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High-pressure vapor + liquid equilibria for the binary system CO₂ + (E)-2-hexenal

*Rafael Villablanca-Ahues^a, Pablo López-Porfiri^b, Roberto I. Canales^c, and Juan C. de la
Fuente^{a,*}*

^aLaboratorio de Termodinámica de Procesos. Departamento de Ingeniería Química y Ambiental.
Universidad Técnica Federico Santa María, Avda. España 1680, Valparaíso, Chile.

^bSchool of Chemical Engineering and Analytical Sciences. Faculty of Science and Engineering.
The University of Manchester, Manchester M13 9PL, United Kingdom.

^cDepartamento de Ingeniería Química y Bioprocesos, Pontificia Universidad Católica de Chile,
Avenida Vicuña Mackenna 4860, Santiago, Chile.

*Fax: (56-32) 2654478. Tel. (56-32) 2654221. E-mail: juan.delafuente@usm.cl

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Abstract

The isothermal vapor + liquid equilibria of carbon dioxide + (E)-2-hexenal (a key apple aroma) was measured using a visual equilibrium cell with an analytic methodology. The selected isotherms were (313.2, 323.2 and 333.2) K, and the pressures assessed ranged from (2.2 to 9.8) MPa. The thermodynamic consistency of the experimental data was verified, and the uncertainties of the molar fractions of the vapor and liquid phases were estimated. The density and dynamic viscosity of pure (E)-2-hexenal were measured at 101.13 kPa and temperatures from (292.2 to 353.2) K. Two equations of state were selected to model the vapor + liquid equilibria. The Peng-Robinson with two different mixing rules, and the Perturbed Chain - Statistical Associating Fluid Theory. The phase envelopes showed a critical pressure, detected at carbon dioxide molar fractions $\geq 95 \text{ \% mol} \cdot \text{mol}^{-1}$.

Keywords: Vapor + liquid equilibria; carbon dioxide; (E)-2-hexenal; density; viscosity; experimental; modeling.

1. Introduction

The aroma of apples is specific to the species and cultivar. The aroma contributes to the overall sensory quality of the fruit, and it is composed by a combination of approximately three hundred volatile organic compounds [1]. The mixture of nearly twenty chemical species, including aldehydes, alcohols, esters, and ketones, usually at very low concentrations, are considered to be the key blend that defines the typical aroma of apples [2]. The aldehyde (E)-2-hexenal (Figure 1) is identified as an essential aroma component for sensory impressions of freshness for green apples as well as in commercial apple juices [3-5].

The conventional procedures for the fractionation and recovery of key volatile organic compounds from concentrated or diluted fruit juice are based on the distillation process. The use of compressed countercurrent carbon dioxide (CO₂) as a solvent in a packed column has proven to be an efficient alternative for the extraction of apple aromas [5,6]. In this process, there is a continuous upward flow of a CO₂-rich phase in contact with a downward flow of a liquid water-rich mixture with fruit juice. The operating temperature (T) and pressure (p) are above the critical values of the CO₂, $T > T_c = 304.1$ K and $p > p_c = 7.38$ MPa. At the supercritical (SC) condition, the CO₂ reveals advantageous characteristics. In general, SC-CO₂ is selective, as well as a solvent with tunable properties with the temperature and pressure. In addition, the use of SC-CO₂ helps to eliminate the risk of thermal damage, and the solvent can be easily removed by decompression [7]. These two aspects are relevant for the fractionation and recovery of high-purity products in food, cosmetics, and for use in the pharmaceutical industry [8].

In order to design and optimize a process for the recovery of key volatile organic compounds using SC-CO₂, the main constraints are defined by the thermodynamic phase equilibria information. Specifically, experimental data as well as models that relate the temperature, pressure, and the mole fraction of the water-rich (liquid, x_i) and CO₂-rich (vapor, y_i) phases at high-pressure equilibrium conditions are required [9]. In addition, pure physicochemical properties of key aroma components such as vapor pressure (p_2^{vap})

[10], density (ρ_i) and dynamic viscosity (η_i) are also needed for a better understanding and modeling of the hydrodynamics process and mass transfer.

López-Porfiri et al., [9] analyzed the data of high-pressure vapor + liquid equilibria (VLE) available in the literature regarding systems containing aroma components and CO₂. The literature suggests that the information could be organized into two main groups. First, the complex systems constituted for extracts of apple aroma components and CO₂, and second, the model systems that include binary and multicomponent mixtures of one or two key aroma components, CO₂, and eventually water [11]. The current state of the available data indicates that there is a need for new and complementary experimental information for high-pressure VLE, and pure component properties. This contribution is a continuation of the work reported by López-Porfiri et al., [9] as well as other works available in the literature [8,10-12]. However, specific data of the high-pressure VLE for CO₂ and (E)-2-hexenal has not been previously reported in the literature. The main goal is to provide physicochemical properties data and modeling required for the development and scale-up of extraction processes, mainly based on packed columns using SC-CO₂ at countercurrent for the recovery of key fruit aroma components.

The specific objective of this work is to contribute with new experimental data (T , p , x_i , y_i) for the isothermal high-pressure VLE of the binary systems CO₂ ($i = 1$) + (E)-2-hexenal ($i = 2$), as well as experimental data of ρ_2 and η_2 for pure (E)-2-hexenal. In addition, we model the experimental measurements using the Peng-Robinson equation of state with the van der Waals and Wong-Sandler mixing rules, as well as the Perturbed Chain - Statistical Associating Fluid Theory (PC-SAFT) equation of state.

2. Materials and Methods

2.1 Materials

(E)-2-Hexenal (99 % purity. CAS: 6728-26-3) was purchased from Sigma-Aldrich (St. Louis. MO). Carbon dioxide (99.99 % purity) and chromatographic carrier gas helium (99.995 % purity) were purchased from Linde-Chile S.A. Reagents were used without further purification.

2.2 High-pressure vapor + liquid equilibrium measurements

The experimental design and procedure used to measure the isothermal high-pressure vapor + liquid equilibria of the binary system CO₂ + (E)-2-hexenal were previously described in detail by López-Porfiri et al. [9], and Bejarano et al. [11]. The temperatures and pressures measured were up to 333.2 K and 10 MPa constrained by the equipment limits and data requirements. The apparatus used a static-analytic methodology, where the main component is a high-pressure view-cell (Thar-Tech. Pittsburgh. PA) of 600 cm³, with ports for direct sampling of the vapor and liquid phases.

The experimental procedure started with approximately 100 cm³ of (E)-2-hexenal loaded into the empty and clean cell. It continued with the setting of the selected temperature in the controller (Digi-Sense Vernon Hills, IL), and the purge of the remaining air with CO₂ at low-pressure. When the temperature was in steady state, the CO₂ was slowly added to the cell with a syringe pump (Teledyne ISCO, 260D, Lincoln, NE) until it reached the previously selected pressure. All the experiments confirmed that after 4 hours of stirring and temperature fluctuations ≤ 0.1 K, the mixture reached the equilibrium condition. The sapphire windows of the cell allowed for the confirmation of the number and type of phases. The molar fraction of the vapor phase was assessed by using an on-line micro-sample injector (ROLSI, Armines, Paris, France) connected to a gas chromatograph (PerkinElmer, Clarus 500, Waltham, MA) to detect CO₂ and (E)-2-hexenal. The capillary column selected was a HayeSep C-ValcoPLOT (VICI Metronics, Houston, TX) 30 m long, 0.53 mm internal diameter, and 20 μ m of thickness. The gas carrier used was helium at 10 cm³·min⁻¹. The temperature of the injector and the thermal conductivity detector was 423 K, and the oven operated at 373 K. The molar fraction of the liquid phase was determined with a micro needle-flow control valve connected to a cold-trap and a wet-test meter. The (E)-2-hexenal

condensed in the cold-trap was weighted with an analytical balance (RADWAG, North Miami Beach, FL). The volume of CO₂ was quantified in the wet-test meter (Ritter, TG05, Germany) at room temperature and atmospheric pressure. The volumetric properties of the CO₂ were calculated with the NIST [13] database. Molar fractions reported were, on average, three solubility measurements, with relative standard deviations lower than 5 %.

The standard uncertainties of temperature ($u(T) = 0.1$ K) and (pressure $u(p) = 0.01$ MPa), as well as the combined expanded uncertainty of the CO₂ (1) mole fractions in vapor ($U_{\text{Comb}}(y_1)$) and liquid ($U_{\text{Comb}}(x_1)$) phases were estimated according to the definitions of Chirico et al. [14]. Specifically, $U_{\text{Comb}}(y_1)$ was estimated using the method proposed by Miller and Miller [15], and $U_{\text{Comb}}(x_1)$ was calculated from the information available for the experimental methodology and measured data [9]. For both uncertainties, a confidence level of 95.45 % was selected, which meant a coverage factor of 2 [9,14].

2.3 Density and dynamic viscosity measurements

Density and dynamic viscosity were measured for (E)-2-hexenal in an Anton Paar Densitometer (DMA4500M, Austria), with a coupled modular Anton Paar Lovis micro-viscometer (2000ME, Austria) [16]. The densitometer uses a vibrating U-tube to provide density measurements, and according to the procedure, this apparatus was previously calibrated with distilled deionized and degassed water and dry air at a pressure of 101.3 kPa. The standard uncertainty reported for the manufacturer is $u(\rho) = 0.05$ kg·m⁻³. The dynamic viscosity measurements are based on the falling ball principle. The micro-viscometer was calibrated using viscosity standards provided by the manufacturer. The viscosity measurements have a reported relative standard deviation of 0.4 %, with a standard uncertainty of $u(\eta) = 0.02$ mPa·s.

2.4 Thermodynamic of phase equilibria modeling

The vapor + liquid equilibrium was modeled using the ϕ - ϕ approach, Eq. (1) [17], following the methodology utilized by López-Porfiri et al. [9].

$$y_i \cdot \bar{\phi}_i^V = x_i \cdot \bar{\phi}_i^L \quad (1)$$

The fugacity coefficients of the vapor phase ($\bar{\phi}_i^V$) and liquid phase ($\bar{\phi}_i^L$) were calculated using two different equations of state, Peng-Robinson (PR) equation of state (EoS) [17], and PC-SAFT [18,19].

For the PR-EoS, two mixing rules were selected. The classical quadratic van der Waals (vdW) mixing rule with two adjustable interaction parameters, k_{12} and l_{12} , and the Wong and Sandler (WS) mixing rule including the Non-Random Two Liquid model (NRTL) for the calculation of the excess Gibbs free energy [20], with four binary interaction coefficients (k_{12} , α_{12} , τ_{12} , τ_{21}).

For PC-SAFT, the CO₂ (1) was considered as a non-polar molecule and the (E)-2-hexenal (2) as a dipolar and non-associating molecule. In this work, the perturbation expansion of the Helmholtz residual energy included the terms hard-chain, dispersion, and dipolar contribution [21]. The four pure-component parameters, number of segments (m_2), segment diameter (σ_2), dispersion energy (ε_2/k_2), and the fraction of dipolar segments in the molecule ($x_{p,2}$), were adjusted from the density and vapor pressure data of (E)-2-hexenal by fixing its experimental dipole moment (μ_2). This value was obtained from the literature for 1-hexenal [22], which is molecularly comparable to (E)-2-hexenal. The three parameters, m_1 , σ_1 and ε_1/k_1 , for CO₂ were obtained from the literature [18]. The Lorentz-Bertherlot mixing rules [18], Eq. (2), were used to calculate the combined segment diameter (σ_{12}) and the combined dispersion energy (ε_{12}) of the mixtures, with one adjusting binary interaction coefficient, k_{12} .

$$\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2) \quad (2a)$$

$$\varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2} (1 - k_{12}) \quad (2b)$$

3. Results and Discussion

3.1 Experimental high-pressure vapor + liquid equilibria data

Table 1 reports the isothermal VLE data measured for the system CO₂ + (E)-2-hexenal at (313.2, 323.2 and 333.2) K, and pressures from (2.2 to 9.8) MPa. This data was analyzed and validated according to

the methodology proposed by López-Porfiri et al. [9], which considered the thermodynamic consistency evaluation, as well as the estimation of the uncertainties. For each isothermal dataset, the experimental mole fractions of the vapor phase were compared with the values estimated by using the Gibbs-Duhem equation to define the thermodynamic consistency. The estimations were performed using the tools available in Aspen Plus v.9 (ApenTech. Bedford. MA) based on the modification of Fredenslund [23]. Table 2 indicates that the isotherms of (313.2 and 333.2) K were thermodynamically consistent. Both isotherms verified that the mean absolute deviations between experimental and estimated molar fractions were lower than the recommended upper limit of $0.01 \text{ mol} \cdot \text{mol}^{-1}$ [23]. For the isotherm of 323.2 K, even though the mean absolute deviations exceed the limit of 2 %, this divergency was considered negligible and the isotherm is considered as thermodynamically consistent. In Table 1, the values of the estimated uncertainties, showing that $U_{\text{Comb}}(y_1) \leq 0.045 \text{ mol} \cdot \text{mol}^{-1}$ and $U_{\text{Comb}}(x_1) \leq 0.016 \text{ mol} \cdot \text{mol}^{-1}$, are shown. In addition, no significant differences were found in the numerical values of the uncertainties between the three isotherms measured.

The experimental information listed in Table 1 was included in Figure 2 and corresponds to the equilibrium between the vapor and liquid phases, without visually detecting any partial immiscibility. The phase envelopes for the three isotherms measured were similar, and their shape can be attributed to the significant differences in the relative volatility of CO_2 and (E)-2-hexenal. The phase envelopes presented a critical pressure at CO_2 molar fractions higher than 95 %. The pressures corresponding to the critical solution points increased with the temperature and were estimated $< 1.1 \text{ MPa}$. No references were found in the literature with information of the VLE for the system $\text{CO}_2 + (\text{E})\text{-2-hexenal}$, nevertheless the phase behavior is comparable to other key apple aroma components studied, for instance, $\text{CO}_2 + \text{hexanal}$ [9,24] and $\text{CO}_2 + \text{ethyl-2-methylbutyrate}$ [9].

3.2 Density and dynamic viscosity of pure (E)-2-hexenal

Experimental density and dynamic viscosity of pure (E)-2-hexenal measured at 101.13 kPa, and temperatures from (293.2 to 353.2) K are reported in Table 3. Both properties decreased with temperature, and the values ranged from (797.45 to 851.87) kg·m⁻³ for density, and from (0.469 to 0.934) mPa·s for viscosity. The (open) literature reports at 293 K a density value with a deviation of 0.39 % [25] from the data measured in this work. Data measured for the dynamic viscosity for pure (E)-2-hexenal was not found in the literature.

Experimental data measured were calculated with PC-SAFT, with a deviation of ±21.1 kg·m⁻³ for the density. The dynamic viscosity was correlated to the temperature using the Vogel-Fulcher-Tamman (VFT) model [26]. The Eq. (3) reports the vales of the adjusted parameters, with a deviation of ±0.002 mPa·s.

$$\eta_2(\text{mPa} \cdot \text{s}) = 0.0416 \cdot \exp\left(\frac{662.7}{T(\text{K}) - 80.23}\right) \quad (3)$$

3.3 Thermodynamic modeling of high-pressure vapor + liquid equilibrium data

3.3.1 Peng-Robinson equation of state

Table 4 reports the properties of pure components for CO₂ (1) and (E)-2-hexenal (2) obtained from the NIST Standard Database v5.0 [13], except for the acentric factor of the (E)-2-hexenal that was estimated with the Lee-Kesler correlation [27]. The critical temperature and pressure, as well as boiling temperature for (E)-2-hexenal, were estimated with the Joback group contribution method [27]. The interaction parameters of the mixing rules were estimated according to López-Porfiri et al., [9] by minimizing the relative root-mean square deviation, $\delta(y_1, x_1)$, defined by the Eq. (4) [14].

$$\delta(y_1, x_1) = \sqrt{\frac{1}{N} \sum_{j=1}^N [\delta(y_1)_j^2 + \delta(x_1)_j^2]} \quad (4)$$

Where N is the total number of experimental data points, $\delta(\xi_1)_j = (\xi_1^{\text{Calc}} - \xi_1)_j / \xi_{1,j}$ represents the individual relative deviation for the molar fraction of CO_2 (1) between calculated $(\xi_{1,j}^{\text{Calc}})$ and measured $(\xi_{1,j})$ values for each phase $(\xi_1 = x_1, y_1)$, and for each data point (j).

[Table 5](#) reports the interaction parameters and deviations obtained for each mixing rule and isotherm. These results showed that when the PR-EoS combined with WS + NRTL mixing rule, with a relative root-mean square deviation of $\delta(y_1, x_1) \leq 1.83 \%$, it had a better performance compared with the two options considered for vdW mixing rule. With $k_{12} \neq 0$ and $l_{12} \neq 0$, the deviations were $\delta(y_1, x_1) \leq 17.33 \%$, on the other hand, with $k_{12} \neq 0$ and $l_{12} = 0$ the values for the deviations were reduced to $\delta(y_1, x_1) \leq 17.33 \% \text{ } 7.95 \%$. An over-fitting problem could explain the improvement of the vdW mixing rule when it was used with three adjusted parameters, $k_{12} \neq 0$ and $l_{12} = 0$, instead of six parameters, $k_{12} \neq 0$ and $l_{12} \neq 0$. The higher deviations were detected for the liquid phase with $\delta(x_1) \leq 17.32 \% \text{ } 7.95 \%$ for vdW with $k_{12} \neq 0$ and $l_{12} = 0$, and $\delta(x_1) \leq 1.82 \%$ for WS+NRTL. These values can be explained considering the theoretical nature of the WS + NRTL mixing rule, which is able to take into account the nonidealities of the liquid phase. On the other hand, the vdW mixing rule considers weaker interactions associated to the van der Waals forces. For the vapor phase, there were no significant differences in the deviations for vdW with $k_{12} \neq 0$ and $l_{12} = 0$, $\delta(y_1) \leq 0.88 \% \text{ } 0.89 \%$, compared with WS + NRTL, $\delta(y_1) \leq 0.87 \%$.

The results of the modeling using the PR-EoS have been included in [Figure 2](#), considering for vdW mixing rule the option with $k_{12} \neq 0$ and $l_{12} = 0$. With both mixing rules, vdW and WS + NRTL, the PR-EoS was able to represent the phase envelope (not shown in [Figure 2](#)) and to detect the critical pressures, estimated for a CO_2 content $> 95 \%$ mol·mol⁻¹. It was verified that the value of the critical pressures

increased with the temperature for both mixing rules. In particular, for WS+NRTL the value of these pressures increased with the temperature from approximately 8.5 MPa at 313.2 K to 1.1 MPa at 333.2 K.

3.3.2 *Perturbed Chain - Statistical Associating Fluid Theory equation of state*

Table 6 reports the pure-component parameters used to model the VLE data measured. For CO₂ (1), these parameters were obtained from Gross and Sadowski [18] and used without further modifications. For (E)-2-hexenal (2), the parameters were adjusted from the density data measured in this work, and the vapor pressure data reported by Meneses et al. [10]. The relative root-mean square deviations between the experimental and calculated values were 0.23 % for density, and 0.61 % for vapor pressure. The CO₂ was considered a non-polar molecule, neglecting its quadrupolar moment contribution [28]. The (E)-2-hexenal was assumed as a non-associating molecule with dipole-dipole interactions, in a similar approach used by Dominik et al. [21] to model ketones.

The modeling of the high-pressure VLE using the PC-SAFT considered two alternatives. First, the use of only the pure-component information as a predictive tool ($k_{12} = 0$), and second, adjusting the binary interaction coefficient to the experimental data ($k_{12} \neq 0$), as a correlation tool. Table 7 reports the relative root-mean square deviations calculated for the molar fraction of the vapor and liquid with both approaches. The results confirmed that the predictive option presented higher deviations, $\delta(y_1, x_1) = 44.76$ %, compared to the correlation with a value of $k_{12} = 0.0752$, $\delta(y_1, x_1) = 9.80$ %. The major differences were observed for the molar fraction of the liquid phase with $\delta(x_1) = 44.75$ % for the prediction, against $\delta(x_1) = 9.78$ % for the correlation. For the vapor phase, both options resulted in comparable deviations, $\delta(y_1) = 0.64$ % for the prediction, and $\delta(y_1) = 0.61$ % for the correlation.

The numerical modeling results can be confirmed in Figure 3 where the experimental information and the calculations with PC-SAFT were plotted. This equation has the capability of predicting the phase envelope, including the existence of a critical pressure for each isotherm at high CO₂ molar fractions.

Moreover, the prediction and correlation of the molar fraction of the vapor phase were higher than the measured values. For the liquid phase, the molar fractions predicted were lower than the experimental, and the correlated molar fractions were higher.

The PR-EoS combined with WS + NRTL mixing rule showed a higher capability of correlating the experimental VLE data than the PC-SAFT EoS. The examination of the relative root-mean square deviations indicated a reduction of 81 % for PR-EoS compared with PC-SAFT. Also, there was a significant disparity in the modeling of the molar fraction of the vapor phase, exhibiting the PR-EoS a reduction of 42 % in the relative deviations regarding to PC-SAFT. The justification is based on the number of adjustable binary interaction coefficients. For the PR-EoS with WS+NRTL, the four coefficients (k_{12} , α_{12} , τ_{12} , τ_{21}) were fixed individually for each isotherm, resulting in a total of twelve parameters. This number decreases significantly to one coefficient (k_{12}) for the PC-SAFT. The values corresponding to the critical pressures estimated for the three isotherms measured were similar for both equations. The open phase envelopes around the critical point obtained with PC-SAFT showed in [Figure 3](#) was as a consequence of the methodology implemented (algorithm) to reproduce specifically the experimental data measured. This made it possible to compare the PC-SAFT capabilities of correlation and prediction. Nevertheless, the PC-SAFT has proved to be able to represent the critical point of mixtures [\[19\]](#). The results described in this work, data and calculations of the molar fraction and the phase envelopes, are relevant to being able to evaluate a process to recover the key aroma components, like (E)-2-hexenal, from liquid mixtures using SC-CO₂ as a solvent in a countercurrent in a packed column.

4. Conclusions

The isothermal vapor + liquid equilibrium of CO₂ + (E)-2-hexenal was measured at (313.2, 323.2 and 333.2) K and pressure lower than 9.8 MPa. The experimental data was validated by a procedure that allowed to verify the thermodynamic consistency, as well as to estimate the combined expanded

uncertainties. Results showed that the uncertainties estimated for the CO₂ mole fractions were ≤ 0.045 mol·mol⁻¹ (vapor) and ≤ 0.016 mol·mol⁻¹ (liquid). The isothermal phase envelopes measured presented a critical pressure at carbon dioxide molar fractions ≥ 95 % mol·mol⁻¹. The pressure corresponding to the critical point increased with temperature, and the values were estimated lower than 1.1 MPa. The density and dynamic viscosity of pure (E)-2-hexenal were measured at 101.13 kPa and temperatures from (292.2 to 353.2) K, with values ranged from (797.45 to 851.87) kg·m⁻³ for density, and from (0.469 to 0.934) mP·s for viscosity. The Peng-Robinson and the Perturbed Chain - Statistical Associating Fluid Theory were the two equations of state selected to model the vapor + liquid equilibria. Both equations were able to represent the phase envelopes. For the Peng-Robinson, two mixing rules were used, the van der Waals classical quadratic and the Wong-Sandler with the Non-Random Two Liquid model. The relative root-mean square deviation calculated simultaneously for the CO₂ molar fractions of vapor and liquid phases using the two mixing rules were, 17.33 % and 1.83 %, respectively. The Perturbed Chain - Statistical Associating Fluid Theory predicted the mole fractions with a deviation of 44.76 %. This value was reduced to 9.80 % when an adjustable binary interaction coefficient was included. According to these results, this last equation would be recommended for the development and scale-up of processes for the recovery of key fruit aroma components.

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Table 1. Experimental temperature (T), pressure (p), molar fraction of liquid (x_1) and vapor (y_1) phases, and its combined expanded uncertainty ($U_{\text{Comb}}(x_1)$, $U_{\text{Comb}}(y_1)$), for the binary system CO₂ (1) + (E)-2-hexenal (2).

$T^{(a)} / \text{K}$	$p^{(b)} / \text{MPa}$	$x_1 / \text{mol}\cdot\text{mol}^{-1}$	$U_{\text{Comb}}(x_1)^{(c)} / \text{mol}\cdot\text{mol}^{-1}$	$y_1 / \text{mol}\cdot\text{mol}^{-1}$	$U_{\text{Comb}}(y_1)^{(c)} / \text{mol}\cdot\text{mol}^{-1}$
CO ₂ (1) + (E)-2-hexenal (2)					
313.2	2.46	0.207	0.009	0.991	0.014
	3.72	0.342	0.014	0.996	0.005
	5.07	0.455	0.014	0.996	0.004
	6.18	0.556	0.015	0.997	0.002
	7.01	0.601	0.014	0.997	0.003
	8.16	0.684	0.013	0.996	0.002
	9.82	0.809	0.016	0.994	0.002
323.2	2.16	0.188	0.005	0.975	0.044
	3.28	0.311	0.004	0.996	0.007
	4.17	0.407	0.003	0.997	0.004
	5.21	0.503	0.002	0.997	0.003
	6.59	0.630	0.002	0.997	0.002
	7.46	0.725	0.001	0.997	0.002
	8.92	0.860	0.001	0.996	0.002
333.2	3.03	0.326	0.008	0.993	0.010
	4.12	0.496	0.011	0.989	0.011
	5.10	0.598	0.012	0.998	0.003
	6.39	0.734	0.014	0.998	0.002
	7.03	0.814	0.014	0.998	0.002
	8.04	0.939	0.015	0.997	0.002

^(a)Standard uncertainty for temperature, $u(T) = 0.1 \text{ K}$.

^(b)Standard uncertainty for pressure, $u(p) = 0.05 \text{ MPa}$.

^(c)Values estimated with a 0.9545 level of confidence [14] for combined expanded uncertainty of molar fraction of CO₂ (1) in the liquid phase, $U_{\text{Comb}}(x_1)$, and vapor phase, $U_{\text{Comb}}(y_1)$.

Table 2. Thermodynamic consistency evaluation of the experimental data measured, based on the point test of van Ness, modified by Fredenslund [23].

T / K	CO ₂ (1) + (E)-2-hexenal (2)	
	Mean absolute deviation	Evaluation
313.2	0.0063	Consistent
323.2	0.0107	Consistent ^(a)
333.2	0.0053	Consistent

^(a)Barely over 0.01 mol·mol⁻¹, the upper limit recommended [23].

Table 3. Experimental temperature (T), density (ρ_2), and dynamic viscosity (η_2) of pure (E)-2-hexenal (2) at 101.13 kPa. The standard uncertainties (u) reported correspond to information from the manufacturer [16].

$T^{(a)} / \text{K}$	$\rho_2^{(b)} / \text{kg}\cdot\text{m}^{-3}$	$\eta_2^{(c)} / \text{mPa}\cdot\text{s}$
293.2	851.9	0.93
298.2	847.5	0.87
303.2	843.1	0.81
308.2	838.6	0.76
313.2	834.1	0.72
318.2	829.7	0.67
323.2	825.1	0.64
328.2	820.6	0.60
333.2	816.1	0.57
338.2	811.5	0.54
343.2	806.8	0.52
348.2	802.2	0.49
353.2	797.5	0.47

^(a)Standard uncertainty for temperature, $u(T) = 0.1 \text{ K}$

^(b)Standard uncertainty for density $u(\rho) = 0.4 \text{ kg}\cdot\text{m}^{-3}$

^(c)Standard uncertainty for dynamic viscosity $u(\eta) = 0.02 \text{ mPa}\cdot\text{s}$

Table 4. Pure component properties for CO₂ (1) and (E)-2-hexenal (2), from literature or estimated in this work.

Property	CO ₂ (1)		(E)-2-hexenal (2)	
	Value	Source (Estimation Method)	Value	Source (Estimation Method)
Molecular weight (Da)	44.01	NIST [13]	98.14	Joback [2726]
Critical temperature (K)	304.2	NIST	625.0	Joback
Critical pressure (MPa)	7.38	NIST	3.24	Joback
Acentric factor (-)	0.225	NIST	0.321	Lee-Kesler [2726]

Table 5. Optimal values of parameters for the Peng-Robinson equation of state with two mixing rules, van der Waals (k_{1i} , l_{1i}) and Wong-Sandler (k_{1i}) plus Non-Random Two Liquid (NRTL) model (α_{1i} , τ_{1i} , τ_{i1}) used to model the vapor + liquid equilibria of CO₂ (1) + (E)-2-hexenal (2).

T / K	Peng-Robinson + van der Waals					Peng-Robinson + (Wong-Sandler + NRTL)						
	k_{12}	l_{12}	$100 \cdot \delta(y_1, x_1) / \%$	$100 \cdot \delta(x_1) / \%$	$100 \cdot \delta(y_1) / \%$	k_{12}	α_{12}	τ_{12}	τ_{21}	$100 \cdot \delta(y_1, x_1) / \%$	$100 \cdot \delta(x_1) / \%$	$100 \cdot \delta(y_1) / \%$
313.2	0.0689	0	6.32	6.30	0.47	0.6260	0.3043	0.1941	0.9348	1.77	1.70	0.47
323.2	-0.0051	0	7.95	7.90	0.89	0.6267	0.47	0.7324	0.2967	1.70	1.46	0.87
333.2	0.0590	0	7.51	7.51	0.26	0.6373	0.4124	0.0053	0.7883	1.83	1.82	0.19
313.2	0.0689	0.0626	17.33	17.32	0.49							
323.2	-0.0051	-0.0862	10.50	10.46	0.88							
333.2	0.0590	0.0009	6.33	6.32	0.31							

$\delta(\xi_{1j}) = (\xi_{1j}^{\text{Calc}} - \xi_{1j}) / \xi_{1j}$: Individual (j) relative deviations between the calculated (ξ_{1j}^{Calc}) and measured (ξ_{1j}) values of molar fractions of CO₂ (1) in liquid phase ($\xi_1 = x_1$) or vapor phase ($\xi_1 = y_1$).

$\delta(y_1, x_1) = \sqrt{\frac{1}{N} \sum_{j=1}^N [\delta(y_1)_j^2 + \delta(x_1)_j^2]}$: Relative root-mean square deviation, the objective function used to fit the interaction parameters.

Table 6. Optimal values of pure-component parameters (m_i , σ_i , ε_i/k_i , $x_{p,i}$, μ_i) for the Perturbed Chain - Statistical Associating Fluid Theory equation of state used to model the vapor + liquid equilibria of CO₂ (1) + (E)-2-hexenal (2).

Component (i)	Molecular characteristic	m_i	σ_i	ε_i/k_i	μ_i	$x_{p,i}$	$100 \cdot \delta(\rho_2) / \%$	$100 \cdot \delta(p_2^{\text{Sat}}) / \%$
Carbon dioxide (1) ^(a)	Non-polar	2.0729	2.7852	169.21	0	0	---	---
(E)-2-Hexenal (2)	Dipolar, non-associating	2.2279	4.1993	325.05	2.5780 ^(b)	0.4857	0.228	0.605

^(a)[18]

^(b)[22]

$\delta(\xi_2) = \sqrt{\frac{1}{N} \sum_{j=1}^N \left[\left(\xi_2^{\text{Calc}} - \xi_2 \right)_j / \xi_{2,j} \right]^2}$: Relative root-mean square deviation, for the individual (j) relative deviations between the calculated ($\xi_{1,j}^{\text{Calc}}$) and measured ($\xi_{1,j}$) values of density ($\xi_2 = \rho_2$), or vapor pressure ($\xi_2 = p_2^{\text{Sat}}$) for (E)-2-hexenal (2).

Table 7. Optimal values of parameters for the Perturbed Chain - Statistical Associating Fluid Theory equation of state used as a predictive tool ($k_{12} = 0$), and as a correlation tool ($k_{12} \neq 0$) to model the vapor + liquid equilibria of CO₂ (1) + (E)-2-hexenal (2).

T / K	Prediction				Correlation			
	k_{12}	$100 \cdot \delta(y_1, x_1) / \%$	$100 \cdot \delta(x_1) / \%$	$100 \cdot \delta(y_1) / \%$	k_{12}	$100 \cdot \delta(y_1, x_1) / \%$	$100 \cdot \delta(x_1) / \%$	$100 \cdot \delta(y_1) / \%$
313.2 } 323.2 } 333.2 }	0	44.76	44.75	0.64	0.0752	9.80	9.78	0.61

$\delta(\xi_1)_j = (\xi_1^{\text{Calc}} - \xi_1) / \xi_{1,j}$: Individual (j) relative deviations between the calculated ($\xi_{1,j}^{\text{Calc}}$) and measured ($\xi_{1,j}$) values of molar fractions of CO₂ (1) in liquid phase ($\xi_1 = x_1$) or vapor phase ($\xi_1 = y_1$).

$\delta(y_1, x_1) = \sqrt{\frac{1}{N} \sum_{j=1}^N [\delta(y_1)_j^2 + \delta(x_1)_j^2]}$: Relative root-mean square deviation, the objective function used to fit the interaction parameters.

Figure 1. Chemical structure of (E)-2-hexenal.

Figure 2. Isothermal vapor + liquid equilibria for the binary system CO₂ (1) + (E)-2-hexenal (2) at temperatures of 313.2 K: (■, □, —, — —); 323.2 K: (●, ○, —, — —); 333.2 K: (▲, △, —, — —). Symbols represent experimental results, full the liquid phase and open the vapor phase. Lines represent the correlation with the Peng-Robinson equation of state using two different mixing rules, van der Waals ($k_{12} \neq 0$ and $l_{12} = 0$) (—), and Wong-Sandler plus Non-Random Two Liquid model (— —).

Figure 3. Isothermal vapor + liquid equilibria for the binary system CO₂ (1) + (E)-2-hexenal (2) at temperatures of 313.2 K: (■, □, —, - -); 323.2 K: (●, ○, —, - -); 333.2 K: (▲, △, —, - -). Symbols represent experimental results, full the liquid phase and open the vapor phase. Lines represent the correlation with the Perturbed Chain - Statistical Associating Fluid Theory equation of state used as a predictive tool ($k_{12} = 0$) (- -), and as a correlation tool ($k_{12} = 0.0752$) (—).