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COMMUNICATION

Effect of Process Variables on Spray-Dried Garlic Juice Quality Evaluated by Multivariate Statistic

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Abstract Garlic juice was spray-dried at different inlet-outlet (110, 130 °C)–(60, 70, 80 °C) air temperatures and different types (gum arabic, DE-10 maltodextrins) and concentrations (0, 0.5, 0.8 g/g dm) of carrier material. Dried product quality was evaluated through moisture, water activity, powder color coordinates, and the retention of allicin and pyruvic acid. A complete 2×3×3 experimental design was developed but some treatments were experimentally nonfeasible. Then, results were analyzed by 1WANOVA and PCA. Drying conditions that maximized allicin retention were maltodextrin at 110 °C, 70 °C of inlet, outlet air temperatures, and 0.5 g carrier/g dm. Under these conditions, retentions were as follows: 76.9 % allicin and 89.9 % pyruvic acid. These results suggest that the obtained powder might be useful as a food additive or ingredient due to the higher retention levels of pyruvic acid than other types of convective drying.

Keywords Spray-dried garlic juice · Process variables · Principal component analysis · Allicin retention · Pyruvic acid retention

Introduction

Garlic (*Allium sativum* L.) has been used in many cultures for thousands of years as food and medicine for its typical flavor, pungency, and pharmacological properties. Many therapeutic properties related to garlic have been attributed to organosulfur compounds, particularly to thiosulfinates, generated when fresh garlic is cut, crushed, or macerated. Garlic essential oils are reported as consisting mainly of allyl; dimethyl; and allyl methyl mono-, di-, and trisulfides, and a few minor components (Block 1985). Among these substances, the main bioactive component of garlic is allicin [*S*-(2-propenyl) 2-propene-1-sulfinothioate] and is the most abundant diallylthiosulfinate (amounts of 30–50 % of total mixture) found in this vegetable (Iberl et al. 1990a; Gil et al. 2011). Allicin is a potential antioxidant (Prasad et al. 1995) and has been shown to inhibit the growth of a variety of microorganisms, including bacterial, fungi, and viruses (Ross et al. 2001; Rahman et al. 2006; Tedeschi et al. 2007). In addition, garlic has antihelminthic, antiprotozoal, antitumor, antithrombotic, anticancer, hypolipidemic, and hypoglycemic properties (Lawson 1998; Khanum et al. 2004; Rahman et al. 2006). Fresh garlic bulb is characterized as having no distinct pungency because the allicin is not present in garlic unless tissue damage occurs and is produced by an enzymatic reaction when garlic is crushed or chopped. The phosphopyridoxal enzyme, allinase, stored in a separate compartment in garlic, combines with alliin (allyl-*S*-cysteine sulfoxide) and produces allicin accompanied by formation of pyruvic acid and ammonia (Schwimmer and Weston 1961). Allicin is a transitory compound, due to its unstable and reactive nature, and once it is produced, it readily changes into other disulfides, thiosulfinates, vinyldithins, and ajoenes (Iberl et al. 1990b; Lawson and Hughes 1992), while the pyruvic acid (2-oxopropanoic acid) has major stability, and therefore, pungency of fresh and dried garlic products can be evaluated indirectly on the pyruvic acid content (Cui et al. 2003). Although garlic is commercialized fresh because it is a semiperishable vegetable, it is necessary to use some methods of conservation in order to extend its shelf life, and drying is

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the most commonly used method. Nowadays, drying is used also in developing garlic products used as food ingredients, natural preservatives, and functional or medicinal foods (Rahman et al. 2009).

It is known that drying method and conditions significantly affect the quality of products; therefore, it is important to select an appropriate method in order to obtain a product with high quality because garlic is sensitive to high temperatures and several volatile compounds may be lost during the process (Pezzutti and Crapiste 1997). In general, convective hot air-drying is a common process used for garlic dehydration (Sharma and Prasad 2001; Cui et al. 2003) but unfortunately affects the quality attributes and increases the loss of nutritional compounds since the products are exposed to high temperatures for a long time. On the other hand, freeze-drying allows to preserve active components, producing high-quality products since it is based on sublimation and uses low operation temperatures; however, this method is very costly in terms of equipment and operating costs. Although a variety of garlic drying methods have been investigated (convective hot air-drying, combined microwave-vacuum and air-drying, freeze-drying, spray-drying of garlic oleoresin) (Madamba 1997; Pezzutti and Crapiste 1997; Condori et al. 2001; Sharma and Prasad 2001; Cui et al. 2003; Sharma and Prasad 2006; Sablani et al. 2007; Ratti et al. 2007; Rahman et al. 2009; Gil et al. 2011), no study has been published on the effect of addition of carrier materials on the retention of allicin and pyruvic acid during spray-drying of garlic juice.

Spray-drying is one of the best drying methods for transforming, in a one-step process, liquid foods or suspensions into solid or semisolid particles (powder). This technology is based on rapid drying rate and a short residence time of products in the drying chamber; therefore, thermal damage to thermosensitive compounds is very low. In addition, spray-drying combined with the addition of carrier materials can be used as an effective way to protect food ingredients against deterioration or to reduce losses of volatile compounds during the process (Ré 1998). Maltodextrins are mainly used to reduce stickiness and agglomeration problems during storage, thereby improving product stability (Bhandari et al. 1992). Spray-drying engineering can be developed with heat and mass transfer-based simulators (Palencia et al. 2002) that relate the input variables (feed state) and service variables (drying air initial state) with respect to process state variables, output variables, and energy requirements. The final product moisture (an output variable) is the main quality variable that defines the performance of the process. However, in food product drying, there are other quality variables that the simulators cannot calculate. In the case of garlic juice spray-drying processing aids (drying carriers) that protect the active compounds (allicin and pyruvic acid) are necessary and therefore, the retention of these active compounds must be considered as a quality variable that must be related with process variables by empirical or statistic techniques because the heat and mass transfer-based simulators cannot predict them. Recently, some works reported response surface methodology (RSM) as the statistic method used to relate quality variable with process variables. For example, Shavakhi et al. (2012) studied the effects of enzymatic liquefaction, maltodextrin concentration, and spray-dryer air inlet temperature on pumpkin powder characteristics by means of RSM; Bakar et al. (2013) optimized by RSM the spray-drying of red pitaya peel; Rouissi et al. (2013) optimized the spray-drying process for the production of *Sinorhizobium meliloti* powder by RSM; and Balasubramani et al. (2013) optimized the spray-drying of garlic oleoresin (not garlic juice) by RSM. This technique is valid only if the relation is analytic, that is, if both quality variables and process variables may be expressed in a continuous interval of real numbers. In spray-drying, process variable combinations that are not able to dry may exist, which produces discontinuous zones in the process variable metric space. Under this situation, RSM is not applied and therefore, statistic methods that allow for the analysis of results in discontinuous metric spaces are necessary [e.g., principal component analysis (PCA) and one-way analysis of variance (1WANOVA)].

Then, the aim of this work was to apply PCA and 1WANOVA in order to study the influence of gum arabic and maltodextrin (DE-10) addition as drying carriers at different spray-drying conditions on dried garlic juice quality. The quality was evaluated through dried powder moisture (X), water activity (a_w), color coordinates (Chro, *Hue* and L), and the retention of allicin (R_{al}) and pyruvic-acid (R_{pa}).

Materials and Methods

Materials

Fresh white garlic (*A. sativum*) was purchased from a local supermarket in Veracruz, Mexico, and stored at 4 °C and 60 % of relative humidity until used for the experiments. Average moisture content of garlic bulbs was 1.85–1.89 g water/g dried solid. Carrier materials used for the study were maltodextrin with dextrose equivalent DE-10 (supplied by Veyco, Puebla, Mexico) and gum arabic (Instruments and Reagents, Veracruz, Mexico). Sodium hydroxide, sodium pyruvate, and 2,4-dinitrophenylhidrazine were supplied by Sigma-Aldrich (Mexico). HPLC-grade methanol was purchased from Baker (Mexico).

Spray-Drying Feed Mixture Preparation

Garlic bulbs were taken out of cold storage and allowed to equilibrate with ambient condition for 12 h, and the bulbs were separated into cloves thereafter. Cloves were manually peeled and damaged ones were discarded. After peeling the garlic cloves, they were placed in a commercial extractor (Sanyo Electric Co., Ltd., Japan) in order to obtain the garlic juice. To minimize losses of allicin, the extraction of juice was quickly done. Carrier material solution was previously prepared by dissolving a required amount of the material in hot distilled water (65–70 °C) and was kept in constant agitation during 1 h until a transparent solution has been obtained. Later, the resulting solution was cooled at room temperature and it was stirred again for 10 min before the juice was added. Feed mixture was prepared by mixing garlic juice (35 % solids), carrier solution (20 % solids), and distilled water in the amounts required to obtain a mixture with 20 % of solids and the solid carrier to solid garlic ratios (0:1, 1:1, and 4:1). The mixture was prepared at room temperature using a magnetic agitator in a hot plate stirred at 600 rpm for 3–5 min (Model Cimarec 2, Thermolyne Barnstead, USA). Both feed mixture preparation and drying experiment were carried out in the same day. The quality of the garlic samples dehydrated by spray-drying process was evaluated by retention of allicin and pyruvic acid, moisture content, color measurement, and water activity. Two commercial spices of garlic powders (called A and B) were purchased to compare with the dried garlic powders produced in this investigation.

Spray-Drying

A mini spray dryer (Büchi B-191, Labortechnik AG, Switzerland) equipped with a 0.7-mm standard-diameter nozzle was used to prepare the spray-dried powders. A cocurrent flow was employed because this flow enables the particles to have a lower residence time within the system and the particle separator (a cyclone) operates more efficiently. The operating conditions for the dryer were as follows: 110 and 130 °C for inlet air temperatures and 60, 70, and 80 °C for outlet air temperatures at a pressure of 1.1 bar. The mixture was fed with a peristaltic pump with variable flow rate to control the outlet air temperature. In order to prevent nozzle blockage, the mixture was adjusted to contain 20 % of solids and continuously stirred before being spray-dried. The total drying time for each experimental run was variable depending on operation conditions, and the range of feed flow was 0.6–9.9 mL/min. The powders were placed in amber vials perfectly sealed and stored in a desiccator at 25 °C for further use in analyses. All analyses reported here were completed within 24 h after spray-drying of the samples.

Moisture Content

The vacuum oven method was used to determine the moisture content of wet and dried garlic samples according to method 925.09 of AOAC (1995). Garlic samples of approximately 1 g were placed in pre-dried aluminum dishes in a vacuum oven (Model 3618-1, Lab-Line Instruments, Melrose Park, IL, USA). The operating temperature was 60 °C with a gauge pressure of 600 mbar, and the sample was kept in the oven until constant weight was reached (18 h approximately). The samples were then taken out of the oven, cooled in a desiccator at room temperature, and weighed using an analytical balance (Model AR2140, Ohaus Corporation, USA) with a sensitivity of 0.0001 g. The fresh and dried weights were used to calculate the moisture content, which was expressed as grams of water per gram of dry solid. All measures were carried out in triplicate.

Water Activity

The water activity (a_w) of spray-dried powders was measured in triplicate at room temperature (25±1 °C) using a water activity meter (AQUA LAB Model CX-2, Decagon Devices Inc., Pullman, WA, USA).

Color Coordinates Measurement

Color coordinates of dried samples were measured by a colorimeter (Hunter Lab Model Mini Scan, USA) in terms of L^* (degree of the lightness or brightness), a^* (degree of redness to greenness), and b^* (degree of yellowness to blueness). The garlic powder contained in a cylindrical plastic dish was placed at the light port. The colorimeter was calibrated against a standard calibration white plate. The color of each sample was measured three times, and the average values of L^*, a^*, and b^* were reported. Chroma (Chro) and hue angle (*Hue*) were calculated with,

$$\mathrm{Chro} = \sqrt{(a*)^2 + (b*)^2} \tag{1}$$

$$\mathrm{Hue} = \tan^{-1}\left(\frac{b*}{a*}\right) \tag{2}$$

Sample Preparation: Allicin in Feed Mixture

A total of 400–800 mg of feed mixture was weighed and placed into a 50-mL tube, adding 25 mL of cold (refrigerated) water to the sample and stirring for 30 s in vortex. Once prepared, the solution was filtered through a 0.45-μm glass filter membrane (Milex-LCR, Millipore), transferred to a vial, and analyzed immediately by HPLC.

Sample Preparation: Allicin Dried Powders

Four hundred to 800 mg of spray-dried powder was weighed and placed into a 50-mL tube, adding 25 mL of cold (refrigerated) water to the sample and mixing for 5 s in vortex to avoid lumps. Then, 25 mL of cold water was added and the solution was stirred for 30 s. Once prepared, the solution was filtered through a 0.45-μm glass filter membrane (Milex-LCR, Millipore), transferred to a vial, and analyzed immediately by HPLC.

Allicin Determination

The allicin content of fresh and dried samples was determined by HPLC procedure as described by Iberl et al. (1990a). A Varian Pro Star HPLC (Model 363, Varian, Inc., USA) equipped with a Waters UV detector (Model 2487, Waters Ltd., Montreal, Canada) and Microsorb-MV 100 C18 column with 150-mm length×4.6-mm ID, 5-μm particle size (Varian, Inc., USA) was used for HPLC analyses. The mobile phase comprising methanol-water (1:1, *v/v*) was pumped at a flow rate of 1.0 mL/min, and the temperature of column was 28 °C.

Allicin was detected at 240 nm and quantified against an isolated allicin external standard prepared from an aqueous extract of garlic powder by solid-phase extraction (Bakerbond SPE C18 column, 1.0 g, 6 mL, J.T.Baker, Inc., USA). The concentration of allicin in the isolated fraction was standardized by measuring the absorbance (Spectrophotometer Model UV1201, Shimadzu, Inc., USA) at both 240 and 254 nm based on the published extinction coefficient. Because allicin has limited stability in solution, samples were analyzed soon after extracting into cold water.

Sample Preparation: Pyruvic Acid in Feed Mixture

Five hundred to 1,000 mg of feed mixture was mixed with 5 mL of distilled water and stirred for 30 s in vortex. The prepared solution was analyzed immediately by spectrophotometry at 515 nm.

Sample Preparation: Pyruvic Acid in Spray-Dried Powders

Four hundred to 500 mg of spray-dried powder was dissolved in 5 mL of distilled water and stirred for 30 s in vortex. The prepared solution was analyzed immediately by spectrophotometry at 515 nm.

Determination of Pyruvic Acid

Pungency is due to enzymatic reactions catalyzed by the allinase and is accompanied by the production of pyruvic acid. Therefore, pungency of fresh and dried products of garlic can be evaluated based on the pyruvic acid content. The pyruvic acid content was determined by modified spectrophotometric method of 2,4-dinitrophenylhidrazine (2,4-DNPH) described by Anthon and Barrett (2003).

Retention of Allicin and Pyruvic Acid

The retention of allicin and pyruvic acid in the final product was calculated as a percent of the compounds originally present in the feed mixture in agreement to Eqs. (3) and (4).

$$R_{\mathrm{al}} = \frac{\mu\mathrm{g\ allicin\ in\ powder/g\ dried\ solids}}{\mu\mathrm{g\ allicin\ in\ feed\ mixture/g\ dried\ solids}}100 \quad (3)$$

$$R_{\mathrm{pa}} = \frac{\mu\mathrm{g\ pyruvic\ acid\ in\ powder/g\ dried\ solids}}{\mu\mathrm{g\ pyruvic\ acid\ in\ feed\ mixture/g\ dried\ solids}}100 \quad (4)$$

Experimental Design and Statistical Analysis

A complete factorial design 2×3×3 (two output temperatures, three input temperatures, and three carrier concentrations) with two replicates was used. However, some treatments were unfeasible to dry. Then, a response surface methodology (RSM) was not applied due that the discontinuities introduced by the treatments unfeasible to dry. Therefore, a principal component analysis (PCA) of the whole responses was developed in order to identify the response variables more sensitive to treatments and the possible correlations between them. The PCA was performed with normalized response variables (y'_{ij}) defined as follows:

$$y'_{ij} = \frac{y_{ij} - \overline{y}_{\cdot j}}{\overline{y}_{\cdot j}} \quad (5)$$

where y_{ij} is the response *j* obtained in the experiment *i* and $\overline{y}_j$ is the arithmetic average of the response *j* on the whole of experiments. The metric space of dried powder quality was defined by j=1,2, ,7 where 1 is the pyruvic acid retention (R_{pa}), 2 allicin retention (R_{al}), 3 $L*$ color coordinate, 4 Hue (*Hue*) color coordinate, 5 Chroma (Chro) color coordinate, 6 moisture content (X), and 7 water activity (a_w), respectively. Additionally, the results were analyzed by 1WANOVA of the drying-feasible treatments.

Results and Discussion

Garlic juice spray-drying at different treatments showed that some variable combinations are unfeasible. The unfeasible conditions to drying are listed in Table 1, in which the treatment code is type of carrier (AG: Arabic gum, M: maltodextrin or anyone)-input temperature-output temperature-carrier concentration (0: anyone, 5: 0.5 mass fraction of solids, or 8: 0.8 mass fraction of solids). There were two causes of no drying: the output temperature cannot be researched even with

Table 1 Causes identified that makes the spray-drying process unfeasible

Treat code	Causes
AG-110-80-5	Feed flow required less than minimum
AG-130-80-5	Feed flow required less than minimum
AG-110-70-8	Feed flow required less than minimum
AG-110-80-8	Feed flow required less than minimum
AG-130-80-8	Feed flow required less than minimum
M-110-60-5	Dried powder glued in drying chamber walls
M-130-60-5	Dried powder glued in drying chamber walls
M-110-80-8	Feed flow required less than minimum
M-130-80-8	Feed flow required less than minimum
110-70-0	Feed flow required less than minimum
110-80-0	Feed flow required less than minimum
130-60-0	Dried powder glued in drying chamber walls

Treatment code: type of carrier (*AG* arabic gum, *M* maltodextrin), input temperature-output temperature-carrier concentration (0: without carrier, 5: 0.5 mass fraction of solids, or 8: 0.8 mass fraction of solids)

the minimal feed flow handle by pump and the powder was glued in the drying chamber walls. The first cause is basically the result of heat lost in the drying chamber, that is, these conditions could be feasible in a drying chamber with thermal insulation. The second cause is related with the thermoplastic properties and moisture of powder within the drying chamber. These conditions must be avoided because the particles are not drying enough to flow in the drying chamber since it is necessary to increase the feed flow in order to decrease the output air temperature. If the feed solution rate is high, the water will not vaporize fully in the short time allotted and the spray-dried powder cannot dry sufficiently. On the other hand, an accumulation of under-dried larger particles on the chamber wall may lead to low process yield. It is important to note that unfeasible conditions by heat loss are not thermally adequate because they are the conditions with minimal difference between input-output air temperatures with the corresponding thermodynamic efficiency falling.

The garlic juice dried powder quality variables obtained at feasible conditions with their respective conclusions of the 1WANOVA are listed in Table 2, and the two main PCAs of the normalized quality variables [Eq. (5)] are plotted in Fig. 1. The main PCA (69.6 % of normalized squared sum of variation) has as its greatest contribution the variables moisture and water activity. This is completely expected because of the natural correlation of moisture with water activity and the fact that drying process variables must have an effect mainly in these two variables. The other variable with some contribution to main PCA is Chroma coordinate, indicating some negative correlation between color intensity with moisture. Although

Table 2 1WANOVA of quality variables at feasible treatments

Treat code	R_{pa}	R_{al}	L	Hue	Chro	X	a_w
M-110-70-5	89.9 ± 2.06^{abc}	76.9 ± 0.50^{a}	89.9 ± 0.05^{e}	101 ± 0.61^{ab}	6.92 ± 0.06^{bc}	2.55 ± 0.09^{de}	0.284 ± 0.004^{ef}
M-130-60-8	89.0 ± 1.32^{abc}	76.1 ± 3.56^{a}	91.9 ± 0.12^{b}	99.3 ± 1.15^{ab}	4.80 ± 0.07	2.91 ± 0.17^{d}	0.335 ± 0.02^{cd}
M-130-80-5	73.8 ± 3.75	58.6 ± 6.92^{b}	90.5 ± 0.06^{d}	102 ± 1.06^{ab}	8.19 ± 0.10^{a}	1.13 ± 0.13	0.199 ± 0.02
AG-110-70-5	73.4 ± 1.61	58.4 ± 3.55^{b}	92.3 ± 0.02^{a}	99.6 ± 1.65^{ab}	7.05 ± 0.24^{bc}	1.63 ± 0.25	0.278 ± 0.004^{ef}
M-130-70-8	88.8 ± 0.97^{abc}	56.6 ± 2.10^{b}	91.4 ± 0.08^{c}	101 ± 1.76^{ab}	5.01 ± 0.02	2.02 ± 0.13	0.252 ± 0.002^{f}
AG-130-60-8	94.2 ± 1.15^{a}	53.7 ± 0.56^{bc}	88.2 ± 0.05^{g}	98.1 ± 0.02^{ab}	5.51 ± 0.11^{f}	2.60 ± 0.41^{de}	0.267 ± 0.01^{ef}
AG-110-60-5	86.9 ± 1.15^{bc}	48.6 ± 3.99^{bcd}	87.2 ± 0.03	90.3 ± 7.71	7.30 ± 0.23^{b}	2.07 ± 0.21^{e}	0.331 ± 0.02^{cd}
AG-130-60-5	90.2 ± 0.01^{abc}	48.4 ± 3.63^{bcd}	88.9 ± 0.02^{f}	98.4 ± 0.14^{ab}	5.07 ± 0.11^{f}	6.98 ± 0.05^{a}	0.496 ± 0.009^{a}
110-60-0	87.4 ± 0.28^{bc}	47.5 ± 2.43^{bcd}	86.6 ± 0.08	99.0 ± 1.18^{ab}	7.41 ± 0.25^{b}	5.05 ± 0.14^{b}	0.390 ± 0.001^{b}
AG-110-60-8	62.8 ± 1.24	44.8 ± 5.24^{bcd}	88.5 ± 0.01^{g}	93.3 ± 2.24	3.98 ± 0.12	6.70 ± 0.33^{a}	0.460 ± 0.006^{a}
AG-130-70-5	88.6 ± 1.00^{abc}	40.0 ± 3.05^{cd}	91.9 ± 0.12^{b}	101 ± 2.01^{ab}	6.22 ± 0.03^{de}	2.47 ± 0.19^{de}	0.129 ± 0.003
M-130-70-5	76.3 ± 0.69	38.5 ± 1.60^{d}	89.0 ± 0.02^{f}	95.1 ± 1.56^{b}	7.40 ± 0.45^{b}	1.71 ± 0.03	0.215 ± 0.006
130-80-0	79.2 ± 0.46^{d}	35.7 ± 2.85^{d}	86.7 ± 0.0	100 ± 0.29^{ab}	6.44 ± 0.02^{cd}	4.09 ± 0.14^{c}	0.302 ± 0.003^{de}
AG-130-70-8	91.7 ± 2.57^{ab}	35.2 ± 0.71^{d}	88.4 ± 0.03^{g}	99.1 ± 1.18^{ab}	4.49 ± 0.13	2.14 ± 0.08^{e}	0.266 ± 0.01^{ef}
130-70-0	85.2 ± 1.04^{cd}	34.9 ± 3.51	86.9 ± 0.03	102 ± 0.63^{ab}	5.72 ± 0.04^{ef}	4.04 ± 0.07^{c}	0.367 ± 0.01^{bc}
M-110-80-5	70.2 ± 1.62	34.9 ± 5.06	87.0 ± 0.03	104 ± 0.01^{a}	8.28 ± 0.02^{a}	1.93 ± 0.17	0.238 ± 0.004
M-110-70-8	89.7 ± 0.45^{abc}	30.0 ± 6.54	88.4 ± 0.01^{g}	97.9 ± 0.19^{ab}	5.25 ± 0.18^{f}	2.48 ± 0.16^{de}	0.225 ± 0.01
M-110-60-8	87.2 ± 0.51^{bc}	26.8 ± 3.31	91.2 ± 0.04^{c}	95.0 ± 0.09	4.77 ± 0.15	3.10 ± 0.12^{d}	0.337 ± 0.01^{cd}
Dif[a]	6.02	15.06	0.34	8.56	0.68	0.75	0.045

Treatment code: type of carrier (*AG* Arabic gum, *M* maltodextrin), input temperature-output temperature-carrier concentration (0: without carrier, 5: 0.5 mass fraction of solids, or 8: 0.8 mass fraction of solids). Different letters represent significant difference between files with Tukey $p<0.05$. Treatment mean±standard deviation. The media with the greatest value are assigned with "a" letter. Only the grater values were indicated

[a] Minimal difference between media required for significant difference with Tukey $p<0.05$

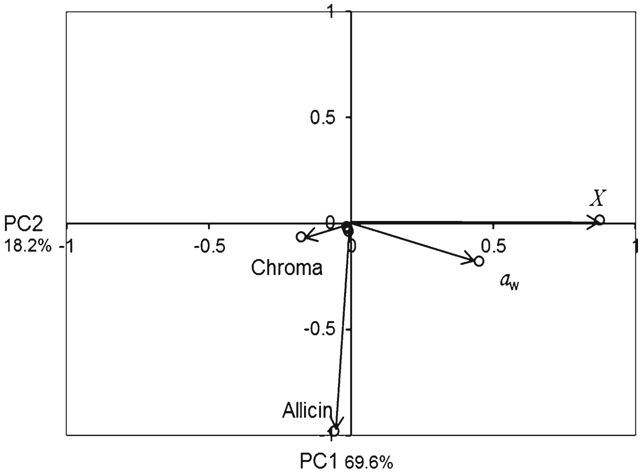

Fig. 1 Principal component analysis (PCA) of normalized quality variables of garlic juice spray-drying

the moisture may be predicted with simulators (Palencia et al. 2002), some discussion is important. The moisture content of the whole feasible treatments was between 1.125×10^{-2} and 6.975×10^{-2} (g water/g dry solid) and the water activity between 0.129 and 0.496. The higher moisture values were obtained from products added with gum arabic as carrier and dried at low output air temperatures, which showed low powder recovery remaining adhered to the drying chamber wall. Because in the investigations published there is no report about water activity of garlic products, for comparison with the results of this research, some commercial products were analyzed and it was found that both water activity values (0.129 to 0.496) and moisture contents (1.125×10^{-2} to 6.975×10^{-2} g water/g dried solid) of our powders were lower than those of commercial products (0.439 to 0.492 for water activity and 5.6×10^{-2} to 6.7×10^{-2} g water/g dried solid for moisture content).

The second PCA (18.2 % of normalized squared sum of variation) has as main contribution variable the allicin retention, with some contribution of water activity. Then, like moisture and water activity which can be calculated from heat and mass balances, the quality variable taken as reference was allicin retention.

The PCA identified allicin retention as the quality variable (additionally to moisture and water activity) most sensitive at process variable change but do not identify the treatment that maximizes the quality. In order to identify the better treatment with respect to quality, the 1WANOVA reported in Table 2 was developed. The Table 2 ANOVA was organized with the treatment with the highest allicin retention as first because this response has the maximum sensitivity and was taken as reference response. From Table 2, it is evident that the best treatments with respect to allicin retention were M-110-70-5 (feed mixture with 50 % dry basis of maltodextrin, 110 and 70 °C of input-output air temperature) and M-130-60-8 (feed mixture with 80 % dry basis of maltodextrin, 130 and 60 °C of input-output air temperature). These two treatments reach 88–89 % of acid pyruvic retention, good moisture and water activity, and tolerable color coordinates. However, the treatment M-130-60-8 is preferred for industrial drying because the greater difference between input-output temperatures assures greater energy efficiency (Palencia et al. 2002). In general, when comparing the feasible treatments with maltodextrins, it can be seen that the lowest values of pyruvic acid retention were obtained with the highest output air temperature (80 °C), while for those feasible with gum arabic, the highest values of pyruvic acid retention were obtained at the highest input air temperature (130 °C) with difference between input-output air temperatures of 60 to 70 °C. On the other hand, for treatments with gum arabic, the lowest allicin retention was obtained when input and output air temperatures of 130 and 70 °C, respectively, were used.

Usually, the quality of garlic products is evaluated based on some sensory attributes, mainly color and pungency or flavor strength, which are very important. Although the pyruvic acid has been considered as an indicator of pungency because of the difficult of allicin determination (Schwimmer and Weston 1961; Sharma and Prasad 2001; Cui et al. 2003), many studies have shown that the therapeutic properties of garlic products are provided by allicin (Prasad et al. 1995; Rahman et al. 2006; Rahman 2007). In spray-drying of garlic juice, the retention of allicin and pyruvic acid by addition of carrier materials may be the key to produce a garlic product with a flavor profile and health benefits as close to fresh garlic as possible. When Gil et al. (2011) evaluated the best encapsulant mixture to elongate the conservation of some bioactive and aromatic compounds of spray-dried garlic oleoresin, they found that 10.38 % of modified starch mixture and 79.62 % of gum mixture (gum arabic and guar gum, 80:20 *w/w*) had better characteristics in the final product; however, it is important to consider that modified starch can produce residual off-suitable flavors or produce less protection against the oxidation of compounds, like that observed in the samples added with modified starch that showed rancid flavors. Bhandari et al. (1992) found that volatile compound retention can be improved at increasing carrier material concentrations of sample, and they observed that retention of this kind of compounds increases at higher inlet air temperature; this was in agreement with the results observed for pyruvic acid retention when gum arabic was used as carrier material in this investigation and the previous results obtained by different authors who used other temperatures, other compounds, and other types of dryers (Rulkens and Thijssen 1972; Reineccius et al. 1982; Rosenberg et al. 1990).

The total content of allicin and pyruvic acid in dry basis in feed mixture and dried powder joint with the results reported in other works at different drying methods and with two commercial spices of dried garlic (called A and B) are listed in Table 3. It was observed that the highest retention levels were obtained with freeze-drying (97 %), whereas similar levels (89 %) to combined microwave-vacuum and convective drying (88 %) and higher than the results obtained by convective air-drying (54 %) were obtained with spray-drying (Cui et al. 2003). On the other hand, the allicin retention can be compared with the results presented by Rahman et al. (2009), listed in Table 3, who evaluated the effect of drying rate, temperature, and level of oxygen on the loss of allicin potential during garlic slices drying in air (50–90 °C), vacuum (50–90 °C), and nitrogen atmosphere (40–60 °C). In agreement with the results of Rahman et al. (2009), the loss of allicin potential increased with increasing drying

Table 3 Content of pyruvic acid and allicin in the treatments of this work with respect to other investigations (Cui et al. 2003; Ratti et al. 2007; Rahman et al. 2009)

Treatment	Content of pyruvic acid[a] (μmol/g total dried solid)		Content of allicin[a] (μg/g dried solid)	
	Initial	Final	Initial	Final
M-110-70-5	115.56±1.75	103.96±3.97	6,467.12±1,431.93	4,967.93±1,068.18
M-130-60-8	43.12±0.12	38.38±0.40	878.05±29.36	667.72±8.34
M-130-80-5	115.50±5.29	85.11±0.42	5,228.22±327.49	3,075.96±553.66
AG-110-70-5	96.28±2.62	70.60±0.37	5,182.04±603.87	3,039.16±536.92
M-130-70-8	42.82±1.56	38.02±0.97	2,593.61±266.15	1,464.34±96.03
AG-110-60-8	39.05±0.32	36.80±0.75	1,250.20±64.81	671.25±41.80
AG-110-60-5	104.10±1.95	90.46±0.49	5,527.48±392.54	2,692.43±409.22
AG-130-60-5	43.77±0.64	39.46±0.57	4,118.55±290.37	1,988.65±9.12
110-60-0	130.22±1.05	113.77±0.58	7,001.05±645.43	3,319.55±136.24
AG-110-60-8	38.35±0.73	24.09±0.01	1,509.87±291.10	668.11±51.21
AG-130-70-5	83.59±0.57	74.07±0.33	5,191.41±776.09	2,089.72±469.41
M-130-70-5	114.09±0.54	87.02±1.22	7,495.39±348.63	2,884.99±253.70
130-80-0	227.83±1.03	180.42±0.27	19,037.71±2,879.42	6,748.99±485.38
AG-130-70-8	40.57±1.68	37.18±0.49	893.71±29.65	314.88±16.75
130-70-0	146.55±4.24	124.88±2.08	10,979.53±375.59	3,825.65±255.15
M-110-80-5	108.26±0.87	75.97±2.36	6487.92±569.22	2,277.26±526.46
M-110-70-8	46.04±0.58	41.28±0.73	1,817.31±92.12	548.09±146.44
M-110-60-8	40.24±0.04	35.10±0.24	2,275.37±326.68	603.44±12.06
Hot air-drying (Cui et al. 2003)	141.00±0.72	84.18±0.78	ND	ND
Freeze-drying (Cui et al. 2003)	141.00±0.72	138.35±0.54	ND	ND
Combined vacuum microwave-convective drying (Cui et al. 2003)	141.00±0.72	126.87±1.29	ND	ND
Hot air-drying at 40 °C (Ratti et al. 2007)	ND	ND	9,224.4±70.4	9,498.2±634.2
Hot air-drying at 60 °C (Ratti et al. 2007)	ND	ND	9,224.4±70.4	7,736.0±51.9
Freeze-drying at 20 °C (Ratti et al. 2007)	ND	ND	9,224.4±70.4	9,286.7±172.8
Freeze-drying at 60 °C (Ratti et al. 2007)	ND	ND	9,224.4±70.4	8,438.3±1,872.0
Air oven at 50 °C (Rahman et al. 2009)	ND	ND	7,000.0±52.0	4,932.0±48.0
Air oven at 90 °C (Rahman et al. 2009)	ND	ND	7,632.0±43.0	3,845.0±326.0
Vacuum oven at 50 °C (Rahman et al. 2009)	ND	ND	7,309.0±33.0	4,655.0±48.0
Vacuum oven at 90 °C (Rahman et al. 2009)	ND	ND	7,620.0±34.0	2,955.0±254.0
Nitrogen atmosphere drying at 40 °C (Rahman et al. 2009)	ND	ND	5,117.0±22.0	3,103.0±109.0
Nitrogen atmosphere drying at 60 °C (Rahman et al. 2009)	ND	ND	8,049.0±3.0	4,103.0±22.0
Commercial powder A	ND	60.99±2.65	ND	3,551.82±463.52
Commercial powder B	ND	60.28±1.44	ND	3,467.95±418.03

Treatment code: type of carrier (*AG* Arabic gum, *M* maltodextrin), input temperature-output temperature-carrier concentration (0: without carrier, 5: 0.5 mass fraction of solids, or 8: 0.8 mass fraction of solids)

ND not determined

[a] Averaged values ± standard deviation

temperature, and drying below 50 °C should be the best drying condition for the retention of this compound. Similar results about the effect of convective hot air-drying and freeze-drying on allicin retention of garlic slices were published by Ratti et al. (2007), listed in Table 3. For freeze-dried garlic slices, the final average values of allicin content were close to those for fresh garlic. The authors concluded that this high allicin content may be due not only to the low temperatures during process but also to the fact that no cutting of the sample was necessary; therefore, no allicin was formed and lost during sample preparation as in the case of air-dried garlic slices.

All of these facts emphasize the PCA results (Fig. 1) which allow identification of allicin as the most sensitive quality variable (except moisture and water activity) with respect to process variable, that is, the pyruvic acid retention obtained was high for the different treatments unlike the retention of allicin. This may be attributable not only to pyruvic acid which is highly stable but also to allicin which is so unstable, because once it is generated, it readily changes into other compounds. Since pyruvic acid is a carboxylic acid which can form more than one set of hydrogen bonds, that is, it can form hydrogen bonds to itself (dimer) or to water molecules, so its molecular weight increases and its boiling point is usually high causing volatility decreases during evaporation. This means that allicin can be taken as reference quality variable, and 1WANOVA results (Table 2) identified M-110-70-5 as the treatment with the highest allicin and pyruvic acid retentions and concentrations (Table 3) in final powder.

Conclusions

Feasible and unfeasible spray-drying conditions of garlic juice in two discontinuous metric spaces (maltodextrin 0–80 % of dry solids 110–130 °C air input temperature and 60–80 °C air output temperature, and arabic gum 0–80 % of dry solids 110–130 °C air input temperature and 60–80 °C air output temperature) were shown. The discontinuities were caused by unfeasible-to-dry process variable combinations. Therefore, the best treatments with respect to more sensitive quality variable (allicin retention) were identified by using multivariate statistic (PCA) and 1WANOVA. Results showed that maltodextrin has better properties with respect to allicin retention and allowed to obtain higher retention levels of pyruvic acid than others types of convective drying. The best treatment with respect to the whole of quality variable was 110, 70 °C of inlet, outlet air temperatures, and 0.5 g of maltodextrin/g dm.

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