

Development of a new functional food from freeze-dried broccoli stalks

Sara Leu-Zürcher ^a; Maria J. Cantalejo ^{a, 1}

^aPublic University of Navarre, Food Technology Department, Campus Arrosadia, Pamplona E-31006, Spain

ARTICLE INFO

Keywords:

broccoli stalks
freeze-drying
functional foods
gazpacho
salmorejo

¹ Correspondence to: Maria J. Cantalejo, Public University of Navarre, Food Technology Department, Campus Arrosadia s/n, Pamplona E-31006, Spain, iosune.cantalejo@unavarra.es

ABSTRACT

Several studies showed that the consumption of broccoli can prevent some diseases and cancer, as broccoli contains important amounts of health-promoting substances like polyphenols, vitamin C and glucosinolates. Just the florets of broccoli are used in the food industry. Although important amounts of the health-promoting compounds are present in the stalks, they are not used. The quantity of health-promoting compounds is reduced significantly when treated thermally. The objective of this study was to obtain a natural functional food product by adding the freeze-dried broccoli stalks to mild-treated products such as gazpacho and salmorejo, in a way that broccoli flavor and odor were not perceived in the final product. To achieve a product with ideal rehydration characteristics and an optimal retention of the health-promoting compounds, the freeze-drying process of broccoli stalks was optimized. The best freeze-drying conditions were a fast freezing rate with a 14 hour primary drying. The maximum addition of broccoli with a minimum of changes on the product was achieved, thanks to viscosity analyses and sensory triangle tests. It is possible to add health-promoting compounds from broccoli stalks to food stuffs without a reduction of the acceptability of the product.

1 Introduction

Broccoli contains important amounts of antioxidant compounds, like polyphenols and vitamin C and other health-promoting substances like glucosinolates. Polyphenols have positive effects against cardiovascular diseases, ageing and various forms of cancer. Glucosinolates are a group of compounds present in cruciferous vegetables which are converted in anti-carcinogen substances by the enzyme myrosinase. This enzyme is released when the vegetable is crushed, chopped or chewed. Due to these factors, several studies showed that the consumption of broccoli can prevent diseases and cancer. For that reason, a frequent ingestion of broccoli in the normal diet is recommended (A. Mahn & Reyes (2012), Gliszczyńska-Świgło, Ciska, Pawlak-Lemańska, Chmielewski, Borkowski & Tyrakowska (2006)). As the flavor and odor of

broccoli is very peculiar and strong, many people don't like this vegetable. On the other hand, there is an increasing awareness of health benefits from eating vegetables and fruits.

The florets of broccoli are used in the industry for the production of frozen broccoli or convenience products containing broccoli. However, the stalks are not used in the food industry or when broccoli is cooked at home. By this, important amounts of the health-promoting compounds, which are present in the stalks as well, are lost (Domínguez-Perles, Martínez-Ballesta, Carvajal, García-Viguera & Moreno (2010)).

In the freeze-drying procedure, the freezing rate, the initial vacuum and the temperature and time of the drying steps can be modified. It is possible to dry the material at different temperatures in subsequent drying steps.

In previous studies, different drying processes and different drying conditions were compared. In those studies, the method using freeze-drying was considered as the mildest one with respect to the quantity of remaining health-promoting compounds. The reason for this is the fact, that the product is not subjected to a thermal treatment (A. Mahn & Reyes (2012), A. Mahn, Zamorano, Barrientos & Reyes (2012), A. V. Mahn, Antoine & Reyes (2011), Sharma, Stähler, Smith & Melton (2011)).

Dominguez-Perles, Moreno, Carvajal & Garcia-Viguera (2011) studied the incorporation of the extract from freeze-dried broccoli stalks and leaves in a drink based on green tea and Banerjee, Verma, Das, Rajkumar, Shewalkar & Narkhede (2012) investigated the possibility to introduce broccoli powder from florets in goat meat nuggets. The authors of both studies concluded that it is possible to add health-promoting compounds from broccoli to foodstuffs without a reduction of the acceptability of the product.

The quantity of health-promoting compounds decreases significantly during thermal treatments and heating of the product in water (Gliszczynska-Świgło, Ciska, Pawlak-Lemańska, Chmielewski, Borkowski & Tyrakowska (2006)). Therefore, it is important to keep the treatments with heat as low as possible, not just when producing the dried broccoli stalks but also when creating a new product with the dried stalks. For that reason, in the present study a cold soup was chosen as base for the new product, more precisely, a gazpacho and a salmorejo. These soups were chosen as they are made with just a mild heating step. These two kinds of cold soups are typically consumed in the South of Spain and are based on crushed tomatoes, other vegetables like cucumber, bell pepper, onion with garlic, olive oil, vinegar and bread. In the case of a gazpacho, no bread is used.

The objective of this study was to obtain a natural functional food based on gazpacho / salmorejo with incorporated freeze-dried broccoli stalks, where the flavor and odor of broccoli is not perceived in the final product. Therefore, the freeze-drying process was optimized, in order to obtain a freeze-dried product with an ideal rehydration characteristic and an optimal retention of the health-promoting compounds. To add value to this by-product, just the stalks were used for creating a new food product.

2 Materials and methods

2.1 Raw matter and sample preparation

The broccoli from Navarre (North Spain), the Don Simon-branded gazpacho and the Al Valle-branded salmorejo, leaders of the Spanish market purchased from the local market were stored at 8 °C until further analyses.

The preparation of the broccoli stalks was carried out immediately before the analyses and further elaboration to preserve sample freshness. The florets were cut with a knife; the stalks were cleaned with tap water and peeled also with a knife to remove the outer layer of the plant.

2.2 Freeze drying treatments

For the lyophilisation, the stalks were cut in 3 mm slices with an automatic cutter with a 3mm knife (CL-52, Robot Coupe, France) and put neatly on the steel plates of the freeze-dryer. The freeze drying was carried out with a pilot plant freeze-dryer type LyoBeta 25 (Telstar, Terrassa, Spain). The freezing temperature was -45 °C, the vacuum for the drying procedure was 25 Pa, and the first primary drying was at 0 °C and the second primary drying at 10 °C. Different freeze-drying conditions with the following parameters were performed: the freezing rate (slow: 9 h; intermediate: 6 h; fast: 3 h), the time of the first primary drying (10 h; 12 h; 16 h) and the time of the second primary drying (none; 2 h; 4 h; 6 h).

2.3 Analyses of fresh and freeze-dried broccoli

For the analyses the stalks were crushed with a blender. The freeze-dried broccoli was triturated with a kitchen mill (Moulinex, France) and the dried and rehydrated broccoli was crushed with a blender when necessary.

The fresh broccoli stalks were analysed to characterize the raw material. The results of these analyses were used to compare the losses during the process under different conditions. The following analyses were performed with the fresh broccoli stalks: Water activity, humidity, colour, pH, total soluble solids, acidity and antioxidant capacity.

To characterize the freeze-dried broccoli and to detect the changes due to the treatment, with the freeze-dried broccoli, the same analyses were performed as with the fresh broccoli. In addition to that, weight loss, shrinkage and rehydration ratio were also measured.

2.3.1 Water activity, humidity and weight loss

The water activity of the ground fresh broccoli stalks and the triturated freeze-dried broccoli was measured with a hygrometer (LabMaster-aw, Novasina, Switzerland).

The humidity of the fresh broccoli was measured according to the ISO norm 665:2000 from AENOR (2001) with some modifications. Shortly, 10 g of the triturated fresh broccoli sample was put in an oven at 102 °C (Binder, Germany) for 24 hours. The difference between the fresh and the dried sample weight is the humidity of the fresh broccoli. To adjust the humidity of the rehydrated broccoli and the gazpacho and salmorejo, the humidity of the cold soups was measured in the same oven at 102 °C for 24 hours. On the other hand, the humidity of the dried broccoli was measured with 3 g of the triturated sample with the infrared humidity analyser (Gram Precision ST-H50 from Gram Precision SL, Hospitalet de Llobregat, Spain).

The weight loss was calculated as the percentage between the weight of the dried product and the weight of the fresh product.

2.3.2 pH, acidity, total soluble solids and colour

The pH of the triturated fresh broccoli stalks and rehydrated freeze-dried broccoli was measured with a pH meter (pH Meter Basic 20, Crison, Spain).

The acidity of the fresh and rehydrated dried broccoli was determined by titration with NaOH (0,1 N) according to the method 942.15 from AOAC (1965). Therefore, 10 g of the crushed samples were homogenized with 90 ml of distilled water. The acidity (A (%)) was calculated with the necessary amount of NaOH to obtain a solution with pH 8.1 by the formula F1:

$$A (\%) = \frac{(ml\ NaOH) * (N_{NaOH}) * (0.07) * 100}{weight\ of\ the\ sample\ (g)} \quad (F1)$$

where the factor 0.07 is the factor of citric acid which is the main acid in broccoli (Gillooly, Bothwell, Torrance, MacPhail, Derman, Bezwoda, Mills, Charlton & Mayet (1983)).

The total soluble solids from the crushed fresh and rehydrated freeze-dried broccoli stalks were measured with a portable refractometer (North China Optical Instrument Factory) according to the norm UNE-EN 12143 from AENOR (1997).

The colour of the fresh and rehydrated freeze-dried broccoli was measured with a colorimeter (Minolta 2500-d, Japan).

2.3.3 Shrinkage, firmness and rehydration ratio

The shrinkage of the dried broccoli stalks was calculated as the percentage between the volume of the dried product and the volume of the fresh product. The volume determined from the length, width and height of the pieces was measured with a caliper.

The firmness of the fresh and rehydrated broccoli slices was analysed by performing a puncture test with the texture analyser (TA.XT Plus, Aname S.L., Spain) equipped with a bar of a diameter of 3.2 mm. The bar penetrated 0.5 mm into the sample with a speed of 2 mm/s after contacting the slice.

To measure the rehydration ratio (RR), the dried broccoli pieces were placed in a 500 ml flask with distilled water. After every half an hour of immersion, the samples were taken out and blotted with tissue paper to eliminate the excess water on the surface. The weight of the samples was measured until stabilisation. The RR was calculated by $RR = W_r/W_f$ according to Doymaz (2014) where W_r is the weight after the rehydration and W_f is the calculated weight of the fresh broccoli pieces.

2.3.4 Antioxidant capacity

The extraction of the fresh and freeze-dried broccoli was carried out according to Mrkic, Cocci, Dalla Rosa & Sacchetti (2006). Shortly, 0.4 g of triturated broccoli was added to 8 ml of the solvent made of methanol and hydrochloric acid with distilled water (50:50, hydrochloric acid:distilled water) (93.7:6.3, methanol:hydrochloric acid with distilled water). The samples were stirred at 200 rpm for 3 hours at room temperature and centrifuged afterwards at 1089 g for 30 minutes with a centrifuge (Medifriger BL-S, JP Selecta S.A., Spain). The supernatant was made up to 10 ml with the solvent. For the analysis of the antioxidant capacity with the DPPH-method, the method described by Bobo-García, Davidov-Pardo, Arroqui, Vírseada, Marín-Arroyo & Navarro (2015) was followed. Briefly, 20 µl of the extract was mixed in microplates with 180 µl of DPPH solution (0.0058 g DPPH in methanol with water 80:20) and the absorption at 515 nm with a spectrophotometer (Thermo Scientific Multiskan Go, Thermo Fisher Scientific Inc., USA) was measured 40 minutes after the beginning of the reaction. The percentage of inhibition of DPPH (inh. DPPH (%)) was calculated with the formula F2. The antioxidant capacity in dry matter was expressed in

trolox equivalences (TE) calculated with the formula F3 which was obtained from the calibration curve.

$$\text{inh. DPPH (\%)} = \left(1 - \left(\frac{\Delta \text{Abs}_S}{\text{Abs}_{BR}} \right) \right) * 100 \quad (F2)$$

where $\Delta \text{Abs}_S = \text{Abs}_{S_{\text{sample}}} - \text{Abs}_{S_{\text{blank sample}}}$ and Abs_{BR} is the blank reactive.

$$\text{mmol TE} = \frac{\text{inhibition DPPH (\%)} - 3.163}{0.139 * 1000} \quad (F3)$$

2.4 Analyses with cold soups

When incorporated in gazpacho and salmorejo, sensory analyses were performed. For the addition of the rehydrated broccoli, the viscosity of gazpacho, salmorejo and the soups with rehydrated broccoli incorporated was evaluated.

2.4.1 Viscosity

The viscosity of the gazpacho, salmorejo and the soups with the rehydrated broccoli was measured with a viscosimeter (Haake RotoVisco, Thermo Fisher Scientific Inc., USA) with a cooling and heating equipment (Haake K15 and Haake DC30) equipped with a cup Z34 and the rotor Z34. The method described by Angós & Fernández (2004) was followed. The shear rate and temperature were controlled. The viscosity profile was measured during the ramp of the shear rate ($\dot{\gamma}$) from 0 to 500 per second in 90 seconds, during holding the shear rate at 500 per second for 90 seconds and during decreasing of the shear rate back to 0 per second in 90 seconds, everything at 20 °C. The shear stress (τ) as well as the viscosity (μ) was recorded in function of the shear rate ($\dot{\gamma}$). The curves were modelled with the model of Ostwald de Waële, the data being fitted to a curve of the type of the Formula F4, where K and n were calculated. Gazpacho, salmorejo and the ones with rehydrated broccoli were measured with the same parameters.

$$\tau = K * \dot{\gamma}^n \quad (F4)$$

where τ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the flow consistency index ($\text{Pa}\cdot\text{s}$) and n is the flow behaviour index.

The thixotropy was also calculated; it is the area between the curve of the ramp of the shear rate from 0 to 500 per second and the curve of the decreasing shear rate.

2.4.2 Sensory analyses

By sensory analysis, the maximum addition of broccoli resulting in a minimum of changes of the

product was evaluated. The broccoli added was rehydrated with the needed amount of water to achieve the same humidity in rehydrated broccoli as in the cold soups. To evaluate the changes of the viscosity by adding broccoli in the product, the viscosity of the products with and without an addition of broccoli was measured.

For the sensory analyses the freeze-dried broccoli was ground and rehydrated with the calculated amount of mineral water to adjust the total solids of the rehydrated broccoli with the one of gazpacho or salmorejo and mixed with the cold soups. To confirm that the mixed product had the same viscosity as the original product, a viscosity profile was made as described before.

A previous evaluation was performed to obtain the best concentrations for the triangle test for each product, gazpacho and salmorejo. In this evaluation the panel evaluated 5 different concentrations equivalent to fresh broccoli between 5.5% and 44%.

By the triangle test, the concentration of introduced broccoli which cannot be perceived was evaluated according to the ISO norm 4120:2004 from AENOR (2008). A team of 12 judges evaluated and compared the products with broccoli with the original products. For that, two different tests with two different concentrations (6 and 8% for gazpacho and 10 and 12% for salmorejo) were made.

2.5 Statistical analysis

The data was subjected to a one-way analysis of variance with $\alpha = 0.05$ with the program Statgraphics (Centurion X64, version 16.2.04, USA). Mean treatments were compared using Fisher LSD with the same $\alpha = 0.05$.

The statistical analysis of the triangle test was evaluated according to the ISO norm 4120:2004 from AENOR (2008). For the similarity evaluation the formula F5 was used.

$$\left[1.5 * \frac{x}{n} - 0.5 \right] + 1.5 * z_{\beta} \sqrt{\frac{(nx - x^2)}{n^3}} \quad (F5)$$

where x is the number of the correct answers, n is the number of judges and z_{β} depends on the significance level used.

When the calculated value lied below the chosen significance level, the samples were concluded to be similar.

3 Results and discussion

3.1 Characterisation of the lyophilized product

The conditions of the different treatments are listed in the Table 1. The first experiment (treatment 1) was used to evaluate a sufficient freeze-drying

process with long drying times. Based on this treatment the other treatments were derived. The humidity and water activity analyses showed that the time of the primary drying is sufficient. In the tables 2 and 3 the results of the analyses to evaluate the fresh and freeze-dried product are represented.

Table 1: Experimental design with different conditions of freeze-drying on broccoli stalks

	Freezing rate	Primary drying at 0 °C (h)	Primary drying at 10 °C (h)	Total primary drying (h)
a) Preliminary treatment				
Treatment 1	Fast (3h)	12	6	18
b) Evaluation of the freezing rate				
Treatment 2	Fast (3h)	12	4	16
Treatment 4	Intermediate (6h)	12	4	16
Treatment 5	Slow (9h)	12	4	16
Treatment 6	Fast (3h)	16	0	16
Treatment 7	Intermediate (6h)	16	0	16
c) Evaluation of the time reduction of primary drying				
Treatment 3	Fast (3h)	10	4	14
Treatment 8	Fast (3h)	12	2	14

Table 2: Analyses of humidity, water activity, weight loss, pH, acidity, total soluble solids of the fresh and freeze-dried broccoli stalks

Treat-ment	Humidity [%]	Water activity	Weight loss [%]	pH	Acidity [%]	Total soluble solids [°Brix]
a) Fresh broccoli stalk						
Fresh	89 ± 0.1	0.96 ± 0.00	n.a.	6.9 ± 0.0	0.14 ± 0.0	9.9 ± 0.3
b) Preliminary treatment						
1	6.26 ± 0.1 (a)	0.228 ± 0.00 (b)	87.8 ± 0.6 (a)	6.3 ± 0.0 (d)	0.05 ± 0.0 (b)	1.8 ± 0.1 (a)
c) Evaluation of the freezing rate						
2	6.70 ± 0.1 (b)	0.228 ± 0.00 (b)	91.2 ± 0.8 (cd)	6.9 ± 0.0 (h)	0.04 ± 0.0 (a)	3.0 ± 0.1 (g)
4	7.71 ± 0.4 (e)	0.245 ± 0.01 (c)	91.1 ± 1.6 (cd)	6.5 ± 0.0 (f)	0.05 ± 0.0 (b)	2.5 ± 0.1 (c)
5	6.69 ± 0.2 (b)	0.212 ± 0.01 (a)	91.0 ± 1.3 (c)	6.0 ± 0.0 (b)	0.08 ± 0.0 (e)	2.4 ± 0.2 (b)
6	7.94 ± 0.3 (f)	0.245 ± 0.01 (d)	91.2 ± 1.0 (d)	6.3 ± 0.0 (c)	0.07 ± 0.0 (d)	3.1 ± 0.1 (h)
7	8.09 ± 0.1 (g)	0.249 ± 0.01 (e)	92.1 ± 0.5 (f)	5.5 ± 0.1 (a)	0.13 ± 0.0 (f)	2.8 ± 0.1 (d)
d) Evaluation of the time reduction of primary drying						
3	7.21 ± 0.2 (d)	0.245 ± 0.00 (d)	90.7 ± 0.7 (b)	6.5 ± 0.0 (e)	0.08 ± 0.0 (e)	2.9 ± 0.2 (e)
8	6.91 ± 0.5 (c)	0.247 ± 0.01 (de)	91.9 ± 0.5 (e)	6.6 ± 0.1 (g)	0.07 ± 0.1 (c)	2.9 ± 0.3 (f)

Results are the means ± SD (n = 3); statistically significance at P < 0.05, n.a. = not analyzed, different letters on the same columns mean significant differences (P < 0.05) among treatments.

Table 3: Analyses of colour, shrinkage, firmness, rehydration rate, antioxidant capacity of the fresh and freeze-dried broccoli stalks

Treat-ment	Colour			Shrinkage	Firmness [N]	Rehydration rate [%]	Antioxidant capacity [mmol TE/g dw]
	L*	a*	b*				
a) Fresh broccoli stalk							
Fresh	78.8 ± 2.0	-3.7 ± 0.5	19.6 ± 1.4	n.a.	7.90 ± 1.33	n.a.	23.92 ± 1.1
b) Preliminary treatment							
1	73.4 ± 2.1 (c)	-1.7 ± 0.5 (c)	18.6 ± 0.9 (cd)	85.7 ± 8.2 (a)	1.44 ± 0.4 (d)	75.5 ± 1.7 (de)	n.a.
c) Evaluation of the freezing rate							
2	71.1 ± 1.8 (a)	-3.2 ± 0.6 (a)	18.3 ± 1.4 (c)	88.2 ± 8.8 (b)	0.51 ± 0.1 (c)	74.7 ± 2.9 (cd)	3.69 ± 0.1 (ab)
4	72.3 ± 1.6 (b)	-1.8 ± 0.6 (c)	18.4 ± 2.4 (cd)	90.6 ± 0.2 (cde)	0.28 ± 0.1 (a)	74.8 ± 7.4 (cd)	3.54 ± 0.1 (ab)
5	76.7 ± 1.3 (d)	-3.2 ± 0.9 (a)	19.6 ± 2.4 (e)	91.5 ± 2.0 (ef)	0.27 ± 0.1 (a)	76.0 ± 5.6 (e)	3.47 ± 0.1 (a)
6	73.8 ± 1.5 (c)	-1.6 ± 0.4 (c)	14.8 ± 0.4 (b)	89.3 ± 7.4 (bc)	0.29 ± 0.1 (a)	74.1 ± 2.1 (c)	n.a.
7	73.5 ± 2.0 (c)	-1.1 ± 0.4 (d)	13.7 ± 0.6 (a)	91.1 ± 3.1 (de)	0.30 ± 0.1 (a)	66.4 ± 3.2 (a)	n.a.
d) Evaluation of the time reduction of primary drying							
3	71.1 ± 2.7 (a)	-2.7 ± 0.7 (b)	15.1 ± 2.6 (b)	92.7 ± 7.4 (f)	0.48 ± 0.0 (c)	75.0 ± 2.9 (cde)	3.42 ± 0.1 (a)
8	77.1 ± 2.7 (d)	-2.5 ± 1.7 (b)	19.2 ± 6.2 (de)	89.8 ± 6.5 (cd)	0.40 ± 0.2 (b)	72.2 ± 3.8 (b)	3.78 ± 0.3 (b)

Results are the means ± SD (n = 3); statistically significance at P < 0.05, n.a. = not analyzed, different letters on the same columns mean significant differences (P < 0.05) among treatments.

3.1.1 *Changes of the properties of the broccoli stalks due to the freeze-drying*

Not only a significant change in humidity, water activity and the total soluble solids could be detected in the freeze-dried broccoli stalks compared to the fresh broccoli stalks, but also in the firmness and the antioxidant capacity. The loss of firmness is due to the destruction of the tissue by the water crystals during freezing of the product (Carbonell, Oliveira & Kelly (2006)). A similar loss of antioxidant capacity could also be analysed by Domínguez-Perles, Martínez-Ballesta, Carvajal, García-Viguera & Moreno (2010) and Wijngaard, Röbke & Brunton (2009), this is due to losses with the water during the sample preparation and the freeze-drying treatment.

3.1.2 *Influence of the conditions of the freeze-drying process on the properties of the lyophilized broccoli stalks*

The humidity was lower with a slow freezing rate and a drying time at 0 °C of 12 hours and 4 hours at 10 °C (treatment 5). But in every case the humidity was 8% or less. The water activity was below 0.27 in all cases and as well as for the humidity the optimal drying time were the conditions of treatment 5. The slow freezing rate results in the lowest water activity. In general the results of the humidity and the water activity were in a narrow range and for the repeatability of the analysis a variation coefficient of a 6.4% for water activity and a 9.2% for humidity was obtained. With the fast freezing rate the weight loss is lower than with intermediate or slow freezing rate.

The analyses of the pH, the acidity, the total soluble solids, the colour and the shrinkage did show differences between the treatments, but the differences were small. The lowest pH and highest acidity was obtained with the treatment 7, the lowest total soluble solids and the lowest shrinkage with treatment 1. These five parameters could not be correlated with any modified condition of the freeze-drying process, which means that these properties are influenced by nature and are different from lot to lot.

The firmness of the rehydrated lyophilized broccoli stalks was influenced by the drying time at 0 °C, at 10 °C and the freezing rate. With fast freezing and 12 hours of drying at 0 °C and 4 hours at 10 °C (treatment 2) the least firm product was obtained which is preferred for an addition of the freeze-dried

broccoli into a liquid product where it is not perceived. The most firm product resulted to be the one from treatment 1.

The rehydration ratio varies between 66 and 76%, where the optimal parameters are the slow freezing rate followed by the fast freezing rate and a drying time of 10 or 12 hours at 0 °C and 4 or 6 hours at 10 °C (treatments 1, 2 and 5). The treatment with the lowest rehydration rate was treatment 7.

The antioxidant capacity lied between 3.42 and 3.78 mmol Trolox equivalents per g dry weight. The conditions for the best retention of the antioxidant capacity were a drying time of 12 hours at 0 °C and 2 hours at 10 °C with a fast freezing rate (treatment 8).

3.1.3 *Selection of the optimal freeze-drying conditions*

First, the optimal freezing rate was evaluated with the treatments 2, 4, 5, 6 and 7. With slower freezing rate the pH and the total soluble solids are decreasing, whereas the acidity, the luminosity (L^*) and the shrinkage are increasing. The rehydration ratio was increasing from treatment 2 to 4 and 5. On the other hand, it decreased from 6 to 7.

With the treatments 3 and 8 the time reduction of the primary drying was evaluated to obtain a shortest possible process to keep down the costs of the lyophilised product. In treatment 3 the product was more firm and with less antioxidant capacity than with treatment 8. With the parameters of this treatment a completely freeze-dried product was obtained.

The optimal conditions are fast freezing rate, a primary drying at 0 °C for 12 hours and a primary drying at 10 °C for 2 hours, these were the conditions of treatment 8. In this treatment not only the values of antioxidant capacity, humidity, firmness and rehydration ratio are best or second best, but also the duration of the process is at least 2 hours less than the others.

3.2 *Introduction in gazpacho and salmorejo*

3.2.1 *Viscosity*

Gazpacho and salmorejo are non-Newtonian fluids, they show pseudo-plastic characteristics. The curves of the viscosity profile showed that they are thixotropic fluids, which means that the fluid loses viscosity when treated mechanically. In Table 4 the results of the viscosity analyses with the model of Ostwald de Waële are listed. The model of Ostwald

de Waële fitted the results with an R^2 between 0.978 and 0.996. Chi^2 lied between 7.4 and 21.9 for gazpacho and 94.3 and 209.5 for salmorejo. This means that the chosen model fitted well to the measured curves.

Table 4: Viscosity analyses of gazpacho and salmorejo

a) Gazpacho			
	K	n	Thixotropy
Gazpacho	3.27 ± 0.2	0.23 ± 0.01	1366 ± 69
Gazpacho with 6% broccoli	3.82 ± 0.9	0.22 ± 0.03	1458 ± 231
b) Salmorejo			
	K	n	Thixotropy
Salmorejo	18.12 ± 1.3	0.21 ± 0.00	6160 ± 96
Salmorejo with 10% broccoli	$15.54 \pm 1.0^*$	$0.24 \pm 0.01^*$	$5623 \pm 276^*$

Results are the means \pm SD (number of replications 3); statistically significance at $P < 0.05$, * means significant differences between the samples.

The viscosity of the original gazpacho and the gazpacho with broccoli, in which the broccoli was rehydrated with the calculated amount of water to obtain the same humidity as gazpacho, did not show any significant differences for the parameters K, n and the thixotropy (Fig. 1).

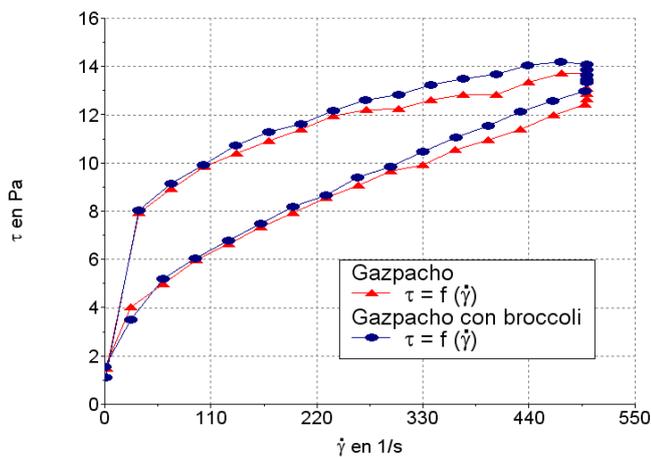


Fig. 1: Shear stress (τ) of gazpacho and gazpacho with broccoli in function of the shear rate ($\dot{\gamma}$)

The evaluated viscosity parameters K, n and the thixotropy of salmorejo samples with and without broccoli were significantly different, but the differences were small. Therefore, equalizing the dry weight between salmorejo and the rehydrated broccoli turned to be more important than the viscosity, as the differences on the viscosity were small (Fig. 2).

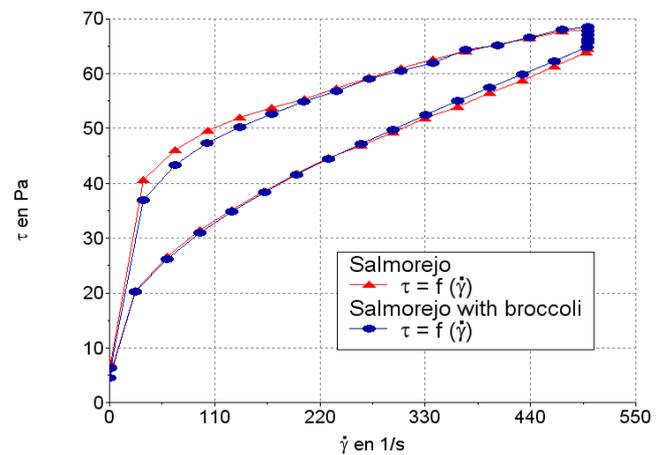


Fig. 2: Shear stress (τ) of salmorejo and salmorejo with broccoli in function of the shear rate ($\dot{\gamma}$)

3.2.2 Sensory analyses

From the previous evaluation performed to obtain the best concentrations for the triangle test for each soup, it was possible to add freeze dried broccoli up to an amount which was equivalent to 6% fresh broccoli in the gazpacho and up to 11% in salmorejo. But the dry weight and the viscosity of the added rehydrated broccoli had to be adjusted to the final product to ensure that no differences between the product with or without broccoli could be perceived. From this evaluation, two concentrations for the triangle test were obtained for each, gazpacho and salmorejo.

The triangle test with the two concentrations, equivalent to 6% and 8% of fresh broccoli, in gazpacho resulted in detecting broccoli in those gazpachos with 8% broccoli, but not in those with 6% ($P < 0.2$).

The triangle tests with both of the two concentrations equivalent to 10 and 12% of fresh broccoli in salmorejo resulted in significantly perceptible differences between the one with broccoli added and the one without it.

But it is important to mention that none of the cold soups was rejected by the judges, most of the judges pointing out that they liked all types they tried.

4 Conclusion

The optimal drying conditions were a fast freezing rate (freezing to $-45\text{ }^{\circ}\text{C}$ in 3 hours), a first primary drying at $0\text{ }^{\circ}\text{C}$ for 12 hours and a second primary drying at $10\text{ }^{\circ}\text{C}$ for 2 hours due to the best retention of the antioxidants in the product and the shortest process.

It is possible to add up to 6% rehydrated freeze-dried broccoli to gazpacho without any sensory changes of the product and even up to 12% to salmorejo without the product being rejected.

Likewise, not just the stalks of broccoli, but also the leaves could be used to take benefit from all the by-products of broccoli. In further studies the introduction of by-products of broccoli in other foodstuffs will be evaluated, such as sauces like guacamole, dip sauces or salad sauces could be enriched with broccoli, or it could be added to prepared meals.

References

- AENOR (1997). Estimation of soluble solids content. Refractometric method (UNE-EN 12143).
- AENOR (2001). Determination of moisture and volatile matter content (ISO 665:2000).
- AENOR (2008). Sensory analysis. Methodology. Triangle test (ISO 4120:2004)
- Angós, I. A., & Fernández, T. (2004). Rheological behaviour of five commercial gazpacho brands. International Conference Engineering and Food (ICEF9-2004). Montpellier, France
- AOAC (1965). Official Method 942.15 Acidity (Titratable) of Fruit Products: AOAC International.
- Banerjee, R., Verma, A. K., Das, A. K., Rajkumar, V., Shewalkar, A. A., & Narkhede, H. P. (2012). Antioxidant effects of broccoli powder extract in goat meat nuggets. *Meat Science*, 91(2), 179-184.
- Bobo-García, G., Davidov-Pardo, G., Arroqui, C., Vírveda, P., Marín-Arroyo, M. R., & Navarro, M. (2015). Intra-laboratory validation of microplate methods for total phenolic content and antioxidant activity on polyphenolic extracts, and comparison with conventional spectrophotometric methods. *Journal of the Science of Food and Agriculture*, 95(1), 204-209.
- Carbonell, S., Oliveira, J. C., & Kelly, A. L. (2006). Effect of pretreatments and freezing rate on the firmness of potato tissue after a freeze-thaw cycle. *International Journal of Food Science and Technology*, 41(7), 757-767.
- Domínguez-Perles, R., Martínez-Ballesta, M. C., Carvajal, M., García-Viguera, C., & Moreno, D. A. (2010). Broccoli-derived by-products - a promising source of bioactive ingredients. *Journal of Food Science*, 75(4), C383-C392.
- Dominguez-Perles, R., Moreno, D. A., Carvajal, M., & Garcia-Viguera, C. (2011). Composition and antioxidant capacity of a novel beverage produced with green tea and minimally-processed byproducts of broccoli. *Innovative Food Science and Emerging Technologies*, 12(3), 361-368.
- Gillooly, M., Bothwell, T. H., Torrance, J. D., MacPhail, A. P., Derman, D. P., Bezwoda, W. R., Mills, W., Charlton, R. W., & Mayet, F. (1983). The effects of organic acids, phytates and polyphenols on the absorption of iron from vegetables. *British Journal of Nutrition*, 49(3), 331-342.
- Gliszczyńska-Świgło, A., Ciska, E., Pawlak-Lemańska, K., Chmielewski, J., Borkowski, T., & Tyrakowska, B. (2006). Changes in the content of health-promoting compounds and antioxidant activity of broccoli after domestic processing. *Food Additives and Contaminants*, 23(11), 1088-1098.
- Mahn, A., & Reyes, A. (2012). An overview of health-promoting compounds of broccoli (*Brassica oleracea* var. *italica*) and the effect of processing. *Food science and technology international = Ciencia y tecnología de los alimentos internacional*, 18(6), 503-514.
- Mahn, A., Zamorano, M., Barrientos, H., & Reyes, A. (2012). Optimization of a process to obtain selenium-enriched freeze-dried broccoli with high antioxidant properties. *LWT - Food Science and Technology*, 47(2), 267-273.
- Mahn, A. V., Antoine, P., & Reyes, A. (2011). Optimization of drying kinetics and quality parameters of broccoli florets. *International Journal of Food Engineering*, 7(2).
- Mrkic, V., Cocci, E., Dalla Rosa, M., & Sacchetti, G. (2006). Effect of drying conditions on bioactive compounds and antioxidant activity of broccoli (*Brassica oleracea* L.). *Journal of the Science of Food and Agriculture*, 86(10), 1559-1566.
- Sharma, K. D., Stähler, K., Smith, B., & Melton, L. (2011). Antioxidant capacity, polyphenolics and pigments of broccoli-cheese powder blends. *Journal of Food Science and Technology*, 48(4), 510-514.
- Wijngaard, H. H., Rößle, C., & Brunton, N. (2009). A survey of Irish fruit and vegetable waste and by-products as a source of polyphenolic antioxidants. *Food Chemistry*, 116(1), 202-207.