CO2 FUTURE at the University of Liège

Prof. Grégoire LEONARD
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
PEPs - Products, Environment and processes

Solid waste and flue gas treatment

CO₂ capture and reuse

Life Cycle Assessment

Hydrodynamics in multiphase systems

Department of Chemical Engineering

http://chemeng.ulg.ac.be

Solvent and reactive extraction

Mixing in (bio)reactors

Computer-Aided Process Engineering (CAPE)

Solid waste and flue gas treatment

CO₂ capture and reuse

Life Cycle Assessment

Hydrodynamics in multiphase systems

Department of Chemical Engineering

http://chemeng.ulg.ac.be

Solvent and reactive extraction

Mixing in (bio)reactors

Computer-Aided Process Engineering (CAPE)
Content

- Context
- CO$_2$ capture
- CO$_2$ re-use and power-to-fuel
- CO$_2$FUTURE platform
The Energy Transition has started…
… but is far from being over!

Global greenhouse gas emissions

Historical Emissions until today
Possible Emissions until 2030 according to INDCs

The Paris Agreement

1. Falling emissions “as soon as possible” (Art. 4.1)
Comparison point for least-cost 2°C target paths: 40Gt (517)

2. Net zero emissions 2050-2100 (=balance between anthropogenic emissions and sinks in second half of the century) (Art. 4.1)
European objectives

- Roadmap for low carbon economy in 2050

<table>
<thead>
<tr>
<th>Table 1: Sectoral reductions</th>
</tr>
</thead>
<tbody>
<tr>
<td>GHG reductions compared to 1990</td>
</tr>
<tr>
<td>Total</td>
</tr>
<tr>
<td>Sectors</td>
</tr>
<tr>
<td>Power (CO₂)</td>
</tr>
<tr>
<td>Industry (CO₂)</td>
</tr>
<tr>
<td>Transport (incl. CO₂ aviation, excl. maritime)</td>
</tr>
<tr>
<td>Residential and services (CO₂)</td>
</tr>
<tr>
<td>Agriculture (non-CO₂)</td>
</tr>
<tr>
<td>Other non-CO₂ emissions</td>
</tr>
</tbody>
</table>

European Commission communication, 2011, COM(2011) 112 final
Possible answers: Trias Energetica
What efforts are needed?

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

World CO₂ emissions abatement in the 450 Scenario (Bridge Scenario 2015-2040), IEA 2015, WEO special report, Energy & Climate Change
2. CO$_2$ Capture technologies & configurations
CO₂ capture configurations
Industrial processes

1. CO₂ not resulting from combustion
   - Cement plants
     - CaCO₃ → CaO + CO₂
     - High Temperature needed
     - Leilac: 21 M€, -60% CO₂
Industrial processes

1. CO₂ not resulting from combustion
   - Steel mills
     - Fermentation of CO into ethanol
     - Steelanol: 87 M€, -70% CO₂

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 CO₂ from combustion gases
   - 2 main focus at ULiège: Process modeling

- IC: -4%
- LVC: -14%
- Split flow: -4%
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 CO₂
- Oxidative degradation
  - Oxidation of amines with O₂ present in flue gas
- Degradation with other flue gas contaminants
  - SOₓ, NOₓ …

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

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$_2$
3. Remove C from the solid fuel by gasification
   - Great Plains Synfuel Plant (US), 8200 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
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\textsubscript{2} emissions
  - Biomass-enhanced CCS
  - Direct air capture

3. CO$_2$ re-use technologies
Technologies and products

- Carbon is root of organic chemistry and materials
  - => Potential of applications for CO₂ 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

![Graph showing energy density of various fuels](image)
Power-to-fuel

- CO₂ 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

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Types of reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phases</td>
<td>Homogeneous (1 phase)</td>
</tr>
<tr>
<td></td>
<td>Heterogeneous (2, 3 or 4 phases)</td>
</tr>
<tr>
<td>Stoichiometry</td>
<td>Simple (1 reaction)</td>
</tr>
<tr>
<td></td>
<td>Complex (multiple reactions, side reactions…)</td>
</tr>
<tr>
<td>Thermodynamics</td>
<td>Irreversible</td>
</tr>
<tr>
<td></td>
<td>Equilibrium</td>
</tr>
<tr>
<td>Kinetics</td>
<td>Limiting factors are physical</td>
</tr>
<tr>
<td></td>
<td>Limiting factors are chemical</td>
</tr>
<tr>
<td>Heat balance</td>
<td>(Strongly) Endothermal ($\Delta H &gt; 0$)</td>
</tr>
<tr>
<td></td>
<td>(Strongly) Exothermal ($\Delta H &lt; 0$)</td>
</tr>
</tbody>
</table>
Power-to-DME

- DME (CH$_3$OCH$_3$)
  - 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
Power-to-methanol

- Conventional methanol synthesis
  - Limiting step: thermodynamic equilibrium (25% $\text{H}_2$ conversion) + exothermal reaction
  - $\Rightarrow$ High P, Low T, large gas recycle
  - $\Rightarrow$ Shell & Tubes reactor

Haldor Topsoe, > 10 000 t/d
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/jcej.2014.10.059
Power-to-methanol

- Novel methanol reactor design
  - Intensification of synthesis reactor for CO$_2$ reduction to methanol

**Diagram:**
- ACM Reactor
- Distillation column
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$_2$FUTURE Platform at ULiege

www.chemeng.uliege.be/CO2Future
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

<table>
<thead>
<tr>
<th>Process</th>
<th>Profit (USD/ton of CO₂)</th>
<th>Profit (USD/ton of product)</th>
<th>Market Share of Product</th>
<th>TRL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enhanced Oil Recovery</td>
<td>-10.79</td>
<td>N/A</td>
<td>4.276%</td>
<td>9</td>
</tr>
<tr>
<td>Concrete</td>
<td>9503.48</td>
<td>95.03</td>
<td>0.261%</td>
<td>5</td>
</tr>
<tr>
<td>Syngas Production</td>
<td>-81.45</td>
<td>-388.78</td>
<td>Naphta: 0.072%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Diesel: 0.023%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dry Reforming: 4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fischer-Tropsch: 6</td>
<td></td>
</tr>
<tr>
<td>Microalgae Production</td>
<td>-452.02</td>
<td>-1674.15</td>
<td>0.275%</td>
<td>5</td>
</tr>
<tr>
<td>Methanol Production</td>
<td>-191.74</td>
<td>-333.46</td>
<td>1.932%</td>
<td>7</td>
</tr>
<tr>
<td>Polymer Production</td>
<td>1377.08</td>
<td>661.74</td>
<td>7769.067%</td>
<td>8</td>
</tr>
<tr>
<td>Urea Production</td>
<td>39.91</td>
<td>29.56</td>
<td>2.442%</td>
<td>9</td>
</tr>
</tbody>
</table>

=> 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.”
Many thanks to the team…
Thank you for your attention!

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

https://vimeo.com/95988841
CO₂ Value Europe

■ Who’s in?

13 Multinational Industry Leaders
Chemicals: Solvay, Total
Equipment manufacturing: CMI Group
Industrial gases: Air Liquide, Praxair, SIAD
Cement: Cemex, HeidelbergCement, Lafarge-Holcim
Lime: Carmeuse, Lhoist
Energy and Power: Engie, Total
Waste Management: Suez

5 Specialized SME's
Atmostat, Carbon 8 Systems, Carbon Recycling Int'l, Econic, Sunfire

4 Clusters
Axelera, Dechema, GreenWin, Port of Antwerp

7 Research Organisations
ECN, IFP-EN, ICIQ, SINTEF, University of Sheffield, VITO, VTT

+ ULiège!