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Microencapsulation of Tomato (*Solanum lycopersicum* L.) Pomace Ethanolic Extract by Spray Drying: Optimization of Process Conditions

Luiz C. Corrêa-Filho, Sofia C. Lourenço, Daniel F. Duarte, Margarida Moldão-Martins and Vítor D. Alves *

LEAF, Linking Landscape, Environment, Agriculture and Food, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal; lucaalbernaz@gmail.com (L.C.C.-F.); sofiaclourenco@isa.ulisboa.pt (S.C.L.); dduarte@isa.ulisboa.pt (D.F.D.); mmoldao@isa.ulisboa.pt (M.M.-M.)
* Correspondence: vitoralves@isa.ulisboa.pt; Tel.: +351-21-365-3546

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Abstract: Microencapsulation by spray-drying is a process used in the stabilization of active compounds from various natural sources, such as tomato by-products, with the purpose to be used as additives in the food industry. The aim of this work was to study the effects of wall material and spray drying conditions on physicochemical properties of microcapsules loaded with lycopene rich extract from tomato pomace. The assays were carried out with ethanolic tomato pomace extract as core material and arabic gum or inulin as wall materials. A central composite rotatable design was used to evaluate the effect of drying air inlet temperature (110–200 °C) and concentration of arabic gum (5–35 wt %) or inulin (5–25 wt %) on the antioxidant activity, encapsulation efficiency, loading capacity, and drying yield. SEM images showed that the produced particles were in the category of skin-forming structures. The most suitable conditions, within the ranges studied, to obtain lycopene loaded microparticles were a biopolymer concentration of 10 wt % for both materials and an inlet temperature of 200 and 160 °C for arabic gum and inulin, respectively. Arabic gum and inulin possessed a good performance in the encapsulation of tomato pomace extract by spray drying. It is envisaged that the capsules produced have good potential to be incorporated in foods systems with diverse chemical and physical properties.

Keywords: microencapsulation; lycopene rich extract; arabic gum; inulin; spray drying; antioxidant activity

1. Introduction

Food industries generate a large quantity of solid by-products that turn into food wastes. As such, they are struggling to reduce organic wastes due to problems, such as accumulation, handling, and disposal costs. By-products obtained may well be suitable for noble purposes, since they are rich in bioactive compounds [1,2]. Many researchers have investigated the potential use of agroindustrial by-products for their inclusion in the human diet, which could correctly solve the problem of waste associated with food processing and reduce industrial costs [3,4].

The tomato is one of the most produced vegetables worldwide. The European Union produced approximately 17.6 million tonnes of tomatoes in 2015, of which around 10% came from Portugal (1.4 million tonnes). Although the tomato is commonly consumed fresh, around 90% of the tomato consumption in Portugal corresponds to processed products, such as tomato juice, paste, puree, ketchup, and sauce [5]. In the case of the tomato processing industry, about 5% of the total raw material is discarded as tomato pomace. It is composed of 44% of seeds and 56% of pulp and skin and is

generally used for animal feeding [2]. Tomato pomace is a rich source of nutrients and bioactive compounds like carotenoids, sugars, and fibers [3].

Natural bioactive compounds, such as carotenoids and polyphenols, are molecules that provide health benefits due to their biological activities, like antioxidant, antihypertensive, anti-proliferative, and anti-inflammatory capacities [6]. Carotenoids as lycopene are antioxidants naturally present in some food products and may be recovered as concentrated extracts from agroindustrial by-products, like tomato pomace. They are referred to be effective against cancer and cardiovascular diseases [7]. Due to the high sensitivity of those compounds to environmental conditions (heat, light, pH, oxygen), bioactive compounds must be protected in order to preserve their expected benefits.

Microencapsulation has been described as a good strategy in the food industry for various purposes, such as preservation of functional properties, masking undesirable flavors, improved handling and utilization of bioactives, development of functional foods, controlled release of the bioactive compounds at the desired time and specific target, and increasing bioavailability of bioactive compounds [8,9].

Among various encapsulation techniques, spray drying is the most common technology applied due to its low cost, flexibility, and production of good quality powder particles [10]. The principle of spray drying is the dissolution of the core (compounds to be protected) in the dispersion of a chosen matrix (wall material). The dispersion is subsequently atomized into heated air, which promotes the rapid removal of the solvent (water) [11]. The quality of the powdered particles may be affected by the type of wall material used and by the spray drying operating conditions, such as the inlet and outlet temperatures, feed flow rate, and inlet air flow rate [12]. The structures formed in the encapsulation process are composed by the core (bioactive compounds) and the protective matrix materials. These materials are commonly polysaccharides (e.g., starches and arabic gum), proteins (e.g., gelatin and casein), lipids (e.g., stearic acid and mono- and diglycerides) and their mixtures [13].

Arabic gum is one of the most common wall materials used in microencapsulation, due to its excellent emulsification properties, high solubility, low viscosity, and good retention of volatiles [14]. It is a highly branched edible polymer exuded from acacia trees, composed of approximately 2% protein and high proportion of carbohydrates (D-galactose, L-rhamnose, L-arabinose, and D-glucuronic acid) [12]. In addition, inulin is also an interesting candidate, as beyond protection, it may act also as a prebiotic, stimulating the activity of colon beneficial microflora, and can improve calcium bioavailability, amongst other benefits [15]. Inulin is a fructooligosaccharide (FOS), insoluble in water at ambient temperature, composed of fructose units with β (2→1) links with glucose at the end of the chain that is present as plant storage carbohydrates in a number of vegetables and plants, including wheat, onion, bananas, garlic, and chicory [14,16]. Inulin is used for a variety of purposes, including as a replacement for fat and sugar, a low caloric sweetener, a texturizing agent, an agent to form gels, and an aid to increase the viscosity of solutions. It is also considered a functional food ingredient, since it affects physiological and biochemical processes, resulting in risk reduction of many diseases [17].

This work goes beyond state-of-the-art, as it deals with the study of the effect of spray drying process parameters on microparticles properties, using a systematic approach of optimization via Surface Response Methodology. As such, the effect of drying air inlet temperature and concentration of the wall material on the drying yield (DY), loading capacity (LC), encapsulation efficiency (EE), and antioxidant activity (AA) of encapsulated carotenoids was assessed simultaneously. In addition, two wall materials (arabic gum and inulin) with distinct physical-chemical properties were studied in parallel, in order to obtain microparticles with diverse properties for future application in the formulation of a range of food products.

2. Materials and Methods

2.1. Materials

Tomato pomace (*Solanum lycopersicum* L.) was supplied by HIT Group (Marateca, Portugal, 2016). arabic gum (LabChem, Lisboa, Portugal, 2016), and inulin (Alfa Aesar, Kandel, Germany, 2016) were used to form the protective matrix.

2,2'-azinobis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) diammonium salt, lycopene, and β-carotene were purchased from Sigma–Aldrich (Steinheim, Germany, 2016). 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) was obtained from Acrós Organics (Geel, Belgium, 2016). Potassium persulfate ($K_2S_2O_8$) and ethanol were purchased from Panreac AppliChem. Acetonitrile, dichloromethane, and ethyl acetate were obtained from Honeywell (Seelze, Germany, 2016).

2.2. Tomato Pomace Extract Preparation

Frozen tomato pomace, comprised of skin and seeds, was lyophilized in a LyoQuest freeze dryer at −47 °C and 0.100 mbar for 48 h, powdered in a cutting mill, and, finally, classified in a system of sieves arranged in columns, in order to separate particles with diameter of less than 0.5 mm. The tomato pomace powder was stored under a vacuum and protected from light.

The extraction of bioactive compounds (mostly lycopene and β-carotene) was carried out in a Soxhlet apparatus, in which 15 g of tomato pomace powder was extracted with 300 ml of ethanol until the solvent became completely colorless (around 5 h). After extraction, the solvent was evaporated with a rotary vacuum evaporator (Rotavapor®R II BUCHI), and the extract obtained was transferred to amber glass flasks and stored at −20 °C until analysis.

2.3. Preparation of Emulsions

Arabic gum was dissolved in distilled water under stirring overnight at room temperature, while inulin was dissolved in distilled hot water (70 °C), at the concentration values indicated in Table 1. After full hydration of the polymer molecules, tomato pomace extract (15%, dry basis) was added into each polymer solution and emulsions were produced by stirring with an Ultra-Turrax T25 (IKA, Staufen, Germany, 2001) at 13,500 rpm for 1 min at ambient temperature. A volume of 50 mL of emulsion was prepared for each experimental condition.

Table 1. Experimental design with coded and decoded values of independent variables and spray drying responses for each wall material.

Arabic Gum						
Drying Conditions			Response Variables			
Test	Arabic Gum (%)	T (°C)	LC	EE	AA	DY
1	9.4 (−1)	123.2 (−1)	1.86	8.5	1.5	44.0
2	9.4 (−1)	186.8 (+1)	2.10	20.5	2.3	38.6
3	30.6 (+1)	123.2 (−1)	1.44	8.0	1.9	29.0
4	30.6 (+1)	186.8 (+1)	1.45	7.3	4.6	26.7
5	20 (0)	155 (0)	1.79	9.3	1.9	27.2
6	20 (0)	155 (0)	1.46	8.1	1.8	29.1
7	20 (0)	155 (0)	1.49	8.4	1.8	27.6
8	5 (−α)	155 (0)	1.51	12.0	4.5	43.4
9	35 (+α)	155 (0)	1.15	3.4	0.9	14.7
10	20 (0)	110 (−α)	1.48	9.8	1.7	34.6
11	20 (0)	200(+α)	1.74	11.8	4.4	35.7

Table 1. *Cont.*

Inulin						
Test	**Inulin (%)**	**T (°C)**	**LC**	**EE**	**AA**	**DY**
1	7.9 (−1)	123.2 (−1)	2.73	19.7	2.5	37.5
2	7.9 (−1)	186.8 (+1)	1.78	15.2	1.0	45.2
3	22.1 (+1)	123.2 (−1)	1.16	7.8	1.6	34.9
4	22.1 (+1)	186.8 (+1)	1.63	14.8	3.4	49.5
5	15 (0)	155 (0)	2.37	20.2	2.5	48.9
6	15 (0)	155 (0)	1.93	17.4	2.6	47.3
7	15 (0)	155 (0)	2.20	19.2	3.0	48.8
8	5 (−α)	155 (0)	3.08	25.3	3.5	37.7
9	25 (+α)	155 (0)	2.54	19.3	2.1	39.7
10	15 (0)	110 (−α)	0.87	6.9	3.2	41.4
11	15 (0)	200(+α)	1.65	14.4	1.4	45.7

T: Temperature; LC: Loading capacity, mg lycopene.g^{-1}particles; EE: Encapsulation efficiency (%); AA: Antioxidant activity, µmol trolox.mg^{-1}lycopene; DY: Drying yield (%).

2.4. Spray Drying Process

The resultant emulsions were fed at a rate of 3.7 mL.min^{-1} to a co-current spray dryer (Lab-Plant SD-05, Huddersfield, England, 1995) equipped with a 0.5 mm diameter nozzle, a drying chamber (500 mm height and 215 mm diameter), and with a cyclone (300 mm height and a bottom diameter of 90 mm). The drying air flow rate was set at 47 m^3/h. The feed solution was kept under magnetic stirring. The pressure of the compressed air was set at 1.7 bar and had a maximum flow rate of 73 m^3/h. The inlet temperature ranged between 110 and 200 °C. Encapsulation of tomato pomace extract with arabic gum (5–35%) or inulin (5–25%) was performed, according to an experimental design (Table 1). Different wall material concentrations were used because inulin solutions concentrations above 25% were highly viscous and could not be processed by spray drying. The dried powders obtained were collected and stored under vacuum and protected from light.

2.5. Experimental Design

Response Surface Methodology (RSM) was used to find the best experimental conditions. The experiments were carried out following a central composite rotatable design, as a function of spray drying inlet temperature (110–200 °C) and the wall material concentration (arabic gum: 5–35% and inulin: 5–25%). The desirability function (Y_i) was applied to experimental results to optimize multiple responses in RSM. A total of 11 experiments were carried out (Table 1): four factorial design points (±1), four star points (±1.414), and three central points (0). The repetition of the central point was used to determine the experimental error, which was assumed to be constant along the experimental domain. The experiments were performed randomly in order to avoid systematic errors.

The experimental data was fitted to 3-dimensional response surfaces as a function of drying inlet temperature (X_1; °C) and arabic gum or inulin concentration (X_2; %). These surfaces were described by a second order polynomial equation, using decoded variables, as follows:

$$Y_i = b_0 + b_1X_1 + b_2X_2 + b_{11}{X_1}^2 + b_{22}{X_2}^2 + b_{12}X_1X_2, \quad (1)$$

where Y_i corresponds to the response variables (total AA, EE, DY, and LC); X_1 and X_2 represent the coded independent variables; b0 is the interception; and b_i, b_j, and b_{ij} (i,j = 1,2) are the linear, quadratic, and interaction coefficients, respectively. The adequacy of the model to the experimental data was verified by applying the ANOVA and the coefficient of determination (R^2) and adjusted R^2 ($R_{adj}{}^2$) [18]. The statistical analysis was carried out using "StatisticTM" software version 7 (Statsoft, Tulsa, OK, USA, 2007).

2.6. Analytical Methods

In order to assess its AA and the concentrations of lycopene an β-carotene, the concentrated extract was diluted into a 1:1 acetonitrile:dichloromethane (ACN:DCM) solution 0.1% (m/v). All analytical measurements were carried out in triplicate.

2.6.1. Carotenoids Content in the Tomato Pomace Extract

The concentration of lycopene and β-carotene in the tomato pomace extract was quantified by HPLC, using an UltiMate-3000 HPLC system (Dionex, Germering, Germany, 2007) equipped with an oven at 30 °C. Carotenoid separation, identification, and quantification were performed using a reversed phase C18 5 μm, 120 Å (4.6 × 150 mm) column by a gradient elution of acetonitrile:water:tetraethylammonioum (900:100:1) as solvent A and ethyl acetate as solvent B. The elution started with a mixture of 75% solvent A and 25% solvent B. After 10.5 min, solvent A was decreased to 59% and, after 20.0 min, to 0%. At 21 min, solvent A returned to the initial condition (75%), remaining constant up to 31 min. The flow rate was 1 $mL.min^{-1}$, and the running time was 31 min. The injection volume of the samples was 20 μL. The identification of carotenoids was based on their retention time of a peak compared with the carotenoids' standards. Calibration curves were carried out using standard lycopene and β-carotene with different concentrations (1–10 $mg.L^{-1}$), using a 1:1 ACN:DCM solution as the solvent. Detection was carried out with a DAD-3000 diode array detector with a wavelength of 475 and 472 nm for lycopene and 440 nm for β-carotene. The amount of β-carotene and lycopene in the samples was expressed as $mg.g_{extract}{}^{-1}$.

2.6.2. Antioxidant Activity

The total AA of samples was evaluated by radical scavenging activity assessment expressed as Trolox Equivalent Antioxidant Capacity (TEAC). An ABTS stock solution was prepared by dissolving ABTS in water at a 7 mM concentration. An ABTS+ solution was produced by reaction of 5 mL of ABTS stock solution and 88 μL of a 140 mM potassium persulfate ($K_2S_2O_8$) solution, to give a final concentration of 2.45 mM. This solution was kept in a dark room at room temperature for 12–16 h. Before analysis, the ABTS+ solution was diluted with ethanol to obtain an initial absorbance value of 0.70 ± 0.05 at 734 nm.

For evaluation of the AA of the tomato pomace extract itself, a volume of 30 μL of diluted extract with the ACN:DCM solution was mixed with 3000 μL of the $ABTS^+$ solution, followed by incubation for 6 min in the dark. Then, the absorbance was measured in a spectrophotometer (Unicam, UV/Vis Spectrometer – UV4, Alva, United Kingdom, 2002) at a wavelength of 734 nm. A calibration curve was performed using Trolox as the standard antioxidant, at the concentration range of 250–2000 μM in ethanol.

2.7. Spray Drying and Microparticles' Characterization

2.7.1. Drying Yield

DY was determined gravimetrically, as the ratio of the mass of microparticles collected at the end of the spray drying process and the mass of solids contained in the feed solutions.

2.7.2. Morphological Characterization of Microparticles

The morphology of the particles obtained by spray drying was observed by SEM. The samples were coated with a mixture of gold (80%) and palladium (20%) in a vacuum chamber and analyzed using a Hitachi S2400 scanning microscope (Scotia, NY, United States, 2000) operated at 10kV with different magnifications (500× to 2000×). Particles size was measured by analyzing SEM images, using the image processing software ImageJ (National Institute of Health, USA, 2017).

2.7.3. Loading Capacity and Encapsulation Efficiency

For the determination of the concentration of the bioactive compounds present in the microparticles, the method described by Rocha et al. [19] was used, with some modifications. A mass of 50 mg of microparticles was added to 50 ml of a mixture of ACN and DCM (1:1). The suspension was homogenized with an Ultra-Turrax T25 (IKA, Germany, 2001) at 13,500 rpm during 3 min, in order to break the particles. After mixing, the suspension was placed in amber glass flasks and kept away from light for about 12 h at 5 °C. Afterwards, the suspension was filtered with a syringe filter (Nylon 25 mm diameter, pore size of 0.45 µm; Fisher Scientific, Hampton, New Hampshire, USA, 2016) into an HPLC vial. The concentration of bioactive compounds in the liquid phase was quantified by HPLC, the same method used for the tomato pomace extract. The LC of the particles was expressed as the mass of carotenoids per mass of particles.

The EE was calculated as by Rocha et al. [19], quantifying the ratio between the mass of carotenoids present in the collected microparticles and the carotenoids' mass initially present in the feed solution.

2.7.4. Antioxidant Activity of the Encapsulated Carotenoids

For the measurement of the AA of the encapsulated molecules, the microparticles' core material was previously extracted with of a 1:1 ACN:DCM, as described in the previous section. Afterwards, a volume of 800 µL of supernatant was mixed with 2200 µL of ABTS+ solution, followed by the steps described in Section 2.6.2 for the fresh extract.

3. Results and Discussion

3.1. Characterization of Tomato Pomace Extract

The concentration of lycopene and β-carotene in the tomato pomace extract was 34.45 ± 1.75 and 0.92 ± 0.04 mg.$g_{extract}^{-1}$, respectively, which corresponded to 14.21 mg lycopene.g^{-1}dry tomato pomace and 0.34 mg β-carotene.g^{-1}dry tomato pomace. In the assessment of AA with ABTS assays, the extract possessed 139.01 ± 4.73 µmol trolox.$g_{extract}^{-1}$, which represented 4.04 ± 0.14 µmol trolox.mg^{-1} lycopene.

The carotenoids' contents obtained in this study were higher than the results reported by Vági et al. [20], which also recovered the carotenoids of the seeds and skins by Soxhlet apparatus using ethanol as the solvent. They found amounts of lycopene and β-carotene of 0.703 and 0.034 mg.$g_{extract}^{-1}$, respectively. Also, Machmudah et al. [21] found that lycopene and β -carotene contents in the tomato by-product (skin/seed) extracted by chloroform Soxhlet extraction for 15 h, were 0.82 ± 0.02 and 1.51 ± 0.06 mg.g^{-1} dry tomato, respectively. The higher amount of lycopene observed in the present work was attributed to the fact that the tomato pomace used in this work was produced from selected tomato cultivars characterized by possessing lycopene high content.

3.2. Microparticles' Morphology

The size of the particles obtained by atomization is an important parameter due to its great influence on appearance, rehydration capacity, solubility, fluidity, and dispensability [22]. Furthermore, it is known that the diameter of the particles depends on various factors, such as the drying conditions, concentration, and viscosity of the encapsulated material and the wall material properties [14]. As examples, particle size distributions of particles dried at 155 °C are presented in Figure 1. They showed a diameter ranging from 0.69 to 26.51 µm and from 0.58 to 21.67 µm for the arabic gum and inulin particles, respectively, with about 45% of them having a diameter between 2.5 and 5 µm and 90% lower than 10 µm. It was not observed as a significant influence of temperature on particle size distribution for both inulin and arabic gum microcapsules. However, an increase in particle size was observed with the increase of the wall material concentration at the temperature of 155 °C. This behavior was clearer for arabic gum particles, as shown in Figure 1. The increased viscosity of the spray drying feed solution may explain this fact. According to Tontul and Topuz [23], the size of the

liquid droplet during atomization varies directly with the viscosity of the liquid at the constant speed of the atomizer, resulting in larger particles. These results are in agreement with other spray drying powders, such as β-carotene in arabic gum [24] and blackberry juice in maltodextrin [24,25].

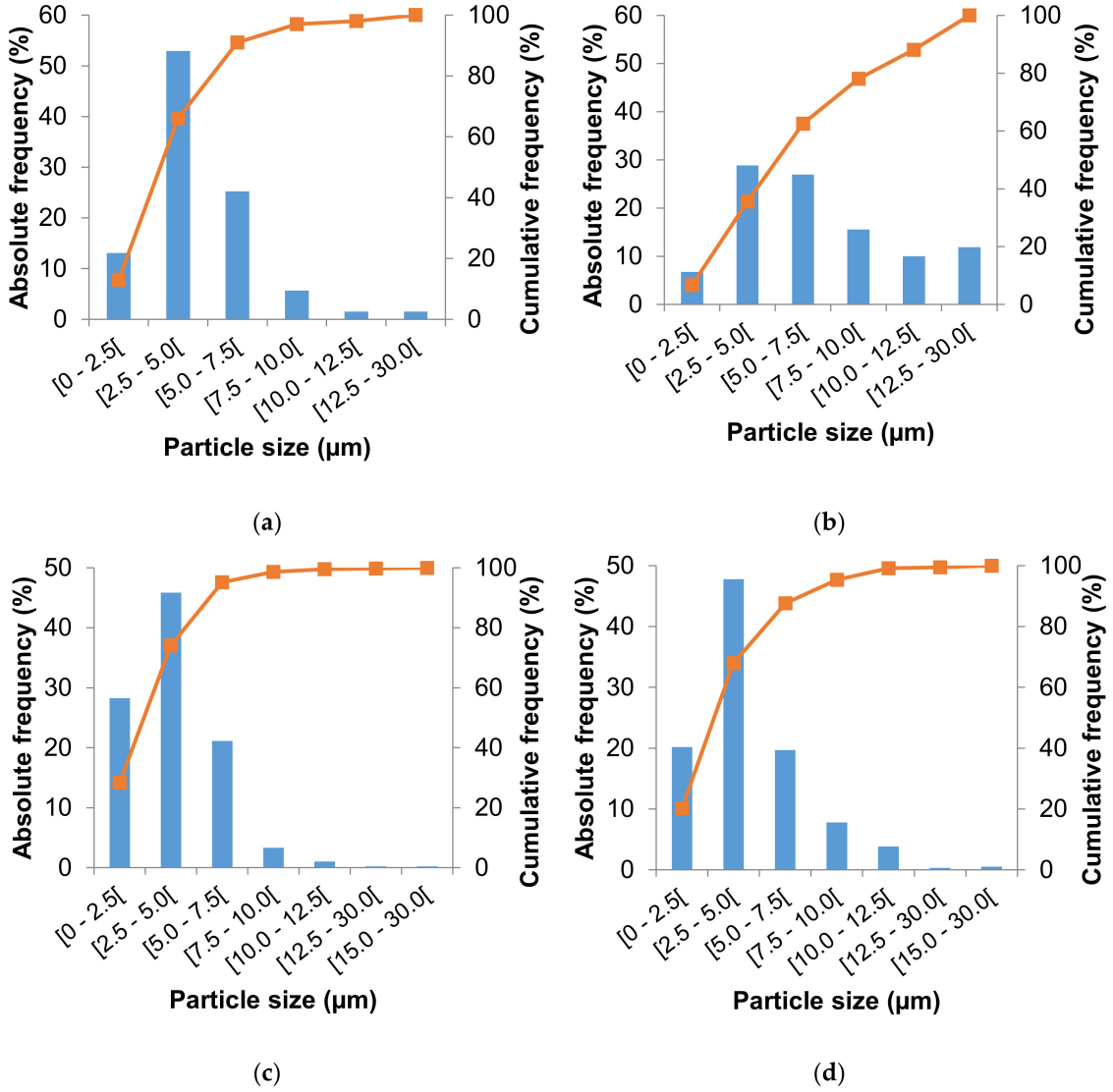


Figure 1. Relative frequency (Bars) and cumulative frequency (Line) equivalent to the diameter of microcapsules: (**a**) 5% AG, 155 °C; (**b**) 35% AG, 155 °C; (**c**) 5% inulin, 155 °C; (**d**) 35% inulin, 155 °C.

Particles collected from spray drying were in the category of skin-forming structures (microcapsules) (Figure 2). These structures are usually formed by fast heat transfer from drying air to feed droplets and water vapor transfer in the opposite direction. When the droplet water content reaches a critical value, the wall material forms a continuous network and a dry outer layer appears at the droplet surface. Afterwards, there is a decrease in the drying rate with the drying front progression that becomes dependent on the water diffusion rate through this layer. Drying is eventually finished when the microcapsule temperature becomes equal to that of the air.

In addition, the results on Figure 2 show that the arabic gum particles presented a different morphology when compared to the inulin ones. The majority of the inulin particles had a smooth outer surface, whereas the arabic gum particles showed the formation of teeth or concavities. However, for the same wall material, there was no difference amongst the particles obtained with different spray drying conditions.

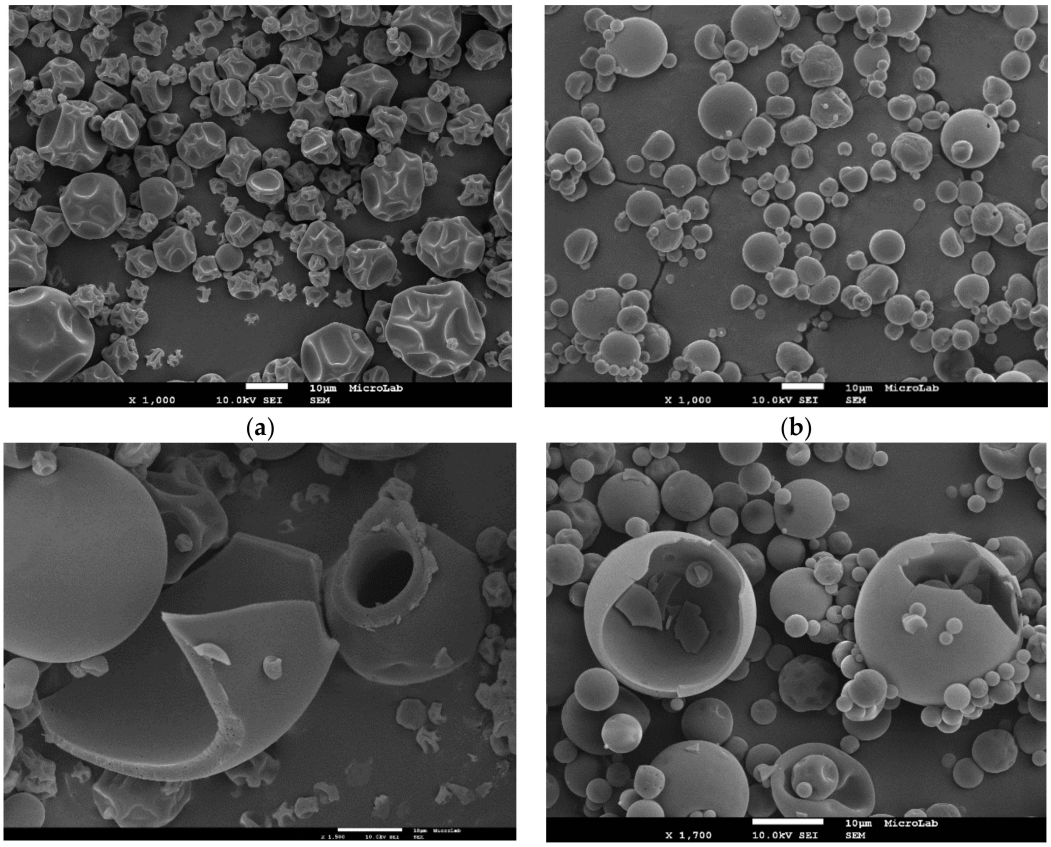


Figure 2. SEM images of microcapsules: (**a**,**c**) arabic gum (Magnification ×1000 and ×1500) and (**b**,**d**) inulin (Magnification ×1000 and ×1700).

This difference in morphology between wall materials may be related to a greater skin rigidity of inulin capsules compared to that of arabic gum, allowing the particles to dry without shrinkage [26]. These results are in agreement with Wilkowska et al. [27] that used two wall materials for the microencapsulation of different wine fruit by spray drying and observed that the inulin particles had a smooth spherical shape, while the particles of the other wall material, hydroxypropyl-β-cyclodextrin, had a spherical shape with wrinkled surfaces. Rocha et al. [19] in analyzing microcapsules using lycopene as the core material and modified food starch as wall material, also found microcapsules with the rounded outer surface showing teeth formation. The authors reported that the appearance of the teeth formed on the surface was due to the rapid evaporation of the liquid droplets during the spray drying process.

In Figure 2c,d, fragmented particles of inulin and arabic gum are depicted. The spray-dried particles were typically hollow, with the core material retained mainly within the wall. The presence of vacuoles was observed in the arabic gum particles throughout the wall where the core material was probably retained. As for the inulin particles, a compacted and homogeneous wall was observed. Aniesrani Delfiya et al. [28] also observed the presence of vacuoles along the entire length of the wall of arabic gum particles, where oleoresin was probably contained. Rocha et al. [19] microencapsulated lycopene using a modified starch and reported that the core material was evenly distributed throughout the wall material.

3.3. Response Variables of Experimental Design

Experimental results of response variables (LC, EE, AA, and DY) are shown in Table 1 for arabic gum and inulin, respectively. Table 2 shows the determination coefficients (R^2 and $R_{Adj}{}^2$) and the

linear and quadratic effects of the independent variables, as well as their interaction on responses for each studied dependent variable. High values for R^2 and $R_{adj}{}^2$ indicated a good fit to the data.

Table 2. Regression coefficients of second-order polynomial equations for each response variable.

Wall Material	Equation	R^2	$R_{Adj}{}^2$
Arabic gum	EE = 13.830 + 1.15306AG* + 0.0001AG^2 − 0.232T + 0.002T^{2*} − 0.009AG.T*	0.91	0.81
	DY = 158.789* − 1.564AG* + 0.01AG^2 − 1.359T* + 0.004T^{2*} + 0.002AG.T	0.93	0.87
Inulin	EE = −59.613 − 3.029In* + 0.023In2 + 1.291T* − 0.005T2* + 0.0127In.T	0.92	0.84
	DY = −25.960 + 1.682In* − 0.093In^{2*} + 0.677T* − 0.002T^{2*} + 0.008In.T	0.87	0.74
	LC = −4.715 − 0.448In* + 0.005In2 + 0.134T* − 0.001T^{2*} + 0.002In.T	0.86	0.72

In: Inulin; AG: Arabic gum; T: Temperature; *: Parameter affecting significantly the response variable, $p > 0.05$.

Experimental data fitted to 3-dimensional response surfaces as a function of drying inlet temperature (T; °C) and arabic gum or inulin concentrations (AG or In; %) are shown in Figure 3.

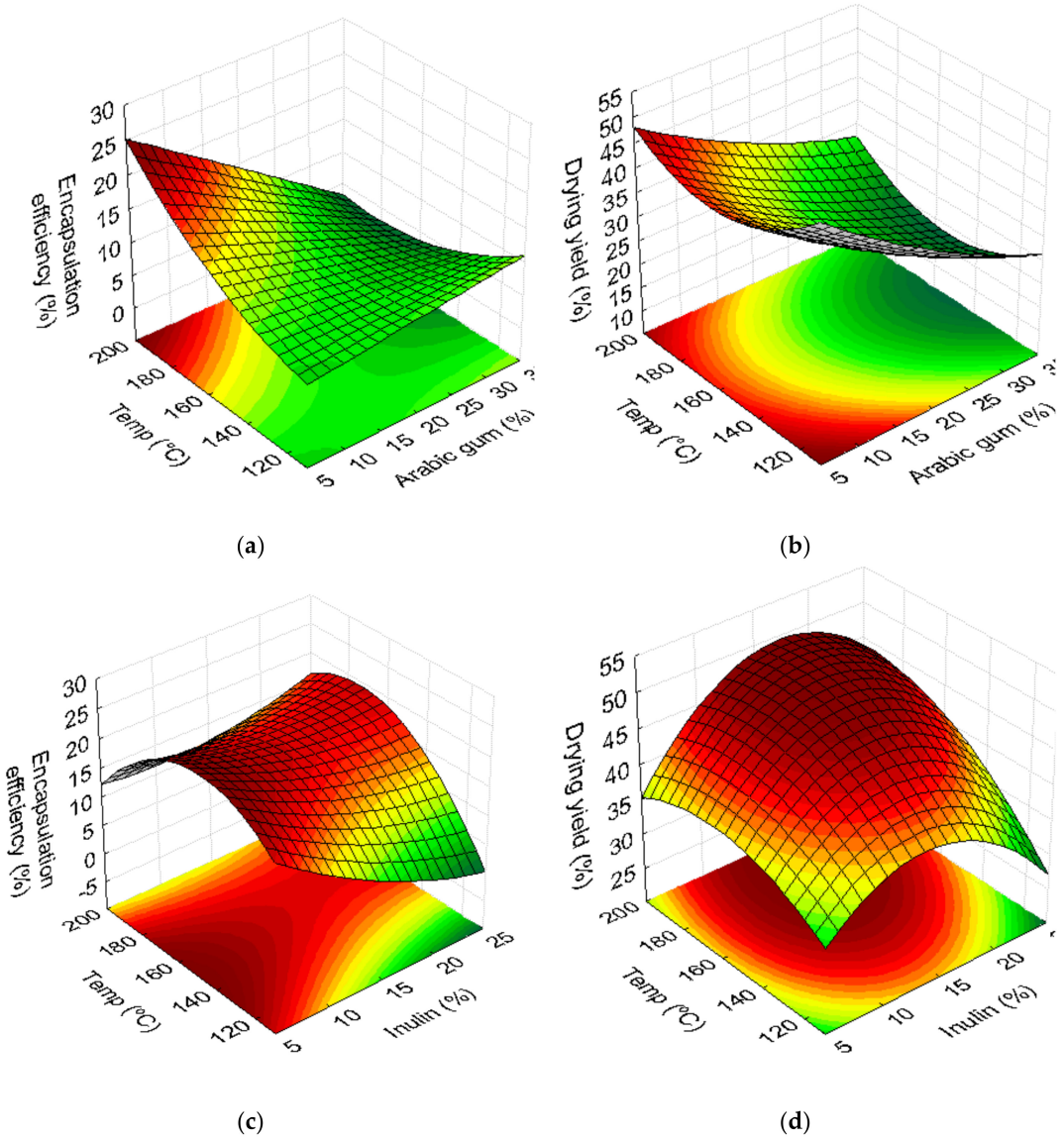


Figure 3. Response surfaces for EE and DY, (**a**,**b**) arabic gum; (**c**,**d**) inulin.

Second order polynomial models, describing those surfaces that have determination coefficients (R^2) higher than 0.70, indicating a good fit to the experimental data [29], are presented in the Table 2.

3.3.1. Encapsulation Efficiency and Loading Capacity

EE is a response variable of great importance in the encapsulation of bioactive compounds, since it indicates the number of bioactive compounds of the feed which, in fact, were encapsulated. According to Fernandes et al. [30], EE is strongly affected by the drying inlet temperature and type and concentration of wall material used. EE values of tomato pomace extract with arabic gum ranged between 3.4 and 20.5% (Table 1), whereas for encapsulation with inulin was slightly higher, ranging from 6.9 to 25.3% (Table 1). These results are in the range of those reported by Rocha et al. [19] for microencapsulation of lycopene in modified starch by atomization in spray drying (between 21.0 and 29.7%) and by Fernandes et al. [30] for the microencapsulation of ginger essential oil using cashew gum as the main wall material and inulin as secondary material (15.8% for the 1:3 mixture of cashew gum and inulin).

For both arabic gum and inulin microparticles, a good fit of Equation 1 to EE experimental data was achieved, with a coefficient of determination (R^2) of 0.91 and 0.92, respectively (Table 2).

The response surfaces are presented in Figure 3a,c. As can be seen, the increase in drying temperature led generally to an increase in the EE in the entire concentration range studied for both wall materials. In the case of arabic gum, EE increased for drying temperature values up to 200 °C. However, with inulin, EE increased when the temperature increased from 110 to 155 °C, but for a further increase up to 200 °C, a decrease of EE was observed. This fact may be due to the effect of air inlet temperature on particle formation that depends on the wall material. High temperatures lead to a fast evaporation of water from the surface of the particle, which results in rapid formation of the surface crust. The formation of this crust protects the bioactive compound during the drying process. Though, for some materials, in the present work, inulin inlet temperatures above a specific value may cause fissures, pores, and broken particles to a larger extent, resulting in the loss of the bioactive compounds and, consequently, reducing EE [31,32].

Regarding the effect of wall material concentration on EE, the surface responses indicated that for both inulin and arabic gum, a decrease of biopolymer concentration led to an increase in the amount of core material encapsulated. This fact may be attributed to the lower viscosity of the feed, which led to a higher water evaporation rate from the liquid droplets with consequent faster dried particles formation.

LC is defined as the number of bioactive compounds, in this study expressed as lycopene, which, in fact, is within the particles produced. LC values ranged from 1.15 to 2.10 mg lycopene.g^{-1} particles and between 0.87 and 3.08 mg lycopene.g^{-1} particles, for arabic gum and inulin, respectively. Overall, the particles obtained with the highest lycopene content were those produced with 9.4% arabic gum at 186.8 °C and with 5% inulin at 155 °C.

The values of LC with arabic gum were not successfully fitted to the second order model. Though, from Table 1, for both wall materials, LC tends to follow a similar trend as EE in what concerns the effect of wall material concentration and drying temperature, the latter up to 155 °C.

Murali et al. [33] studied the microencapsulation of black carrot using tapioca starch, arabic gum, and maltodextrin as wall material and indicated a greater loss of anthocyanins content of the particles obtained for each wall material by increasing the drying inlet temperature.Kha et al. [34] also indicated that the increase in input drying temperature and maltodextrin concentration (wall material) led to the reduction of both the LC and EE in the microencapsulation of bioactives of the gac fruit. In both works this behavior was attributed to thermal degradation and oxidation of the bioactives. Similar to the present work, Quek et al. [35] observed lower LC values of lycopene and total carotenoids with increasing concentration of maltodextrin, upon encapsulation of watermelon juice.

3.3.2. Drying Yield

The yield of microparticles depends both on the type and concentration of the wall material and also on the configuration of the equipment, inlet air temperature, feed temperature, and feed flow rate used for encapsulation [36]. Losses in the recovery of the microparticles in the spray drying process may be due to deposition of the powder on the wall of the drying chamber or cyclone. In this study, this behavior was observed mainly for the trials with higher concentration of the wall material. A similar observation was also reported by several authors. For example, according to Santana et al. [37], the retention of the product in the wall of the dryer or cyclone, for long time, is undesirable as it affects the quality of the product. Due to a more intense heat treatment, this product accumulated on the surface of the drying chamber may have different properties, such as solubility, color, or moisture content.

DYs of tomato pomace extract with arabic gum ranged between 14.7 and 44.0%, and the highest DY values were obtained with 9.4% of arabic gum at a drying temperature of 123.2 °C (Table 1). With inulin as wall material, DYs were higher, ranging from 34.9 to 49.5%, with the highest value obtained for the inulin concentration of 22.1% and drying temperature of 186.8 °C (Table 1). Other researchers have also found values of DY lower than 60%. Nunes and Mercadante [36] found an average DY of 51% when encapsulating lycopene crystals with a mixture of arabic gum and sucrose. In addition, Santana et al. [37], who studied the microencapsulation of pequi pulp extract by spray drying using arabic gum as the encapsulating agent, found DY values that ranged from 25.8 to 56.1%.

A second order model was fitted to the experimental data of the DY for both the arabic gum and inulin assays. ANOVA showed that a satisfactory adjustment was obtained, since the coefficient of determination was acceptable ($R^2 > 0.7$), and the value of the lack of fit was not significant ($P > 0.05$) for a confidence level of 95%. Figure 3b,d show the surface response relative to the DY for the arabic gum and inulin assays, respectively.

As shown in Table 2, the drying inlet temperature had a significant positive effect on the DY in both inulin and arabic gum assays. The increase of the drying inlet temperature resulted in the increase of the DY. This behavior can be attributed to higher heat and mass transfer processes at higher temperatures, leading to the increase of the water evaporation rate. On the other hand, the concentration of the wall material showed a significant negative effect on the DY, that is, increasing the concentration of arabic gum or inulin decreased the DY. Again, a lower water evaporation rate in droplets of emulsions with a higher viscosity was envisaged. These results are in agreement with Santana et al [37] and Tonon et al. [38] upon microencapsulation of pequi pulp extract and açai pulp, respectively.

3.3.3. Antioxidant Activity

The AA values of encapsulated tomato pomace extract with arabic gum ranged from 0.9 to 4.6 μmol trolox.mg^{-1} lycopene, whereas that with inulin particles varied between 1.0 and 3.5 μmol trolox.mg^{-1} lycopene. These results showed a loss of AA after encapsulation ranging from 0 to 77.7% and from 13.4 to 75.2% for arabic gum and inulin particles (Table 1), respectively. Similarly, Simon-Brown et al. [39] observed the loss of approximately 72% of AA when encapsulating the ginger extract with maltodextrin and arabic gum by spray drying. This decrease is attributed mainly to the exposure of the feed solution to inevitable environmental factors, such as oxygen and light, during the spray drying process.

The second order model did not fit the AA experimental data obtained for both arabic gum and inulin particles, since a coefficient of determination below 0.70 was observed. Nevertheless, looking at Table 1, the value of AA of bioactives encapsulated in arabic gum particles tended to increase with increasing drying temperature, for the same wall material concentration. This might have been due to the formation of a rapid crust on the surface protecting the bioactive compounds from degradation. Though, the results obtained for the inulin particles (Table 1) showed that AA values tended to decrease with increasing drying temperature in most cases. For example, with 15% inulin, the AA decreased

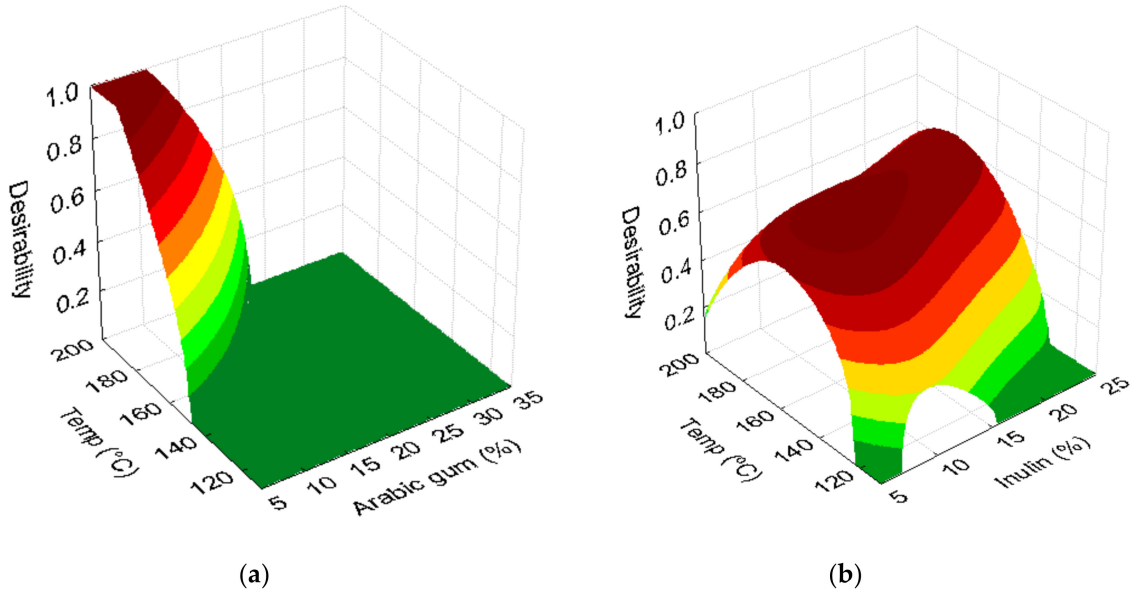
from around 2.6 to 1.4 μmol trolox.mg^{-1} lycopene, and from 3.2 to 1.4 μmol trolox.mg^{-1} lycopene, when the temperature was changed from 155 to 200 °C and from 110 to 200 °C, respectively.

Regarding the effect of wall material concentration on AA, from Table 1, a decrease of AA when increasing the biopolymer content on the feed was envisaged. In fact, for a fixed drying temperature of 155 °C, increasing the arabic gum concentration from 5% to 35% led to an AA decrease from 4.5 to 0.9 μmol trolox.mg^{-1} lycopene. In the case of inulin, increasing its concentration from 5% to 25% led to an AA decrease from 3.5 to 2.1 μmol trolox.mg^{-1} lycopene. These results are in line with those reported above for the variation of EE and LC with wall material concentration, and might be related to lower droplets drying rates occurring when the feed viscosity is higher.

3.4. Spray Drying Process Analysis

The most suitable conditions for the production of tomato pomace extract loaded microcapsules by spray drying were determined by taking into account the maximum value of the response variables, within the range values of the independent variables studied. The multicriteria methodology was used to find an optimal point for taking into account the different responses studied at the same time. The desirability function is the most current multicriteria methodology used in optimization processes that contains several responses. In the desirability function, each response obtained under the operating conditions was transformed into a dimensionless desirability scale ranging from 0 (fully undesirable response) to 1 (totally desired response) [40].

The desirability function was employed for the simultaneous analysis of the responses, and the response variables values considered as the most suitable were the ones leading to desirability values above 0.7 [41]. To obtain microcapsules under the ideal conditions for each wall material studied, namely arabic gum and inulin, only the variable responses that presented a good fit to the experimental model were considered. For arabic gum particles, EE and DY responses were simultaneously analyzed, and for inulin particles, EE, DY, and LC responses were used. The desirability surface curves are shown in Figure 4.



(**a**) (**b**)

Figure 4. Desirability surface curves for optimal conditions: (**a**) Using EE and DY for arabic gum assays; (**b**) using EE, LC, and DY for inulin assays.

The most suitable condition found for the inlet drying temperature was 200 and 160 °C for arabic gum and inulin, respectively. Concerning the most suitable value of the wall material concentration, a concentration of 10% was estimated for both inulin and arabic gum. Under these conditions, the predicted EE and DY were 21.5% and 43.3%, respectively, for arabic gum

particles. Also, the predicted EE, DY, and LC for inulin particles were 21.2%, 45.9%, and 2.5 mg lycopene.g^{-1}particles, respectively.

4. Conclusions

In this study, an ethanolic tomato pomace extract was successfully encapsulated by spray drying, using arabic gum and inulin as wall materials. Both wall materials enabled the formation of microparticles loaded with tomato pomace carotenoids, mostly lycopene. However, the particles' morphology, the carotenoids loading, and the AA of the encapsulated material were quite dependent on the wall material used. Furthermore, from the study of the effect of the spray drying conditions (inlet drying temperature and biopolymer concentration of the feed) for each wall material, the ones that enabled the better performance, not only in terms of carotenoids loading but also in terms of DY and EE, were a wall material concentration of 10% and drying temperatures of 160 and 200 °C for inulin and arabic gum, respectively.

Overall, arabic gum and inulin presented good potential for encapsulation of tomato pomace extract by spray drying, originating loaded microcapsules with different properties, and envisaging their application in food formulations with diverse physical and chemical characteristics.

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