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Alaa Hajlaoui, J-M Andanson, L Rodier, Y Coulier, W Khay, et al.. Suitable working fluids for CO<sub>2</sub>-based absorption chillers. International Seminar on Sustainable Refrigeration, Jun 2024, Cnam Paris, France. hal-04731436

**HAL Id: hal-04731436**

**<https://hal.science/hal-04731436v1>**

Submitted on 10 Oct 2024

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> International Seminar on Sustainable Refrigeration 2024

# Suitable working fluids for CO<sub>2</sub>-based absorption chillers

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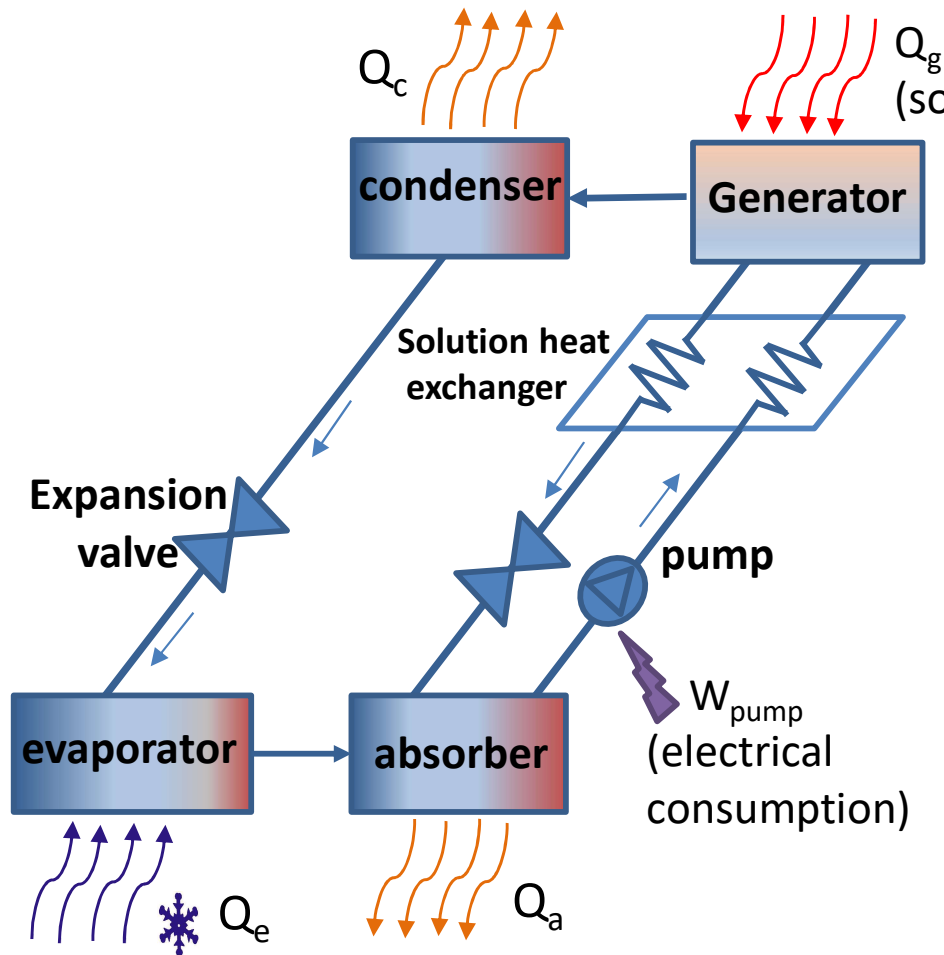
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# Context

## > Conventional absorption refrigeration process



- Uses low-grade heat
- Uses natural refrigerants
- Conventional working fluid pairs
  - $\text{NH}_3 + \text{H}_2\text{O}$
  - $\text{H}_2\text{O} + \text{LiBr}$
  - Outstanding thermodynamic properties
  - But...

$\text{NH}_3$  /  $\text{H}_2\text{O}$

Corrosion  
Toxicity  
Rectifier

$\text{H}_2\text{O}$  /  $\text{LiBr}$

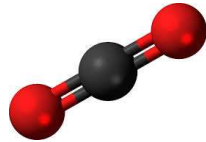
Corrosion  
Crystallization  
 $T_{\text{evap}} > 0^\circ\text{C}$

# Objectives

## > Improving of working fluid pairs

Refrigerant

**CO<sub>2</sub> (R744)**



- ODP=0
- GWP=1
- Non-flammable
- Non-toxic
- High thermal conductivity
- High latent heat
- Cooling below 0°C

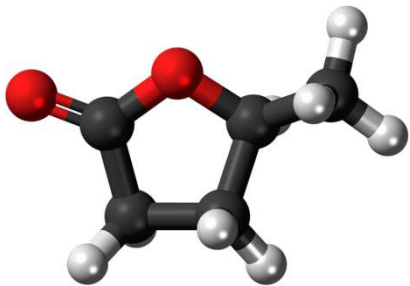
+ Absorbent

**Bio-Based Solvent  
(BBS)**

- Non-hazardous
- Low toxicity
- Environmentally benign
- Biodegradable

# Objectives

- > Required absorbent thermophysical properties :
  - Low volatility compared to the refrigerant
  - No crystallization or solidification
  - Low heat of mixing of refrigerant and absorbent
  - High solubility of the refrigerant in the absorbent

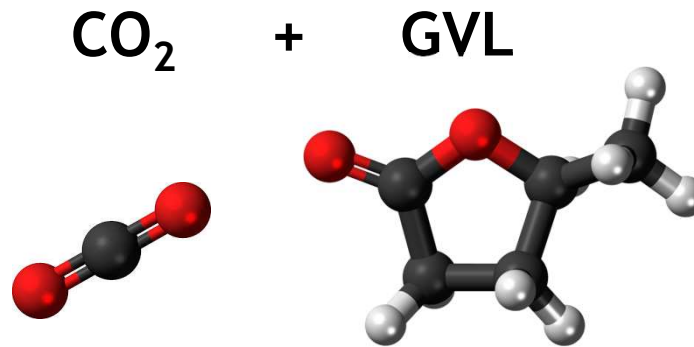


**γ-valerolactone**

Abbreviation	MW /g·mol <sup>-1</sup>	Melting point /°C	Boiling point /°C	Viscosity /cP	Flash point /°C
GVL	100.12	-31.15	206.85	2.2	98.35

# Thermodynamic characterization

## > Literature experimental data



Available Vapour Liquid Equilibria (VLE) data ( $T, P, x$ )	
Low pressure [1]	283.15 – 323.15 K and 0.04 – 0.56 MPa
High pressure [2]	308.2 – 393.2 K and 7.25 – 24.41 MPa

Solubility (VLE)

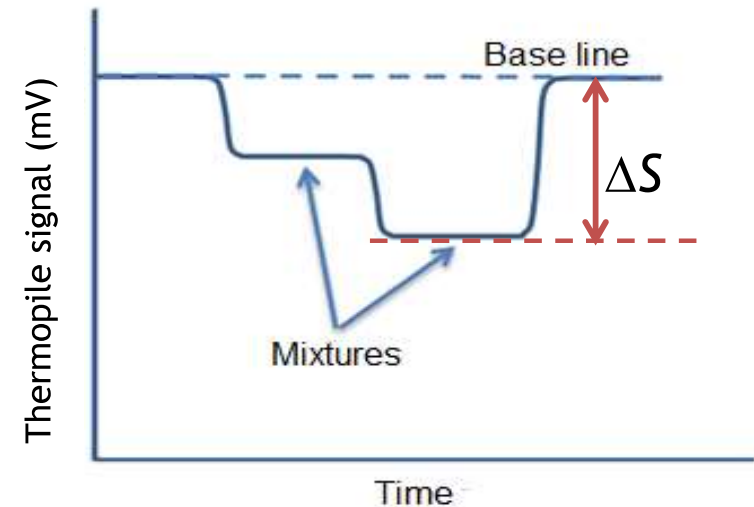
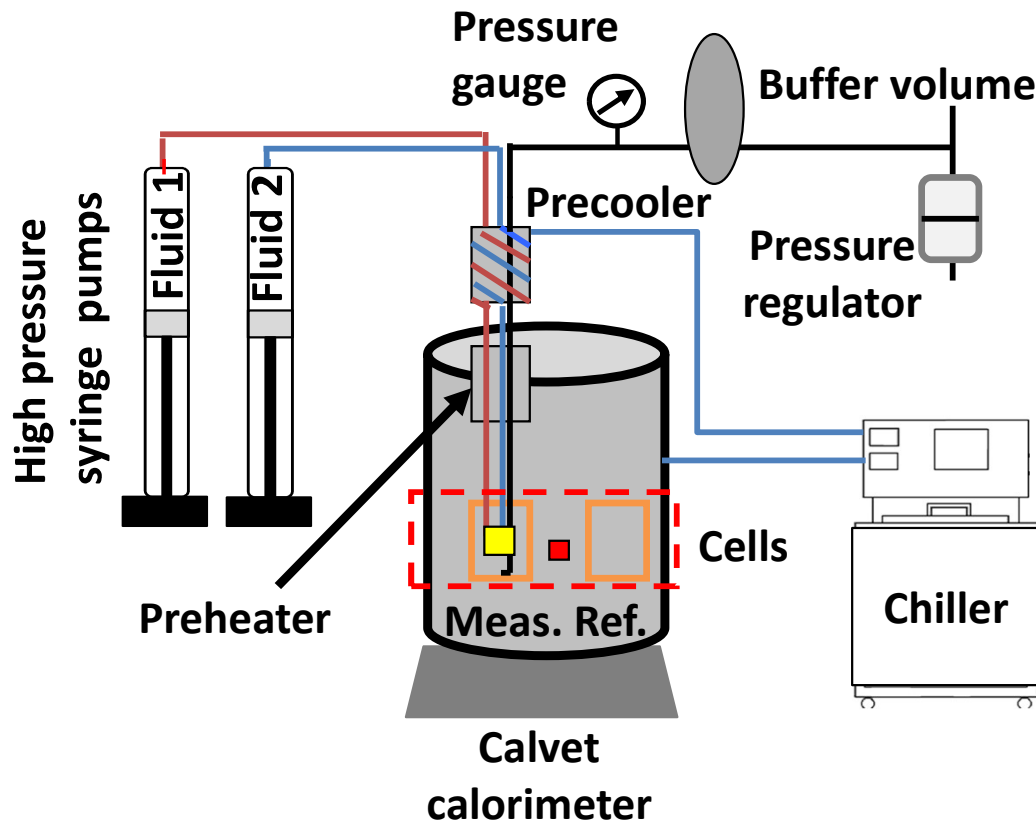
Excess Enthalpy

[1] D. Deng, G. Han, Y. Jiang, and N. Ai, J. Chem. Eng. Data, vol. 60, no. 1, pp. 104-111, Jan. 2015

[2] Y. Hou, W. Wu, and M. Poliakoff, J. Chem. Eng. Data, vol. 54, no. 1, pp. 118-126, Jan. 2009

# Thermodynamic characterization

- > Experimental approach : heat of mixing
  - Flow calorimetric technique at constant  $T$  and  $P$



$$\Delta_{\text{mix}}H (\text{J} \cdot \text{mol}^{-1}) = \frac{\Delta S}{K \cdot \dot{n}}$$

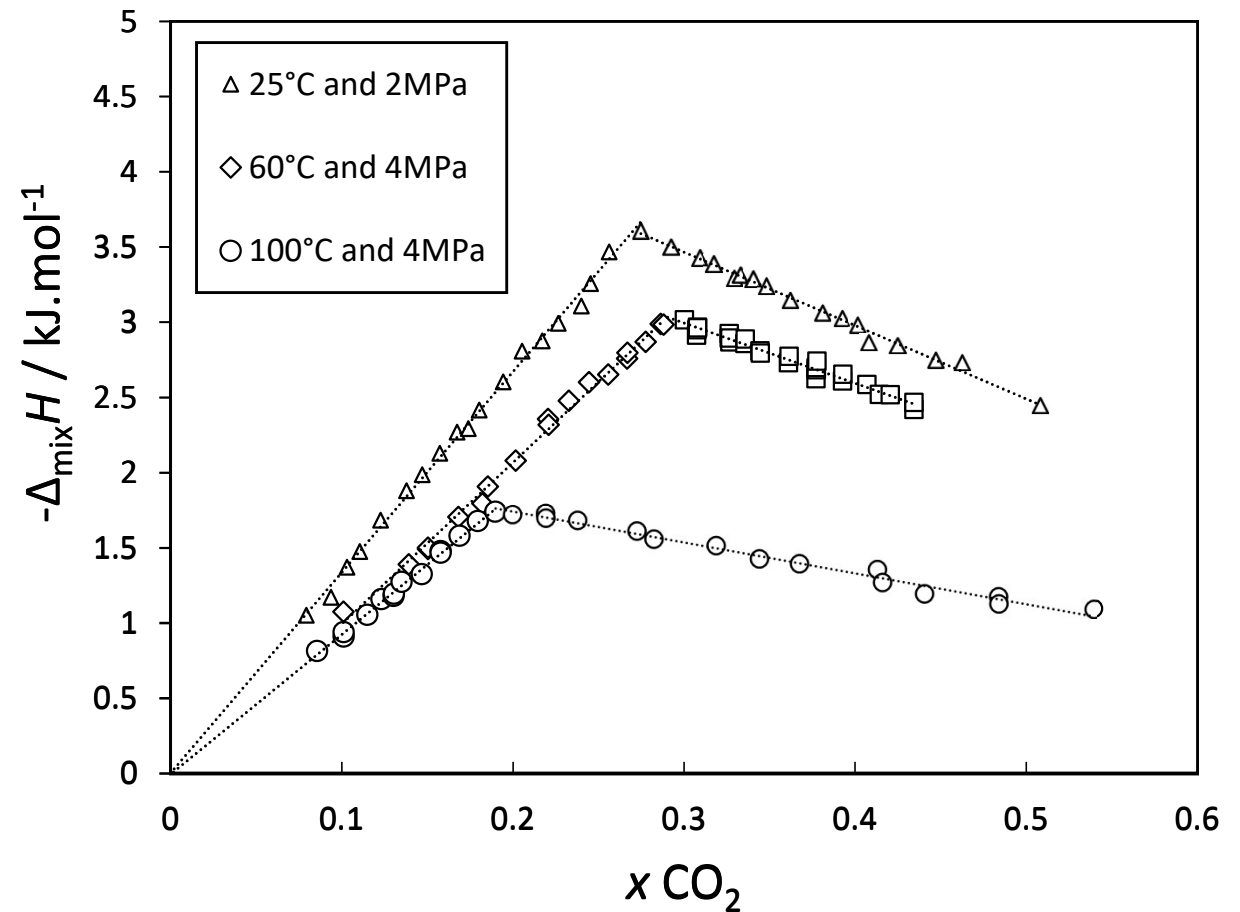
$T$ : from  $-90^{\circ}\text{C}$  to  $200^{\circ}\text{C}$   
 $P$ : up to 20 MPa

# Thermodynamic characterization

- > Experimental results : heat of mixing
  - VLE

Mixing	Gas+Liquid
Fluid 1	CO <sub>2</sub>
Fluid 2	γ-valerolactone
Property	Δ <sub>sol</sub> H, VLE
Precision	±5%

$$\Delta_{\text{mix}}H (\text{J} \cdot \text{mol}^{-1}) = \frac{\Delta S}{K \cdot \dot{n}}$$



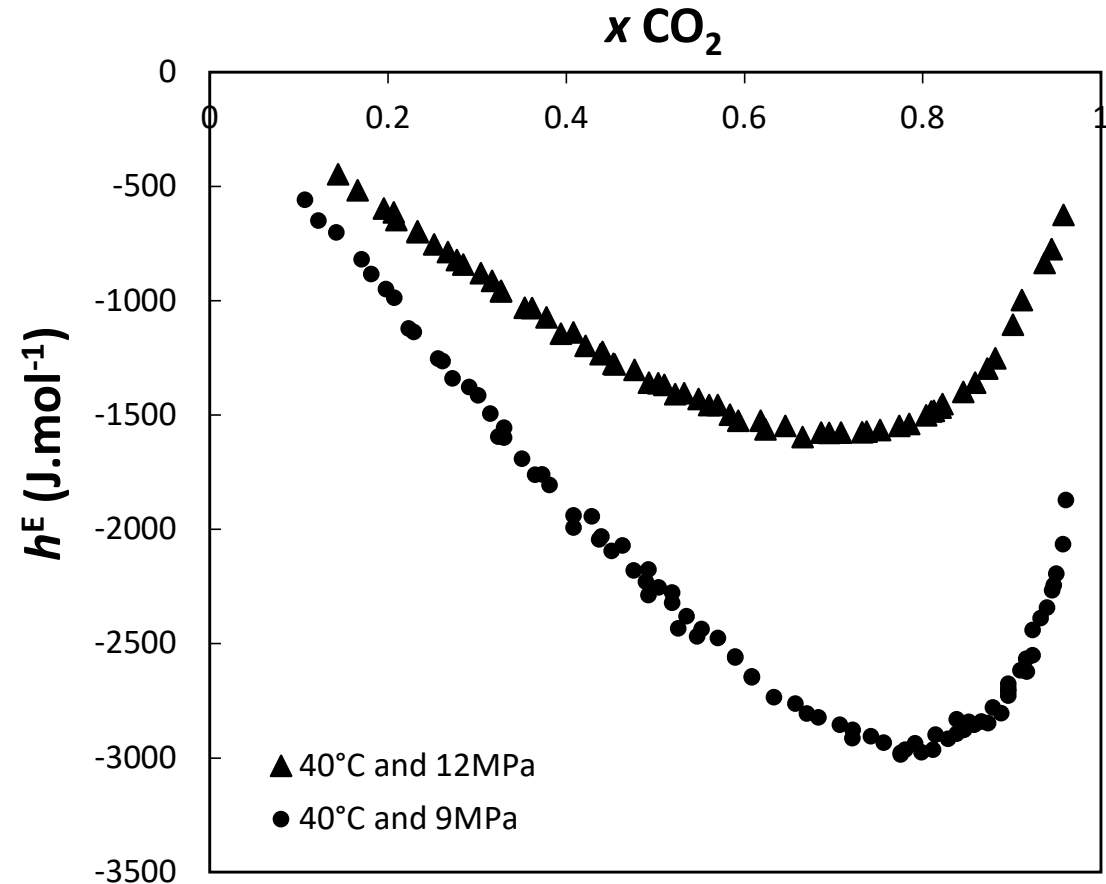


# Thermodynamic characterization

- > Experimental results : heat of mixing
  - Excess enthalpy

Mixing	Liquid+Liquid
Fluid 1	CO <sub>2</sub>
Fluid 2	γ-valerolactone
Property	$h^E$
Precision	±3%

$$h^E(\text{J} \cdot \text{mol}^{-1}) = \frac{\Delta S}{K \cdot \dot{n}}$$



# Thermodynamic modeling

## > Equation of state

- Peng Robinson (1978) : 
$$P = \frac{RT}{v - b_m} - \frac{a_m}{v(v + b_m)}$$

- Standard mixing rules : 
$$b_m = \sum_{i=1}^N x_i b_i$$

$$a_m = \sum_{i=1}^N \sum_{j=1}^N x_i x_j (a_i \alpha_i a_j \alpha_j)^{1/2} (1 - k_{ij})$$

- Alpha function : 
$$\alpha_i(T) = \left[ 1 + m_i \left( 1 - \left( \frac{T}{T_{ci}} \right)^{1/2} \right) \right]^2$$

$$m_i = 0.379642 + 1.48503\omega_i - 0.164423\omega_i^2 + 0.016666\omega_i^3$$

- Margules binary interaction parameters : 
$$k_{ij} = x_i k_{ij}^0 + x_j k_{ji}^0$$

- Required parameters :  $P_c$ ,  $T_c$ ,  $\omega$  for pure fluids and binary interaction parameters ( $k_{ij}^0$  and  $k_{ji}^0$ )

# Thermodynamic modeling

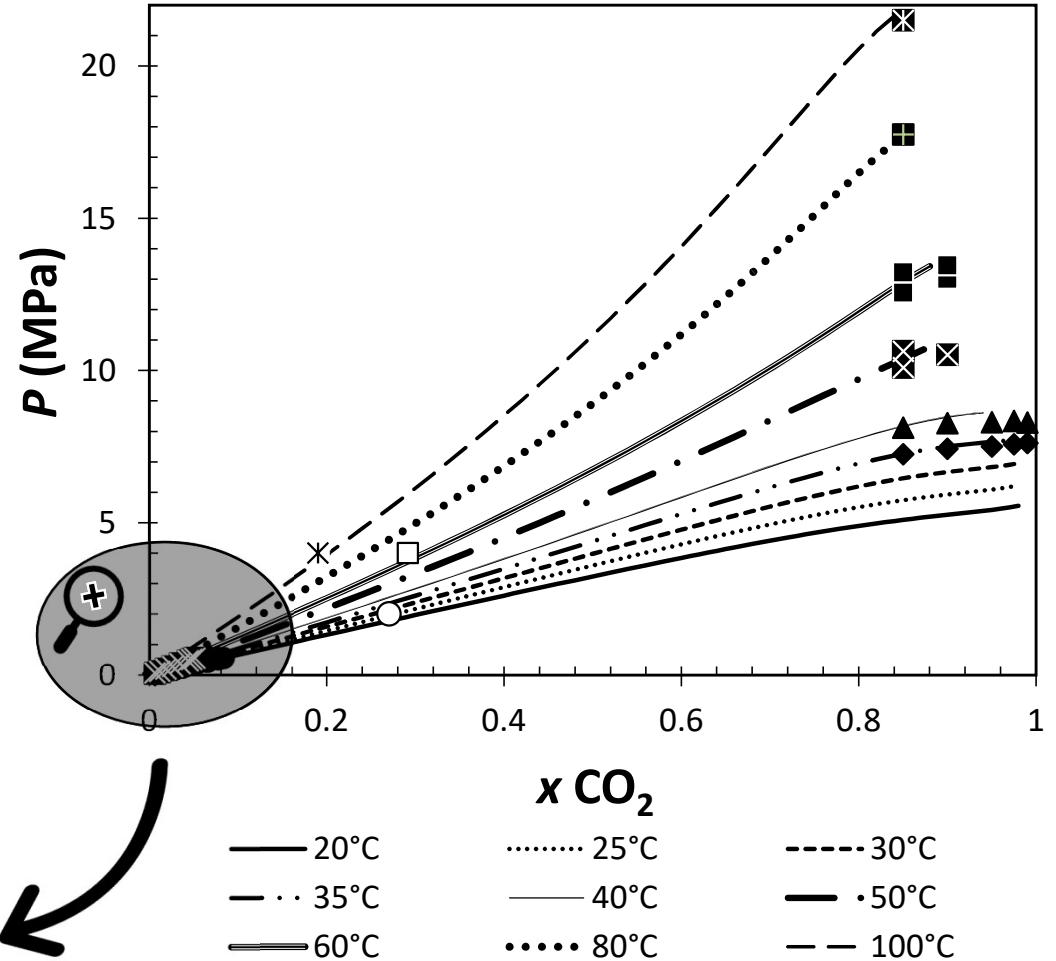
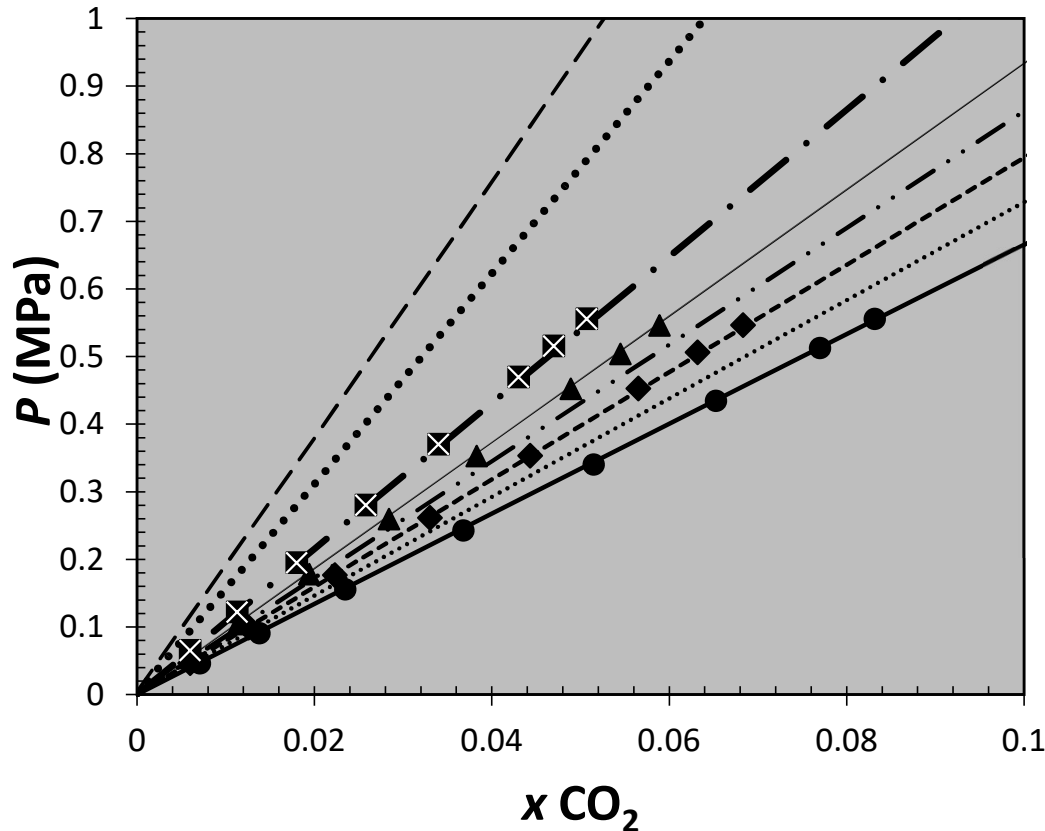
## > Model parameters determination

- Literature VLE data (65 data)
- Our experimental VLE and excess enthalpy data (152 data)
- Simulis thermodynamics software
- Objective function

$$F = F_{\text{VLE}} + F_{h^E} f_w \text{ with } \left\{ \begin{array}{l} F_{\text{VLE}} = \sum_i \left( \frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{P_i^{\text{exp}}} \right)^2 \\ F_{h^E} = \sum_i \left( \frac{h_i^{E,\text{exp}} - h_i^{E,\text{cal}}}{h_i^{E,\text{exp}}} \right)^2 \\ f_w \text{ Weighting factor} \end{array} \right.$$

# Thermodynamic modeling

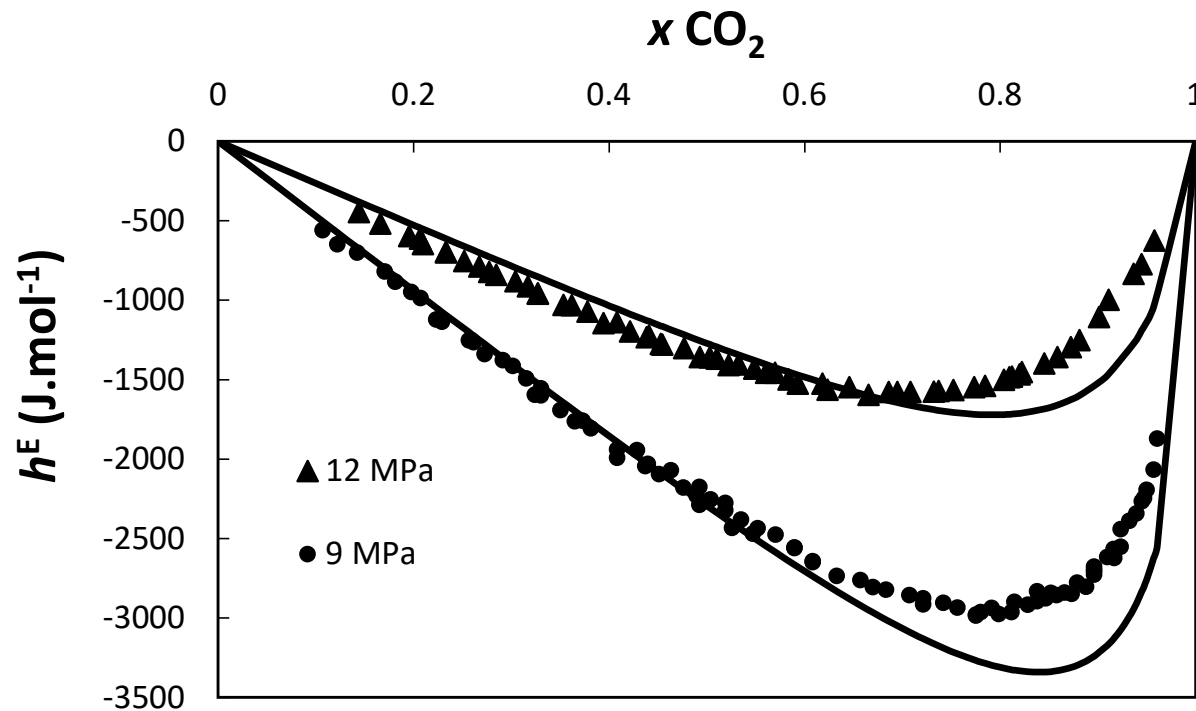
## > Results for VLE modeling



Opened symbols : our work  
Filled symbols : literature data  
Lines : Thermodynamic model

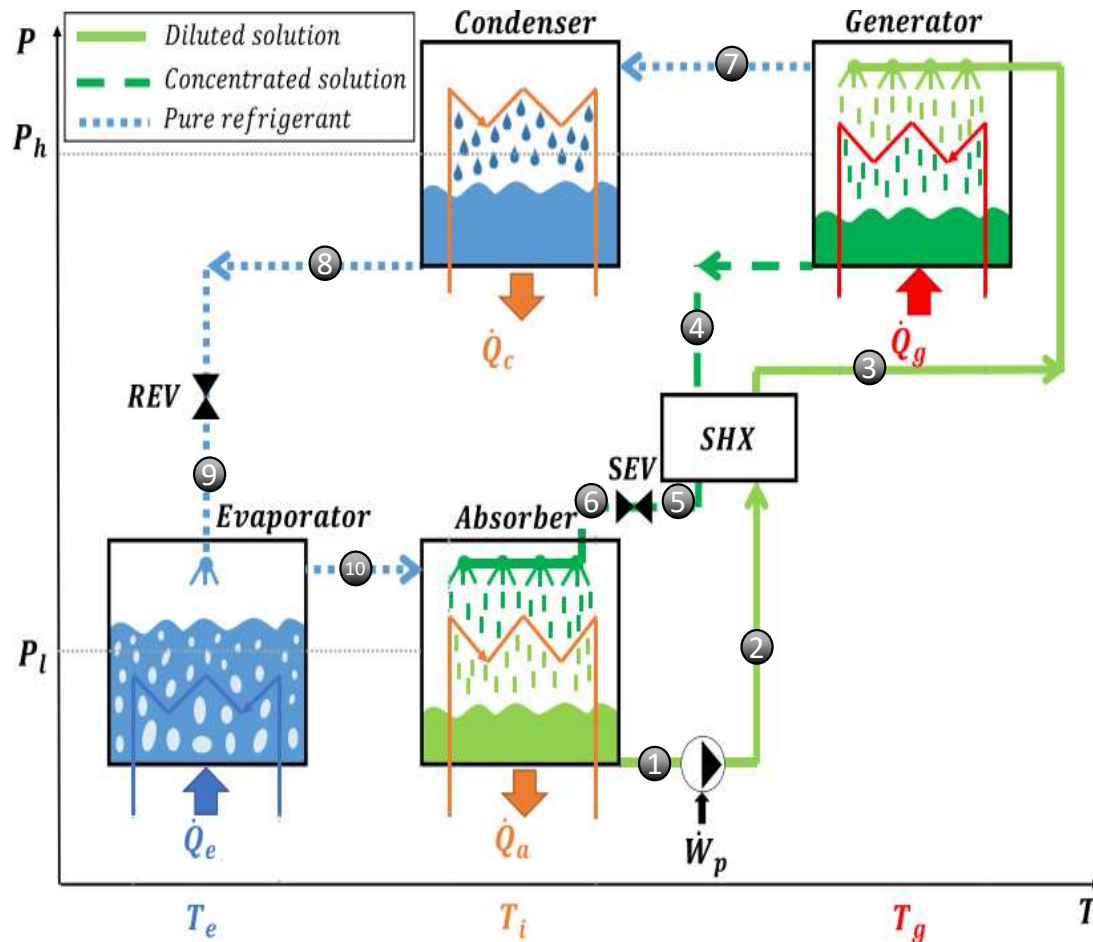
# Thermodynamic modeling

> Results for excess enthalpy modeling (40 °C)



# System efficiency evaluation

## > Process modeling



Schematic representation of the studied configuration of a single-stage CO<sub>2</sub>-GVL absorption cycle. [3]

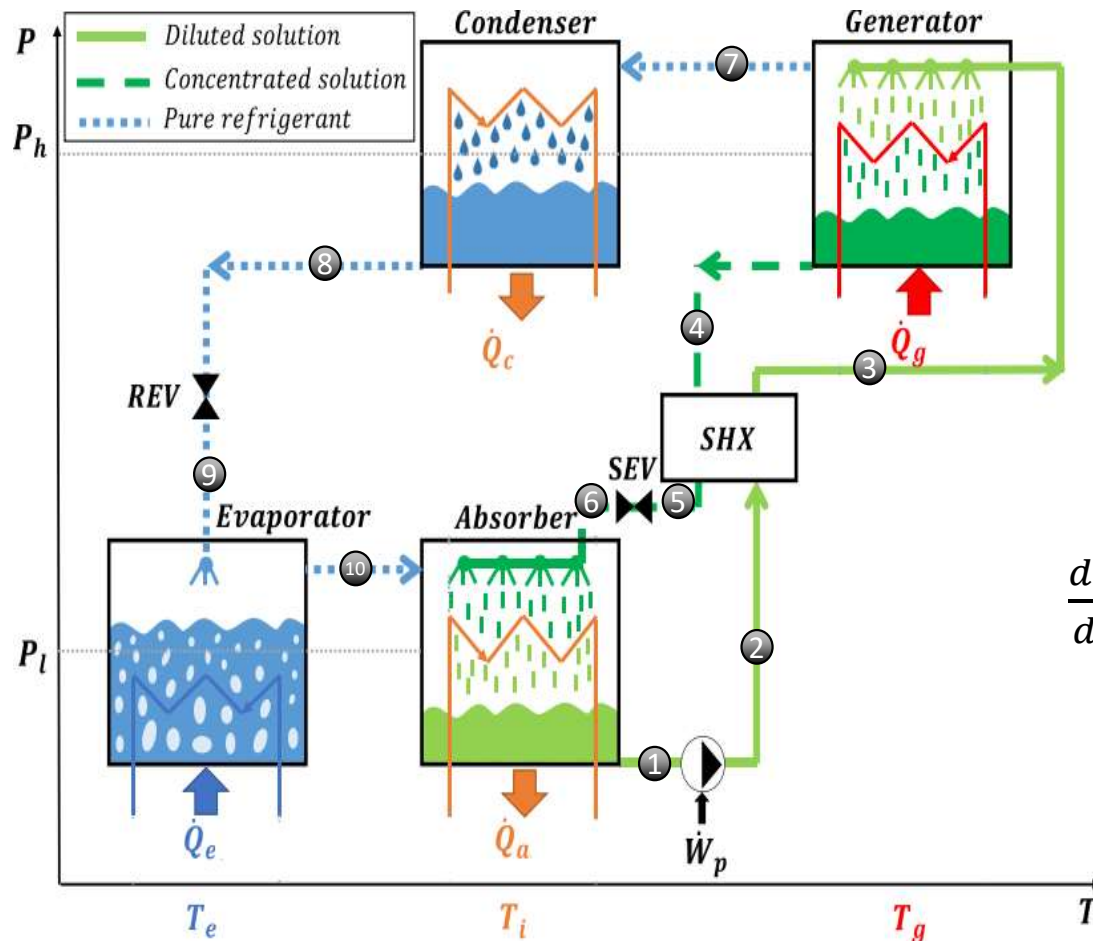
## Simplifying assumptions:

- Steady-state conditions
- Negligible pressure drop and heat losses to the surroundings
- The condenser and the absorber are cooled by the same fluid ( $T_a = T_c = T_i$ )
- The solution at the outlet of the sorption elements (state 1 and 4) is under equilibrium conditions
- The refrigerant at the outlet of the condenser and evaporator (states 8 and 10) is under saturated conditions
- Vapor leaving generator is assumed in equilibrium with incoming solution stream concentration (state 3)
- $\epsilon_{SHX} = 0.8$  and ideal heat exchangers for the rest of the components

[3] C. Maragna, A. Altamirano, B. Tréméac, F. Fabre, L. Rouzic, and P. Barcellini, *Applied Energy*, vol. 364, p. 123102, Jun. 2024

# System efficiency evaluation

## > Process modeling



Schematic representation of the studied configuration of a single-stage CO<sub>2</sub>-GVL absorption cycle. [3]

## Mass balance

$$\sum \dot{m}_i = \sum \dot{m}_o$$

$$\sum (\dot{m}_i w_i) = \sum (\dot{m}_o w_o)$$

## Energy balance

$$\frac{dE}{dt} = \sum ((\dot{m}_i h_i) - (\dot{m}_o h_o)) + \sum \dot{W} + \sum \dot{Q}_{i/o} = 0$$

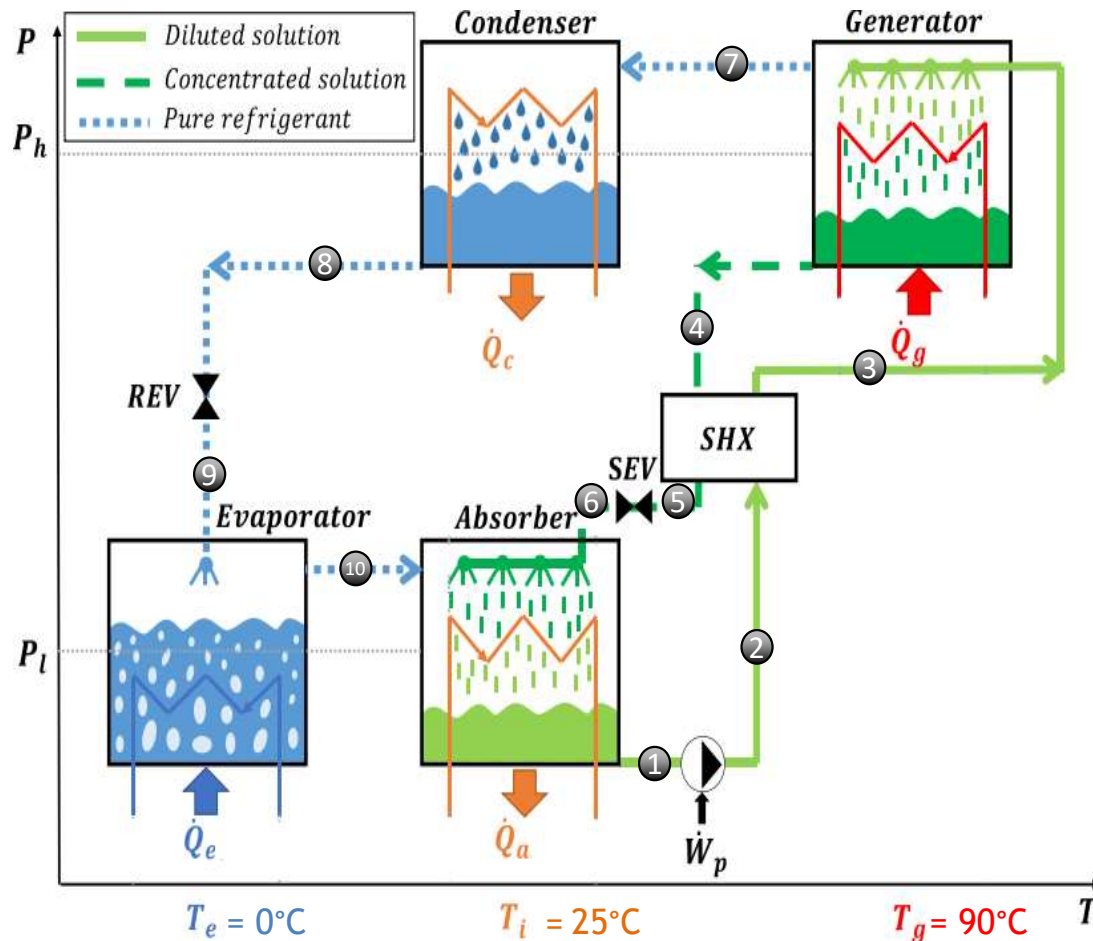
## Coefficient of performance

$$COP_{th} = \dot{Q}_e / \dot{Q}_g$$

[3] C. Maragna, A. Altamirano, B. Tréméac, F. Fabre, L. Rouzic, and P. Barcellini, Applied Energy, vol. 364, p. 123102, Jun. 2024

# System efficiency evaluation

## > Process modeling



## Nominal conditions

input temperatures	
Evaporator outlet	$T_{10} = 0\text{ }^{\circ}\text{C}$
Condenser outlet	$T_8 = 25\text{ }^{\circ}\text{C}$
Absorber outlet	$T_1 = 25\text{ }^{\circ}\text{C}$
Generator outlet	$T_4 = 90\text{ }^{\circ}\text{C}$

$\dot{m}_1$   
 ↑  
 Cooling capacity,  $\dot{Q}_e = 20\text{ kW}$

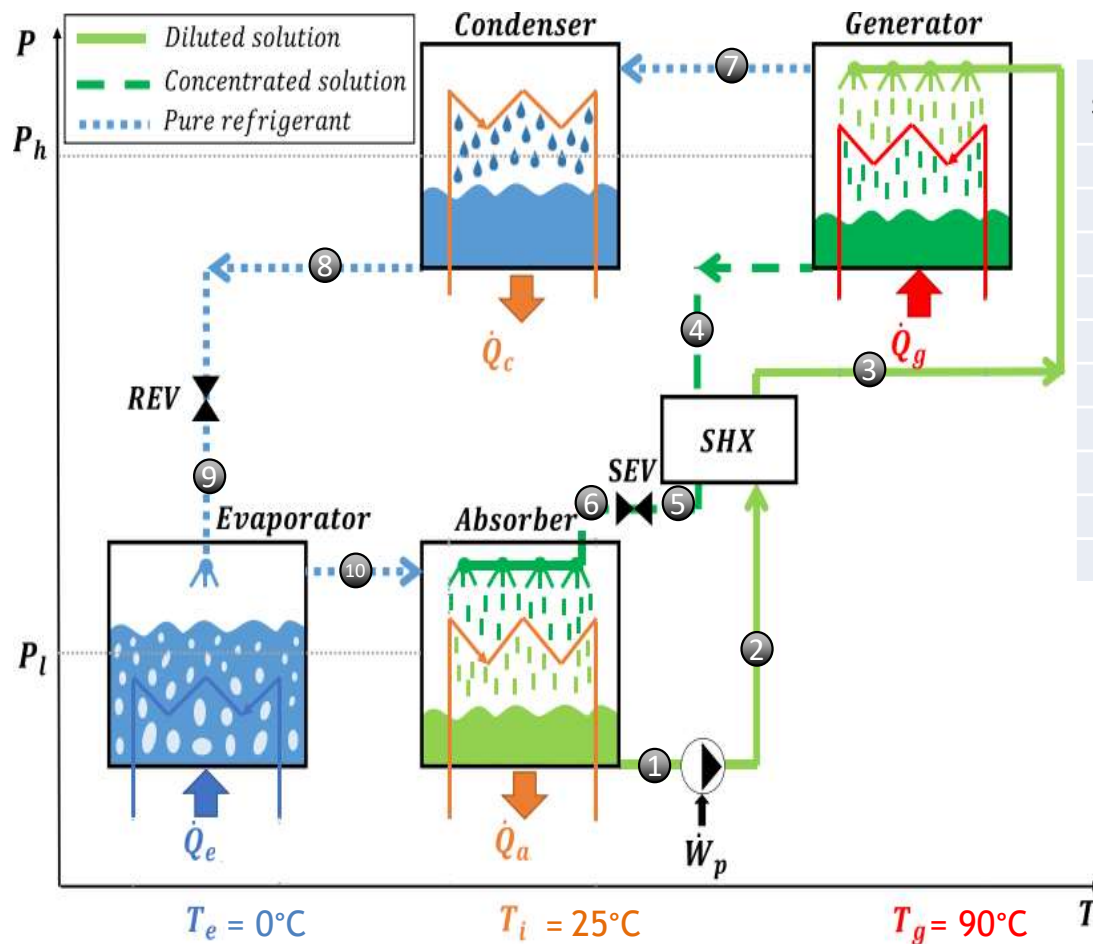
Schematic representation of the studied configuration of a single-stage CO<sub>2</sub>-GVL absorption cycle. [3]

[3] C. Maragna, A. Altamirano, B. Tréméac, F. Fabre, L. Rouzic, and P. Barcellini, Applied Energy, vol. 364, p. 123102, Jun. 2024



# System efficiency evaluation

## > Process modeling



## Nominal conditions

state point	h (KJ/kg)	mass flow rate $\dot{m}$ (kg/s)	T (°C)	absorbent mass fraction w (kg/kg)
1	-420.22	0.9657	25	0.709
2	-420.22	0.9657	25	0.709
3	-326.99	0.9657		0.709
4	-322.86	0.8418	90	0.813
5	-429.81	0.8418	38	0.813
6	-429.81	0.8418	38	0.813
7	-31.63	0.1240	59.64	0
8	-238.33	0.1240	25	0
9	-238.33	0.1240		0
10	-76.95	0.1240	0	0

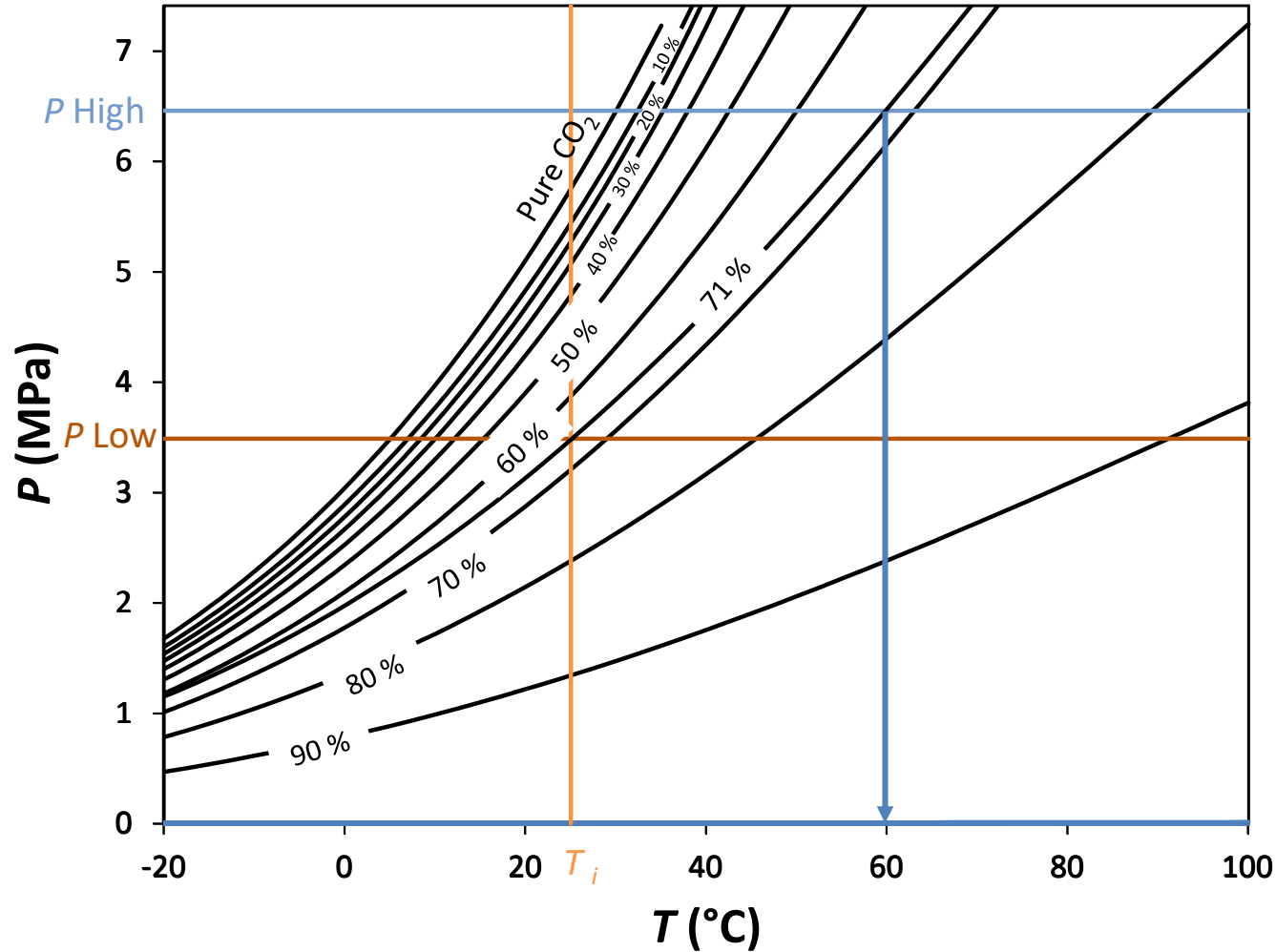
high pressure (MPa)	6.450
low pressure (MPa)	3.477
$\dot{Q}_a$ (kW)	34.48
$\dot{Q}_g$ (kW)	40.09
$\dot{Q}_e$ (kW)	20.00
$\dot{Q}_c$ (kW)	25.62
COP	0.4989

[3] C. Maragna, A. Altamirano, B. Tréméac, F. Fabre, L. Rouzic, and P. Barcellini, Applied Energy, vol. 364, p. 123102, Jun. 2024

> International Seminar on Sustainable Refrigeration 2024, 24 June

# System efficiency evaluation

## > Dühring diagram

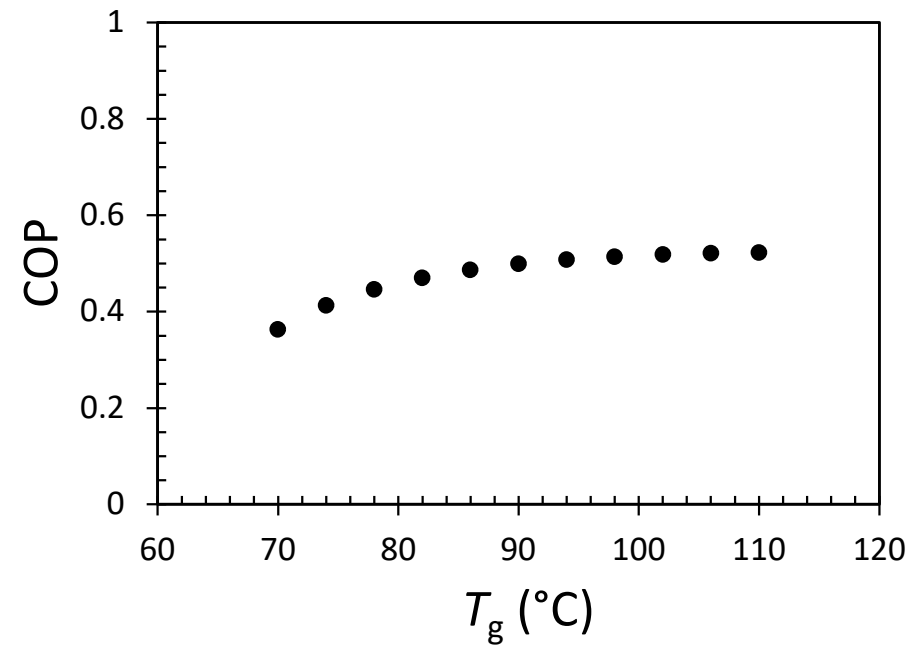
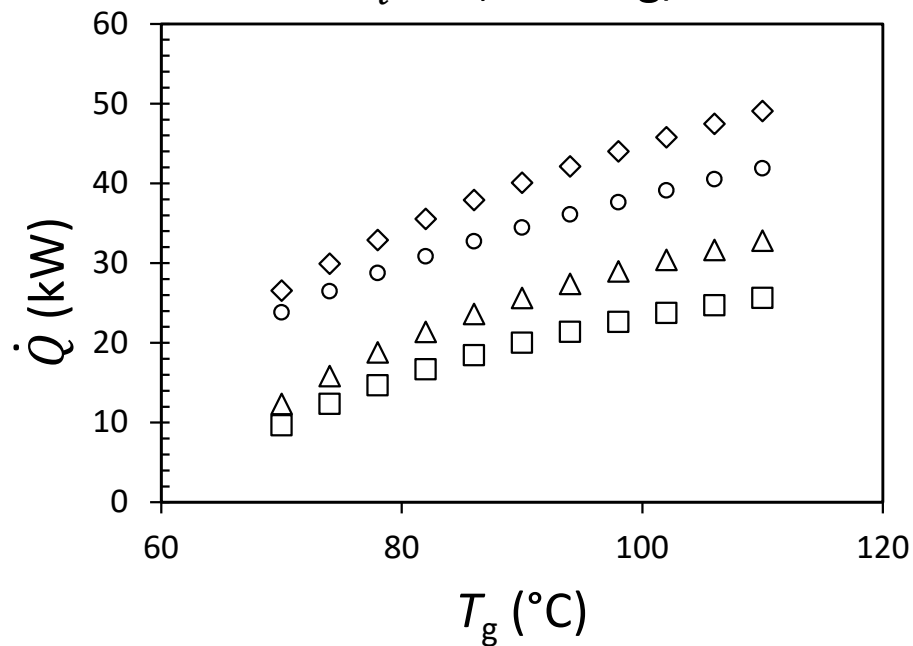


# System efficiency evaluation

## > Parametric analysis

- Generator temperature effect

- $T_i = 25^\circ\text{C}$
- $T_g$  varies from  $70^\circ\text{C}$  to  $110^\circ\text{C}$
- $T_e = 0^\circ\text{C}$
- $\dot{m}_i = 0,9657 \text{ kg/s}$

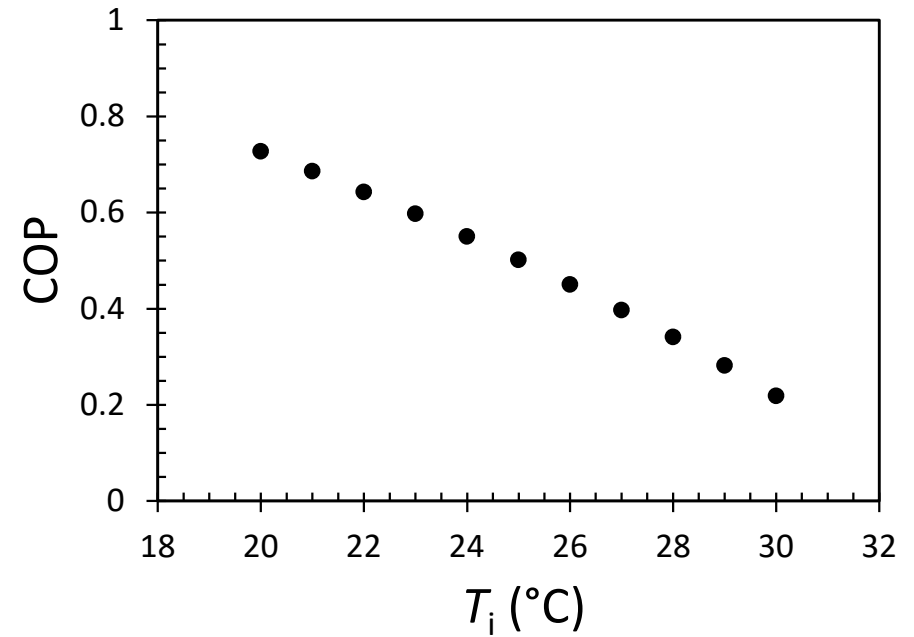
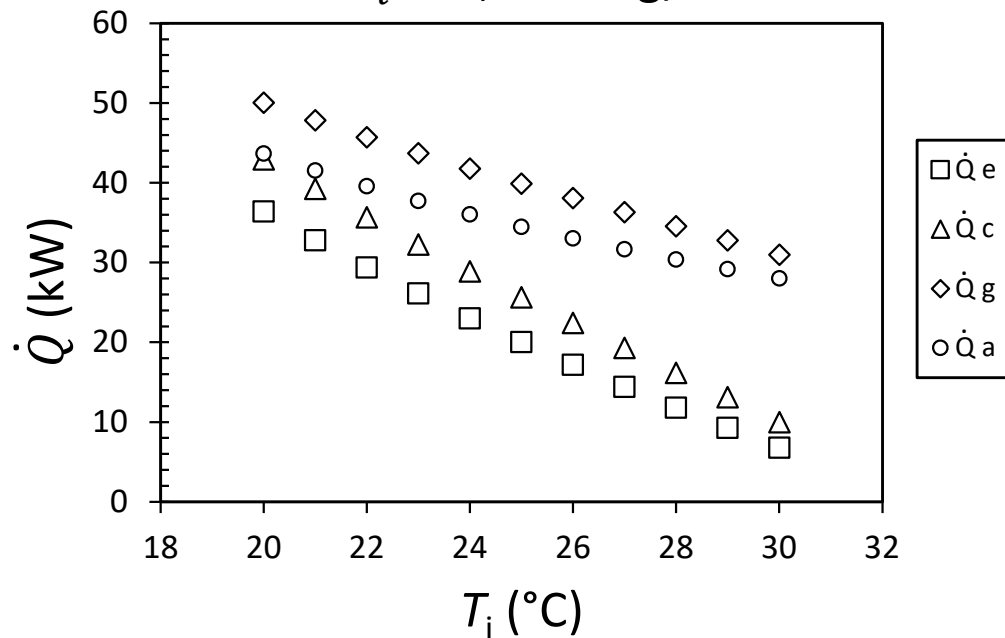


# System efficiency evaluation

## > Parametric analysis

- Intermediate temperature effect ( $T_a$  and  $T_c$ )

- $T_i$  varies from 20°C to 30°C
- $T_g = 90^\circ\text{C}$
- $T_e = 0^\circ\text{C}$
- $\dot{m}_i = 0,9657\text{ kg/s}$

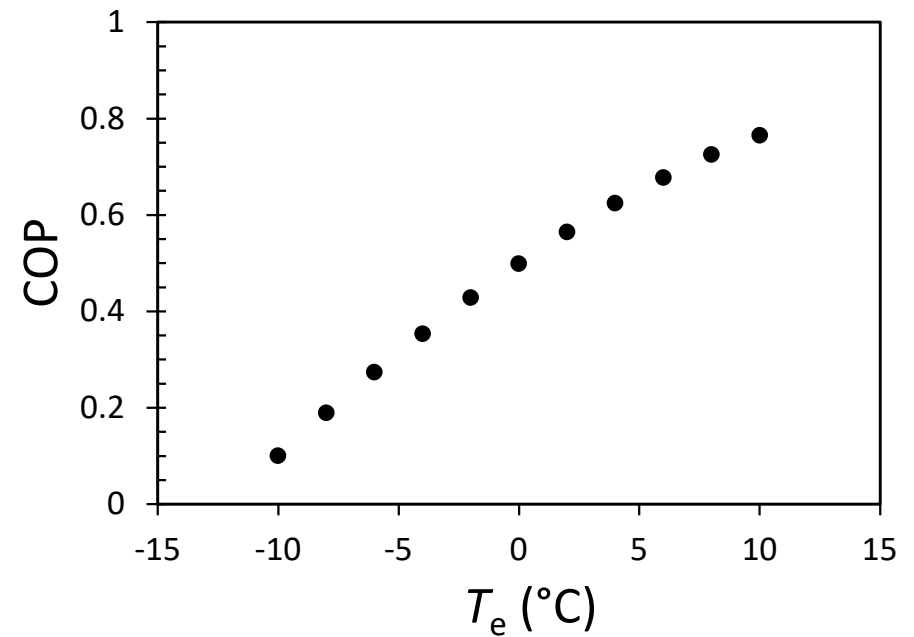
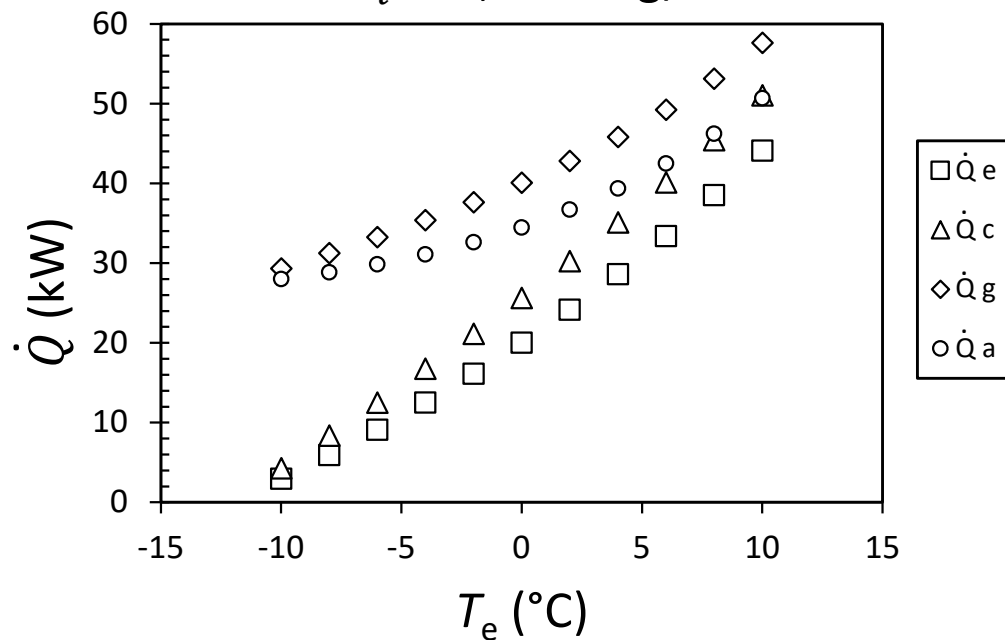


# System efficiency evaluation

## > Parametric analysis

- Evaporator temperature effect

- $T_i = 25^\circ\text{C}$
- $T_g = 90^\circ\text{C}$
- $T_e$  varies from  $-10^\circ\text{C}$  to  $10^\circ\text{C}$
- $\dot{m}_i = 0,9657 \text{ kg/s}$



# Conclusion and future work

## > Conclusion

- Use of experimental data to fit the Peng Robinson equation of state
- Process modeling results :
  - Possibility of using low-temperature heat sources
  - Preference for lower intermediate temperature
  - Possibility of producing negative cold, but the preference to remain at temperatures close to zero

## > Perspective

- Addition of other thermodynamic data to improve the equation of state
- Diffusion and thermal stability studies for a complete overview
- Comparison with conventional working fluid pairs
- Extension of the analysis to other bio-based absorbents currently under investigation to enable comparative studies

> International Seminar on Sustainable Refrigeration 2024, 24 June



Thank you for your attention

