# Investigation of catalysts used for the regeneration step of an amine-based absorption-regeneration $CO_2$ capture process

Célia Pasté, Lionel Dubois, Diane Thomas

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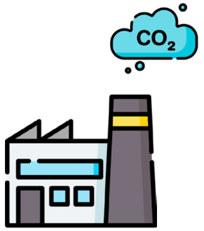
*Chemical & Biochemical Process Engineering Unit*

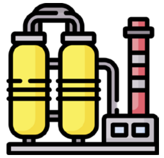
*Faculty of Engineering - University of Mons (Belgium)*

## CCUS chain



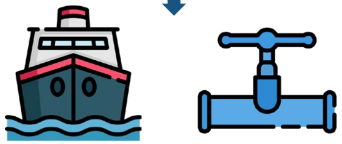

**$CO_2$ sources**

↓



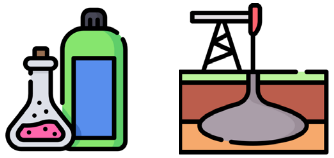
**$CO_2$ Capture**

↓



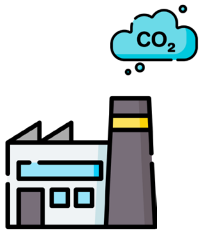
**Transportation**

↓



**Utilization or Storage**

## CCUS chain



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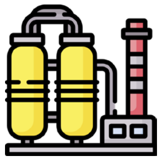

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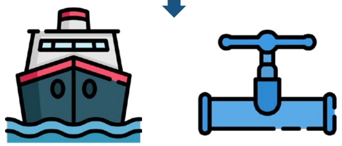
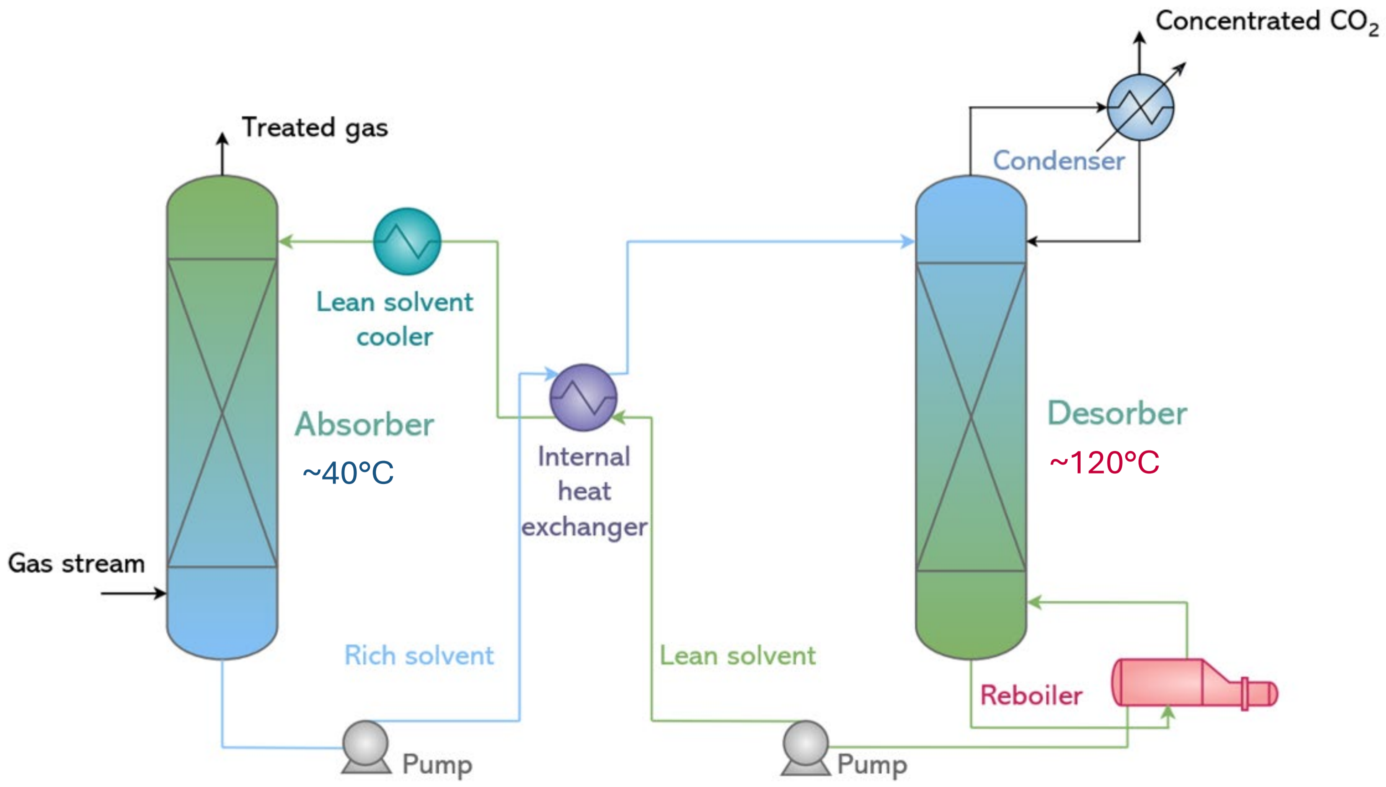


**Transportation**

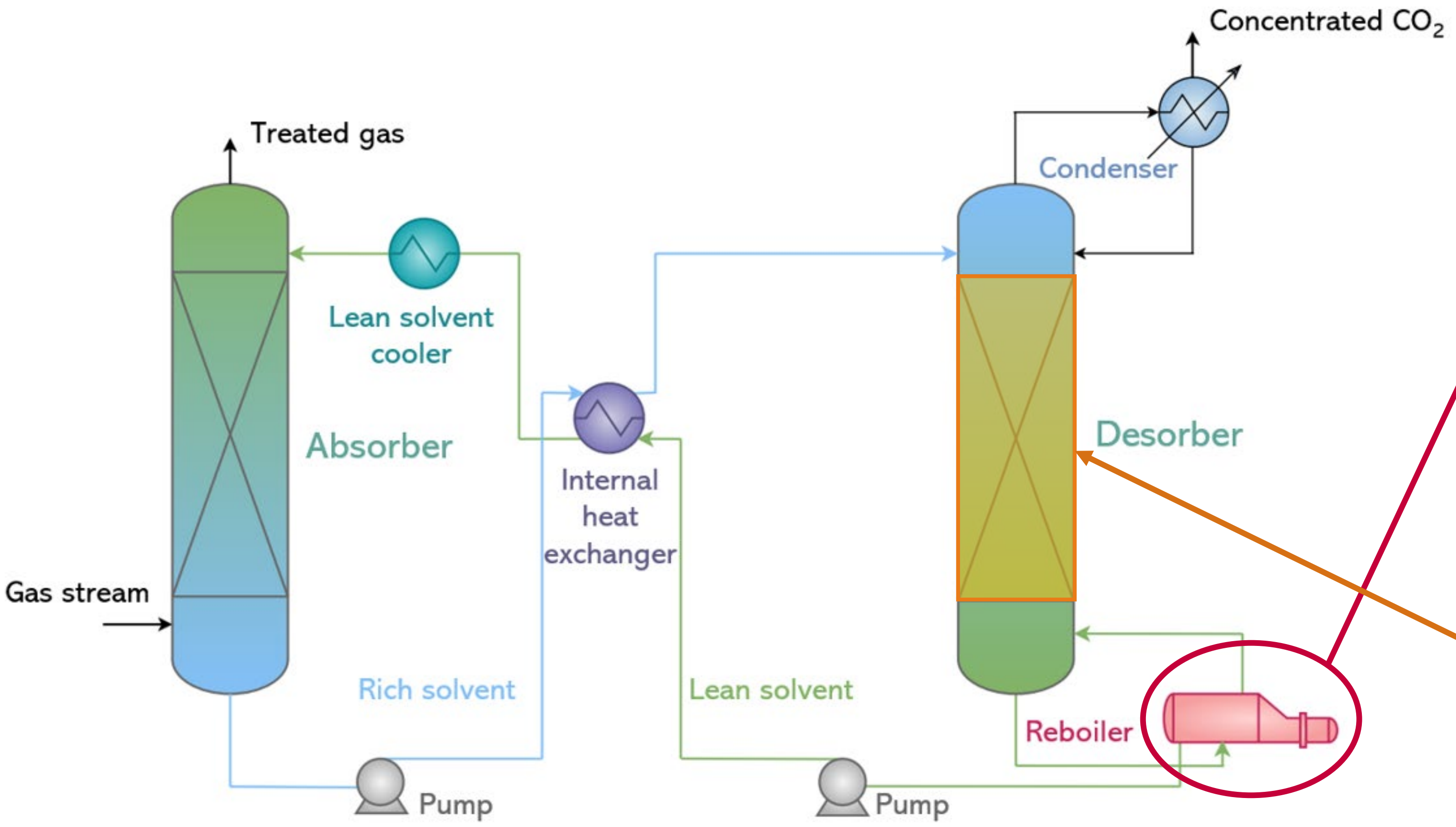
**Utilization or Storage**

### Absorption – Regeneration process using amine-based solvent




**Mature technology: TRL 9**

## Absorption – Regeneration process using amine-based solvent




**Drawback**

**High regeneration energy**
**3.5-4 GJ/t$CO_2$ (for MEA 30 wt%)**

**Reduction of energy consumption by:**

Innovative solvents

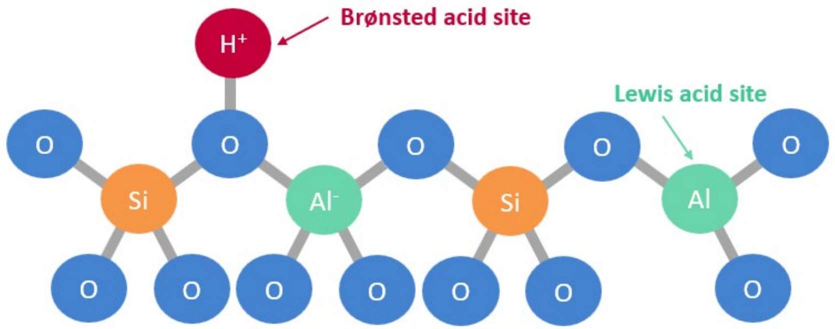
Process optimization

Use of catalyst

Catalyst

# Catalytic Regeneration

- **Innovative strategy introduced by *Idem et al. (2011)***




*Solid acid catalyst*

**Desorption reactions:** *(with primary and secondary amines)*

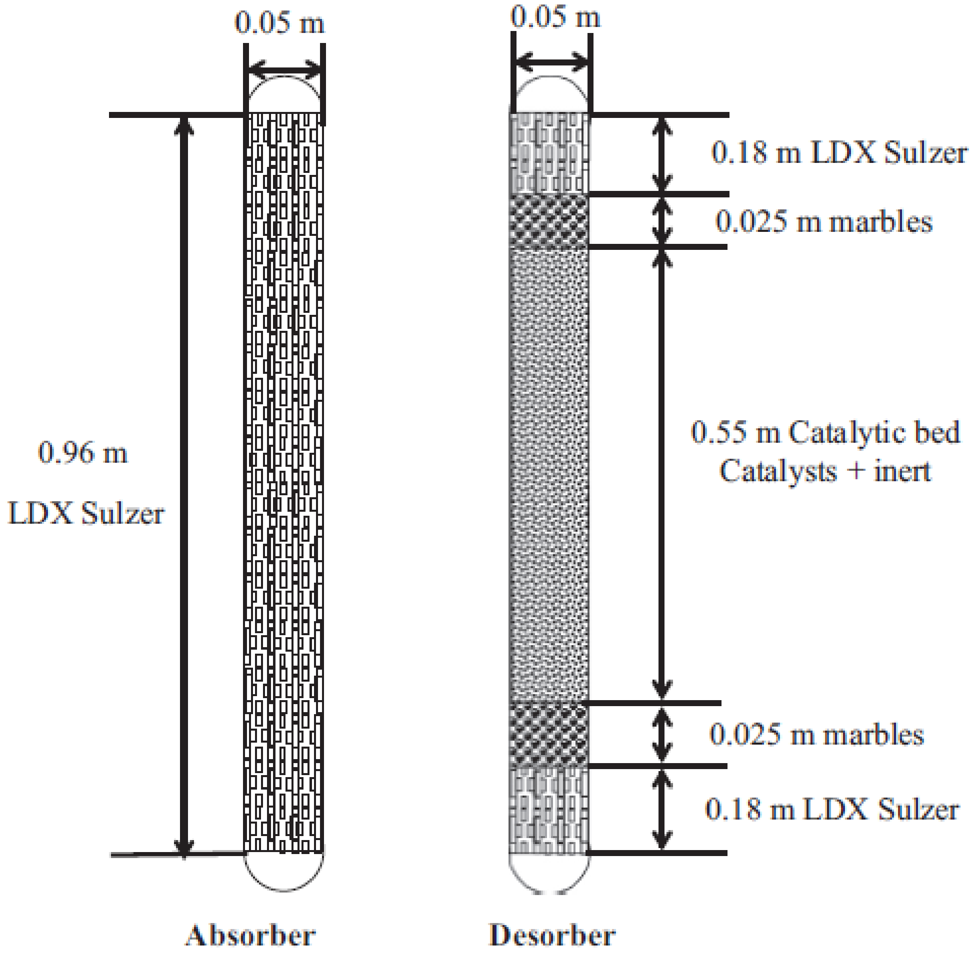
$$RN^+H_3 + H_2O \rightleftharpoons RNH_2 + H_3O^+$$

$$RNHCOO^- + H_3O^+ \rightleftharpoons RNH_2 + CO_2 + H_2O$$ *carbamate breakdown reaction*

$$RNHCOO^- + RN^+H_3 \rightleftharpoons 2RNH_2 + CO_2$$ ***Endothermic***

- **Micro-pilot study from literature**

*Sriang et al. (2017)*



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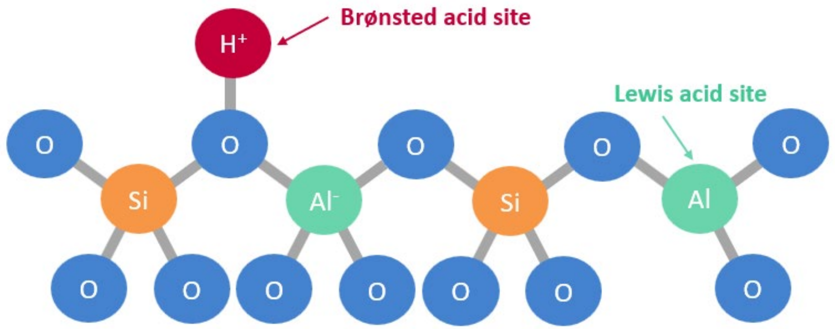


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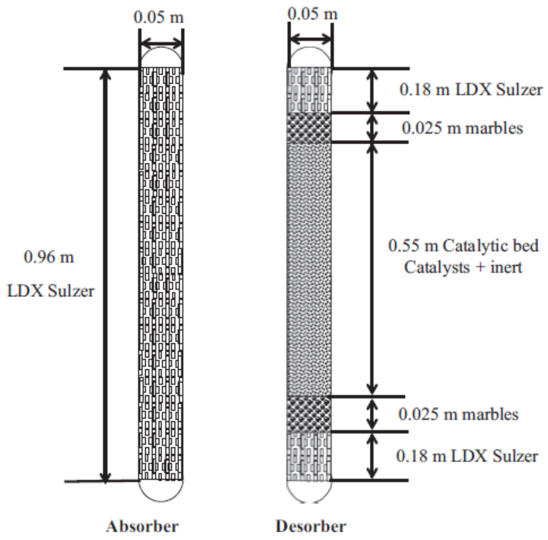


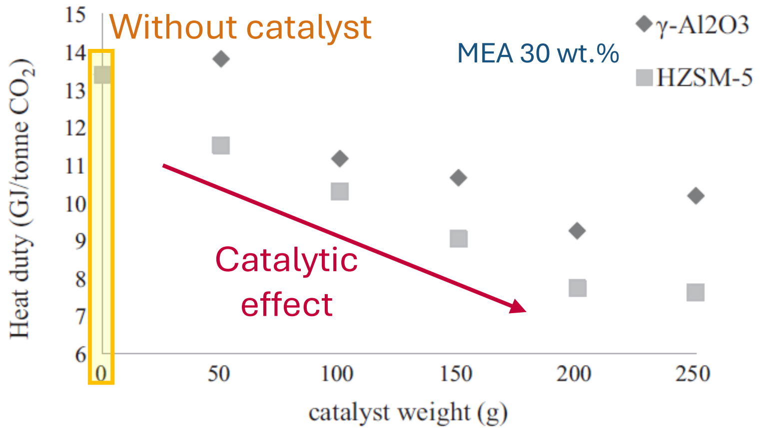

# Catalytic Regeneration

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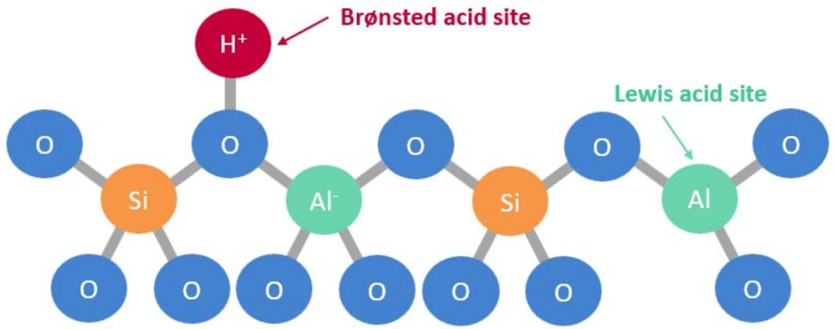


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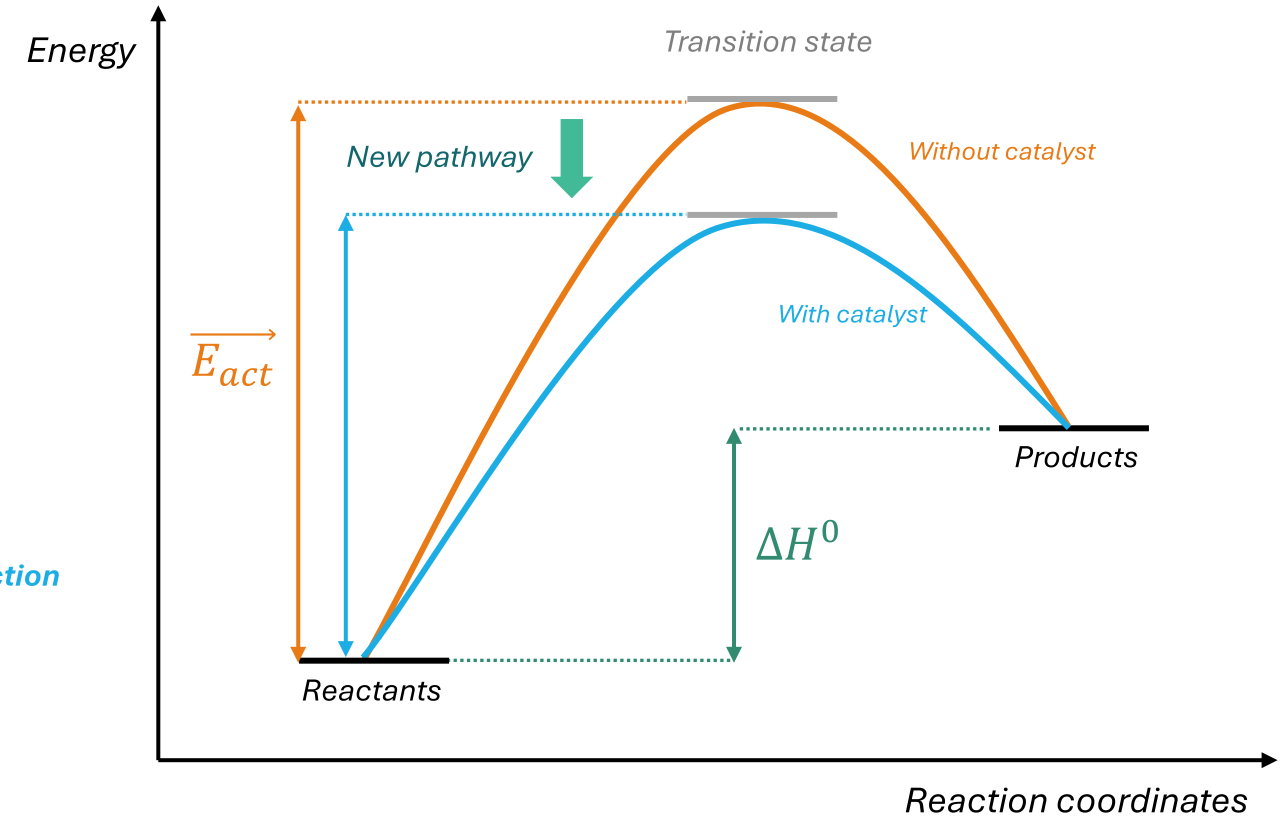
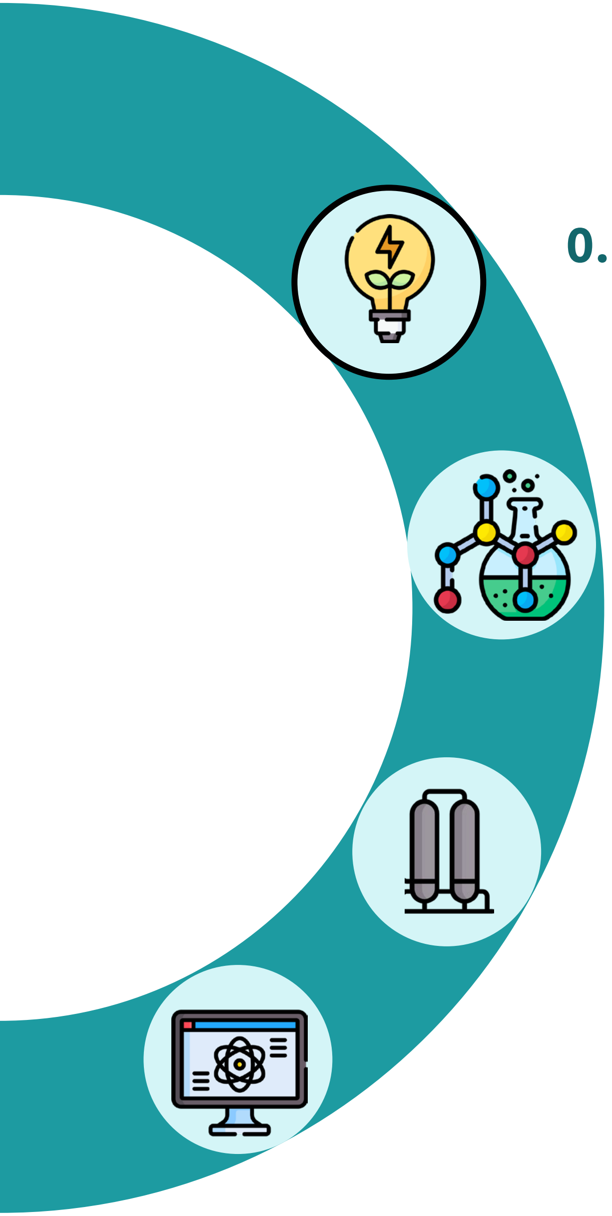
$$RNHCOO^{-} + RN^{+}H_3 \rightleftharpoons 2RNH_2 + CO_2$$ ***Endothermic***

- **Catalyst reduces Eact**

$$\nearrow r_j = k_0 \exp\left(\frac{-\overset{\nearrow}{E}_{act;j}}{RT}\right)$$



# Scope of the ATLANTIS project

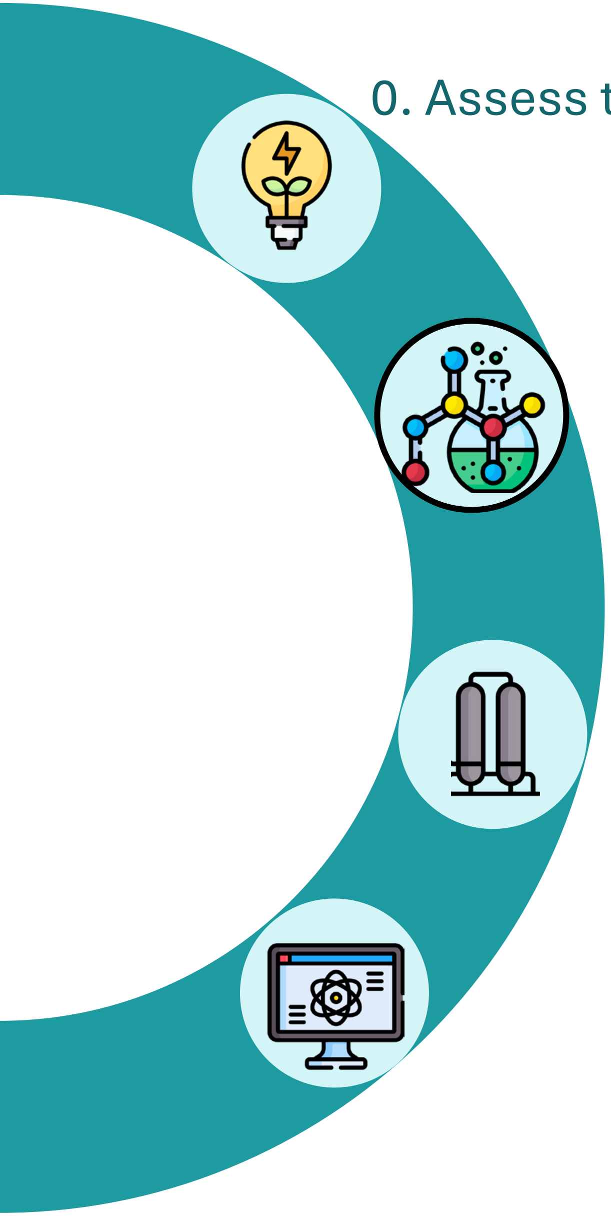


**0. Assess the potential energy gain from adding a catalyst**

**Simulations in Aspen Plus® V14**

→ **Effect on $E_{act}$ in a process ?**

# Scope of the ATLANTIS project



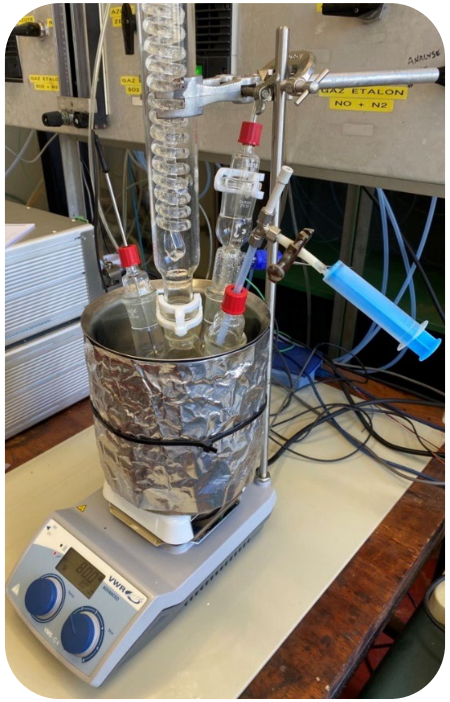
0. Assess the potential energy gain from adding a catalyst

**1. Identify solvent/catalyst pairs**

**Selection of candidates from literature data**

→ **Catalyst characterization** → 
- **Acidity**
- **Textural properties**

→ **Lab-scale experiments:**
- **Aqueous amine solvents**



*Batch reactor for regeneration*

# Scope of the ATLANTIS project

0. Assess the potential energy gain from adding a catalyst

1. Identify solvent/catalyst pairs

**2. Micro-pilot experiments**

**Powder**

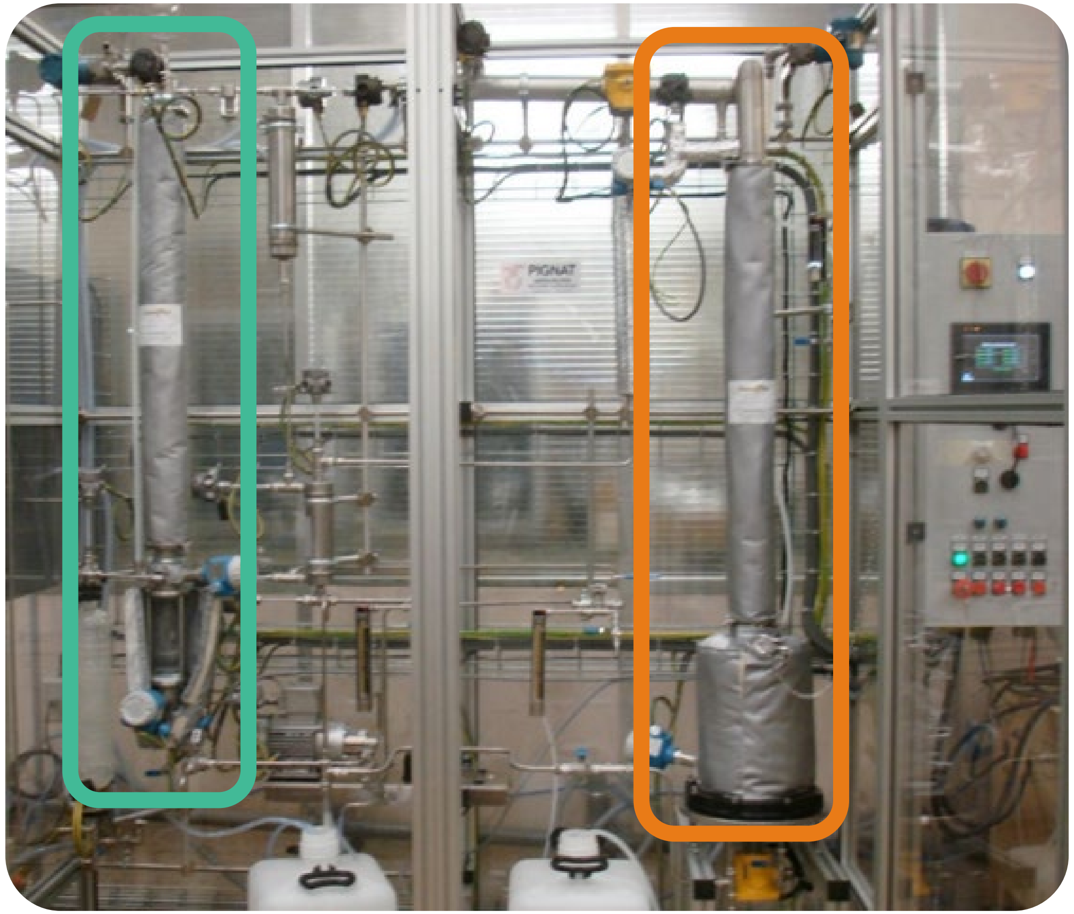
**Pellets**

***Continuous process***

**Absorption column**

**UMONS Micro-pilot unit**

**Regeneration column**



# Scope of the ATLANTIS project

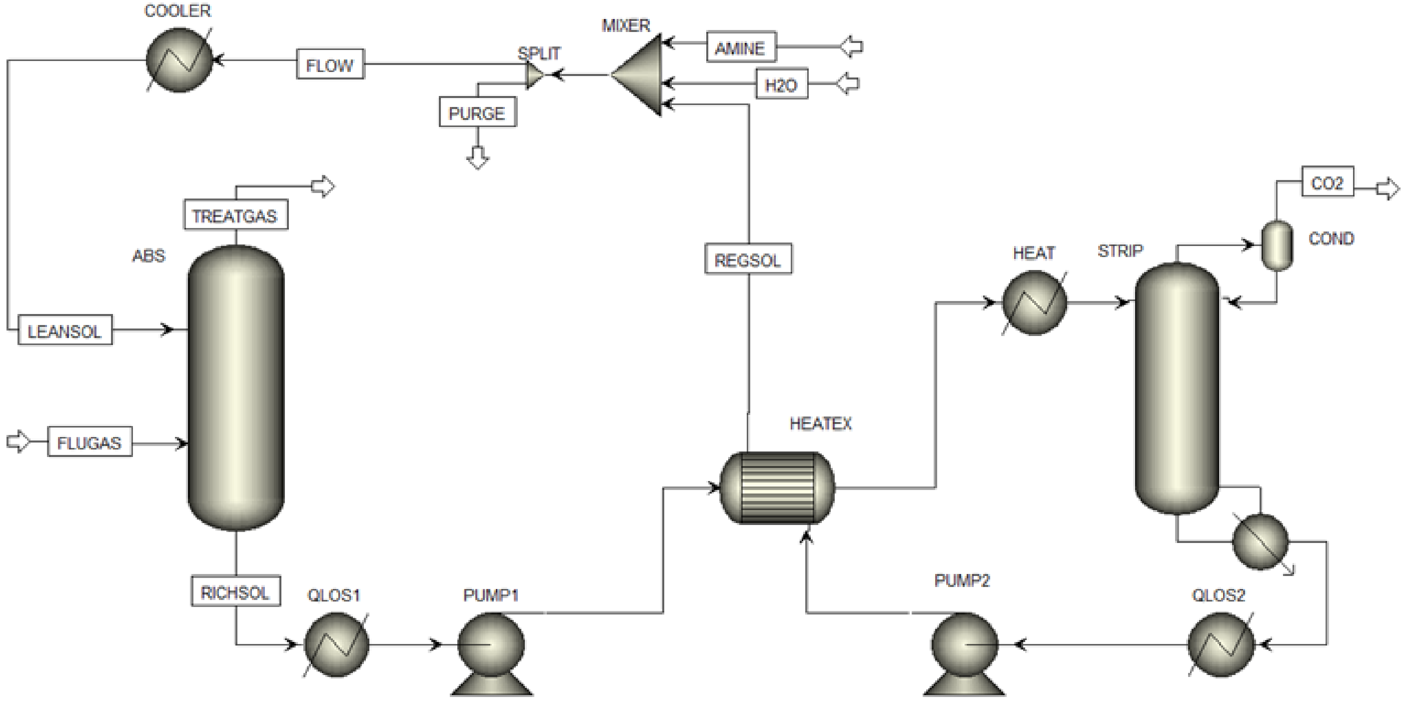
0. Assess the potential energy gain from adding a catalyst

1. Identify solvent/catalyst pairs

2. Micro-pilot experiments

**3. Simulations**

**Micro-pilot unit flowsheet**




**Kinetic parameters determination**

# Scope of the ATLANTIS project

**0. Assess the potential energy gain from adding a catalyst**

**1. Identify solvent/catalyst pairs**

**2. Micro-pilot experiments**

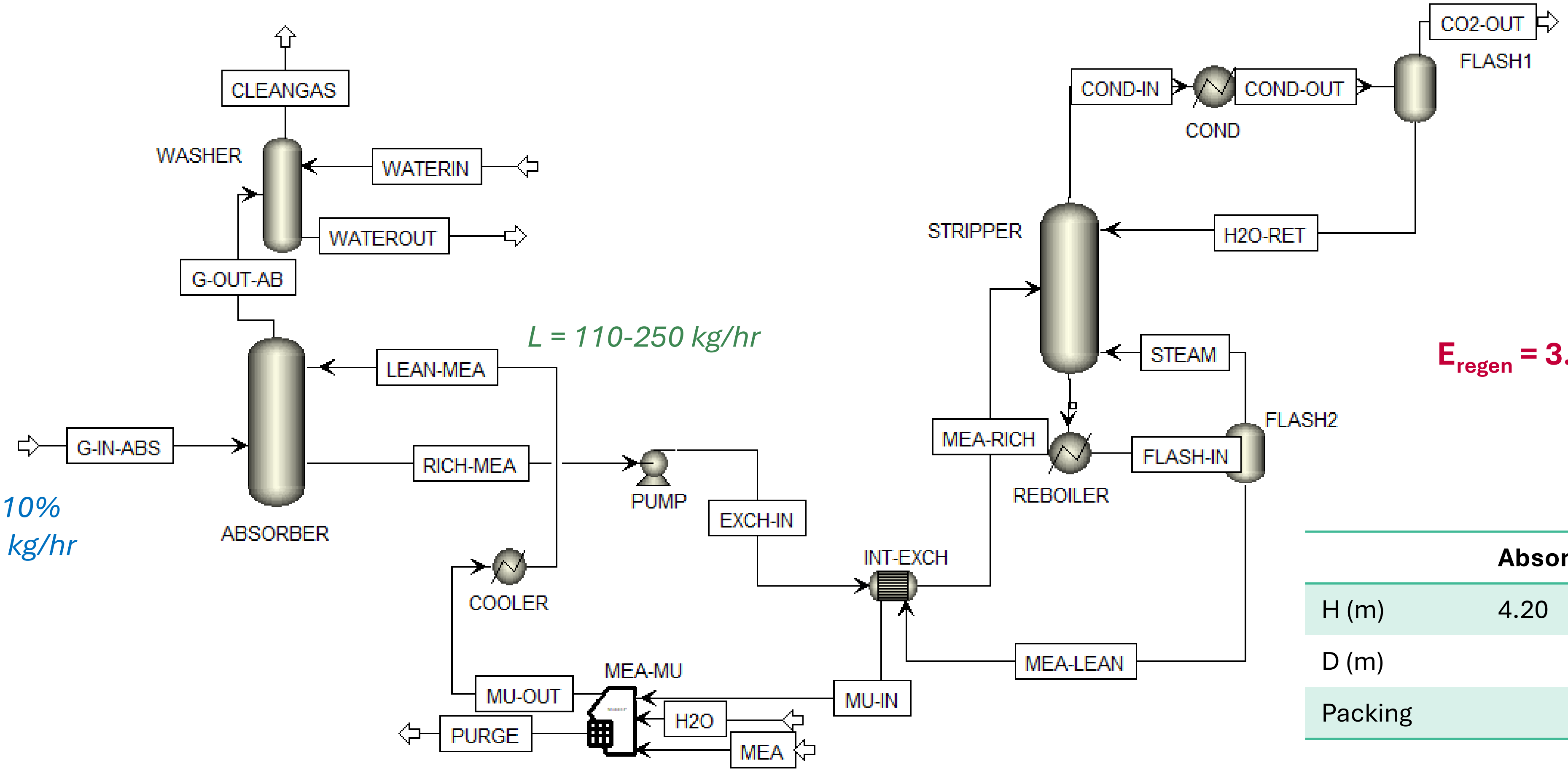
**3. Simulations**

# 0. Catalyst reduces $E_{act}$ – Energy gain ?

## Preliminary simulations in Aspen Plus® V14

- **Pilot plant with available data (Notz et al., 2012)**
- **Regeneration energy representative of the industrial scale**

| | |
|---|---|
| Solvent | MEA 30 wt% |
| Thermodynamic model | ENRTL-RK |




*L = 110-250 kg/hr*

*$y_{CO2} \approx 10\%$*
*G = 80 kg/hr*

**$E_{regen}$ = 3.58 GJ/t$CO_2$**

| | Absorbeur | Stripper |
|---|---|---|
| H (m) | 4.20 | 2.55 |
| D (m) | 0.125 | |
| Packing | BX 500 | |

# 0. Catalyst reduces $E_{act}$ – Energy gain ?

## Preliminary simulations in Aspen Plus® V14

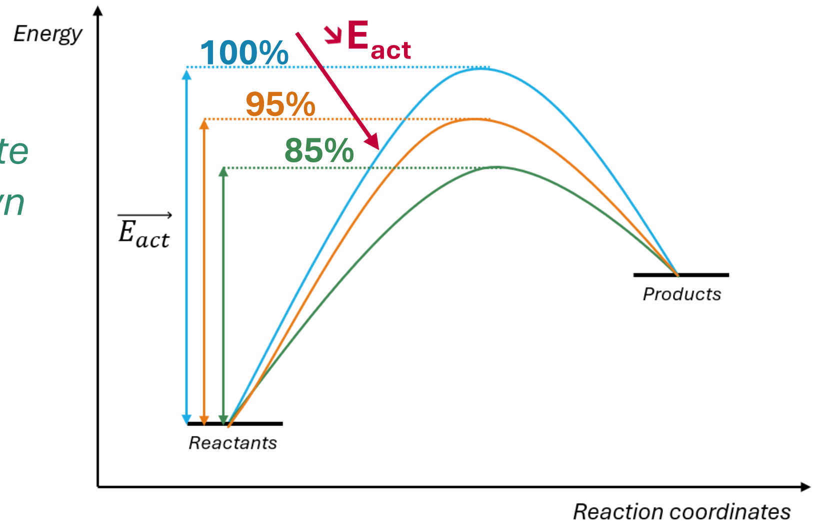
### Virtual integration of the catalyst into the process

Reactions set in the stripper:

**Kinetics:**

| |
|---|
| $MEA + CO_2 + H_2O \rightarrow MEACOO^- + H_3O^+$ |
| $MEACOO^- + H_3O^+ \rightarrow MEA + CO_2 + H_2O$ |
| $CO_2 + OH^- \rightarrow HCO_3^-$ |
| $HCO_3^- \rightarrow CO_2 + OH^-$ |

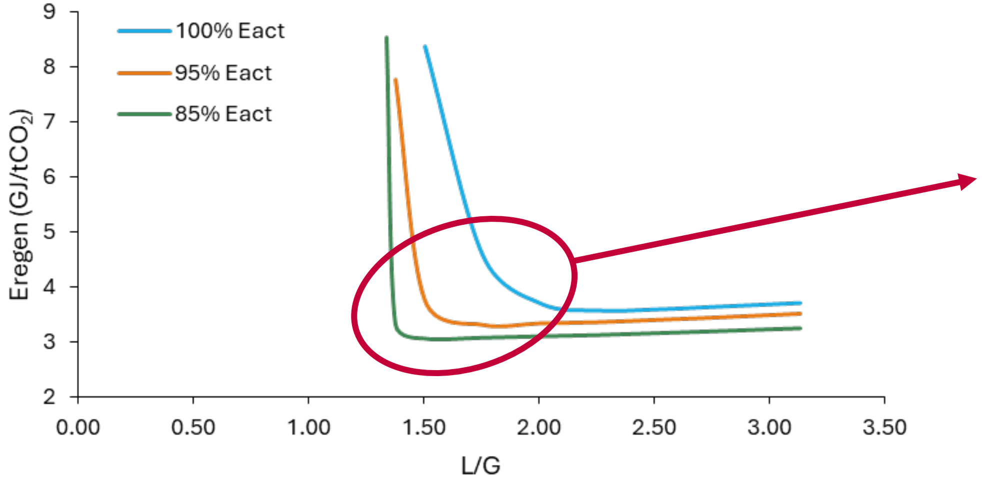
*Carbamate breakdown*

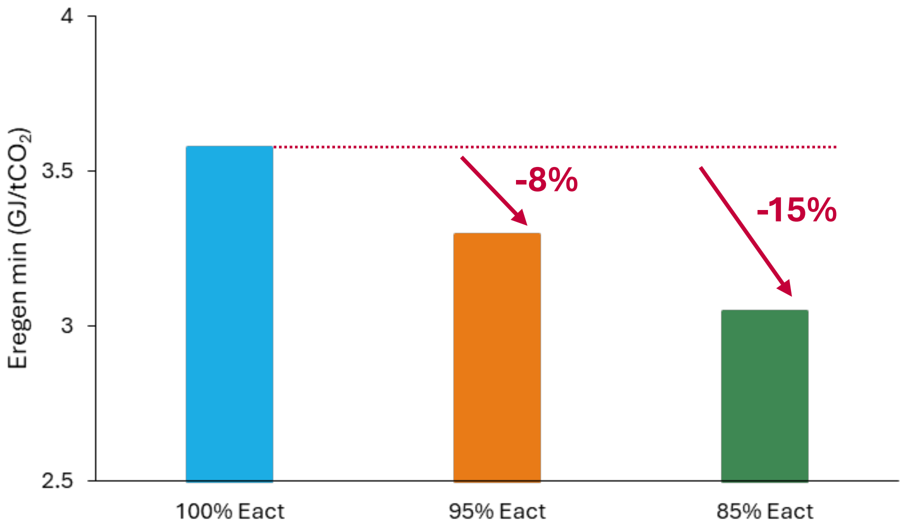



## Influence of $E_{act}$:

**Performance:**

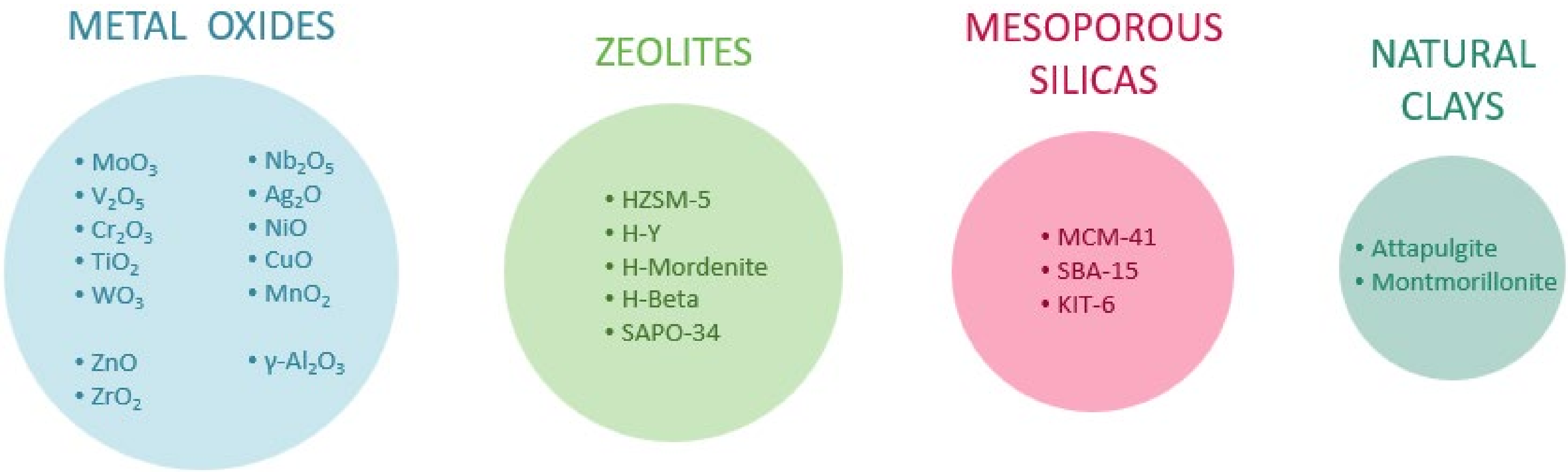
| | |
|---|---|
| Capture rate | 95% |
| Purity | 99.6% |



## Selection of candidates from literature data

**23 candidates**



# 1. Identify solvent/catalyst pairs

**Selection** – Characterization - Lab scale experiments

## Selection of candidates from literature data

**23 candidates**

METAL OXIDES

- $MoO_3$
- $V_2O_5$
- $Cr_2O_3$
- $TiO_2$
- $WO_3$
- $Nb_2O_5$
- $Ag_2O$
- NiO
- CuO
- $MnO_2$
- ZnO
- $ZrO_2$
- $\gamma$-$Al_2O_3$

ZEOLITES

- HZSM-5
- H-Y
- H-Mordenite
- H-Beta
- SAPO-34

MESOPOROUS SILICAS

- MCM-41
- SBA-15
- KIT-6

NATURAL CLAYS

- Attapulgite
- Montmorillonite

**4 criteria**

- Performances based on literature data
- Physicochemical properties
- Economic criterion
- Safety criterion

**Selected catalysts**

5 METAL OXIDES: $\gamma$-$Al_2O_3$, $ZrO_2$, $Nb_2O_5$, $Cr_2O_3$, $MoO_3$

3 ZEOLITES: H-ZSM5, H-Mord, H-Beta

# 1. Identify solvent/catalyst pairs



## Selection of candidates from literature data

### 23 candidates

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- $MoO_3$
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- NiO
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17th International Conference on Greenhouse Gas Control Technologies, GHGT-17

20th -24th October 2024 Calgary, Canada

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*Chemical and Biochemical Process Engineering Unit, University of Mons (UMONS), Place du Parc 20, 7000 Mons*

# 1. Identify solvent/catalyst pairs



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**4 criteria**

- Performances based on literature data
- Physicochemical properties
- Economic criterion
- Safety criterion

**Selected catalysts**

- $\gamma$-$Al_2O_3$
- H-ZSM5

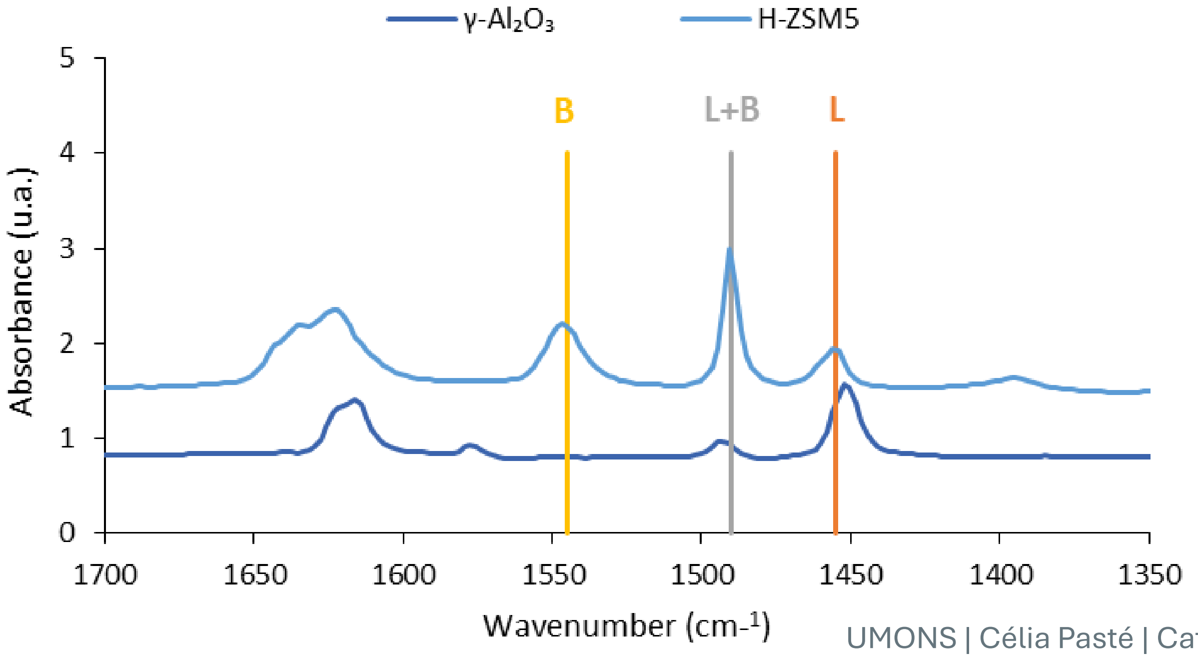
# Catalyst characterization

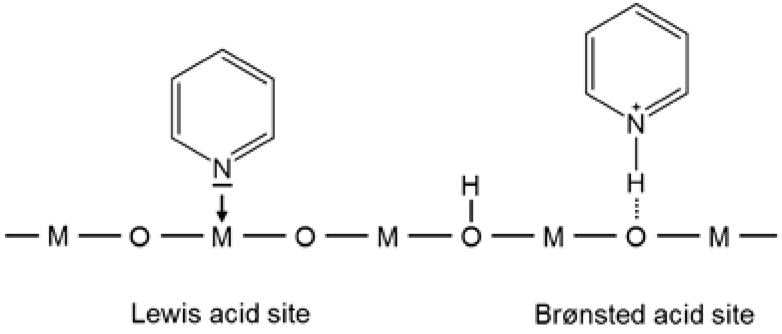
## Acidity: $NH_3$-Temperature Programmed Desorption (TPD)

- $NH_3$ Adsorption (150°C)
- $NH_3$ Desorption 150-800°C (10°C/min)

| | $\gamma$-$Al_2O_3$ | H-ZSM5 |
|---|---|---|
| Weak [mmol/g] | 0 | 0 |
| Medium [mmol/g] | 0.056 | 0.290 |
| Strong [mmol/g] | 0 | 1.292 |
| **Total [mmol/g]** | **0.056** | **1.582** |

## Acidity Lewis and Brønsted sites: Pyridine-IR




| | $\gamma$-$Al_2O_3$ | H-ZSM5 |
|---|---|---|
| Lewis sites [µmol/g] | 99.3 | 170.3 |
| Brønsted sites [µmol/g] | 0.0 | 522.5 |

The catalyst will be in contact with the solvent

## Catalyst characterization

### Textural properties

| | $\gamma$-$Al_2O_3$ | H-ZSM5 |
|---|---|---|
| Surface area (BET) [$m^2/g$] | 131.19 ± 0.46 | 421.90 ± 1.26 |
| $S_{microporous}$ [$m^2/g$] | 41.09 | 319.90 |
| Pore volume (Halsey) [$cm^3/g$] | 0.26 | 0.11 |

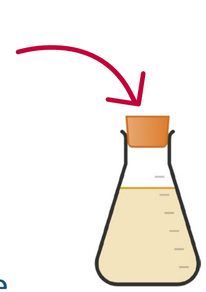
*Tristar II 3020 Micrometrics®*

# Lab-scale experiments

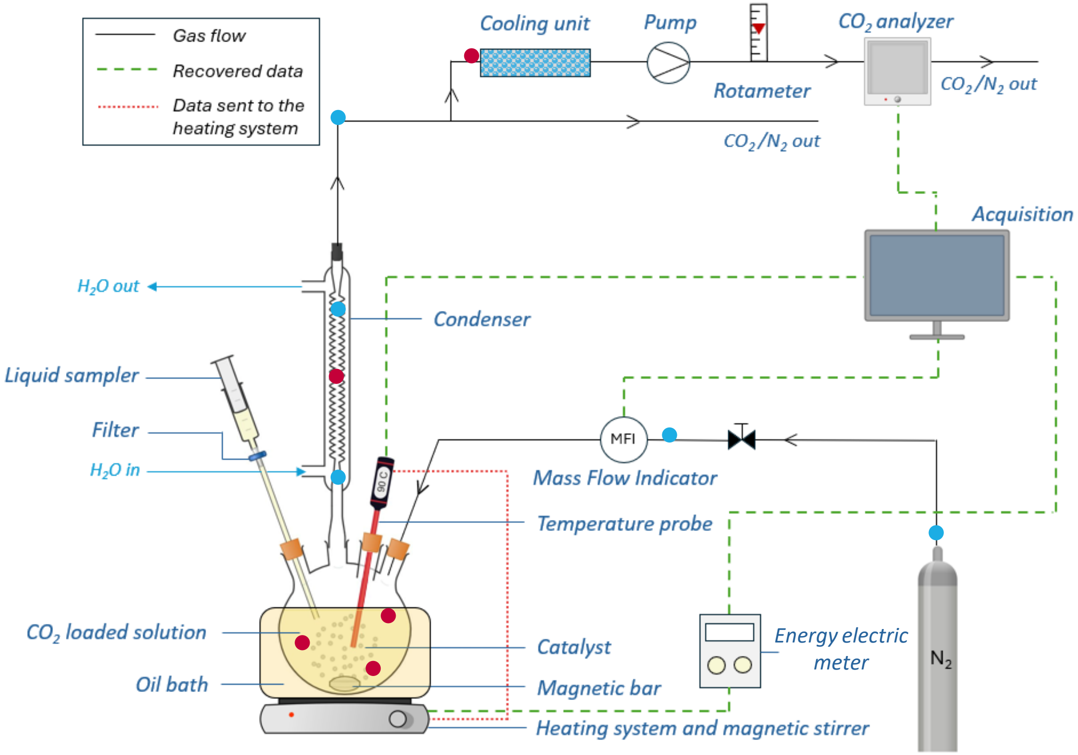
## Materials and methods

1. **Amine-based solvent preparation**
   - → aq. MEA 30 wt%
   - → aq. CESAR1 (AMP 27 wt% + PZ 13 wt%)

2. **$CO_2$ loading (absorption)**
   - → Maximal $CO_2$ loading
     - MEA: ≈ 0.60 mol $CO_2$/ mol Amine
     - CESAR1: ≈ 0.80 mol $CO_2$/ mol Amine




3. **$CO_2$ Desorption**



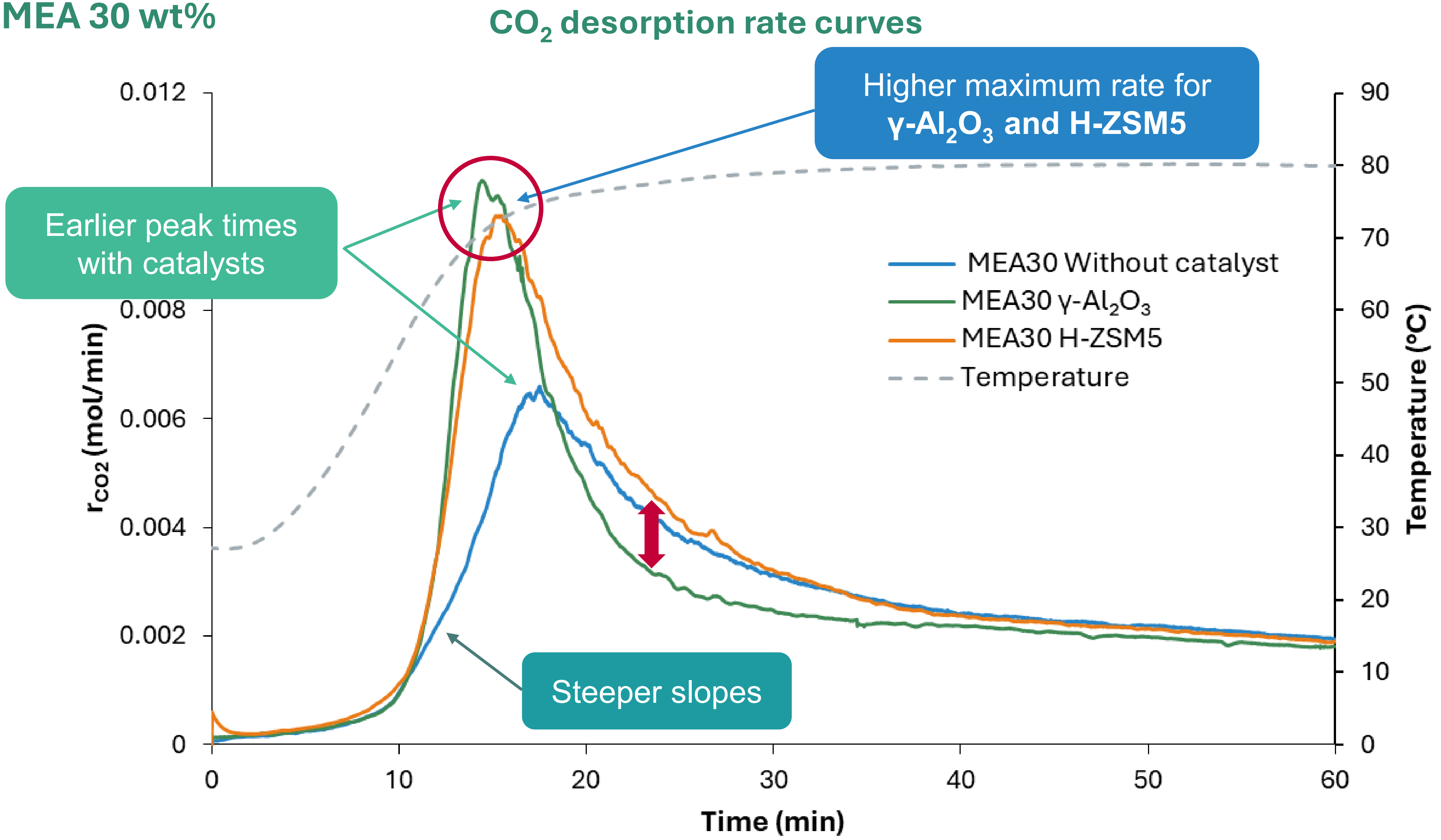

**Operating conditions:**

| | |
|---|---|
| **V solution** | 300 mL |
| **$N_2$ flow rate** | 0.8 NL/min |
| **Desorption temperature** | 80 °C |
| **Catalyst concentration** | 25 g/L |
| **Desorption time** | 60 min |
| **Stirring speed** | 300 rpm |

# 1. Identify solvent/catalyst pairs

## Lab-scale experiments

### Results – MEA 30 wt%

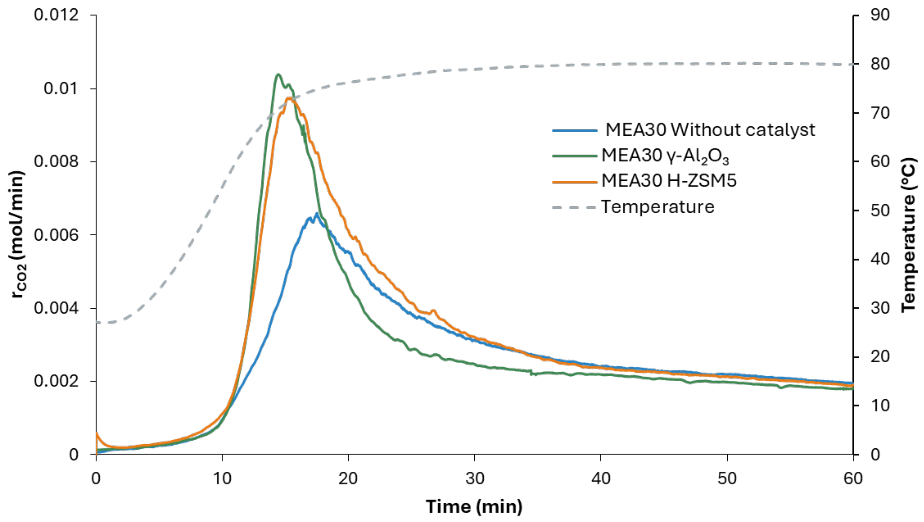


# Lab-scale experiments

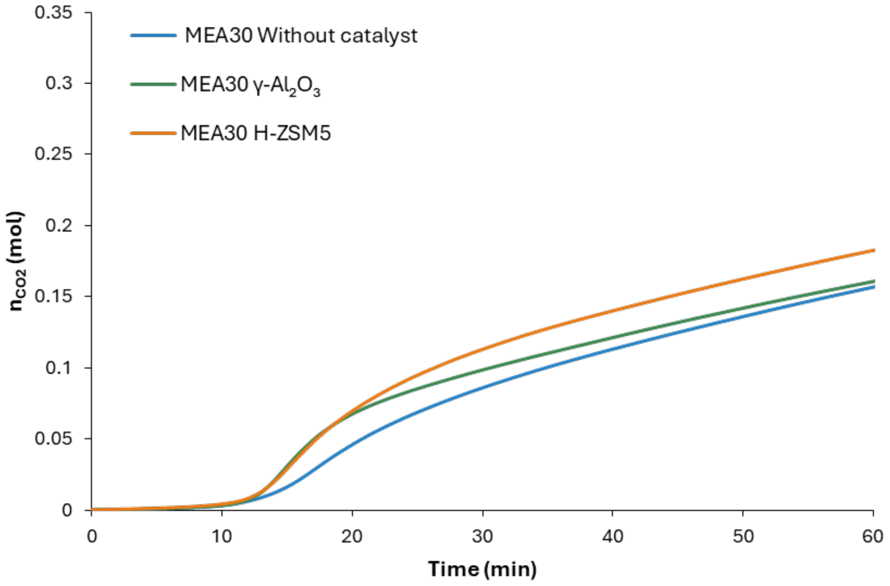
## Results – MEA 30 wt.%

$$n_{CO_{2,desorbed}}(t) = \int_0^t r_{CO_2}\, dt$$

CO$_2$ desorption rate curves

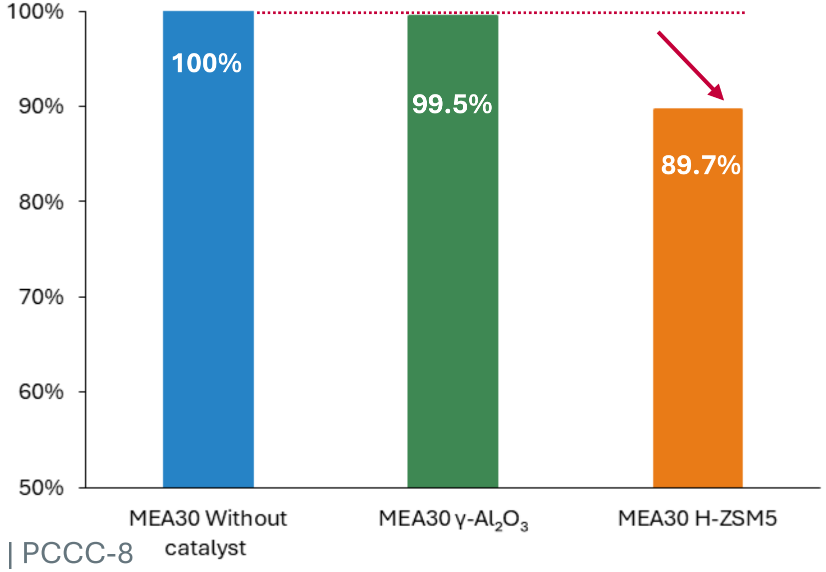



Amount of CO$_2$ desorbed




$$HD = \frac{Energy\ input}{n_{CO_{2,desorbed}}}$$

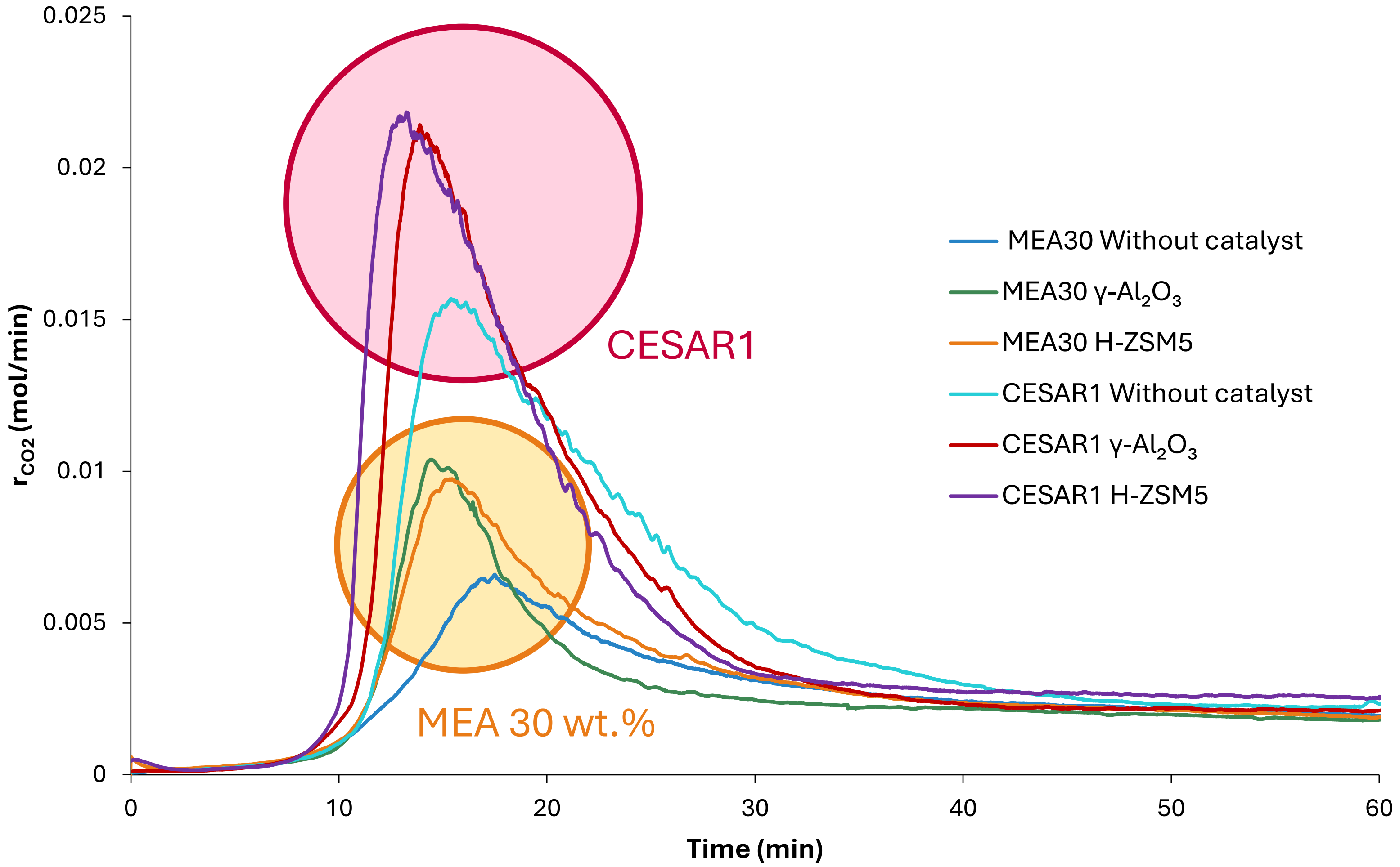
Relative Heat Duty



# 1. Identify solvent/catalyst pairs

## Lab-scale experiments

### Results - MEA 30 wt.% - CESAR1



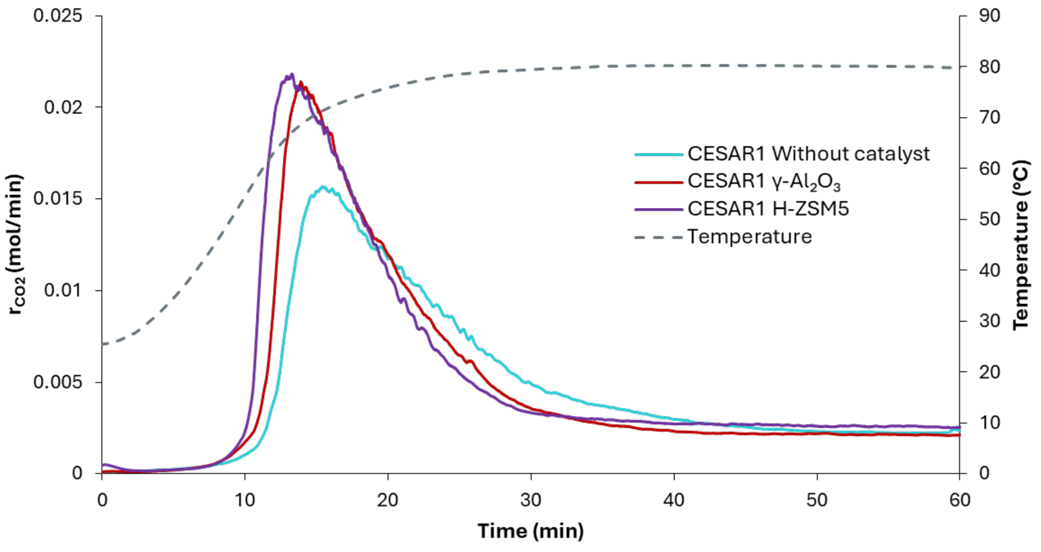
# 1. Identify solvent/catalyst pairs

## Lab-scale experiments

### Results - CESAR1

$$n_{CO_{2,desorbed}}(t) = \int_0^t r_{CO_2}\, dt$$

$CO_2$ desorption rate curves

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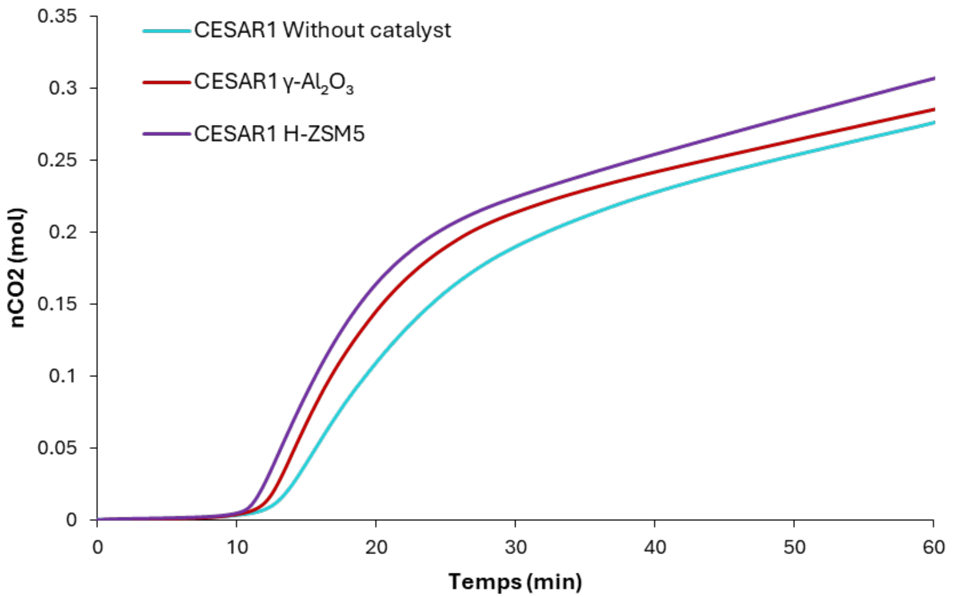


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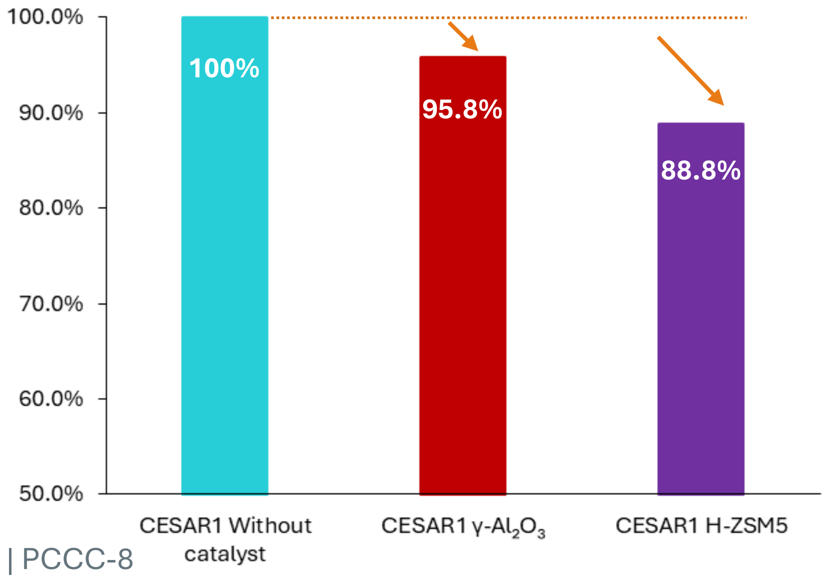
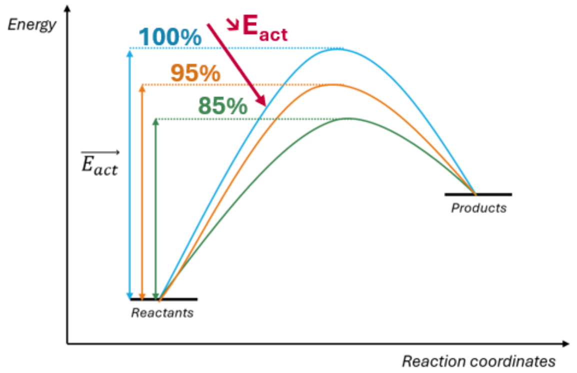
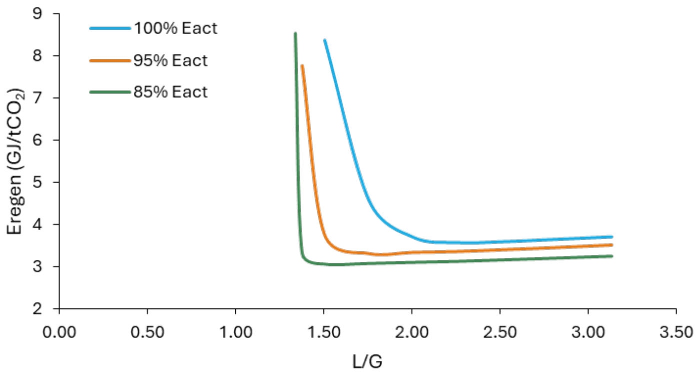


# Conclusion

## Catalyst reduces $E_{act}$ – Energy gain ?

$E_{activation}$ ↘ → $E_{regen}$ ↘



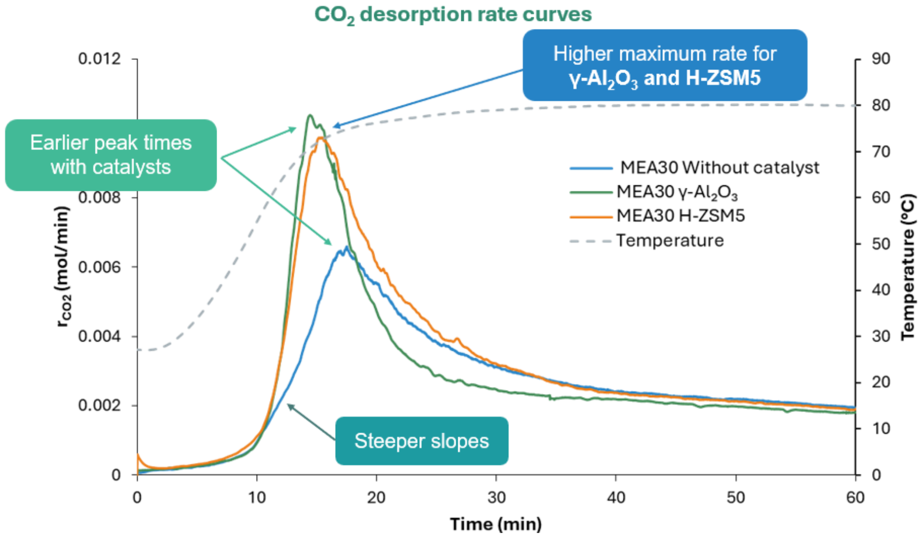



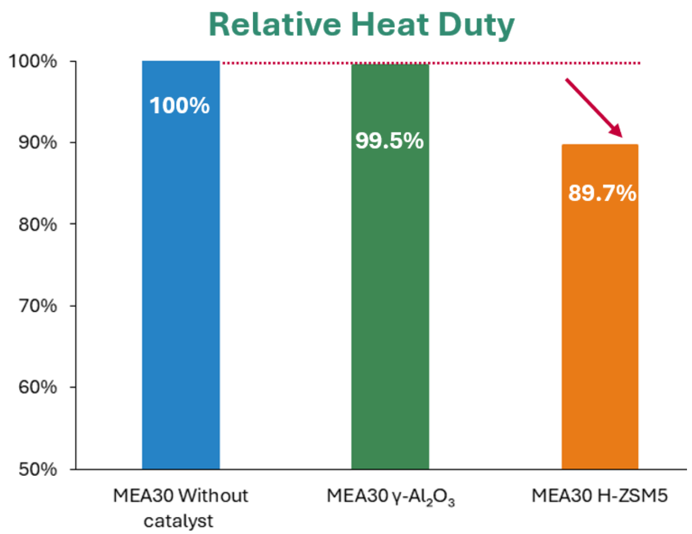

## Catalyst characterization

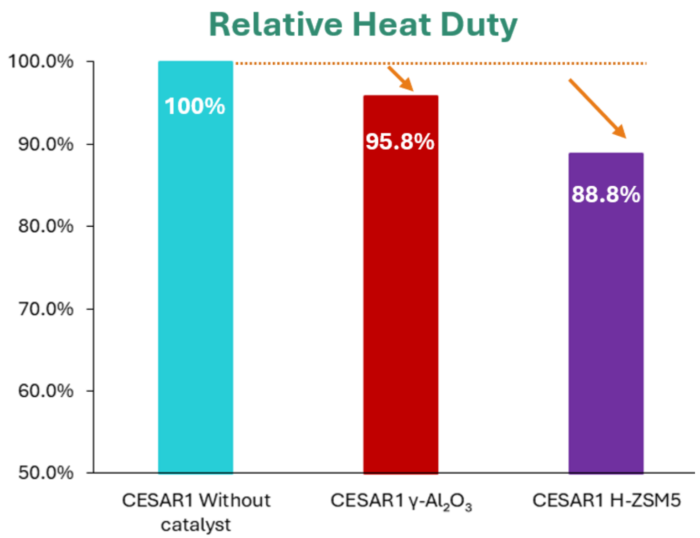
| | Acidity | Surface area |
|---|---|---|
| $\gamma\text{-}Al_2O_3$ | ✗ | Mostly **mesoporous** |
| H-ZSM5 | ✓ | Mostly **microporous** |

Better results with a better acidity

## Lab-scale results



# Perspectives

## 0. Assess the potential energy gain from adding a catalyst

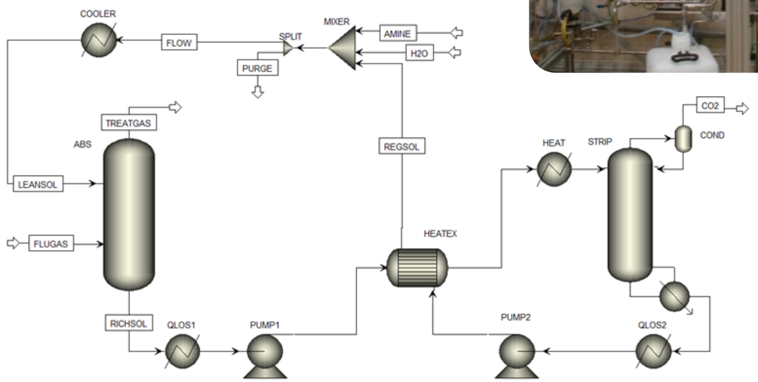
## 1. Identify solvent/catalyst pairs

5 METAL OXIDES
- $\gamma$-$Al_2O_3$
- $ZrO_2$
- $Nb_2O_5$
- $Cr_2O_3$
- $MoO_3$

3 ZEOLITES
- H-ZSM5
- H-Mord
- H-Beta

## 2. Micro-pilot experiments

## 3. Simulations



THANKS VERY MUCH FOR YOUR ATTENTION!

QUESTIONS?

PCCC-8 conference, Marseille, France - Session 4B – 17th September 2025

**Célia Pasté (PhD Student)**

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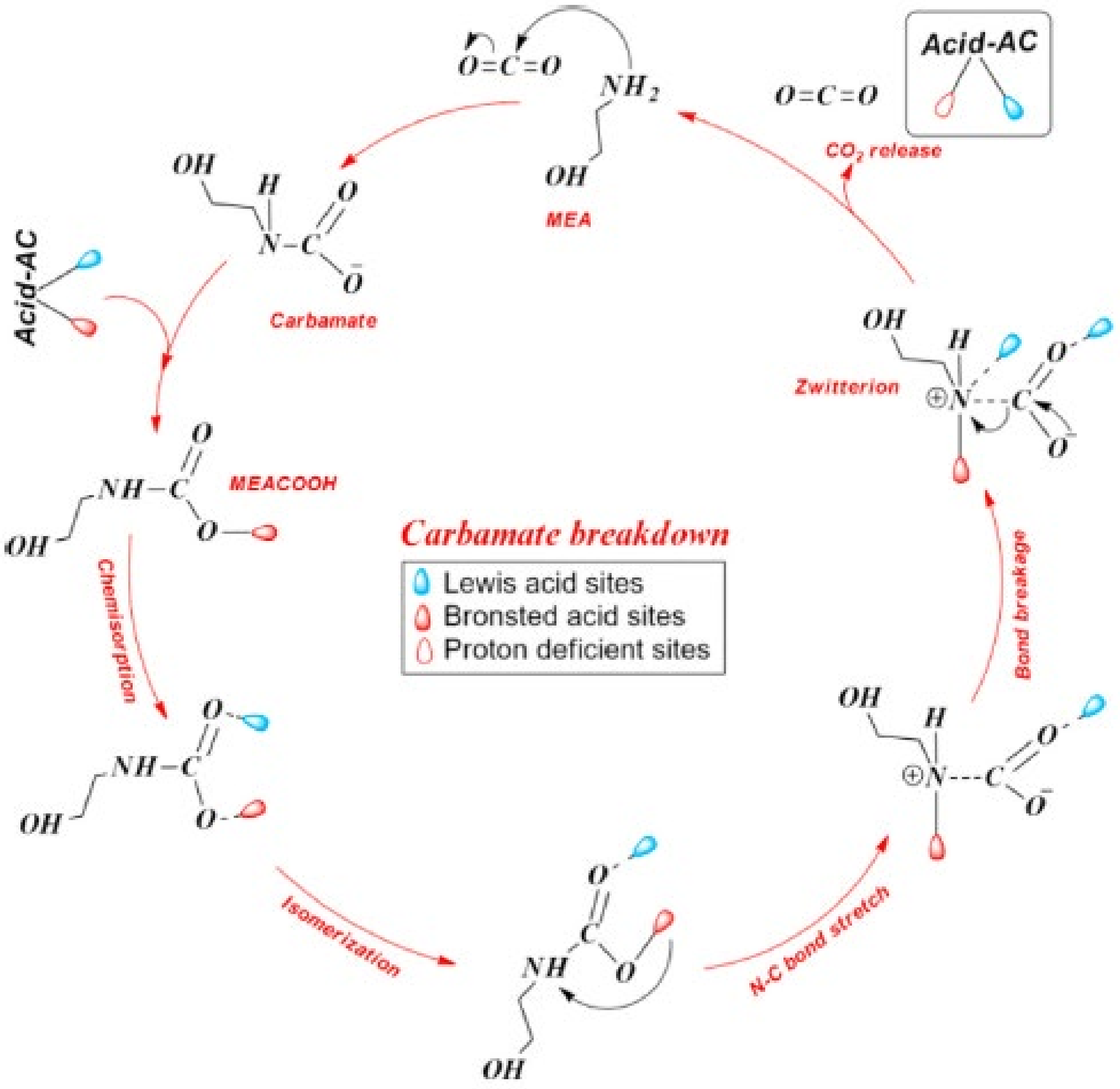
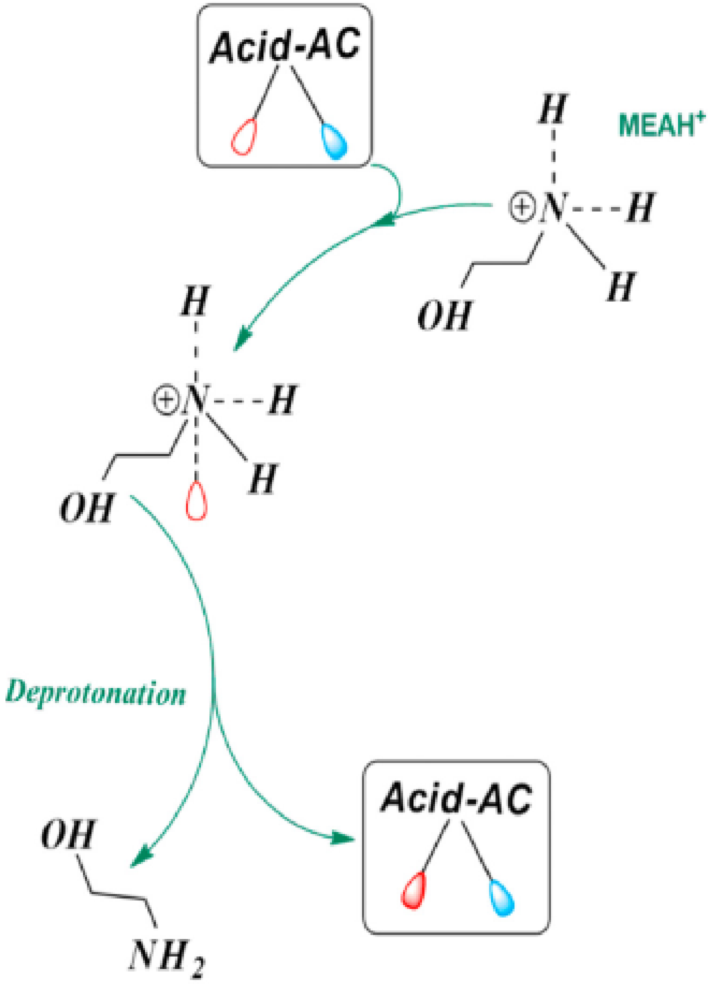
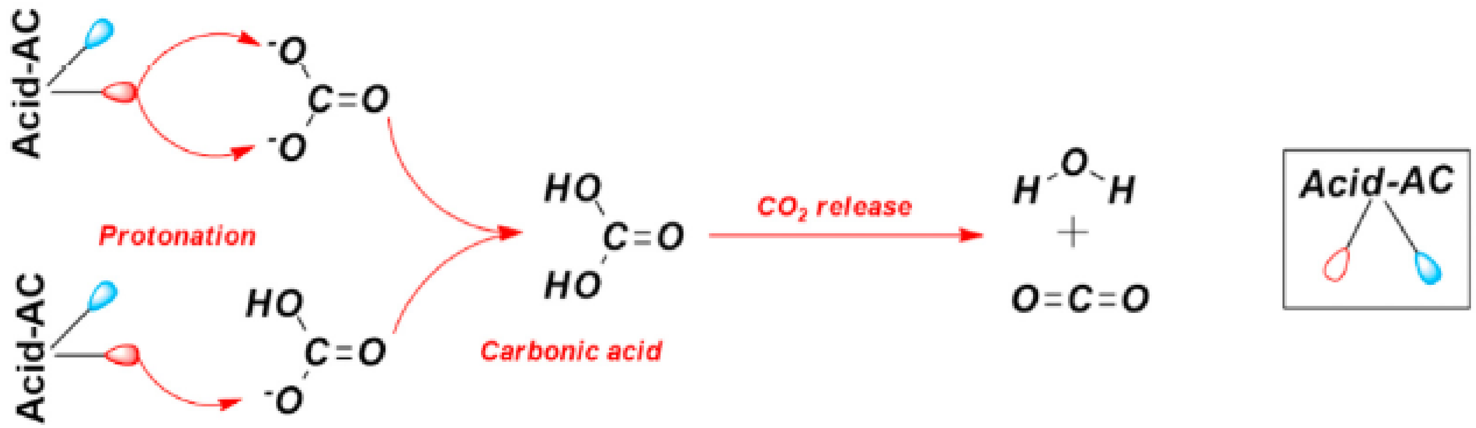
*Faculty of Engineering - University of Mons (Belgium)*


Acid-AC
O=C=O
MEA
CO2 release
Carbamate
Acid-AC
MEACOOH
Carbamate breakdown
Lewis acid sites
Bronsted acid sites
Proton deficient sites
Zwitterion
Bond breakage
Chemisorption
Isomerization
N-C bond stretch


Acid-AC
MEAH+
H
N
H
H
OH
H
N
H
H
OH
Deprotonation
OH
NH2
Acid-AC



Acid-AC
Protonation
Acid-AC
Carbonic acid
CO2 release
Acid-AC