Modeling post-combustion CO_2 capture with assessment of solvent degradation

Modélisation du captage post-combustion de CO_2 avec évaluation de la dégradation des solvants

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Global context

Environnemental issues

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Growing energy demand (esp. electricity)

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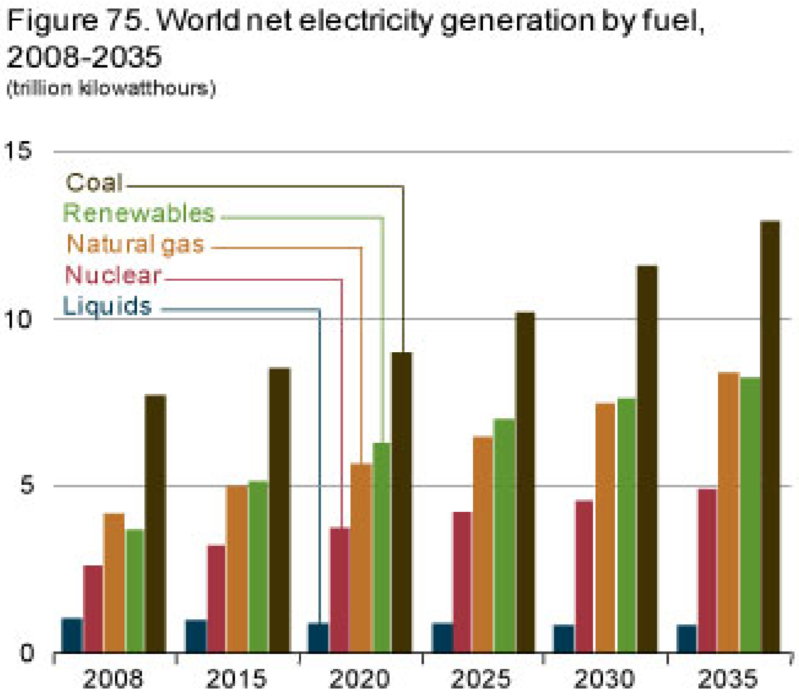
Large contribution of fossil fuels for electricity generation

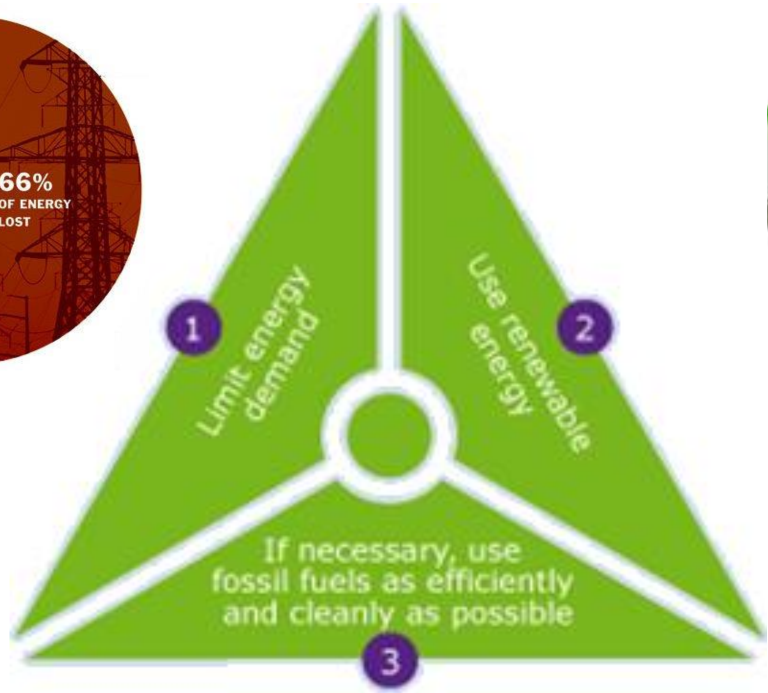


International Energy Outlook 2011

$\Rightarrow$ ***Big challenge!***

Global context

⇒3 possible answers : TRIAS ENERGICA



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

Outline

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1. Introduction: CO_2 capture and solvent degradation
2. Experimental study of solvent degradation
3. Simulation of the CO_2 capture process with assessment of solvent degradation
4. Conclusion and perspectives

1. Introduction

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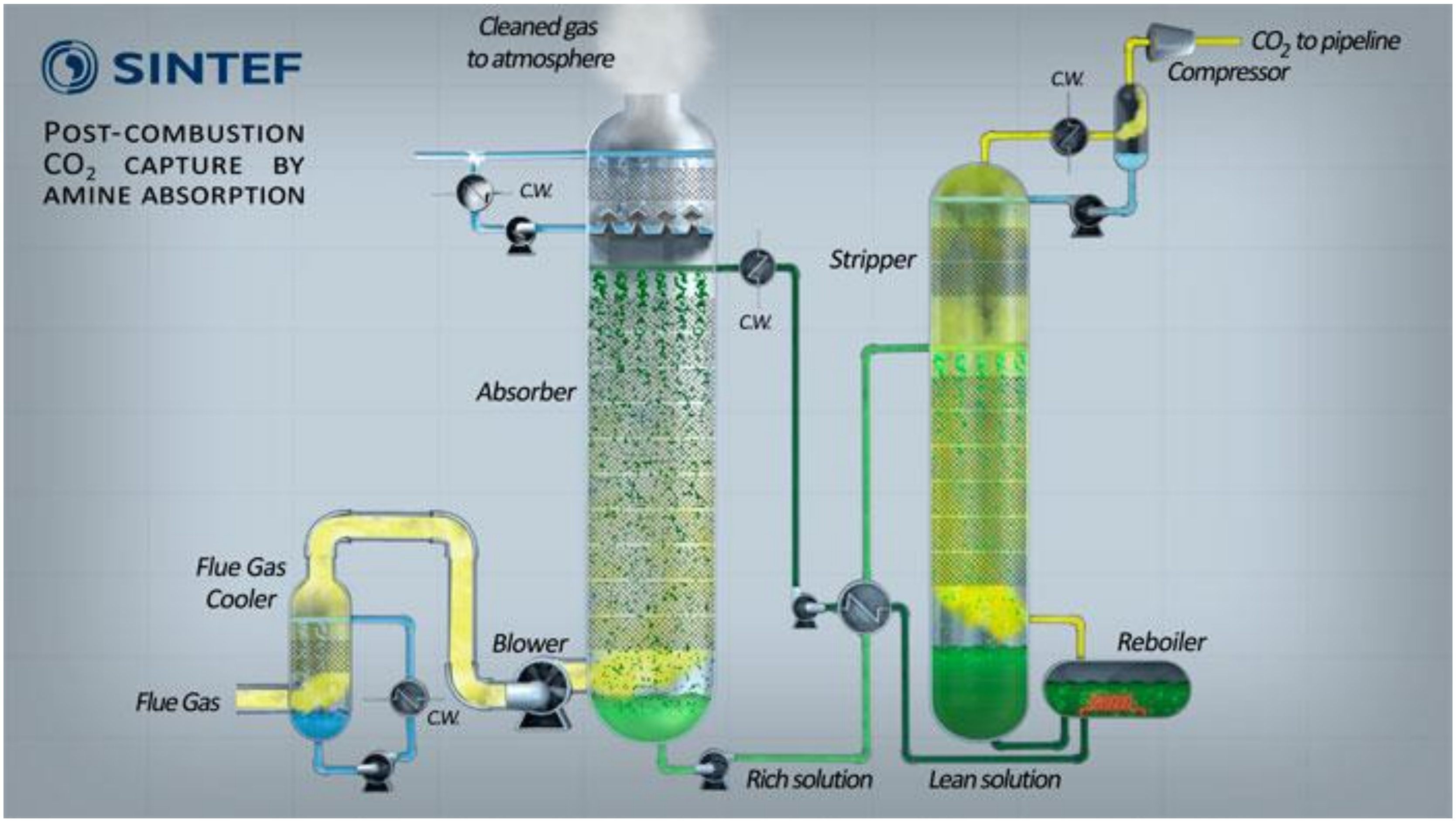
Post-combustion CO_2 capture



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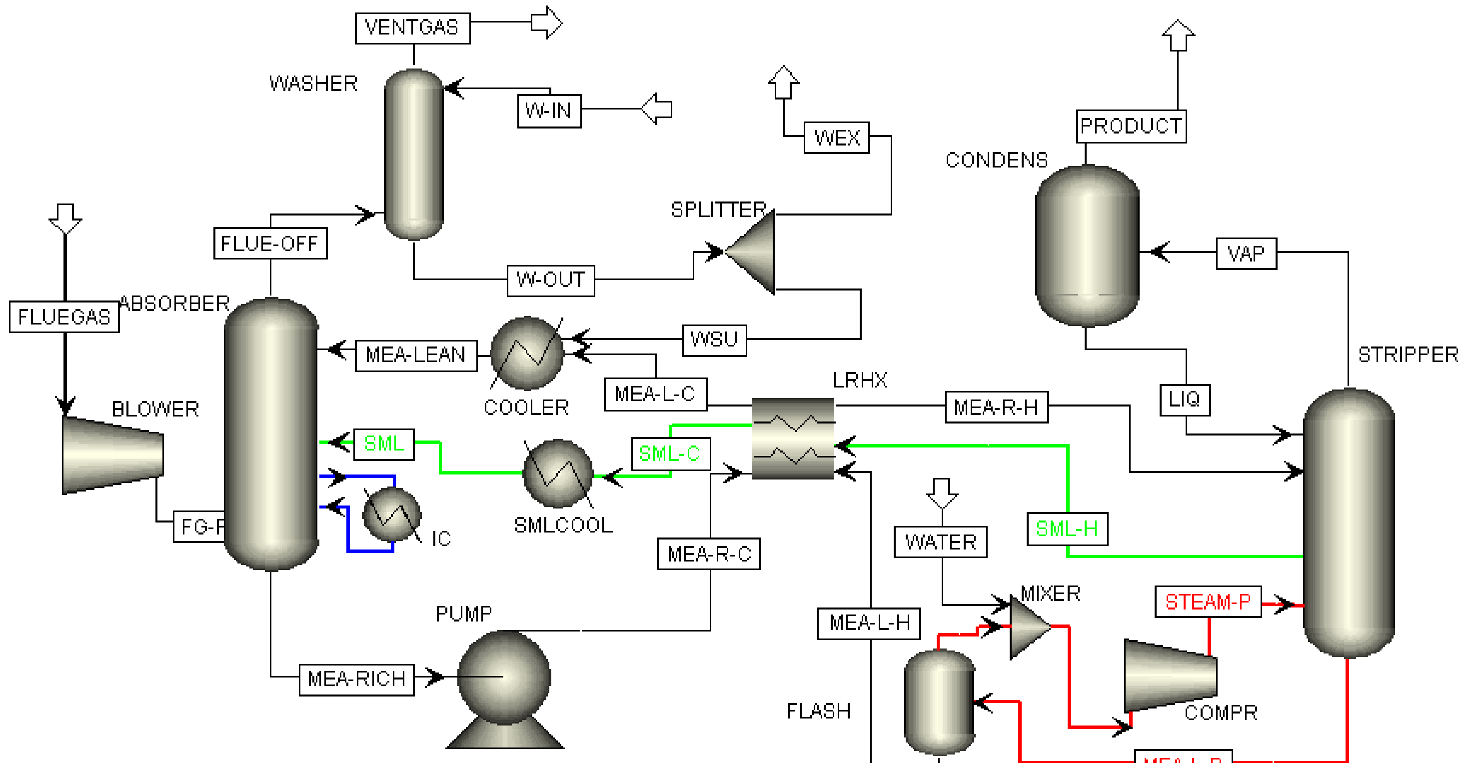
Most studies on CO_2 capture: the energy penalty

=> New solvents

=> Process intensification

=> …



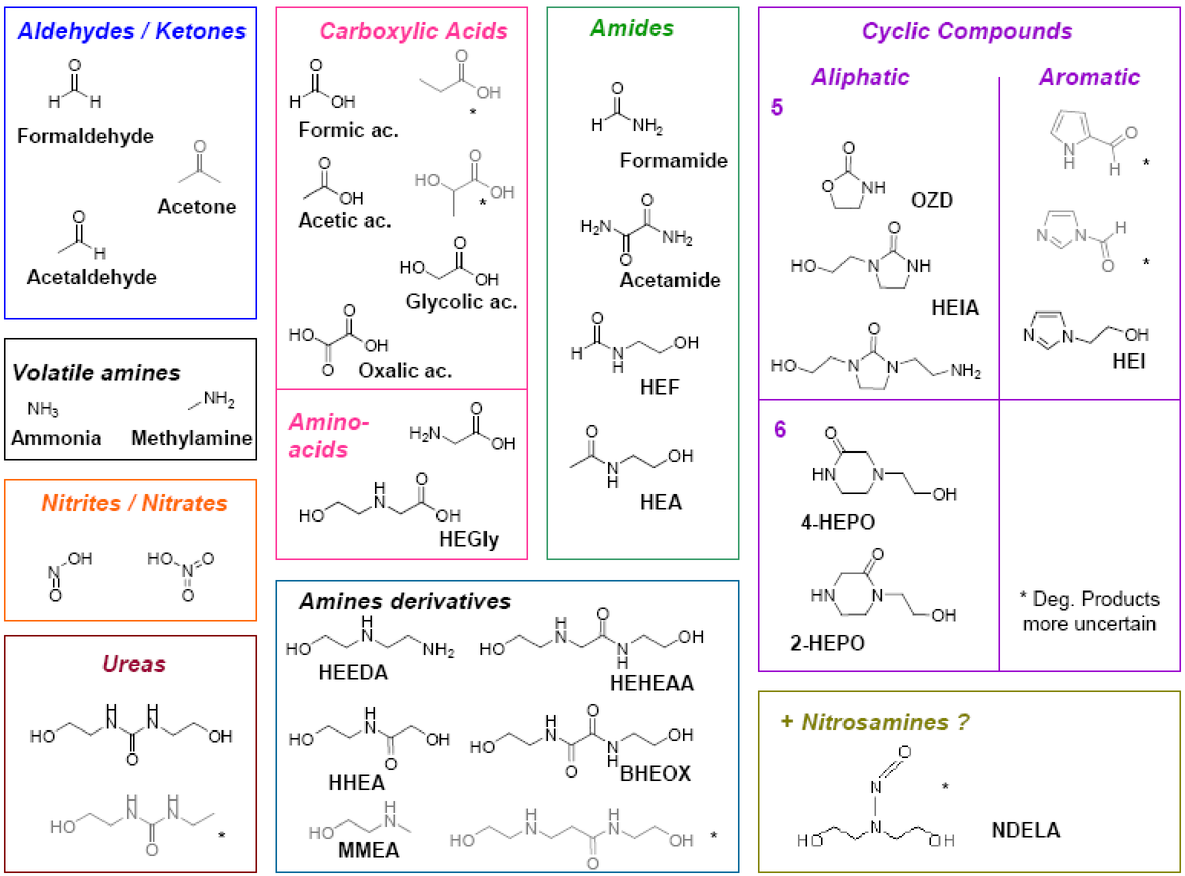
Léonard G. and Heyen G., 2011. Optimisation du procédé de captage de CO_2 dans des solvants aminés. Récents Progrès en Génie des Procédés, 101.

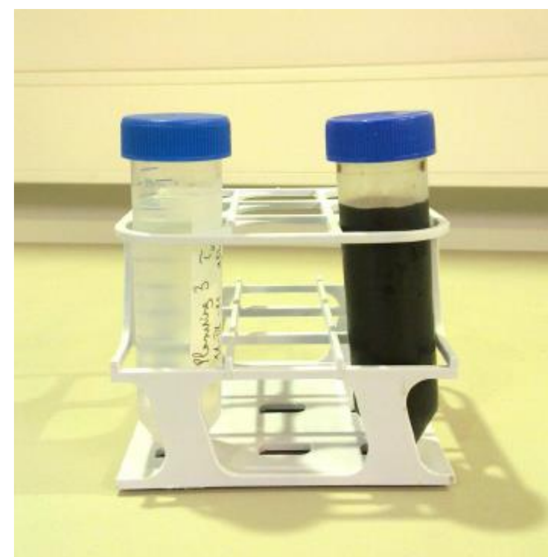
1. Introduction

However, solvent degradation is not considered!

=> Solvent replacement cost

=> Effect of degradation products (emissions, solvent properties, …)





1. Introduction

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The goal of this work is 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 of solvent dégradation

2. Experimental study

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

⇒ Accelerated conditions:

- 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
- 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:

?

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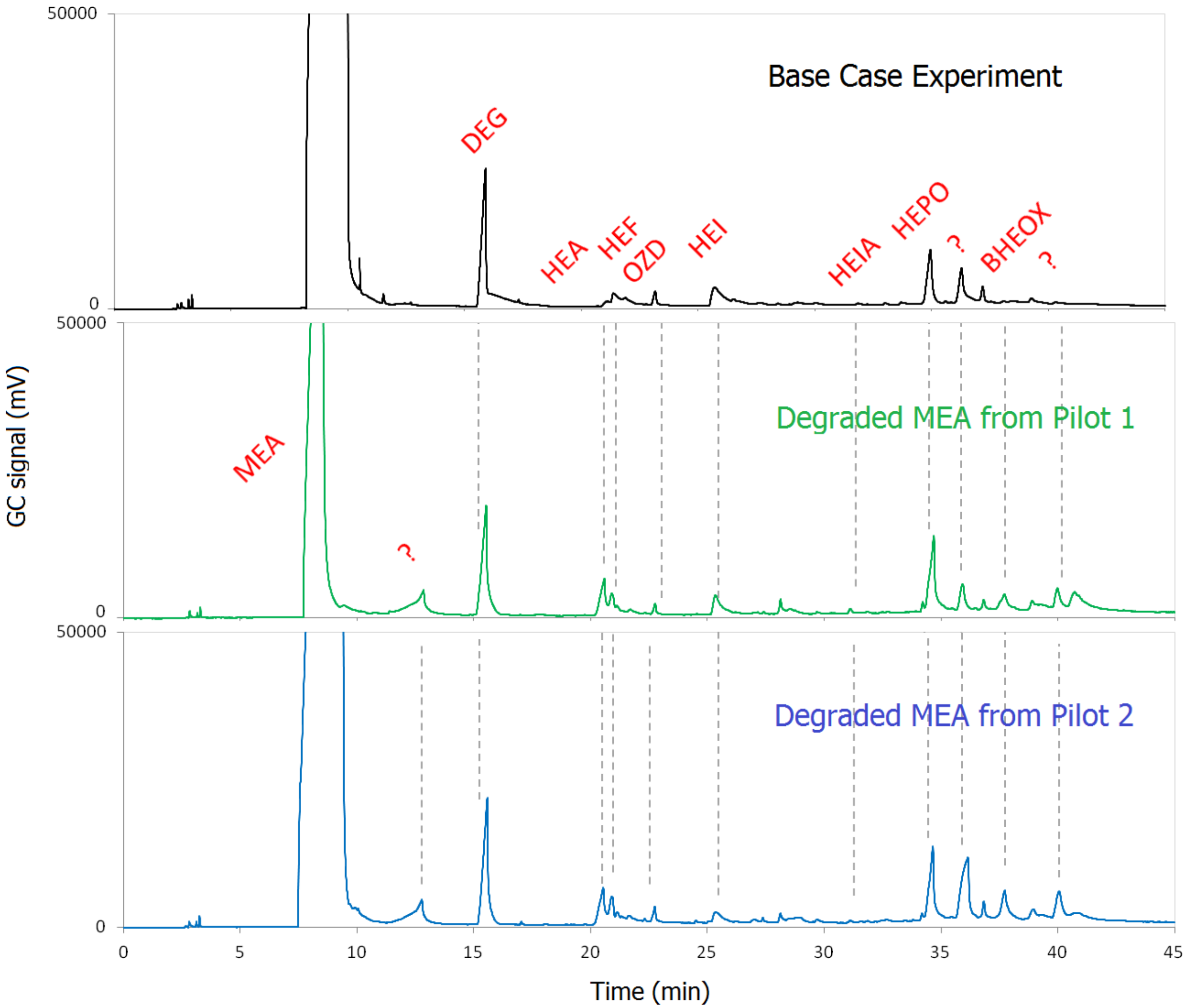
Similar degradation products (GC spectra)!



=> 20% degradation after 7 days!

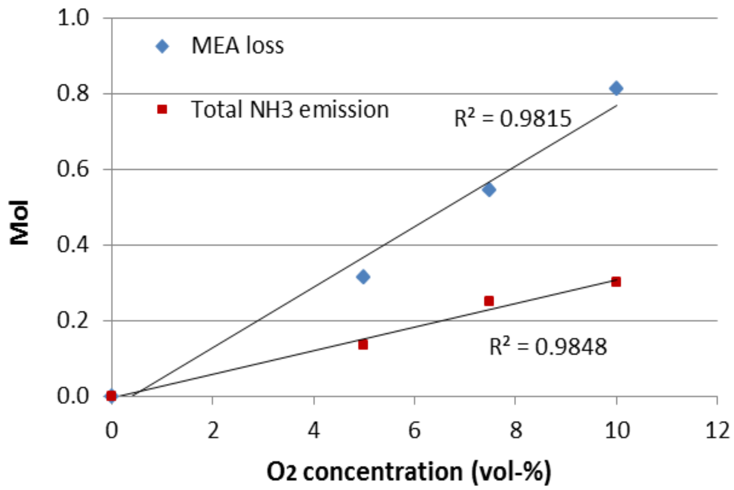
=> Nitrogen mass balance can be closed within 10%

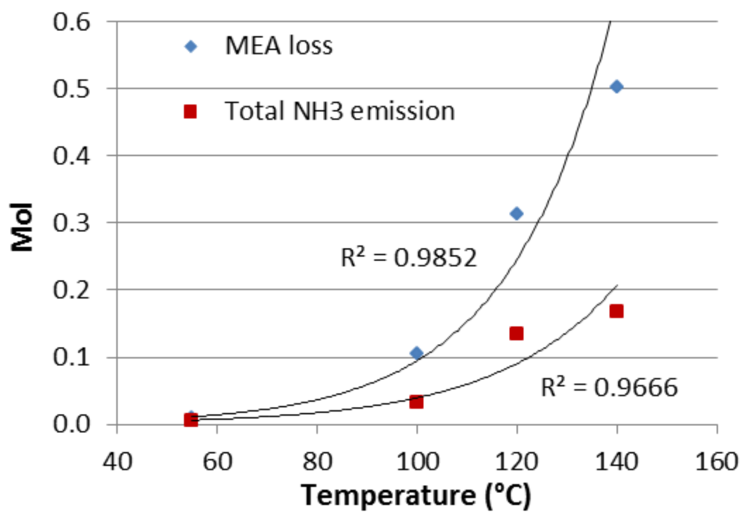
=> Repetition experiments lead to similar results (<5% deviation)

2. Experimental study

Study of the influence of operating variables:

=> Feed gas 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

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

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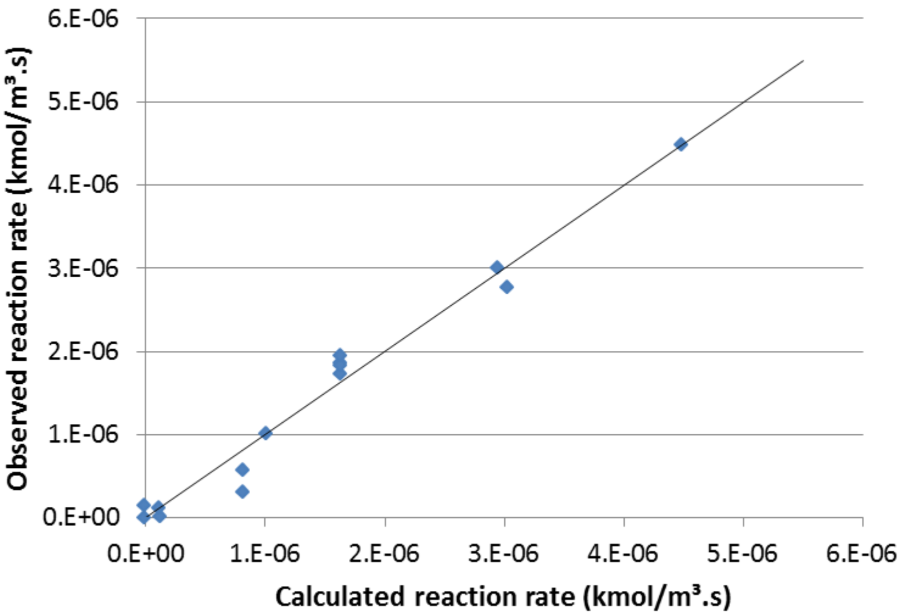
Arrhenius kinetics (kmol/m³.s):

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

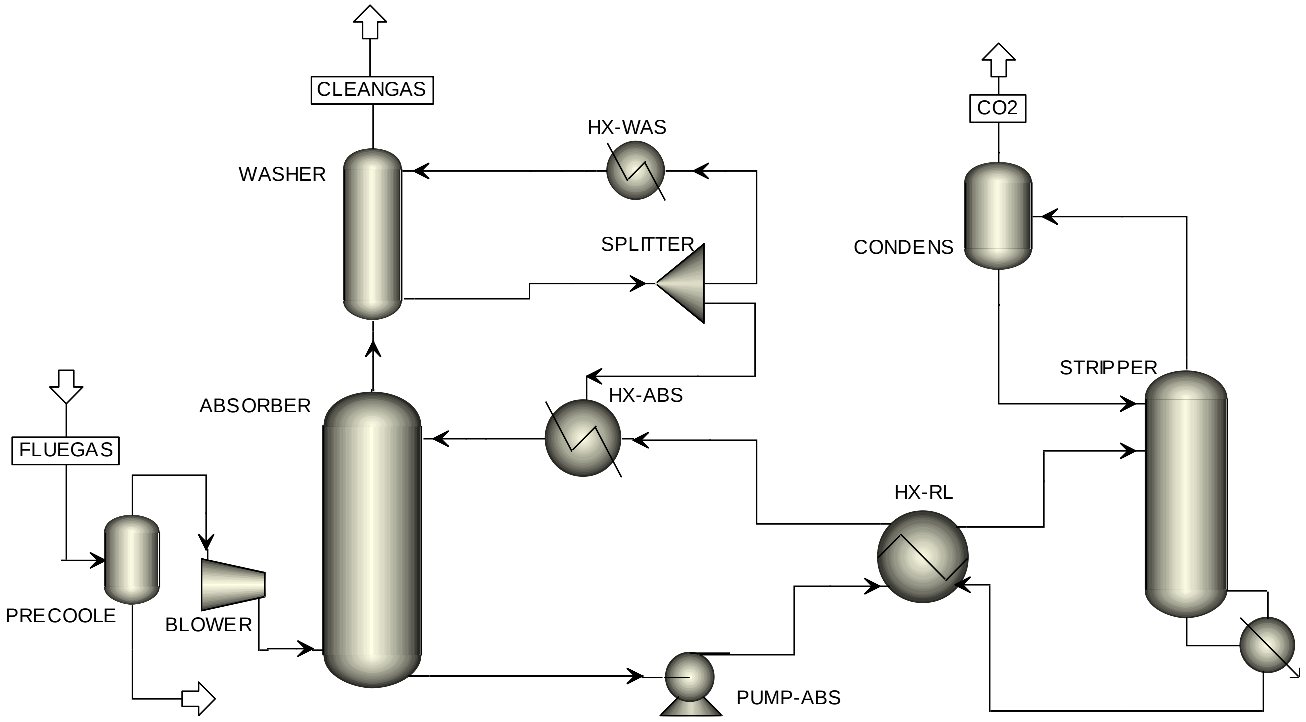
- Oxidative degradation: $r = 535\,209 . e^{-\frac{41\,730}{8{,}314.T}} . [O_2]^{1{,}46}$
- Thermal degradation with CO_2: $r = 6{,}27.1011 . e^{-\frac{143106}{8{,}314.T}} . [CO_2]^{0{,}9}$



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

Degradation model has been included into a global process model built in Aspen Plus[1]

=> Additional equations in the column rate-based models



Leonard G. and Heyen G., 2011. Modeling post-combustion CO_2 capture with amine solvents. Computer Aided Chemical Engineering 29, 1768-1772.

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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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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

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=> 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 324kg MEA/day at large-scale!)

=> 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.

3. Process simulation

Influence of process variables on solvent degradation:

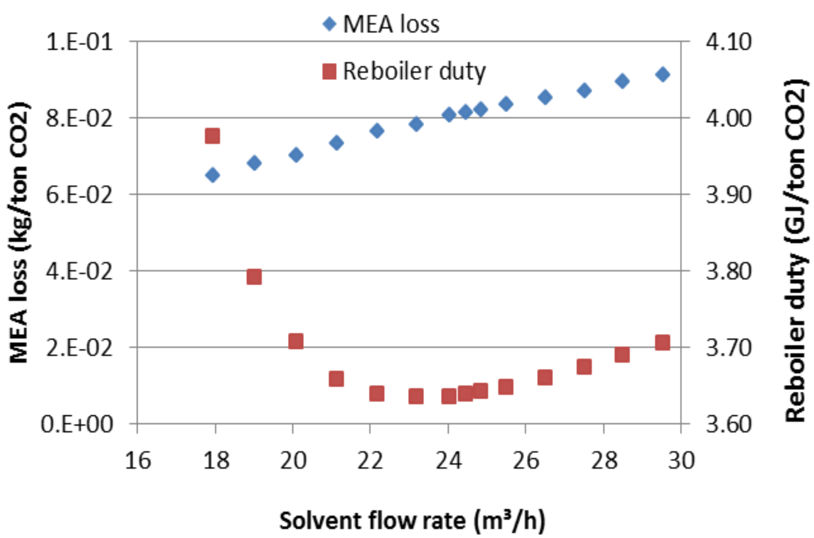
=> Solvent flow rate

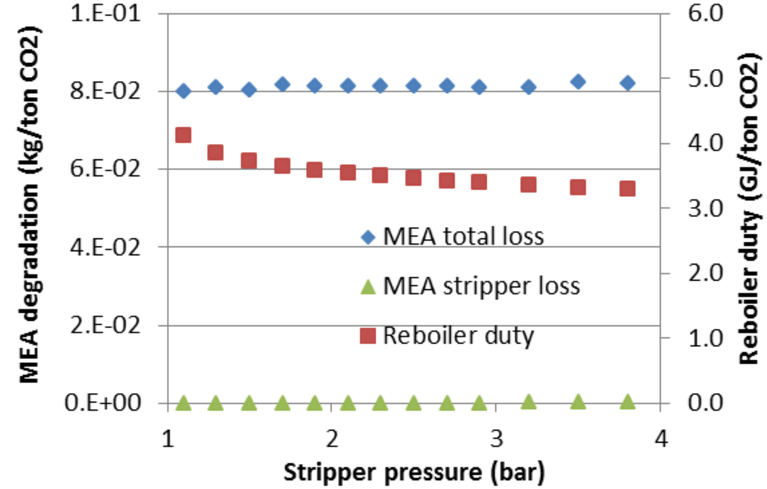
=> Regeneration pressure

=> Oxygen concentration in the gas feed

=> MEA concentration

=> …





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

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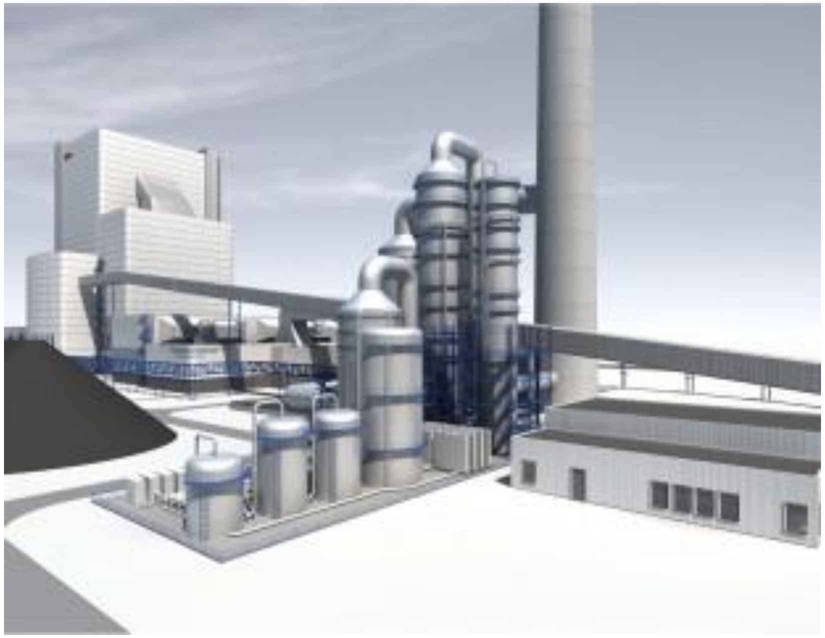
Many challenges are still up to come for the CO_2 capture process!

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

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



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Thank you for your attention!

Lyon, 14th SFGP congres, 2013