Carbon capture, re-use and storage technologies: Research results at the University of Liège

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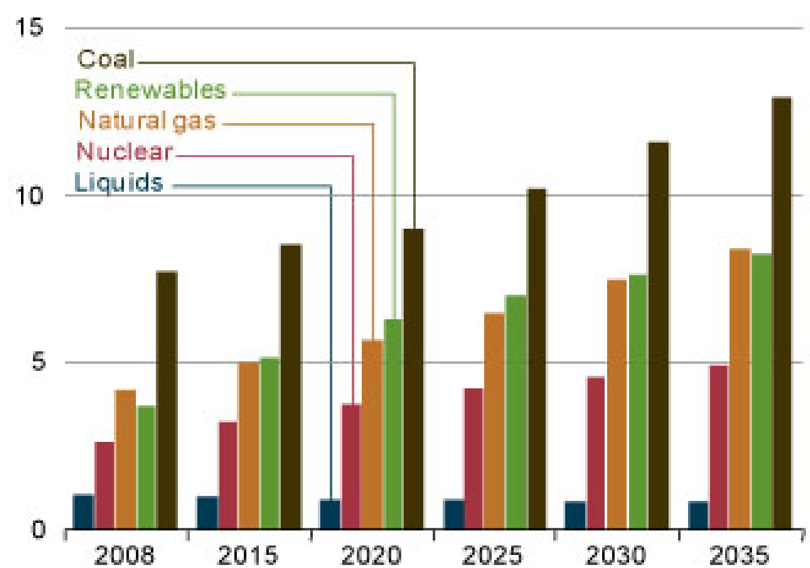
Lenfest Center for Sustainable Energy, Group meeting, November 2014

CO_2 capture, re-use and storage as a possible answer to

- Environmental issues
- Growing energy demand and large contribution of fossil fuels

Figure 75. World net electricity generation by fuel, 2008-2035
(trillion kilowatthours)



International Energy Outlook 2011

Outline

1. CO_2 capture, re-use and storage

2. Experimental study of solvent degradation

3. Simulation of the CO_2 capture process with assessment of solvent degradation

4. Conclusion and perspectives

1. CO_2 capture

1. CO_2 Capture

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CO_2 capture = technology existing for decades

=> Commercial capture of CO_2

=> Which uses?

1999 Malaysia
(200 T/D Max)
Urea Production

2005 Japan
(330 T/D max)
General Use

2006 India (2 locations)
(450 T/D x 2 units)
Urea Production

But…

- Relatively low scale => scale is the main challenge!
- Capture cost very high! Power plant efficiency reduced by 33%!

1. CO_2 Capture

3 main technologies:

1. Capture the CO_2 that is formed during the combustion in flue gas (separation between CO_2 and flue gas = mainly N_2)

=> Decarbonisation of flue gases **= Post-combustion capture**

2. Capture the C out of the fuel (separation between CO_2 and H_2 after solid fuel gazification)

=> Decarbonisation of fuel **= Pré-combustion capture**

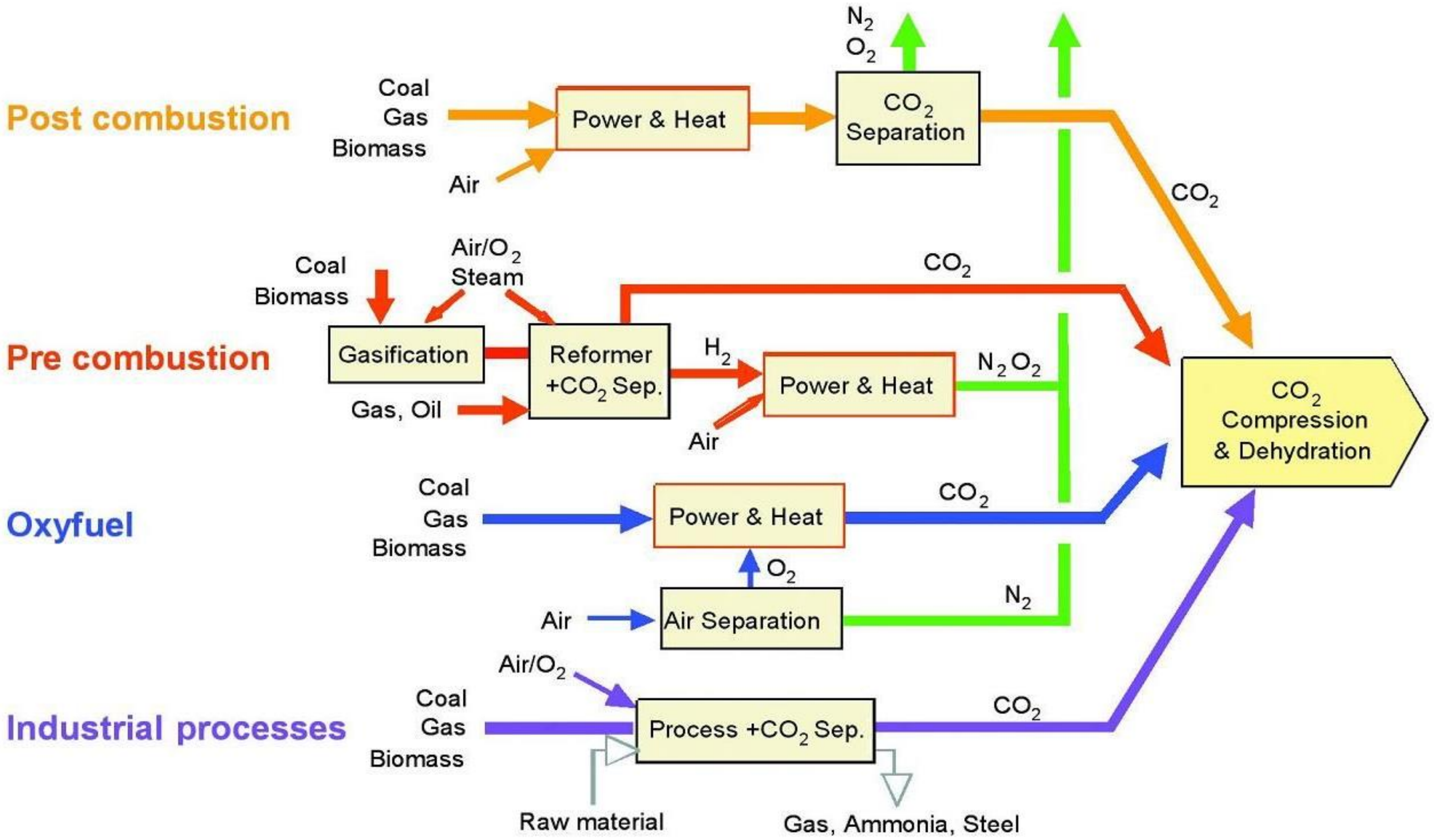
3. Burn the fuel with pure oxygen (separation between CO_2 and water)

=> **Oxyfuel combustion**

Source : Mathieu, 2011

1. CO_2 Capture

Overview of CO2 capture processes and systems



SRCCS Figure TS-3

1. CO_2 Capture

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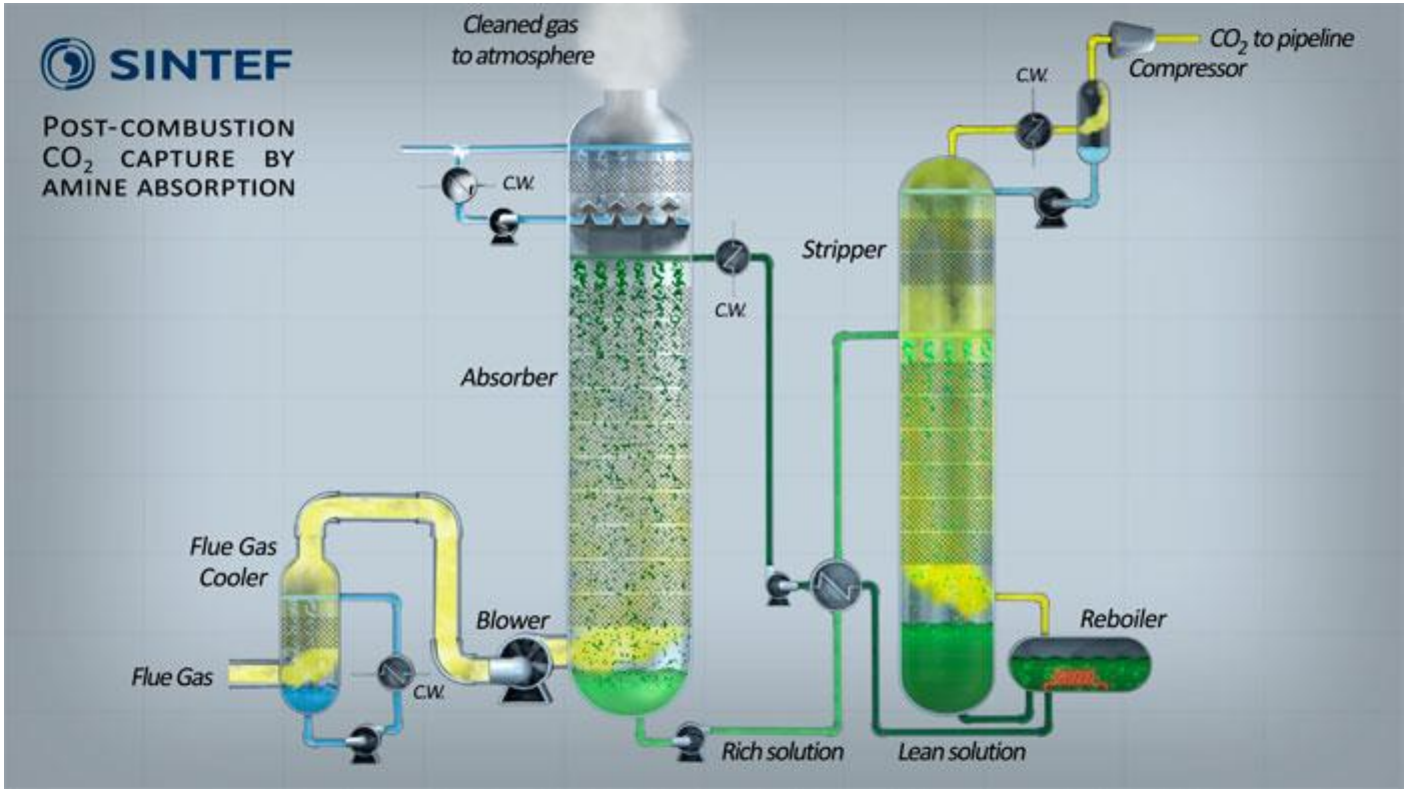
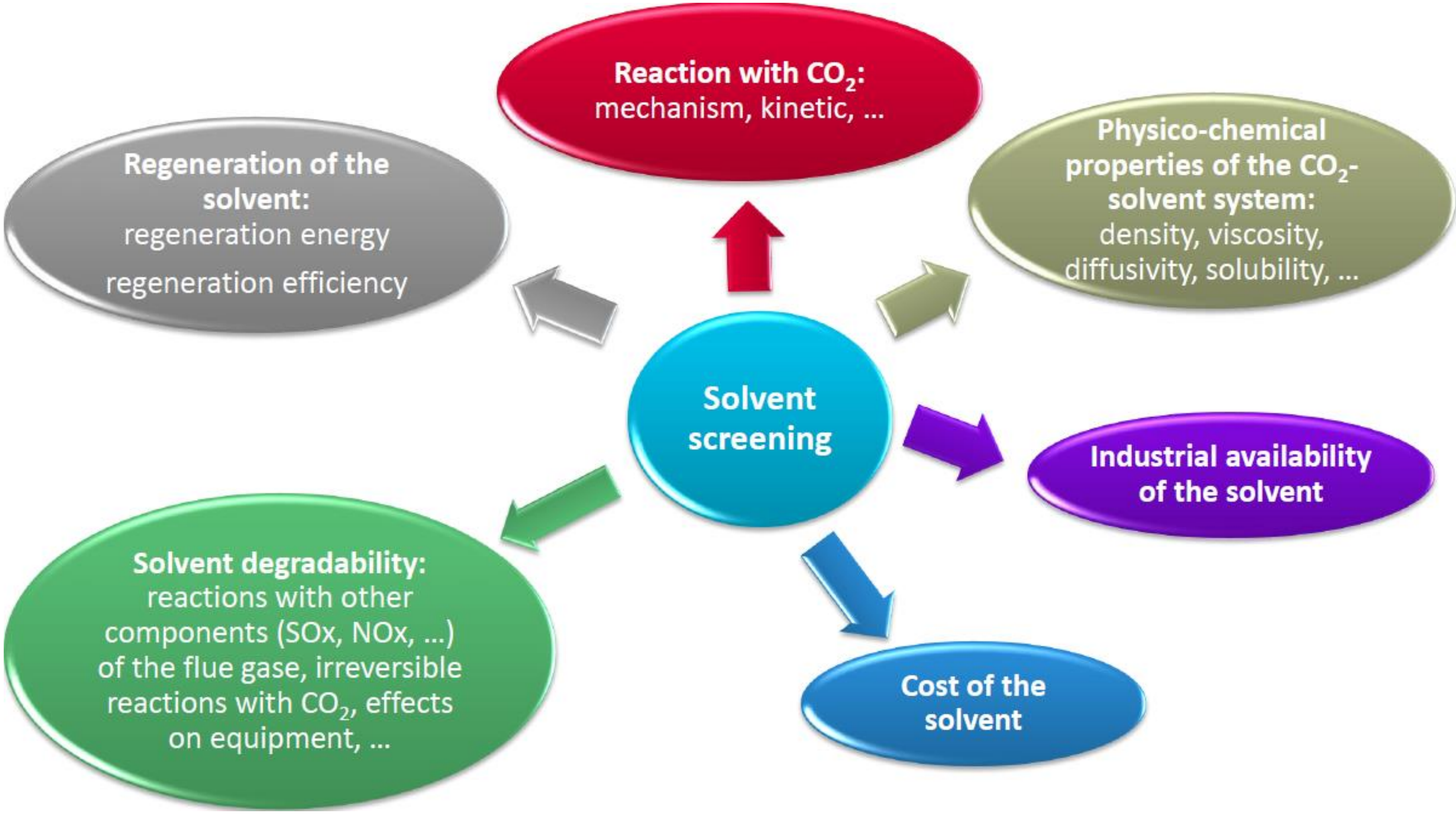
Post-combustion Capture



1. CO_2 Capture

Chemical solvent characteristics:

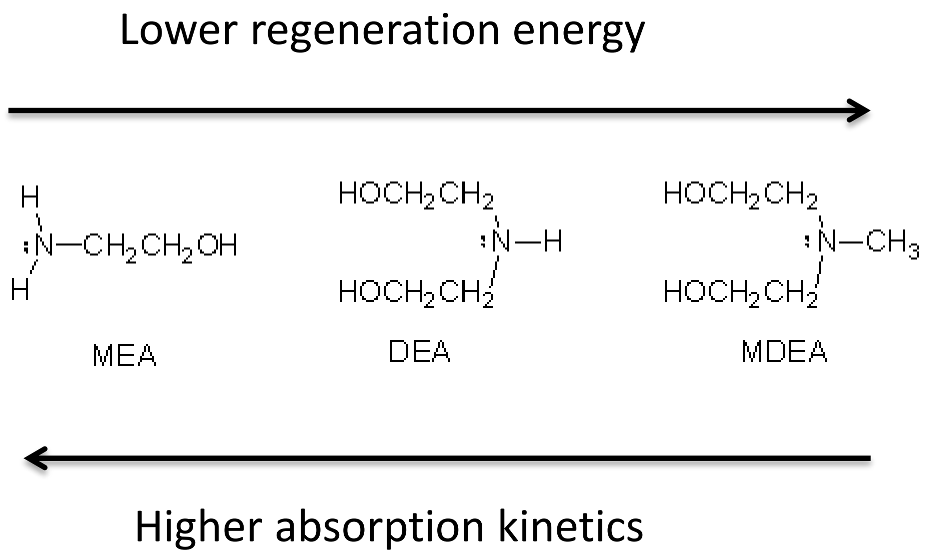


Source : Lionel Dubois, UMons, 2011

1. CO_2 Capture

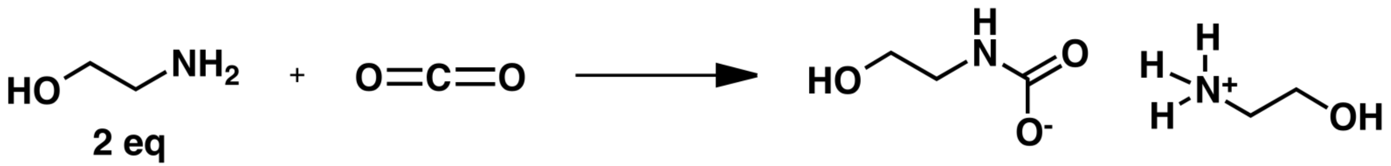
Usually: Amines

=> primary, secondary or tertiary (MEA, DEA, MDEA)



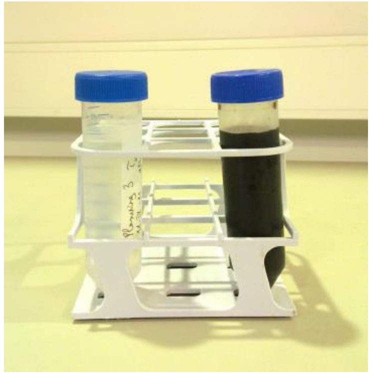
1. CO_2 Capture

Benchmark solvent: Monoethanolamine 30 wt% in water



Advantages: High absorption kinetics, availability, cost, mature

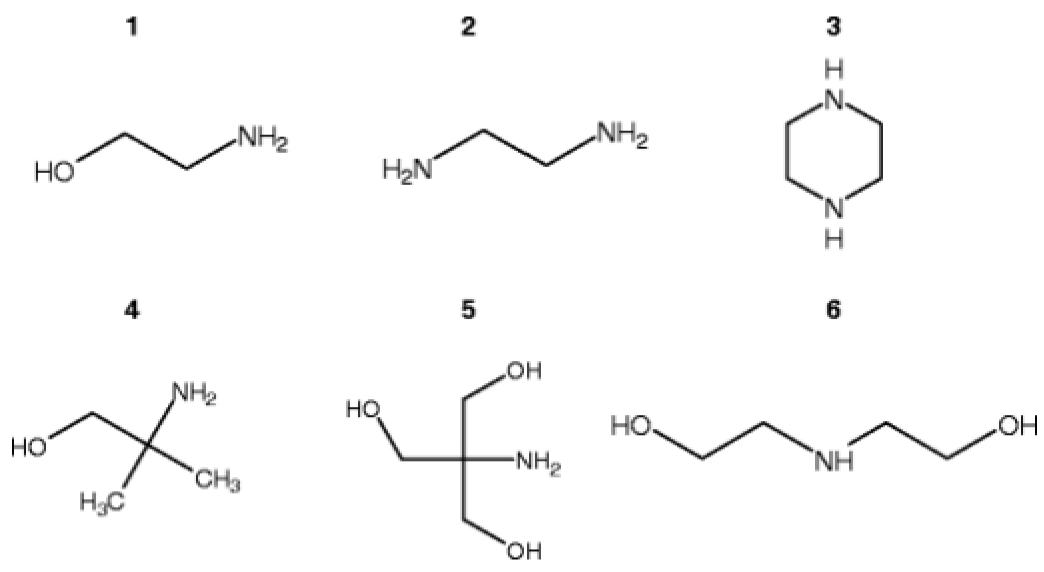
Drawbacks: High regeneration energy, degradation, corrosion



1. CO_2 Capture

MEA, DEA and some alternatives:

- 1 = ethanolamine, MEA
- 2 = ethylenediamine
- 3 = piperazine (PZ)
- 4 = 2-amino-2-methyl-1-propanol (AMP);
- 5 = 2-amino-2-(hydroxymethyl)propane-1,3-diol (Tris);
- 6 = 2,2'-iminodiethanol (diethanolamine, DEA)
- …

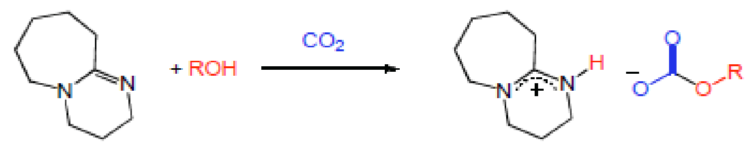


Source : Jackson P, Fisher KJ, Attalla MI - J. Am. Soc. Mass Spectrom. (2011)

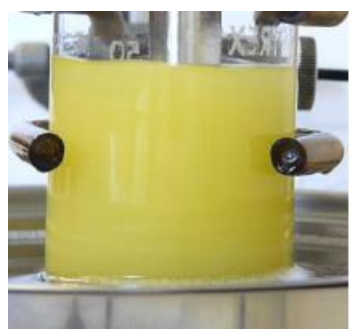
1. CO_2 Capture

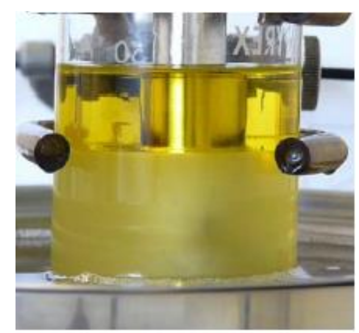
Other alternatives:

- Chilled Ammonia
- Potassium Carbonate: K_2CO_3
- Amino-acids (non volatile, O_2 resistant)
- Organic liquids (no water)



- Demixing solvents



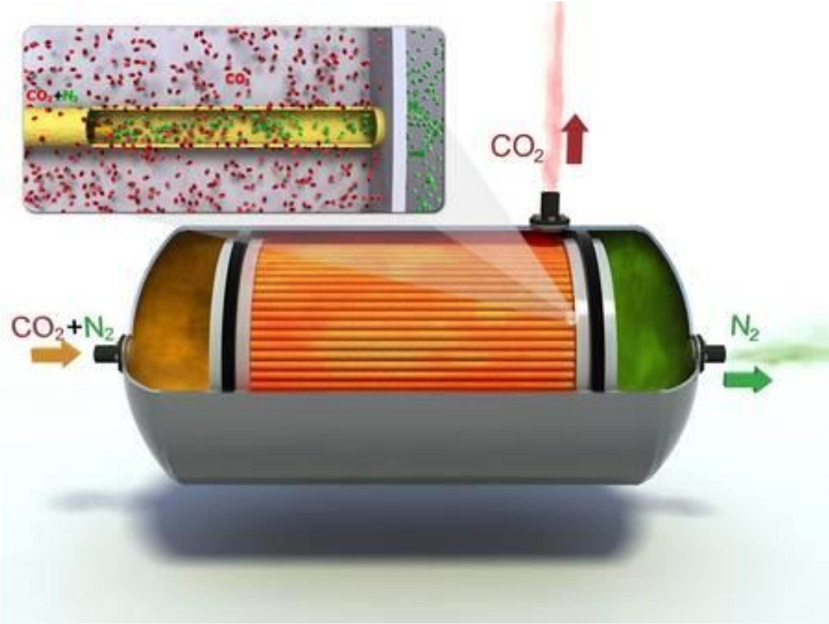


=> Looking for the holy grail…

Source : Heldebrant et al., 2009; Raynal et al., IFP, 2011

1. CO_2 Capture

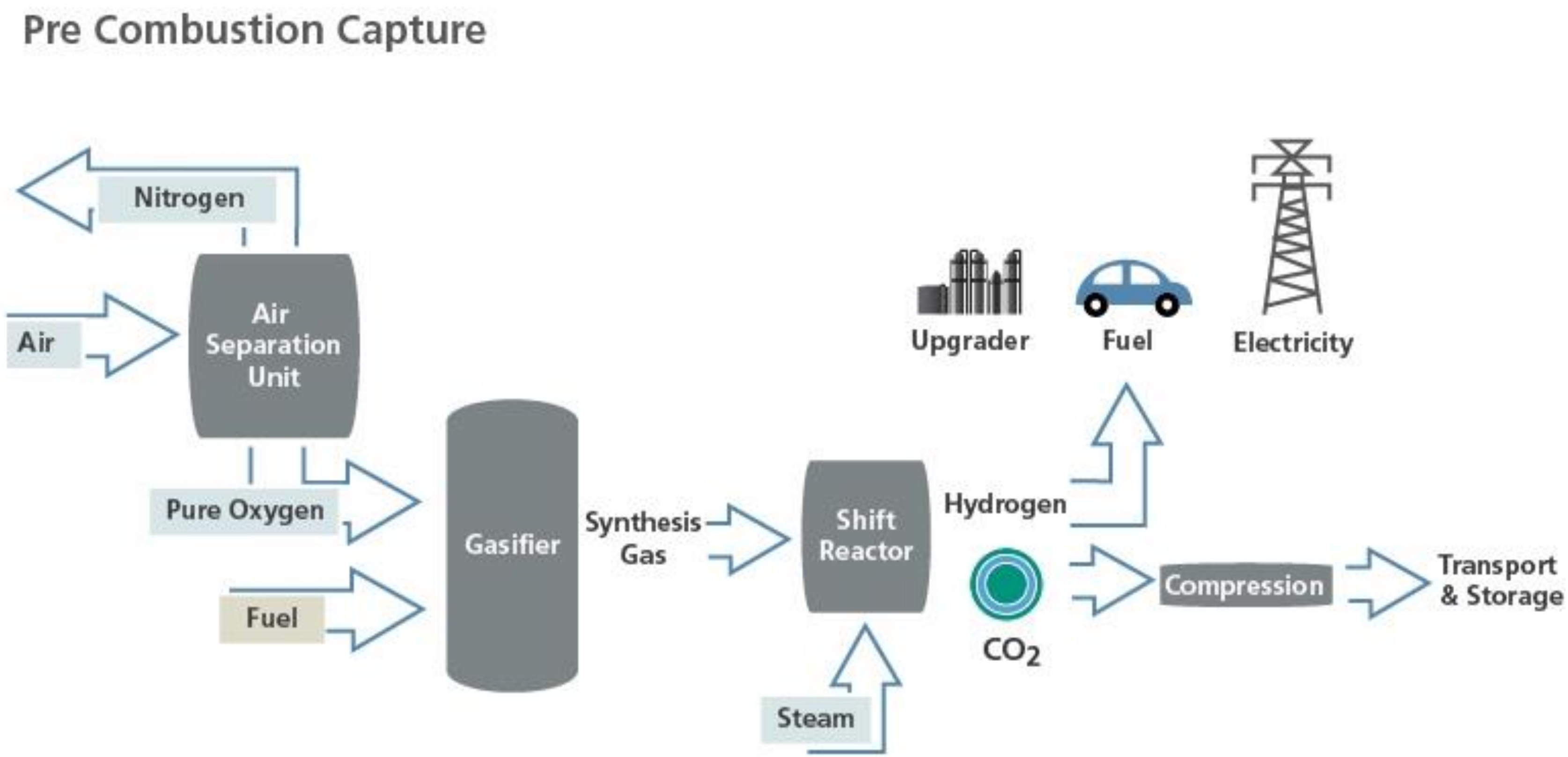
Alternative to chemical solvents: => Membranes



Challenges: Cost, Scale, Flue gas impurities…

Source : Bellona

1. CO_2 Capture

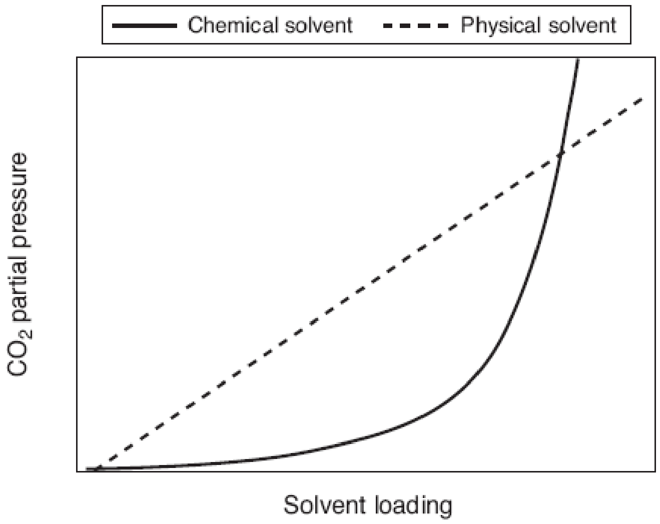


1. CO_2 Capture

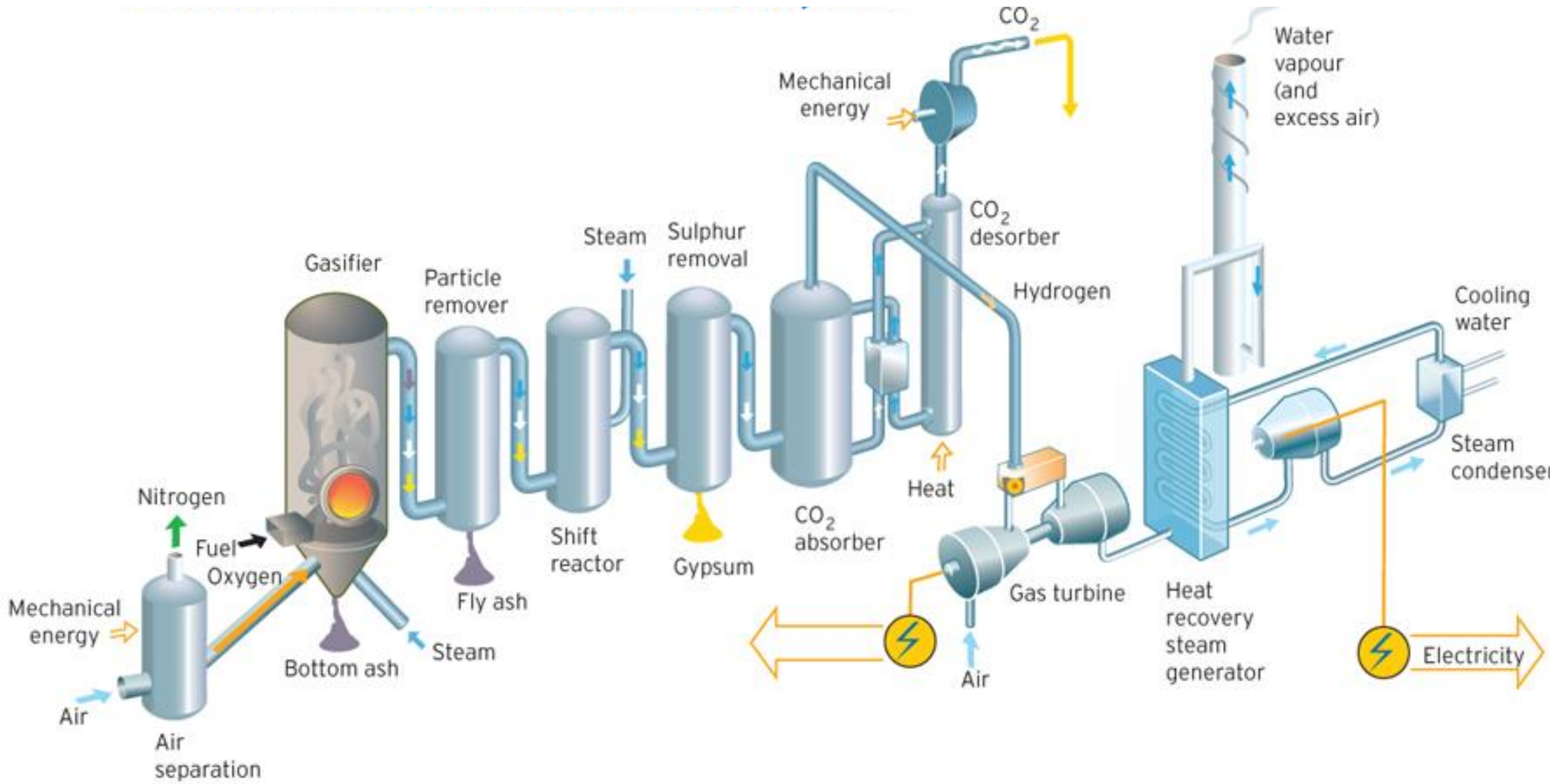
Main reactions:

Reaction	Name	Equation	Reaction enthalpy (MJ/kmol CH_4)
1	Steam reforming	$CH_4 + H_2O \Leftrightarrow CO + 3H_2$	206,2
2	Partial oxidation	$CH_4 + ½\ O_2 \Leftrightarrow CO + 2H_2$	-35,7
3	Water-shift reaction	$CO + H_2O \Leftrightarrow CO_2 + H2$	-41

Notice: Physical absorption may become interesting since CO_2 is more concentrated in this process



Case study: IGCC (integrated gasification combined cycle)



1. CO_2 Capture

Pre-combustion capture:

- Still in development, close to maturity, but studied less intensively in the last few years
- Partial combustion => generation of NOx
- Hydrogen as an energy carrier
- Gaz turbine with H_2 must be improved

1. CO_2 Capture

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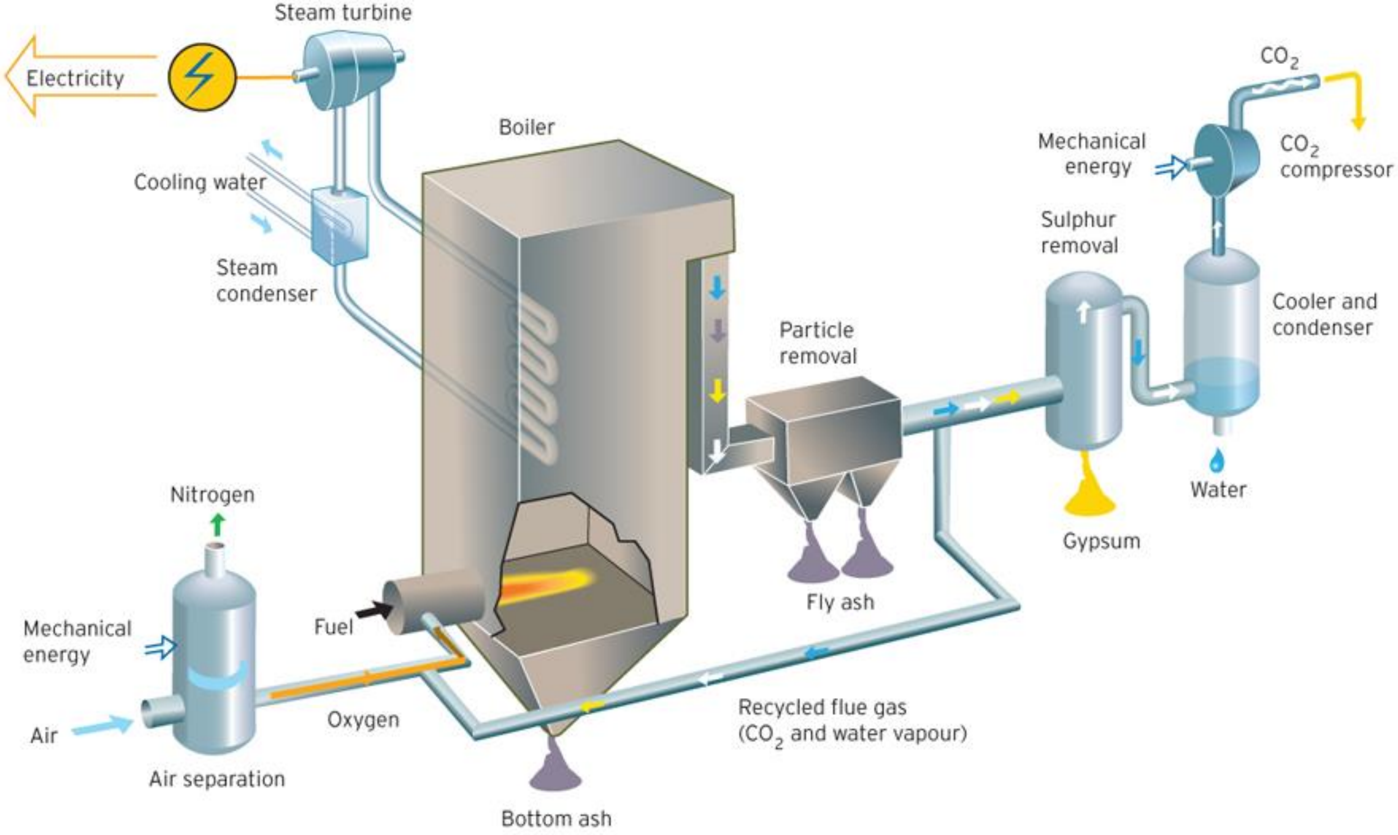
Oxy-combustion



1. CO_2 Capture

Oxy-combustion: Challenges

- Air separation: Cost and flow rates (14Mt/j – 3.6Mt/j so far)
- Enriched oxygen environnement => materials and security
- Flame temperature and characteristics

Combustion à l'air

Combustion oxyfuel

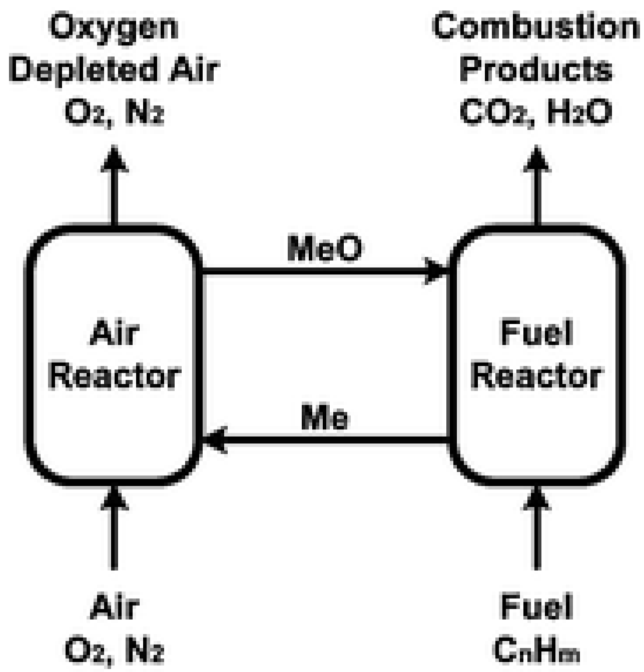
=> Pilot plants (Germany: 30 MWth) launched in 2008, but closed in 2014

Source : Strömberg et al., Energy procedia 1, 581-589, 2009

1. CO_2 Capture

Chemical looping

- No conventional Air Separation Unit
- But combustion with oxygen only



- **Oxidation : exothermic**

$$M + \frac{1}{2}O_2 \rightarrow MO$$

- **Reduction : endothermic**

$$CH_4 + 4MO \rightarrow CO_2 + 2H_2O + 4M$$

M : metal, MO : metal oxide

1. CO_2 Capture

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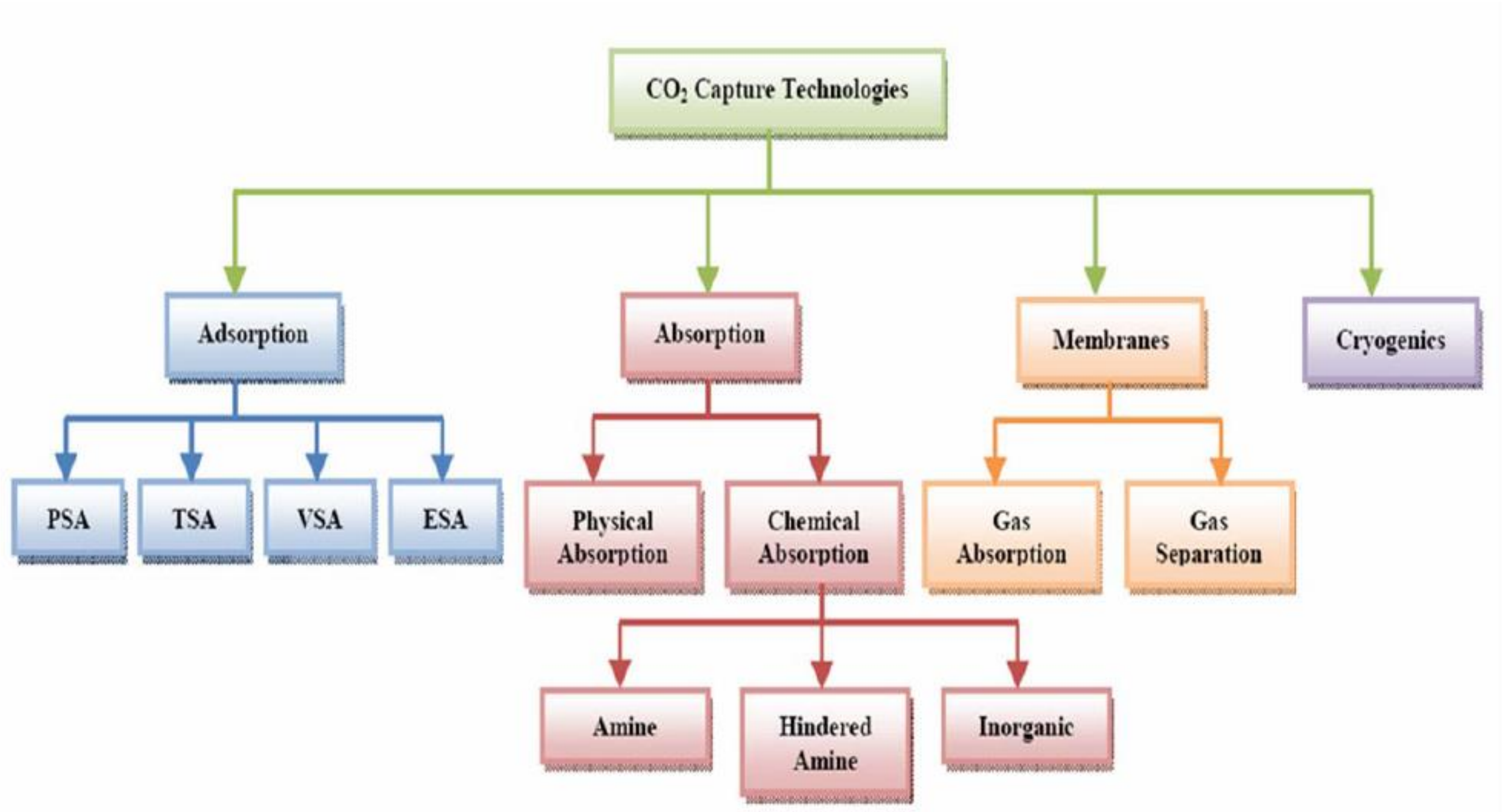
Method	Advantages	Challenges
Post-combustion	• Mature • Rétrofit (CCR)	• Energy penalty • Secondary emissions
Pre-combustion	• H_2 • Cost	• No retrofit • NOx • Gaz turbines for H_2
Oxycombustion	• Cost • Simple process • Combustion quality • 100% capture rate	• Air Separation • Difficult retrofit • O_2 enriched env. (materials)
Chemical looping	• Energy penalty is lower	• Metal selection (reaction kinetics) • Ashes • Not mature yet
Other	• Costs?	• Development in progress

1. CO_2 Capture



+ biotechnologies: algae, micro-organisms, …

+ CO_2 capture from air?

1. CO_2 Capture

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1. CO_2 re-use

Algae

=> Many applications

But: - land use (12t CO_2/an at Niederaussem)

- reprocessing

1. CO_2 re-use

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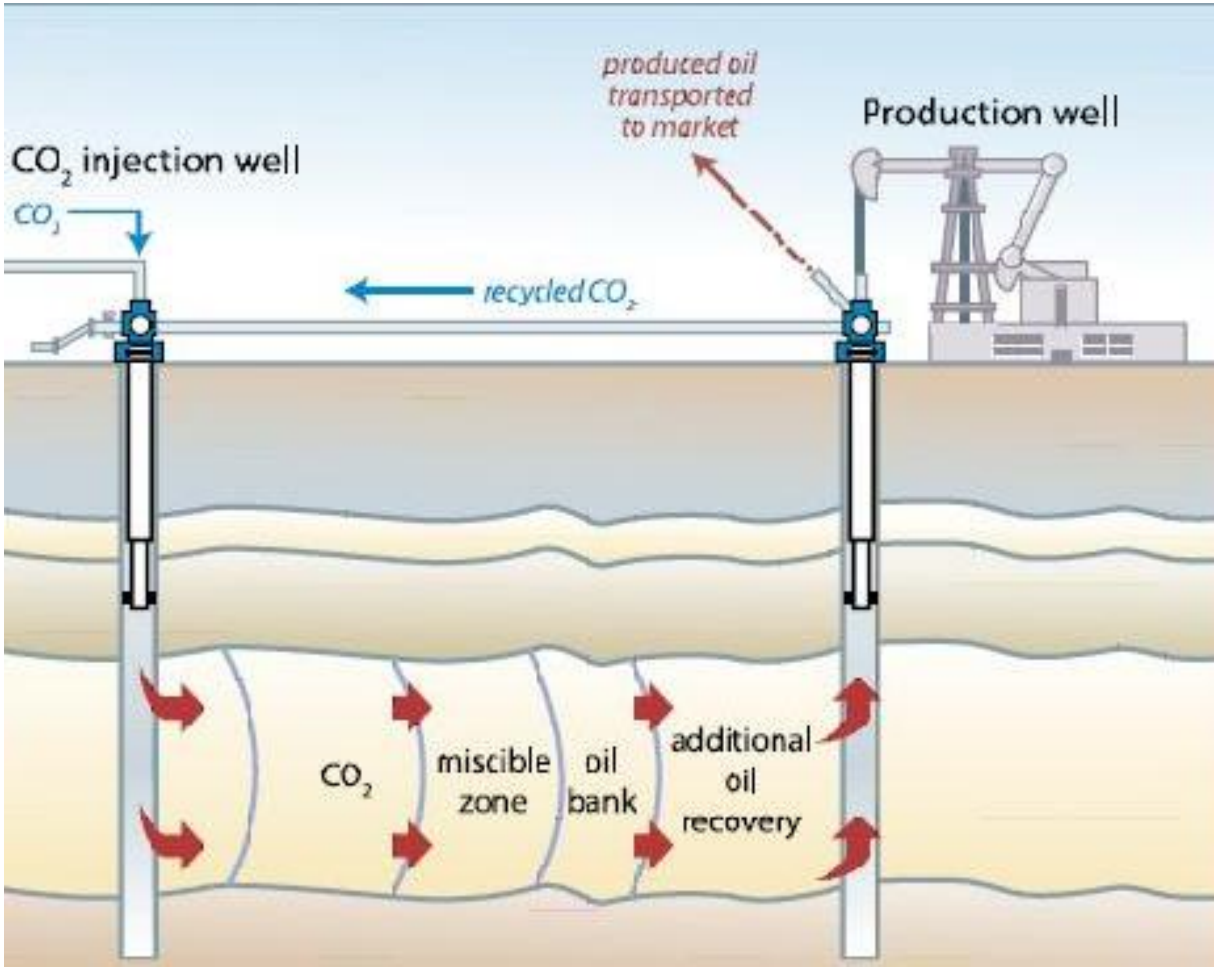
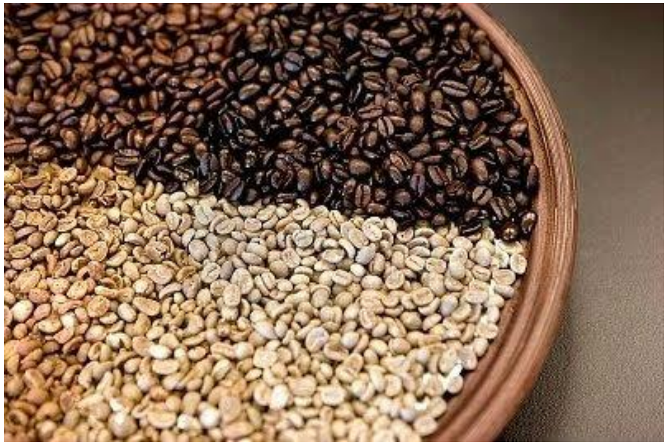
Enhanced oil recovery: 40 Mt CO_2/year (2008)



1. CO_2 re-use

Industrial use of CO_2: 20 Mt CO_2/year, no long-term storage





1. CO_2 re-use

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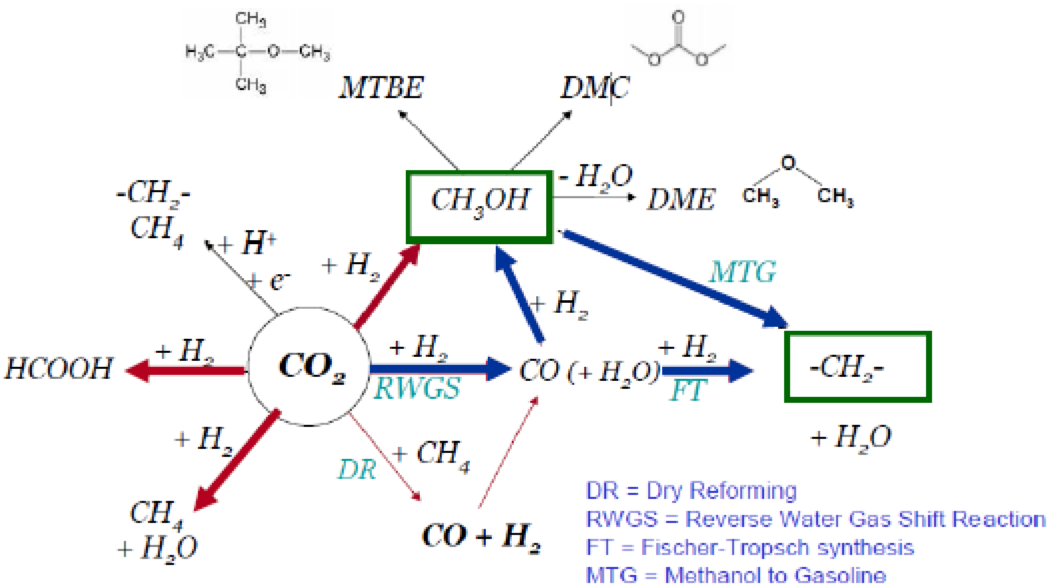
Re-use for organic synthesis: 100Mt CO_2/y

1. CO_2 re-use

Other cases of CO_2 to chemicals:



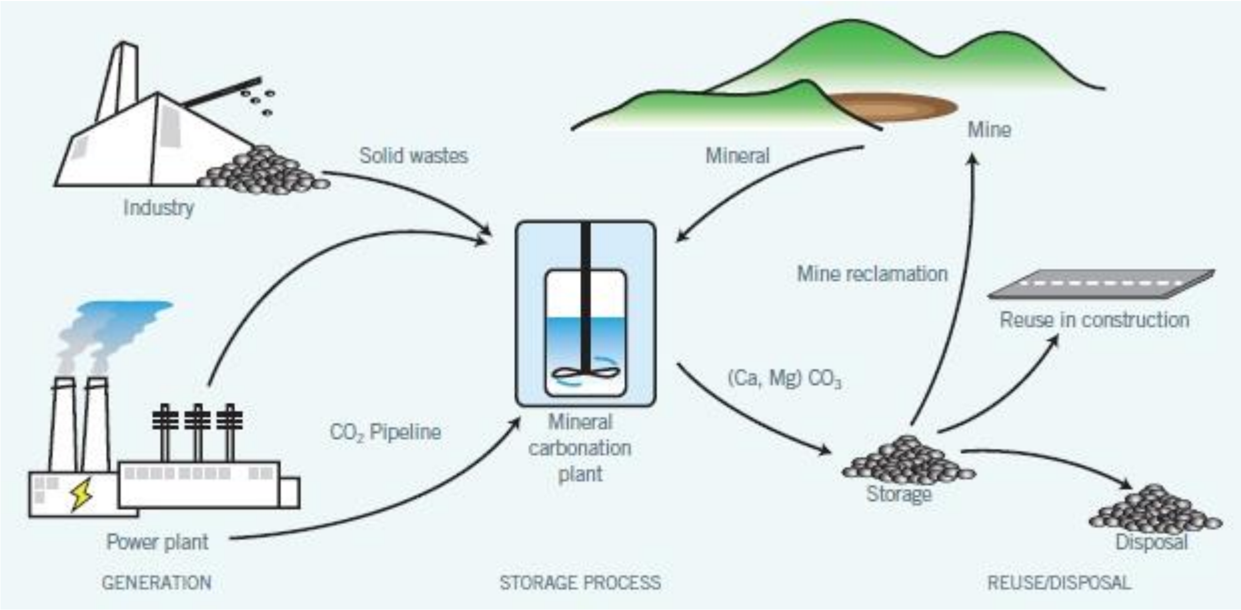
But…

- CO_2 contains few energy
- need for renewable energy source to make such processes sustainable

1. CO_2 re-use

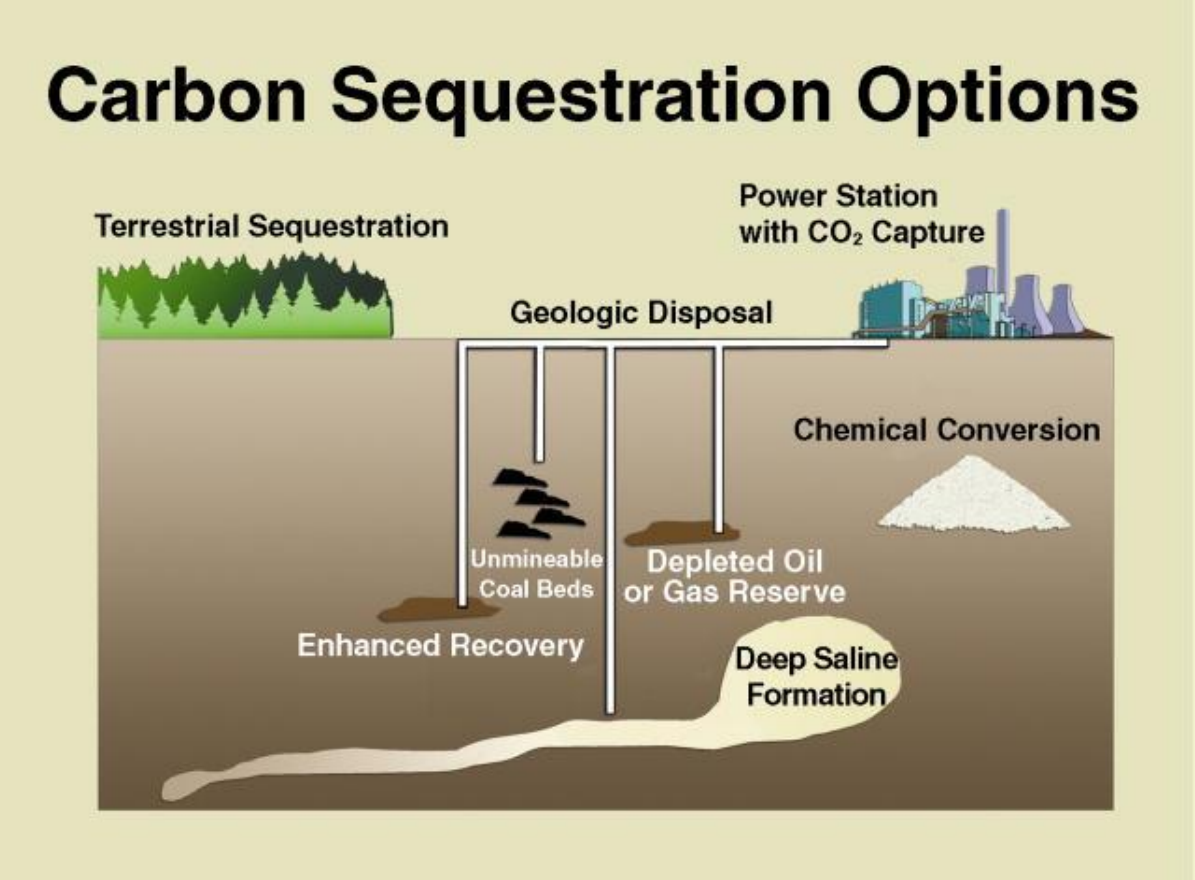
Carbonatation (mineralisation):

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$



- Use of mining ores or industrial wastes as raw materials
- Spontaneous reaction, but slow

1. CO_2 storage



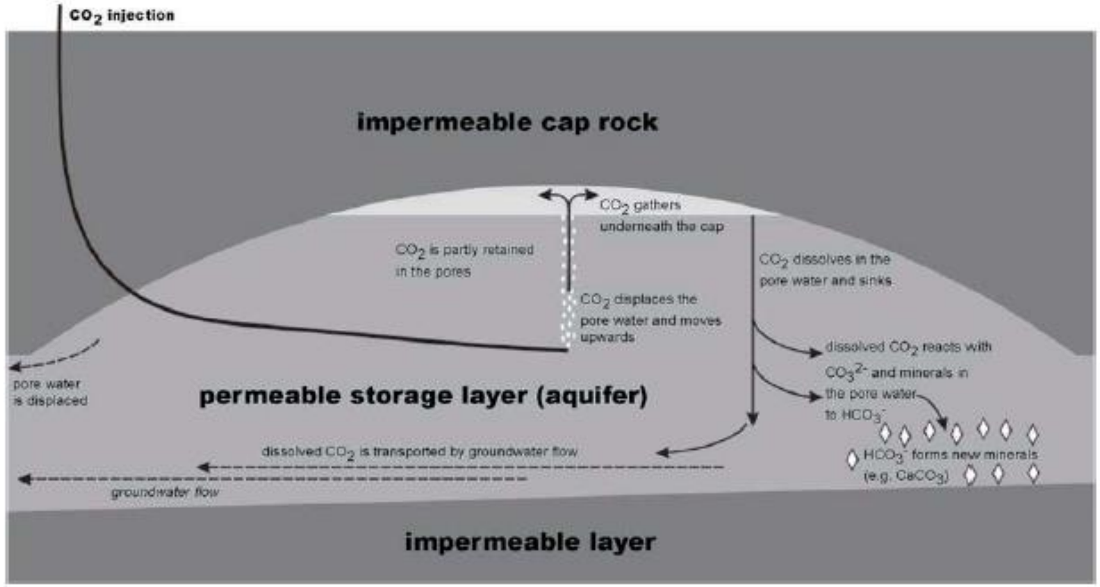
1. CO_2 storage

Selection of storage site:

- Capacity: related to the size and the porosity of the storage site

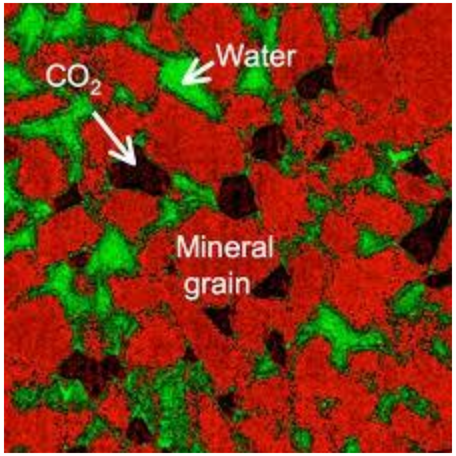
- Injectability: related to the permeability of rocks

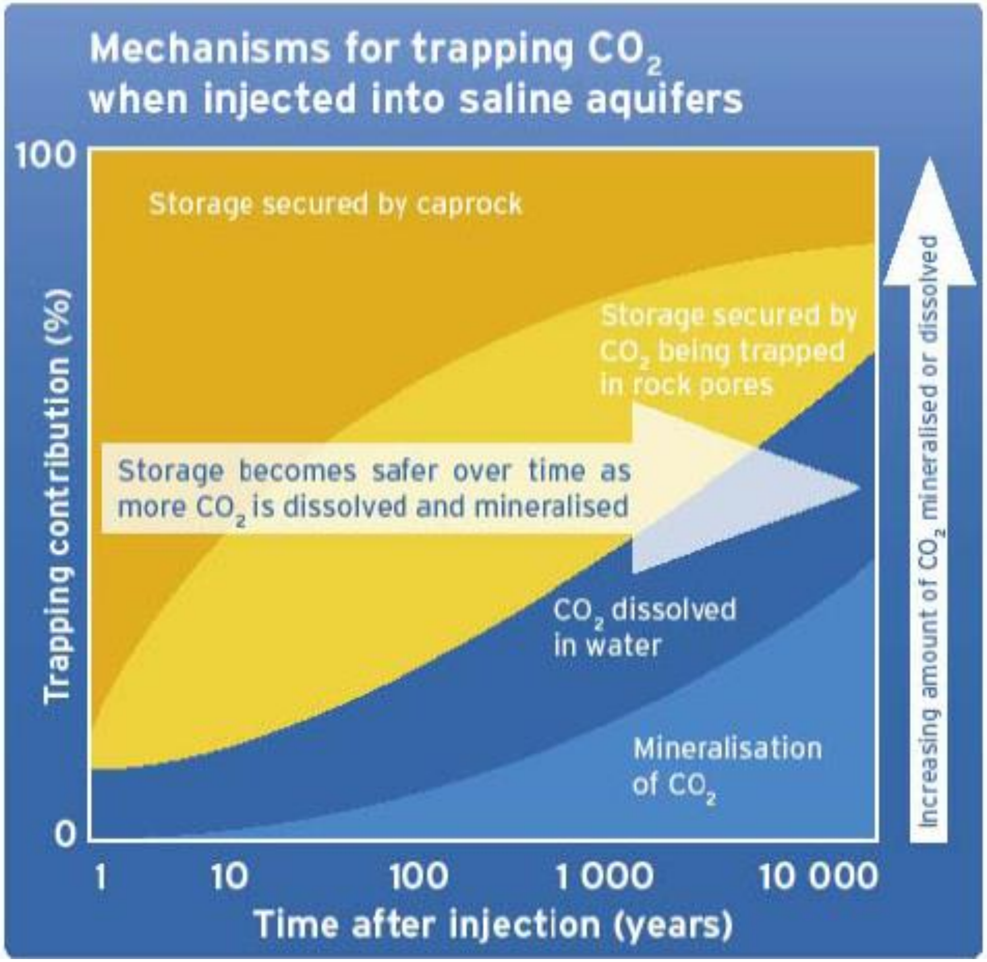
- Stability: impermeable cap rock



1. CO_2 storage

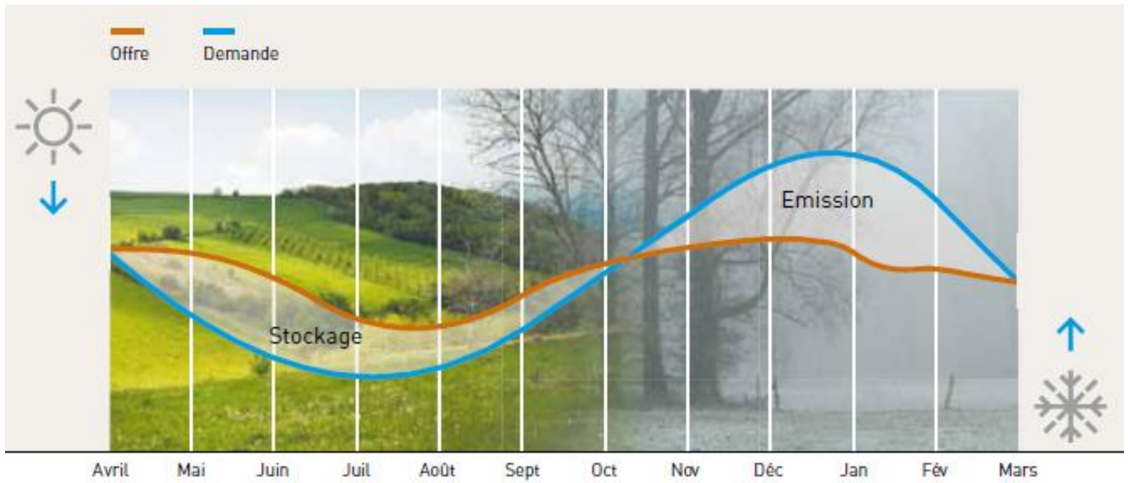
In-situ mineralisation



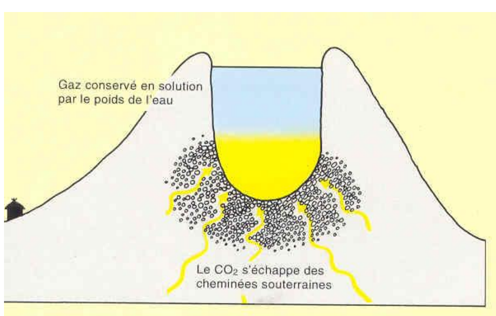


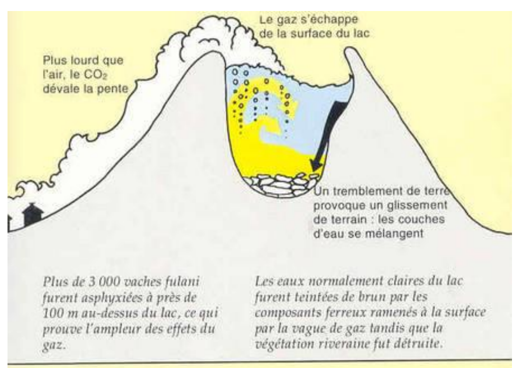
1. CO_2 storage

Risk management: Seasonal NG storage



Lake Nyos (Cameroun, 1986): 1700 casualties



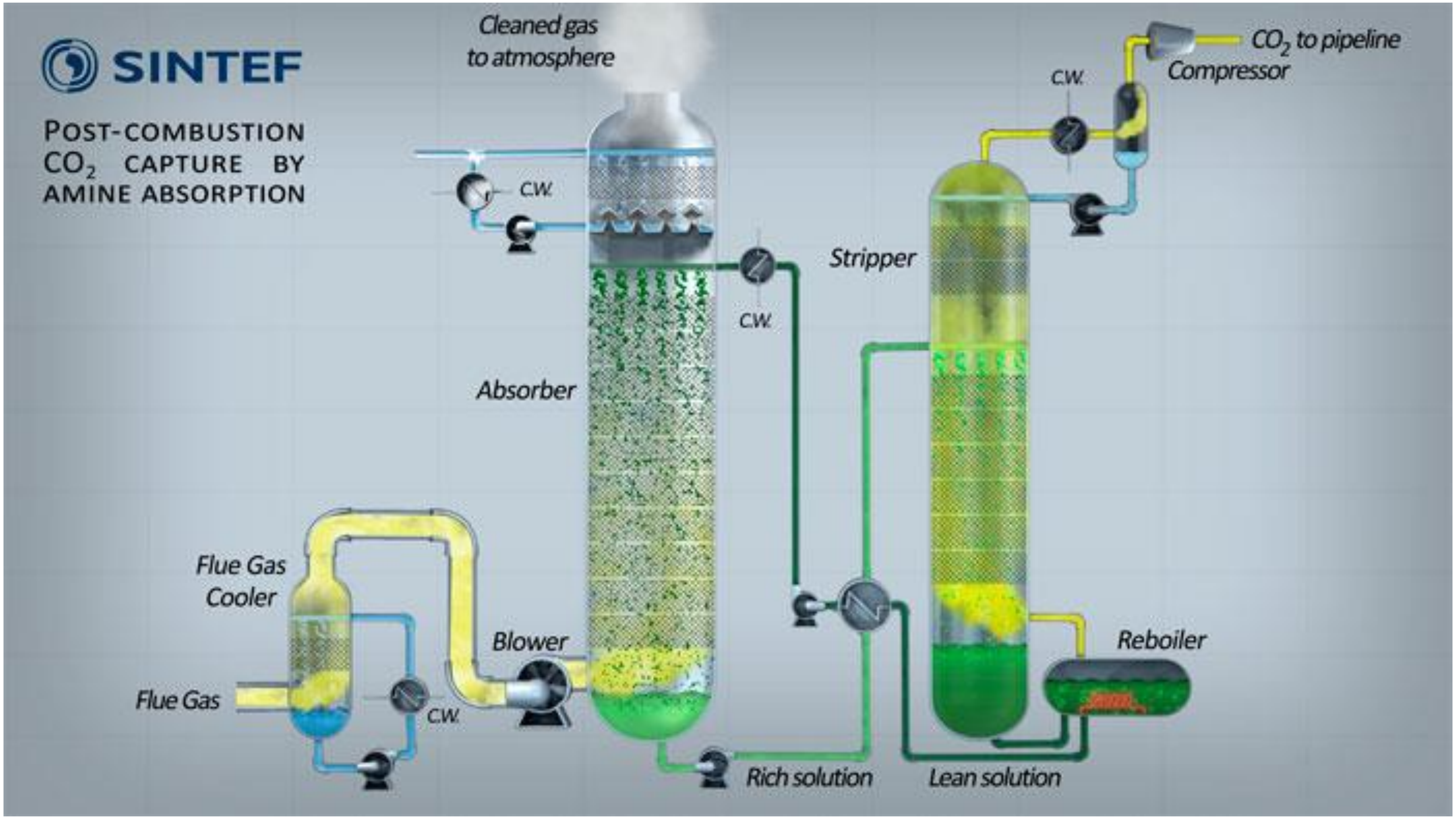


Source : www.fluxys.com

2. Experimental study of solvent degradation

2. Solvent degradation

Post-combustion CO_2 capture

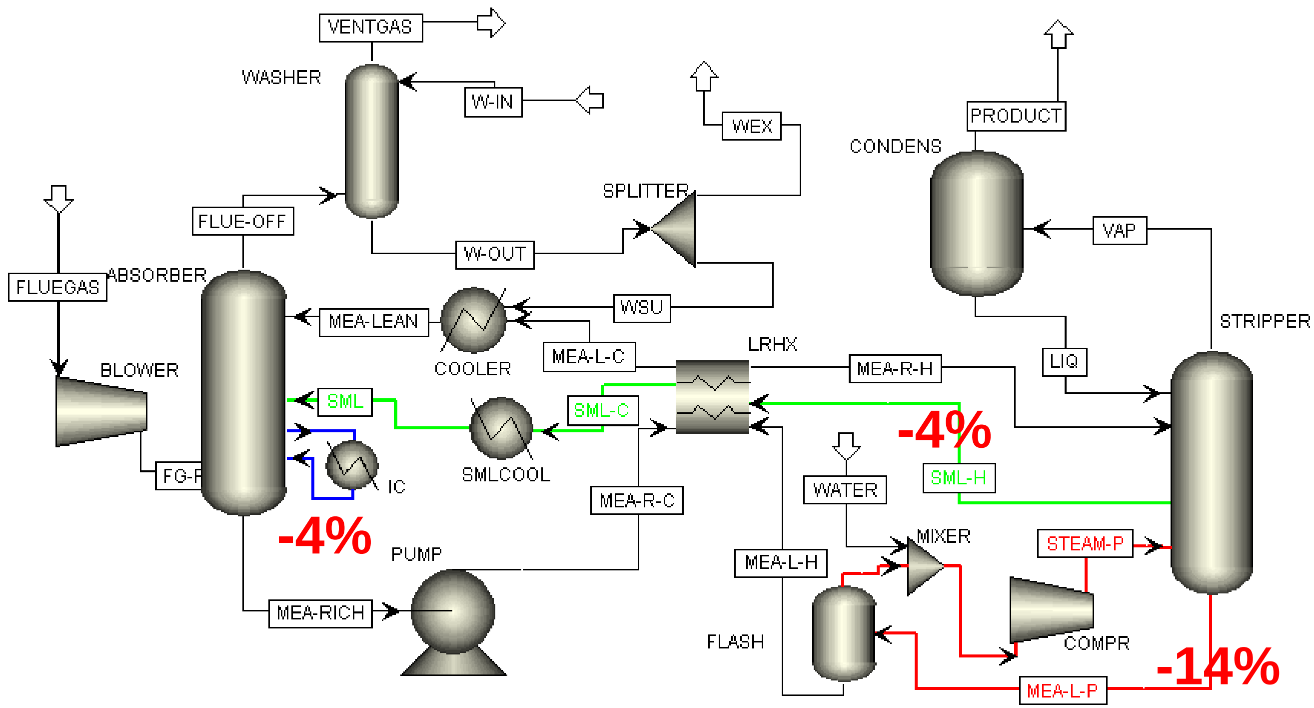


www.bellona.org

2. Solvent degradation

Most studies on CO_2 capture with amines: energy penalty

⇒ New solvents, Process intensification…



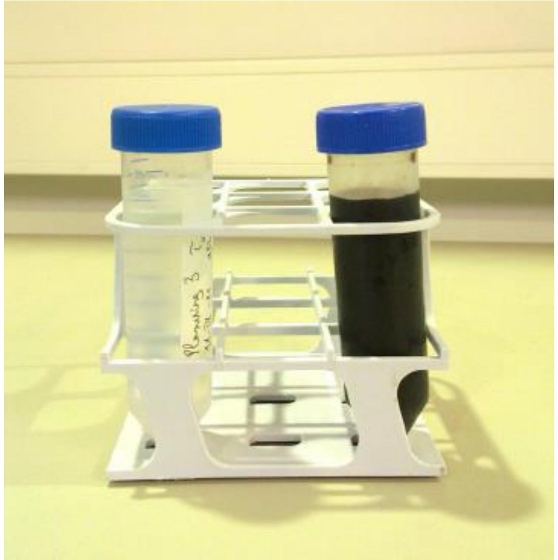
However, simulation does not consider all important parameters!

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

2. Solvent degradation

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.

2. Solvent degradation

The goal of this work was to develop a 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)

2. Experimental study

Degradation is a slow phenomenon (4% in 45 days[1]).

⇒ Accelerated conditions (base case):

- 300 g of 30 wt% MEA
- Loaded with CO_2 (~0,40 mol CO_2/mol MEA)
- 120°C, 4 barg, 600 rpm
- 7 days
- Continuous gas flow: 160 Nml/min,
  5% O_2 / 15% CO_2 / 80% N_2

[1] Lepaumier H., 2008. Etude des mécanismes de dégradation des amines utilisées pour le captage du CO_2 dans les fumées. PhD thesis, Université de Savoie.

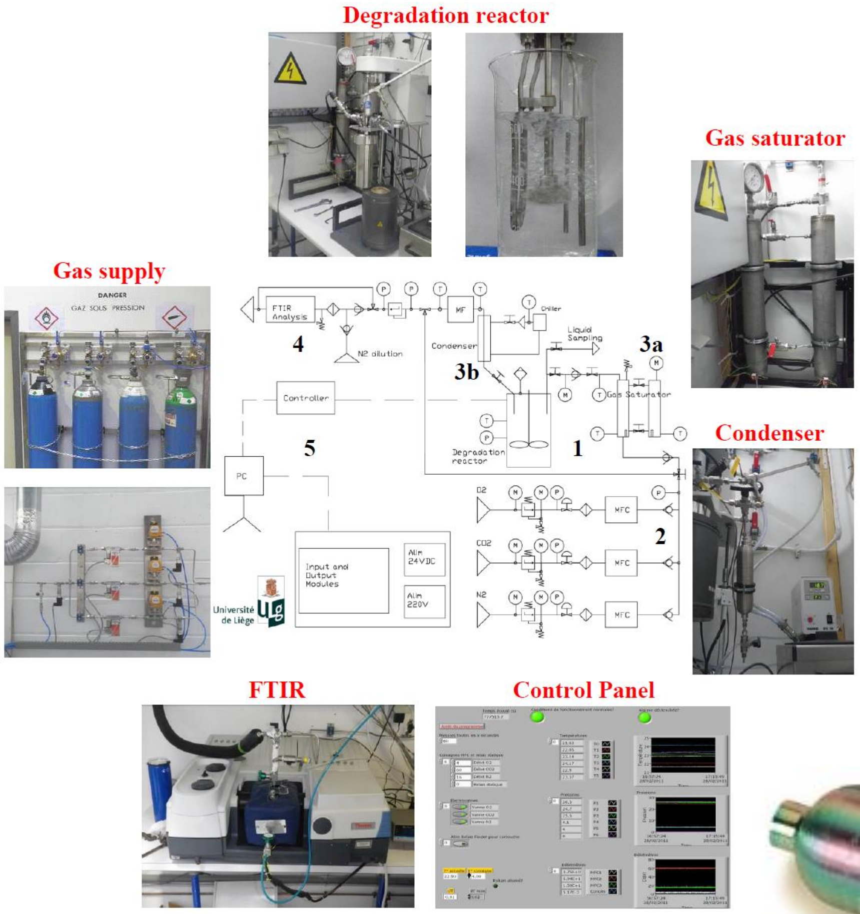
2. Experimental study

Identification of degradation products:

- HPLC-RID
  => *MEA*
- GC-FID
  => *degradation products*
- FTIR
  => *Volatile products (NH_3)*

2. Experimental study

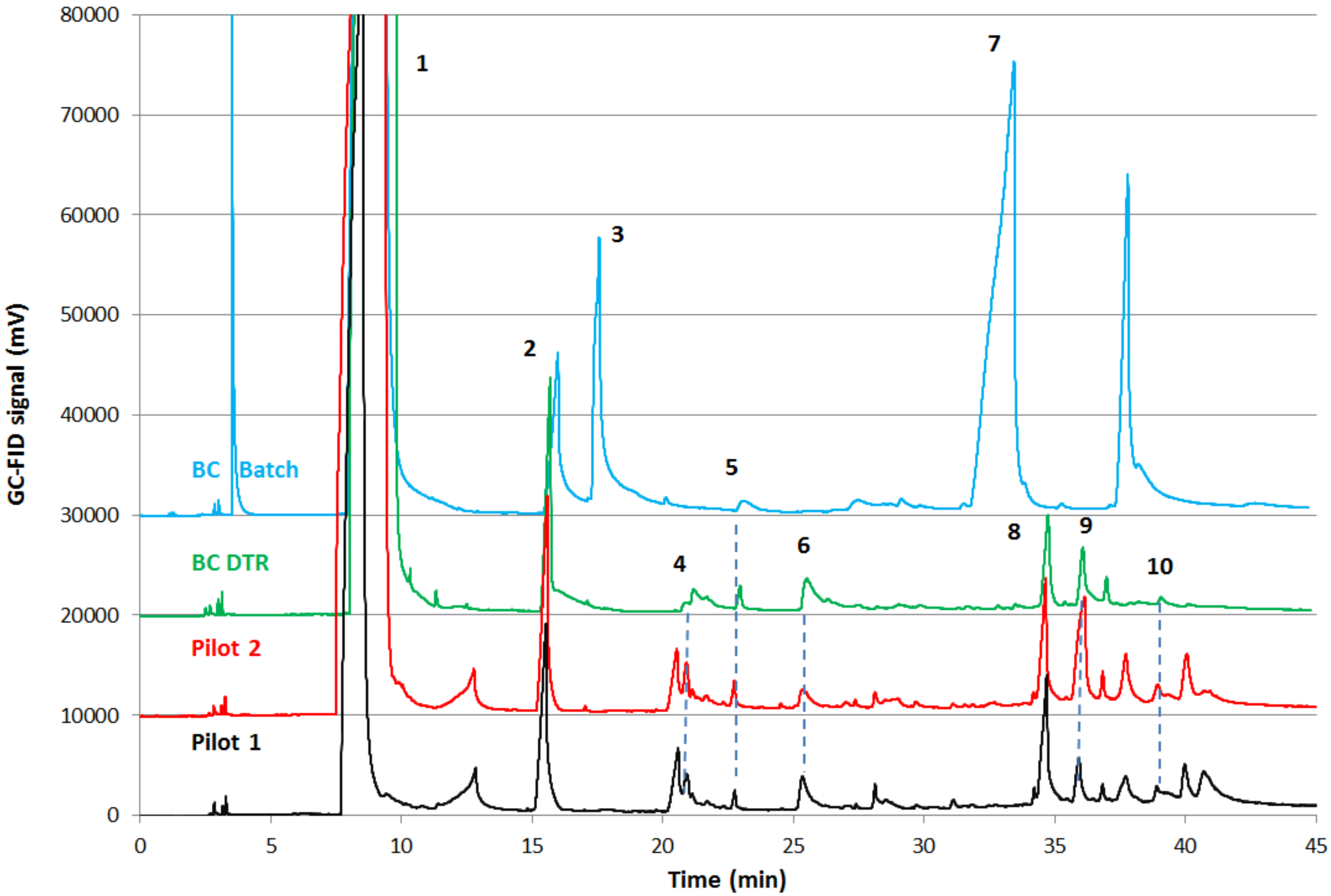
Comparison of the base case with degraded samples from industrial pilot plants:



?

2. Experimental study

Similar degradation products (GC spectra)!



=> 20% degradation after 7 days!

=> Nitrogen mass balance can be closed within 10%

=> Repetition experiments lead to similar results (<5% deviation)

2. Experimental study

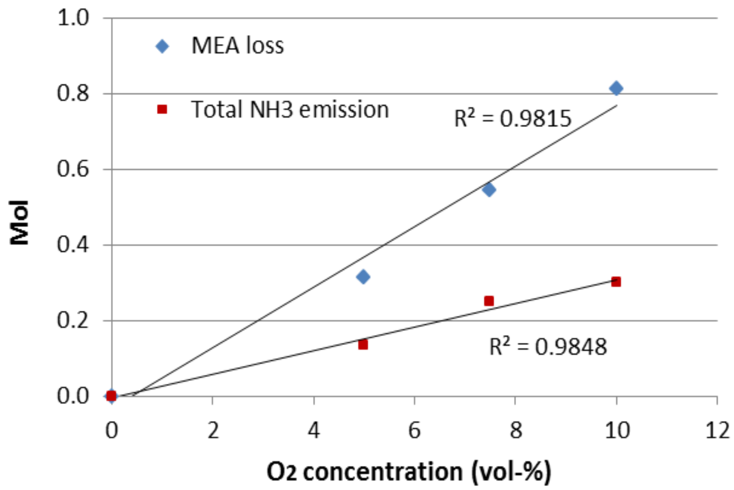
Study of the influence of operating variables:

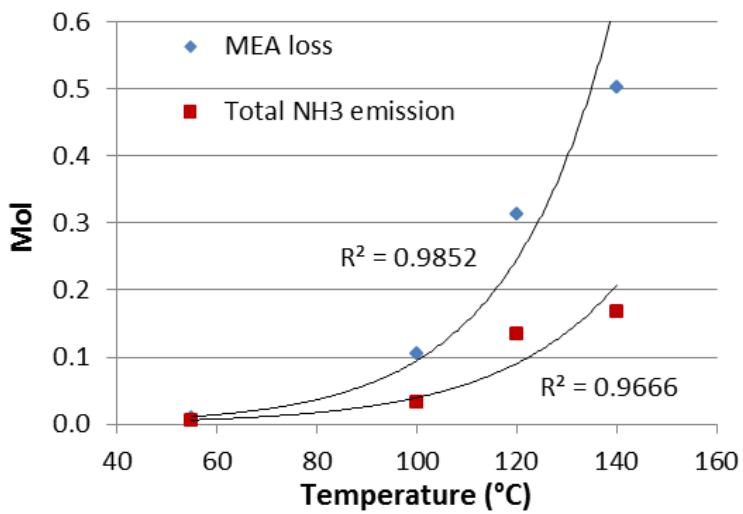
=> Gas feed flow rate and composition (O_2, CO_2)

=> Temperature

=> Agitation rate

=> Presence of dissolved metals and degradation inhibitors





2. Experimental study

Leads to a kinetic model of solvent degradation:

=> 2 main degradation mechanisms

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

Oxidative degradation

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

Thermal degradation with CO_2

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

2. Experimental study

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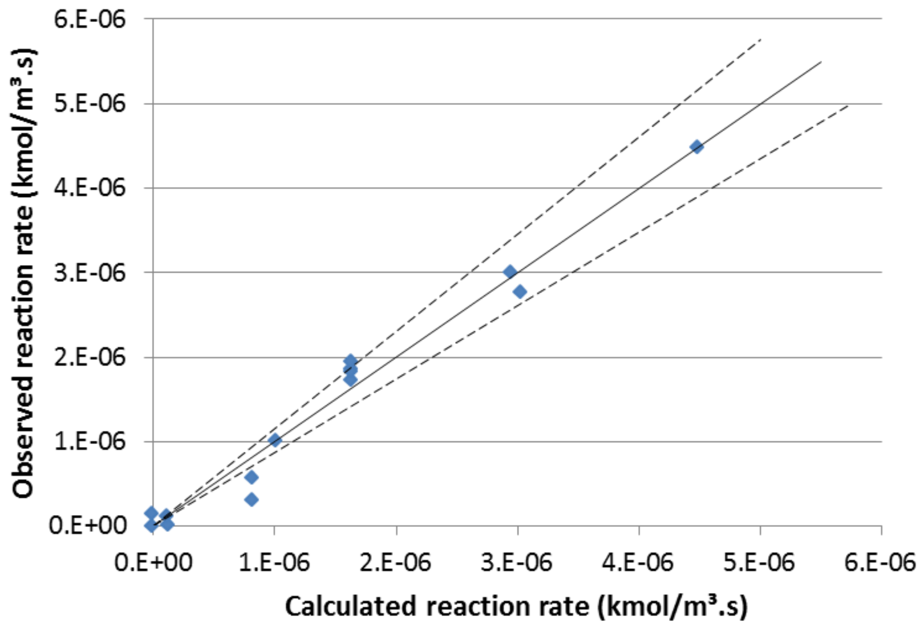
Arrhenius kinetics (kmol/m³.s):

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

- Oxidative degradation: $r = 535\,209.\,e^{-\frac{41\,730}{8{,}314.T}}.\,[O_2]^{1{,}46}$
- Thermal degradation with CO_2: $r = 6{,}27.1011.\,e^{-\frac{143106}{8{,}314.T}}.\,[CO_2]$



3. Simulation of the CO_2 capture process with assessment of solvent degradation

3. Process simulation

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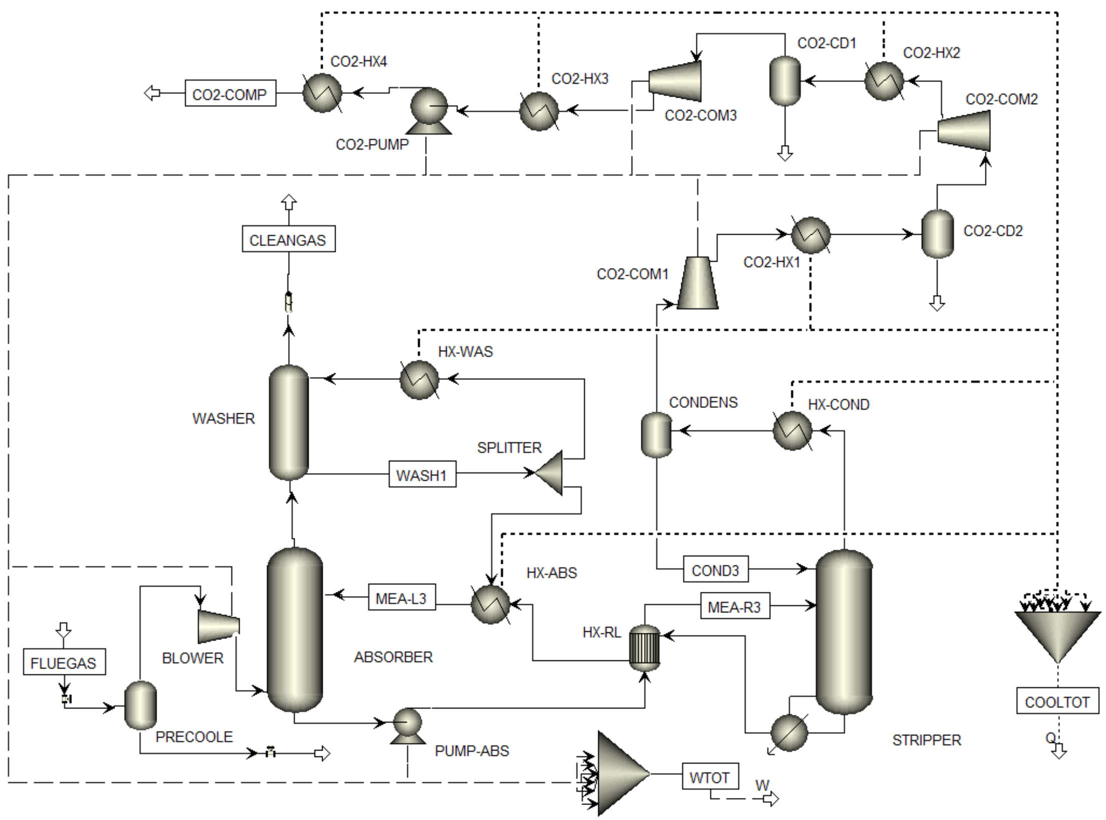
Degradation model has been included into a global process model built in Aspen Plus

⇒ Steady-state simulation, closed solvent loop

⇒ Additional equations in the column rate-based models



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

3. Process simulation

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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

3. Process simulation

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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

=> Oxidative degradation is more important than thermal degradation with CO_2

3. Process simulation

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

=> Ammonia is the main emitted degradation product after washing, coming from both absorber and stripper

3. Process simulation

Comparison with industrial CO_2 capture plants:

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

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

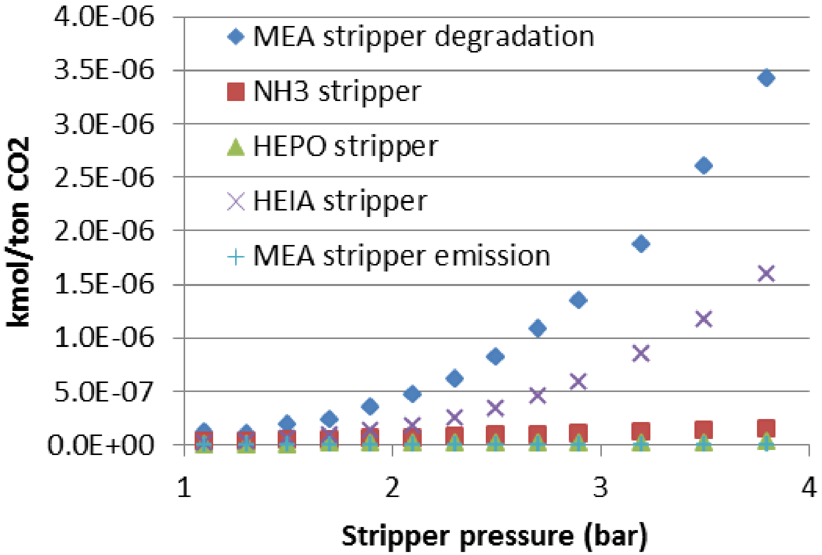
=> Maybe due to simplifying assumptions:

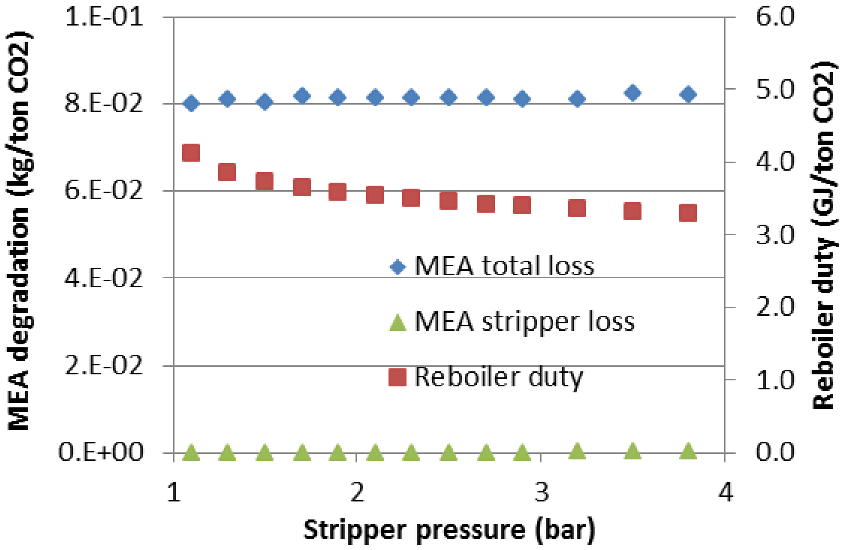
- Modeling assumptions for the degradation kinetics
- Presence of SO_x et NO_x neglected
- Influence of metal ions neglected

[1] Moser P., Schmidt S. and Stahl K., 2011. Investigation of trace elements in the inlet and outlet streams of a MEA-based post-combustion capture process. Energy Procedia 4, 473-479.

Influence of process variables on solvent degradation:

=> Regeneration pressure

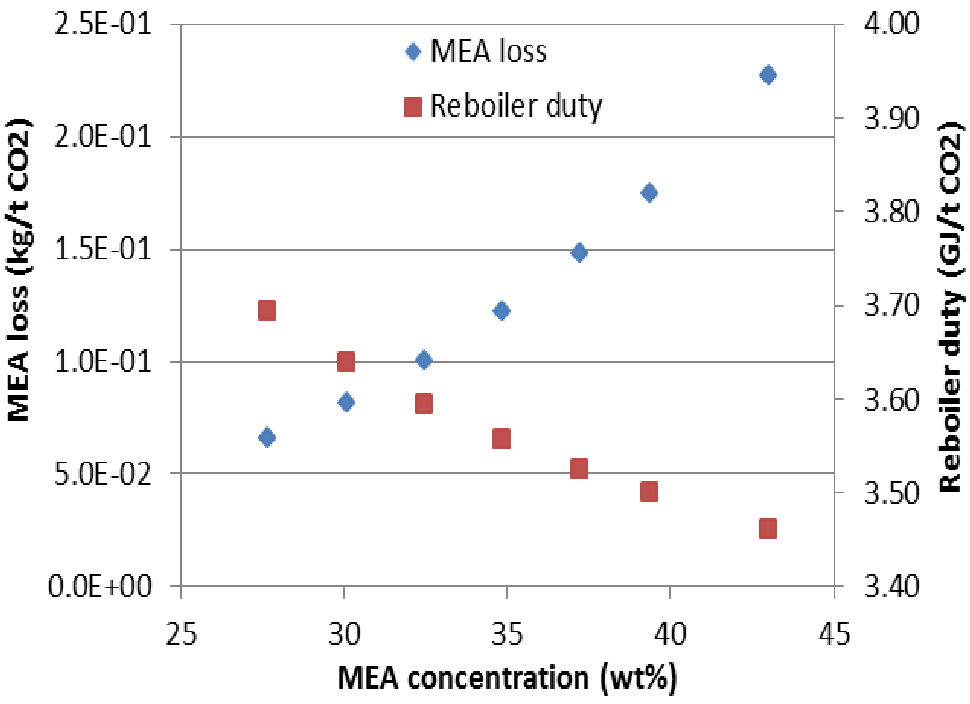




Exponential increase of the thermal degradation, but still much lower than oxidative degradation

Influence of process variables on solvent degradation:

⇒ MEA concentration



Influence of MEA concentration on the O_2 mass transfer!

⇒ Identification of optimal process operating conditions for the CO_2 capture process:

- *Concentrated MEA solvent: 40 wt% MEA (if degradation inhibitors are available).*

- *Optimized solvent flow rate: 24 m^3/h in the simulated configuration.*

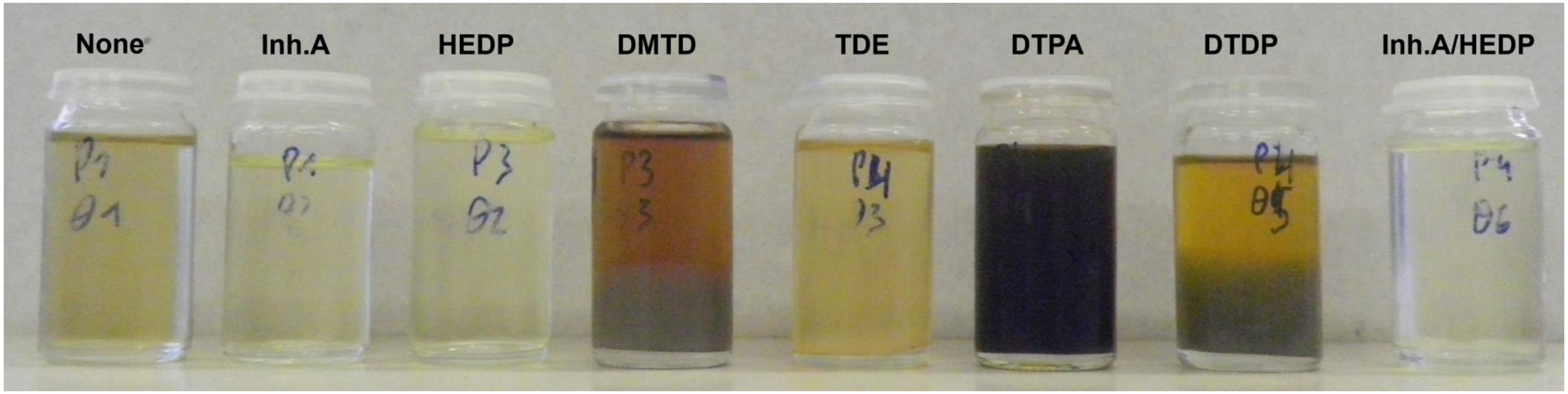
- *Low oxygen concentration in the flue gas: 0% O_2 (or minimum)*

- *High stripper pressure: 4 bar.*

- *Equipment for absorber intercooling and lean vapor compression.*

3. Other studies

- Influence of oxidative degradation inhibitors on thermal stability of the solvent



- Dynamic study of the CO_2 capture unit
  - Control strategies
  - Regulation of the process water balance

4. Conclusion and perspectives

4. Conclusion

Two of the main CO_2 capture drawbacks are considered:

- Solvent degradation is experimentally studied and a kinetic model is proposed
- This model is included into a global process model to study the influence of process variables

=> Both energy and environmental impacts of the CO_2 capture are considered!

=> This kind of model could and should be used for the design of large-scale CO_2 capture plants.

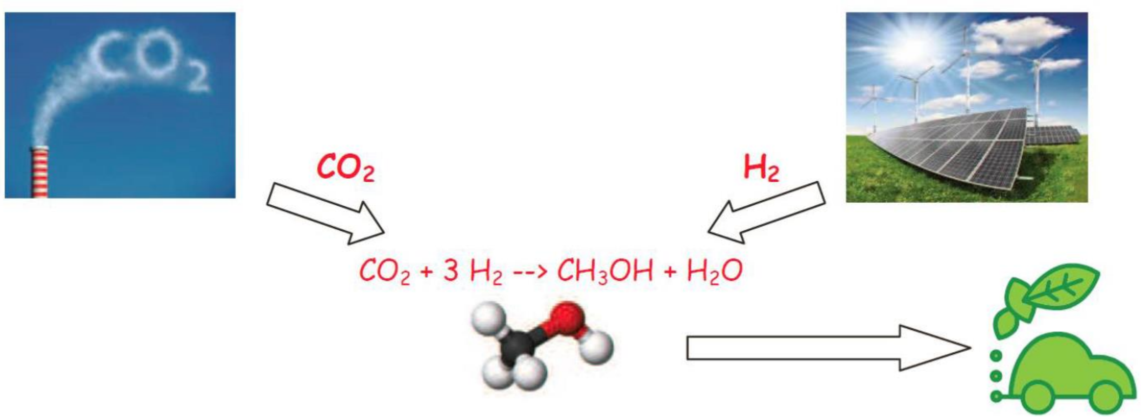
4. Conclusion

- Many challenges are still up to come for the CO_2 capture process!

=> ~ 1 Mton CO_2 has been emitted during this presentation

- Demonstration plants are the next step to evidence large-scale feasibility!

- Further works: CO_2 re-use for fuel synthesis

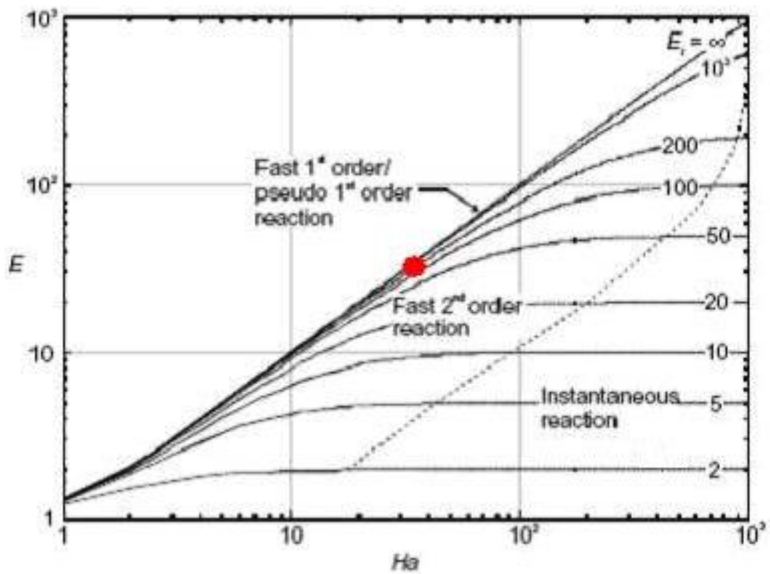


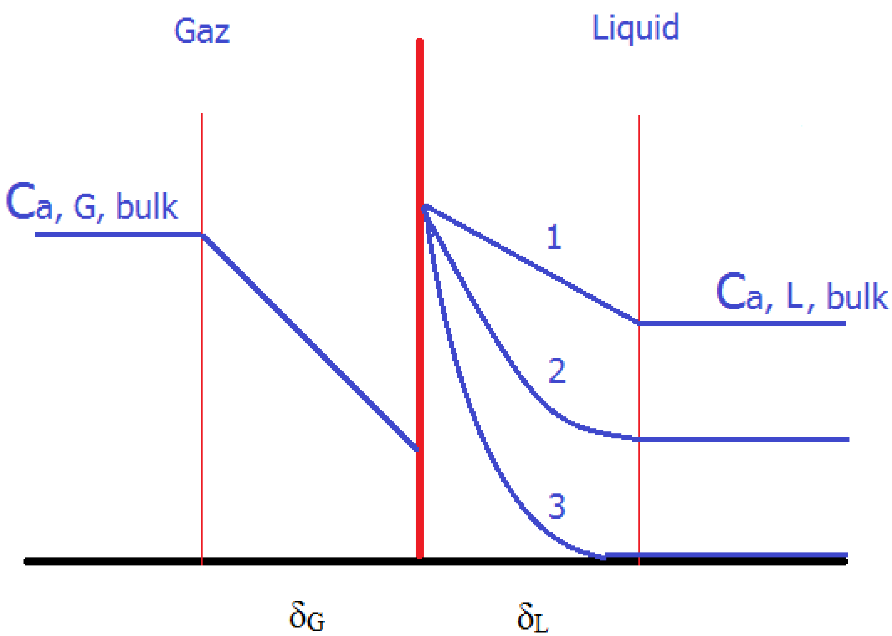
Thank you for your attention!

Lenfest Center for Sustainable Energy, Group meeting, November 2014

Back-up slides

- Mass transfer enhancement due to the chemical reaction in the liquid film





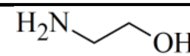
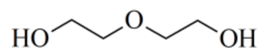
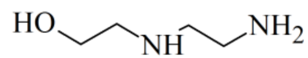
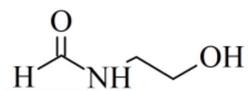
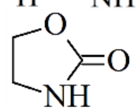
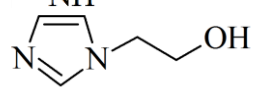
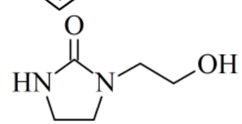
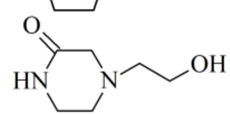
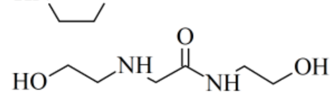
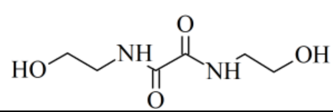
$$N_{O2} = k_L.a.\left(C_{O2}^{interface} - C_{O2}^{bulk}\right).E$$

$$E = Ha = \frac{\sqrt{D_{A,L}.k.C_{B,L}}}{{K_L}^0}$$

Back-up slides

Université de Liège

Table 1. Main peaks identified in GC spectra of degraded MEA samples

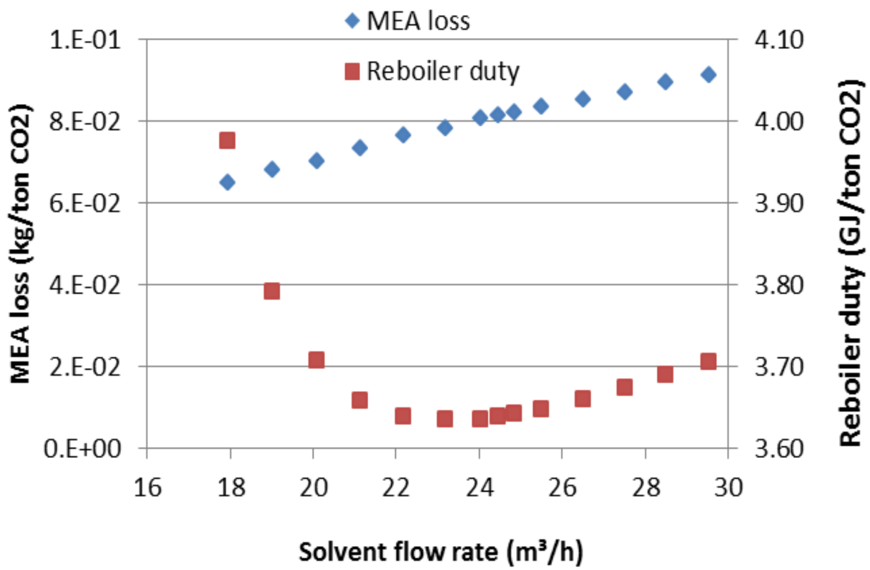
		Compound	Structure	Retention time (min)	Type
1	MEA	monoethanolamine		7.6	Start amine
2	DEG	diethylene glycol		15.0	Internal standard
3	HEEDA	*N*-(2-hydroxyethyl)ethylenediamine		17.0	Quantified
4	HEF	*N*-(2-hydroxyethyl)formamide		21.1	Identified
5	OZD	2-oxazolidinone		22.5	Quantified
6	HEI	*N*-(2-hydroxyethyl)imidazole		24.9	Quantified
7	HEIA	*N*-(2-hydroxyethyl) imidazolidinone		31.5	Quantified
8	HEPO	4-(2-hydroxyethyl)piperazine-2-one		34.3	Quantified
9	HEHEAA	*N*-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide		36.8	Identified
10	BHEOX	*N,N'*-bis(2-hydroxyethyl)oxamide		38.7	Quantified

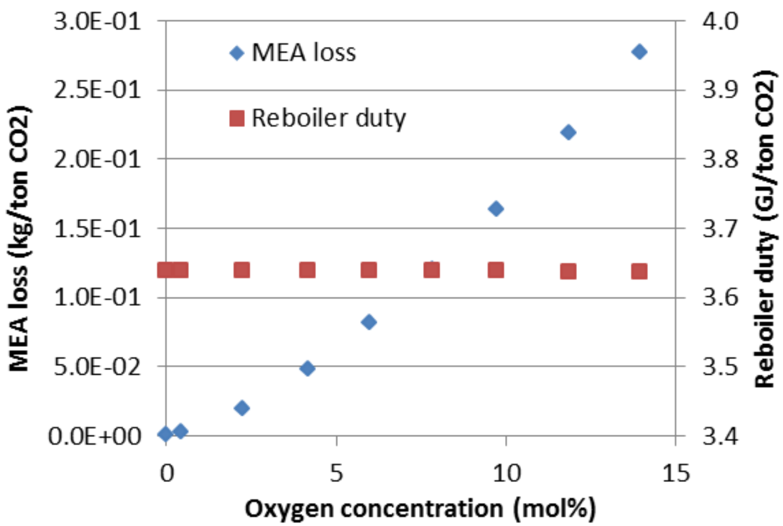
3. Process simulation

Influence of process variables on solvent degradation:

=> Solvent flow rate

=> Oxygen concentration in the gas feed





Minimum in the solvent flow rate has been experimentally evidenced.