Solvent degradation

Grégoire Léonard

22nd August 2011

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1. Introduction and objectives

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1. Introduction and objectives

PhD thesis in the field of chemical engineering, subject is divided into two main parts:

1. *Simulation and optimal conception of the post-combustion CO_2 capture process*

2. *Experimental study of solvent degradation*

Establishing a link between those two parts is the main objective of this PhD thesis

1. Introduction and objectives: Litterature review

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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, O2, Temperature and stirring	230ml	Discontinuous with gas feed to compensate for pressure losses	120-150	2,41-3,45 bar O2	MEA (2-11mol/L)	GCMS	2 - 12 days
Lawal and Idem, 2005; Lawal et al. 2005&2006	Influence of O2, CO2, MDEA-MEA-ratio, Temperature, amine concentration + Product formation mechanisms, Ecotoxicity	450ml		55-120	2,5 bar O2/CO2	MEA-MDEA blends (7-9mol/L)	GCMS (+HPLC from 2006)	6 - 22 days
Bello and Idem, 2005	Pathways of degradation reaction, influence of O2, CO2, Temperature, MEA concentration, ...	230ml		55-120	2,5-3,5 bar O2/CO2	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 O2/CO2	MEA (5 mol/L)	GCMS, HPLC, CE	18-24 days
Bello and Idem, 2006	Influence of the corrosion inhibitor NaVO3 on Degradation kinetics	230ml		55-120	3,5-4,5 bar O2/CO2	MEA (5-7 mol/L)	HPLC	6-30 days
Uyanga and Idem, 2007	Influence of the corrosion inhibitor NaVO3 and of SO2 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 O2 and SO2-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 CO2-loading and inhib (Fe, Bicine, EDTA) on NH3 production rate	500ml	5L/min Air/N2/Air+2%CO2	55	1	MEA (13-42 wt-%)	FTIR	up to 8 hours
Goff and Rochelle 2004; Goff, 2005; Goff and Rochelle 2006	Importance of O2-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 degradation	550 g	Up to 8L/min Air/Air + CO2	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%CO2/98%02) and high flow (7,5 L/min Air/N2/2%CO2)	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 +CO2	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 O2/CO2/N2	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%N2, 30%O2, 30%CO2	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 N2/O2/CO2	40-120	1-4	MEA	GC-FID	14 days
Notz 2009	Thermal degradation	7 ml	Batch	140-180	N2 atmosphere	MEA (30wt-%)	GC-FID	7 days
Knudsen et al., 2007	Results from test campaigns on Esbjerg pilot	~20m³/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 N2/CO2/Air	150	1,2	Different amines	GC	Several months
Lepaumier, 2008; Lepaumier et al., 2008	Degradation Mecanisms and products for differents amines	100ml	Batch O2/CO2/N2/Air	140	20	Different amines	GCMS, RMN	2weeks

1. Introduction and objectives

It has been decided to design and build a degradation test rig at the University of Liège in order to:

- obtain **our own experimental data on MEA** degradation that will be used for Process Modeling

- allow us to work at **extrem temperature and pressure** conditions to accelerate degradation reactions

- get the possibility of testing the degradation of **newly developed solvents**, as well as the influence of **additives**

2. Degradation Test Rig

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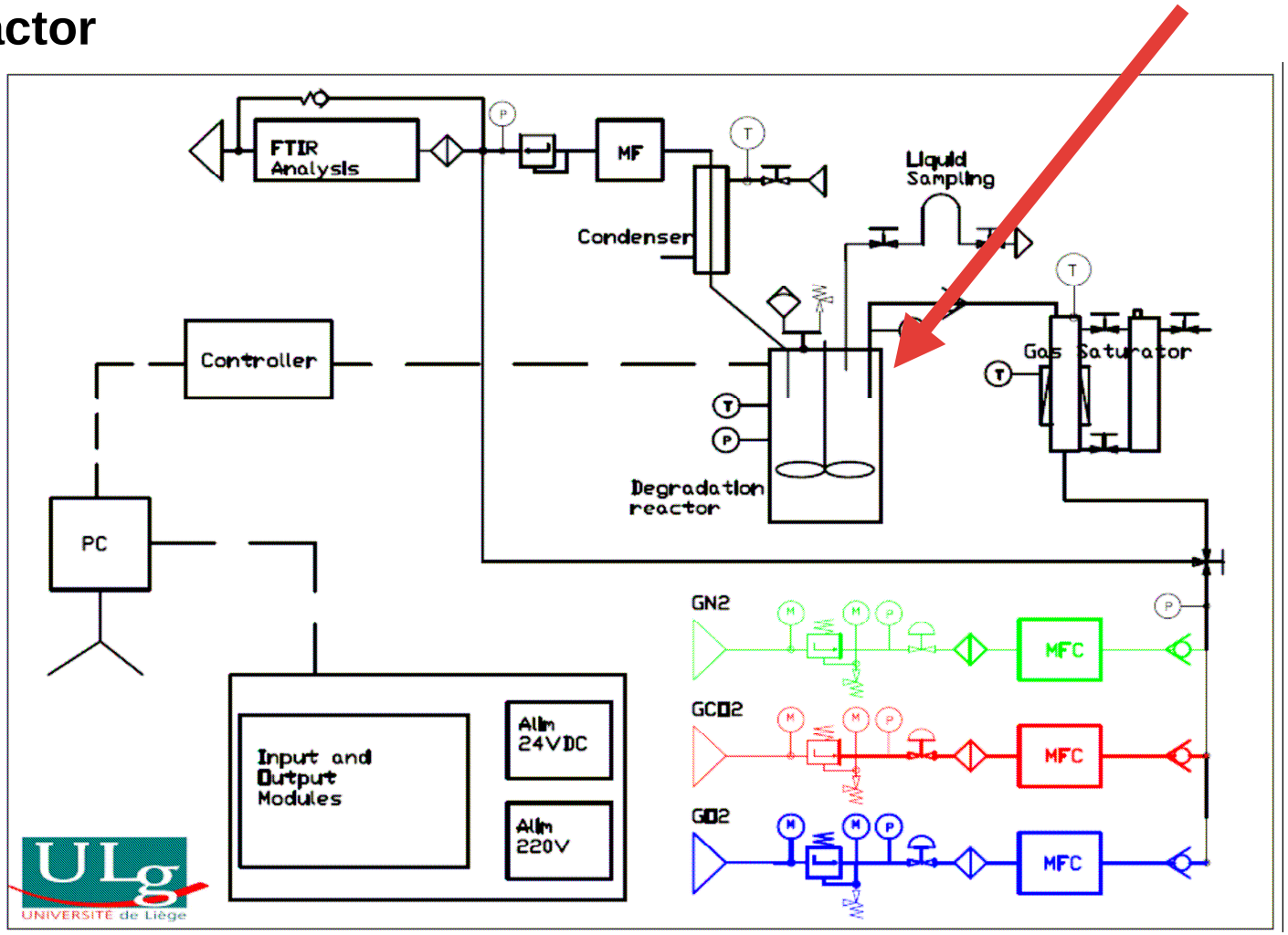
2. Degradation Test Rig

Elements:

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

2. Degradation Test Rig

1. Reactor



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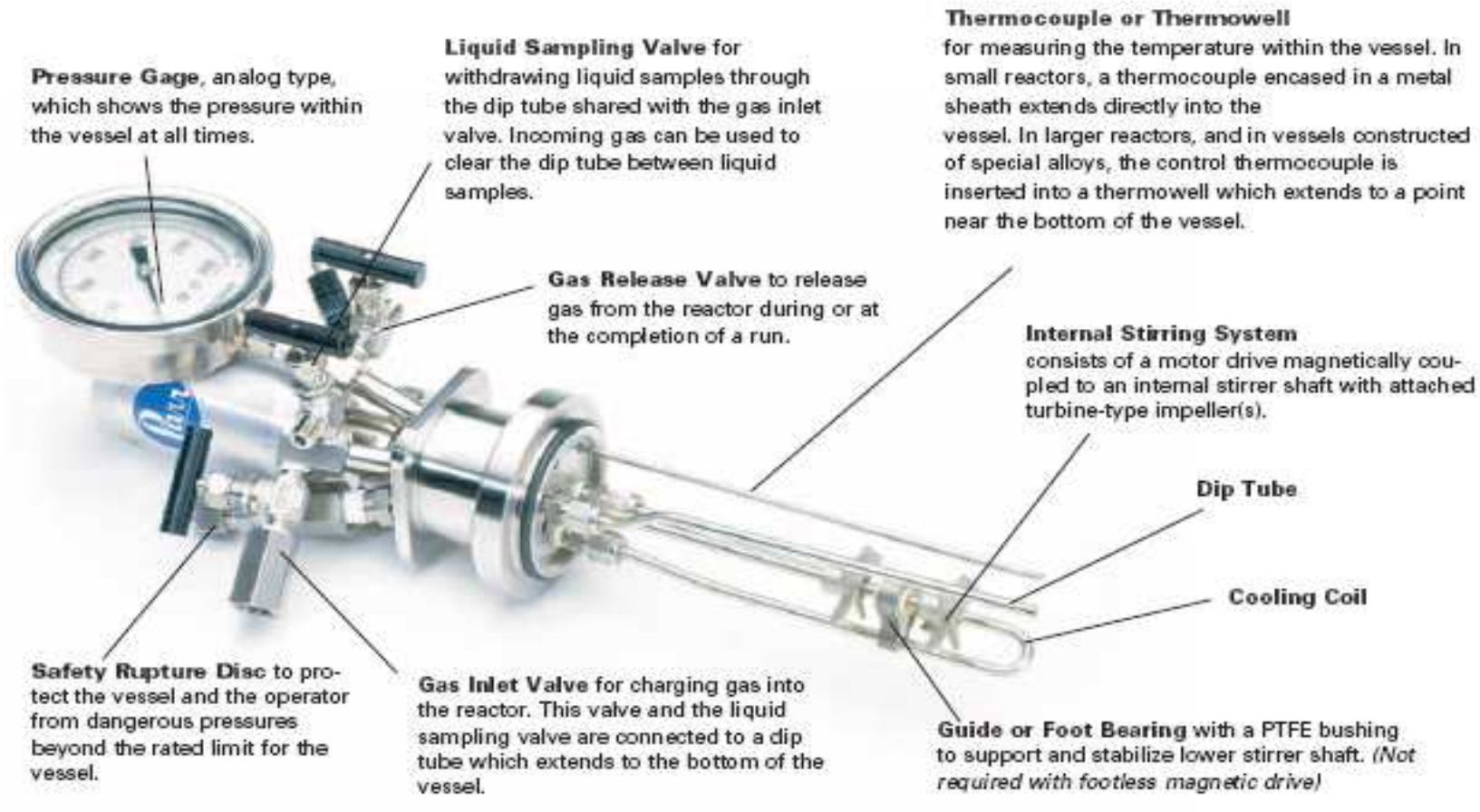
1. Reactor

- Parr reactor
- 600 ml
- Max temperature : 500℃
- Max pressure: 200 bar
- T316 Stainless Steel
- Heating mantle controls the temperature
- Agitation rate is set by the operator

Model 4544 High Pressure Reactor, 600 mL, Moveable Style Vessel, with heater lowered, and a 4848 Controller shown with optional Expansion Modules.

2. Degradation Test Rig



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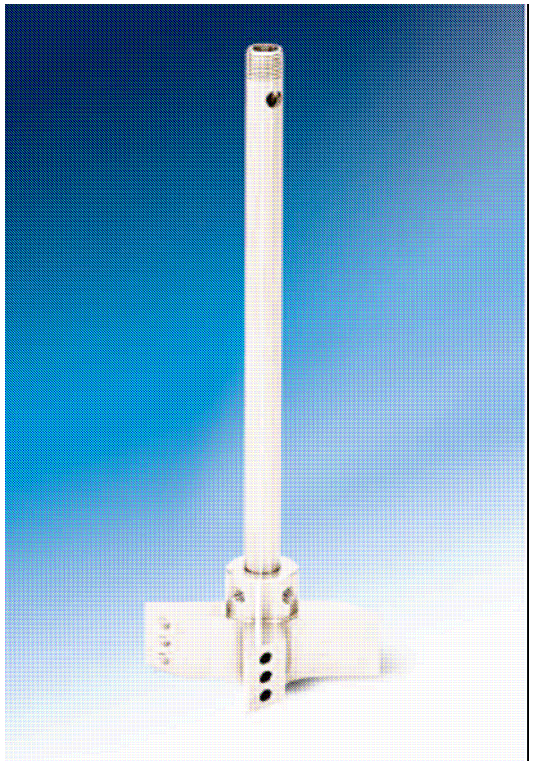
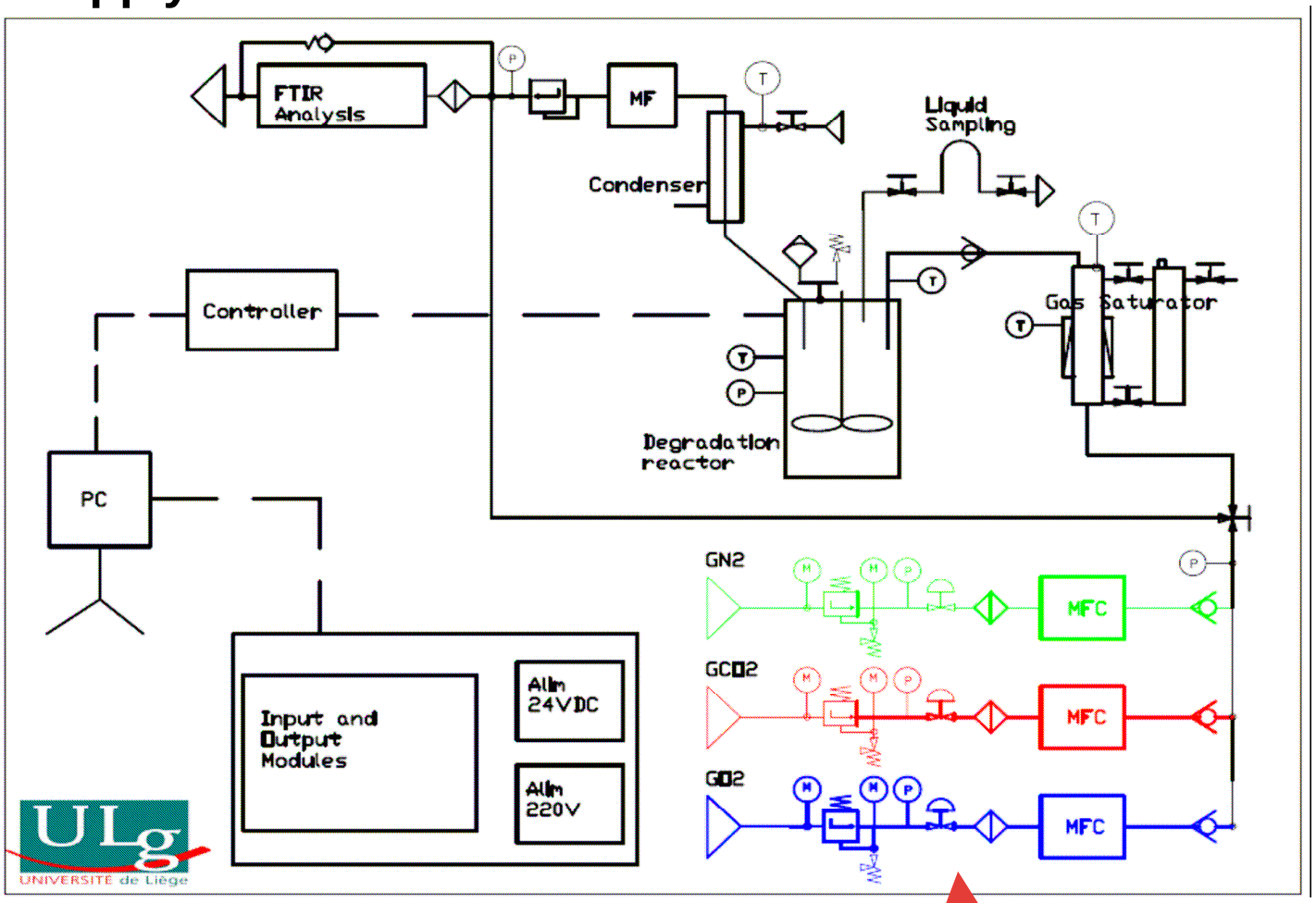
Hollow shaft for a better gas-liquid contact



2. Gas supply


FTIR Analysis
MF
Condenser
Liquid Sampling
Controller
Gas Saturator
Degradation reactor
PC
Input and Output Modules
Alim 24VDC
Alim 220V
GN2
GCO2
GO2
MFC
MFC
MFC
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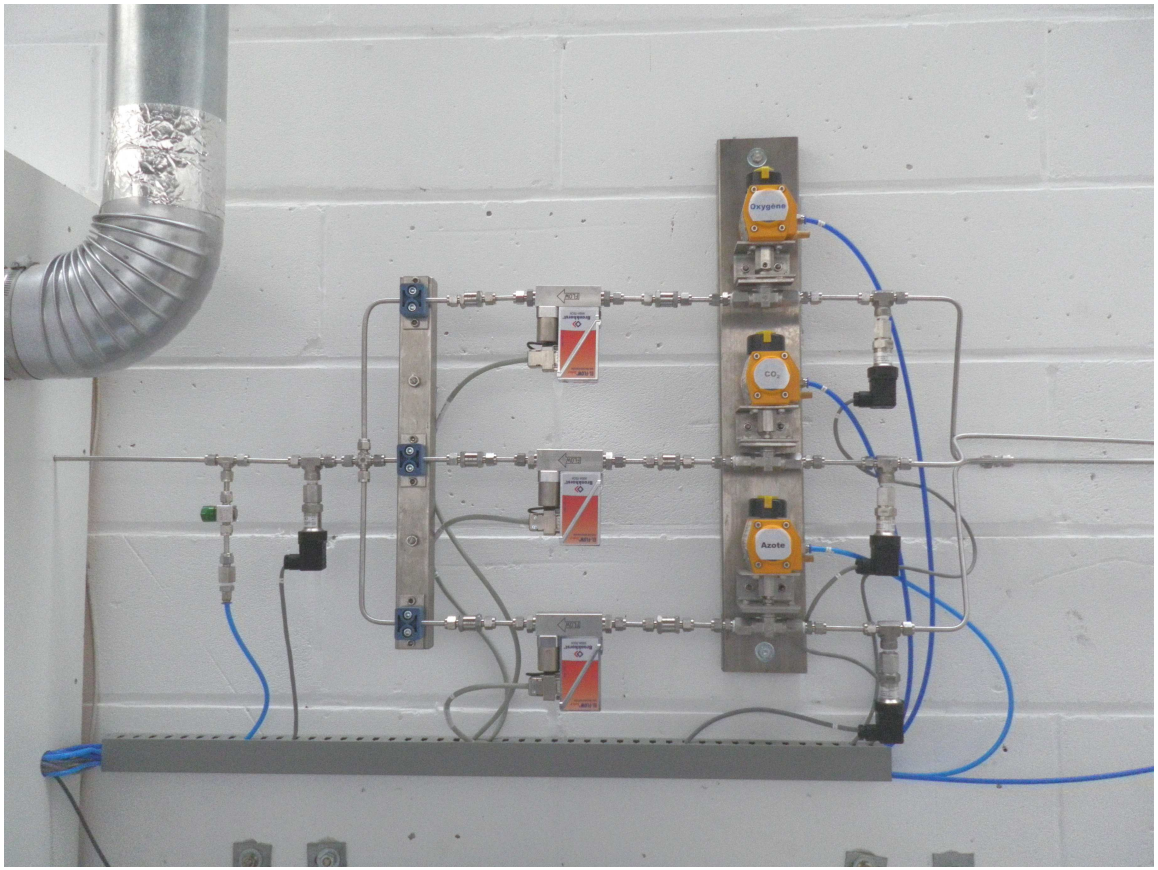
2. Gas supply

- N_2 - CO_2 - O_2
- Compressed Air

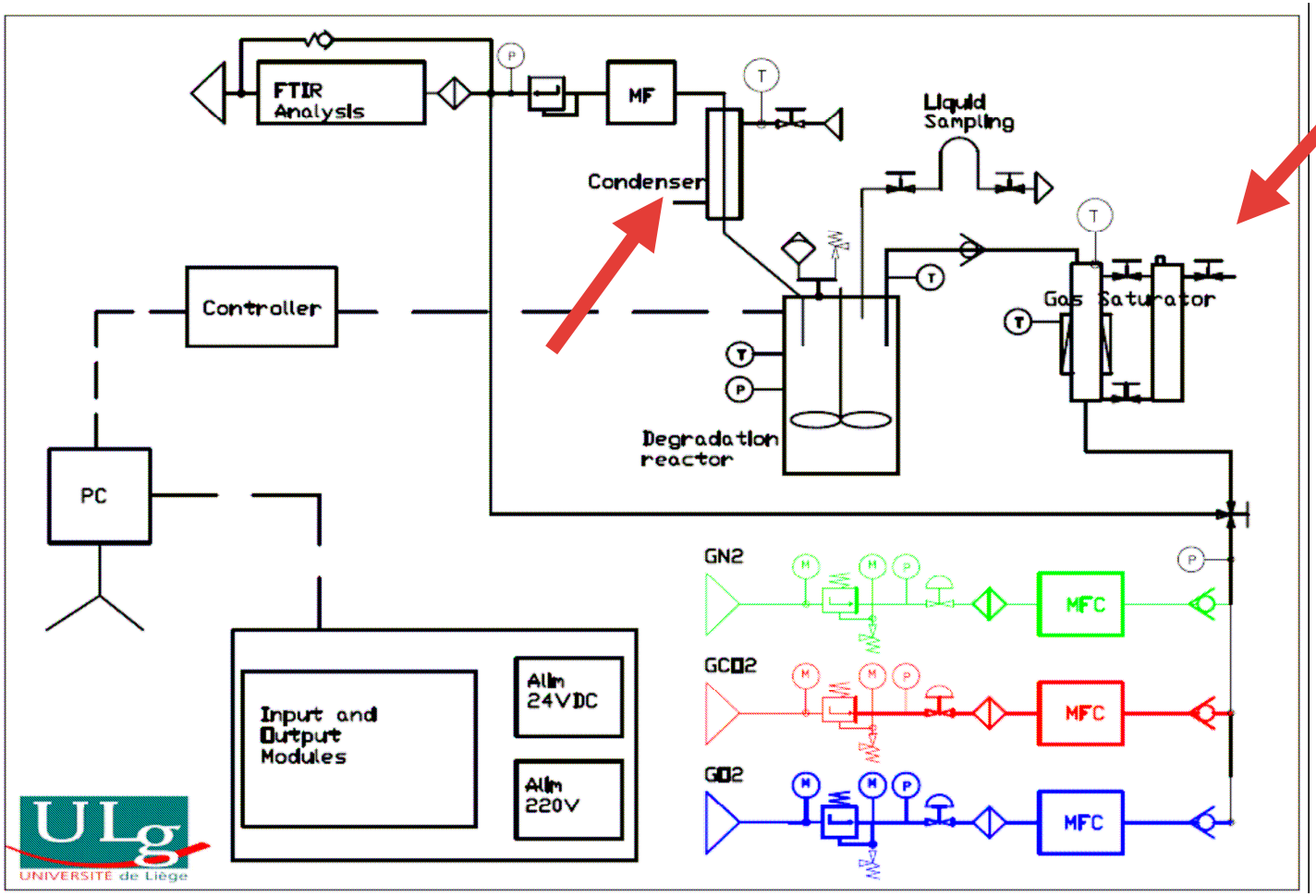
- Bottle Rack
- Pressure regulator
- Risk indications

2. Gas supply

- Pressure transducers
- Security valves
- Filters
- Mass flow controllers
- Check valves
- Valve for air pruge



3. Water balance



3. Water Balance: Saturator

- Tank filled with destillated water
- Saturation of the inlet gas with water
- Water temperature controled from 25℃ to 70℃
- Gas pressure up to 25bar

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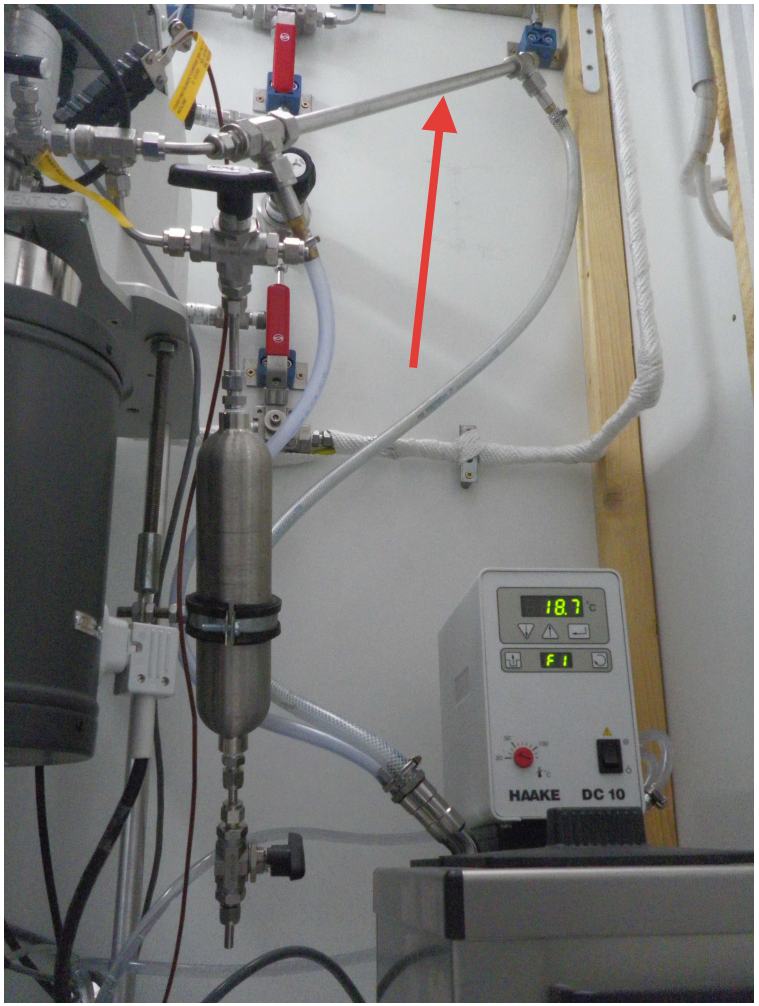
3. Water balance: Condenser

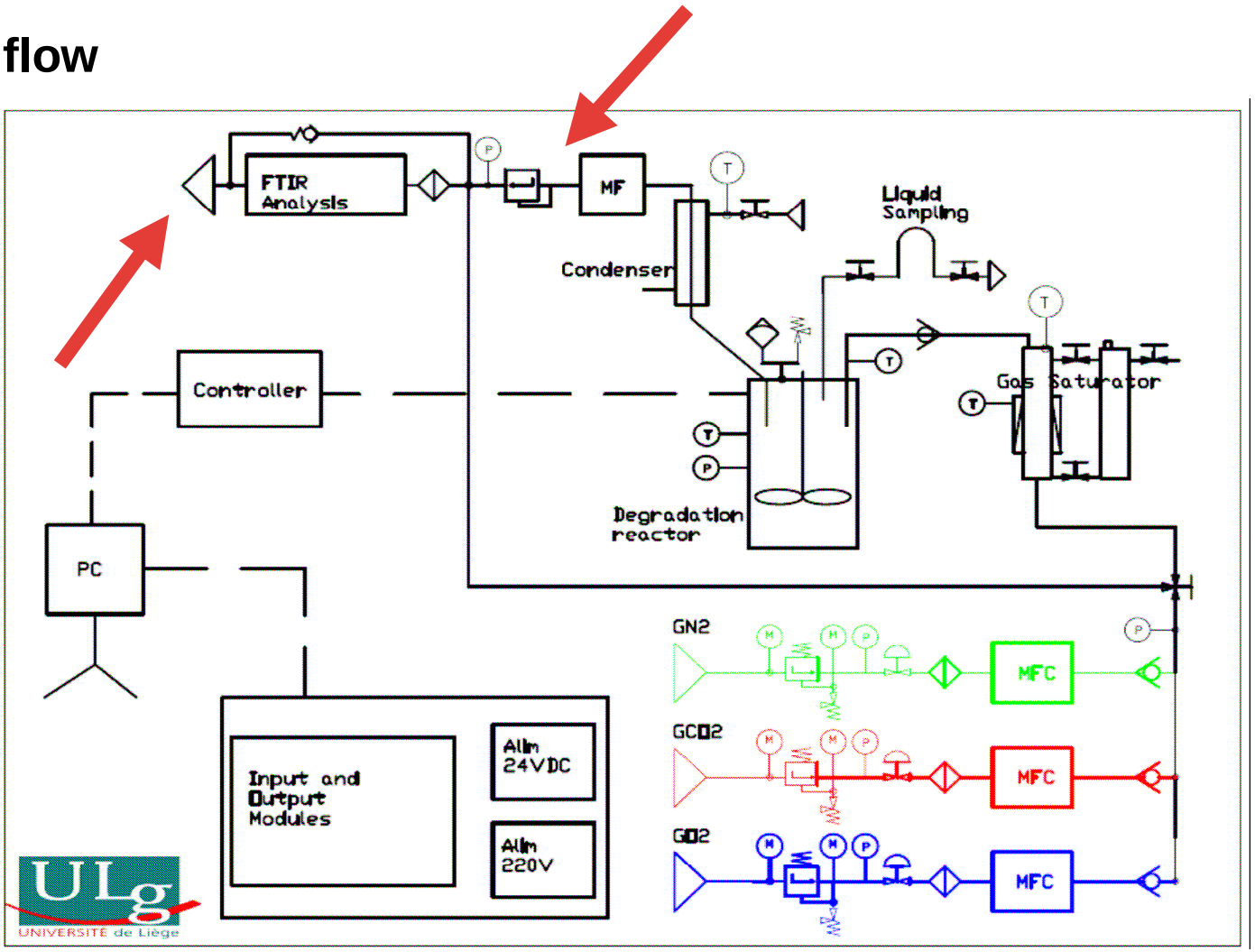
- Reactor outlet gas flows into the intern tube; cooling water flows into the mantle (extern tube)

- Temperature controled from 20℃ to 70℃

- Condensat sampling possible



4. Gas flow


FTIR Analysis
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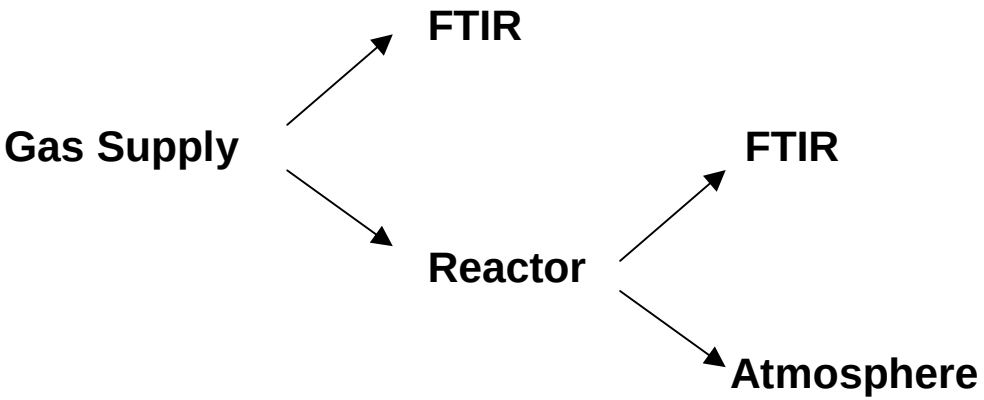
Gas Saturator
Degradation reactor
PC
Input and Output Modules
Alim 24VDC
Alim 220V
GN2
MFC
MFC
MFC

4. Gas flow

- To the reactor via the saturator
- Then to the FTIR analyser or to the atmosphere
- Possibility of diluting the gas sample with N_2



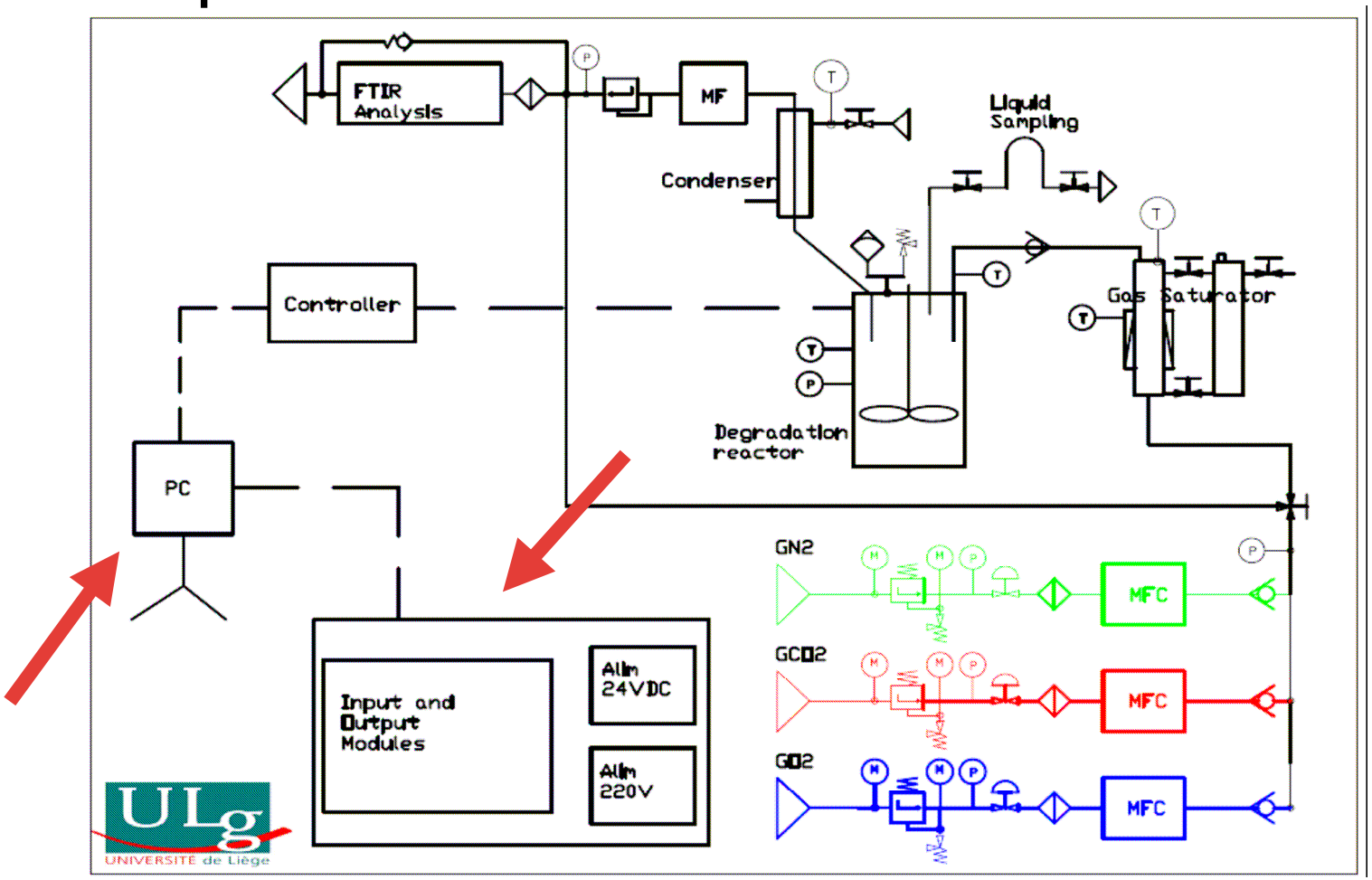
4. Gas flow

- Biphasic Coriolis flow meter
- Back pressure regulation
- Heating rope to prevent the gas flow from condensing in the tubing

4. Gas flow

- Gas release to the atmosphere
- Ventilated local to prevent any incident
- Relief valves and FTIR exhaust are redirected to the atmosphere as well

5. Control panel

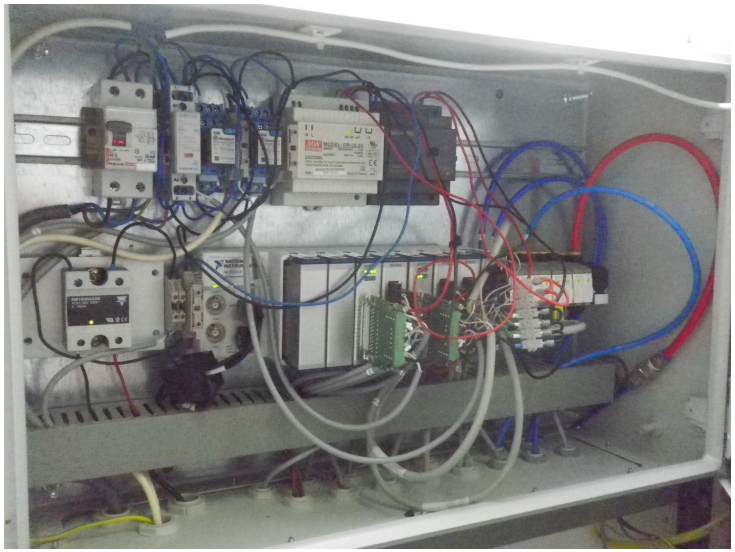


5. Control Panel

Labview

- Data acquisition (Pressures, Temperatures, Mass flows)

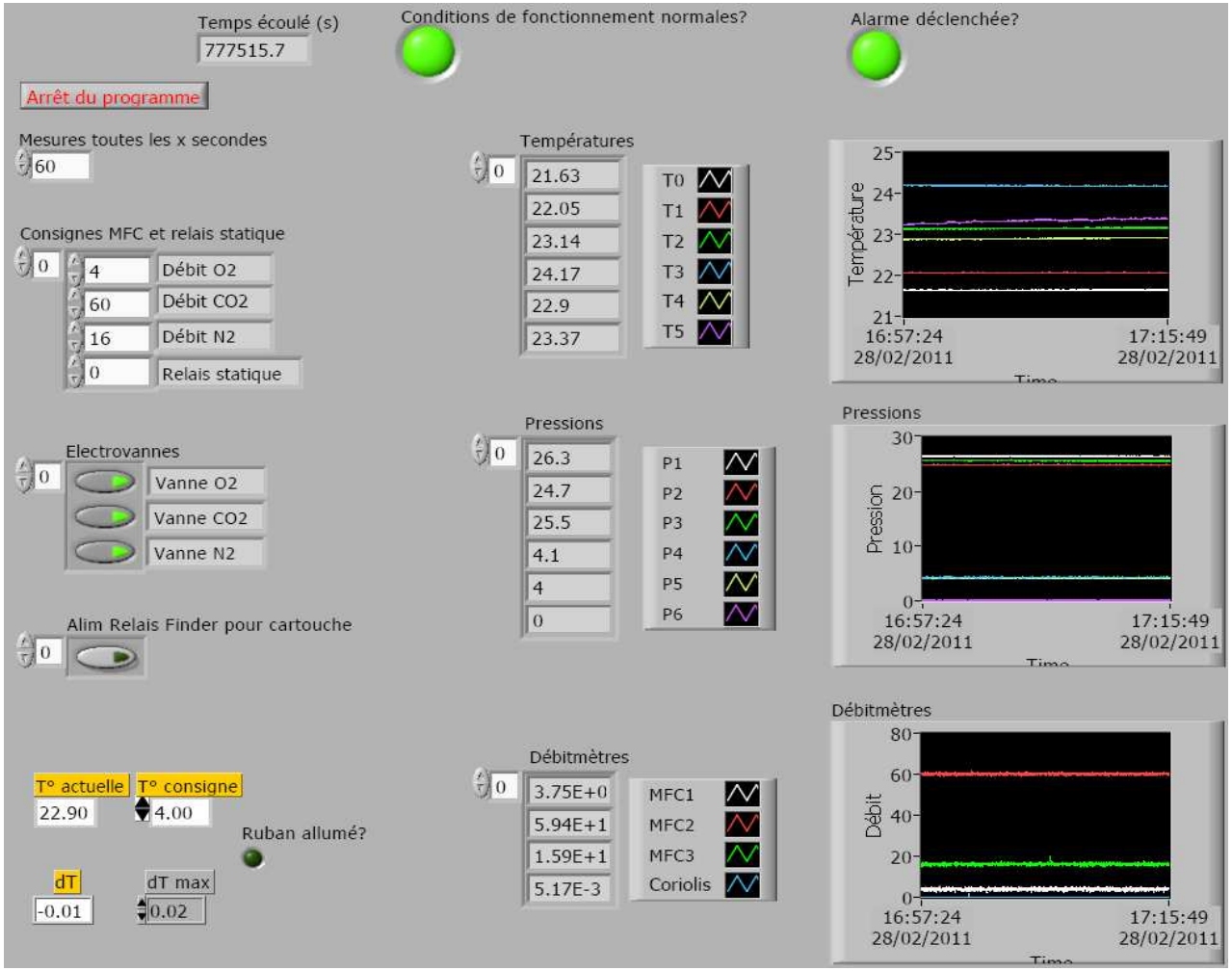
- Control of the installation (Mass flow, heating elements, compressed air for security valves)



5. Control Panel

Labview control panel

- Data acquisition
- Regulation



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5. Control Panel

Reactor controller

- Temperature control
- Agitation rate control
- Pressure display
- High temperature and pressure security

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5. DTR Control Panel

- Data acquisition
- Regulation

Risk analysis

- Deparis method: « Dépistage Participatif des Risques »

- Electrical risks, explosions, gas and liquid leakages, chemicals contamination, fire, earthquake have all been envisaged.

- Risk analysis reviewed by the prevention expert at Laborelec as well as at the University of Liège.

- Emergency procedure has been detailed and software alarms have been implemented

2. Degradation Test
Rig: Risk analysis

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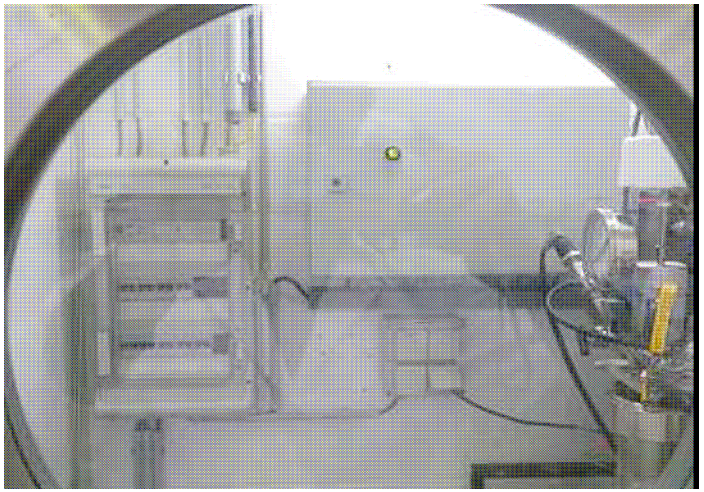
Some performed improvements



3. Results of performed experiments

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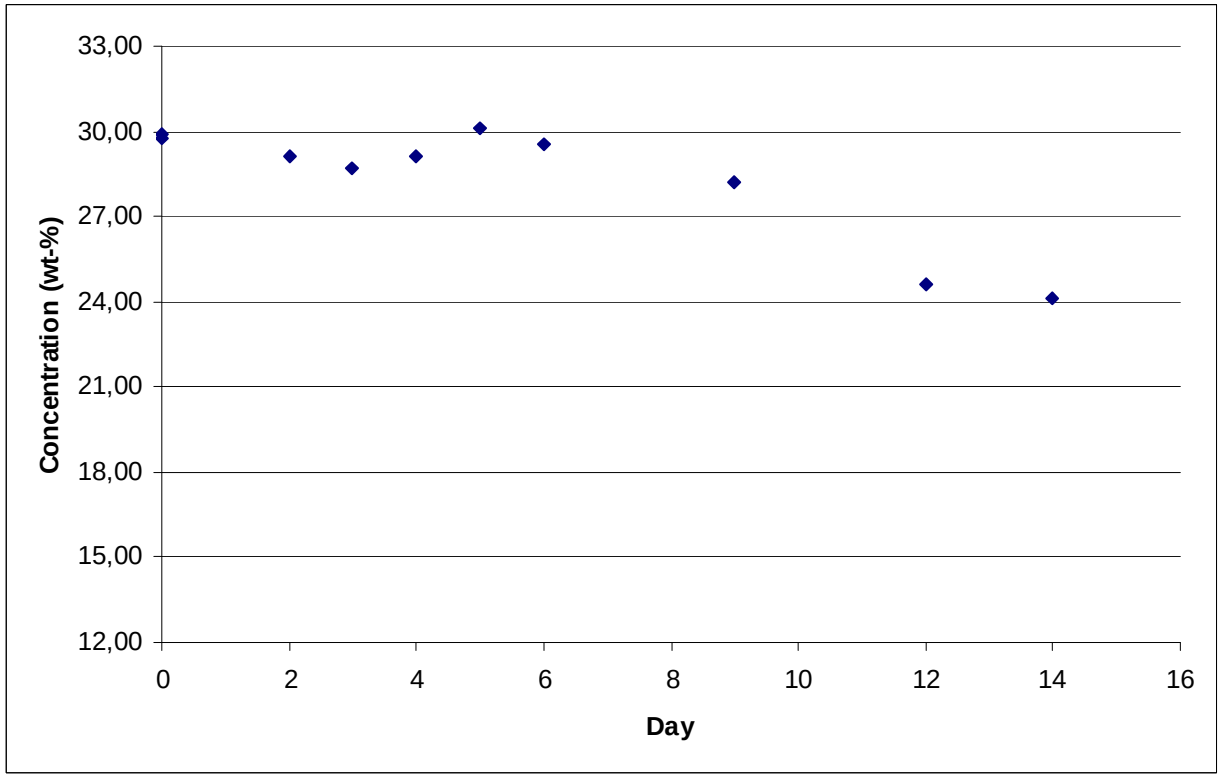
3. Results of performed experiments

- Results of the first experiments performed

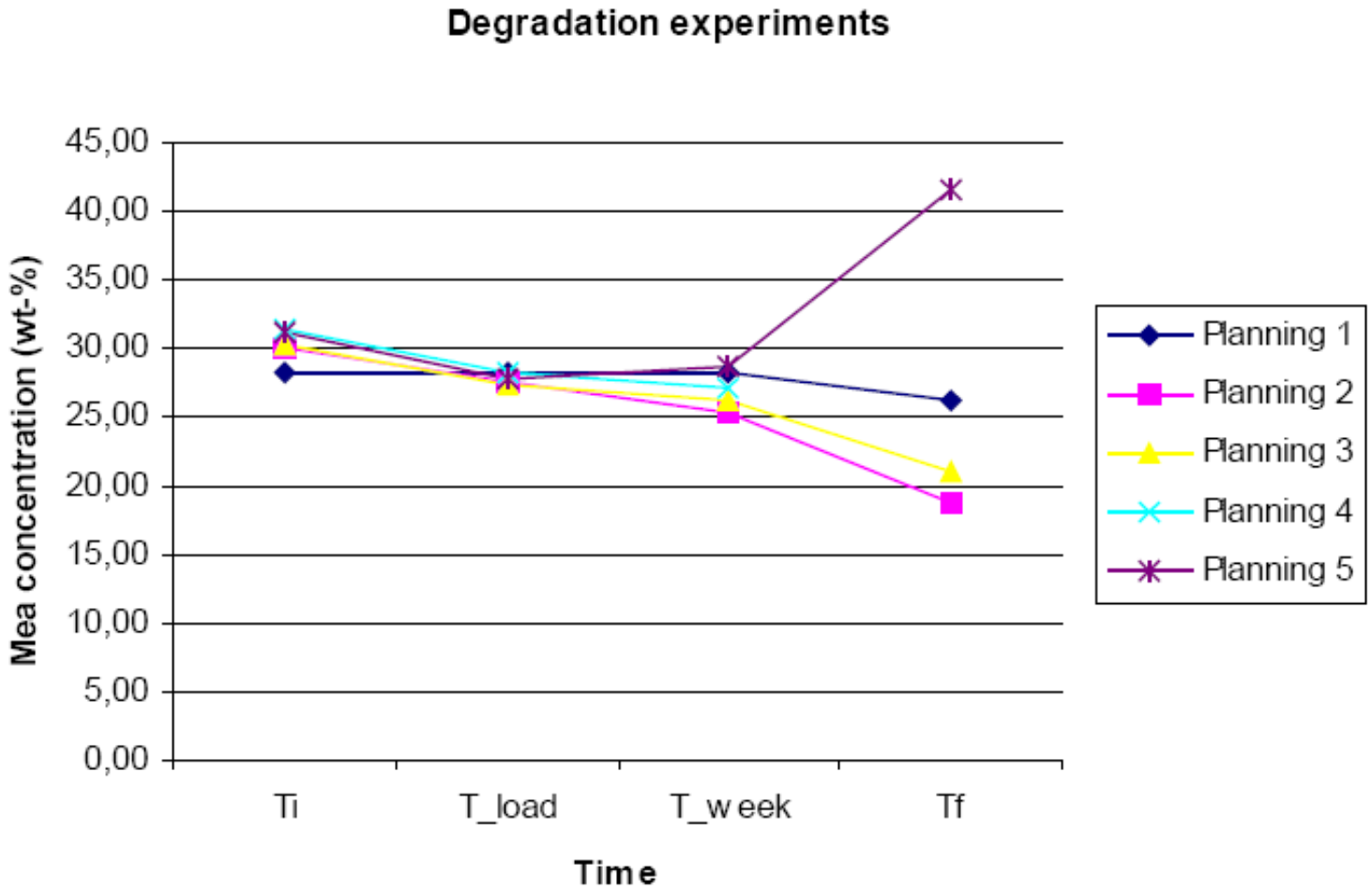
Operating conditions												
Name	Experiment Start	Experiment end	Length [Days]	Parameter tested	T [°C]	P_{tot} [bar]	P_{O2} [bar]	P_{CO2} [bar]	P_{N2} [bar]	Gas flow [mln/min]	Solvent [wt% MEA]	Problems
Test 1	19/02/2011	5/03/2011	14	Base case	120	4	0,2	3	0,8	80	30,00	Pressure variations, sampling frequency higher than in following experiments
Test 2	24/03/2011	5/04/2011	12	Exp. Length/strong cond.	140	20	1	15	4	200	30,00	Gas exhaust stopped due to cristal formation at the condenser, pressure reached up to 25 bar in the end
Test 3	11/04/2011	25/04/2011	14	Temperature	120	20	1	15	4	200	30,01	-
Test 4	10/05/2011	19/05/2011	9	Pressure (N2)	140	20	0,2	3	16,8	500	30,05	Foaming, temperature sensor defectuous => heating stopped automatically
Test 5	27/05/2011	10/06/2011	14	Repetability	120	4	0,2	3	0,8	80	30,01	Cristal formation at the condenser bottom, pressure rose to 20 bar for a few hours, Mass losses (200g)
Test 6	1/07/2011	15/07/2011	14	Repetability	120	4	0,2	3	0,8	80	30,02	Mass losses (150g)
Test 7	20/07/2011	3/08/2011	14	Batch	120	20	0,2	3	0,8	0	29,99	Corrosion of the temperature sensor, green layer on the vessel's walls

3. Results of performed experiments

Degradation profile over 14 days



3. Results of performed experiments



3. Results of performed experiments

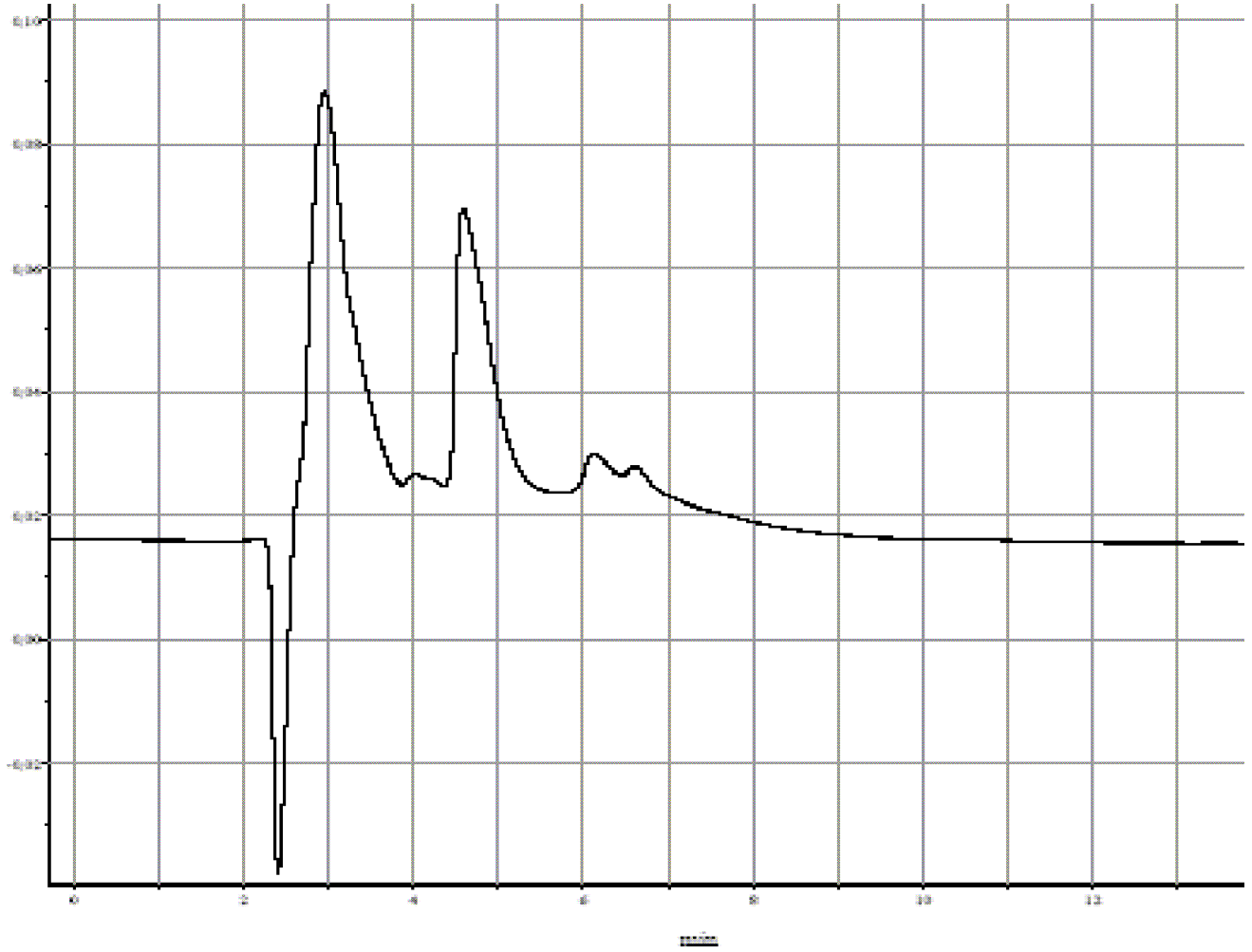
First conclusions:

- Two weeks degradation gives better results
- High temperature enhances the degradation
- High oxygen-content enhances the degradation

- Last experiments still have to be analysed

- HPLC method is sufficient for following the MEA concentration, but seems very imprecise for screening degradation compounds

3. Results of performed experiments



4. Analytical methods

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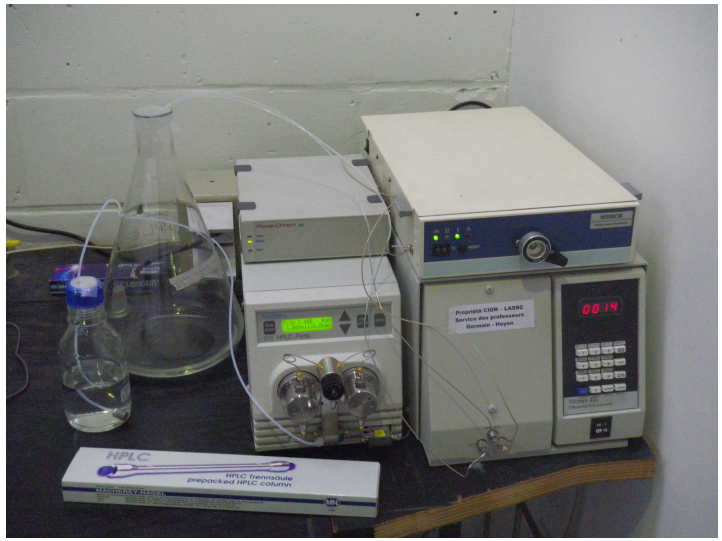
4. Analytical methods

- Liquid sample

  => High Pressure Liquid Chromatography

  => Gas Chromatography-Flamme Ionization Detector



- Gas Sample:

  => Fourier Transformed Infra Red Spectrometer

4. Analytical methods: HPLC

HPLC:

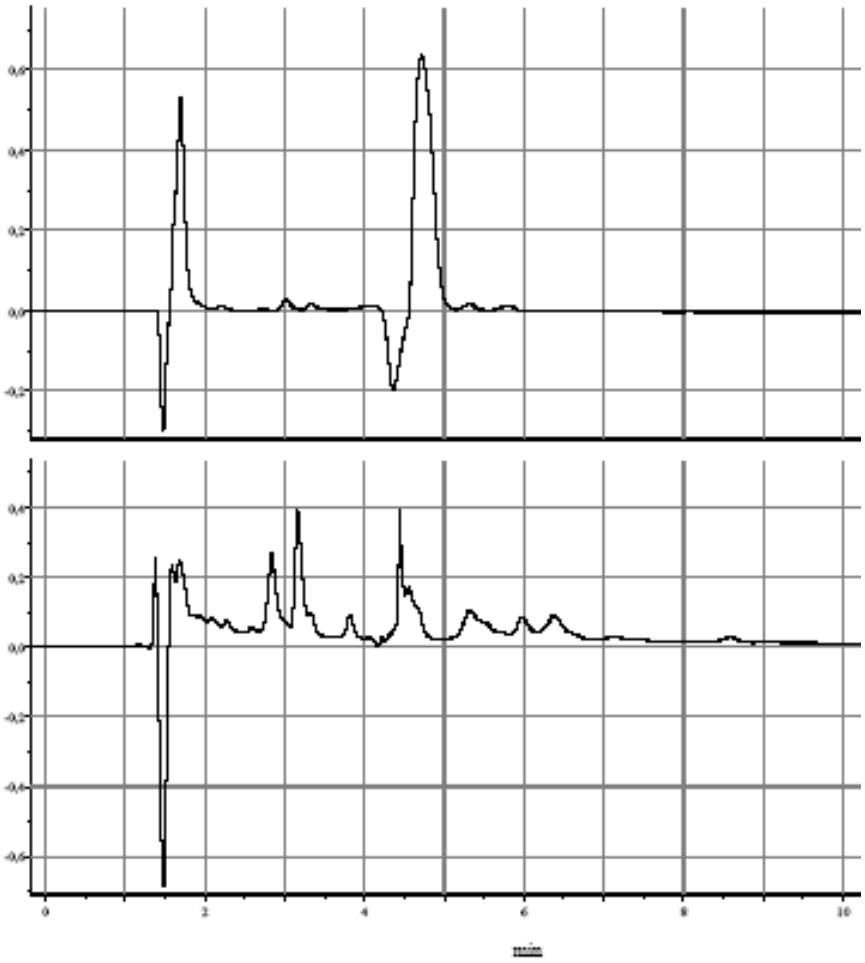
- Influences of eluent, salt concentration, pH, temperature, flow rate

have been studied quite unsuccessfully. For more details see progress report, June 2011.

A new column is beeing tested.

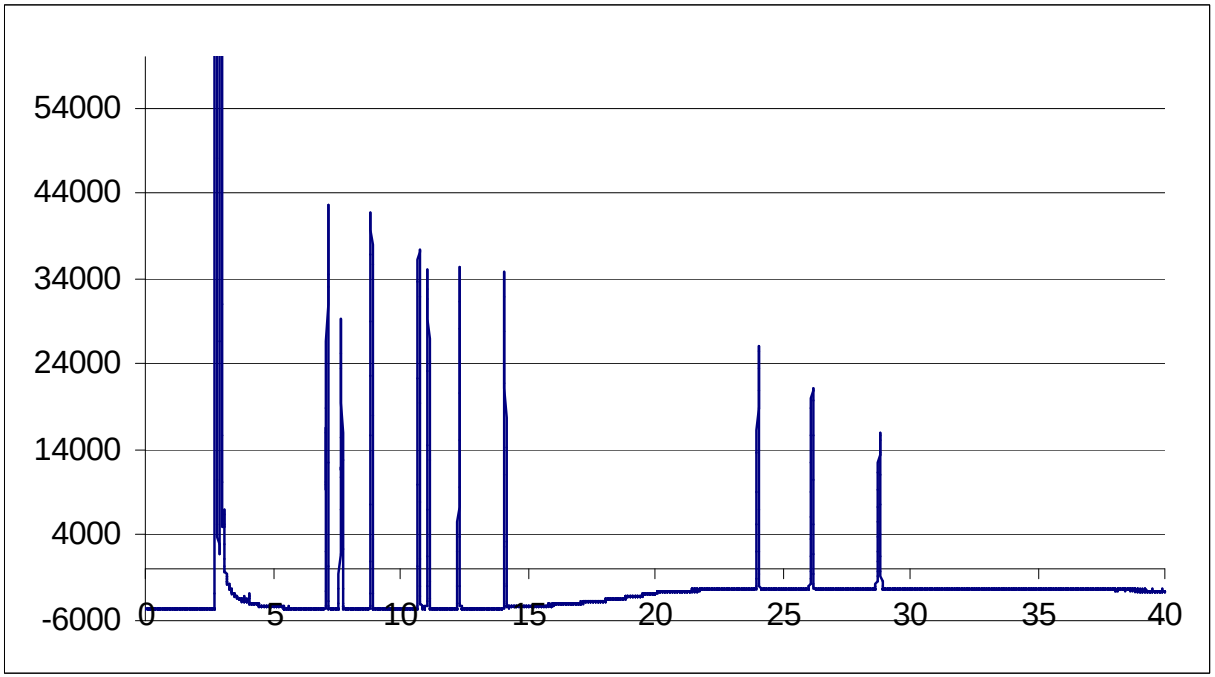
4. Analytical methods: HPLC

Degraded MEA, Eluent 75:25 ACN:Buffer (NH4Ac 24mM pH 3.8); Mass flow 1.2ml/min; T=30℃, UV @ 215nm



4. Analytical methods: GC-FID

- GC-FID: First results seem very promising, repetability has been demonstrated



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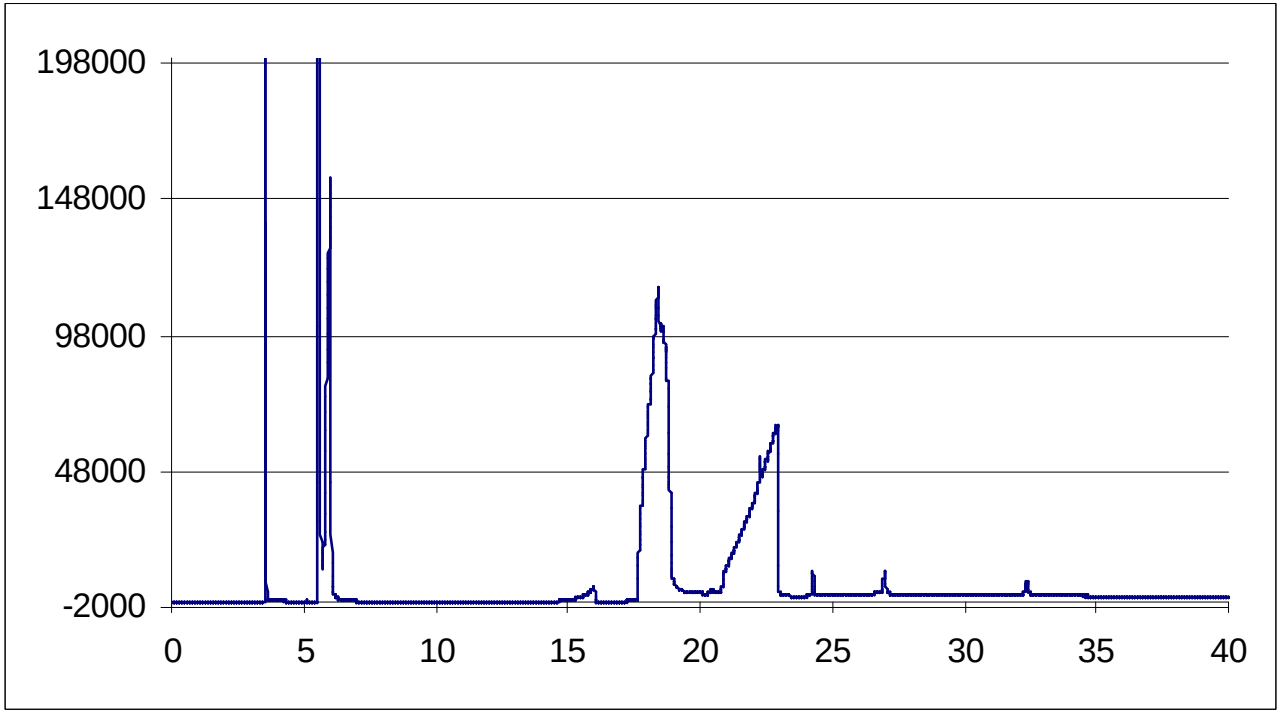
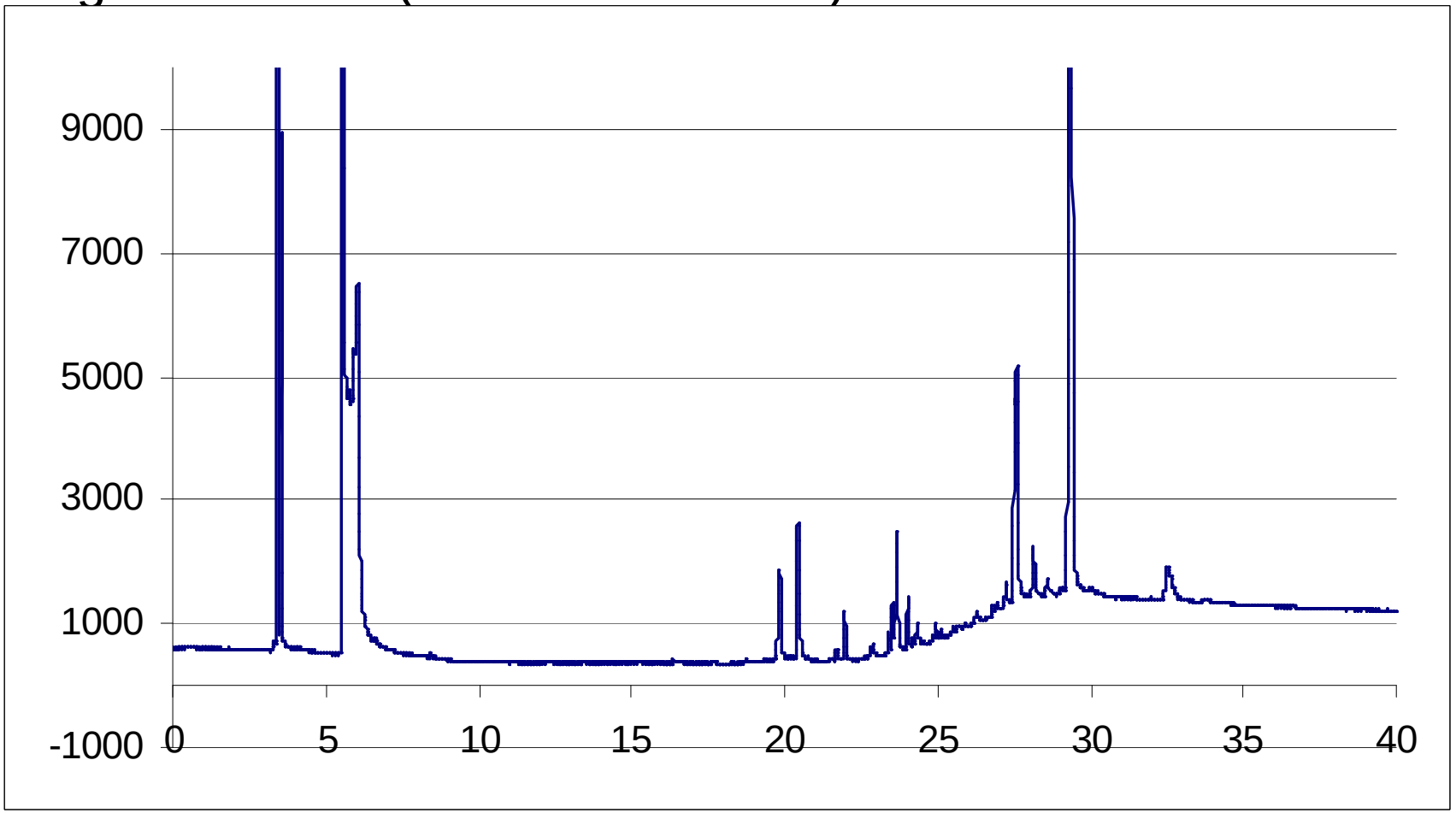
Standard solution (MEA, AEAE, HEA, EDA) 1:100

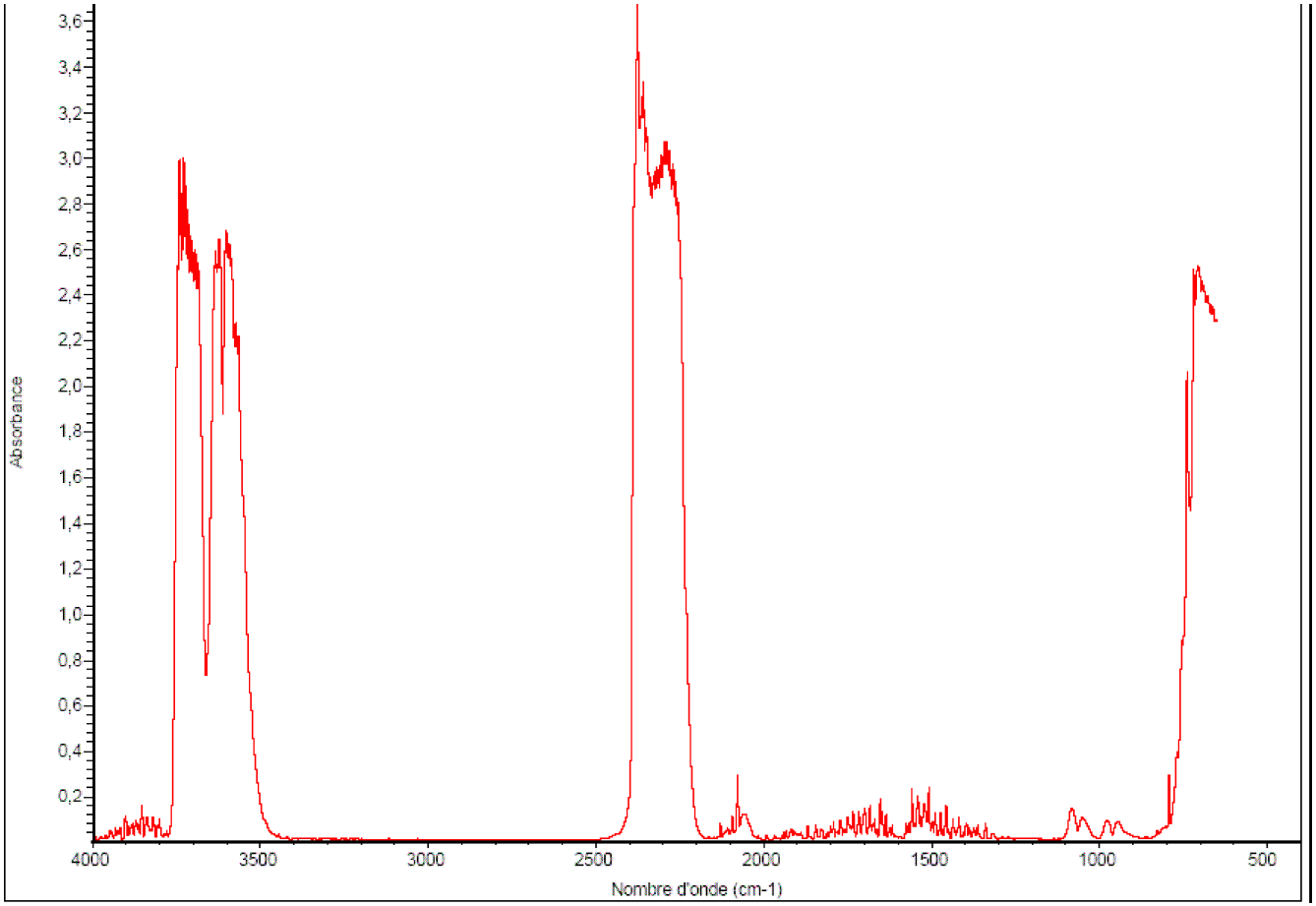


4. Analytical methods: GC-FID

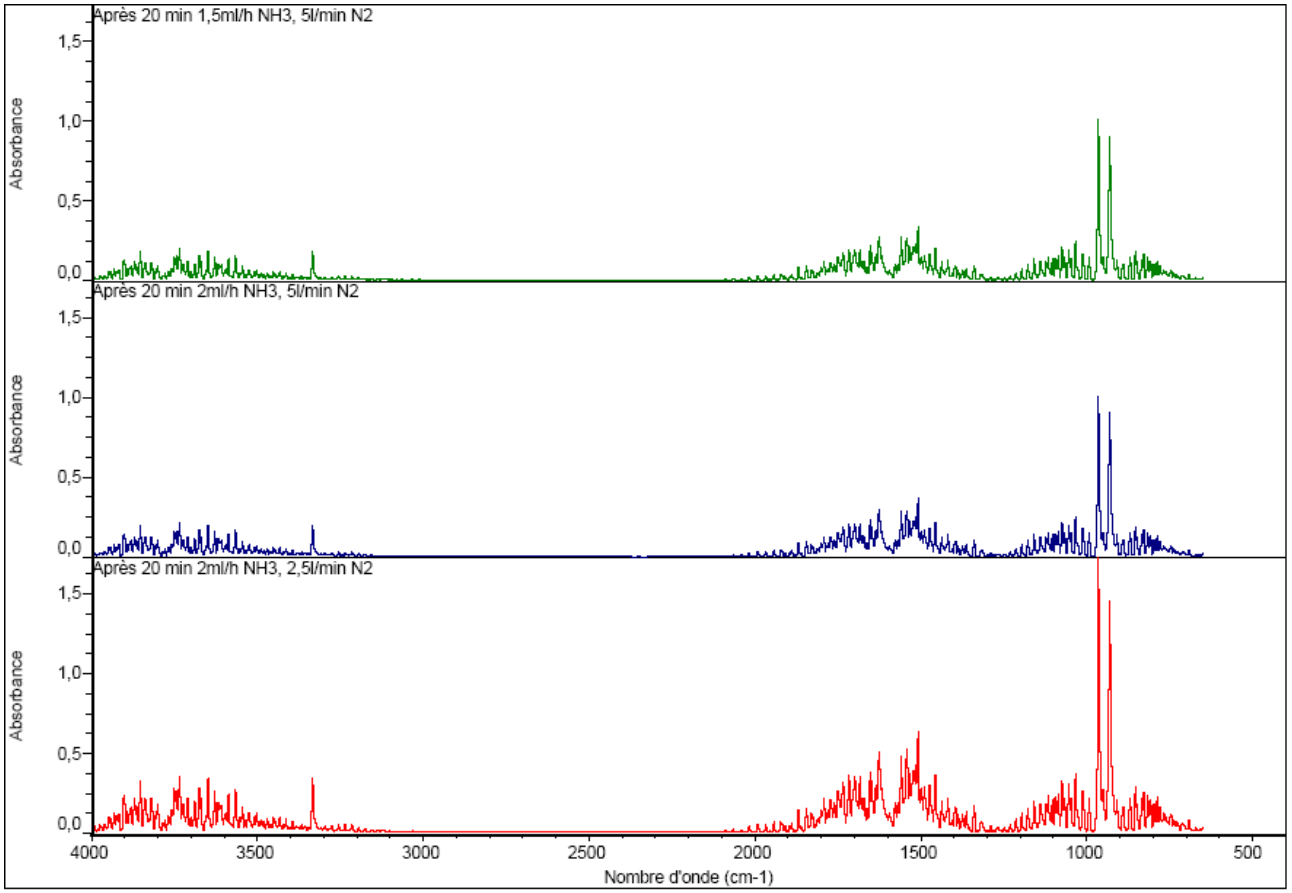
Degraded MEA (dil 1:100 in water)



Gas phase analysis: gas calibration : CO_2

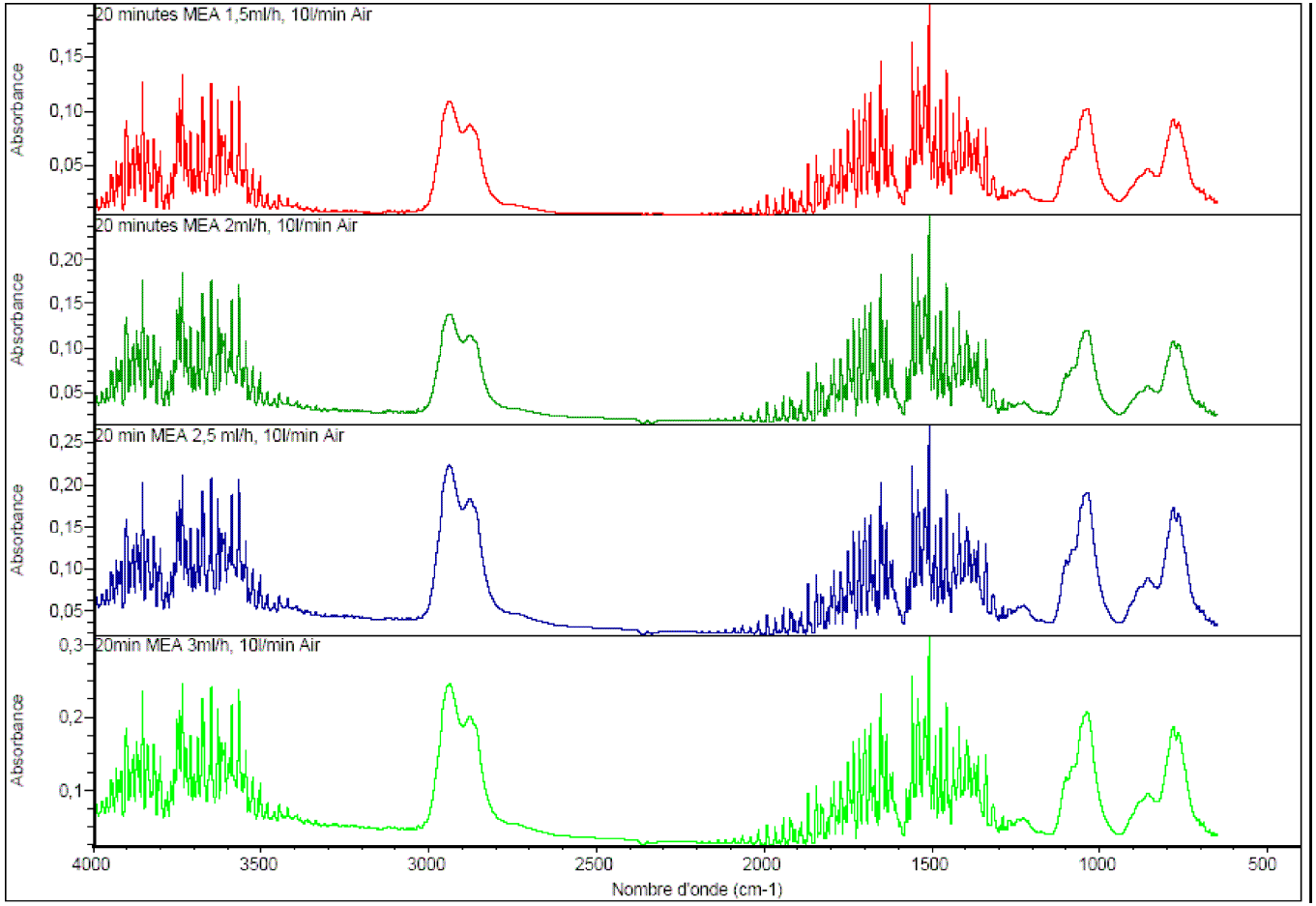


NH3 calibration (910-1196cm^{-1}, 3219-3396cm^{-1})



4. Analytical methods: FTIR

- MEA calibration (980-1119cm^{-1}, 2624-3150cm^{-1})



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Corrosion is followed thanks to this analysis

	Fe	Cr	Ni	Si	Cl	F
Planning 1 T0	0,44	< 0.10	< 0.10	-[a]	< 2.00	38,94
Planning 1 Tf	7,57	1,55	4,24	-[a]	< 2.00	416,08
Planning 2 Tf	22,40	8,60	9,75	13,01	513,16	1826,18
Planning 3 Tf	6,80	3,10	2,66	10,66	522,32	869,35
Planning 4 Tf	1,90	1,30	1,01	15,57	291,36	307,13
Washing water 1[b]	4,82	0,02	0,51	3,06	0,74	0,05
Washing water 2[b]	0,01	< 0.01	0,20	2,03	0,08	0,04

[a] Silicon has not been measured for the two first samples

[b] Washing water from the washing realized after experiment "Planning 4"

5. Conclusion

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5. Conclusion

- Degradation test rig has been constructed
- Experiments are running
- Development of analytical methods in process

5. Conclusion

Making the link between simulation and degradation

=> Objective:

- having a reliable simulation model
- taking solvent degradation into account
- that can be used for predicting the most appropriated operating conditions for post-combustion capture

Multi-objectives process optimization:

- Energy savings (costs)
- Solvent savings (lower solvent make-up)
- Lower environmental impact due to solvent degradation

Thank you for your attention!

Questions are welcome!