Second ECRA Chair Scientific Event

9th-10th November 2016 – Mons (Belgium)

ECRA Chair research activities on CO_2 Capture, Purification and Conversion

Dr Lionel DUBOIS

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Chemical & Biochemical Process Engineering Unit

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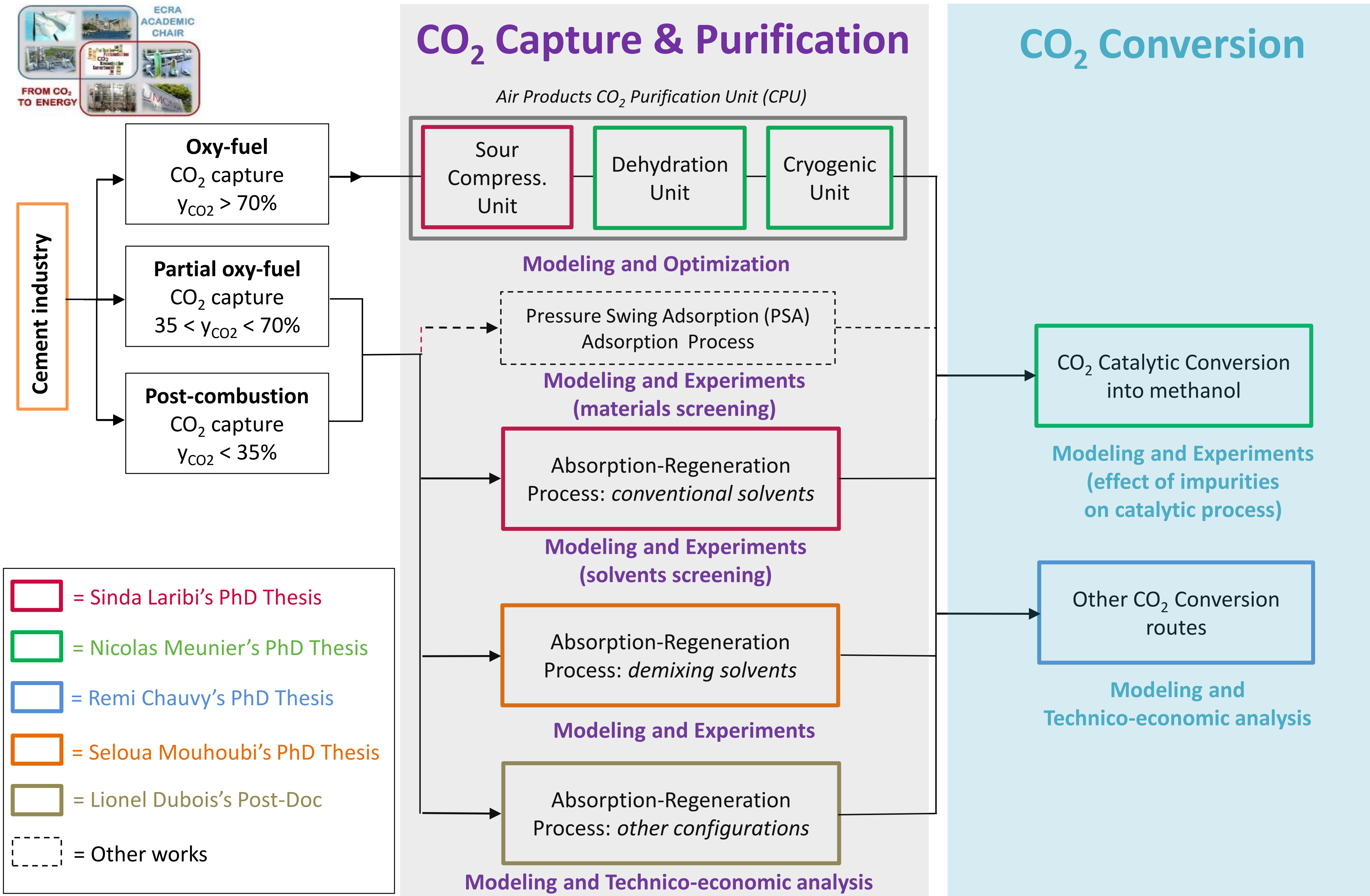
General framework of the ECRA Chair



ECRA Academic Chair Timeline

Phase 1 (2013-2016)

Phase 2 (2016-2019)

2013 2014 2015 2016 2017 2018 2019

HEIDELBERGCEMENT **POST-DOC – L. DUBOIS**

PhD THESIS 1 – N. MEUNIER fnrs LA LIBERTÉ DE CHERCHER

PhD THESIS 2 – S. LARIBI

PhD THESIS 3 – R. CHAUVY

HEIDELBERGCEMENT **PhD THESIS 4 – S. MOUHOUBI**

+ UNDERGRADUATE STUDENTS WORKS

Works of undergraduate students

→ **« Purification of rich-CO_2 flue gases coming from oxy-fuel cement kilns – Water elimination by adsorption »**
Pol BLANCHARD & Ilyas ZARIOH
Bachelor 3 student project, *Thermodynamics Unit, May 2015*

→ **« Experimental study of CO_2 absorption into amine(s) based solvents: application to cement flue gases coming from partial-oxyfuel kilns »**
Guillaume PIERROT
Master thesis, Chemical and Biochemical Process Engineering Unit, May 2015

→ « **Modeling and optimization of PSA processes for the treatment of gaseous effluents rich in CO_2** »
Nicolas DEBAISIEUX (*UMONS*)
Master thesis, *Thermodynamics Unit, June 2016*

→ « **Technical, economical and environmental evaluations of CO_2 capture techniques** »
Lucas LE MARTELOT (*ECOLE SUPERIEURE DE CHIMIE ORGANIQUE ET MINERALE (ESCOM), Compiègne (France)*)
Master thesis*, Chemical and Biochemical Process Engineering and Thermodynamics Units, August 2016*

ECRA Chair presentations agenda

Modeling and simulation of post-combustion CO_2 capture process using demixing solvents applied to cement flue gases
by Seloua Mouhoubi

Capture & Purification processes applied to CO_2 derived from cement industry
by Sinda Laribi

Simulations of various configurations of the post-combustion CO_2 capture process applied to a cement plant flue gas
by Lionel Dubois
--*Question phase 1*--

Methodological selection of CO_2 conversion pathways: First outlook of technico-environmental assessment
by Remi Chauvy

CO_2 conversion into methanol
by Nicolas Meunier
--*Question phase 2*--

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Modeling and simulation of post-combustion CO_2 capture process using demixing solvents applied to cement flue gases

Ir Seloua MOUHOUBI

PhD Student

Chemical & Biochemical Process Engineering Unit

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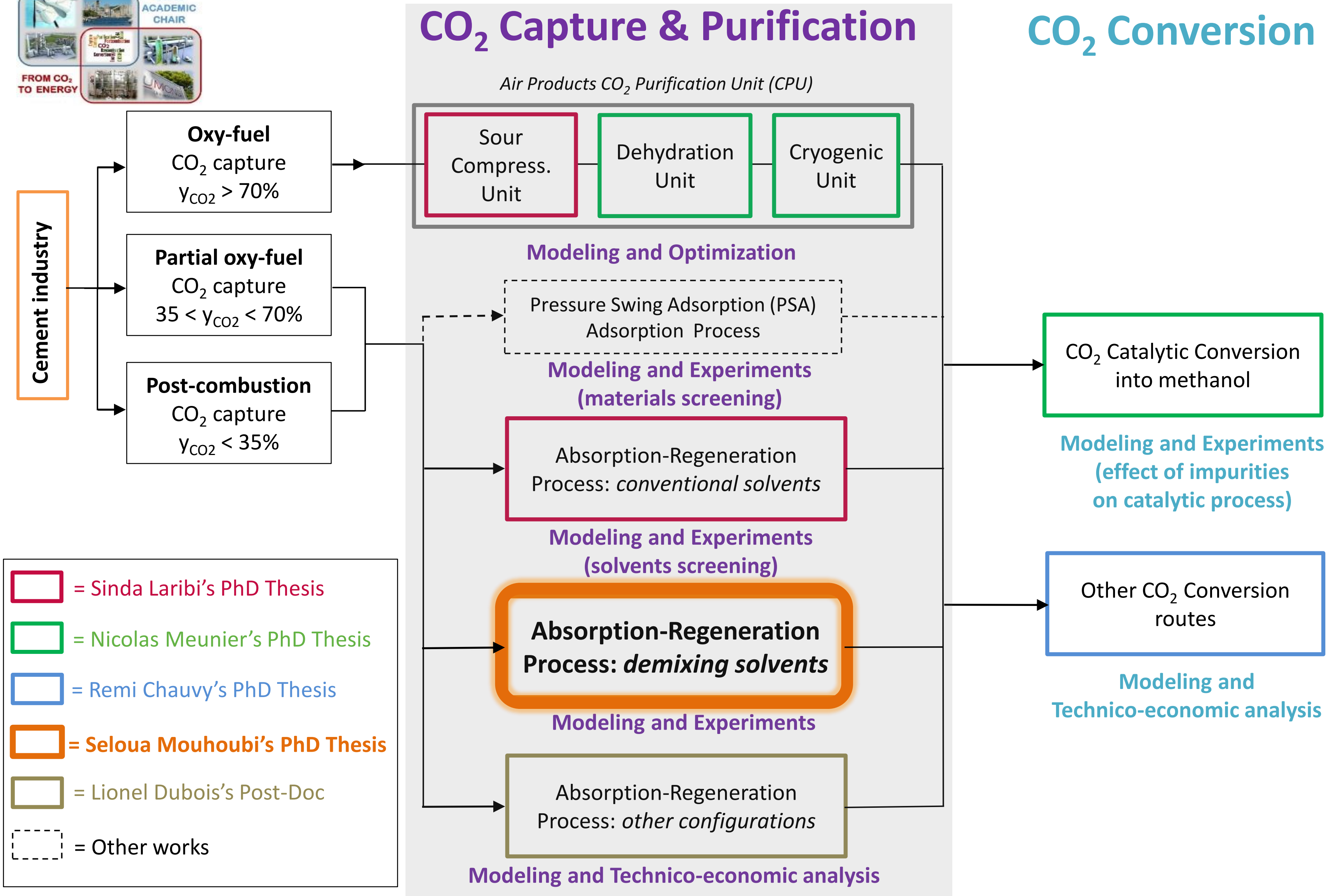
General framework of the ECRA Chair



Outline

1. CO_2 capture by absorption-regeneration
2. Context of the study
3. CO_2 capture using demixing solvents
4. Conclusion and future works

1. CO_2 capture by absorption-regeneration

Solvents

First generation

Chemical solvents:
Alkanolamine, alkylamines & diamines
Ex: MEA, MDEA, PZ, …

Physical solvents:
Mainly alcohols
Ex: Selexol, Rectisol, …

Second generation

Solvents blend:
Chemical: MDEA+PZ, …

❖ **Innovative solvents**
Demixing solvent (MAPA + DEEA, …)

Hybrid: Blend of chemical + physical solvents
Ex: Sulfinol

Third generation

Ionic Liquids (IL):
Molten salts (liquid at room temperature)

Ex: Imidazolium, Pyridinium, Ammonium, Sulfonium, Alkylsulfate, …

Fourth generation

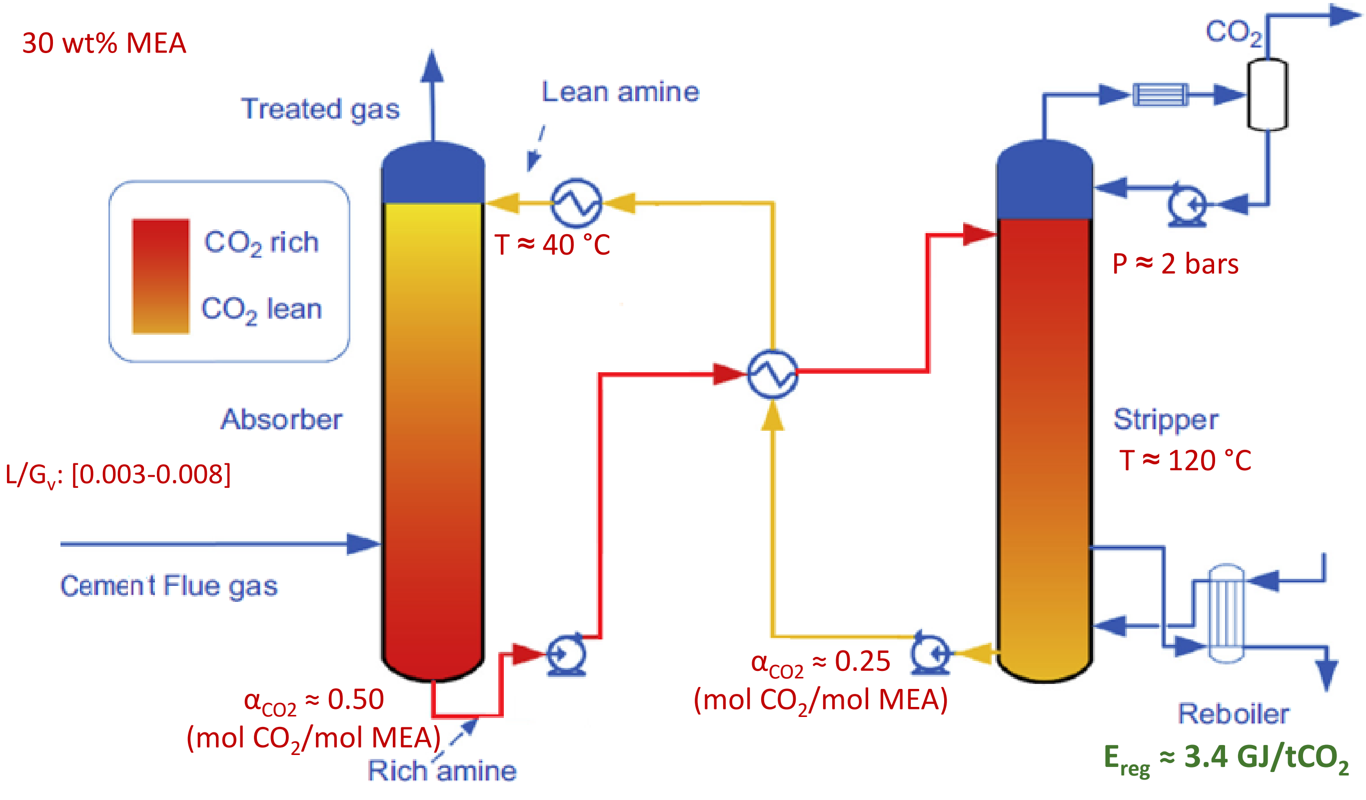
Enzymatic solvents:

Amine based solvents
+
Biocatalyzer (ex: carbonic anhydrase)

1. CO_2 capture by absorption-regeneration 2/2

- Researches on post-combustion CO_2 capture ⟶ MEA conventional process

MEA conventional process



CO_2 loading:

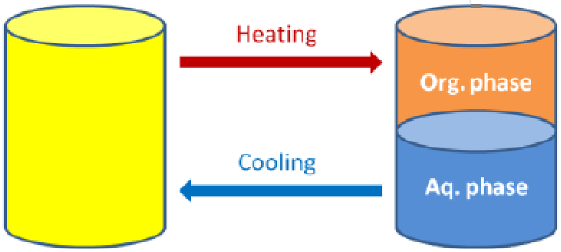
$$\alpha_{CO_2} = \frac{C_{CO_2}\left[\frac{mol}{l}\right]}{C_{Amine}\left[\frac{mol}{l}\right]}$$

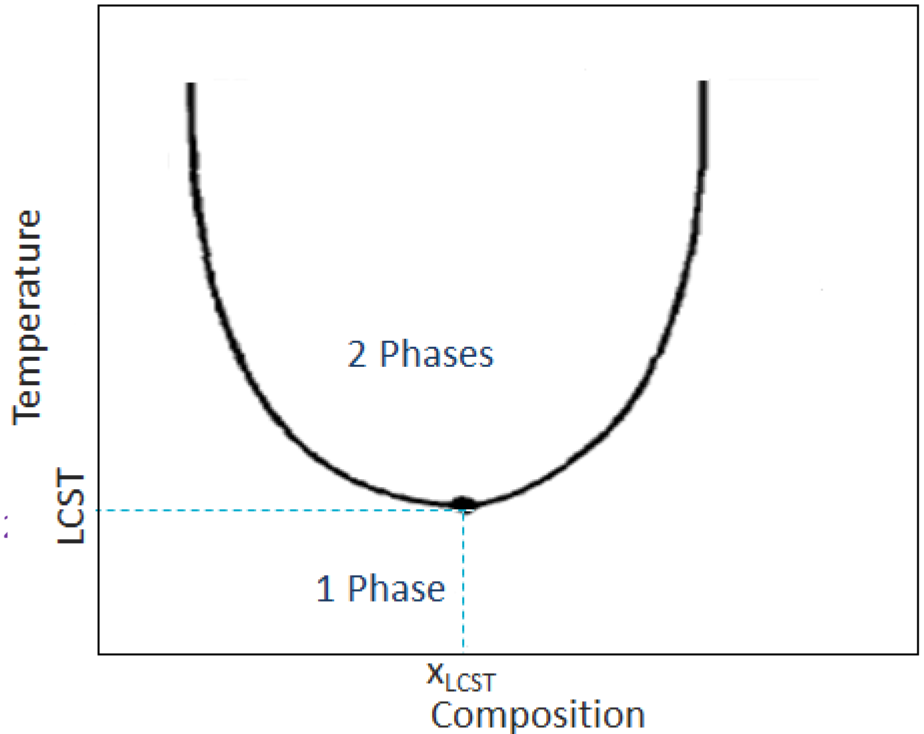
2. Context of the study

New technologies to reduce the capture cost → Demixing solvents

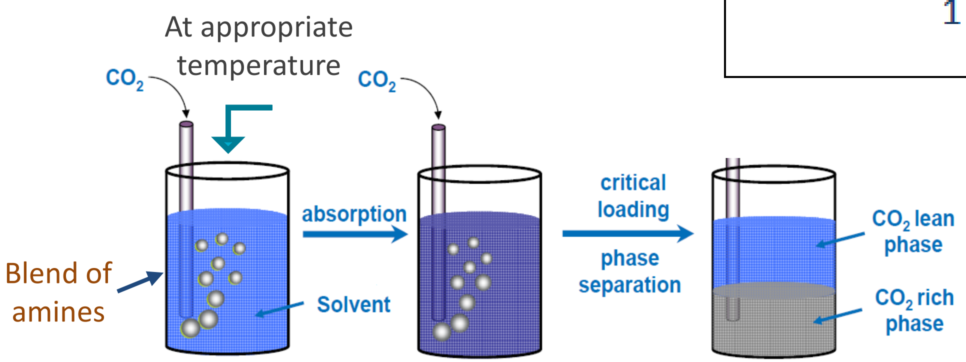
Demixing concept

- Biphasic even without CO_2



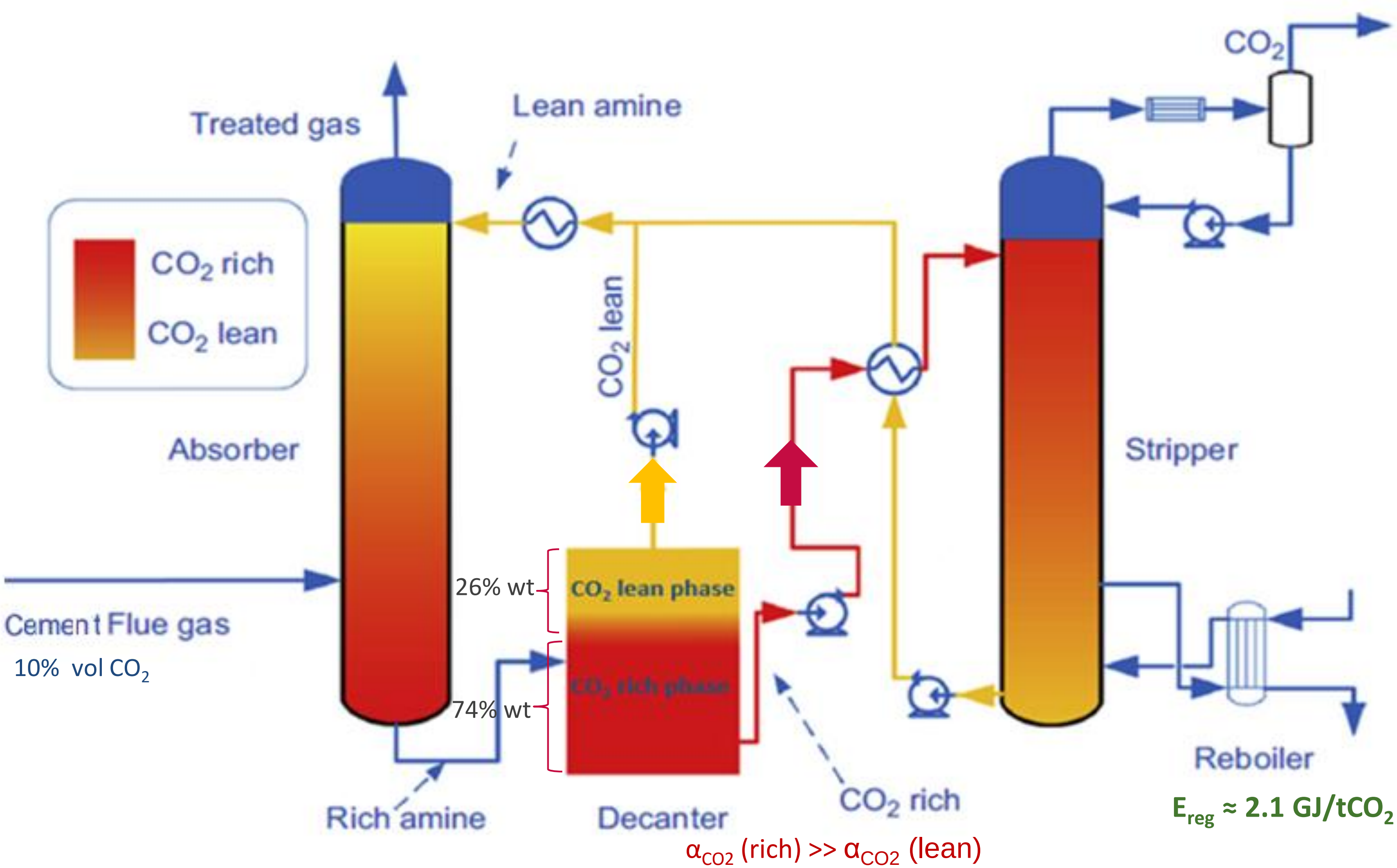


- Biphasic only in presence of CO_2



2. Context of the study

IFP Energies Nouvelles DMX process



≈ 40% decrease of the regeneration energy comparing to MEA 30 wt%

3. CO_2 capture using demixing solvents

Demixing solvents

- DEEA-BDA blend
- DEEA-MAPA blend
- DEEA-TETA blend
- Thermomorphic biphasic solvents — MCA, DMCA, …
- Self-concentrating solvents — Amine + alcohol
- DMX solvents — Blend of amines

Absorber
+
Phase separator
~~Stripper~~

Amines formula

DEEA: Diethylaminoethanol

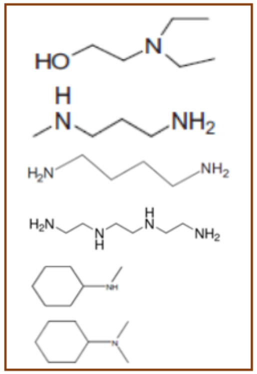
MAPA: N-Methyl-1,3Propanediamine

BDA: 1,4-Butanediamine

TETA: Triethylenetetramine

MCA: N-methylcyclohexylamine

DMCA: N,N-dimethylcyclohexylamine

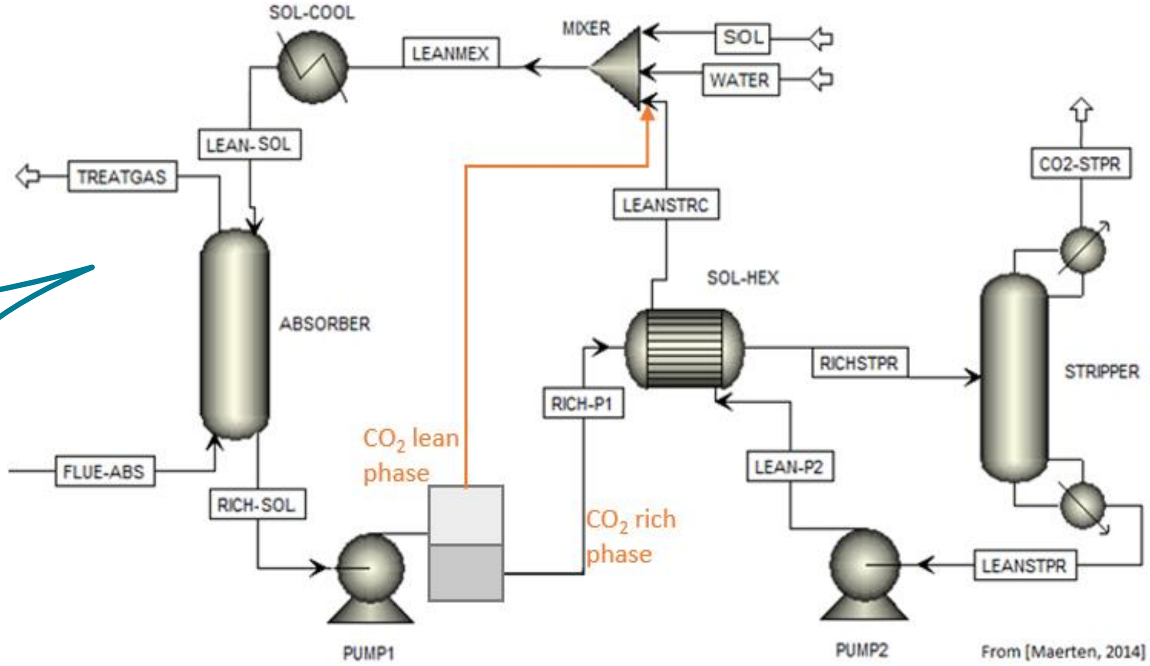


3. CO_2 capture using demixing solvents 2/2

- Lack of data on demixing solvents in the literature
- No Aspen simulation with the demixing solvents

Aspen plus absorption- regeneration process flowsheet

Develop a model to simulate the process



4. Conclusion and future works

Bibliographies review ✓

-Study of the different phase change CO_2 capture processes

-Focus on liquid biphasic solvents

→ Identification of the appropriate biphasic solvent

Experimental section

-Equilibrium tests

-Kinetic tests

-Absorption-regeneration tests in micro pilot

↔ Determination of equilibrium and kinetic parameters for the simulations

Modeling and simulation

-Equilibrium modeling

-Kinetic modeling

-Aspen simulation of biphasic process

Technico-economic investigations → Determination and estimation of the gain

Thank you for your attention

References

-Gomez, A., Briot, P., Raynal, L., Broutin, P., Gimenez, M., Soazic, M., Saysset, S. ACACIA Project – Development of a Post-Combustion CO 2 Capture Process . Case of the DMX TM Process, 69(6), 2014.

-Jiafei, Z. Study on CO2 Capture Using Thermomorphic Biphasic Solvents with Energy-Efficient Regeneration. Dortmund, 2013.

-Raynal, L., Alix, P., Bouillon, P. A., Gomez, A., Le Febvre De Nailly, M., Jacquin, M., Trapy, J. The DMX TM process: An original solution for lowering the cost of post-combustion carbon capture. Energy Procedia, 4, 779–786, 2011.

-Shi, F., & Morreale, B. Novel Materials for Carbon Dioxide Mitigation Technology. 2015.

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Capture and purification processes applied to CO_2 derived from cement industry

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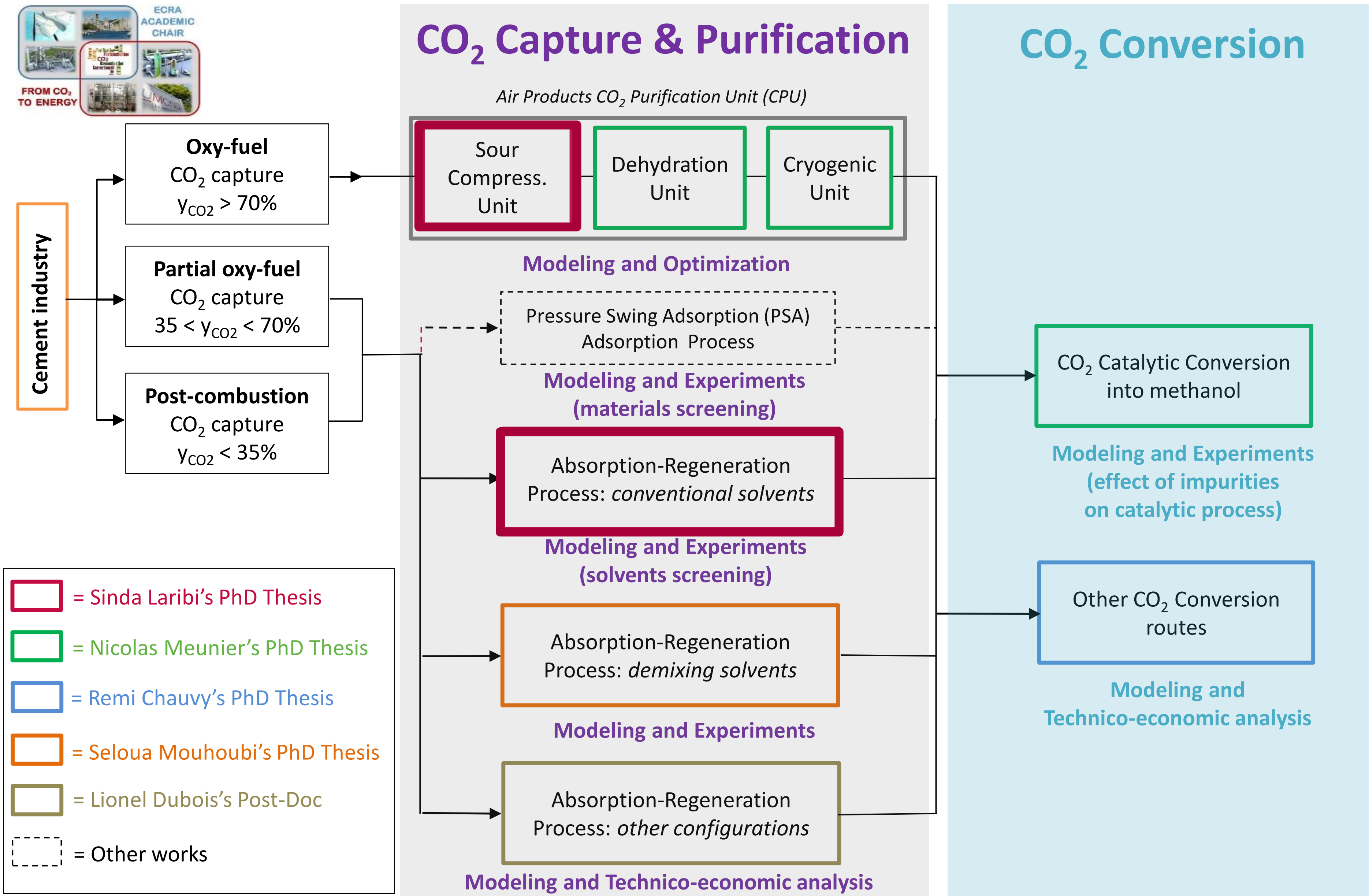
General framework of the ECRA Chair



Considered combustion technologies

Cement production using conventional combustion

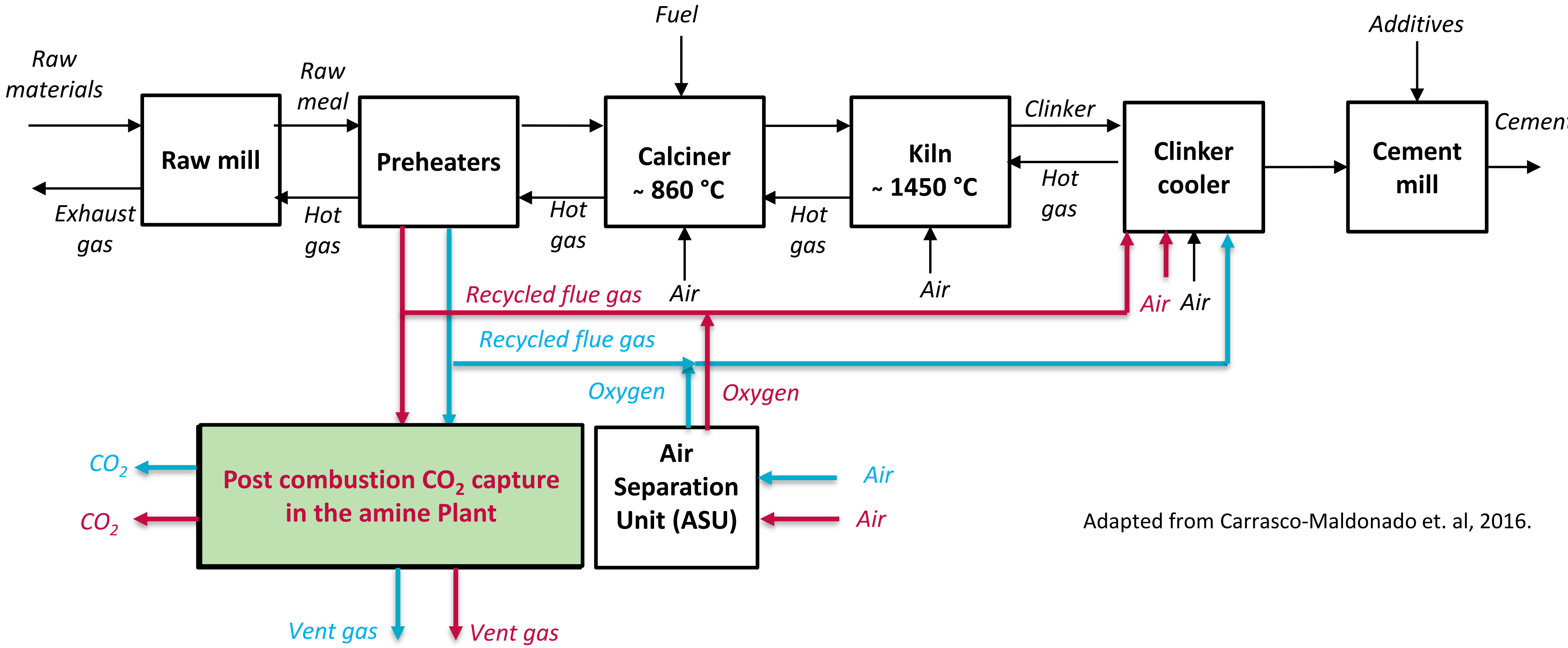
$y_{CO2, out}$ =20-30%

Partial oxyfuel combustion

30%<$y_{CO2, out}$<70%

Full oxyfuel combustion

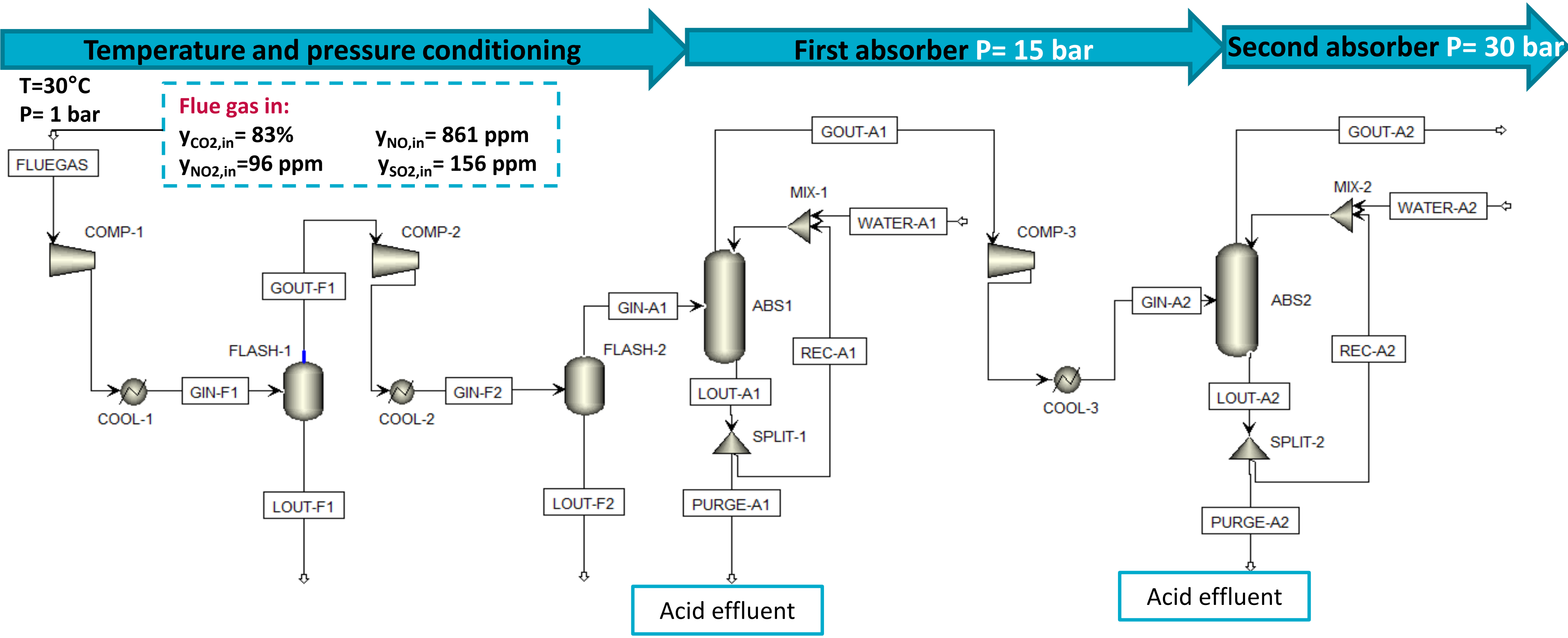
70%<$y_{CO2, out}$<90%



Adapted from Carrasco-Maldonado et. al, 2016.

PART 1: CO_2 purification process (de-SO_x & de-NO_x) applied to full oxy-fuel combustion

Flowsheet of the Sour-compression Unit (SCU)

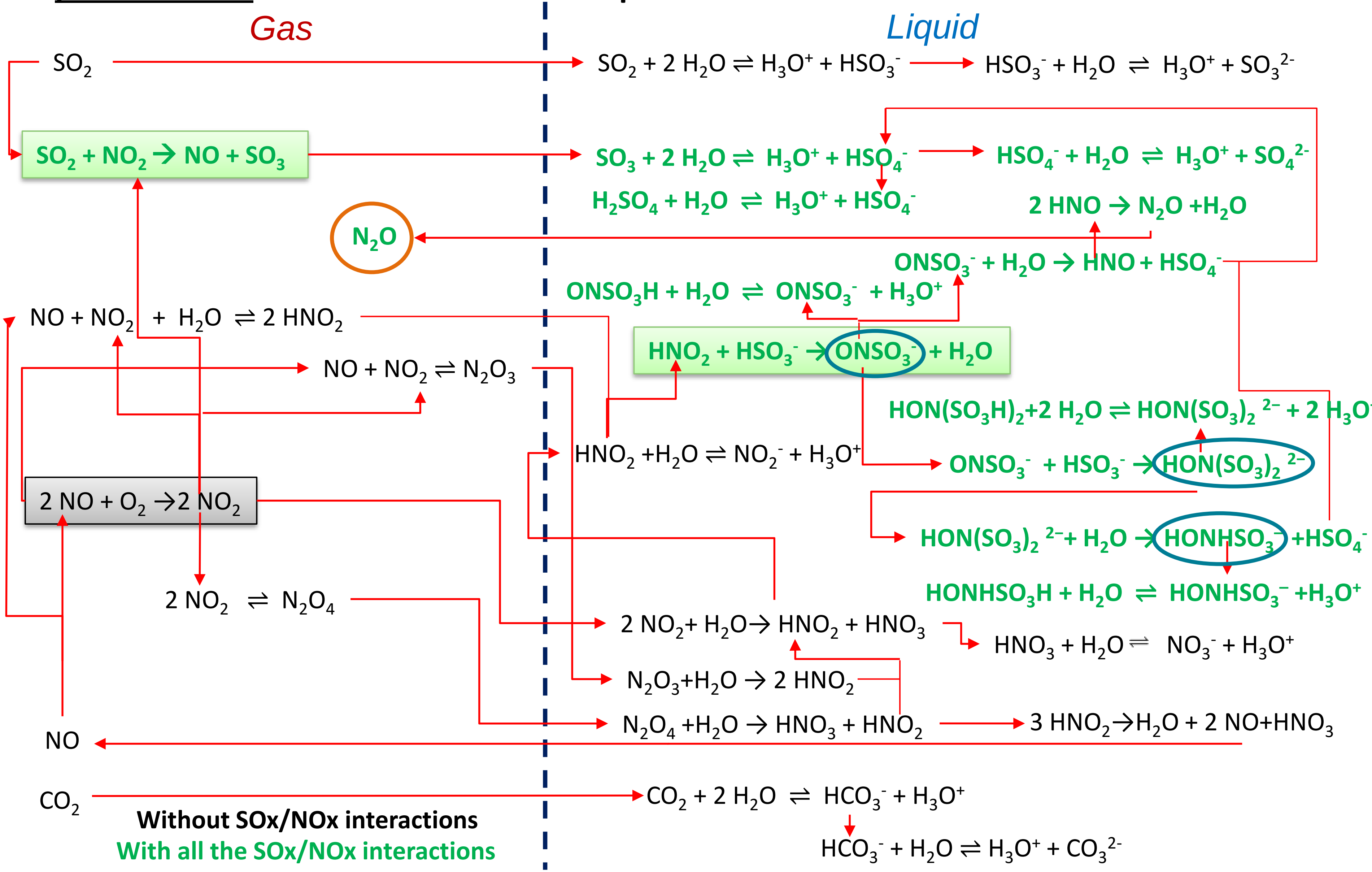


Modelling characteristics:

- Aspen Plus V8.6
- ELEC-NRTL model for electrolyte systems
- Rate-based calculations in the contactors
- Flue gas compositions from ECRA oxyfuel combustion simulations.

New chemical mechanism considered

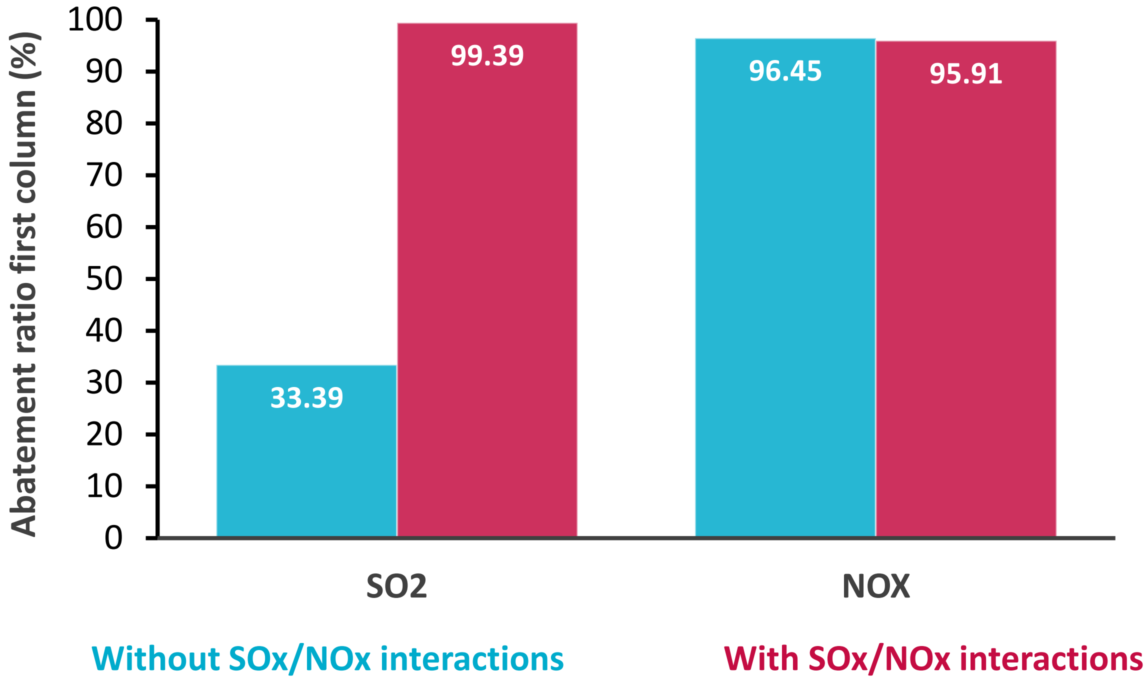
➢ **pH influence: Reactions selected for 1≤pH≤4**



Interaction effect on the simulation results

Liquid phase composition analysis: 1≤pH≤4

Gas phase composition analysis:



- Interaction effect: SO_2 abatement ratio ↗
- Same NOx abatement ratio for the mechanisms with and without interactions.

Conclusions & prospects of the SCU

Full oxyfuel combustion

CO_2 De-SOx & De-NOx: Sour-Compression Unit (SCU)

FLUE GAS TREATMENT TECHNOLOGIES

Conclusions

- ✓ SCU Chemical mechanism completed considering SOx/NOx interactions under $1 \leq pH \leq 4$.
- ✓ New chemical mechanism implemented in Aspen Plus™ .
- ✓ Interest of considering interaction reactions proved.

Prospects

- Optimization of the SCU by parametric study (in progress).
- SCU: from two-column process to one-column process.

Objectives:

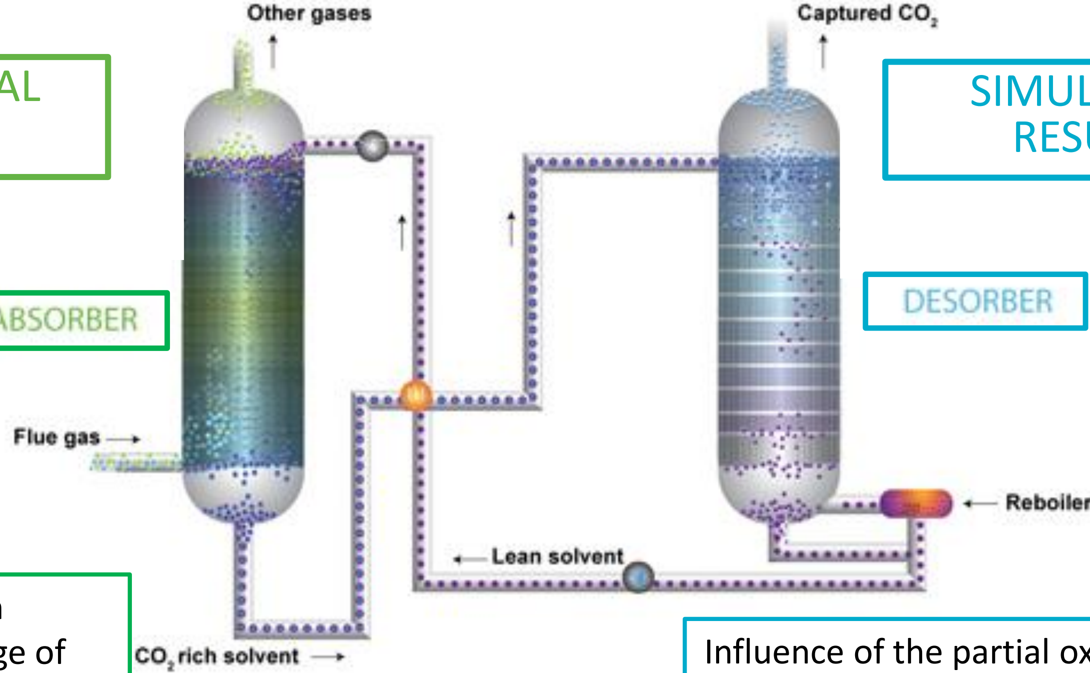
Design and optimize CO_2 purification process for re-use & ↘ E_{tot} of the global process.

PART 2: Post-combustion CO_2 capture process applied to partial oxy-fuel combustion

Absorption-regeneration process

Post-combustion capture: absorption-regeneration in amine based solvents.

EXPERIMENTAL RESULTS



From http://www.co2crc.com.au/

SIMULATION RESULTS

Evaluation of the absorption performances of a wide range of solvents in high CO_2 content conditions

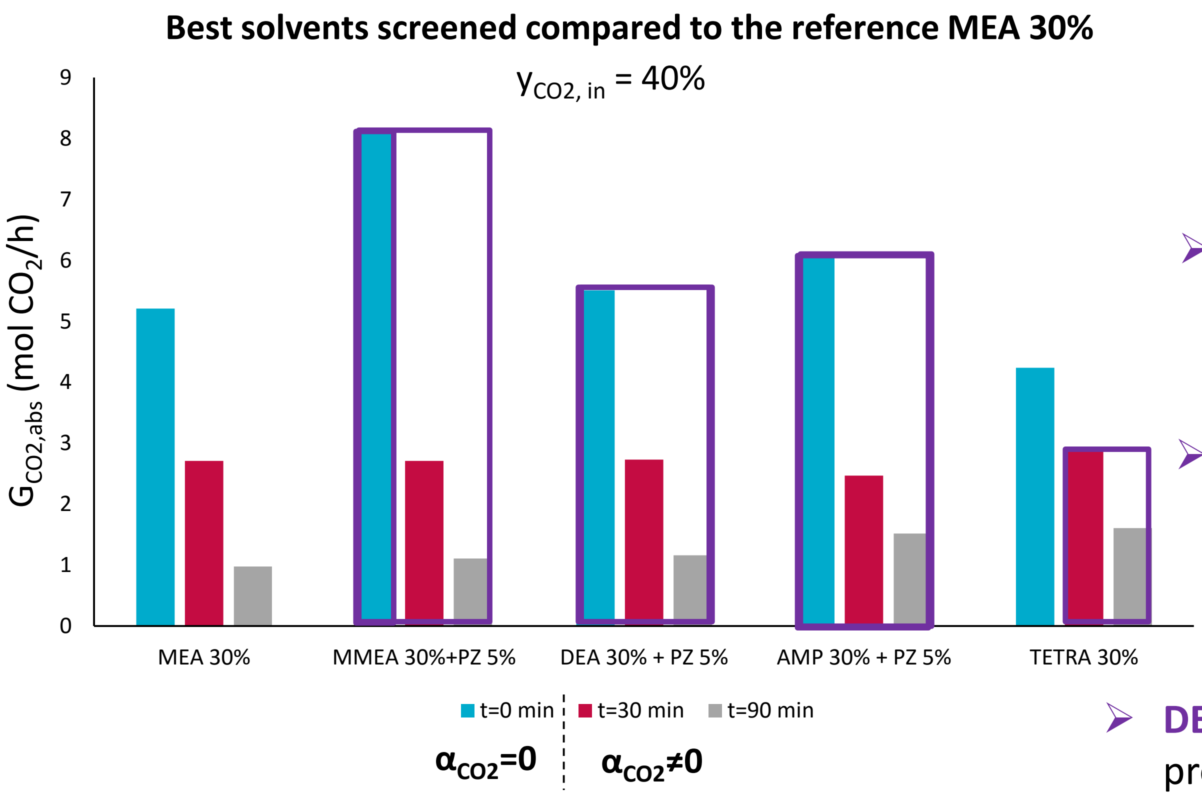
→ Lab scale screening of solvents
→ Micro-pilot tests
of the best solvents screened

Influence of the partial oxyfuel combustion conditions on the regeneration energy

Aspen Hysys™ simulations:
→ of the micro-pilot unit
→ of an industrial unit

Lab scale: experimental results of the Screening of solvents

- **Lab scale tests of the solvents absorption performances.**

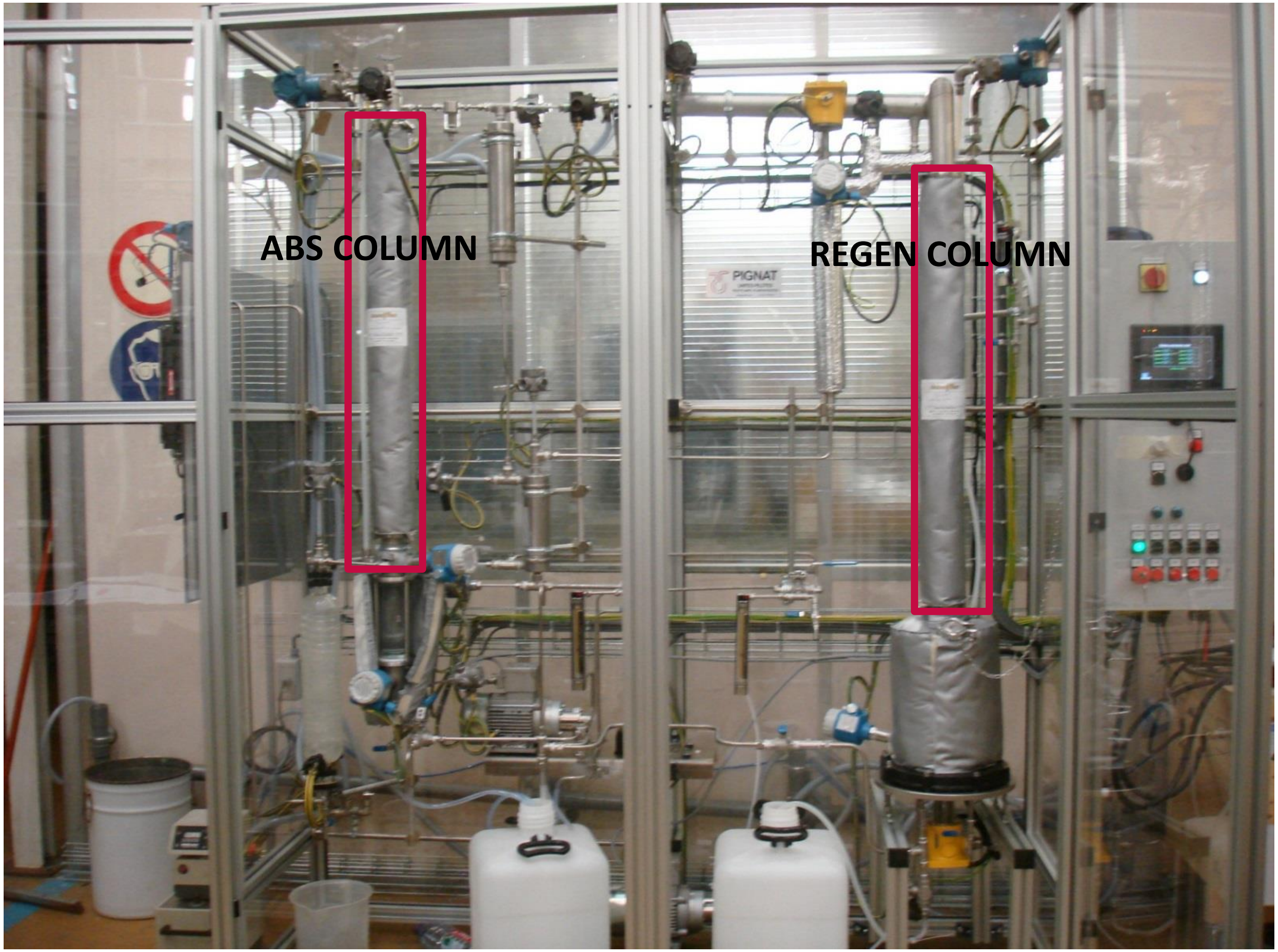


Master thesis G. Pierrot, 2015.

- **MMEA 30%** presents the best absorption capacity among the unloaded solvents without necessity of using an activator (**+ PZ 5%**)
- **PZ 5%** is the best activator (compared to tetra)
- **TETRA 30%** has the best absorption performances among CO_2 loaded simple solvents
- **DEA 30% + PZ 5%** and **AMP 30% + PZ 5%** present good absorption performances at the beginning of the test and significant CO_2 loadings

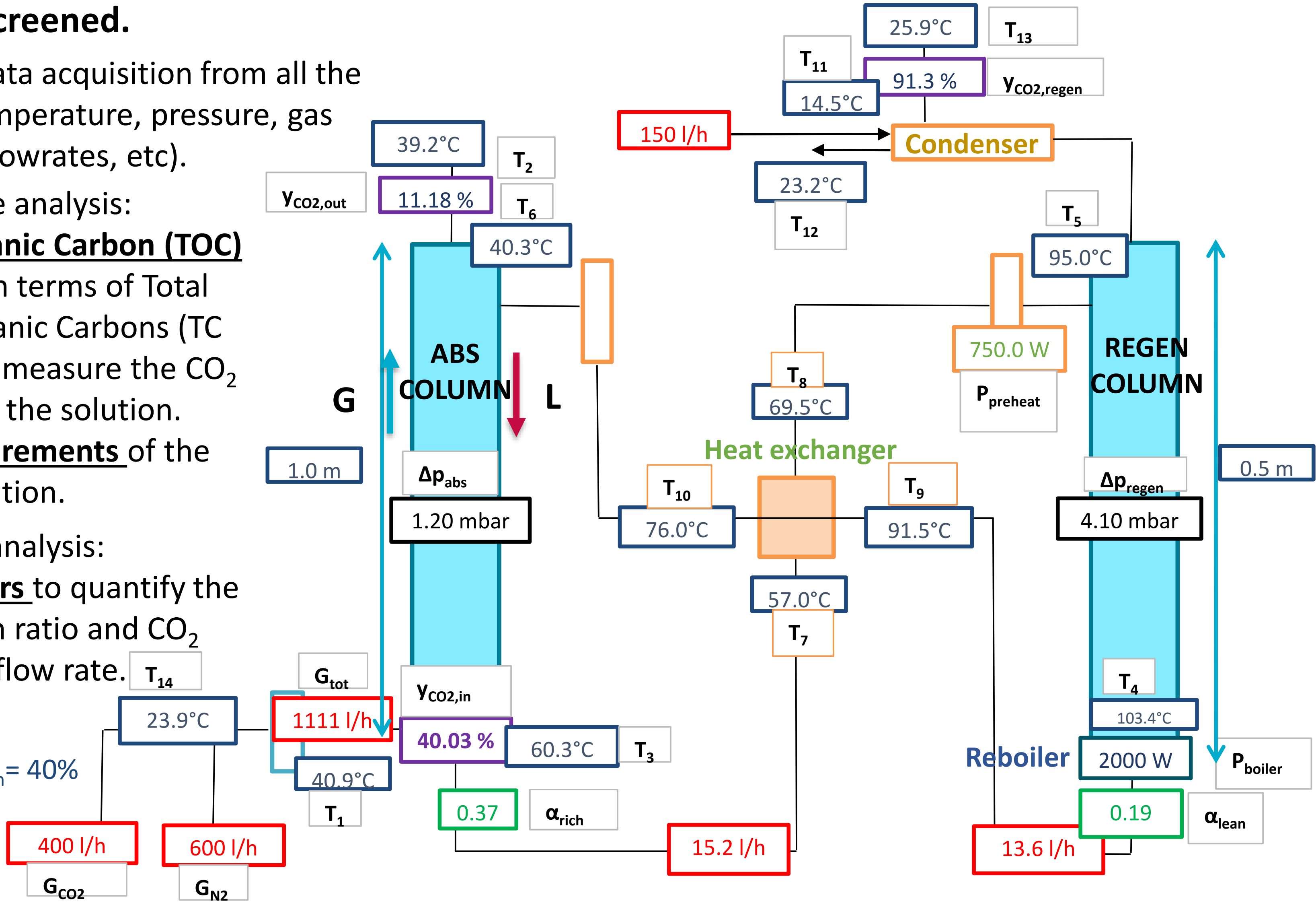
Micro-pilot tests of the best solvents screened

- **Micro-pilot tests→ Absorption-regeneration tests using the micro-pilot unit for the best solvents screened.**



Micro-pilot tests of the best solvents screened

- **Micro-pilot tests→ Absorption-regeneration tests using the micro-pilot unit for the best solvents screened.**
- Temporal data acquisition from all the sensors (temperature, pressure, gas and liquid flowrates, etc).
- Liquid phase analysis:
  - **Total Organic Carbon (TOC)** analyzer in terms of Total and Inorganic Carbons (TC and IC) to measure the CO_2 loading of the solution.
  - **pH measurements** of the liquid solution.
- Gas phase analysis:
  - **IR analysers** to quantify the absorption ratio and CO_2 absorbed flow rate.

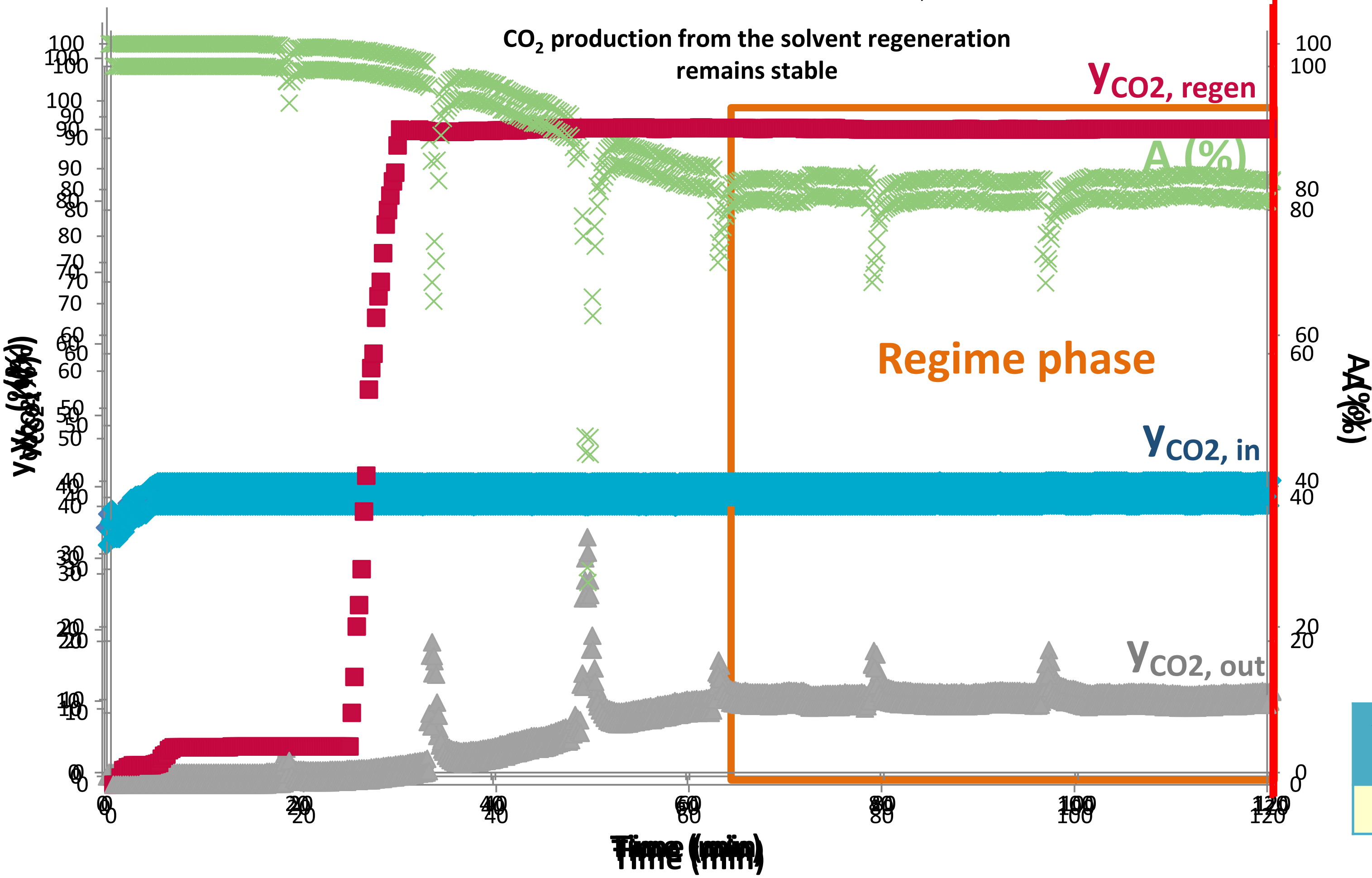


MEA 30% ,$y_{CO2, in}$= 40%

Micro-pilot scale: experimental results

➤ **Temporal evolutions of $y_{CO2,in}$, $y_{CO2,out}$, $y_{CO2,regen}$ and A for MEA 30% at $y_{CO2,in}$ = 40%**

$$A\ (\%) = \frac{Gin\ \ y_{CO2,in}\ -\ Gout\ \ y_{CO2,out}}{Gin\ \ y_{CO2,in}}\ 100$$



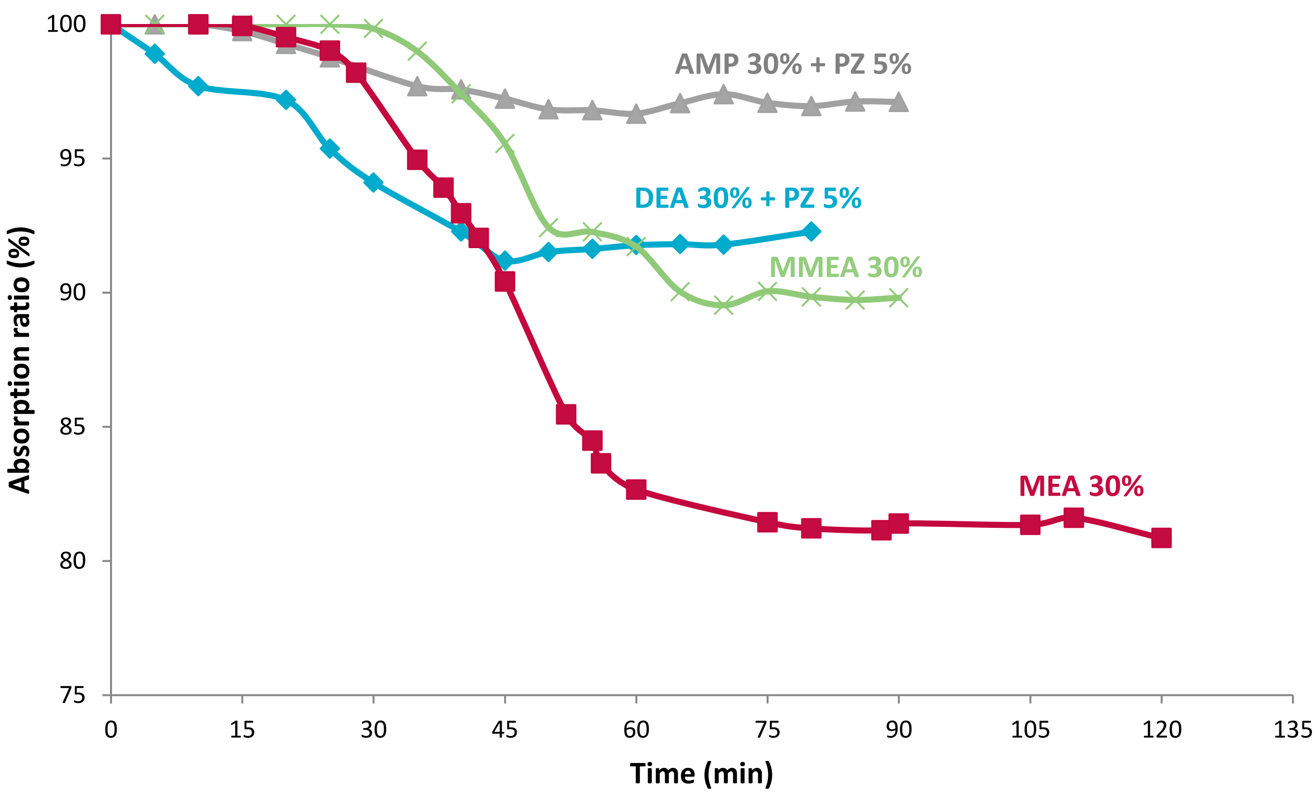
$y_{CO2,in}$ (%)	L (l/h)	G (l/h dry)
40	14	1030

Internship L. Le Martelot, 2016.

Micro-pilot scale: experimental results

- **Comparison of the temporal evolutions of absorption performances at $y_{CO2,\,in}$ = 40%**

$$A\ (\%) = \frac{Gin\ \ y_{CO2,in} - Gout\ \ y_{CO2,out}}{Gin\ \ y_{CO2,in}}\ 100$$



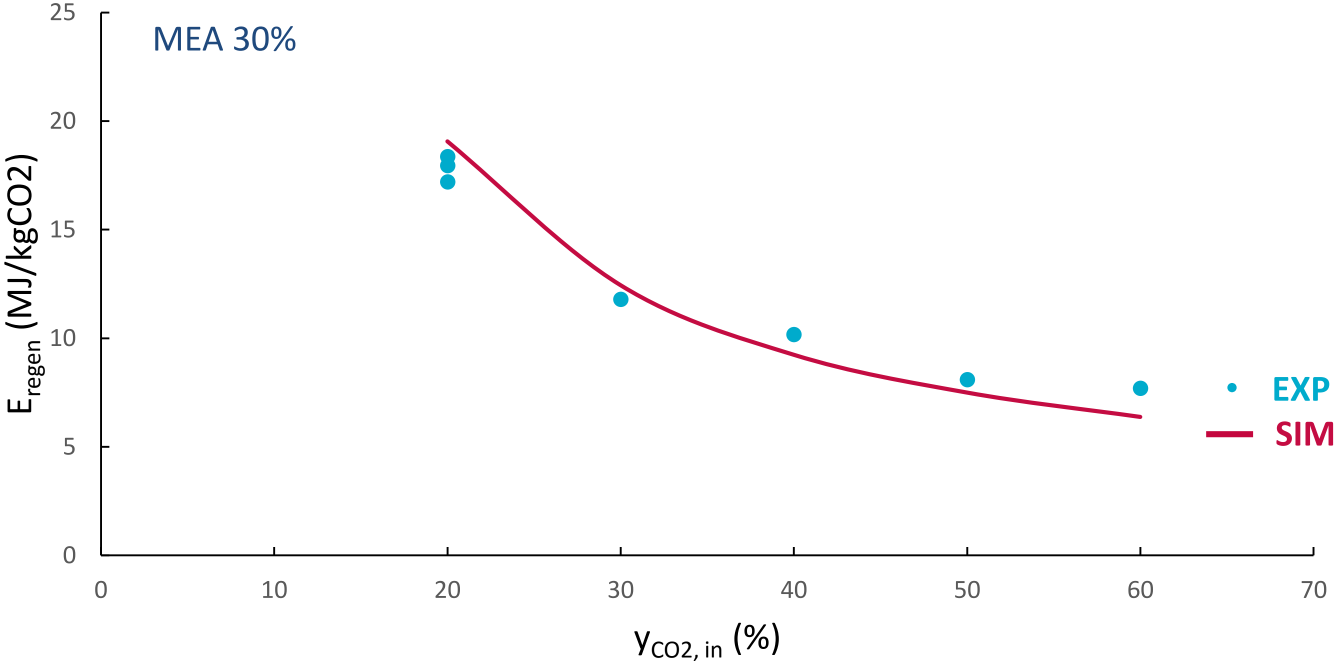
$y_{CO2,\,in}$ (%)	L (l/h)	G (l/h dry)
40	14	1030

Internship L. Le Martelot, 2016.

Micro-pilot scale: experimental results

➢ **Evolution of the solvents regeneration energy (E_{regen}) with increased CO_2 content in the gas to treat**

$$E_{regen}\left(\frac{MJ}{kg_{CO2}}\right) = \frac{Q_{reboiler}\left(\frac{MJ}{h}\right)}{G_{CO2,regen}\left(\frac{kg_{CO2}}{h}\right)}$$



A= ± 90%

$y_{CO2, in}$ (%)	L (l/h)	G (l/h dry)
20	8	1030
30	11	1030
40	14	1030
50	16	1030
60	19	1030

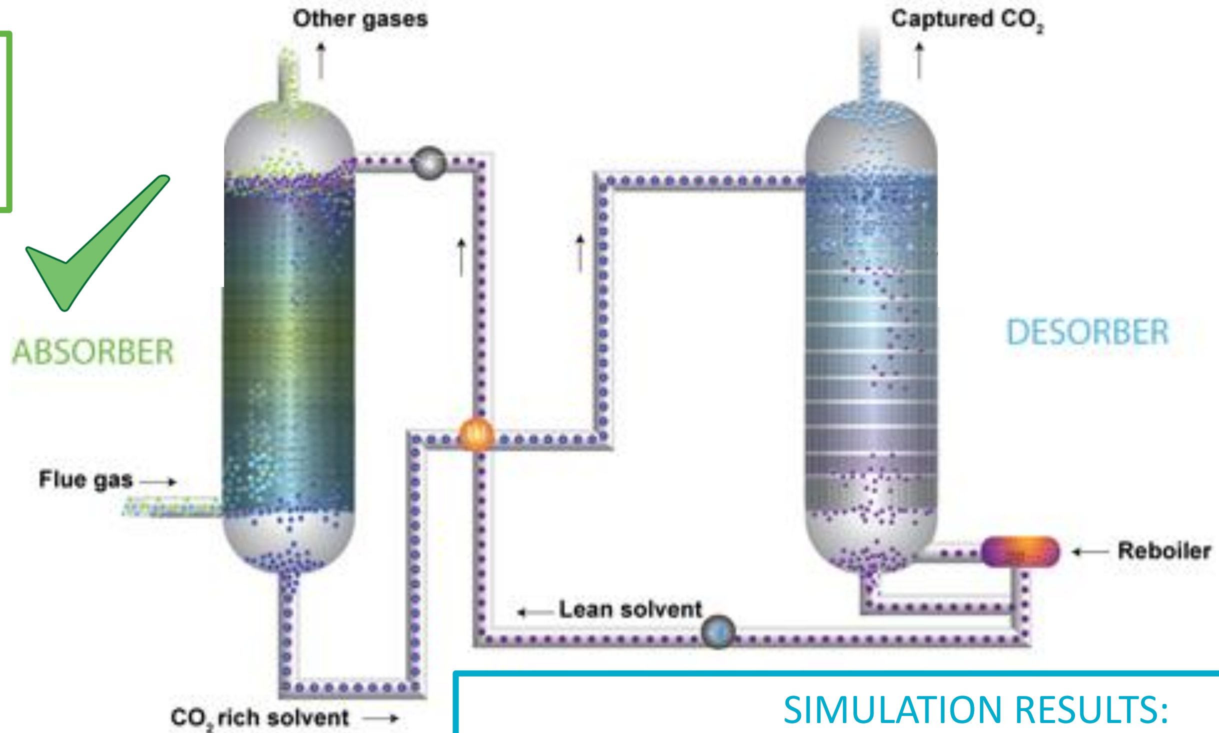
When $y_{CO2, in}$ increases, E_{regen} decreases

Comparison E_{regen} EXP/SIM ✓

Internship L. Le Martelot, 2016.

Purpose of simulations

EXPERIMENTAL RESULTS



SIMULATION RESULTS:
Influence of the partial oxy-fuel combustion conditions on the regeneration energy
→ **Aspen Hysys™ simulations**

General principles of the simulations

NORCEM
HEIDELBERGCEMENT Group
Brevik Cement plant

G_{in} = 4000 m³/h
$y_{CO_2,in}$ = 20.4 mol.%

CASTOR/CESAR pilot

$G_{CO_2,regen}$ = 1.5 t CO_2/h
A = 90 mol.%
Produced CO_2 purity=98mol.%

Brevik cement plant = ECRA reference
First European project for testing CO_2 capture from cement industry

CASTOR/CESAR pilot= reference
European projects
All data available

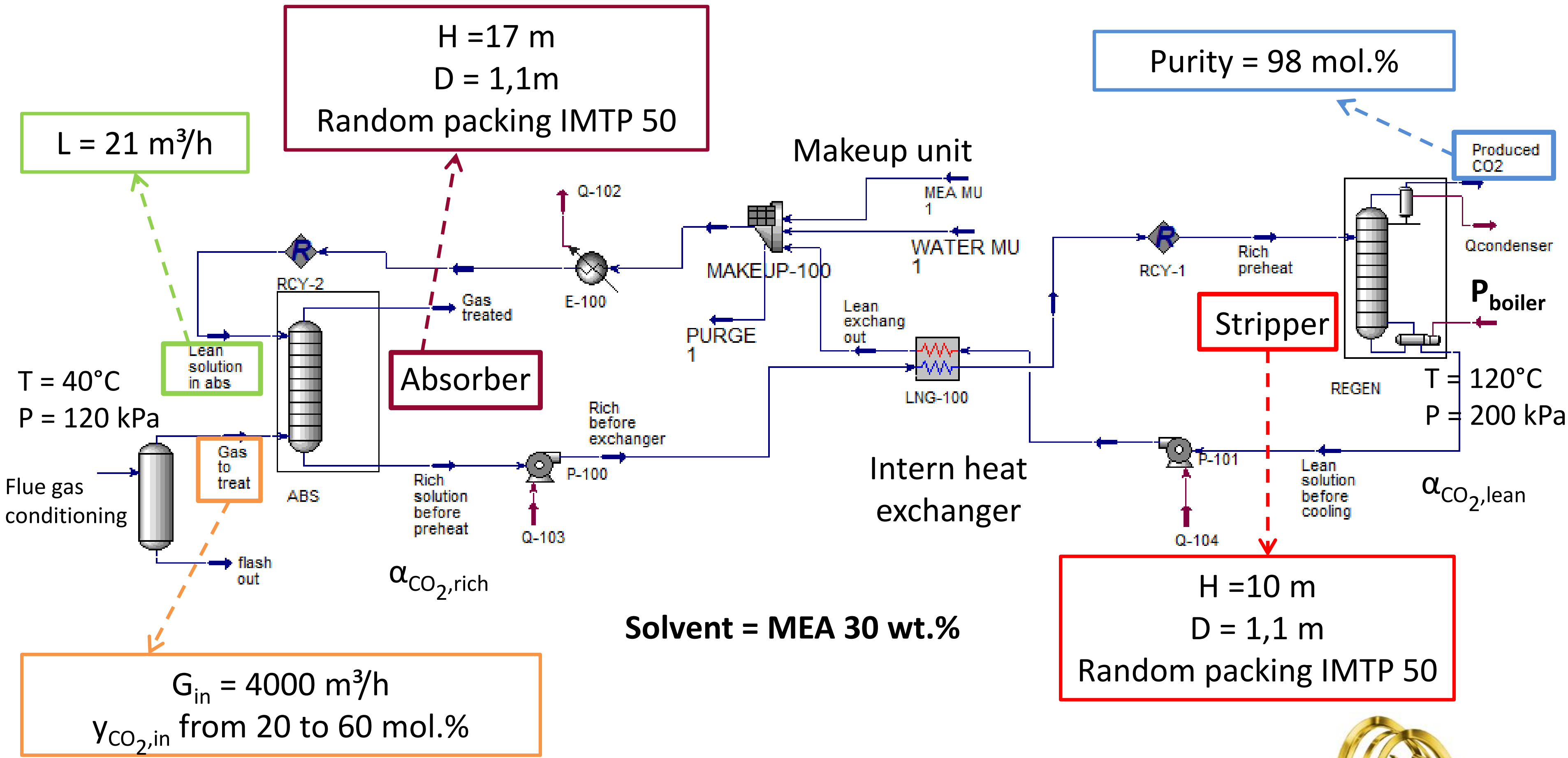
Modelling Characteristics:

- Aspen Hysys V8.6
- Acid gas package
- Thermodynamic models: Peng-Robinson (gas) and e-NRTL (liquid)
- Solvent: MEA 30%
- Reactions sets included in the package (validated by literature)

Simulations for different CO_2 contents in the gas to treat:

- Base case: flue gas from Brevik ($y_{CO_2,in}$ = 20.4 mol.%)
- Other cases: simulations of partial oxyfuel combustion for high y_{CO2} (compositions provided by ECRA).

Flowsheet of the simulations



Determined → $E_{regen} = \dfrac{P_{boiler}}{G_{CO_2,regen}}$

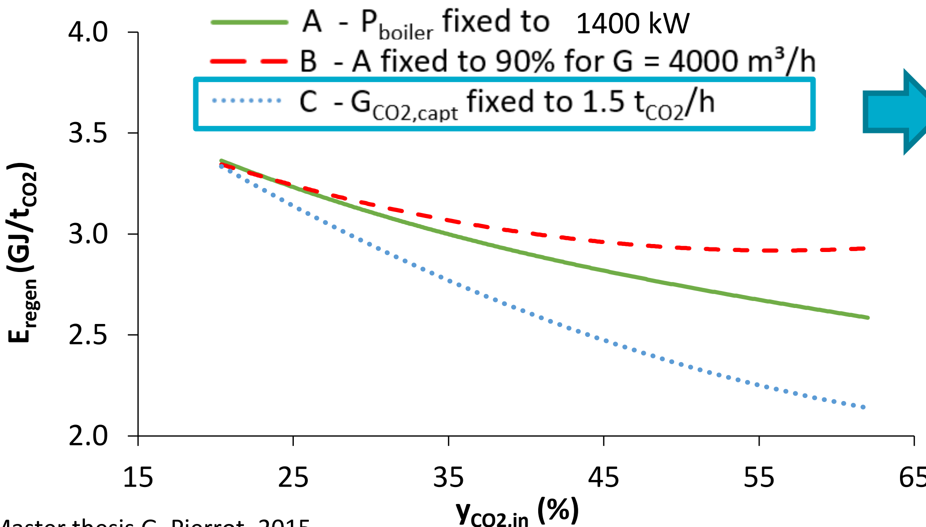
P_{boiler} → [GJ/h]

$G_{CO_2,regen}$ → t_{CO2}/h

Simulations results: $E_{regen} = f(y_{CO_2,in})$

Results for the tested cases:

	Base case	Case 1	Case 2	Case 3	Case 4
$y_{CO2,in}$ (%)	20.4	31	44.1	51.44	62.03
E_{regen} (GJ/ t CO_2)	3.39	2.96	2.56	2.48	2.30
E_{regen} saving / base case		**12.61%**	**24.31%**	**26.79%**	**31.99%**
$\alpha_{CO_2,rich}$	0.508	0.536	0.562	0.557	0.590
$\alpha_{CO_2,lean}$	0.198	0.232	0.264	0.259	0.285



Master thesis G. Pierrot, 2015.

If $y_{CO_2,in}$ ↗
- E_{regen} ↘ for $y_{CO_2,in}$ from 20 to 44% — **E_{saving} = 24%**
- Costs for O_2 production ↗

Conclusions & prospects of the post-combustion capture

Conventional & Partial oxyfuel combustions

FLUE GAS TREATMENT TECHNOLOGIES

Post-combustion CO_2 capture: Absorption-regeneration

Conclusions

- ✓ Interesting solvents screened in lab and micro-pilot scales.
- ✓ Determination of E_{regen} (EXP and SIM values) : when $y_{CO2, in}$ ↗ E_{regen} ↘
  => Interest of post-combustion capture applied to partial oxyfuel combustion.

Prospects

- Evaluation of E_{tot} for CO_2 capture under partial oxyfuel conditions for more complete conditions→ considering the oxygen production cost, E_{ASU}.

Objectives:

Design and optimize CO_2 capture process for re-use & ↘ E_{tot} of the global process.

Thank you for your attention.

Questions?

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Simulations of various configurations of the post-combustion CO_2 capture process applied to a cement plant flue gas

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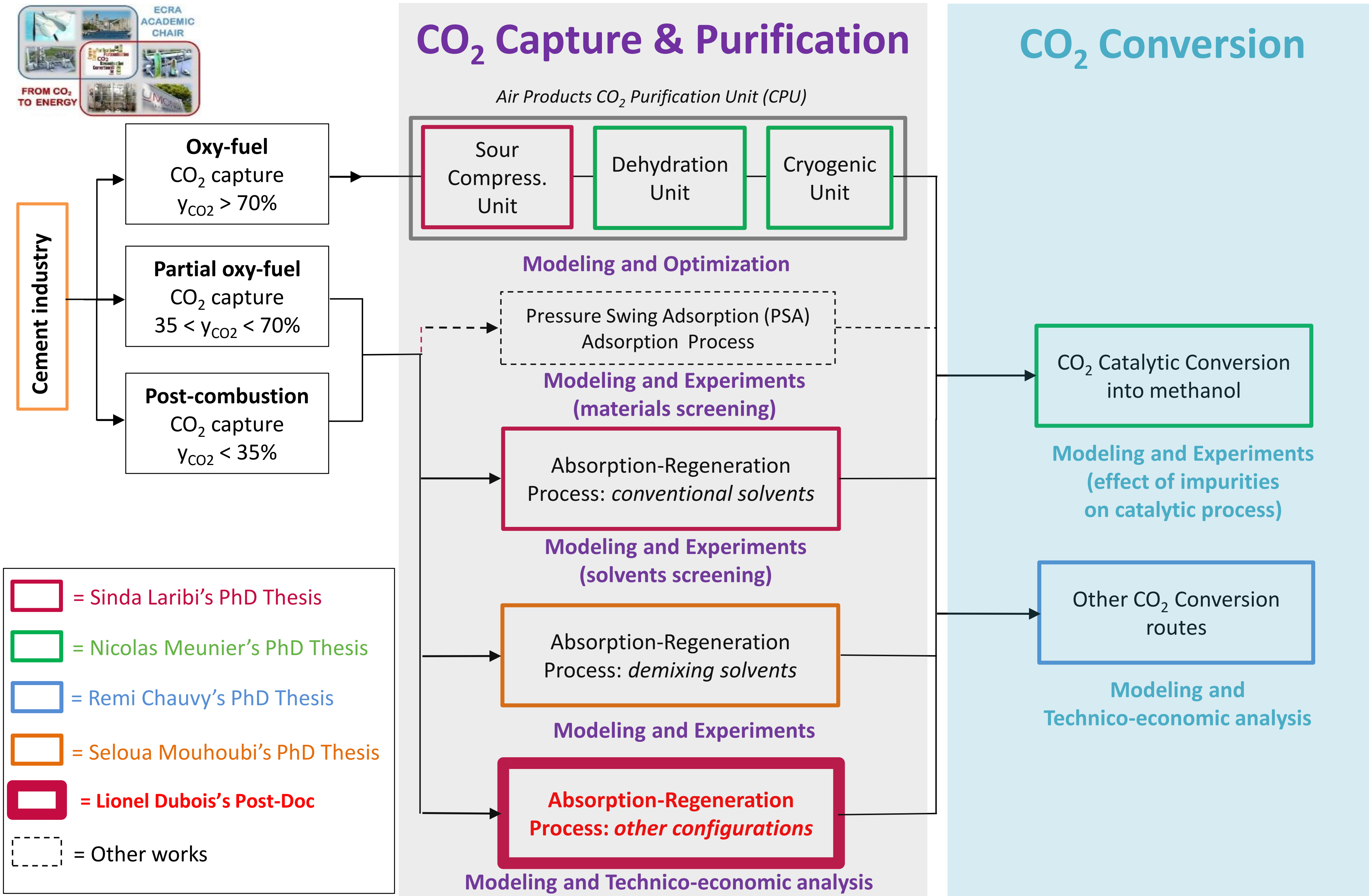
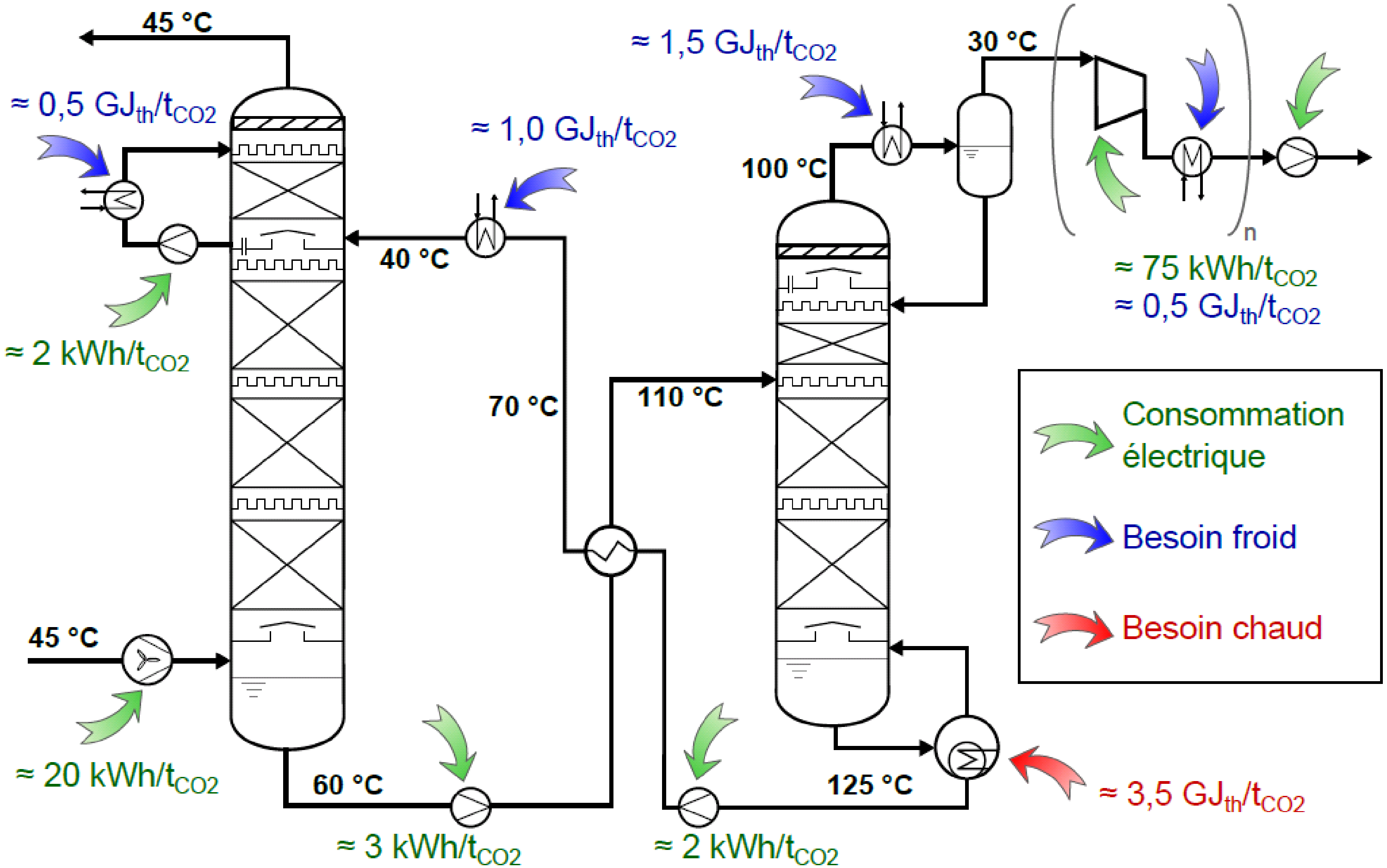
General framework of the ECRA Chair



Post-combustion CO_2 capture

Conventional process:



Ordres de grandeur des différentes dépenses énergétiques (thermiques et électriques) du procédé conventionnel opérant à la MEA [Th. Neveux, 2013]

Post-combustion CO_2 capture

Improvements of the process:

- New solvents
- New packings & equipment
- **New configurations of the process**

Process configurations

Improvements of the process:

A

Promoting absorption

thanks to temperature levels adjustments

B

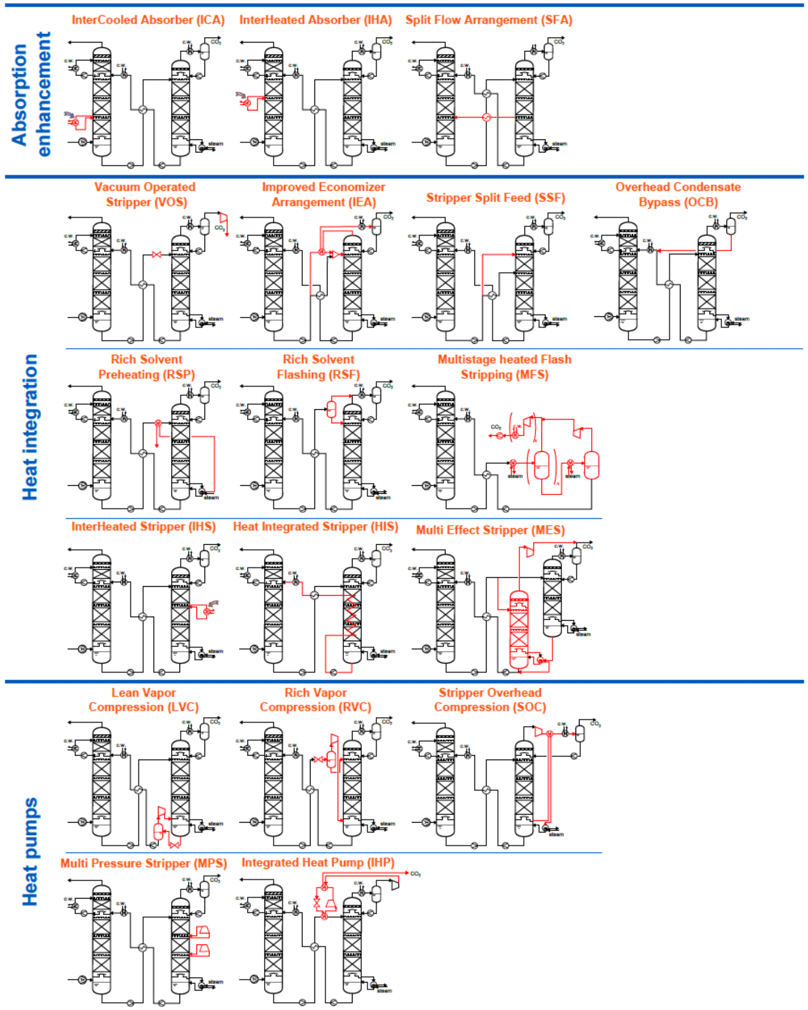
Promoting energy integration

thanks to enhancement of the heat exchanges between the fluids

C

Promoting heat recovery

thanks to heat quality adjustments



Classification des modifications individuelles de procédés (Le Moullec, Neveux, Hoff, et Chikukwa, 2013)

General principles of the simulations

NORCEM

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G_{in} = 4000 m³/h

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→

CASTOR/CESAR pilot

→

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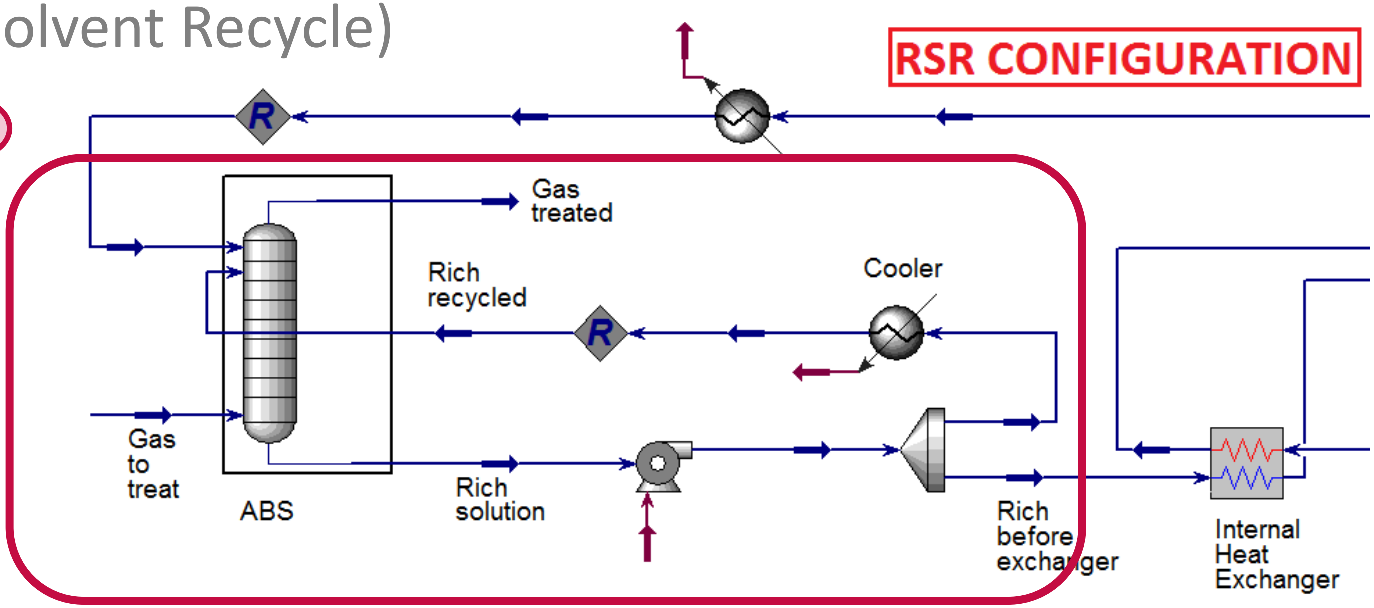
- Thermodynamic models: Peng-Robinson (gas) and e-NRTL (liquid)
- Reactions sets included in the package (validated by literature)

→ **Simulations for different process configurations & for 3 solvents (MEA, PZ & MDEA+PZ)**

Process configurations

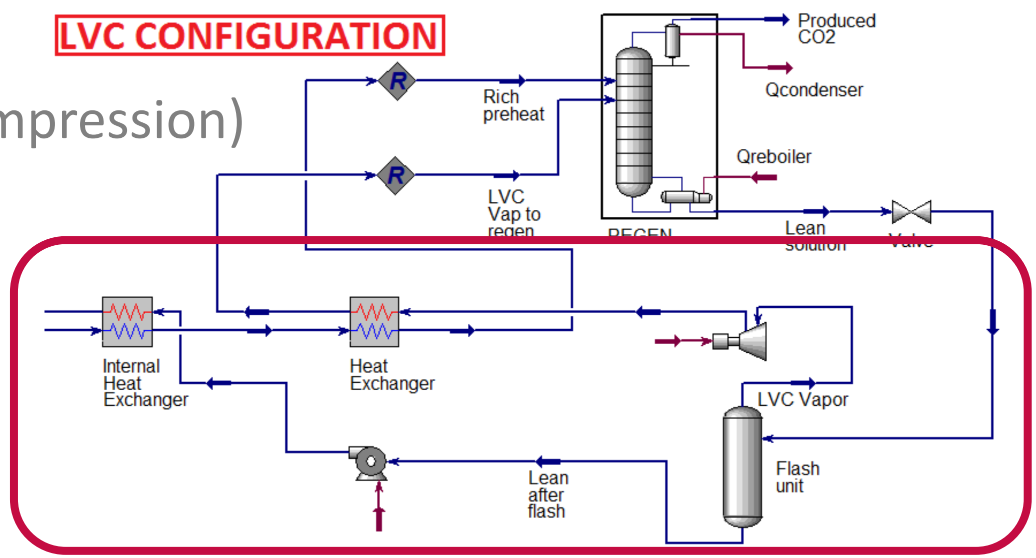
RSR (Rich Solvent Recycle)

A



LVC (Lean Vapor Compression)

C



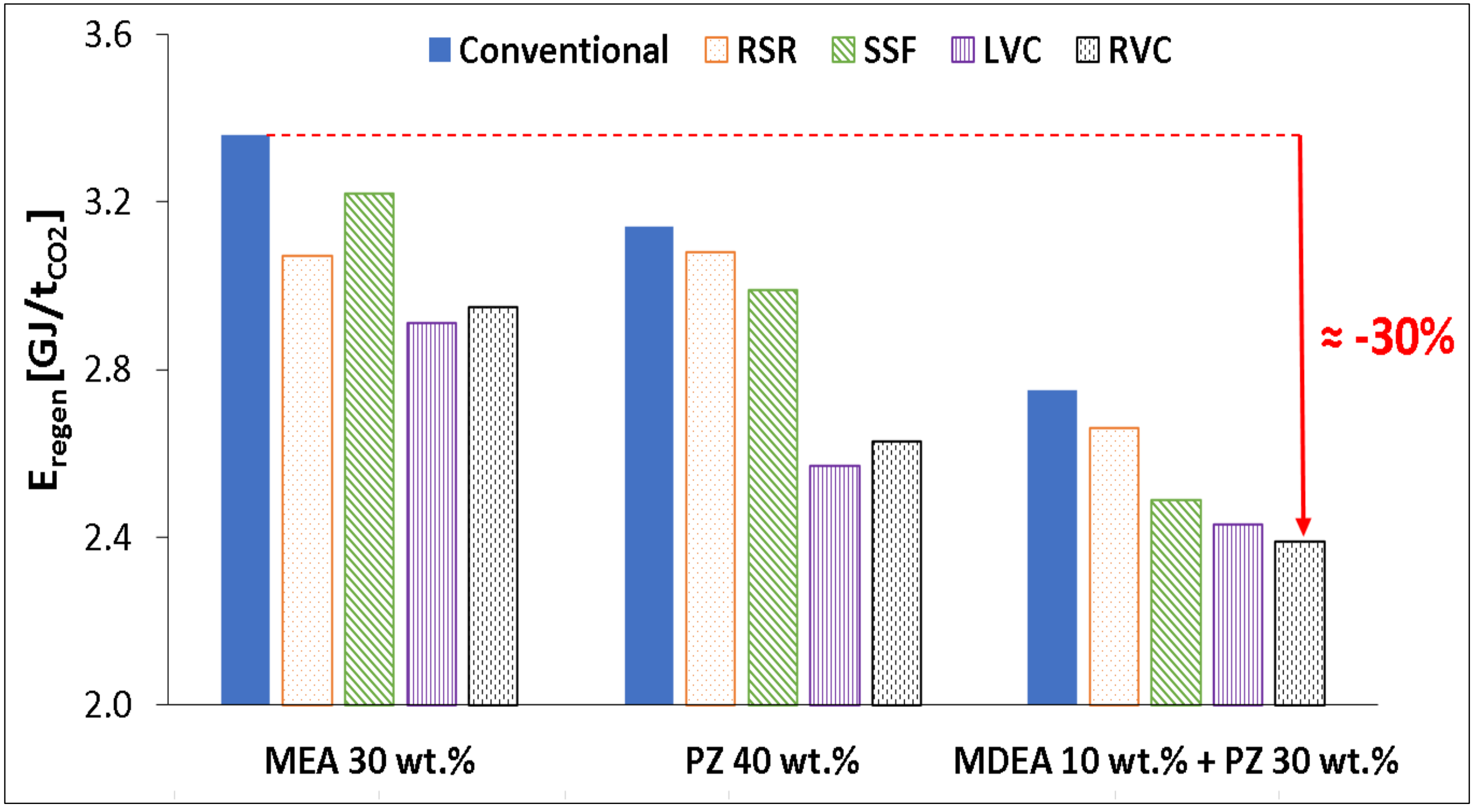
Parametric study

Type of variable	Conventional	RSR	SSF	LVC	RVC
Flow rate ratio	(L/G)	(L/G)	(L/G)	(L/G)	(L/G)
Level	Injection level into the stripper	Re-injection level into the absorber	Injections level of the cold solution into the stripper Injections level of the preheated solution into the stripper	-	-
Temperature	-	Re-injection temperature into the absorber	-	-	-
Flow fraction	-	Re-injected fraction	Split fraction	-	-
Pressure	-	-	-	Flash pressure	Flash pressure

➔ Each parameter varied separately in a first step and then cross variation in a second step

Simulations results

Summary of the results for the three solvents



➔Lower E_{regen} with MDEA 10 wt.% + PZ 30 wt.%

➔**LVC** and **RVC** configurations leading to the minimum of E_{regen} (heat recovery process modifications)

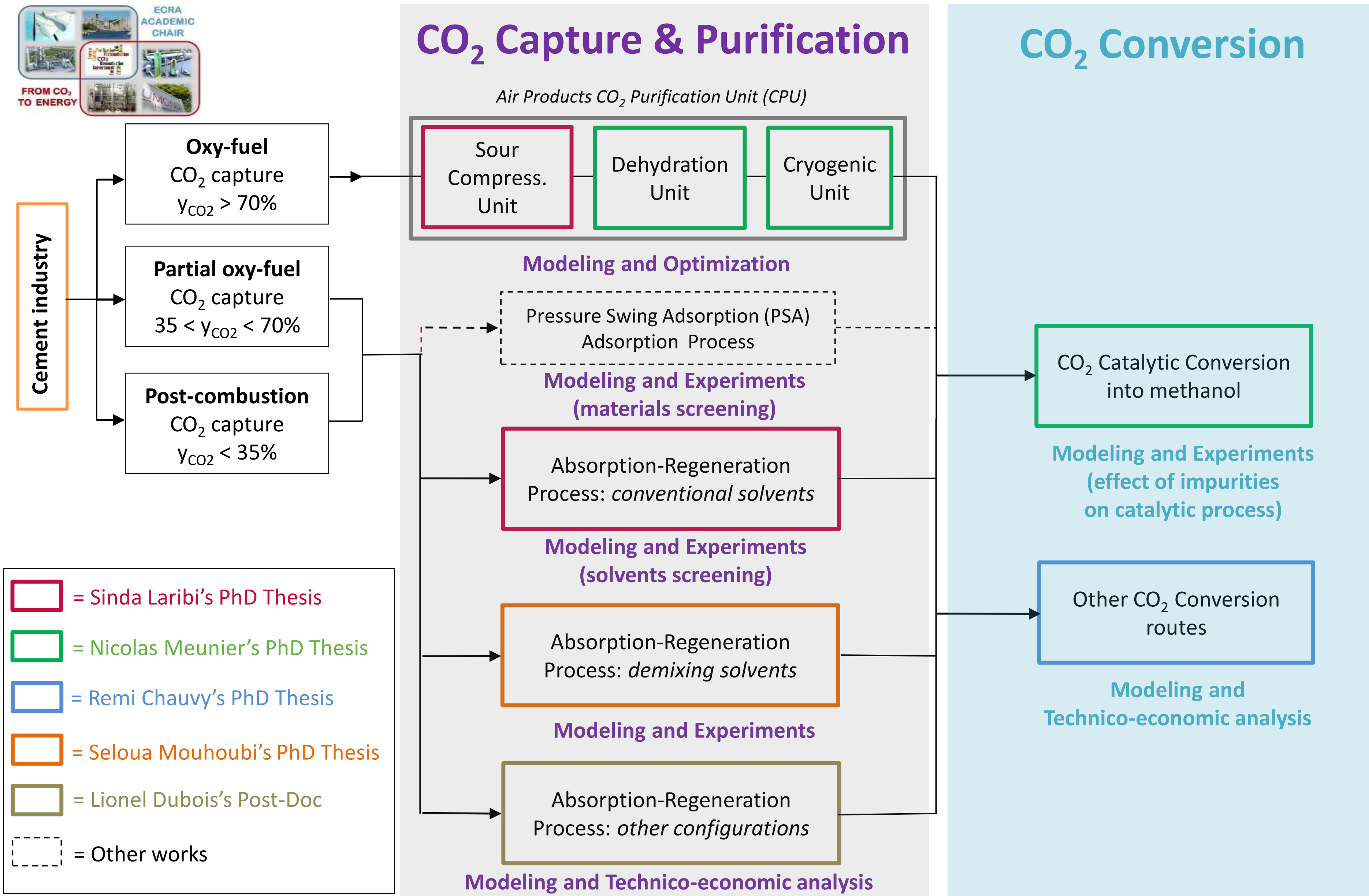
Conclusion & Perspectives

- Interest of alternative process configurations
- Heat recovery modifications (LVC/RVC) to ↓ E_{regen}
- PZ-based solutions lead to the lower E_{regen} values
- In progress with:
  - Other process configurations (e.g. intercooling)
  - Other solvents (e.g. demixing solvents)
  - Other cement flue gas (partial oxy-fuel = high y_{CO2})
  - Etc.

Thank you for your attention!

Questions?

General framework of the ECRA Chair



CO_2 Conversion:

Selection of routes and application to methanol

Ir Remi Chauvy

Ir Nicolas Meunier

Ph.D. Students

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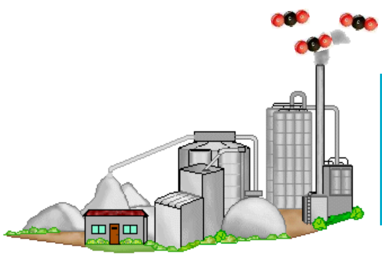
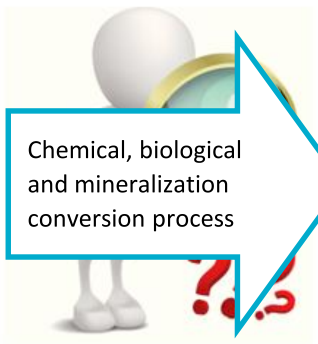
CO_2 capture and utilization



CO_2 capture process



Chemical, biological and mineralization conversion process

CO_2 sources
Cement plant

Capture
Amine scrubbing
Membrane
Pressure Swing Adsorption etc.

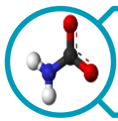
Conversion
Chemicals
Mineralization
Biological
Electrochemical etc.

Fuels
methane, methanol, ethanol, diesel etc.

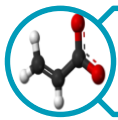
Intermediates & Chemicals
formic acid, acrylic acid, acetic acid, syngas, methanol, ethanol, methane etc.

Polymers
polycarbonates, polyurethane etc.

Inorganic and organic carbonates
calcium carbonate, sodium carbonate, dimethylcarbonate etc.



Carbamates

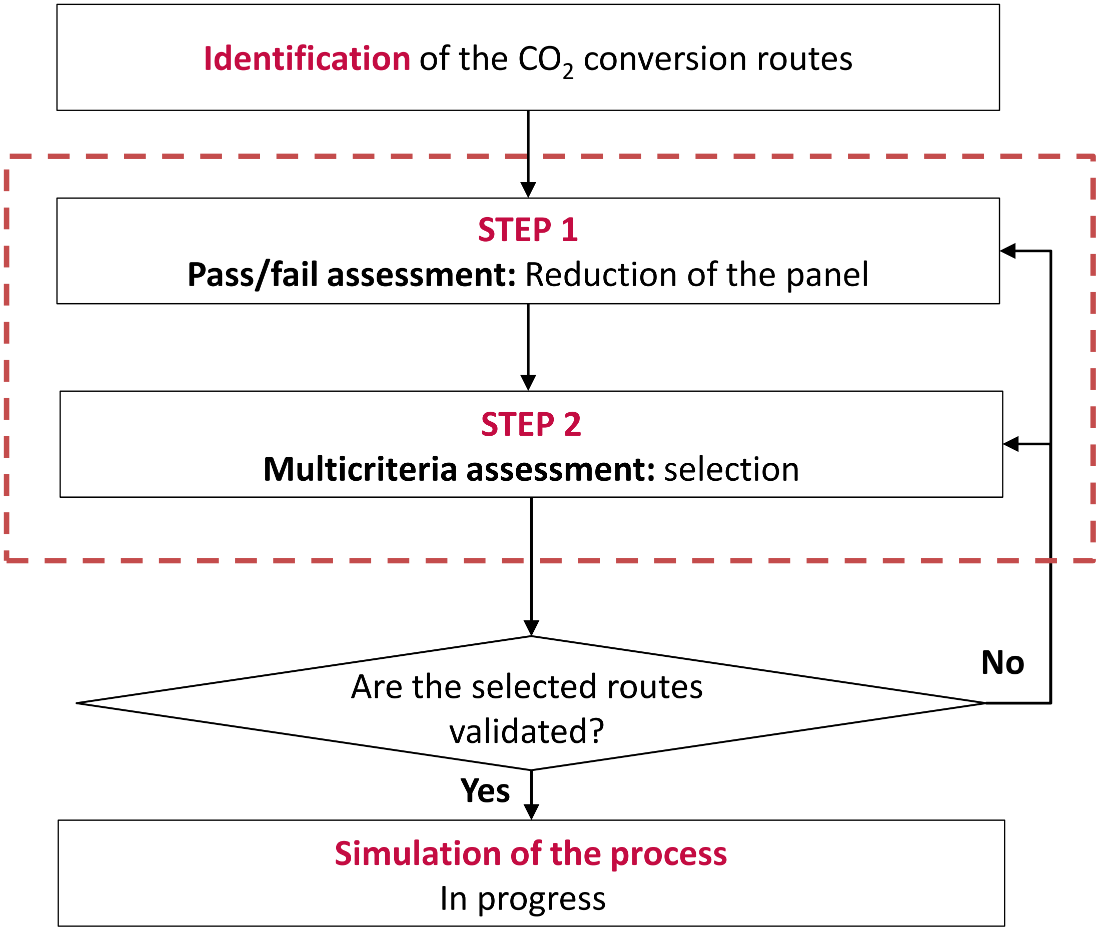


Carboxylates and lactones

Biomass

Microalgae

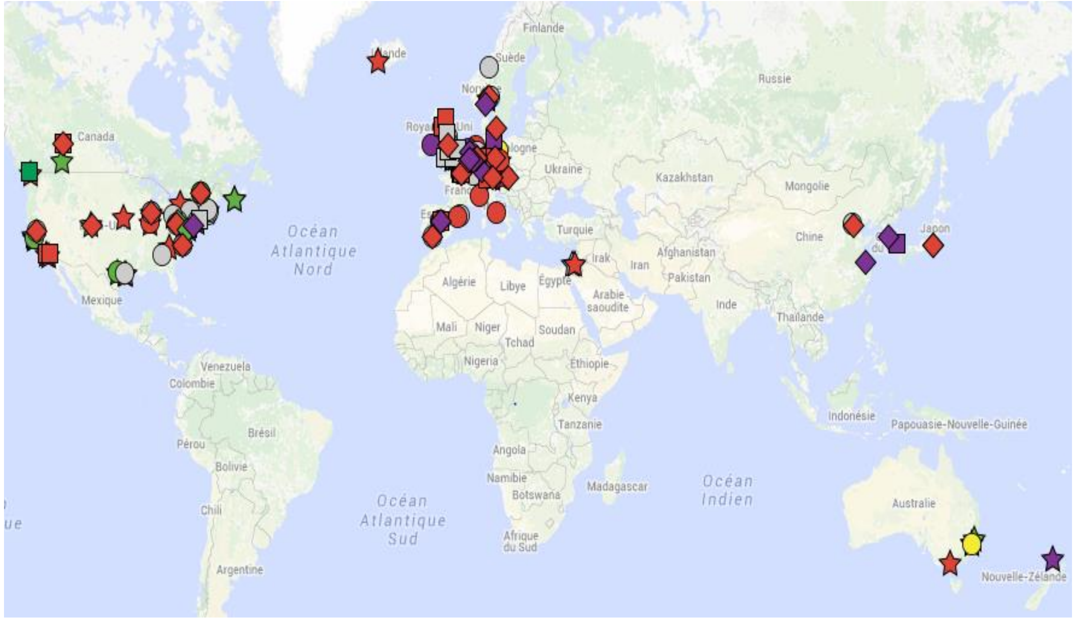
Methodological framework



Identification of the CO_2 conversion routes

Up to date:

- 60 start-ups, 90 projects, 25 Research Centers referenced
- Over **30 routes** identified
  - Final CO_2-based products
  - Technologies of conversion
- Large number of processes and chemical reactions at different levels of maturity and performances.



Carbon dioxide usage activities

Ref.: https://www.google.com/maps/d/viewer?mid=zc9HSeNKIBAs.kekirE1Q9t1c

➡ Need for selection

STEP 1: Pre-selection

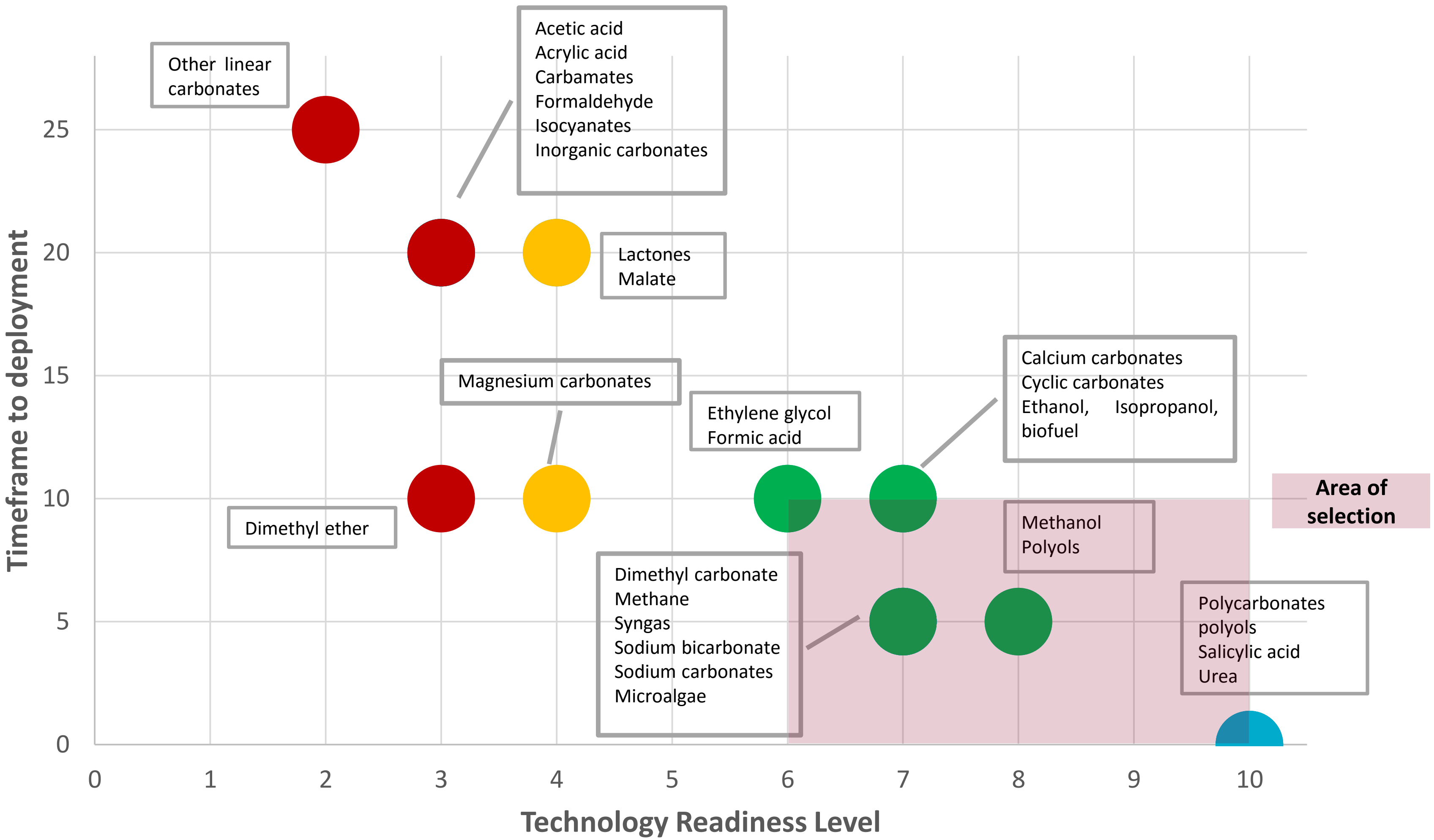
Initial assessment: Qualitative study

- Reduction of the panel based on:
  - **Timeframe to deployment:** short to mid-term period, set at 10 years
  - **Level of maturity:** use of the Technology Readiness Level (TRL): threshold of TRL 6
  - **Size of CO_2 utilization:** evaluated using the specific mass, i.e. the amount of CO_2 which is necessary to produce one ton of a product based on the stoichiometry of the chemical reaction, and the world production in ton per year.

- Short list of about 10 CO_2-based alternatives

STEP 1: Pre-selection

Initial assessment: Level of maturity & timeframe to deployment



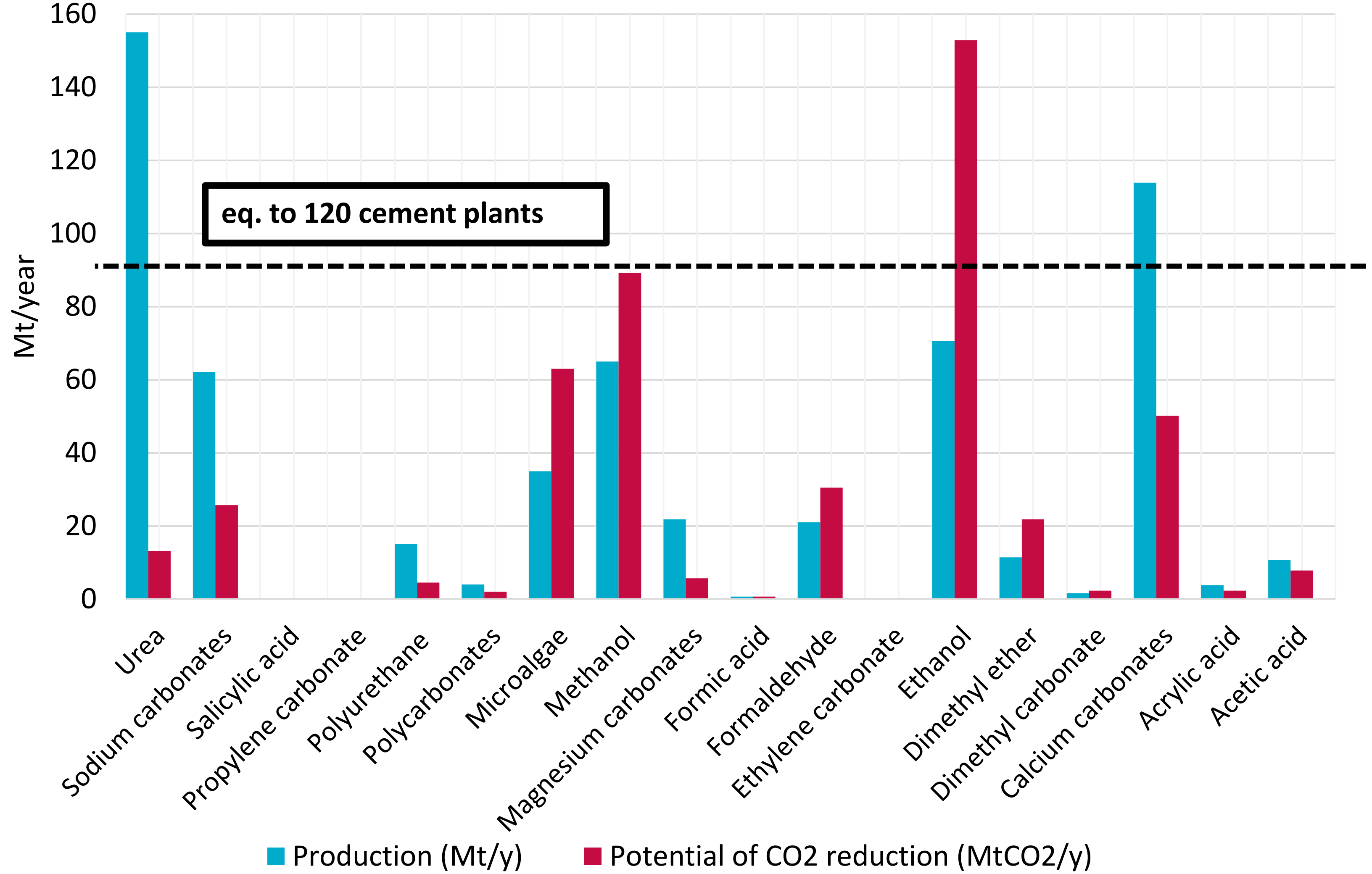
STEP 1: Pre-selection

Initial assessment: Size of CO_2 utilization

No Equivalent of cement plant:

$$\frac{Potential\ of\ CO2\ reduction}{CO2\ emissions\ of\ 1\ BAT\ cement\ plant}\ \frac{[Mt/y]}{[Mt/y]}$$

With: $CO2\ emissions\ of\ 1\ BAT\ cement\ plant$ = **0.74 Mt/y**



STEP 1: Pre-selection

Initial assessment: Results

Shortlist of CO_2 conversion options for the cement industry

CO_2-based compound	CO_2-conversion process	Conventional production
Calcium carbonates	Mineralization (mineral carbonation)	Extraction (mining)
Ethanol	Microbial process	Hydration of ethylene; Fermentation
Formic acid	Electrochemical reduction Electrolysis	Synthesis from methyl formate
Methane	Catalytic hydrogenation	Upgrade of raw natural gas
Methanol	Catalytic hydrogenation	Steam reforming of natural gas
Microalgae	Biological process	NA
Sodium carbonates	Mineralization (mineral carbonation)	Solvay Process; Use of the mineral trona

STEP 2: Selection

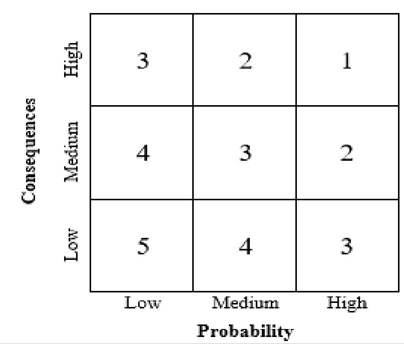
Multicriteria assessment: Criteria and indicators

Definition of the criteria and indicators

Criterion	Indicator
Maturity of the process	i. Level of maturity ii. Timeframe to deployment iii. Risks and uncertainties (SWOT matrix)
Economic potential	i. Size of the market ii. Market competition with other technologies iii. Economic viability (literature review) iv. Energy costs
CO_2 reduction potential	i. Specific mass of CO_2 ii. CO_2 avoidance potential
Environmental, health and safety performance	i. Initial environmental assessment ii. health and safety considerations
Energetic performance and operating conditions	i. Energy requirements ii. Operating conditions, (T, P, kinetics) and conditions of CO_2 feedstock (concentration, purity)

STEP 2: Selection

Multicriteria assessment: Scoring guide for the double weighted matrix

Criterion	Indicator	Definition	Method for the evaluation	Scale	Score
Maturity of the process	*Technological maturity*	Level of maturity and performances	Use of the Technology Readiness Level (TRL)	TRL6	1
				TRL7	2
				TRL8	3
				TRL9	4
				Commercially available	5
	Timeframe to deployment	Estimated time needed to reach commercial technological maturity	Literature review	5 to ≤ 10 years	1
				< 5 years	2
				Commercially available	3
	Risk and Uncertainty	How risks and uncertainties may impact the industrial expansion and the dynamic of growth	Use of a SWOT matrix Development of a risk matrix for evaluation	Risk matrix with the scores associated. Final score calculation: Average of the scores; truncation 	

STEP 2: Selection

Multicriteria assessment: Construction of the double weighted matrix

Criteria	Weight w_{crit}	Indicators	Weight w_{ind}	Alternative 1: Score Sc	Alternative 1: Weighted $Sc \times w_{ind}$	Alternative 2: Sc	Alternative 2: $Sc \times w_{ind}$
Maturity of the process		Technological maturity					
		Timeframe					
		Risk and uncertainty					
				Total			
Economic potential		Size of the market					
		Competiveness with other technologies					
		Economic viability					
		Energy costs					
				Total			
CO_2 reduction potential		Specific mass of CO_2					
		CO_2 reduction potential					
				Total			
Environmental, health and safety performance		Environmental potential					
		Health and safety					
				Total			
Energetic performance & operating conditions		Energy requirements					
		Operating conditions	NA				
		Conditions on inlet CO_2	NA				
				Total			
		Total score (TSc)					
		Total weighted score (TWSc) FINAL SCORE					
		Solution of interest					

STEP 2: Selection

Multicriteria assessment: Construction of the double weighted matrix

Criteria	Weight w_{crit}	Indicators	Weight w_{ind}	Alternative 1: Score Sc	Alternative 1: Weighted $Sc \times w_{ind}$	Alternative 2: Sc	Alternative 2: $Sc \times w_{ind}$
Maturity of the process		Technological maturity					
		Timeframe					
		Risk and uncertainty					
				Total			
Economic potential		Size of the market					
		Competitiveness with other					
CO							
Env... safety performance		Environmental potential					
		Health and safety					
Energetic performance & operating conditions		Energy requirements					
		Operating conditions	NA				
		Conditions on inlet CO_2	NA				
				Total			

Total score (TSc)		
Total weighted score (TWSc)		
FINAL SCORE		
Solution of interest		

Weig

Five-p
-> 1 ve
-> 5 ve

Definit

Weighted score

$$WSc_{ind,i} = Sc_i \times w_{ind}$$

$$TWSc = \sum WSc_{crit,j}$$

with

$$WSc_{crit,j} = w_{crit,j} \times \sum WSc_{ind,i,j}$$

Weighting factors (w_{crit})

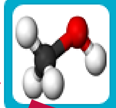
Assigned to each criterion
Defined the level of importance in percentage

STEP 2: Selection

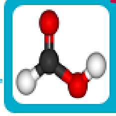
Multicriteria assessment: Results and discussion

Ranking of CO_2 conversion options for the cement industry

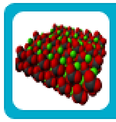
CO_2-based product	Conversion process	TRL	Timeframe	Size of CO_2 utilization	Score
Calcium carbonates	Mineral carbonation	TRL 7	Timeframe to deployment 5 to 10 years	Market: 113.9 Mt (2013) CO_2 avoidance potential: 50.08 Mt	**
Ethanol	Microbial process	TRL 7	Timeframe to deployment 5 to 10 years	Huge market Competition with other bioethanol ec.	*
Formic acid	Electrolysis reduction	TRL 6	Timeframe to deployment 5 to 10 years	Market: 0.6 Mt (2013) CO_2 avoidance potential: 0.57 Mt	**
Methane	Catalytic hydrogenation	TRL 7/8	Timeframe to deployment < 5 years	Huge market Competition with biogas / natural gas	****
Methanol	Catalytic hydrogenation	TRL 8/9	Timeframe to deployment < 5 years	Market: 50 Mt (2013) CO_2 avoidance potential: 68.65 Mt	*****
Microalgae	Biological process	TRL 7	Timeframe to deployment 5 to 10 years	Important market But limited application	***
Sodium carbonates	Mineral carbonation	TRL 6	Timeframe to deployment 5 years	Market: > 62 Mt (2013) CO_2 avoidance potential: 25.73 Mt	**



Methanol *via* catalytic hydrogenation



Formic acid *via* electrochemical reduction



Both **calcium & sodium carbonates** *via* mineral carbonation

CO_2 Conversion:
Application to methanol

Methanol Utility & Applications

Key points:

- ✓ Liquid at ambient condition (ease of storage)
- ✓ High energy density
- ✓ Hydrogen mass balance methanol vs. methane
- ✓ Global demand of 70 million tons/year in 2015
- ✓ Generates more than $55 billion/year and creates over 90,000 jobs

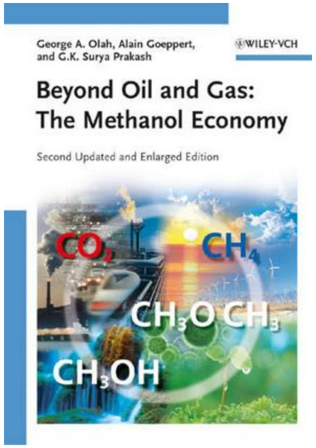
Applications:

- Energy (Automotive & Marine fuels, Biodiesel, Dimethyl ether (LPG), …)
- Chemicals (Formaldehyde, Acetic acid, Dimethyl ether (adhesives), Solvents, …)
- Waste Water Treatments (Denitrification)

Methanol Utility & Applications

Methanol Rally Racing
Junior WRC 2013 - Greece

CO_2 Methanol Plant
(Carbon Recycling International – CRI)
Svartsengi, Iceland



The Methanol Economy
George A. Olah

GreenPilot Boat (Stela Line)
Sweden

Thermodynamics & Kinetics

Reactions

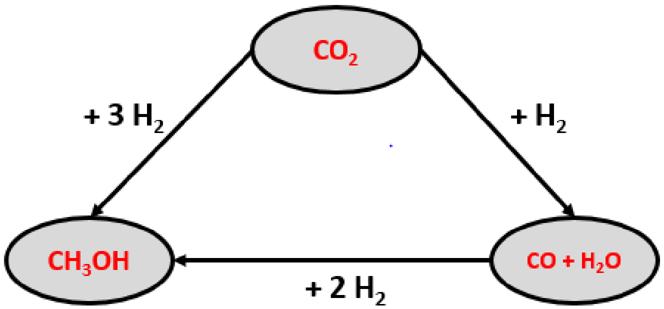
$$\begin{cases} CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O \\ CO + 2H_2 \Leftrightarrow CH_3OH + H_2O \\ CO_2 + H_2 \Leftrightarrow CO + H_2O \end{cases}$$

Kinetics

$$r'_{CH_3OH,A_3} = \frac{k'_{ps,A_3}\, K_{CO}\left[f_{CO}\, f_{H_2}^{3/2} - f_{CH_3OH}/\left(f_{H_2}^{1/2} K_{p1}^0\right)\right]}{\left(1 + K_{CO}\ f_{CO} + K_{CO_2}\, f_{CO_2}\right)\left[f_{H_2}^{1/2} + \left(K_{H_2O}/K_{H_2}^{1/2}\right)\, f_{H_2O}\right]}$$

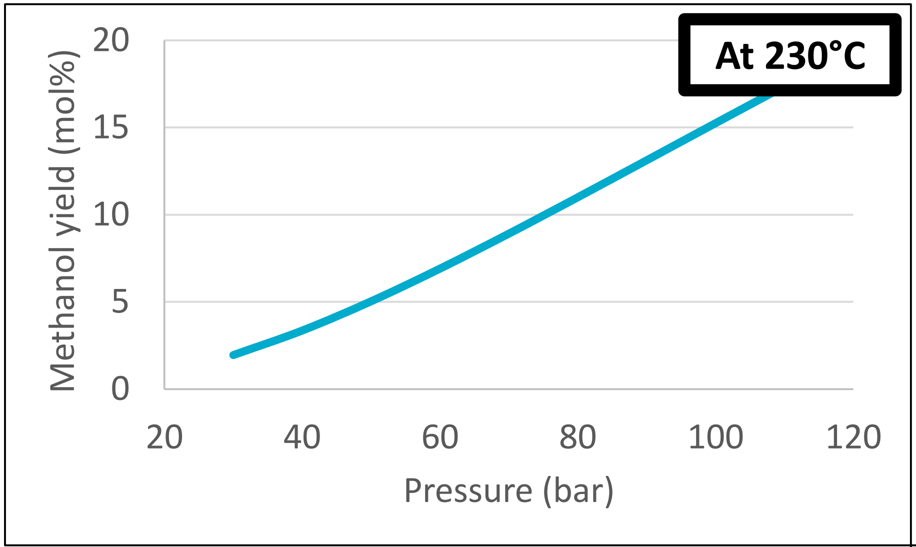
$$r'_{H_2O,B_2} = \frac{k'_{ps,B_2}\, K_{CO_2}\left[f_{CO_2}\, f_{H_2} - f_{H_2O}\, f_{CO}/K_{p2}^0\right]}{\left(1 + K_{CO}\ f_{CO} + K_{CO_2}\, f_{CO_2}\right)\left[f_{H_2}^{1/2} + \left(K_{H_2O}/K_{H_2}^{1/2}\right)\, f_{H_2O}\right]}$$

$$r'_{CH_3OH,C_3} = \frac{k'_{ps,C_3}\, K_{CO_2}\left[f_{CO_2}\, f_{H_2}^{3/2} - f_{CH_3OH} f_{H_2O}/\left(f_{H_2}^{3/2}\, K_{p3}^0\right)\right]}{\left(1 + K_{CO}\ f_{CO} + K_{CO_2}\, f_{CO_2}\right)\left[f_{H_2}^{1/2} + \left(K_{H_2O}/K_{H_2}^{1/2}\right)\, f_{H_2O}\right]}$$



- **Carbon monoxyde** (CO) and **water** also have an influence on the methanol conversion yield !

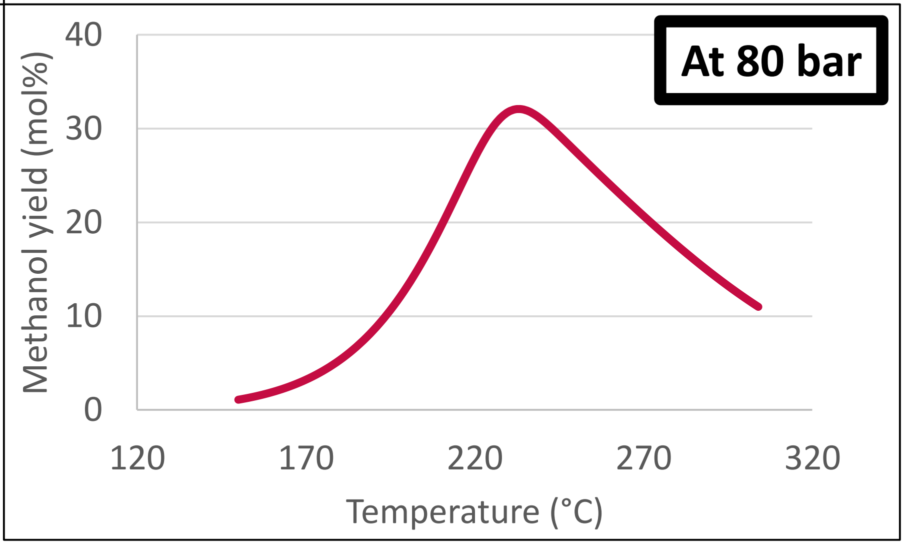
Thermodynamics & Kinetics



GHSV : 10,000h^{-1}

- The optimal operative pressure is set to **<u>80 bar</u>** as a trade-off between <u>performances</u> and compression <u>costs</u> !

- There is an optimal operative temperature of ~**<u>230°C</u>** !



Methanol Catalysts

CuO/ZnO – type catalysts:

- Typically CuO/ZnO/$\mathbf{Al_2O_3}$
- Firstly designed for **pure CO** conversion

➢ **Promoters** required to enhance the selectivity of **pure $\mathbf{CO_2}$** conversion

✓ Collaboration with the **European School for Catalysts, Polymers and Materials of Strasbourg** (**ECPM**)

✓ Elaboration of **new generation** catalysts

(ex: CuO/ZnO/$\mathbf{ZrO_2}$)

➢ Promising preliminary tests !

CuO/ZnO/Al_2O_3 catalyst

Methanol Catalysts

Deactivation pathways:

- **Very sensitive** to all common deactivation problems:
  - ✓ Sensitive to **thermal sintering** above 180°C
  - ✓ Sensitive to **coke deposition**
  - ✓ Sensitive to **sulfur** poisoning (H_2S and SO_x)
  - ✓ Sensitive to **water** poisoning

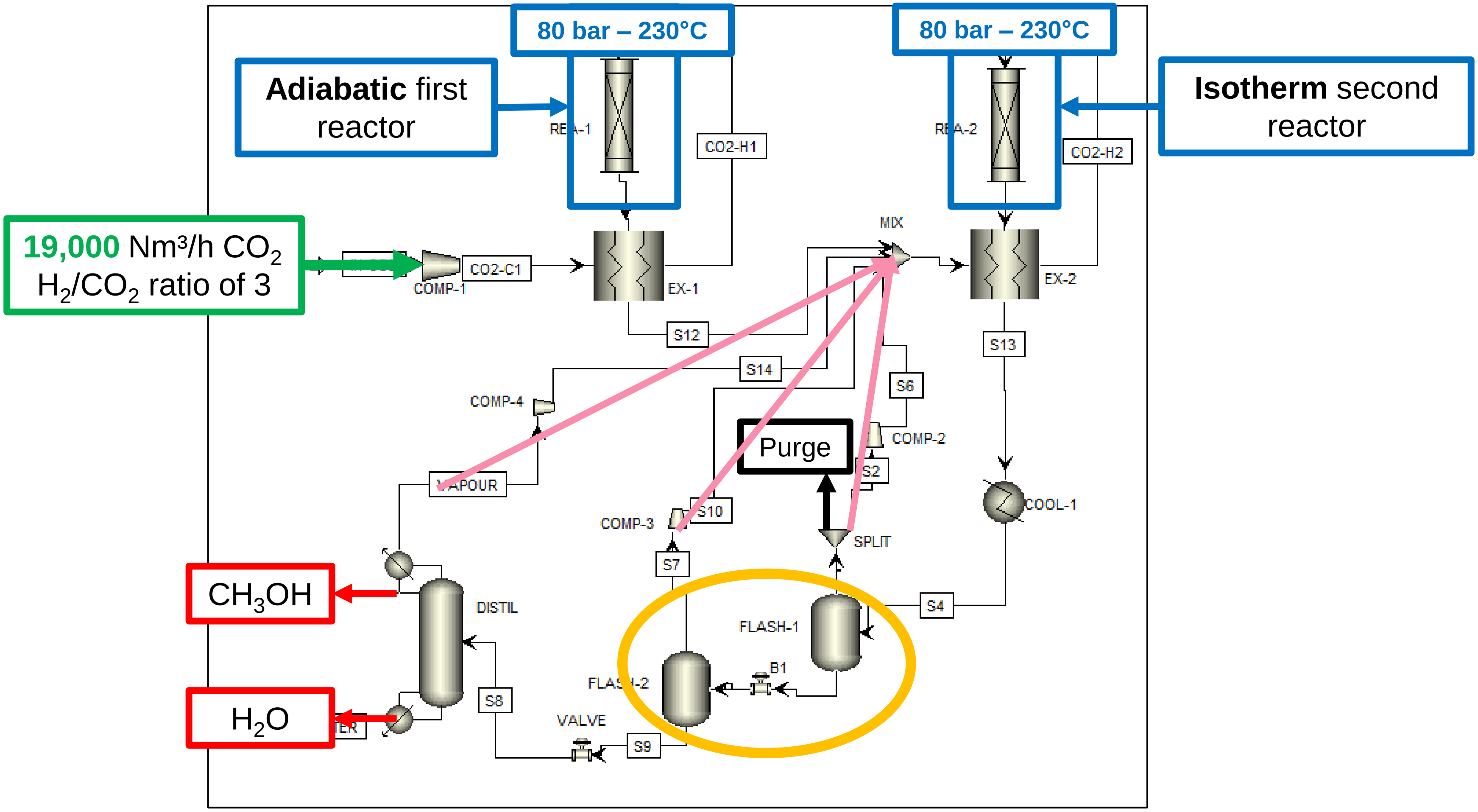
✓ Generally, this kind of catalysts has a lifetime of **3 years**

✓ Very important for **OPEX** considerations !

✓ **No** possible **recycling** of catalysts → **Metal recovering** !

Understanding the process

Simulations with *Aspen Plus* v8.4.



Methanol Conversion Process

On the path of *optimization*

Main purposes:

- Ensure a constant methanol **purity** stream (currently **99 mol%)**
- Maximize the **productivity** of the installation
- Improve the performances of **catalysts**
- Reduce the **CAPEX** and **OPEX** of the methanol conversion process

Sensitivity analysis:

- **Pressure of the reactors**
- **Size of the reactors**
- **Temperature of the flash**
- **Purge ratio**
- **Sizing of the distillation column**
- **Innovative alternative configurations !**

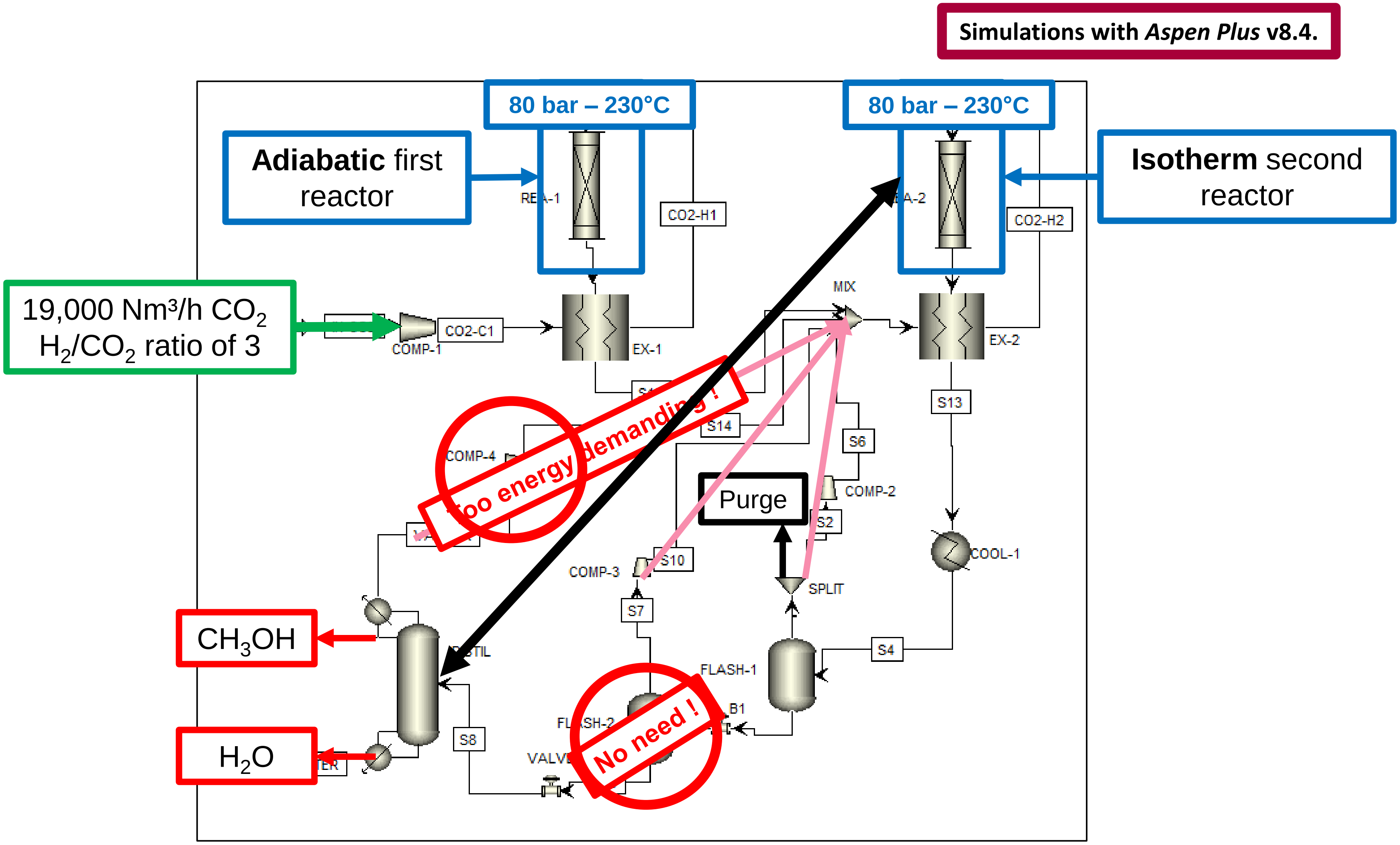
Energetic factors:

- **Electrical consumption**
- **Heat demand**

Economic factors:

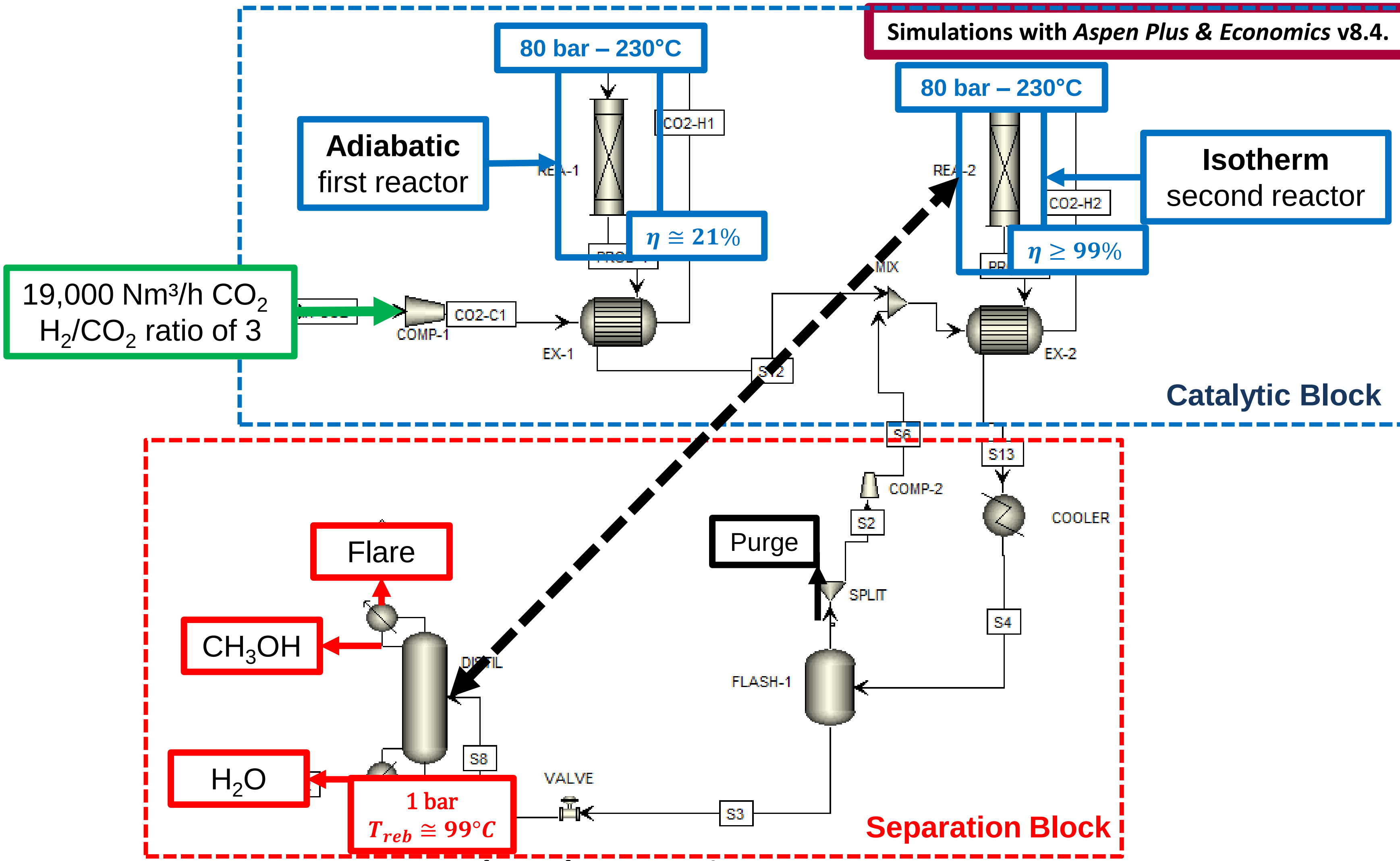
- **CAPEX & OPEX**
- **Incomes**

Understanding the process



Methanol Conversion Process

The Upgraded Process

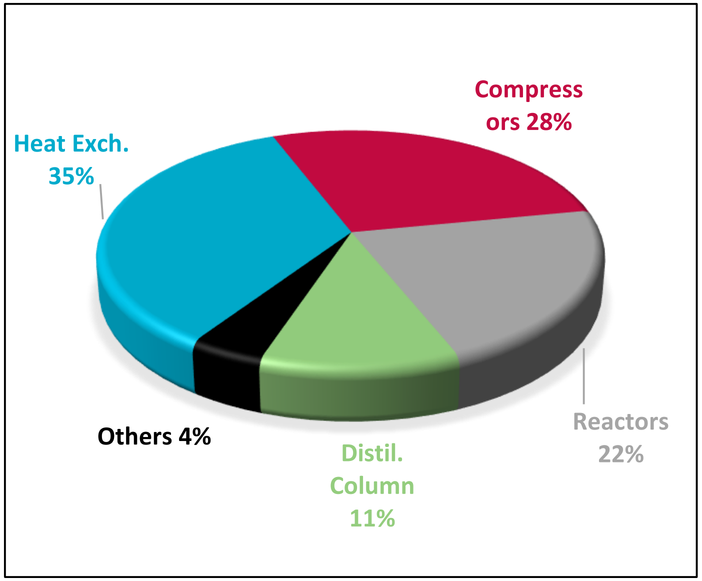


Methanol Conversion Process

CAPEX & OPEX Estimations

CAPEX estimations:

- The upgraded process is designed to treat **35%** of the **CO_2 emissions** coming from a **3,000 tpd clinker** cement plant
- The global CAPEX of the upgraded proces is estimated to reach **21,000 k€**
- **39%** (i.e. 8,300 k€) dedicated to the purchase of the equipment



CAPEX estimations (equipment)

With the **upgrades** in the process design:

✓ *<u>Reduction of the CAPEX by **12%** !</u>*

CAPEX & OPEX Estimations

OPEX estimations:

- The **OPEX** related to our upgraded process are currently estimated to reach **18.6 €/ton CO_2 converted** (i.e. **28 €/ton CH_3OH produced**)
- The **OPEX** estimations show that more than **69%** (i.e. 4,065 k€/year) of the energy expenses are dedicated to the **reboiler heating**
- The replacement of the **catalyst** accounts for **4%** of the global **OPEX**

		k€/year	€/ton CO_2	€/ton CH_3OH
Electricity	1st Compr.	1,036	5.1	7.7
	2nd Compr.	576		
Heat	Steam	4,065	12.8	19.3
Deprec.	Catalyst	225	0.7	1.1

OPEX estimations

With the **upgrades** in the process design:

✓ *Reduction of the heat demand by **20 – 40%** !*

✓ *Reduction of the electricity duty by over **70%** !*

Prospects

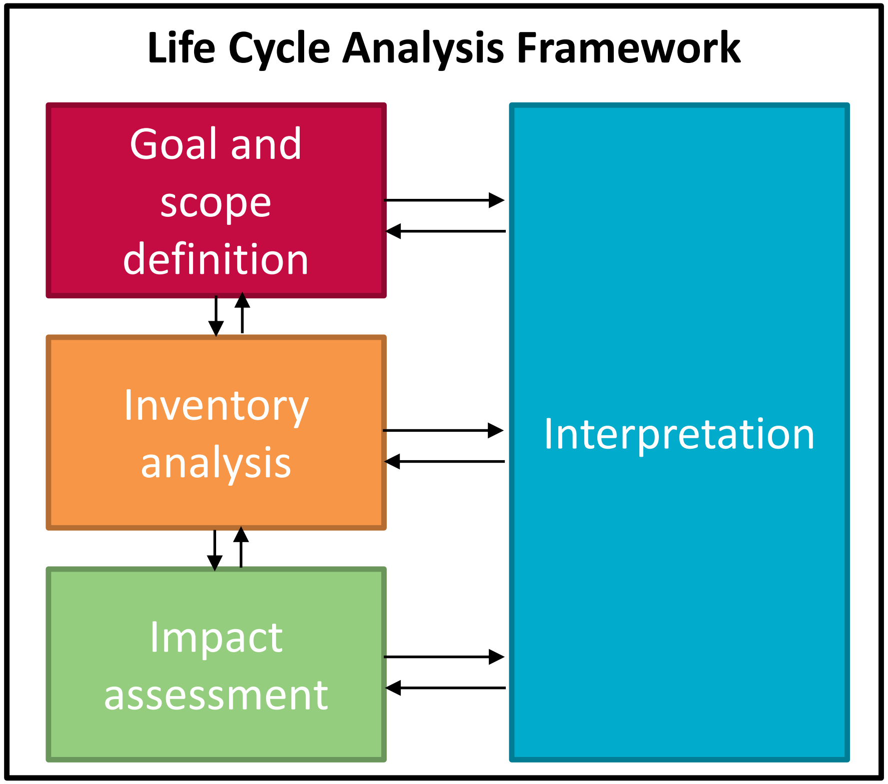
- Investigation of **modifiers** to improve **catalyst performances and stability** (with the **European School for Catalysts, Polymers and Materials of Strasbourg**)
- Experiments on several **CuO/ZnO shaped** catalysts with **CO_2/H_2** mixtures on our homemade semi-pilot installation
- **Check** and **Update** of the **kinetic** data related to catalysts
- Better **optimization** of the **methanol conversion process** (**CAPEX** & **OPEX**)
- Influence of **SOx** and **NOx** on **catalyst** performances, stability and aging

- **Life Cycle Analysis** (LCA) of the methanol conversion process (with **Remi Chauvy**)

- Propose an **environmentally friendly**, **integrated** and **optimized** **CO_2 purification** and **conversion** process applied to the **cement sector** !

Environmental assessment
Background information

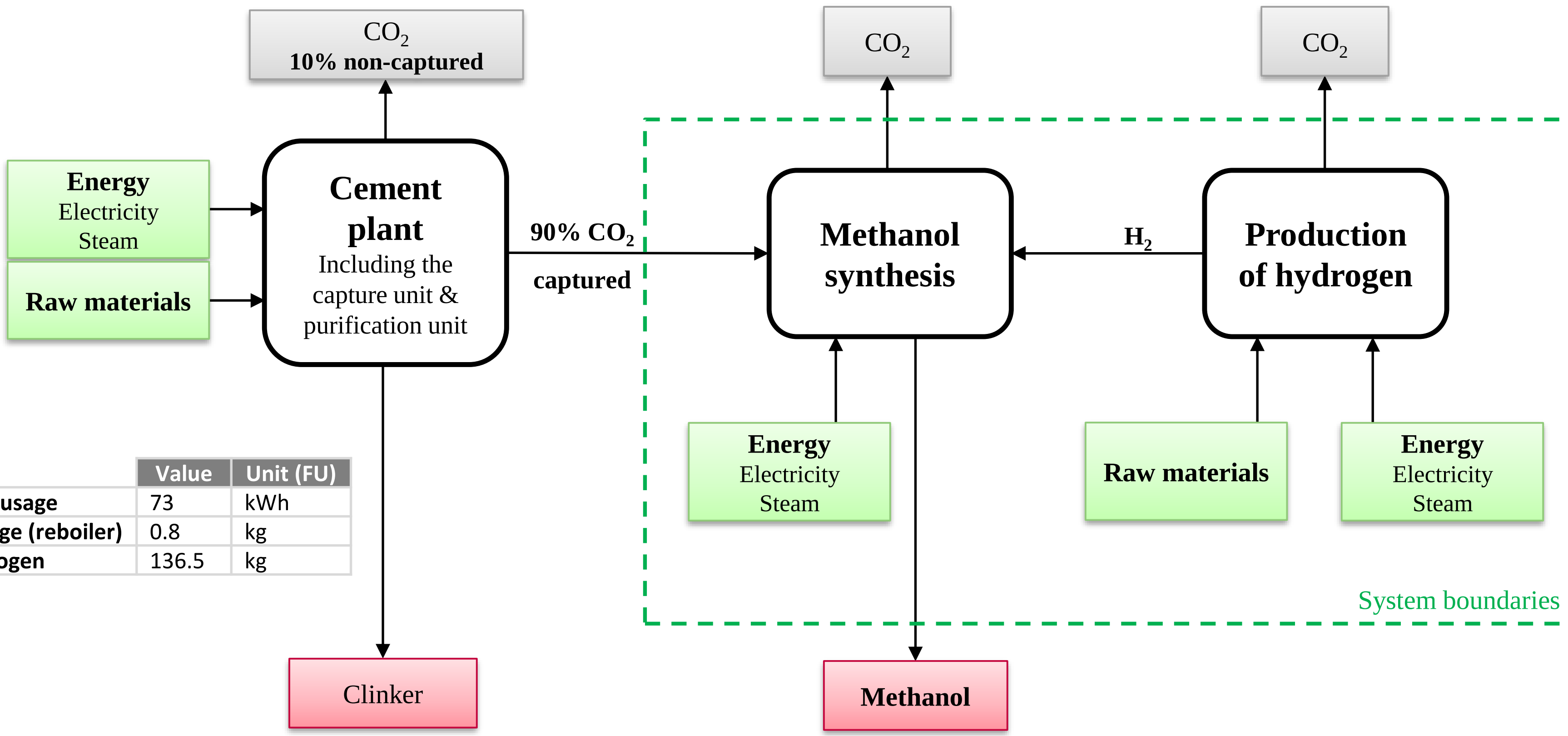
- Life Cycle Analysis (LCA) based on ISO 14040 & 14044:



Environmental assessment

Background information

- **Functional unit**: Conversion of 1 ton of CO_2 into methanol via catalytic hydrogenation
- **System boundaries**:



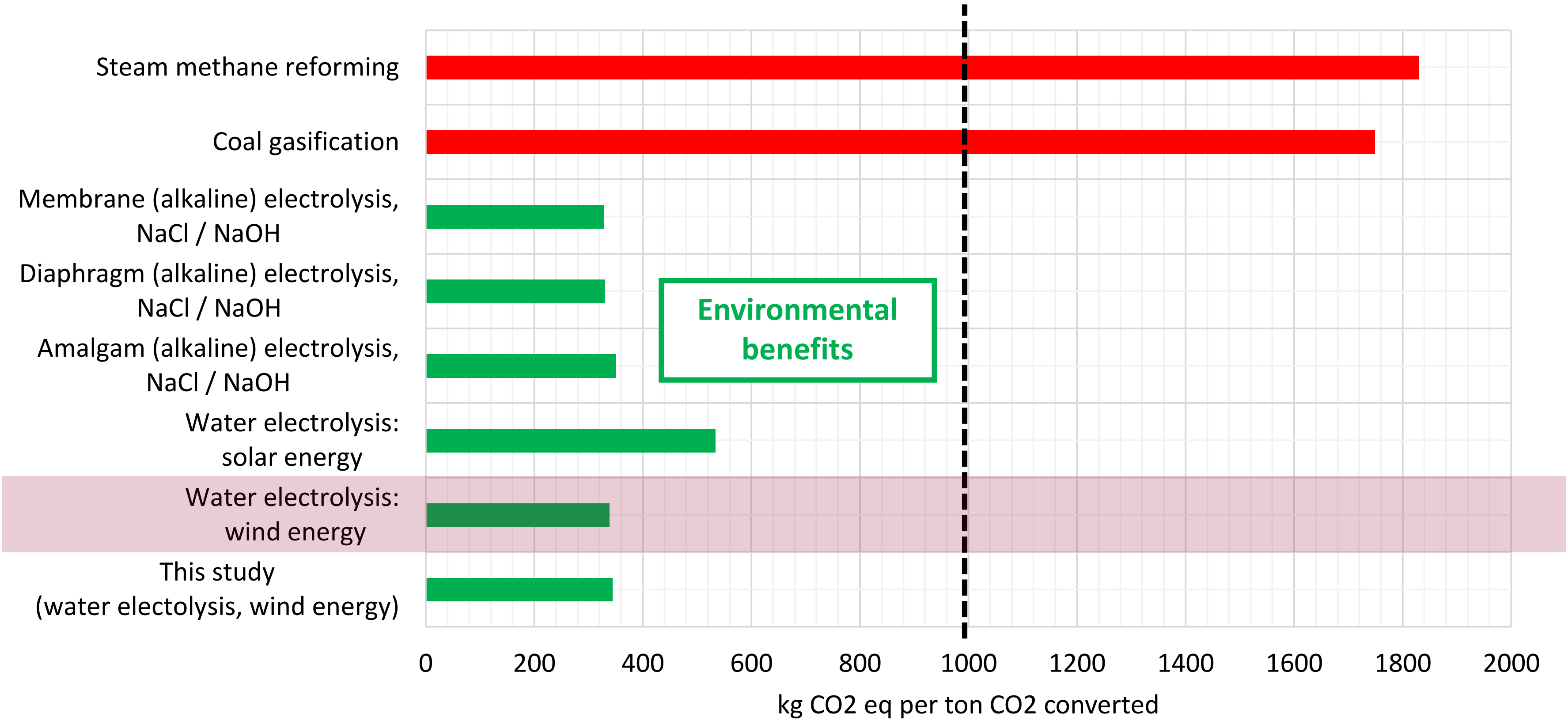
	Value	Unit (FU)
Electricity usage	73	kWh
Steam usage (reboiler)	0.8	kg
Feed hydrogen	136.5	kg

Environmental assessment

First results

Sensitivity analysis

Influence of the production of hydrogen on the global warming impact category for the conversion of 1 t of CO_2

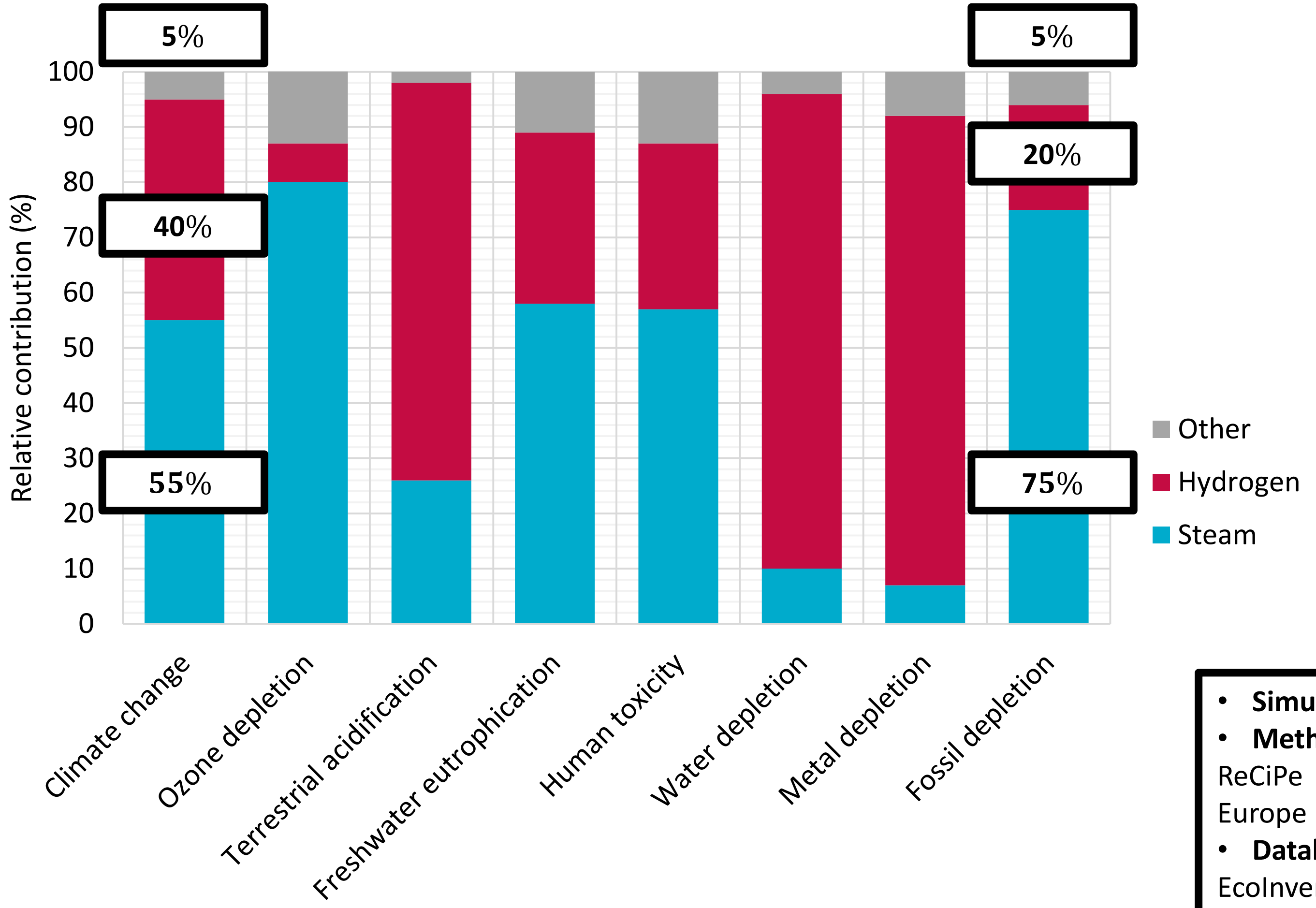


Environmental assessment

First results

Impact assessment for the conversion of 1 ton of carbon dioxide

Relative contribution on the selected impacts categories



- **Simulations with SimaPro**
- **Method of characterization:** ReCiPe Midpoint (H) V1.12 / Europe Recipe H
- **Database:** EcoInvent database v3.2

Environmental assessment

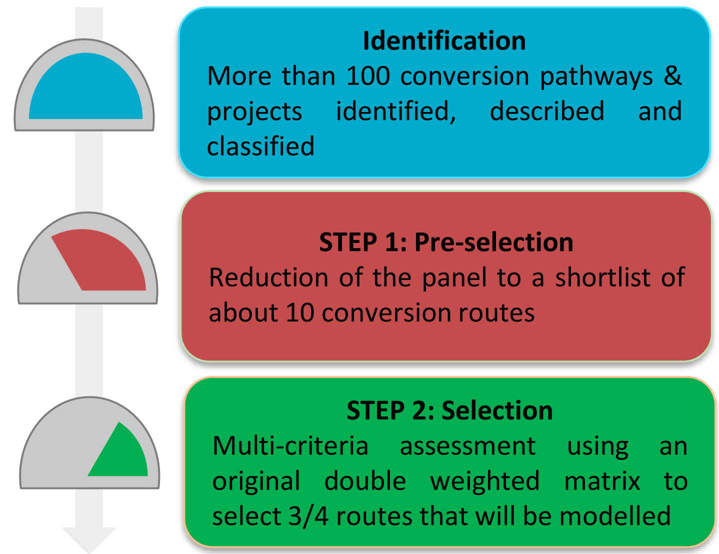
Discussion

- **Up to date**: no straight conclusion can be drawn
- **Need to implement**:
  - Construction and decommissioning of the infrastructures and equipment,
  - The use of the catalyst,
  - The environmental impact of the downstream process, i.e. linked to the capture and purification of the carbon dioxide from a cement plant.

- **These first results tend to demonstrate that this process may have an environmental benefit regarding the global warming**

Conclusion and prospects

- An original method to select most suitable CO_2 conversion pathways in the framework of the ECRA Academic Chair
  - Two-step method
  - Multicriteria assessment
  - Original score system
  - Double-weighted matrix



- Study and simulation of the selected processes under Aspen Plus
  - Process design and economics (OPEX / CAPEX) (Aspen Economics)
  - Environmental assessment and impacts characterization (SimaPro)
  - Integration and optimization

Thank you for your attention

Questions?

Ir Remi Chauvy

Ir Nicolas Meunier

Ph.D. Students

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