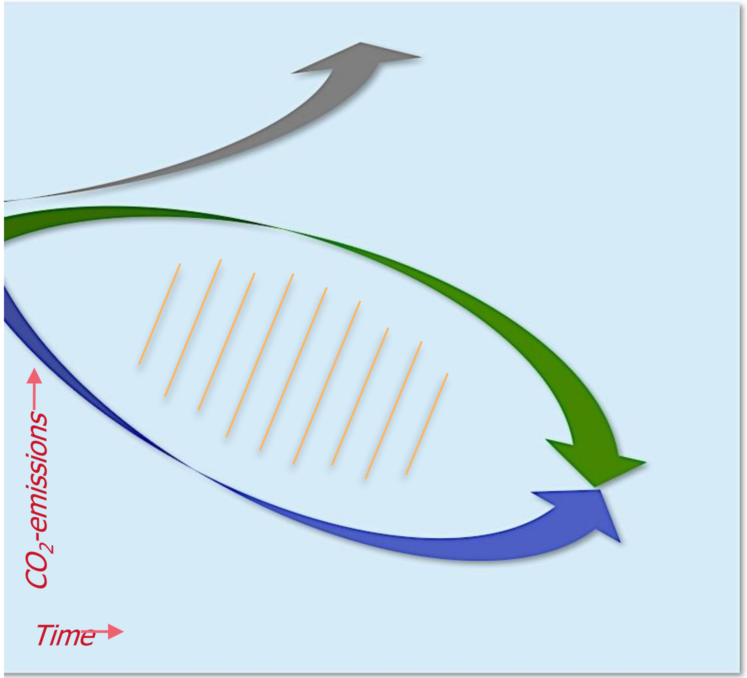


Illustration demonstrates the impact levels from emissions by the three different qualities of hydrogen.

Shaded area demonstrates the CO_2 reductions that can be achieved with blue hydrogen in the short term.

Grey hydrogen | Blue hydrogen | Green hydroge

ACCELERATOR AND PIONEER

- By speeding up CO_2-reductions H-vision accelerates the energy transition
- Potential CO_2-reduction of 2 million tons in 2025, ascending to 6 million tons annually in 2030
- Blue hydrogen paves the way for the infrastructure needed for green hydrogen and installations of end-users (no lock-in)
- H-vision plants provide a back-up system within a large scale green hydrogen economy

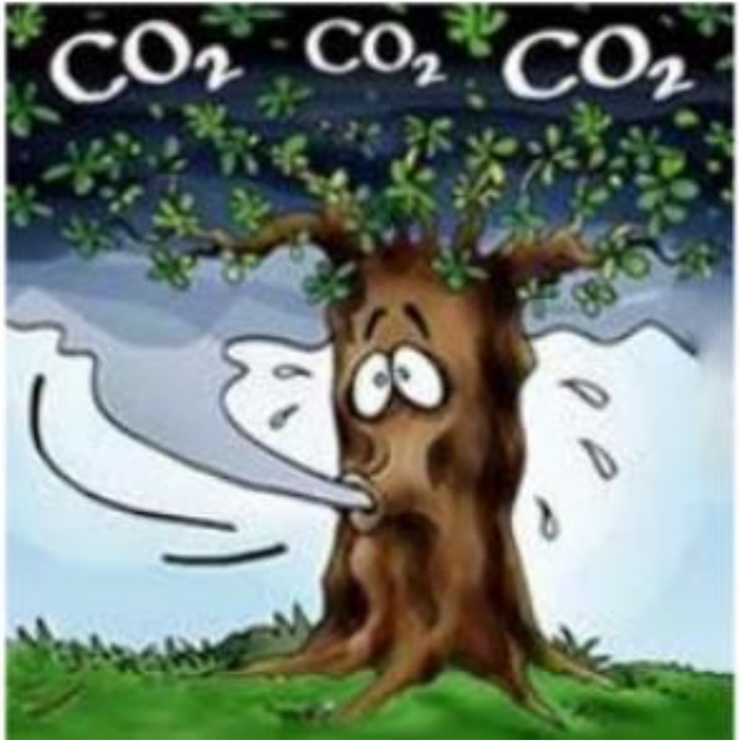
BLUE HYDROGEN COSTS

- With blue hydrogen, substantial reductions in CO_2-emissions can be achieved quickly and cost efficient
- CO_2 abatement for H-vision is part of the feasability study
- Studies blue hydrogen:
  - 110-150 €/tons CO_2 (Sintef)
  - 110-130 €/tons CO_2 (Berenschot and TNO)
  - 140 €/tons CO_2 (studie ”Waterstofroutes Nederland”)
- Studies green hydrogen:
  - nearly 700 €/tons CO_2 (CE-Delft)
- Results of the feasability study will provide more clarity on the costs for H-vision, early 2019

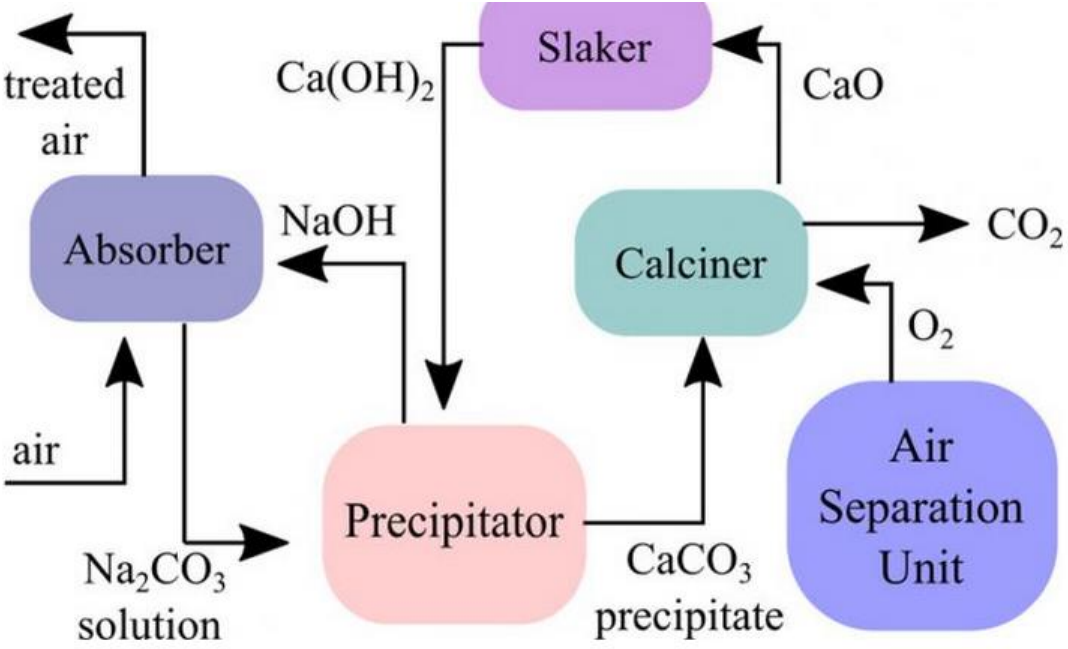
PORTHOS (ROTTERDAM)

- https://rotterdamccus.nl/en/

AIR CAPTURE



CAPTURE OPTIONS



Air Capture: Collection & Regeneration

Ion exchange resin as sorbent, regeneration with humidity

1 Collection

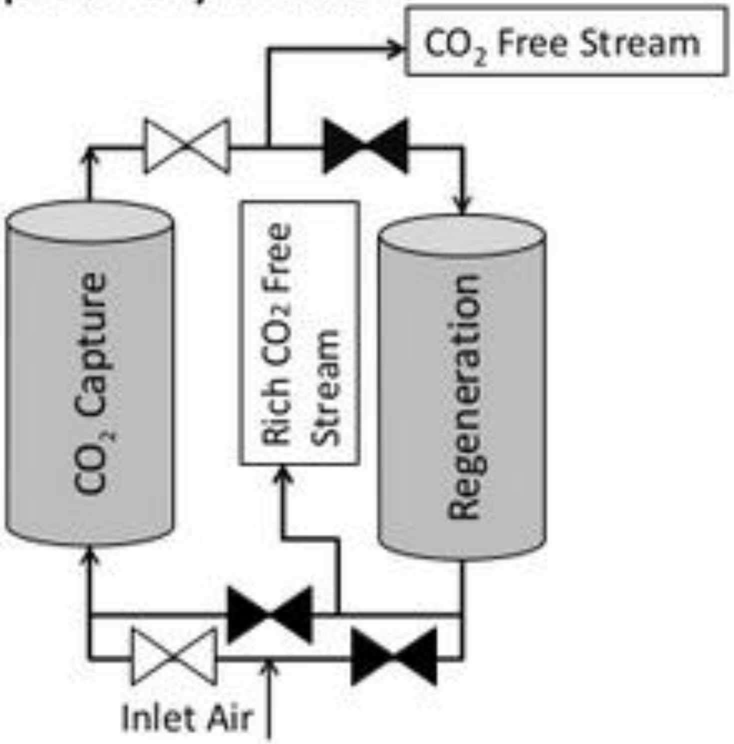
- Natural wind carries CO_2 through collector
- CO_2 binds to surface of proprietary sorbent materials

2 Regeneration

- CO_2 is recovered with:
  - low-temperature water vapor
  - plus optional low-grade heat
- Regenerated solid sorbent is reused over and over for years

Dry Air Capture Systems

- Adsorption/Chemisorption process
- Regeneration needed
- Degradation of sorbents in cycles



Some examples mentioned in literature related to air capture

Clime workx

Crucial is modularisation and
creating low energy consuming air flow through the capture devices

FINANCE & INNOVATION

Bill Gates Is Investing in a Technology That Turns CO2 into Clean Fuel

Bill Gates is planning to strip CO2 from the air and turn it into clean fuel

How Bill Gates aims to c planet

It's a simple idea: strip CO2 from the air and u carbon-neutral fuel. But can it work on an inc

Bill Gates haalt CO2 uit de lucht en maakt er brandstof van

Lucht veranderen in benzine: het klinkt misschien te mooi om waar te zijn, maar Microsoft-topman Bill Gates hoopt op deze manier de opwarming van de aarde een halt toe te roepen.

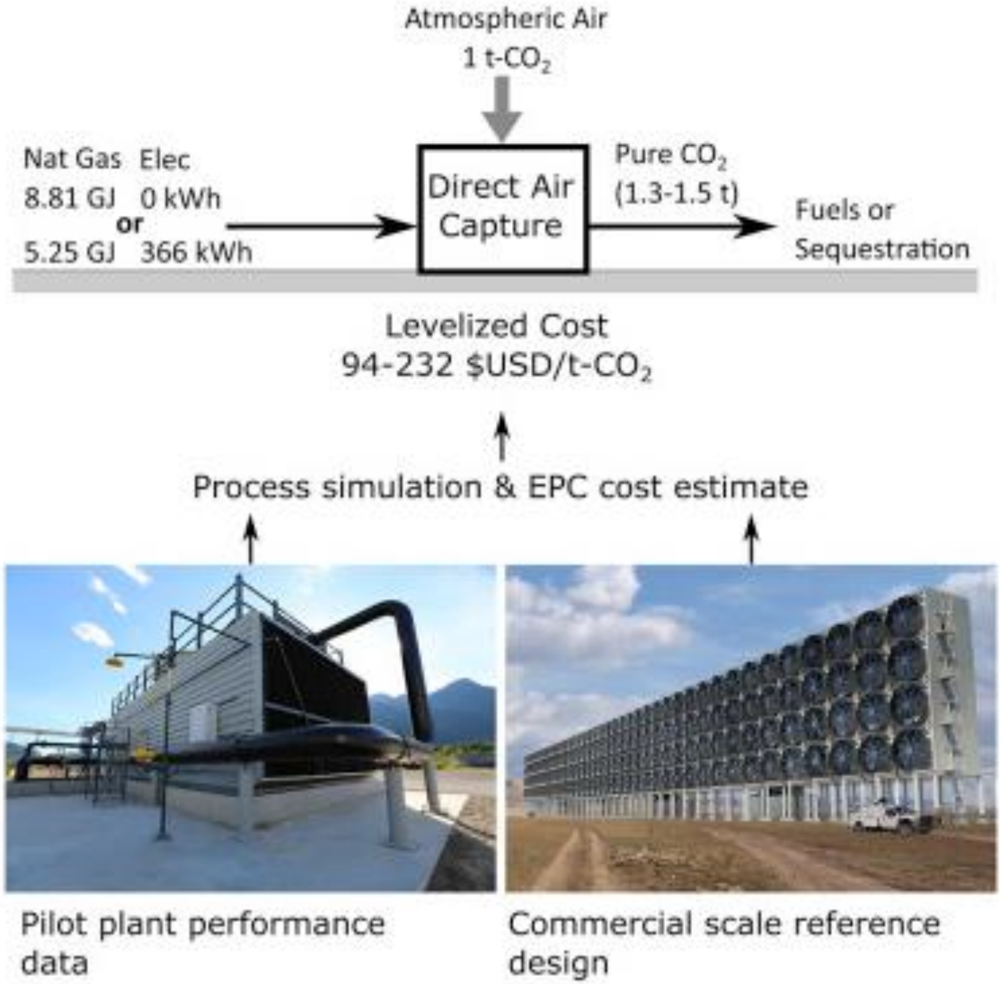
Sustainable Energy

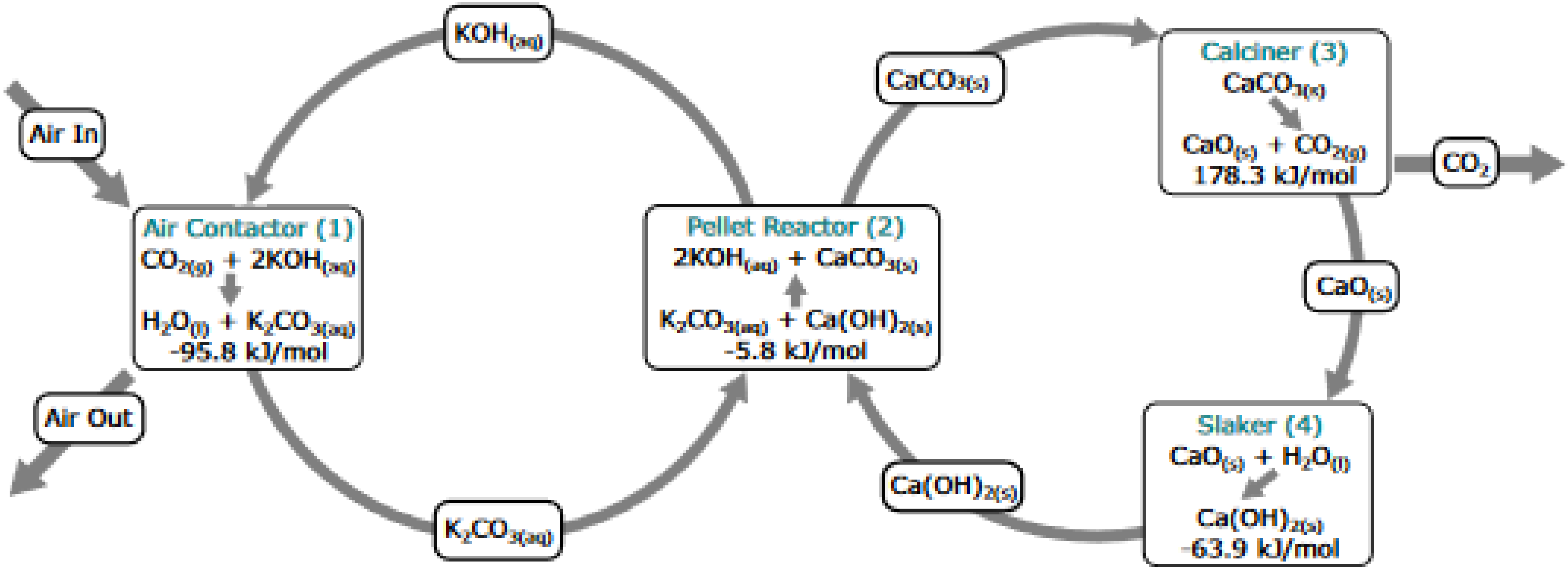
Maybe we can afford to suck CO_2 out of the sky after all

A new analysis shows that air capture could cost less than $100 a ton.

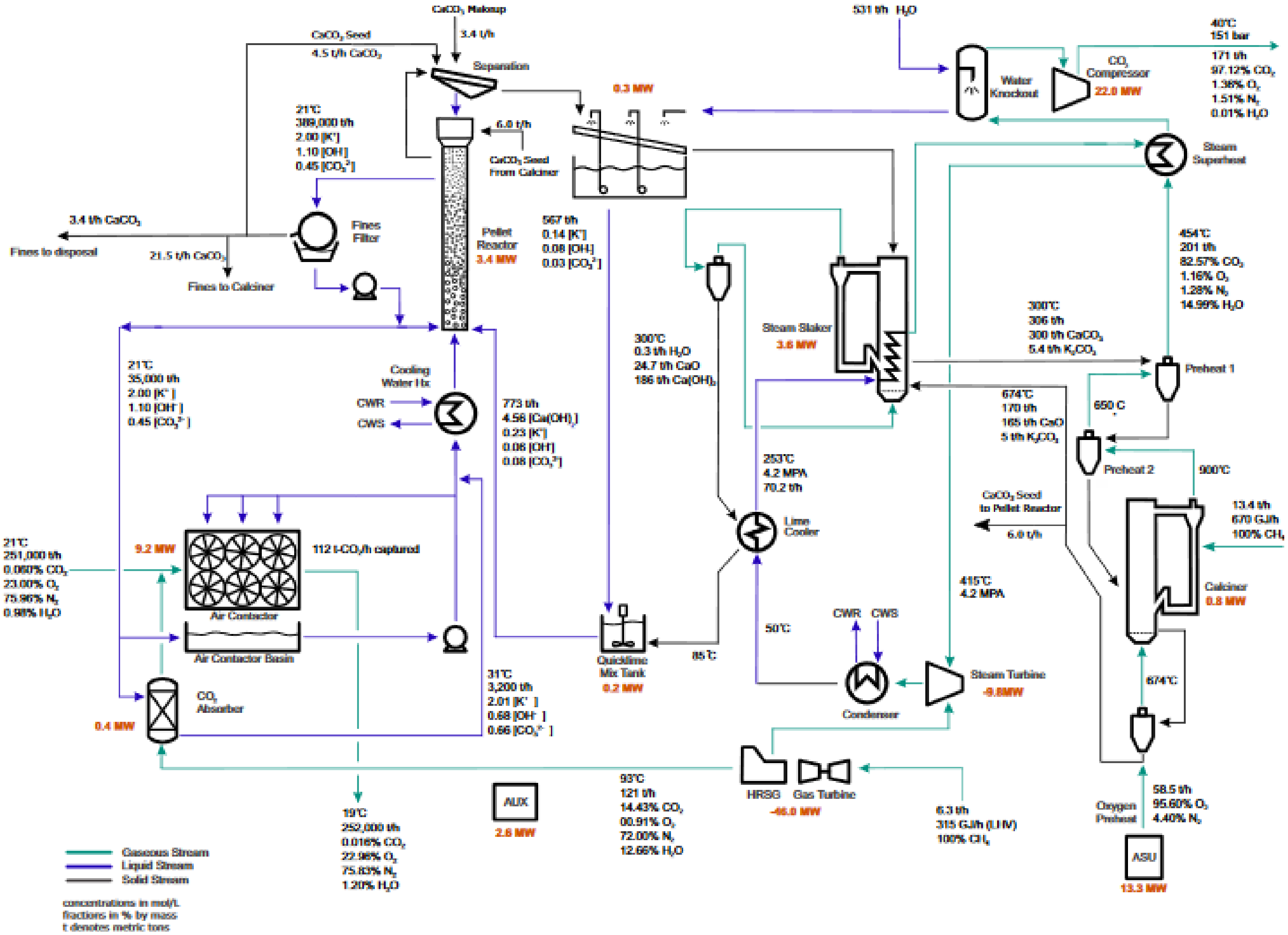
Key 'step forward' in cutting cost of removing CO2 from air

The pilot plant has been built in British Columbia and is extracting about a tonne of CO2 every day


Atmospheric Air
1 t-CO2
Nat Gas Elec
8.81 GJ 0 kWh
or
5.25 GJ 366 kWh
Direct Air Capture
Pure CO2
(1.3-1.5 t)
Fuels or Sequestration
Levelized Cost
94-232 $USD/t-CO2
Process simulation & EPC cost estimate
Pilot plant performance data
Commercial scale reference design



Joule 2, 1573–1594, August 15, 2018


CaCO$_3$ Makeup
3.4 t/h
CaCO$_3$ Seed
4.5 t/h CaCO$_3$
Separation
0.3 MW
531 t/h H$_2$O
Water Knockout
CO$_2$ Compressor
22.0 MW
40°C
151 bar
171 t/h
97.12% CO$_2$
1.36% O$_2$
1.51% N$_2$
0.01% H$_2$O
21°C
389,000 t/h
2.00 [K$^+$]
1.10 [OH$^-$]
0.45 [CO$_3^{2-}$]
6.0 t/h
CaCO$_3$ Seed From Calciner
Steam Superheat
3.4 t/h CaCO$_3$
Fines to disposal
Fines Filter
21.5 t/h CaCO$_3$
Fines to Calciner
Pellet Reactor
3.4 MW
567 t/h
0.14 [K$^+$]
0.08 [OH$^-$]
0.03 [CO$_3^{2-}$]
454°C
201 t/h
82.57% CO$_2$
1.16% O$_2$
1.28% N$_2$
14.99% H$_2$O
Steam Slaker
3.6 MW
300°C
0.3 t/h H$_2$O
24.7 t/h CaO
186 t/h Ca(OH)$_2$
300°C
306 t/h
300 t/h CaCO$_3$
5.4 t/h K$_2$CO$_3$
Preheat 1
21°C
35,000 t/h
2.00 [K$^+$]
1.10 [OH$^-$]
0.45 [CO$_3^{2-}$]
Cooling Water Hx
CWR
CWS
773 t/h
4.56 [Ca(OH)$_2$]
0.23 [K$^+$]
0.06 [OH$^-$]
0.08 [CO$_3^{2-}$]
674°C
170 t/h
165 t/h CaO
5 t/h K$_2$CO$_3$
650 C
Preheat 2
900°C
253°C
4.2 MPA
70.2 t/h
CaCO$_3$ Seed to Pellet Reactor
6.0 t/h
13.4 t/h
670 GJ/h
100% CH$_4$
Lime Cooler
21°C
251,000 t/h
0.060% CO$_2$
23.00% O$_2$
75.96% N$_2$
0.98% H$_2$O
9.2 MW
112 t-CO$_2$/h captured
Air Contactor
Air Contactor Basin
415°C
4.2 MPA
Calciner
0.8 MW
CWR CWS
50°C
85°C
Quicklime Mix Tank
0.2 MW
674°C
CO$_2$ Absorber
0.4 MW
31°C
3,200 t/h
2.01 [K$^+$]
0.68 [OH$^-$]
0.66 [CO$_3^{2-}$]
Condenser
Steam Turbine
-9.8MW
19°C
252,000 t/h
0.016% CO$_2$
22.96% O$_2$
75.83% N$_2$
1.20% H$_2$O
AUX
2.8 MW
93°C
121 t/h
14.43% CO$_2$
00.91% O$_2$
72.00% N$_2$
12.66% H$_2$O
HRSG
Gas Turbine
-46.0 MW
6.3 t/h
315 GJ/h (LHV)
100% CH$_4$
Oxygen Preheat
58.5 t/h
95.60% O$_2$
4.40% N$_2$
ASU
13.3 MW
Gaseous Stream
Liquid Stream
Solid Stream
concentrations in mol/L
fractions in % by mass
t denotes metric tons

OUR APPROACH

1

TNO innovation for life

Electrodialysis route to Formic acid & NaOH

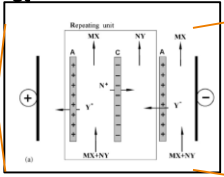
-Multiple papers with homogeneous catalysts
-At least one paper with heterogeneous catalyst

$NaOH + CO_2 \rightarrow NaHCO_3$

$NaHCO_3 + H_2 \rightarrow NaFa$

Electrodialysis

Formic acid +NaOH



HCO3- +H2
→HCO2- +H2O

Change of standard Gibbs energy is +3.62 kcal/mole.
→ High H2 pressure needed (74.7% yield, **23h** (!), 70 ℃, **60 atm** H2 pressure)
→ Pd on C catalyst

(Wiener 1988)

Power:	0,88 kWh /acid
Membraan:	0,08 € / kg acid
Electrodes/maintenance	0,01 €/ kg acid

(Bailly 2002)

Formic acid price (85%): 0,55 €/kg
→ 100%: 0,64 €/kg

(https://www.icis.com/resources/news/2006/07/26/2015258/chemical-profile-formic-acid/)

2

Sodium formate to oxalate to CO

NaOH+CO2 → NaHCO3

↓

NaHCO3+ H2 → NaFa

↓

Oxalate

↓

C
O

- Conversion to Oxalate is preferred at 350-400°C (otherwise alkali metal formate will go to carbonate and eventually CO_2

  $2HCOOM \rightarrow M_2C_2O_4 + H_2$

- Oxalate decomposes to carbonate & CO

  $M_2C_2O_4 \leftrightarrow M_2CO_3 + CO$

- Nitrogen atmosphere gives oxalate, oxygen atmosphere give carbonate.

(Meisel 1975)

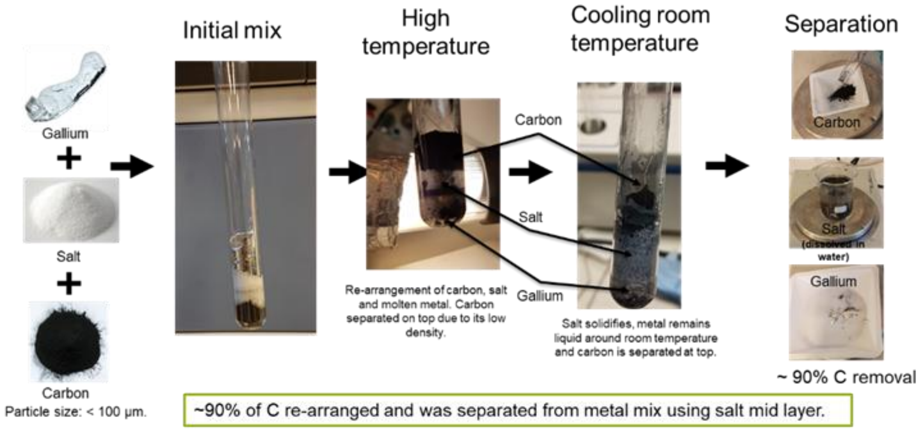
Valid for lithium, sodium, potassium, rubidium & caesium formates

DECARBONIZED HYDROGEN PRODUCTION

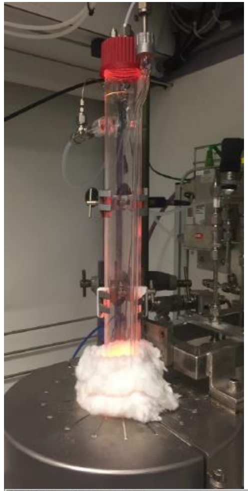
Methane reforming*	$CH_4 + H_2O \rightarrow CO + 3H_2$	206 KJ/mol
CO_2 reforming	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	247 KJ/mol
Hydrolysis	$H_2O \rightarrow ½\, O_2 + H_2$	283 KJ/mol
Pyrolysis	$CH_4 \rightarrow C + 2H_2$	75 KJ/mol

Costs (Eur/ ton) **150 – 400** **200 - 1000** **1500 - 3000**

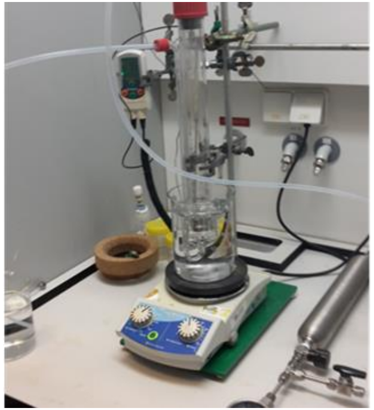
* Water gas shift accompanies this reaction resulting in production of CO_2

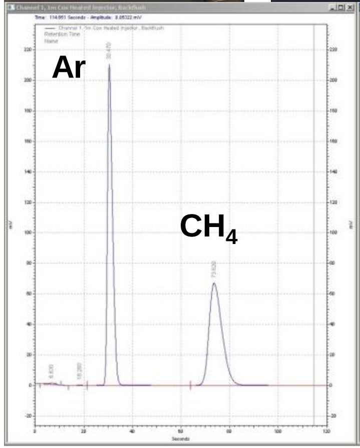


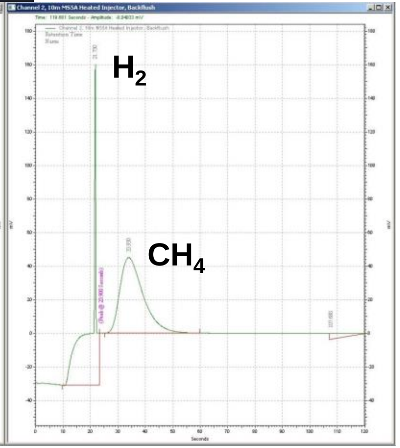
Who: Rajat, Marco, Willem, Hans, Arjen, Earl.



+ H_2 separation







CO_2 UTILISATION

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Text-only start sheets can be added using
‘New slide/Nieuwe dia’

TNO innovation for life

EXAMPLES OF CO_2 CONVERSION PRODUCTS

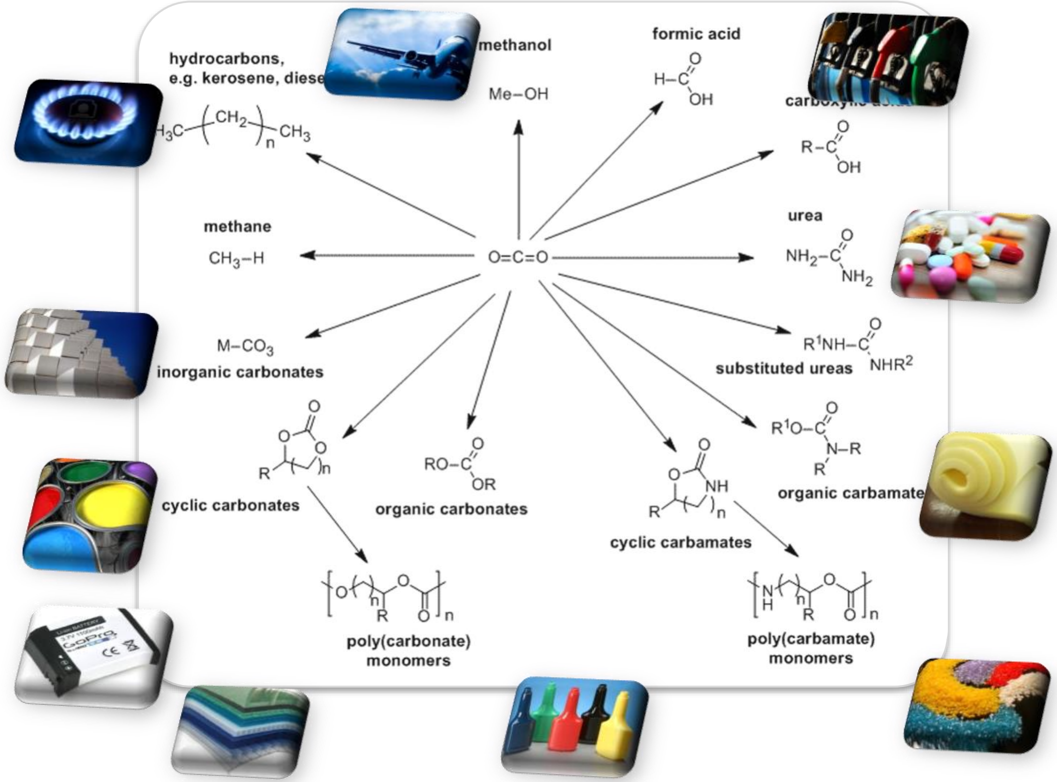


Chart source: "Carbon capture and utilization in the green economy," Center for Low Carbon Futures, 2011

Using unwanted CO_2 is a seductive idea but…

Source: Graham Turner for the Guardian

Source: Venex_jpb/Creative Commons

Source: JMR_Photography

Source: CliNKer

- People assume that "geological storage is **costly** and simply hides our waste; it's like landfill"
- "CO_2 is a **valuable resource**; we're running out of carbon"
- "CO_2 utilisation **makes money** from normal consumer demand not from artificial markets like CO_2 certificates"
- "CO_2 utilisation stimulates **innovation** and competitiveness and will generate green growth"

There are reasons to be cautious:

- What if CO_2 utilisation **doesn't prevent emissions**?
- Extracting carbon from CO_2 requires lots of **extra energy**
- Many products from CO_2 utilisation are **low volume**
- Competitiveness on its own is **not energy policy**

CCU contribution to CO_2 emissions reduction needs to be demonstrated on life-cycle basis

CONVERSION TECHNOLOGIES

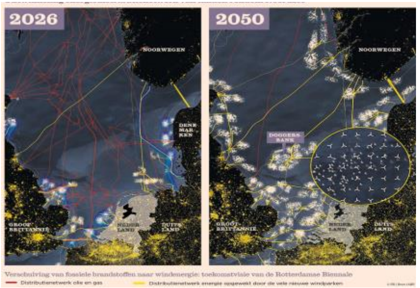
1. Catalytic Hydrogenation
2. Direct Electrochemical

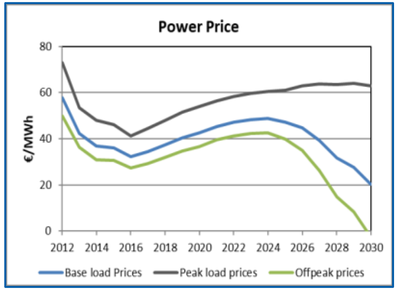
Electrification

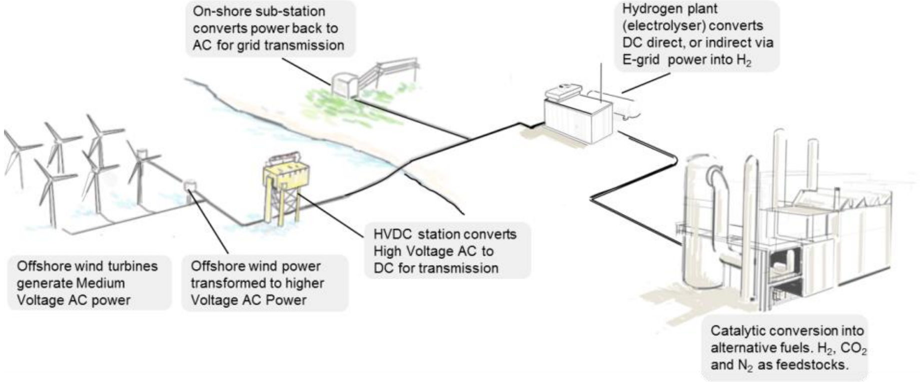
3. Polymerization
4. Biochemical
5. Mineralisation

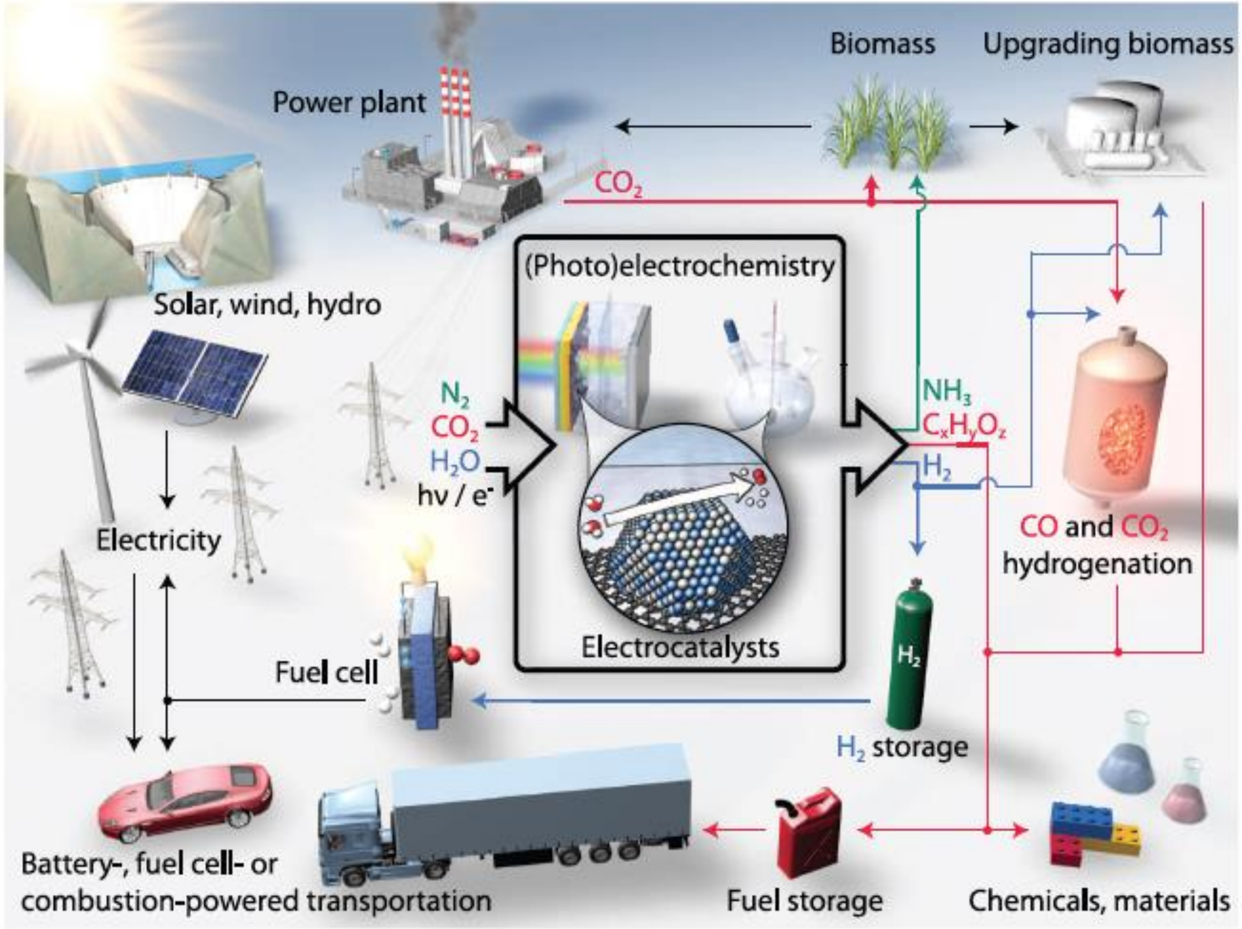
RENEWABLES WILL CREATE OPPORTUNITIES

0.9 GW (2016) → 4.5 GW (2023) → 250? GW (2050)



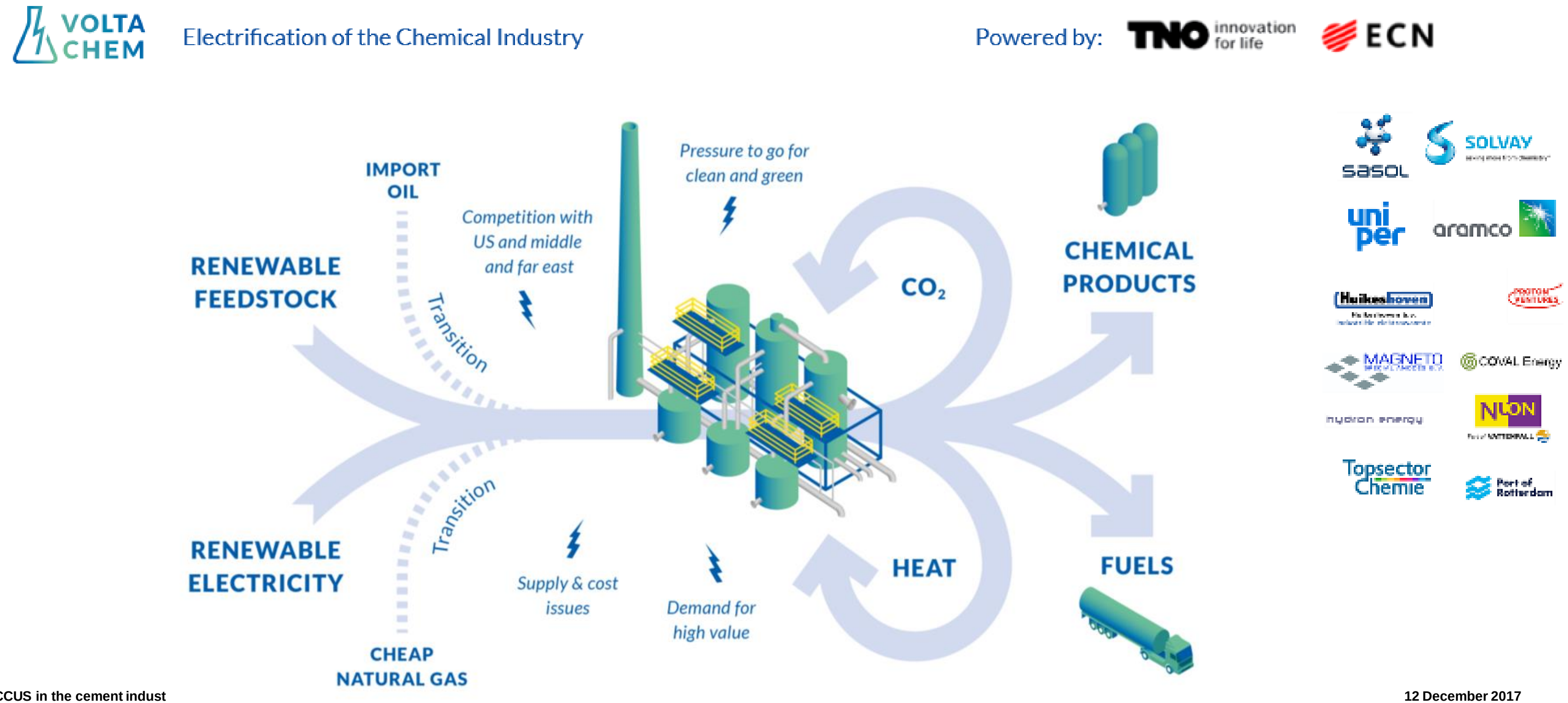


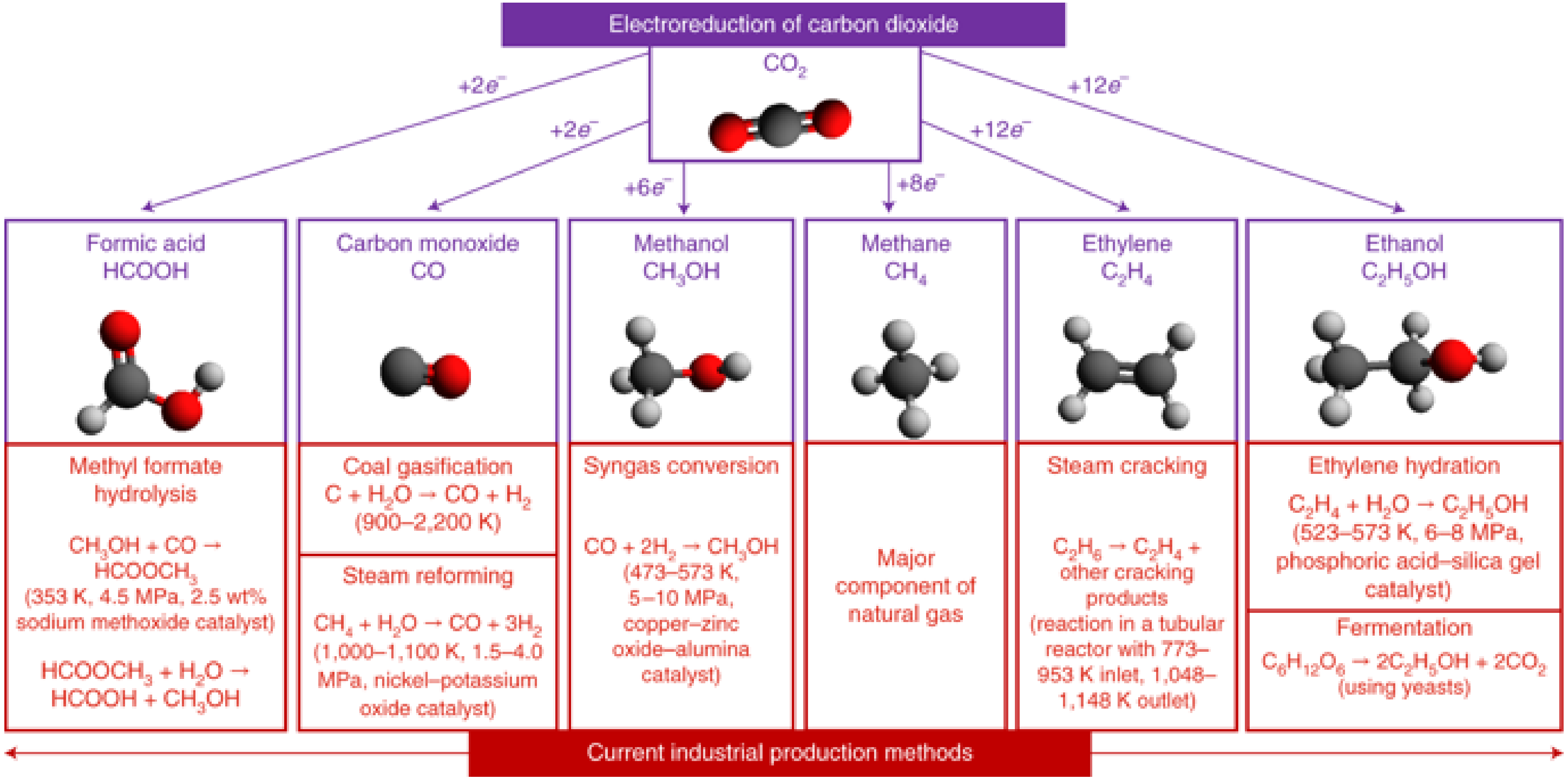




Z. She et al, Science, 355 (2017)

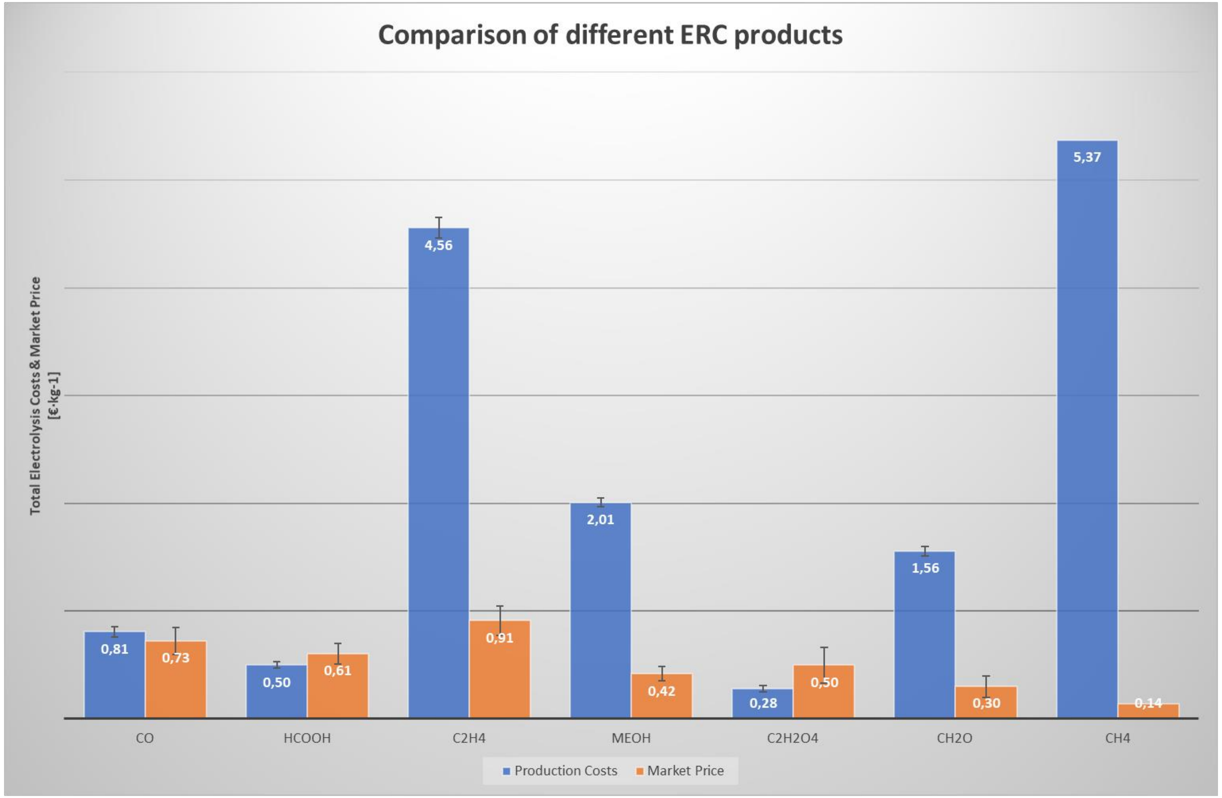
C1 CHEMISTRY: FUTURE VISION



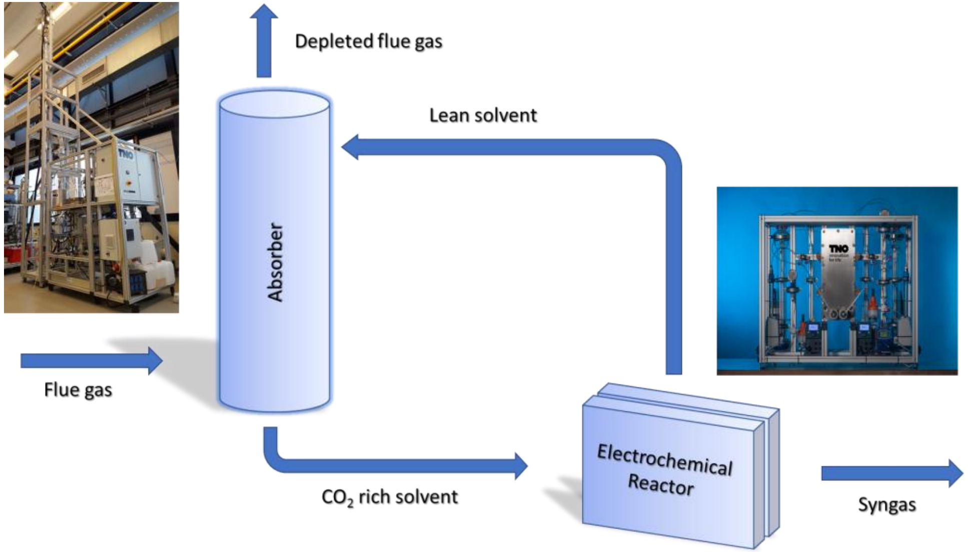


Sumit Verma, Shawn Lu & Paul J. A. Kenis, Nature Energy (2019)

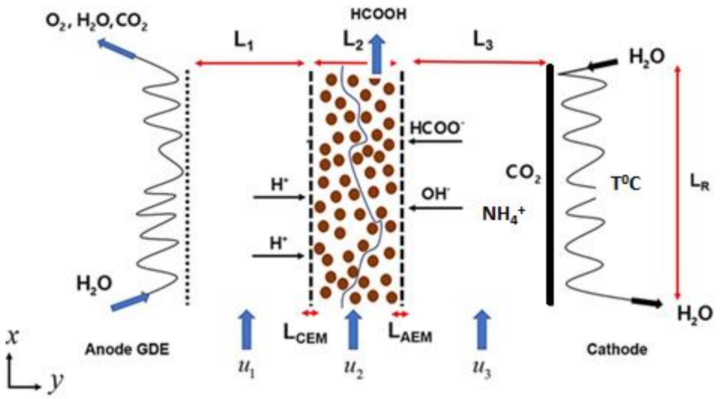
DIRECT ELECTROCHEMICAL REDUCTI



INTEGRATION CO_2 CAPTURE AND CONVERSION



CO_2 ELECTROLYSIS IN AMMONIA ELECTROLYTE CONCEPT

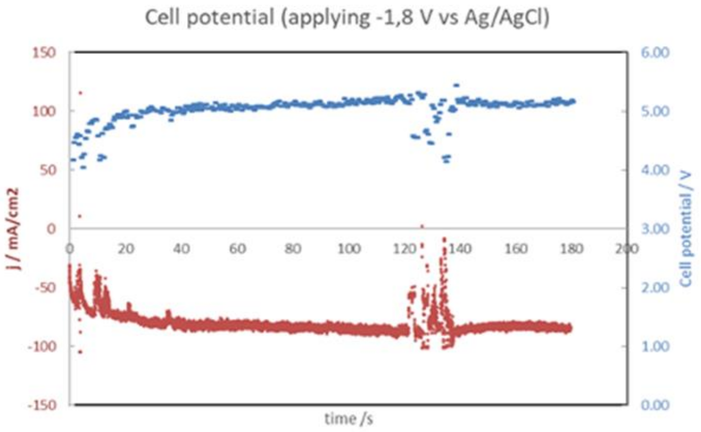


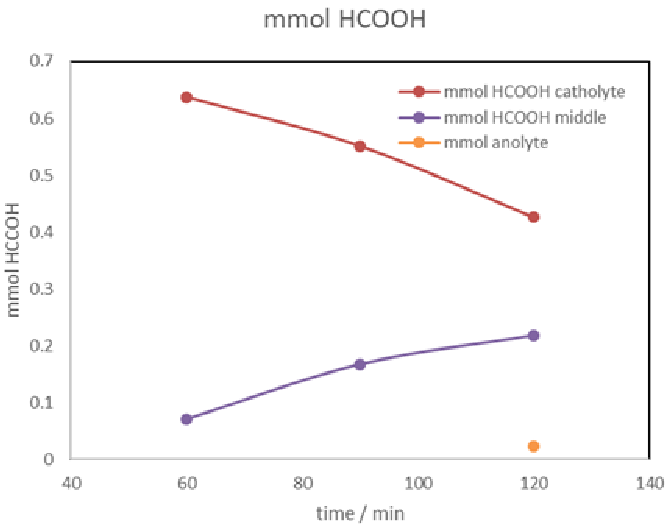
- CO_2 rich ammonia loaded at the catholyte
- Formate produced by electrolysis
- Formic acid separated in situ in the middle compartment

Formate is synthesized at the cathode, H^+ at the anode and they combine in the middle to form formic acid!

EXPERIMENTAL PROOF OF CONCEPT

IN SITU SEPARATION FORMIC ACID FROM AN AMMONIA SOLUTION



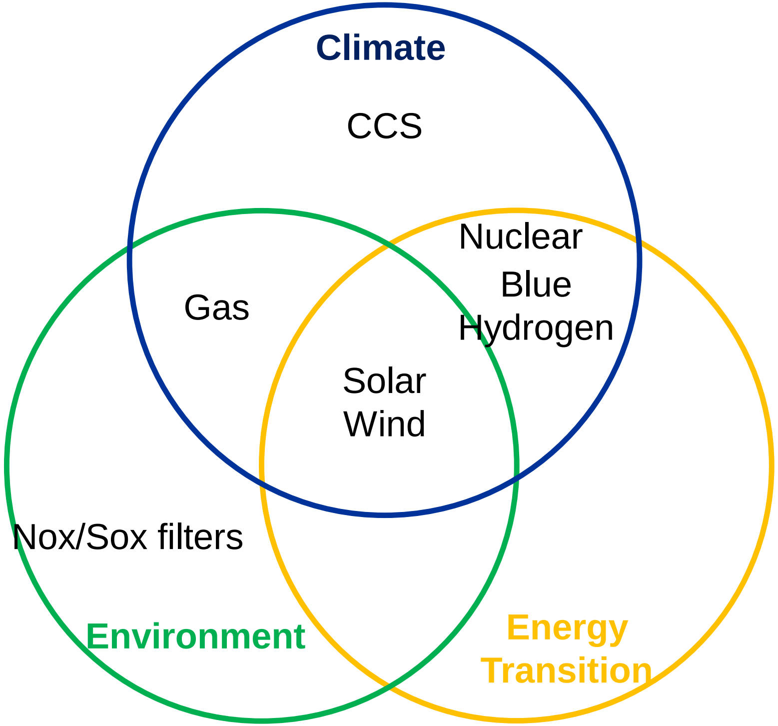


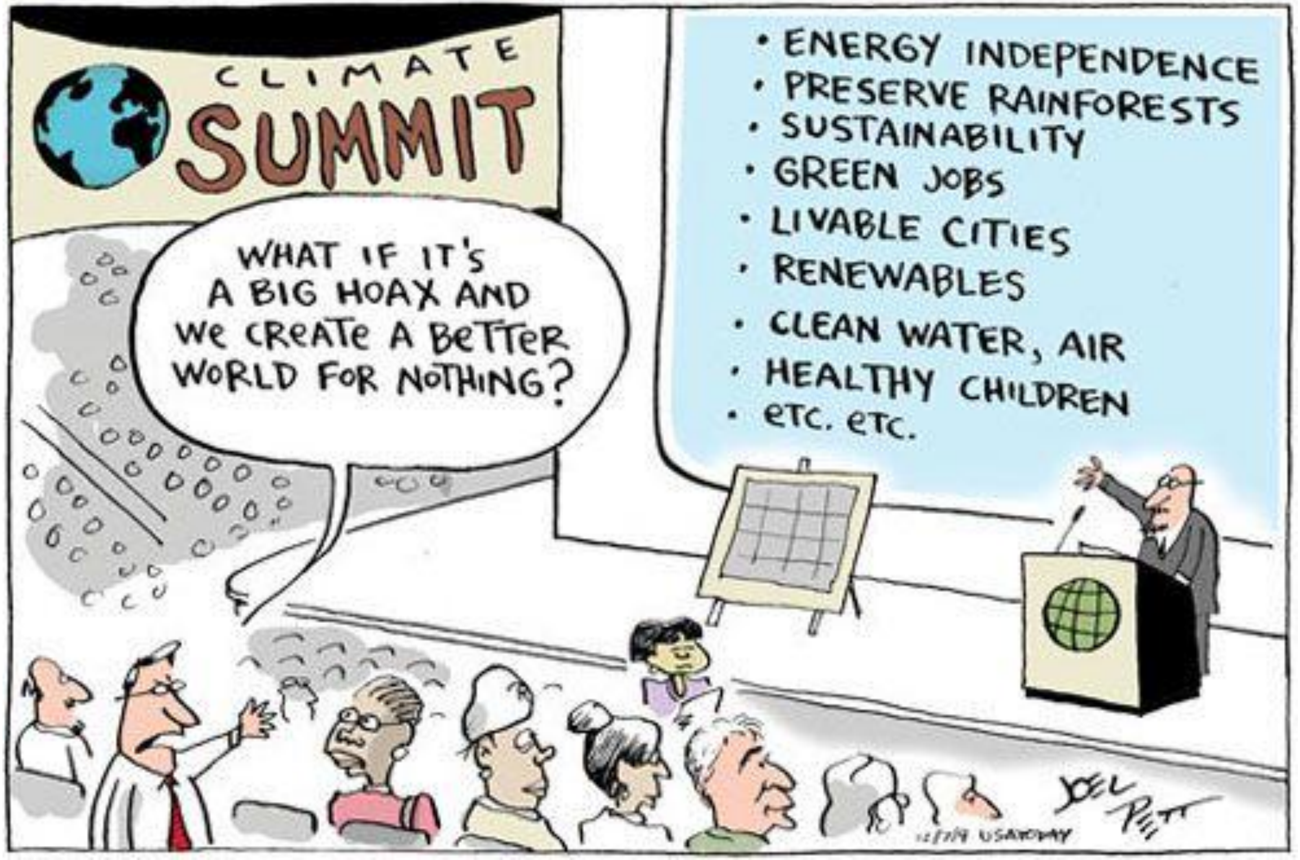
Chronoamperometry at -1.8 V vs Ag/AgCl

Temperatures: Warm up cathode at 85°C

Cool down catholyte at 15°C

MESSAGE: CLIMATE, ENVIRONMENT & TRANSITION





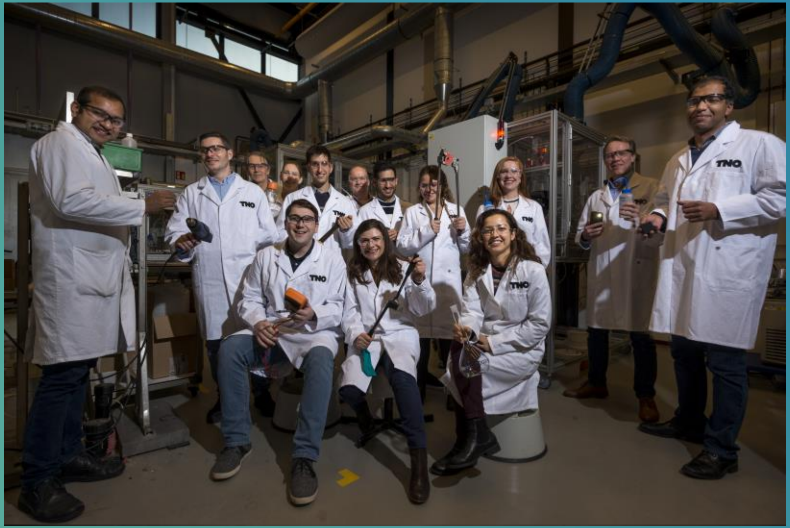
https://www.thoughtco.com/global-warming-cartoons-4122873

FINAL MESSAGE:

In the Netherlands, the signs are on green

at least today…

LET'S ENERGIZE INNOVATION TOGETHER!



www.voltachem.com

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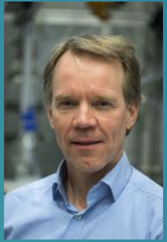

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