CO_2 Research at the University of Liège

Prof. Grégoire LEONARD

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University of Liège - ULiège

- Liège: 3rd urban area in Belgium
  - ~750 000 inh.
- ULiège, a pluralist university
  - 11 faculties, 23 000+ students, 122 Nationalities
  - 38 bachelor study lines, more than 200 master study lines

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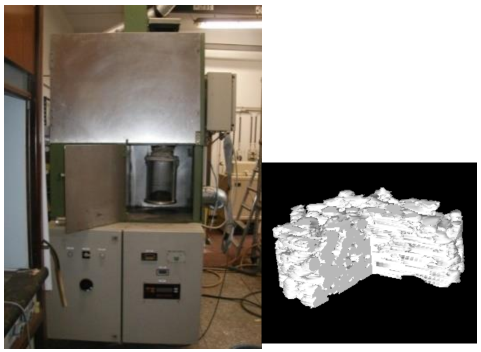
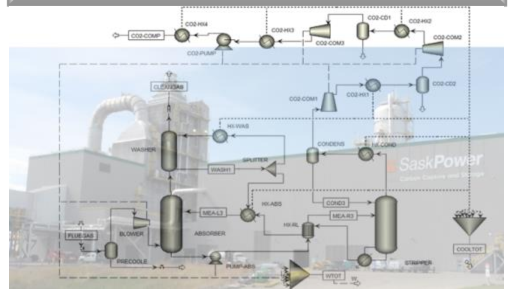
PEPs - Products, Environment and processes

Solid waste and flue gas treatment



CO_2 capture and reuse



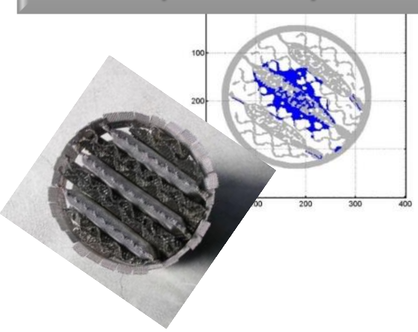
Life Cycle Assessment

Department of Chemical Engineering

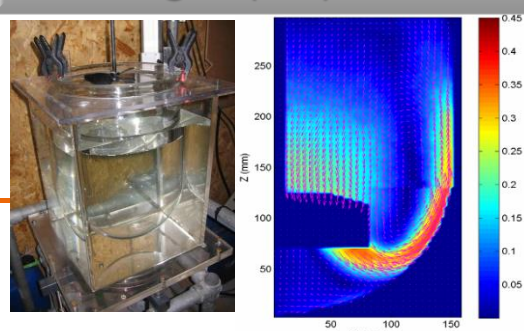
http://chemeng.ulg.ac.be

Solvent and reactive extraction

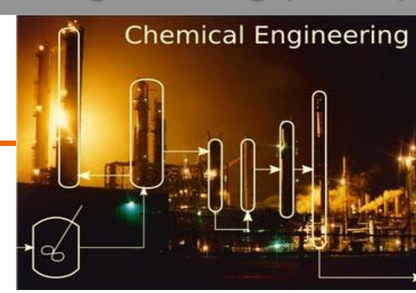
Hydrodynamics in multiphase systems



Mixing in (bio)reactors



Computer-Aided Process Engineering (CAPE)



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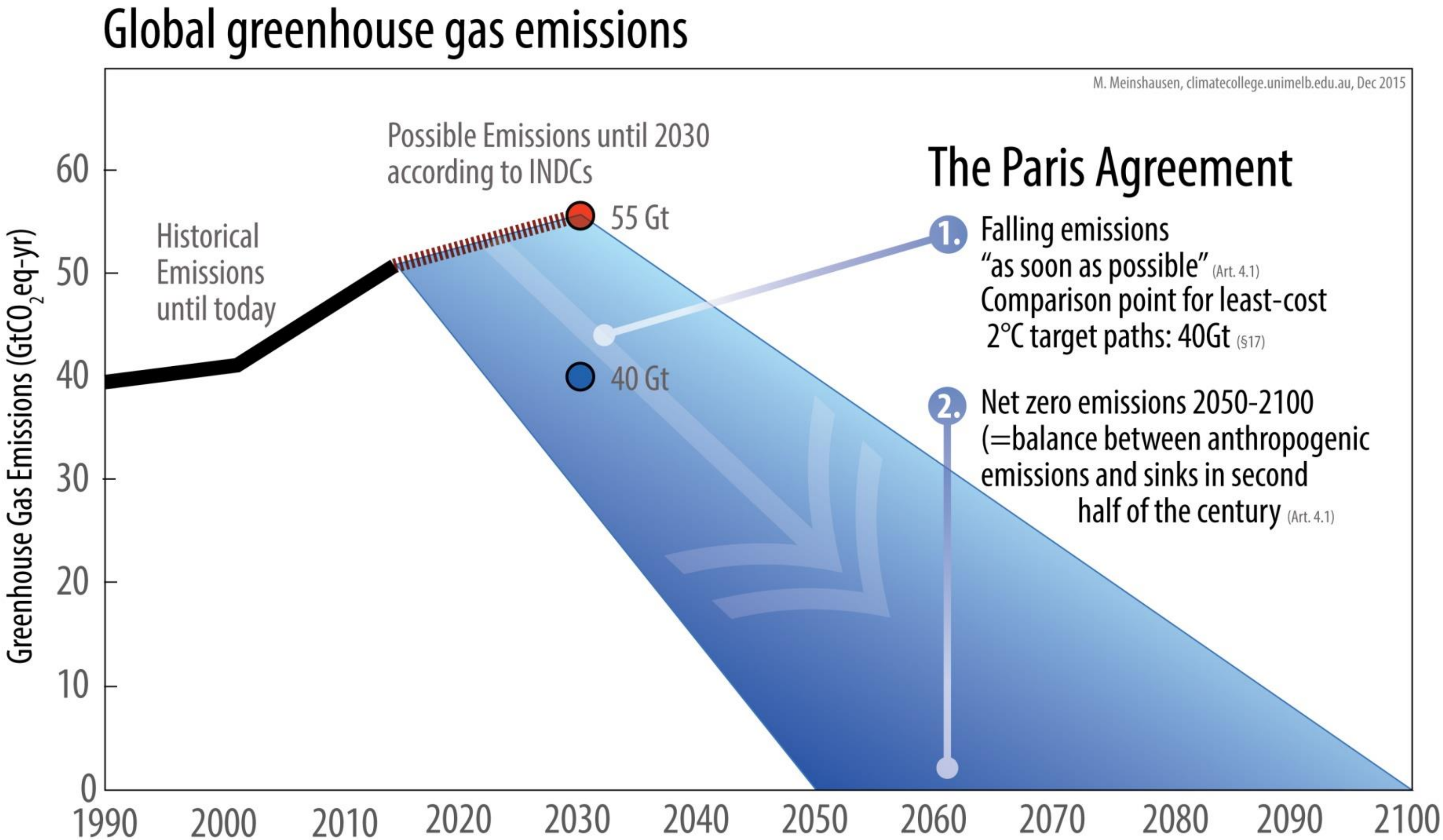
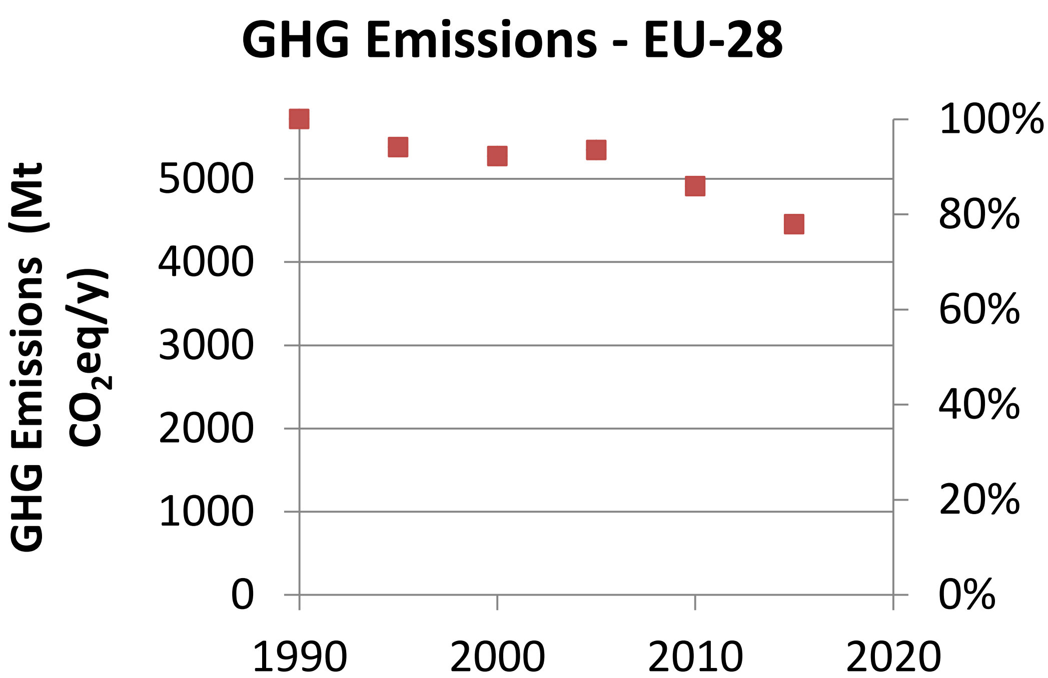
Content

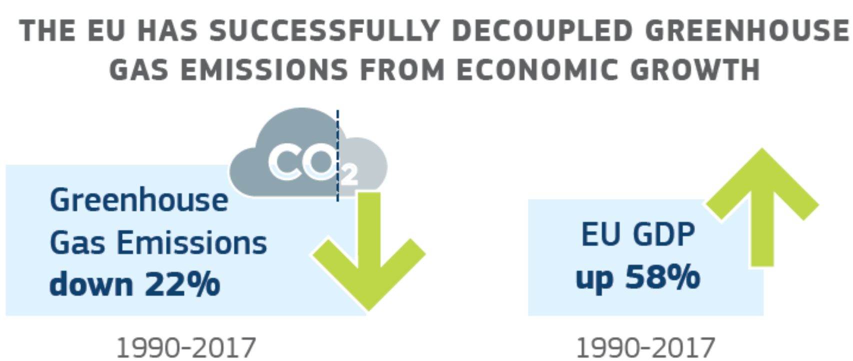
- Context
- CO_2 capture
- CO_2 re-use and power-to-fuel
- FRITCO$_2$T Platform

The Energy Transition has started… but is far from being over!



European achievements



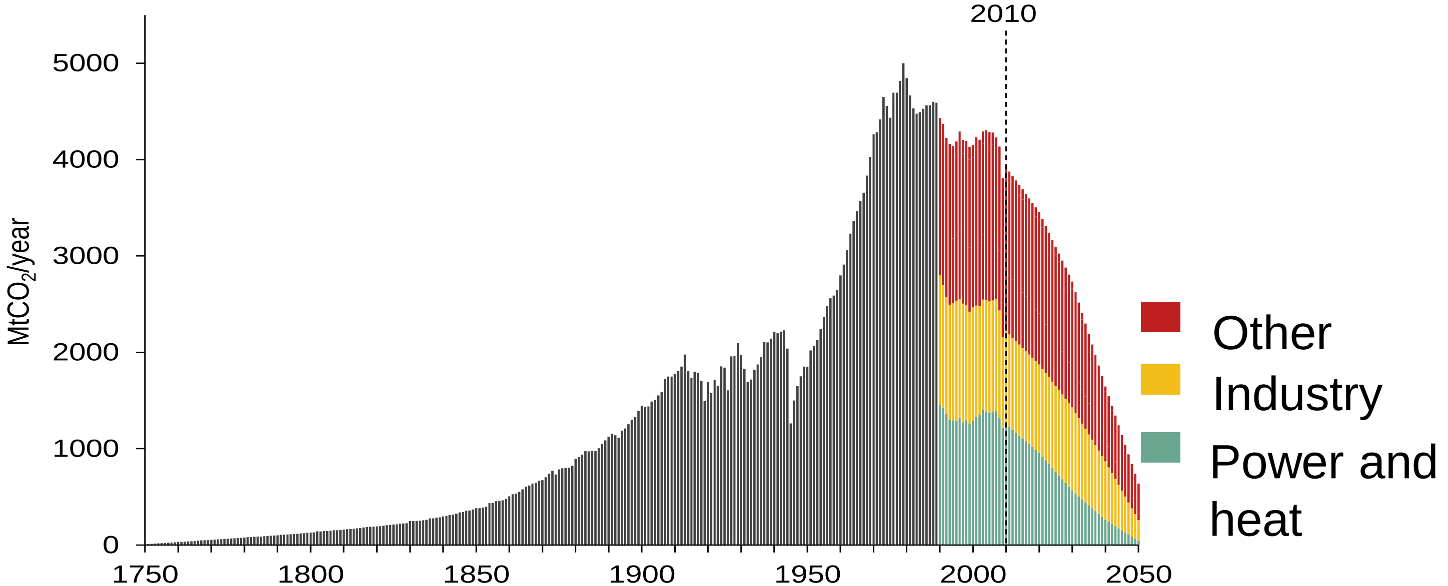


Eurostat, 2017. Greenhouse gas emission statistics - emission inventories

European Ojectives

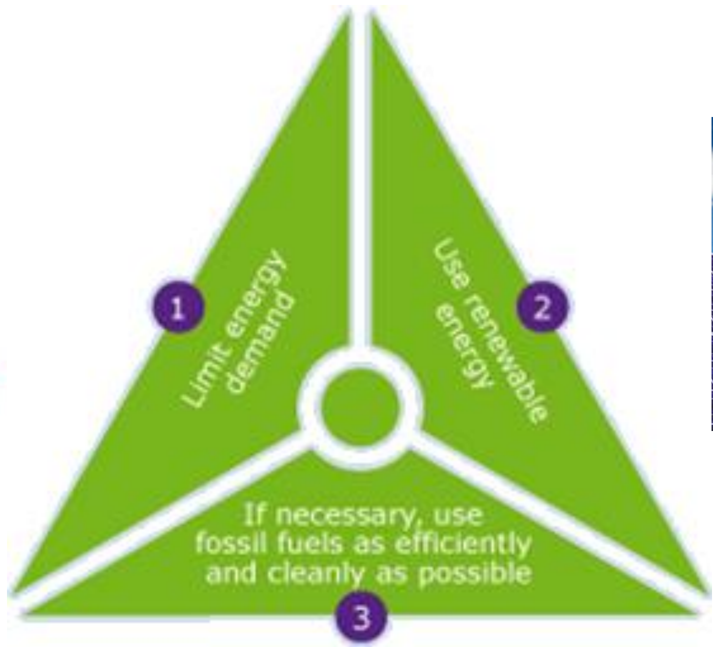
European targets: -80% CO_2

- - 93 to 99% CO_2 in power and heat
- - 83 to 87% CO_2 in the industry



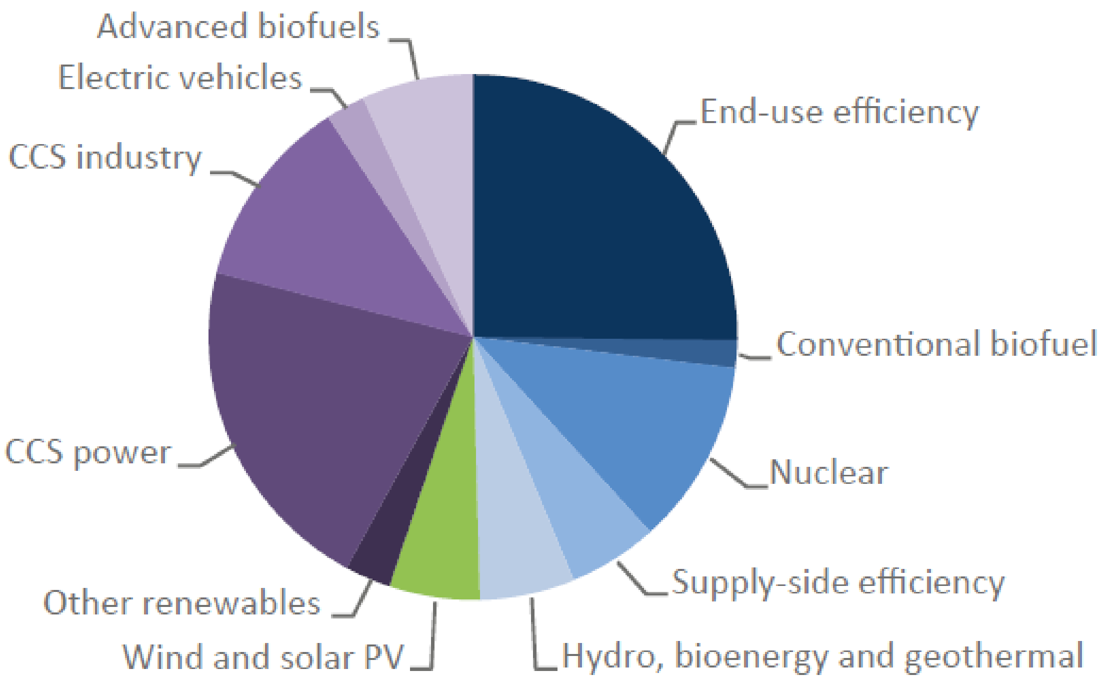
Data sources: [Boden et al., 2010; EC-JRC/PBL, 2009; European Commission 2011; EEA, 2015]

Possible answers: Trias Energetica



Lysen E., The Trias Energica, Eurosun Conference, Freiburg, 1996

What efforts are needed?



World CO_2 emissions abatement in the 450 Scenario (Bridge Scenario 2015-2040), IEA **2015**, WEO special report, Energy & Climate Change

- **CCS:** mature technology, but cost only!
- **CCU:** may help to create viable business

2. CO_2 Capture technologies & configurations

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CO_2 capture & storage

- Idea: recover the CO_2 instead of emitting it, so it does not reach the atmosphere. Then re-use or store it.

- Purity of sources varies between 0.04% and 100%!
  - => Fluid separation
  - Solvents, sorbents, membranes, cryo…
  - Technology existing for more than 50 years

- Pros and cons:
  - Almost mature, flexible
  - But expensive…

India, 2006, Urea production, 2x450 tpd CO_2

CO_2 capture configurations

1. Industrial processes (cement, steel…)

=> CO_2 resulting **from process**

2. Capture CO_2 from combustion gas

=> **Post-Combustion** capture

3. Remove C from fuel

=> **Pre-combustion** capture

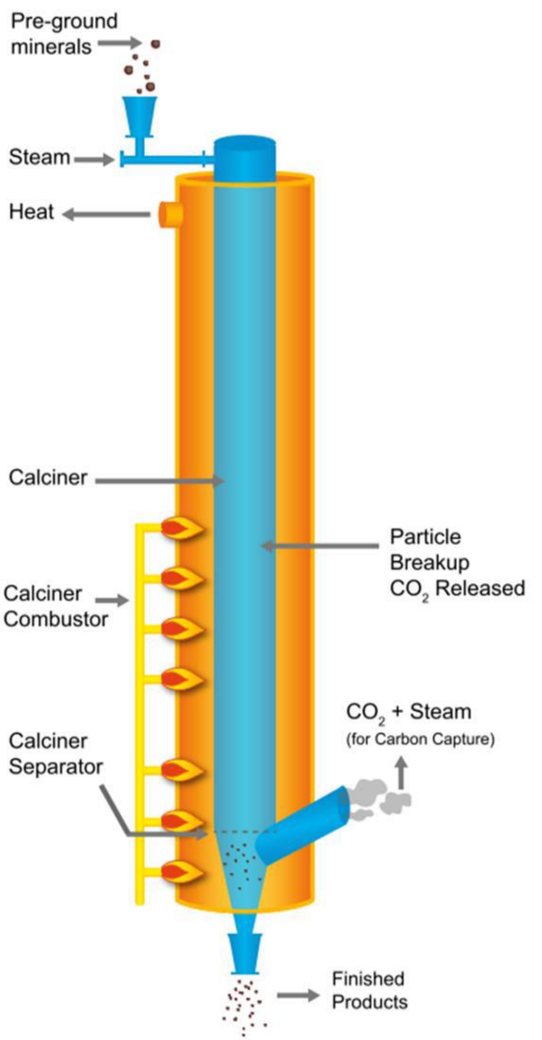
4. Burn fuel with pure oxygen

=> **Oxyfuel combustion**

Industrial processes

1. **CO_2 not resulting from combustion**
   - Cement plants
     - $CaCO_3 \rightarrow CaO + CO_2$
     - Potential gain: -60% CO_2
     - High temperature → 1000°C

     - Pilot plant close to Liège
     - End of construction: 2019
     - Investment: 21 M€



LEILAC public preFEED report, 2016

Post-combustion capture

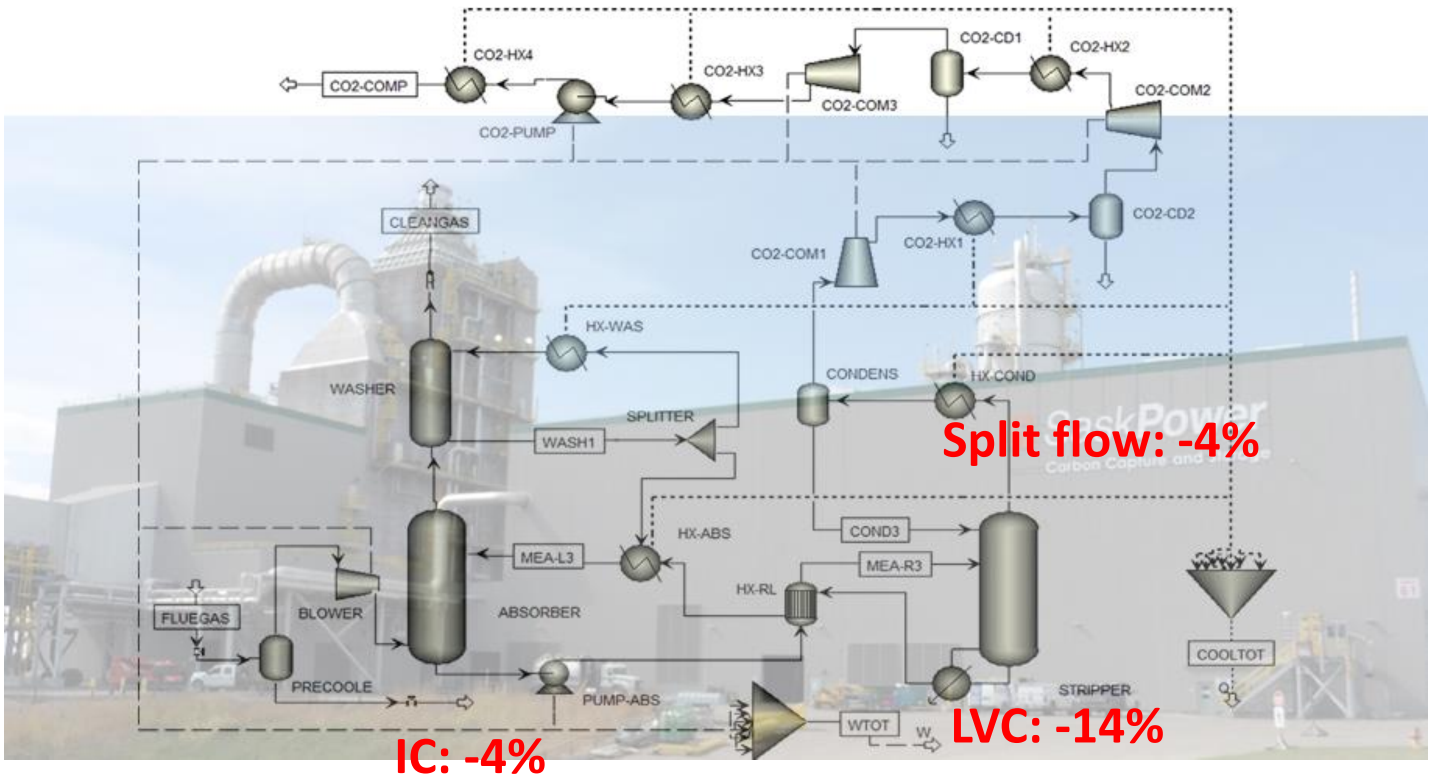
2. **Capture CO_2 from combustion gases**

- Absorption – Regeneration with chemical solvents
- Boundary Dam (Ca), 2700 tCO_2/day from Coal PP
  - Flue gas: 180 Nm^3/s ; Solvent: 550 L/s

Post-combustion capture

2. **Capture CO_2 from combustion gases**

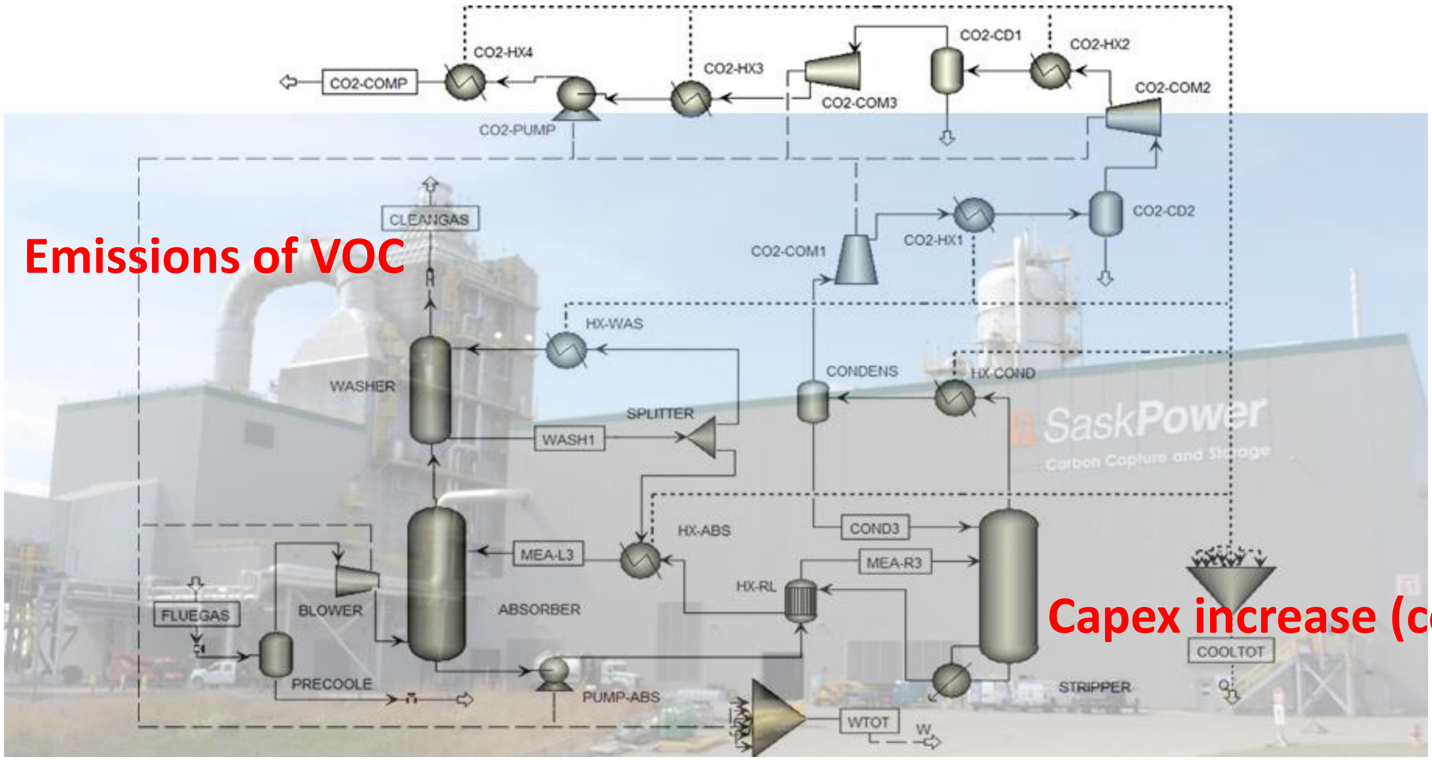
- 2 main focus at ULiège: Process modeling



Post-combustion capture

2. **Capture CO_2 from combustion gases**

- 2 main focus at ULiège: Solvent stability

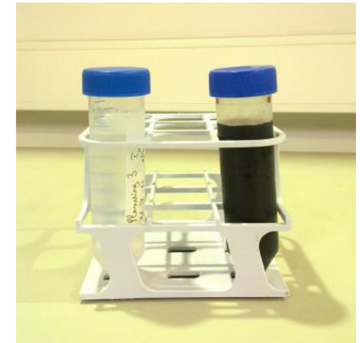


Emissions of VOC

Capex increase (corrosion)

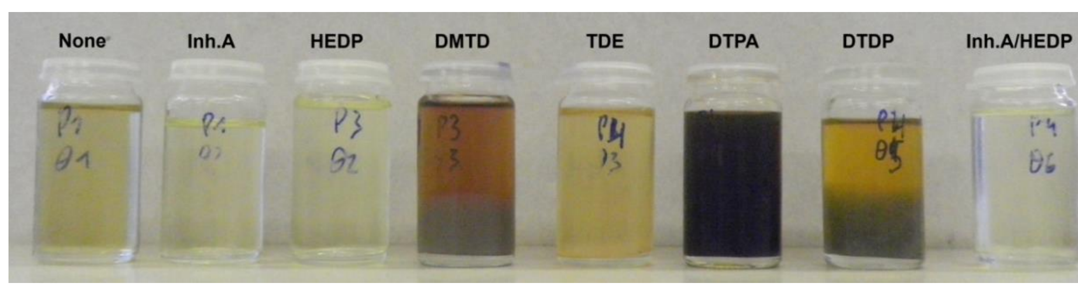
OPEX increase: viscosity, solvent properties…

Post-combustion capture



Solvent stability

- Thermal degradation (120< T <140°C)
  - Irreversible reactions with CO_2
- Oxidative degradation
  - Oxidation of amines with O_2 present in flue gas
- Degradation with other flue gas contaminants
  - SO_X, NO_X …



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Léonard et al., 2014. DOI:10.1021/ie5036572

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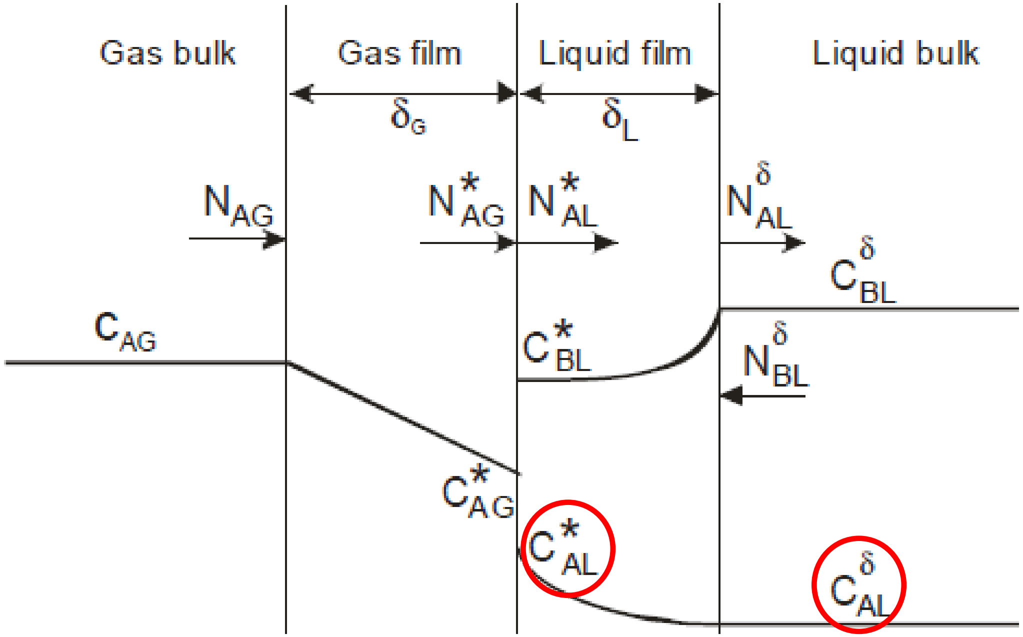
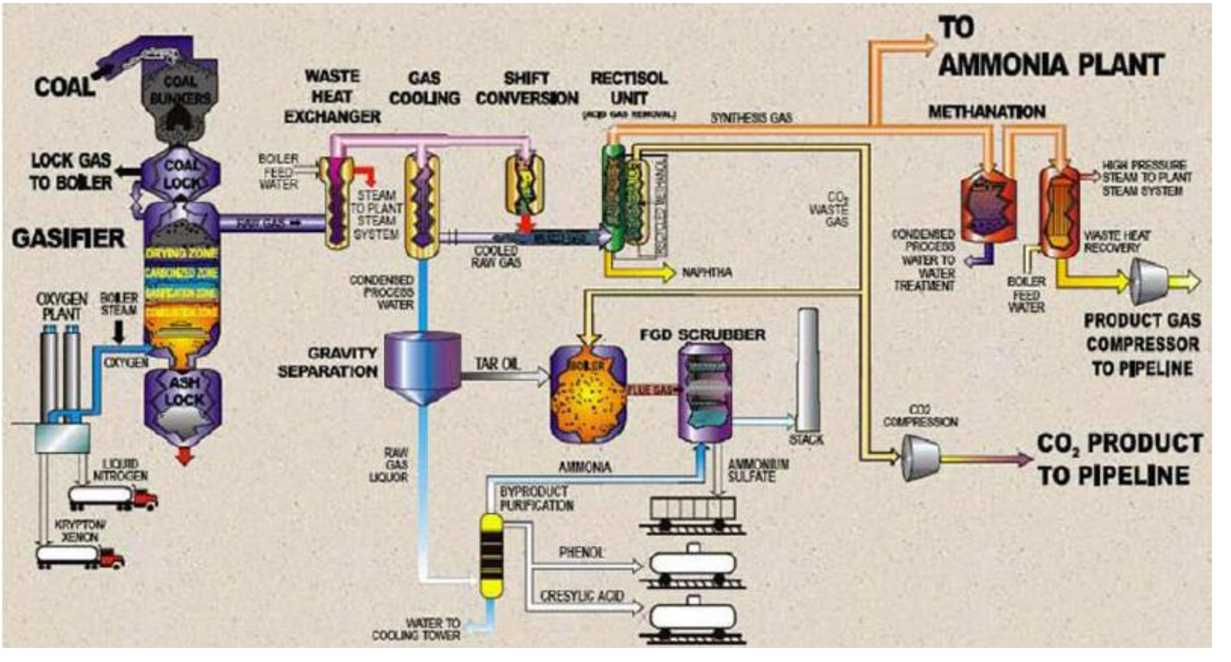
Post-combustion capture

- PhD student Hana Benkoussas
  - Experimental study of solvent ageing for CO_2 capture
  - Kinetic modeling of mass-transfer
  - SO_2-induced degradation



Pre-combustion capture

3. **Remove C from the solid fuel by gasification**
   - Great Plains Synfuel Plant (US), 8 200 tCO_2/day
   - Rectisol process: physical absorption in cold methanol
     - Largest utility consumption and largest plant bottleneck

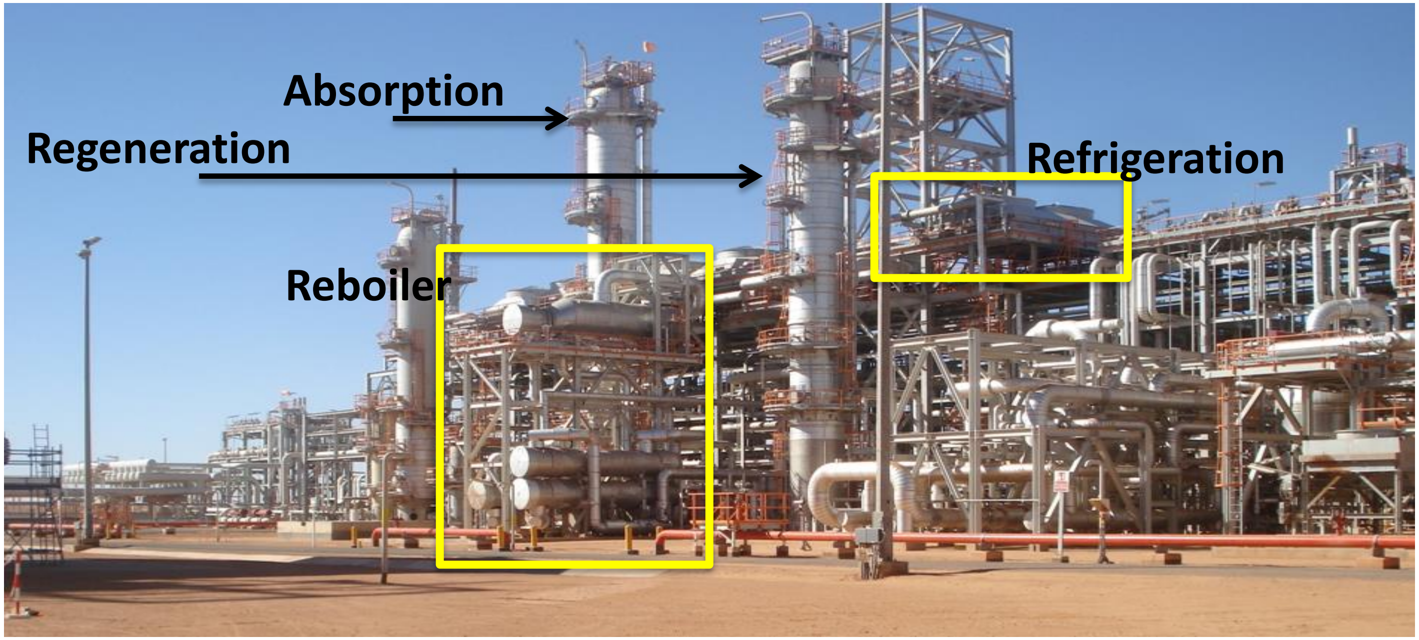


http://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/great-plains

Pre-combustion capture

3. **Remove C from the fuel => Natural gas sweetening**

- Conventional process: absorption with solvents
- From 80 to 2 vol%; down to 50 ppm if liquefaction

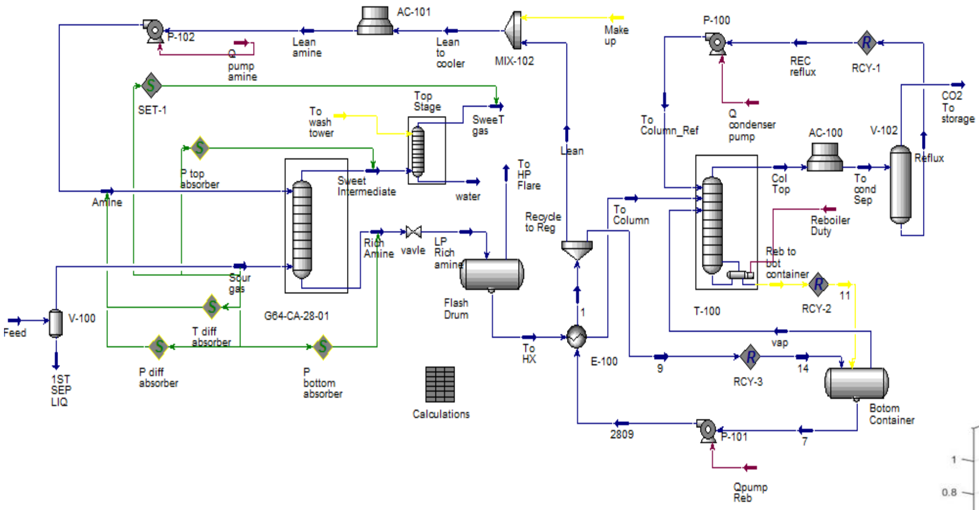


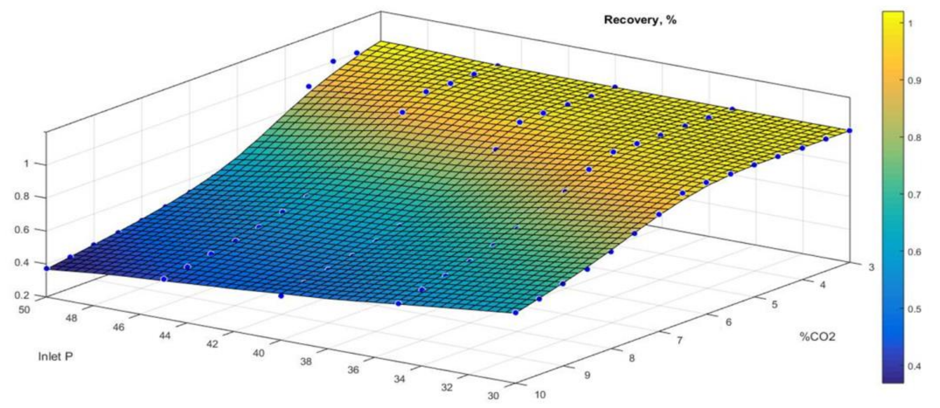
- => Multi-objective optimization of sour natural gas sweetening processes

Picture: Berchiche M. (2017).

Pre-combustion capture

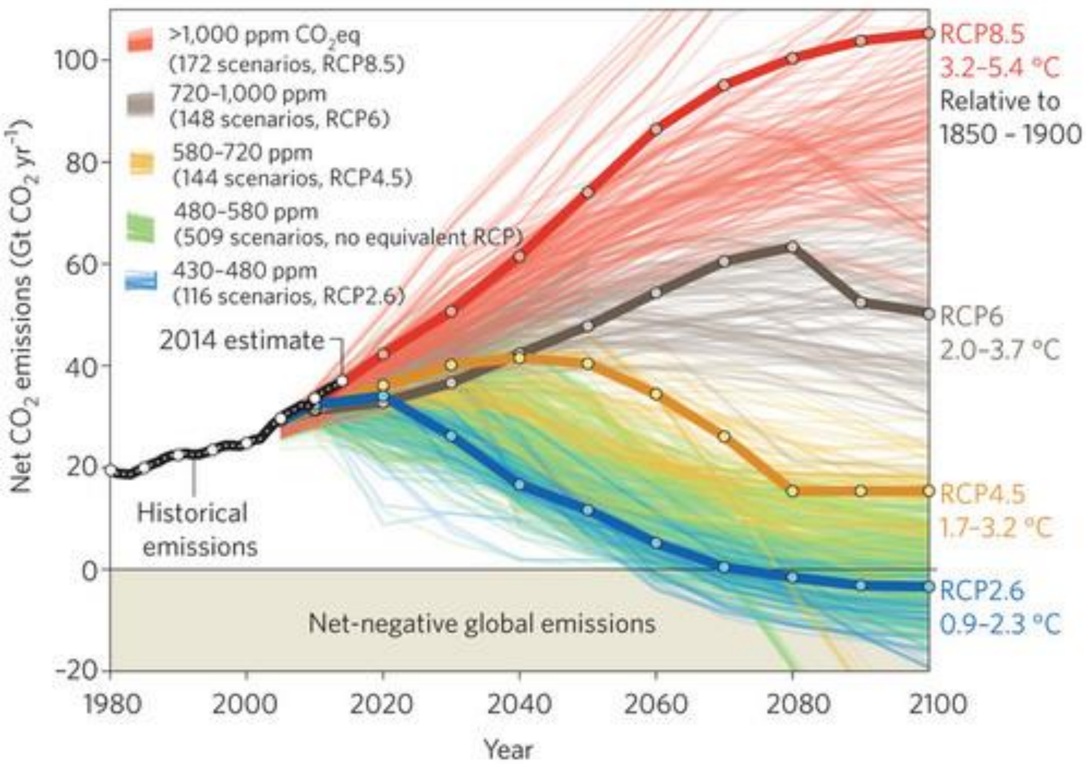
- PhD student Mohamed Berchiche
  - CO_2 capture for Natural gas sweetening operations
  - Process multi-objective optimization





Trends and challenges

- Negative CO_2 emissions
  - Biomass-enhanced CCS
  - Direct air capture



Fuss et al, Nature, 2014, doi:10.1038/nclimate2392

Trends and challenges

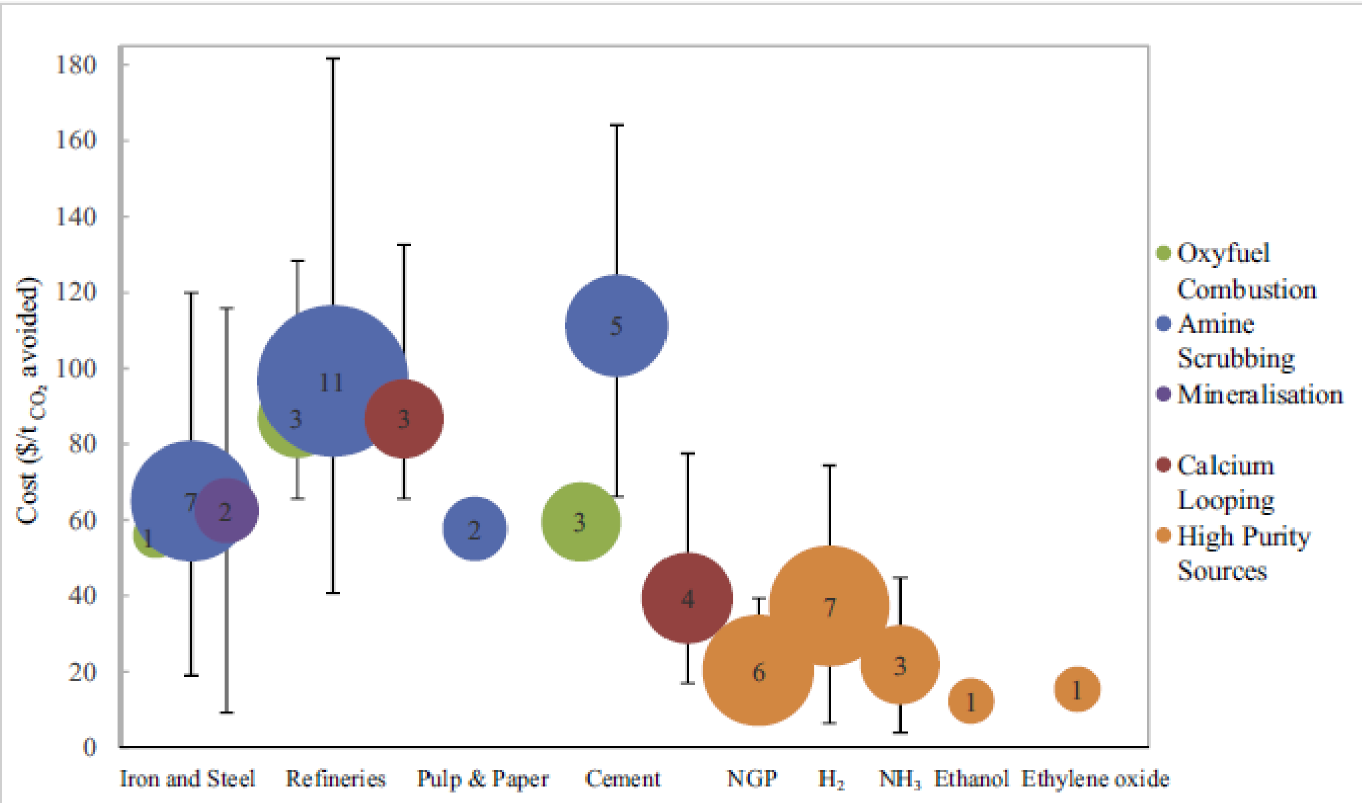
Exclusive: Carbon Engineering CEO discusses recent funding for DAC technology

By Molly Burgess | 24 April 2019

Last month, Carbon Engineering, a Canadian clean energy company announced the completion of an equity financing round of $68m, marking the largest private investment made into a Direct Air Capture (DAC) company to date.

Cost of CO_2 capture

- Merit curve for CO_2 capture
- NB: DAC ~100$/ton



Leeson et al, 2017, DOI: 10.1016/j.ijggc.2017.03.020

CO_2 market

- European Emissions Trading System (ETS)
- CO_2 price now reaches 25 €/t!

https://markets.businessinsider.com/commodities/co2-emissionsrechte

3. CO_2 re-use technologies

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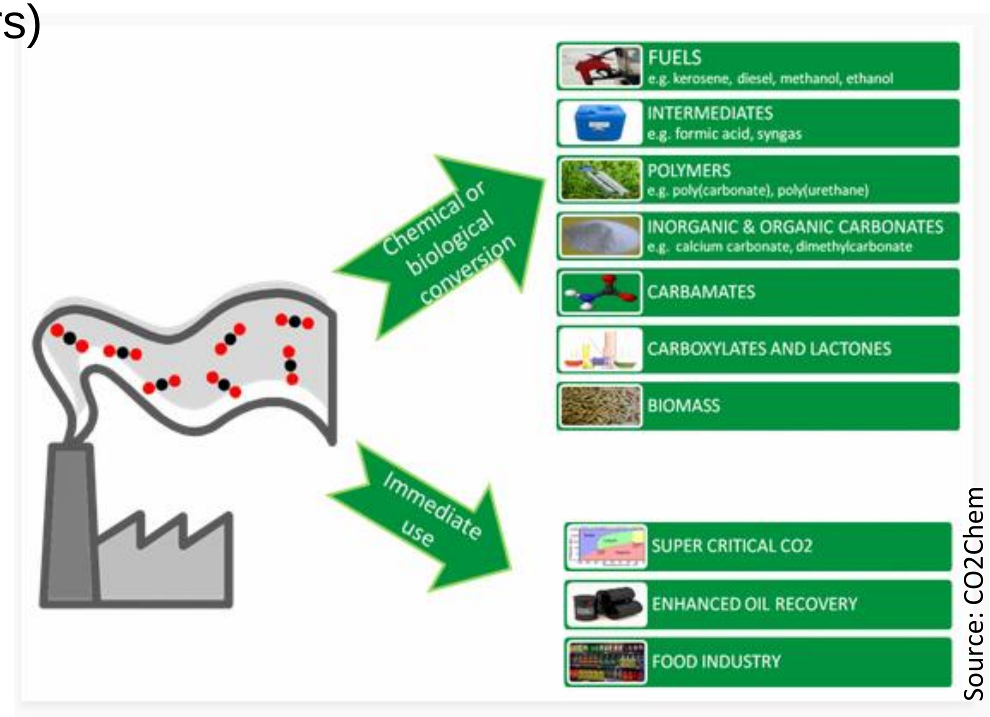
CCUS: New technologies and products

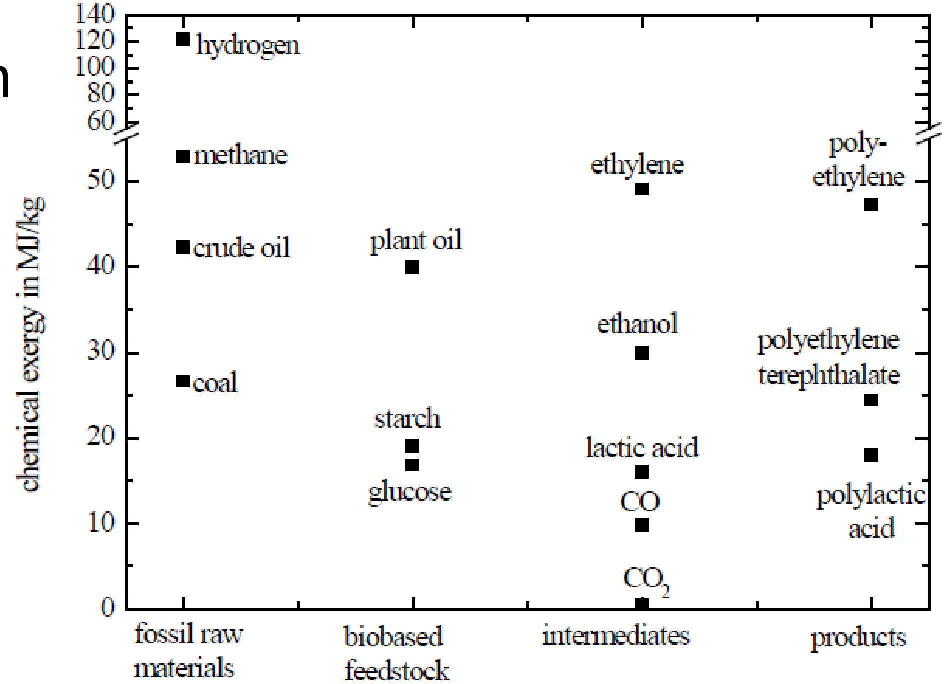
- Future source for C in organic products?
  - Biomass or CO_2
- Huge potential of applications : 4 Gtpa CO_2
  - 2016: ~ 250 Mt CO_2 reused (120 Mt CO_2 on site: 15% CCS, 50% Urea, 35% others)



Koytsumpa et al, 2018. https://doi.org/10.1016/j.supflu.2017.07.029

Main CO_2 re-use pathways

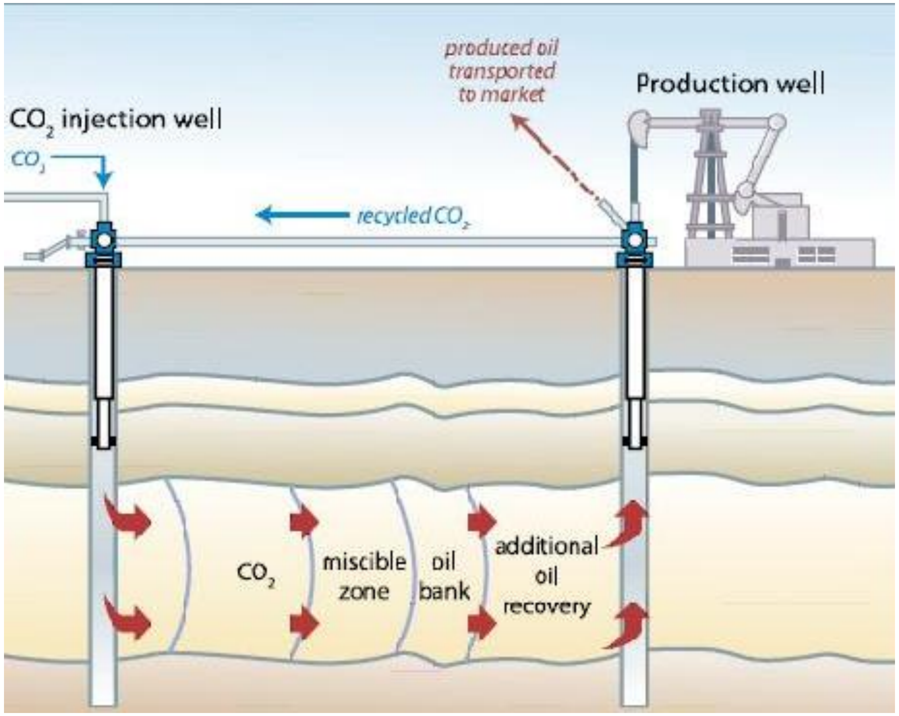
- Direct use, without transformation
  - Enhanced oil recovery
  - Use as solvent…
- With biological transformation
  - Algae, plants…
- With chemical transformation
  - To lower energy state
    - Carbonatation
  - To higher energy state
    - Fuels
    - Plastics
    - Chemicals…

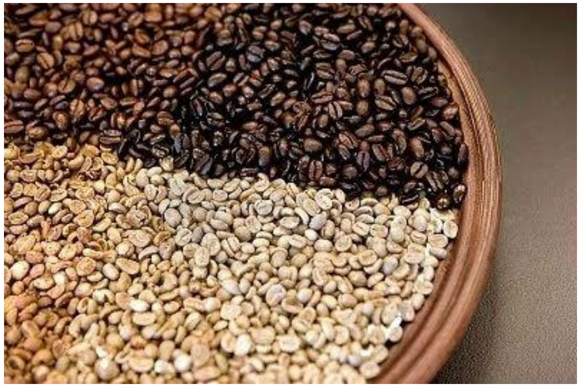


=> At large scale, need to make sure that energy comes from renewables!

Frenzel et al, 2014. Doi:10.3390/polym6020327

Direct industrial use





Biological transformation

- Photosynthesis
  - Microalgae

  - Drawbacks:
    - Area for cultivation (+- 120 t CO_2/ha)
    - Energy for post-processing

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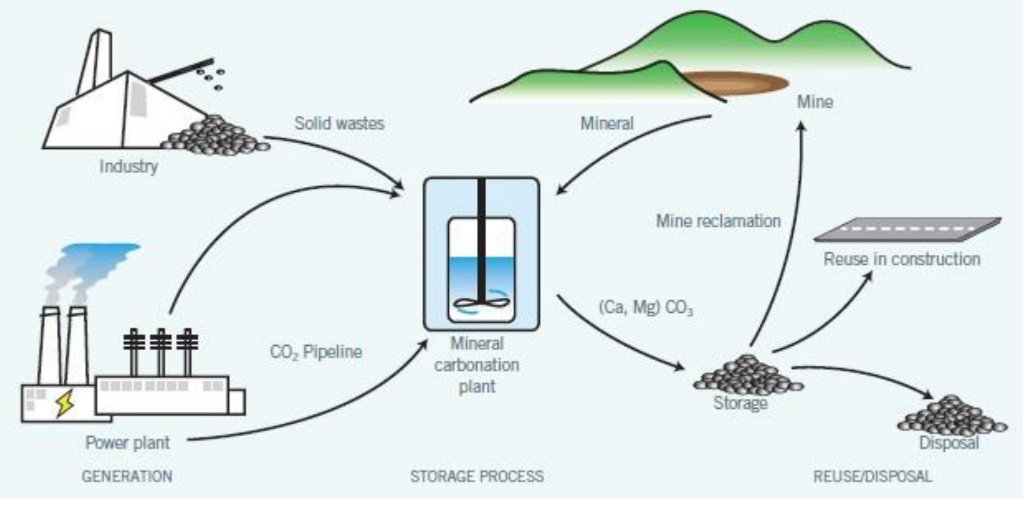
Chemical transformation to lower energy

- Mineralization - Carbonatation
  - $CaO + CO_2 \rightarrow CaCO_3$
  - $MgO + CO_2 \rightarrow MgCO_3$
  - $Mg_2SiO_4 + 2\ CO_2 \rightarrow 2\ MgCO_3 + SiO_2$

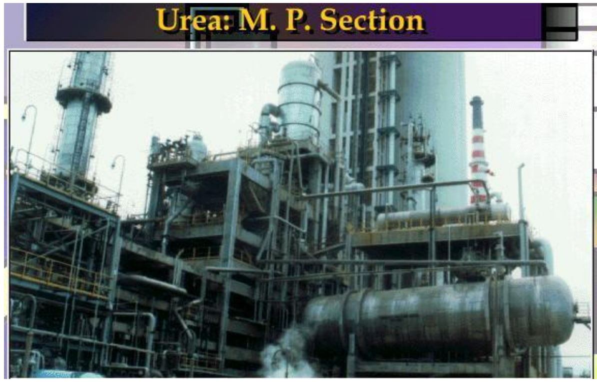


Source: Hemcrete, 2015

- Spontaneous but slow reaction

CO_2 to chemicals

- Urea
  - $2\ NH_3 + CO_2 \leftrightarrow H_2N\text{-}COONH_4$
  - $H_2N\text{-}COONH_4 \leftrightarrow (NH_2)_2CO + H_2O$
  - Already large use (120 $MtCO_2$/an)



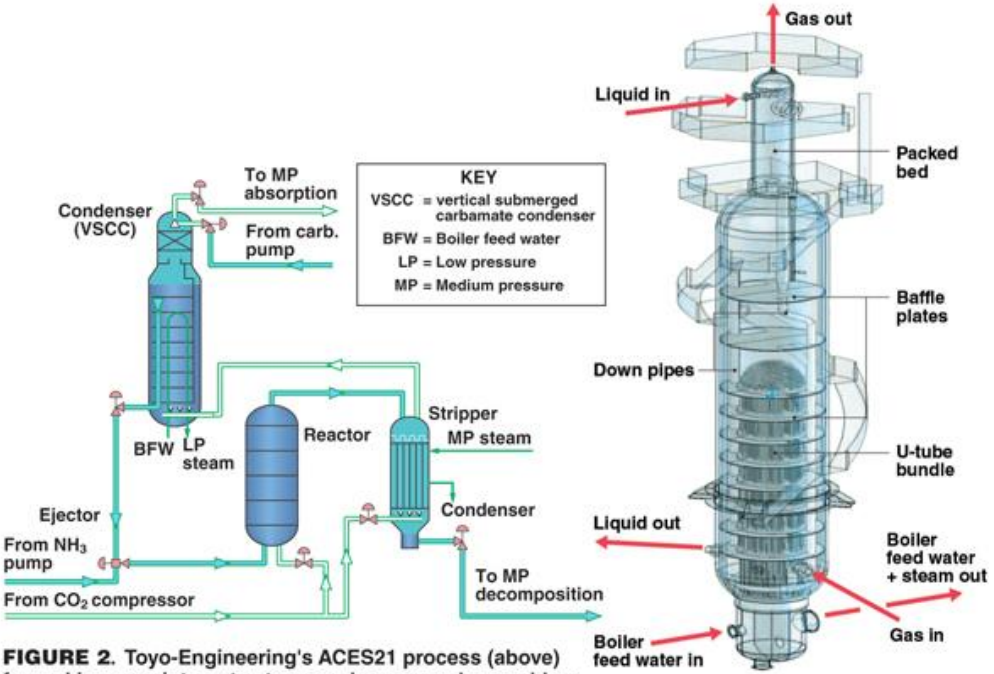


FIGURE 2. Toyo-Engineering's ACES21 process (above) for making urea integrates two condensers and a scrubber into a single condenser (right), which has a vertical, submerged carbamate-condensing section

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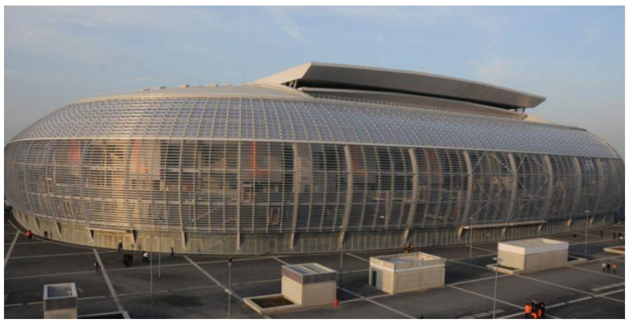
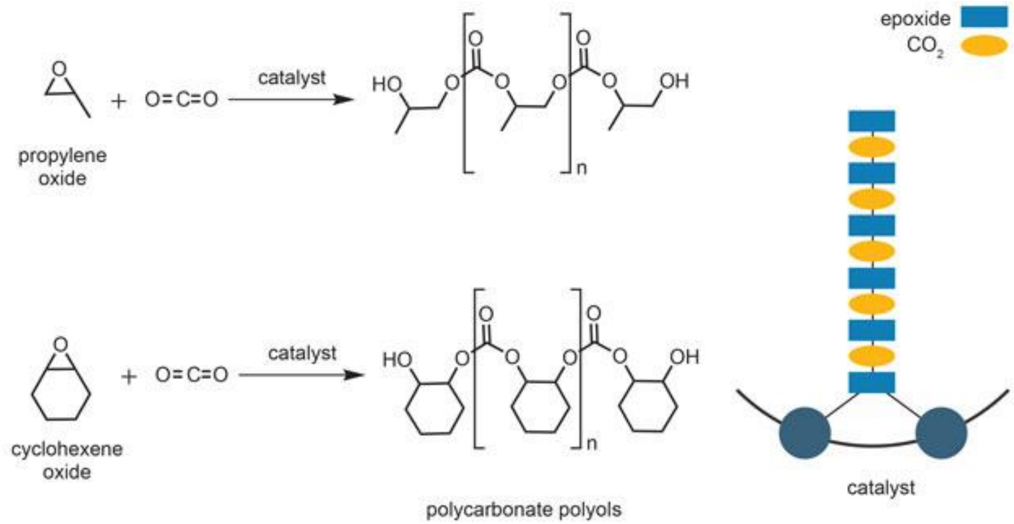
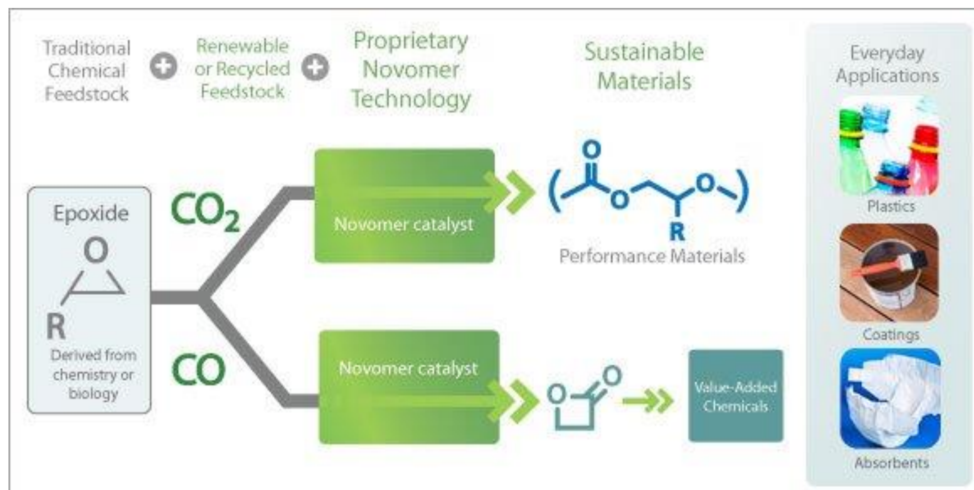
CO_2 to chemicals

- Polycarbonates
  - CO_2 + epoxides





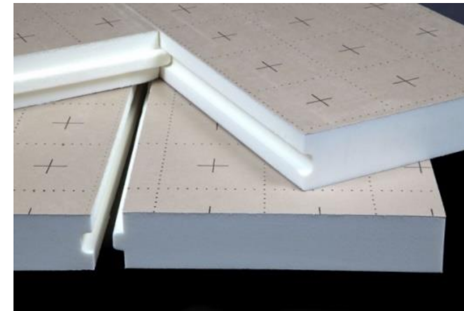
  - Other polyols
    - Up to 40% CO_2 in the plastic!

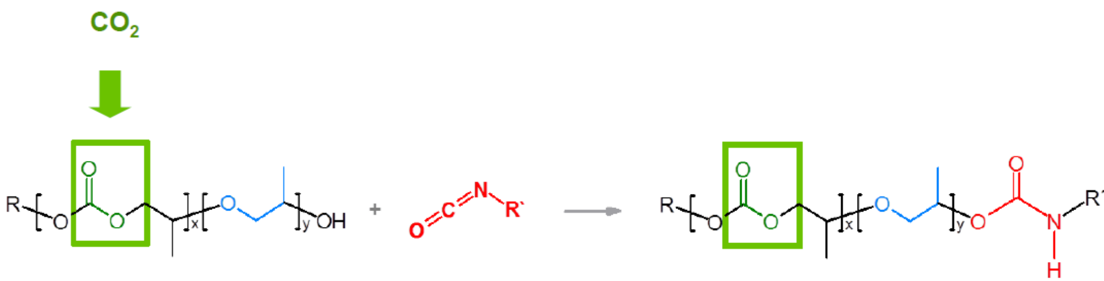


breakingenergy.com, 2014

CO_2 to chemicals

- Polyurethanes
  - 18 Mtpa market
  - 20% CO_2 in the final plastic





Polyol Isocyanate Polyurethane

  - Covestro: 5000 t/a pilot reactor

  - Next step: remove isocyanates => NIPU
    - Grignard B. et al., Green Chem., 2016, 18, 2206

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CO2-production-line at Bayer Material Sciences' site in Dormagen, Germany.
ChemEurope.com, June 2015

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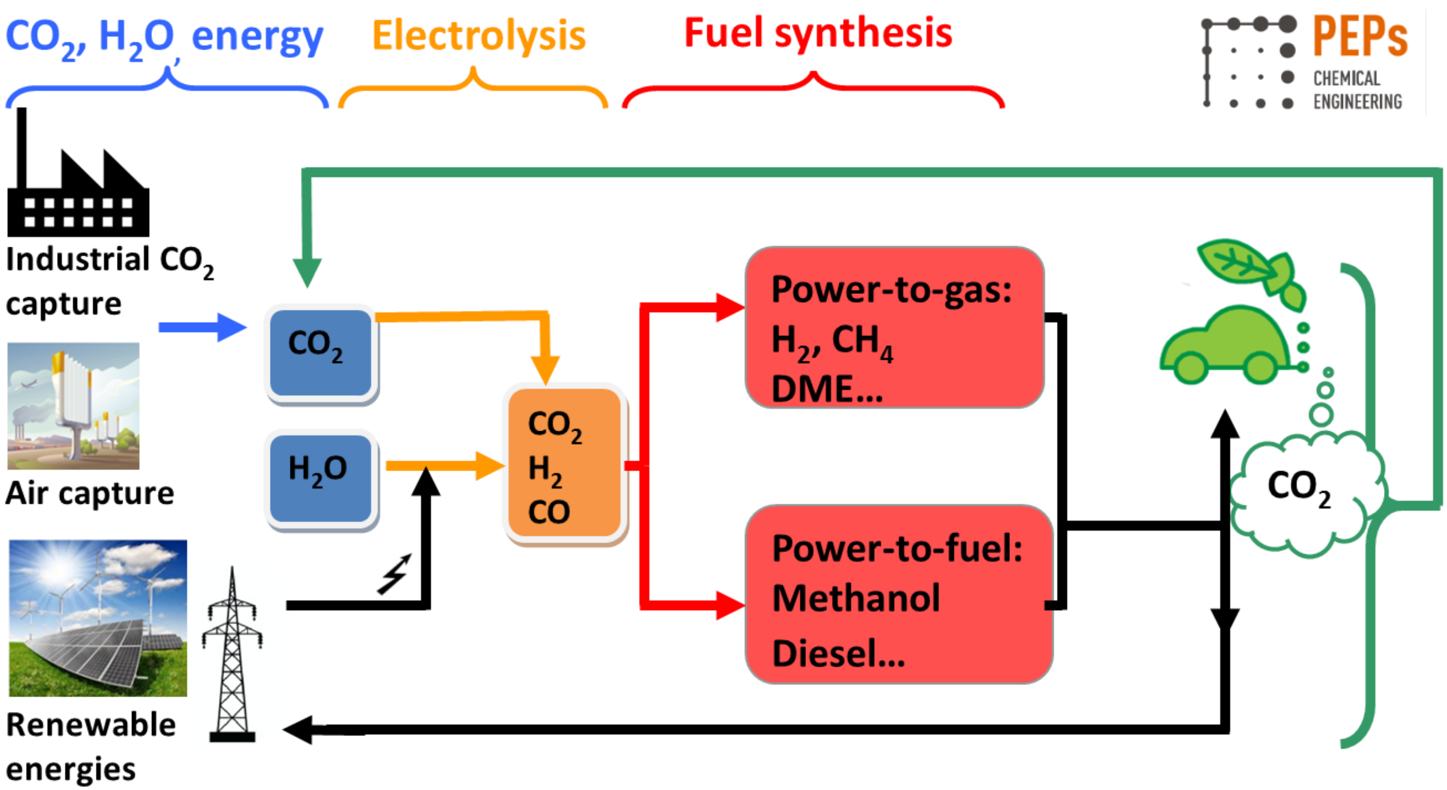
CO_2 to fuels

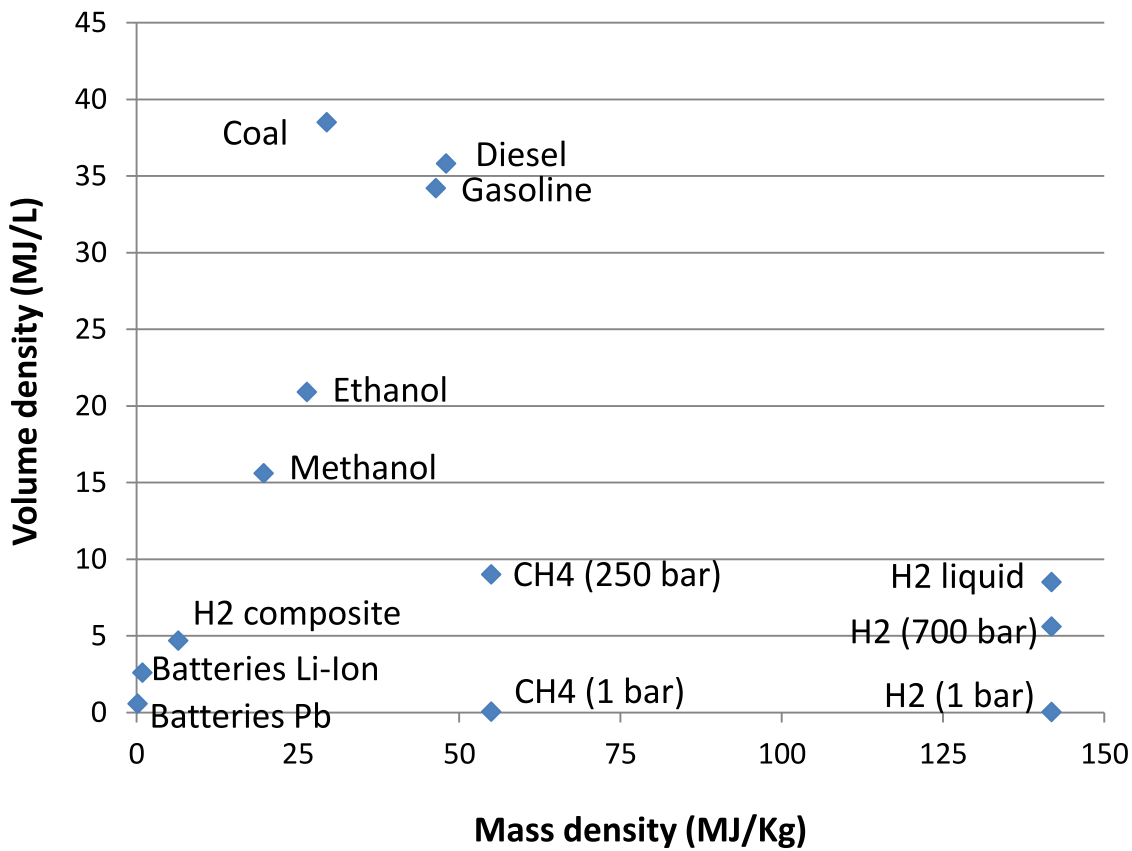
- Power-to-liquid, power-to-gas



=> Sustainability is possible with carbonated fuels!

CO_2 to fuels

- Decisive advantage: a fantastic energy density!
  - => Inteseasonal energy storage becomes possible



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CO_2 to fuels

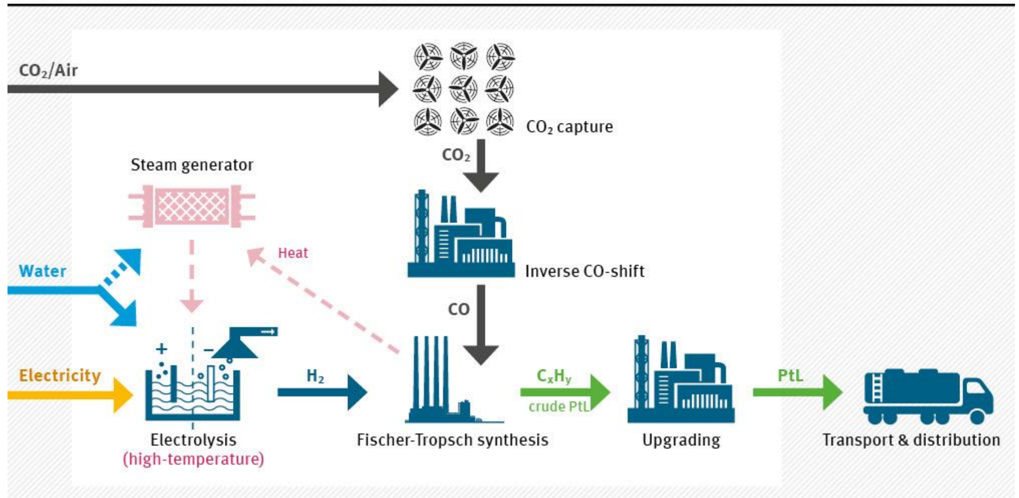
- Methanol
  - $CO + 2\ H_2 \rightarrow CH_3OH$
  - $CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$
  - 4000 T/a, Efficiency ~50%

- DME (CH_3-O-CH_3)
  - Drop-in fuel
  - Stored under pressure

- Fischer-Tropsch fuels
  - Similar to gasoline
  - 58 m^3/a, Efficiency ~70%

Figure 3

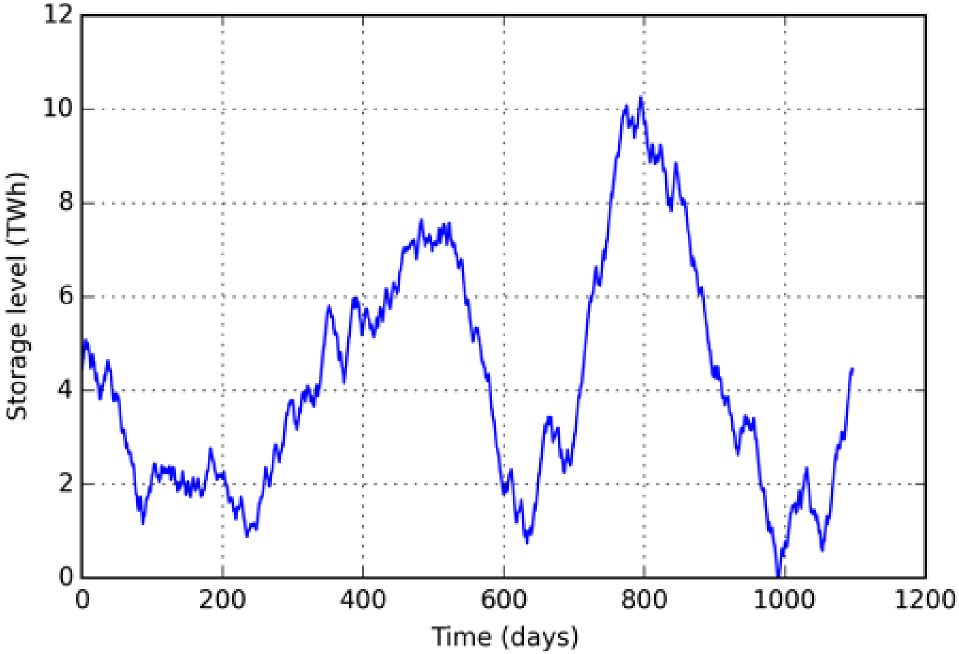
PtL production via Fischer-Tropsch pathway (high-temperature electrolysis optional)



Source: LBST

Research ULiège at system scale

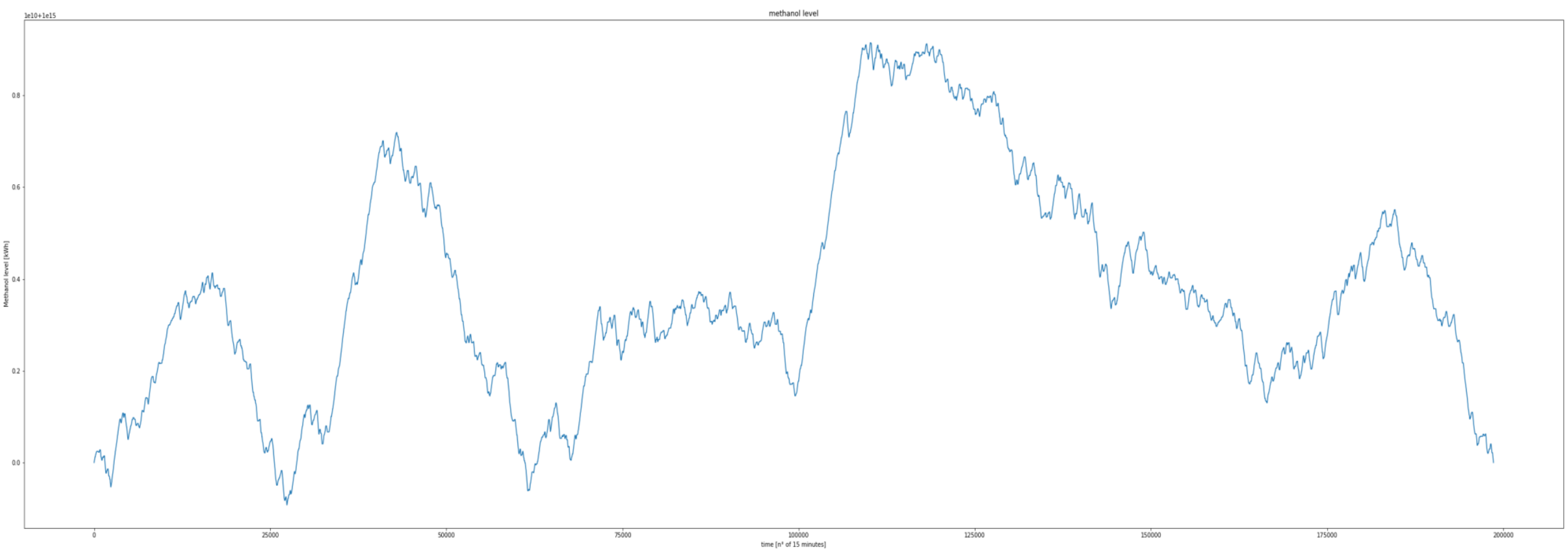
- Energy model with 100% variable renewables + storage for electricity grid:
  - Based on historical belgian data for load and capacity factors
  - Vary the installed capacity to minimize system costs and avoid black-outs



Léonard et al., 2015. Electricity storage with liquid fuels in a zone powered by 100% variable renewables, IEEE 978-1-4673-6692-2.

Research ULiège at system scale

- With addition of On- and off-shore wind, solar, biomass, PV, PHS, batteries
- Results
  - Inter-seasonal storage is needed!
  - Electricity cost ~150€/MWh



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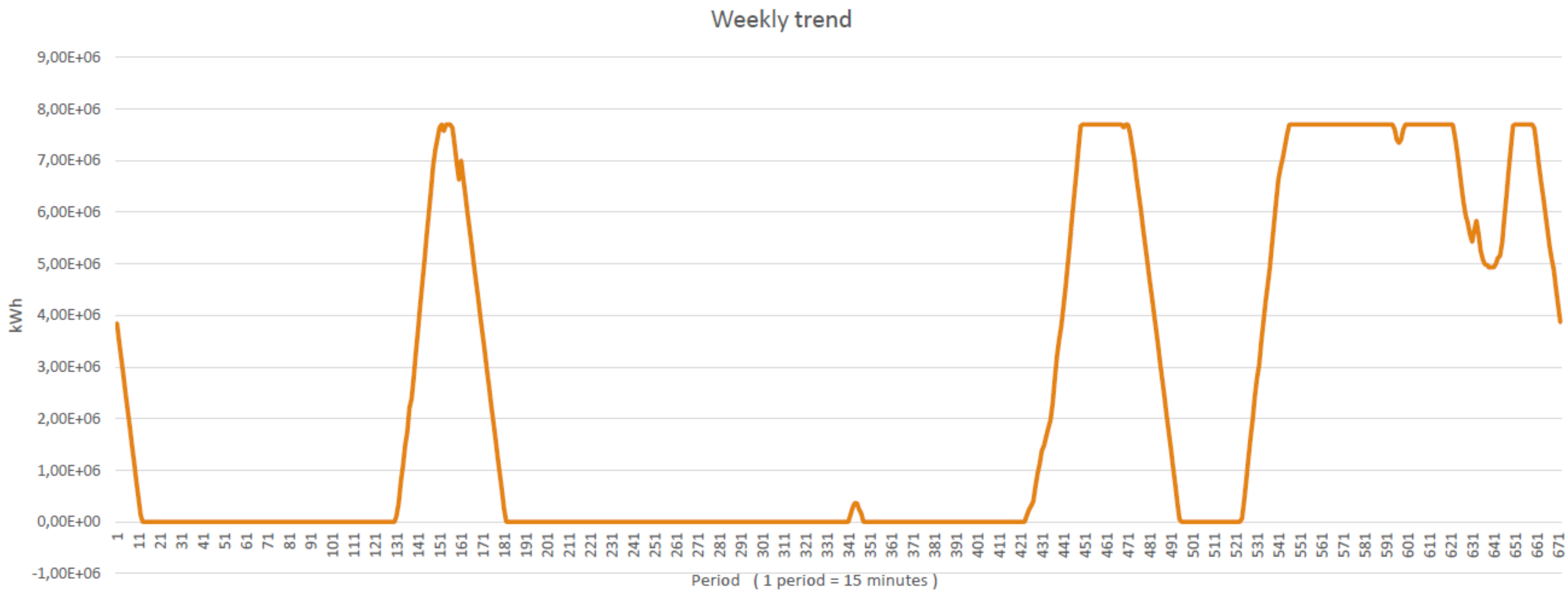
- Example of result: weekly trend for PHS

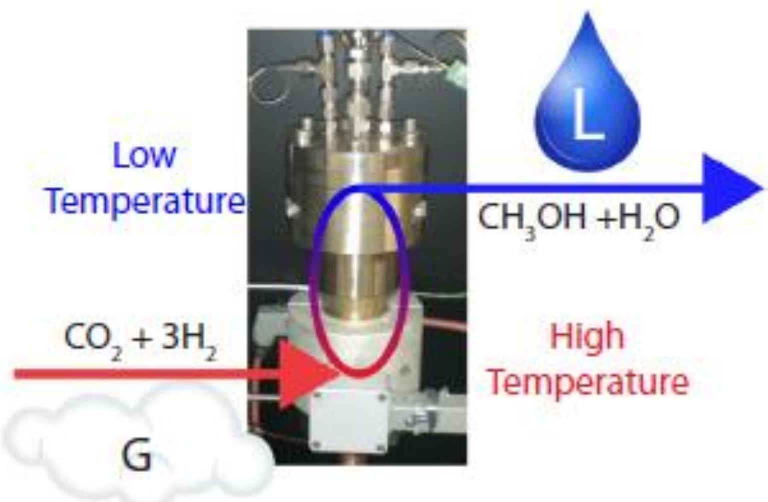


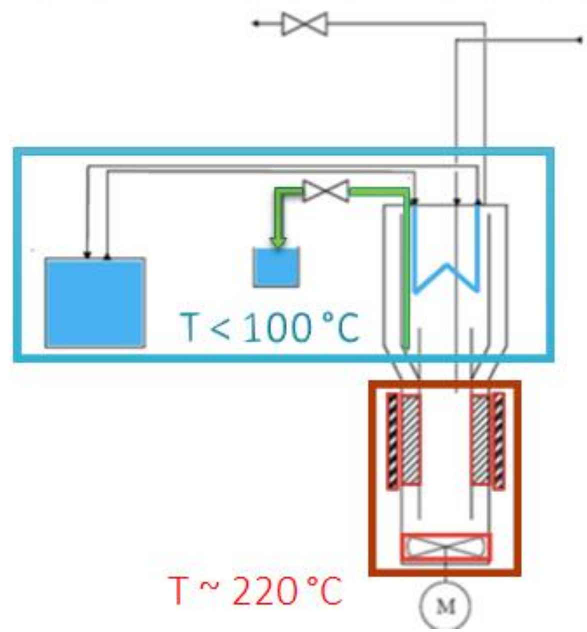
96 periods = 1 day	672 periods = 1 week

Question: how much would you pay for long-term storage?

Research ULiège at process scale

- Novel methanol reactor designs
  - Remove the thermodynamic limitation
  - Displace the equilibrium
  - Conversion reaches 99.9%!

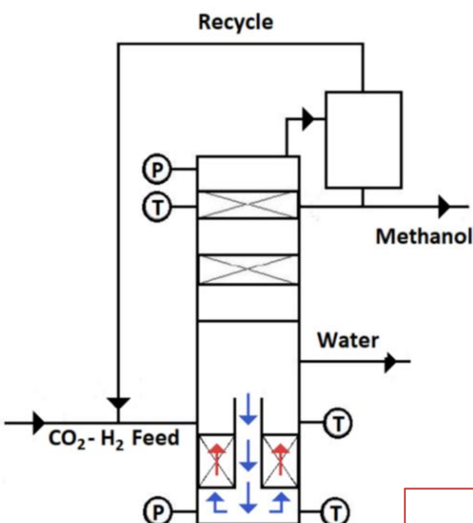


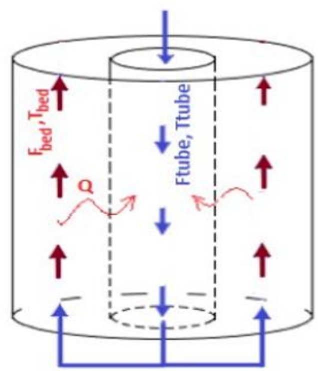


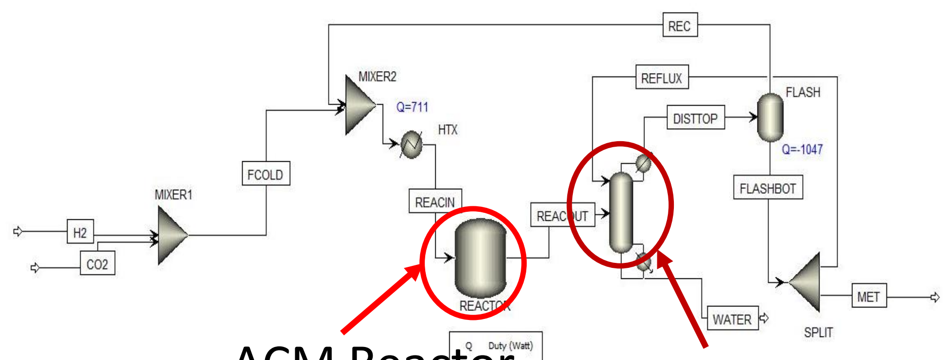
Bos and Brilman, 2014. DOI: 10.1016/j.cej.2014.10.059

Research ULiège at process scale

- Novel methanol reactor design
  - Intensification of synthesis reactor for CO_2 reduction to methanol







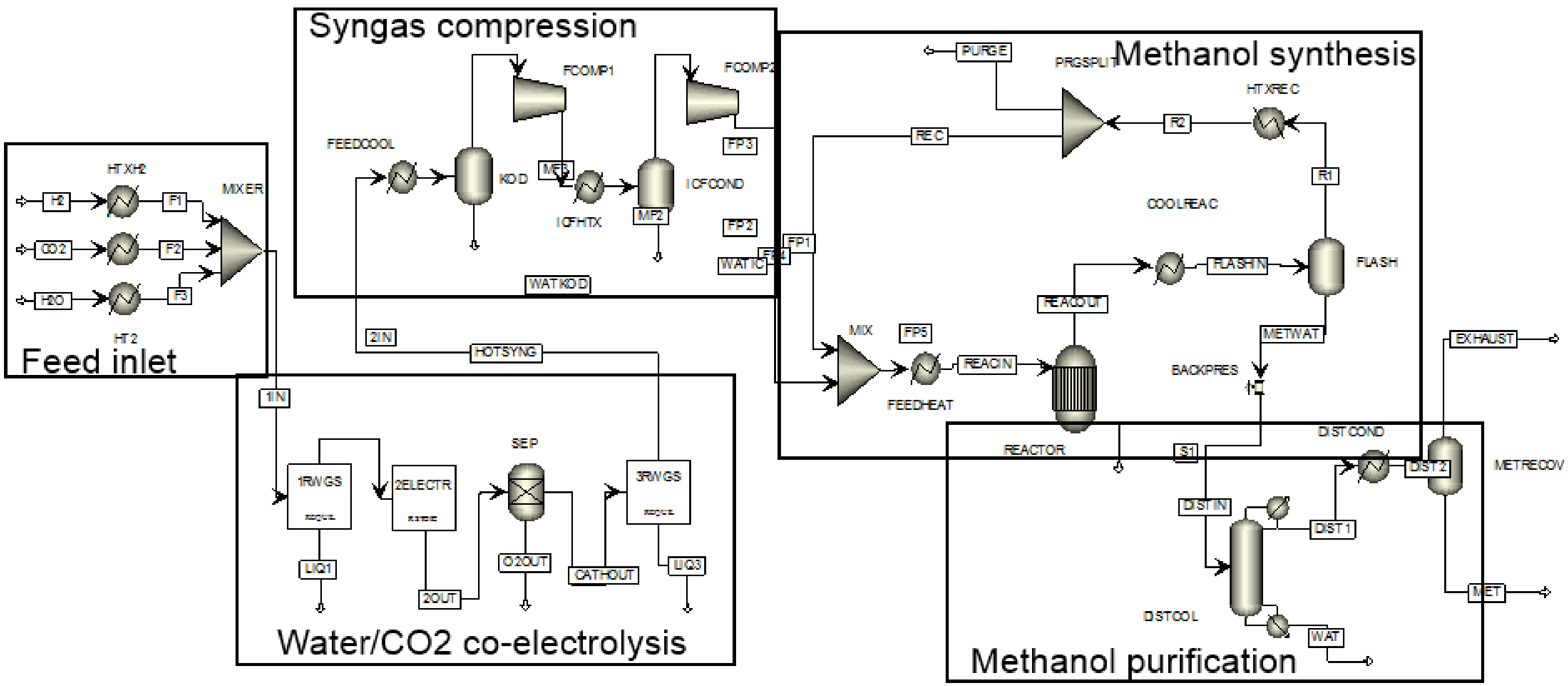
$$r_{MeOH} = \frac{k'_{5a}K'_2K_3K_4K_{H2}p_{CO2}p_{H2}[1-1/K^*(\frac{p_{H2O}p_{CH3OH}}{p^3_{H2}p_{CO2}})]}{(1+K_{H2O}/K_8K_9K_{H2})(\frac{p_{H2O}}{p_{H2}}+\sqrt{K_{H2}p_{H2}}+K_{H2O}p_{H2O})^3}$$

$$r_{RWGS} = \frac{k'_1p_{CO2}[1-K^*_3(\frac{p_{H2O}p_{CO}}{p^3_{H2}p_{CO2}})]}{(1+K_{H2O}/K_8K_9K_{H2})(\frac{p_{H2O}}{p_{H2}}+\sqrt{K_{H2}p_{H2}}+K_{H2O}p_{H2O})^3}$$

Vanden Bussche K.M and Froment G.F, 1996. Journal of catalysis, 161, pp. 1-10.

Research ULiège at process scale

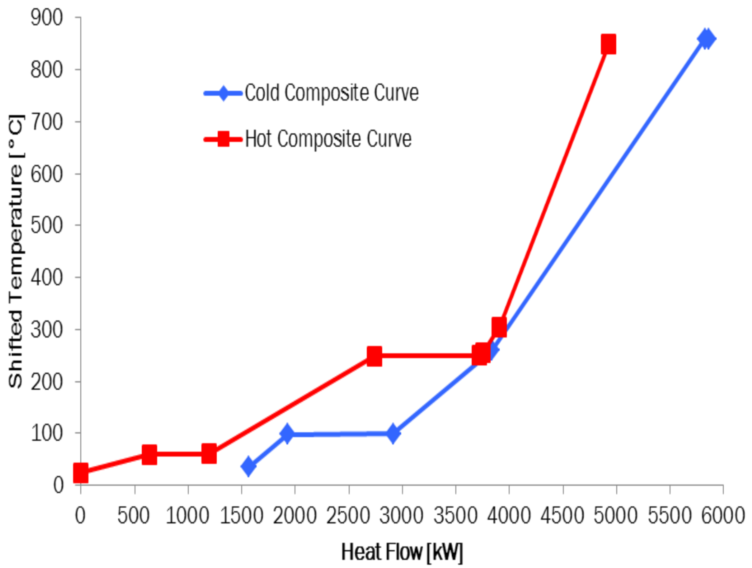
- Process integration
  - Models for electrolysis, CO_2 capure and fuel synthesis

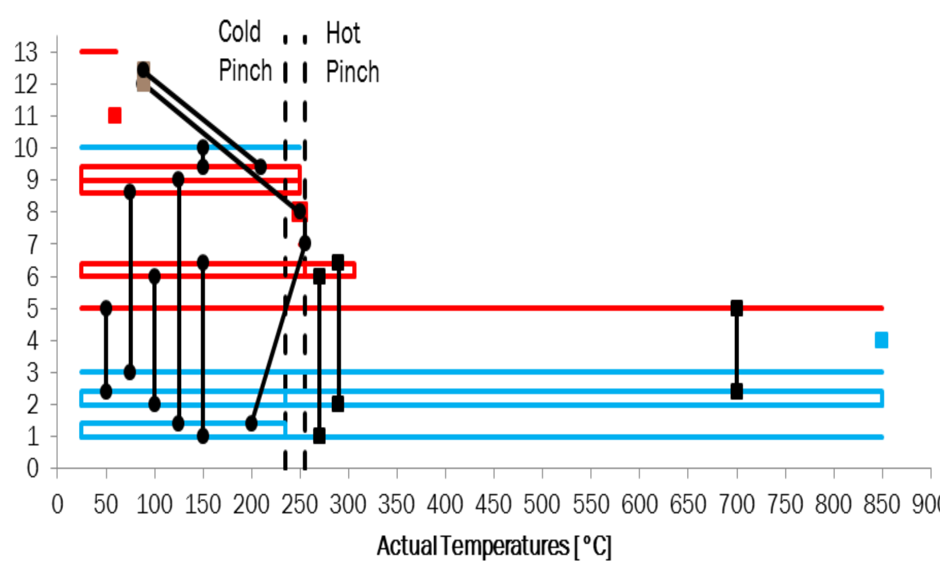


Léonard et al., 2016. Computer aided chemical engineering *38*, 1797.
DOI: 10.1016/B978-0-444-63428-3.50304-0

Research ULiège at process scale

- Heat integration and intensification
  - Heat integration to improve LHV conversion efficiency
  - Design of a heat exchanger network
  - ε increases from 40.1 to 53.0% !





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4. The FRITCO$_2$T Platform at ULiege

www.chemeng.uliege.be/FRITCO2T

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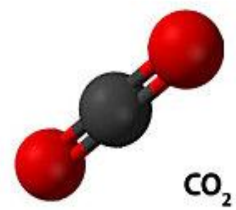
The FRITCO$_2$T Platform

Chemical Transformation

Synthetic Fuels

Monomers & Polymers

Mineralization



Sourcing

Capture & Purification

Physical Use

Pharmaceutics & Cosmetology

Direct CO_2 use (solvent, foaming…)

Transversal WP

Process sustainability (LCA and economics)

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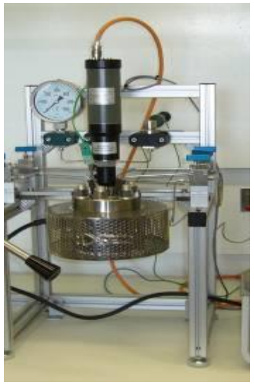
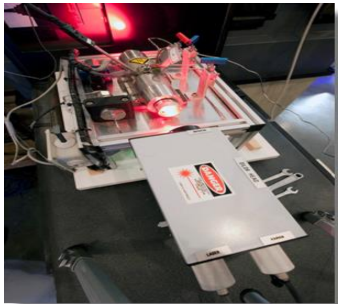
Success stories

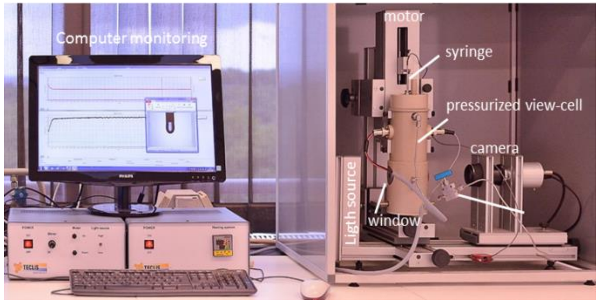
- **More than 45 research projects** in the last 20 years, 10 on-going
- About **12 M€ funding** achieved, > 3 M€ unique equipment available
- > 200 publications, patents, communications…

From lab to pilot scale



High performance analytical tools

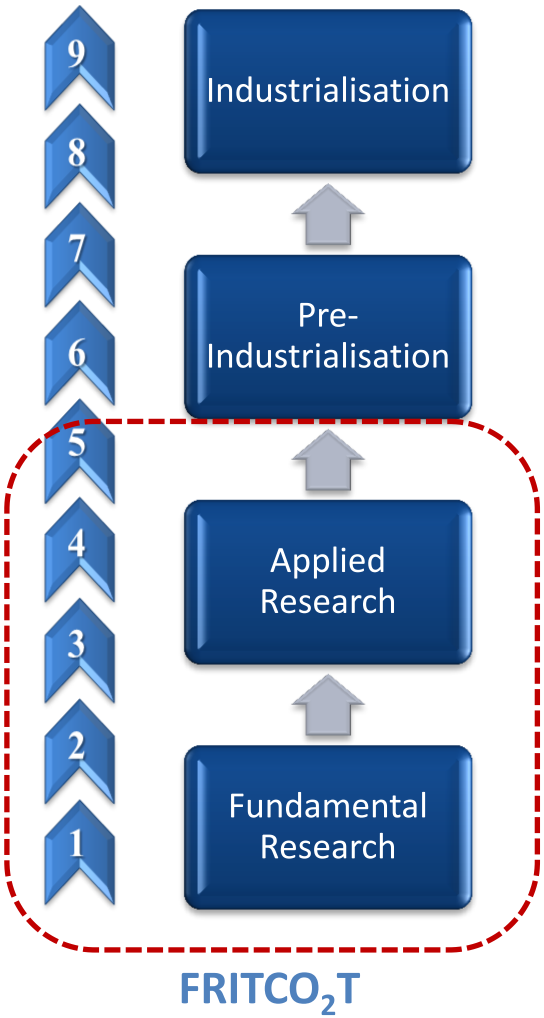




CO_2-assisted processes

Missions of the $FRITCO_2T$ Platform

- Market needs, fundamentals push
  - Many fundamental problems to be tackled
  - **Accelerate climbing of the TRL scale**
- Lead large-scale research projects
  - From Regional to European projects
- Support technological developments
  - Give rationals and scientific backgrounds to new ideas
  - Support for operational issues
  - Holistic view: Circular economy and life cycle thinking



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Many thanks to the team…

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Thank you for your attention!

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