Modelling of CO₂/acetone fluid mixture thermodynamic properties for compression/resorption refrigeration systems

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Abstract. Compression/resorption refrigeration systems are similar to conventional vapor compression systems but using zeotropic mixtures with large boiling temperature difference, similar to the refrigerant/absorbent mixtures used in absorption technology. A resorber and a desorber replace the conventional condenser and evaporator, respectively. As the saturation temperature in both desorber and resorber change with the composition, there is a gliding temperature that can reduce the irreversibility of the heat transfer with external sensible heat and sink sources. Another advantage of these systems is that they operate at lower pressures and pressure ratios than the conventional ones. CO₂/acetone mixture was proposed for automotive air-conditioning with compression/resorption systems. In this paper, different methods are evaluated for modelling the thermodynamic properties, using experimental data. The selected thermodynamic model will be used to study the performance of the compression/resorption refrigeration cycle.

1. Introduction
Nowadays, vapour-compression refrigeration is the technology most commonly used for refrigeration purposes. The refrigerants typically used in vapour-compression cycles are hydrofluorocarbons (HFCs) that are potent greenhouse gases. Although vapour-compression refrigeration is a well-known technology and provides very good performance, the need to reduce environmental impacts has renewed interest in the use of natural refrigerants.

Compression/resorption refrigeration is a very interesting technological alternative that provides more flexible design options compared to conventional systems. The concept of compression/resorption is similar to the conventional vapour compression cycle but the refrigerant is a zeotropic binary mixture with a large boiling temperature difference, and the evaporating and condensing processes are not completed as in conventional vapour-compression cycles. The evaporation and condensation taking place at the evaporator and condenser at constant pressure and temperature (for pure refrigerants) in the conventional systems are replaced by desorption and absorption processes at non-isothermal conditions (Lorentz Cycle) in the desorber and the resorber, respectively. As the evaporation in the desorber of the refrigerant/absorbent mixture is partial, along with the vapor stream a residual solution stream is produced and once pumped returns to the resorber in the so-called “resorption circuit”. The vapour stream leaving the desorber is compressed in the compressor and sent to the resorber after joining with the solution stream from the desorber. The two pressure levels in the conventional vapor-compression cycle are fixed by the refrigerant condensing and evaporating temperatures; however, in the resorption cycle, the operating pressures depend also on
the composition of the refrigerant/absorbent mixture, providing great flexibility in terms of cycle design. Thus, these cycles can operate at lower high pressures and lower pressure ratio than the compression cycles working with the refrigerant fluid.

Ammonia/water is the most commonly used working pair in compression/resorption refrigeration systems, but due to the toxicity of ammonia that limits its use in some applications, other mixtures based on carbon dioxide were proposed by several researchers. A complete review on compression/resorption refrigeration technology was published by Groll [1] in 1997.

The first reference of compression/resorption cycles, also called vapor compression cycle with solution circuit, with CO$_2$/acetone is from Groll and Kruse [2] based on the Ph.D. thesis of Groll [3] for refrigeration and air conditioning applications. In 2000, Spauschus and Hesse [4] published two patents about the use of CO$_2$ based mixtures and different absorbents for air conditioning in the automotive sector. The compression process performed in these documents is a two-phase compression, so the liquid and vapour streams leaving the desorber are compressed together by a wet compressor. As a result, the complexity and number of components in the cycle are reduced and due to the reduction of the discharge temperature at the compressor, the performance is improved. Mozurkewich et al. [5] studied by numerical simulation the performance of a wet compression/resorption cycle operating with CO$_2$/acetone and compared with other absorbents as N-methyl-2-pyrrolidone, neopentylglycol diacetate, and g-butyrolactone operating under the same pressure conditions as automotive air conditioning equipment with R134a. It was used property data of pure fluid and experimental data from Henderson [6]. They concluded that the performance with CO$_2$/acetone was better than with the other mixture. Yongming et al. [7] developed and tested a compression/resorption air conditioner working with mixtures based on CO$_2$. Wujek et al. [8] studied also the use of Ionic Liquids as absorbents of CO$_2$ for similar applications.

Most of these research works are based on thermodynamic properties of CO$_2$/acetone mixtures calculated with different methods, in general not based on experimental data because they were not available. For these reasons, in 2016 our research group launched a research project to complete the measurement and modelling of the thermodynamic properties of these mixtures for compression/resorption systems in refrigeration and air-conditioning applications.

The objective of this work is the evaluation of the methods for estimating the thermodynamic properties of CO$_2$/acetone in order to select the most convenient one to study the performance of the compression/resorption systems for refrigeration and air-conditioning applications.

2. Literature data and evaluation of thermodynamic property models

The first experimental data for CO$_2$/acetone found in the open literature are the vapour-liquid equilibrium data reported by Katayama et al. [9]. In 1991, Kato et al. [10] also measured the vapour-liquid equilibrium and compared with Kayatama’s values obtaining similar results. Between 1996 and 1998, Day et al. [11], Chang et al. [12] and Ja et al. [13] measured vapour-liquid equilibria and densities. Day et al. [11] corrected some of the data published in a previous paper. Adrian and Maurer [14] determined the solubility of CO$_2$ in acetone. In addition, liquid phase density and the critical pressure were determined. The authors obtained deviations of 10 % between the density calculated with the equation of state and the measured values. Reaves et al. [15] measured the critical pressure and temperature for CO$_2$/acetone diluted mixtures.

Chen et al. [16] measured vapour-liquid equilibrium and densities. Bamberger and Maurer [17], Steivano and Elvassore [18], and Hsieh and Vrabec [19] measured vapour-liquid equilibrium. Wu et al. [20] and Chiu et al. [21] measured phase boundaries. Zahran et al. [22] determined by isothermal calorimetry, the excess enthalpies of CO$_2$/acetone. The results obtained show that the mixing is exothermic at all the conditions studied with large effects of pressure and temperature on the excess enthalpy. Höhler et al. [23] measured the solubility of CO$_2$ in acetone. In our group, Ramírez-Ramos [24] determined experimentally the vapour-liquid equilibrium (VLE) in a temperature range from 283.1 K to 353.1 K in a range of composition. VLE data were correlated using the RKS EoS.
obtaining a good agreement between experimental and calculated data with deviations lower than 1.5%.

These experimental data can be used to select a suitable method, accurate and simple, to estimate the thermodynamic properties of CO\textsubscript{2}/acetone. In the first step, the experimental vapour-liquid equilibria data collected from different sources are analysed in order to exclude those data sets presenting large deviations from the rest. The deviations between calculated and experimental data were obtained using the Peng Robinson and the Redlich-Kwong-Soave equations of state with the binary interaction parameter equal to zero. The results show that the deviations for most of the vapour pressure data sets analysed are below 5% except for three references [18, 21, 28]. In Figure 1 can be seen that the selected experimental data sets cover almost completely the window for cooling applications using the compression/resorption refrigeration cycle, e.g., temperature range from -20 °C to 60 °C, and pressure up to 40 bar. In a second step, the binary interaction parameters were obtained by regression of the selected vapour-liquid equilibria data, in order to identify the method having lower deviations. The equations of state selected are Lee-Kesler-Plöcker (LKP), Peng-Robinson (PR) and Redlich-Kwong-Soave (RKS). Both cubic equations of state were evaluated with their original alpha-functions (PR and RKS) and with the Boston-Mathias one (PR-BM and RKS-BM), recommended for polar compounds (acetone in this case) and the supercritical region.

![Figure 1. Experimental CO\textsubscript{2}/acetone VLE data overlaying working window for cooling applications with compression/resorption refrigeration cycle.](image)

In the case of Lee-Kesler-Plöcker equation of state [26] the mixing rule to calculate the pseudo-critical temperature for the mixture can be written as:

\[ T_{cm} = \frac{x_1^2 \cdot V_{1c}^{0.25} \cdot T_{c1} + x_2^2 \cdot V_{2c}^{0.25} \cdot T_{c2} + 2 \cdot x_1 \cdot x_2 \cdot V_{12}^{0.25} \cdot T_{c12}}{V_{cm}^{0.25}} \]  \hspace{1cm} (1)

where sub-indexes 1 and 2 refer to CO\textsubscript{2} and acetone respectively, \( V_{cm} \) is the molar pseudo-critical volume for the mixture, which is based upon the pure components critical volume \( V_{c1} \) and \( V_{c2} \). Equation (3), \( V_{12} \) is the critical volume term calculated using Equation (3), and \( T_{c12} \) is the critical temperature term calculated from the critical temperature of pure components, \( T_{c1} \) and \( T_{c2} \), and a binary interaction parameter, \( k_{12} \), Equation (4).

\[ V_{cm} = x_1 V_{c1} + x_2 V_{c2} \]  \hspace{1cm} (2)
The binary interaction parameter \( k_{12} \) is obtained by regression of experimental VLE data. Regarding the cubic equations of state, they can be written in a polynomial form of the compressibility factor \( Z \) as:

\[
0 = Z_m^3 - Z_m^2 + Z_m(A_m - B_m - B_m^2) - A_mB_m
\]

(5)

\[
0 = 3^3 - (1 - B_m)Z_m^2 + Z_m(A_m - 2B_m - 3B_m^3) - (A_mB_m - B_m^2 - B_m^3)
\]

(6)

where Equation (5) corresponds to Redlich-Kwong-Soave EoS and Equation (6) for Peng-Robinson EoS. The coefficients \( A_m \) and \( B_m \) can be expressed with the following mixing rules:

\[
A_m = x_1^2 A_1 + x_2^2 A_2 + 2x_1x_2(A_1A_2)^{0.5}(1 - k_{12})
\]

(7)

\[
B_m = x_1 B_1 + x_2 B_2
\]

(8)

Coefficients \( A_1, A_2, B_1 \) and \( B_2 \) for the pure components are calculated as in a conventional way. The binary interaction parameter \((k_{12})\) can be expressed in a temperature dependent form as:

\[
k_{12} = a + bT + \frac{c}{T}
\]

(9)

where \( a, b \) and \( c \) are parameters obtained by regression of VLE data.

In this work, the Maximum Likelihood method is used to minimize the objective function \( OF \) and obtain the best values for \( k_{12} \). The objective function \( OF \) is defined as

\[
OF = \sum_{i=1}^{N} \left[ \left( \frac{p_{exp} - p_{calc}}{\sigma_p^2} \right)^2 + \left( \frac{T_{exp} - T_{calc}}{\sigma_T^2} \right)^2 + \left( \frac{x_{1,exp} - x_{1,calc}}{\sigma_{x_1}^2} \right)^2 + \left( \frac{y_{1,exp} - y_{1,calc}}{\sigma_{y_1}^2} \right)^2 \right]
\]

(10)

where \( \sigma^2 \) is the statistical variance of associated measured variables (Pressure \( P \), Temperature \( T \), liquid mole fraction \( x \), and vapor mole fraction \( y \)), and “exp” and “calc” indices refer to experimental and calculated values of \( P, T, x \) and \( y \) variables. Additionally, the Root-Mean-Square Deviation (RMSD) indicator, useful to evaluate the accuracy of the different methods in estimating the vapour-liquid equilibrium properties, is defined as follows:

\[
RMSD = \frac{OF}{\sqrt{N - n}}
\]

(11)

here \( N \) is the total number of experimental \( P, T, x, y \) data and \( n \) is the total number of parameters regressed.

In Table 1, the RMSD values for the selected equations of state and the values of the binary interaction parameter are shown. The deviations for the Lee-Kesler-Plöcker EoS with \( k_{12}=0 \) are much higher than the values obtained with other equations in the same conditions. However, when the binary interaction parameter is obtained by regression, in all the cases, the best results are obtained when \( k_{12} \) is independent of the temperature. It can be seen also that there is not any improvement in using the Boston-Mathias alpha-function.

Additionally, each of the proposed cubic equations of state has practically the same performance in estimating the VLE of CO\(_2\)/acetone. Reasonable results were achieved even without introducing a temperature dependence term in the binary interaction equation (7). As accuracy is not an issue anymore, either one of the cubic equations of state considered can be fairly used for modelling the thermodynamic properties necessary to study the performance of the cycle. Thus, we have selected the Redlich-Kwong-Soave equation to calculate the thermodynamic properties of the fluid mixture to study the performance and operating conditions of the cycle. Figure 2 shows the values of the maximum absolute deviation and the RMSD for the RKS equation.
In Figure 2(a), it can be seen that experimental data from [22] present the maximum absolute deviation for the temperature of 11 K with a RMSD of approximately 1.5 %. Regarding the liquid mole fraction, experimental data from [25] present the biggest deviation of 0.17 mol/mol that represents a value of 17% for RMSD (Figure 2(b)). Similarly, in Figure 2(c), it can be seen that the maximum deviation for pressure, about 7 bar, is found in [24,27,28,30] representing a RMSD value greater than 10 % for [23, 26]. Figure 2(d) shows that a maximum deviation value of about 0.03 mol/mol is obtained for vapour mole fraction representing a RMSD value lower than 1% in all cases.

### 3. Modelling of the thermodynamic properties

The thermodynamic properties of CO₂/acetone mixtures needed to study the performance and operating conditions of the compression/resorption system for refrigeration and air condition applications are vapour-liquid equilibrium (pressure, temperature, liquid, and vapour phase compositions) and vapour and liquid densities, enthalpies, and entropies. This section discusses the modelling of these properties. As explained in the cycle modelling section, the cycle design is based on the assumption that some states of the working fluid are at saturated conditions; thus, it is fundamental that the selected property calculation method computes adequately the vapour-liquid equilibrium. The VLE computation is a key factor to define the flow streams compositions throughout the cycle and may influence hugely on the cycle designing choices. Additionally, both liquid and vapour densities are essential in some component performance as the pump and compressor. Important to point out that the compressor energy requirement is a very important aspect for the cycle performance. Finally, thermodynamic properties such as enthalpy and entropy are crucial to foresee the energy performance in the cycle heat exchangers.

According to the results on the evaluation above presented, the Redlich-Kwong-Soave equation of state with the original alpha function, and $k_{12} = -0.008$ has been selected to perform the calculation of most of the thermodynamic properties needed.

The calculation procedure to calculate the VLE with equation of states is well-known [28]. Once the pressure and the composition of the vapor phase ($P$, $y$) at equilibrium conditions are fixed, the temperature and liquid phase composition ($T$, $x$) are calculated. In case that the input variables are the temperature and the liquid phase composition ($T$, $x$) at equilibrium conditions, the corresponding pressure and vapour-phase composition ($P$, $y$) are determined using the equation of the state.

| EOS       | Parameter          | RMSD  |
|-----------|--------------------|-------|
| LK-LOCK   | $k_{12} = 0$       | 373   |
|           | $k_{12} = 7.2 \times 10^{-2}$ | 81.7  |
| PENG-ROB  | $a = -6.2 \times 10^{-3}$; $b = 0$ | 81.4  |
|           | $a = -1.0 \times 10^{-2}$; $b = 3.5 \times 10^{-4}$; $c = 0$ | 81.3  |
|           | $a = 4.6$; $b = -7.5 \times 10^{-3}$; $c = -698.1$ | 72.2  |
| PR-BM     | $k_{12} = 0$       | 76.5  |
|           | $a = 0.0052$; $b = 0$ | 77.4  |
|           | $a = 0.15$; $b = -0.0053$; $c = 0$ | 71.0  |
| RKS       | $k_{12} = 0$       | 79.2  |
|           | $a = 0.008$; $b = c = 0$ | 79.6  |
|           | $a = 0.016$; $b = 0.00031$; $c = 0$ | 70.4  |
| RKS-BM    | $k_{12} = 0$       | 79.1  |
|           | $a = 0.0078$; $b = c = 0$ | 79.4  |
|           | $a = 0.059$; $b = -0.0022$; $c = 0$ | 79.4  |
|           | $a = 4.7$; $b = -0.0076$; $c = 721.7$ | 79.5  |
The density of the vapour phase can be computed by finding three roots of the cubic equation of state, Equation (5), for a given state: the largest one corresponds to the vapour phase, the smallest to the liquid phase [30]. Figure 3 shows a comparison between the vapour density calculated with the selected RKS-EoS and experimental data from [12] against the correspondent equilibrium liquid phase composition at different temperatures. It can be seen a good agreement between experimental and computed values through the EoS for the vapour phase density.

Figure 2. Maximum deviation and Residual Root Mean Deviation between calculated values using RKS-EoS and experimental data from different sources.

Figure 3 Comparison of experimental [14] and calculated saturated vapour density using Redlich-Kwong-Soave equation as a function of the correspondent equilibrium liquid-phase mole fraction at different temperatures.

Because the liquid density is
usually not accurately calculated by cubic equations of state [28], the modified Rackett model [30] is used in this work to estimate it. The corresponding mixing rule to calculate the critical temperature term ($T_{c,m}$) for the mixture has been calculated with the following equation:

$$T_{c,m} = \frac{x_1^2 V_{c1} T_{c1} + x_2^2 V_{c2} T_{c2} + 2x_1x_2 V_{c1} V_{c2} (T_{c1} T_{c2})^{0.5} (1 - k_{12})}{V_{cm}}$$

(12)

where $T_{ci}$ and $T_{cj}$ is the critical temperature of the pure components, $V_{cm}$ is the critical volume term and $k_{12}$ a binary interaction parameter. The critical volume term is calculated with Equation (2). The binary interaction parameter can be expressed in function of the temperature as:

$$k_{12} = a + b T + c T^2$$

(13)

where $a$, $b$ and $c$ are obtained (Table 2) through experimental data regression from literature [11, 13, 16, 29].

**Table 2.** Coefficients of the binary interaction parameter for Equation (13).

| Parameter | Value | Units |
|-----------|-------|-------|
| $a$       | 0.12  | -     |
| $b$       | -0.00038 | K$^{-1}$ |
| $c$       | 3.272 x 10$^{-06}$ | K$^2$ |

The regression yields a maximum absolute deviation of 92.97 kg/m$^3$ and a RMSD of 2.3 % (Figure 4).

**Figure 4.** Comparison of calculated and experimental values of saturated liquid density using the modified Rackett model (lines) and literature data (symbols) [13, 14, 17, 30].

Regarding the energy-related properties, only Zahran et al. [22] measured excess enthalpy for CO$_2$/acetone. However, for a good understanding of the cycle behaviour, both the fluid mixture enthalpy and entropy are necessary: the former for the operation of heat exchangers such as desorber and resorber and the later for the compressor model, respectively. In this work, enthalpy and entropy are evaluated through departure function expressions corresponding to the RKS equation of state. Thus, the enthalpy of the binary fluid mixture $H$ at a given state defined by the pressure $P$, temperature $T$, and total composition $z$ is calculated as follows:

$$H(P, T, z) = H^0(T, z) - H^d(P, T, z)$$

(14)
where $H^0$ and $H^d$ are the ideal gas enthalpy and the departure enthalpy, that can be obtained using the following equations:

\[ H^0(T, z) = \int_{T_{ref}}^{T} \left[ z C_{P,1}^0 + (1 - z) C_{P,2}^0 \right] dT \]  

\[ C_p^0 = A + B \left( \frac{E}{\sinh \left( \frac{E}{T} \right)} \right)^2 + D \left( \frac{E}{\cosh \left( \frac{E}{T} \right)} \right)^2 \]  

\[ H^d(P, T, z) = - \frac{A_m \alpha}{RT B_m} \ln \left( \frac{2V}{2V + B_m} \right) + 1 - Z_m \]  

where $C_{P,1}^0$ and $C_{P,2}^0$ are the ideal gas heat capacity of the pure components, CO$_2$ and acetone respectively, calculated using equation (15) and the parameters $A$ to $E$ are pure fluid dependent taking the values indicated in Table 3. The enthalpy at the reference state is zero being the reference temperature $T_{ref}$ equals to 298.15 K.

**Table 3.** Pure fluid coefficient values for the ideal gas heat capacity equation (15).

| Fluid          | $A$ [J/mol K] | $B$ [J/mol K] | $C$ [K] | $D$ [J/mol K] | $E$ [K] |
|----------------|---------------|---------------|--------|---------------|--------|
| Carbon dioxide | 29.37         | 34.54         | 1428   | 26.4          | 588    |
| Acetone        | 57.04         | 163.2         | 1607   | 96.8          | 731.5  |

For the entropy calculation, the procedure is similar but using the following expressions:

\[ S(P, T, z) = S^0(T, z) - S^d(P, T, z) \]  

\[ S^0(T, z) = \int_{T_{ref}}^{T} \left[ z C_{P,1}^0 + (1 - z) C_{P,2}^0 \right] dT \]  

\[ S^d = \frac{dA_m \alpha}{RT B_m} \ln \left( \frac{2V}{2V + B_m} \right) - \ln \left( Z \left( 1 - \frac{B_m}{V} \right) \right) \]  

### 4. Modelling of the compression/resorption refrigeration cycle

Figure 5 shows the scheme of the compression/resorption cycle, being the main components: the resorber, the desorber, the compressor, the solution heat exchanger, the solution pump and the throttling valve. The CO$_2$ concentrated solution, also known as rich solution, with a mass CO$_2$ fraction $x_{rich}$ and a mass flow rate $\dot{m}_{rich}$, is partially evaporated in the desorber at the low pressure $P_{low}$ producing a cooling effect $Q_D$, and leaving it with a vapor quality $q_7$ and a low temperature $T_7$. Then, the two-phase flow produced is separated into two streams. The solution stream, called weak solution, with a lower CO$_2$ mass fraction $x_{weak}$ and a mass flow rate $\dot{m}_{weak}$, is pumped to the high pressure $P_{high}$ and mixed with the compressed vapor stream, $\dot{m}_{vapor}$, before entering the resorber.

The absorption process of the vapor stream by the weak solution is completed in the resorber where the heat produced $Q_R$ is delivered to the sink. The rich solution leaves the resorber at a high temperature $T_a$, and return to the desorber after being throttled in the expansion valve. The solution heat exchanger, with effectiveness $\varepsilon_{HX}$, placed in the solution circuit, also known as resorption circuit, subcools the rich solution in order to increase the cooling effect in the desorber. The vapor stream from the separator is compressed by the compressor to the high pressure $P_{high}$, being $\dot{W}_c$ the
mechanical power consumed in the process. The power consumed by the solution pump is $W_p$. The efficiency of the refrigeration cycle is expressed in terms of the Coefficient of Performance, COP, defined as

$$\text{COP} = \frac{Q_D}{W_C + W_p}$$ (21)

The solution circulation ratio $f$ is defined as the ratio of the rich solution and vapour mass flow rates.

$$f = \frac{m_{\text{rich}}}{m_{\text{vapor}}}$$ (22)

The compression pressure ratio is defined as the ratio of the high and low-pressure values.

$$\text{CPR} = \frac{P_{\text{high}}}{P_{\text{low}}}$$ (23)

![Compression/resorption refrigeration cycle scheme](image)

**Figure 5.** Compression/resorption refrigeration cycle scheme.

The cycle modelling is based on the mass and energy balances (Tables 4 and 5) and in the following assumptions:
- the two-phase flow leaves the desorber at the temperature $T_7$ and pressure $P_{\text{low}}$ in equilibrium conditions;
- the rich solution with a CO$_2$ mass fraction $x_{\text{rich}}$ leaves the resorber at the temperature $T_4$ and pressure $P_{\text{high}}$ fluid mixture in saturated conditions;
- the processes in the solution pump and the compressor are isentropic;
- the throttling process in the expansion is considered isenthalpic;
- the process in the separator and the mixing process before the resorber are adiabatic;
- the effectiveness of the solution heat exchanger is 1;
- pressure drops and heat losses in pipes and other components are not considered.

The independent variables are:
- solution temperature at the resorber outlet: $T_4$;
- fluid mixture temperature at the outlet of the desorber: $T_7$;
- rich solution composition, $x_{\text{rich}}$;
- difference between rich and weak solution compositions (in terms of CO$_2$ mass fraction) $\Delta x = x_{\text{rich}} - x_{\text{weak}}$;
- vapour mass flow rate $\dot{m}_{\text{vapor}}$ is taken as a reference equal to 1 kg/s.

**Table 4.** Energy balances in the main components of the compression/resorption cycle.

| Component                  | Energy balances                                                                 |
|----------------------------|---------------------------------------------------------------------------------|
| Compressor                 | $W_C = \dot{m}_{\text{vapor}}(h_2 - h_1)$                                      |
| Resorber                   | $Q_R = \dot{m}_{\text{vapor}}[f \ h_4 - h_2 - (f - 1)h_{10}]$                     |
| Solution heat exchanger SHX| $\dot{Q}_{\text{SHX}} = \dot{m}_{\text{vapor}}(h_4 - h_5) = \dot{m}_{\text{vapor}}((f - 1)(h_{10} - h_9))$ |
| Expansion valve            | $h_5 = h_6$                                                                      |
| Desorber                   | $\dot{Q}_D = \dot{m}_{\text{vapor}}[h_1 + (f - 1)h_{10} - f \ h_6]$               |
| Solution pump              | $W_p = \frac{\dot{m}_{\text{weak}}(P_{\text{high}} - P_{\text{low}})}{\rho_0}$ |

**Table 5.** Mass balances in the separator.

| Component   | Mass balances                                                                 |
|-------------|--------------------------------------------------------------------------------|
| Separator   | $\dot{m}_{\text{rich}} = \dot{m}_{\text{vapor}} + \dot{m}_{\text{weak}}$       |
|             | $x_{\text{rich}}\dot{m}_{\text{rich}} = y_1 \dot{m}_{\text{vapor}} + x_{\text{weak}}\dot{m}_{\text{weak}}$ |

The cycle can be represented graphically in the Dühring diagram for the CO$_2$/acetone mixture. This diagram, also known as PTXY diagram, is drawn using the RKS equation of state obtained in section 3. In Figure 6, has been represented the solution circuits corresponding to the typical temperature conditions of an air-conditioning application (e.g. $T_s = 35^\circ$C, $T_l = 10^\circ$C based on [31]). These temperature levels are obtained considering a cooling water inlet temperature of 30$^\circ$C in the resorber and chilled water returning temperature of 15$^\circ$C in the desorber. In both cases, the composition of the rich solution is the same $x_{\text{rich}}=50\%$ in CO$_2$ mass fraction but the values of the rich and weak solution compositions are $\Delta x = 0.2$ (case 1: blue circuit) and $\Delta x = 0.3$ (case 2: red circuit). As can be seen in this figure, the high pressure is the same in both cases $P_{\text{high}} = 40$ bar, because it depends on $x_{\text{rich}}$ and $T_s$, being the low pressure different $P_{\text{low}} = 13.94$ bar (case 1) and $P_{\text{low}} = 9.4$ bar (case 2), because it depends on the composition of the weak solution ($x_{\text{weak}} = x_{\text{rich}} - \Delta x$) and the temperature $T_l$. The corresponding pressure ratio values are 2.69 and 3.99 and the composition of the vapor stream in the compressor are $y_1 = 98.6\%$ (case 1) and $y_1 = 98\%$ (case 2) in CO$_2$ mass fraction. The solution circulation ratio values are 3.43 (case 1) and 2.6 (case 2). Finally, the cooling capacity, the power consumed by the compressor and pump, and the COP are shown in Table 6:

**Table 6.** Performance indicators for typical air-conditioning application.

| Indicators   | Case 1  | Case 2  |
|--------------|---------|---------|
| $\dot{Q}_D$(kW) | 230.7   | 240.4   |
| $W_p$(kW)    | 7.34    | 5.73    |
| $W_C$(kW)    | 57.1    | 82.9    |
| COP          | 3.58    | 2.71    |
Figure 6. Compression/resorption cycle for air conditioning application in a pressure-temperature-composition (PTXY) diagram of CO$_2$/acetone mixture.

5. Conclusions
The open literature review on the experimental vapor-liquid equilibrium data of CO$_2$/acetone mixtures revealed the existence of enough data to cover the working window for the cooling applications of the compression/resorption system. These data sets were evaluated using the cubic equations of state of Peng Robinson and Redlich-Kwong-Soave with their original and the Boston-Mathias alpha-functions and the binary interaction parameter equal zero. The data sets with deviations lower than 5% in the pressure estimation, were used for the binary interaction parameter regression of the equations of state considered. The most suitable method, accurate and simple, found is the Redlich-Kwong-Soave with the original alpha-function and the binary interaction parameter $k_{12} = -0.008$.

Based on the estimation thermodynamic property method selected, it has been developed a thermodynamic model of the compression/resorption cycle. This model is useful to design the cycle and study the performance and operating conditions for cooling applications. The compression/resorption cycle have been represented graphically in the Dühring diagram for CO$_2$/acetone mixture in typical thermal conditions for air-conditioning.

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