

Optimal design of a CO₂ absorption unit and assessment of solvent degradation

Mid-term Presentation

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14th December 2011

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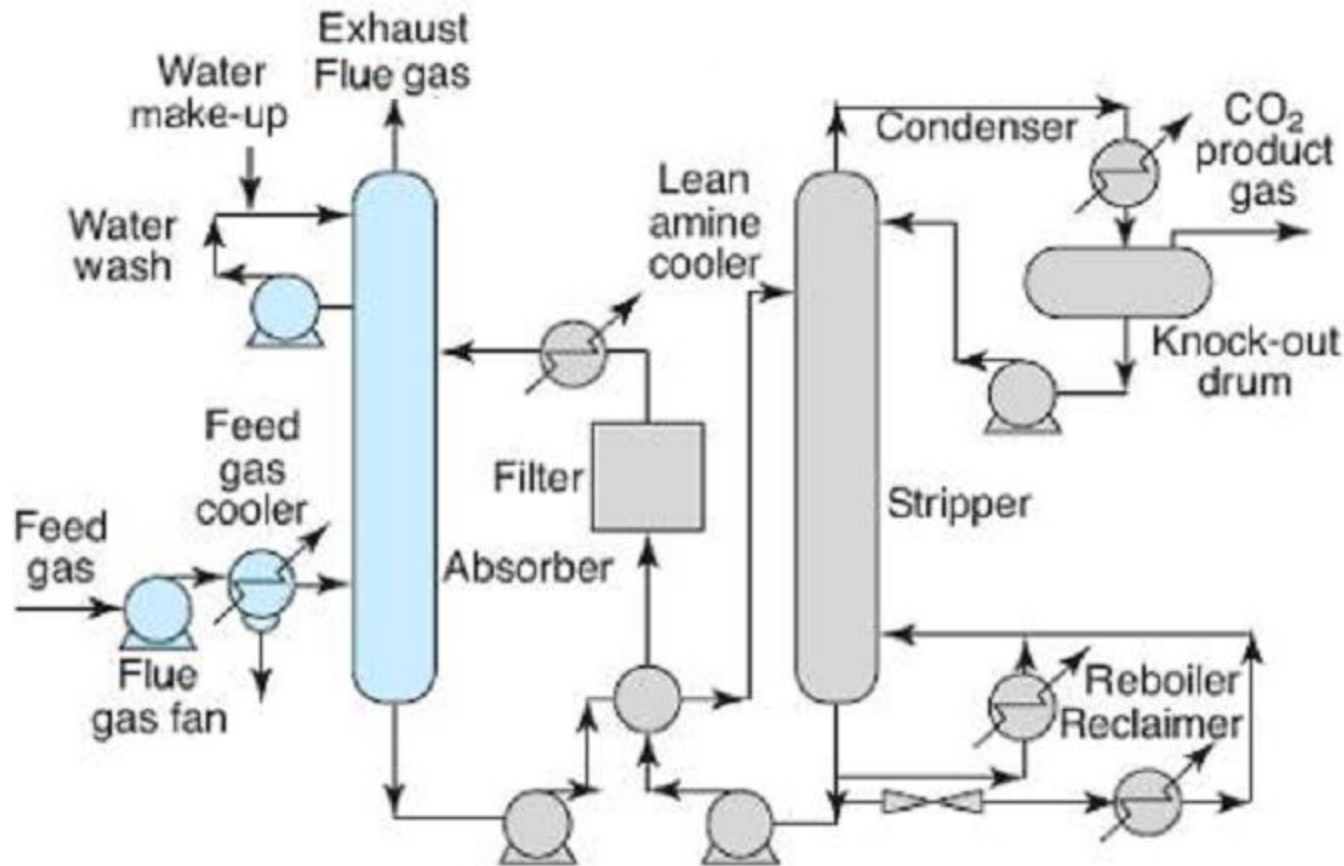
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5. Conclusion and perspectives

1. Introduction

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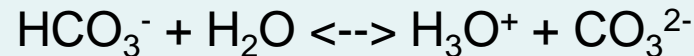
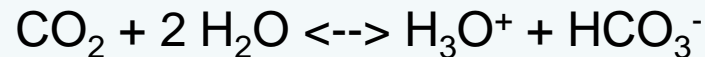
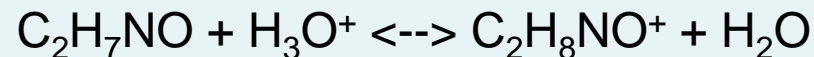
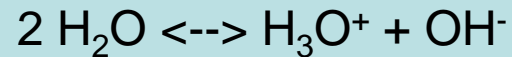
1. Introduction

CO₂ capture in coal power plants



1. Introduction

Chemical reactions taking place during the CO₂ capture in Monoethanolamine (MEA):

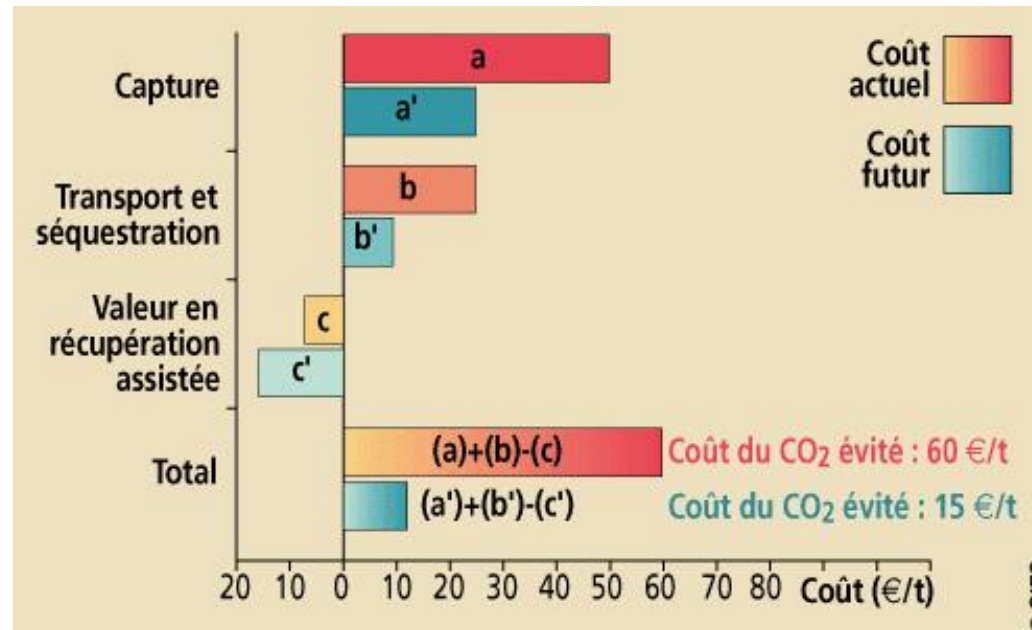


2. Objectives

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2. Objectives

Context: reduction of the CO₂ capture cost for large scale power plants



=> Energy requirement and degradation induced costs are among the largest operative costs!

2. Objectives

- To establish a link between **modeling** and **degradation**

2. Objectives

- To establish a link between **modeling** and **degradation**
- The result will be
a proposal
 - ... for **optimal operating conditions** in the CO₂ capture process
 - ... taking into account **process efficiency** and **solvent degradation**
 - ... i.e. **cost** and **environmental impacts** of PCC







3. Modeling and optimal design

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3.1 Objectives

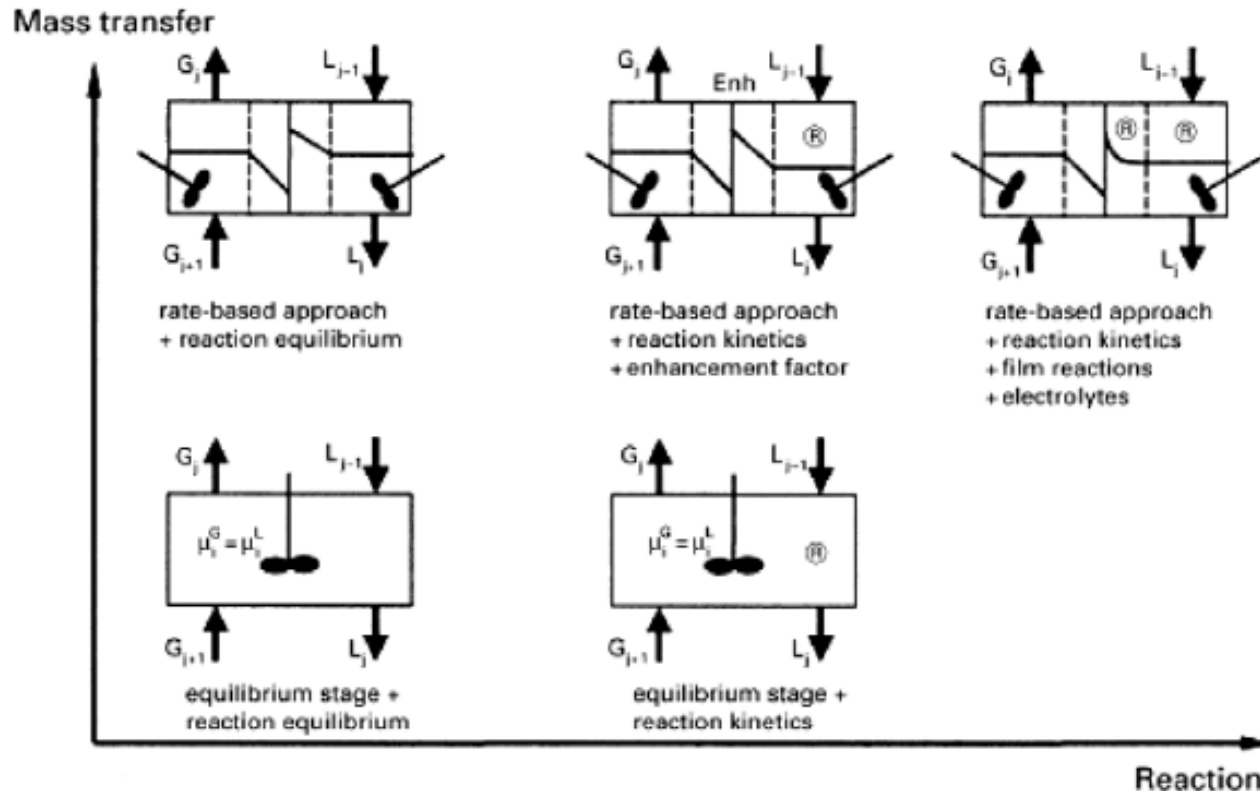
- Model building
- Sensitivity study of key parameters
- Simulation of process improvements
- Validation based on experimental results
- Implementation of degradation results
- Multi-objective optimization

3.1 Objectives

- Model building 
- Sensitivity study of key parameters 
- Simulation of process improvements 
- Validation based on experimental results 
- Implementation of degradation results 
- Multi-objective optimization 

3.2 Model Building

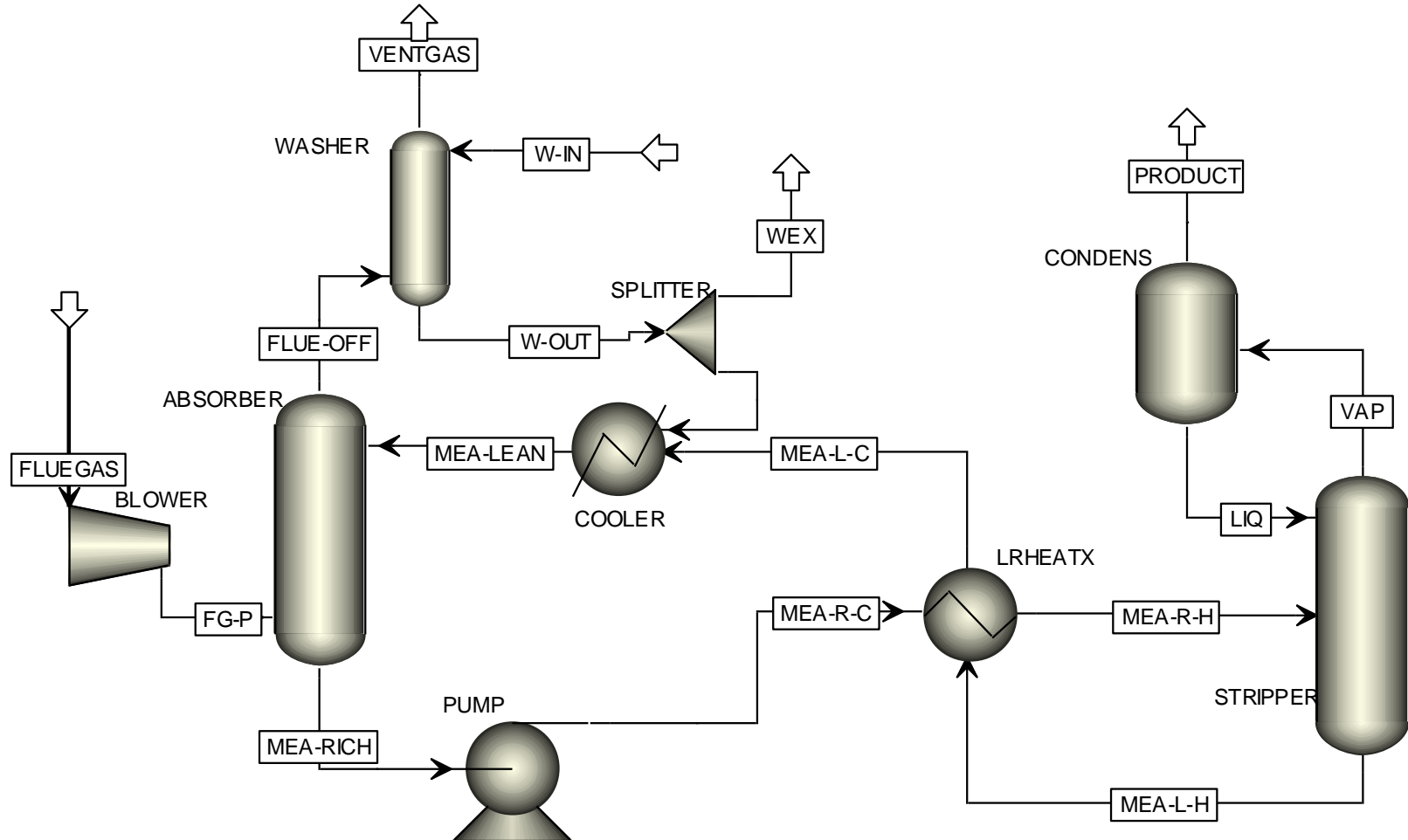
Two different modeling approaches



Model parameters: 2500 NM^3 flue gaz, 14vol-% CO_2 ,
90% Capture rate, MEA 30wt-%

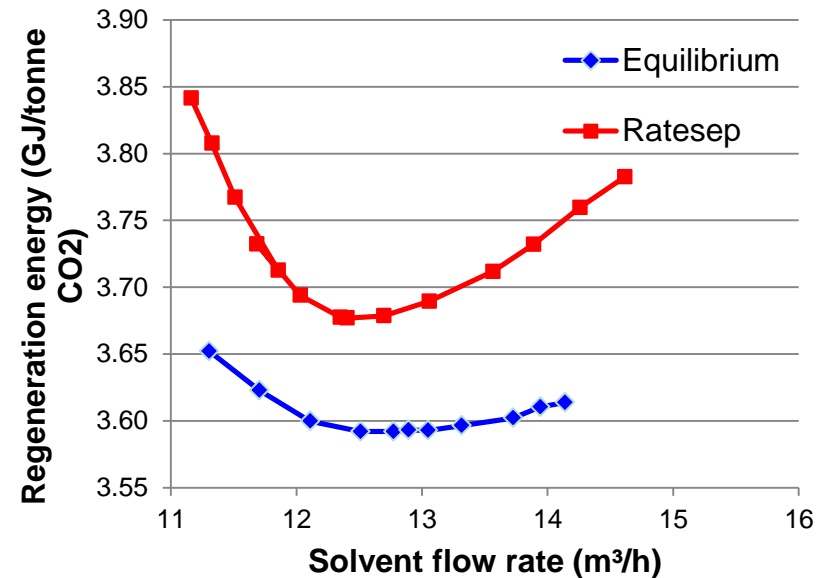
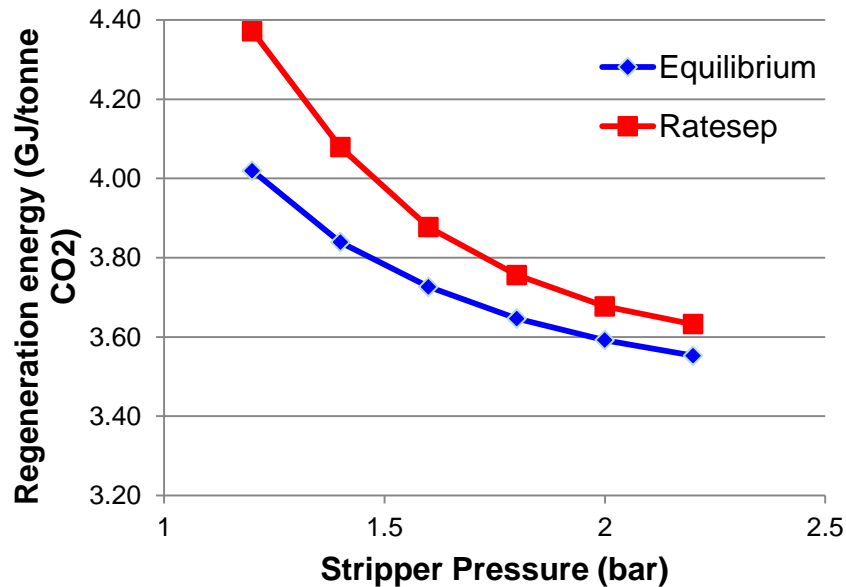
3.2 Model Building

Simulation tool: Aspen Plus V7.2



3.3 Sensitivity study

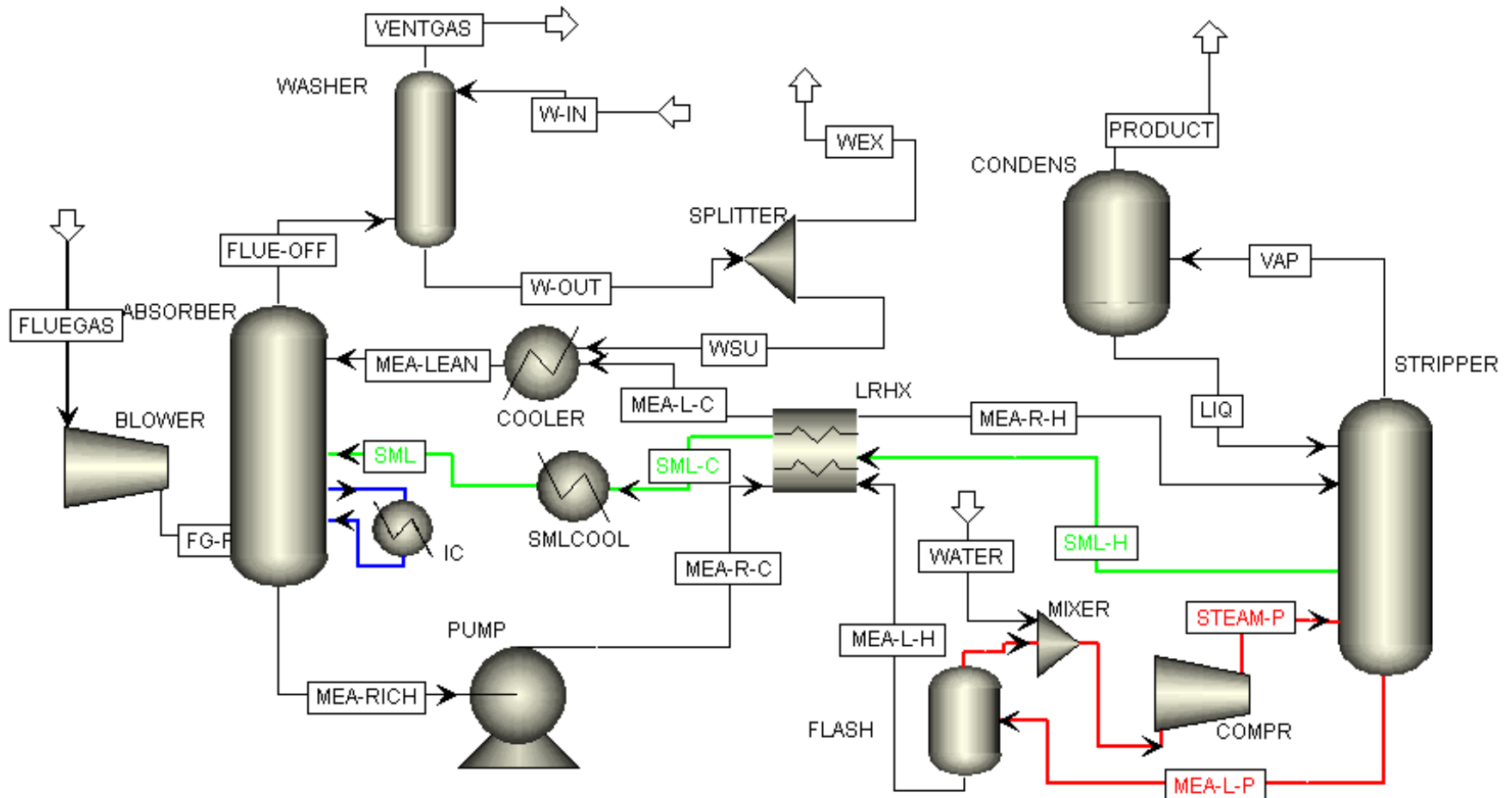
Sensitivity study of process key variables



Results	Stripper Pressure	Solvent concentration	Solvent flow rate
Base Case Value	1.2 bar	30 wt-%	15 m³/h
Optimized Value	2.2 bar	37 wt-%	12.4 m³/h
Gain in regeneration energy	-16.9%	-5.4%	-2.8%

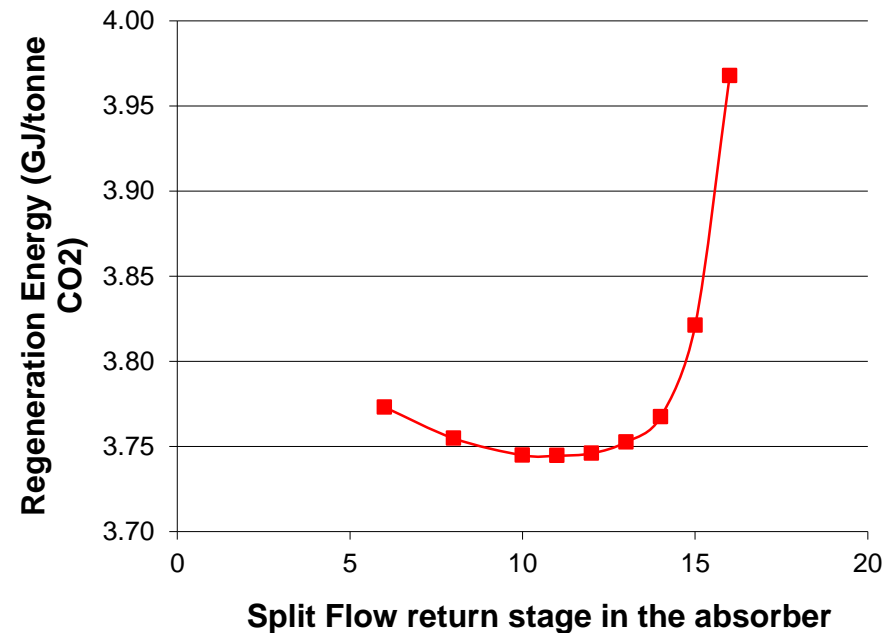
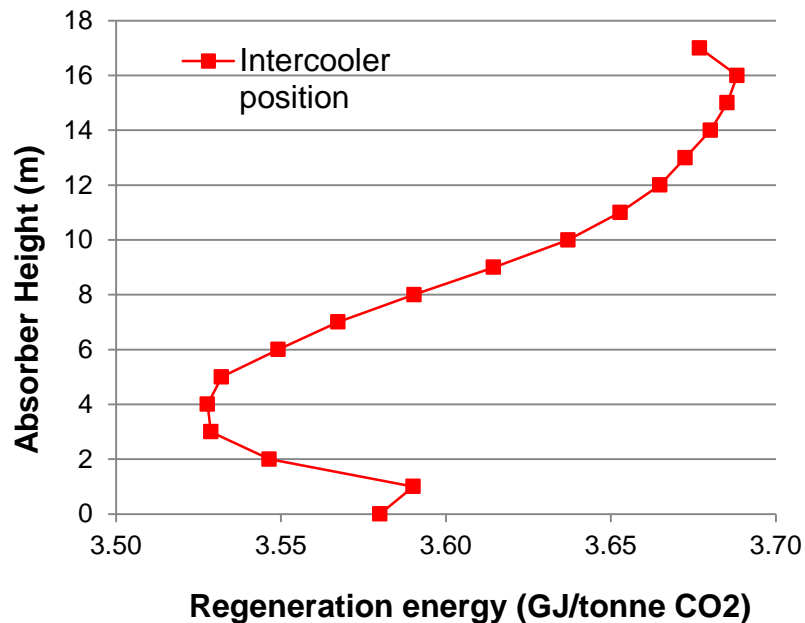
3.4 Model improvements

Impact study of process improvements



3.4 Results summary

Impact study of process improvements



Process modifications	Lean vapor compression	Absorber intercooling	Split-flow configuration
Gain in regeneration energy	-14% (exergy)	-4%	-4%

3.5 Conclusion

- It is possible to identify optimal operating conditions using modeling
- Simulation results are less costly than lab experiments and can help to the decision for process improvements
- Good model knowledge has been gained and can be useful for further simulation
- However, simulation results still don't take secondary effects into account (degradation, corrosion, ...)

3.6 Perspectives

- Writing of an article and submission for publication to a journal in the field *Energetics and Engineering*
=> planed at the beginning of 2012.
- Validation of the model may occur soon, depending on pilot experimental results
=> validation based on:
 - Regeneration energy = $f(\text{solvent flow rate})$
 - Absorber and stripper temperature profiles
 - Solvent lean and rich loading

3.6 Perspectives

- Follow-up of a master thesis with subject « Simulation of the dynamic behavior of a pilot plant for CO₂ capture »
 - => First semester 2012
 - => Objective is to develop a dynamic model using Aspen Dynamics
 - => Eventually modeling of process improvements
- First tests for the implementation of degradation parameters in Aspen Plus







4. Solvent degradation

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4.1 Objectives

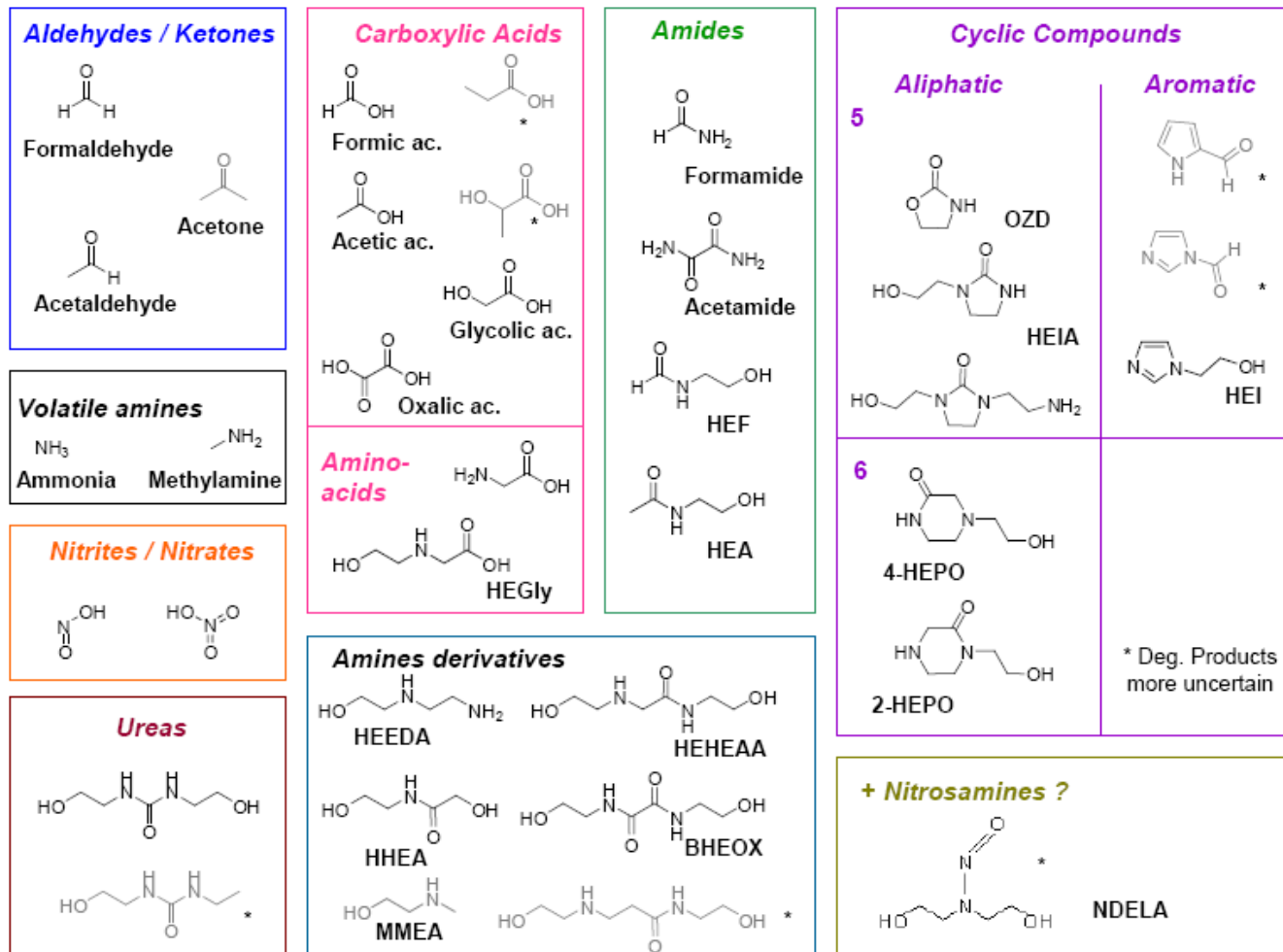
- Design and construction of a degradation test rig
- Detailed screening of MEA degradation
- Study of the impact of operating conditions
(temperature, gas composition, flow, ...)
- Study of the effect of additives (degradation inhibitors, metal)
- Test of 1 or 2 other solvents
- Results implementation in the process model

4.1 Objectives

- Design and construction of a degradation test rig 
- Detailed screening of MEA degradation 
- Study of the impact of operating conditions
(temperature, gas composition, flow, ...) 
- Study of the effect of additives (degradation inhibitors, metal) 
- Test of 1 or 2 other solvents 
- Results implementation in the process model 

4.2 Literature review

3 types of degradation mechanisms: Temperature, O₂, CO₂

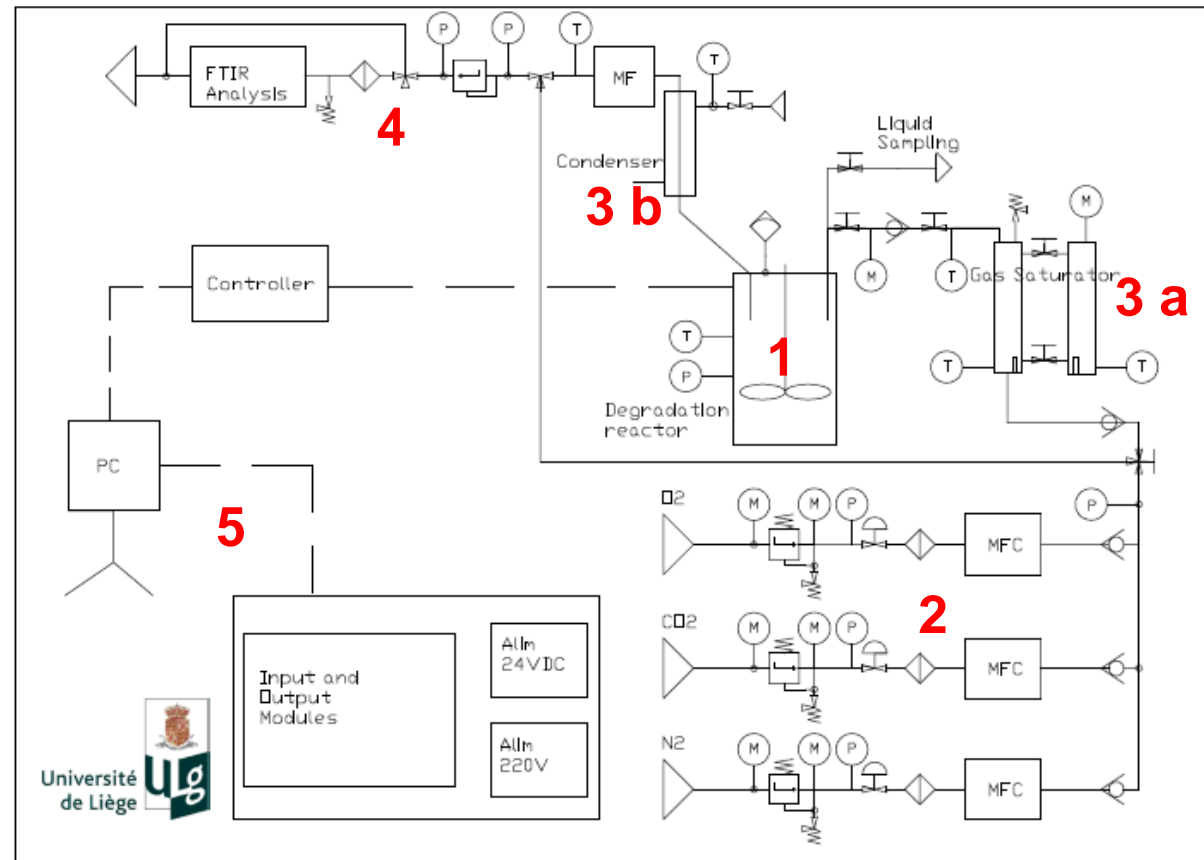


4.2 Literature review

Reference	Description	Volume	Gas feed mode	T (°C)	P (bar)	Solvent	Analysis	Run time
Supap et al., 2001	Kinetic law for MEA-degradation in function of solvent concentration, O ₂ , Temperature and stirring	230ml		120-150	2,41-3,45 bar O ₂	MEA (2-11mol/L)	GCMS	2 - 12 days
Lawal and Idem, 2005; Lawal et al. 2005&2006	Influence of O ₂ , CO ₂ , MDEA-MEA-ratio, Temperature, amine concentration + Product formation mechanisms, Ecotoxicity	450ml		55-120	2,5 bar O ₂ /CO ₂	MEA-MDEA blends (7-9mol/L)	GCMS (+HPLC from 2006)	6 - 22 days
Bello and Idem, 2005	Pathways of degradation reaction, influence of O ₂ , CO ₂ , Temperature, MEA concentration, ...	230ml	Discontinuous with gas feed to compensate for pressure losses	55-120	2,5-3,5 bar O ₂ /CO ₂	MEA (5-7 mol/L)	GCMS	6 - 30 days
Supap et al. 2006	Analysis techniques: comparizon and methods	450ml		55-120	2,5-4,5 bar O ₂ /CO ₂	MEA (5 mol/L)	GCMS, HPLC, CE	18-24 days
Bello and Idem, 2006	Influence of the corrosion inhibitor NaVO ₃ on Degradation kinetics	230ml		55-120	3,5-4,5 bar O ₂ /CO ₂	MEA (5-7 mol/L)	HPLC	6-30 days
Uyanga and Idem, 2007	Influence of the corrosion inhibitor NaVO ₃ and of SO ₂ on kinetics. Kinetics model	450ml		55-140	2,5 bar O ₂ /N ₂ /CO ₂ /SO ₂	MEA (3-7 mol/l)	HPLC	5-10 days
Supap et al., 2009	Kinetics data for O ₂ and SO ₂ -induced Degradation	450ml		55-120	2,5 bar O ₂ /N ₂ /CO ₂ /SO ₂	MEA (3-7 mol/l)	HPLC	6-13 days
Chi and Rochelle, 2000	Influence of CO ₂ -loading and inhib (Fe, Bicine, EDTA) on NH ₃ production rate	500ml	5L/min Air/N ₂ /Air+2%CO ₂	55	1	MEA (13-42 wt-%)	FTIR	up to 8 hours
Goff and Rochelle 2004; Goff, 2005; Goff and Rochelle 2006	Importance of O ₂ -mass transfer and agitation rate, influence of Fe-Cu and of the presence of degradation products on degradation rate, Test of several oxydative degradation inhibitors for Fe-Cu catalysed deegradation	550 g	Up to 8L/min Air/Air + CO ₂	55	1	MEA (6-85 wt-%)	FTIR	8- 17 hours
Sexton, 2008; Sexton and Rochelle, 2009	Test of different gas flow rate, influence of degradation catalysts (Fe, Cr-Ni, Cu, V) and inhibitors, test of MEA-PZ blends, amine screening	350-400ml	Low flow (100ml/min 2%CO ₂ /98%O ₂) and high flow (7,5 L/min Air/N ₂ /2%CO ₂)	55	1	MEA (42 wt-%)	FTIR, IC (AC&CC), HPLC	12-15 days
Davis and Rochelle, 2009; Davis 2009	Dependance of Degradation rate on Temperature, Pressure and amine concentration. Thermal degradation of different amines, Kinetics model.	10ml	Batch +CO ₂	100-150	1-8	MEA (15-40wt-%)	IC (cationic), HPLC, MS	Few days to several months
Bacot et al., 2007	Degradation and corrosion screening for 20 amines	Not reported	Batch	140	5 bar O ₂ /CO ₂ /N ₂	Different amines	GC, GCMS, HPLC, IC	14 days
Notz et al., 2007	Degradation rate of primary, secondary amines, and activator (PZ).	350g	10 nml/min 40%N ₂ , 30%O ₂ , 30%CO ₂	90	1	Different amines	GC, RMN	14 days
Notz 2009	Solvent degradation induced by contact with gas, Castor 1&2, MEA	350g	10 - 20nml/min N ₂ /O ₂ /CO ₂	40-120	1-4	MEA	GC-FID	14 days
Notz 2009	Thermal degradation	7 ml	Batch	140-180	N ₂ atmosphere	MEA (30wt-%)	GC-FID	7 days
Knudsen et al., 2007	Results from test campaigns on Esbjerg pilot	~20m ³ /h	Plant conditions	up to 125°C	max 2 bar	MEA (30wt-%) +Castor1&2	Not reported	Several months
Captech, 2007	Degradation studies for the Captech program. Few details available.	100ml	350 ml/min N ₂ /CO ₂ /Air	150	1.2	Different amines	GC	Several months
Lepaumier, 2008; Lepaumier et al., 2008	Degradation Mecanisms and products for differents amines	100ml	Batch O ₂ /CO ₂ /N ₂ /Air	140	20	Different amines	GCMS, RMN	2weeks

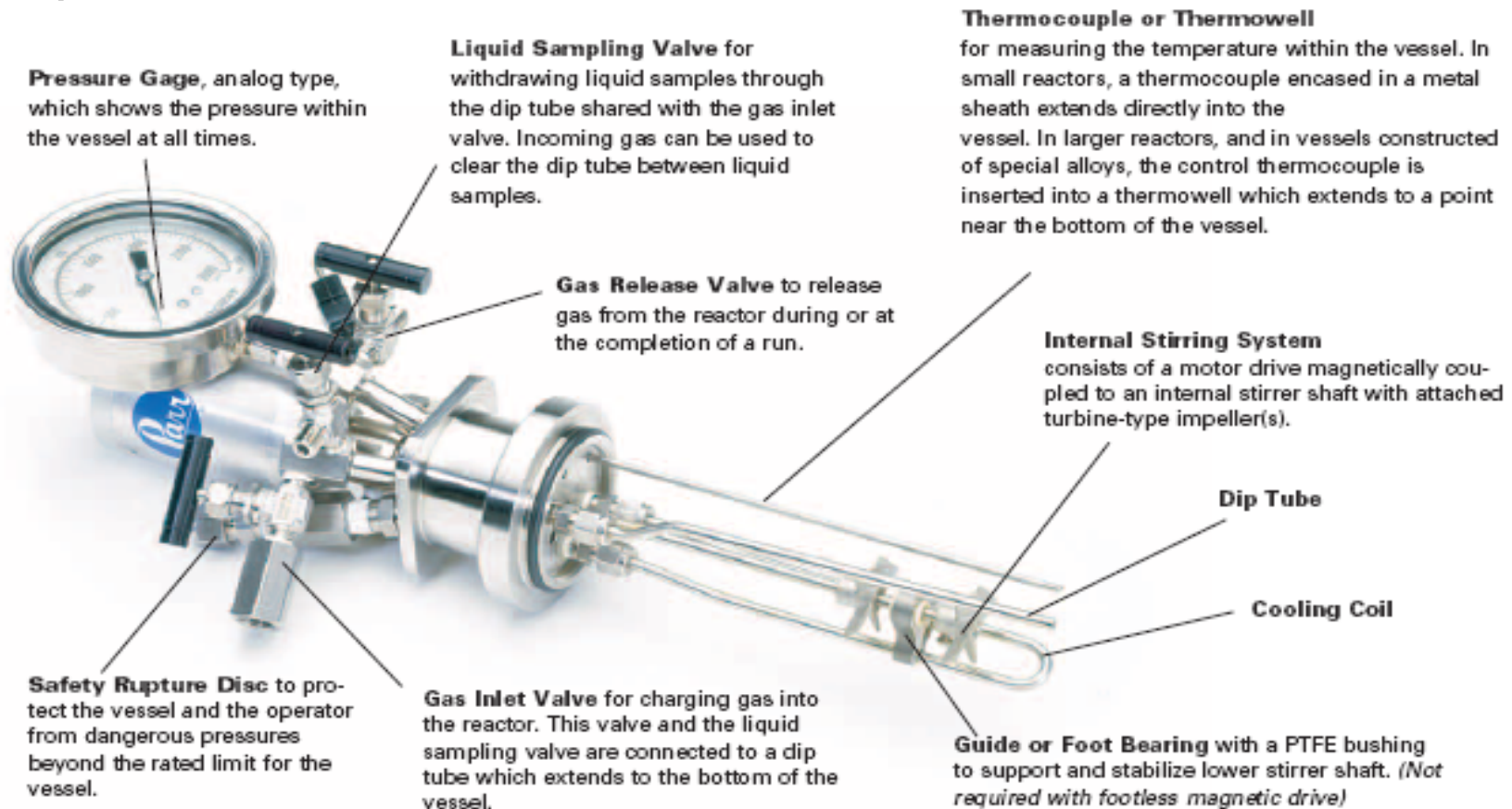
4.3 Degradation Test Rig

1. Reactor
2. Gas supply
3. Water balance
4. Gas flow
5. Control panel



4.3 Degradation Test Rig

Test rig continuously improved to face experimental problems



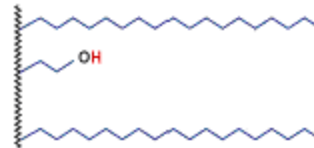
4.4 Analytical Methods

- Liquid phase:
 - **HPLC** (High Pressure Liquid Chromatography): MEA quantification
 - **GC-FID** (Gas Chromatography): identification & quantification of the degradation products
 - **IC** (Ionic Chromatography): quantification of organic anions
 - **Karl-Fischer** Titration: water quantification
 - **AAS** (Atomic Absorption Spectroscopy) and **CE** (Capillar Electrophoresis): quantification of inorganic ions
- Gas phase:
 - **FTIR** (Fourier Transform Infrared Spectroscopy):
NH₃ and MEA quantification

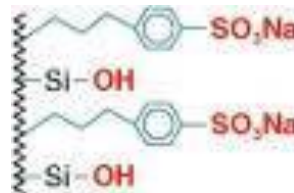
4.4.1 HPLC

Quantification of MEA: 3 different columns have been tested

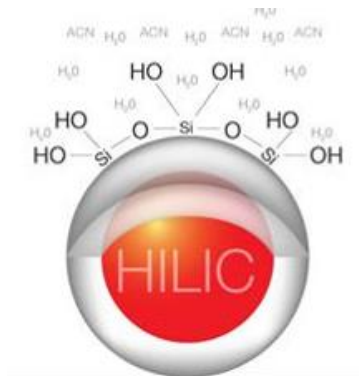
- C18 Pyramid



- Nucleosil 100-5 SA



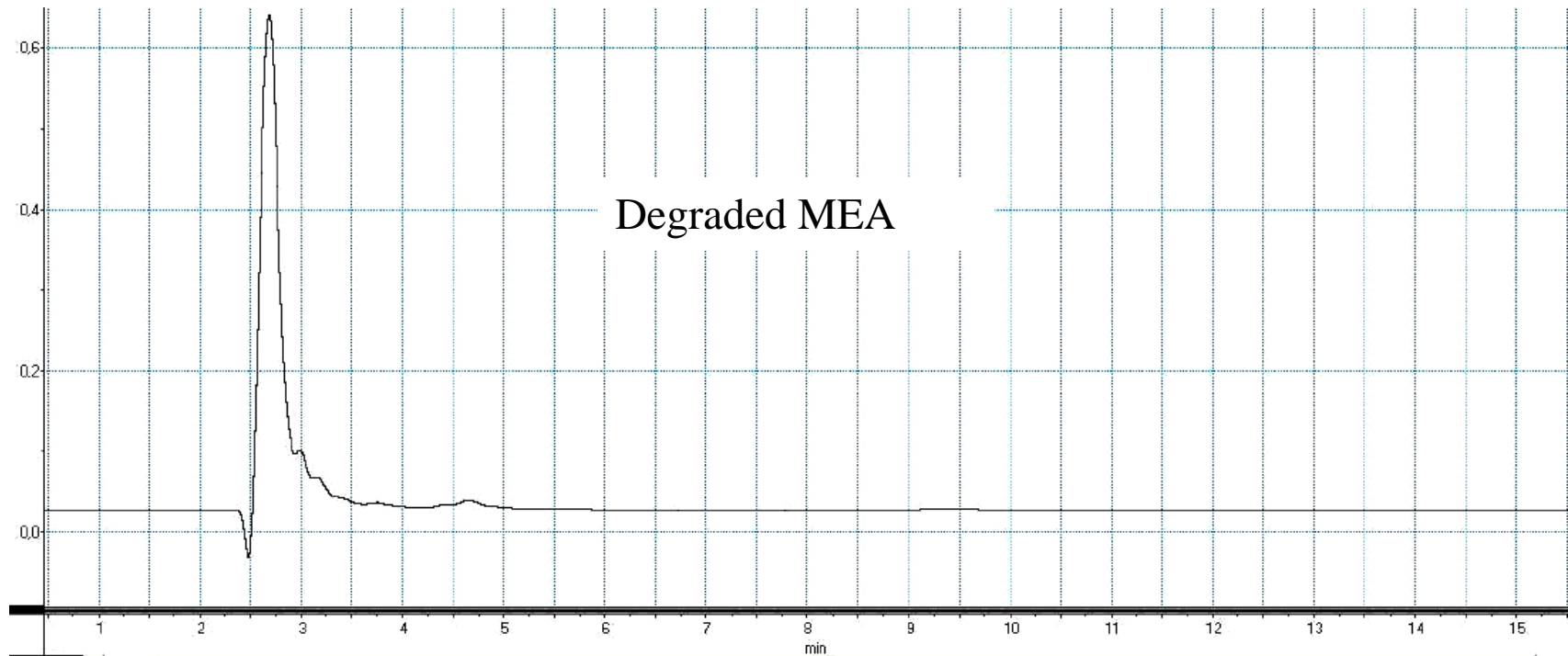
- HILIC



4.4.1 HPLC

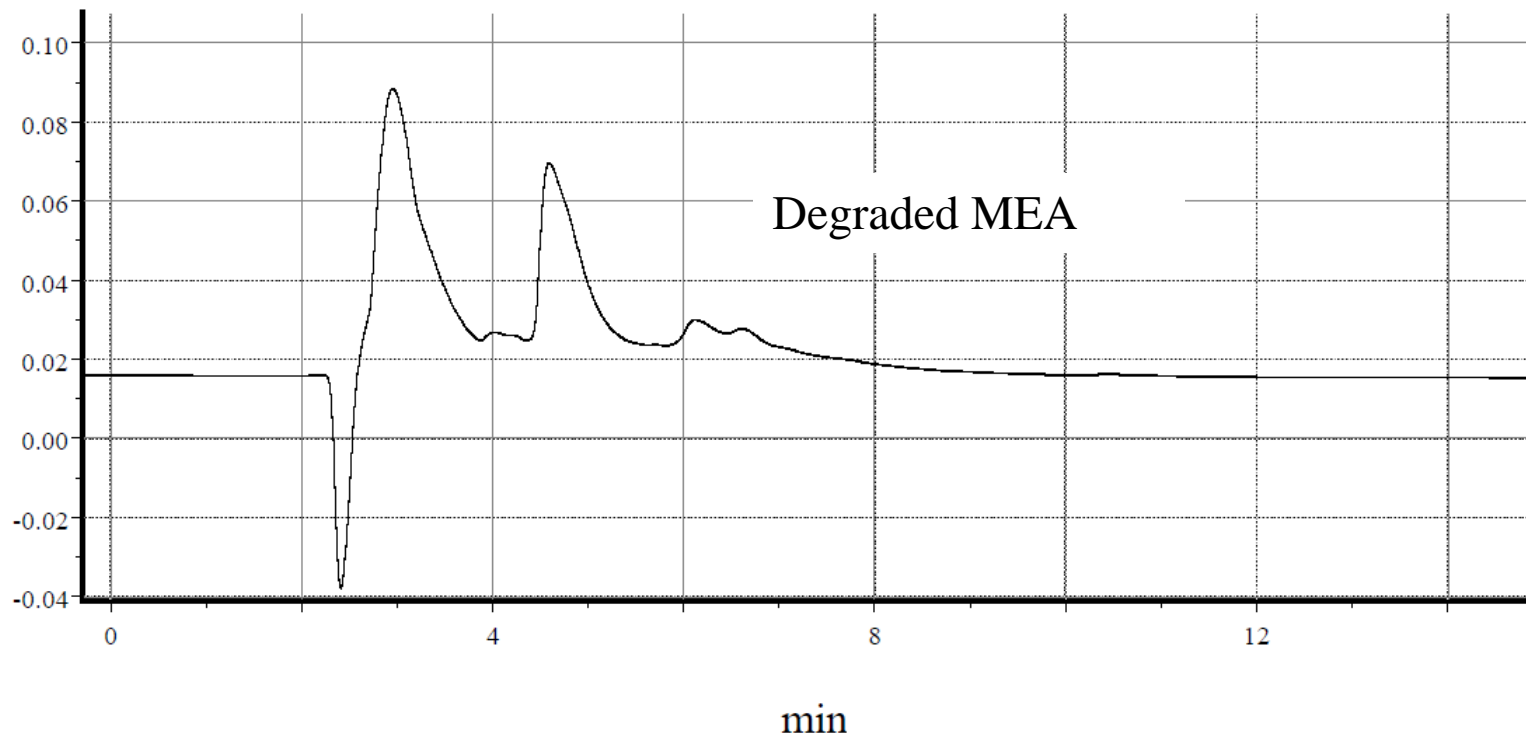
With different results...

- C18: no retention



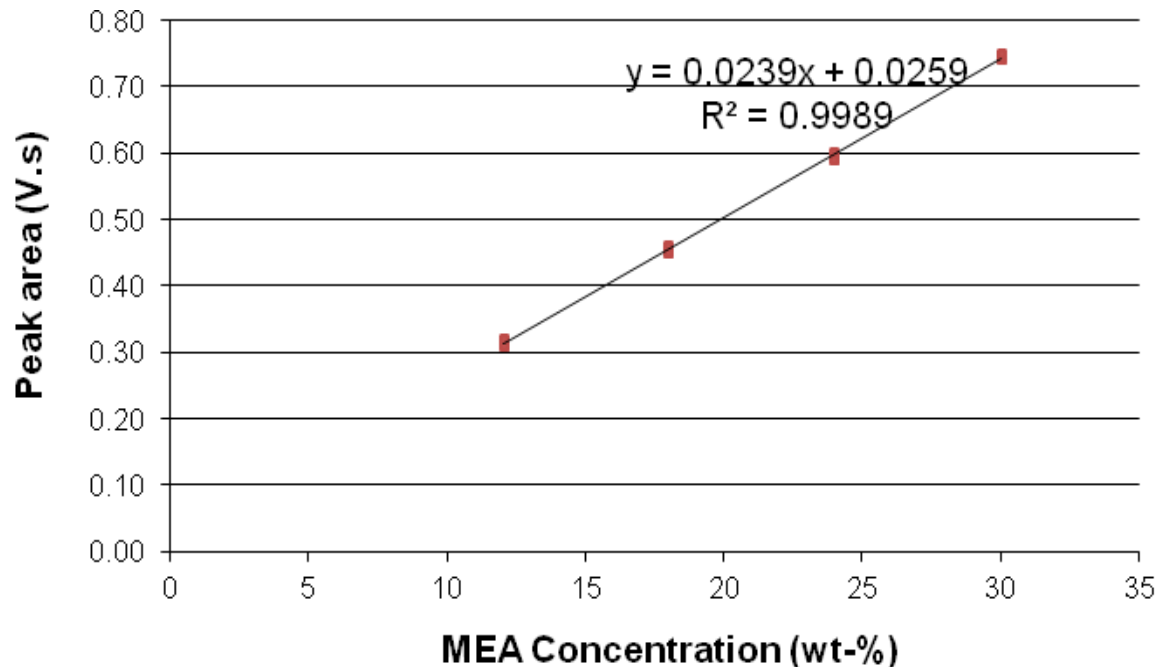
4.4.1 HPLC

- Nucleosil 100-5 SA: Better separation but bad peak shape



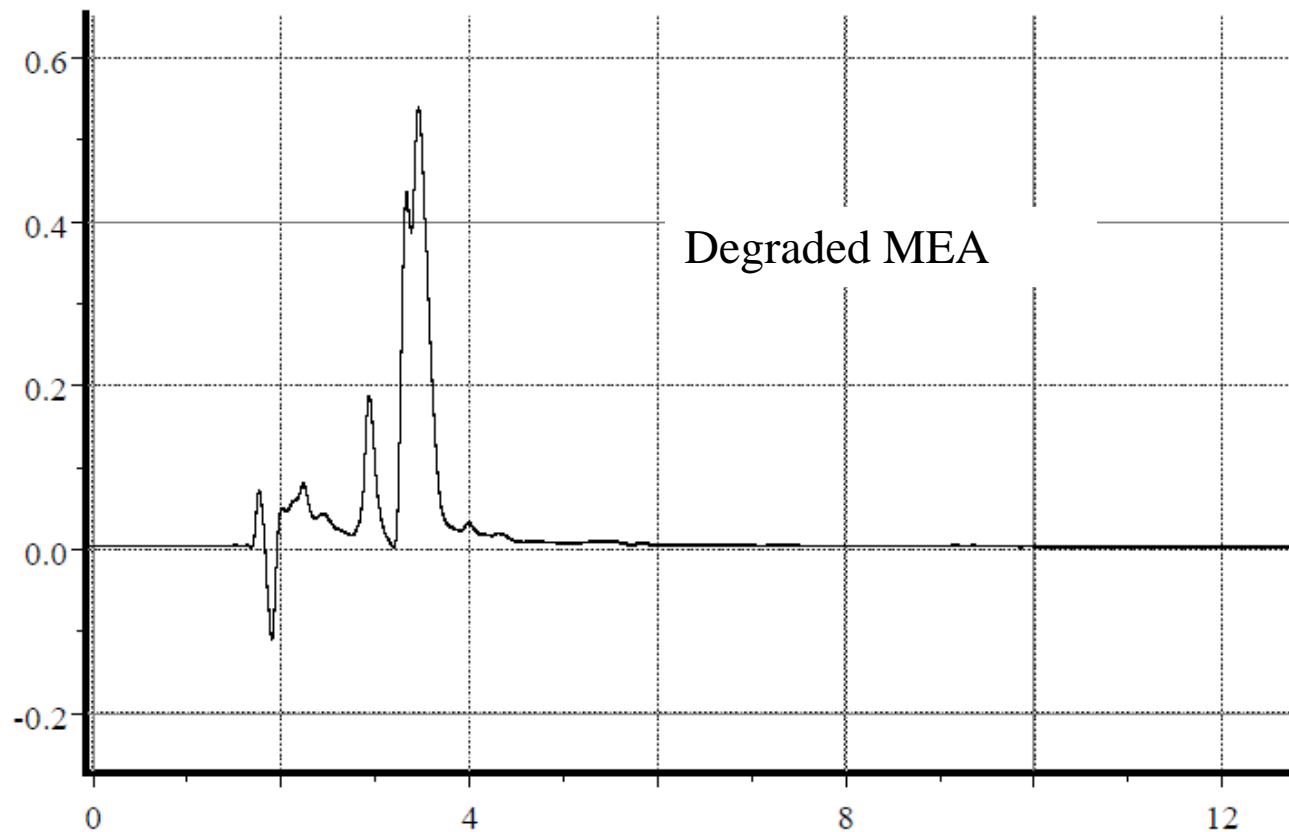
4.4.1 HPLC

- Nucleosil 100-5 SA: quantification of MEA possible:
=> calibration curve



4.4.1 HPLC

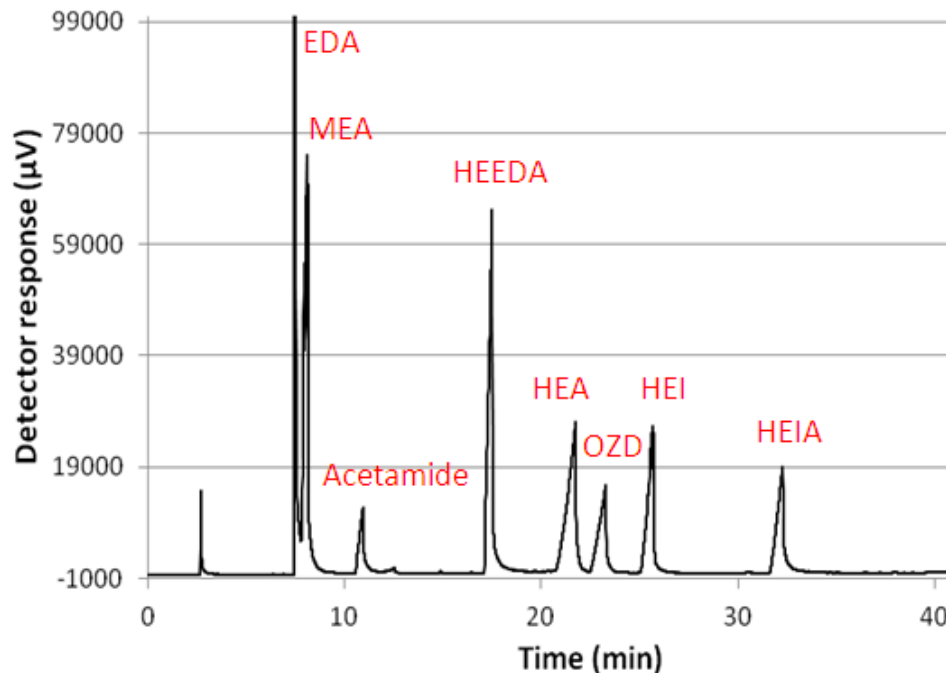
- HILIC: Better peak shape but separation still to be improved...



4.4.2 GC-FID

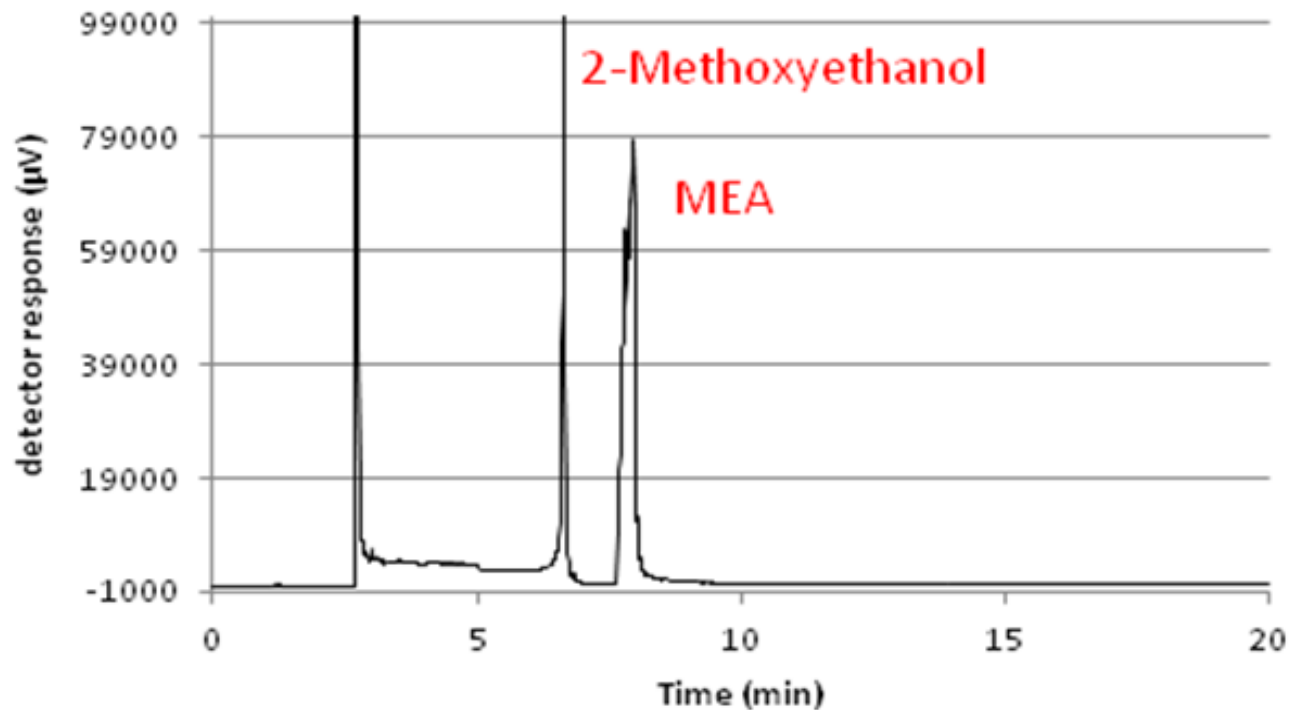
GC-FID:

- Analytical method has been developed
- Identification of degradation products possible



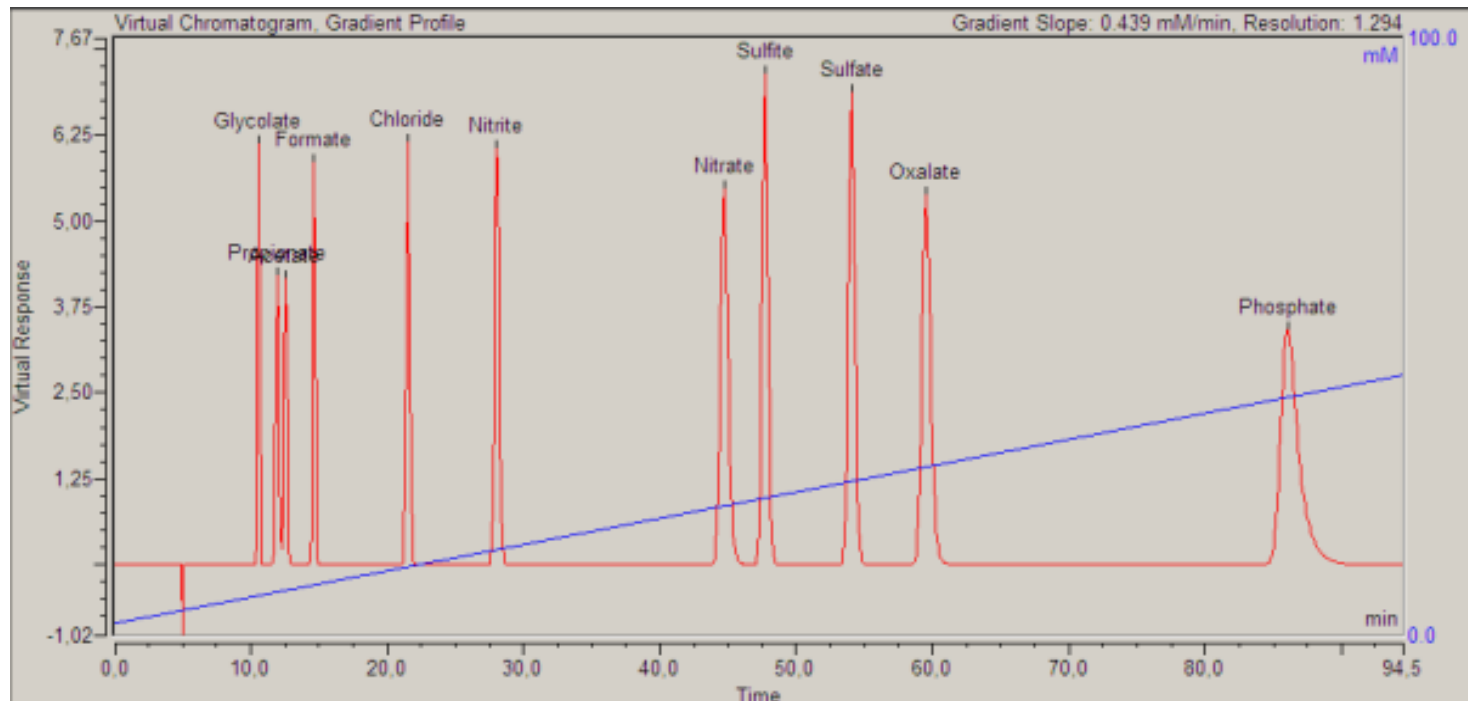
4.4.2 GC-FID

- Quantification using an internal standard (1% of 2-Methoxyethanol)



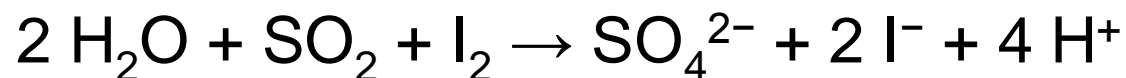
4.4.3 Organic Ions Analysis

- Organic ions may lead to heat stable salts (HSS)
- HSS can not be regenerated and lead to a loss of efficiency
- Analysis of Formate, Acetate, Glycolate, Oxalate



4.4.4 Karl Fischer Titration

Potentiometric titration of water based on the equation:



=> Water quantification in degraded amine samples

=> In relation with the mass balance



4.4.5 Inorganic Ion Analysis

Quantification of elemental ions because their presence can be directly related to corrosion

Ion	Method
Fe	Atomic absorption
Cr	Atomic absorption
Ni	Atomic absorption
Si	Atomic absorption
F	Capillary electrophoresis
Cl	Capillary electrophoresis

Fe, Cr, Ni: components of SS 316

Si: found in many analyses

F, Cl: corrosion accelerator

4.4.6 FTIR

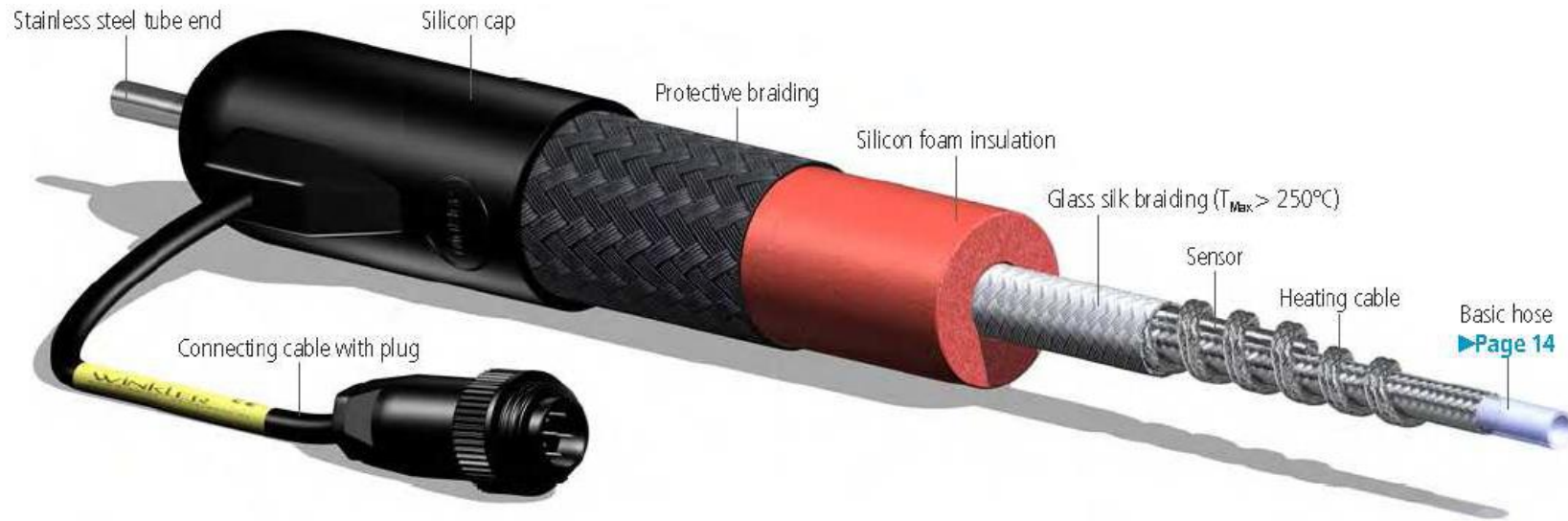
- Quantification of NH_3 and MEA in the gas phase at the reactor exhaust
- Quantification of H_2O , CO_2 , MEA and NH_3



Compound	Wavelength interval (cm^{-1})
CO_2	926 – 1150
MEA	2700 – 3200
H_2O	3200 – 3401
NH_3	910 – 1150

4.4.6 FTIR

- Heating rope from reactor to FTIR



- => Combined with a pre-heating of the dilution gas
- => Prevents condensation of the gas sample in the line

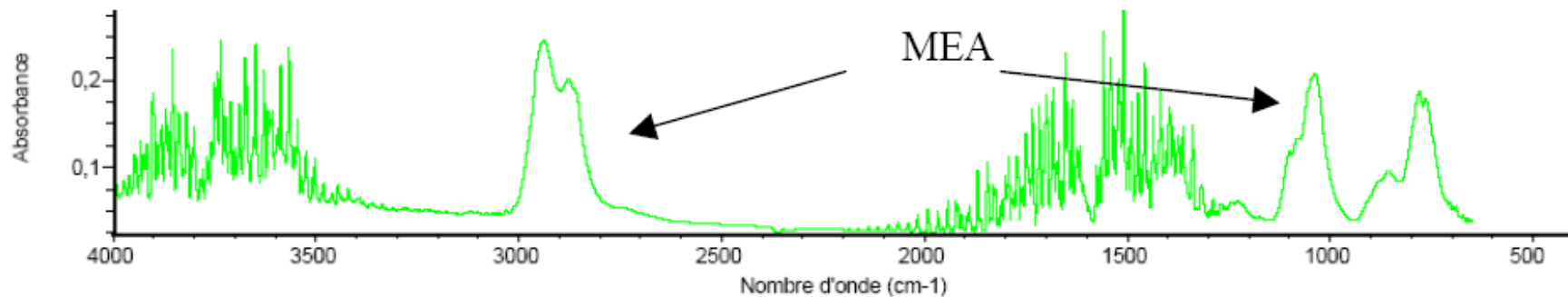
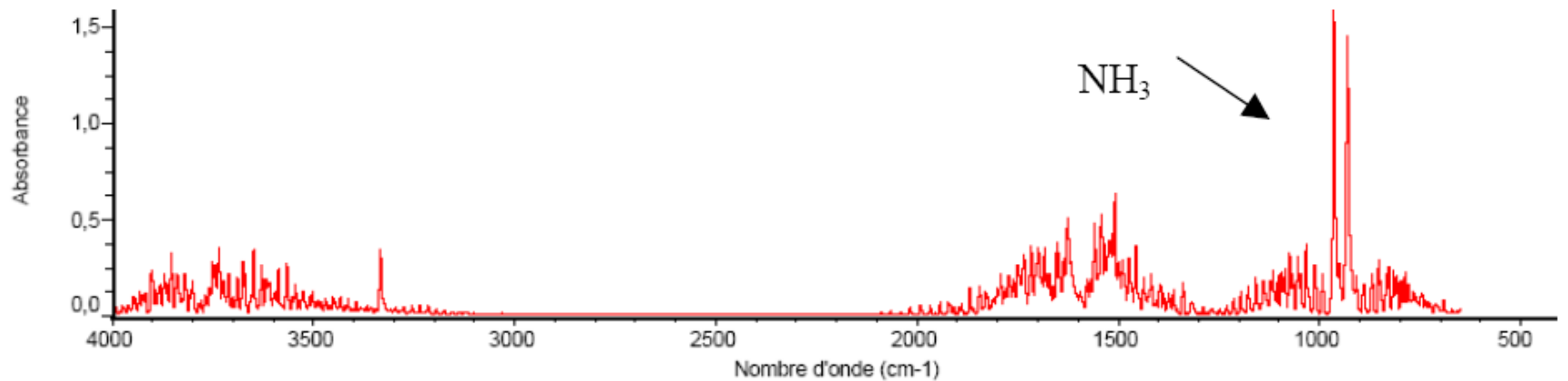
4.4.6 FTIR

- Calibration of liquid samples



4.4.6 FTIR

- Calibration of NH_3 and MEA



4.5 Results Summary

Name	Operating conditions												Problems
	Experiment Start	Experiment end	Length [Days]	Parameter tested	T [°C]	P _{tot} [bar]	P _{O2} [bar]	P _{CO2} [bar]	P _{N2} [bar]	Gas flow [mln/min]	Solvent [wt% MEA]	Mass balance [%]	
Experiment 1	19/02/2011	5/03/2011	14	Base case	120	4	0.2	3	0.8	80	30.00	not recorded	-
Experiment 2	24/03/2011	5/04/2011	12	Exp. Length/strong cond.	140	20	1	15	4	200	30.00	-3.33	Gas exhaust stopped due to crystal formation in the condenser, pressure up to 25 bar
Experiment 3	11/04/2011	25/04/2011	14	Temperature	120	20	1	15	4	200	30.01	10.07	-
Experiment 4	10/05/2011	19/05/2011	9	Pressure (N ₂)	140	20	0.2	3	16.8	500	30.05	-1.43	Foaming, temperature sensor defectuous => heating stopped automatically
Experiment 5	27/05/2011	10/06/2011	14	Repetability	120	4	0.2	3	0.8	80	30.01	-62.33	Crystal formation in the condenser, pressure up to 20 bar for a few hours, mass losses
Experiment 6	1/07/2011	15/07/2011	14	Repetability	120	4	0.2	3	0.8	80	30.02	-47.60	Mass losses (150g)
Experiment 7	20/07/2011	3/08/2011	14	Batch	120	20	0.2	3	0.8	0	29.99	-0.33	Corrosion of the temperature sensor
Experiment 8	24/08/2011	31/08/2011	7	Temperature and gas flow	120	20	0	0	20	20	30.00	-2.33	-
Experiment 9	31/08/2011	9/09/2011	9	Temperature and gas flow	120	20	0	0	20	200	30.00	-3.70	Gas bottle empty (2 days), current shortage
Experiment 10	13/09/2011	27/09/2011	14	New base case	120	4	0.2	0.6	3.2	160	29.99	-11.30	Mass losses

4.5 Results Summary

Experimental feed-back of the 1st test campaign

- Corrosion
- Crystal formation
- Mass balance regulation
- Temperature regulation
- Agitation

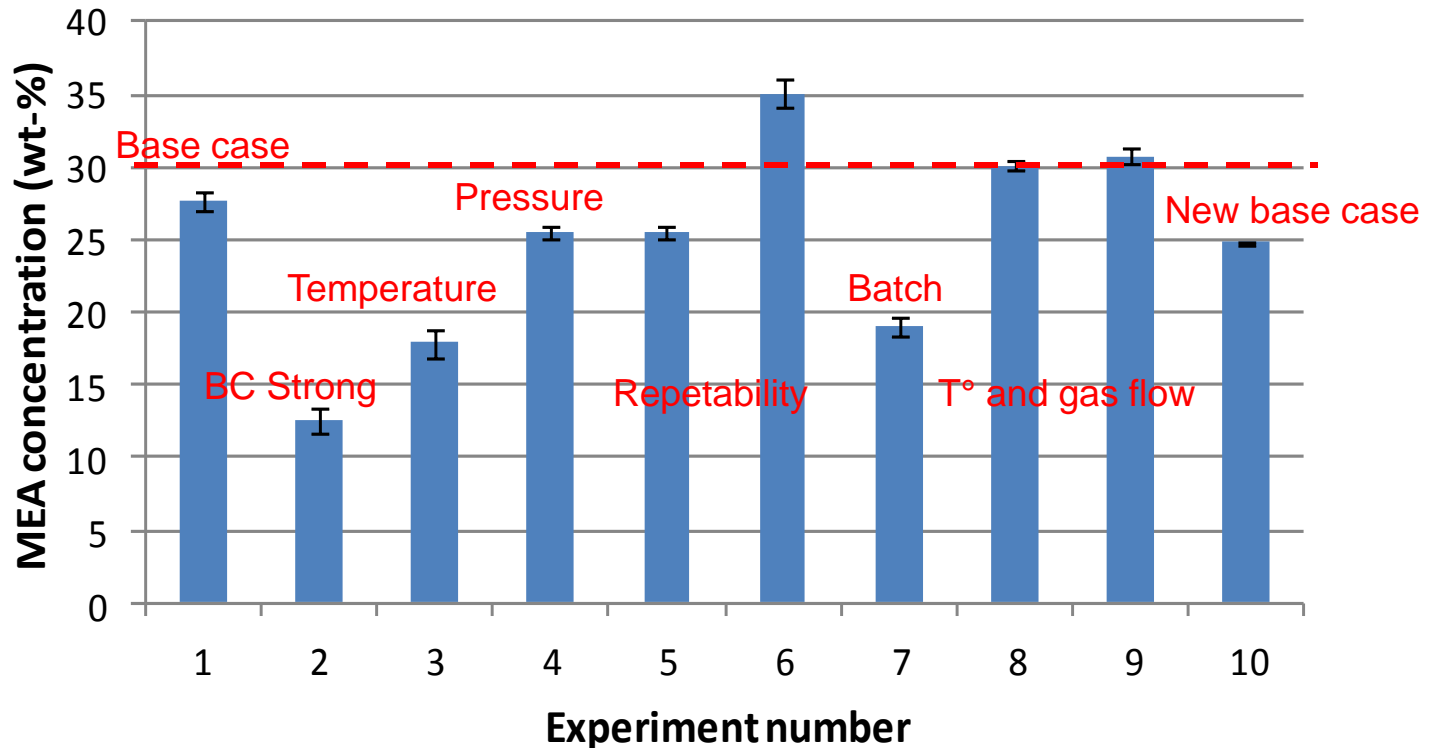


Model 854 High Pressure Reactor, 500 mL, Movable Style Vessel, with heater lowered, and a 8045 Controller shown with optional Expansion Module.



4.5.1 HPLC

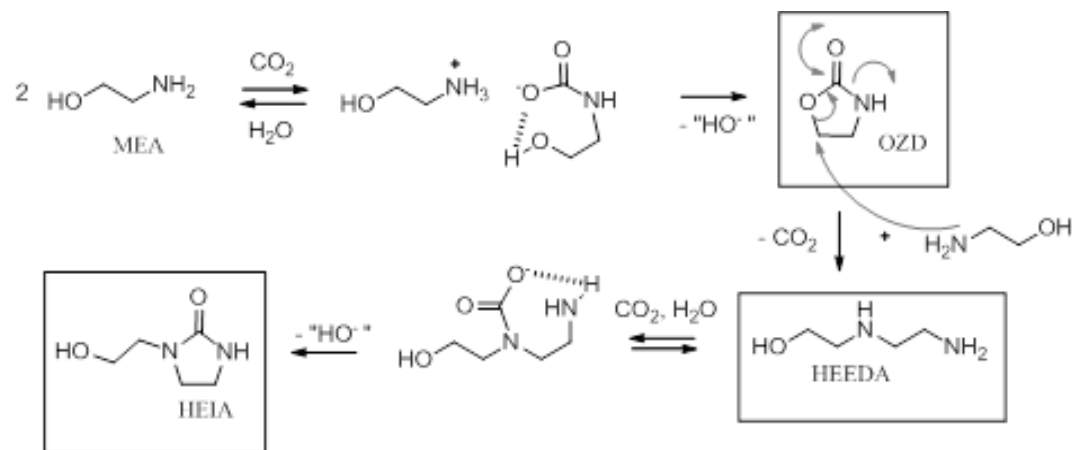
HPLC quantification of MEA in degraded samples



4.5.2 GC-FID

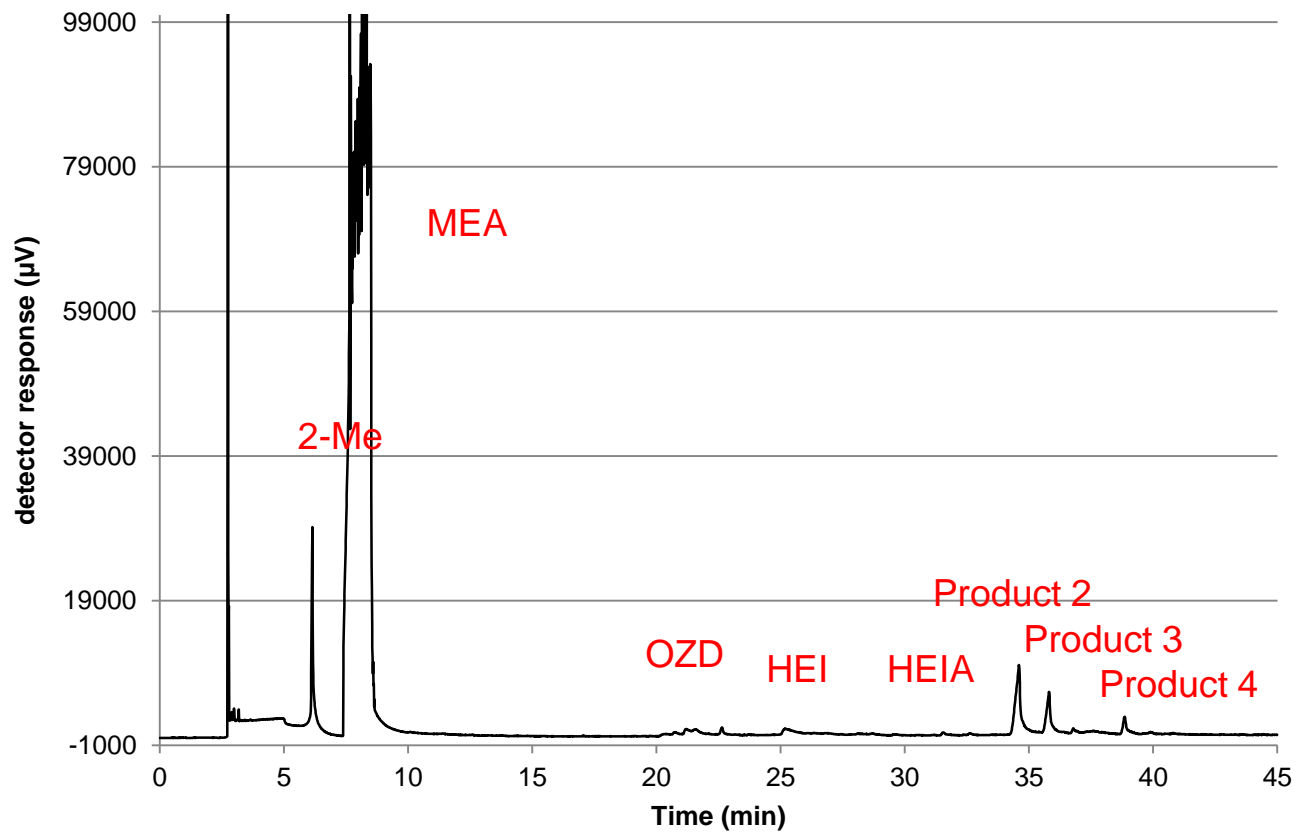
GC Identification of degradation products

Std \ Exp	1	2	3	4	5	6	7	8	9	10
Acetamide		?	?		?	?	?			
HEEDA					X	X	X			
HEA									X	
OZD	X	X	X	X	X	X	X			X
HEI	X	X	X	X	X	X	X			X
HEIA	X	X		X	X	X	X			



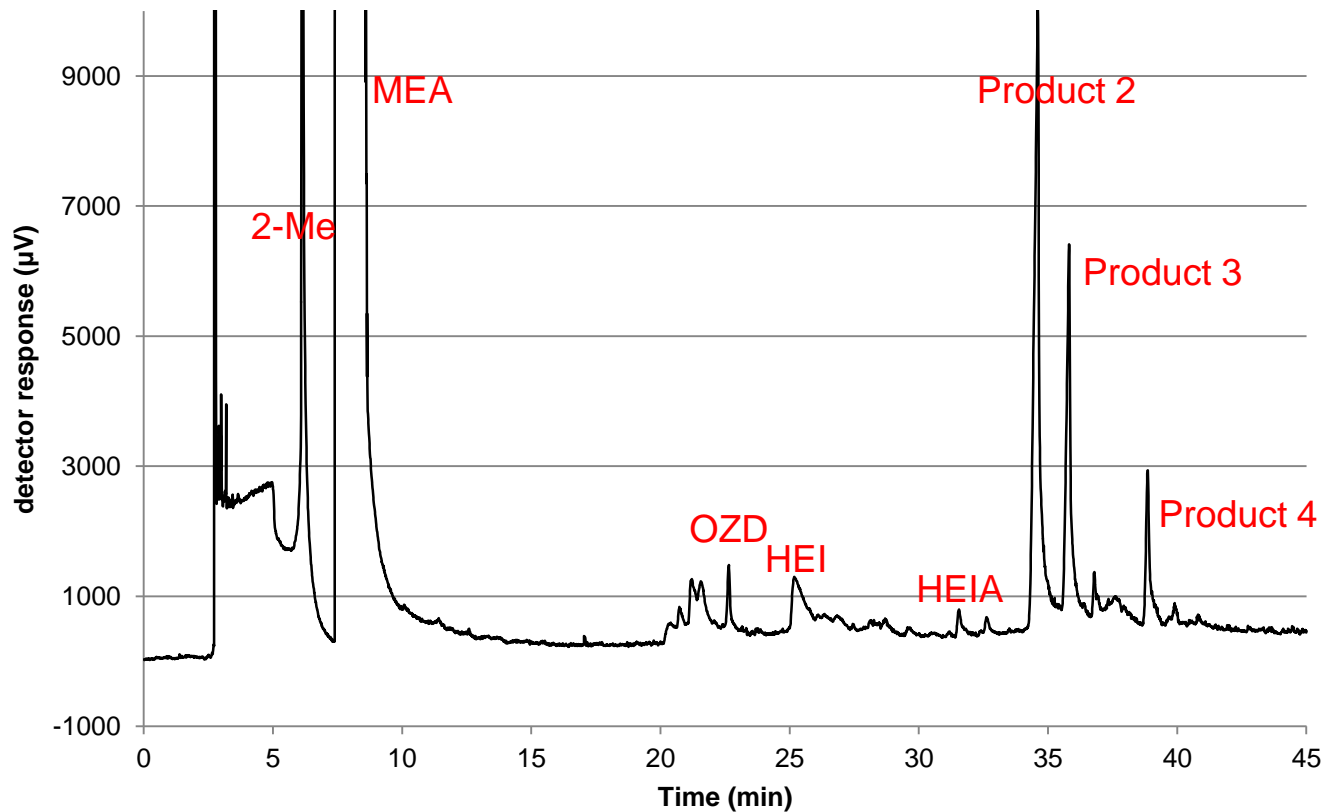
4.5.2 GC-FID

GC Identification of degradation products: Experiment 10



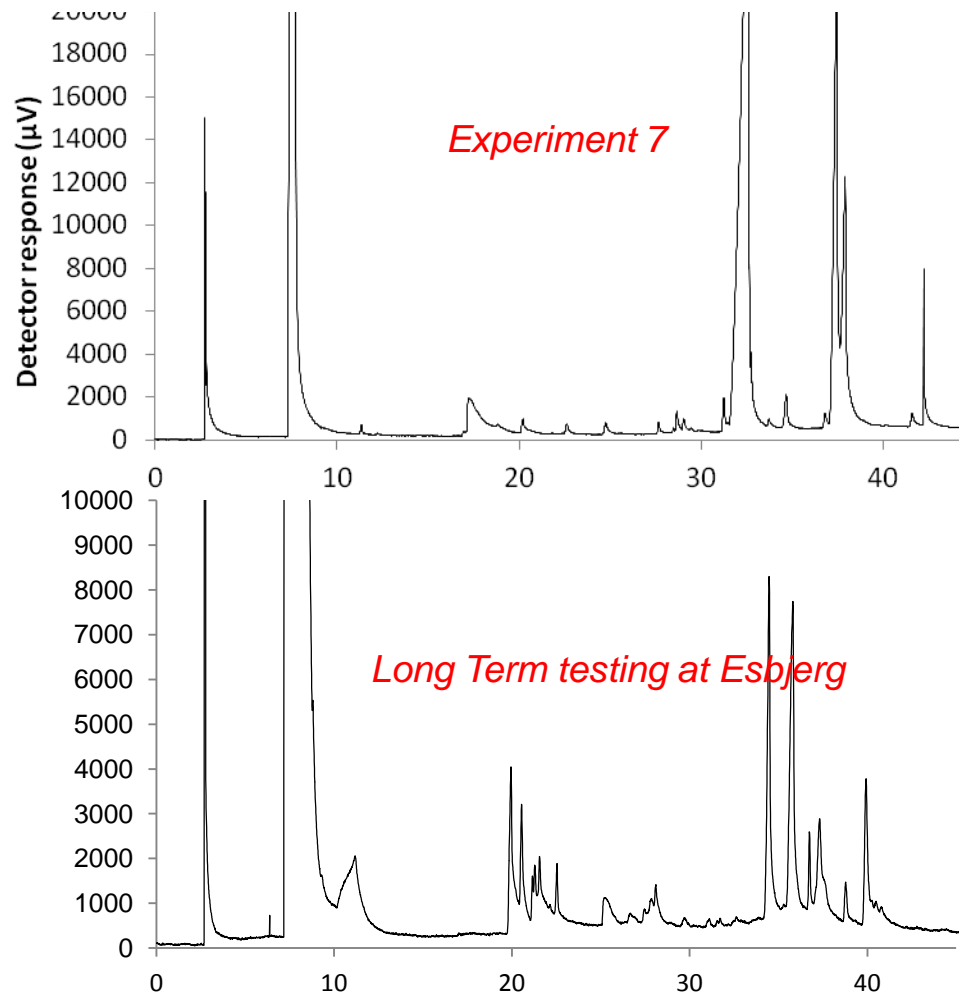
4.5.2 GC-FID

GC Identification of degradation products: Experiment 10



4.5.2 GC-FID

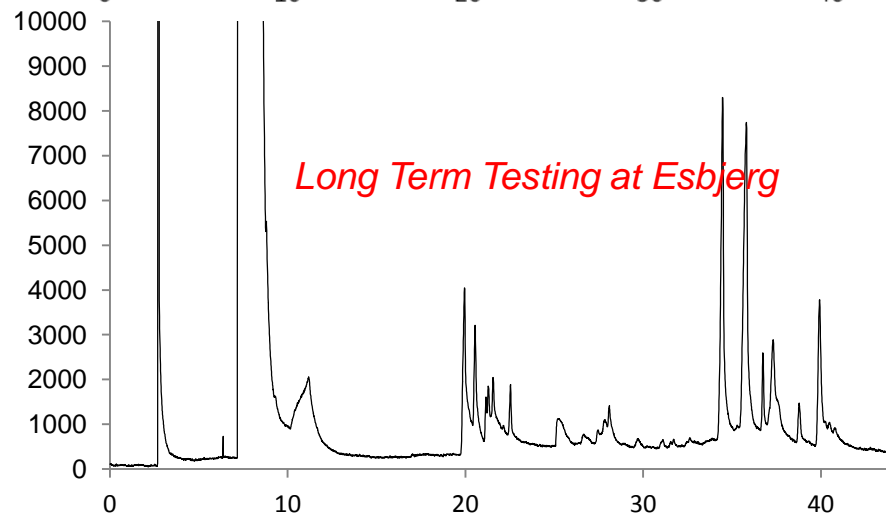
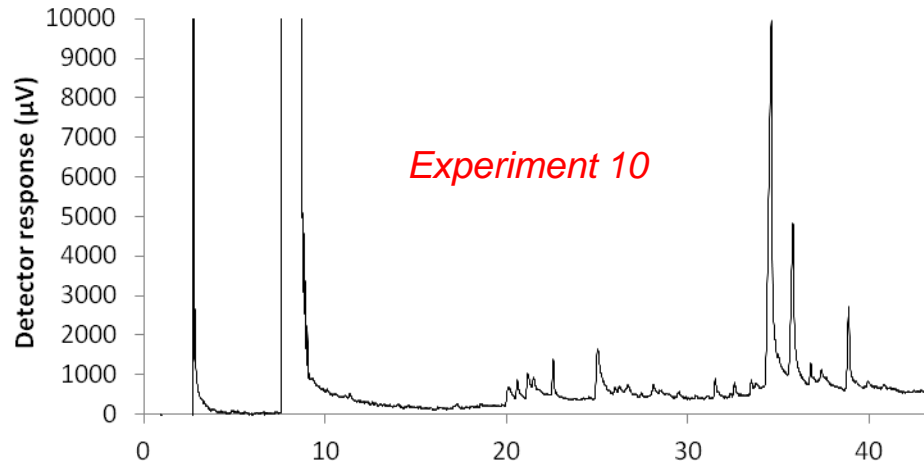
GC Comparison with pilot plant results



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4.5.2 GC-FID

GC Comparison with pilot plant results



=> Experiment 10 has been chosen as the new base case for next test campaign:

- 120°C
- 4 bar
- 5%O₂, 15%CO₂, 80%N₂
- 160 mln/min gas flow
- 2 weeks

4.5.3 Inorganic Ions

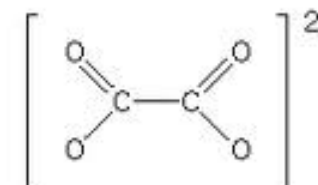
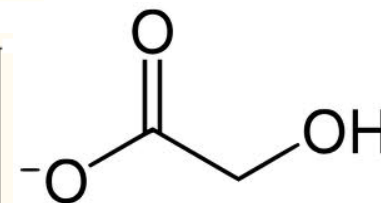
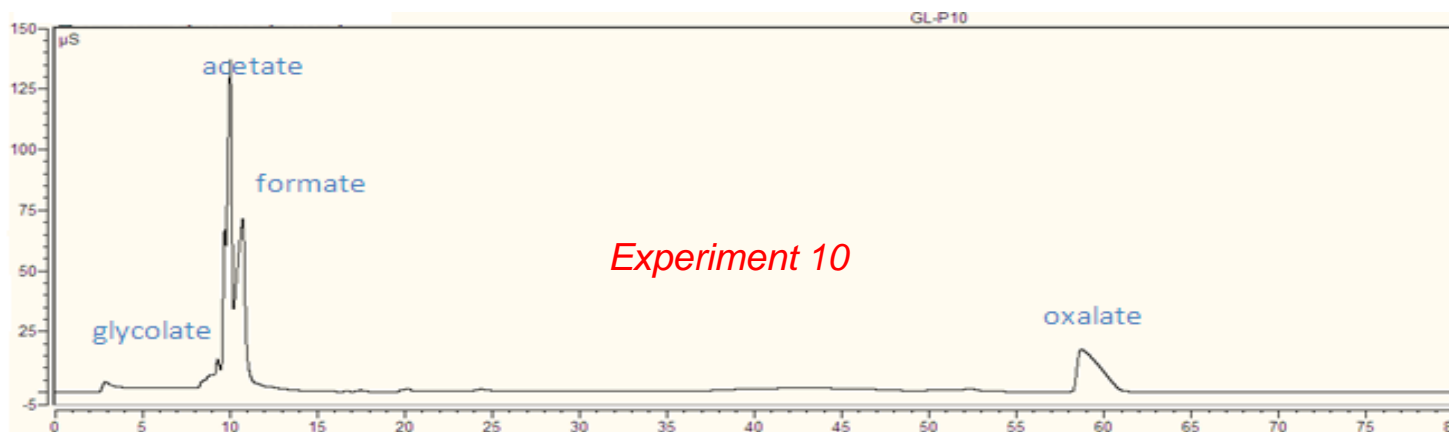
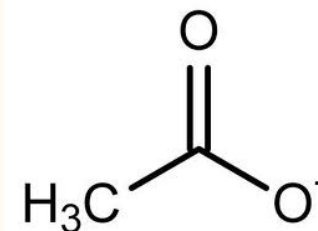
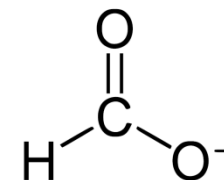
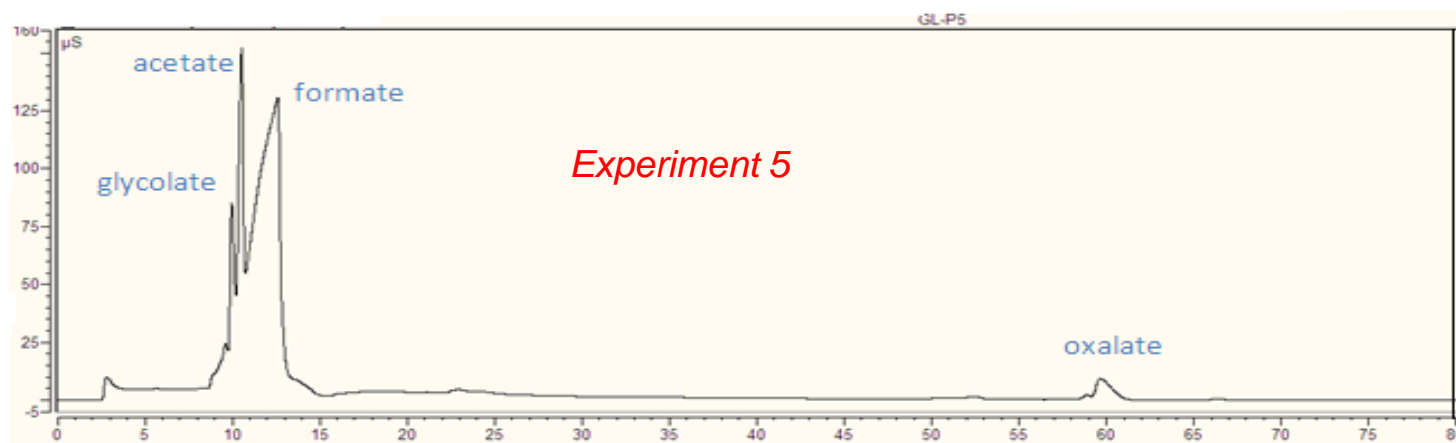
Quantification of inorganic ions

	Fe	Cr	Ni	Si	Cl	F
MEA 30%	0.44	< 0.10	< 0.10	-	< 2.00	38.944
Experiment 1	7.57	1.55	4.24	-	< 2.00	416.08
Experiment 2	22.40	8.60	9.75	13.01	513.16	1826.18
Experiment 3	6.80	3.10	2.66	10.66	522.32	869.35
Experiment 4	1.90	1.30	1.01	15.57	291.36	307.13
Experiment 6	14,70	2.75	159	2754.21	< 5.00	594.62
Experiment 7	66.10	7.50	571	147.78	< 5.00	321.14
Experiment 8	0.19	2.27	0.69	94.80	< 5.00	251.55
Experiment 9	0.14	2.39	0.51	95.55	< 5.00	276.30
Experiment 10	3.46	6.41	0.87	557.55	29.34	532.38

=> More ions during Experiments 2, 6 and 7

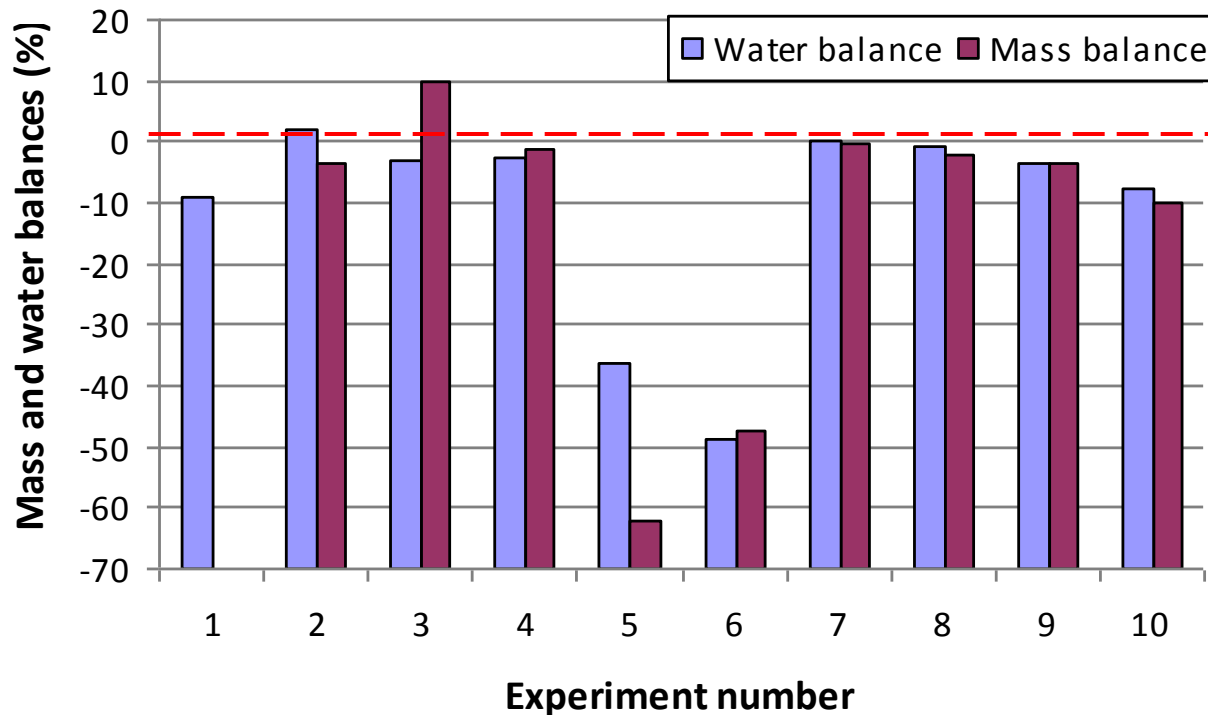
4.5.4 Organic Ions

Identification of organic ions performed at Laborelec



4.5.5 Karl Fischer Titration

- Quantification of water in degraded amine sample
- Good correspondance with mass balance results!



4.6 Conclusion

- First test campaign has brought practical experience using the degradation test rig that may be very useful for future experiments
- Analysis methods are numerous and allow for a complete screening of MEA degradation
- Observed degradation products were expected and may be explained in relation with previous studies
- Unexpected degradation products are also obtained, but similar to pilot plant results

4.6 Conclusion

- First tests have permitted the definition of a new base case, with results similar to pilot plant's
- Influence of temperature, gas flow rate, gas composition and pressure may already be observed. Results are in accordance with previous literature
- Corrosion follow-up is pursued

4.7 Perspectives

- Development of analytical methods, especially FTIR and GC-FID for quantification of degraded products
- Next degradation tests must ensure repeatability
=> the new base case experiment will be repeated
- Second test campaign with MEA to determine more precisely the influence of gas composition and temperature
=> first experiments will study the influence of O₂ and CO₂ separately

4.7 Perspectives

- Bibliography studies about degradation inhibitors and additives that may be tested with MEA
- Test of alternative solvents furnished by Laborelec
- Collaboration with the University of Mons in order to determine the influence of degradation on the CO₂ capture process
- Participation to a conference at the University of Texas in Austin

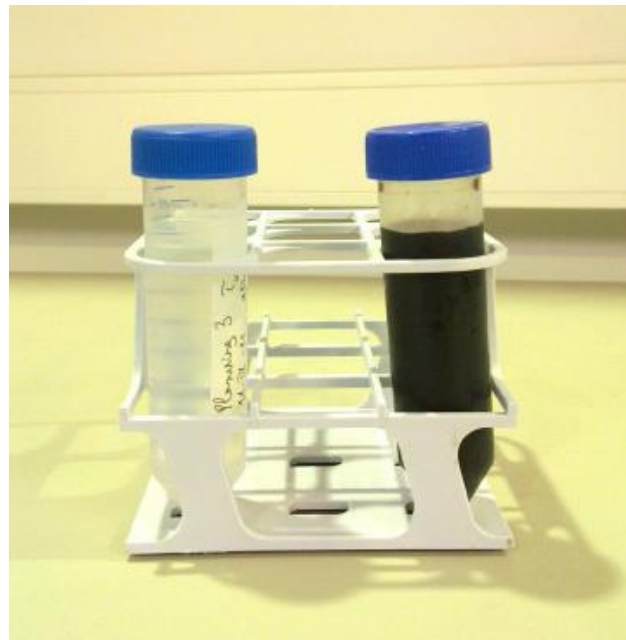
5. Conclusion and perspectives

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5 Conclusions

- Good knowledge about the CO₂ capture process considers the **energetical efficiency** but also takes **solvent degradation** into account!
- Results prove that the study of MEA degradation under accelerated conditions can be related to pilot scale results
- In the coming year, the construction of a **model including solvent degradation** parameters will begin. This model will have to be **validated** with experimental data in order to perform a **multi-objective optimisation** of the CO₂ capture process.

Thanks for your attention!



14th December 2011