Progress Report

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8th April 2011

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1. Introduction

1. Introduction

- PhD thesis in the field of chemical engineering

- Partnership between Laborelec and the University of Liège

- Subject divided into two main parts:

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

2. Experimental study of solvent degradation

2. Objectives

8^{th} April 2011

2. Objectives

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

- The result will be

⇒ a proposal
⇒ for optimal operative conditions in the CO_2 capture process
⇒ taking into account process efficiency and solvent degradation
⇒ i.e. cost and environmental impacts of post-combustion capture

3. Modeling and optimal design

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3.1 Objectives

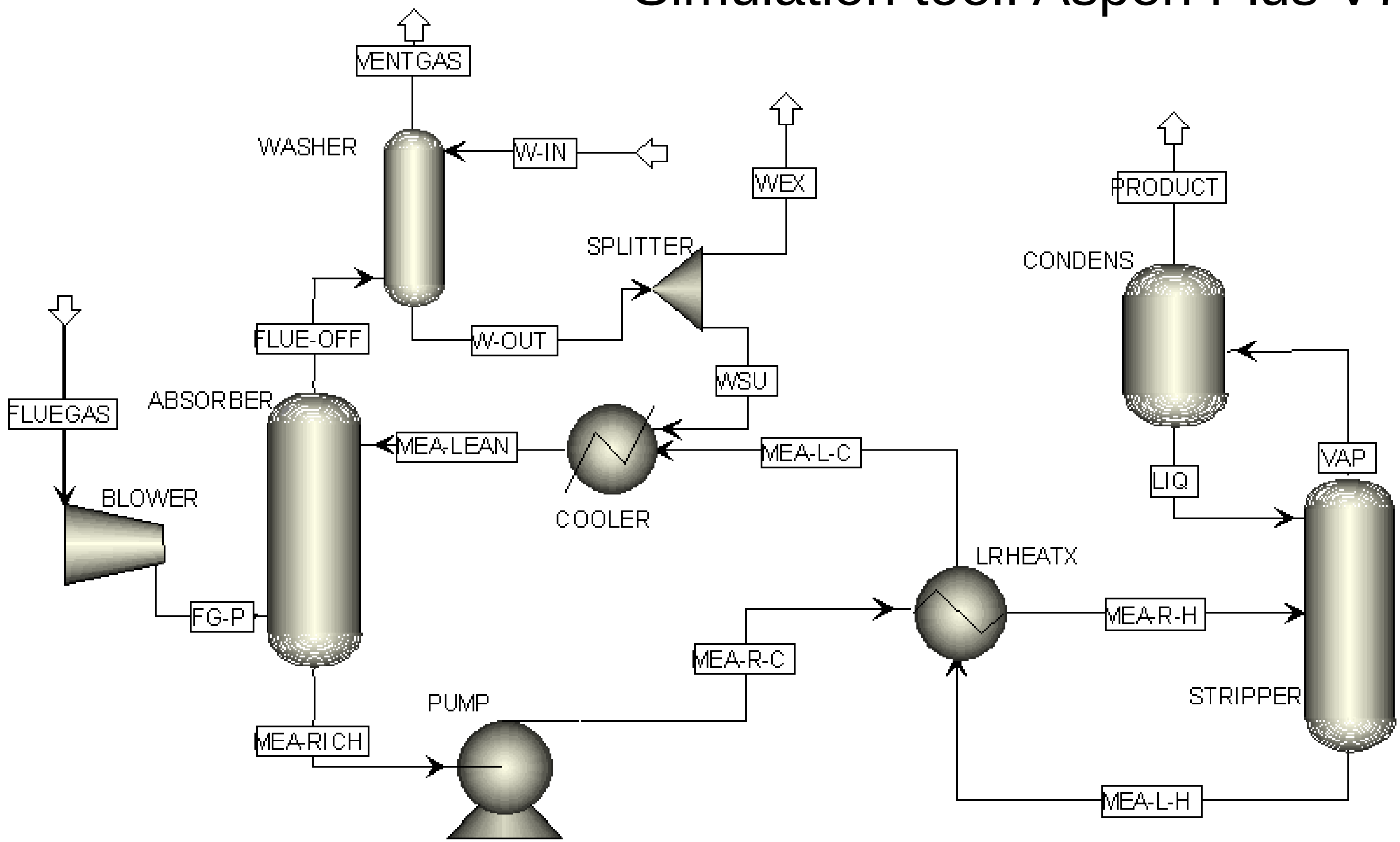
- Modeling and optimization of the existing carbon capture process with MEA
- Proposal and simulation of flowsheet improvements
- Adaptation of the model to novel CCS solvents
- Adaptation of the model to the Hitachi pilot in order to dispose of a model available for the test campains
- *Dynamic model of the capture process*

3.2 Achievements

- Master thesis: Equilibrium model
- Rate-based model
- Sensitivity analysis focusing on key parameters
- Simulation of flowsheet modifications
- Writing of a article for a symposium in June 2011
- Model available for accompagnying the Hitachi test campaigns

3.3 Results Summary

Simulation tool: Aspen Plus V7.2



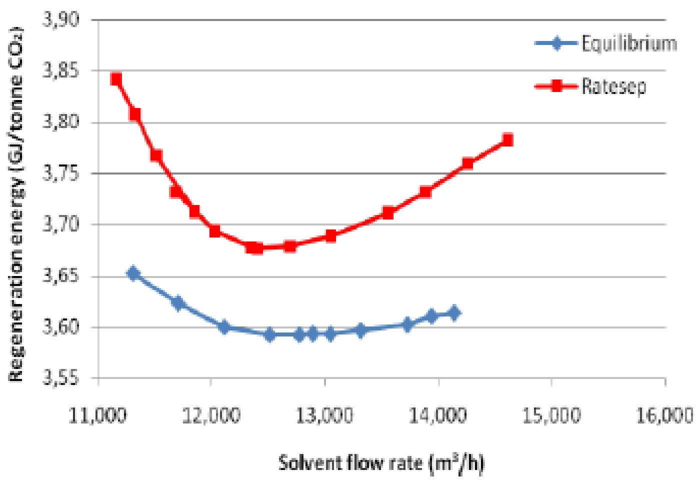
3.3 Results summary

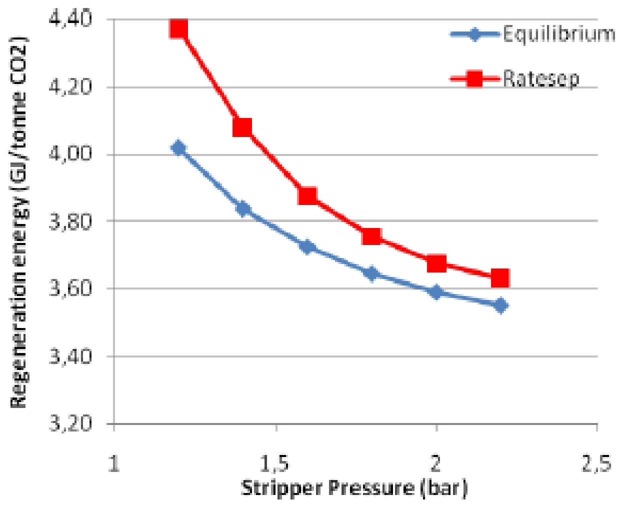
Process optimization:

	Stripper pressure	Solvent concentration	Solvent flow rate
Equilibrium model			
Basecase value	1.2 bar	30 wt-%	15 m^3/h
Optimum value	2.2 bar	37 wt-%	13.9 m^3/h
Regeneration energy	-11.6%	-8.2%	-1.6%
Rate-based model			
Basecase value	1.2 bar	30 wt-%	15 m^3/h
Optimum value	2.2 bar	37 wt-%	12.4 m^3/h
Regeneration energy	-16.9%	-5.4%	-2.8%

Process optimization:

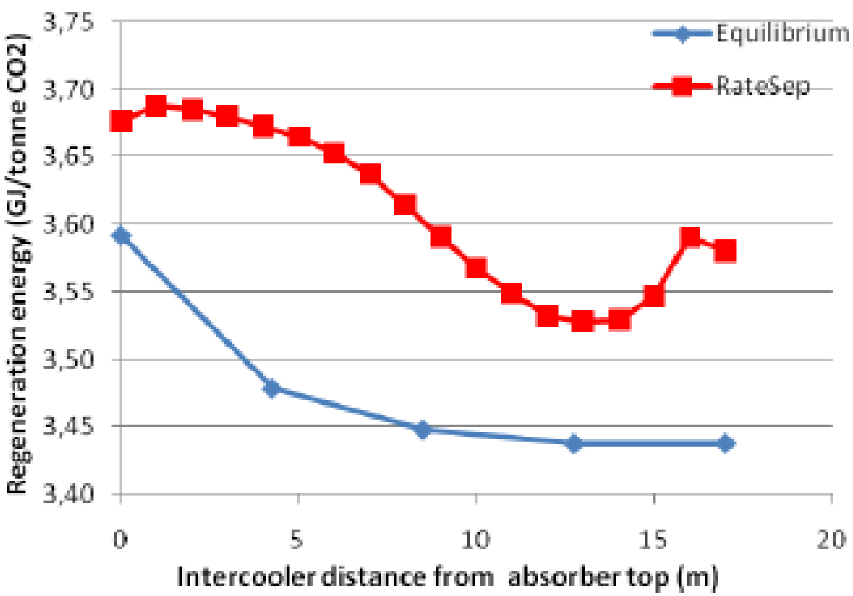
Solvent flow rate and stripper pressure

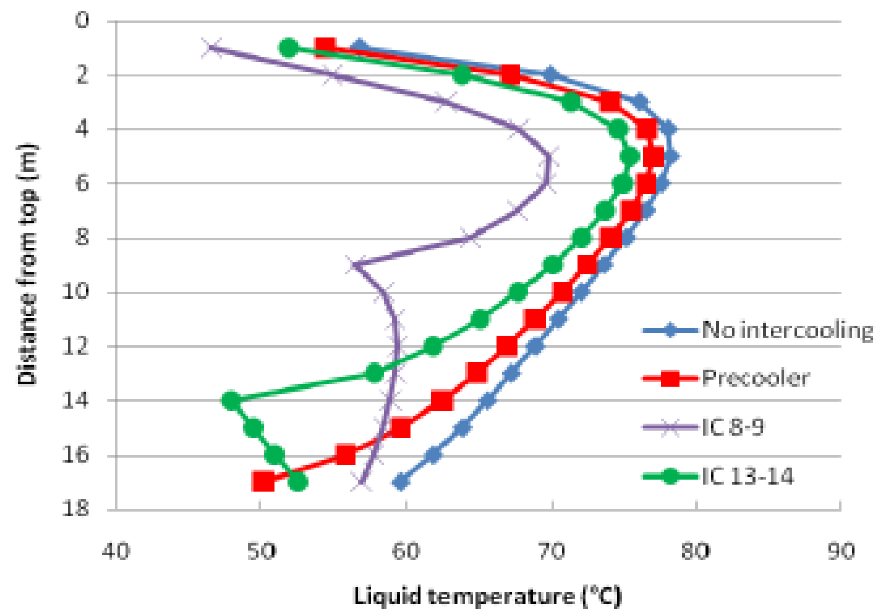




3.3 Results summary

Flowsheet improvements: effect of absorber intercooling





3.4 Met problems

- Not possible to establish a direct link between Matlab and Aspen Plus

  => Sensitivity study made using Excel

- Thermodynamical data not accurate, varying from one model to the other

  => The chosen parameter set seems to give good results, but the model still has to be validated based on pilot data

4. Assessment of solvent degradation

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4.1 Objectives

- Design and construction of a test bench for experimental study of CCS solvent degradation
- Comparison of the degradation rate of classical and newly developed solvent systems
- Impact of operative conditions and degradation inhibitors on solvent degradation
- *Experimental study of the reclaiming process*

4.2 Achievements

1. Degradation Test Rig (DTR) has been designed and built
2. Detailed risk analysis available
3. Analytical methods development in progress
4. Test of classical solvents started

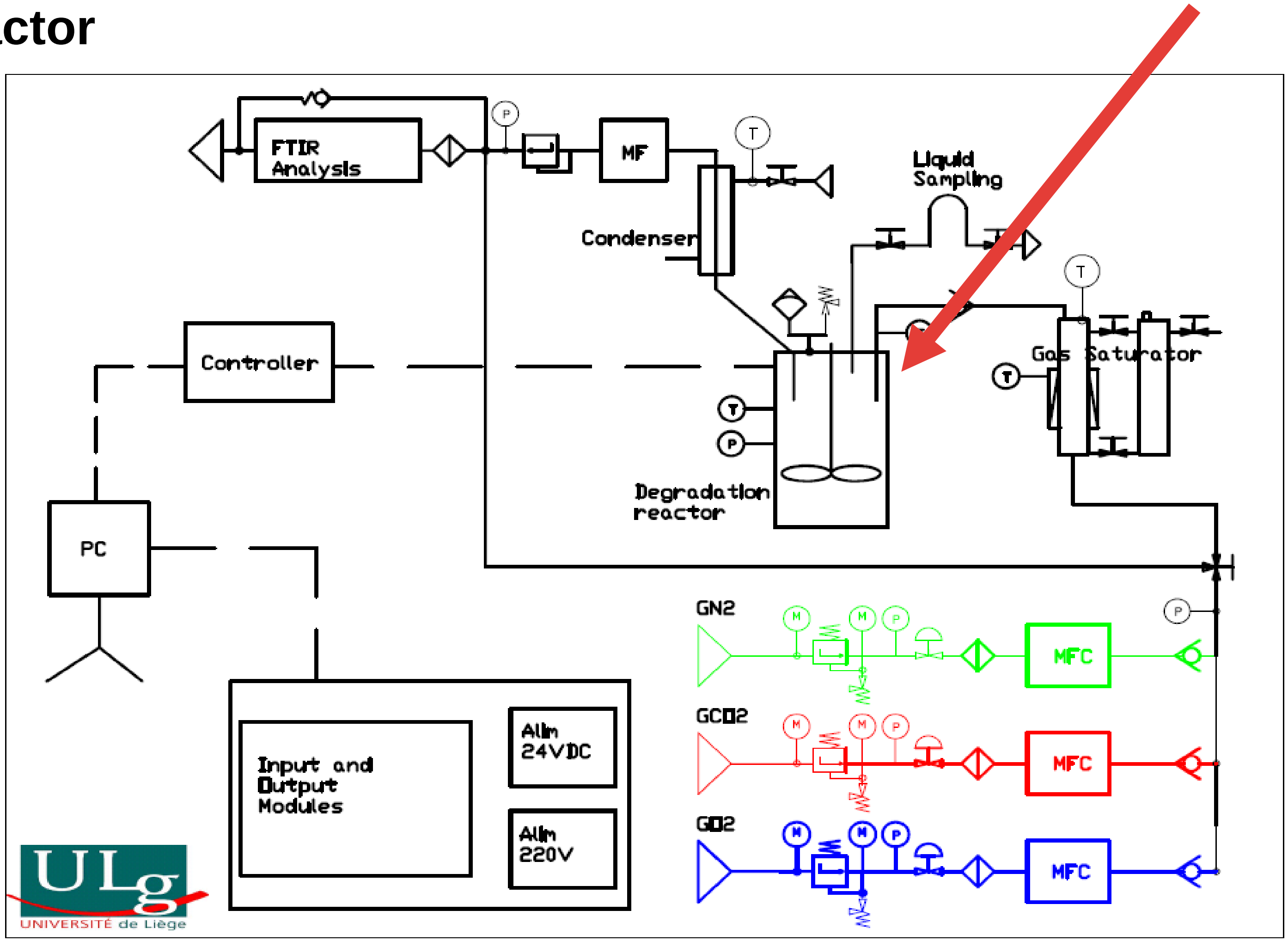
4.2.1 Degradation Test Rig (DTR)

Elements:

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

4.2.1 Degradation Test Rig (DTR)

1. Reactor

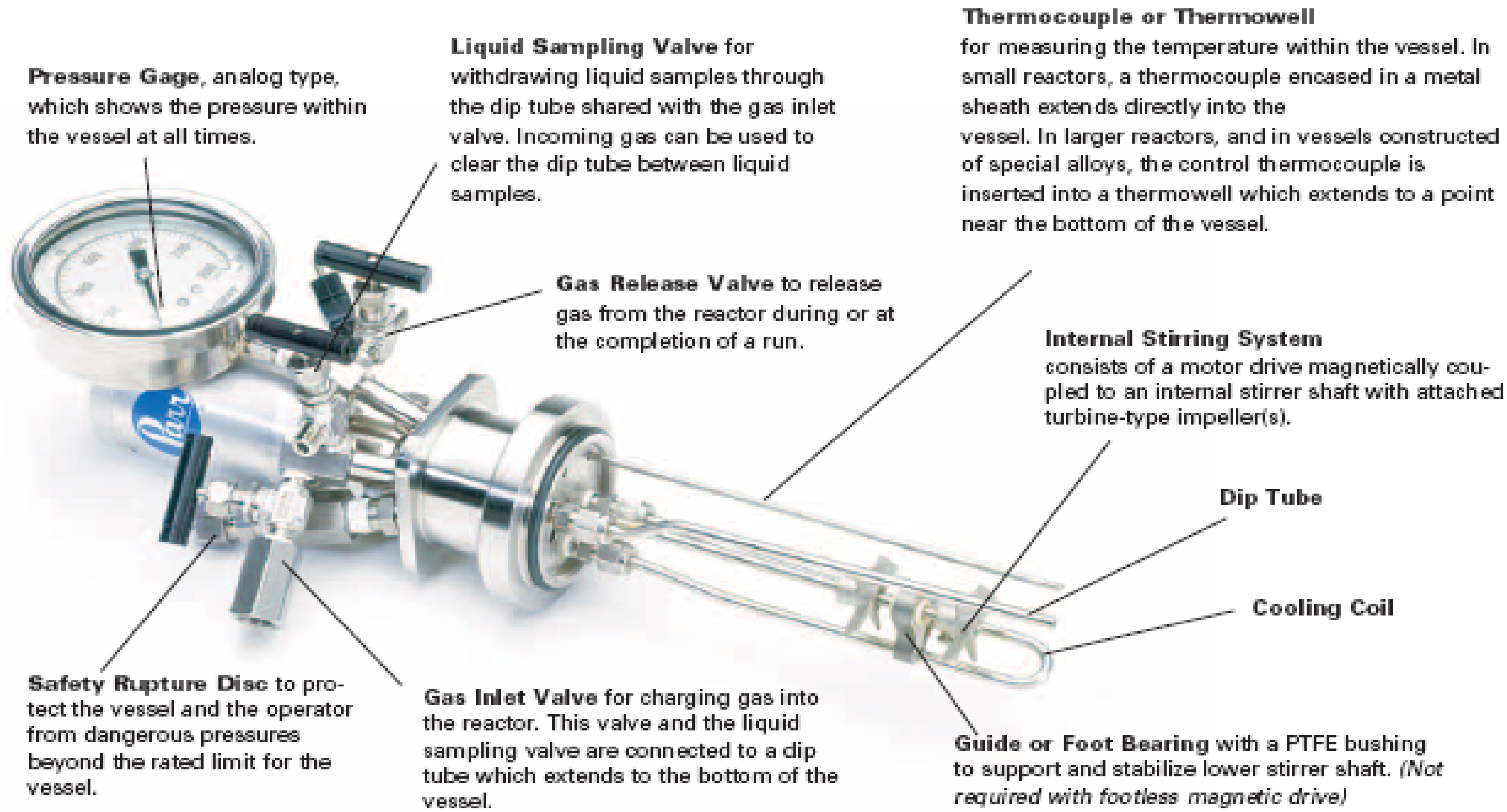


1. Reactor

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

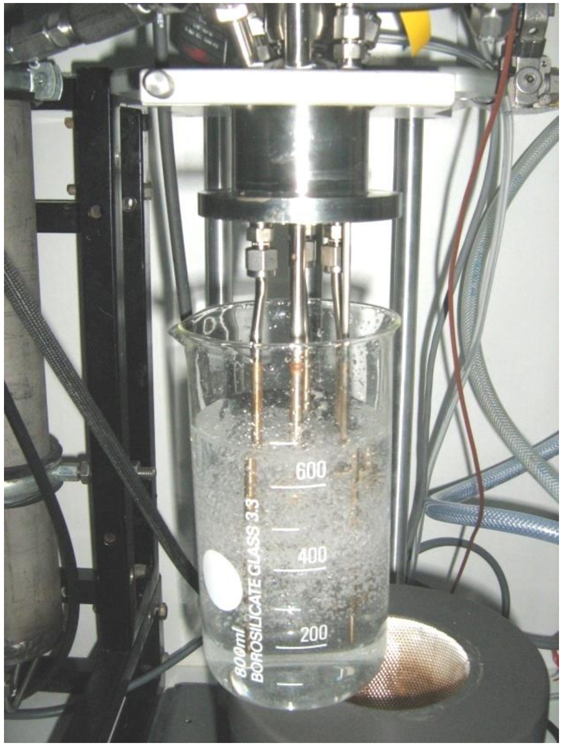
Model 4544 High Pressure Reactor, 600 mL, Moveable Style Vessel, with heater lowered, and a 4848 Controller shown with optional Expansion Modules.

4.2.1 Degradation Test Rig (DTR)

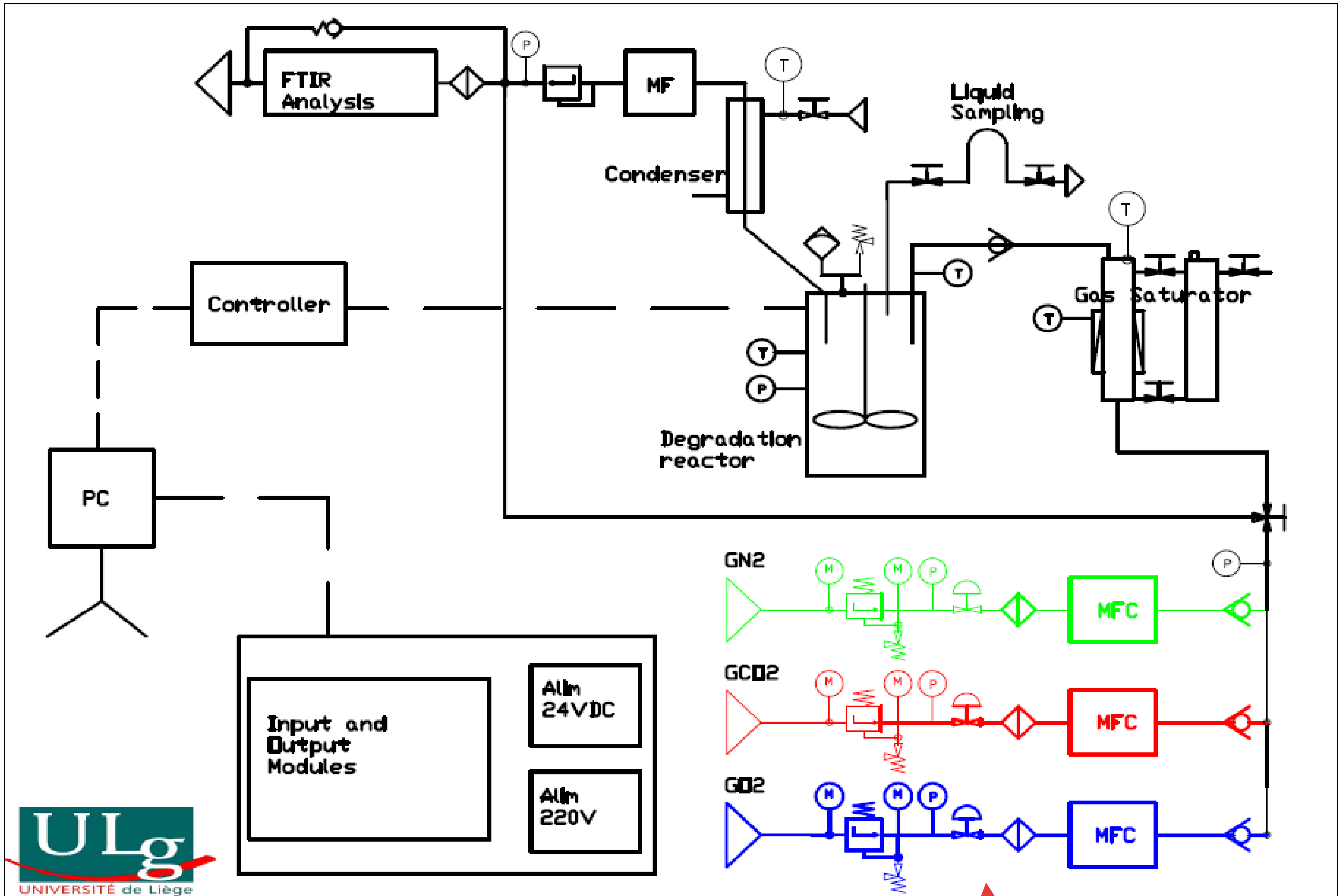


4.2.1 Degradation Test Rig (DTR)

Hollow shaft for a better gas-liquid contact



2. Gas supply



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

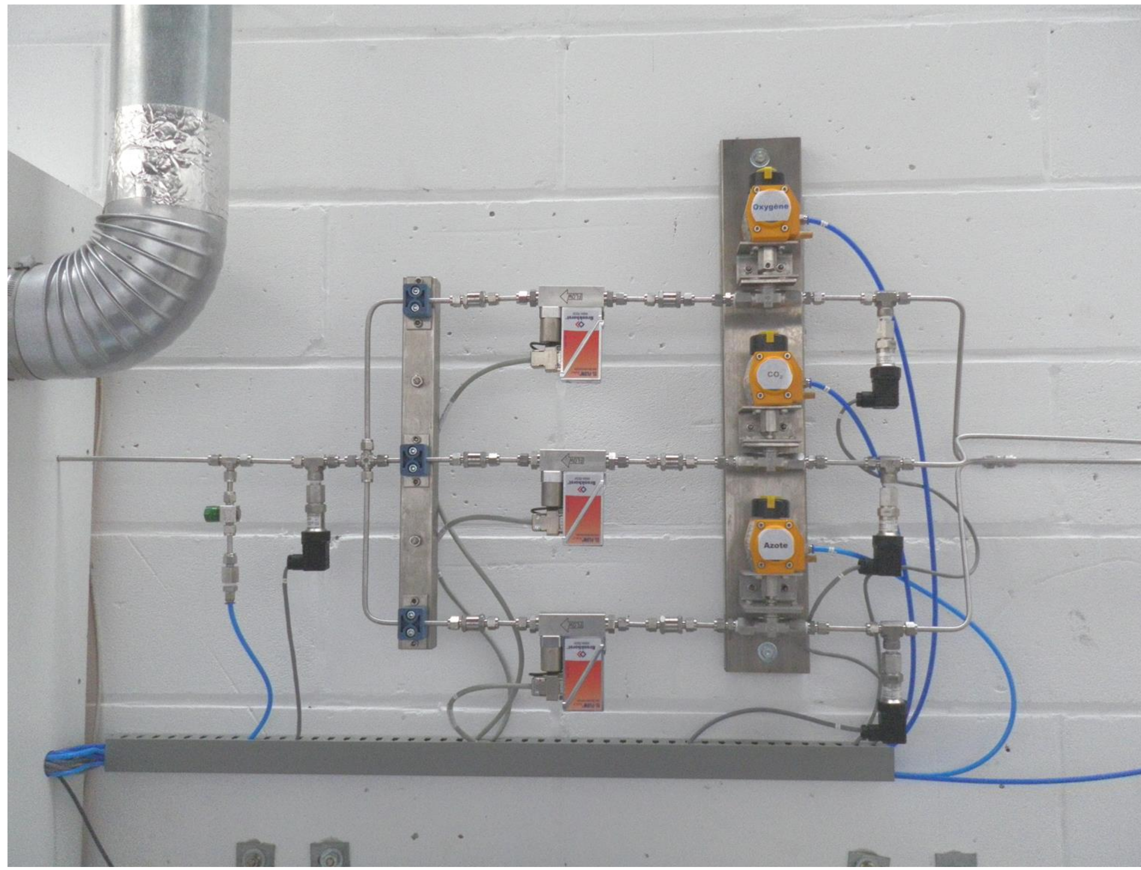
2. Gas supply

- N_2 - CO_2 - O_2
- Compressed Air

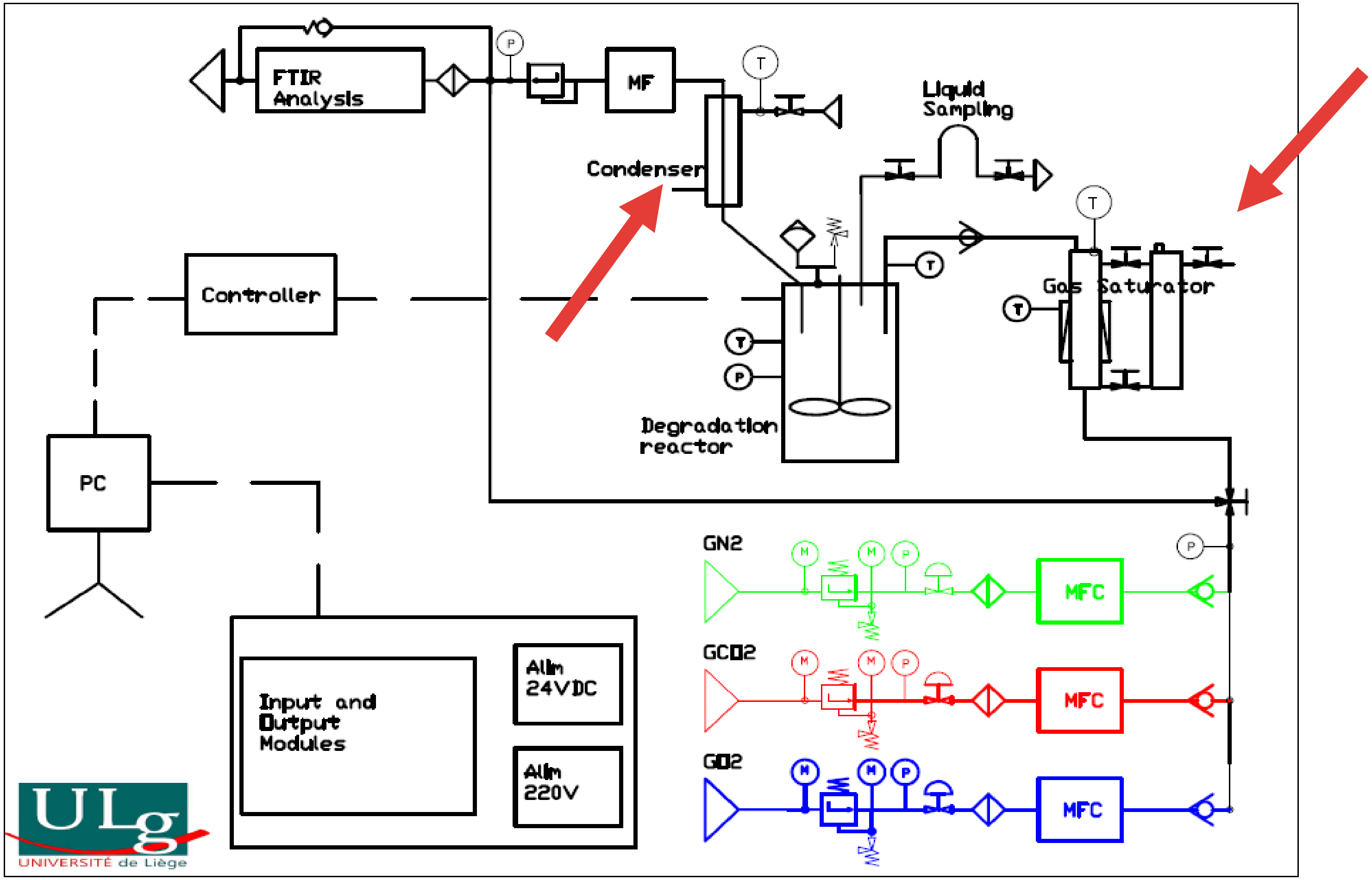
- Bottle Rack
- Pressure regulator
- Risk Indications

2. Gas supply

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



3. Water balance



3. **Water Balance:** Saturator

- Saturation of the inlet gaz with water
- Re-filling under pressure possible
- Relief valve set at 40bar
- Temperature controled thanks to a solid state relay
- Outlet connected to the reactor

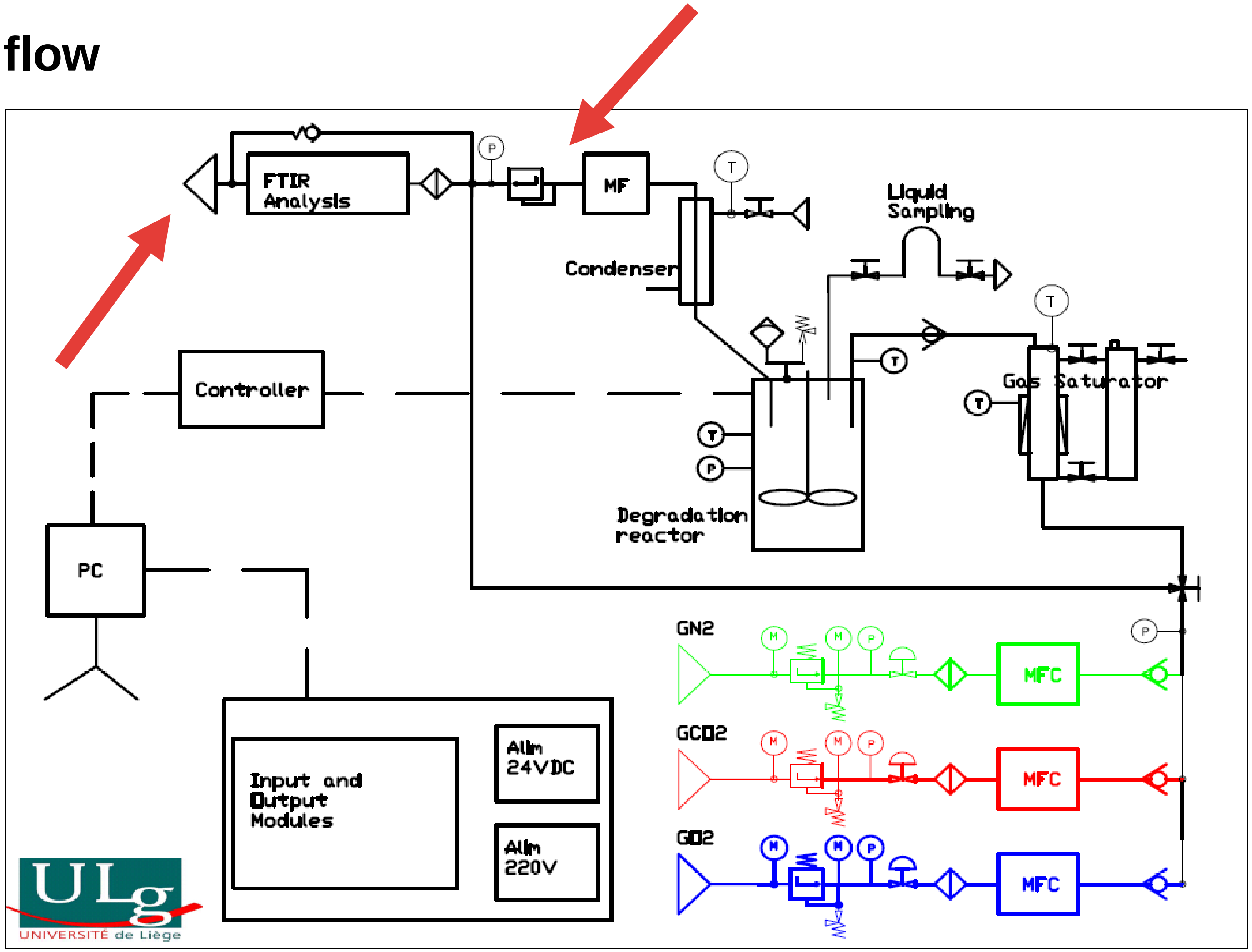
4.2.1 Degradation Test Rig (DTR)

3. Water balance: Condenser

- Reactor exit gas flows into the intern tube
- Waters flows into the mantle (extern tube)
- Temperature control thanks to the heating bath
- Range: 15°C – 70°C
- Condensat sampling possible

4.2.1 Degradation Test Rig (DTR)

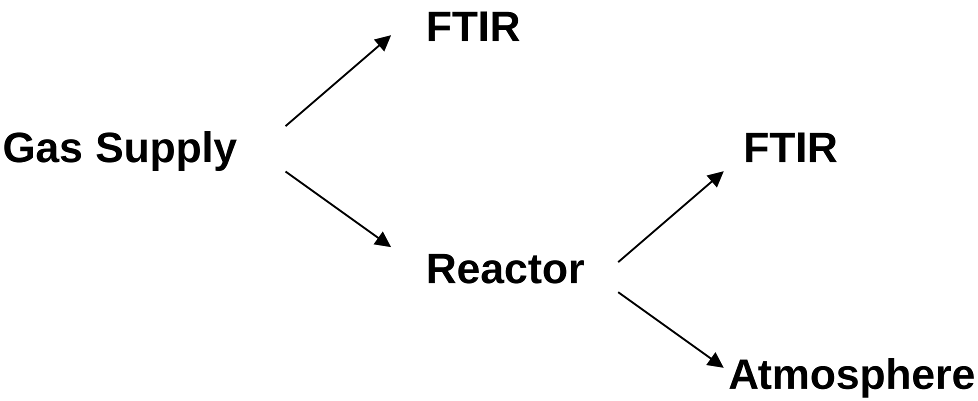
4. Gas flow



4.2.1 Degradation Test Rig (DTR)

4. Gas flow

- To the reactor via the saturator
- Then to the FTIR analyser or to the atmosphere
- Or directly to the FTIR analyser for calibration



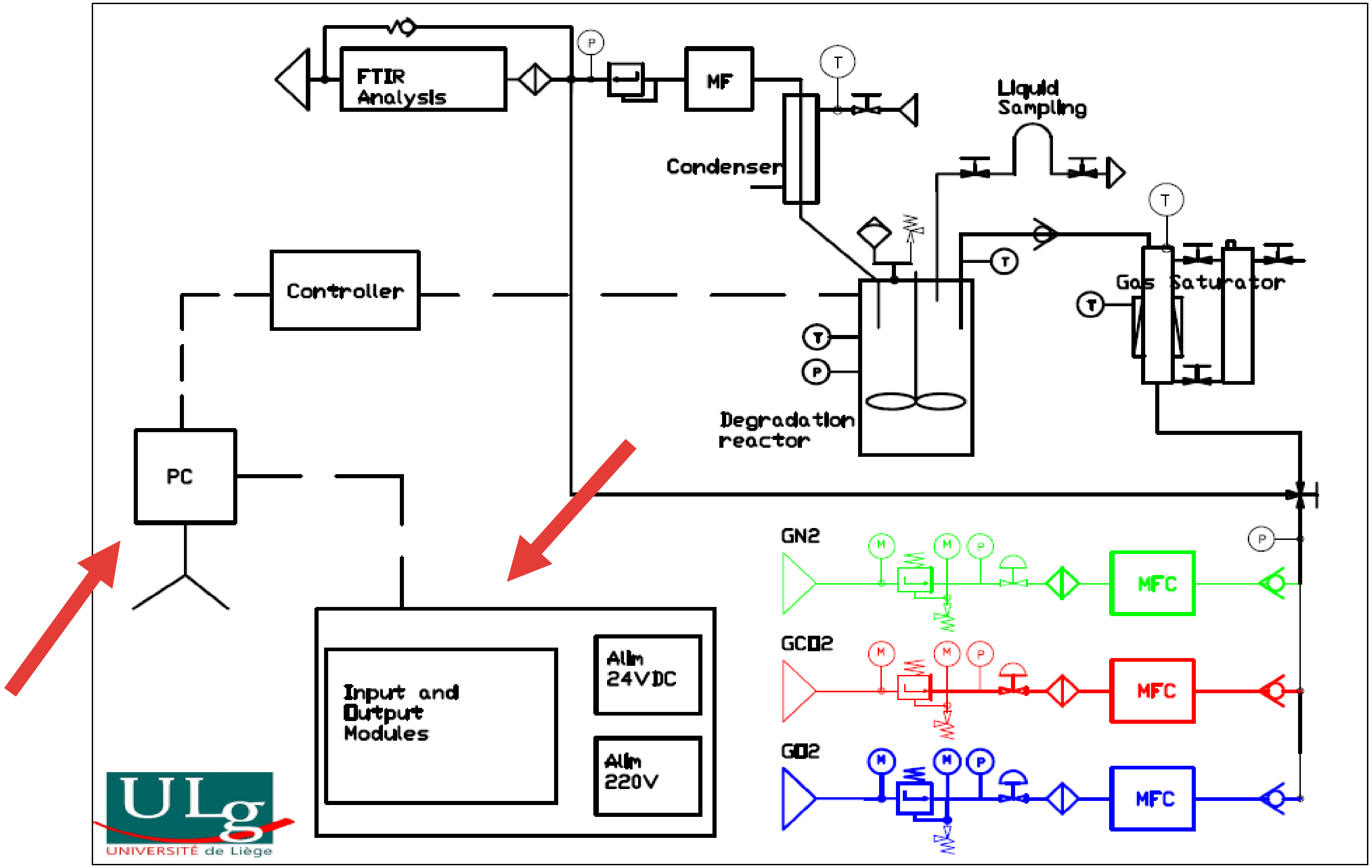
4. Gas flow

- 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. DTR control panel

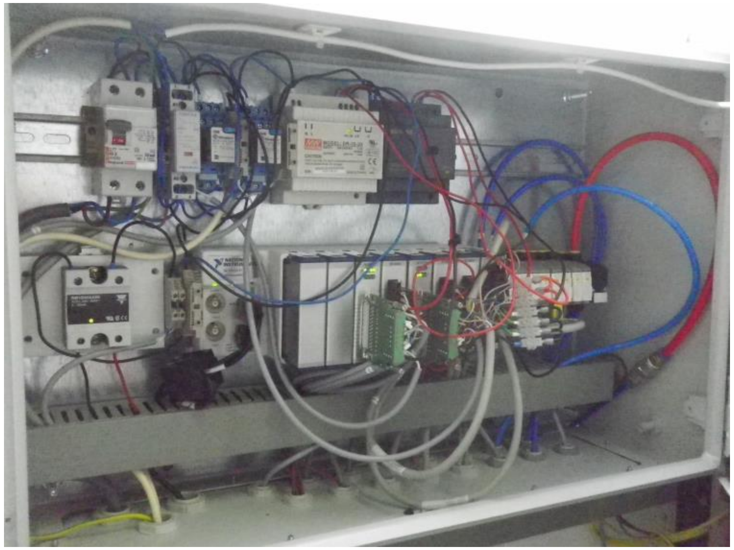


5. DTR Control Panel

Labview

- Data acquisition (Pressures, Temperatures, Mass flows)

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



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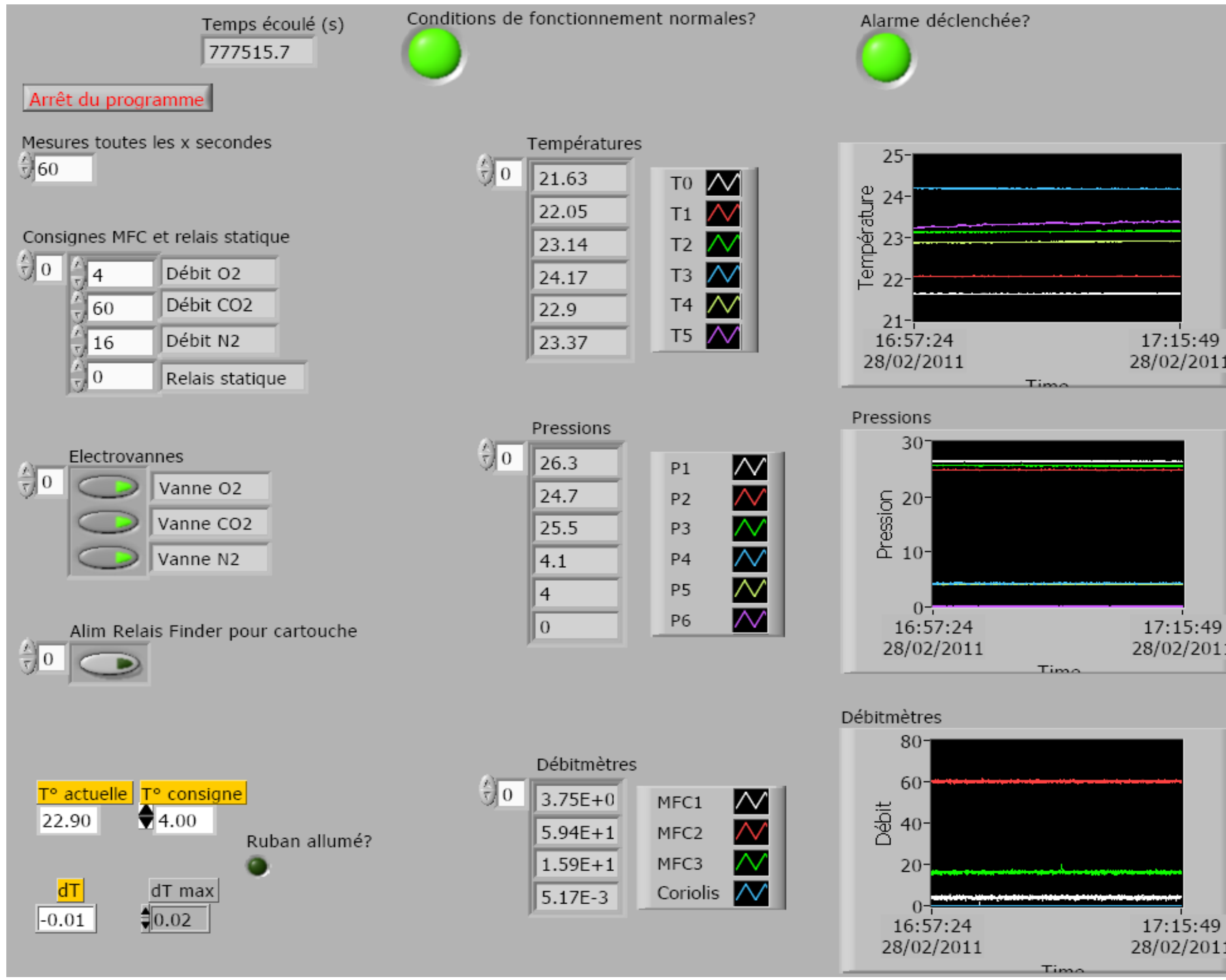
5. DTR Control Panel

Labview control panel

- Data acquisition
- Regulation



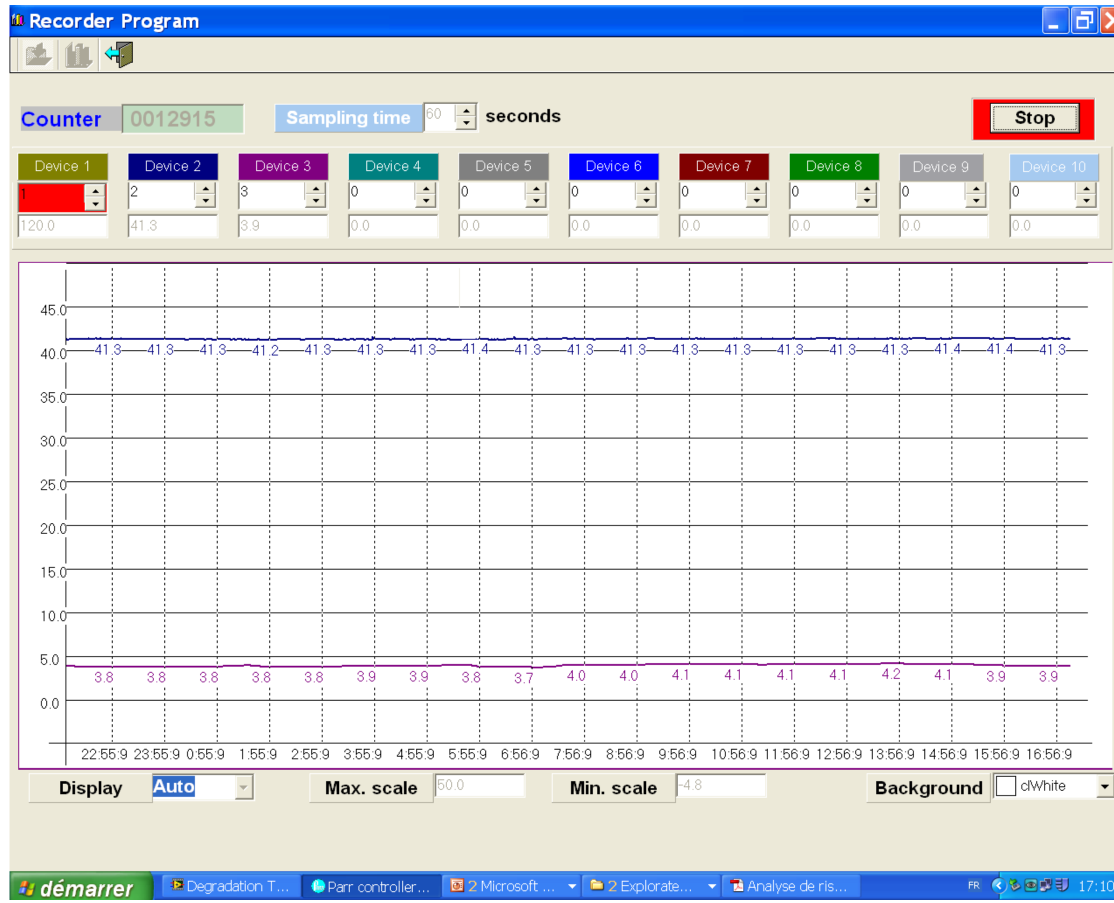
5. DTR Control Panel

Reactor controller

- Temperature control
- Agitation rate manual control
- Pressure display
- High temperature security

5. DTR Control Panel

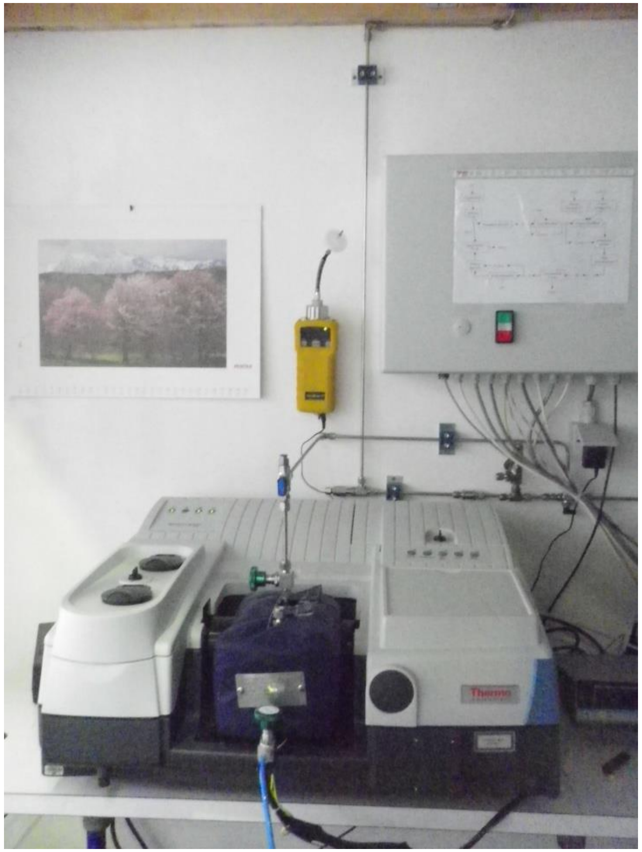
- Computer is only used for data acquisition
- Regulation is performed via the Controller



6. Analytics

- Liquid phase: HPLC, GC-MS

- Gas phase: FTIR



4.2.2 Risk analysis

- Risk analysis has been performed according to the Deparis method: « Dépistage Participatif des Risques »

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

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

Some performed improvements

4.2.2 Risk analysis

- Emergency procedure has been detailed

- Software alarms have been implemented

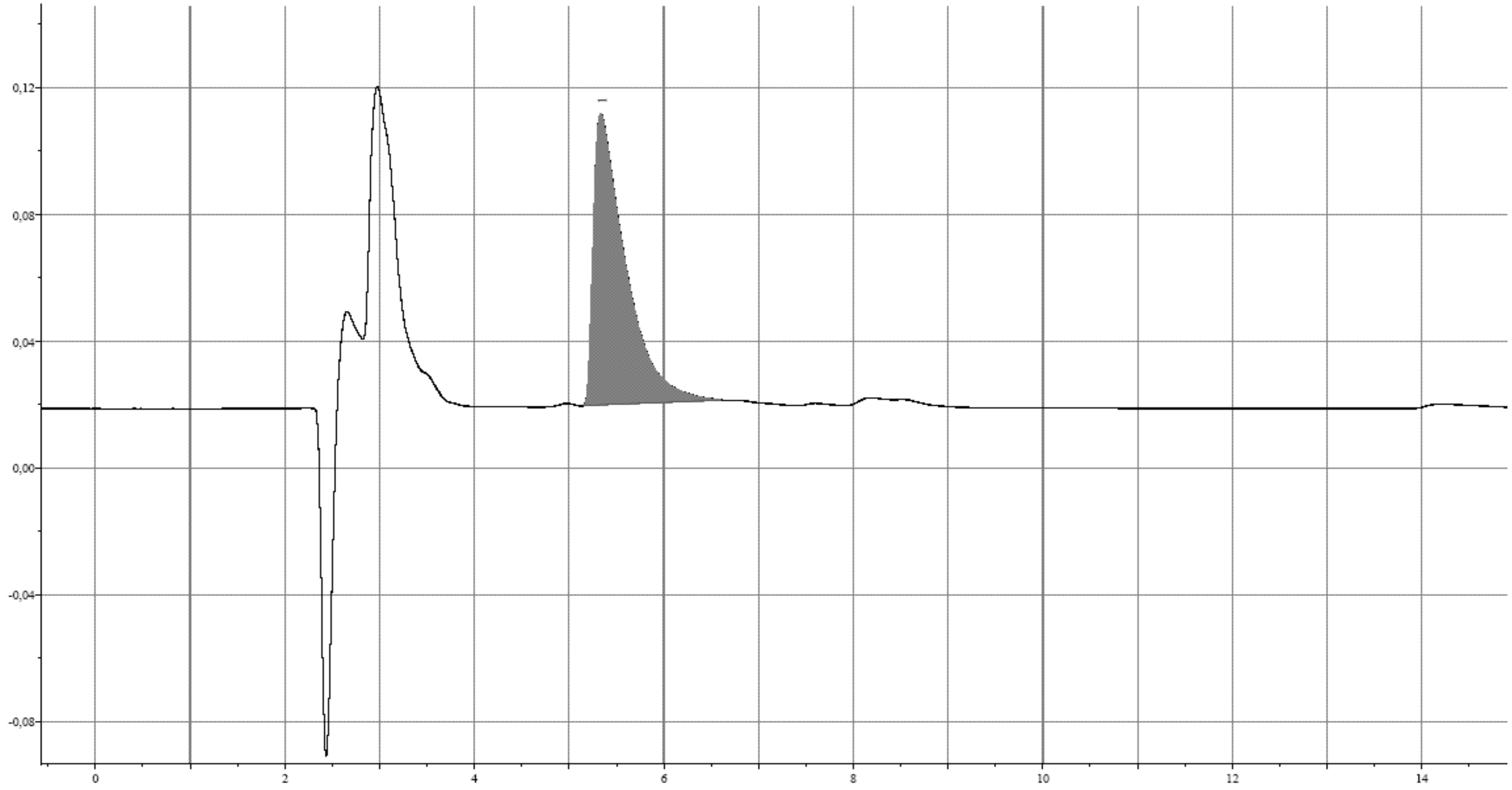
Example: In case of electrical power outage or if the maximal admitted values are overcome, the software shuts the DTR safely down: gas arrival is stopped by the safety valves, heating system is shut down.

4.2.3 Analytical methods

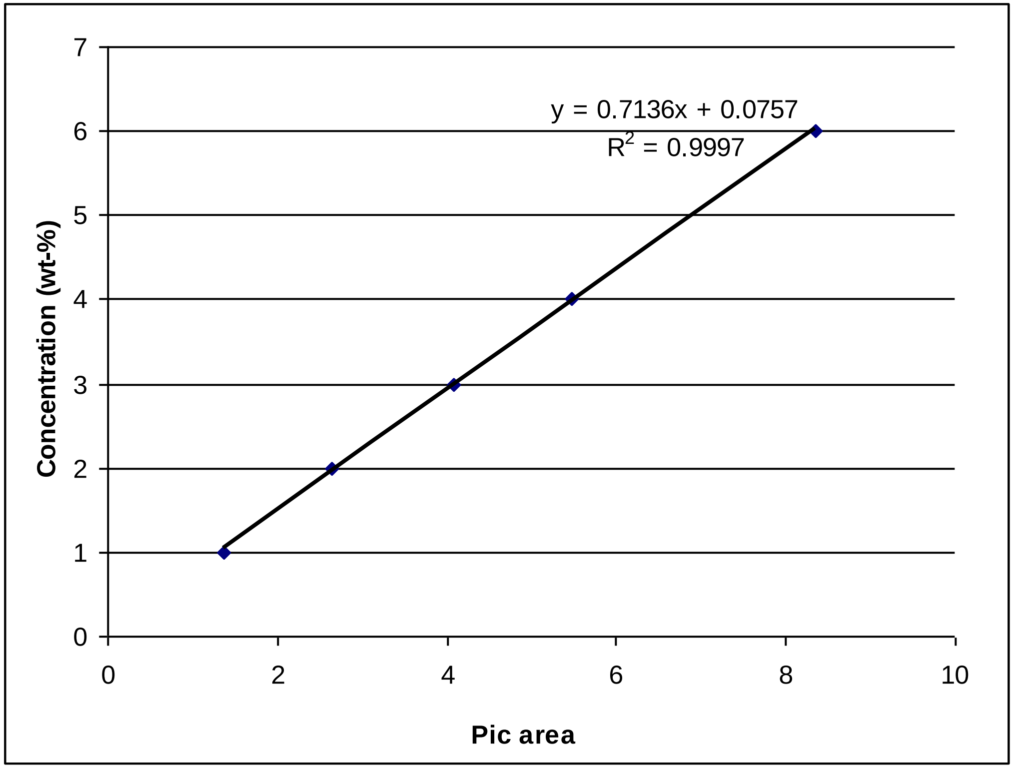
- Liquid sample: degraded solution or condensat
  => High Pressure Liquid Chromatography
  => Gas Chromatography-Mass Spectroscopy

- Gas Sample: gas exhaust from reactor
  => Fourier Transform Infra Red

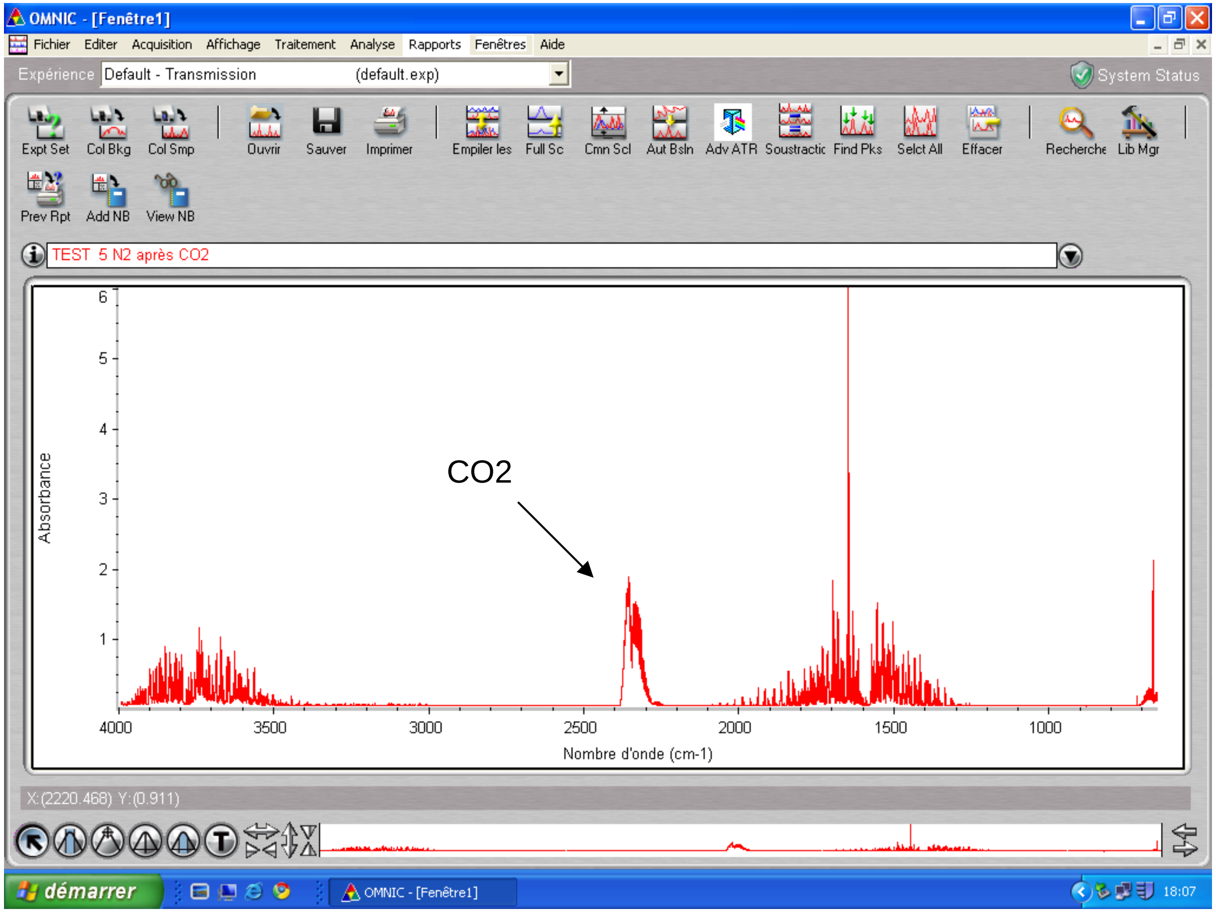
Liquid phase analysis: HPLC-spectrum of degraded solution



Liquid phase analysis: HPLC calibration curve



Gas phase analysis: first spectra



4.3 Results Summary

DTR operationnal:

- Operating temperature: Ambient up to 140°C
- Operating pressure: Ambient up to 25 barg
- Enhanced gas-liquid contact
- Water balance regulation at temperature varying between 15 and 70°C
- Batch and semi-batch experiments both possible
- Liquid (degraded solution and condensat) and gas analysis
- Study of all kinds of degradation possible
- Possibility of studying the reclaiming process

4.3 Results Summary

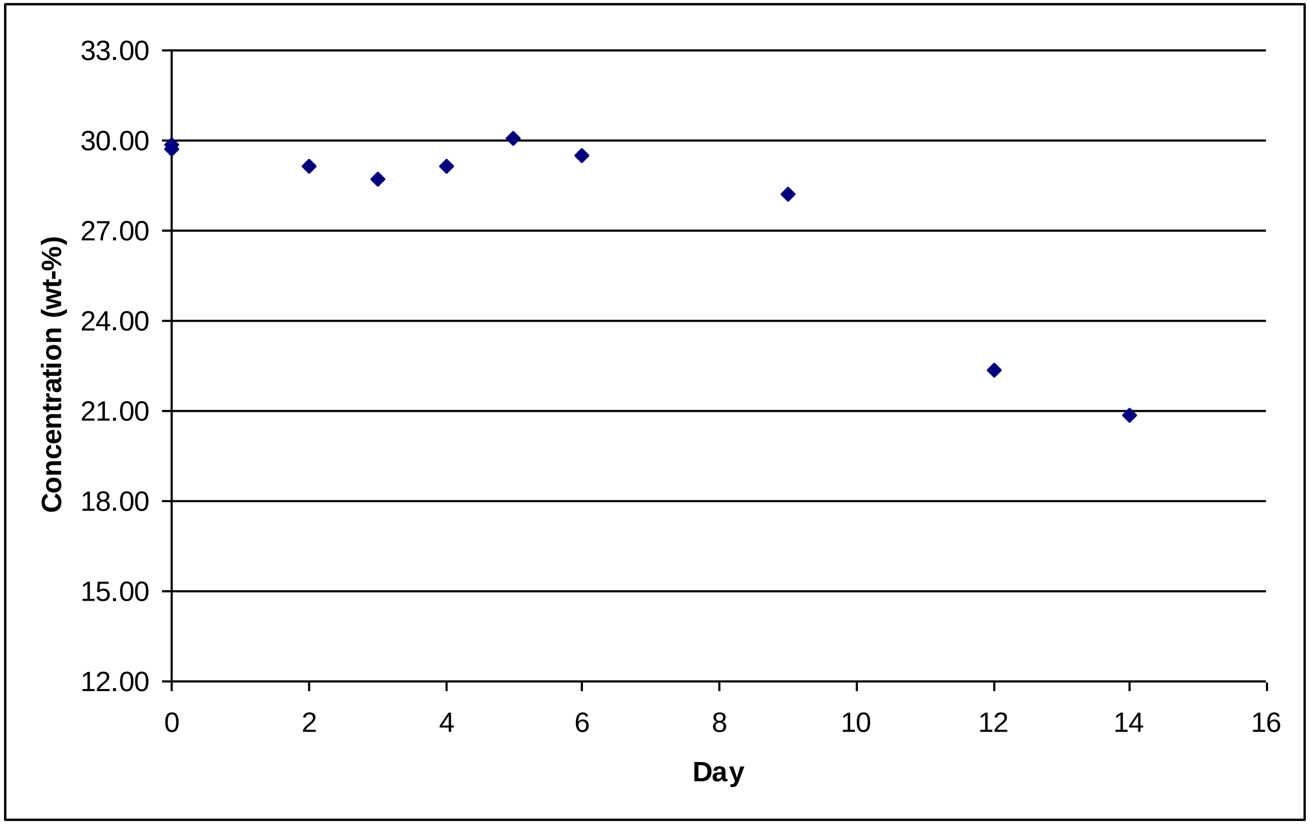
Limitations:

- Only one vessel => not possible to study different solvent systems or conditions in the same time
- Comparative study between different solvents, identification of influence factors, but no absolute results!
- Is it relevant to increase the pressure and temperature conditions that much? Perhaps could it lead to completely different degradation mechanisms.

4.3 Results Summary

First test of classical solvents : MEA 30 wt-%

Analytical method has still to be refined



4.4 Met problems

- Water balance difficult to regulate

  => Finally, gas saturator and condensator maintain the mass balance according to

  $$T_{sat} = T_{cond} \neq T_{reactor}$$

- Delay during the construction, mainly due to suppliers delays (up to 2 months for some pieces of equipment!)

- Extra safety procedure due to the presence of pure oxygen

  => Cleaning of all pieces with Tri-Chloroethylen in the beginning, but replaced with Aceton

4.4 Met problems

- Corrosion problems in the vessel due to destillated water

  => Passivation of the vessel with nitric acid

- HPLC spectra not clean

  => Method does not take the begining of the spectrum into account

- FTIR spectra polluted with CO_2, gas from the air compressor not clean

  => drying of the compressed air, so that CO_2 condenses

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5. Planning and perspectives

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Long-term planning

- => December 2011: Screening of MEA degradation
- January - July 2012: Degradation screening of some alternative solvent systems
- July - December 2012: Integration of degradation results into the simulation model
- January - June 2013: Thesis submission and public defense

5.1 Screening of MEA degradation

1. Influence of the experiment length
2. Study of the washing process
3. Influence of the pressure
4. Influence of the temperature
5. Influence of the gas composition (O_2, CO_2)

5.1 Screening of MEA degradation

Run	Parameter tested	Temp [°C]	P(O2) [bar]	P(CO2) [bar]	P(N2) [bar]	SOx, NOx	Metal ions	Inhibitor	Length [week]	Exp. Start
1	Base case	120	0.2	3	0.8	-	-	-	2	12/03/2011
2	Exp. Length	**140**	**1**	**15**	**4**	-	-	-	2	24/03/2011
3	Repetability	**140**	**1**	**15**	**4**	-	-	-	1	26/04/2011
4	Condensate recycling	**140**	**1**	**15**	**4**	-	-	-	1	5/05/2011
5	Temperature	120	**1**	**15**	**4**	-	-	-	1	14/05/2011
6	Pressure (N2)	**140**	0.2	3	**16.8**	-	-	-	1	23/05/2011
7	P(CO2)	**140**	**1**	3	**16**	-	-	-	1	1/06/2011
8	P(O2)	**140**	0.2	**15**	4.8	-	-	-	1	9/06/2011
9	Additives	**140**	**1**	**15**	4	**x**	-	-	1	
10	Additives	**140**	**1**	**15**	4	-	**x**	-	1	
11	Inhibitors	**140**	**1**	**15**	4	-	-	**x**	1	
12	Additives + Inhibitors	**140**	**1**	**15**	4	**x**	-	**x**	1	
13	Additives + Inhibitors	**140**	**1**	**15**	4	-	**x**	**x**	1	

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Planning of experiments

5.1 Screening of MEA degradation

- Influence of the experiment length

=> Objective: time savings if it is possible to reduce the experiment length down to 1 week

- Reference conditions :

MEA 30 wt-%, 2 weeks, 120°C, 4 barg

80mln/min gas supply: 75% CO_2 - 5% O_2 - 20% N_2

- Strong conditions:

MEA 30 wt-%, 2 weeks, 140°C, 20 barg

200mln/min gas supply: 75% CO_2 - 5% O_2 - 20% N_2

5.1 Screening of MEA degradation

- Influence of the washing process

=> Objective: study the composition of condensate and its influence on the degradation and the properties of the solvent

=> Based on the advice of Pr Hallvard Svendsen

- No condensate recycling conditions:

Same conditions as before but with condensate not recycled

- Influence of the condensation temperature on the gas exhaust composition:

Same conditions as before but with condensation performed at 70°C

5.1 Screening of MEA degradation

- Influence of the temperature

=> Objective: compare the results with data from the litterature to see if same trends can be found on the DTR than in other labs

- Low temperature conditions:

MEA 30 wt-%, 1 or 2 weeks, 120°C, 20 barg

150mln/min gas supply: 75% CO_2 - 5% O_2 - 20% N_2

5.1 Screening of MEA degradation

- Influence of the pressure

=> Objective: be sure that high pressure doesn't lead to completely different degradation mechanisms, so that strong degradation conditions remain relevant for assessment of solvent degradation

- High pressure conditions:

MEA 30 wt-%, 1 or 2 weeks, 140°C, 20 barg

150mln/min gas supply: 15% CO_2 - 1% O_2 - 84% N_2

5.1 Screening of MEA degradation

- Influence of gas composition

=> Objective: study the influence of the oxygen content on the degradation to evaluate the part due to oxydative degradation

- High oxygen conditions:

MEA 30 wt-%, 1 or 2 weeks, 140°C, 20 barg

80mln/min gas supply: 75% CO_2 - 25% O_2

- Low CO_2 conditions:

MEA 30 wt-%, 1 or 2 weeks, 140°C, 20 barg

80mln/min gas supply: 95% N_2 - 5% O_2

5.1 Screening of MEA degradation

- Influence of additives on the degradation process

=> Objective: study the benefit gained with degradation inhibitors, the influence due to corrosion inhibitors, …

- Standard conditions (see previous test, strong conditions)

- + addition of knowm amounts of chemicals (Metallic ions, degradation inhibitors, additives, SO_2 …)

- Possibility of ions quantification at the University of Liège (Laboratory of Geochemistry)

- Operating conditions will have to be determined!

5.1 Screening of MEA degradation

- 12 experiments to perform (shall be discussed!)
- 1 or 2 weeks per experiment? The decision will have a large influence on the planning

5.2 Screening of other solvent degradation

- Comparison of different solvents for CO_2 capture

=> Objective: degradation comparative study of different solvents

- Standard conditions (see previous test, strong conditions)
- We work with 30 wt-% solutions of amines
- Proposal for new solvents from Laborelec
- Depending on the most influent parameters identified for MEA, a standard campaign of experiments will be applied to those solvents
- Operating conditions will have to be determined! Hazardous to do it now!

5.3 Reclaiming

- Process used to regenerate the amine

=> Objective: study the temperature reclaiming process which is actually not well-described in the litterature

- Experimental conditions and DTR configuration radically change
- Temperature much higher
- Condensate corresponds to condensated MEA
- Analysis of the remaining sludge which is potentially toxic and ecologically harmful, …
- Operating conditions will have to be determined!

5.4 Degradation & Simulation

- Making the link between simulation and degradation

=> Objective:

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

- Multi-objectives process optimization:
  - Energy savings (costs)
  - Solvent savings (lower solvent make-up)
  - Lower environmental impact due to solvent degradation

6. Conclusion

- Degradation test rig has been constructed
- Experiments are running
- Analytical means available but still to be improved
- Still a long way to do

Thank you for your attention!

Questions are welcome!

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