Grégoire LEONARD

Reactors for CO_2 utilization

PEPS group

Products, Environment and Processes

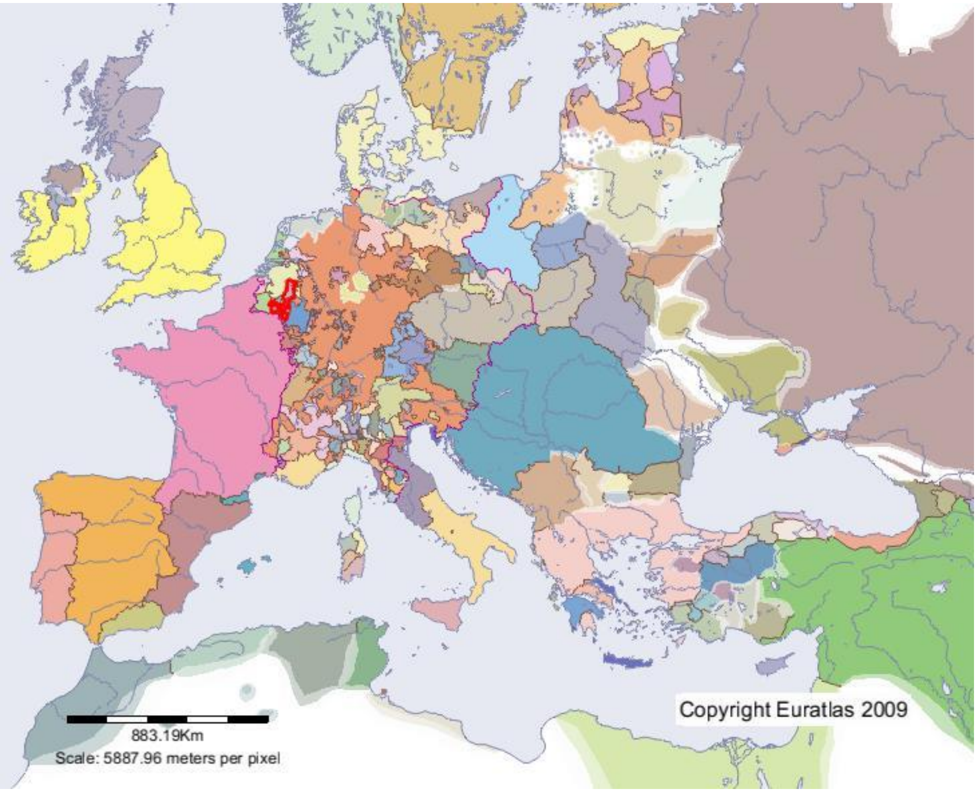
Université de Liège

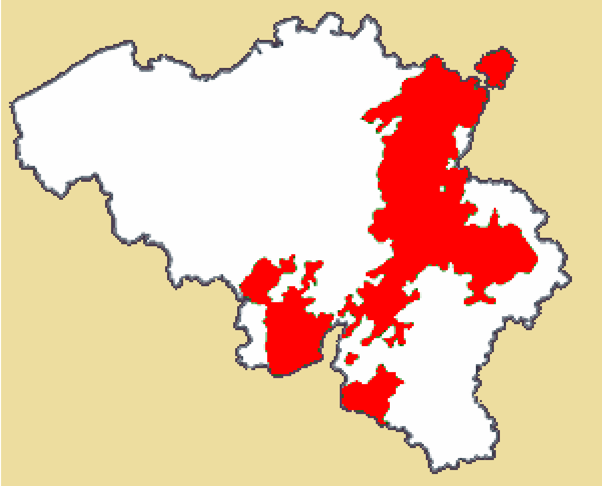
January 2016

PEPs CHEMICAL ENGINEERING

Liège

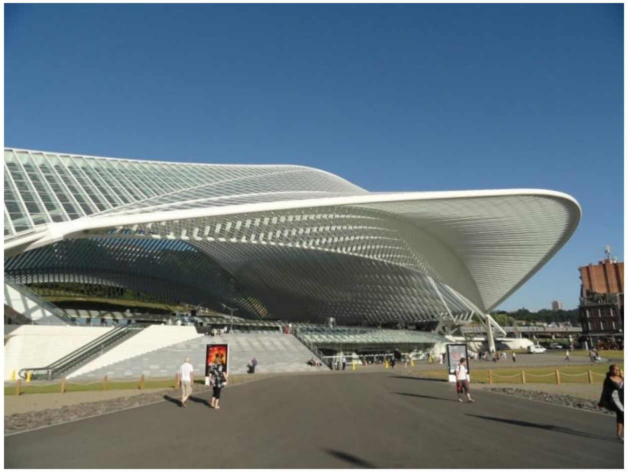
- Former independent Prince-bishopric, in the heart of North-western Europe (980-1789)





Liège

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



University of Liège

- 11 faculties, 20 000+ students, 122 Nationalities

Philosophy & Letters

Applied Sciences

Law and Criminology school

Veterinary Medecine

Sciences

Psychology and Education

Medecine

gembloux
agro bio tech

Architecture

HEC ULg
Management School - University of Liege

Human and Social Sciences

- ✓ 38 bachelors
- ✓ 194 masters
- ✓ 68 complementary masters

Outline

1. General introduction to chemical reactors

2. Reactors for CO_2 reuse routes
   1. CO_2 to fuels
   2. CO_2 to chemical building blocs
   3. CO_2 to monomers and polymers

3. Related research topics at ULg

1. General introduction

Industrial/chemical process:

- A process is a series of matter and energy transformation steps
- These steps are known as unit operations (UO)
- The reactor is the step where chemical reaction(s) are implied

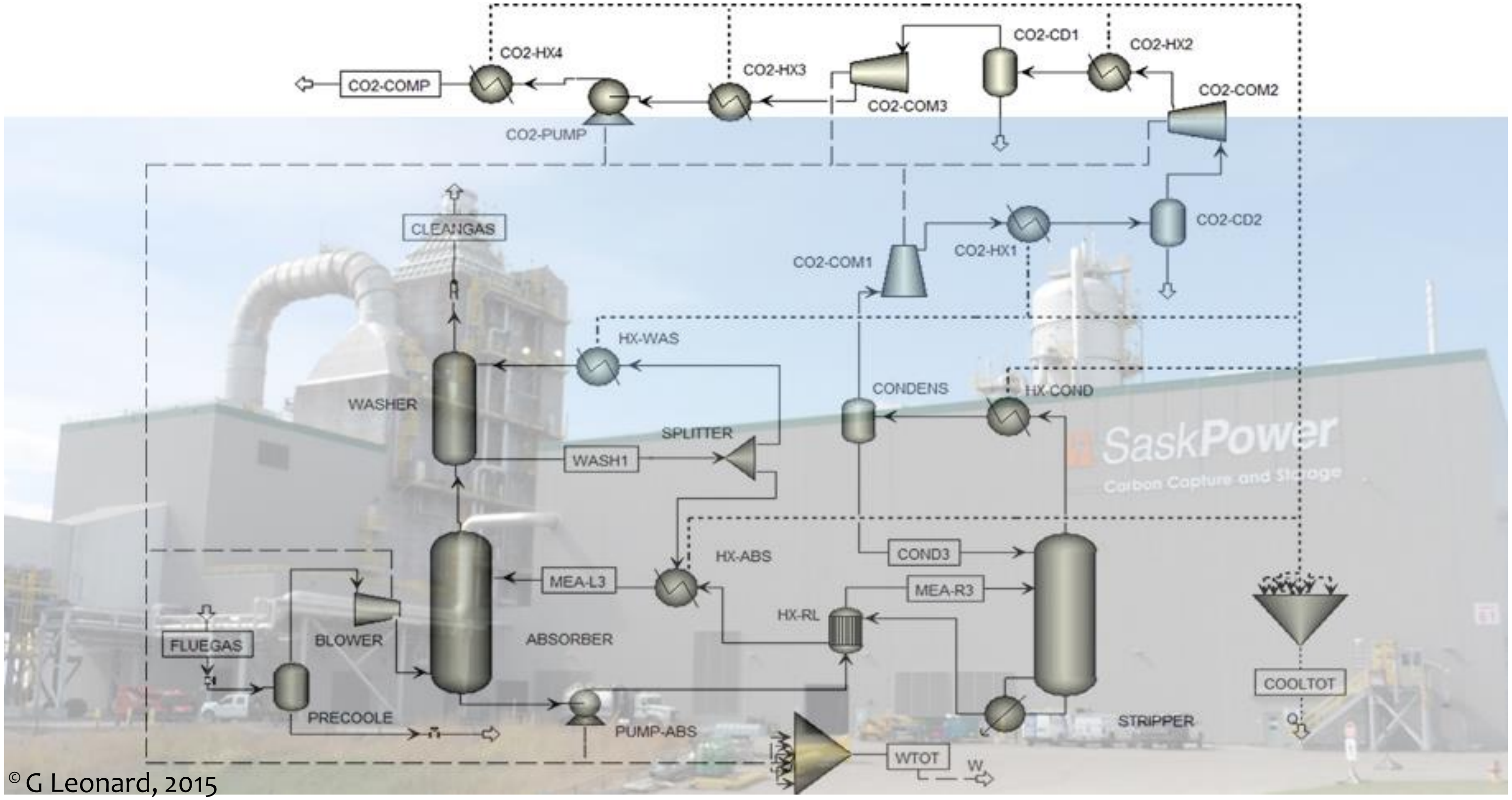
1. General introduction

Example: CO_2 capture from flue gas

© G Leonard, 2015

1. General introduction

Example: CO_2 capture from flue gas

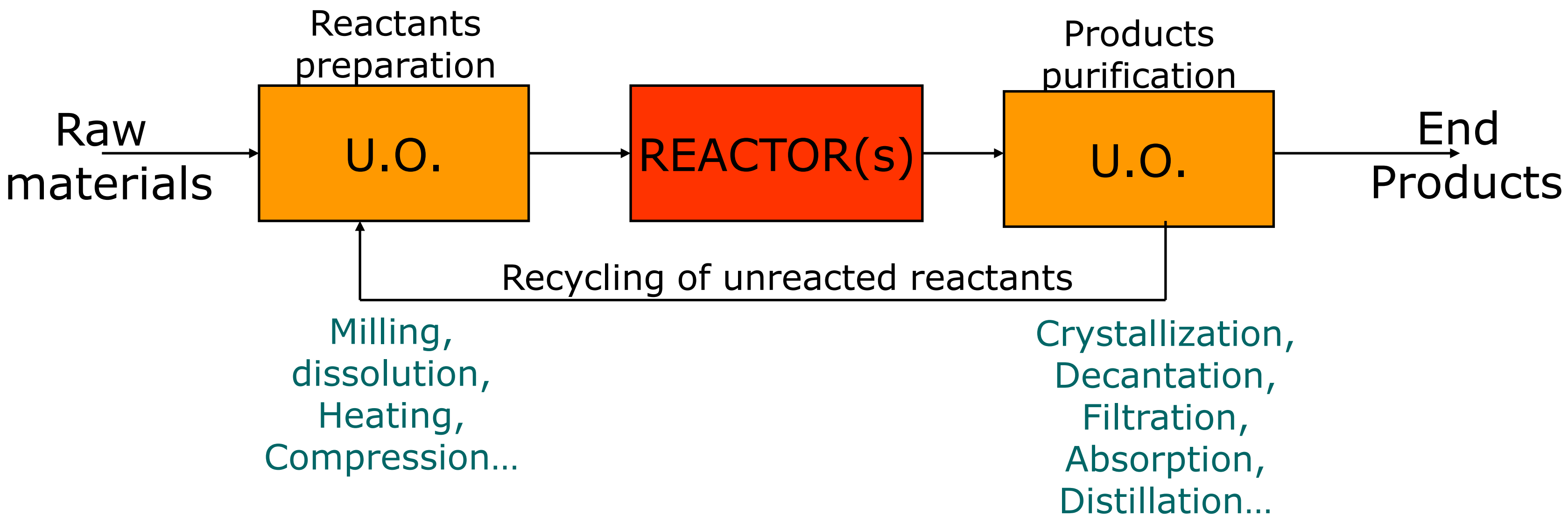


© G Leonard, 2015

1. General introduction

The reactor is the heart of the process

- Large influence on process costs and efficiency
- Usually a small part of the investment in itself (~10%).



1. General introduction

How to choose the right reactor?

- High variety of reactions and operating conditions
- Close links between physical and chemical phenomena, non-linear behaviors
- Rational analysis of processes needed to identify limiting factors

⇒ No "one-size-fits-all" solution!

1. General introduction

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 ($\Delta H < 0$)

1. General introduction

Criterion	Types of reactions
Feed mode	Batch reactor Semi-batch Continuous reactor
Time dependency	Steady-state Transitory
Mixing quality	Perfectly stirred reactor Plug flow reactor
Flow configuration	Cocurrent Countercurrent Cross flow

1. General introduction

Goal of reactor design:

- Achieve the best possible coupling between
  - The reaction(s)
  - The reactor

=> optimize reaction conditions and reach optimal production and selectivity

1. General introduction

Main types of industrial reactors:

- Homogeneous reactors:
  - Stirred tank reactor (liquid phase)
  - Tubular reactor (liquid or gas phase)

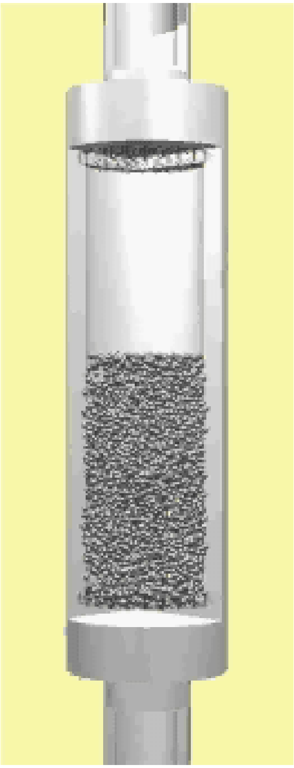
- Heterogeneous reactors:
  - Slurry, fixed-bed, moving-bed, fluidized-bed, bubble column…
  - Often due to the presence of solid catalyst
  - Pseudo-homogeneous modelling: use of apparent kinetics, which includes heat and mass transfer limitations

1. General introduction

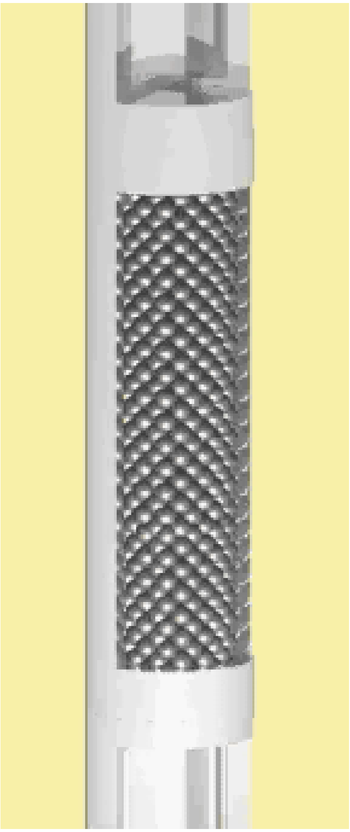
- Heterogeneous reactors:

Stirred-tank slurry

Fluidized-bed reactor



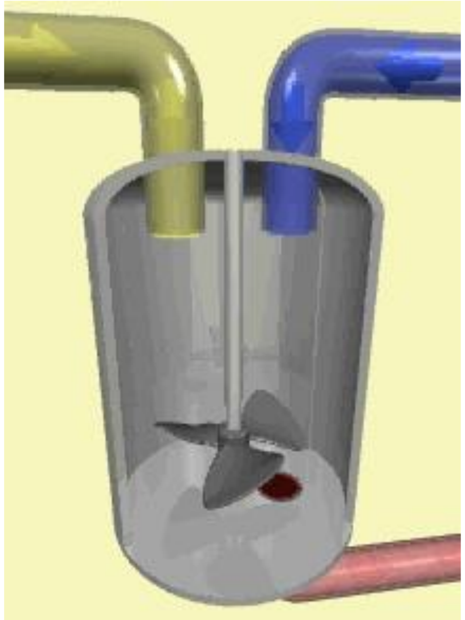
Fixed-bed reactor



1. General introduction

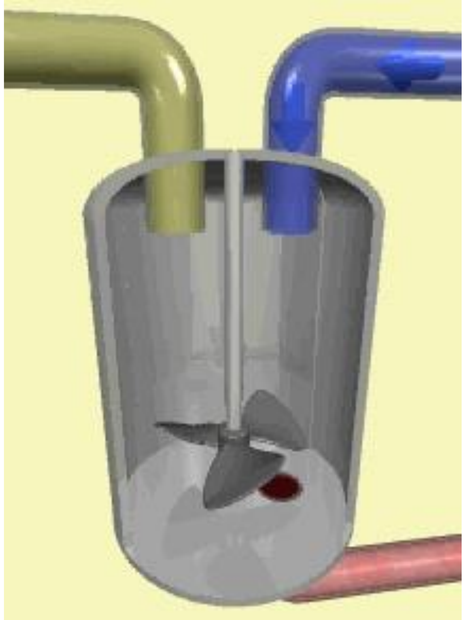
- Homogeneous reactors

Batch



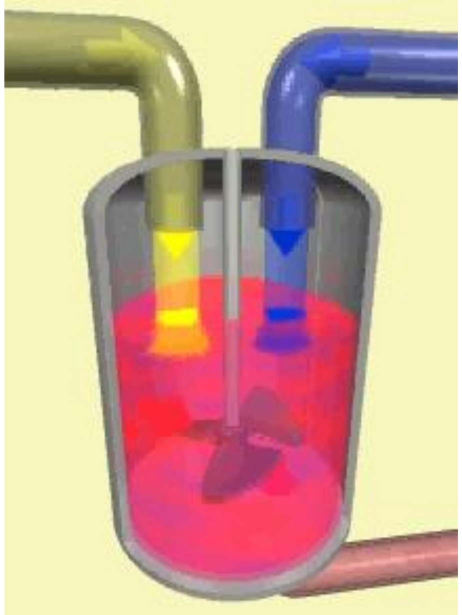
- Small production volumes
- Flexible equipment
- Complex reactions

Semi-batch



- Strongly exothermal reactions
- Equilibrium-limited reactions

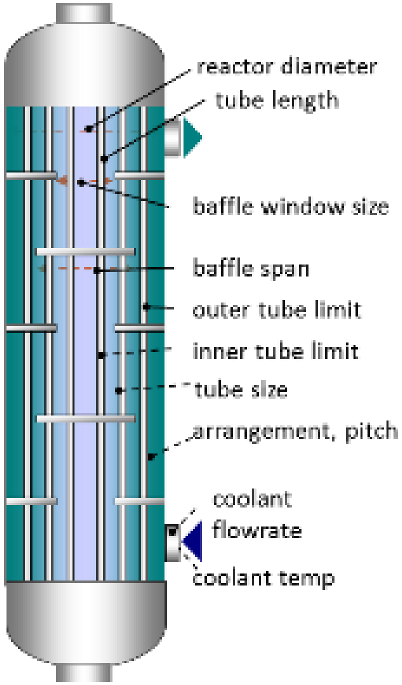
Continuous



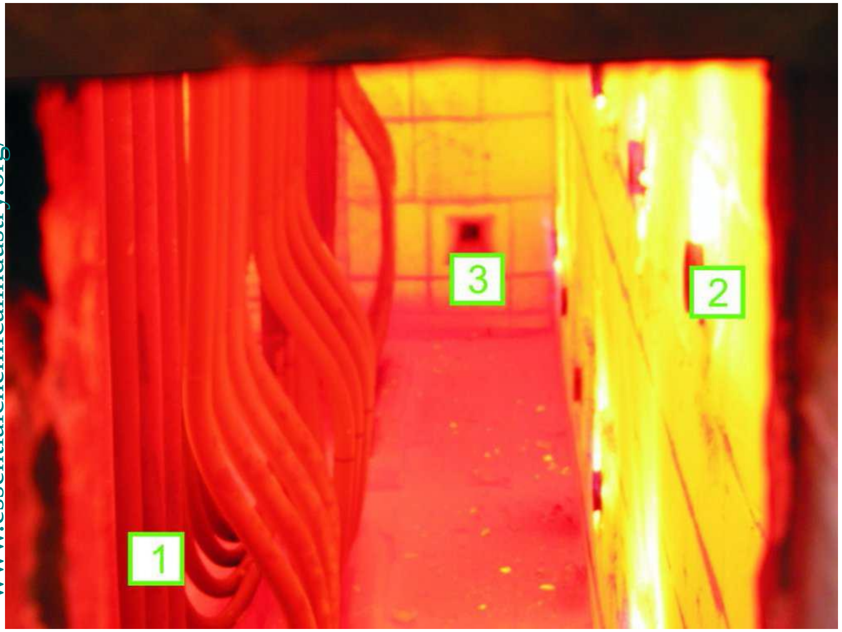
- Larger prod. volumes
- Continuous operation

1. General introduction

- Tubular reactors



www.psenterprise.com



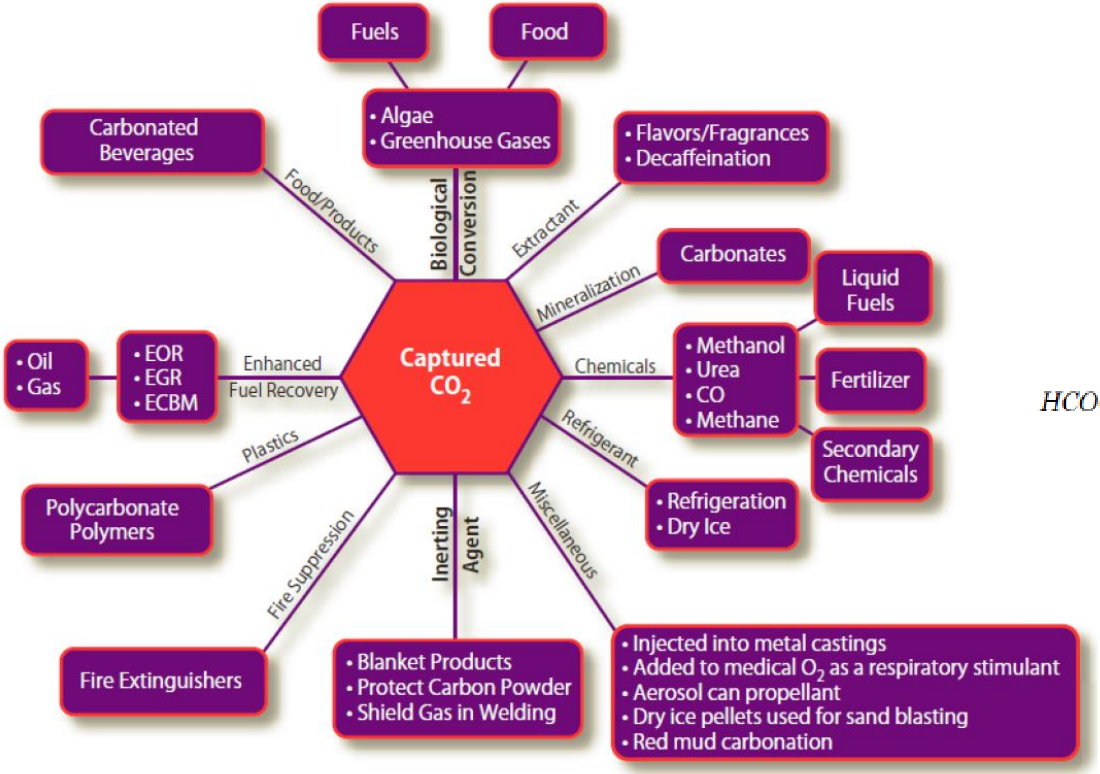
www.essentialchemicalindustry.org/

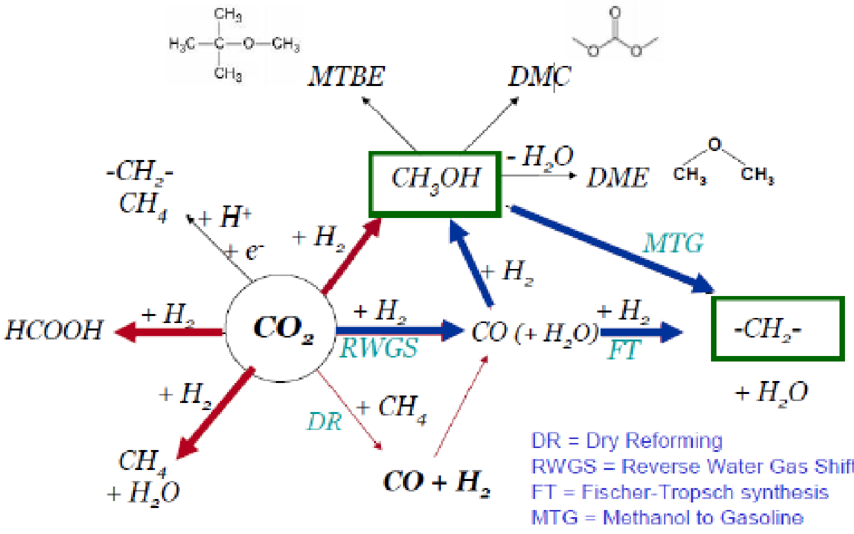
Tubular reactor for naphtha cracking

- Good heat management
- Reaction under vacuum or high pressure
- Continuous
- Fast reactions

2. CO_2 re-use reactors

- Chemical re-use pathways…



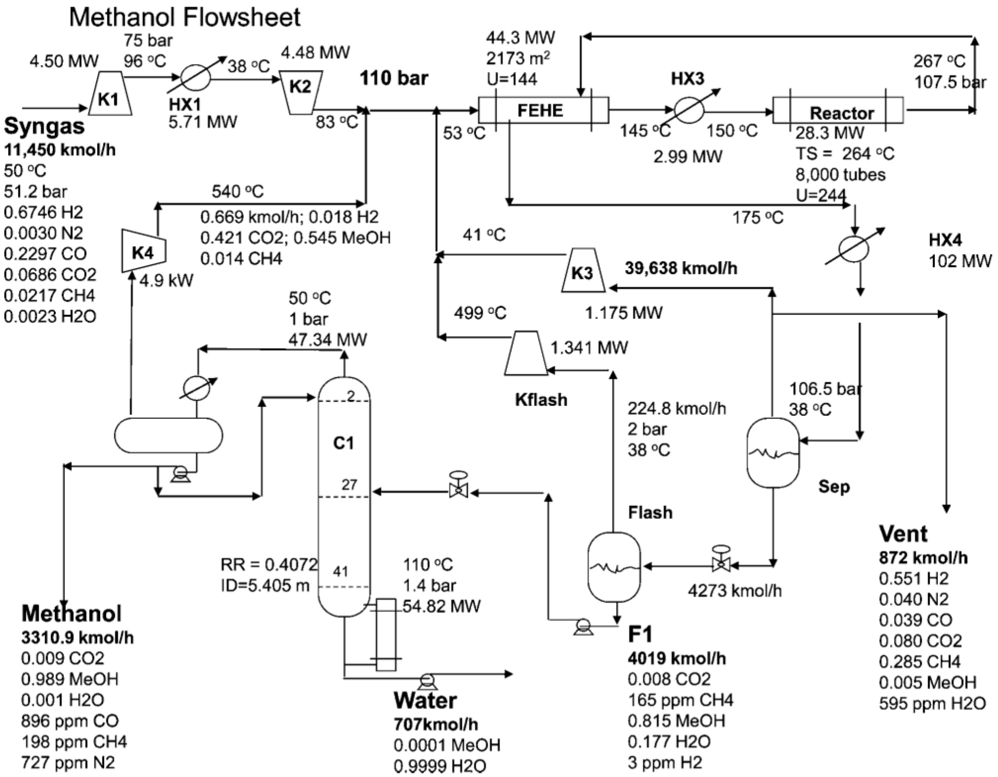


DR = Dry Reforming
RWGS = Reverse Water Gas Shif
FT = Fischer-Tropsch synthesis
MTG = Methanol to Gasoline

=> CO_2 can be a useful source of carbon, it's just that you need energy…

2.1 CO_2 to fuels

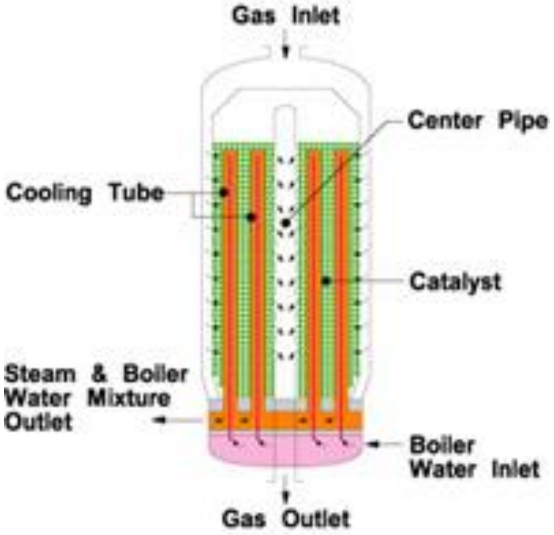
- Conventional methanol synthesis
  - Limiting step: thermodynamic equilibrium (25% H_2 conversion)
  - => High P, Low T
  - Gas recycle



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

2.1 CO_2 to fuels

- Conventional methanol synthesis



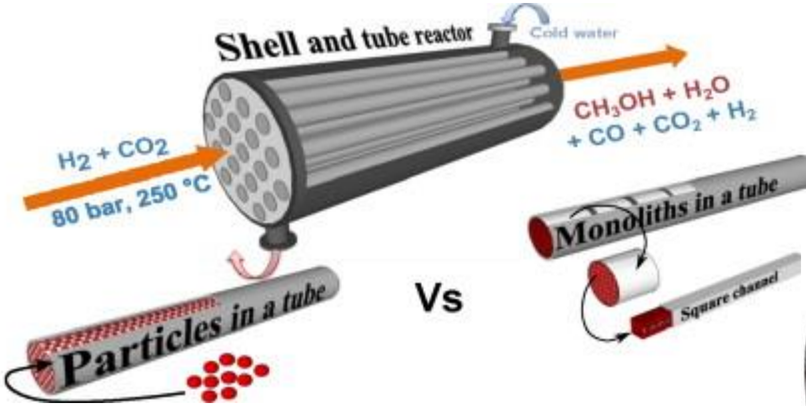
3,000 t/d methanol plant at Oman Methanol Company L.L.C., TOYO Engineering

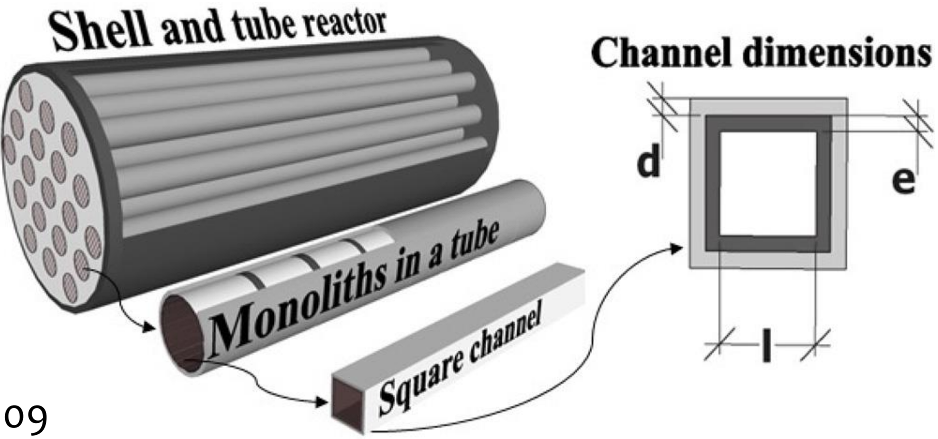
Haldor Topsoe, > 10 000 t/d

=> assuming syngas availability!

2.1 CO_2 to fuels

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

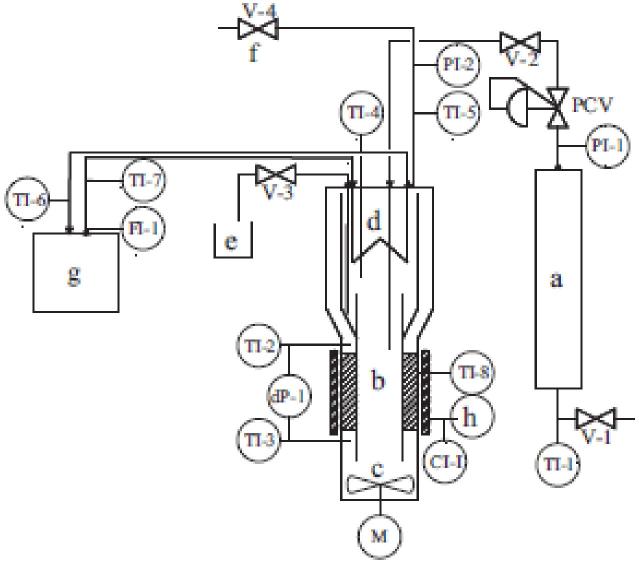




Arab S. et al., 2014. DOI: 10.1016/j.cherd.2014.03.009
Montebelli et al., 2013. DOI: 10.1016/j.cattod.2013.02.020

2.1 CO_2 to fuels

- 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

2.1 CO_2 to fuels

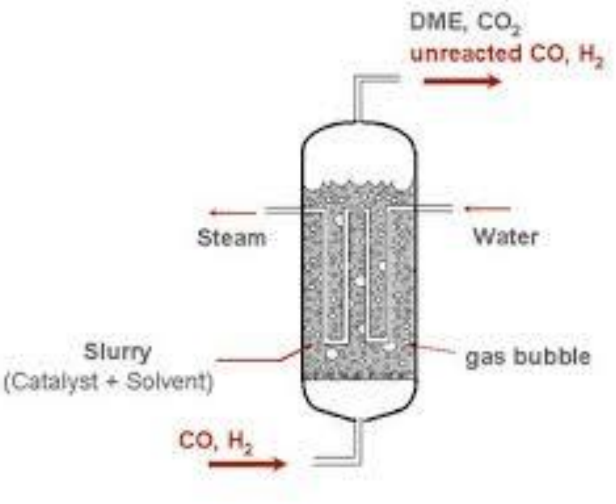
- Syngas
  - Water-gas shift
    - $CO_2 + H_2 \rightarrow CO + H_2O$
  - (Dry) Reforming
    - $CO_2 + CH_4 \rightarrow 2\ CO + 2\ H_2$
  - Co-electrolysis:
    - $H_2O \rightarrow H_2 + 0.5\ O_2$
    - CO2 -> $CO + 0.5\ O_2$

NETL, WGSR

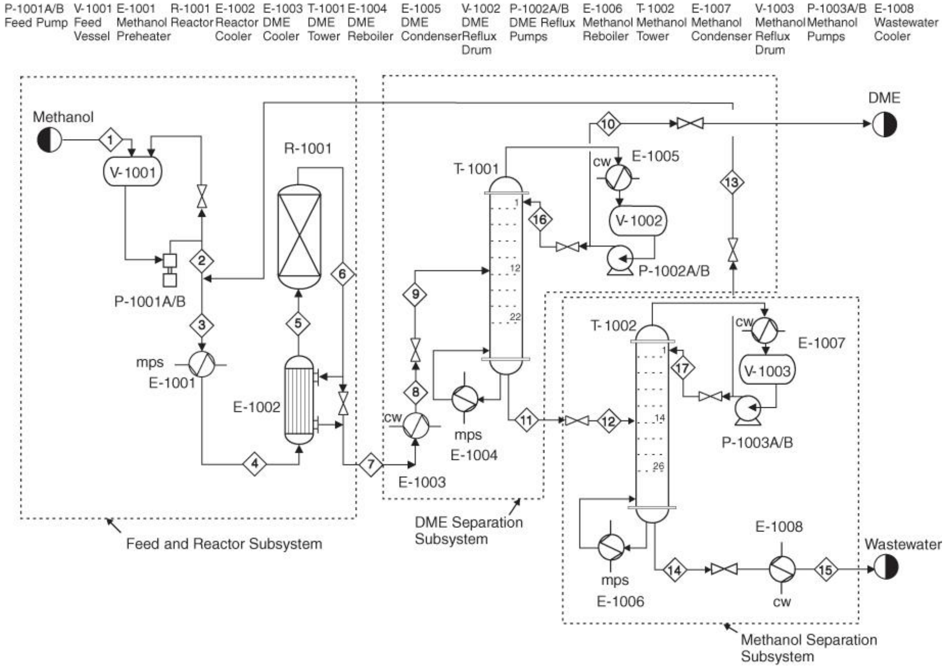
Wikipedia, SOEC

2.1 CO_2 to fuels

- 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

2.1 CO_2 to fuels

- Fischer-Tropsch fuels
  - Need for efficient heat removal
    - HT: 330-350°C
    - LT: 220-250°C
    - HT: Circulating fluidized bed
      => Sasol advanced synthol
    - LT: Multi-tubular fixed bed
      => Slurry reactor

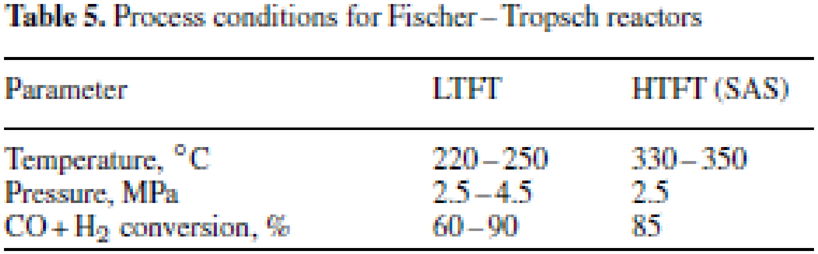
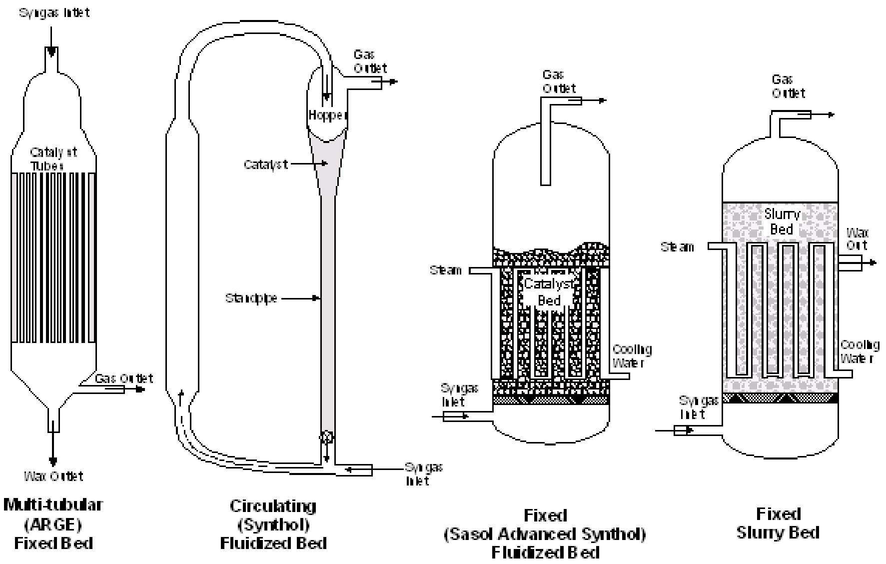


Table 5. Process conditions for Fischer – Tropsch reactors

Parameter	LTFT	HTFT (SAS)
Temperature, °C	220 – 250	330 – 350
Pressure, MPa	2.5 – 4.5	2.5
$CO + H_2$ conversion, %	60 – 90	85

Ullman encyclopedia, Coal liquefaction, 2005

Figure 2—Types of Fischer-Tropsch synthesis reactors



Multi-tubular (ARGE) Fixed Bed

Circulating (Synthol) Fluidized Bed

Fixed (Sasol Advanced Synthol) Fluidized Bed

Fixed Slurry Bed

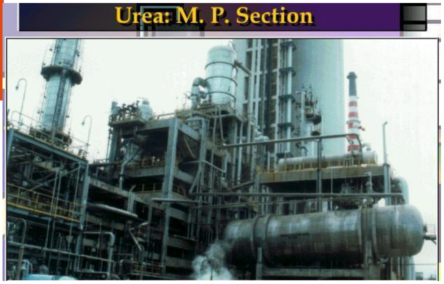
Source: P.L. Spath and D.C. Dayton, Preliminary screening—technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomas-derived syngas, National Renewable Energy Laboratory, NREL/TP-510-34929, December, 2003.

2.2 CO_2 to chemical building blocs

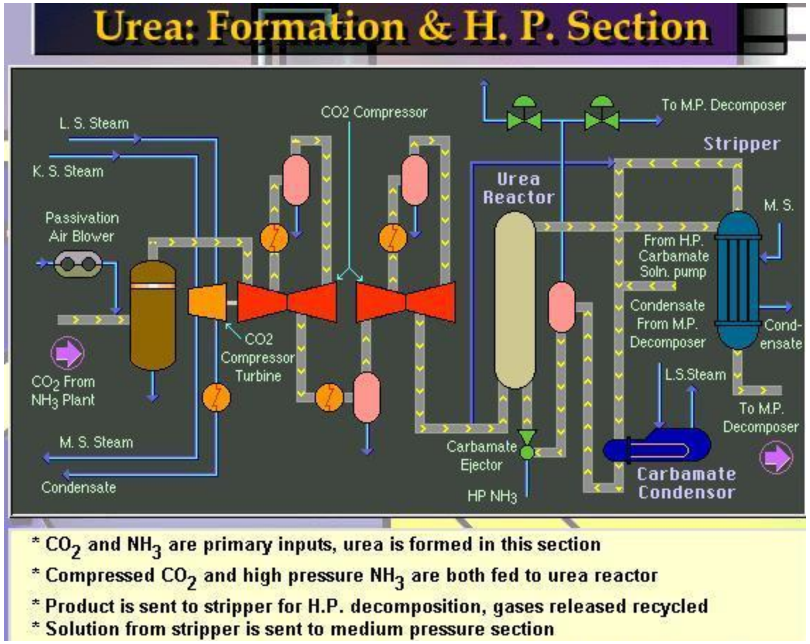
- Formic acid
  - Main route: CO + H_2O + methanol catalyst
  - Alternative: CO_2 + H_2
    - Reaction in liquid phase, need for basic conditions
    - Low TRL

Blair and Berman, University of Central Florida, WO 2014/089537 A1

2.2 CO_2 to chemical building blocs



- Urea
  - $2\ NH_3 + CO_2 \leftrightarrow H_2N\text{-}COONH_4$
  - $H_2N\text{-}COONH_4 \leftrightarrow (NH_2)_2CO + H_2O$



* CO_2 and NH_3 are primary inputs, urea is formed in this section

* Compressed CO_2 and high pressure NH_3 are both fed to urea reactor

* Product is sent to stripper for H.P. decomposition, gases released recycled

* Solution from stripper is sent to medium pressure section

Engineers Guide, http://enggyd.blogspot.be, 2016

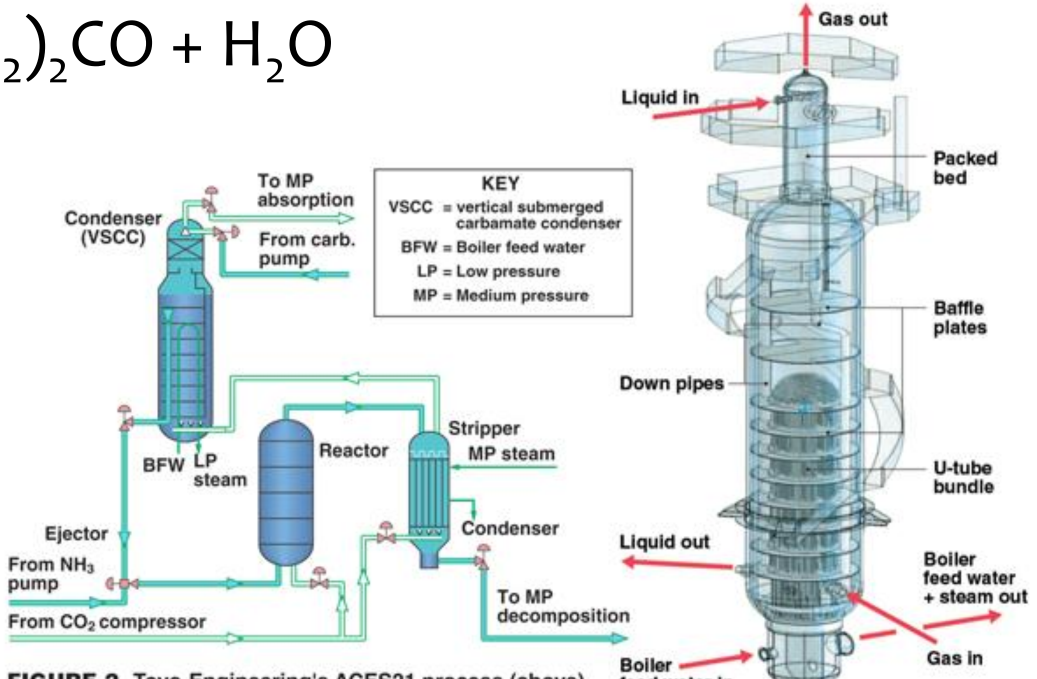


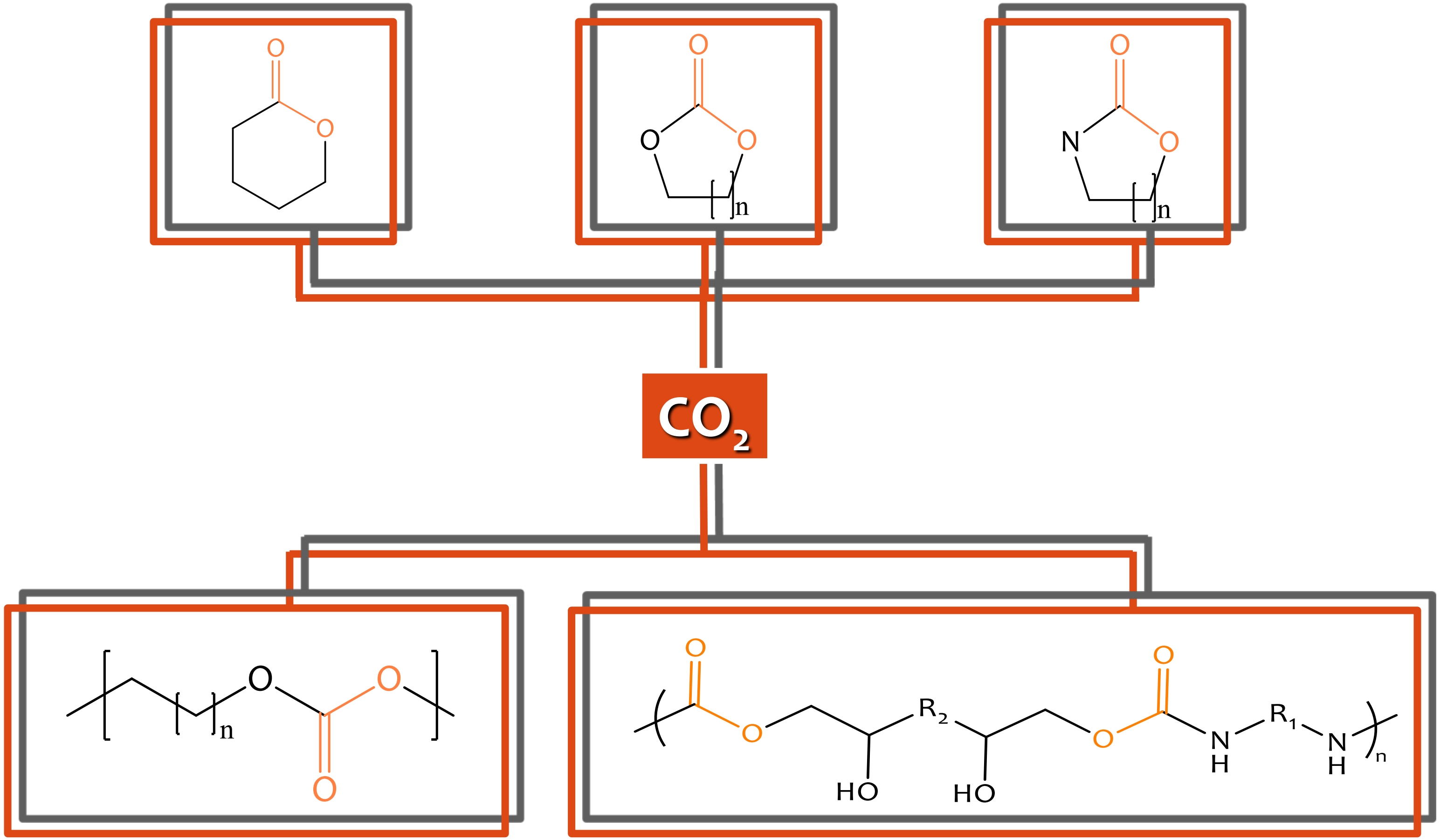
FIGURE 2. Toyo-Engineering's ACES21 process (above) for making urea integrates two condensers and a scrubber into a single condenser (right), which has a vertical, submerged carbamate-condensing section

2.2 CO_2 to chemical building blocs

- Mineralization
  - Formation of Ca and Mg carbonates

Recoval, 2015

2.3 CO_2 to monomers and polymers



Gennen & al., ***Chemsuschem***, 2015, 11, 1845-1849; Alves & al., **RSC Adv.**, 2015, 5, 53629-53636; Alves & *al.*, ***Catal. Sci. Technol.***, 2015, 5, 4636-4643, Poussard & al., ***Macromolecules***, 2016, accepted

2.3 CO_2 to monomers and polymers

- Polycarbonates
  - Usually using Phosgene => environment, safety!
  - Or diphenyl carbonate => High T needed!

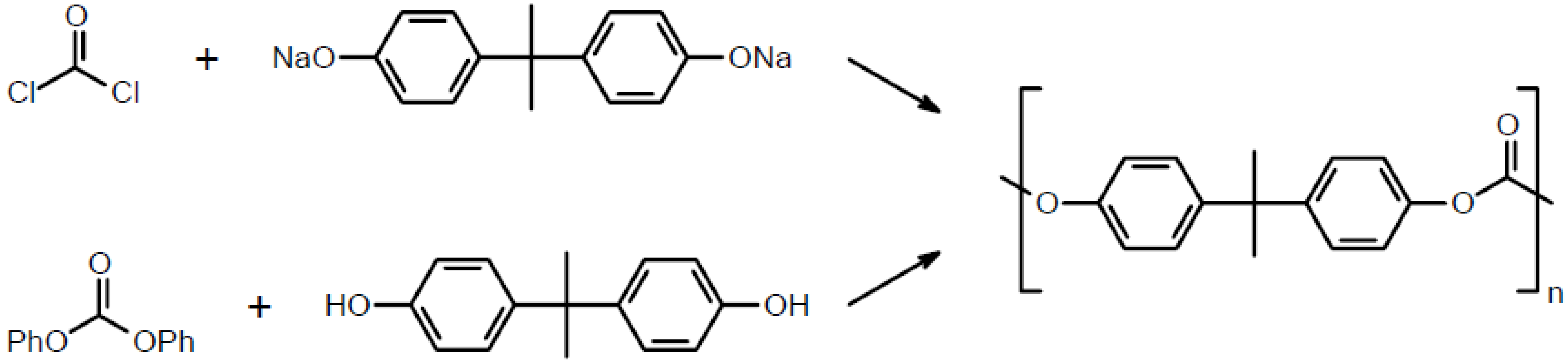


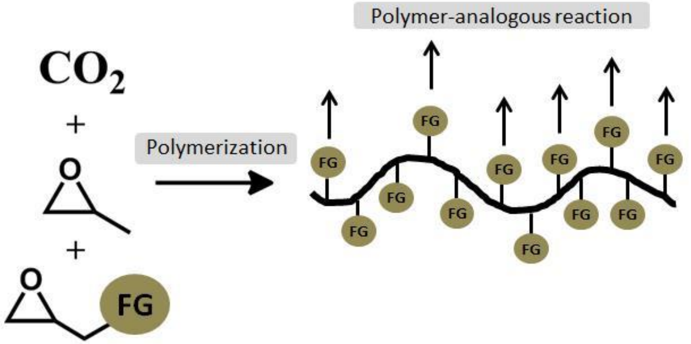
Figure 1-1. Industrial routes to poly(bisphenol-A carbonate).[1]

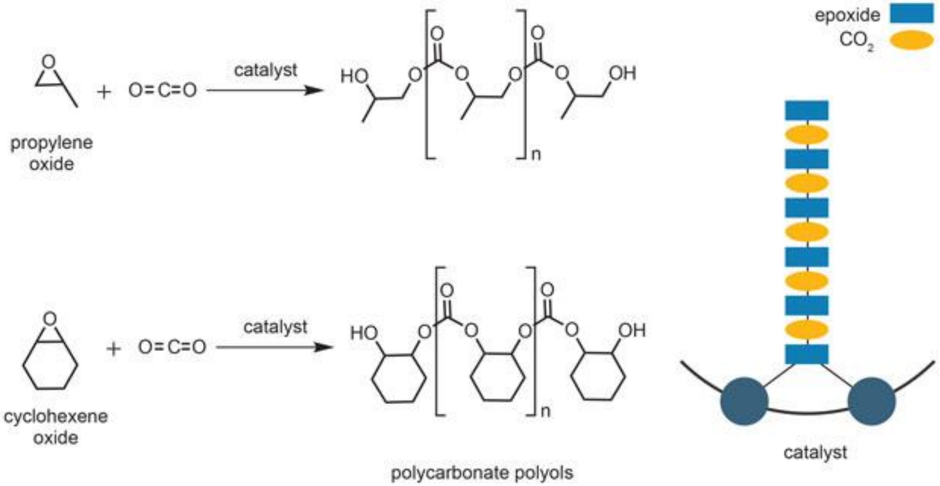
Wouter Johannes van Meerendonk, PhD thesis, U. of Eindhoven

2.3 CO_2 to monomers and polymers

- Polycarbonates

Prof. Frey, U. of Mainz, 2016

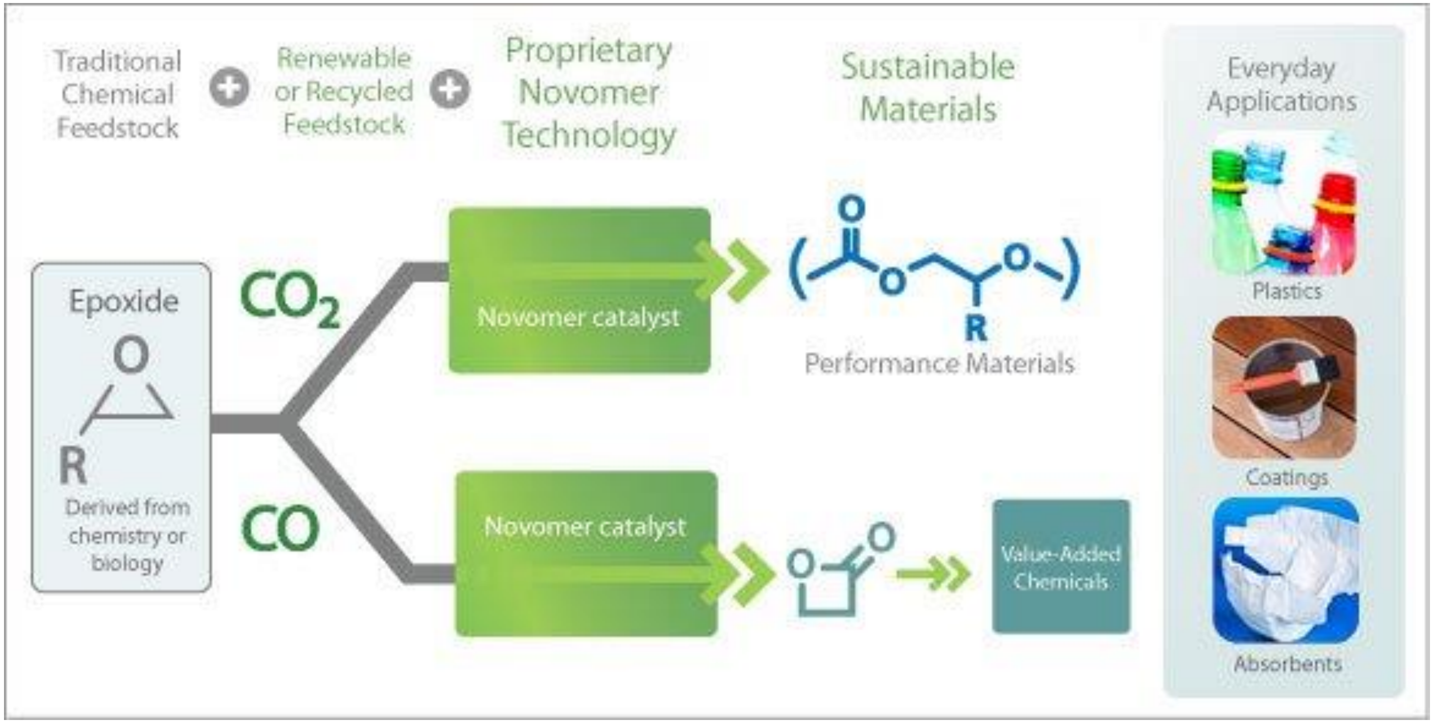




Econic's bimetallic catalysts produce polyols form a variety of epoxides © Royal Society of Chemistry

2.3 CO_2 to monomers and polymers

- Other polyols…
  - 40% CO_2 in the final plastic

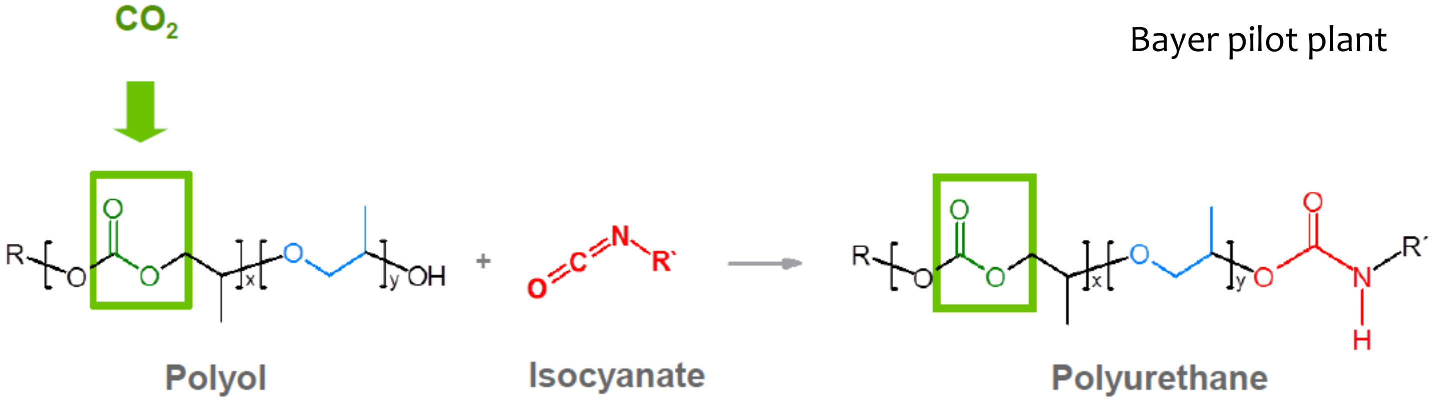


breakingenergy.com, 2014

2.3 CO_2 to monomers and polymers

- Polyurethanes
  - Polyols
  - Isocyanate
  - => “Dream material”

Bayer pilot plant



2.3 CO_2 to monomers and polymers

- Polyurethanes
  - 5000 t/a
  - 20% CO_2 in the final plastic

Little by little the customized reactor glides into the very heart of the new CO2-production-line at Bayer Material Sciences' site in Dormagen, Germany.
ChemEurope.com, June 2015

3. Related research topics at ULg

- Transfaculty platform for CO_2 re-use

Capture	Transformation	Processing	Pharma/biomaterials	Industrialization
Solvent degradation Modeling	Methanol Molecules Monomers Polymers	Solvent Extraction Synthesis Materials Foaming	Anti-solvent process Impregnation Capsuling Micronization Sterilisation	Intensification Process design Reactor design Modeling

Life Cycle Analysis

- ☐ About 20 researchers
- ☐ 50 research projects in less than 10 years
- ☐ Specific equipment, unique in Wallonia

LTPB Laboratoire de Technologie Pharmaceutique & Biopharmacie

CERM

Université de Liège

PEPs CHEMICAL ENGINEERING

3.1 Post-combustion CO_2 capture

Acceleration of solvent degradation to mimic industrial degradation

Pressure ?

Temperature ?

Flue gas composition ?

→

Mass transfer?

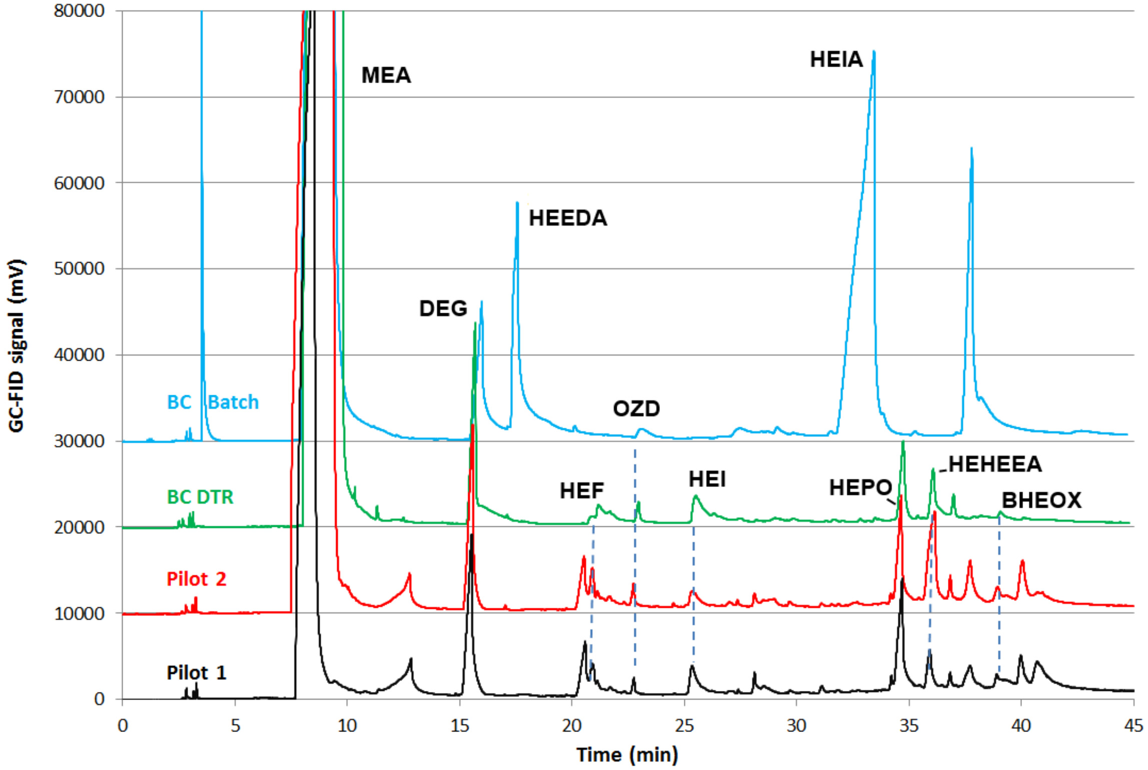
Metal ions ?

Inhibitors ?

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

3.1 Post-combustion CO_2 capture

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



=> Similar degradation products (GC spectra)!

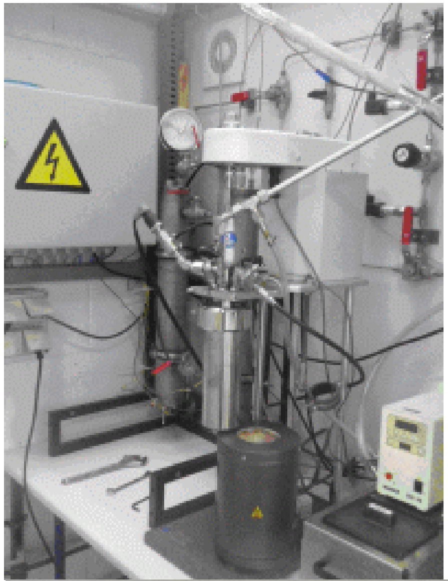
=> Identification and quantification of influence parameters

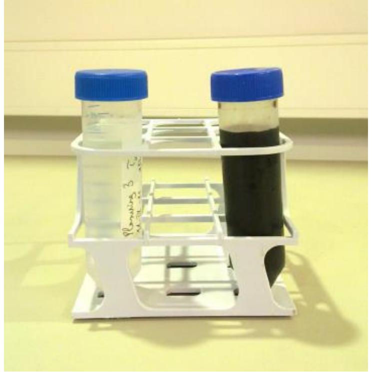
=> Kinetic model for degradation reactions

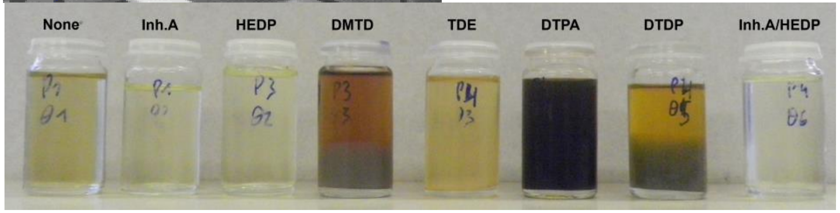
Léonard et al., 2014. DOI 10.1002/cjce.22094

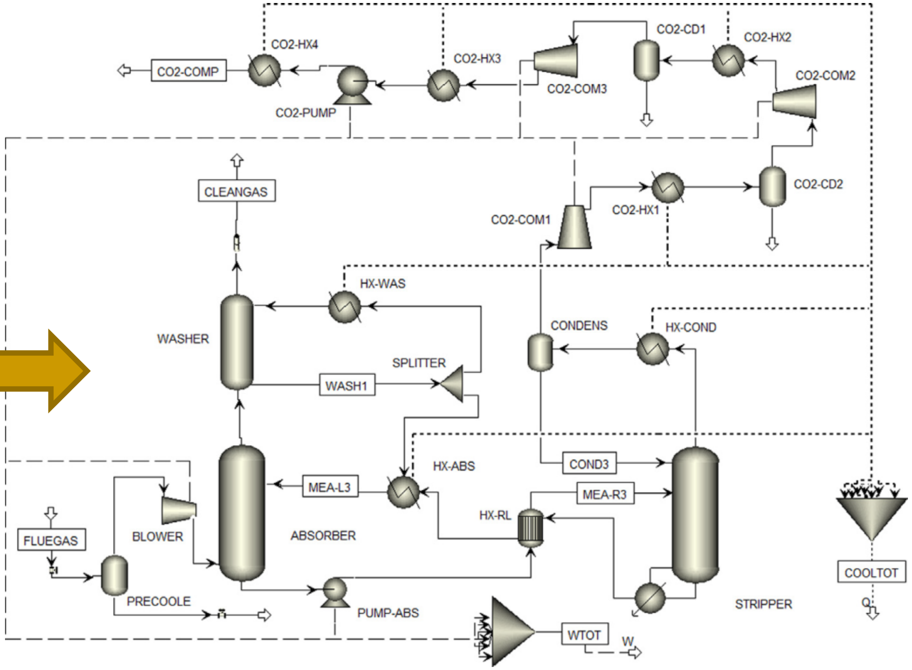
3.1 Post-combustion CO_2 capture

- Modelling of CO_2 capture with assessment of solvent degradation







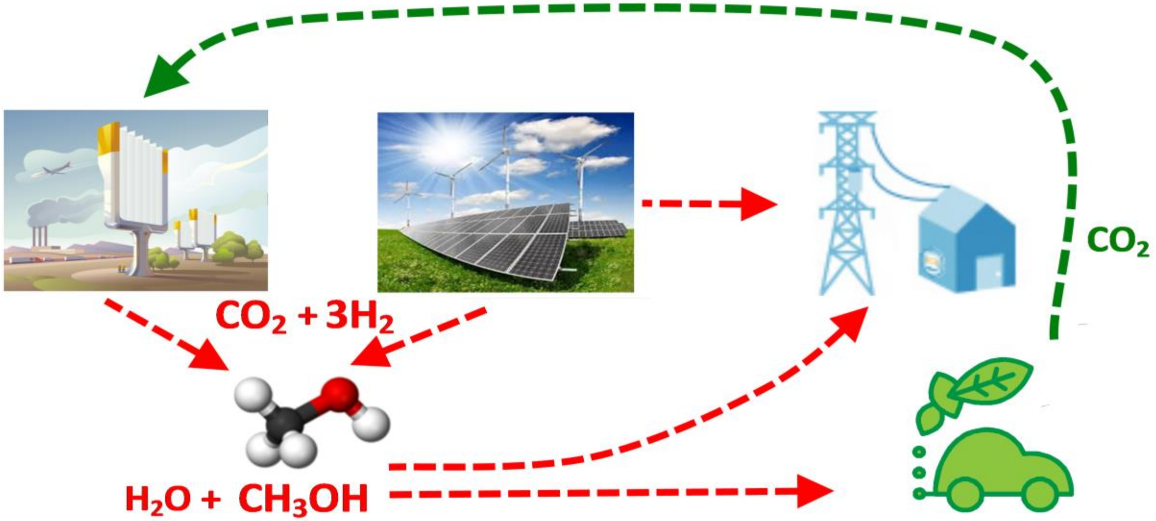


DOI: 10.1016/j.compchemeng.2015.05.003

DOI:10.1021/ie5036572

3.2 CO_2 re-use for Power-to-fuel

- Power-to-fuel
  - ❑ Long-term energy storage
  - ❑ => Addresses time imbalance generation – consumption of variable energy sources
  - ❑ CO_2 capture, electrolysis and fuel synthesis



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

3.2 CO_2 re-use for Power-to-fuel

- 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)

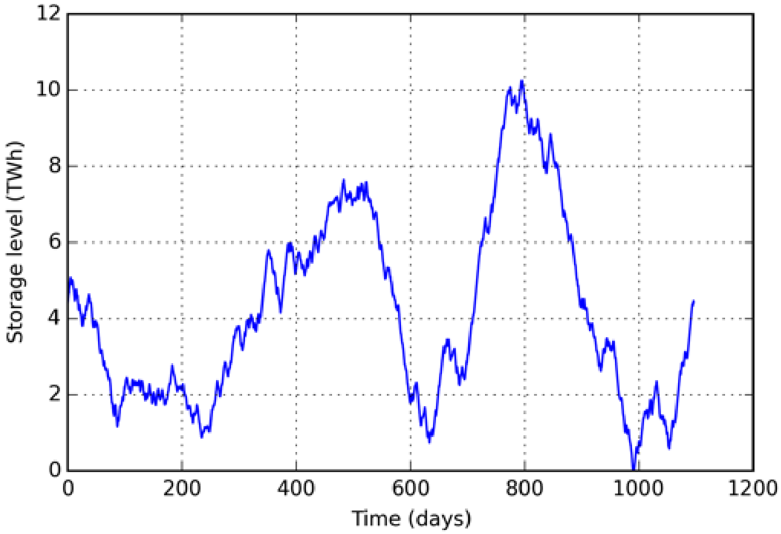
=> Cheap long-term energy storage

=> Easy transportation

Stena Teknik

3.2 CO_2 re-use for Power-to-fuel

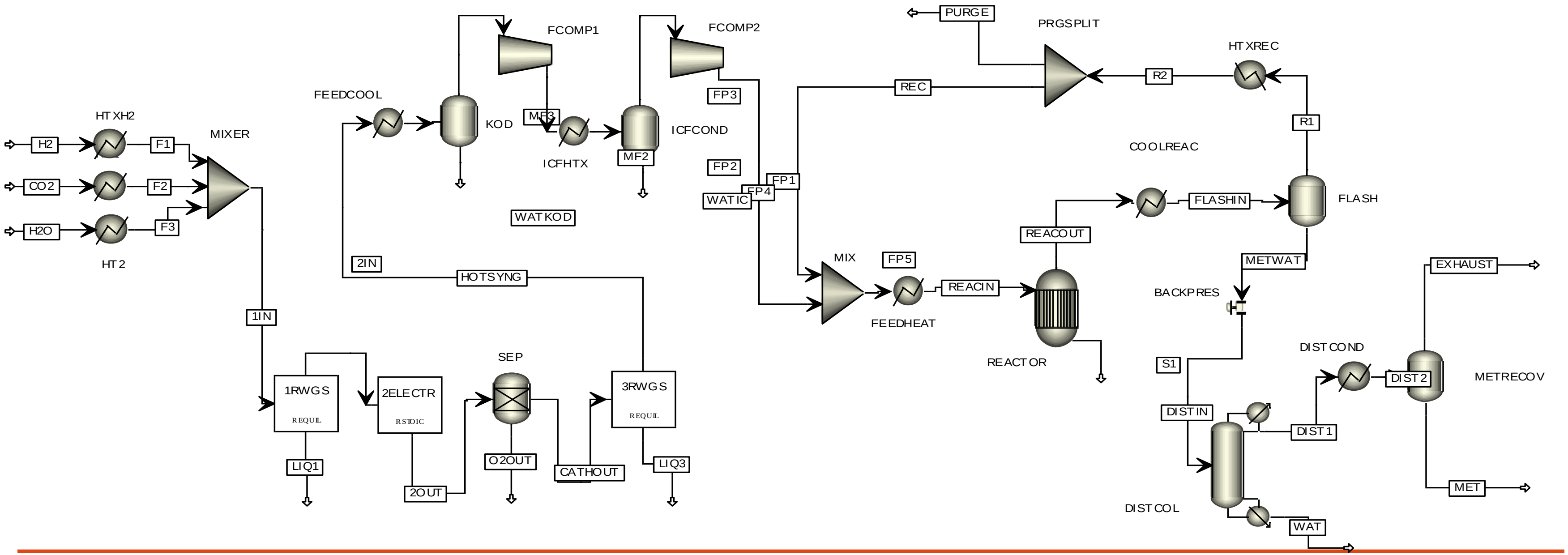
- Energy system analysis
  - Study of an electricity zone powered with 100% variable renewables and storage units
    - Second and minute scale for frequency regulation
    - Inter-seasonal scale: power-to-gas, power-to-fuel
    - Reasonable electricity cost (83.4 €/MWh)



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

3.2 CO_2 re-use for Power-to-fuel

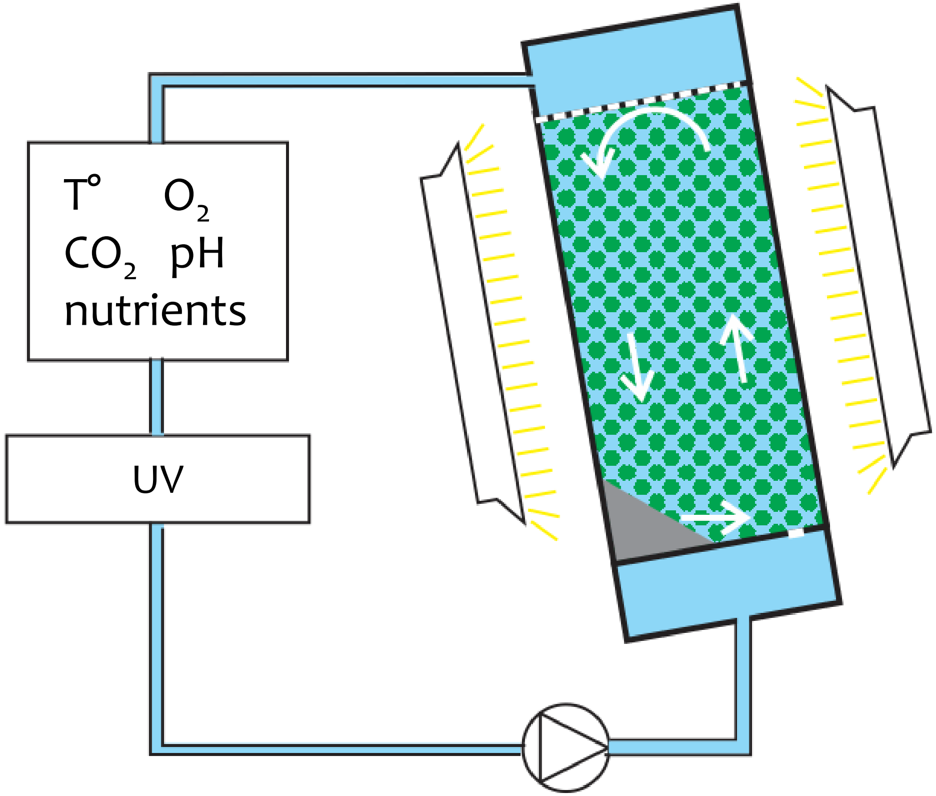
- Process integration and intensification
  - Low thermodynamic efficiency (50% conversion efficiency, LHV, Sunfire)
  - Modelling and experimental work (in progress)



Léonard et al. Design and evaluation of a high-density energy storage route with CO_2 re-use, water electrolysis and methanol synthesis. Computer aided chemical engineering, in press.

3.2 CO_2 reuse: microalgae culture

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



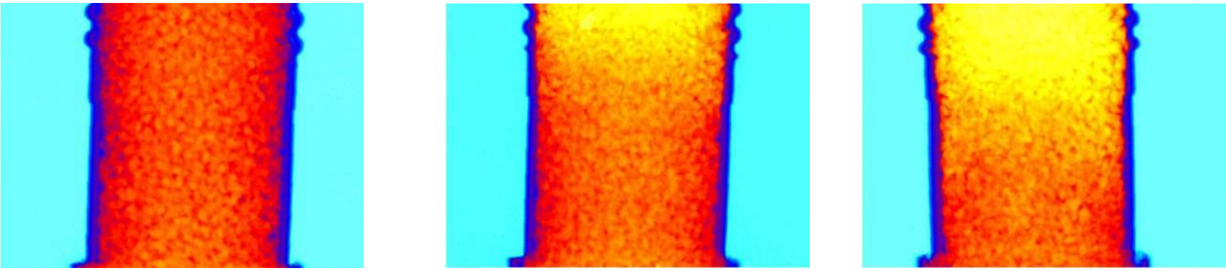
Photobioreactor **modelling** and **scale up** based on a **coupled characterisation** of :

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

3.3 Hydrodynamics in multiphase systems

- Solid waste and flue gas treatment
- Aerosol capture, VOC adsorption, CO_2 capture

VOC adsorption on activated carbon filter



Visualisation of adsorption front by X-ray microtomography

3.3 Hydrodynamics in multiphase systems

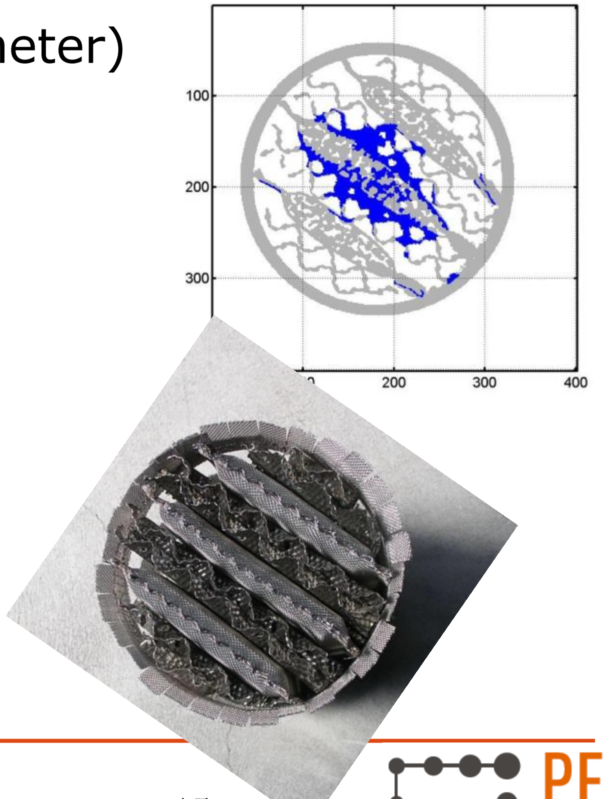
- Use and development of non invasive techniques to characterize phases distribution in multiphase systems and to visualize flows

✓ 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

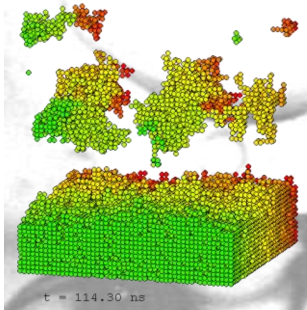


3.3 Hydrodynamics in multiphase systems

- 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

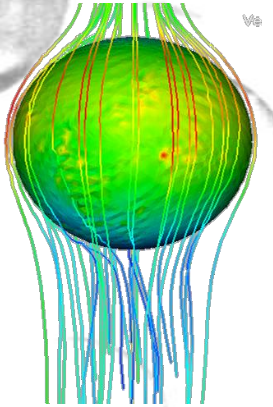
3.4 Solvent&reactive extraction: on all scales

Understanding for the fundamentals of mass and momentum transfer ...

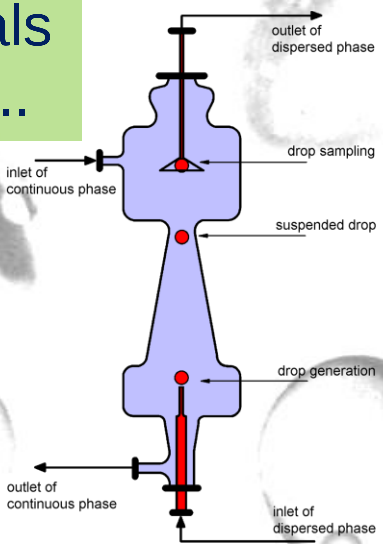


molecules

interfaces



drops



lab-cells for single drops

extraction column

… for the development and scale-up of new extraction processes

3.5 Life cycle analysis

- 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 …

3.6 Process modelling

- Solid streams modelling
- Biomass, wastes and sludge valorization
- Better use of raw materials: (Urban) mining processes, reverse metallurgy …

Conclusion

- Integration within PEPs
  - *Products, Environment and Processes*
  - Department of Chemical Engineering
  - 4 Professors + post-docs, PhDs, technical staff…

- G.leonard@ulg.ac.be

Thank your for your attention and welcome in Liège!

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

https://vimeo.com/95988841

Thank you for your attention!

g.leonard@ulg.ac.be

Université de Liège

PEPs
CHEMICAL
ENGINEERING