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# **Countercurrent fractionation of aqueous apple aroma constituents using supercritical carbon dioxide**

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**Highlights**

A super-concentrated apple aroma extract (*E*-2-hexenal and hexanal) was obtained by CC-SFF

Extraction yield of aromas was >86% for all experiments

*S/F* had the most significant effect on the extraction of C-6 apple aroma compounds

40 °C, 14 MPa, and *S/F* = 5 would be optimal conditions for CC-SFF of C-6 apple aromas

**Abstract**

A newly acquired CounterCurrent Supercritical Fluid Fractionation (CC-SFF) packed column was putted into operation by studying the separation of key apple aroma constituents from aqueous solutions using supercritical carbon dioxide (CO<sub>2</sub>). This work studied the effect of temperature (40 to 60 °C), pressure (8 to 14 MPa) and solvent-to-feed ratio (*S/F*) (5 to 15 kg·kg<sup>-1</sup> CO<sub>2</sub>/feed) on the fractionation and concentration of characteristic six-carbon (C-6) apple aromas ((*E*)-2-hexenal and hexanal) from less important compounds such as 1-hexanol and water. At the selected temperatures and pressures CO<sub>2</sub> densities were in the range of 192 to 763 kg·m<sup>-3</sup>. Very high separation factors from water were observed (~10<sup>4</sup>). Two separate phases were obtained in the extract, demonstrating that CC-SFF of aqueous apple aromas is highly capable of producing a water-free super-concentrated product. However, little fractionation of aromas from less important compounds such 1-hexanol was achieved. The highest concentration of C-6 apple aromas in the total extract was approx. 20% w/w, and the extraction yield of aromas was >86%. Response Surface Methodology (RSM) with a Box-Behnken design was used to investigate and optimize the process variables. Significant surface models (P-values <0.0001) for the total yield of extraction and the organics' loading showed that the *S/F* had the most significant effect on the extraction of C-6 apple aroma compounds. Additionally, according to the RSM models 40 °C, 14 MPa, and *S/F*= 5 to would be optimum condition to concentrate C-6 apple aromas.

**Keywords:** Apple aroma; Carbon dioxide; Countercurrent Supercritical Fluid Fractionation; (*E*)-2-Hexenal, Hexanal; 1-Hexanol; Packed column

## 1. Introduction

Supercritical Fluid Extraction (SFE) is a process that uses gases at high pressures as solvents to extract valuable materials. In contrast to SFE from solid matrices, in which the compounds of interest are directly extracted from its natural source, the SFE from liquid mixtures is typically used to fractionate materials extracted by conventional methods [1], typically carried out continuously on packed columns operated in the countercurrent mode [2], and known as CounterCurrent Supercritical Fluid Fractionation (CC-SFF).

Early developments of the CC-SFF technology and its advantageous characteristics were first described in the late 1970's [3,4]. However, the number of industrial applications of CC-SFF nowadays is limited mainly because the process has to be designed for each application, and the required know-how is not universally shared by all members of the chemical engineering community [5].

CC-SFF has been applied mainly to edible oil mixtures and derivatives (e.g., PUFAs from fish oil), essential oils (e.g., dewatering of citrus oils), and alcoholic beverages (e.g., dealcoholization). Extensive reviews on CC-SFF applications are available in literature [2,5–8]. Concentration and fractionation of aroma constituents from aqueous solutions has been mainly applied to alcoholic beverages [9–15]. The recovery of aromas from other liquid mixtures such as juices is even more limited. Señoráns et al. [16] and Simó et al. [17] isolated by CC-SFF and analyzed the antioxidant compounds in orange juice. The authors studied the effect of the solvent-to-feed ratio ( $S/F$ ) on the content of antioxidant compounds of the extracts. They found that when operating at low  $S/F$  ( $\sim 3$ ) the antioxidant compounds were more concentrated in the extract.

In the late and mid 70's Schultz et al. [18] studied the extraction of volatiles from apple essences with different solvents including dense  $\text{CO}_2$ . Later, Schultz [19] patented the process, performed selective extraction of apple aroma [20], and built a pilot plant for the extraction of volatiles from fruit essences using liquid  $\text{CO}_2$  [21]. However, to the best of the authors knowledge further research on the subject is not available.

Chile is among the eleven top world producers of apples with 1.5% of the world production [22]. Nearly 55% of the domestic production of apples is used to make concentrated juice with 95% being exported [23]. This process is usually carried out by evaporation, and a significant amount of

volatile aromas are lost. Actually, few companies in Chile recover the aroma fraction lost in the evaporation stage of the concentrated juice manufacturing process. Traditionally, fruit aromas are recovered from the concentrated juice using techniques based on distillation/evaporation or partial condensation [24,25]. CC-SFF can be used as an alternative technology to concentrate and fractionate natural fruit aroma essences with large amounts of water as described by Mukhopadhyay [26]. A super-concentrated aroma extract obtained by CC-SFF would be a product of higher added value than the fresh fruit, concentrated juice, and aqueous essences obtained by condensation. Therefore, the use of CC-SFF could be attractive to producers of concentrated fruit juices.

The objective of this work was to put into operation a new packed column designed for SFF by studying the effect of temperature, pressure, and  $S/F$  on the concentration and fractionation of a model aqueous apple aroma solution composed by two six-carbon aldehydes which contribute to the apple aroma, (*E*)-2-hexenal and hexanal; and a six-carbon alcohol which is not relevant for the apple aroma, 1-hexanol. Although (*E*)-2-hexenal and hexanal are not in significant amounts in the whole fruit, they are mainly responsible for sensory impressions, such as ‘green, fresh, estery’ in commercial apple juices [27]. Moreover, Koch [28] demonstrated the importance of (*E*)-2-hexenal in the odor of apple essences. The concentration of these compounds in apple juice, apple, and essence varies from ca. 1 to 2400 mg·kg<sup>-1</sup> [29–32]. Response Surface Methodology (RSM) with a Box-Behnken Design (BBD) was used to investigate and optimize the process variables. This approach is an effective statistical method to define the effects of multiple independent variables and their interactions on the process response, and to optimize the process variables [33,34]. The values of the variables used in the BBD were chosen based on previous ternary phase equilibrium measurements [27] to explore reasonable operating values. Experimental values of temperature ranged from 40 to 60 °C, pressure from 8 to 14 MPa, and  $S/F$  from 5 to 15 kg·kg<sup>-1</sup> CO<sub>2</sub>/feed. At the selected temperature and pressure conditions CO<sub>2</sub> densities were in the range of 191.6 to 763.3 kg·m<sup>-3</sup> [35].

## 2. Materials and Methods

### 2.1 Materials

Food grade CO<sub>2</sub> (≥99.9%) was supplied by Indura S.A. (Santiago, Chile). *E*-2-hexenal (≥99.5%), hexanal (98%), and 1-hexanol (≥99%) were purchased from Sigma-Aldrich (Saint Luis, MO).

LiChrosolv® methanol ( $\geq 99.9\%$ ) was acquired from Merck (Darmstadt, Germany). Distilled water was used in all experiments. All materials were used without further purification.

## 2.2 *Experimental apparatus and procedure*

The new pilot-scale CC-SFF column was purchased from Eurotechnica GmbH (HPCC-500, Bargteheide, Germany) and was coupled to an existing SFE plant as depicted in Figure 1. The main component of the experimental apparatus is the high-pressure column (1) of 4 m height and an internal diameter of 38 mm. Top operation condition of the column is 50 MPa at 100 °C. The column is equipped with structured packing Sulzer CY, and with a sapphire window to observe the wetting behavior of falling liquid in the middle section of the column (2). The column temperature inside the column is controlled by the temperature of the CO<sub>2</sub> entering at the bottom of the column and by two heating mantles covering the upper (3) and bottom (4) part of the column. The temperature of the CO<sub>2</sub> entering at the bottom of column is adjusted in the heating thermostatic water bath (5) (8205, PolyScience, Niles, IL) and a 500 cm<sup>3</sup> preheater filled with glass beads (6). The temperatures inside the column are measured by three type-k thermocouples, located at the top, middle, and bottom part of the column. The upper and bottom thermocouples are connected to the temperature controllers (7) (HT42-10P, Hillesheim GmbH, Waghäusel, Germany) of the heating mantles (3,4). All three temperatures are monitored and displayed in the column control panel. A backpressure regulator (8) (BPR-A-200B1, Thar Technologies, Pittsburgh, PA) controls the pressure inside the column and it is displayed in the column control panel by a pressure transmitter (A-10 Wika, Klingenberg, Germany). The liquid phase is pumped by a piston pump (9) (Novados H1, SPX Bran+Luebbe, Norderstedt, Germany) from the liquid feed storage tank (10). The liquid feed pump is equipped with a variable frequency drive to control the liquid mass flow rate which is measured by a Coriolis mass flow meter (11) (MASS 2100, SITRANS FC MASSFLO®, Siemens, Nordborg, Denmark). Liquid CO<sub>2</sub> is pumped by a two piston pump (12) (P-200A-220V, Thar Technologies, Pittsburgh, PA) from the buffer tank (13) of the solvent recovery cycle (14). A cooling thermostatic water bath (15) (9106A12E, PolyScience, Niles, IL) is installed at the suction side of the pump in order avoid gaseous CO<sub>2</sub> entering the pump head, and to achieve higher CO<sub>2</sub> mass flow rates. The CO<sub>2</sub> mass flow rate is measured and controlled by a Coriolis mass flow meter (16) (CNF010M324NU, Micro Motion Inc., Boulder, CO).

Sampling was done as follows. Dissolved substances in CO<sub>2</sub> coming out from the top of the column were collected in two 250 cm<sup>3</sup> cyclonic separators (17,18). The pressure inside the CO<sub>2</sub> supply tank determined the pressure of both separators (5.0 MPa). The first separator was heated to 40 °C in order to avoid ice formation while sampling causing a controlled expansion while taking samples. The second separator (18) was cooled with water (at ~ -5 °C) from the cooling thermostatic water bath (15) to diminish aroma losses in the first separator (due to relative high temperature) and to the solvent cycle. Additional losses were quantified by a homemade cold-trap (19) set-up composed by a needle valve (20) (HiP model 15-11AF1, Erie, PA, USA), an expansion and flow control valve (21) (Butech, SFPMMV26V, Erie, PA, USA), and a wet-test meter (22) (Ritter, TG 05/5, Bochum, Germany) to measure the CO<sub>2</sub> content using density data [35]. Finally, CO<sub>2</sub> was recycled through the solvent cycle (14) before passing through a molecular sieve (23) to avoid clogging of pipes by gas hydrates. The raffinate was collected at the bottom of the column and withdrawn via a heated vessel (24) for gradual expansion to avoid ice formation. The temperature of the liquid in the feed tank (10) and the raffinate expansion vessel (24) is measured and controlled by a Pt-100 temperature sensor connected to a temperature controller (25) (AKO-D14726, Madrid, Spain).

The experimental procedure was as follows. Cooling of the solvent cycle (14) and cooling thermostatic water bath (15) were turned on, and the column was pressurized by opening slowly the CO<sub>2</sub> storage tank (26). The operating temperature of the column was set on the column controllers (7) and on the heating bath (5). When the temperature values inside the column were near the set point and the buffer tank (13) was filled with liquid CO<sub>2</sub>, the CO<sub>2</sub> flow rate was set on the flow controller (16) and CO<sub>2</sub> pump (12) was turned on. The desired operation pressure was set on the automatic back-pressure regulator (8), which was initially closed up to when the pressure reached the set point when it began to open until a stable pressure within the column was achieved. When stable temperature and pressure conditions in the column were achieved, a previously prepared homogeneous aqueous liquid solution of 1750 mg·kg<sup>-1</sup> of organics (500 mg·kg<sup>-1</sup> of (*E*)-2-hexenal, 250 mg·kg<sup>-1</sup> of hexanal, and 1000 mg·kg<sup>-1</sup> of 1-hexanol) was fed to the liquid feed tank (10) and the magnetic stirrer (27) turned on. To establish the desired *S/F* the liquid flow rate was adjusted in the liquid pump mass flow controller (11) according to the CO<sub>2</sub> mass flow rate. The concentration of

the feed solution was chosen so that the 1-hexanol-to-(*E*)-2-hexenal ratio, in apple essence, was similar to that reported in literature (~2) [31].

In order to establish steady state conditions the phase composition of the raffinate was monitored at the bottom of the column as a function of time (60, 80, 100, 110, and 120 min). Fig. 2 shows the composition of (*E*)-2-hexenal, hexanal, and 1-hexanol *versus* time. Based on this observation the extraction time was set to 2 h. This period of time was used in all experiments and was found to be in agreement with those in literature [11,13,36–40] for a similar type of application and operation conditions.

The estimation of the aroma losses to the solvent cycle was as follows. After the first hour of constant operation, both separators (17,18) and the heated raffinate collector (24) were emptied, and the cold trap was slightly opened in order to quantify the aroma losses to the solvent cycle. Overall and component mass balances were checked for the next hour of operation. At the end of that period samples from both extract and raffinate were collected. The mass balance was checked with overall recovery value of >93%, >90% for (*E*)-2-hexenal, >80% hexanal, and >90% for 1-hexanol. The extract that remained in the walls of the separators was collected by cleaning with pure methanol and samples were stored in the dark at -18 °C until analysis.

### 2.3 Analyses and quantification

The extract, raffinate, and feed samples were sent to a certified analytical laboratory at *Universidad Técnica Federico Santa María*. All samples were analyzed by Gas Chromatography (GC) and Solid Phase Micro Extraction (SPME). Calibration curves were constructed for each compound in order to quantify the amount of organics ((*E*)-2-hexenal, hexanal, and 1-hexanol) in each sample. The amount of water in each sample was determined by difference. All samples were analyzed in triplicate and the estimated experimental uncertainty was <12.0 mg·kg<sup>-1</sup> for (*E*)-2-hexenal, 3.1 mg·kg<sup>-1</sup> for hexanal, and <49.2 mg·kg<sup>-1</sup> for 1-hexanol.

### 2.4 Data analysis and statistics

Statistical calculation and analysis were performed in R [41] using the package RcmdrPlugin.DoE [42]. The significance of the models was determined through the ANalysis Of Variance (ANOVA),



the significance of each variable was determined by ANOVA followed by Fisher's statistical test (F-test).

### 3. Results and discussion

The experimental conditions of each experiment used in the BBD are listed in Table 1. All compounds were identified by numbers as follows: (*E*)-2-hexenal (*i*=1), hexanal (*i*=2), 1-hexanol (*i*=3), and water (*i*=4). Additionally, Table 1 lists the results of the mass fraction of each compound in the extract ( $y_i$ ) and raffinate ( $x_i$ ). Other response variables such as the Organics' Loading (OL), aroma extraction yield ( $Y_A$ ), and selectivity of aroma from 1-hexanol ( $\alpha_{A,3}$ ) were also considered and are listed in Table 1. The OL was expressed as the mg of extract dissolved per kilogram of CO<sub>2</sub>, and the  $Y_A$  and  $\alpha_{A,3}$  were calculated using the following equations:

$$Y_A (\%) = 100 \cdot \frac{q_E (y_1 + y_2)}{q_F (z_1 + z_2)}, \text{ and} \quad (1)$$

$$\alpha_{A,3} = \frac{k_A}{k_3} = \frac{(y_1 + y_2)/y_3}{(x_1 + x_2)/x_3}, \quad (2)$$

where  $q_E$  and  $q_F$  are the solvent-free extract and feed mass flow rates,  $x_i$ ,  $y_i$ , and  $z_i$  are the mass fractions of compound *i* in the raffinate, extract, and feed streams, and  $k_A$  and  $k_3$  are the partition coefficients of apple aroma constituents (*E*)-2-hexenal and hexanal, and 1-hexanol ( $k_i=y_i/x_i$ ) between CO<sub>2</sub> and water.

#### 3.1 Extraction yield of aromas and mass fractions of extract and raffinate streams

In all experiments, a good concentration of the apple aroma constituents was achieved (Table 1). The organic compounds were practically removed completely from the feed solution. The amount of organic compounds in the raffinate was <200 mg·kg<sup>-1</sup> in all experiments, and the minimum value was found to be 11 mg·kg<sup>-1</sup>. Fig. 3 shows the mass fraction of each component in the feed, raffinate, and extract for the best run (first line in Table 1). This experimental run showed the highest organic compounds content in the extract, and the  $Y_A$  was around 93%. The mass fraction of organics in the best run was nearly 43% w/w (14% w/w of (*E*)-2-hexenal, 6% w/w of hexanal, and 23% w/w of 1-hexanol), raffinate composition was near 174 mg·kg<sup>-1</sup> (26 mg·kg<sup>-1</sup> of (*E*)-2-hexenal, 3 mg·kg<sup>-1</sup> of hexanal, and 145 mg·kg<sup>-1</sup> of 1-hexanol).

Results of Table 1 and Fig. 3 show that the apple aroma constituents (*E*)-2-hexenal and hexanal were not successfully fractionated from the less relevant compound 1-hexanol. However, as it can be seen in Fig. 4, the extract collected in the separator was highly concentrated so that two separate phases were formed.

None of the RSM models gave satisfactory results for the  $Y_A$ , aroma selectivity (from 1-hexanol and water), and mass fractions of each compound in the extract ( $y_i$ ) and raffinate ( $x_i$ ) streams. The number of significant effects, the magnitude of the regressed parameters, and the determination coefficient ( $R^2$ ) were low. This means that variability of the responses was not successfully explained by the variation of the chosen variables ( $T$ ,  $P$ , and  $S/F$ ) and such statistical models were not considered valid. Qualitatively, however, consistent results were obtained for all the mass fractions; in general, low temperatures and  $S/F$  levels, and pressures in the range of 11 to 14 MPa tend to increase the mass fraction of relevant apple aroma compounds in the extract.

For all experiments,  $Y_A$  was  $>86\%$ . Fig. 5 shows  $Y_A$  versus  $\text{CO}_2$  density at fixed temperatures:  $Y_A$  remained practically constant around 90% at all pressures and  $S/F$ . This result suggests that no relevant difference was observed in  $Y_A$  by varying temperature, pressure, or  $S/F$ . This may be due to the low solubility of the organic compounds in water so that when in contact with a non-polar solvent such as  $\text{CO}_2$  they are extracted easily. The solubility of alcohols in water varies with chain length and temperature. At near ambient temperature (15 °C), it decreases from 81,510  $\text{mg}\cdot\text{kg}^{-1}$  for 1-butanol to 6,745  $\text{mg}\cdot\text{kg}^{-1}$  for 1-hexanol [43]. At 50 °C, the solubility of hexanal in water is near 3,511  $\text{mg}\cdot\text{kg}^{-1}$  [44]. To the best of the authors' knowledge there is no data of the solubility of (*E*)-2-hexenal in water reported in literature.

Even though  $Y_A$  didn't vary significantly in all experiments, the highest  $Y_A$  was found to be at a temperature of 50 °C and showed a maximum of 95% near 500  $\text{kg}\cdot\text{m}^{-3}$  which occurred at  $S/F = 10 \text{ kg}\cdot\text{kg}^{-1}$ , and at a pressure of 11 MPa. These results agree with those of Señoráns et al. [12] and da Porto and Decorti [36] who obtained the highest extraction yield of volatiles at a  $S/F$  of  $\sim 7 \text{ kg}\cdot\text{kg}^{-1}$  for similar aqueous systems. These results are consistent with the observed tendency of the mass fractions in the extract and raffinate streams discussed above. In order to increase mass fraction of relevant apple aroma compounds in the extract, and maximize water and 1-hexanol content in the

raffinate low values of temperature and  $S/F$ , and pressures in the range of 11 to 14 MPa would be preferable.

### 3.2 Total extraction yield of organic compounds and organics' loading

The experimental data of the total extraction yield of organic compounds ( $Y_{tot}$ ) and the Organics' Loading (OL) was fitted to the quadratic response surface model depicted by Eq. (3) where  $Y$  is the estimated response, the  $X_i$ s are the independent coded variables ( $X_1$  for temperature,  $X_2$  for pressure, and  $X_3$  for  $S/F$ ) depicted by equations (3a) to (3c), and  $\beta_0$ ,  $\beta_j$ ,  $\beta_{jj}$ , and  $\beta_{ij}$  are the regression coefficients for the intercept, First Order (FO), Pure Quadratic (PQ), and Two-Factor Interaction (TFI), respectively.

$$Y = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} X_i X_j \quad (3)$$

$$X_1 = \frac{T\{^{\circ}\text{C}\} - 50}{10} \quad (3a)$$

$$X_2 = \frac{P\{\text{MPa}\} - 11}{3} \quad (3b)$$

$$X_3 = \frac{S/F - 10}{5} \quad (3c)$$

The significance of the models was determined through the ANOVA, and the results, for both estimated responses,  $Y_{tot}$  and OL, are summarized in Table 2. A large F-value indicates that most of the variation in the response can be explained by the regression model, Eq. (3). The results of the ANOVA indicated that both models showed a satisfactory representation of the relationship between the independent variables and responses. In order to simplify the mathematical expressions of  $Y_{tot}$  and OL, the parameters of non-significant effects were excluded from the regression analysis. However, care was taken in order to maintain the significance of the expressions.

For  $Y_{tot}$ , all FO parameters were significant (P-values <0.05), the PQ parameters of temperature and  $S/F$  were also significant (P-values <0.05), and only the TFI parameter of pressure and  $S/F$  was significant (P-value= 0.05). For OL, only the FO parameters of pressure and  $S/F$  showed high significance (P-values <0.01), none of the TFI parameters were significant, and the PQ parameter of  $S/F$  was highly significant (P-value <0.01). The PQ parameter of pressure was not significant (P-value >0.05), nevertheless the removal of this parameter causes that the lack of fit to become significant and the  $R^2$  drops to unacceptable values.

The regression coefficient analysis of the models for the responses  $Y_{\text{tot}}$  and OL are summarized in Table 3 along with the list of coefficients of each model. Regression analysis results also show that the  $R^2$  and adjusted- $R^2$  values were 0.96 and 0.92 for the  $Y_{\text{tot}}$  model and 0.995 and 0.992 for the OL model, respectively. These results indicate the accuracy of the models.

The response surface generated from the regression model of  $Y_{\text{tot}}$  is shown in Fig. 6. As it can be seen from Fig. 6A,  $Y_{\text{tot}}$  decreases rapidly from approx. 96 to 86% when pressure decreased from 14 to 8 MPa. The  $S/F$  affected  $Y_{\text{tot}}$  differently, with a slight convex tendency, due to the significance of the  $S/F$  PQ term.  $Y_{\text{tot}}$  increased when  $S/F$  decreased from 10 to 5 to find a maximum near 96% at  $S/F = 5 \text{ kg}\cdot\text{kg}^{-1}$ . Fig. 6B shows the effect of temperature and pressure on  $Y_{\text{tot}}$ . The maximum  $Y_{\text{tot}}$  was found to be at the lowest temperature (40 °C) and the highest pressure (14 MPa). As the temperature and  $S/F$  decreased,  $Y_{\text{tot}}$  increased (Fig. 6C). The slight curvature of  $Y_{\text{tot}}$  in Fig. 6 is explained by the significance of the PQ parameters of temperature and  $S/F$ .

On the other hand, only the  $S/F$  and pressure showed significant effect on the OL. Fig. 7 shows the response surface plot for OL. As it can be observed, the OL decreased rapidly from ~270 to ~100  $\text{mg}\cdot\text{kg}^{-1} \text{ Org}/\text{CO}_2$  when the  $S/F$  increased from 5 to 15  $\text{kg}\cdot\text{kg}^{-1}$ . Pressure showed a very slight, almost undetectable effect on OL due to the magnitude of the PQ coefficient of the  $S/F$ .

As mentioned before, these results were found to be in good agreement with those found in literature [12,36]. The highest extraction yield of volatiles was observed at values of  $S/F \sim 7 \text{ kg}\cdot\text{kg}^{-1}$ , and this variable was found to be the one with the most significant effect on the extraction of volatiles from similar aqueous systems.

### 3.3 Selectivity of CO<sub>2</sub> for aromas from 1-hexanol and water

The fractionation capability of CC-SFF for aqueous apple aromas (*E*)-2-hexenal and hexanal from 1-hexanol and water was analyzed by the comparison of the selectivity factor ( $\alpha_{ij}$ ). Fig. 8 shows the selectivity factor of the apple aroma constituents aromas (*E*)-2-hexenal and hexanal from 1-hexanol ( $\alpha_{A,3}$ ) versus CO<sub>2</sub> density at fixed temperatures. In general the  $\alpha_{A,3}$  showed a decreasing tendency with increasing CO<sub>2</sub> density. At a temperature of 50 °C,  $\alpha_{A,3}$  decreases from a maximum of 6.3 near 200  $\text{kg}\cdot\text{m}^{-3}$  to 1.2 near 750  $\text{kg}\cdot\text{m}^{-3}$ . At temperatures of 60 °C and 40 °C the decreasing tendency was less steep than at 50 °C. At 60 °C,  $\alpha_{A,3}$  decreased slowly approximately from 4 to 1.5. At 40 °C,  $\alpha_{A,3}$

started approximately at 4 near  $300 \text{ kg}\cdot\text{m}^{-3}$  and decreased to 2.5 near  $750 \text{ kg}\cdot\text{m}^{-3}$ . However, near  $680 \text{ kg}\cdot\text{m}^{-3}$  and  $S/F = 15$  the selectivity was approximately 4.5. This decreasing tendency  $\alpha_{A,3}$  with increasing  $\text{CO}_2$  density is a typical behavior of competence of selectivity *versus* yield. The solvent power of  $\text{CO}_2$  increases at higher density (liquid-like), and thus extraction yield, but at expense of a lower selectivity. Even though  $\alpha_{A,3}$  showed reasonable values for feasible separation with CC-SFF ( $>1.3$  [8]), the presence of water made the fractionation of the relevant aroma constituents (*E*)-2-hexenal and hexanal from 1-hexanol unsuccessful.

As expected high separation factors between organic compounds and water were achieved. Fig 9 compares the selectivity of individual aromas from water ( $\alpha_{i,4}=k_i/k_4$ ) calculated from column experiments and from (vapor + liquid) equilibria (VLE) data [27].

Selectivity values of (*E*)-2-hexenal from water ( $\alpha_{1,4}=k_1/k_4$ ) calculated from column experiments were  $\sim 10^4$  and were found to be in reasonable good agreement with those calculated from VLE data [27] (Fig. 9A). This result suggests that only one stage of equilibrium was achieved in the column, this could be explained by poor hydrodynamic characteristics inside the column due to high interfacial tension of aqueous systems and perhaps inappropriate packing type. However, typical values of the height equivalent of a theoretical stage (HETS) in CC-SFF of aqueous systems ranges from 1 to 3 m [45,46]. As it can be seen from Fig. 9B the separation factors for hexanal ( $\alpha_{2,4}=k_2/k_4$ ) were higher than those calculated from VLE data nearly by an order of magnitude ( $\sim 10^4$ ). The maximum separation factor was observed at  $50 \text{ }^\circ\text{C}$  and  $\text{CO}_2$  density of  $500 \text{ kg}\cdot\text{m}^{-3}$ . Nearly one order of magnitude lower ( $\sim 10^3$ ) were the observed separation factors for 1-hexanol ( $\alpha_{3,4}=k_3/k_4$ ) (Fig. 9C). This behavior is explained by the higher polarity of alcohols compared with that of aldehydes. However, a clear increasing tendency with increasing  $\text{CO}_2$  density was observed for all temperatures suggesting that low pressure would be preferable for obtaining low separation factors between 1-hexanol and water. No experimental data was available to compare. However, from the behavior of (*E*)-2-hexenal and hexanal the  $\alpha_{3,4}=k_3/k_4$  should not differ greatly from those calculated from VLE data.

As mentioned before, despite the higher polarity of alcohols compared to that of aldehydes, these were not sufficient for fractionation of 1-hexanol from the aroma compounds. This could explain

why fractionation was not possible; the predominant effect was the concentration of organics in the extract.

#### 4. Conclusions

CC-SFF of aqueous C-6 apple aromas is highly capable of producing a water-free super-concentrated product. Very high separation factors of individual aromas over water were observed ( $\sim 10^4$ ). Therefore, all organic compounds were practically removed completely from the feed solution and a two-phase extract was collected in the separator. However, polarity differences between (*E*)-2-hexenal, hexanal, and 1-hexanol were not sufficient for separation of 1-hexanol from the aldehydes (aroma compounds) and, consequently the predominant effect was the concentration of organics in the extract. The extraction yield of aromas was  $>86\%$  for all experiments and the highest organic compounds composition in the extract was 43% w/w. The *S/F* had the most significant effect on the extraction of apple aroma compounds as observed by other authors and, according to the RSM models, the optimal conditions to concentrate C-6 apple aromas would be 40 °C, 14 MPa, and *S/F* = 5.

#### Acknowledgements

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#### Nomenclature

##### Acronyms

ANOVA	ANalysis Of VAriance
BBD	Box-Behnken Design
CC-SFF	CounterCurrent Supercritical Fractionation
FO	First Order
GC	Gas Chromatography
PQ	Pure Quadratic
RSM	Response Surface Methodology
SFE	Supercritical Fluid Extraction
SPME	Solid Phase Micro Extraction

S/F	Solvent-to-Feed ratio
TFI	Two-Factor Interaction

*Variables and parameters*

$k_i$	Partition coefficient [-]
OL	Organics' Loading [ $\text{mgOrg}\cdot\text{kgCO}_2^{-1}$ ]
$P$	Pressure [MPa]
$q_E$	Extract mass flow rate [ $\text{g}\cdot\text{min}^{-1}$ ]
$q_F$	Feed mass flow rate [ $\text{g}\cdot\text{min}^{-1}$ ]
$q_R$	Raffinate mass flow rate [ $\text{g}\cdot\text{min}^{-1}$ ]
S/F	Solvent-to-Feed ratio [ $\text{kg}\cdot\text{kg}^{-1}$ ]
$T$	Temperature [ $^{\circ}\text{C}$ ]
$x_i$	Solute i mass fraction in the raffinate stream [ $\text{g}\cdot\text{min}^{-1}$ ]
$Y_A$	Extraction yield of aromas [%]
$y_i$	Solute i mass fraction in the extract stream [%w/w]
$Y_{\text{tot}}$	Total extraction yield of organic compounds [%]
$z_i$	Solute i mass fraction in the feed stream [%w/w]

*Greek symbols*

$\alpha_{ij}$	Selectivity factor of compound i over compound j [-]
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**Table 1.** Box-Behnken design and observed responses. Operational conditions of temperature ( $T$ ), pressure ( $P$ ), solvent-to-feed ratio ( $S/F$ ), CO<sub>2</sub> density ( $\rho$  CO<sub>2</sub>), mass flow rates of feed ( $q_F$ ), extract ( $q_E$ ) and raffinate ( $q_R$ ); mass fractions of component  $i$  in extract ( $y_i$ ) and raffinate ( $x_i$ ) streams; selectivity of aromas (A) from 1-hexanol ( $\alpha_{A,3}$ ) and water ( $\alpha_{A,4}$ ); extraction yield of aromas ( $Y_A$ ) and total organics ( $Y_{tot}$ ), and Organics' Loading (OL).

Operational Conditions							Mass Fractions								Selectivity		Extraction Yield		Loading
$T$ ( $X_1$ )	$P$ ( $X_2$ )	$S/F$ ( $X_3$ )	$\rho$ CO <sub>2</sub>	$q_F$	$q_E$	$q_R$	$y_1$	$y_2$	$y_3$	$y_4$	$x_1$	$x_2$	$x_3$	$x_4$	$\alpha_{A,3}$	$\alpha_{A,4}$	$Y_A$	$Y_{tot}$	OL
50 (0)	8 (-1)	5 (-1)	219	20.2	0.1	20.7	14.2	5.9	23.1	56.9	26	2.8	145	14.2	4.4	12232	93.4	87.4	261
50 (0)	14 (1)	5 (-1)	672	20.4	0.2	20.7	6.1	2.1	12.1	79.7	2.5	1.5	7.00	6.1	1.2	25622	94.5	96.0	273
50 (0)	8 (-1)	15 (1)	219	10.9	0.1	10.1	6.0	2.3	11.0	80.7	18	3.5	178	6.0	6.3	4804	90.6	88.8	107
40 (-1)	8 (-1)	10 (0)	278	15.5	0.1	15.8	5.6	2.0	10.5	81.9	17	1.6	112	5.6	4.3	4875	90.3	88.6	150
60 (1)	11 (0)	5 (-1)	358	21.5	0.3	20.7	4.0	1.3	7.60	87.1	11	2.5	47.0	4.0	2.5	4635	93.6	93.1	281
40 (-1)	11 (0)	5 (-1)	684	19.5	0.2	19.3	3.9	1.4	8.11	86.5	4.1	1.5	12.6	3.9	1.5	11095	87.4	95.5	267
40 (-1)	11 (0)	15 (1)	684	10.4	0.1	10.1	3.4	1.1	6.68	88.8	4.7	0.6	34.0	3.4	4.3	9538	91.2	93.4	106
40 (-1)	14 (1)	10 (0)	763	15.4	0.3	15.8	2.9	0.9	5.55	90.6	4.2	1.6	20.2	2.9	2.4	7276	94.0	95.9	165
60 (1)	8 (-1)	10 (0)	192	10.0	0.2	10.7	2.1	0.8	4.38	92.7	17	1.1	94.4	2.1	3.6	1803	89.6	87.3	140
60 (1)	14 (1)	10 (0)	561	15.5	0.4	15.9	1.9	0.7	3.96	93.5	5.7	1.6	18.3	1.9	1.6	3733	89.9	94.9	162
50 (0)	14 (1)	15 (1)	672	10.5	0.3	10.5	1.6	0.6	3.47	94.3	4.6	1.5	16.7	1.6	1.7	3809	86.7	92.5	108
60 (1)	11 (0)	15 (1)	358	10.3	0.3	10.2	1.5	0.6	2.93	95.1	5.8	0.3	24.8	1.5	2.8	3491	89.4	91.7	105
50 (0)	11 (0)	10 (0)	503	15.6	0.3	16.1	2.3	1.1	4.52	92.1	14	0.2	41.9	2.3	2.3	2677	92.0	89.4	157
50 (0)	11 (0)	10 (0)	503	15.6	0.3	15.3	2.3	1.0	4.36	92.3	9.2	0.5	26.9	2.3	2.1	3723	95.2	91.8	158
50 (0)	11 (0)	10 (0)	503	15.6	0.3	14.3	2.2	1.1	4.46	92.3	11	0.2	33.3	2.2	2.2	3192	89.5	89.5	156

( $E$ )-2-hexenal ( $i=1$ ); hexanal ( $i=2$ ); 1-hexanol ( $i=3$ ); water ( $i=4$ )

$[T] = ^\circ\text{C}$ ;  $[P] = \text{MPa}$ ;  $[S/F, \alpha_{A,3}, \alpha_{A,4}] = -$ ;  $[\rho\text{CO}_2] = \text{kg}\cdot\text{m}^{-3}$ ;  $[q] = \text{g}\cdot\text{min}^{-1}$ ;  $[y_i], [x_4] = \%$  w/w;  $[x_i] = \text{mg}\cdot\text{kg}^{-1}$ ;  $[Y_{tot}] = \%$ ;  $[\text{OL}] = \text{mgOrg}\cdot\text{kgCO}_2^{-1}$

**Table 2.** Analysis of variance (ANOVA) of total yield of organics ( $Y_{tot}$ ) and Organics Loading (OL) models. First Order (FO), Two Factor Interaction (TFI), Pure Quadratic (PQ).

Source	Degrees of freedom	Sum of squares	Mean squares	F-value	Pr (>F)
<b><math>Y_{tot}</math></b>					
FO ( $X_1, X_2, X_3$ )	3	101	33.6	45.6	< 0.001 (***)
PQ ( $X_1, X_3$ )	2	19.0	9.52	12.9	0.003 (**)
TFI ( $X_2, X_3$ )	1	6.04	6.04	8.16	0.021 (*)
Residuals	8	5.92	0.740		
Lack of fit	6	2.35	0.391	0.219	0.938
Pure error	2	3.57	1.78		
<b>OL</b>					
FO ( $X_2, X_3$ )	2	$5.40 \cdot 10^4$	$2.70 \cdot 10^4$	855	< 0.001 (***)
PQ ( $X_2, X_3$ )	2	$4.05 \cdot 10^3$	$2.02 \cdot 10^3$	64.1	< 0.001 (***)
Residuals	10	316	31.6		
Lack of fit	4	158	39.5	1.50	0.313
Pure error	6	158	26.3		

Significance levels: (\*\*\*), 0.1%; (\*\*), 1%; (\*), 5%.

**Table 3.** Regression coefficient analysis for total yield model ( $Y_{\text{tot}}$ ) and Organics Loading (OL) models. Coded variables  $X_1$  temperature,  $X_2$  pressure, and  $X_3$ , solvent-to-feed ratio; regressed coefficients ( $\beta_0, \beta_{ii}, \beta_{ij}$ ); and model determination coefficient ( $R^2$ ).

Coefficient	Estimated value	Standard error	t value	P-value (Pr >  t )
<b><math>Y_{\text{tot}}</math></b>				
Intercept ( $\beta_0$ )	90.0	0.413	218	< 0.001 (***)
$X_1$ ( $\beta_1$ )	-0.791	0.304	-2.60	0.032 (*)
$X_2$ ( $\beta_2$ )	3.39	0.304	11.2	< 0.001 (***)
$X_3$ ( $\beta_3$ )	-0.704	0.304	-2.32	0.049 (*)
$X_1^2$ ( $\beta_{11}$ )	1.89	0.446	4.23	0.003 (**)
$X_3^2$ ( $\beta_{33}$ )	1.38	0.446	3.10	0.015 (*)
$X_2 \cdot X_3$ ( $\beta_{23}$ )	-1.23	0.430	-2.86	0.021 (*)
$R^2$	0.955			
Adjusted $R^2$	0.922			
F-statistic	28.4			< 0.001 (***)
<b>OL</b>				
Intercept ( $\beta_0$ )	157	2.70	58.2	< 0.001 (***)
$X_2$ ( $\beta_2$ )	6.30	1.99	3.17	0.001 (**)
$X_3$ ( $\beta_3$ )	-81.9	1.99	-41.2	< 0.001 (***)
$X_2^2$ ( $\beta_{22}$ )	-2.60	2.92	-0.893	0.393
$X_3^2$ ( $\beta_{33}$ )	32.64	2.92	11.2	< 0.001 (***)
$R^2$	0.995			
Adjusted $R^2$	0.992			
F-statistic	460			< 0.001 (***)

Significance levels: (\*\*\*), 0.1%; (\*\*), 1%; (\*), 5%.

## Figure captions

**Fig. 1.** Schematic flow diagram of experimental apparatus. (1), packed column; (2), sapphire window; (3) and (4), upper and bottom heating mantles; (5), heating bath; (6) preheater; (7), temperature controllers; (8), backpressure regulator; (9), liquid piston pump; (10), liquid storage tank; (11), liquid mass flow meter; (12), CO<sub>2</sub> piston pump; (13), CO<sub>2</sub> buffer tank; (14), CO<sub>2</sub> recovery cycle; (15), cooling bath; (16), CO<sub>2</sub> mass flow meter; (17) and (18), cyclonic separators; (19), cold-trap; (20), needle valve; (21), flow control valve; (22), wet test-meter; (23), molecular sieve; (24), raffinate expansion tank; (25), temperature controller; (26), CO<sub>2</sub> storage tank; (27), magnetic stirrer.

**Fig. 2.** Raffinate mass fraction over time for steady state time estimation. (---○---), 1-Hexanol; (—□—), (*E*)-2-Hexenal; (----Δ----), Hexanal. Open symbols represent experimental values and lines signals trends.

**Fig. 3.** Aroma content in Feed, Raffinate, and Extract samples of best experimental run (first line of Table 1). (■), (*E*)-2-Hexenal; (⚡), Hexanal; (■), 1-Hexanol; (□), Water.

**Fig. 4.** Super-concentrated extract, two-phase separation.

**Fig. 5.** Aromas ((*E*)-2-Hexenal, Hexanal) extraction yield ( $Y_A$ ). (---○---), 60 °C; (—□—), 50 °C; (----Δ----), 40 °C. Open symbols represent experimental values and lines signals trends.

**Fig. 6.** Response surface plot for total organics extraction yield ( $Y_{tot}$ , %)

$$Y_{tot} = 89.97 - 0.79X_1 + 3.39X_2 - 0.70X_3 + 1.89X_1^2 + 1.38X_3^2 - 1.23X_2X_3.$$

(A), effect of pressure and solvent-to-feed ratio; (B), effect of temperature and pressure; (C), effect of temperature and solvent-to-feed ratio.

**Fig. 7.** Response surface plot for Organics loading (OL, mg·kg<sup>-1</sup> Org/CO<sub>2</sub>).

$$OL = 157.06 - 6.30X_2 - 81.88X_3 - 2.60X_2^2 + 32.64X_3^2.$$

Effect of pressure and solvent-to-feed ratio.

**Fig. 8.** Selectivity of apple aroma constituents (*E*)-2-Hexenal, Hexanal from 1-Hexanol

( $\alpha_{A,3} = k_A/k_3$ ). (---○---), 60 °C; (—□—), 50 °C; (----Δ----), 40 °C. Open symbols represent experimental values and lines signals trends.

**Fig 9.** Selectivity of individual aromas from water ( $\alpha_{i,4}=k_i/k_4$ ) calculated from column experiments and (vapor + liquid) equilibria (VLE) data [27]. (A), (*E*)-2-hexenal; (B), Hexanal; (C), 1-hexanol; (- - - ○ - - -), 60 °C; (- - □ - -), 50 °C; (- - - Δ - - -), 40 °C. Open symbols represent experimental values, closed symbols experimental values from VLE, and lines signal trends.



## Apple C-6 aromas

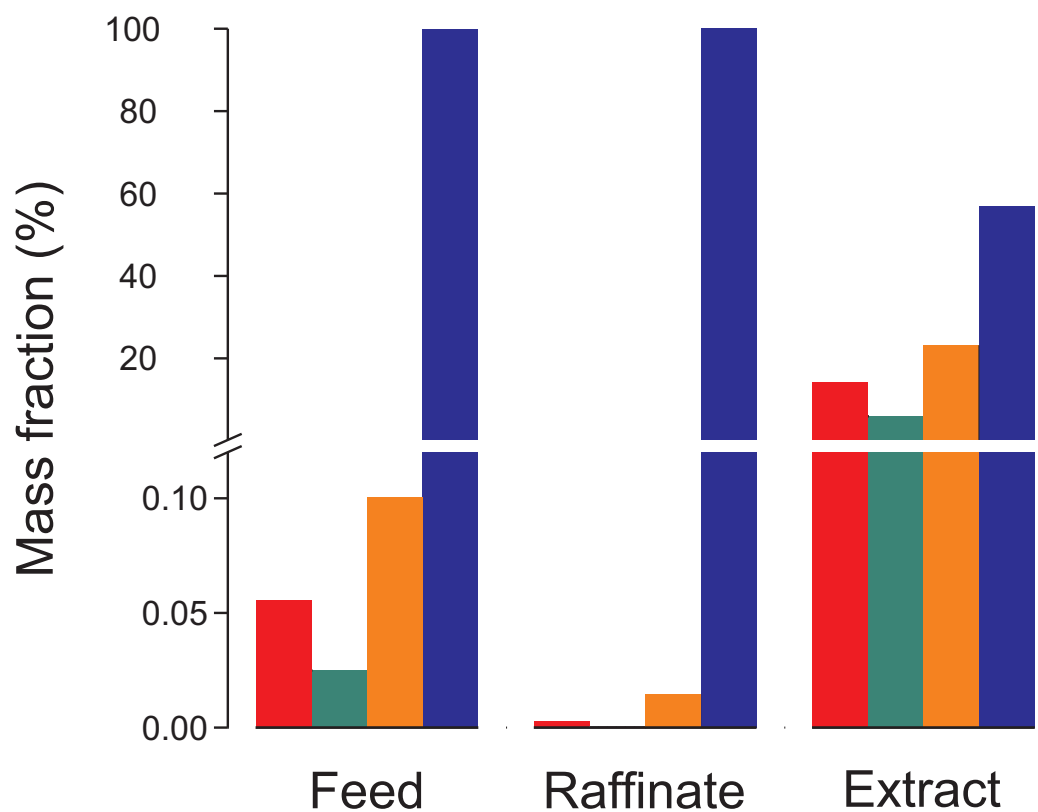


Figure 1

