Assessment of Solvent Degradation within a Global Process Model of Post-Combustion CO_2 Capture

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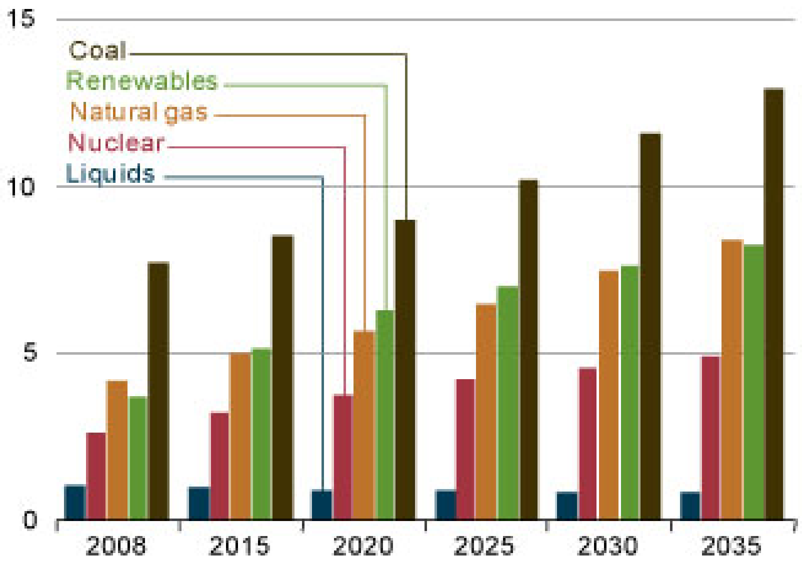
Budapest, Escape 24, June 2014

Global context

CO_2 capture 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. 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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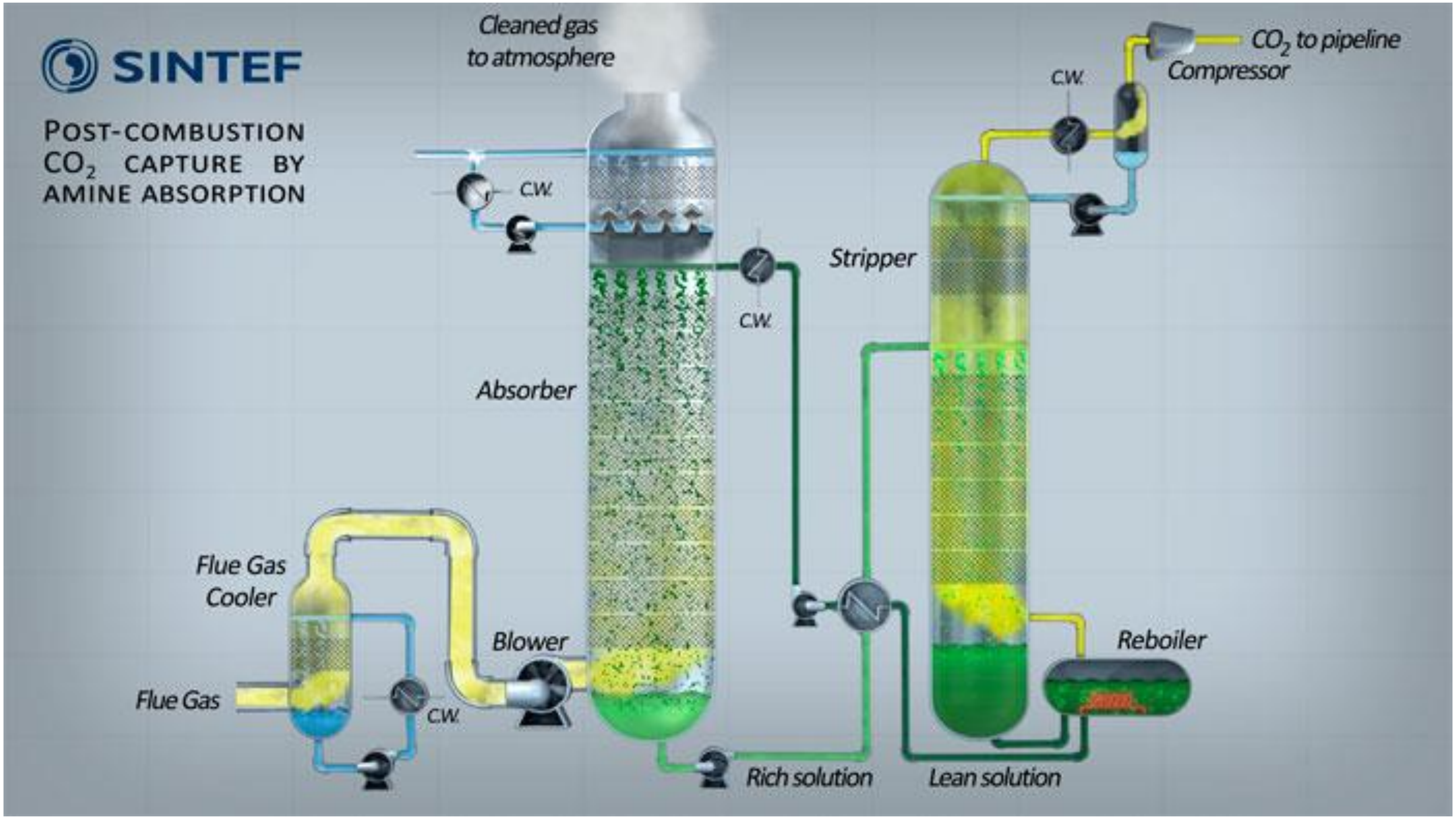
Post-combustion CO_2 capture



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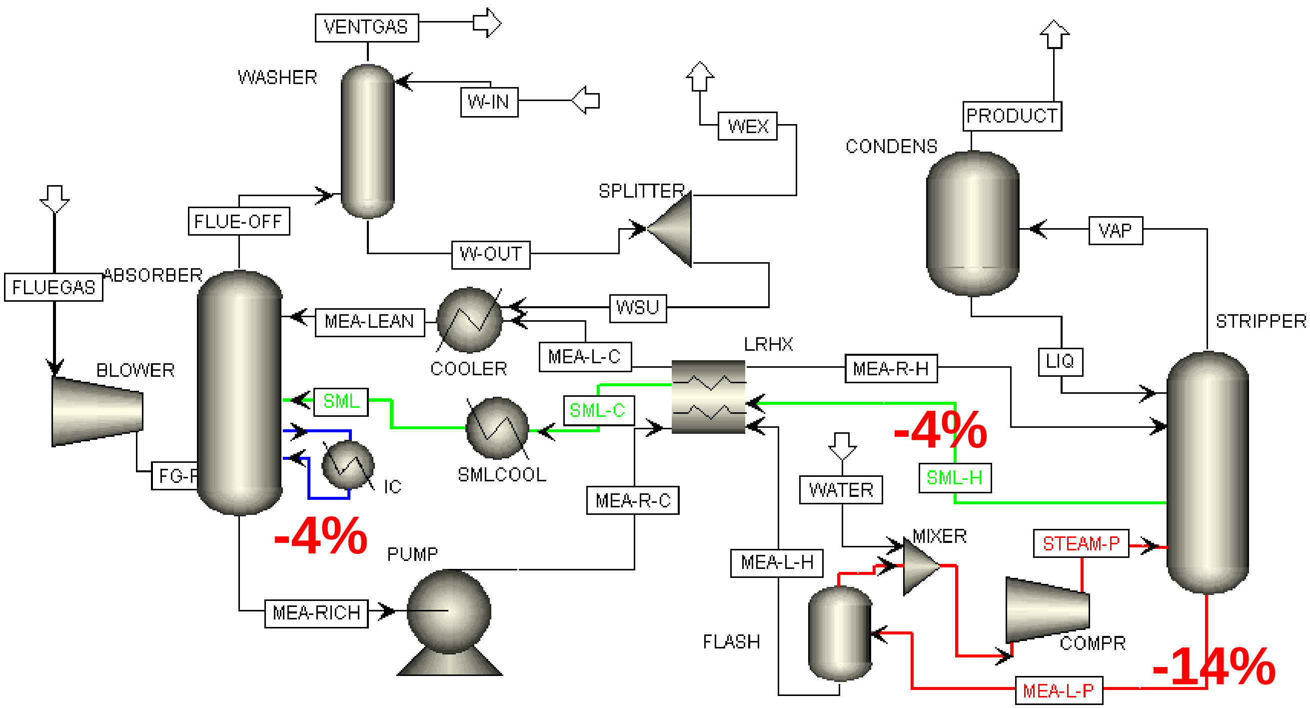
1. Introduction

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.

1. Introduction

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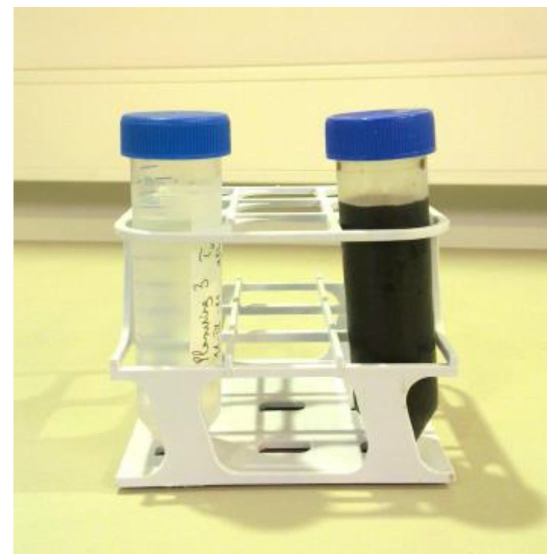
Focus set on solvent degradation

- 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.

1. Introduction

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 degradation

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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

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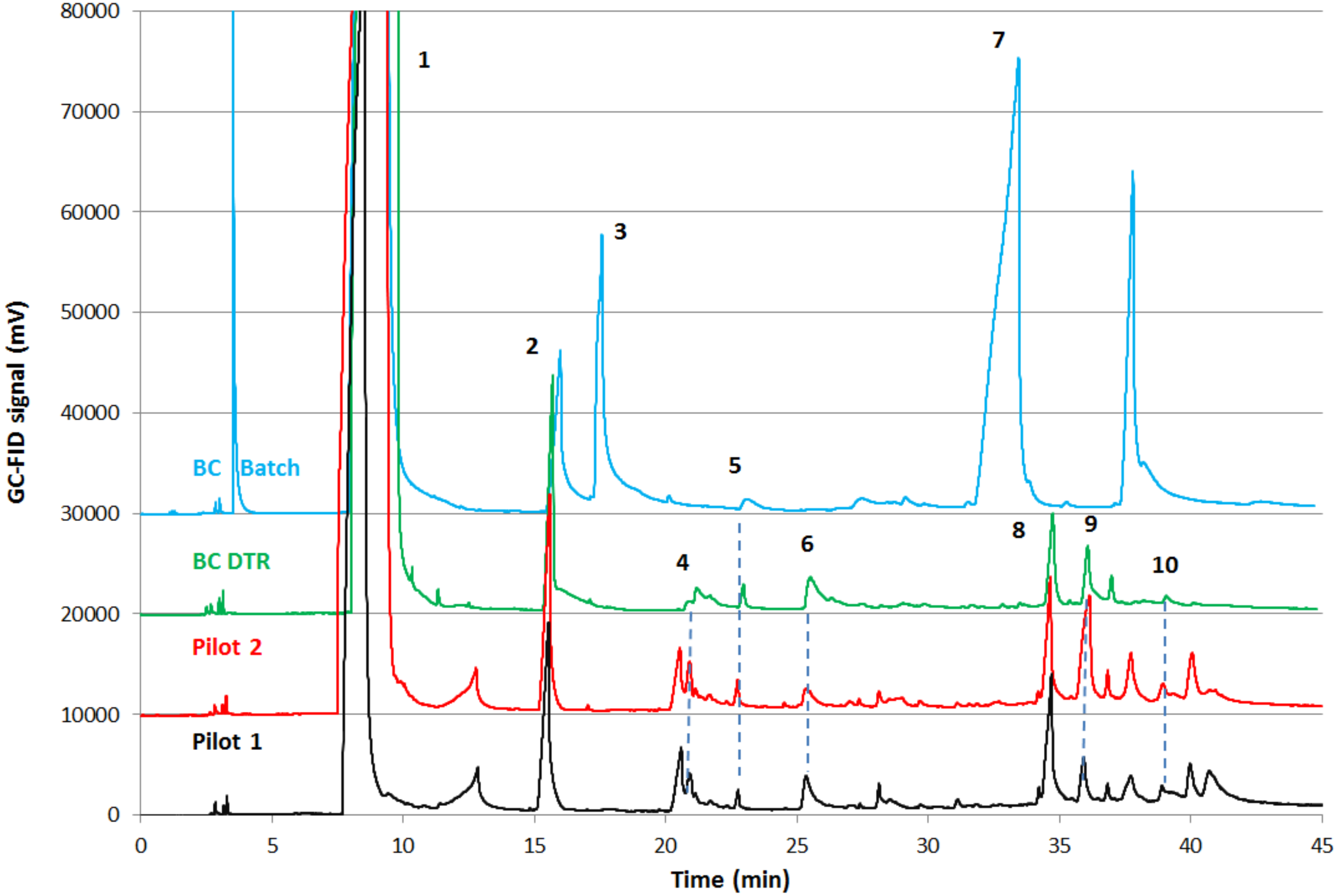
Similar degradation products (GC spectra)!



=> 20% degradation after 7 days!

=> Nitrogen mass balance can be closed within 10%

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

2. Experimental study

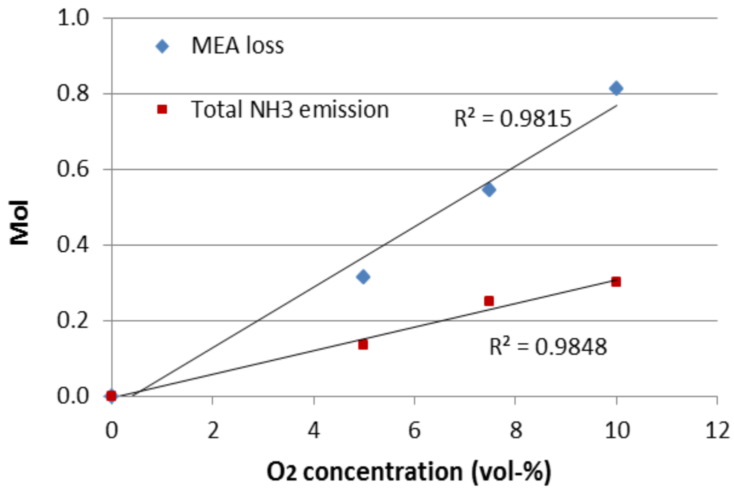
Study of the influence of operating variables:

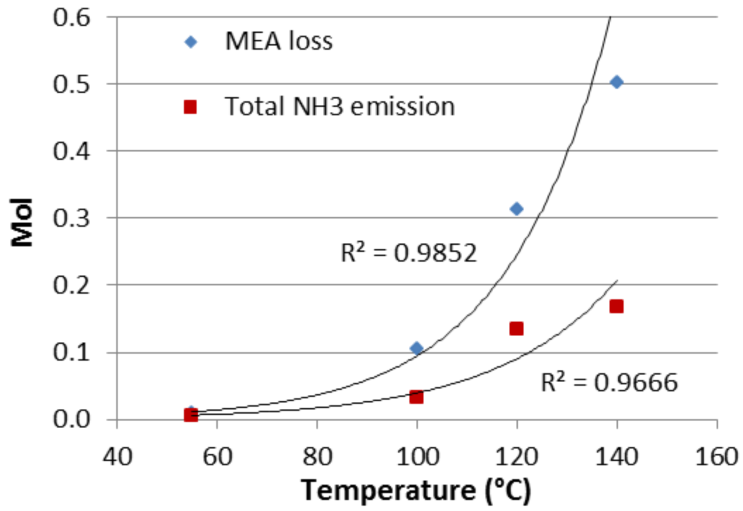
=> Gas feed flow rate and composition (O_2, CO_2)

=> 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

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

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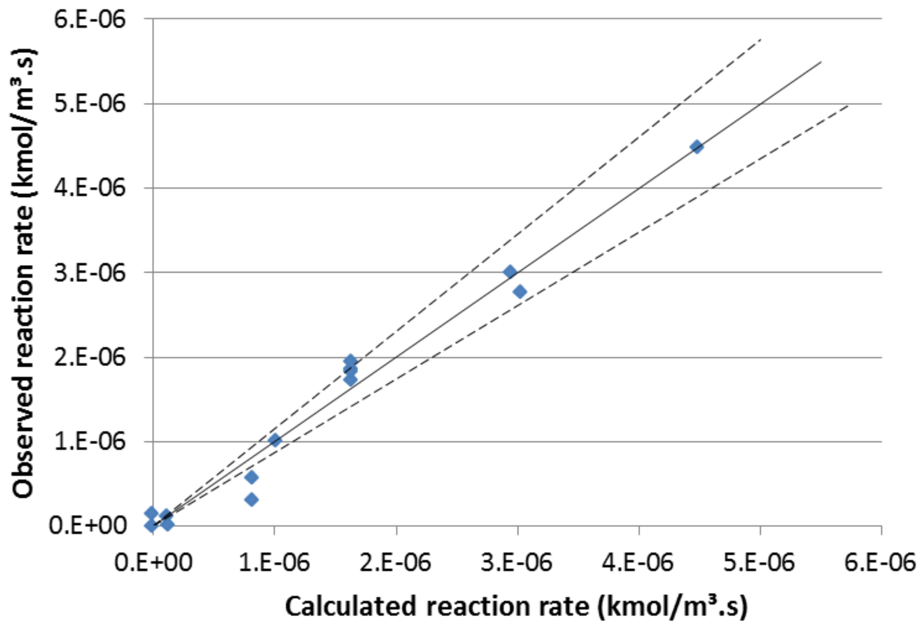
Arrhenius kinetics (kmol/m³.s):

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

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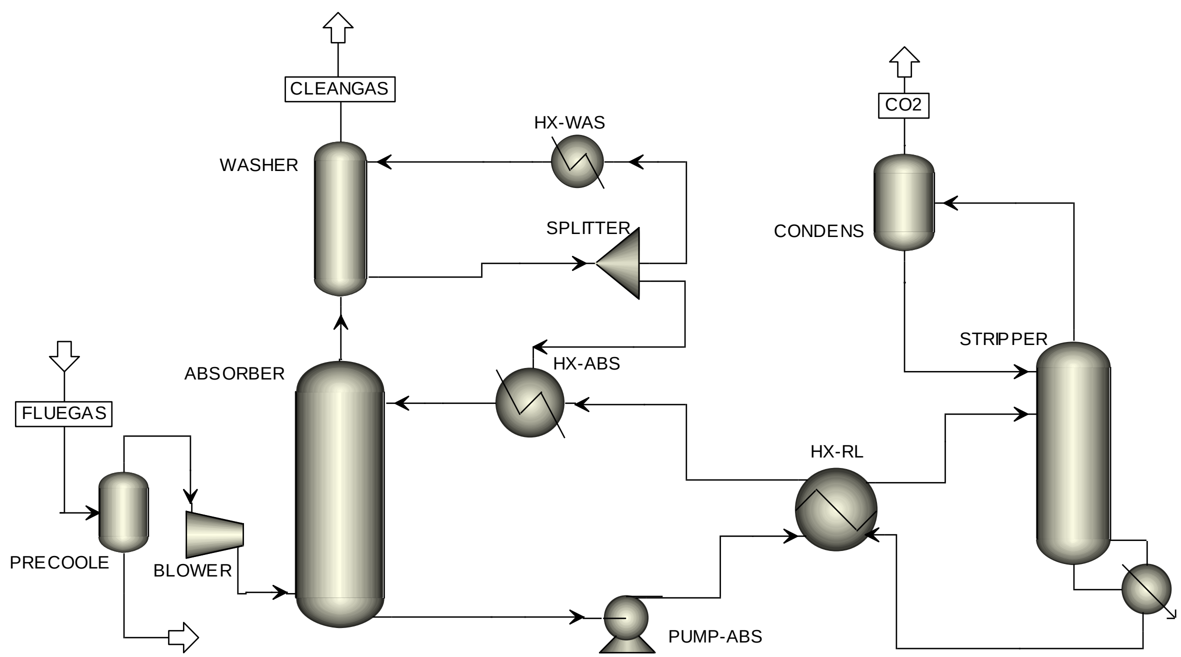
Degradation model has been included into a global process model built in Aspen Plus

⇒ 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

Base case degradation:

Parameter	Unit	Absorber	Stripper	Total
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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:

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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 324kg MEA/day at large-scale ~ 4000 tCO_2/day)!

=> Maybe due to simplifying assumptions:

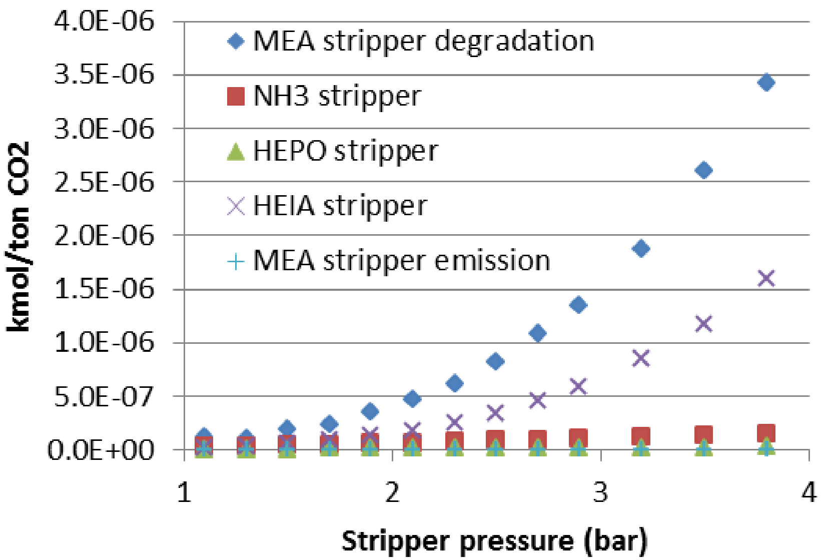
- Modeling assumptions for the degradation kinetics
- Presence of SO_x et NO_x neglected
- Influence of metal ions neglected

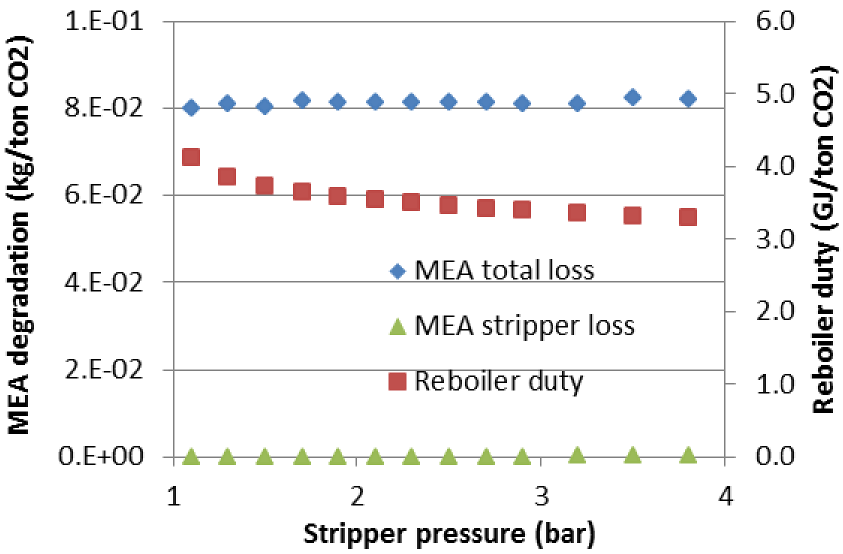
[1] Moser P., Schmidt S. and Stahl K., 2011. Investigation of trace elements in the inlet and outlet streams of a MEA-based post-combustion capture process. Energy Procedia 4, 473-479.

3. Process simulation

Influence of process variables on solvent degradation:

=> Regeneration pressure





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

3. Process simulation

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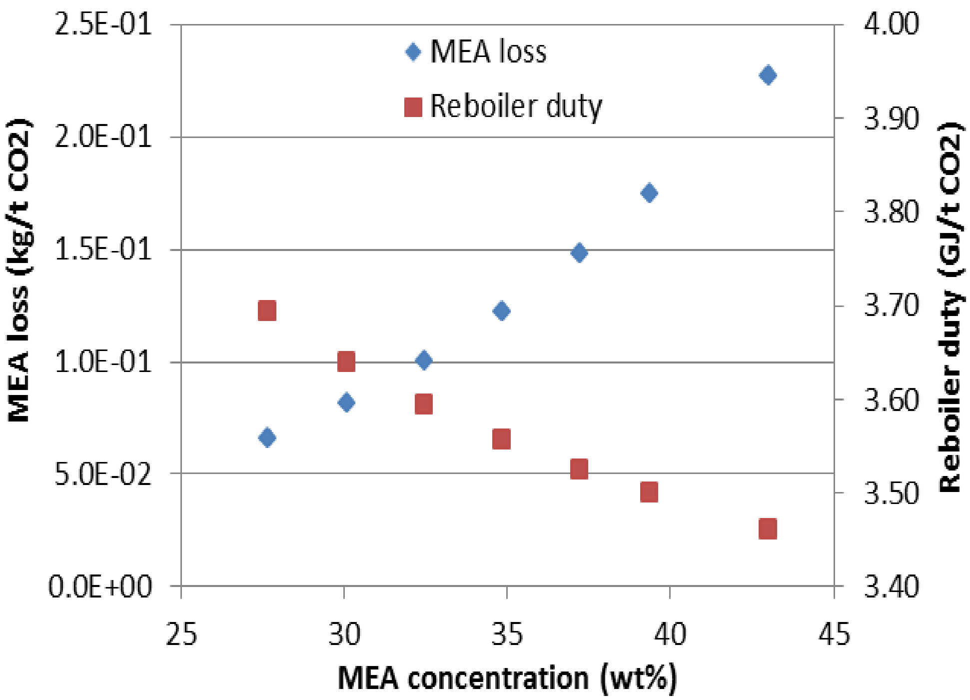
Influence of process variables on solvent degradation:

⇒ MEA concentration



Influence of MEA concentration on the O_2 mass transfer!

3. Process simulation

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⇒ 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.*

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.

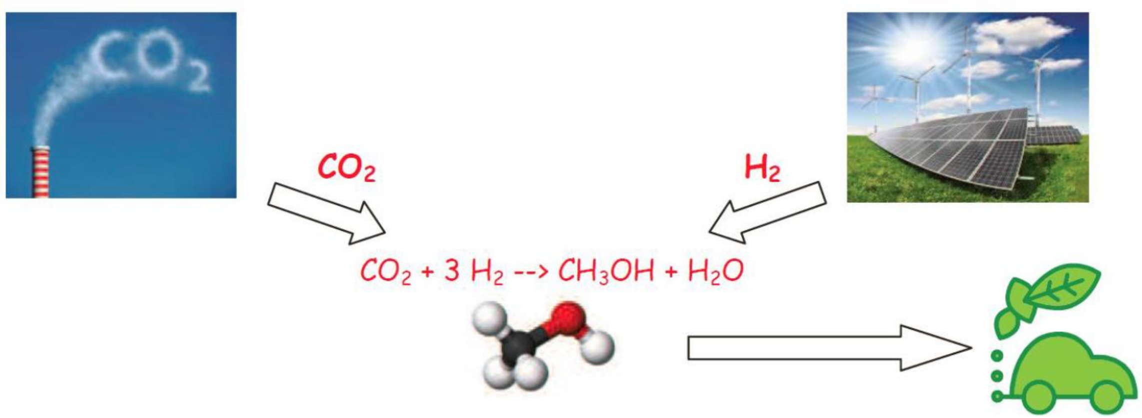
4. Conclusion

- 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 methanol synthesis



Thank you for your attention!

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Back-up slides

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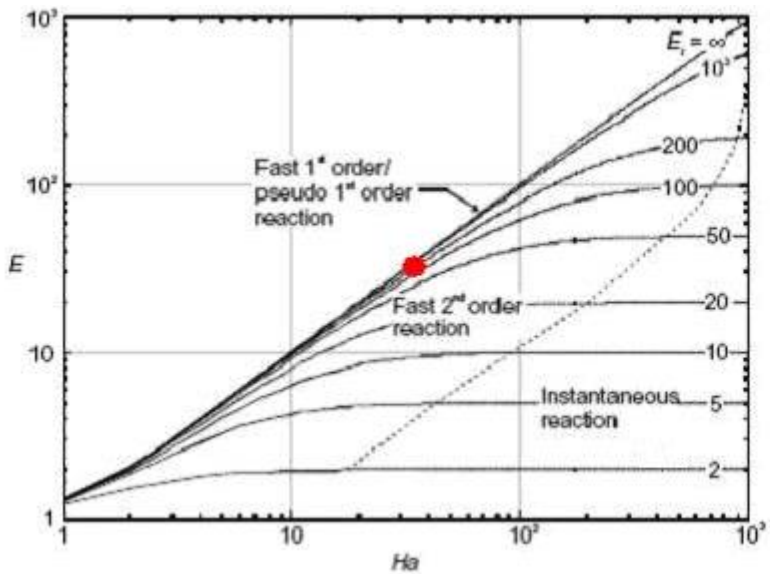
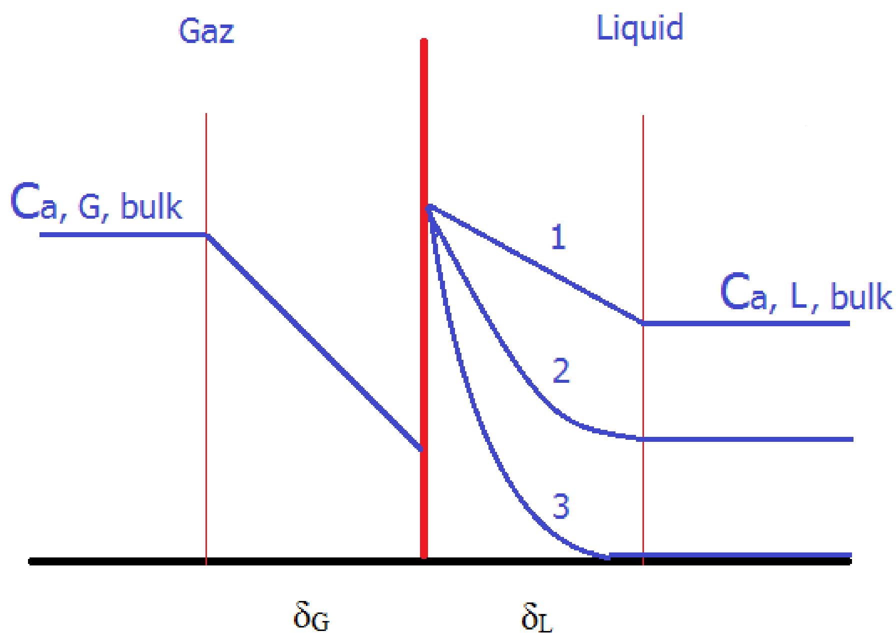
- Mass transfer enhancement due to the chemical reaction in the liquid film





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

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

Back-up slides

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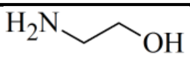
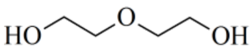
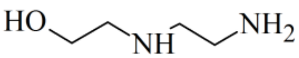
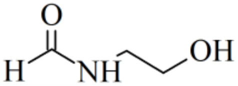
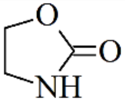
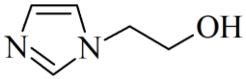
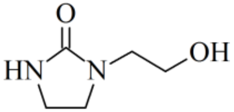
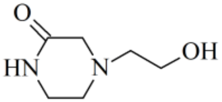
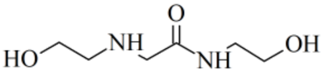
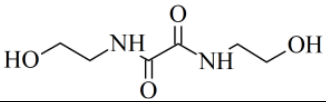
Table 1. Main peaks identified in GC spectra of degraded MEA samples

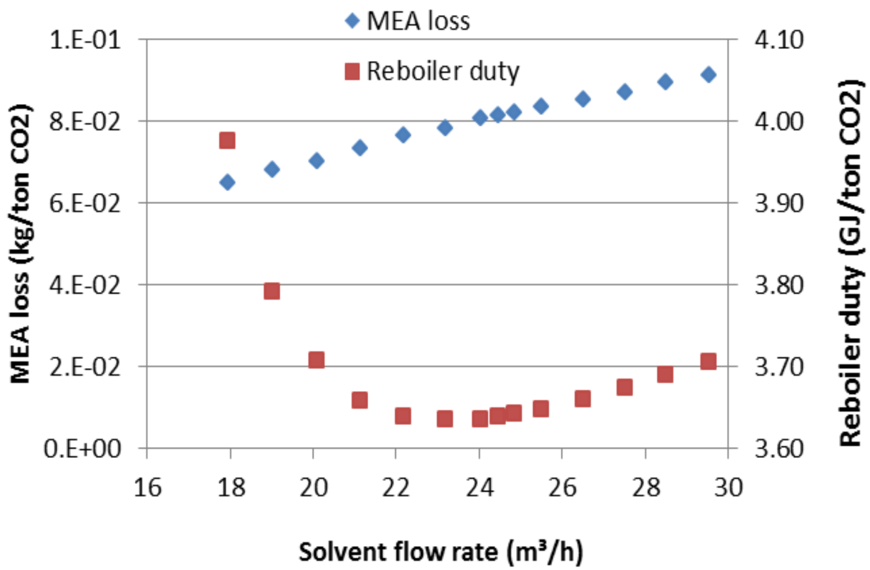
		Compound	Structure	Retention time (min)	Type
1	MEA	monoethanolamine		7.6	Start amine
2	DEG	diethylene glycol		15.0	Internal standard
3	HEEDA	*N*-(2-hydroxyethyl)ethylenediamine		17.0	Quantified
4	HEF	*N*-(2-hydroxyethyl)formamide		21.1	Identified
5	OZD	2-oxazolidinone		22.5	Quantified
6	HEI	*N*-(2-hydroxyethyl)imidazole		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

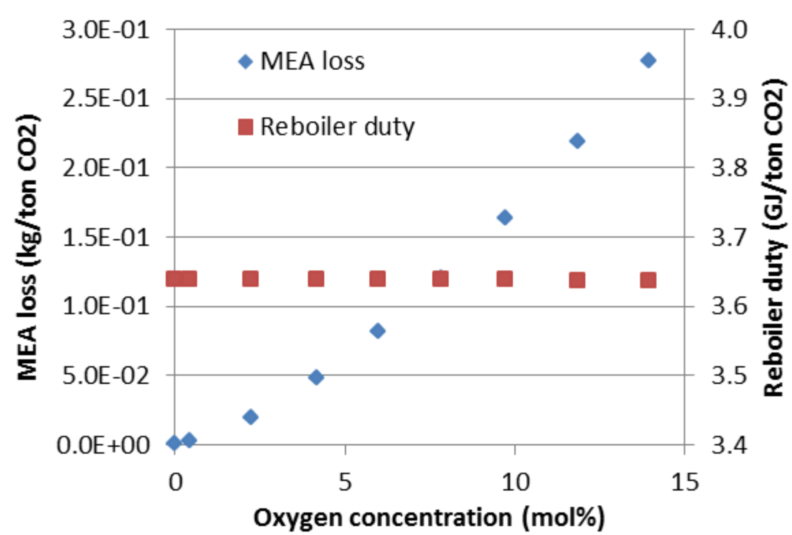
3. Process simulation

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.