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Supercritical CO_2 drying of food matrices

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Abstract

This work explore the use of supercritical CO2 drying as alternative technique for the obtainment of pasteurized and high quality dried product. Several tests were conducted on animal, vegetable and fruit matrixes in order to investigate the effectiveness of SC-CO2 drying process at different process conditions. Design of experiment was performed to find the optimal process conditions for vegetable and fruit matrices, using the final water activity of the products as key indicator for the drying efficiency. The inactivation of naturally present microorganisms and inoculated pathogens demonstrated the capability of SC-CO2 drying process to assure a safe product. Moreover, retention of nutrients was compared with conventional drying methods. Results suggest that supercritical drying is a promising alternative technology for food drying.

Keywords: *supercritical drying; carbon dioxide; food drying; microbial inactivation*

1. Introduction

Fresh food products, in particular ripped fruits and vegetables, are rich sources of nutrients with an important role in human health [1]. However, fresh products are seasonal and an optimal cold chain is needed to prolong their limited shelf life.
An alternative is represented by food dehydration, which is one of the oldest and widely used processes for the long-term maintenance of food products. By reducing the amount of moisture, the microbial and enzymatic activities are inhibited, promoting the extension of the product's shelf-life [2,3]. Conventional hot air-drying is one of the most commonly used dehydration process in food industry. Nevertheless the overall quality of the final product is often reduced by the combination of high temperatures and the presence of oxygen which promotes physical, structural, chemical and nutritional changes [4,5]. Higher retention of those compounds can be achieved using freeze-drying technology [6], however it is an expensive and very slow process, making it suitable only for high value foods [3,7].
Recently the use of carbon dioxide at supercritical conditions (Sc-CO_2) has been investigated as alternative drying food process, specifically for carrots [8], basil [9], mango and persimmon [10] and coriander [11], demonstrating to be a promising process for the retention of the original structure and the preservation of the most valuable compounds.
Within Sc-CO_2 drying the vapour-liquid interface can be avoided meaning that the water is removed as a liquid dissolved in the supercritical fluid. The result is a minor capillary stress for the product, which allows a better preservation of the original structure. Moreover, the critical point, and consequently the critical temperature (31.1°C), is low, which allows to operate at lower temperatures than conventional air drying, helping the prevention of the heat sensitive degradation's reactions and thus giving a final product with higher quality [8,9]. Sc-CO_2 have been largely investigated as alternative food pasteurization at low temperature [12] because it is able to inactivate microorganisms and enzymes.

The present work explore the use of Sc-CO_2 for drying and simultaneous pasteurization of foodstuff. The influence of process parameters (temperature, pressure, flow rate and treatment time) on the final water activity were studied within a Box Behnken Design method. Overall the results demonstate the possibility to obtain a high quality product microbiologically safe.

2. Materials and Methods

2.1 Sample preparation

Different types of food products were daily bought in the local market in Padua (Italy): red bell peppers (*Capsicum annuum, L.*), coriander (*Coriandrum sativum*), strawberry (*Fragaria ananassa*), apple (*Golden delicious*) and chicken breast fillet. The vegetables were cut into slices while coriander leaves were removed from the stem. The chicken breast fillet was cut into small cubes with a weigh of approximately 1g.

2.2 Sc-CO_2 drying apparatus and procedure

The high pressure carbon dioxide apparatus consists of a sapphire high pressure visualization cell (Separex S.A.S., Champigneulles, France) with an internal volume of 50 mL designed to withstand up to 400 bar and 100 °C. The plant includes a CO_2 tank, kept at room temperature, a chiller reservoir (M418-BC MPM Instruments, Milan, Italy), a HPLC pump (307 Gilson, Milan, Italy), and a thermostatic water bath (ME-Julabo, Seelbach, Germany) to keep the vessel at the desired temperature. Further details of the reactor and drying procedure are reported elsewhere [11,13]. Experiments were carried out between 40/60°C and 100/140 bar up to 16 hours of drying for red peppers, while 40°C and 100 bar were chosen for the other food products.

2.3 Experimental design

The Box Behnken Design was used to study the effect of supercritical CO_2 drying process parameters on the final water activity of treated red peppers. To quantify the relationship between the controlled input and the accomplished responses, a second order regression model was used. All the calculations were done using Minitab®.

2.4 Physical and chemical analysis

Water activity was measured (Hygropalm Rotronic, Bassersdorf, Switzerland) at the end of the process. Samples were weighted before (W_{start}) and after (W_{end}) the treatment and the weight loss in terms of percentage ΔW was calculated as $(W_{start}-W_{end})/W_{start}$. Chemical characterization was performed for flavonoids as previously described [11]. For all the HPLC analysis an Agilent 1260 system equipped with Diode array (126 series) and Ion trap Mass spectrometer (Varian/Agilent MS500) were used. For vitamin C 200 mg of grinded powder plant material were xtracted three times for 10 minutes in an ultrasound bath with 8 ml of solution composed of water with 1% (v/v) formic acid. Zorbax SB C3 4.6x 150mm (DTO Servizi, Spinea, Italy) was used for the stationary phase. Isocratic conditions of elution used two solutions: solution A was acetonitrile while solution B was water 1% formic acid. For the quantification, standard solutions of ascorbic acid (Sigma Aldrich, Milano, Italy) were used to build up a calibration curve in the range 3-120 ug/mL.

2.5 Microbial analysis

Mesophilic bacteria, mesophilic bacterial spores and yeasts and molds were counted before and after the treatments by means of the standard plate count technique, as previously described [11]. Breefly, mesophilic bacteria and spores were cultured using total plate count agar (Microbial Diagnostici, Catania, Italy) at 30°C within pour plate, while yeasts and molds were cultured with DRBC agar (Bitec S.r.l., Grosseto, Italy) supplemented with chloramphenicol at 22°C within spread plate. For the enumeration of mesophilic spores, the first dilution tubes were inserted in a thermostatic bath at 80°C for 10 min before plating. The incubation time for mesophilic bacteria and spores was 72 h, while 72-120 h for yeast and

molds. The enumeration was referred to the weight of initial fresh product and expressed in CFU/g. Reductions are expressed as $\log(N_0/N)$ where N_0 was the number of initial microorganisms in the untreated sample and N the number of viable microorganisms after the treatment, in CFU/g of fresh product. The limit of quantification was set to 200 CFU/g for the mesophilic bacteria and mesophilic bacterial spores, 2000 CFU/g for yeast and molds while the limit of detection was < 10 CFU/g < 100 CFU/g respectively. Experiments with inoculated pathogens (*E.coli*, *Salmonella* and *Listeria monocytogenes*) were performed on coriander, apple slices and strawberry slices following the protocol by Bordeaux et al [14]. Results were analyzed with one-way analysis of variance to compare effects of the different treatments with significance at $\alpha = 0.05$.

3. Results and Discussion

The drying kinetics, in terms of water activity and weight loss, were determined by increasing the drying time till a complete water removal. Figure 1 shows the water loss and water activity obtained during the drying of the red pepper. Similar behaviours were observed for the others food samples (data not shown).

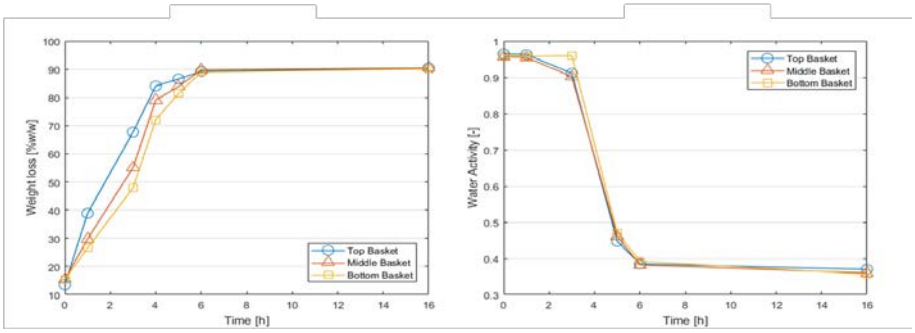

Fig. 1. Water loss (left) amd water activity (right)at different drying times for red pepper. Data are reffered to three different hights of the reactors. Experiments were carried out at 40°C, 100bars and 150kg/h flow rate.

The response surface methodology was chosen to quantify the relationship between the controllable input parameters and the obtained response surfaces, in order to find the influence of the process conditions over the product quality. Fig 2 shows results obtained at 40°C and 16 hours drying that highlight the influence of pressure and pump frequency on the final water activity of the sample. Response surface analysis on strawberry demonstrated a similar behavior (data not shown). To demonstrate the capability of the technology to retain the active components of the fresh products, some chemical analyses were performed on the Sc-CO_2 dried product.

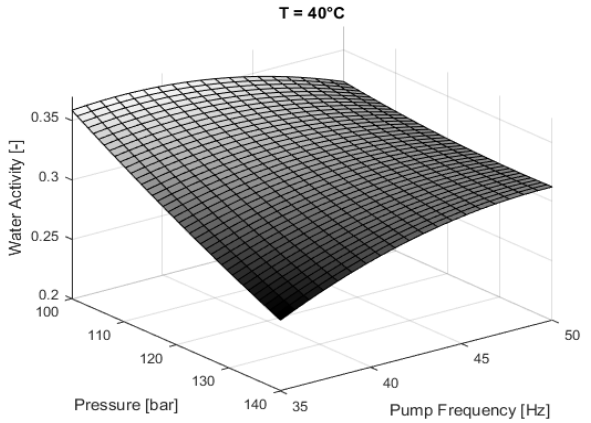

Fig. 2. Response surface for the water activity at 40°C and 16h drying as function of Pressure and Pump frequency.

For red pepper, the amount of flavonoids obtained was about 880 mg/100g of dried sample, reported in Table 1, are consistent with the literature; for instance Deepa et al. (2007) [1] reported phenolics in the range of 20–40 mg/100g of fresh product, which is similar to our results considering a loss of weight of 90% compared to the fresh product.

Table 1. Flavonoid and ascorbic acid content in dried red pepper (40°C. 100bar, 100kg/h flow rate)

Flavonoid [mg/100 g dry product]	**Ascorbic acid [mg/100g dry product]**
880.45 ± 2.4	1163.20 ± 5.3

The average content of ascorbic acid in fresh bell pepper is in the range of 64-220mg/100g of fresh product [1, 15]. As for flavonoids, we measured a higher content of ascorbic acid after Sc-CO_2 drying compared to the fresh product; the data can be explained with an apparent concentration of micronutrients caused by water removal during the process. Considering a water loss of about 90%, data of dried and fresh products are comparable and we can assert that SC-CO_2 drying technique is able to preserve the ascorbic acid content in the red pepper.

Microbiological inactivation was demonstrated on coriander, apple, strawberry and chiken breast fillet for the natural flora and specific pathogens (data not shown). Supercritical drying was able to complete inactivate yeasts and molds in all the samples considered; as regards bacteria, only the most sensitive mesophilia were inactivated on fruits, while a complete inactivation was possible on chicken. *E.coli, Salmonella* and *Lysteria monocytogen* were completely inactivate in all the food samples up to 8 log reduction.

4. Conclusions

Overall the results highlighted the potential of Sc-CO_2 drying technology to obtain a safe and dried products with unaltered nutritional value.

5. Acknowledgements

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