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Exploring Novel Supercritical CO_2 Drying Combined with High Power Ultrasounds: a Case on Peas and Apples

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The current global population stands at 8.1 billion people and is projected to reach 9 billion by 2037. The food sector will need to undergo significant transformations to ensure food security. In this context, drying plays an important role in enhancing global food security by facilitating the safe storage of agricultural products and food. In this study, we employed two innovative drying methods: supercritical carbon dioxide ($scCO_2$) drying and its combination with high-power ultrasound ($scCO_2$+HPU) to assess their performance in drying seeds and fruits such as peas and apples. Among drying methods, supercritical carbon dioxide is emerging as a promising technology in the food drying industry. So far, the use of $scCO_2$ has yielded promising results in the drying of spices, meat, and vegetables, but further studies are needed. High-power ultrasound has shown substantial potential in enhancing water mass transfer and microbial inactivation when coupled with technology. The outcomes of our experimental implementation demonstrated a significantly greater reduction in weight, moisture content and a notably lower water activity level for $scCO_2$+HPU compared to $scCO_2$ alone. These findings validate the significant potential of this integrated technology, which warrants further exploration in diverse food matrices.

1. Introduction

Addressing the nutritional needs of the expanding global population presents a major challenge, as forecasts suggest an increase from today's 8.1 billion individuals to between 9.6 and 12.3 billion by the year 2100 (FAO, 2023). Meeting this challenge will necessitate comprehensive transformations in food production, storage, distribution, and consumption practices to ensure global food security (Xiao and Mujumdar, 2020). A critical component among these solutions is the drying process, pivotal for the safe storage of agricultural products and food (Chojnacka *et al.*, 2021). By effectively reducing the moisture content, drying impedes microbial growth, reduces moisture-driven deteriorative biochemical reactions, and lowers costs related to packaging, transportation, storage, and processing. This, in turn, minimises postharvest losses, prolongs shelf-life, and increases the added value of food products (Filková *et al.*, 2014).
In the past, drying has been extensively investigated, and among various techniques, convective drying, microwave vacuum drying, and freeze-drying are some of the most widely used methods in the industry (Chojnacka *et al.*, 2021). In the pursuit of more efficient and safer drying methods, significant research has been dedicated to innovative and combined drying technologies. Notably, the application of supercritical carbon dioxide ($scCO_2$) has emerged as a promising alternative, yielding encouraging results in the drying of various foods such as fruits (Braeuer *et al.*, 2017; Zambon *et al.*, 2021; Zambon *et al.*, 2022), herbs (Bourdoux *et al.*, 2018), vegetables (Tomic *et al.*, 2020), and poultry (Morbiato *et al.*, 2019). The growing interest in $scCO_2$ technology is attributed to its physical properties, particularly its ability to avoid the formation of vapour-liquid interfaces during drying. This feature allows for rapid penetration of CO_2 into the food's structure without the capillary-induced tensile stresses typically observed during air-drying, thereby preserving the food's integrity (Pravallika *et al.*, 2023). Additionally, the low critical temperature and pressure of CO_2 allow for the process to

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be conducted at low temperatures, offering a considerable advantage over conventional drying methods. Specifically, $scCO_2$ drying is able to preserve the food's original structure and prevent degradation reactions, arising from the absence of a vapour-liquid interface and leveraging its relatively low critical point. Moreover, $scCO_2$ is recognized for its broad-spectrum antimicrobial effects in both solid and liquid products (Zambon *et al.*, 2022a).

$scCO_2$ drying can be coupled with high-power ultrasounds (HPU) accelerating the water removal in solid foods (Morbiato *et al.*, 2019). Moreover, coupling $scCO_2$ and HPU has been shown to have a synergistic effect on microbial inactivation (Michelino *et al.*, 2018; Morbiato *et al.*, 2019). Nevertheless, only a few studies have evaluated the performance of $scCO_2$ and HPU in food drying, and investigations focusing on seeds and fruits, such as peas and apples, are still lacking.

This preliminary study aims to investigate the drying performance (*i.e.* weight loss, moisture content, water activity) and appearance quality (*i.e.* colour) of peas and apples using two drying methods: $scCO_2$ drying and its combination with high-power ultrasound ($scCO_2$+HPU).

2. Materials and methods

2.1 Sample preparation

Fresh *Golden Delicious* apples were purchased from a local market in Padova (Italy), stored at 4 °C and treated within 3 days after the purchase. Unwashed fruits were cut into 1.5 X 1.0 X 1.0 cm rectangular parallelepiped, each weighing 1.0 ± 0.1 g, before being processed. Similarly, frozen peas were purchased from the same market, stored at -20 °C, and thawed at 4°C for 12 hours before processing. For each test, peas and apples were equally distributed in 4 metallic baskets (*i.e.* 2 baskets for each matrix) yielding 4.0 ± 0.2 g of product.

2.2 Supercritical carbon dioxide drying

Supercritical carbon dioxide drying alone ($scCO_2$) or combined with high-power ultrasounds ($scCO_2$+HPU) was carried out in a lab-scale reactor with recirculation (Separex S.A.S., Champigneulles, France). It was equipped with drying and regenerative vessels of different sizes, as described by Zambon *et al.* (2022a) and Zambon *et al.* (2022b). In brief, the equipment comprises a CO_2 tank (Nippon gasses, carbon dioxide 4.0, Milan, Italy), a chiller reservoir, pumps for pressurisation and recirculation, a heat exchanger, and automated control via LabVIEW software for monitoring pressure, temperature, and flow rate.

Experiments were conducted at 40°C, 13.3 MPa, and 300 min drying time, with a CO_2 flow rate of 19 kg/h, and featured pressurisation and depressurisation rates of 0.4 and 1.3 MPa/min, respectively. A piezoelectric sonotrode (Aktive Arc Sarl, La Vue-des-Alpes, Switzerland) was coupled with an ultrasonic generator (AA-WG1-Special, Trento, Italy) to generate 40 kHz ultrasounds, using a configuration similar to that reported by Morbiato *et al.* (2019). When the HPU were coupled, experiments were conducted at a consistent 10 ± 3 W by utilising the HPU during the drying phase. The sonotrode's oscillation amplitude was manually adjusted using the ultrasound generator to maintain a constant applied power. Two drying batches were performed for each method.

2.3 Drying performances and colour assessment

Drying performances were evaluated considering moisture, weight loss and water activity of the dried products as reported by Zambon *et al.* (2022b). Briefly, before and after the treatment, the weight of each sample was accurately determined using a precision balance (Radwag, PS 6000 R2, Poland) with weight sensitivity of 0.001 g. Weight loss was calculated according to Equation 1:

$$Weight\ loss = \left(1 - \frac{W_{dry}}{W_{fresh}}\right) * 100\%$$

where W_{fresh} and W_{dry} represent the sample weight before and after the drying treatment, respectively.

To determine moisture content, both treated and untreated samples were placed in an incubator (G-Cell 035, Fratelli Galli, Italy) at 70°C for 2–4 hours until a constant weight was achieved. The moisture content, defined as the proportion of water content in the dried products relative to that of the fresh samples, was calculated according to Equation 2:

$$Moisture\ \% = \left(1 - \frac{W_{dry} - W_{sm}}{W_{fresh}}\right) * 100\%$$

where W_{sm} is the solid matter weight, corresponding to the sample weight after the complete dehydration.

The water activity of fresh and treated products was measured with HygroPalm HP23-AW-A (Rotronic AG, Switzerland). Lastly, the sample's surface colour was assessed with a Tristimulus colourimeter (NR100, 3nh, China) within the CIE 1976 (L*, a*, b*) colour space parameters. In this context, L* represents the lightness index, which ranges from 100 (white) to 0 (black); a* indicates the redness index, transitioning from positive values (indicating red) to negative values (indicating green); and b* denotes the yellowness index, shifting from positive (indicating yellow) to negative (indicating blue). Treatment-induced colour alterations were quantified as the total colour change (ΔE), calculated according to Pathare *et al.* (2013).

2.4 Statistical analysis

Statistical analyses were performed using R version 4.0.5 (R Foundation for Statistical Computing, Vienna, Austria). Normal distribution and homogeneity of variance were tested using the Shapiro-Wilk and Levene lest (Royston, 1982; Schultz, 1985). Mean values were used to compare drying performance and colour parameters obtained from fresh and treated products. The existence of significant differences ($\alpha = 0.05$) between the treatments was evaluated using ANOVA for weight reduction and total colour difference. Multiple comparisons between treatments were conducted using Tukey's honestly significant difference test (Abdi and Williams, 2010). All p-values from multiple comparisons were adjusted using the Benjamini and Hochberg (1995) correction method.

3. Results

The summary of the drying performance of $scCO_2$ and $scCO_2$+HPU for peas are reported in Table 1.

Method	Moisture (%)	Water activity	Weight reduction (%)
Untreated	72.16 ± 1.15^a	0.937 ± 0.008^a	-
$scCO_2$	25.31 ± 0.79^b	0.686 ± 0.019^b	66.32 ± 4.60^a
$scCO_2$+HPU	19.43 ± 1.02^c	0.551 ± 0.019^c	74.32 ± 1.63^b

Both treatments yielded significantly lower moisture content and water activity compared to the untreated product. Dried peas have a water activity lower than 0.7 and 0.6, after $scCO_2$ and $scCO_2$+ HPU, respectively. These methods inhibit the growth of pathogenic bacteria reaching water activities below 0.85 (Tapia *et al.*, 2020), and the combined method also prevents yeast and moulds when the value decreases below 0.62 (Rahman and Labuza, 2007). Moreover, the weight reduction observed differed significantly between $scCO_2$ and $scCO_2$+HPU, with the latter treatment resulting in a substantial decrease. Specifically, the combined method was able to achieve a higher reduction in percentage of 23, 19, and 11% for moisture content, water activity, and weight reduction, respectively, compared with the $scCO_2$ alone. A similar pattern was observed in the drying performances of apples (Table 2).

Method	Moisture (%)	Water activity	Weight reduction (%)
Untreated	85.23 ± 1.05^a	0.941 ± 0.008^a	-
$scCO_2$	24.93 ± 1.29^b	0.563 ± 0.029^b	81.15 ± 0.69^a
$scCO_2$+HPU	21.94 ± 1.17^c	0.419 ± 0.015^c	83.55 ± 1.09^b

In the drying of apples, both $scCO_2$ and $scCO_2$+HPU yielded moisture content and water activity values capable of inhibiting microbial growth. However, all the mentioned parameters, including weight reduction, significantly varied according to the drying treatment. The $scCO_2$+HPU combination achieved the lowest moisture content and water activity, along with the highest weight reduction. Tao and Sun (2015) reported that HPU significantly enhances the speed of the food drying process by improving heat and mass transfer and facilitating water removal. High-intensity acoustic waves, integral to HPU, can cause the cavitation of water molecules within the solid matrix, aiding in the removal of firmly bound moisture (Aslam *et al.*, 2022). This cavitation effect is also prominent in the combined $scCO_2$+HPU process, contributing to increased micro-mixing and contact between the solvent and water, thereby enhancing extraction, as described by Ortuño *et al.* (2012). Moreover, the 'sponge effect' created by high-power ultrasounds, characterised by alternating squeezing and releasing because of rapid compression and expansion movements caused by sound waves, facilitates fluid movement in the micro-channels (Zhang and Abatzoglou, 2020). These studies collectively support the synergistic effects of combining $scCO_2$+HPU, as observed in our findings on the drying of peas and apples. Furthermore, despite the initial moisture differences at the beginning of the drying process, the differences between the $scCO_2$ and $scCO_2$+HPU methods were more pronounced for peas than for apples. The behaviour might be caused by the different porosity of the products, however, considering the absence of comparative studies on the porosity in literature, further research should investigate this hypothesis.Lastly, we evaluated the colour differences connected to the drying treatment (Table 3)

Table 3. L, a*, b* colour parameters and ΔE for peas and apple samples kept untreated and dried with $scCO_2$ or $scCO_2$+HPU. L* represents the lightness index; a* indicates the redness index, and b* denotes the yellowness index. ΔE represents the colour difference after the treatment referred to the fresh product.*

Matrix	Method	L*	a*	b*	ΔE
Pea	Untreated	39.12 ± 1.49^a	-11.33 ± 5.12^a	26.21 ± 1.44^a	-
	$scCO_2$	55.77 ± 2.36^b	-2.96 ± 1.11^b	18.65 ± 2.96^b	15.12 ± 2.91^a
	$scCO_2$+HPU	55.03 ± 2.19^b	-2.34 ± 0.67^b	17.47 ± 1.19^b	14.83 ± 1.16^a
Apple	Untreated	52.03 ± 5.43^a	0.03 ± 0.22^a	12.88 ± 0.82^a	-
	$scCO_2$	63.27 ± 2.79^b	1.08 ± 0.96^b	14.76 ± 1.67^a	11.67 ± 2.13^a
	$scCO_2$+HPU	63.16 ± 1.02^b	1.84 ± 0.82^b	13.70 ± 1.31^a	11.37 ± 1.05^a

Significant differences in L*, a*, and b* colour parameters were observed between fresh and processed food for both processes and in both matrices. Despite undergoing $scCO_2$ and $scCO_2$+HPU treatments, both apples and peas maintained their distinct colour coordinates. This suggests a uniform alteration in colour characteristics across various foods and processing methods. Generally, each drying method significantly increased the lightness index (L*) compared to the fresh matrices. The redness (a*) and yellowness (b*) index showed different behaviours between the matrices. For peas, a significant increase in redness and decrease in yellowness index was observed between processed products and untreated ones. For apples, both indices increased in comparison to the fresh product. There were no significant differences observed between $scCO_2$ and $scCO_2$+HPU for all colour parameters, including total colour difference. The total colour difference (ΔE) values, when compared to the fresh product, exceeded the threshold of 3. This threshold is commonly regarded as the point at which colour differences become distinctly noticeable to the average observer (Pathare *et al.*, 2013). Similar results on total colour differences were obtained in the drying with only $scCO_2$ of apples and carrots (Brown *et al.*, 2008; Pravallika *et al.*, 2023). The results can be visually appreciated in Figure 1 through a photographic comparison.

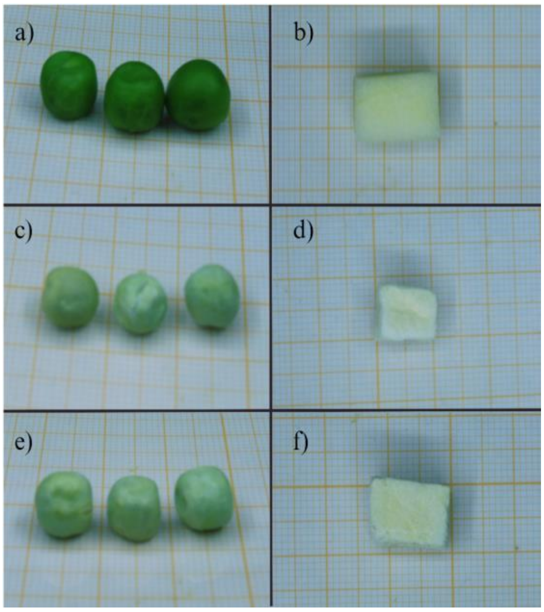

Figure 1. Images of peas and apples before and after drying treatments: a) and b) untreated peas and apples, c) and d) peas and apples dried using $scCO_2$, e) and f) peas and apples dried using $scCO_2$+HPU.

4. Conclusions

This preliminary study underscores the efficacy of two innovative drying methods ($scCO_2$ and $scCO_2$+HPU) in enhancing the preservation of perishable food items such as peas and apples. The findings reveal that both $scCO_2$ and $scCO_2$+HPU are effective in significantly reducing the moisture content and water activity in these foods. The $scCO_2$+HPU treatment obtained the greatest weight reduction and lowest values of moisture and water activity, resulting in a more stable product compared to the $scCO_2$ treatment alone. After the drying treatment, both apples and peas maintained their distinct colour. The observed changes in colour parameters indicated a noticeable difference between the fresh and processed products but not between the two methods. The study contributed valuable insights into the field of food technology but also paved the way for further research into the optimisation of these drying techniques for various matrices. The synergistic effects of combining HPU with $scCO_2$, underscore the potential to enhance weight reduction, water activity, and moisture content simultaneously, presenting a promising avenue for future exploration, and offering a potential solution to the pressing need for more effective food preservation strategies.

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