A Study about the Effects of Supercritical Carbon Dioxide Drying on Apple Pieces

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***Abstract*—The work explores the feasibility of supercritical carbon dioxide (SC-CO_2) as alternative drying food process. Experiments carried out with apple pieces at 10 MPa and 35 ℃, aimed to investigate the effect of the drying time (5÷120 min) and the addition of a pre-dehydration step in graded ethanol (EtOH) solutions on the dehydration of the final product in terms of weight loss and structure. The treatment with pure EtOH leaded to a weight reduction of 50.0 ± 0.2 % after 120 min while SC-CO_2 induced a reduction down to 18.53±1.57 % after the same drying time. Significant improvements in terms of weight loss were obtained when apples were first dehydrated in pure EtOH for 40 min, and subsequently in SC-CO_2 for 10 min reaching a final reduction of 11.67±2.55%. Color measurements indicated that both SC-CO_2 and EtOH-SC-CO_2 drying treatments induced a significant increase of L*, while an increase of a* and b* parameters was detected only for SC-CO_2 dried apples. The overall changes in color ΔE did not shown significant differences between the two dried samples. SEM images indicated that the EtOH-SC-CO_2 dried apples presented more shrinking and a wider pore distribution compared to the SC-CO_2 dried ones. EtOH-SC-CO_2 drying confirmed the potential to apply the technology for drying apple slices in short time.**

***Index Terms*—apple; drying, supercritical carbon dioxide, weight loss, microstructure, color**

I. Introduction

Food drying is one of the most common process used to improve food stability, since it considerably decreases the water activity of the material, and therefore it reduces microbiological activity minimizing physical and chemical changes during the product storage [1]. Although these positive benefits, the loss of moisture during drying may inflict undesirable effects on the product's microstructure, influencing its nutritional characteristics and chemical/physical properties [2], [3]. For instance after hot air drying, that is the most common dehydration process in food and chemical industry, low porosity and high apparent density are observed [4]. In addition, the high temperatures commonly used (typically 65–85 ℃) may damage the microstructure and negatively influence the color, texture, taste, aroma and nutritional value of the product.

Recently, several alternative techniques have been proposed to overcome the main drawback of the traditional air-drying process [5]. Despite their innovation and benefits, they show several limitations. For example, microwave drying promotes a quick drying but also difficulties in controlling the rapid dehydration rate that can negatively affect the microstructure of the product [6], while freeze-drying technique leads to products with good quality attributes but higher porosity than those of air-drying [7]. In addition, some of these alternative technologies, as microwave [8] and vacuum drying [9] are very expensive and energy-consuming [10].

Supercritical carbon dioxide (SC-CO_2) has been shown to have potentials as green technology in several fields of food processing. SC-CO_2 extraction has already found several applications such as the removal of caffeine from coffee [11] or the recovery of flavors, fragrances and oils from fruits and vegetable matrices [12]. SC-CO_2 has been also shown a good alternative to thermal treatments for the pasteurization of liquid [13] and solid foodstuffs [14] making it attractive for food manufacturing.

Concerning food drying, SC-CO_2 has been applied on fresh cut fruits [15], carrot [16], agar gels [17], apple slabs [18] and basil [19]. Lee et al. [18] showed that SC-CO_2 treatment of 120 min at 35 ℃,15 MPa followed by a thermal dehydration at 70 ℃ induced a weight loss of 17.5% with a constant water reduction rate during 60 min and a final water content of 3.6% after 120 min of thermal treatment.

For products other than food, the process has found applications for drying gels composed of silica [20] or chromia [21] to produce aerogels or to create other inorganic porous structures [22], [23].

The interest towards this technology comes from the physical properties of SC-CO_2, in particular from its ability to avoid the formation of the vapor-liquid interfaces during the process. Consequently, capillary-induced tensile stresses, observed during air-drying, can be avoided, allowing CO_2 rapid to penetrate into the pores of food structure, preserving its structure. Additionally, as CO_2 has a low critical temperature (31.1 ℃) it is possible to exploit the process at relatively low temperatures, much lower than in a conventional drying.

On the other hand, it is worth noticing that, as SC-CO_2 is a non-polar solvent with modest water solubility, thus a

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co-solvent such as ethanol needs to be added to the fluid [24]. Although this scenario depicting the advantages of SC-CO_2 processing for food dehydration, limited information on this process are available. The present work aims to investigate the potential of supercritical drying of foods on apples using both pure SC-CO_2 and ethanol-modified SC-CO_2. We analyzed the potential of this novel technology in terms of drying profiles, color and microstructure of the final product.

II. Materials and Methods

A. Materials

Fresh apples (Golden Delicious variety) were purchased from a local market and stored at 4 ℃ prior their use. CO_2 (carbon dioxide 4.0, purity 99.990%) was supplied by Rivoira (Verona, Italy). Pure ethanol (EtOH, 99.9%) was supplied by Carlo Erba (Milan, Italy).

B. Sample Preparation

Samples were prepared using a scalpel, cutting square pieces (1x1 cm) of 0.2 cm of thickness, and analyzed or dried within 10 min after their preparation, in order to avoid the degradation and enzymatic browning. The initial moisture content of the apple pieces was measured by drying the samples at 80 ℃ in an oven until reaching a final constant mass, which value was then compared to the initial weight.

C. Sample Preparation

The high-pressure drying reactor used for this study was purchased by Separex S.A.S. (Champigneulles, France) and represented in "Fig. 1". The reactor has an internal volume of 50mL and is equipped with a thermostatic bath to assure a constant temperature of 35 ℃ during the process, a HPLC pump (Gilson 25SC; Gilson S.A.S, France) and a cryostat bath (MPM Instruments, Milan, Italy). An on-off valve and a micrometric valve placed at the outlet of the reactor, electrically heated, are used to avoid CO_2 freezing during the flushing. Liquid CO_2 was injected inside the reactor with a constant flow rate (23mL/min) until reaching the set-up pressure of 10 MPa. Afterward, the on-off and micrometric valves were opened to ensure a continuous flow during the entire treatment time. Samples were dried up to 120 min when only CO_2 was used, otherwise the SC-CO_2 drying was reduced to 80 min when the samples were firstly dehydrated for 40 min with a graded EtOH solution. In this second case, the preliminary dehydration was performed dipping the samples in graded EtOH series solutions (50%, 75%, 95%, and 99.8%) at 20 ± 2 ℃.

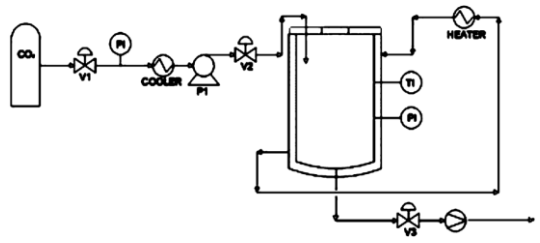

Figure 1. SC-CO_2 semi-continuous system.

The process conditions (10 MPa and 35 ℃) used in this study were optimized on the base of previous researches. We have shown that above 10 MPa CO_2 solubility is a weak function of pressure [25], [26]. We also demonstrated that a pressure increase from 10 to 30 MPa did not influence significantly CO_2 solubility in the water contained in samples [26]. Temperature was fixed at 35 ℃ to exploit CO_2 properties in supercritical phase. Experiments at higher temperatures were not taken into account based on CO_2 solubility, which decreases as temperature increases [25]. Moreover, higher temperatures could damage and irreversibly degrade the sample.

D. Drying Efficiency

Samples weights were measured before and after each treatment using a microbalance (OHAUS® Explorer, Nänikon, CH); the percentage of weight loss was expressed as W_{fin}/W_{in}, where W_{fin} and W_{in} correspond to the weight of the sample after and before the treatment, respectively. All the experiments were performed at least in triplicate. Water activity was also measured at the end of the process by the use of HygroPalm23-AW (Rotronic Italia srl, Milano, Italy).

E. Color Measurement

Color was measured with a high-resolution miniature spectrometer (HR2000+, Ocean Optics Inc., Dunedin, FL) as previous reported [28]. Briefly, the probe transmitted the light from a halogen lamp to the sample by an illuminating fiber while the reflected light from the sample was acquired by the reading fiber and measured by the spectrometer. The sample was placed at 1 cm from the fiber using a custom support. After the calibration of the signal, the reflectance spectrum of the samples was acquired by a specific software (Spectra Suite®, Ocean Optics Inc., Dunedin, FL, USA) providing L* (the lightness ranging from the darkest black at L* = 0, and the brightest white at L* = 100), a* (the red/green opponent colors, with green at negative (-100) a* values and red at positive (+100) a* values), and b* (the yellow/blue opponent colors, with blue at negative (-100) b* values and yellow at positive (+100) b* values) parameters. Color measurements were performed at least in triplicate, and mean values and standard deviations were evaluated.

Total color difference (ΔE) between the untreated and dried samples was calculated from the numerical values of *L**, *a** and *b**, as in (1):

$$\Delta E = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2} \quad (1)$$

F. Scanning Electron Microscope Observations

FEI QUANTA 200 was used for scanning electron microscope (SEM) observation on raw and dried samples (30 min in milliQ water at room temperature). In order to avoid sample degradation and water removal, samples were analyzed at low vacuum (pressure of 0.07 MPa in the samples chamber) processing one sample at the time.

G. Statistical Analysis

Differences between mean values were tested using the analysis of variance followed by multiple comparisons

between means with the Duncan test. The general procedure of Statistica 7.0 software (StatSoft Inc., Tulsa, OK, U.S.A.) was used. All the data were analyzed at a significance level of $p>0.05$.

III. Results and Discussion

A. Drying

"Fig. 2" shows the weight reduction for three different dehydration treatments as function of treatment time.

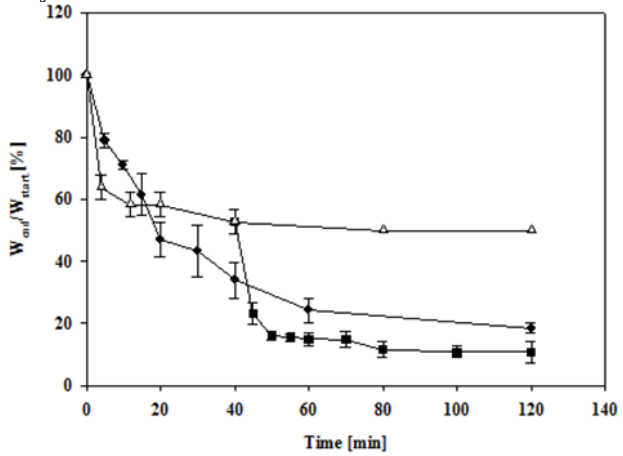

Figure 2. Drying profiles of raw apple pieces treated with graded EtOH series solutions (50%, 75%, 95%, and 99.8%) ( ), SC-CO_2 (•,120 min at 10 MPa, 35 ℃), and EtOH-SC-CO_2 (■, 40min in EtOH at 20±2 ℃ followed by SC-CO_2 at 10 MPa, 35 ℃, 10÷80min).

When apples were dried in pure EtOH for 120 min, a weight reduction of 50±0.2% was observed, while a higher weight reduction of 18.53±1.57% were observed with pure SC-CO_2 after the same drying time. It is worth noticing that the dehydration in pure EtOH did not show any further decrease of weigh after 40min of total resident time. Significant improvements were obtained when a combined treatment was used by coupling the dehydration with EtOH with the SC-CO_2. After 40 min of pure EtOH, the SC-CO_2 drying was applied from 10 up to 40min. The maximum reduction equal to 11.67±2.55% was achieved with a combined treatment of 40 min of pure EtOH followed by 10min of SC-CO_2.

Additionally, no significant weight reductions were observed increasing the time from 50 (40 min of EtOH pre-treatment followed by 10 min of SC-CO_2) to 120 min (40 min of EtOH pre-treatment followed by 80 min of SC-CO_2). The results indicated that 10 min of SC-CO_2 were enough to reach the maximum weight reduction when the process was preceded by a 40 min dehydration with EtOH.

Based on these results and consideration, the color and the microstructure of EtOH-SC-CO_2 dried samples were just measured for samples dried for 40 min with EtOH and subsequently for 10 min at 10 MPa and 35 ℃ with SC-CO_2. For the sample measured, the water activity was lower than 0.4 (data not shown).

Experimental evidences shown in "Fig. 2" confirmed that the addition of a co-solvent favorably influence the solubility of polar substances in SC-CO_2, as reported in several works on different application of CO_2 processes [16], [29]. Their mechanism of action is thought to involve specific chemical and physical interactions that exist between the co-solvent and solute, including hydrogen bonding and dipole–dipole attractions [30].

On the other hand, our results showed that when apples are processed in an environment of pure, unmodified SC-CO_2, a considerable quantity of water could be extracted from the matrix. About 80% of the original moisture content was lost, indicating that CO_2 drying is a feasible drying method for apples.

B. Color

"Fig. 3" shows the untreated (A), EtOH-SC-CO_2 (B) and SC-CO_2 (C) apple pieces. The differences in color between the treated and untreated samples are visible. Both EtOH-SC-CO_2 and SC-CO_2 samples are lighter compared to the untreated meaning that the drying treatment inactivated polyphenol oxidase enzyme.

Figure 3. Images of apple pieces untreated (A), EtOH-SC-CO_2 (B) treated for 40 min in EtOH and 10 min in SC-CO_2 at 10 MPa, 35 ℃, and SC-CO_2 (C) treated for 120 min at 10 MPa, 35 ℃

Furthermore, L*, a*, and b* color parameters for the raw, SC-CO_2 (120 min at 10 MPa, 35 ℃) and EtOH-SC-CO_2 (40min in EtOH and 10 min in SC-CO_2 at 10 MPa, 35 ℃) dried apples were also measured and reported in Table I.

TABLE I. Color Parameters and ΔE Values for Raw and Dehydrated Apples After SC-CO_2 (120 min at 10 MPa, 35 ℃) and EtOH+SC-CO_2 (40 min in EtOH at 20 ±2 ℃ and 10 min in SC-CO_2 at 10 MPa, 35 ℃).

	L*	a*	b*	ΔE
Raw apple	89.7±3.7^a	5.03±5.5^a	23.53±2.0^a	
EtOH+SC-CO_2 dehydrated apple	97.1 ±5.1^b	4.3 ±0.6^a	17 ±3.4^b	9.88±3.03^a
SC-CO_2 dehydrated apple	97.3±6.5^b	8.0±0.8^b	29.5±4.2^a	10.96±3.05^a

Data are mean values ± standard deviations. Values with similar letters within rows are not significantly different (Duncan's test, $p > 0.05$).

SC-CO_2 and EtOH-SC-CO_2 drying processes induced a significant increase of the lightness (L*) of the samples probably due to CO_2 extraction properties. An increase of a* and b* parameters was detected only for SC-CO_2 dried apples, meaning that the samples appeared more brown probably due to polyphenol oxidase, which started its activity at the first instants of the treatment. As regards EtOH-SC-CO_2 dried apples, a* parameter was not significantly influenced while b* significantly decreased compared to the raw sample, as it was probably affected by EtOH. The overall changes in color ΔE were also calculated. An absolute threshold value for human color discrimination has only been determined for few specific products [31], nevertheless, a ΔE value of 4 is usually considered a clearly distinguishable color difference to

the average person. Based on this assumption, perceivable color differences could be observed for both dried samples compared to the raw one. Similar results were also observed for carrot dried with SC-CO_2 in terms of L* parameters showing a paler color compared to the untreated samples [16]. Additionally, the evaluation showed no significant differences between the two dried samples (Table I).

C. Microstructure

"Fig. 3" shown the images obtained by SEM of the surfaces of the raw, SC-CO_2 (10 MPa, 35 ℃, and 120 min) and EtOH-SC-CO_2 (40 min in EtOH and 10 min in SC-CO_2 at 10 MPa, 35 ℃) dried apples. The surface of the EtOH-SC-CO_2 dried apples showed more shrinking and a wider pore distribution compared to the raw and the pure SC-CO_2 dried apples. Furthermore, a high pores distribution was also observed probably associated to the higher cell disruption caused by the fast loss of cell moisture. SC-CO_2 dried apples also reported a high pores distribution compared to the raw one, but it was, anyhow, lower than the one observed for the EtOH-SC-CO_2 dried apples.

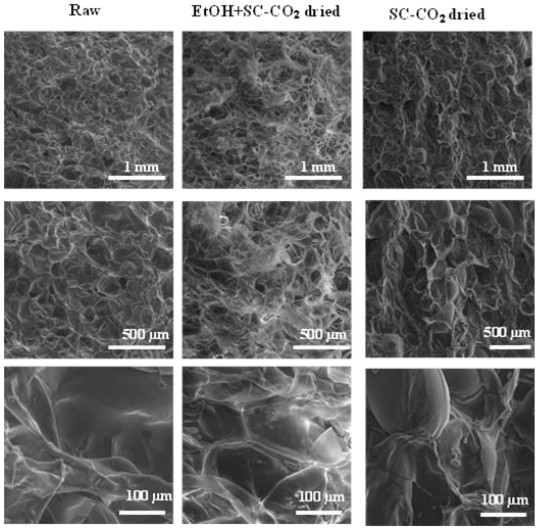

Figure 4. SEM images showing the raw apple, the raw apple dried at 10 MPa, 35 ℃ for 120 min with pure SC-CO_2 and rehydrated at 20±2 ℃, and the raw apple dried for 40 min in EtOH and 10 min in SC-CO_2 at 10 MPa, 35 ℃ and rehydrated at 20±2 ℃.

Lee *et al*. [18] reported similar results showing that the apples pretreated with SC-CO_2 had a wider pore distribution compared to the one dried only with the thermal treatment. They also observed that samples treated at higher temperatures 45 and 55 ℃ and pressures from 15 to 25 MPa showed more cell disruption, and more pores were observed.

IV. Conclusions

The results of the present work showed that apples firstly dehydrated with EtOH for 40 min and subsequently treated with SC-CO_2 at 10 MPa, 35 ℃ for 10 min lead to a satisfactory weight reduction (11.67 ± 2.55%), while the drying profiles of pure SC-CO_2 showed a lower degree of dehydration, a 18.53±1.57% after 120 min.

The color of the samples, measured after 120 min of SC-CO_2 drying and after a first step of 40 min in EtOH solutions and a subsequent drying of 10 min in SC-CO_2, showed significant increase of L*, while an increase of a* and b* parameters was detected only for SC-CO_2 dried apples. The overall changes in color ΔE did not shown significant differences between the two dried samples. SEM images indicated that the surface of presented more shrinking and a higher pores distribution compared to the raw and the SC-CO_2 dried samples.

In conclusion, the results of the present work are promising for a possible exploitation of such a technologies as alternative drying method. Nevertheless, more investigations are needed to understand the effect of the treatment on the rehydration properties of the apples and to investigate the acceptability of EtOH-SC-CO_2 dried apples in terms of sensorial perception by the consumers.

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