

# PHYSICOCHEMICAL AND THERMAL STABILITY OF MICROCAPSULES OF CINNAMON ESSENTIAL OIL BY SPRAY DRYING

PEDRO HENRIQUE CAMPELO FELIX,<sup>1,3</sup> VIVIANE SANTOS BIRCHAL,<sup>2</sup> DIEGO ALVARENGA BOTREL,<sup>1</sup> GERSON REGINALDO MARQUES<sup>1</sup> and SORAIA VILELA BORGES<sup>1</sup>

<sup>1</sup>Department of Food Science, Federal University of Lavras, Lavras, Brazil

<sup>2</sup>Department of Chemical Engineering, Federal University of Minas Gerais, Belo Horizonte, Brazil

<sup>3</sup>Corresponding author.

TEL: + 55 31 34337656;

FAX: + 55 35 38291401;

EMAIL: pcampelo.felix@gmail.com

Received for Publication October 9, 2015

Accepted for Publication February 9, 2016

doi:10.1111/jfpp.12919

## ABSTRACT

Many studies on the cinnamon essential oil has attracted the attention of researchers because of their antimicrobial and antifungal properties. The objective of this study was to evaluate the influence of different wall material on the physicochemical characteristics of microencapsulated cinnamon essential oil. Microcapsules produced with combinations of wall materials (gum arabic, whey protein isolate and maltodextrin) were evaluated with regard to moisture, solubility, hygroscopicity, bulk density, tapped bulk density and microscopic analysis. The encapsulation efficiency was based on cinnamaldehyde retention in relation to the content of the pure oil. The results showed that blends of gum arabic and maltodextrin obtained better retention of cinnamaldehyde (50%). The presence of maltodextrin together with whey protein isolate favored the formation of more spherical particles. Transmission electron microscopy images clearly showed the oil dispersed in the wall materials. Thermogravimetric curves showed higher thermal stability for microcapsules with whey protein isolated. Based on the physicochemical characteristics analyzed, the best wall material for the process of microencapsulation essential oils of cinnamon was the combination of gum arabic and maltodextrin.

## PRACTICAL APPLICATIONS

This paper aims to add knowledge about the microencapsulation process of essential oils, promoting greater stability to oils.

## INTRODUCTION

Essential oils are generally derived from one or more plant parts such as flowers, leaves and bark that also contain volatile compounds, mainly alcohols and aldehydes. These oils have significant organoleptic characteristics, and are finding increasing use in research and industry, especially the food, pharmaceutical and cosmetics sectors (Bizzo *et al.* 2009).

In recent years, many consumers have sought new alternatives for overly processed foods, including those that are nearly free of synthetic preservatives. This has created an expanding and lucrative niche market in which essential oils play important roles (Bizzo *et al.* 2009).

The replacement of synthetic products is a significant challenge industrially because of the inherent instability

when stored for long periods. Thus, investment in research in this area has been growing throughout the world, focusing on reducing losses through storage, transportation and unsuitable environmental conditions such as undesirable levels of oxygen, pH and light (Santana *et al.* 2013).

Cinnamon (*Cinnamomum zeylanicum*) is one of the oldest and best-known spices in the world. Usually is sold in powder form or as curled rolls of bark, commonly used in foods and pharmaceuticals and cosmetics, because of its unique organoleptic characteristics. In addition, because of its antimicrobial, fungicidal and insecticidal activities, cinnamon is widely used as a preservative and additive in food packaging (Cheng *et al.* 2006; Wang *et al.* 2009).

Drying may be defined as a unit operation consisting of the removal of the solvent from a product by techniques

based on temperature, osmotic potential and/or pressure variations. The drying process is one of the most effective methods for the preservation of products, especially food being operationally simple, inexpensive, adaptable and widely available and therefore attractive to industry (Chen and Mujumdar 2008).

The sensory qualities of food products should be preserved throughout its shelf life. This can be accomplished in part by preserving its volatile components for longer periods of time. During storage, factors such as changing temperature, pH and oxygen levels can modify the basic structure of these compounds, degrading them and making them disagreeable to the consumer. As an effective solution to for these issues, microencapsulation is gaining momentum in the global scientific community, as it provides stability to the encapsulated material, by protecting volatile compounds against degradation and volatilization. The microencapsulation process stores compounds within protective capsules that insulate the stock from the external environment, thus avoiding unwanted reactions and product degradation (Passos and Ribeiro 2009).

Some of the most important considerations when studying microencapsulation are the type, quality and concentration of the microparticle wrap materials (wall material), along with the optimal operating conditions such as temperature and feed rate. The choice of the wall material should consider both physical and chemical properties; it would be undesirable that the final product would degrade or even react with the wall material (Costa *et al.* 2013; Vasisht 2014).

The atomization method of spray drying is the most used in microencapsulation processes because it economical, easily adjusted and operated and offers a good quality product (Solval 2011). When the compounds in a food are very reactive or when there is a need to control the onset and rate of release of the core product the technique of microencapsulation is valid and interesting (Mozafari *et al.* 2008).

The process of microencapsulating essential oils is extremely important for industries that use these very volatile and fragile raw materials during production because the process protect them from chemical and organoleptic changes under different operating conditions, ensures the final product quality throughout storage and transport (Botrel *et al.* 2012; Fernandes *et al.* 2014a, 2014b).

The antimicrobial properties of essential oils suggest their uses as differentiated and attractive forms of natural preservatives. The concentration of the oil and their application method are considered important as their misuse can cause organoleptic changes and preclude consumption of the product (Solórzano-Santos and Miranda-Novales 2012).

Due to the fragility of food, parameters such as hygroscopicity, sorption behavior and thermal stability require constant monitoring (Hijo *et al.* 2015; Costa *et al.* 2015).

**TABLE 1.** COMPOSITION IN THE FORMULATION OF MICROPARTICLES OF CINNAMON ESSENTIAL OIL WITH GUM ARABIC, WHEY PROTEIN ISOLATE AND MALTODEXTRIN

Code	GA (%)	WPI (%)	MD (%)	Cinnamon essential oil (g 100/g)
GA	100	–	–	1.5
WPI	–	100	–	1.5
GA/MD	50	–	50	1.5
WPI/MD	–	50	50	1.5

Thermogravimetric is a technique that can continuously measure the loss of mass of a substance with heating. The mass loss in microencapsulated can characterize the changes of composition or structure of the polymer used (Giron 2002).

This paper present a method to conserve the volatile compounds from cinnamon essential oil by spray drying with the evaluation of the physicochemical and thermal properties of different encapsulation materials.

## MATERIALS AND METHODS

### Materials

Cinnamon essential oil (FERQUIMA, São Paulo, Brazil) extracted from the leaves was used as the microencapsulation material. The wall materials consisted of gum arabic (GA; Nexira, São Paulo, Brazil); whey protein isolate 9400 (WPI; HILMAR INGREDIENTS, Hilmar, CA) and maltodextrin Maltogil 20% dextrose (MD; CARGILL FOODS, São Paulo, Brazil).

### Experimental Design

The experiments were conducted in a completely randomized experimental design with 3 as shown in Table 1. A one-way analysis of variance (ANOVA) and Tukey test at  $P < 0.05$  were used to compare the effects of the drying composition on the product properties using the software Statistica (version 8; Stat Soft. Inc., Tulsa, OK). All of the measurements were performed in triplicate.

### Methods

Initially, wall materials (150 g) were mixed with water (350 g) and let to stand for 12 h to hydration. Emulsions were prepared with 30% wall material. The emulsions were subjected to drying in a Spray Dryer (Model MSD 1.0; Labmaq, Ribeirão Preto, Brazil). The inlet and outlet air temperatures were maintained at  $180 \pm 3$  and  $120 \pm 3$  C, respectively. The feed rate was maintained at 0.9 L/min.

**TABLE 2.** MEAN AND STANDARD DEVIATION VALUES FOR MOISTURE, SOLUBILITY, HYGROSCOPIC, BULK AND BULK TAPPED DENSITIES AND WETTABILITY FOR THE PRODUCED POWDERS

Wall materials	Moisture (%)	Solubility (%)	Hygroscopic (%)	Pbulk (g/mL)	Ptapped (g/mL)	Wettability (min)
GA	3.56 ± 0.47 <sup>a</sup>	49.57 ± 0.91 <sup>a</sup>	42.21 ± 0.86 <sup>a</sup>	0.29 ± 0.01 <sup>a</sup>	0.34 ± 0.01 <sup>a</sup>	8.75 ± 0.31 <sup>a</sup>
WPI	1.77 ± 0.24 <sup>a</sup>	48.87 ± 0.83 <sup>a</sup>	31.12 ± 0.82 <sup>b</sup>	0.24 ± 0.01 <sup>b</sup>	0.29 ± 0.01 <sup>b</sup>	17.99 ± 0.47 <sup>b</sup>
GA/MD	4.34 ± 0.27 <sup>a</sup>	37.38 ± 0.25 <sup>b</sup>	31.10 ± 0.36 <sup>b</sup>	0.31 ± 0.01 <sup>a</sup>	0.36 ± 0.02 <sup>a</sup>	5.41 ± 0.56 <sup>c</sup>
WPI/GA	1.85 ± 0.48 <sup>a</sup>	33.04 ± 0.27 <sup>c</sup>	22.9 ± 0.30 <sup>c</sup>	0.25 ± 0.01 <sup>b</sup>	0.29 ± 0.01 <sup>b</sup>	9.77 ± 0.68 <sup>a</sup>

<sup>a,b,c,d</sup>Values with different letters in the same column differ significantly ( $P < 0.05$ ). GA, gum arabic; WPI, whey protein isolate and MD, maltodextrin.

### The moisture content was determined by the gravimetric method, at 105C for 24 h

For the determination of bulk density, powders were gently loaded into a 100 mL tared graduated cylinder, filled to 100 mL and weighed. The volume read directly from the loaded cylinder was used to calculate the bulk density ( $\rho_{\text{bulk}}$ ) according to the mass/volume relationship (Jinapong *et al.* 2008). For the determination of the tapped bulk density ( $\rho_{\text{tapped}}$ ), powder (approximately 5 g) was poured into a 25 mL graduated cylinder which was then repeatedly tapped by lifting and dropping it under its own weight until a negligible difference in volume between successive measurements was observed. The volume read directly from the loaded cylinder was then used to calculate the bulk density tapped ( $\rho_{\text{tapped}}$ ) according to the mass/volume relationship (Goula and Adamopoulos 2008).

The solubility of the powder was evaluated according to the method proposed by Cano-Chauca *et al.* (2005) with modifications. The powders (1 g) were stirred in distilled water (25 mL) for 5 min using a mixer. The solution was centrifuged at  $3,000 \times g$  for 10 min. A 20 mL aliquot of the supernatant was transferred to preweighed Petri dish and dried at 105C overnight. Solubility (%) was calculated as the percentage of dried supernatant compared to the amount initially added powder.

Hygroscopicity was determined according to the method proposed by Cai and Corke (2000) with some modifications. Samples of each powder (about 1 g) were placed in a vessel with a saturated NaCl solution (75.29% relative humidity) at 25C for 1 week. Then the samples were weighed and the hygroscopicity was determined as the weight in grams of adsorbed moisture per 100 g of dry solid (%).

The wettability of the powders was determined using the method described by Fuchs *et al.* (2006). The powder (1 g) was sprinkled in 100 mL of distilled water at 20C without agitation. The time taken for the powder particles to sediment, sink and disappear from the water's surface was recorded and used to compare the extent of wettability of the samples.

The particle size distribution was measured using a laser light diffraction instrument (model 12 LA Sympatech Hellos

(cidade), Switzerland). A small sample of powder was suspended in ethyl alcohol with agitation and the particle size distribution was monitored until successive readings were consistent. The distribution of the sizes of the particles were recorded and the span, which represents the distribution's homogeneity, was calculated using Eq. (1), as follows:

$$\text{Span} = \frac{d_{90} - d_{10}}{d_{50}} \quad (1)$$

where  $d_{90}$ ,  $d_{50}$  and  $d_{10}$  are the volume diameters at 90%, 50% and 10% of the cumulative volume, respectively (Jinapong *et al.* 2008).

Because the essential oil of cinnamon have high volatility is inconsistent evaluate the encapsulation efficiency by the total surface oil in the microparticle. Therefore, we consider the efficiency factor in the encapsulation process of essential based on the final concentration of cinnamaldehyde (major compound) considering the crude oil as a standard. So, we can define Encapsulation efficiency by Eq. (2):

$$C_{\text{ef}} = 100 * \left( \frac{C_m}{C_o} \right) \quad (2)$$

where  $C_{\text{ef}}$  is the encapsulation efficiency;  $C_m$  is the cinnamaldehyde microcapsules content; and  $C_o$  is the cinnamaldehyde pure oil content on the initial emulsion (dry basis).

To evaluate the composition of the oil before and after microencapsulation gas chromatography (GC) analysis was performed on an HP 7820A GC (Agilent) equipped with a flame ionization detector. The samples (~50 mg) were kept in chloroform (500  $\mu\text{L}$ ) in an ultrasonic bath for 10 min. After centrifugation at 6,500 rpm, an aliquot (2  $\mu\text{L}$ ) of the supernatant was injected into the GC for analysis. An HP5 column was used 30 m  $\times$  0.32 mm  $\times$  0.25  $\mu\text{m}$  (Agilent). The initial column temperature was 100C, which was ramped at 5C/min to 200C, injector (splitless), and detector temperatures were 200 and 220C, respectively. Hydrogen was used as the carrier gas (3 mL/min) and injection volume was 2  $\mu\text{L}$ . Data were acquired using the software EZChrom Compact Elite (Agilent).

The morphologies of the cinnamon essential oil microcapsules were examined by scanning electron microscopy (SEM). Microcapsules samples were distributed over a piece

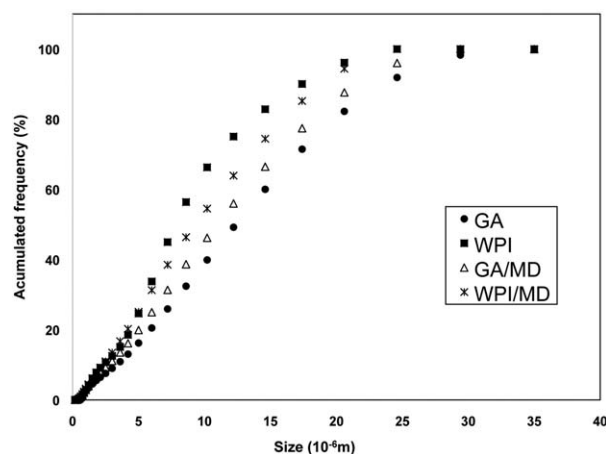


FIG. 1. PARTICLE SIZE OF ALL TESTS GA, WPI, GA/MD AND WPI/MD

of double-sided carbon tape adhered to a metallic support (stub). Then, the samples were analyzed with scanning electron microscopy JSM-6360 (JEOL; Tokyo, Japan), with an accelerating voltage of 15 kV. To view the internal morphology of the microparticles, transmission electron microscope (TEM) FEI Tecnai G2-12 (SpiritBiotwin; OR) was performed with an accelerating voltage of 120 kV. The samples were embedded in EpoFix Hardener resin and cut an ultramicrotome to a slice thickness of approximately 50 nm. The sections were mounted on lacey carbon screens.

The thermal stability of microcapsules of cinnamon essential oil was evaluated by TGA in Shimadzu TG-DTA 50H (Shimadzu Corporation, Japan). The analysis were performed under nitrogen as a flow rate of 50 mL/min. The samples temperature was raised at a rate of 10C/min from 30 to 600C (Hijo *et al.* 2015).

## RESULTS AND DISCUSSION

The particle characteristics are summarized in Table 2. The final moisture content (Table 2) is an important parameter for predicting the shelf life of a food product. Among the samples, there was no significant difference ( $P > 0.05$ ) in the moisture content, and therefore, the different wall materials do not impact these values. The moisture contents in all samples were very low (1.77–4.34%), in agreement with the findings of Costa (1.11–4.16%) (Costa *et al.* 2013) and Botrel *et al.* (1.3–3.65%) (Botrel *et al.* 2012) for the micro-

TABLE 3. D10, D50, D90 AND SPAN VALUES OF ALL SAMPLES

Code	d10 ( $\mu\text{m}$ )	d50 ( $\mu\text{m}$ )	d90 ( $\mu\text{m}$ )	Span ( $\mu\text{m}$ )
GA	3.32	12.37	23.81	1.65
WPI	2.31	7.81	17.38	1.92
GA/MD	2.70	10.92	21.72	1.74
WPI/MD	2.28	9.31	19.07	1.80

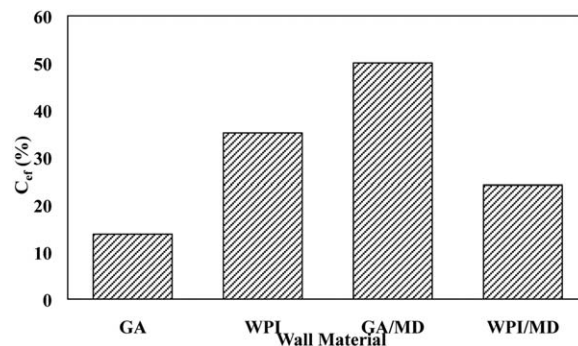


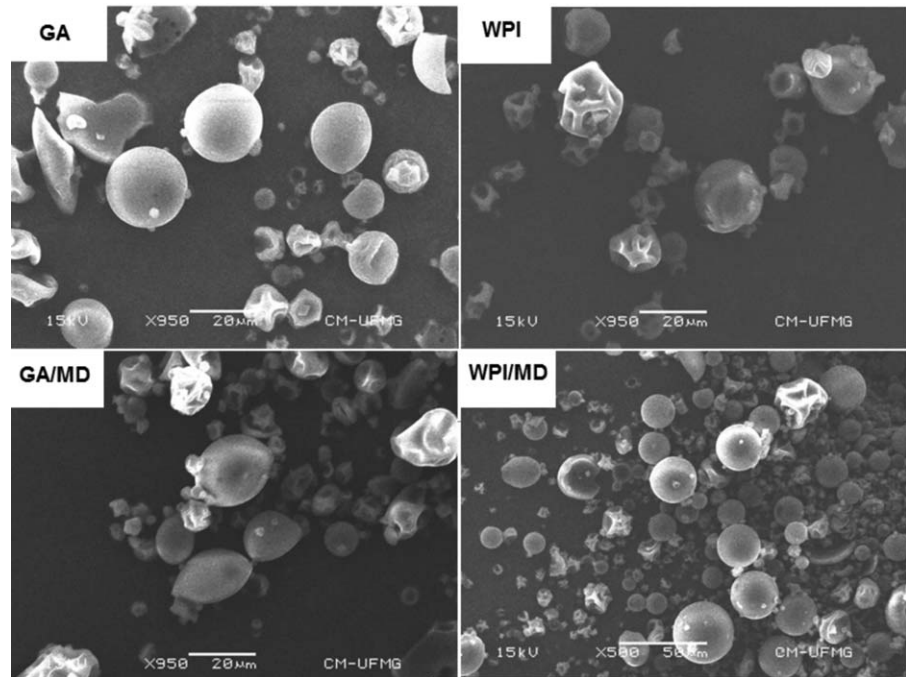
FIG. 2. CINNAMALDEHYDE EFFICIENCY OF GA, WPI, GA/MD AND WPI/MD

encapsulation of essential oils using spray drying. The final moisture content of a powdered product is one of the most important parameters in the study of microencapsulation; this factor determines the ultimate quality of the product, which could be prone to deterioration at high moisture levels (Chen and Mujumdar 2008).

Because of the hydrophobic nature of essential oils, microencapsulation can facilitate their solubility in water by preventing phase separation (Botrel *et al.* 2012) GA and WPI samples showed higher solubility compared to GA/MD and WPI/MD samples. Fernandes *et al.* (2013) also observed similarly decreased levels of solubility in the presence of MD. The variation in the solubility tests with and without MD (0.25–0.36 g/mL). This can be explained by the hydrophobic properties of the cinnamon essential oil, decreasing the solubility of the microparticles.

The hygroscopicities of the samples ranged from 22.9 to 42.21%. Because of its hydrophilic properties, GA interacts easily with water, confirming the high hygroscopicity values for the GA samples. The addition of MD significantly reduces the hygroscopicity of the powders ( $P < 0.05$ ) compared with pure GA and WPI samples. Fernandes *et al.* (2014a,b) observed hygroscopicities values ranged from 15.7 to 17.1% to rosemary essential oil microcapsules used whey protein isolated with wall material. In another study using gum arabic as wall material, Fernandes *et al.* (2013) obtained hygroscopicity values between 15.87 and 18.90%.

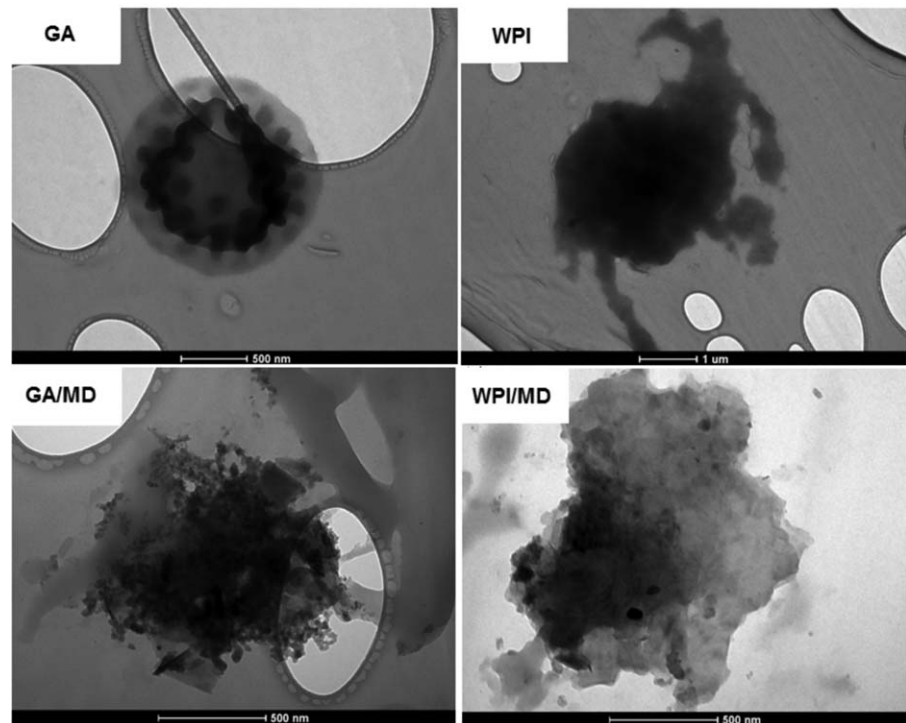
The values of bulk and tapped densities ranged from 0.24 to 0.31 and 0.29 to 0.36 g/mL, respectively. The samples with gum arabic (GA and GA/MD) exhibited higher values than those with whey protein isolate (WPI and WPI/MD). Also, the addition of MD increased the final bulk and tapped density values. Fernandes *et al.* (2013) also observed an increase in bulk density when MD was added to GA (0.28–0.31 g/mL). The bulk density results for mixtures of WPI and MD obtained by Bae and Lee (2008) in the microencapsulation of avocado oil also corroborate this work (0.27  $\pm$  0.001 g/mL).



**FIG. 3.** SEM MICROGRAPHS OF THE PARTICLES CONTAINING CINNAMON ESSENTIAL OIL USING THE FOLLOWING WALL MATERIALS: GUM ARABIC (GA), WHEY PROTEIN ISOLATE (WPI), GUM ARABIC/MALTODEXTRIN (GA/MD) AND WHEY PROTEIN ISOLATE/MALTODEXTRIN (WPI/MD)

Wettability is the ability to maintain a liquid in contact with a solid surface. The wettability time of powders depends on the balance between the forces binding the solid and the liquid. If the chemical bonds are strong, the solid

has a greater ability to wet (Kim *et al.* 2002). In this work, the wettability of the GA samples (Table 2) is lower compared to the WPI-based materials. Also, the addition of MD reduces the wettability (8.75–5.41 min for GA-based



**FIG. 4.** TEM MICROGRAPHS OF THE PARTICLES CONTAINING CINNAMON ESSENTIAL OIL USING THE FOLLOWING WALL MATERIALS: GUM ARABIC (GA), WHEY PROTEIN ISOLATE (WPI), GUM ARABIC/MALTODEXTRIN (GA/MD) AND WHEY PROTEIN ISOLATE/MALTODEXTRIN (WPI/MD)

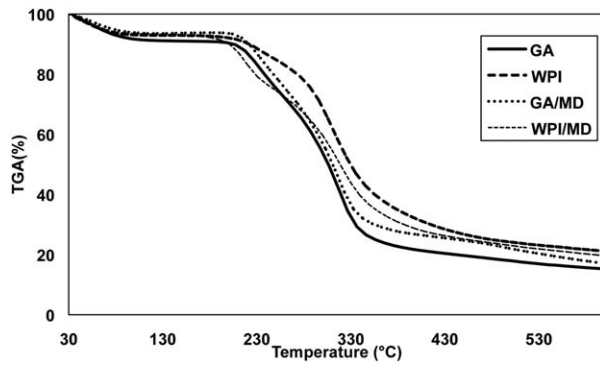


FIG. 5. MASS LOSS (%) AS A FUNCTION OF TEMPERATURE FOR EACH SAMPLE

materials and 17.99–9.77 min for those based on WPI, facilitating the reconstitution of the powder in water. Frascareli *et al.* (2012), during a study of the microencapsulation of coffee oil, observed a declining trend in microcapsule wettability values when MD was added. Wettability is influenced by the particle size, porosity and intermolecular bonds (Schubert *et al.* 2003).

Figure 1 shows the particle size distribution for the microencapsulated cinnamon essential oil samples. WPI-based microcapsules were smaller in size when compared with microcapsules prepared with GA. The addition of MD (GA/MD and WPI/MD) did not have impact on the variation of particles size. Increased particles size for GA matrices and decreased particles size for WPI matrices were observed. Compared to the span values reported in Table 3, the ranges found (Costa *et al.* 2013) and (Botrel *et al.* 2012) and (2.06–2.83 and 1.79–2.59  $\mu\text{m}$ , respectively) were close to those found in our study (1.65–1.92  $\mu\text{m}$ ). Which represent a good homogeneity of the particles size distribution. At the same temperature used in this work, Aghbashlo *et al.* (2012) found a mean particle size near 1.48  $\mu\text{m}$  when WPI micro-particles of fish oil were produced by the atomizing process. Fernandes *et al.* (2013) also observed the largest particle size when the wall material was GA (13.4  $\mu\text{m}$ ). The particle size is an extremely important factor in microencapsulation processes mainly because it can interfere with the dispersion of powders into fluids (Reineccius 2004).

Figure 2 shows the values for the cinnamaldehyde efficiency ( $C_{ef}$ ) (the most abundant volatile compound) in the microencapsulated samples. While the cinnamaldehyde concentration in the crude oil was nearly 62.30  $\mu\text{g}/\text{mL}$ , this value was reduced to 13.79% in the GA-based material. The samples with WPI, GA/MD and WPI/MD also exhibited lower final concentrations, with efficiency approximate values of 35.17, 50.00% and 24.13%, respectively. In general, volatile loss can occur due to three situations: (1) large surface area in atomization may facilitates the volatilization; (2) when the microcapsules membrane is not rapidly formed, facilitating the diffusion of the volatile substances or (3) when volatiles material is transported due to vapor bubbles inside the microcapsules (King 2007).

In their study of the effects of different combinations of wall materials in the microencapsulation of orange essential oil, Ascheri *et al.* (2003) obtained results that corroborate this work. The formulations with higher concentrations of GA gave the worst results, with a loss of more than 80% of the initial concentration of the essential oil of orange volatiles. Goubet *et al.* (1998) explain that there is still no studies on the interactions between the wall material and the encapsulated compound. Operating conditions and the molecular weight of the wall material may be considered important factors in the retention of volatiles in the microcapsules.

Figure 3 presents SEM images of the microencapsulated essential oil of cinnamon particles for all test samples. The GA-based material produced particles of spherical shape, and that based on WPI produced rougher particles. The addition of MD resulted in lower roughness for the WPI-based particles, but increased the roughness of the particles with GA. Fernandes *et al.* (2013) observed smoother, more spherical microcapsules when GA was used as the carrier material in the microencapsulation of the essential oil of rosemary. Bae and Lee (2008) observed rougher particles using WPI and MD as the wall materials for the microencapsulation of avocado oil, in agreement with the observations of this work. The morphology of the particles is an important factor in microencapsulation processes because the presence of cracks influences the loss of volatile compounds from the essential oil microcapsules (Fernandes *et al.* 2014a,b). No cracks were evidenced in this study.

TABLE 4. THERMOGRACIMETRIC ANALYSIS OF CINNAMON ESSENTIAL OIL MICROENCAPSULES WITH DIFFERENT WALL MATERIALS.

Samples	First stage			Second stage			Third stage		
	$T_{onset}$ (°C)	$T_{endset}$ (°C)	$M_{loss}$ (%) ( $T_{onset} - T_{endset}$ )	$T_{onset}$ (°C)	$T_{endset}$ (°C)	$M_{loss}$ (%) ( $T_{onset} - T_{endset}$ )	$T_{onset}$ (°C)	$T_{endset}$ (°C)	$M_{loss}$ (%) ( $T_{onset} - T_{endset}$ )
GA	33.76	109.42	8.64	207.53	351.83	64.19	371.73	598.72	8.04
WPI	33.55	106.26	7.04	204.81	418.02	50.43	432.57	590.87	15.31
GA/MD	31.30	101.55	7.32	199.86	345.05	62.46	371.11	600.97	11.41
WPI/MD	35.18	107.47	6.61	171.01	378.91	51.79	408.61	598.72	8.01

In the TEM images, the GA test sample (Fig. 4) shows a higher concentration of the essential oil (black colour) in the centre of the particle, whereas the other samples exhibit greater dispersions of the essential oil over the entire area of the wall material (gray colour). These images confirm the SEM views of the more spherical shapes for the GA test, and more irregular shapes for the other particles. The images also corroborate the EE data, in which the least amount of oil retained in the wall material was for the GA test sample, and the efficiency was higher value for test and gum arabic maltodextrin.

Kim and Morr (1996), who studied the encapsulation of orange essential oil in different wall materials, observed a tendency for the oil to concentrate in the centre of the particle in experiments with GA, and noted a greater dispersion along the wall material for experiments with WPI.

Figure 5 shows the relationship between mass loss (%) and the temperature of cinnamon essential oil microcapsules. We can be observed 3 (three) degradation stages. During heating, it can be noted that the microcapsules containing gum arabic (GA and GA/MD) as wall material had lower thermal stability. Minor degradations were observed with the microcapsules whey protein isolated (WPI and WPI/MD). The addition of maltodextrin reduced the thermal stability of whey protein isolated particles. The first stage in the temperature range of 30–130C with an average loss of 7.40%. In all cases, a relative thermal stability was observed up to 100C. In the first stage (Table 4), samples containing GA obtaining higher mass loss due to high humidity. This was confirmed because the gum arabic has a higher hygroscopicity among the wall materials used, with higher humidity. In this stage, loss of volatile compounds and of moisture adsorbed on the surface of the microparticles can also be considered and moisture adsorbed on the surface of the microcapsules (Hijo *et al.* 2015).

The second stage in the temperature range of 230–330C was observed for all samples with mass loss average of 57.22%. This stage can be characterized the decomposition of the microcapsules wall material. The degradation of the wall materials can be explained the large loss of mass at this stage. The addition of maltodextrin did not interfere significantly in the thermal stability of the microcapsules (Osorio *et al.* 2010; Garnero *et al.* 2013). Waste wall materials can be founded at the end of this stage (Mothé and Rao 2000). Gum arabic has a higher degradation at temperatures above 200C (Mothé and Rao 2000; Cozic *et al.* 2009; Klein *et al.* 2015). Similar behavior TGA curves studies for whey protein isolated was founded for other authors with decomposition temperature of approximately 300C (Sharma *et al.* 2008; Hundre *et al.* 2015; Winkler *et al.* 2015). Otálora *et al.* (2015) and Klein *et al.* (2015) obtained a thermogram of maltodextrin pure and they observed a temperature range of degradation of 150–300C. Fernandes *et al.* (2008) observed degradation second stage of gum arabic and maltodextrin

blends at temperatures above 200C in essential oil microencapsulation *Lippia sinoides*, corroborating this work.

In the temperature higher than 330C was observed a little mass loss for all samples with mass loss average of 10.69%. This little mass variation over heating can be evidenced the formation of ash of the compounds of the microcapsules (Hijo *et al.* 2015; Silva and Meireles 2015). Hazra *et al.* (2002) observed essential oil degradation of pure cinnamon in a temperature range of 100–200C. Compared to the thermogravimetric studies of this work, it can be agreed that the microencapsulation processes improve the thermal stability of essential oils, increasing its degradation temperature.

## CONCLUSION

Wall materials composed of carbohydrates (GA and MD) achieved the best results for the encapsulation efficiency and the highest cinnamaldehyde retention (50 %). The TGA curves showed higher degradation of microcapsules using gum arabic as wall material. Microcapsules with WPI showed increased thermal stability and similar to GA/MD samples. The micrographs showed spherical microcapsules ways to GA and GA/MD and dispersal of essential oil of cinnamon throughout matrix, with good protection to environmental factors.

## ACKNOWLEDGMENTS

The authors thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Brazil, Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG), and Pró-Reitoria de Pesquisa da UFMG (PRPq-UFMG) for the financial suport.

## REFERENCES

- AGHBASHLO, M., MOBLI, H., MADADLOU, A. and RAFIEE, S. 2012. Influence of wall material and inlet drying air temperature on the microencapsulation of fish oil by spray drying. *Food Bioprocess Technol.* 6, 1561–1569.
- ASCHEI, D.P.R., MARQUEZ, M.O.M. and MARTUCCI, E.T. 2003. Microencapsulação de óleo essencial de laranja: seleção de material de parede. *Cienc. Tecnol. Aliment.* 23, 1–6.
- BAE, E.K. and LEE, S.J. 2008. Microencapsulation of avocado oil by spray drying using whey protein and maltodextrin. *J. Microencapsulation.* 25, 549–560.
- BIZZO, H.R., MARIA, A., HOVELL, C. and REZENDE, C.M. 2009. Óleos Essenciais no Brasil: Aspectos gerais, desenvolvimento e perspectivas. *Quím. Nova.* 32, 588–594.
- BOTREL, D.A., BORGES, S.V., FERNANDES, R.V.B., VIANA, A.D., COSTA, J.M.G. and MARQUES, G.R. 2012. Evaluation of spray drying conditions on properties of microencapsulated oregano essential oil. *Int. J. Food Sci. Technol.* 47, 2289–2296.

- CAI, Y.Z. and CORKE, H. 2000. Production and properties of spray-dried amaranthus betacyanin pigments. *J. Food Sci.* **65**, 1248–1252.
- CANO-CHAUCA, M., STRINGHETA, P.C., RAMOS, A.M. and CAL-VIDAL, J. 2005. Effect of the carriers on the microstructure of mango powder obtained by spray drying and its functional characterization. *Innovative Food Sci. Emerg. Technol.* **6**, 420–428.
- CHEN, X.D. and MUJUMDAR, A.S. 2008. *Drying Technologies in Food Processing*, Blackwell Publishing, Oxford, England.
- CHENG, S.-S., LIU, J.-Y., HSUI, Y.-R. and CHANG, S.-T. 2006. Chemical polymorphism and antifungal activity of essential oils from leaves of different provenances of indigenous cinnamon (*Cinnamomum osmophloeum*). *Bioresour. Technol.* **97**, 306–312.
- COSTA, J.M.G., BORGES, S.V., HIJO, A.A.C.T., SILVA, E.K., MARQUES, G.R., CIRILLO, M.A. and AZEVEDO, V.M. 2013. Matrix structure selection in the microparticles of essential oil oregano produced by spray dryer. *J. Microencapsulation.* **30**, 717–727.
- COSTA, J.M.G., SILVA, E.K., HIJO, A.A.C.T., AZEVEDO, V.M. and BORGES, S.V. 2015. Physical and thermal stability of spray-dried swiss cheese bioaroma powder. *Drying Technol.* **33**, 346–354.
- COZIC, C., PICTON, L., GARDA, M.R., MARLHOUX, F. and LE CERF, D. 2009. Analysis of arabic gum: Study of degradation and water desorption processes. *Food Hydrocoll.* **23**, 1930–1934.
- FERNANDES, L.P., OLIVEIRA, W.P., SZTATISZ, J. and NOVÁK, C. 2008. Thermal properties and release of Lippia sidoides essential oil from gum arabic/maltodextrin microparticles. *J. Therm. Anal. Calorim.* **94**, 461–467.
- FERNANDES, R.V.B., BORGES, S.V. and BOTREL, D.A. 2013. Influence of spray drying operating conditions on microencapsulated rosemary essential oil properties. *Cienc. Tecnol. Aliment.* **33**, 171–178.
- FERNANDES, R.V.B., BORGES, S.V. and BOTREL, D.A. 2014a. Gum arabic/starch/maltodextrin/inulin as wall materials on the microencapsulation of rosemary essential oil. *Carbohydr. Polym.* **101**, 524–532.
- FERNANDES, R.V.B., BORGES, S.V., BOTREL, D.A. and DE OLIVEIRA, C.R. 2014b. Physical and chemical properties of encapsulated rosemary essential oil by spray drying using whey protein-inulin blends as carriers. *Int. J. Food Sci. Technol.* **49**, 1522–1529.
- FRASCARELI, E.C., SILVA, V.M., TONON, R.V. and HUBINGER, M.D. 2012. Effect of process conditions on the microencapsulation of coffee oil by spray drying. *Food Bioprod. Process.* **90**(3), 413–424.
- FUCHS, M., TURCHIULI, C., BOHIN, M., CUVELIER, M.E., ORDONNAUD, C., PEYRAT-MAILLARD, M.N. and DUMOULIN, E. 2006. Encapsulation of oil in powder using spray drying and fluidised bed agglomeration. *J. Food Eng.* **75**, 27–35.
- GARNERO, C., ALOISIO, C. and LONGHI, M. 2013. Ibuprofen-maltodextrin interaction: Study of enantiomeric recognition and complex characterization. *Pharmacol. Pharm.* **4**, 18–30.
- Giron, D. 2002. Applications of thermal analysis and coupled techniques in pharmaceutical industry. *J. Therm. Anal. Calorim.* **68**, 335–357.
- GOUBET, I., LE QUERE, J.L. and VOILLEY, A.J. 1998. Retention of aroma compounds by carbohydrates: Influence of their physicochemical characteristics and of their physical state. A review. *J. Agric. Food Chem.* **46**, 1981–1990.
- GOULA, A.M. and ADAMOPOULOS, K.G. 2008. Effect of maltodextrin addition during spray drying of tomato pulp in dehumidified air: II. Powder properties. *Drying Technol.* **26**, 726–737.
- HAZRA, A., DOLLIMORE, D. and ALEXANDER, K. 2002. Thermal analysis of the evaporation of compounds used in aromatherapy using thermogravimetry. *Thermochim. Acta.* **392–393**, 221–229.
- HIJO, A.A.C.T., COSTA, J.M.G., SILVA, E.K., AZEVEDO, V.M., YOSHIDA, M.I. and BORGES, S.V. 2015. Physical and thermal properties of Oregano (*Origanum vulgare* L.) essential oil microparticles. *J. Food Process Eng.* **38**(1), 1–10.
- HUNDRE, S.Y., KARTHIK, P. and ANANDHARAMAKRISHNAN, C. 2015. Effect of whey protein isolate and  $\beta$ -cyclodextrin wall systems on stability of microencapsulated vanillin by spray-freeze drying method. *Food Chem.* **174**, 16–24.
- JINAPONG, N., SUPHANTHARIKA, M. and JAMNONG, P. 2008. Production of instant soymilk powders by ultrafiltration, spray drying and fluidized bed agglomeration. *J. Food Eng.* **84**, 194–205.
- KIM, E.H.-J., CHEN, X.D. and PEARCE, D. 2002. Surface characterization of four industrial spray-dried dairy powders in relation to chemical composition, structure and wetting property. *Colloids Surf. B.* **26**, 197–212.
- KIM, Y.D. and MORR, C.V. 1996. Microencapsulation properties of gum arabic and several food proteins: Spray-dried orange oil emulsion particles. *J. Agric. Food Chem.* **44**, 1314–1320.
- KING, C.J. 2007. Spray drying: Retention of volatile compounds revisited. *Drying Technol.* **13**, 1221–1240.
- KLEIN, T., LONGHINI, R., BRUSCHI, M.L. and DE MELLO, J.C.P. 2015. Microparticles containing guaraná extract obtained by spray-drying technique: Development and characterization. *Rev. Bras. Farm.* **25**, 292–300.
- MOTHÉ, C.G. and RAO, M.A. 2000. Thermal behavior of gum arabic in comparison with cashew gum. *Thermochim. Acta.* **357–358**, 9–13.
- MOZAFARI, M.R., KHOSRAVI-DARANI, K., BORAZAN, G.G., CUI, J., PARDAKHTY, A. and YURDUGUL, S. 2008. Encapsulation of food ingredients using nanoliposome technology. *Int. J. Food Prop.* **11**, 833–844.
- OSORIO, C., ACEVEDO, B., HILLEBRAND, S., CARRIAZO, J., WINTERHALTER, P. and MORALES, A.L. 2010.

- Microencapsulation by spray-drying of anthocyanin pigments from corozo (*Bactris guineensis*) Fruit. *J. Agric. Food Chem.* *58*, 6977–6985.
- OTÁLORA, M.C.C.C., CARRIAZO, J.G.G.G., ITURRIAGA, L., NAZARENO, M.A.A.A. and OSORIO, C. 2015. Microencapsulation of betalains obtained from cactus fruit (*Opuntia ficus-indica*) by spray drying using cactus cladode mucilage and maltodextrin as encapsulating agents. *Food Chem.* *187*, 174–181.
- PASSOS, M.L. and RIBEIRO, C.P. 2009. *Innovation in Food Engineering*, CRC Press, Boca Raton, FL.
- REINECCIUS, G.A. 2004. The spray drying of food flavors. *Drying Technol.* *22*, 1289–1324.
- SANTANA, A.A., KUROZAWA, L.E., DE OLIVEIRA, R.A. and PARK, K.J. 2013. Influence of process conditions on the physicochemical properties of pequi powder produced by spray drying. *Drying Technol.* *31*, 825–836.
- SCHUBERT, H., AX, K. and BEHREND, O. 2003. Product engineering of dispersed systems. *Trends Food Sci. Technol.* *14*(1–2), 9–16.
- SHARMA, S., HODGES, J.N. and LUZINOV, I. 2008. Biodegradable plastics from animal protein coproducts: Feathermeal. *J. Appl. Polym. Sci.* *110*, 459–467.
- SILVA, E.K. and MEIRELES, M.A.A. 2015. Influence of the degree of inulin polymerization on the ultrasound-assisted encapsulation of annatto seed oil. *Carbohydr. Polym.* *133*, 578–586.
- SOLÓRZANO-SANTOS, F. and MIRANDA-NOVALES, M.G. 2012. Essential oils from aromatic herbs as antimicrobial agents. *Curr. Opin. Biotechnol.* *23*, 136–141.
- SOLVAL, K.M.S. 2011. *Spray Drying Technology for the Production and Processing of Microencapsulated Omega-3 Fish Oil With Egg Powder*, Escuela Agrícola Panamericana, Department of Food Science, Escuela Agrícola Panamericana, El Zamorano, Honduras.
- VASISHT, N. 2014. Selection of materials for microencapsulation. In *Microencapsulation in the Food Industry* (A.G. Gaonkar, N. Vasisht, A.R. Khare and R. Sobel, eds.) pp. 173–180, Elsevier, London.
- WANG, R., WANG, R. and YANG, B. 2009. Extraction of essential oils from five cinnamon leaves and identification of their volatile compound compositions. *Innovative Food Sci. Emerg. Technol.* *10*, 289–292.
- WINKLER, H., VORWERG, W. and SCHMID, M. 2015. Synthesis of hydrophobic whey protein isolate by acylation with fatty acids. *Eur. Polym. J.* *62*, 10–18.