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> International Seminar on Sustainable Refrigeration 2024

Suitable working fluids for CO₂-based absorption chillers

Alaa HAJLAOUI¹, J-M. ANDANSON¹, L. RODIER¹, Y. COULIER¹, W. KHAY¹
A. ALTAMIRANO²

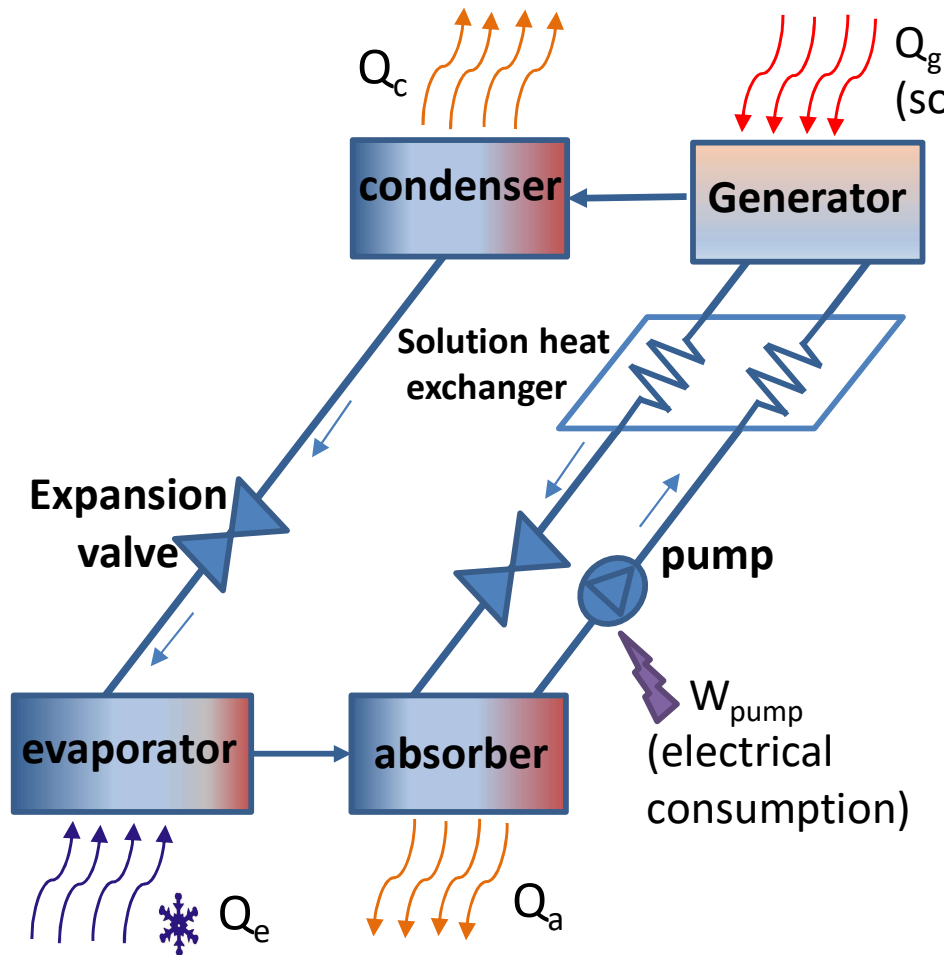
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² : Laboratoire du froid et des systèmes énergétiques et thermiques (Lafset), Conservatoire national des arts et métiers, HESAM Université, F-75003 Paris, France



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...

NH_3 / H_2O

Corrosion
Toxicity
Rectifier

H_2O / LiBr

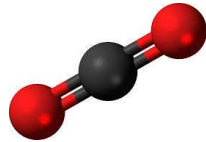
Corrosion
Crystallization
 $T_{\text{evap}} > 0^\circ\text{C}$

Objectives

> Improving of working fluid pairs

Refrigerant

CO₂ (R744)



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

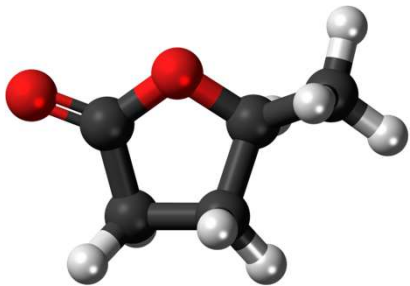
+ Absorbent

**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

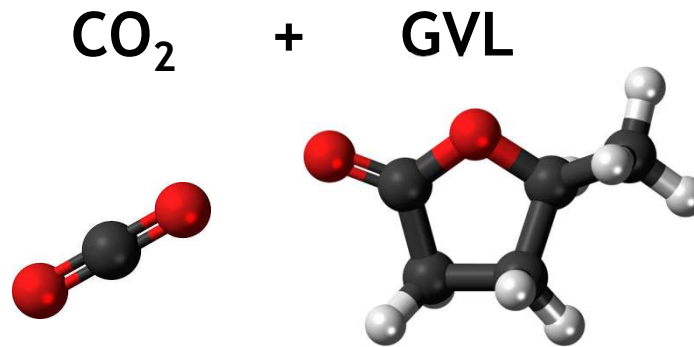


γ-valerolactone

Abbreviation	MW /g·mol ⁻¹	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)

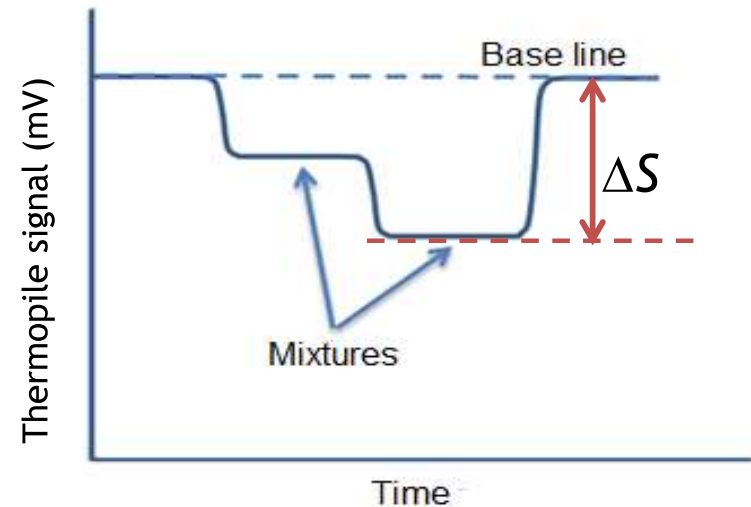
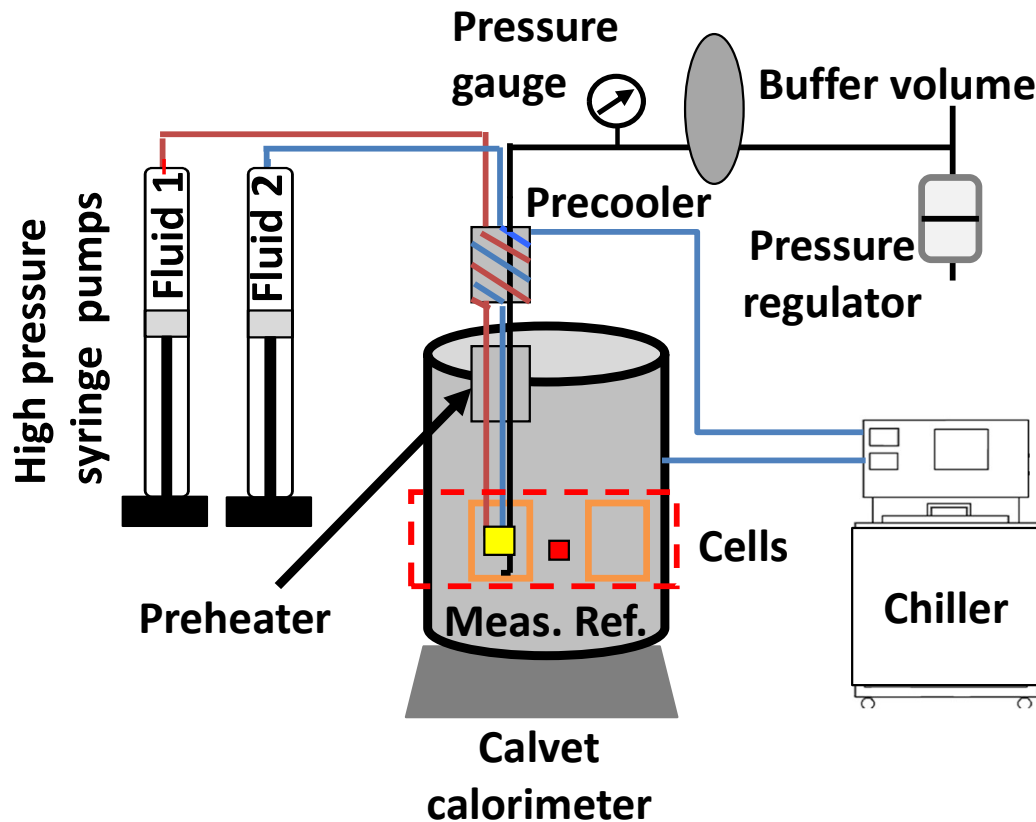
Excess Enthalpy

[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



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

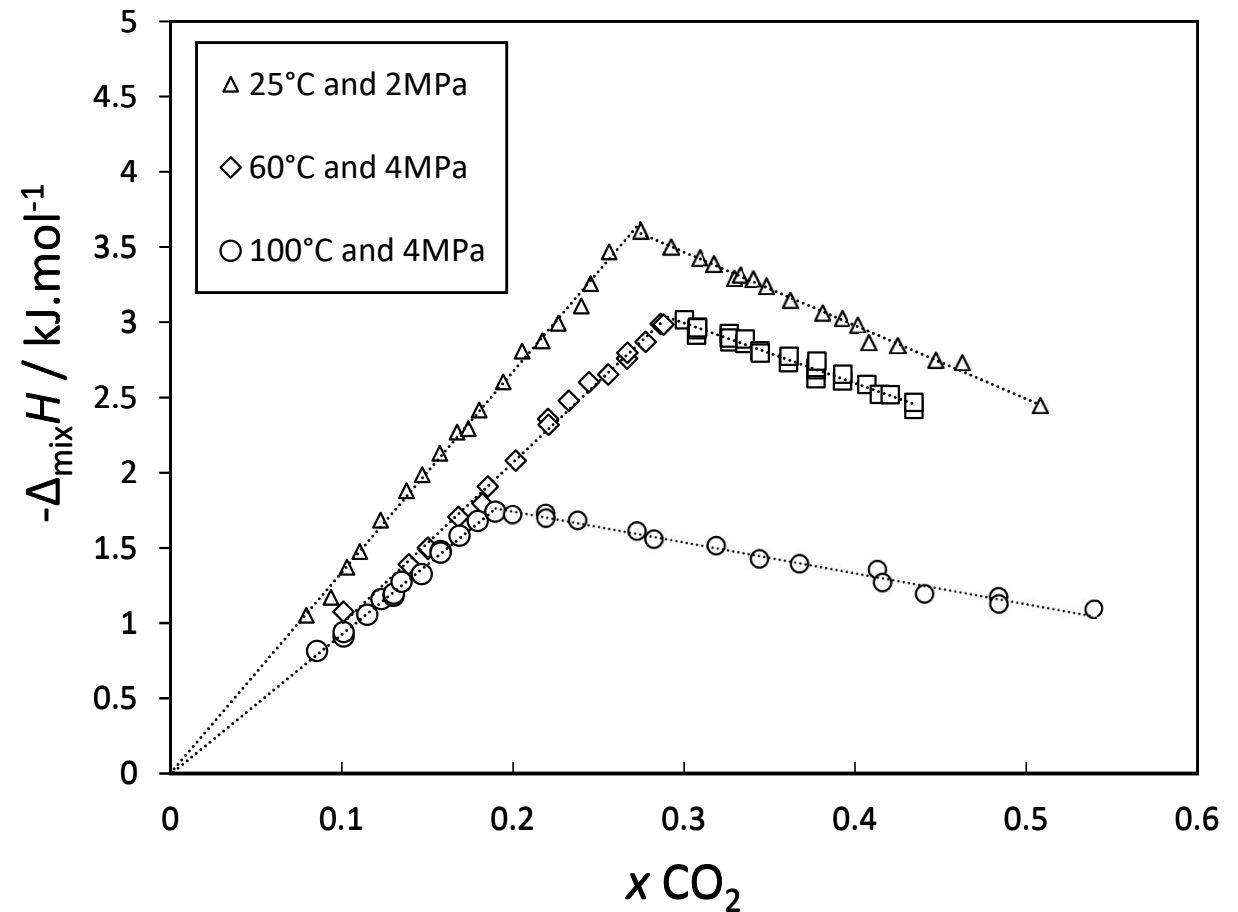
T : from -90°C to 200°C
 P : up to 20 MPa

Thermodynamic characterization

- > Experimental results : heat of mixing
 - VLE

Mixing	Gas+Liquid
Fluid 1	CO ₂
Fluid 2	γ-valerolactone
Property	Δ _{sol} H, VLE
Precision	±5%

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

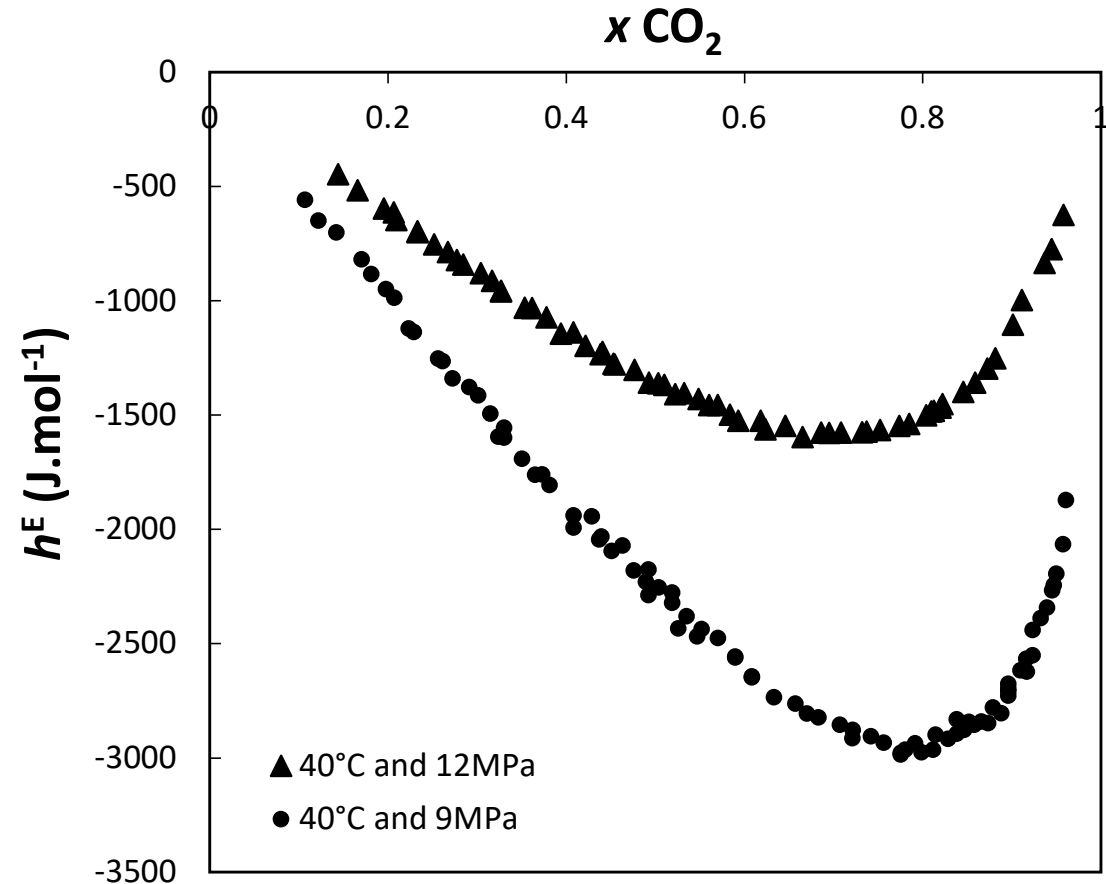


Thermodynamic characterization

- > Experimental results : heat of mixing
 - Excess enthalpy

Mixing	Liquid+Liquid
Fluid 1	CO ₂
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 , ω for pure fluids and binary interaction parameters (k_{ij}^0 and k_{ji}^0)

Thermodynamic modeling

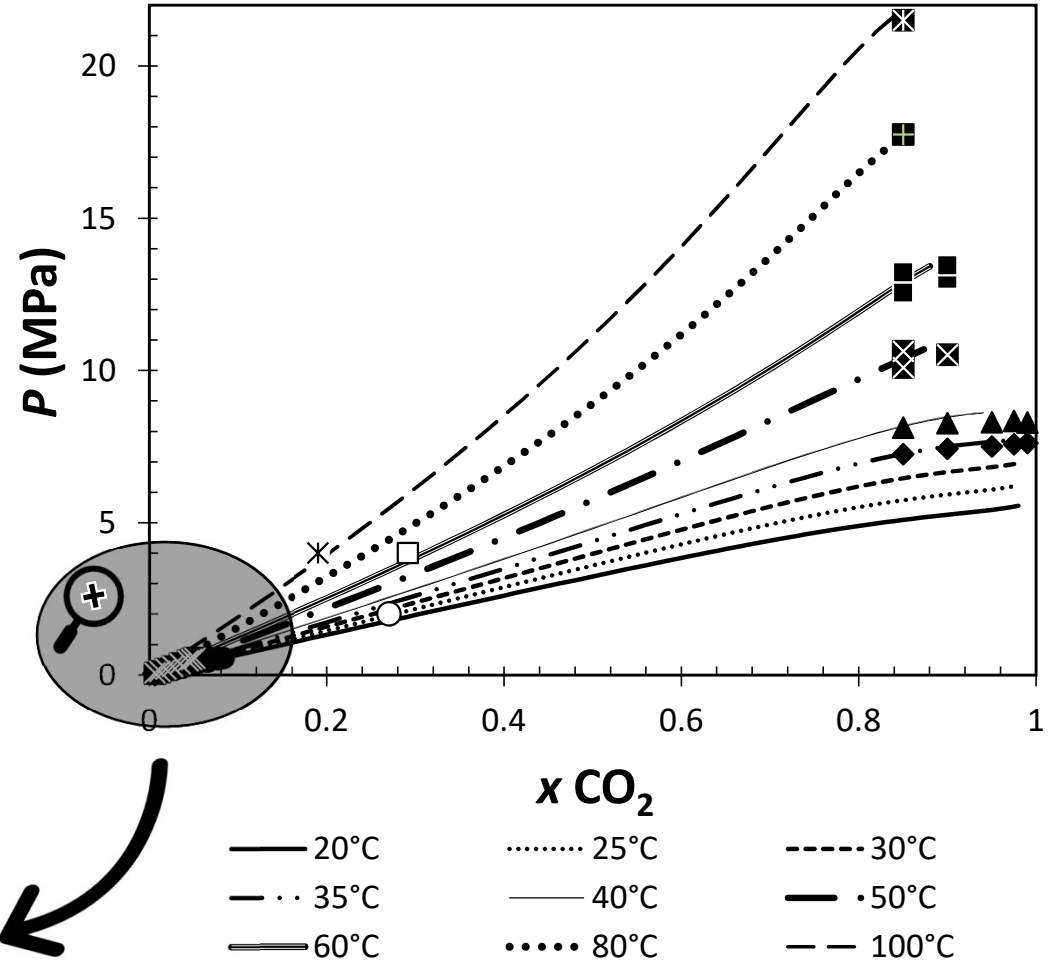
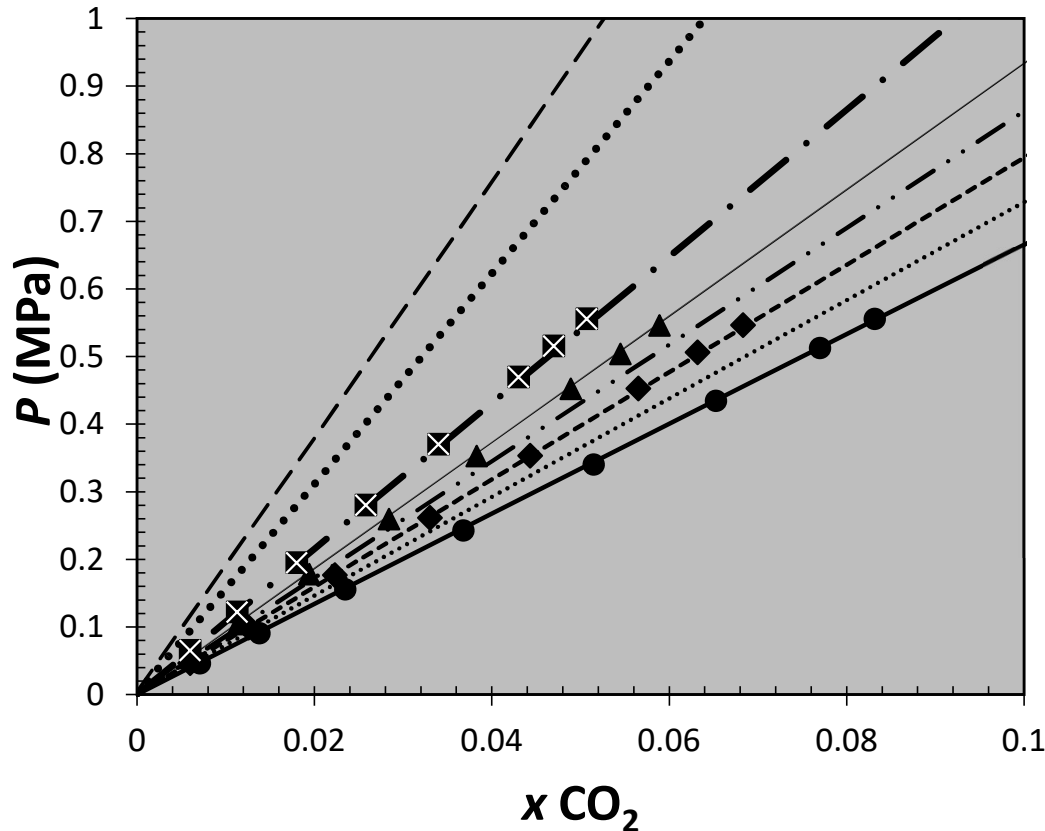
> Model parameters determination

- 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

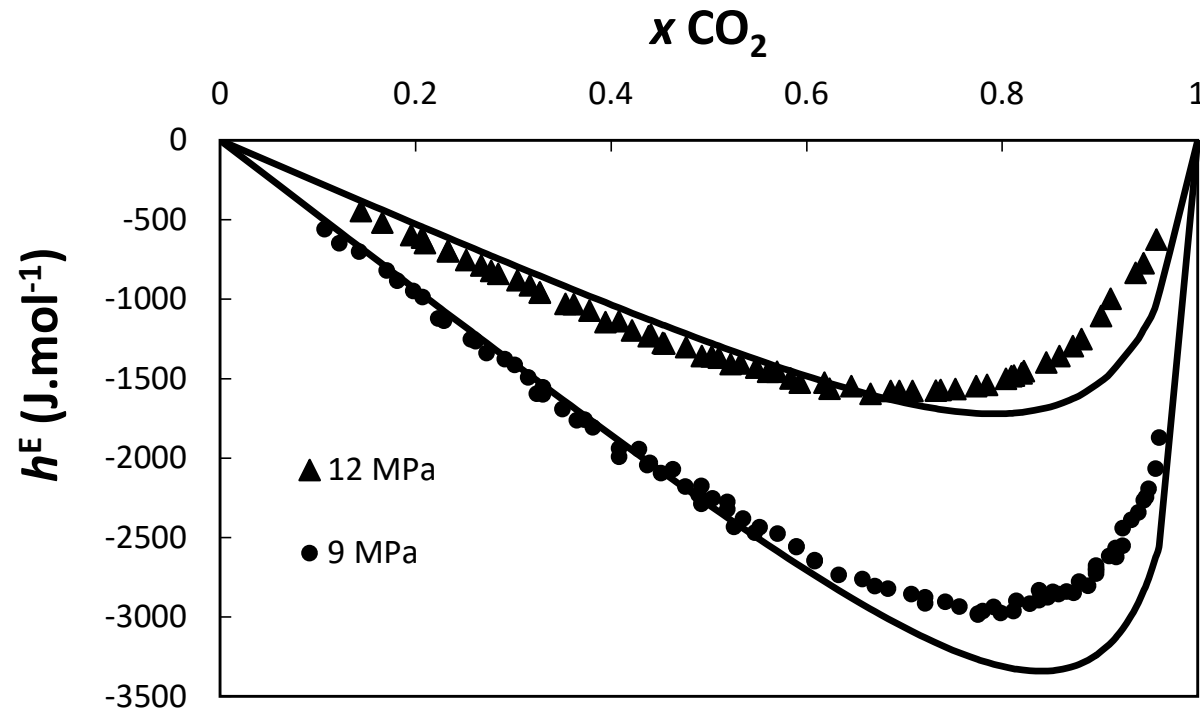
> Results for VLE modeling



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

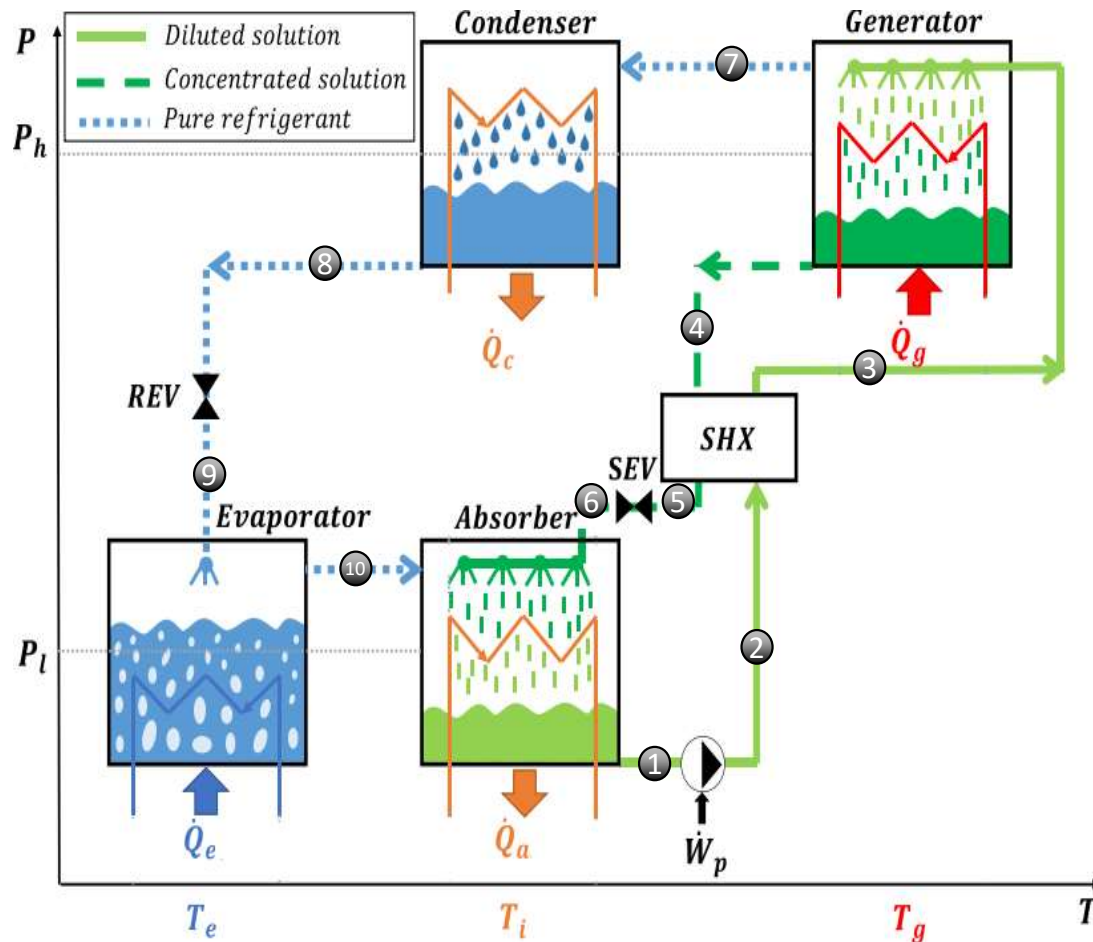
Thermodynamic modeling

> Results for excess enthalpy modeling (40 °C)



System efficiency evaluation

> Process modeling



Schematic representation of the studied configuration of a single-stage CO₂-GVL absorption cycle. [3]

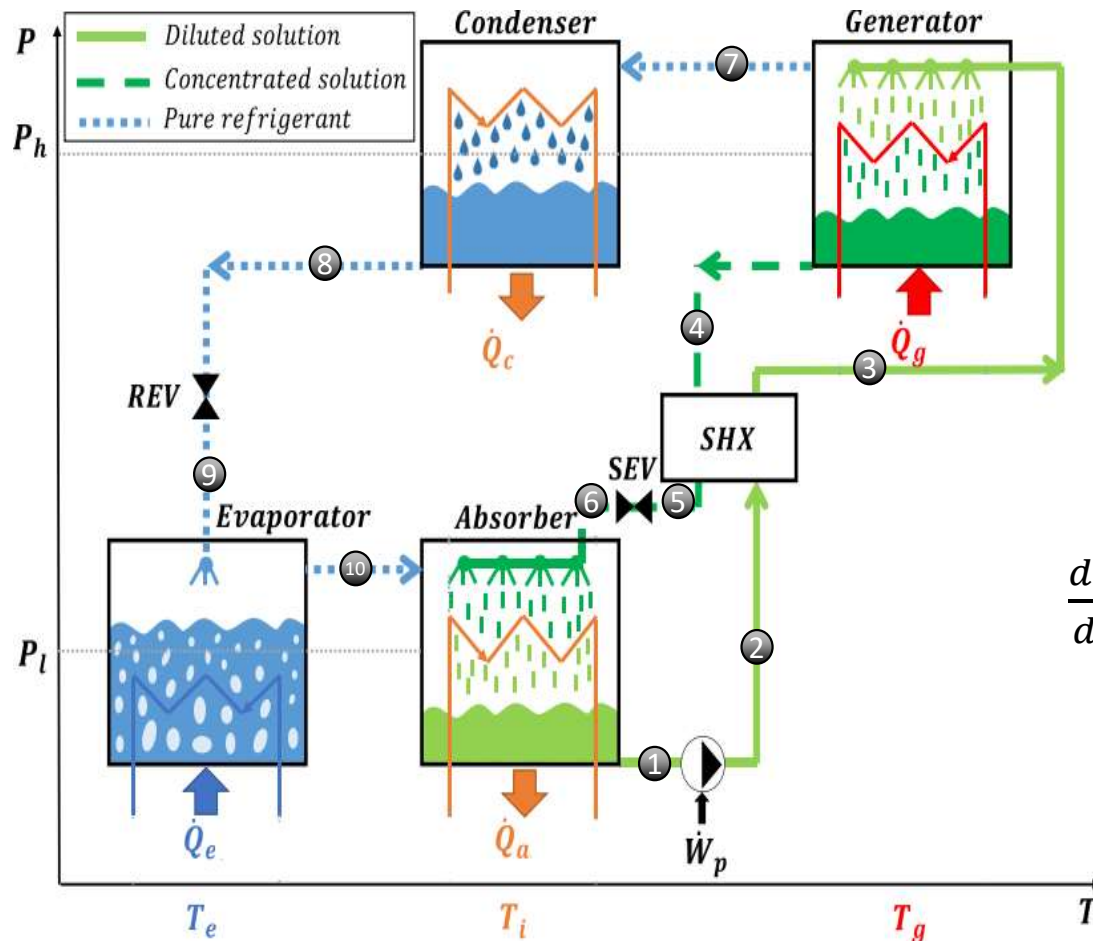
Simplifying assumptions:

- 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 CO₂-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

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

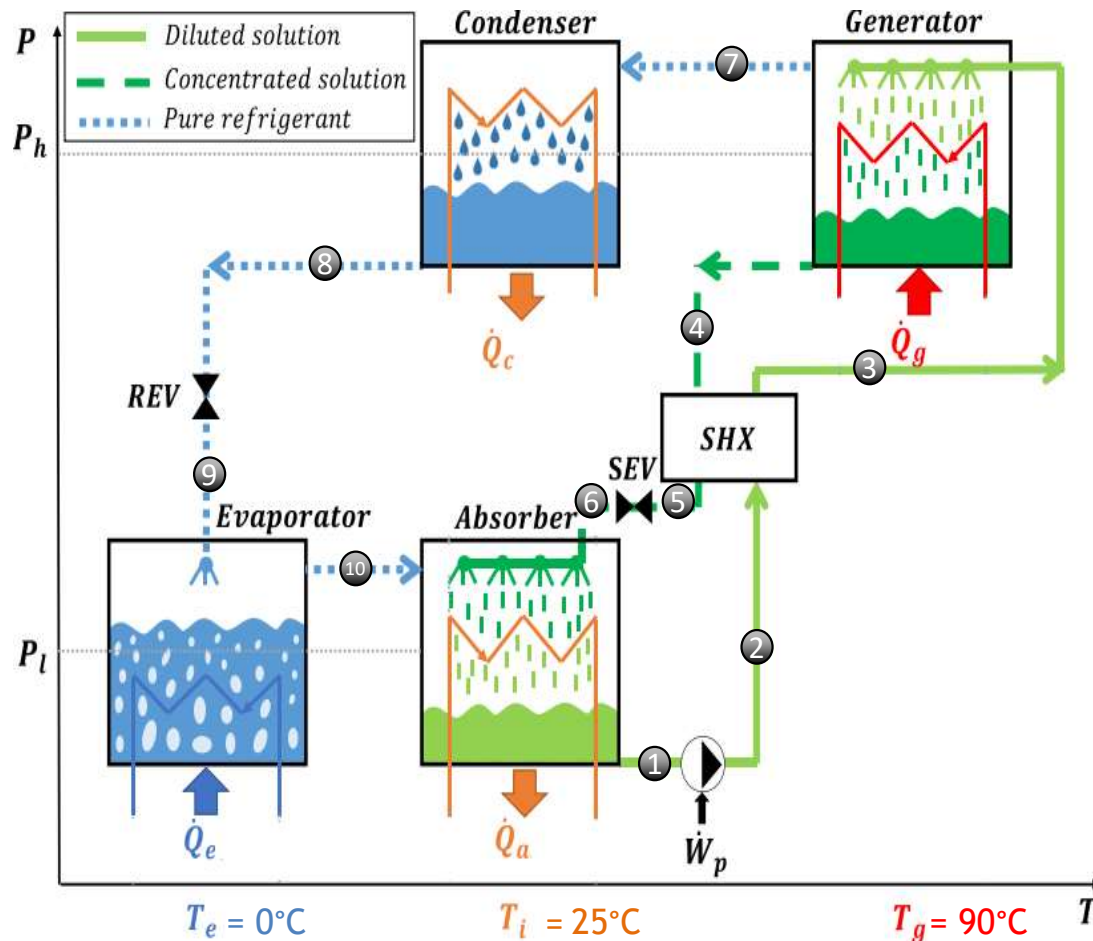
Coefficient of performance

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

[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

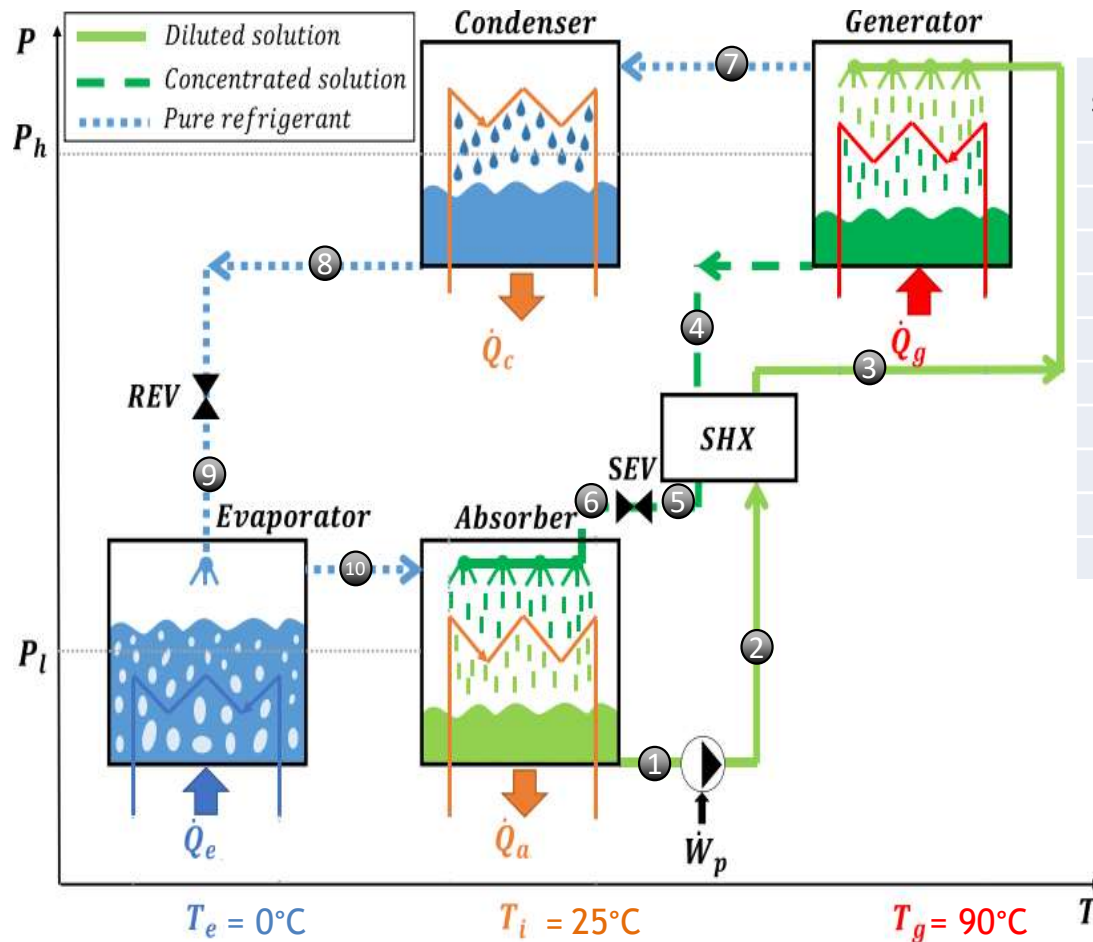
input temperatures	
Evaporator outlet	$T_{10} = 0\text{ }^{\circ}\text{C}$
Condenser outlet	$T_8 = 25\text{ }^{\circ}\text{C}$
Absorber outlet	$T_1 = 25\text{ }^{\circ}\text{C}$
Generator outlet	$T_4 = 90\text{ }^{\circ}\text{C}$

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

[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

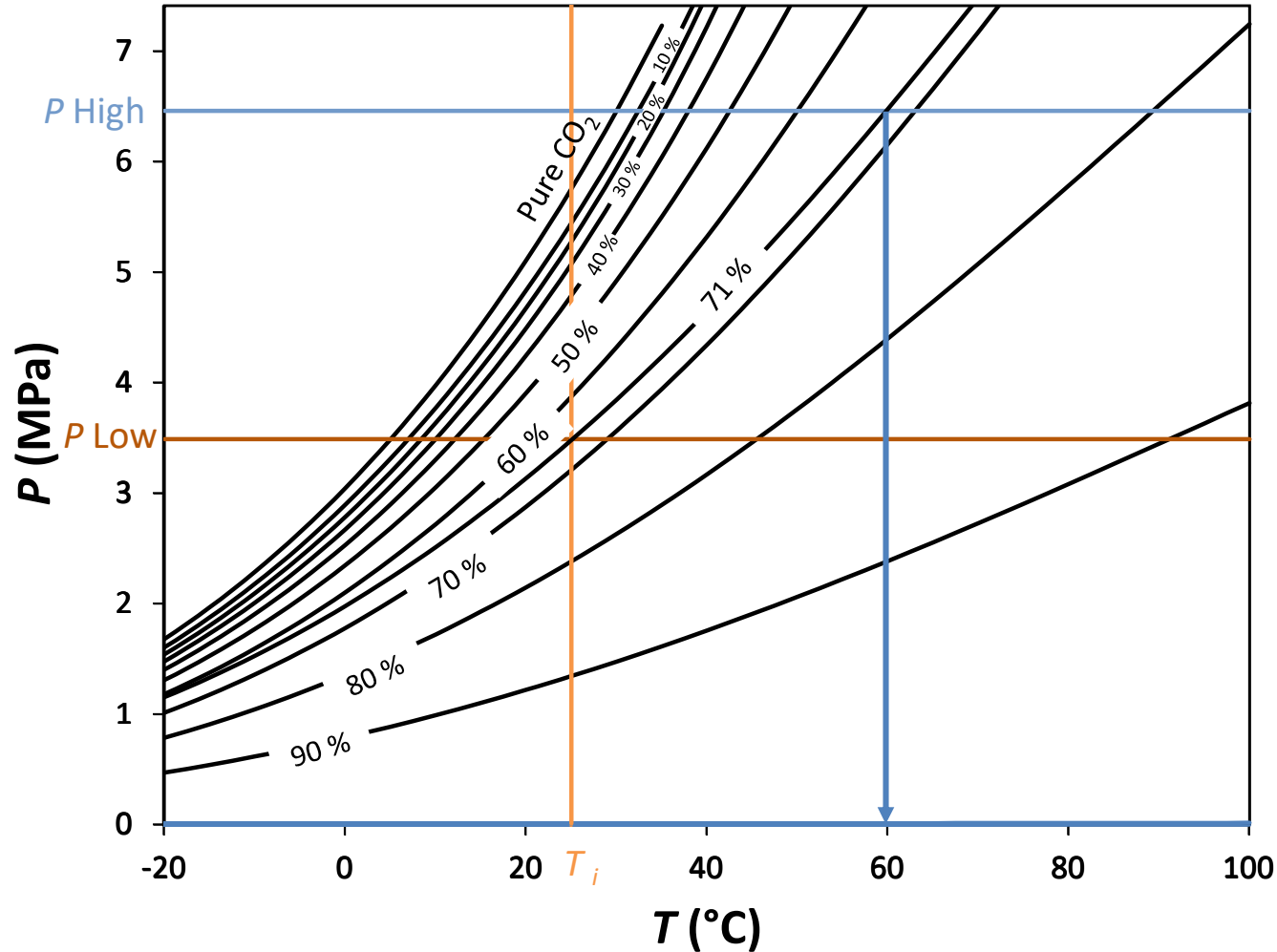
high pressure (MPa)	6.450
low pressure (MPa)	3.477
\dot{Q}_a (kW)	34.48
\dot{Q}_g (kW)	40.09
\dot{Q}_e (kW)	20.00
\dot{Q}_c (kW)	25.62
COP	0.4989

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

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System efficiency evaluation

> Dühring diagram

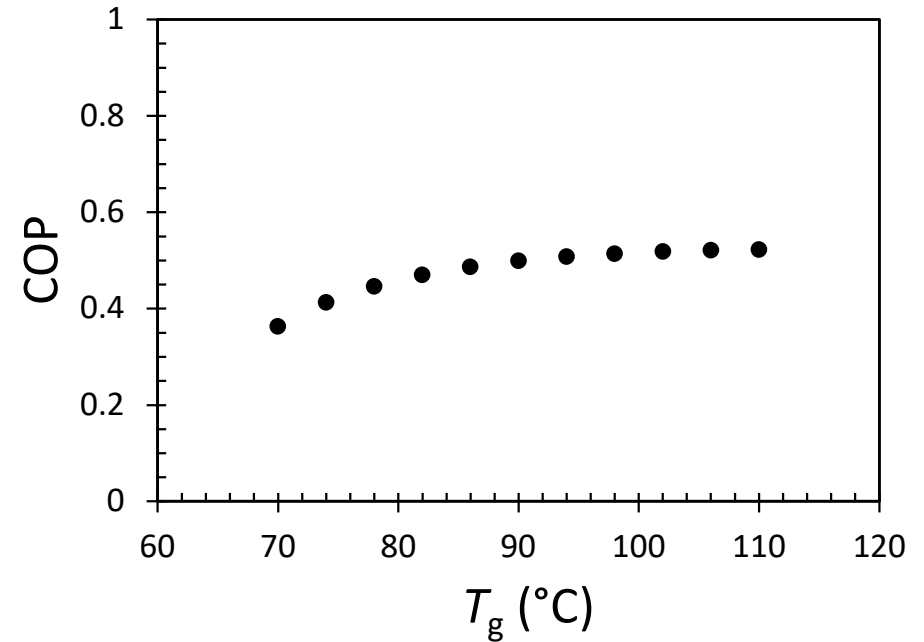
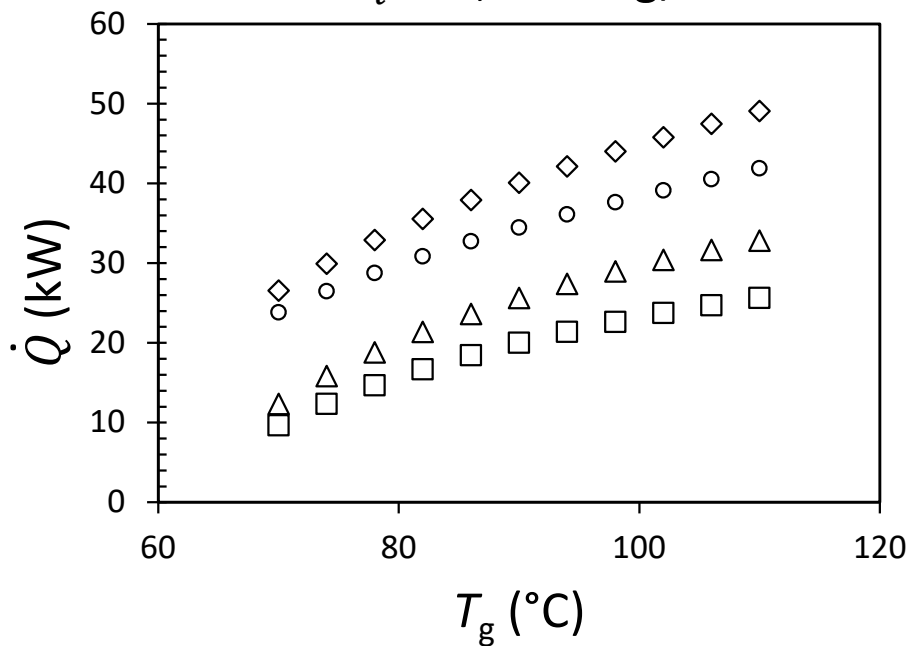


System efficiency evaluation

> Parametric analysis

- Generator temperature effect

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

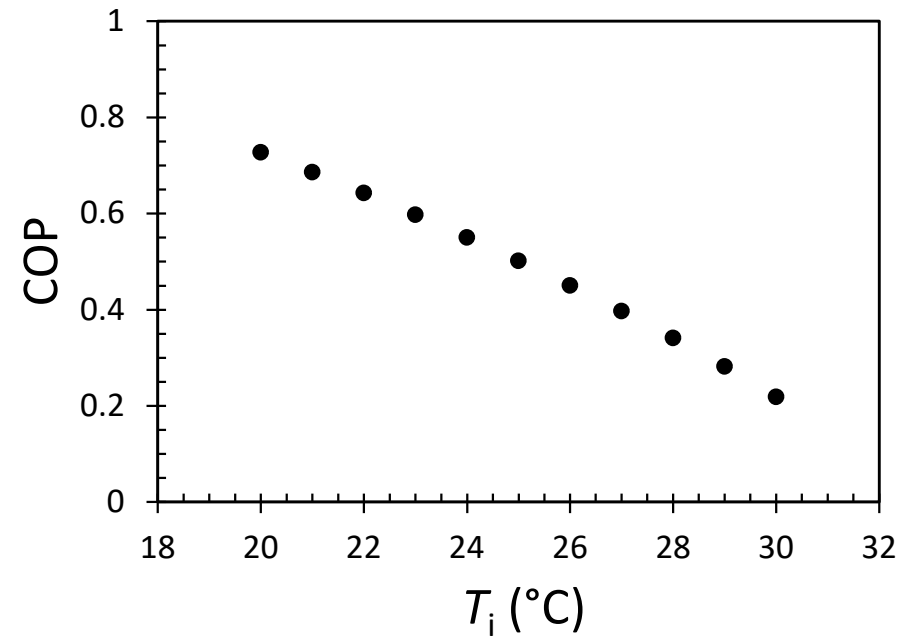
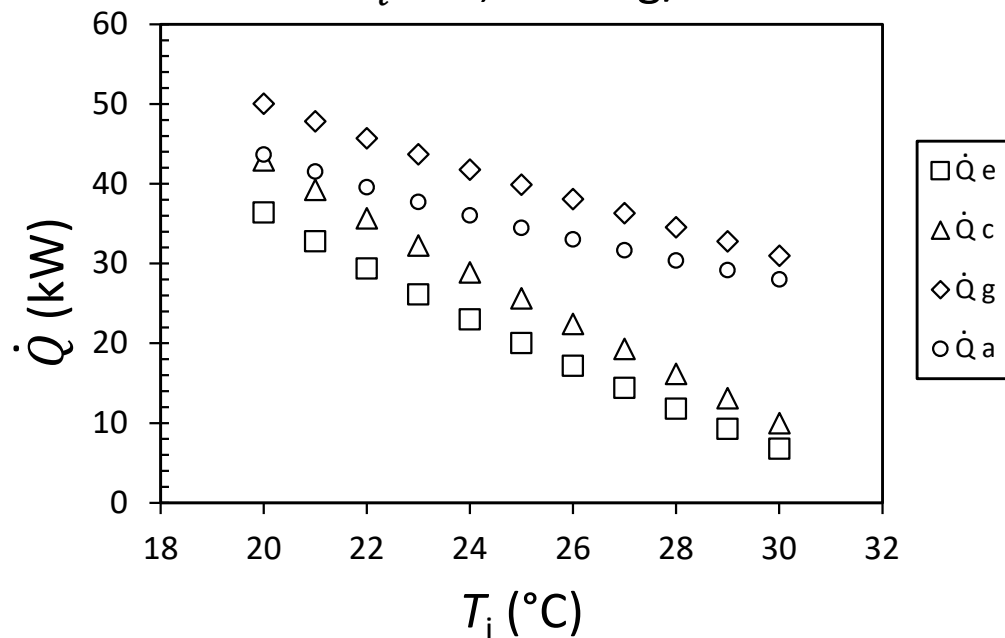


System efficiency evaluation

> Parametric analysis

- Intermediate temperature effect (T_a and T_c)

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

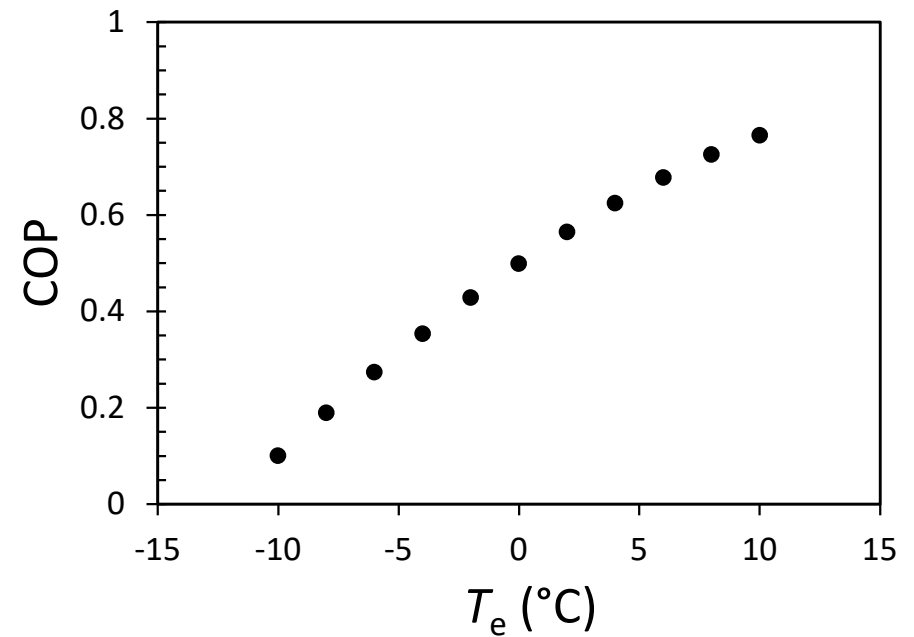
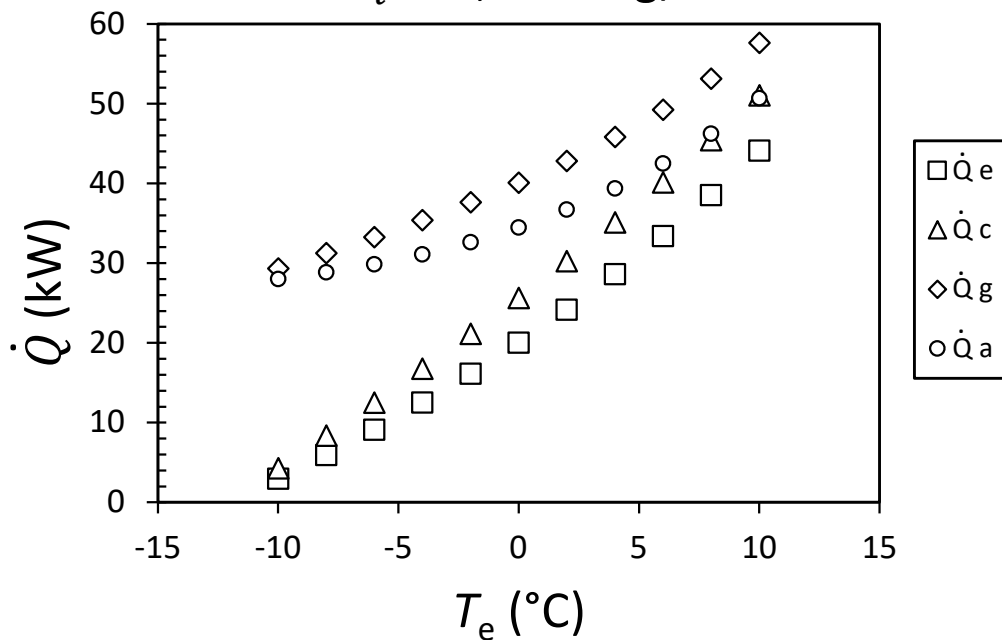


System efficiency evaluation

> Parametric analysis

- Evaporator temperature effect

- $T_i = 25^\circ\text{C}$
- $T_g = 90^\circ\text{C}$
- T_e varies from -10°C to 10°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

