CO2 FUTURE at the University of Liège

Prof. Grégoire LEONARD

PEPs CHEMICAL ENGINEERING

Universitas Leodiensis

LIÈGE université

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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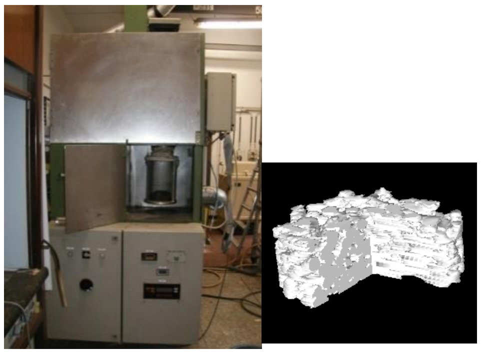
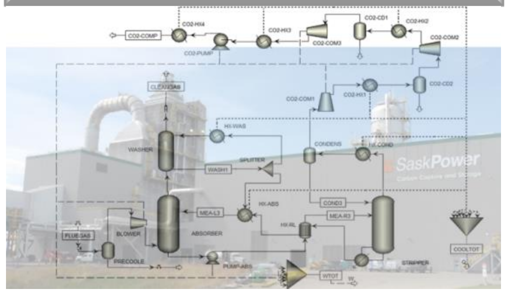
PEPs - Products, Environment and processes

Solid waste and flue gas treatment



CO_2 capture and reuse



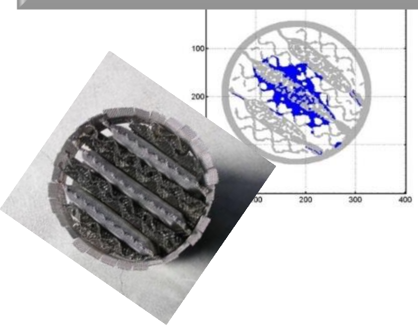
Life Cycle Assessment

Department of Chemical Engineering

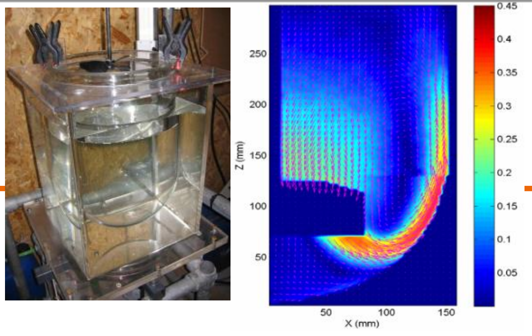
http://chemeng.ulg.ac.be

Solvent and reactive extraction

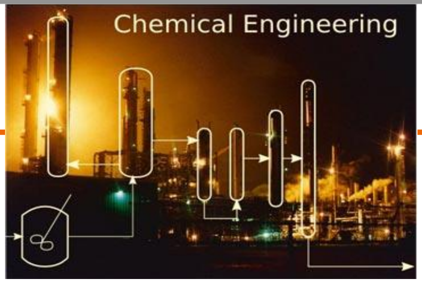
Hydrodynamics in multiphase systems



Mixing in (bio)reactors



Computer-Aided Process Engineering (CAPE)



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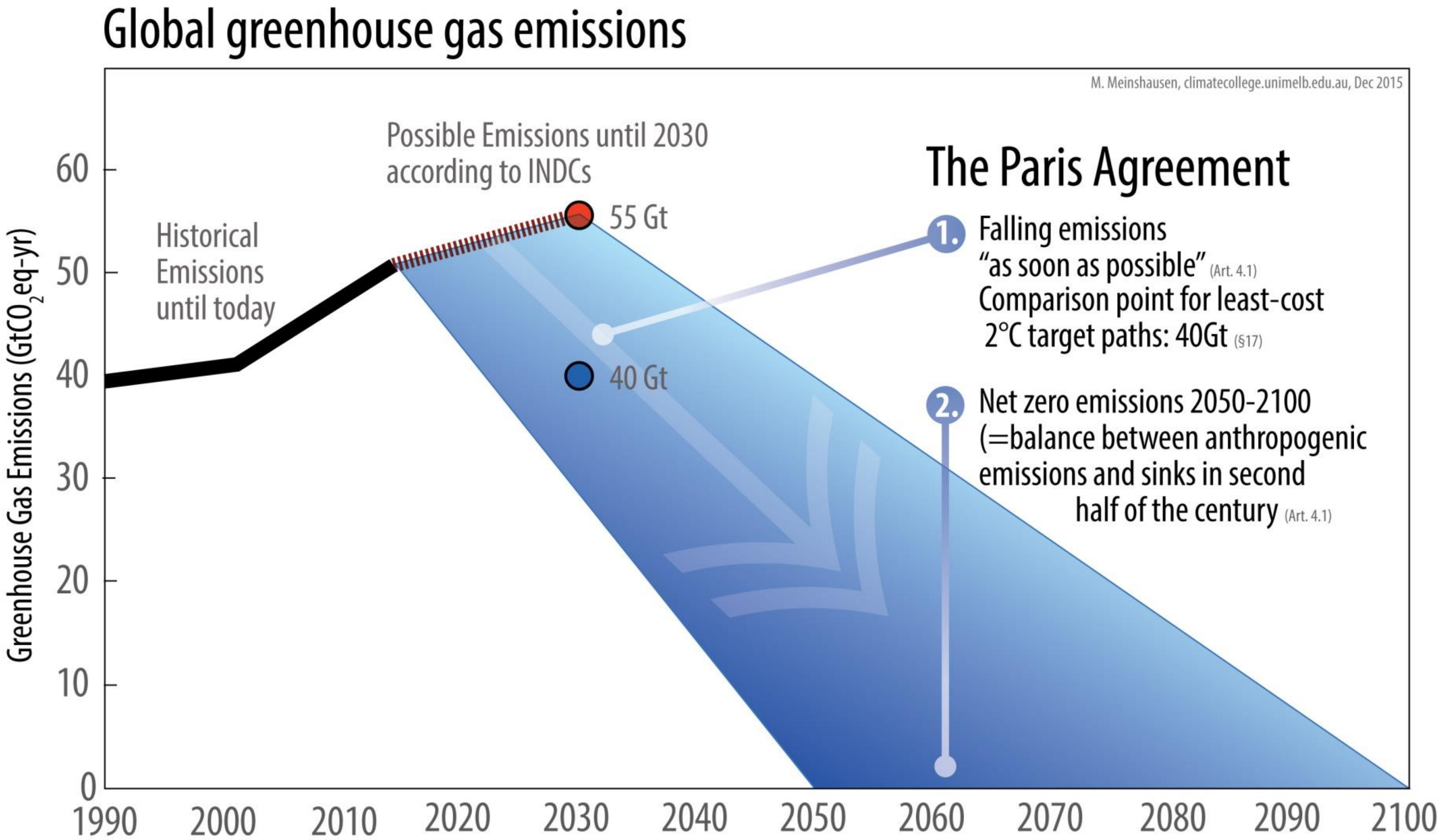
Content

- Context
- CO_2 capture
- CO_2 re-use and power-to-fuel
- CO_2FUTURE platform

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



European objectives

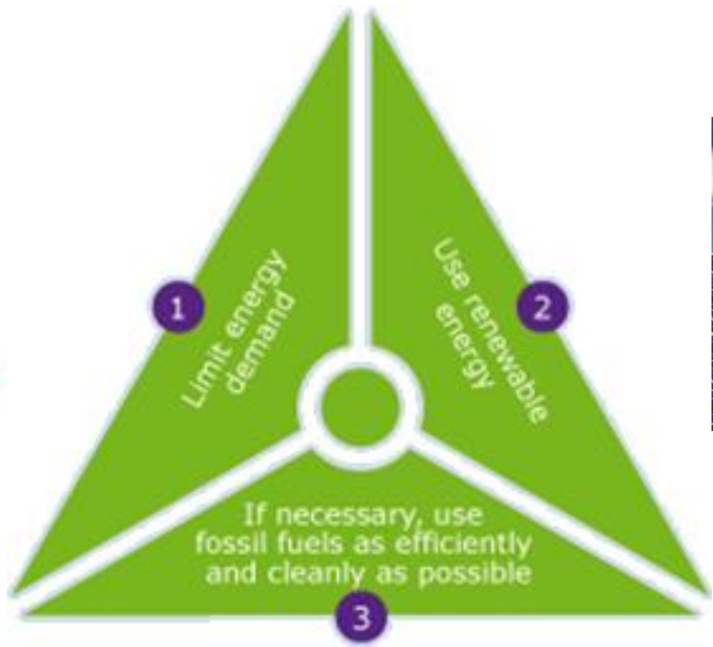
- Roadmap for low carbon economy in 2050

Table 1: Sectoral reductions

GHG reductions compared to 1990	2005	2030	2050
Total	-7%	-40 to -44%	-79 to -82%
Sectors			
Power (CO_2)	-7%	-54 to -68%	-93 to -99%
Industry (CO_2)	-20%	-34 to -40%	-83 to -87%
Transport (incl. CO2 aviation, excl. maritime)	+30%	+20 to -9%	-54 to -67%
Residential and services (CO_2)	-12%	-37 to -53%	-88 to-91%
Agriculture (non-CO_2)	-20%	-36 to -37%	-42 to -49%
Other non-CO_2 emissions	-30%	-72 to -73%	-70 to -78%

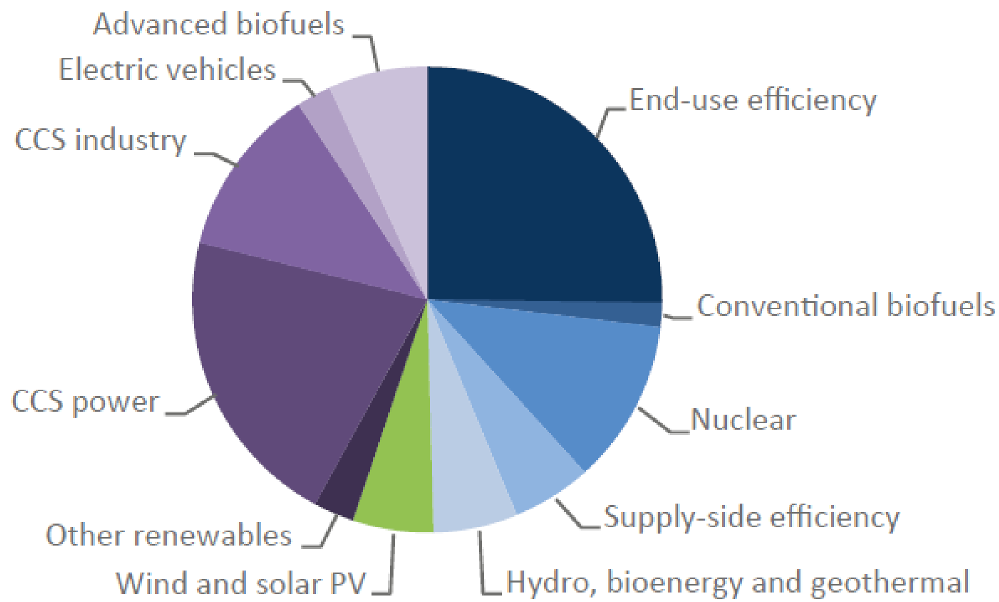
European Commission communication, 2011, COM(2011) 112 final

Possible answers: Trias Energetica



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

What efforts are needed?

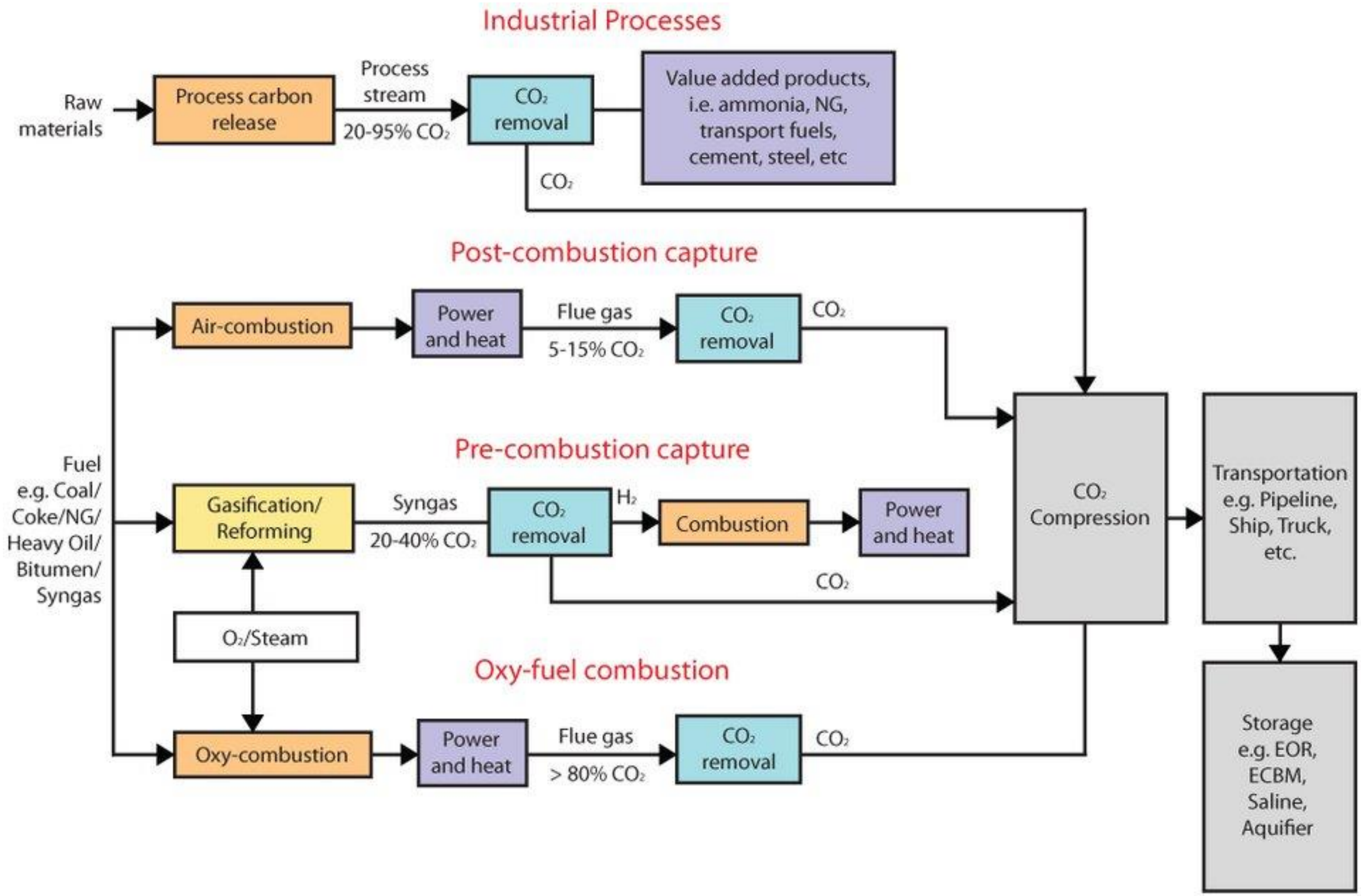


World CO_2 emissions abatement in the 450 Scenario (Bridge Scenario 2015-2040), IEA **2015**, WEO special report, Energy & Climate Change

- **CCS** mature technology, but cost only!
- **CCU**: different maturity levels, depending on product

2. CO_2 Capture technologies & configurations

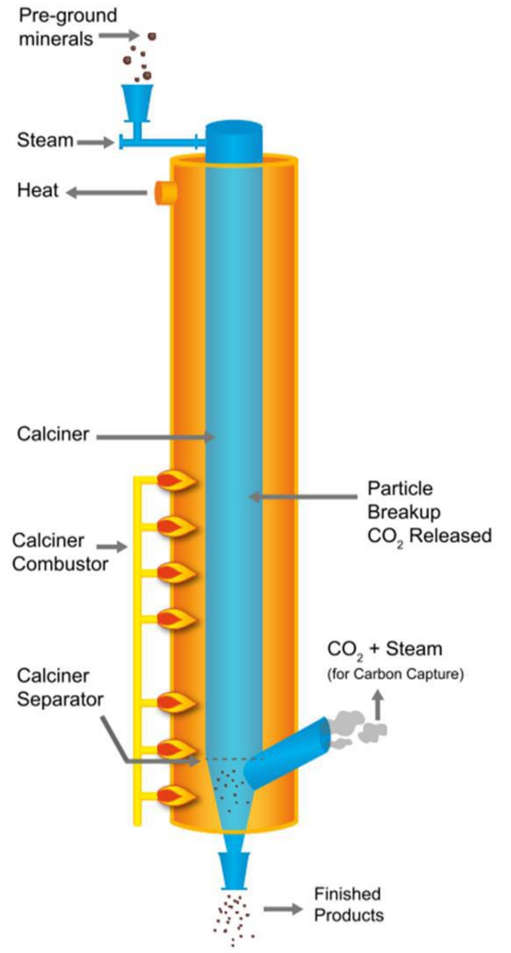
CO_2 capture configurations



Industrial processes

1. CO_2 not resulting from combustion

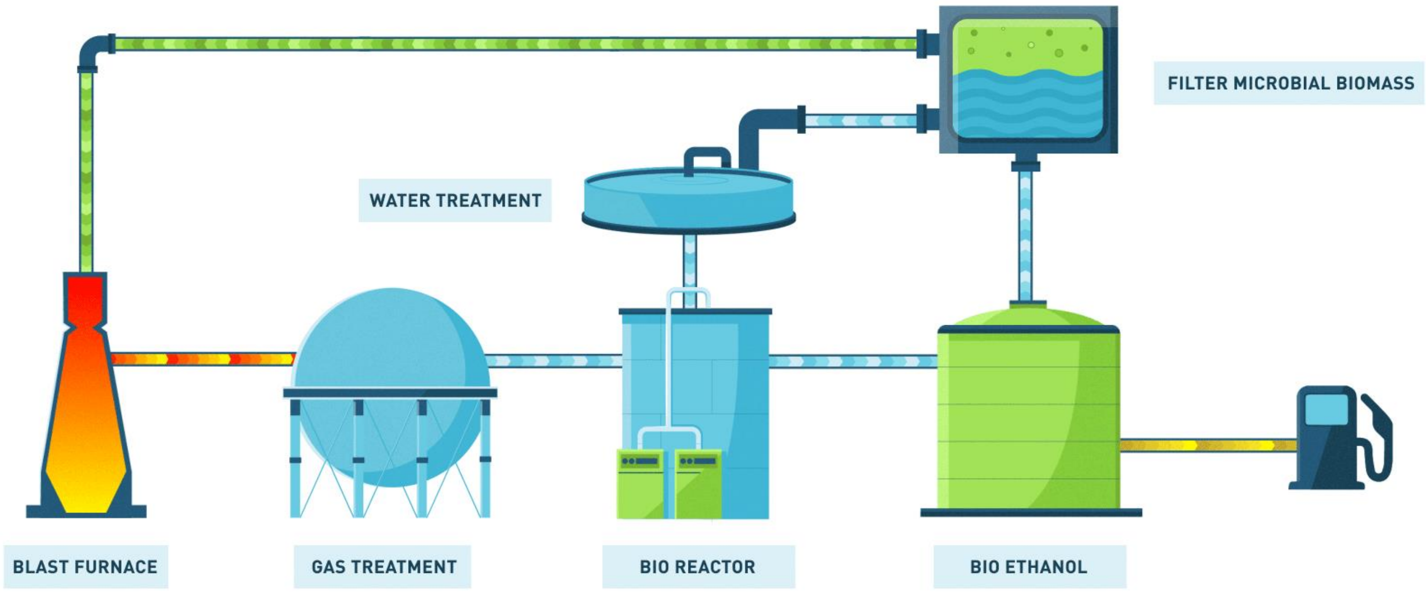
- Cement plants
  - $CaCO_3 \rightarrow CaO + CO_2$
  - High Temperature needed
  - Leilac: 21 M€, -60% CO_2



LEILAC public preFEED report, 2016

Industrial processes

1. **CO_2 not resulting from combustion**
   - Steel mills
     - Fermentation of CO into ethanol
     - Steelanol: 87 M€, -70% CO_2



www.steelanol.eu

Post-combustion capture

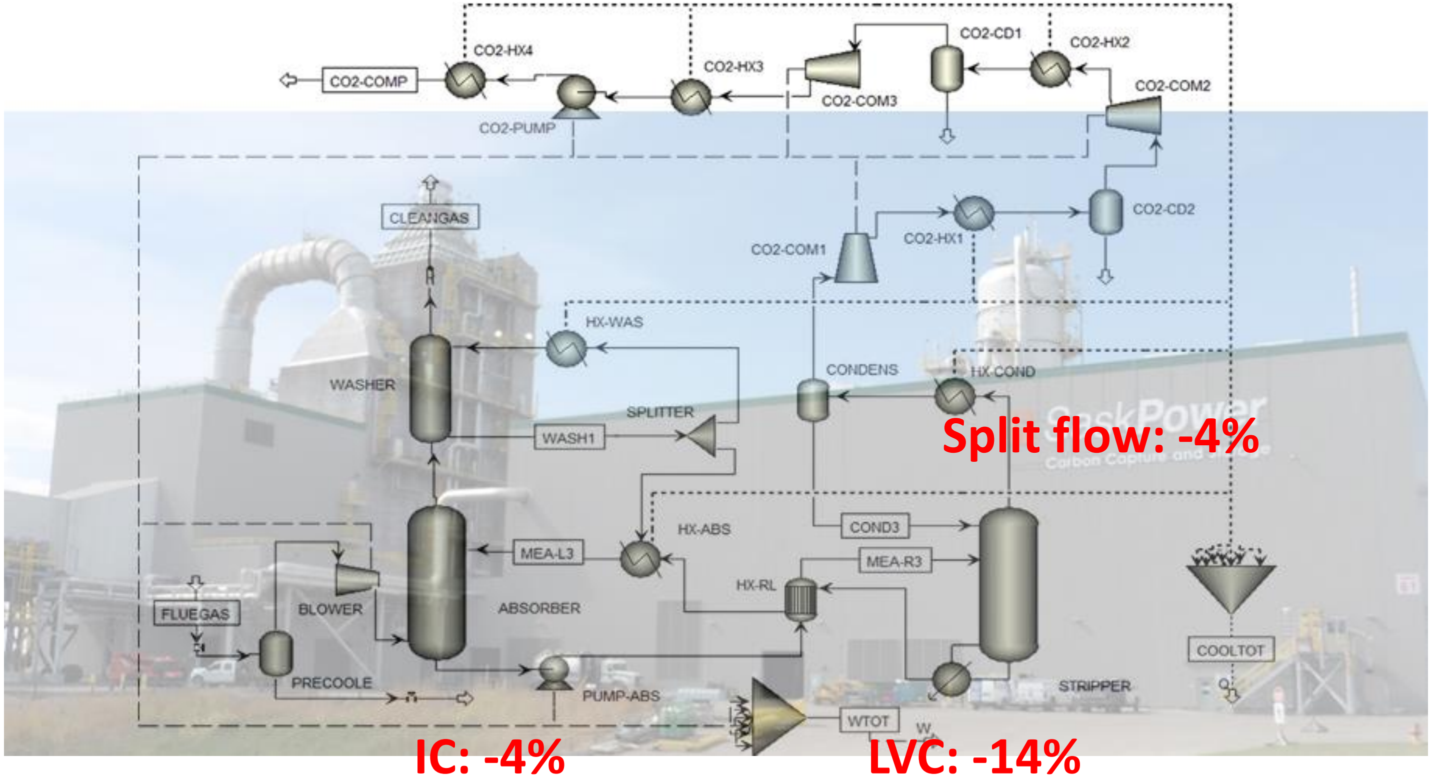
2. **Capture CO_2 from combustion gases**

- 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**

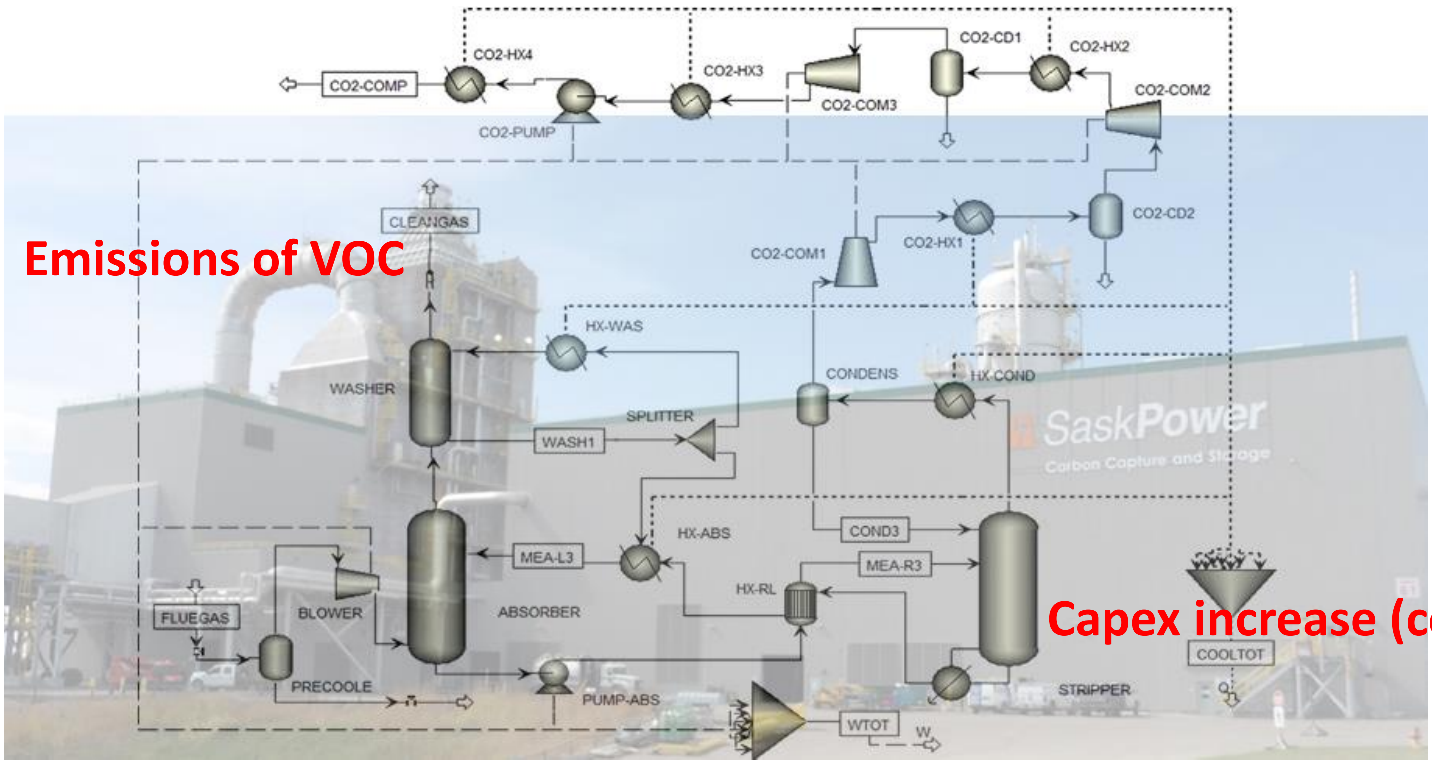
- 2 main focus at ULiège: Process modeling



Post-combustion capture

2. **Capture CO_2 from combustion gases**

- 2 main focus at ULiège: Solvent stability

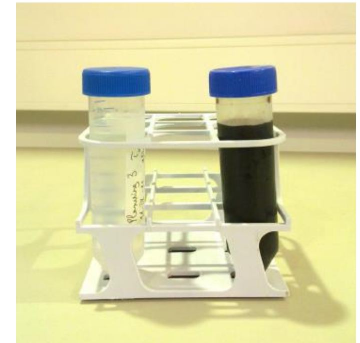


Emissions of VOC

Capex increase (corrosion)

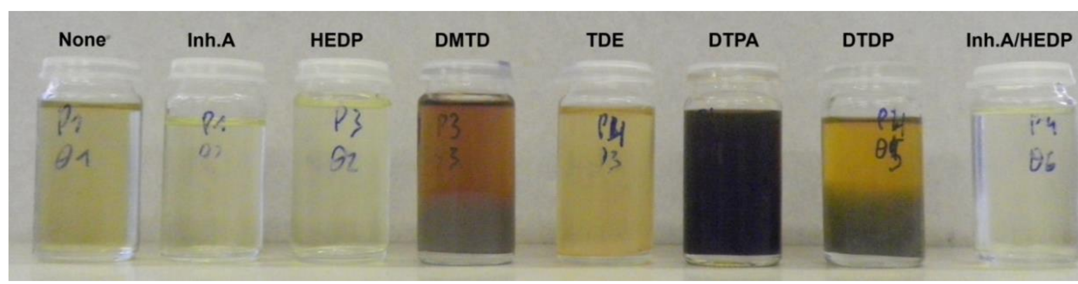
OPEX increase: viscosity, solvent properties…

Post-combustion capture



4 main types of solvent degradation

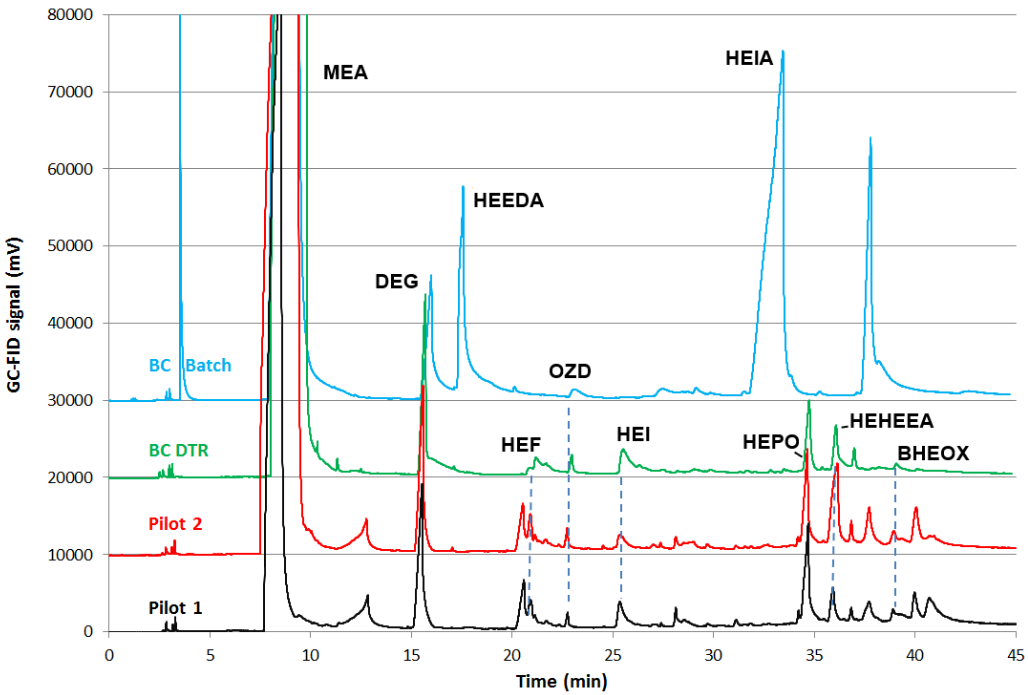
- Thermal decomposition > 200°C
- Thermal degradation (120< T <140°C)
  - Irreversible reactions with CO_2
- Oxidative degradation
  - Oxidation of amines with O_2 present in flue gas
- Degradation with other flue gas contaminants
  - SO_X, NO_X …



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

Post-combustion capture

1st Objective: Representativity of accelerated degradation versus industrial degradation

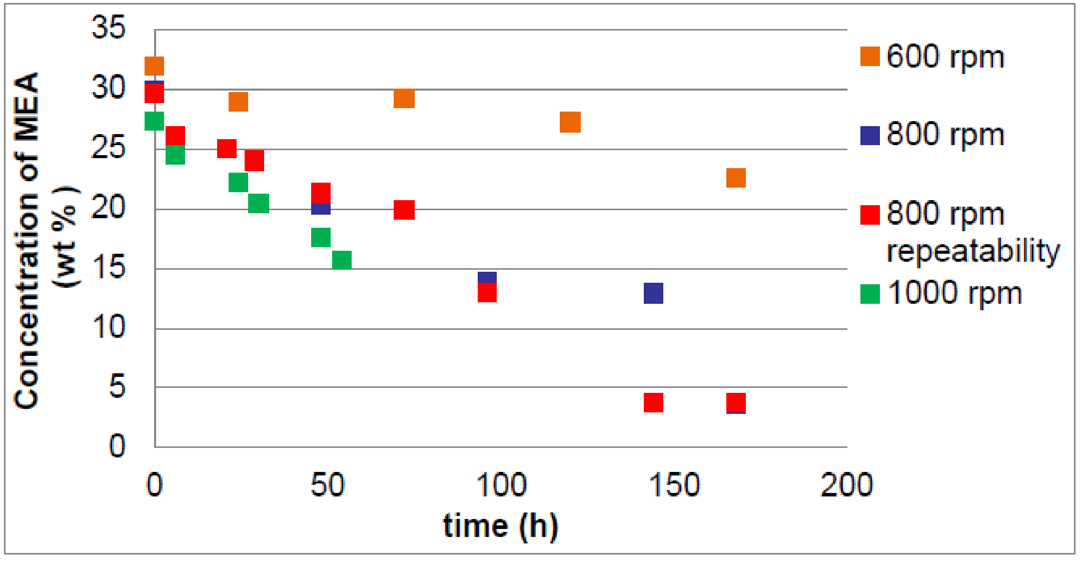


=> 21% MEA loss after 7 days vs. 4% loss in 45 days

[1] Léonard et al., 2014. Int. J. Greenhouse Gas Control 30, 171. DOI: 10.1016/j.ijggc.2014.09.014

Post-combustion capture

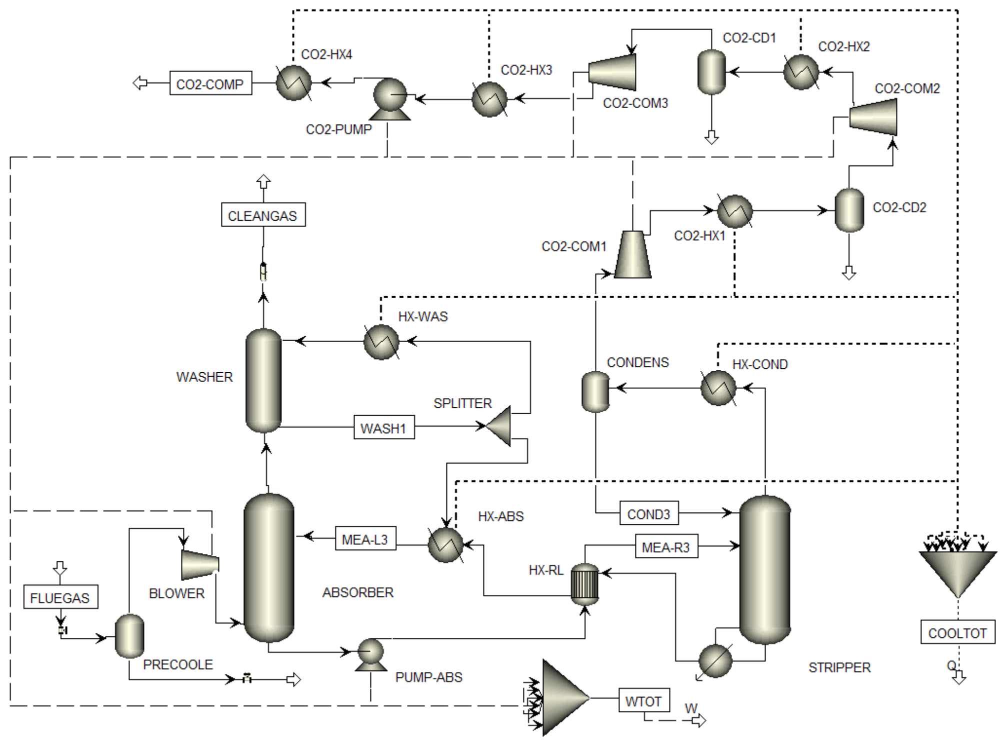
- Influence of operating conditions on solvent degradation
  - O_2, CO_2 content in flue gas
  - Temperature & Mass transfer
  - Additives (dissolved metals, degradation inhibitors, SOx…)



=> kinetic model for oxidative and thermal degradation

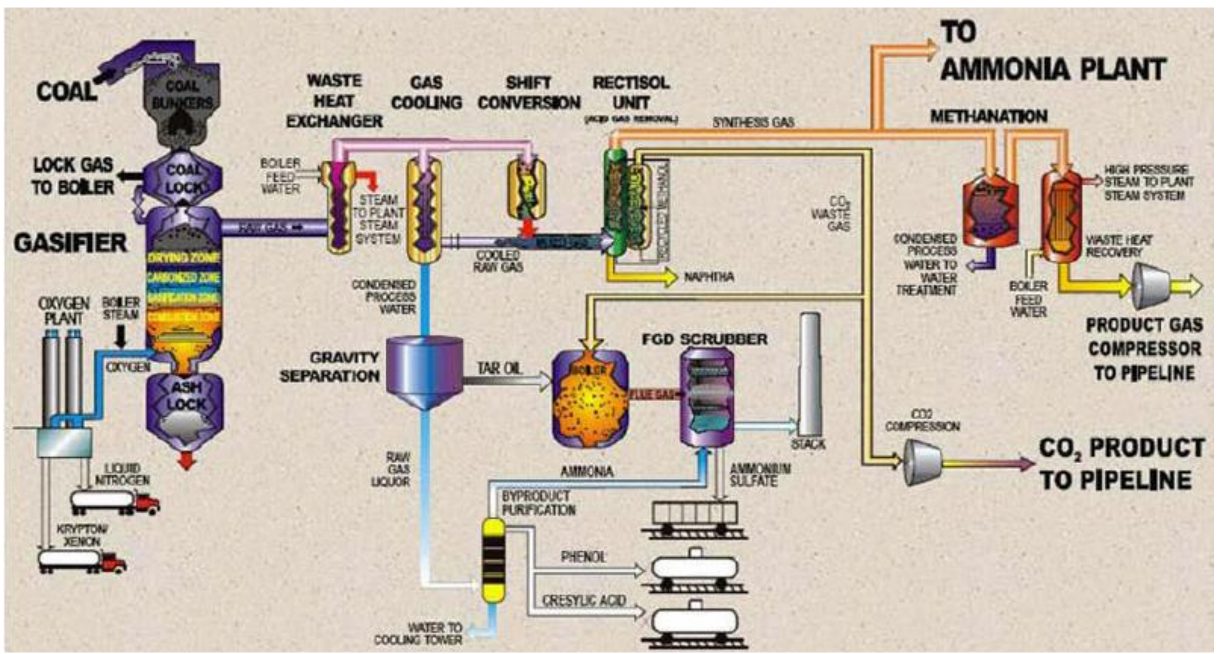
Post-combustion capture

- This kinetic model is implemented in process models
  - => predict degradation depending on operating conditions
  - 81 g MEA/ton CO_2 < 284 g MEA/ton CO_2



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

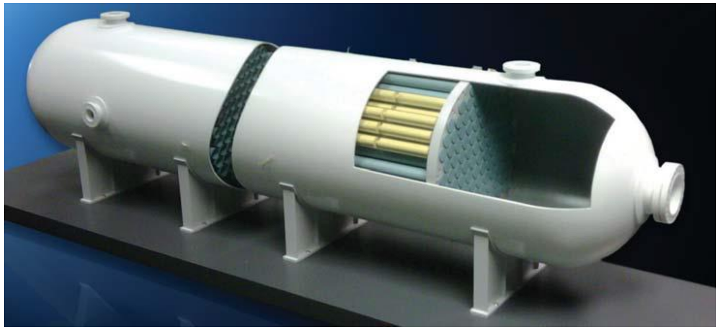


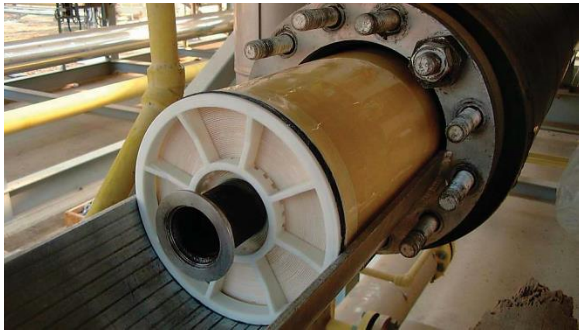
http://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/great-plains

Pre-combustion capture

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

- Off-shore platforms: possibly use membranes



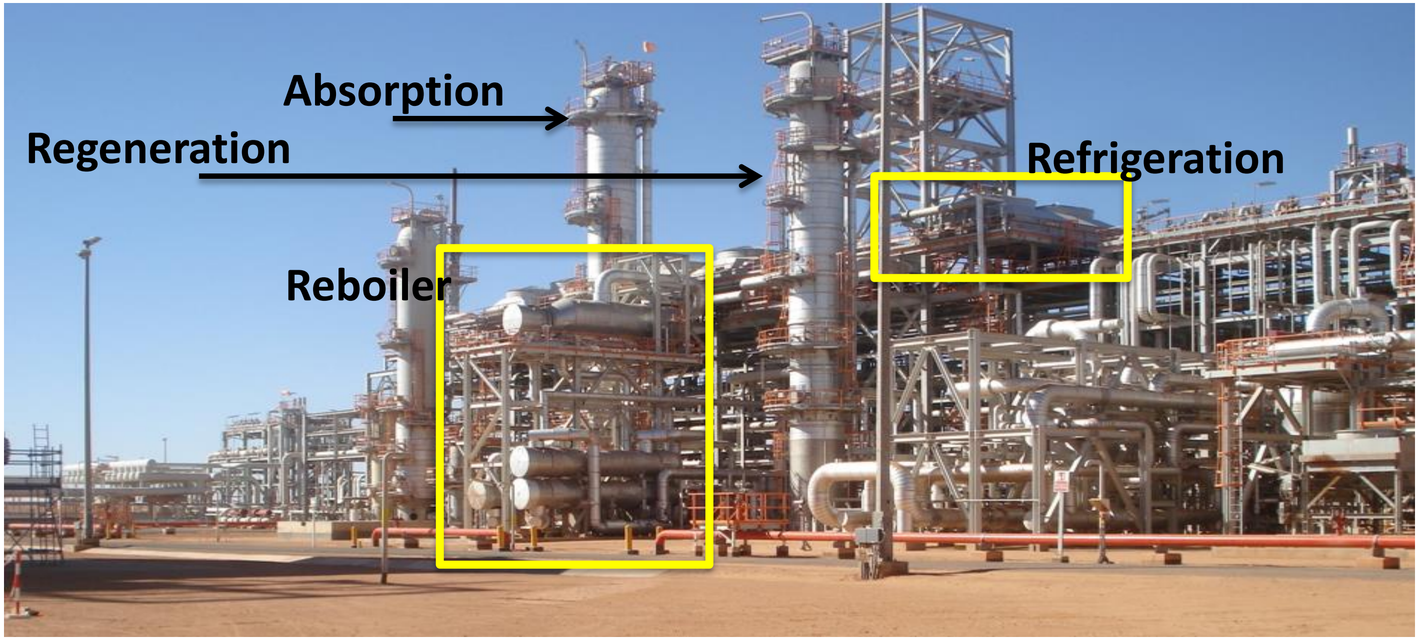


UOP Separex™ Membrane Systems, UOP LLC, 2011

Pre-combustion capture

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

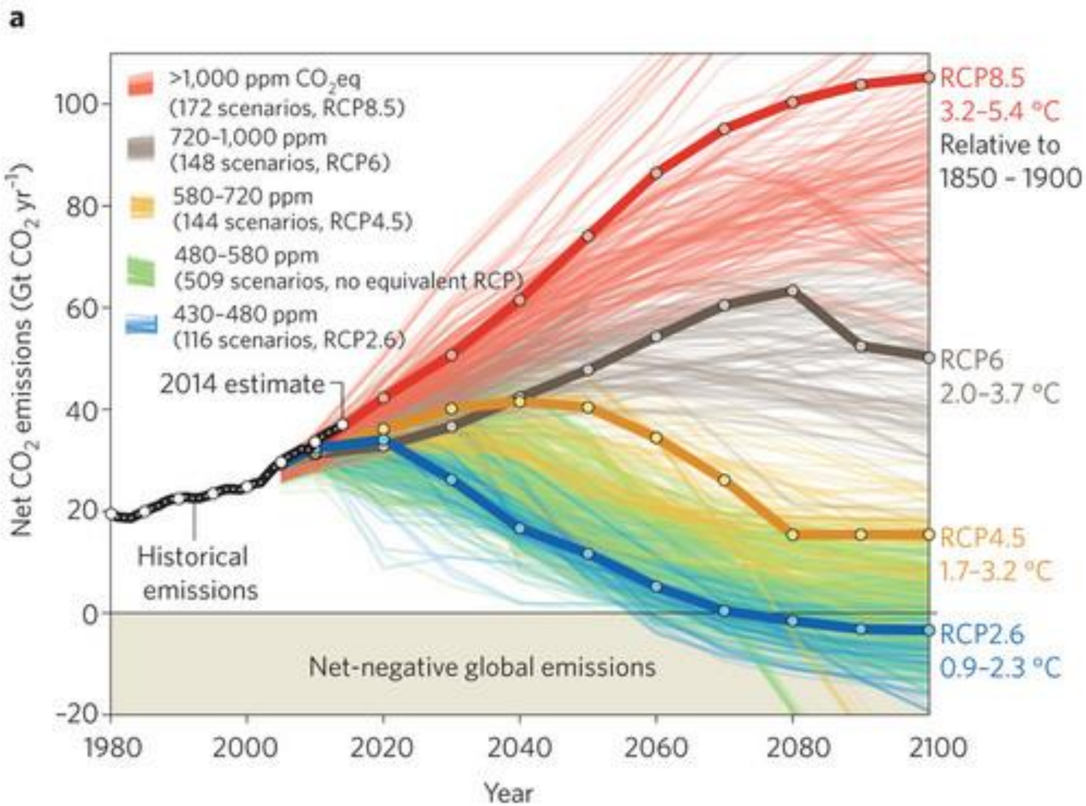
- Conventional process: absorption with solvents
- From 80 to 2 vol%; down to 50 PPM if liquefaction



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

Trends and challenges

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

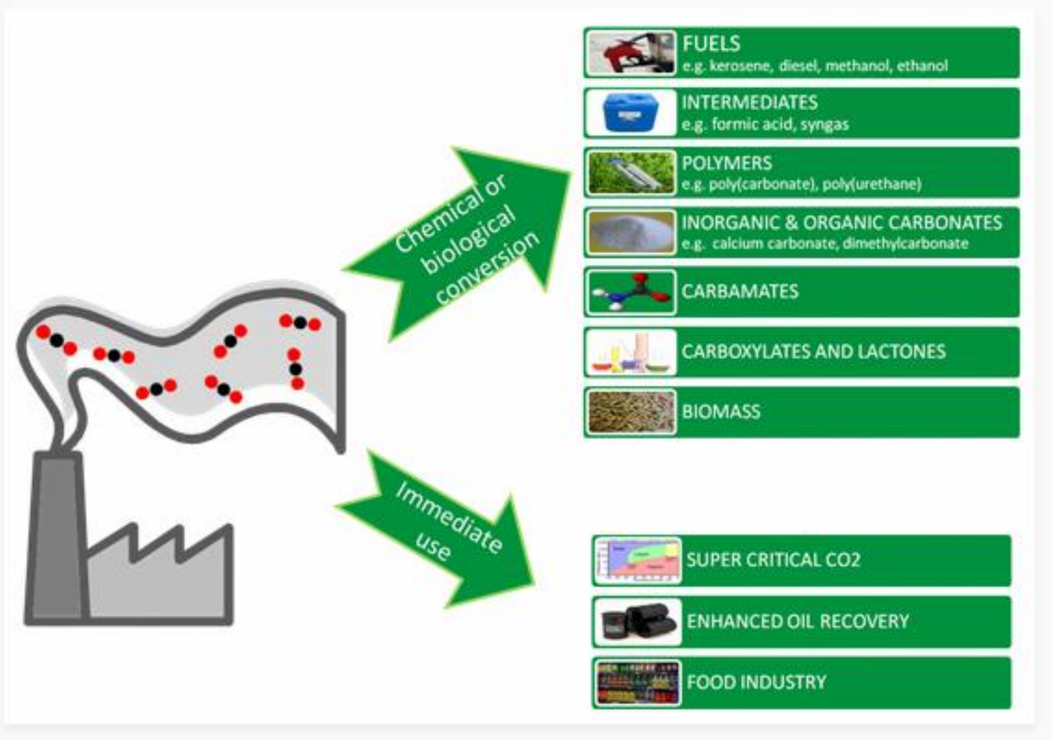


Fuss et al, Nature, 2014, doi:10.1038/nclimate2392

3. CO_2 re-use technologies

Technologies and products

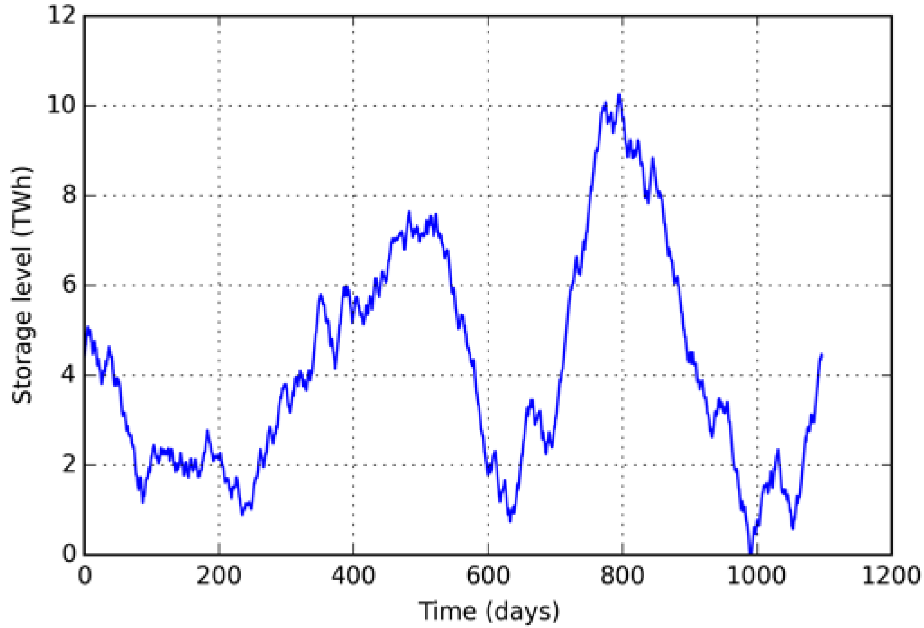
- Carbon is root of organic chemistry and materials
  - => Potential of applications for CO_2 is huge
    - New products
    - New technologies



Source: CO2Chem

Power-to-fuel

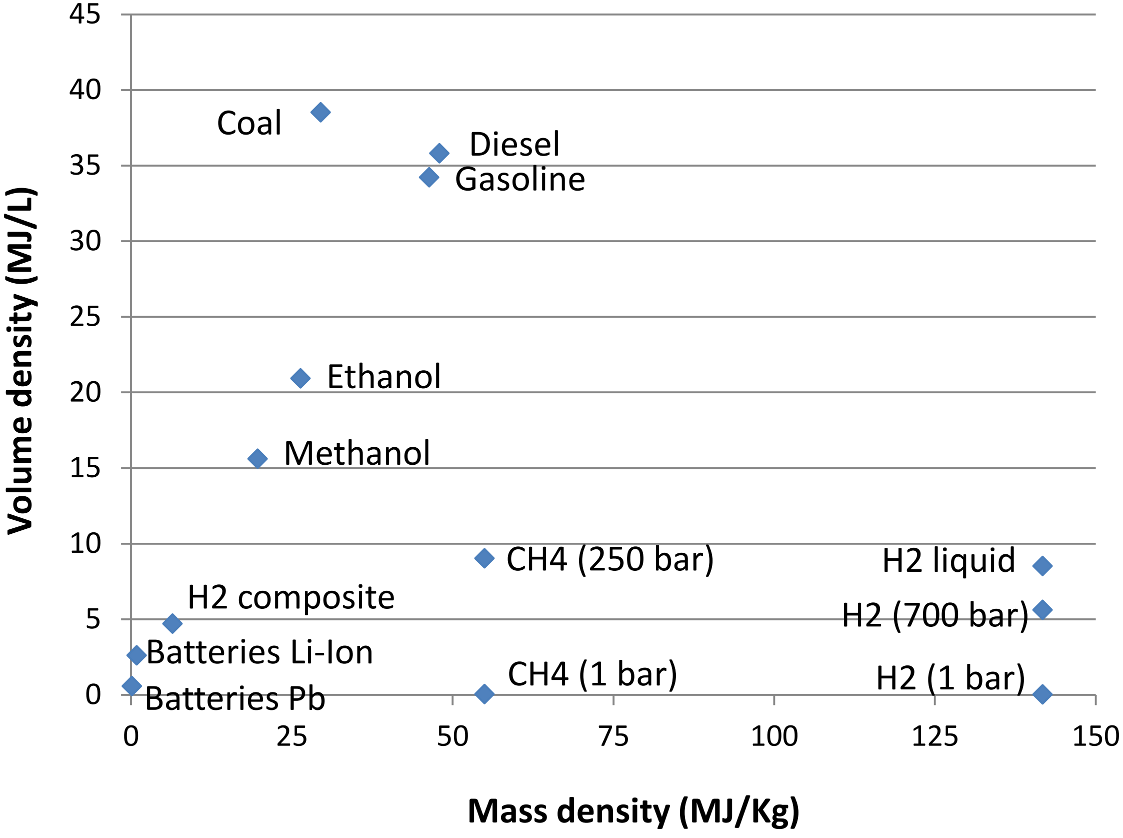
- Study with 100% variable renewables + storage for electricity grid:
  - Reasonable electricity cost (83.4 €/MWh)
  - Second and minute scale storage for frequency regulation
  - Inter-seasonal scale also needed!



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

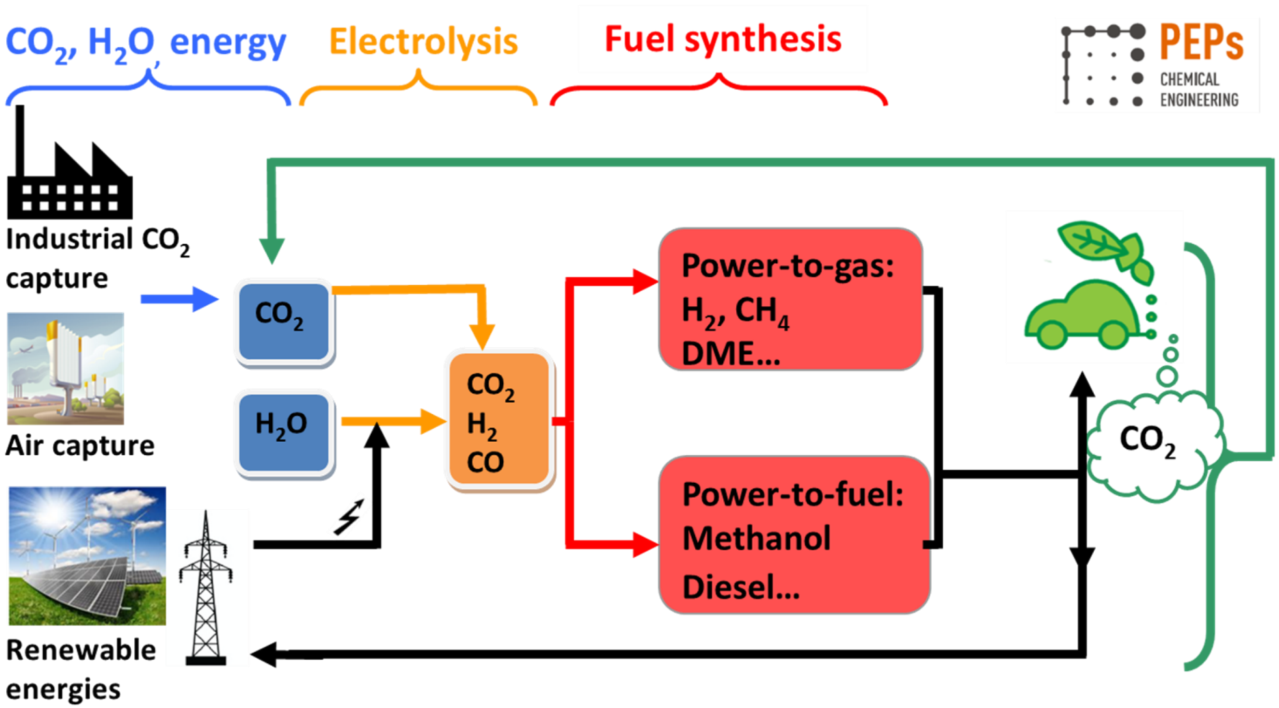
Power-to-fuel

- High energy density is required for long-term storage



Power-to-fuel

- CO_2 capture, water electrolysis, fuel synthesis



Power-to-fuel

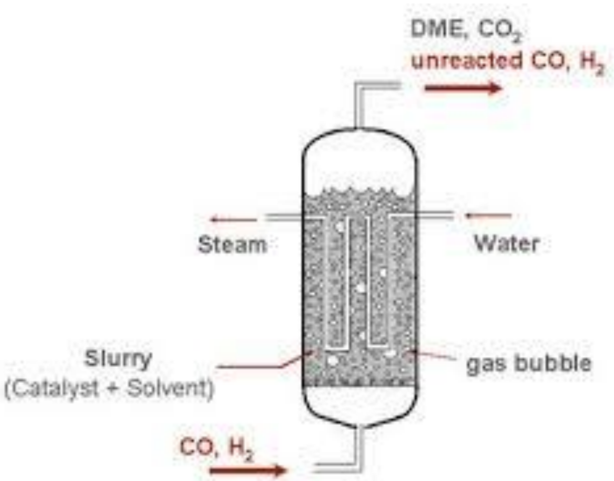
How to choose the right reactor?

- High variety of reactions and operating conditions
- Rational analysis of processes to identify limiting factors

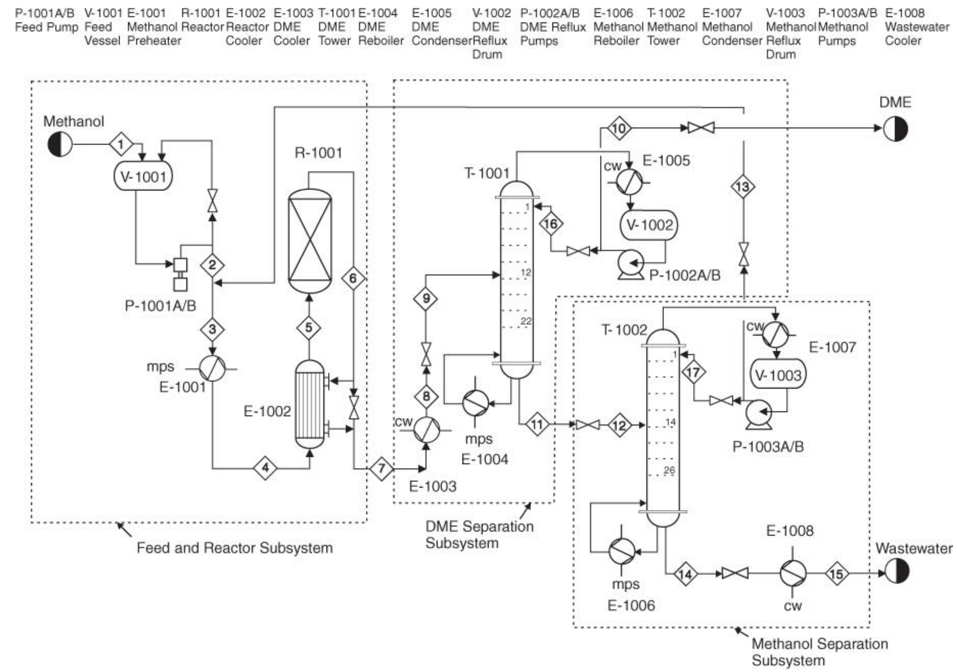
Criterion	Types of reactions
Phases	Homogeneous (1 phase) Heterogeneous (2, 3 or 4 phases)
Stoichiometry	Simple (1 reaction) Complex (multiple reactions, side reactions…)
Thermodynamics	Irreversible Equilibrium
Kinetics	Limiting factors are physical Limiting factors are chemical
Heat balance	(Strongly) Endothermal ($\Delta H > 0$) (Strongly) Exothermal ($\Delta H < 0$)

Power-to-DME

- DME (CH_3OCH_3)
  - Directly from syngas => more exothermal => slurry
  - From methanol => fixed bed gas reactor



Yagi et al., 2010. DOI: 10.2202/1542-6580.2267



Turton et al., Prentice Hall, 2012

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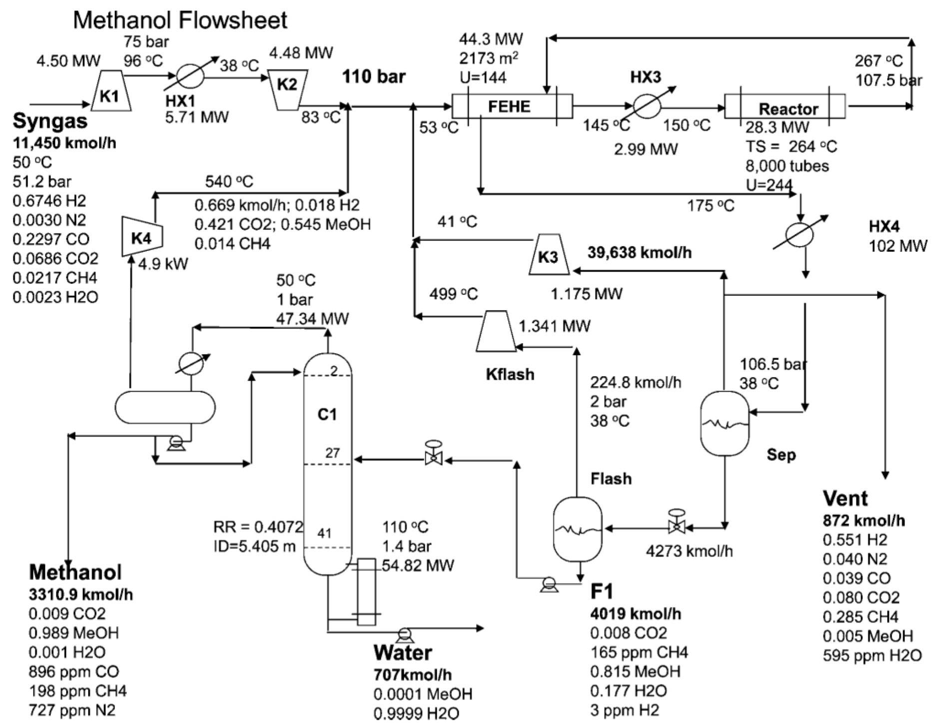
Power-to-methanol

- Conventional methanol synthesis
  - Limiting step: thermodynamic equilibrium (25% H_2 conversion) + exothermal reaction
  - => High P, Low T, large gas recycle
  - => Shell & Tubes reactor

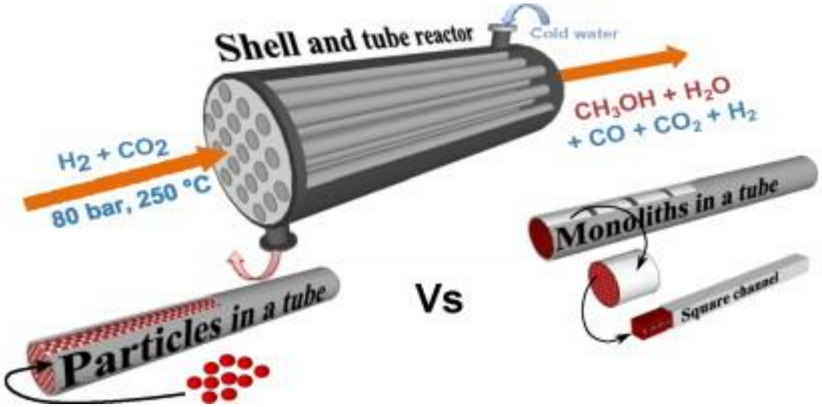


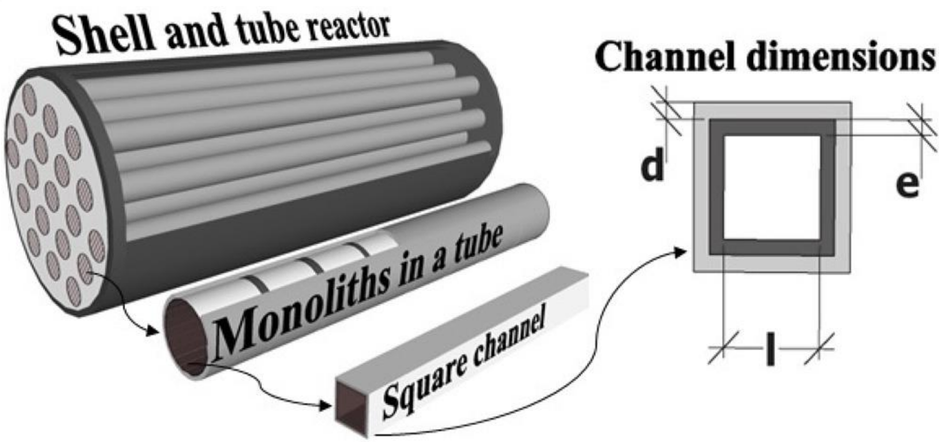
Haldor Topsoe, > 10 000 t/d

Ind. Eng. Chem. Res., Vol. 49, No. 13, 2010

Power-to-methanol

- Novel methanol reactor designs
  - Improve the heat management
  - Lower ΔP at high flow rates

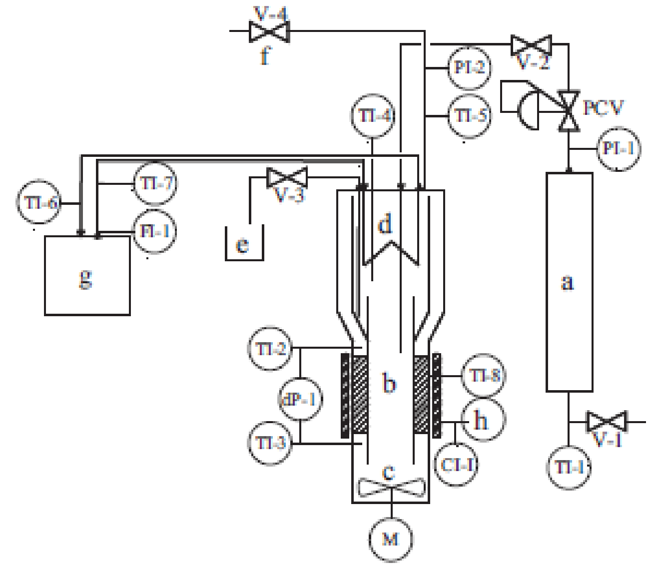




Arab S. et al., 2014. DOI: 10.1016/j.cherd.2014.03.009
Montebelli et al., 2013. DOI: 10.1016/j.cattod.2013.02.020

Power-to-methanol

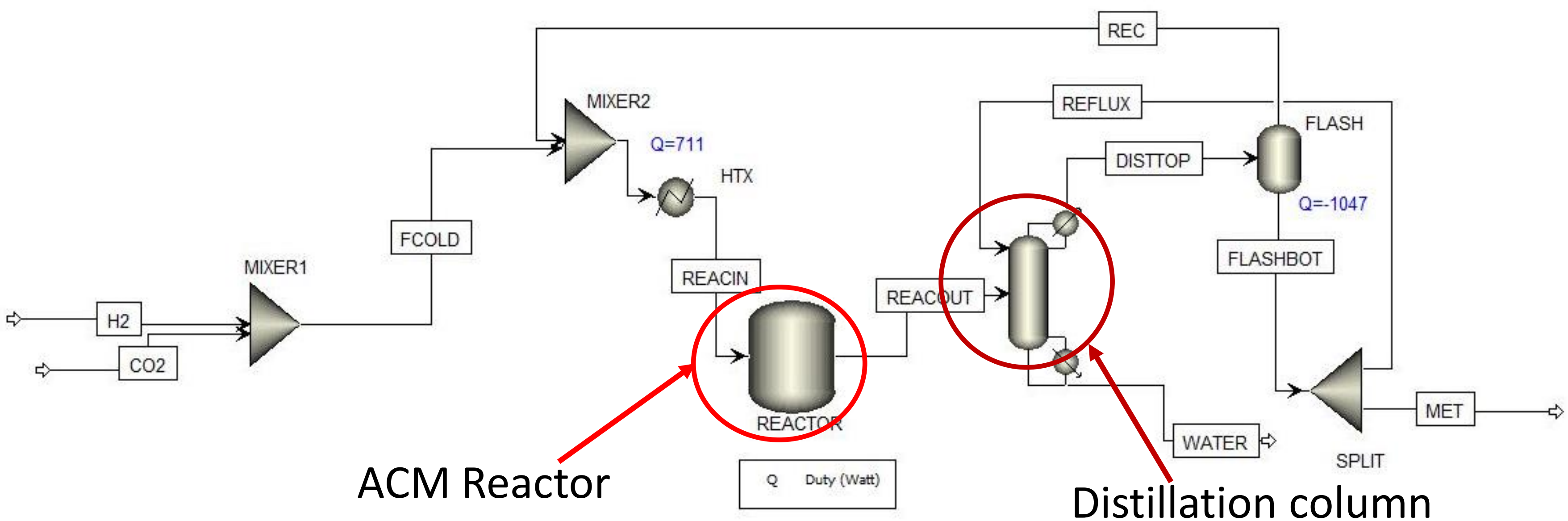
- Novel methanol reactor designs
  - Remove the thermodynamic limitation
  - Displace the equilibrium
  - Conversion reaches 99.9%!



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

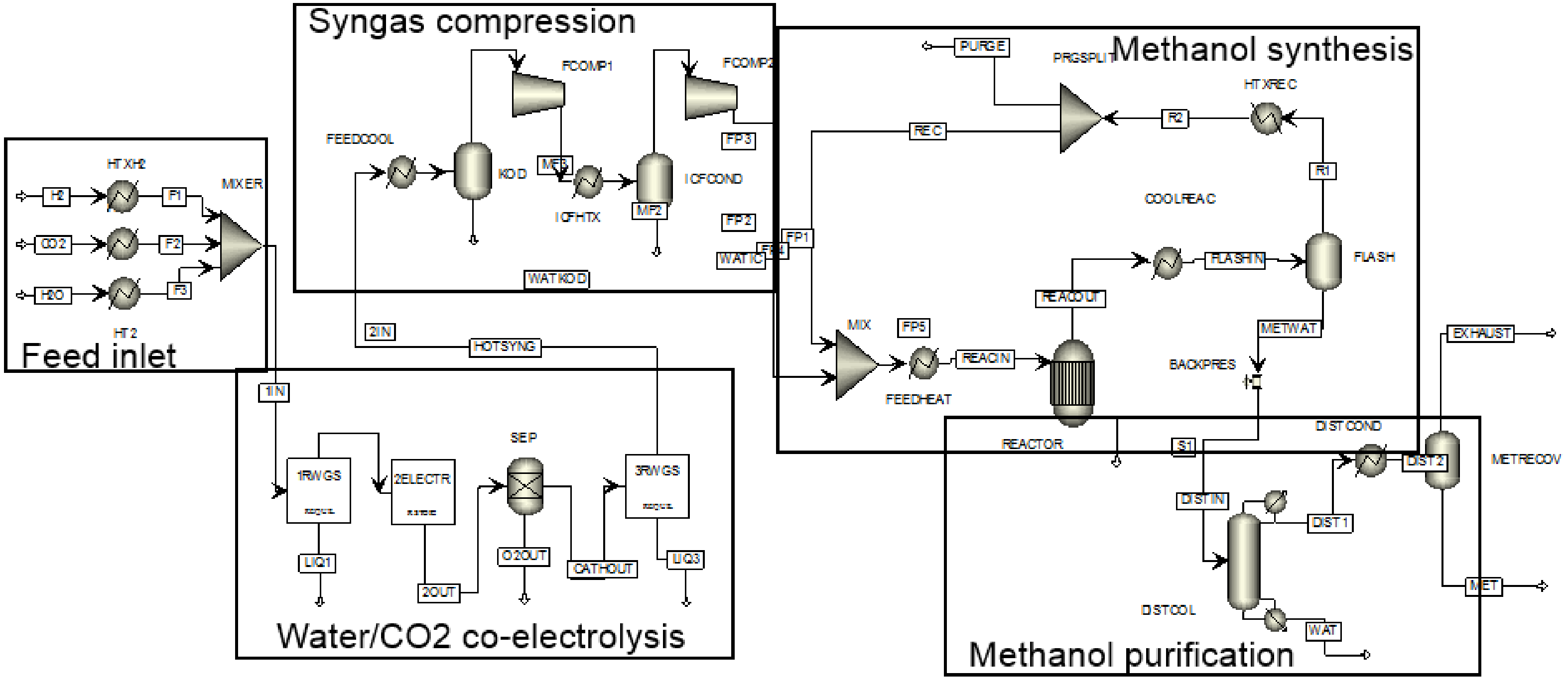
Power-to-methanol

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



Power-to-methanol

- Improved heat integration
  - Electricity to fuel efficiency 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

4. The CO_2FUTURE Platform at ULiege

www.chemeng.uliege.be/CO2Future

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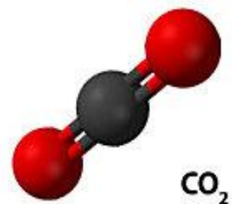
CO_2FUTURE

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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CO_2FUTURE

- Industrial partner in Brazil
  - Produces sugar, ethanol and various other products
  - Convert CO_2 waste into new products => 400 tCO_2/h
  - Looking for brazilian research partners

A flavor of teaching

- Case study for grad students in Chemical Engineering

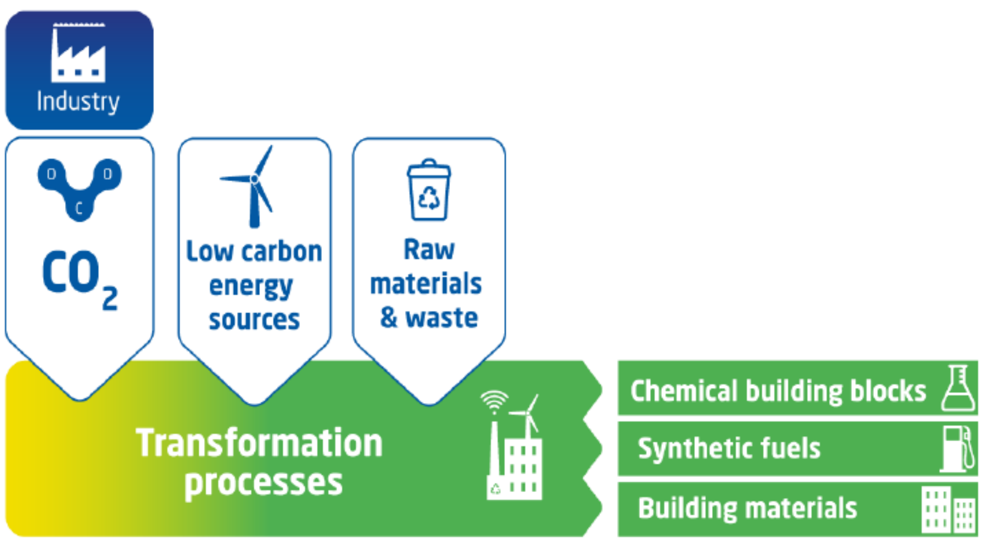
Process	Profit (USD/ton of CO_2)	Profit (USD/ton of product)	Market Share of Product	TRL
Enhanced Oil Recovery	-10.79	N/A	4.276%	9
Concrete	9503.48	95.03	0.261%	5
Syngas Production	-81.45	-388.78	Naphta: 0.072% Diesel: 0.023%	Dry Reforming: 4 Fischer-Tropsch: 6
Microalgae Production	-452.02	-1674.15	0.275%	5
Methanol Production	-191.74	-333.46	1.932%	7
Polymer Production	1377.08	661.74	7769.067%	8
Urea Production	39.91	29.56	2.442%	9

=> Urea production process will be studied in Q2

CO_2 Value Europe

- 30.11.2017: Creation of CO_2 Value Europe, an Association for promoting:

"the development and market deployment of sustainable industrial solutions that convert CO_2 into valuable products, in order to contribute to the net reduction of global CO_2 emissions and to the diversification of the feedstock base."



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Many thanks to the team…

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Thank you for your attention!

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

https://vimeo.com/95988841

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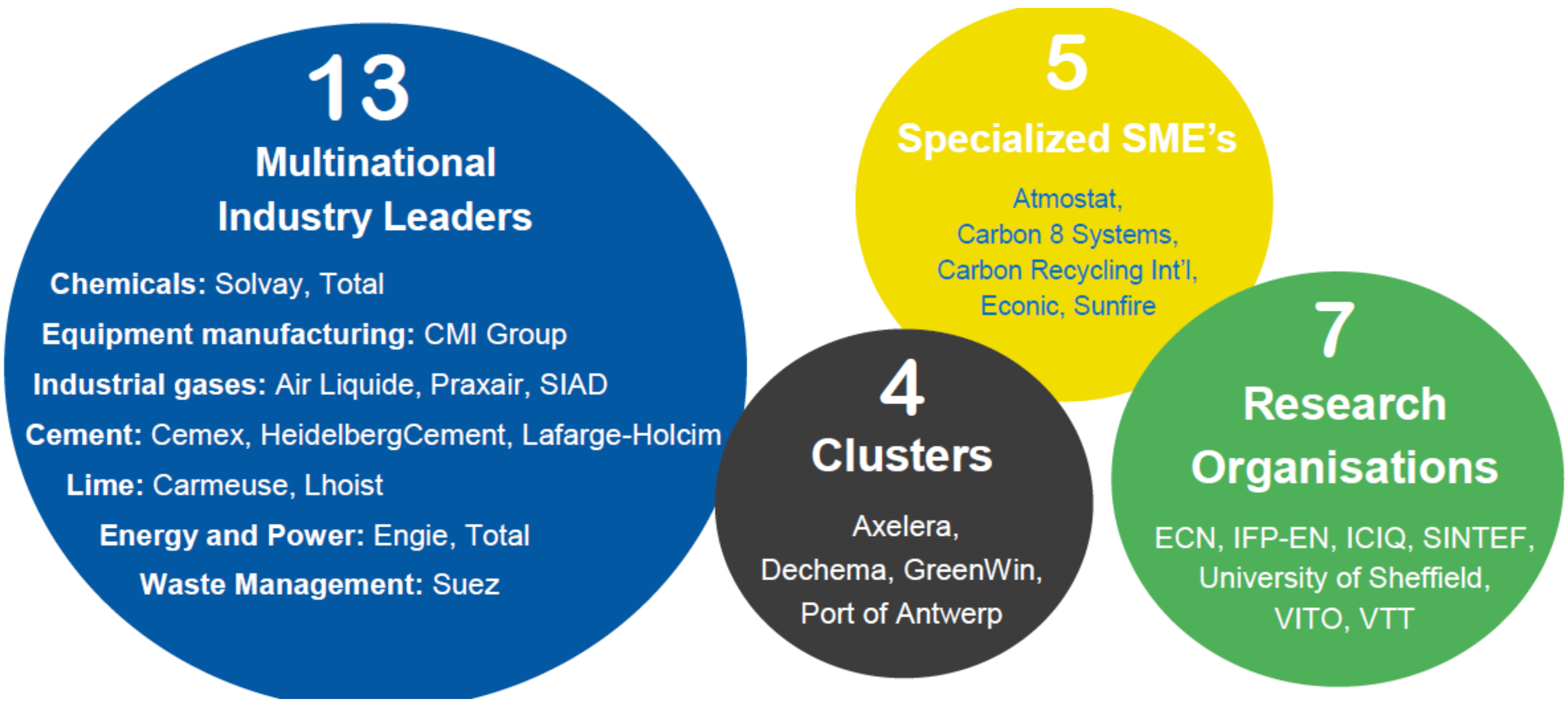
CO_2 Value Europe

- Who's in?



+ ULiège!