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Influence of spray-drying operating conditions on sunflower oil powder qualities

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ABSTRACT

The main aim of the study was to develop a vegetable oil (VO) microencapsulation process using a spray drying technique with the aid of the response surface methodology (RSM). The specific objectives were to evaluate the operating condition effect on VO powder qualities and analyze the microstructure and rancidity on VO microcapsules obtained under set conditions that lead to high solid yields. Maltodextrin and hydroxypropylmethylcellulose were used as wall materials. The influence of spray drying process variables over solid yield (SY), moisture content (MC), surface oil (SO) and encapsulation efficiency (EE) was studied. All experiments led to high values of EE, while SY and MC were significantly affected by modifying spray drier conditions, allowing the enhancement of SY when the optimization process was applied. The optimized VO microcapsules presented an external surface with a continuous wall and no apparent pores; with low moisture content, high VO content retained into microcapsules and low peroxide value.

1. Introduction

Unsaturated fatty acids (UFA) (omega-3, omega-6 and omega-9) are essential fatty acids commonly found in marine and vegetable oils (VO). They are nutritionally important for good health and are especially beneficial for individuals suffering from coronary heart disease, diabetes, and immune response disorders [1,2]. For this reason, the use of these fatty acids in health food formulations was increased in the last years. Nevertheless, the susceptibility of UFA to oxidative degradation during food processing and storage is always a concern. Fatty acids are chemically unstable in the presence of oxygen, light, moisture and heat. Microencapsulation of oils in polymeric matrices has been used in order to protect UFA against oxidative degradation [3,4]. The efficiency of protection or controlled release of the core material mainly depends on the composition and structure of the wall material [5,6]. However, the operating conditions (temperature, pH, pressure, humidity) employed during the encapsulation process may strongly affect the encapsulation efficiency, the stability of microcapsules and the shelf-life of the core material. Biopolymer blends have been successfully used as wall materials [7,8]. Among them, carbohydrates have showed to improve the yield and efficiency of microencapsulation [9,10]. Lactose, sucrose, cellulose, maltose, maltodextrins, cyclodextrins and gums are the most commonly used [11]. Kolanowski et al. [12] and Davidov-Pardo et al. [13] have reported that the use of modified celluloses, such as methylcellulose and hydroxypropyl methylcellulose improves the stability, encapsulation efficiency and morphology of fish oil powders obtained by spray drying. Several researches also indicate that maltodextrins have protective effects on microencapsulated oils [14,3]. The use of maltodextrin has several advantages such as low viscosity, good solubility and low cost [15,16].

Spray drying involves the atomization of emulsions into a drying medium with high temperature which leads to very fast water evaporation, resulting in quick crust formation and quasi-instantaneous entrapment of the core material [3,16,17]. The advantages of this method are its ability to handle heat-sensitive materials, its availability of machinery and its variety, its good keeping qualities of microcapsules, a variety of particle sizes that can be produced and an excellent dispensability of particles in aqueous media. The disadvantage of this technology is the high temperature conditions necessary for drying and access of air [18]. Spray drying technology requires well-adjusted operating conditions as well as adequate composition of the solution that contains the active compounds. The former include factors such as inlet air temperature, atomization airflow, liquid flow rate, aspirator suction velocity and solid concentration, among others [19]. The response surface methodology (RSM) is a statistical analysis tool that predicts appropriate levels of independent variables for optimizing response variables. Factorial designs are frequently used in experiments involving several factors where it is necessary to study the joint effect of the factors on a response. In this study, RSM was applied to obtain a high solid yield of sunflower oil microcapsules by using a spray drying process. The specific objectives of the work were to evaluate the influence of operating

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conditions on VO powder qualities and analyze the microstructure and rancidity in the optimized VO microcapsules.

2. Materials and methods

2.1. Materials

Sunflower (*Helianthus annuus*) oil (Natura, AGD, Córdoba, Argentina), certified as organic product, was used as a model of VO for microencapsulation experiments. This VO was rich in polyunsaturated essential fatty acids (64%) and monounsaturated fatty acids (26%). Hydroxypropyl methylcellulose (HPMC, Methocel K99, Ciclo Química, Argentina) and maltodextrin (MD, DE15, Distribuidora Nicco, Argentina) were used as wall materials. Soya lecithin (food grade, Distribuidora Nicco, Argentina) was used as emulsifying agent.

2.2. Spray drying emulsion preparation

A suspension of MD/HPMC was prepared as follow: MD (6%) was dissolved in distilled water at room temperature; HPMC (3%) was slowly added, the whole mixture was blended for 5 min using a typical kitchen mixer at 200 r.p.m. (Philips, China), and it was stored for 24 h at 4 °C. For the emulsion preparation, a blend of soybean lecithin (0.15%) and sunflower oil was incorporated to the MD/HPMC/water suspension at a ratio of 2:1 (MD/HPMC:sunflower oil), by using an Ultraturrax T18 homogenizer at 18000 r.p.m. for 10 min at 10 °C. The obtained emulsion (200 mL) was stored at 4 °C until use.

2.3. Emulsion viscosity

Emulsion viscosity was measured at 10 °C by means of steady-shear flow curves (shear stress × shear rate), using a controlled stress Physica MCR301 rheometer (Anton Paar, Graz, Austria) with stainless steel plate–plate geometry (25 mm in diameter and 2 mm in gap). Three flow ramps (up, down and up-cycles) were obtained in a range of shear stress corresponding to shear rates from 0 to 100 s^{-1}, in order to eliminate any possible thixotropic effect. Trials were performed in triplicate by using a new sample for each repetition. Rheograms were analyzed according to empirical models and viscosity was calculated as the relationship between shear stress and shear rate.

2.4. Spray drying and experimental design

The spray drying process was performed by using a laboratory-scale Mini Spray Dryer (Büchi B-290, Büchi Labortechnik AG). A two-fluid nozzle with a cap orifice diameter of 0.5 mm was used. Air atomizing pressure was kept constant at 6 bars for all the experiments.

The following parameters were selected as independent variables: (A) drying air inlet temperature, (B) atomization air volumetric flow rate, (C) feed volumetric flow rate, and (D) drying air volumetric flow rate. Table 1 summarizes the levels of the operating variables which were selected on the basis of what was recommended for the experimental unit [20], and from several trial experiments [19].

Experiments were planned applying a ratable central composite design (response surface methodology, RSM, Statgraphics plus 5.0) with four factors and five levels (2^{-4} design) to assess the effect of the operating variables on the responses: solid yield (SY, percentage of solid material recovered in the dryer), surface oil (SO, percentage of VO on the microcapsules surface), encapsulation efficiency (EE, percentage of VO present into the microcapsules) and moisture content (MC, moisture content on SY). All experimental runs were performed in randomized order to eliminate any possible sources of bias. Four replicates were made at the center point of design to allow the estimation of the pure error at the sum of the square. The experiment design is shown in Table 2.

Results were analyzed by a multiple regression method. The quality of the models' fitness was evaluated by ANOVA (Statgraphics plus 5.0, USA). The experimental results were applied to obtain the regression models. The fit of each model to the experimental data was given by the determination coefficient (R^2) which explains the extent of the variance in a modeled variable that can be understood with the model. Multiple regression equations included only significant coefficients ($p < 0.05$). Only models with high determination coefficients were included in this study. Three-dimensional response surface plots were generated for each response variable.

Calculation of the optimal processing conditions for the solid yield production was performed using a multiple response method called desirability [21]. This optimization method incorporates desires and priorities for each of the variables.

2.5. Powder analysis

2.5.1. Solid yield (SY)

It was calculated as the ratio of the powder weight collected after every spray drying experiment to the initial amount of solids in the sprayed dispersion volume (g of solid in 200 mL of emulsion).

Table 1
Process variables levels.

Parameter independent formulation	Low (−)	High (+)	Units
A (air inlet temperature)	130	200	°C
B (atomization air flow rate)	400	800	L/h
C (pump setting)	5	15	%
D (aspirator setting)	80	100	%

Table 2
Experimental matrix according to a 2^{-4} central composite design and studied responses.

Run	A	B	C	D	MC*	SY*	SO*	EE*
1[a]	165	600	10	90	3.95	23.47	20.22	79.78
2	200	400	15	80	3.24	33.69	25.66	74.34
3	200	800	15	80	4.31	15.04	22.62	77.38
4	200	400	5	100	2.96	39.34	22.13	77.87
5	130	800	15	80	4.86	9.00	19.09	80.91
6[a]	165	600	10	90	3.73	23.41	16.31	83.69
7	165	600	2	90	3.56	20.17	19.42	80.58
8	200	800	15	100	3.47	26.13	23.65	76.35
9	130	400	5	100	2.35	38.95	18.18	81.82
10	130	400	5	80	2.55	29.41	24.46	75.54
11	130	800	5	80	3.97	10.30	13.93	86.07
12	130	400	15	100	3.88	27.35	26.87	73.13
13	200	800	5	80	3.88	5.44	15.68	84.32
14	200	800	5	100	3.21	17.87	20.99	79.01
15	165	279	10	90	2.93	38.68	22.90	77.10
16	165	600	18	90	4.67	19.91	22.62	77.38
17	109	600	10	90	4.12	22.03	18.73	81.27
18	130	800	5	100	4.78	23.07	21.02	78.98
19	200	400	15	100	3.18	39.88	17.75	82.25
20	130	800	15	100	4.41	18.51	17.45	82.55
21	130	400	15	80	4.63	21.76	18.69	81.31
22[a]	165	600	10	90	3.09	25.56	16.37	83.63
23	221	600	10	90	2.63	28.63	15.44	84.56
24	165	600	10	74	3.14	15.42	13.70	86.30
25	165	600	10	106	3.27	33.21	16.16	83.84
26[a]	165	600	10	90	3.41	25.44	13.00	87.00
27	200	400	5	80	2.71	33.05	25.69	74.31
28	165	921	10	90	3.94	10.90	17.60	82.40

A: Drying air inlet temperature. B: Atomization air volumetric flow rate. C: Feed volumetric flow rate. D: Drying air volumetric flow rate.

[a] Central point.

* Experimental responses: MC (moisture content, %); SY (solid yield, %); SO (surface oil, %); EE (encapsulation efficiency, %).

2.5.2. Surface oil (SO) and encapsulation efficiency (EE)

The SO was measured on 500 mg of powder contained in a filter paper, at room temperature, by adding twice 30 mL of petroleum ether for 2 min and 30 s, respectively. The solution containing the extracted oil was transferred to a clean flask, which was left to evaporate and then was dried at 60 °C until constant weight was reached. The SO weight was calculated based on the difference between that of the clean flask and that of the flask containing the extracted oil residue. Total oil was assumed to be equal to the initial oil, since preliminary tests revealed that all the initial oil was retained.

The EE was obtained by indirect measurement from VO-retention level in the powders, and was calculated by means of the following equation:

$$EE = (TO - SO)/TO * 100$$

where TO is the total oil content and SO is the surface oil content.

2.5.3. Moisture content (MC)

Powder MC was determined by a moisture analyzer with halogen heating (model M45, OHAUS). Sample moisture content analysis was performed immediately after the spray drying step.

2.5.4. Particle morphology

Particle morphology was evaluated by scanning electron microscopy (SEM). Powders were attached to a double-sided adhesive tape mounted on SEM stubs, coated with 3–5 mA gold/palladium under vacuum and examined with a FEG SEM scanning electron microscope (Carl Zeiss — Sigma, Germany).

2.5.5. Peroxide value (PV)

In order to evaluate the rancidity of VO after the microencapsulation process, the PV of optimized powder was determined after the spray drying step by means of the method used by Kolanowski et al. [12] with minimal modifications. A powder sample of 2.0 g was dissolved in 7 mL chloroform. Immediately, 10 mL glacial acetic acid was added, and the mixture was stirred for a few seconds to ensure mixing. After addition of 0.5 mL saturated potassium iodide solution, the mixture was kept 1 min under darkness. Immediately, 30 mL purified H_2O were added and the mixture was titrated with 0.01 N $Na_2S_2O_3$ using starch solution (1%) as an indicator. As control system, 2.0 g of VO without encapsulation was treated in the same way as the VO powders.

2.5.6. Statistical analysis

Both surface oil and peroxide value analysis were carried out in triplicate, while for moisture content trials were made in duplicate. The data obtained were statistically treated by variance analysis, while the means were compared by the Fisher LSD test at a significance level of 0.05. In both cases the INFOSTAT statistical software (Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba, Argentina) was used.

3. Results and discussion

3.1. Statistical evaluation of the experimental design

3.1.1. Solid yield

The global yield of the microencapsulation process could be improved by changing spray drying conditions in order to decrease particle sticking to the dryer chamber surfaces. Table 2 shows the yields, based on the collected powder, achieved for each experiment. The lowest yield was for test 13 (5.44%) while the highest one was for the experiment 19 (39.88%). All significant linear effects and two-factor interactions on SY are reported in Table 3. On the one hand, air inlet temperatures (A) and aspirator settings (D) had positive linear effects on SY, as shown by the significant coefficients (Table 3), while the opposite effect was obtained from atomization air flow rate (B). On the other hand, the two-factor interactions were AA, AB, AC, BC, BD and CC.

Table 3
Significant coefficients (95% confidence interval) of the design of the regression fitting model for the powder characteristics.

Factor	SY (%)	MC (%)	SO (%)	EE (%)
Constant	91.3	−14.2	43.8	−95.3
A	0.262	−0.034	ns	ns
B	−0.081	0.006	ns	ns
C	ns	0.407	ns	ns
D	0.569	ns	ns	ns
AA	0.97×10^{-3}	ns	ns	ns
AB	-0.22×10^{-3}	ns	ns	ns
AC	0.016	ns	ns	ns
AD	ns	ns	ns	−0.006
BC	0.002	ns	ns	ns
BD	0.57×10^{-3}	ns	ns	ns
CC	−0.048	0.009	ns	−0.078
R^2	0.99	0.84	0.95	0.66

ns: No significant effect at level < 5%, R^2: adjusted square coefficient of the fitting mode (indicates the percentage of variability for which the model accounts).

The main effect plot showed that high A and D values improved SY; while high B values decreased it (Fig. 1). Positive and negative quadratic effects of interactions between operating variables indicated that they had optimum values from which SY increased and decreased, respectively.

High air inlet temperatures increased water evaporation, which in turn increased the amount of dried powder produced. Tonon et al. [22] informed that inlet air temperature had significant effects on the process yield of spray drying of *Euterpe oleraceae* extract. Gallo et al. [19] showed that the most significant main factors on the spray drying yield of *Rhamnus purshiana* extract were aspiration, pump setting and air inlet temperature. They found that higher aspiration values led to a better separation rate in the cyclone, higher thermal levels in the spray chamber, and higher drag forces, which improved the process yield. Also, at low pump rates, water loading was almost completely evaporated decreasing the probability of particle adhesion on the chamber walls and, thus, giving better process yields.

The influence of the processing variables on the collected powder is well-defined by the wide range of powder yield values obtained on the experimental design. In spite of the fact that solid yield was improved due to the changes of A, B and D parameters, the values were at the limit of what is acceptable for lab-scale spray dryers. Similar results were reported by Gallardo et al. [6], who observed a very low yield on linseed oil microencapsulated which had methylcellulose and maltodextrin as coating material. These researches argued that their observation could be a consequence of the different nature of the oil or some small variations in the preparation procedure, comparing with previous results obtained for fish oil encapsulated with the mixture methylcellulose/maltodextrin in similar conditions [13].

3.1.2. Surface oil (SO) and encapsulation efficiency (EE)

The SO parameter did not change as a consequence of process variable combination (Table 3). All experiments showed low values of VO on microcapsule surface (Table 2). These results led to a high EE% of VO in MD/HPMC matrix. According to Table 2, EE% varied from 73.13% to 87.00% which can be considered an adequate level for oil powders. Encapsulation efficiency determines the grade of oil protection and is dependent on many factors, among which the nature of encapsulated material, composition of the blend coating material, homogeneity of dried slurry and spray drying parameters can be found. In spite of this, it is important to note that, in this work, the EE% was not significantly influenced by processing conditions as it was showed by the low R^2 value (0.66) (Table 3).

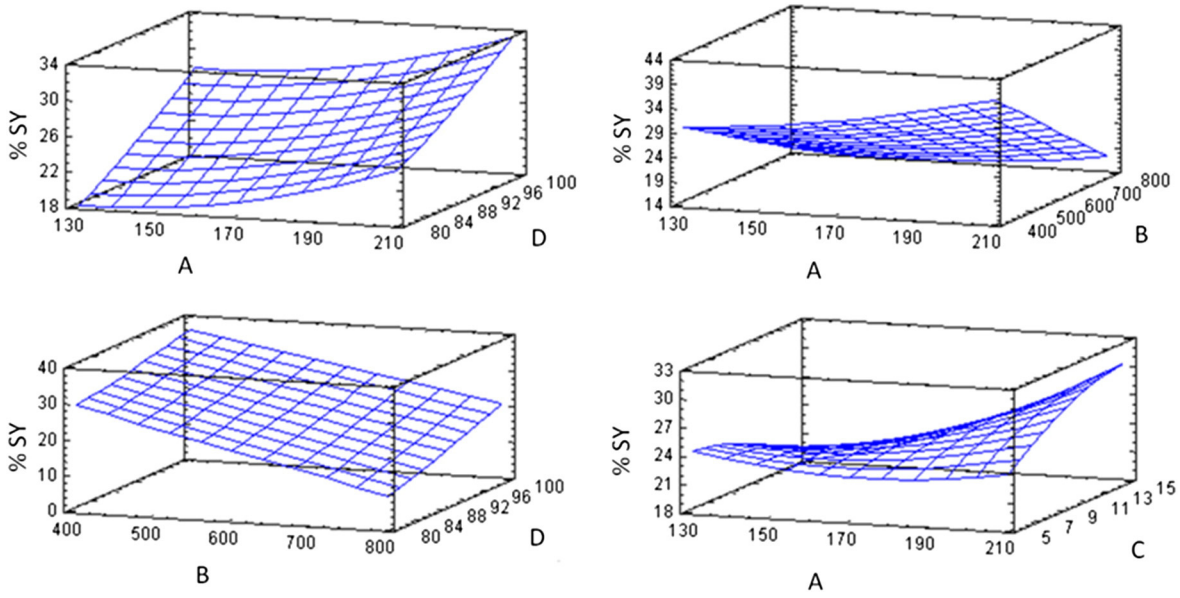

Fig. 1. Response surface plots for solid yield (SY). (A) Air inlet temperature, (B) atomization air flow, (C) pump setting, (D) aspiration setting.

Since the process variables did not affect the EE values, the high VO retained into microcapsules could be due to the nature of wall material and their mixtures and emulsion quality and stability. As stated before, several researches informed the good properties of MD and HPMC for encapsulated oils [12,13]. In this work, MD was mainly chosen as it provided good oxidative stability to encapsulated oil; however, as MD exhibited poor emulsifying capacity [16], HPMC was proposed as part of wall materials due to their good emulsifying properties and effective microencapsulation of oils [12,16]. Besides, lecithin was included in the formulation to assure the stability of feeding emulsions before spray drying [23]. Moreover, since microencapsulated VO was formulated with the aim to incorporate on foods, the selected wall material was a compromise between cost, easy manipulation, availability and effectiveness as protective materials.

The wall material to core ratio is another variable to consider. It is generally accepted that a wall material to core ratio between 2:1 and 4:1 (w/w) should be suitable for most applications. A ratio lower than 2 would probably lead to an unacceptable increase of surface oil, while a ratio higher than 4 would result in a powder with a very low oil content, which is not desirable for food applications [6]. In this work, the MD/HPMC:VO proportion was 2:1, selected according to previous studies [6,13]. Consequently, the good EE% was probably due to a combination of the nature of coating material and the adequate wall material to core ratio selected for VO microencapsulation.

The total solid content had a positive effect on the encapsulation efficiency. Higher solid content implies shorter time to form a crust, making the oil diffusion to the drying particle surface difficult [24]. Both the wall material used for oil microencapsulation and the total solid content have influence on the emulsion characteristics, mainly on viscosity. The MD/HPMC suspension was formulated with a solid percentage lower than 10% w/v since an increment of HPMC content means the increase of system viscosity. As stated before, the viscosity of emulsions was determined through steady-shear flow curves. The most appropriate mathematical model to describe the flow characteristics of the emulsion produced with VO and MD/HPMC was the Newton model, according to which viscosity is constant with shear rate, with a value of 0.2604 Pa·s, $R^2 = 0.9873$, Rheoplus software. Carneiro et al. [25] observed the same behavior in emulsions produced with flaxseed oil and maltodextrin in combination with other surface active biopolymers. However they informed lower viscosities (inferior to 0.1 Pa·s) compared to those observed in this work. Adhikari et al. [26] and Tonon et al., [22] evaluated the increment of viscosity of feed emulsion as a function of maltodextrin concentration. However, the higher viscosities (maltodextrin 40%) informed by these authors were half the viscosity value of MD/HPMC/VO obtained on this study. Therefore, MD exhibits a low viscosity even at concentrated solutions, which allows increasing the solid content of emulsions. Then, and due to the fact that vegetable oil incorporation decreases the emulsion viscosity [17,27], the high viscosity value of MD/HPMC/VO mixture was due to HPMC nature.

3.1.3. Moisture content

The MC was in the range of 2.35–4.86 wt.% (Table 2). Most of MC values obtained through the experimental design were under the minimum moisture specification of dried powder in the food industry which is between 3 and 4 g/100 g [28]. The moisture content of biopolymers may affect the accessibility of oxygen to the oil, thus, the low water contents are usually associated with low water activities, which might prevent lipid oxidation.

The MC variable was mainly affected by the drying air inlet temperature (A), atomization air flow rate (B) and pump setting (C) (Table 3). On the one hand, the main effect's plot showed that high values of B and C produced powders with the highest MC; while high values of A parameter decreased the MC of powders (Fig. 2). On the other hand, the significant quadratic effect of C variable indicated that pump setting had a value in which the MC is the lowest.

Bhandari et al. [14] reported a direct relationship between the viscosity of the feed emulsion and the moisture content of the drying powder. Taking into account that the viscosities of the emulsions used in this work were the same for all experiments, the drying inlet temperature and the powder moisture content were the independent variables of greater importance.

The effect of the increase of air inlet temperature on low moisture content of dried powder was informed in previous studies, which tested different core and wall materials by spray drying methodology [19,22,29]. The air inlet temperature is directly proportional to the microcapsule drying rate and the final water content. When the air inlet temperature is low, the low evaporation rate causes the formation of microcapsules with high-density membranes, high water content, poor fluidity, and ease of agglomeration. However, a high air inlet temperature causes an excessive evaporation and results in cracks in the

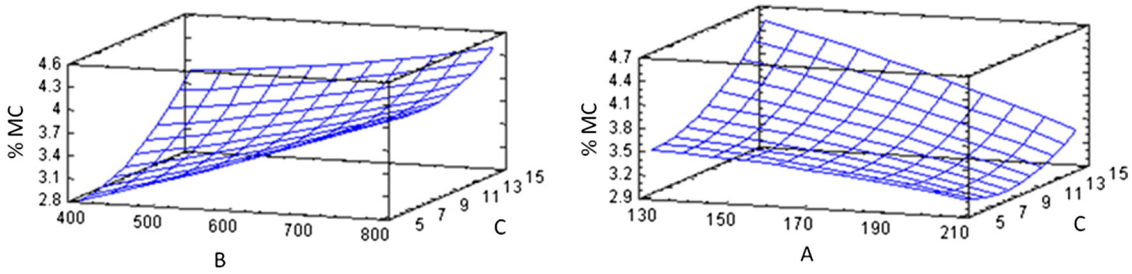

Fig. 2. Response surface plots for moisture content (MC). (A) Air inlet temperature, (B) atomization air flow, (C) pump setting.

membrane inducing subsequent premature release and a degradation of the encapsulated ingredient [16,30].

Other authors observed similar results when investigating the effect of air inlet temperature and pump rate on the final water content of spray drying powders. Tonon et al. [22] informed that the feed flow rate negatively affected the powder moisture content on açaí microcapsules. These researches reported that high flow rates imply in short contact time between the feed and the drying air, making the heat transfer less efficient and resulting in lower water evaporation. In addition, Hong and Choi [31] verified that the powder moisture content increased with increasing pump rate and with decreasing inlet air temperature on powder material from *Agaricus blazei* Murill.

3.2. Optimization

The best spray drying conditions are a compromise between high air temperature, high solid concentration of the solution, and easy pulverization and drying without expansion and cracks of final particles [32]. Other researches investigated the microencapsulation efficiency of microencapsulated sunflower oil with respect to sunflower oil concentration, proportion of milk protein isolates to coating wall, soy lecithin concentration and homogenizing pressure using response surface methodology [33].

Taking into account that unsaturated fatty acids ($\omega-3$, $\omega-6$ and $\omega-9$) are chemically unstable in the presence of oxygen, light, moisture and heat; the optimization procedure of multiple response was applied reducing the maximum value of the inlet air temperature (190 °C) in order to maximize the SY% and to preserve the oil chemical and sensorial quality. The optimized response suggested that a combination of A: 163 °C, B: 279 L/h, C: 10% and D: 100% would lead to SY of 41.94%. The results showed that no significant differences were found between the estimated value by the model and the experimental observed value for solid yield which suggested a good fit of the model to experimental data (Table 4).

3.2.1. Analysis of optimized powder

In order to determine the microcapsule quality, the efficiency on VO encapsulation, powder moisture content and oxidative stability of VO was analyzed. Table 5 shows the analytical characterization of VO microcapsules obtained according to the optimized response. Under these conditions, the powder characteristics did not changed with respect to the values observed for the MC, SO and EE on the original experimental design (Table 2). The MC value was near the minimum value obtained in the previous runs, and the SO and EE values indicated a high VO retained into microcapsules. Moreover, the peroxide value was not adversely affected by the spray drying process applying the optimum level of independent variables.

3.2.2. Powder morphology

The resulting powders obtained after the optimized response had particles with a wide range of sizes (Fig. 3, A). Most of the particles showed a rounded external surface with a continuous wall and no apparent fissures or cracks, which is important to provide lower permeability to gasses, better protection and core retention. Moreover, surfaces were concave and shriveled (Fig. 3, B), which is typical of microcapsules produced by spray drying process [34]. This type of morphology was also observed by Bertolini et al. [35] and Trindade and Grosso [36] who microencapsulated monoterpenes and ascorbic acid respectively, using gum arabic as wall material. In the same way, other authors informed this morphology on microcapsules using maltodextrin and modified cellulose as wall materials [12,13]. The formation of hollow particles as usual characteristic of spray drying process can be explained by the formation of a "vacuole" inside the particles, immediately after the crust development. This crust inflates when the particle temperature exceeds the local ambient boiling point and the vapor pressure within the vacuole rises above the local ambient pressure [37]. The lack of pores on the microcapsule surface was related to the good encapsulation efficiency obtained in the experimental design. Besides, the low surface oil content was a consequence of a continuous wall surface. All of these led to an effective protection of vegetable oil quality, as was indicated for the absence of peroxide content.

4. Conclusions

The results obtained in this study support the fact that the spray drying method is suitable for microencapsulated VO. Besides the use of RSM design is a good alternative in order to identify, in a relatively fast and simple way, those combinations of spray-drying operating

Table 4
Predicted and observed values of solid yield (SY) for the combination of design variables that maximize the desirability function.

Process variable	Level	SY (predicted value)	SY (observed value)	%Error*
A (air inlet temperature)	163 °C	41.94%	39.94%	3.45%
B (atomization air flow)	279 L/h			
C (pump setting)	10%			
D (aspiration setting)	100%			

% Error* error percentage obtained from the predicted and the observed values for solid yield parameter (SY).

Table 5
Powder analysis of VO microcapsules under conditions of optimal model point.

Process variable	Optimum level	Powder analysis	
A (°C)	163	MC (%)	2.75 ± 0.22
B (L/h)	279	SO (%)	20.57 ± 0.12
C (%)	10	EE (%)	79.43 ± 0.12
D (%)	100	PV (meq O_2 kg^{-1} oil)	ND

A: Air inlet temperature. B: Atomization air flow. C: Pump setting. D: Aspiration setting. MC: Moisture content. SO: Surface oil. EE: Encapsulation efficiency. PV: peRoxide value. ND: Not detected.

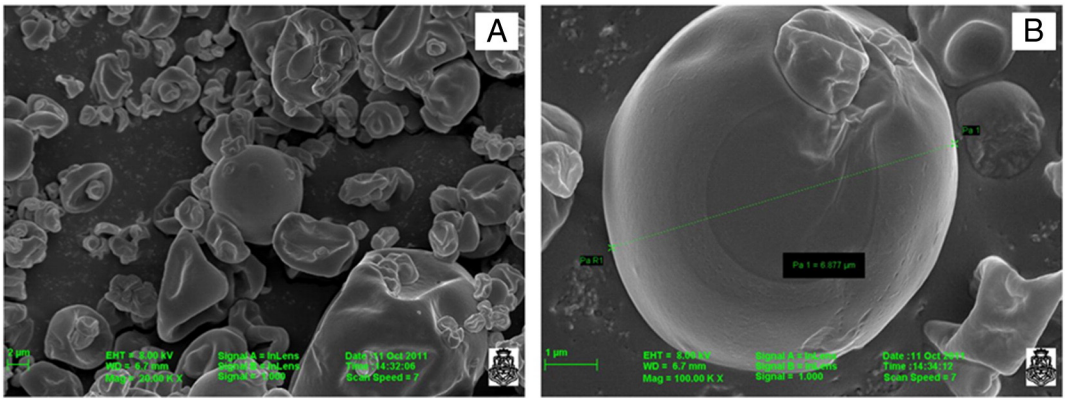

Fig. 3. Micrographs of the surface topology of microcapsules produced under the optimal model point conditions: air inlet temperature (A), 163 °C; atomization air flow rate (B), 279 L/h; pump setting, 10% and aspirator setting, 100%.

conditions that allow for the production of powders with good encapsulation efficiency and solid yield.

However, according to the analysis of the results obtained in this work and in comparison to those reported by other authors, it can be concluded that the optimal spray-drying operating conditions for a given oil/carrier system cannot be directly extrapolated from other formulations.

The fact that EE% was not significantly influenced by processing conditions proves the high microencapsulation capacity of coating material combination. Since SY was affected by all process variables, the optimization procedure was carried out to maximize the powder yield. The best processing combination achieved the best SY for the utilized wall material with an effective protection of vegetable oil quality. The results provide a good start for other microencapsulation approaches.

Acknowledgments

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References

[1] C. Galli, F. Marangoni, N−3 fatty acids in the Mediterranean diet, P. L. E. F. A. 75 (2006) 129–133.
[2] G. Dobson, Analysis of fatty acids in functional foods with emphasis on ω3 fatty acids and conjugated linoleic acid, in: W.J. Hurst (Ed.), Methods of Analysis for Functional Foods and Nutraceuticals, Boca Raton, United States of America, 2008, pp. 85–145.
[3] M. Fuchs, C. Turchiuli, M. Bohin, M.E. Cuvelier, C. Ordonnaud, M.N. Peyrat-Maillard, E. Dumoulin, Encapsulation of oil in powder using spray drying and fluidized bed agglomeration, J. Food Eng. 75 (2006) 27–35.
[4] T.C. Kha, M.H. Nguyen, P.D. Roach, Effects of spray drying conditions on the physicochemical and antioxidant properties of the Gac (*Momordica cochinchinensis*) fruit aril powder, J. Food Eng. 98 (2010) 385–392.
[5] P. Calvo, M. Lozano, A. Espinosa-Mansilla, D. González-Gómez, In-vitro evaluation of the availability of ω−3 and ω−6 fatty acids and tocopherols from microencapsulated walnut oil, Food Res. Int. 48 (2012) 316–321.
[6] G. Gallardo, L. Guida, V. Martinez, M.C. López, D. Bernhardt, R. Blasco, R. Pedroza-Islas, L.G. Hermida, Microencapsulation of linseed oil by spray drying for functional food application, Food Res. Int. 52 (2013) 473–482.
[7] M. Jimenez, H.S. Garcia, C.I. Beristain, Spray-dried encapsulation of conjugated linoleic acid (CLA) with polymeric matrices, J. Sci. Food Agric. 86 (2006) 2431–2437.
[8] C. Pérez-Alonso, J. Cruz-Olivares, J.F. Barrera-Pichardo, M.E. Rodríguez-Huezo, J.G. Báez-González, E.J. Vernon-Carter, DSC thermo-oxidative stability of red chili oleoresin microencapsulated in blended biopolymers matrices, J. Food Eng. 85 (2008) 613–624.
[9] S.L. Young, X. Sarda, M. Rosenberg, Microencapsulating properties of whey proteins—combination of whey proteins with carbohydrates, J. Dairy Sci. 76 (1993) 2878–2885.
[10] M.E. Neil, K.M. Younger, Microencapsulation of marine oils with a view to food fortification, in: M.J. Sadler (Ed.), Saltmarsh Functional Foods: the Consumer, the Product and the Evidence, Berlin, Heilderberg, New York, 1998, pp. 149–158.
[11] J. Velasco, C. Dobarganes, G. Márquez-Ruiz, Variables affecting lipid oxidation in dried microencapsulated oils, Grasas y Aceites 54 (2003) 304–314.
[12] W. Kolanowski, G. Laufenberg, B. kunz, Fish oil stabilization by microencapsulation with modifies cellulose, Int. J. Food Sci. Nutr. 55 (2004) 333–343.
[13] G. Davidov-Pardo, P. Roccia, D. Salgado, A.E. León, R. Pedroza-Islas, Evaluation of the different wall materials to microencapsulate fish oil and its behavior in bread products, Am. J. Food Technol. 3 (2008) 384–393.
[14] B.R. Bhandari, E.D. Dumoulin, H.M.J. Richard, I. Noleau, A. Lebert, Flavour encapsulation by spray drying: application to citral and linalyl acetate, J. Food Sci. 57 (1992) 217–221.
[15] A. Madene, M. Jacquot, J. Scher, S. Desobry, Flavour encapsulation and controlled release — a review, Int. J. Food Sci. Technol. 41 (2006) 1–21.
[16] A. Gharsallaoui, G. Roudaut, O. Chambin, A. Voilley, R. Saurel, Applications of spray-drying in microencapsulation of food ingredients: an overview, Food Res. Int. 40 (2007) 1107–1121.
[17] R.V. Tonon, C.R.F. Grosso, M.D. Hubinger, Influence of emulsion composition and inlet air temperature on the microencapsulation of flaxseed oil by spray drying, Food Res. Int. 44 (2011) 282–289.
[18] S.K. Kanawija, V. Pathania, S. Singh, Microencapsulation of enzymes, microorganisms and flavours and their applications in foods, Indian Dairyman 44 (1992) 280–287.
[19] L. Gallo, J.M. Llabot, D. Allemandi, V. Bucalá, J. Piña, Influence of spray-drying operating conditions on *Rhamnus purshiana* (Cáscara sagrada) extract powder physical properties, Powder Technol. 208 (2011) 205–214.
[20] Mini Spray Dryer B-290, 29th October, http://www.buchi.com/Pro-ducts.176.0.html2010.
[21] E. Del Castillo, D.C. Montgomery, D.R. McCarville, Modified desirability functions for multiple response optimization, J. Q. T. 28 (1996) 337–345.
[22] R.V. Tonon, C. Brabet, M.D. Hubinger, Influence of process conditions on the physicochemical properties of açai (*Euterpe oleraceae* Mart.) powder produced by spray drying, J. Food Eng. 88 (2008) 411–418.
[23] J.L. Courthaudon, E. Dickinson, W.W. Christie, Competitive adsorption of lecithin and beta-casein in oil-in-water emulsions, J. Agric. Food Chem. 39 (1991) 1365–1368.
[24] S.M. Jafari, E. Assadpoor, Y. He, B. Bhandari, Encapsulation efficiency of food flavours and oils during spray drying, Dry. Technol. 26 (2008) 816–835.
[25] H.C.F. Carneiro, R.V. Tonon, C.R.F. Grosso, M.D. Hubinger, Encapsulation efficiency and oxidative stability of flaxseed oil microencapsulated by spray drying using different combinations of wall materials, J. Food Eng. 115 (2013) 443–451.
[26] B. Adhikari, T. Howes, A. Shrestha, B.R. Bhandari, Effect of surface tension and viscosity on the surface stickiness of carbohydrate and protein solutions, J. Food Eng. 79 (2007) 1136–1143.
[27] E.C. Frascareli, V.M. Silva, R.V. Tonon, M.D. Hubingera, Effect of process conditions on the microencapsulation of coffee oil by spray drying, Food Bioprod. Process. 90 (2012) 413–424.
[28] W. Klaypradit, Y.W. Huang, Fish oil encapsulation with chitosan using ultrasonic atomizer, LWT — Food Sci. Technol. 41 (2008) 1133–1139.
[29] S.Y. Quek, N.K. Chok, P. Swedlund, The physicochemical properties of spray-dried watermelon powders, Chem. Eng. Process. 46 (2007) 386–392.
[30] A.J. Zakarian, C.J. King, Volatiles loss in the zone during spray drying of emulsions, Ind. Eng. Chem. Process. Des. Dev. 21 (1982) 107–113.
[31] J.H. Hong, Y.H. Choi, Physico-chemical properties of protein-bound polysaccharide from *Agaricus blazei* Murill prepared by ultrafiltration and spray drying process, Int. J. Food Sci. Tech. 42 (2007) 1–8.
[32] J.J. Bimbenet, C. Bonazzi, E. Dumoulin, Drying of foodstuffs, Proceeding of the 13th International Drying Symposium IDS 2002, Beijing, China, 2002, p. 64.
[33] J.H. Ahn, Y.P. Kim, Y.M. Lee, E.M. Seo, K.W. Lee, H.S. Kim, Optimization of microencapsulation of seed oil by response surface methodology, Food Chem. 107 (2008) 98–105.
[34] M.I. Ré, Microencapsulation by spray drying, Drying Technol. 16 (1998) 1195–1236.
[35] A.C. Bertolini, A.C. Siani, C.R.F. Grosso, Stability of monoterpenes encapsulated in gum Arabic by spray-drying, J. Agr. Food Chem. 49 (2001) 780–785.
[36] M.A. Trindade, C.R.F. Grosso, The stability of ascorbic acid microencapsulated in granules of rice starch and in gum Arabic, J. Microencapsul. 17 (2000) 169–176.
[37] J.J. Nijdam, T.A.J. Langrish, The effect of surface composition on the functional properties of milk powders, J. Food Eng. 77 (2006) 919–925.

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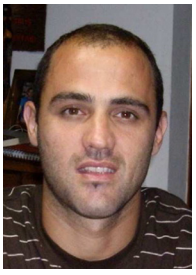

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