CO_2 activities at the University of Liège

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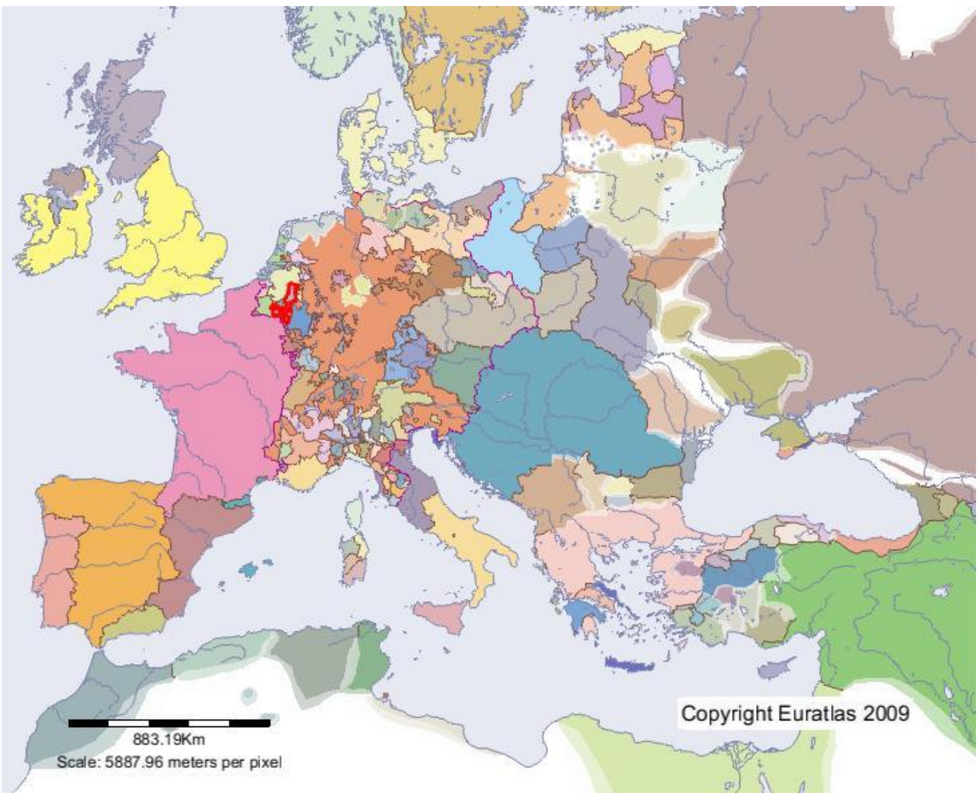
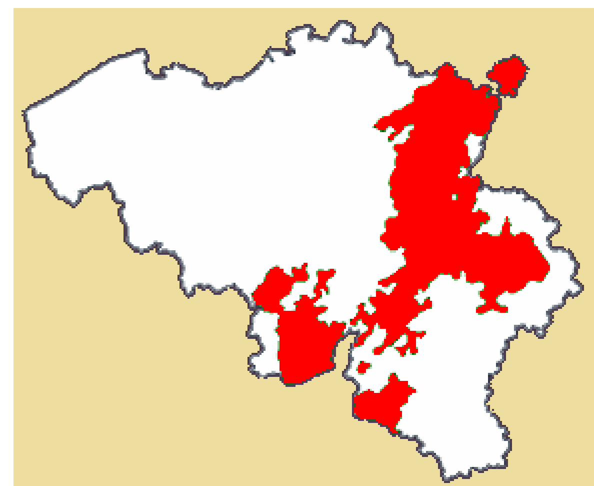
Liège

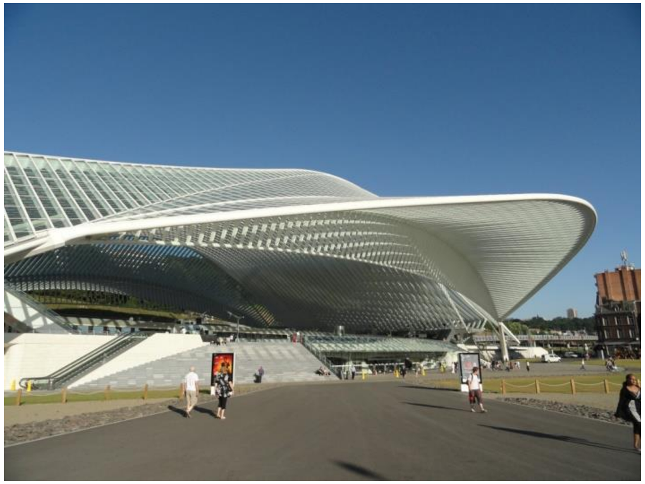
- Former independent Prince-bishopric, in the heart of North-western Europe (980-1789)





Liège

- Now 3rd urban area in Belgium, ~750 000 inh.



University of Liège

- 11 faculties, 20 000+ students, 122 Nationalities
- 38 Bachelor, 194 Master, 68 complementary masters

Philosophy & Letters

Applied Sciences

Law and Criminology school

Veterinary Medecine

Sciences

Psychology and Education

Medecine

gembloux agro bio tech

HEC ULg Management School - University of Liege

Architecture

Human and Social Sciences

Faculty of Applied Sciences

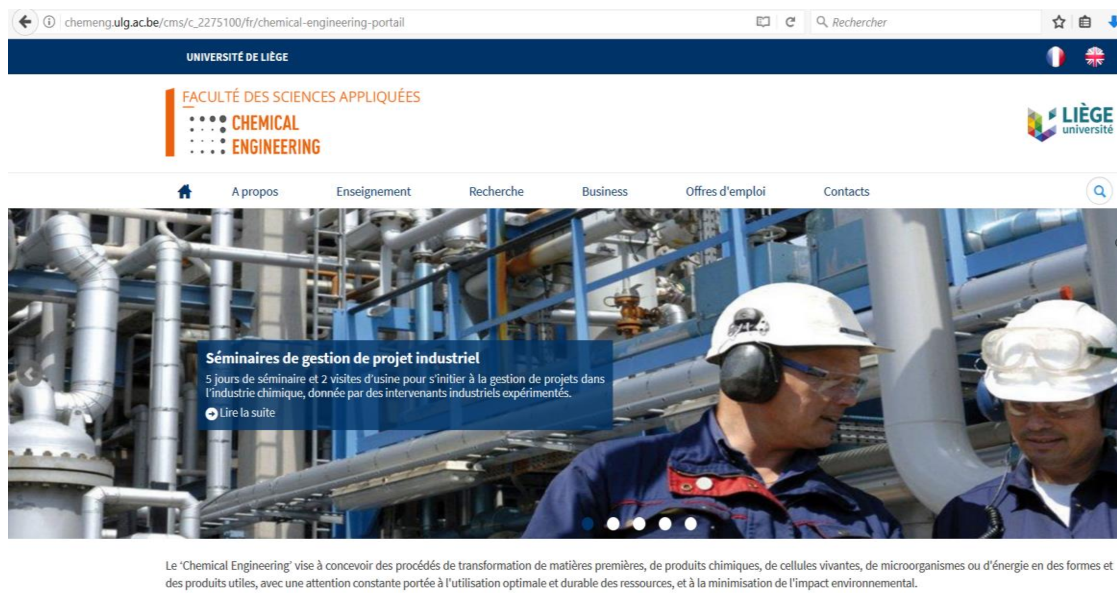
- 4 research units
  - Aerospace and Mechanical Engineering
  - ArGEnCO = Architectural, Geological, Environmental and Civil Engineering
  - Electrical Engineering and Computer Science
  - Chemical Engineering

Chemical Engineering

3 groups, about 60 persons

- CRYO - Cryotechnology
- NCE - Nanomaterials, Catalysis, Electrochemistry
- PEPs – Products, Environment, Processes

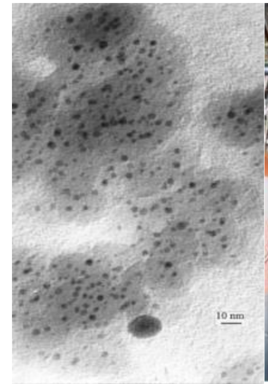
http://chemeng.ulg.ac.be

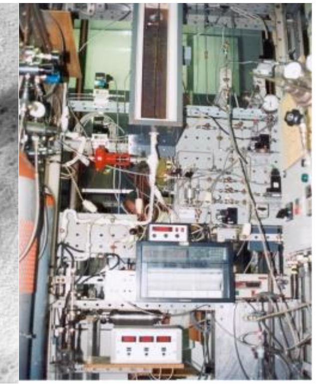


Chemical Engineering

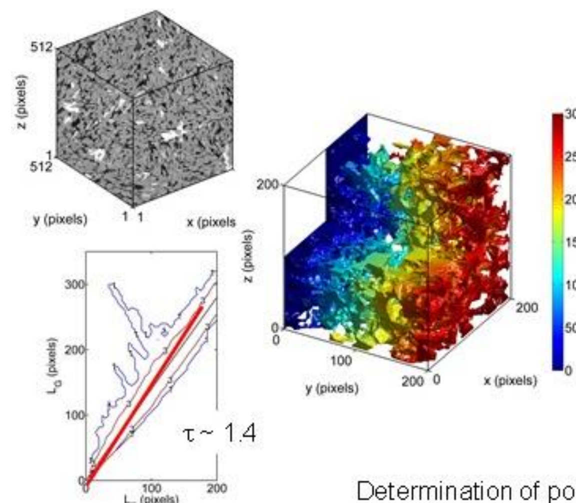
Cryotechnology – Ariane rocket

Catalytic processes



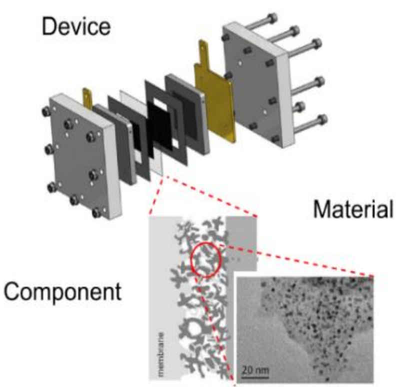


Porous materials modeling



Determination of pore tortuosity

Batteries – fuel cells



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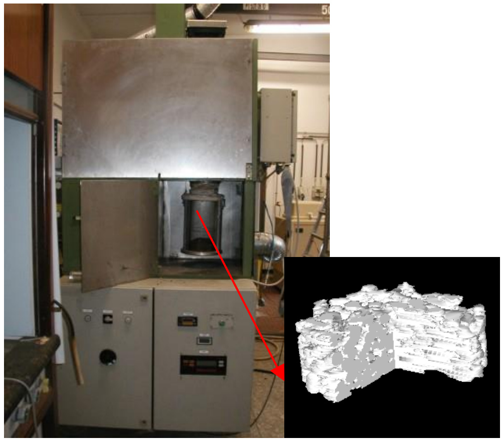
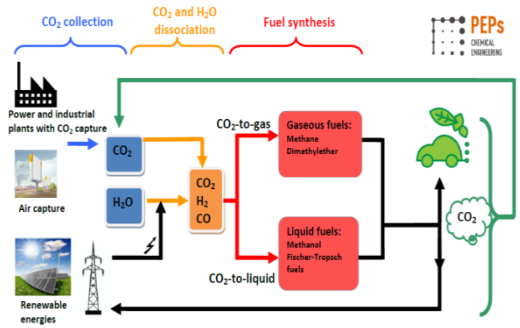
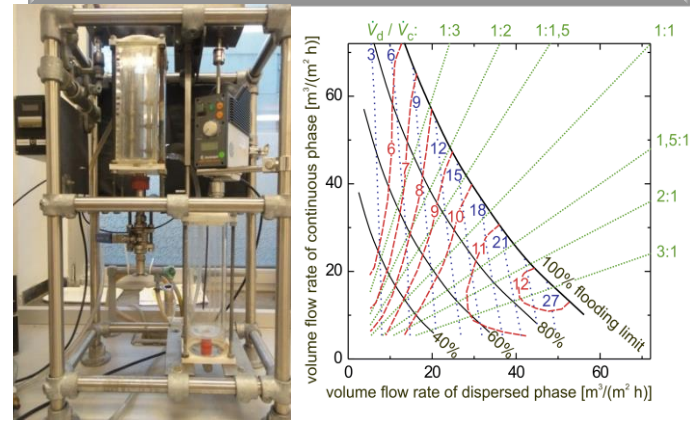
Solid waste and flue gas treatment



CO_2 capture and reuse

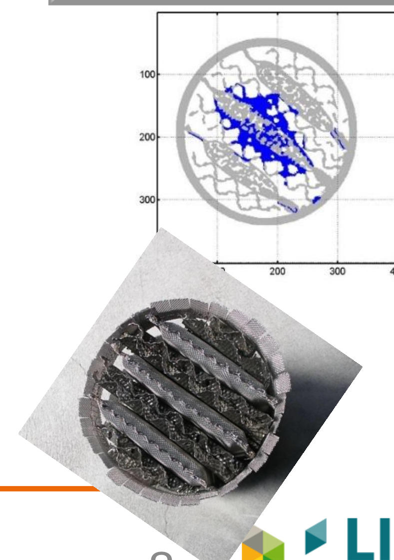


Solvent and reactive extraction

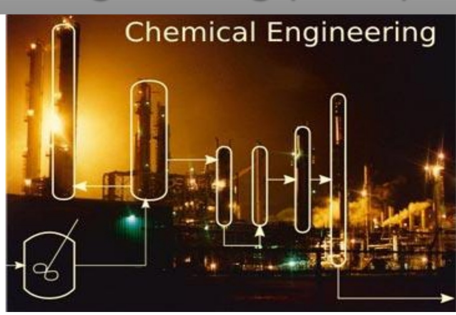


Life Cycle Assessment

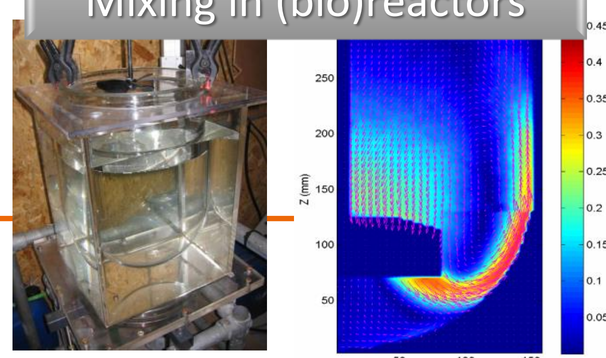
Hydrodynamics in multiphase systems



Computer-Aided Process Engineering (CAPE)



Mixing in (bio)reactors



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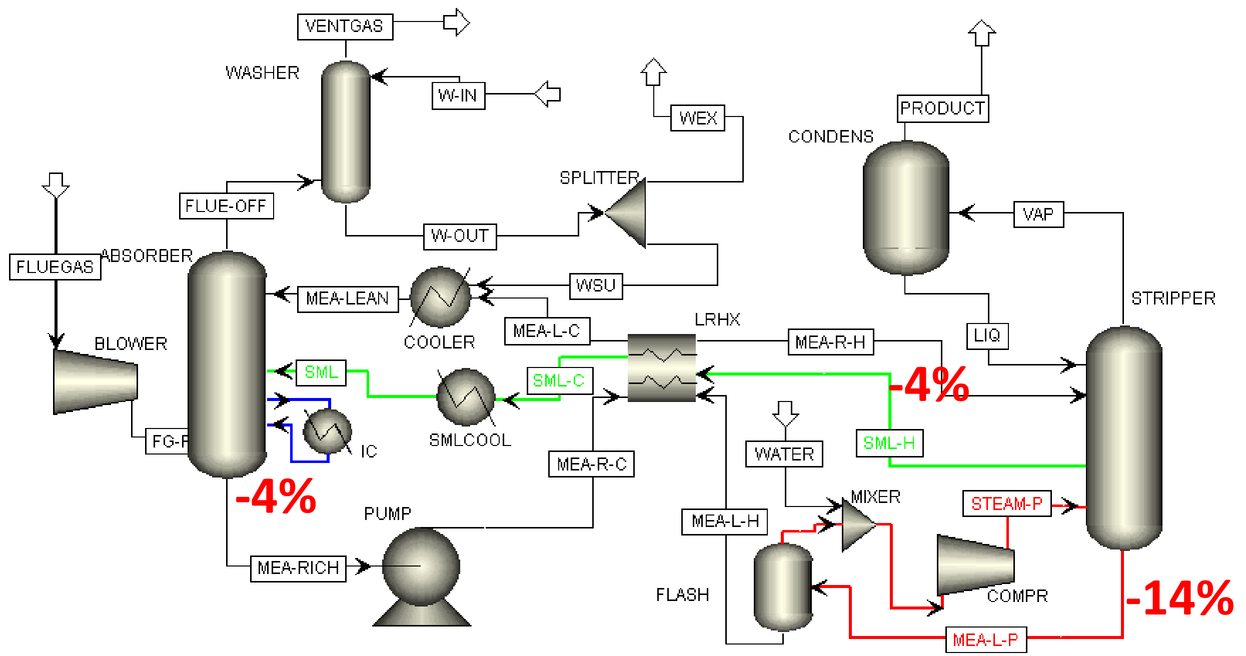
Activities in the field of CO_2

- Post-combustion CO_2 capture
- CO_2 re-use for energy storage
- Other process and CO_2 related topics
- CO_2 research platform at ULiège

Post-combustion CO_2 capture

Most studies on CO_2 capture with amines: energy penalty

=> New solvents, process integration…



However, simulation does not consider all important parameters!

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Léonard and Heyen, 2011. *Computer Aided Chemical Engineering 29,* 1768-1772

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Post-combustion CO_2 capture

Focus set on solvent degradation

- Process operating costs:

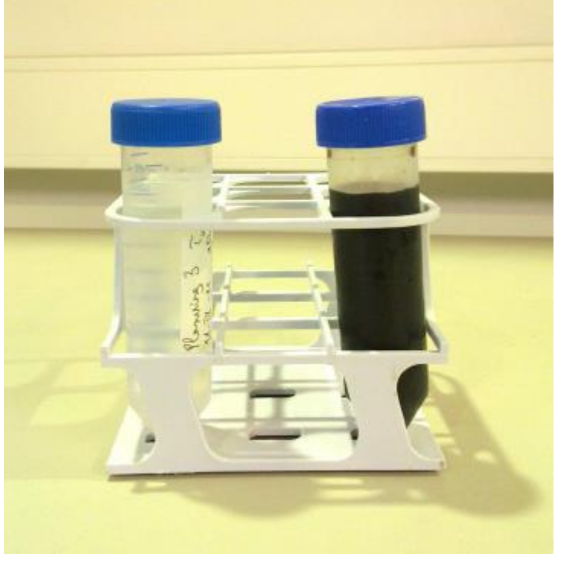
  - Solvent replacement: up to 22% of the CO_2 capture OPEX[1]!
  - Removal and disposal of toxic degradation products

- Process performance:

  - Decrease of the solvent loading capacity
  - Increase of viscosity, foaming, fouling…

- Capital costs
  - Corrosion

- Environmental balance
  - Emission of volatile degradation products!



[1] Abu Zahra M., 2009. Carbon dioxide capture from flue gas, PhD Thesis, TU Delft, The Netherlands.

Post-combustion CO_2 capture

PCCC research at ULiège focusses on the interaction between process operation and solvent degradation

=> Process model assessing both energy consumption and solvent degradation

Two steps:

- ***Experimental study*** of solvent degradation
- ***Process modeling*** with assessment of solvent degradation

Methodology based on 30 wt% MEA (Monoethanolamine)

Post-combustion CO_2 capture

Acceleration of solvent degradation to mimic industrial degradation

Pressure ?

Temperature ?

Flue gas composition ?

Mass transfer?

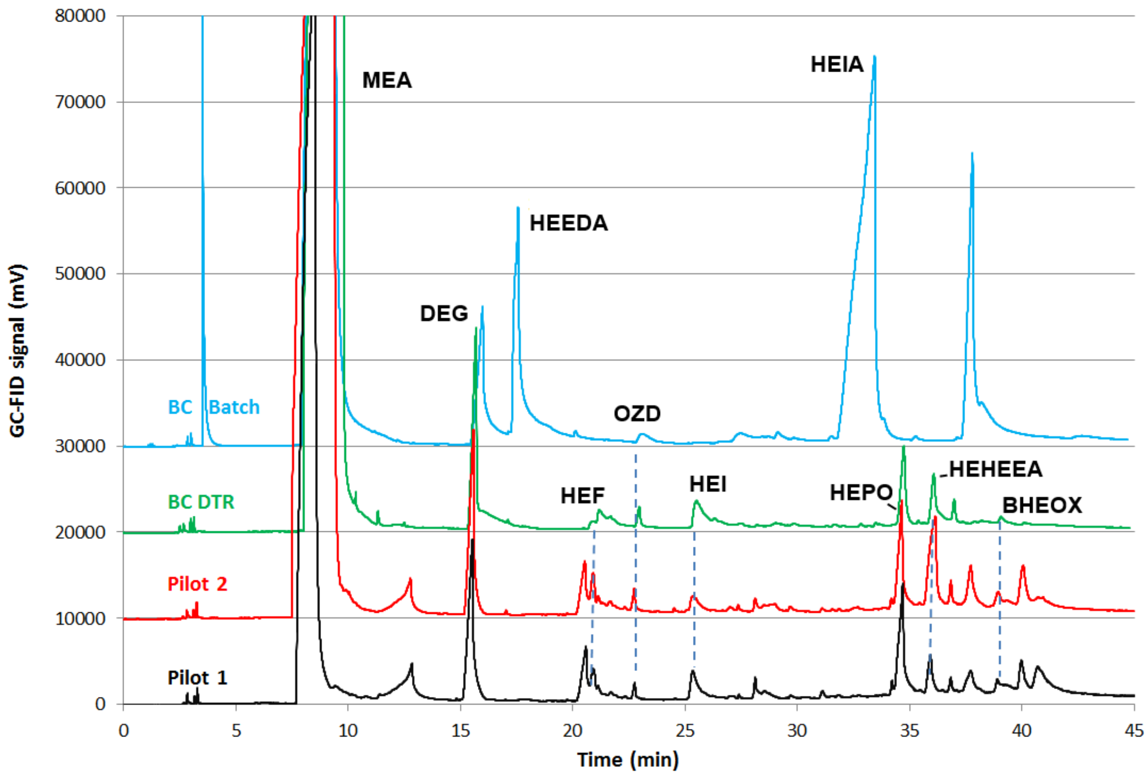
Metal ions ?

Inhibitors ?

Léonard et al., 2014. International Journal of Greenhouse Gas Control 30, 171.
DOI: 10.1016/j.ijggc.2014.09.014

Post-combustion CO_2 capture

=> 21% degradation after 7 days vs. 4% loss in 45 days (Pilot vs. lab)



=> Similar degradation products (GC spectra)!

=> Identification and quantification of influence parameters

=> Kinetic model for degradation reactions

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Léonard et al., 2014. Canadian Journal of Chemical Engineering 93 (2), 348.
DOI 10.1002/cjce.22094

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Post-combustion CO_2 capture

Comparison of the laboratory degradation with degradation in industrial pilot plants

	Unit	Industrial conditions	Lab conditions
Degradation rate	wt-%/day	0.026	0.9
k_La	s^{-1}	$0.01 < k_La < 0.04$[1]	$k_La \sim 0.003$
P_{O2}	Pa	~ 6,000	~ 25,000
T	°C	40-60	120

=> Temperature and pressure are the main parameters that have been used for the accelerated degradation experiments

=> Alternative to degradation acceleration by high agitation!

[1] Typical k_La in Mellapak structured packing depending on packing geometry and hydrodynamics: De Brito M., 1991. PhD thesis n° 984, EPFL.

Post-combustion CO_2 capture

Leads to a kinetic model of solvent degradation:

=> 2 main degradation mechanisms

=> Equations balanced based on the observed proportion of degradation products

Oxidative degradation

$$\begin{array}{c} MEA + 1{,}3\ O_2 \\ \downarrow \\ 0{,}6\ NH_3 + 0{,}1\ HEI + 0{,}1\ HEPO + 0{,}1\ HCOOH + 0{,}8\ CO_2 + 1{,}5\ H_2O \end{array}$$

Thermal degradation with CO_2

$$MEA + 0{,}5\ CO_2 \rightarrow 0{,}5\ HEIA + H_2O$$

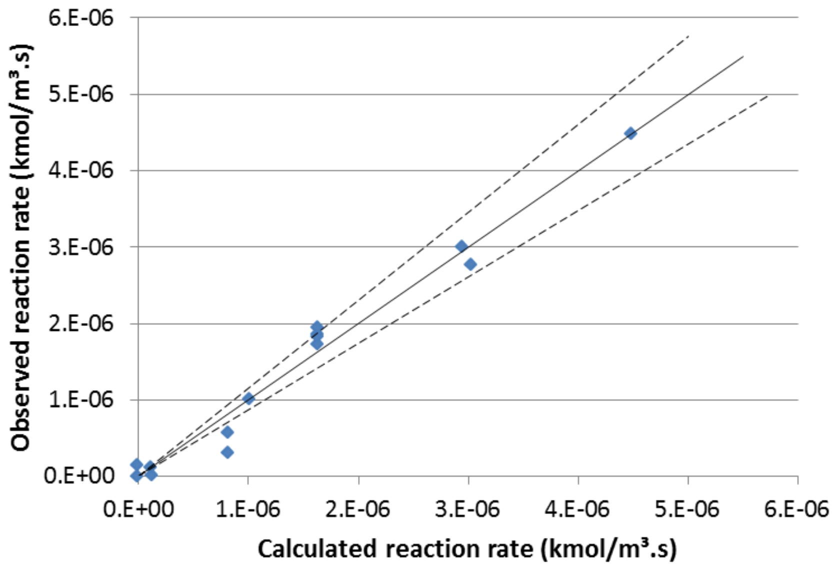
Léonard et al., 2014. DOI 10.1016/j.ijggc.2014.09.014

Post-combustion CO_2 capture

Arrhenius kinetics (kmol/m³.s):

Parameters are identified by minimizing the difference between calculated and observed degradation rates.

- Oxidative degradation: $r = 5.35\ 10^5 . e^{-\frac{41\,730}{8.314\,T}} . [O_2]^{1.46}$
- Thermal degradation with CO_2: $r = 6.27 . 10^{11} . e^{-\frac{143\,106}{8.314\,T}} . [CO_2]^{0.9}$



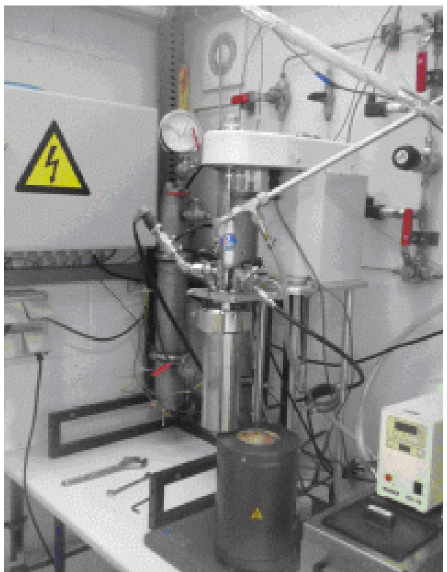
Léonard et al., 2014. DOI 10.1016/j.ijggc.2014.09.014

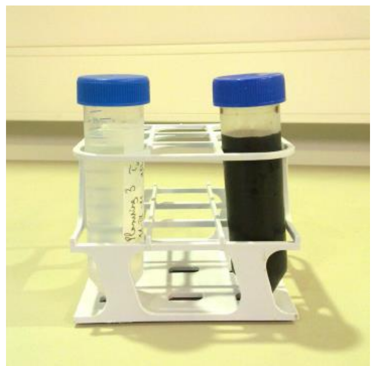
Post-combustion CO_2 capture

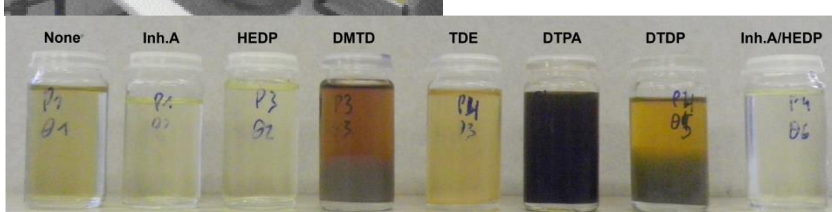
Degradation model has been included into a global process model built in Aspen Plus

⇒ Steady-state simulation, closed solvent loop

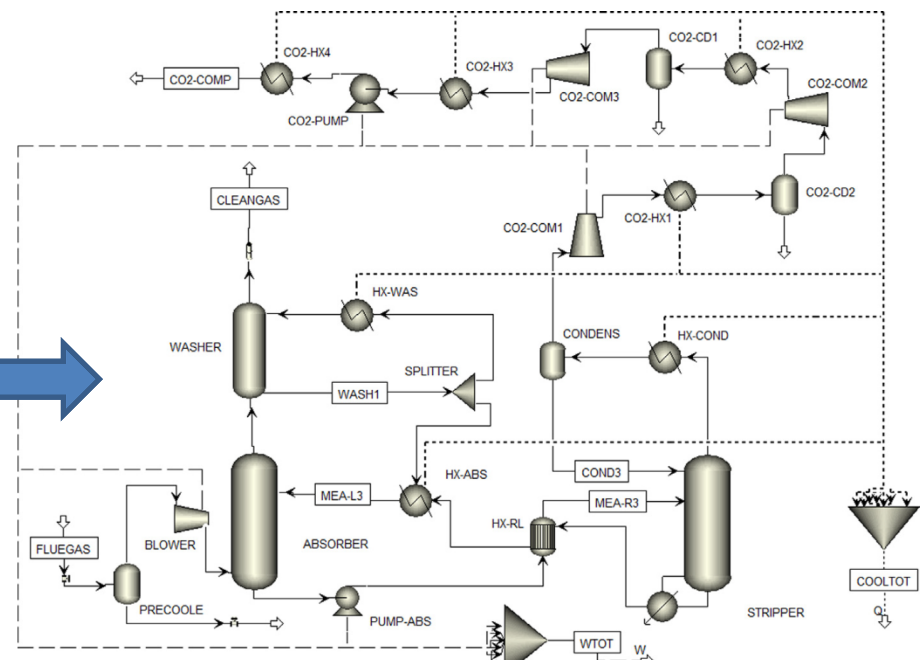
⇒ Additional equations in the column rate-based models







DOI:10.1021/ie5036572



DOI: 10.1016/j.compchemeng.2015.05.003

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Post-combustion CO_2 capture

Base case degradation:

Parameter	Unit	Absorber	Stripper	Total
MEA degradation	kg/ton CO_2	8.1e-2	1.4e-5	8.1e-2
NH_3 formation	kg/ton CO_2	1.4e-2	8.4e-7	1.4e-2
HEIA formation	kg/ton CO_2	1.1e-5	1.1e-5	2.2e-5
MEA emission	kg/ton CO_2	8.7e-4	9.4e-9	8.7e-4
NH_3 emission	kg/ton CO_2	9.5e-3	3.0e-3	1.3e-2
HCOOH emission	kg/ton CO_2	1.1e-4	1.4e-5	1.2e-4

=> Degradation mainly takes place in the absorber:

=> 81 g MEA/ton CO_2

Post-combustion CO_2 capture

Base case degradation:

Parameter	Unit	Absorber	Stripper	Total
MEA degradation	kg/ton CO_2	8.1e-2	1.4e-5	8.1e-2
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HEIA formation	kg/ton CO_2	1.1e-5	1.1e-5	2.2e-5
MEA emission	kg/ton CO_2	8.7e-4	9.4e-9	8.7e-4
NH_3 emission	kg/ton CO_2	9.5e-3	3.0e-3	1.3e-2
HCOOH emission	kg/ton CO_2	1.1e-4	1.4e-5	1.2e-4

$\Rightarrow$ Oxidative degradation is more important than thermal degradation

$\Rightarrow$ Ammonia is the main emitted degradation product after washing, coming from both absorber and stripper

Post-combustion CO_2 capture

Comparison with industrial CO_2 capture plants:

81 g MEA/ton CO_2 < 284 g MEA/ton CO_2[1]

=> Degradation under-estimated (but still 324 kg MEA/day at large-scale ~ 4000 tCO_2/day)!

=> Maybe due to simplifying assumptions:

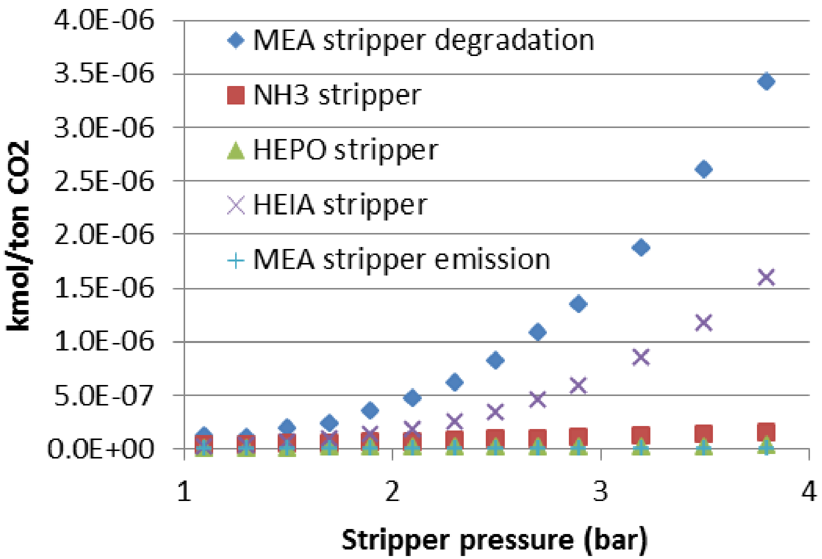
- Modeling assumptions for the degradation kinetics
- Presence of SO_x et NO_x neglected
- Influence of metal ions neglected

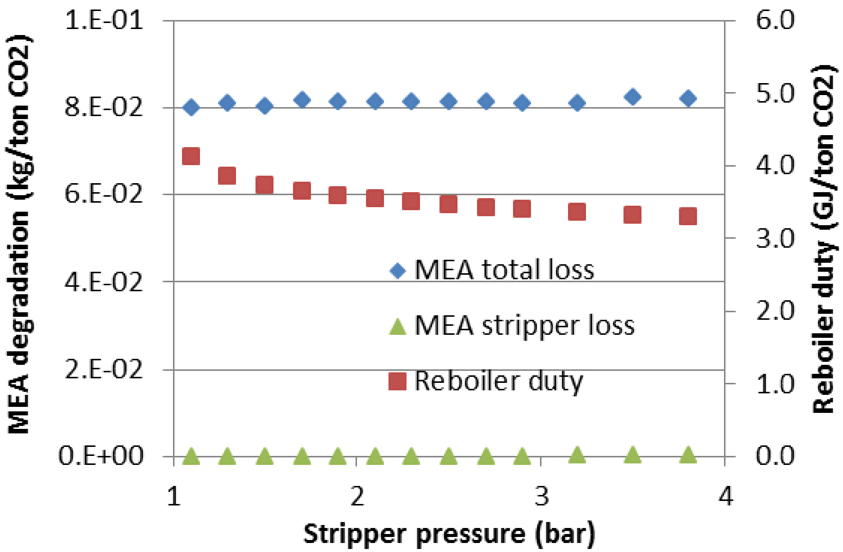
[1] Moser P., Schmidt S. and Stahl K., 2011. Energy Procedia 4, 473-479.

Post-combustion CO_2 capture

Influence of process variables on solvent degradation:

⇒ Regeneration pressure



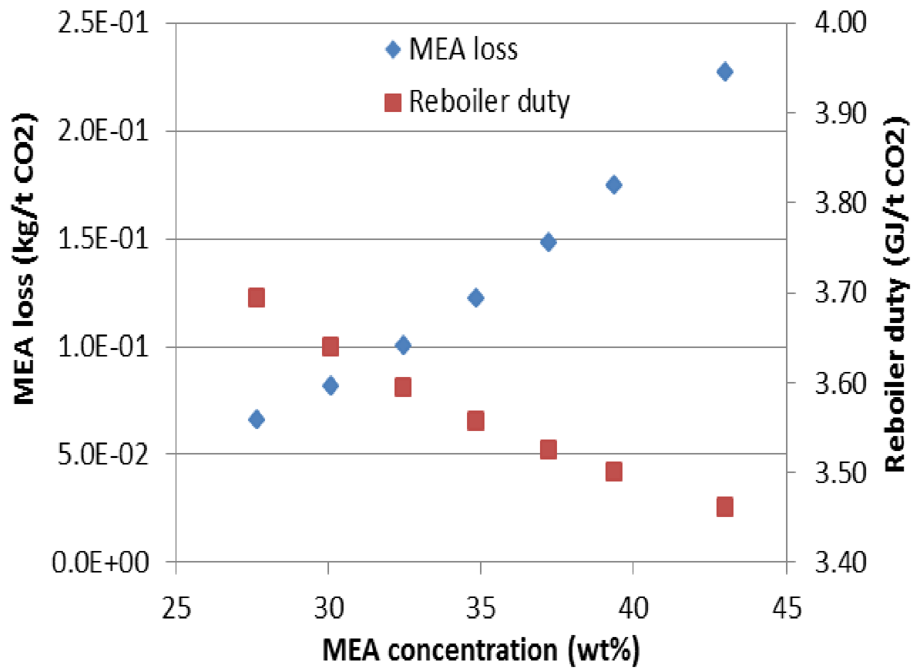


Exponential increase of the thermal degradation, but still much lower than oxidative degradation

Post-combustion CO_2 capture

Influence of process variables on solvent degradation:

⇒ MEA concentration



Influence of MEA concentration on the O_2 mass transfer!

Post-combustion CO_2 capture

In conclusion:

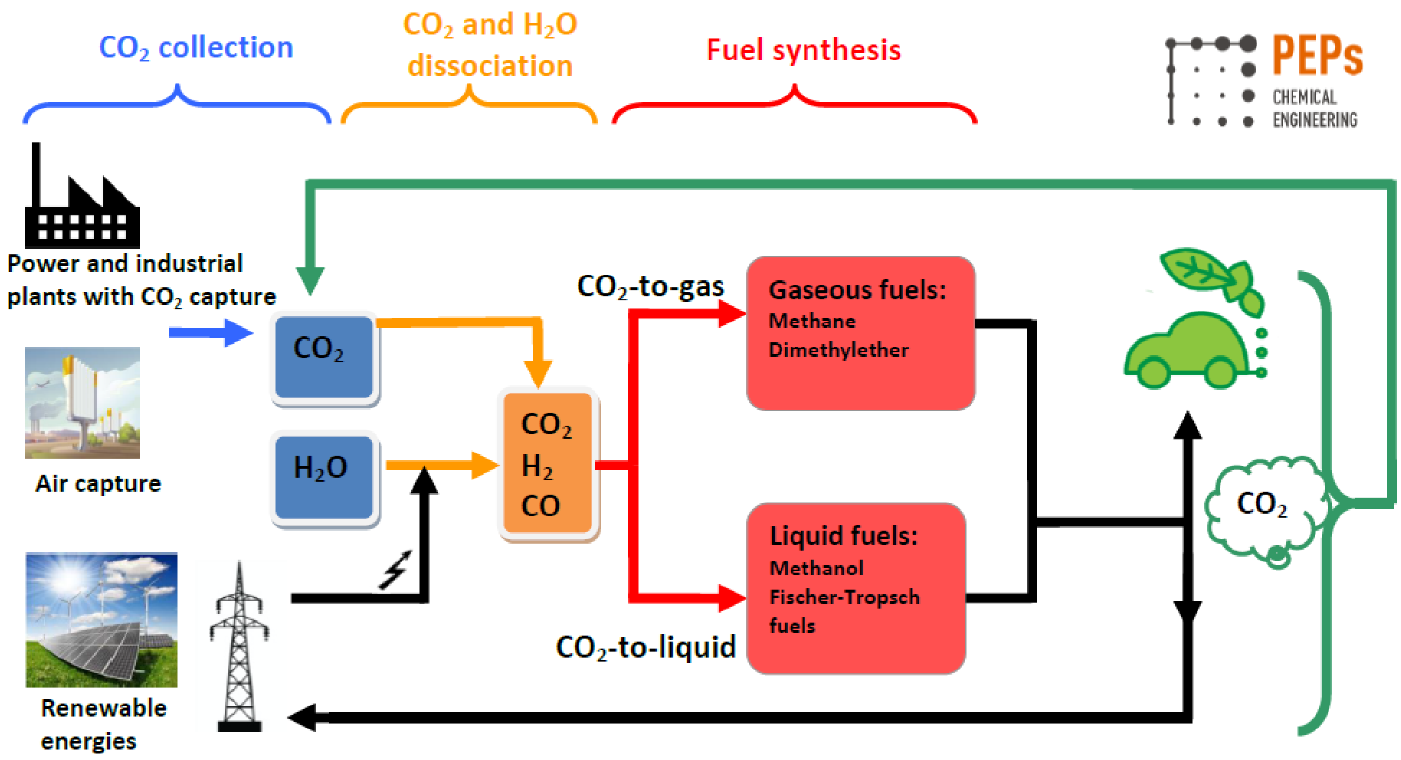
- Solvent degradation is experimentally studied under accelerated conditions
- Methodology is validated with degraded samples from pilot plants
- A kinetic model is proposed for solvent degradation
- Degradation is included into a global process model

=> Two of the main CO_2 capture drawbacks, environmental and energy, are considered within a unique process model!

=> This kind of model should support the design of large-scale CO_2 capture plants.

CO_2 re-use

- Power-to-fuel
  - Long-term energy storage
  - => addresses time imbalance generation – consumption



CO_2 re-use

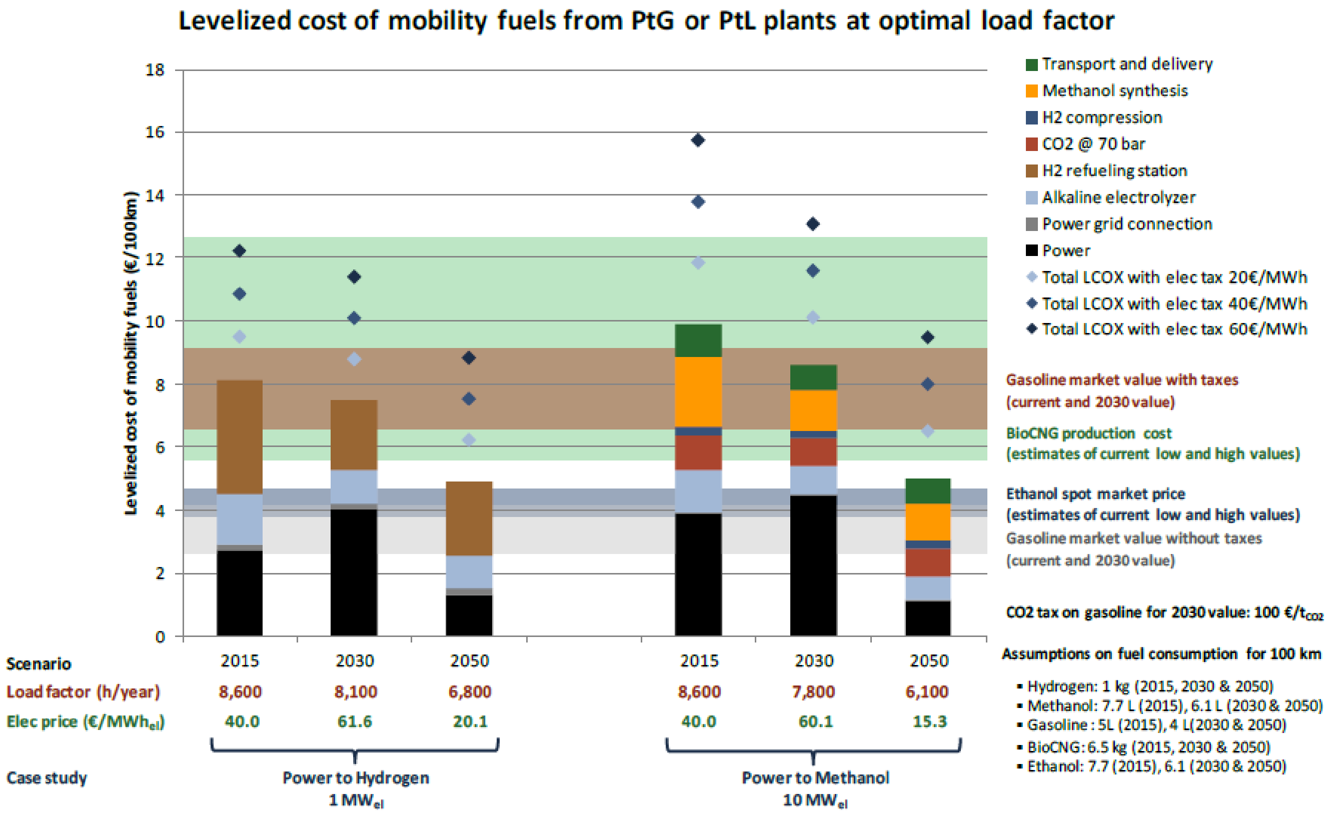
- Why liquid fuels?
  - High energy density at ambient conditions
    - 22.4 MJ/kg (methanol) vs. < 1 MJ/kg (batteries, PHS)
    - 17.8 MJ/L vs. 0.01 – 0.03 MJ/L (H_2, CH_4)
  - CO_2 neutral if air capture and renewable energies
  - Flexibility of use
    - Back to electricity
    - Transportation fuel (can contribute to displace fossil fuels in mobile applications)

=> Cheap long-term energy storage

=> Easy transportation

CO_2 re-use

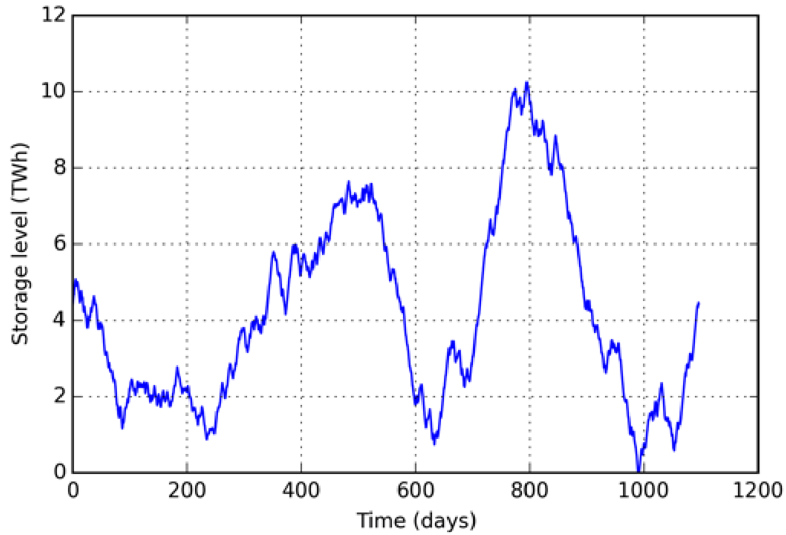
- Technology challenges
  - Round-trip efficiency ~ 50%
  - Capital cost is critical (Electrolyser, methanol synthesis)
  - Dynamic operation, Domestic applications?



Source: Enea report, 2016

CO_2 re-use

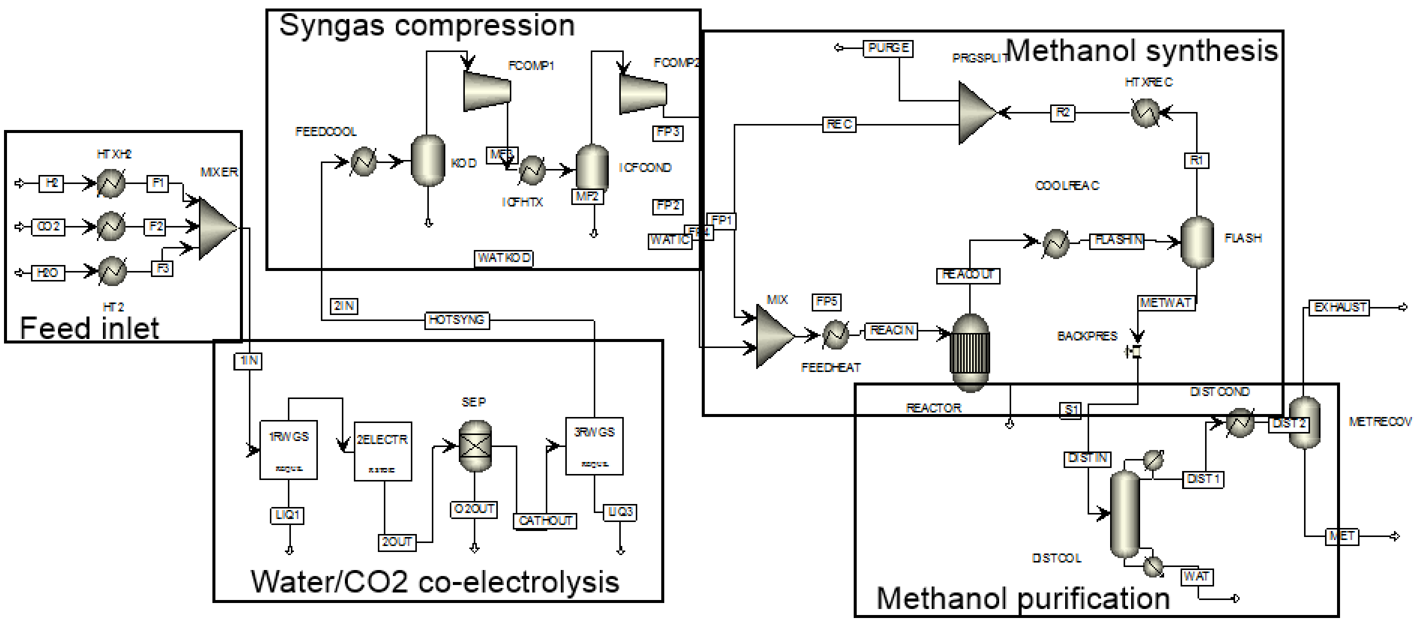
- Energy system & cost analysis
  - Study of an electricity zone powered with 100% variable renewables and storage units
    - Second and minute scale for frequency regulation
    - Inter-seasonal scale: power-to-gas, power-to-fuel
    - Reasonable electricity cost (83.4 €/MWh)



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

CO_2 re-use

- Process integration and intensification
  - Low thermodynamic efficiency (50% conversion efficiency, LHV, Sunfire)
  - Modelling and experimental work (in progress)



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

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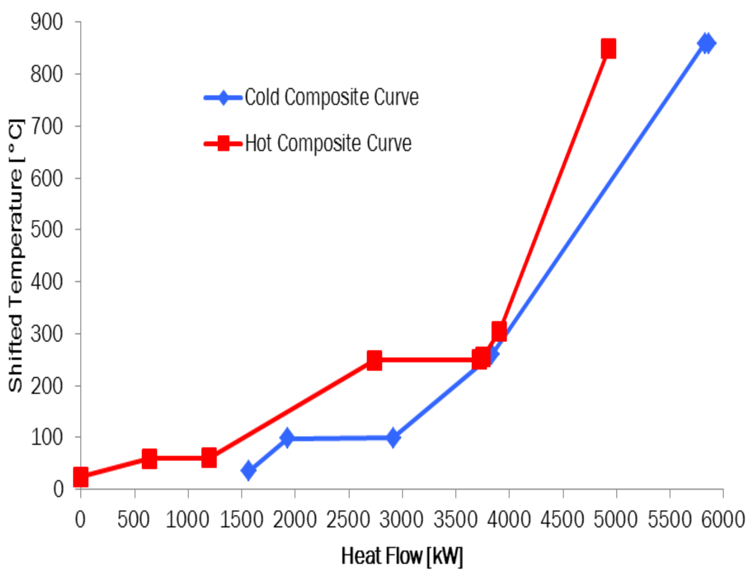
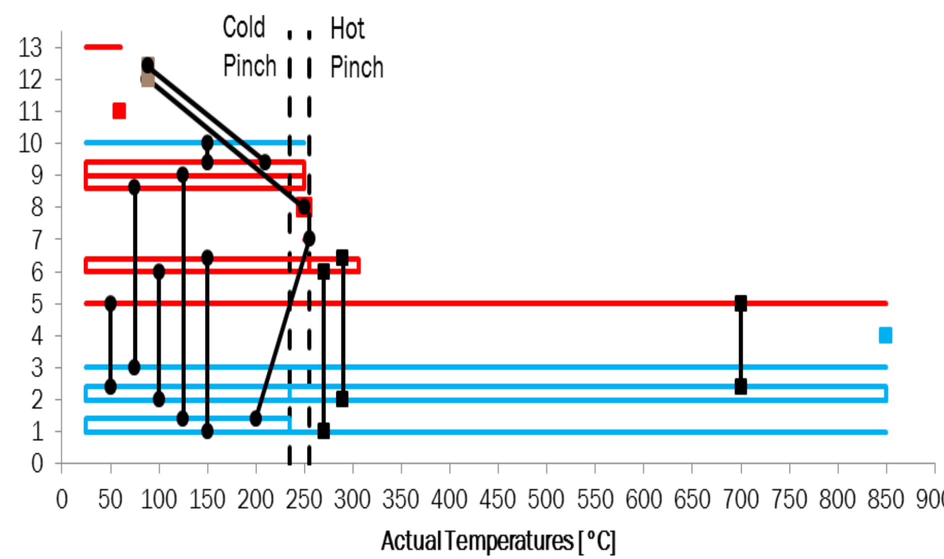
CO_2 re-use

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

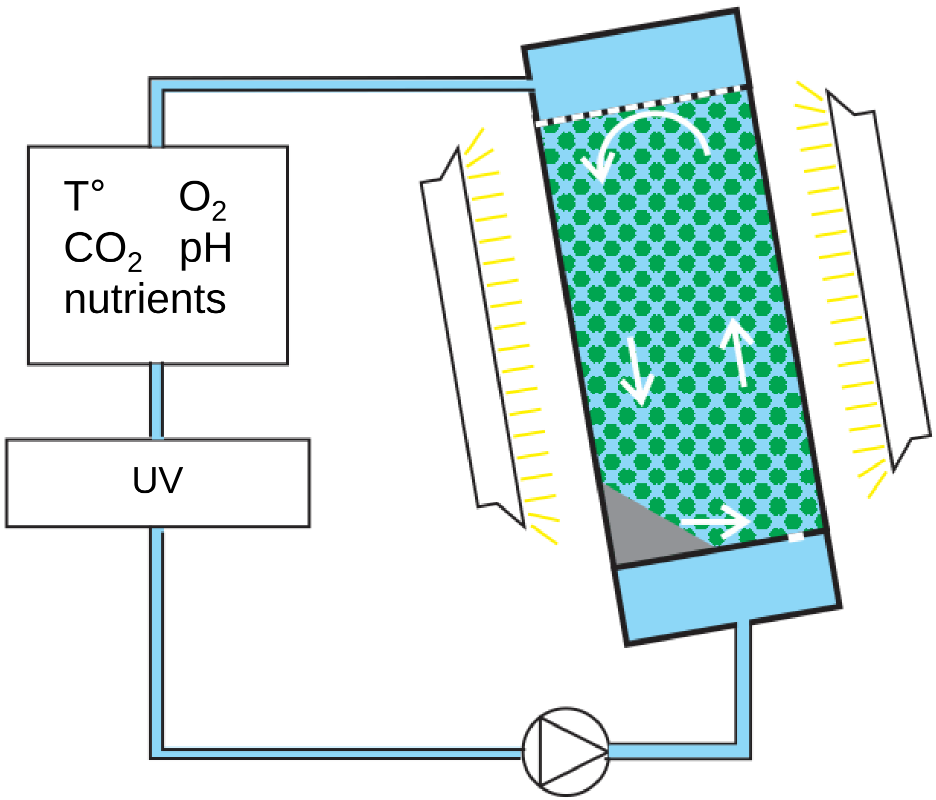




Léonard et al., 2016. Computer aided chemical engineering *38*, 1797.
DOI: 10.1016/B978-0-444-63428-3.50304-0

Other process and CO_2 research

- Photobioreactor designed to cultivate microalgae encapsulated in an hybrid matrix (beads)



Photobioreactor **modelling** and **scale up** based on a **coupled characterisation** of :

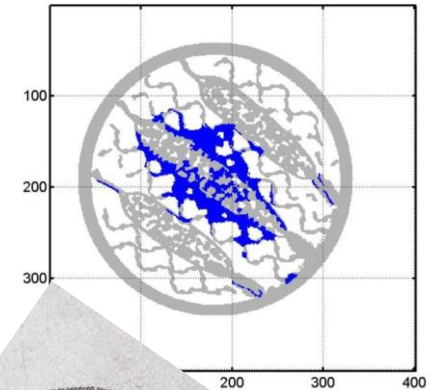
- Liquid and solid phase hydrodynamics;
- Light distribution;
- Biological activity

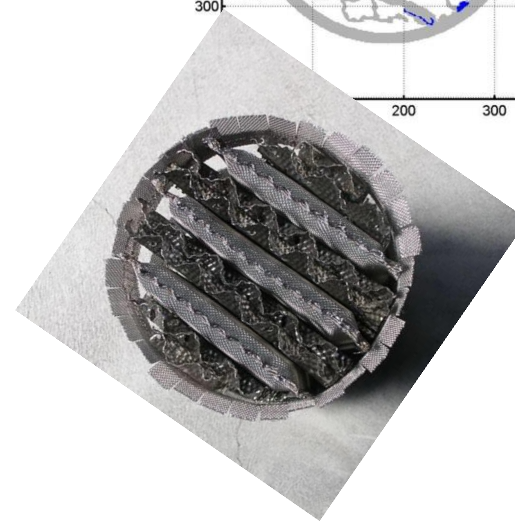
Other process and CO_2 research

- Use and development of non invasive techniques to characterize phases distribution in multiphase systems and to visualize flows

✓ Packed columns (from 0.1 to 0.6 m diameter)

- X-ray tomography (420 kV)





✓ Bubble columns

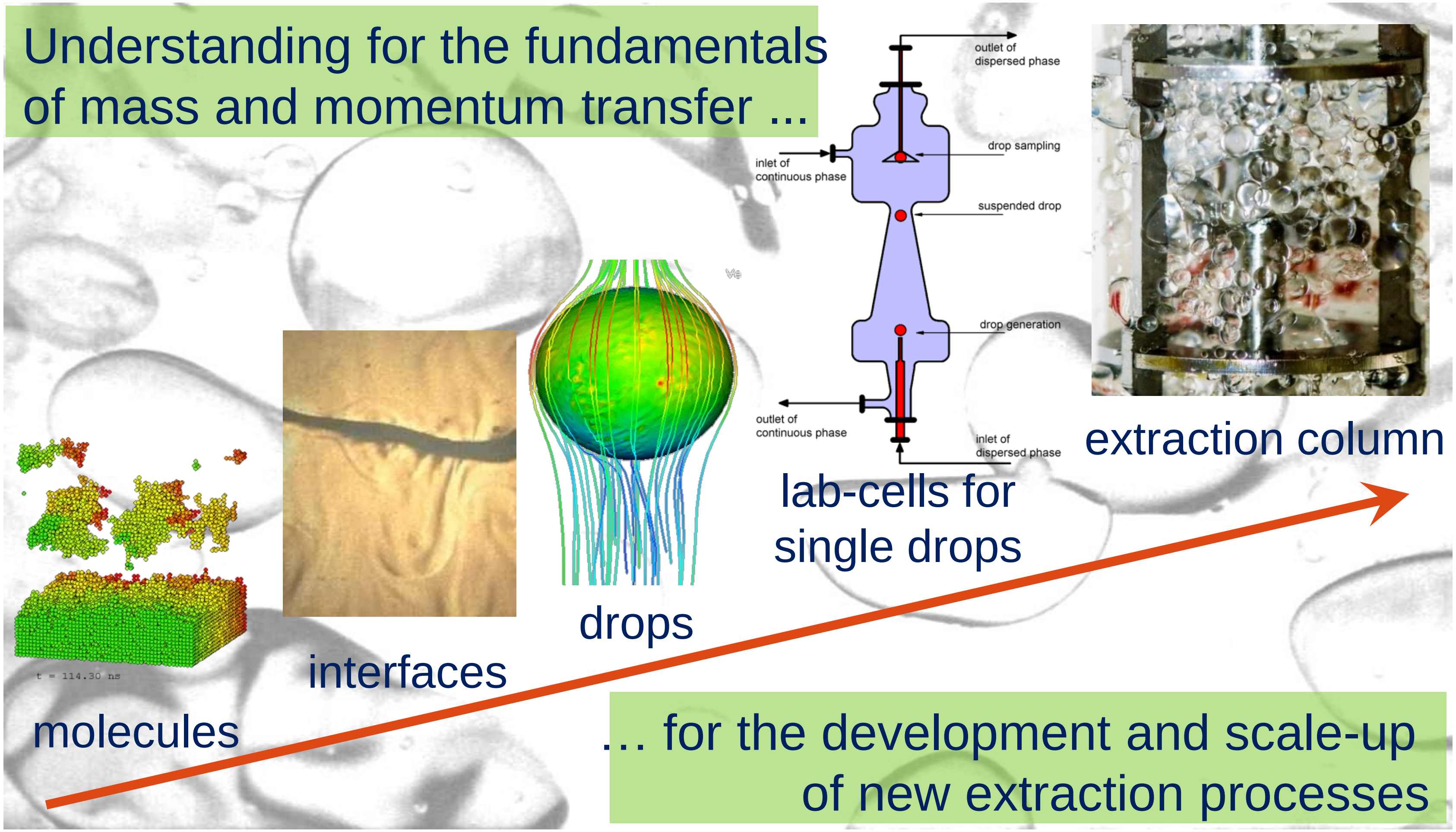
- Particle Image Velocimetry (biphasic)
- Parietal probes
- Optical probes

Other process and CO_2 research

- Large scale, high energy X-ray tomography setup
- Cold mock-ups of packed columns (Ø : 0.1 – 0.4 m) (h : 2 – 4 m)
- Examples of application
  - Absorption columns
  - Adsorption beds (active carbon)
  - Distillation and reactive distillation packings
  - Fixed bed bioreactors

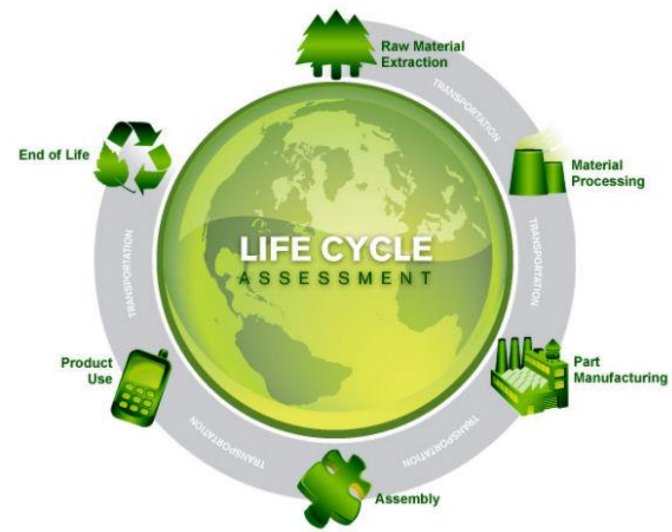
Other process and CO_2 research

- Solvent & reactive extraction: on all scales



Other process and CO_2 research

- Life Cycle Assessment, environmental reporting
  - Evaluation of the environmental impact of processes
  - Development of databases
  - Academic research + external studies
  - Participation to several regional and European projects
  - Training programs



- References
  - Knauf Insulation, Prayon, Intradel, Total Petrochemicals, Materia Nova, Pierre et marbres de Wallonie, Aseptic Technologies …

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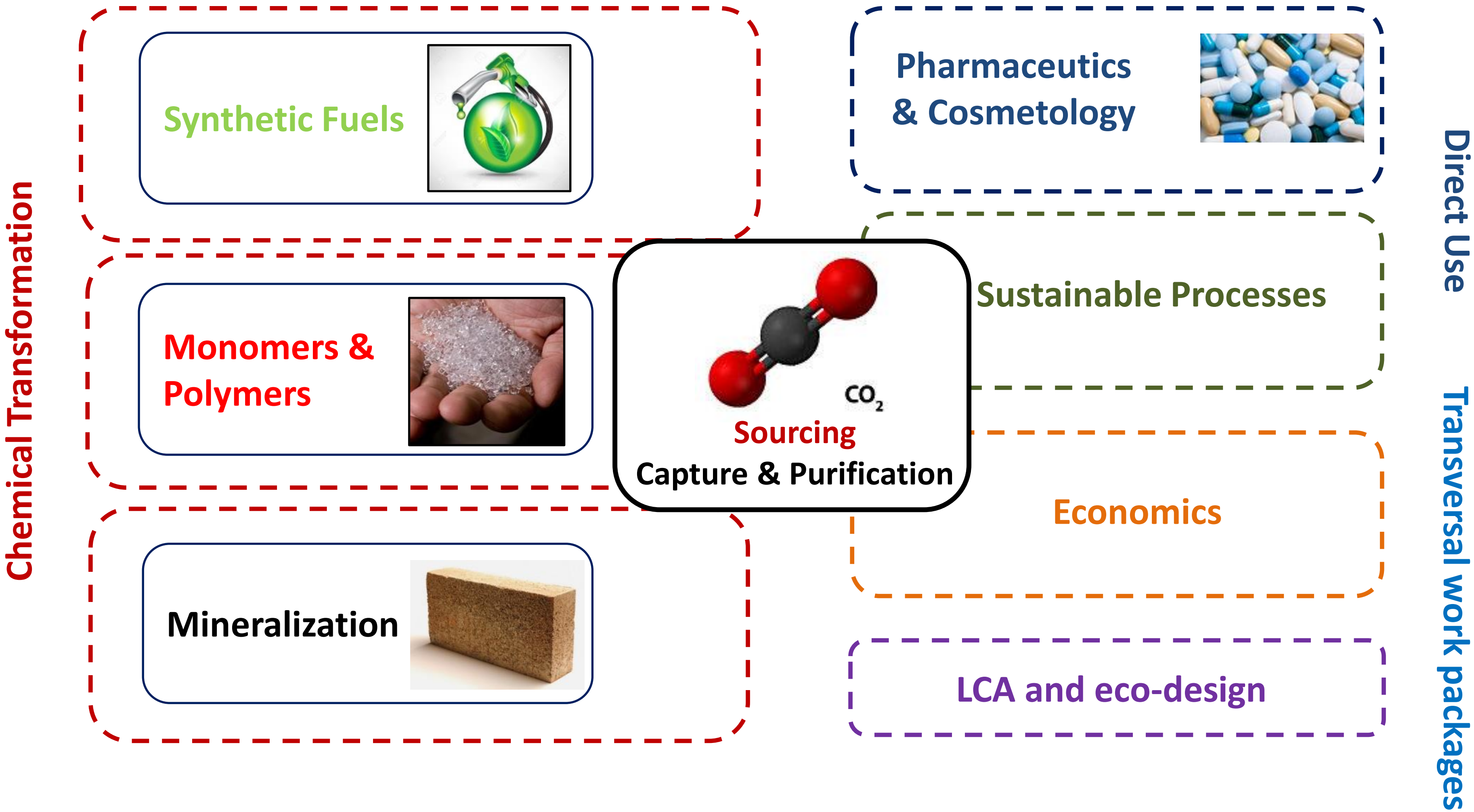
Other process and CO_2 research

- Process modelling
  - Steady-state and dynamic models
  - Process integration
  - Biomass, wastes and sludge valorization
  - Better use of raw materials: (Urban) mining processes, reverse metallurgy …
  - Techno-economic assessment

CO_2 research platform at ULiège



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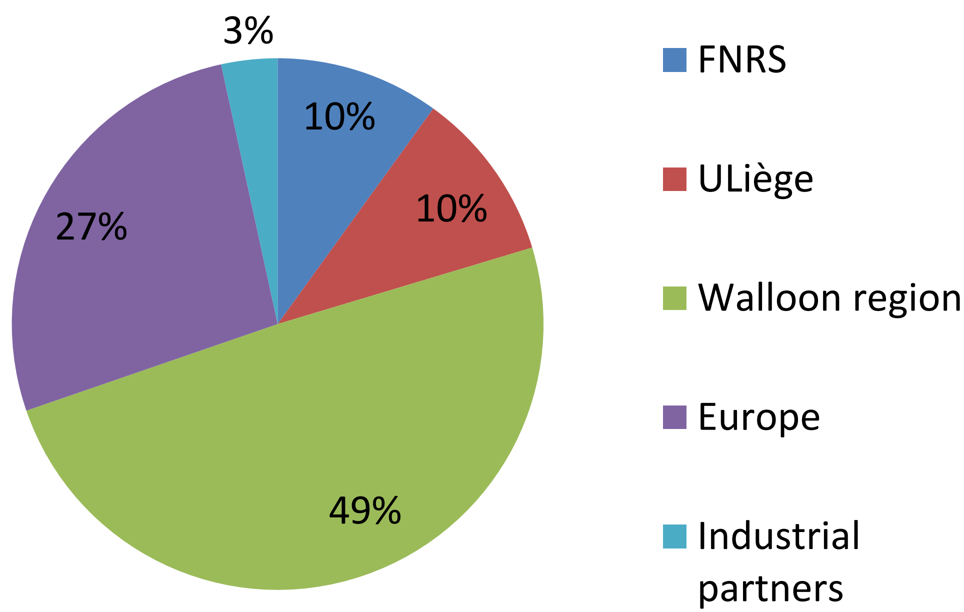
CO_2 research platform at ULiège

- More than 40 research projects in the last 20 years
  - Almost 12 M€ funding achieved
  - More than 10 projects currently on-going
    - + many projects submitted and waiting for decision



Funding organisms

CO_2 research platform at ULiège

- Equipment and know-how available on-site at ULiège
  - 83 people implied throughout the years
  - Among them, almost 30 PhD
  - 27 people still active in the field
- About 200 publications
- Support received from many industrial partners

Welcome to Liège!

http://kleesbutterfly.com/2015/03/22/where-the-heck-is-liege/

https://vimeo.com/95988841

Thank you for your attention!

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