REGIANE VICTÓRIA DE BARROS FERNANDES BOTREL

ÓLEO ESSENCIAL DE GENGIBRE (*Zingiber officinale* L.) MICROENCAPSULADO POR *SPRAY DRYING* EM DIFERENTES MATRIZES POLIMÉRICAS

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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós- Graduação em Ciência dos Alimentos, área de concentração em Ciência dos Alimentos, para a obtenção do título de Doutor.

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APROVADA em 01 de fevereiro de 2016.

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LAVRAS – MG

2016

A Deus,
aos meus amores, Diego e Beatriz,
aos meus amados pais, Regina e Roberto,
à minha irmã, Roberta,
DEDICO

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RESUMO GERAL

A secagem por atomização é um importante método utilizado pela indústria de alimentos na produção de aromas microencapsulados, melhorando suas propriedades de manuseio, dispersão, liberação dos componentes ativos e auxiliando no desenvolvimento de novos produtos. Foi avaliado o efeito da substituição parcial de goma arábica por maltodextrina e inulina, utilizados como materiais de parede, nas características da emulsão e do óleo essencial de gengibre microencapsulado através de secagem por atomização. Além disso, foi também realizado o estudo da substituição parcial do isolado proteico de soro por maltodextrina e inulina. A mistura de goma arábica e maltodextrina, e isolado proteico de soro e maltodextrina, materiais de parede que apresentaram boas propriedades físicas e químicas, entre elas, a alta retenção de voláteis, são alternativas de encapsulantes para o óleo essencial de gengibre. Apesar da adição de inulina ter reduzido a retenção de óleo, os tratamentos mostraram que este encapsulante é interessante substituto para a goma arábica em alimentos. Este fato contribui para aumentar as possibilidades de novas formulações de encapsulantes e coloca a inulina, uma fibra com atividades funcionais comprovadas, como uma alternativa de encapsulante na produção de alimentos. O uso combinado de goma do cajueiro e inulina pode também ser considerado uma alternativa no processo de encapsulação de óleos essenciais e no desenvolvimento de novos produtos com a utilização de biopolímeros naturais não convencionais. O óleo essencial microencapsulado na matriz de goma do cajueiro e inulina na proporção de 3:1, m/m, apresentou as melhores características físicas e químicas, principalmente em relação à eficiência de encapsulação. Através do processo de otimização da matriz isolado proteico de soro e inulina (1:1 m/m), considerando as variáveis molhabilidade, eficiência de encapsulação e dispersibilidade, os resultados indicaram que a concentração de material de parede de 22 % e a temperatura de entrada do ar de 170 °C são as melhores condições para o processo de secagem por atomização de óleo essencial de gengibre.

Palavras-chave: Inulina. Goma do cajueiro. Goma arábica. Isolado proteico de soro. Encapsulação.

GENERAL ABSTRACT

Spray drying is an important method used by the food industry in the production of microencapsulated aromas, improving its handling properties, dispersion, release of active components and aiding in the development of new products. We evaluated the effect of the partial substitution of gum Arabic for maltodextrin and inulin, used as wall materials, over the emulsion properties and microencapsulated ginger essential oil by means of spray drying. In addition, we studied the partial substitution of the whey protein isolate for maltodextrin and inulin. The mixture of gum Arabic and maltodextrin, and whey protein isolate and maltodextrin, wall materials that presented good physical and chemical properties, among which high volatile retention, are alternatives for encapsulating ginger essential oil. Despite the addition of inulin having reduced oil retention, the treatments showed that this encapsulating agent is an interesting substitute for gum Arabic in food. This contributes for increasing the possibilities of new encapsulating formulations and places inulin, a fiber with proven functional activities, as an alternative for encapsulating agent in food production. The combined use of cashew gum and inulin can also be considered an alternative in the process of encapsulating essential oils and in the development of new products using non-conventional natural biopolymers. The essential oil microencapsulated in the matrix of the cashew gum and inulin in the proportion of 3:1, m/m, presented the best physical and chemical properties, especially concerning encapsulation efficiency. By means of optimizing the whey protein isolate and inulin matrix, and considering the variables wettability, encapsulation efficiency and dispersity, the results indicated that the concentration of wall material of 22 % and the inlet air temperature of 170 °C are the best conditions for the spray drying process of ginger essential oil.

Keywords: Inulin. Cashew gum. Gum Arabic. Whey protein isolate. Encapsulation.

SUMÁRIO

PRIMEIRA PARTE

1 INTRODUÇÃO

Na indústria de alimentos, a aplicação de técnicas de microencapsulação para diversos compostos funcionais está sob crescente interesse. A microencapsulação é um processo no qual substâncias bioativas são cobertas ou incorporadas a um material de parede. O encapsulante adequado é escolhido com base no processo de encapsulação utilizado, tipo de material de núcleo, custo, estabilidade durante a estocagem e funcionalidade na aplicação final. Dentre os vários métodos utilizados para a encapsulação, destaca-se a secagem por atomização ou *spray drying*.

O óleo essencial de gengibre vem sendo bastante estudado devido às suas atividades antimicrobiana e antioxidante, além de ser um potencial ingrediente na indústria de alimentos contribuindo para diferenciar o produto alimentício. A estabilidade dos componentes dos óleos essenciais é de grande interesse, pois sua relação com a qualidade e aceitação é grande. A escolha do tipo de polímero e as condições de alimentação do processo e secagem são variáveis de interesse com importância nas propriedades físicas e químicas do composto microencapsulado. Estes atributos justificam o desenvolvimento de diversos produtos utilizando o óleo essencial de gengibre.

Nesse contexto, objetivou-se com este trabalho avaliar a influência de diferentes matrizes poliméricas nas características da emulsão e nas propriedades de óleo essencial de gengibre microencapsulado por secagem por atomização, utilizando-se goma arábica, isolado proteico de soro, maltodextrina e inulina como agentes encapsulantes. A goma do cajueiro, um biopolímero emergente na área de microencapsulação, também foi aplicada como material encapsulante para avaliar as características das micropartículas de óleo essencial de gengibre. Nesse sistema, também foram avaliadas diferentes matrizes com a

aplicação da inulina. Além disso, os efeitos da concentração de material de parede, e temperatura do ar de entrada em variadas propriedades foram avaliados por meio de um delineamento experimental fatorial completo. Após o processo de otimização, a influência da concentração de inulina e isolado proteico de soro, utilizados como materiais de parede, e da temperatura do ar de entrada nas características de óleo essencial de gengibre microencapsulado, também foram avaliadas.

2 REFERENCIAL TEÓRICO

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2.1 Introduction

Synthetic flavorings, essential oils, and natural oleoresins are the main aromatic components used by the food industry. Recently, the aroma market has focused on using aromatic substances originating from natural sources to substitute for synthetic aromas. Essential oils are used as flavorings and aromas in foods, cosmetics, and personal hygiene products because of their chemical and functional properties. Moreover, the antimicrobial and anti-oxidant properties of these essential oils are increasingly being studied. Essential oils are liquid products obtained from plants, generally by means of hydrodistillation. These oils contain many components, including secondary metabolites from plants, and are mainly composed of mono- and sesquiterpene hydrocarbons and their oxygenated derivatives, among others. The stability of essential oil components is of great interest, since it is related to quality and consumer acceptance of products. Essential oils are highly susceptible to changes caused by external factors such as light, oxygen, and temperature, in addition to being

prone to evaporating. To reduce these effects, the process of microencapsulation has become an alternative. Microencapsulation is a technique in which the material of interest is encapsulated in a polymeric matrix, with spray drying being the most commonly used technique. The choice of polymer type, matrix stability, and feed and drying conditions are variables of interest, with importance for the properties and characteristics of the final product. Studies on the drying processes and the search for new formulations and polymer types are trends in this sector.

2.2 Essential Oils

Essential oils have been widely used worldwide, and their use is increasing because of high demand for pure and natural ingredients in diverse market segments. Essential oils of plant origin are commonly used as flavoring agents in food and drink, perfume, pharmaceuticals, and cosmetic products. In addition to these applications, they present antimicrobial properties that may make them efficient alternatives to the use of antibiotics (which are responsible for the increase in resistant bacteria) and chemical additives (which are potentially carcinogenic).

Considerable quantities of essential oils are produced worldwide to supply these industries. The prices of these products vary and are related to the supply of raw materials, harvest-related issues, climatic factors, and the extraction yield. Around 3000 essential oils have been produced, 300 of which are commercially important. Many factors affect the chemical composition of essential oils, including genetic variation, plant type or variety, plant nutrition, fertilizer application, plant geographic location, climate, seasonal variations, stress during growth or maturation, as well as post-harvest drying and storage. Moreover, the type of plant material used and the extraction method determine

the yield and composition of an essential oil, thus influencing its functional properties. For example, an essential oil extracted from different parts of the plant, such as flowers (rose and jasmine), leaves (rosemary and eucalyptus), stems (clove), roots (ginger), fruits (anise), and bark/peel (cinnamon and orange) show different biological and pharmaceutical properties (RAUT; KARUPPAYIL, 2014). Essential oils are normally extracted by distillation, cold pressing, or maceration, and their biological or antimicrobial activities are directly correlated with the presence of bioactive volatile components (CALO et al., 2015; MAHMOUD; CROTEAU, 2002).

Because of the various processes and parameters involved, essential oils are complex matrices, consisting of hundreds of compounds with varied structures and functional groups. This chemical diversity may also result from chemical modifications that occur during the extraction process, for example, thermal activation of chemical reactions and the drying of the fresh raw materials (DO et al., 2015). Chemically, essential oils are composed of compounds of terpene, alcohols, acids, esters, epoxides, aldehydes, ketones, and amines (BAKKALI et al., 2008; CALO et al., 2015).

The diversity of chemical functions found in essential oils provides for a variety of properties and consequently diverse applications. On the other hand, these compounds may also have undesirable properties, such as allergenicity or toxicity, resulting in safety concerns. For this reason, standards and specifications have been established by national authorities and international organizations to limit and control the use of essential oils (DO et al., 2015).

Due to their hydrophobic nature and density, often lower than water, essential oils are generally lipophilic, soluble in organic solvents, and not miscible with water. Extraction methods may be classified into two categories: conventional/classic methods (hydrodistillation, carrying by steam, extraction by organic solvents, and cold pressing) and advanced/innovative methods

(extraction with supercritical fluids, and microwave-assisted). The search for new technologies in recent decades has led to the emergence of newer, more efficient extraction processes, with reduced extraction time and energy consumption, increased extraction yield, and better-quality essential oils (ASBAHANI et al., 2015).

Essential oils are normally liquid at room temperature and contain volatile and unstable compounds. As such, if unprotected from external factors, they may easily be degraded by oxidation, volatilization, heat, and light. Because essential oils are not soluble in aqueous media, it is often necessary to perform some type of transformation before use (CENTINI et al., 2007; SZENTE; SZEJTLI, 2004; UEKAMA; HIRAYAMA; IRIE, 1988). The components from essential oils may be protected by applying microencapsulation technologies, thus extending their performance and controlling their release by external means. These methods are usually economically viable, fast, and efficient.

Essential oils, especially those rich in monoterpenes, are generally used as flavoring ingredients (GHARSALLAOUI et al., 2007). Many investigations have studied various process variables involving microencapsulation by spray drying of essential oils, such as oregano (BOTREL et al., 2012), rosemary (FERNANDES et al., 2013a,b), mint (SARKAR et al., 2013), and lemon (JANISZEWSKA; JEDLINSKA; WITROWA-RAJCHERT, 2015). Their use in flavoring, however, is limited by the quantity of raw material allowed to be added to the product. The aromas of essential oils may be transmitted in excess to food, which negatively influences consumer acceptance. Moreover, the stability of the flavor components in foods has attracted attention because of its relationship to the quality and acceptability of the food products containing them (JUN-XIA; HAI-YAN; JIAN, 2011).

All the potential attributes of essential oils and the increasing demand for natural additives in the food industry have led to interest in their use as potential antimicrobial agents in applications such as food preservatives (BURT, 2004), and to inhibit the pathogens responsible for food-borne illness, such as *Listeria monocytogenes*, *Salmonella typhimurium*, *Clostridium perfringens*, *Pseudomonas putida*, and *Staphylococcus aureus* (ASBAHANI et al., 2015). Numerous studies have demonstrated the efficiency of these components at low doses against pathogenic bacteria found in the food industry (OUSSALAH et al., 2006, 2007).

Several studies have suggested that the antimicrobial action of essential oils may be attributed to their capacity to penetrate through bacterial membranes into the cell, inhibiting functional activities. The phenolic nature of essential oils also causes an antimicrobial response against pathogenic food-borne bacteria. Action mechanisms may be related to the ability of phenolic compounds to change the permeability of the microbial cell, damage the cytoplasmic membrane, and interfere in the cellular energy generation system (BAJPAI; BAEK; KANG, 2012; BURT, 2004; CALO et al., 2015; FISHER; PHILLIPS, 2009; FRIEDLY et al., 2009; GUINOISEAU et al., 2010; LI et al., 2011; SMITH-PALMER; STEWART; FYFE, 1998). Some examples of microencapsulated essential oils and their application in foods with antimicrobial activity are clove oil in tofu (CUI; ZHAO; LIN, 2015) and rosemary in fresh dough (TEODORO et al., 2014).

Essential oils also have anti-oxidant properties, as reported by many studies. Teixeira et al. (2013) reported that essential oils from celery seeds, citronella, clove, oregano, salsa, tarragon, and thyme were capable of inhibiting 50 % of the 2,2-diphenylpicrylhydrazil (DPPH) radical elimination activity. Moreover, the anti-oxidant activity of clove and oregano essential oils is similar to that found for the synthetic anti-oxidant butylated hydroxytoluene (BHT). The

strong activity of clove essential oil may be caused by the presence of eugenol, the principal constituent of the oil, while for oregano essential oil the activity is caused in part by the presence of carvacrol. Both components are known to have high anti-oxidant activity. The use of essential oils as anti-oxidants has been evaluated in different types of food, and research is currently being done to optimize the process. Essential oils from different parts of plants have shown different anti-oxidant properties, with those from leaves generally presenting greater activity (LÓPEZ-MEJIA; LÓPEZ-MALO; PALOU, 2014; NIKOLIC et al., 2014; OLMEDO; ASENSIO; GROSSO, 2015).

2.3 Spray Drying Process

Various techniques may be used to produce microcapsules, including spray drying, spray chilling or cooling, extrusion coating, fluidized bed coating, liposome entrapment, coacervation, and centrifugal extrusion. The most common way to promote component entrapment, however, is through microencapsulation by spray drying, which transforms a liquid into dry particles by feed atomization in hot air (SOOTTITANTAWAT et al., 2005).

Spray drying technology is commonly used in the food industry, and it is one of the oldest and best-defined encapsulation methods (GOUIN, 2004; JAFARI et al., 2008). The food industry uses diverse types of spray dryers, which differ basically in size, shape, and atomizer type. Other advantages of this process are equipment availability, low processing cost, a large selection of encapsulating solids, good retention of volatiles, and good stability of the produced flavoring (REINECCIUS, 2004). Figure 1 illustrates an operational scheme of the spray drying process.

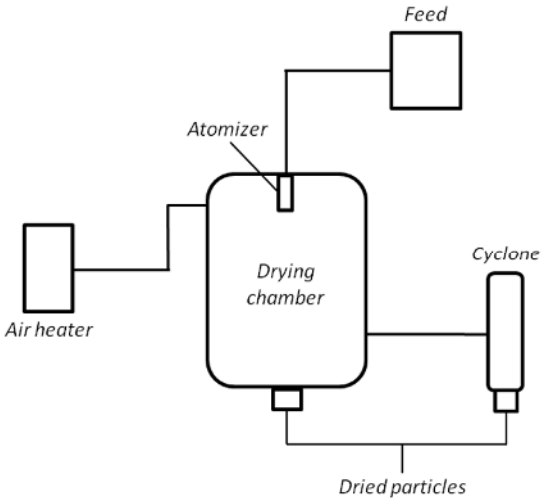

Figure 1 General operation system of a spray dryer, containing the air heater, feed system, atomizer, and the drying and cyclone chambers.

The use of spray drying minimizes volume and weight compared to particles in liquid or gel form, making them easier to store and transport. In addition to these factors, the benefits of the spray drying technique include the capacity to produce powders with a specific particle size and moisture content, independent of dryer capacity. Spray drying is a continuous operation, automatically controlled with a rapid time response, and is applicable to both sensitive and heat-resistant materials (KESHANI et al., 2015). The use of high working temperatures during the drying process, however, may induce degradation by heat and alter thermosensitive products; thus, this parameter should be well evaluated beforehand. Dried solid particles are obtained by drying the liquid droplets with the help of hot air, produced at the top of the chamber. Drying occurs fairly rapidly during a particle's descent to the bottom of the chamber because of its contact with the dry air stream (BOTREL et al., 2014).

The process is characterized in five basic steps: solution preparation, emulsion dispersion (e.g., lipids in a dense wall material solution), dispersion homogenization, spray drying of the feed solution, and spray-dried particle dehydration (SHAHIDI; HAN, 1993). To optimize the process, at least four groups of criteria may be considered: wall material properties, core material characteristics, feed solution specification, and drying conditions. The drying conditions are very important for determining encapsulation process quality. Parameters to be considered include air flow rate, inlet air humidity, inlet air temperature, feed rate, feed concentration, feed formulation, rheological properties, thermodynamic properties, and spray dryer specification (KESHANI et al., 2015).

Atomization is an important step during drying, since it controls droplet formation by means of the two most commonly used techniques: rotary atomization by centrifugal energy and two-fluid nozzle atomization. In the first case, the solution is placed on a rotary disc that spreads it onto a thin film at the edge of the disc. Disc rotation and friction with the surrounding air cause the film to disintegrate into droplets. A wide variety of particle sizes may form and can be controlled by manipulating rotational speed. Since there are no small openings to be blocked, clogging is rarely observed. The rotary disc method is commonly used in the food industry. When the spray drying process is applied by means of a nozzle injector, the solution passes through a nozzle of a certain size under high pressure (with help of the pressurized air). The liquid leaves the nozzle, forming a thin film at the edge of the opening, but disintegrates rapidly into droplets. Droplet size may be controlled by various parameters, among them the nozzle diameter. This type of atomization technique is prone to clogging and may present problems if used with high-viscosity solutions (BUREY et al., 2008).

A fundamental problem in the spray drying process is the deposition of particles on the walls of the equipment, which indirectly affects product quality by degrading the deposited particles. Understanding this problem provides insight into selecting dryer operating conditions that will minimize wall deposition, and therefore help to improve product quality (KESHANI et al., 2015).

The spray drying technique is categorized as a glass encapsulation system, which uses amorphous glassy matrices to retain compounds. The glass transition temperature (T_g) is an important concept for separating the two phases, the glassy state and the rubbery state. T_g accounts for an important function in storage and processing. During storage, the matrix must be maintained in the glassy state to avoid volatile component loss. During processing, T_g must also be considered in relation to matrix viscosity (YULIANI et al., 2004). The decrease in T_g occurs by the increase in humidity and temperature while the powder material is stored, in addition to other factors.

Due to its complexity, a good understanding of the particle formation process is required for successful particle engineering. This drives larger studies on the mechanisms that control the drying process and particle formation (VEHRING; FOSS; LECHUGA-BALLESTEROS, 2007). The principal challenge to producing powders by spray drying is developing powders with desirable properties and reduced costs. For the specific case of essential oils, research into microencapsulation by means of spray drying has concentrated on improving encapsulation efficiency and retaining volatiles (FERNANDES et al., 2014a), in addition to trying to extend the maximum product shelf life.

2.4 Microencapsulation by Spray Drying

The spray drying microencapsulation process consists of transforming a solution, suspension, or emulsion from a liquid state to a solid state to create a protective coating surrounding the material of interest. The microencapsulated product presents some advantages compared to its original form, with regard to transport, manipulation, and use in food matrices. Removing water from the aqueous phase by spray drying allows dry emulsions to be obtained in powdered form, where oil droplets are dispersed in the solid matrix polymer. For encapsulation to be efficient, however, the proportion of non-encapsulated components on the particle surface must be low, and to improve handling properties, the powder must present good fluidity and the ability to mix, and must allow reconstitution of the initial emulsion by means of rehydration in water (CHRISTENSEN; PEDERSEN; KISTENSEN, 2001; TURCHIULI et al., 2014).

The transformation of liquid essential oils to solid form may make the product suitable for use in powdered foods, in view of the dosage and handling of dry powders, with a consequent reduction in storing and packaging costs. Based on the properties of the wall material, the encapsulated product presents better stability in the presence of environmental factors such as light, heat, and oxygen, is less volatile, and can mask undesirable aromas and flavors. Microencapsulation in food products mostly aims to protect and isolate volatile and labile components, which may also apply to essential oils extracted from various plants, and provide potential applications in food products.

As previously described, essential oils are complex mixtures of volatile and labile components that have their physicochemical and sensory characteristics altered by oxidation and volatilization processes. These negative

effects are minimized by microencapsulation, which helps to retain volatile components and protect the most sensitive components.

In a general way, the microencapsulation process is based on the formulation of an initial emulsion by the core material mixture, in this case the essential oil and the wall material, which had been previously dissolved in water. The emulsion is then sent to the spray dryer, where water evaporates by exchanging heat with the heated air passing through the drying chamber, and subsequently microparticles are formed containing the essential oil. The size of the formed particles may vary generally from 1 μm to 100 μm.

Figure 2A shows microcapsules produced by spray drying, using rosemary essential oil as the core material and modified starch as the wall material. The hollow structure of the microcapsule produced by the spray drying technique is highlighted (Figure 2B). The coating formed by the polymeric matrix containing modified starch and maltodextrin, and the oil droplets distributed in this matrix, may also be observed in this picture.

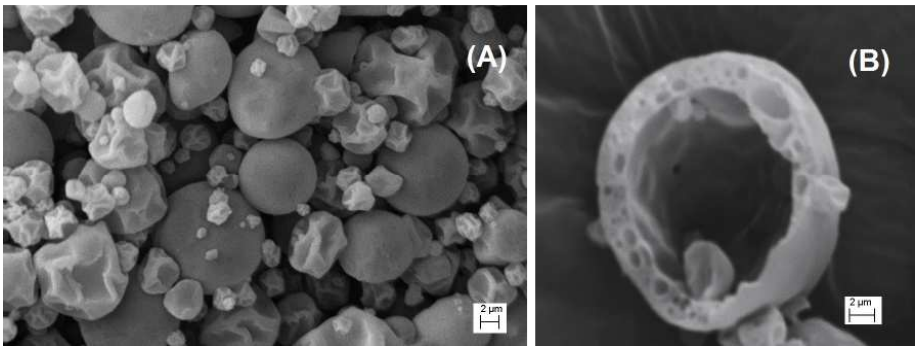

Figure 2 Scanning electron micrographs of essential oil microcapsules produced by spray drying. (A) Rosemary essential oil encapsulated in a modified starch matrix dried at 170 °C; (B) oregano essential oil encapsulated in modified starch matrix and maltodextrin dried at 180 °C.

The choice of wall material or the ideal mixture of wall materials for each system is of extreme importance, since the encapsulating material determines many of the physicochemical characteristics of the product in powdered form, as well as its behavior during storage. The stability, viscosity and droplet size of the emulsion also influence the characteristics of the final product. Moreover, process parameters, such as the temperature and humidity of the drying air, feed rate of the system, and the concentrations of solids and core materials in the emulsion, strongly influence the properties of the particles produced.

Another important point in evaluating the encapsulated powder produced by spray drying is the quantity of core material components present on particle surfaces. The presence of lipophilic materials causes the particle surface to be hydrophobic, thereby decreasing its wettability and dispersability. Hydrophobic products on the surface act to reduce particle fluidity. This material is also readily susceptible to oxidation (KIM; CHEN; PEARCE, 2005).

2.5 Wall Material Properties

The wall material in essential oil microencapsulation systems consists of polymers containing chemical groups with hydrophilic and hydrophobic properties, such as modified starches, milk and soy proteins, and gums that form a polymeric network holding the material of interest encapsulated within the matrix created. The use of combined polymers is generally preferred, since it improves barrier properties compared to their use in single form. In addition to the emulsifier properties and ability to form films, wall materials should present low viscosity in solutions with a high concentration of solids, not present flavor or odor, release the core constituent when required, and still be low in cost. Each material has unique characteristics that define its ability to function as a good

encapsulant; thus, the correct selection of material or mixture of materials is a critical point in the microencapsulation process.

Carbohydrates and proteins may be considered the principal classes of wall materials available and suitable for encapsulation by spray drying, with gum arabic being one of the most commonly applied materials. In addition to gum arabic, other materials have also been studied as microencapsulating agents of essential oils, as shown in Table 1.

Table 1 Wall materials and drying temperatures used in microencapsulation of essential oils by spray drying.

Essential Oil	Matrix/Wall Material	Air Drying Temperature	Reference
Rosemary	Gum arabic, inulin, maltodextrin, modified starch	170°C	Fernandes et al., 2014a
Rosemary	Maltodextrin, modified starch	190°C	Fernandes et al., 2014b
Mint	Gum arabic, guar gum, modified starch	160°C	Sarkar et al., 2013
Oregano	Modified starch, gum arabic, maltodextrin	132–188°C	Botrel et al., 2012
Oregano	Whey protein concentrate, skim milk powder	190°C	Baranauskiene et al., 2006
Oregano	Inulin	120–190°C	Beirão-da-Costa et al., 2013
Basil	Gum arabic	180°C	Garcia et al., 2012
Chia	Whey protein concentrate, mesquite gum, gum arabic	135°C	Rodea-González et al., 2012
Lemon	Maltodextrin, gum arabic	160°C	Janiszewska et al., 2015
Pepper-rosmarin	Cashew tree gum, alginate	170°C	Oliveira et al., 2014
Pepper-rosmarin	β-Cyclodextrin	160°C	Fernandes et al., 2009
Cardamom	Mesquite gum	200°C	Beristain et al., 2001
Lime	Gum arabic, maltodextrin	180, 200, 220°C	Bringas-Lantigua et al., 2012
Orange	Modified starch, maltodextrin, trehalose	175°C	Sosa et al., 2014
Lemon myrtle	Modified starch, whey protein concentrate, maltodextrin	180°C	Huynh et al., 2008

Carbohydrates are widely used in encapsulation thanks to their ability to interact with the components to be encapsulated, in addition to their diversity and low cost. Gums, polymers of long chains and high molecular weight, are among the most frequently used carbohydrates. Moreover, these materials

present other properties of interest for an encapsulating agent, such as low viscosity, high solids content, and good water solubility. Carbohydrates with shorter chains (e.g., maltodextrin) act as filling agents and matrix formers. The principal disadvantage of most carbohydrates as encapsulating materials is their low emulsifying capacity and lower volatile retention, but they are being increasingly studied for use in polymeric mixtures.

Gum arabic, or acacia gum, is a heteropolysaccharide of high molecular weight, a product of the natural exudation of *Acacia senegal*. It is a polymer that consists primarily of the acids D-glucuronic, L-rhamnose, D-galactose, and L-arabinose, with approximately 5 % protein. This protein portion is responsible for the emulsification property of the gum, which makes it suitable for encapsulating lipid components by spray drying. Gum arabic shows low viscosity in aqueous solutions, and moreover is considered a natural product in many countries. Solutions of 50 % concentration may be obtained, but above this value the dispersion presents gel-like characteristics. Other types of gum form viscous solutions at very low concentrations of solids, making them unsuitable for use as encapsulants. The powders produced using gum arabic as wall material are slightly hygroscopic, and are protected from oxidation and volatilization. On the other hand, the cost and availability of gum arabic are subject to fluctuations (DAMODARAN; PARKIN; FENNEMA, 2008; SHAHIDI; HAN, 1993).

Starch constitutes another class of interest in microencapsulation. It is a homopolymer of branched glucose, with α-(1-4) in the linear bonds and α-(1-6) in the branched bonds. Native starches have limited use as microencapsulation agents as a result of their low solubility in water. Therefore, its chemical structure is often modified to generate products with diverse properties. The functionality of the starches may be modified principally by chemical and physical processes. As discussed, to emulsify essential oils, it is necessary to

have lipophilic and hydrophilic groups in the encapsulating polymer. In this way, an alternative to gum arabic is the use of the derivatized starch with octenyl succinic anhydride (n-OSA starch).

When modified with octenyl succinic anhydride, the waxy starch becomes partially hydrolyzed and gains a hydrophobic element in the form of octenyl groups, resulting in molecules with an amphiphilic character. A small amount of substitution results in a product with excellent volatile retention during spray drying, which may be used at high concentrations in the feed system, producing emulsions with good stability (SHAHIDI; HAN, 1993; SWEEDMAN et al., 2013). The viscosity of the solutions containing the modified starch is substantially lower than for gum arabic, and it is therefore possible to use high levels of solids in the feed solution. Solutions containing gum arabic are limited to 35 %, while solutions containing modified starch may be used at concentrations up to 50 %, which reduces the loss of volatiles (SHAHIDI; HAN, 1993).

Maltodextrin is a partially hydrolyzed starch product formed by chains of D-glucose, presenting different dextrose equivalent (DE) values as a function of the size of its chains. To be considered maltodextrin, it must have a DE value of < 20. Maltodextrins are produced by means of acid hydrolysis, enzymatic processes, or a combination of the two. In a general manner, maltodextrins are products of low hygroscopicity, lacking in sweet flavor, and widely used to improve the body of food products. Despite maltodextrin not promoting good retention of volatile components during spray drying, and lacking emulsifying properties, it is used as a secondary carrier material because of its ability to protect the encapsulated ingredients from oxidation. The retention ability of the maltodextrins changes significantly with different DE values. Systems containing starch hydrolysates with high DE values are less permeable to oxygen and therefore present better protection against oxidation. On the other

hand, these systems are more prone to caking during storage because of their high hygroscopicity (ANANDARAMAN; REINECCIUS, 1986; KENYON; ANDERSON, 1988; REINECCIUS, 2004; SHAHIDI; HAN, 1993). Thus, an optimal point for the DE value must be found when choosing hydrolyzed starches to be applied as secondary wall materials in essential oil microencapsulation.

Diverse protein sources are used as microencapsulation agents, with milk and gelatin proteins being the most commonly used. Among the properties of these proteins, their solubility and emulsification capacity are desirable characteristics.

Milk proteins, such as whey protein concentrate (WPC), skim milk powder (SMP), and caseinates, have been widely studied in essential oil encapsulation. During the emulsification step, these proteins change their conformation and are positioned in the oil-water interface, and contribute to the repulsive forces that make emulsions significantly more stable (JAFARI et al., 2008). Gelatin is a protein derived from collagen that is nontoxic and commercially available. It has film-forming properties and solubility in water. Changes in the pH of the aqueous solution may result in polycationic and polyanionic effects being exhibited by the gelatin. This property is applied in coacervation processes (SHAHIDI; HAN, 1993).

Encapsulation efficiency may be increased by means of selecting wall materials that present different functional properties. The partial replacement of WPC by carbohydrates containing surface active groups increased the volatiles retention in the encapsulation of essential oil of caraway during spray drying. On the other hand, the opposite tendency was observed in the use of SMP matrices, where the substitution of SMP by carbohydrates resulted in reduced volatiles retention, resulting in even lower protection against oxidation (BYLAITĖ; VENSKUTONIS; MAPDPIERIENĖ, 2001).

2.6 Volatile Component Retention

The retention of volatile components in microencapsulated essential oils through spray drying is of great interest, since it indicates the quantity of oil entrapped within the matrix, and thus the quantity that will be released when required. This variable is strongly related to the type of wall material used, solids concentration of the feed solution, and the temperature applied during the process.

At the beginning of the spray drying process a semipermeable membrane is formed that acts as a barrier to the majority of volatile components of essential oils, while remaining permeable to water molecules, reducing losses of components of interest (HUYNH et al., 2008). The increase in wall material concentration has a positive effect on the yield of the encapsulated product, although it appears that optimal quantities must be determined for each process and each type of essential oil. The increase in feed solids concentration is related to the reduced formation time of the semipermeable membrane, ensuring a higher quantity of the microencapsulated oil. On the other hand, excessive concentration leads to reduced encapsulated material yield, since it directly affects the viscosity of the emulsion (FERNANDES et al., 2014; SOOTTITANTAWAT et al., 2005). Each wall material has its optimal concentration, which is related to an optimum viscosity for volatile component retention. If a solution is highly viscous, the formation of discrete particles is reduced during spray drying, but low-viscosity media slow the formation of the semipermeable membrane, increasing the loss of volatiles (REINECCIUS, 2004).

Some emulsion properties must be evaluated, such as stability, viscosity, and droplet size, since emulsions with low stability are more prone to producing

particles with lower volatile retention, since their components are not efficiently emulsified and therefore more susceptible to volatilization.

The influence of the inlet air temperature on volatile retention has also received much attention, with temperatures between 130 °C and 200 °C commonly used. The use of high temperatures allows the semipermeable membrane to form rapidly on the surface of the droplets, but the use of very high temperatures may cause damage due to excessive heat exposure, bubble formation, and ruptures on the particle surfaces, leading to reduced volatile components in the essential oil. In accordance with the theory of selective diffusion, when the water concentration on the surface decreases to 7-23 % (a_w < 0.90), the dried surface acts as a semipermeable membrane, allowing continuous loss (or diffusion) of the water while efficiently retaining volatile organic molecules present in the essential oil (REINECCIUS, 2001, 2004). The process of evaporating water from the solidified encapsulating material is very rapid, causing the internal temperature of the particles to stay below 100 °C.

In the process of microencapsulating volatile components, it is important to evaluate the changes that occurred during spray drying. In producing microencapsulated rosemary essential oil by spray drying, Fernandes et al. (2014b) observed that there were no significant alterations in the profile of the principal components of this essential oil, using an inlet air temperature equal to 190 °C and maltodextrin and modified starch as wall materials. Adamiec and Kalemba (2006) verified that the composition of peppermint essential oil did not undergo significant changes when microencapsulated by spray drying with the help of maltodextrin and surfactant Tween 80, under air drying at 150 °C.

2.7 Controlled Release of Microencapsulated Essential Oils

Controlled release may be defined as the process in which one or more active agents or ingredients are released in a desired location, and at a specific time and rate. For encapsulating systems applied to volatile components, the release depends on various independent processes, such as diffusion of the component through the matrix, particle type and geometry, transfer from the matrix to the environment, and degradation/dissolution of the wall material (MADENE et al., 2006; POTHAKAMURY; BARBOSA-CANOVAS, 1995). Advantages include the fact that in controlled release systems the active component is released over prolonged periods of time, the loss of components during processing may be reduced, and reactivity or incompatibility between components may be avoided.

The controlled release of food ingredients and additives, at the right place and time, is a key functionality provided by microencapsulation. Timely and standardized release improves the effectiveness of food additives, extends application possibilities over a range of food ingredients, and ensures optimal dosage, thus improving cost efficiency for food manufacturers (GOUIN, 2004). For a system of encapsulated core ingredients, a controlled release is necessary to provide valuable and useful effects for the final and specified uses. The wall material is capable of preventing damage from the external environment, such as acidity, alkalinity, evaporation, heat, oxidation, light, or humidity, which degrade the active ingredients. Microparticles still allow the controlled release of active substances from the core in a targeted manner, for example, the core ingredients can be controlled to be released all at once or gradually and moderately (LAM; GAMBARI, 2014).

Different bioactive compounds may be encapsulated in the interior cavities of the microparticles and may be released in a well-controlled manner.

Controlled release systems based on polymeric matrices are usually used due to their low cost and versatility. This technology therefore has promising applications in the release of food compounds as well as for pharmaceuticals. For these applications to be viable, however, the system should include factors such as biofunctionality and the use of nontoxic materials. The use of natural materials is therefore promising for microparticle formation and applications (PINHEIRO et al., 2015).

For microencapsulated volatile components in polymeric matrices, the release of the incorporated polymer component is controlled by the initial charge of the core (encapsulated material) in the polymer, and the ability of the molecules to diffuse through the polymeric barrier to the surrounding environment. Interactions between the encapsulated molecules and the polymeric matrix, together with the vapor pressure of the volatile substances on each side of the matrix, are the principal driving forces that influence diffusion. The final characteristics of the microencapsulated essential oil are the result of the release rates of each component. Therefore, understanding the release profile of each component is essential in order to predict the change of the perceived aromas over time (SANSUKCHAREARNPON et al., 2010).

Diverse factors are used for the release of the encapsulated ingredient, such as changes in pH, temperature, mechanical stress, enzymatic activity, and the presence of solvents, among others. Some considerations, however, must be studied for application in the food industry, especially the costs, which may be much higher compared to the pharmaceutical or cosmestic industries.

The selection of appropriate wall materials deserves attention. The nature, morphology, and glass transition temperature of the polymer will influence core material diffusion. The most common method of controlled release in the food industry involves activation by solvent. Active components are released from dry microcapsules in drinks or mixtures of powder products as

soon as water is added (GIBBS et al., 1999). Various mechanisms have been reviewed on the characteristics of release of encapsulated aromas. In the study of Baranauskiene et al. (2007), where peppermint essential oil was microencapsulated by spray drying, the authors observed that the effect of water activity on the release of encapsulated materials is associated with structural changes in the coating matrix. In this work, the slower release of the volatiles at low water activity (a_w) was probably caused by the lower mobility of flavor molecules in the glassy state of the microparticle matrices. At elevated a_w levels, the matrix started to plastify, resulting in greater volatile component mobility, and higher release rates.

The release rate of the essential oil components from the matrix has a direct influence on the perception of aroma in food products, and on the contribution of each component. The microencapsulation of essential oils allows their use in solid products, and the possibility of controlling the release of flavor as necessary, for example, during consumption. Various studies have focused on the development of microparticles to stabilize and protect active compounds, increase their solubility in the media used, and especially to achieve an efficient controlled release.

3 CONSIDERAÇÕES GERAIS

O uso de tecnologias como a microencapsulação pela secagem por atomização proporciona às indústrias de alimentos ferramentas para o desenvolvimento de produtos com características sensoriais apropriadas e com mínimas perdas dos compostos aromáticos. O desenvolvimento e estudo da otimização das condições de secagem, em diferentes materiais de parede, possibilita o uso de novos encapsulantes emergentes, disponíveis em maior escala. O uso de diversas técnicas analíticas é importante para entender o comportamento do processo em diferentes matrizes encapsulantes, e também, para gerar dados para estudos e aplicações em alimentos.

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SEGUNDA PARTE - ARTIGOS

ARTIGO 1 Microencapsulation of ginger essential oil emulsion produced by ultrasound using gum Arabic, maltodextrin and inulin as encapsulating matrices

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MICROENCAPSULATION OF GINGER ESSENTIAL OIL EMULSION PRODUCED BY ULTRASOUND USING GUM ARABIC, MALTODEXTRIN AND INULIN AS ENCAPSULATING MATRICES

Abstract

The aim of this study was to evaluate the effects of the ultrasound-assisted emulsions of ginger essential oil on physical and chemical characteristics of the microparticles obtained from spray drying using gum Arabic, maltodextrin and inulin as wall materials. The emulsions obtained by using ultrasound were more stable and presented smaller droplets. The use of maltodextrin and inulin together with gum Arabic improved the wettability of the powders and the presence of maltodextrin contributed to lower the level of higroscopicity. The partial replacement of gum Arabic by maltodextrin affected considerably the encapsulation efficiency showing the higher value for this parameter. Larger particles were observed in the powders prepared with gum Arabic or a mixture of gum arabic with maltodextrin. The physical and chemical properties of the microparticles were substantially modified by using inulin or maltodextrin together with gum Arabic. Based on the studied properties, the microparticles produced with gum Arabic and maltodextrin were considered to present the better characteristics for wettability, encapsulation efficiency and higroscopicity.

Keywords: spray drying; carbohydrates; emulsion.

1 Introduction

Synthetic flavourings, essential oils, and natural oleoresins are the main aromatic components used by the food industry. Ginger (*Zingiber officinale*) is a plant that belongs to the *Zingiberaceae* family with antioxidant and antimicrobial activities, being considered important for the treatment of various diseases and disorders (Nile & Park, 2015). This product is widely used in food production such as jams, beverages and bakery products (Mesomo et al., 2013) and is valued for its pungency (Kumar et al., 2014). The essential oil produced by *Zingiber officinale* rhizomes varies in colour from pale yellow to light-amber and can be extracted with yields ranging approximately from 1.5 % to 3.0 % depending on the quality of the crop (Bellik, 2014).

Spray drying belongs to the rather complex multiphase convective-drying processes which involve the atomization of droplets, particle transport, evaporation of droplets as well as the interaction between particles and/or droplets and/or dryer walls (Blei & Sommerfeld, 2011; Schmitz-Schug et al., 2016). The emulsification process requires an energy input to blend two immiscible fluids when a proper emulsifier is not added to mixture. In order to overcome this limitation, ultrasound emulsification provide major advantages over other techniques, primarily due to the energy-efficiency, low production cost, ease of system manipulation and better control over formulation variables of ultrasound (Silva et al., 2015a).

Different parameters can be controlled during the spray drying process in order to obtain desired characteristics in the final product. The wall material system is commonly used in order to avoid these technological problems and the choice of the appropriate carrier depends on the desired physico-chemical properties and the final application of the powdered product (Daza et al., 2016). It is necessary to choose the wall materials with high efficiency for microencapsulation by spray-drying because they are playing an important role

in encapsulation efficiency and microcapsule stability (Bakry et al., 2016). Gum Arabic, which it is one of the most common wall materials used in microencapsulation by spray drying, is the most commonly used biopolymer emulsifier in flavour emulsions (Niu et al., 2016). Maltodextrin is produced by partial hydrolysis of starch and is commonly used as secondary wall material in microencapsulation by spray drying, offering advantages such as relatively low cost, neutral aroma and taste, low viscosity at high solids concentrations and good protection against oxidation (Otálora et al., 2015). However, the greatest limitation of this wall material is its low emulsifying capacity, so it is generally mixed with other materials. All the commercial inulin types present very high purity and different powder characteristics and carbohydrate compositions (Botrel et al., 2014). Inulin is a natural fructan composed by a linear chain of fructose monomers with a terminal glucose unit. It has a degree of polymerization that ranges from 10 to 60, and the lengths of its molecular chains are associated with its technological properties (Silva & Meireles, 2015). As well as maltodextrin, inulin can provide protection to encapsulated core materials, although these carbohydrates lack any emulsifying properties and need the addition of other encapsulants. Moreover, the use of inulin in foods, at certain levels, provide benefits to consumer health.

There are few published works reporting the effect of different types of homogenization process and the use of wall materials, particularly inulin, on the encapsulation efficiency and the particle properties of microencapsulated ginger essential oil. This study evaluated the effects of the ultrasound-assisted emulsions of ginger essential oil on the physical and chemical characteristics of the microparticles obtained from spray drying using gum Arabic, maltodextrin and inulin as wall materials.

2 Materials and methods

2.1 Materials

Ginger (*Zingiberofficinale*) essential oil (Ferquima, Vargem Grande Paulista, Brazil) was used as the core material. Gum Arabic (Colloides Naturels Brasil, São Paulo, Brazil), inulin (degree of polymerisation >10, Orafti®GR, BENEO-Orafti, Tienen, Belgium) and maltodextrin (Maltogil DE 10, Gargil, São Paulo, Brazil) were used as wall materials.

2.2 Preparation of ginger essential oil emulsions

The volume of each emulsion was set at 400 mL. The ratio between the ginger essential oil and each biopolymer was 1:4 (w/w) (Fernandes et al., 2014a). Each polysaccharide suspension, gum Arabic (GA), gum Arabic + maltodextrin (1:1; w/w) (GA:MD) and gum Arabic + inulin (1:1; w/w) (GA:IN), was prepared by dissolving the material at 20 % (w/w) (Fernandes et al., 2013a,b) in distilled water. The solutions were prepared the day before emulsification and stored at room temperature for 12 h to ensure complete saturation of the molecules of the materials.

The ginger essential oil was slowly incorporated into each polysaccharide suspension by mechanical stirring at 1000 rpm for 5 min, using a rotor-stator blender (Ultra-Turrax IKA T18 basic, Wilmington, USA), to form emulsions (H). For the treatments where the ultrasound was applied (H/U), after the homogenization process by mechanical stirring, the samples were submitted to ultrasonication at 160 W of nominal power (Branson Digital Sonifier®, Model S-450D, Branson Ultrasonics Corporation, Danbury, USA), 20 kHz, for 2 min. The height contact between the ultrasonic probe and the emulsions was standardized to 30 mm. The experiment was conducted according to Table 1 with three replicates.

Table 1. Composition of the feed emulsions and emulsion processes used in the experiments.

Feed emulsion ($g.100g^{-1}$)				Emulsion step	
GA	**MD**	**IN**	**Oil**	**Homogenization (H)**	**Ultrasonication (U)**
20	-	-	5	x	
20	-	-	5	x	x
10	10	-	5	x	
10	10	-	5	x	x
10	-	10	5	x	
10	-	10	5	x	x

GA: gum Arabic; MD: maltodextrin; IN: inulina

2.3. Characterisation of the emulsions

2.3.1.Emulsions viscosity

Rheological measurements were conducted using a concentric cylinder viscosimeter (Brookfield DVIII Ultra, Brookfield Engineering Laboratories, Stoughton, MA, USA), assembled with a cylindrical sample chamber 13R/RP (19.05 mm of diameter and depth of 64.77 mm), and a spindle SC4-18 (17.48 mm of diameter and 35.53 mm length). For each test, the filled sample cup (6.7 mL) and spindle were temperature equilibrated (at 25 °C). Flow curves were obtained at shear rates of 0.1-80 s^{-1}. The power law model (Eq. 1) was used to analyze the flow properties of the emulsified samples, as follows:

$$\boldsymbol{\tau = k.\gamma^{n}} \quad (\mathbf{1})$$

where τ = shear stress (Pa), γ = shear rate (s^{-1}), k = consistency index ($Pa.s^{n}$), and n = flow behaviour index (Silva et al., 2015b). Apparent viscosity of the emulsion was calculated as the ratio between the shear stress and the shear rate at 20 s^{-1}.

2.3.2.Emulsion droplet size

The droplet size distribution of the emulsions was determined by light scattering using laser diffraction (Mastersizer 2000 Malvern Instruments Ltd., Malvern, UK). The average diameter was calculated based on the average diameter of an area of a similar sphere, the surface mean diameter (d_{32}), while the volume surface mean diameter (d_{43}) and the polydispersity index (PDI) were determined according Eq. (2), (3) and (4), respectively. The samples were analyzed in triplicate for each repetition of the evaluated emulsion by the wet method with dispersion in water and a refractive index of 1.52. The measurements were performed at 25 °C.

$$\mathbf{d_{32}} = \frac{\sum \mathbf{n_i d_i^3}}{\sum \mathbf{n_i d_i^2}} \quad (\mathbf{2})$$

$$\mathbf{d_{43}} = \frac{\sum \mathbf{n_i d_i^4}}{\sum \mathbf{n_i d_i^3}} \quad (\mathbf{3})$$

$$\mathbf{PDI} = \frac{\mathbf{d_{90} - d_{10}}}{\mathbf{d_{50}}} \quad (\mathbf{4})$$

where d_i is the average droplet diameter; n_i is the number of drops; and d_{10}, d_{50} and d_{90} are the diameters at 10 %, 50 % and 90 % cumulative volume, respectively.

2.3.3. Optical microscopy

Optical microscopy of emulsions was performed immediately after their preparation. The samples were poured onto microscopes slides, covered with glass cover slips and observed using a Carl Zeiss Model MF-AKS 24 x 36 Expomet optical microscope (Zeiss, Germany).

2.3.4.Creaming stability

The creaming index (CI) of the ginger essential oil emulsions was analyzed as described by Silva & Meireles (2015). Immediately after emulsion preparation, 25 mL aliquots of each emulsion were poured into a cylindrical graduated glass tube (internal diameter = 1.8 cm, height = 16.5 cm), sealed and stored at 25 °C for 30 h. The emulsion stability was measured by the height of the upper phase over the storage period. The CI was determined according to Eq. (5):

$$\mathbf{CI}\ (\%) = \left(\frac{\mathbf{Hc}}{\mathbf{Ht}}\right)\mathbf{x100} \qquad (\mathbf{5})$$

where Ht represents the initial height of the emulsion and Hc is the upper phase height (cream phase).

2.4 Microencapsulation by spray drying

The spray drying process was conducted only for the emulsions obtained when applying the ultrasonication step (H/U). The feed emulsions were dried using a spray-dryer (model MSD 1.0; Labmaq do Brasil, Ribeirão Preto, Brazil) equipped with a two-fluid nozzle atomiser. The following operational conditions were used, as described in previous studies: inlet temperature of 170 °C and feed rate of 0.8 Lh^{-1} (Fernandes et al., 2013a,b). The atomasing air flow was kept in 35 $L.min^{-1}$. The dried powder was collected and stored in opaque airtight containers at 4 °C for further analysis. The effects of the encapsulating systems were evaluated.

2.5. Characterisation of the microcapsules

2.5.1. Moisture content

The moisture content of the powder was determined gravimetrically by oven-drying at 105 °C to constant weight (Association of Official Analytical Chemists [AOAC], 2007).

2.5.2. Reconstitution properties

The wettability of the powders was determined using the method described by Fuchs et al. (2006). One gram of powder was sprinkled over the surface of 100 mL of distilled water at 20 °C without agitation. The time taken for the powder particles to sediment, sink, be submersed and disappear from the water's surface was recorded and used for a comparison of the extent of wettability of the samples.

The solubility of the powders was evaluated according to the method proposed by Cano-Chauca et al. (2005), with modifications. The powders were weighed (1 g) and stirred into 25 mL of distilled water for 5 min using a blender. The solution was then centrifuged at 760×g or 10 min. An aliquot of 20 mL of the supernatant was transferred to a pre-weighed Petri dish and oven-dried at 105 °C overnight. The solubility (%) was calculated as the percentage of dried supernatant in relation to the amount of powder originally added (1.0 g).

2.5.3.Essential oil encapsulation efficiency

Ginger essential oil content in the microparticles was determined as described by Li & Lu (2016), with some modifications. 1000 mg of sample was dissolved in 20 mL distillate water at 45 °C in glass tubes assisted by ultrasound at 160 W of nominal power (Branson Digital Sonifier®, Model S-450D, Branson Ultrasonics Corporation, Danbury, USA), 20 kHz, for 1 min, followed by 10 mL hexane addition and mixing for 1 min. Essential oil was extracted with

hexane by heating the sample in glass tubes at 45 °C in a water bath with intermittent mixing during 30 min. The tubes were cooled to room temperature and hexane was separated from the aqueous phase by centrifugation at 3000 rpm for 5 min. The extraction was performed four times. The amount of ginger essential oil in hexane was quantified by measuring absorbance at 270 nm in a UV-visible spectrophotometer (Bel Photonics, Piracicaba, Brazil) and its concentration was calculated using a calibration curve. Essential oil encapsulation efficiency (EE) was determined using Eq. (6):

$$\mathbf{EE}(\%) = \frac{\mathbf{M}}{\mathbf{M_0}}\mathbf{x\ 100} \qquad (\mathbf{6})$$

where M is the amount (mg) of oil in microparticles and M_o is the initial oil amount (mg) added to the emulsion.

2.5.4. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy was performed on the pure essential oil, the wall materials and the powders. These measurements were taken at ambient temperature, in the range of 400–4000 cm^{-1}, using a Fourier transform infrared Jasco 4100 spectrometer.

2.5.5. Moisture sorption isotherms

The sorption isotherms for the treatments were determined using the gravimetric static method with a saturated saline solution at 25 °C. The seven saturated saline solutions (NaCl, K_2CO_3, $MgCl_2$, LiCl, $Mg(NO_3)_2$, KCl and K_2SO_4) had water activities ranging from 0.12 to 0.98. The moisture sorption isotherm data were correlated to the water activity (relative humidity) using the following mathematical models: GAB, Halsey, Henderson and Oswin and Smith (Toledo Hijo et al., 2015).

The parameters of these equations were estimated by correlating the mathematical models to the experimental data using a quasi-Newton nonlinear regression. The model that was considered most suitable was based on the low mean relative percentage deviation modulus (E), defined as follows in Eq. (7):

$$\mathbf{E} = \frac{\mathbf{100}}{\mathbf{N}} \sum_{\mathbf{i=1}}^{\mathbf{N}} \frac{\left|\mathbf{m_i} - \mathbf{m_{pi}}\right|}{\mathbf{m_i}} \qquad (\mathbf{7})$$

where m_i is the experimental value, m_{pi} is the predicted value and N is the population of experimental data.

2.5.6. Thermogravimetric analysis

The thermogram curves were obtained using TGA50H thermobalance (Coorporation Shimadzu, Kyoto, Japan) under the following operating conditions: alumina pan; dynamic nitrogen atmosphere with flow of 100 mL min^{-1}; heating rate: 10 °C min^{-1}; temperature range: 50-550 °C. Approximately 5 mg of sample were used.

2.5.7. X-ray diffraction

Samples of products were placed in a support for powder and covered with a glass sheet. Measurements were performed using a Shimadzu X-ray diffractometer (model XRD-6000) using Cu-Kα1 radiation with a wavelength of 1.54 Å at 30 kV and 30 mA. Samples were analyzed at angles from 4° to 40° in 2 h with an increment of 0.02° (1.2° min^{-1}).

2.5.8. Particle morphology and size distribution

The particle morphology of the samples was evaluated using scanning electron microscopy (SEM). The powders were attached to a double-sided adhesive tape mounted on SEM stubs with a diameter of 1 cm and a height of 1 cm, coated with gold in a vacuum evaporator and examined using an MEV 1430

VP – LEO scanning electron microscope (Electron Microscopy Ltd., Cambridge, UK). The SEM was operated at 20 kV with magnification of 900–1200x.

The particle size distribution was determined for all of the samples using a Mastersizer 2000 laser light diffraction instrument (model Hydro 2000 MU, Malvern Instruments, Malvern, UK). A small sample of powder was suspended in ethanol with agitation and the particle size distribution was monitored during each measurement until successive readings were consistent. The area-weighted mean diameter (d_{32}), the volume-weighted mean diameter (d_{43}) and the polidispersity index (PDI) were calculated using Eq. (2), (3) and (4).

2.6 Statistical analysis

Analysis of variance in factorial design was performed to evaluate the effect of the emulsion step and the feed composition on the emulsion parameters studied. One way analysis of variance was performed to evaluate the effect of encapsulating matrices composition on the properties of the microparticles. Significant differences ($p<0.05$) between the treatments mean values were examined by *Duncan* test. The experiments were performed in triplicate.

3. Results and discussion

3.1. Emulsion characterisation

Emulsion viscosity, at optimal values, could affect encapsulation efficiency by a reduction of oscillation and circulation of internal oil droplets during the spray drying, improving oil retention. However, if viscosity increases excessively, oil retention may decreases due to slower droplet formation and longer exposure during atomization (Botrel et al., 2014; Jafari et al., 2008a). According to Battista et al. (2015) the viscosity of the liquid in the feed of spray drying should be lower than 300 mPa.s to ensure good atomization. Therefore, the emulsion study is of extreme importance when studying the

microencapsulation of essential oils. The viscosity-shear rate profiles of the emulsions obtained by applying homogenization (H) and homogenization followed by ultrasound (H/U) processes are presented in Fig. 1. The higher viscosity values were obtained for the emulsions prepared with gum Arabic when applying in both treatments, H (43.8 mPa.s) and H/U (46.0 mPa.s) both at 20 s^{-1} shear rate (Table 2). The higher viscosity observed for the emulsions prepared using gum Arabic is related to its protein content, which is associated with higher water retention and binding ability which could contribute to the increase in the viscosity. Moreover, gum Arabic is also used as a thickening agent in foodstuffs, showing a ramified structure with long chains, which can be responsible for its higher viscosity (Carneiro et al., 2013). Aqueous solutions of maltodextrin commonly present low viscosity (Santiago-Adame et al., 2015) due due to its hydrolyzed chains and may decrease the overall viscosity when mixtured with gum Arabic. Similar behavior was observed, when inulin was used.

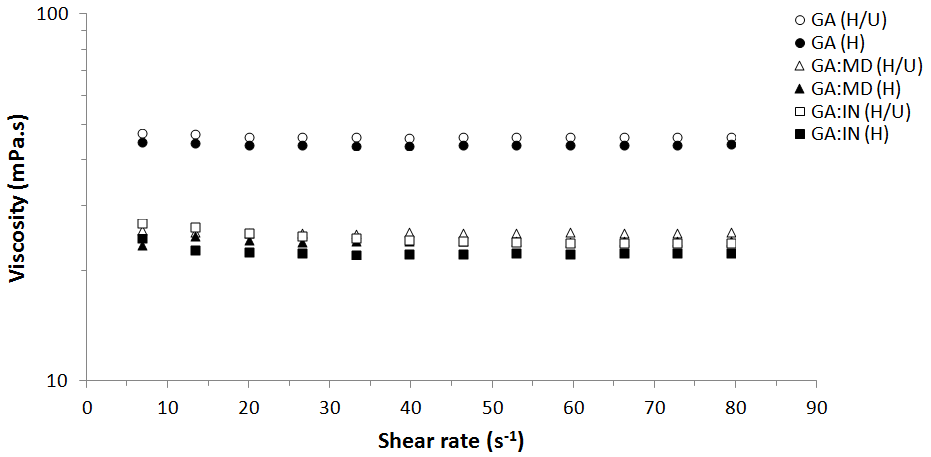


Fig 1. Viscosity-shear rate profiles obtained for the emulsions submitted to the homogenization (H) and homogenization followed by ultrasound (H/U) processes. GA: gum Arabic, MD: maltodextrin, IN: inulin.

Table 2. Valued for apparent viscosity (mPa.s) of the emulsions produced using different wall materials and by homogenization (H) and ultrasonication (H/U).

Wall material	Emulsification process	
	H	H/U
	Apparent viscosity (mPa.s)	
GA	43.82 ± 0.77^{aB}	45.99 ± 1.16^{aA}
GA:MD	24.25 ± 1.04^{bA}	25.26 ± 1.04^{bA}
GA:IN	22.58 ± 1.51^{bB}	25.26 ± 0.77^{bA}

Values with different letters (lower case) for the same emulsification process and different letters (upper case) using the same wall material differ significantly ($p<0.05$) by Duncan test. GA: gum Arabic, MD: maltodextrin, IN: inulin.

Power law model was well fitted to the experimental data having high values for determination coeficient and low values for mean relative error (Table 3). Emulsions were considered to present newtonian fluid behavior. It can be found an increased viscosity for the emulsions when H/U process was applied, except for the treatment using GA:MD. Silva & Meireles (2015) also observed that the annatto seed oil emulsion stabilized by gum Arabic had the apparent viscosity at 97 s^{-1} increased from 13.9 to 23.7 mPa.s when ultrasound was applied in the emulsification process. These authors reported that the changes in the rheological behavior on this emulsion can be associated with application of ultrasonic waves that result in pressure fluctuations that propagate through the material. The sonication process, mainly related to the high shear stress, may be associated with the significant increase observed in the apparent viscosity of the emulsion stabilized with gum obtained using the H/U process.

Table 3. Rheological parameters for the emulsions produced using different wall materials and by homogenization (H) and ultrasonication (H/U).

Treatments					
Wall material	**Emulsification process**	**K (mPa.s^n)**	**n**	**R^2**	**E(%)**
GA		0.04	1.01	0.99	3.97
GA:MD	**H**	0.02	1.00	0.99	1.09
GA:IN		0.02	1.00	0.99	6.65
GA		0.05	1.00	0.99	1.27
GA:MD	**H/U**	0.03	1.00	0.99	4.34
GA:IN		0.03	0.96	0.99	6.66

GA: gum Arabic, MD: maltodextrin, IN: inulin. K: consistency index; n: flow behavior index; E: mean relative error.

The combination of ultrasonic emulsification methods with the application of biopolymers as emulsion stabilizers can produce materials that meet high technological standards and are safe for human consumption (Silva et al., 2015a). The method used to prepare the mixtures significantly influenced the emulsion droplet size as can be observed in Fig. 2. The mean diameter of the droplets in emulsified food products typically falls somewhere in the range of 0.1 to 100 μm (McClements, 2007). The emulsification processes for the ginger essential oil and the different wall materials combinations resulted in emulsions with droplet diameter (d_{43}) ranging from 1.97 to 8.17 μm (Table 4). Treatment GA:MD produced under H/U process reached the smallest value of droplet diameter. Emulsions submitted to ultrasonication process produced particles with smaller sizes when compared to emulsions submitted only to the homogenization step. This fact is also related to the higher shear stress provided by the ultrasound process which leads to a higher level of particles disruption.

Table 4. Particle size distribution of the emulsion droplets produced by homogenization (H) and ultrasound process (H/U) for the evaluated treatments.

Wall material	EP	d_{43} (µm)	d_{32} (µm)	d_{10}	d_{50}	d_{90}	PDI
GA		$4.95^{cA} \pm 0.03$	$2.69^{cA} \pm 0.01$	1.16	4.32	9.74	1.98
GA:MD	**H**	$5.95^{bA} \pm 0.34$	$2.80^{bA} \pm 0.06$	1.14	4.92	12.44	2.30
GA:IN		$8.17^{aA} \pm 0.05$	$3.71^{aA} \pm 0.02$	1.48	6.85	16.96	2.26
GA		$2.68^{bB} \pm 0.03$	$1.34^{cB} \pm 0.01$	0.68	1.57	5.68	3.19
GA:MD	**H/U**	$1.97^{cB} \pm 0.05$	$1.46^{bB} \pm 0.02$	0.81	1.72	3.46	1.54
GA:IN		$5.30^{aB} \pm 0.02$	$2.03^{aB} \pm 0.01$	0.92	2.63	14.24	5.06

Values with different letters (lower case) for the same emulsification process (EP) and different letters (upper case) using the same wall material differ significantly ($p<0.05$) by Duncan test. GA: gum Arabic, MD: maltodextrin, IN: inulin.

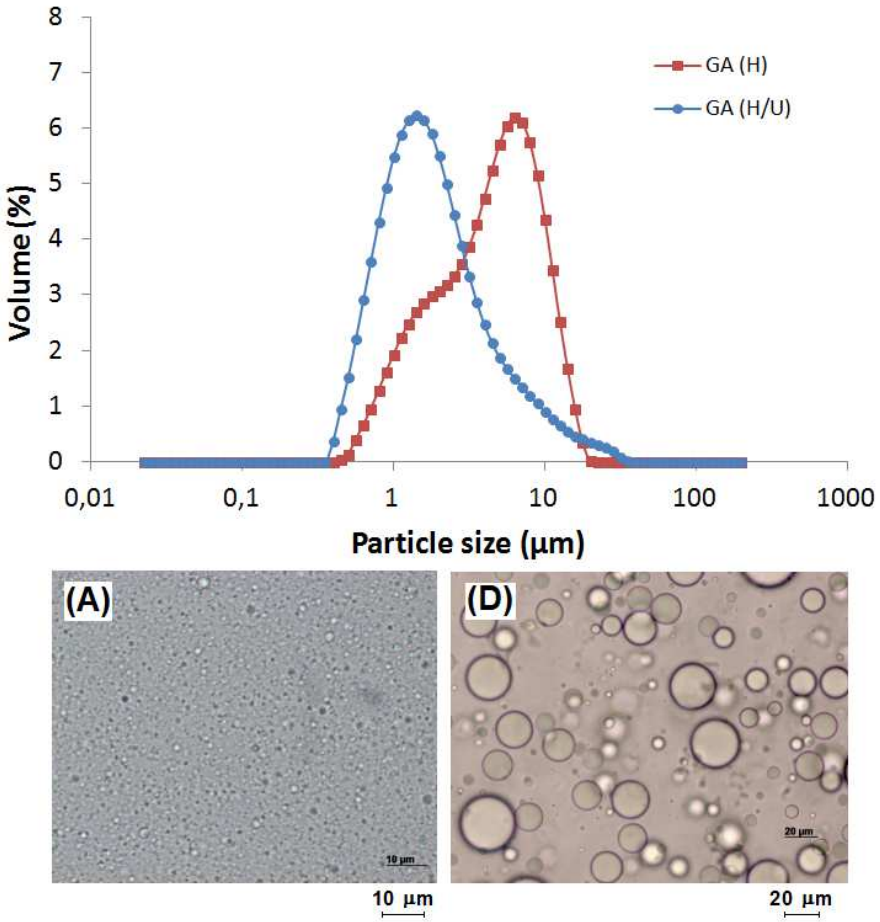
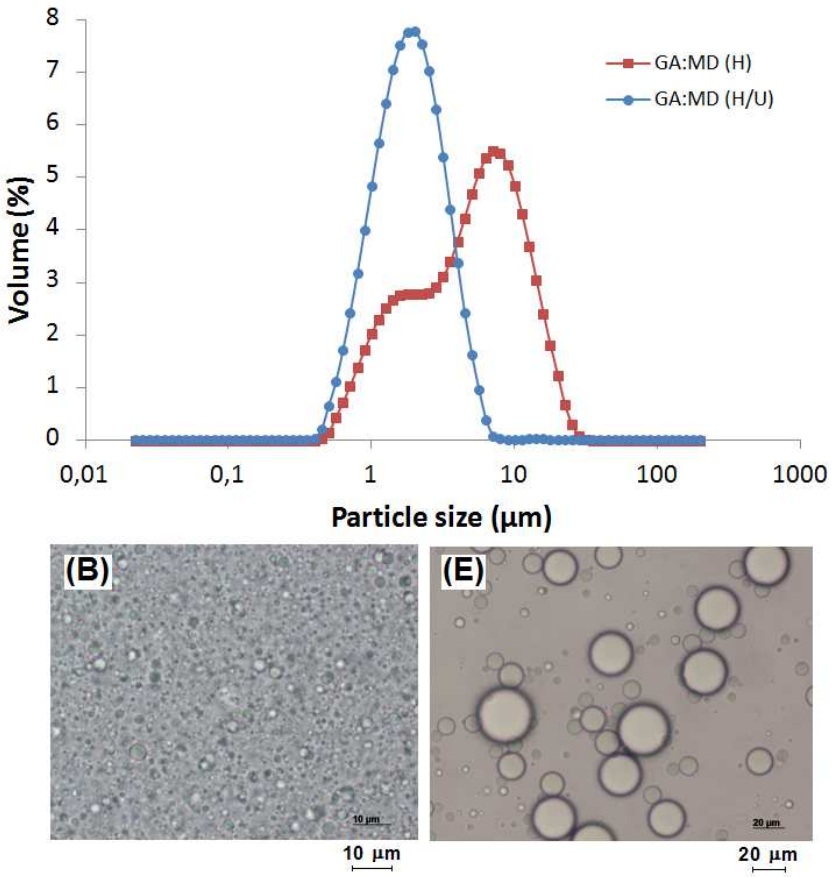


Fig.2. Droplet size distribution curves of the ginger essential oil emulsions processed by homogenization (H) and homogenization plus ultrasound (H/U) and optical micrograph of the ginger essential oil emulsions processed by homogenization plus ultrasound (H/U) (A,B, C) and homogenization (H) (D,E, F). GA: gum Arabic, MD, maltodextrin, IN: inulin. (…to be continued…)



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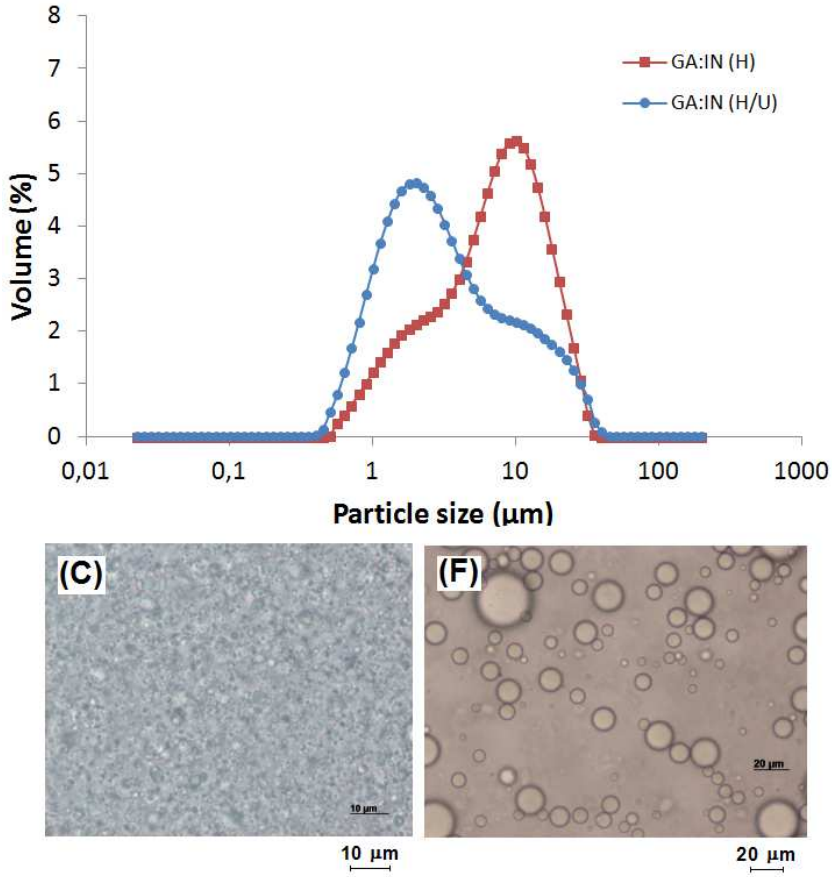

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Processing of blends by ultrasonication after a previous homogenization rendered emulsions with smaller droplet sizes than other treatments which is related to the formation of microscopic bubbles that collapse within a few milliseconds, which is referred to as the cavitation phenomenon as described

before. Moreover, differences between droplet size distribution were observed depending on the carbohydrate used in the formulation of emulsions. Carneiro et al. (2013) found emulsion droplet sizes varying from 1.73 to 2.19 μm (flaxseed oil plus different carbohydrates) produced using a homogenizer. The results confirmed that reduction in emulsion droplet size does not exclusively depend on the type of energy provided to the system (H or H/U). The physicochemical properties of the stabilizer material directly influence emulsion characteristics such as droplet size and viscosity (Silva & Meireles, 2015).

Fig. 2 shows also the microstructure of the emulsions created by the different emulsification process and carbohydrates. The micrographs confirm the results obtained in the droplet size distribution. It is observed that the processes result in different colloidal systems and in the benefits of the H/U process, independent of the biopolymer used in the emulsification of ginger essential oil. A similar effect was observed by Silva et al. (2015b) in the micrographs obtained in the study of ultrasound-assisted formation of annatto seed oil emulsions stabilized by biopolymers (gum Arabic, whey protein isolate, modified starch, polyethylene glycol and inulin).

The emulsion produced using GA:MD showed a narrower droplet size distribution when compared to the other formulations. By the other hand, the emulsion produced using GA:IN showed particles with higher PDI. The efficient development and production of high quality emulsion-based products depends on knowledge of their physicochemical properties and stability (McClements, 2007). The stability of the emulsions to creaming was shown in Fig. 3.

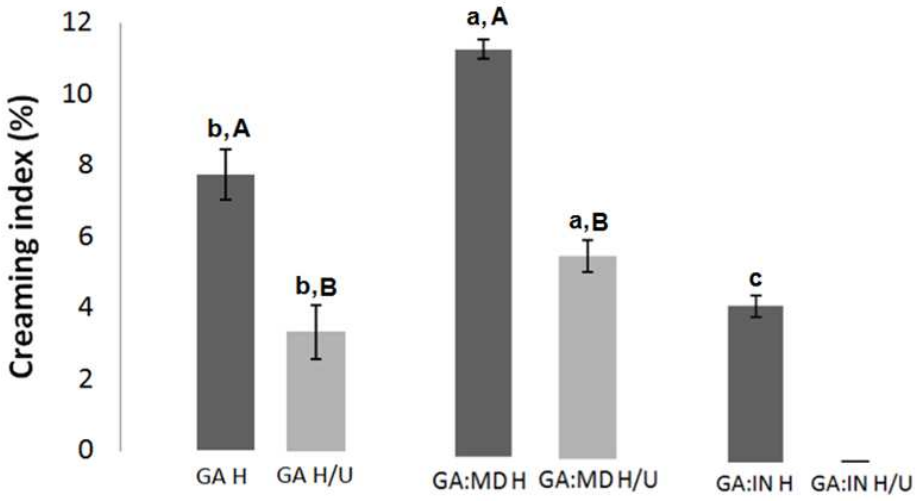

Fig. 3. Effect of the emulsification process and the wall material system on the creaming index (%) of the emulsions. Values with different letters (lower case) for the same emulsification process and different letters (upper case) using the same wall material differ significantly ($p<0.05$) by Duncan test. GA: gum Arabic, MD: maltodextrin, IN: inulin

The purpose of these experiments was to examine the influence of different methods of homogenization and wall materials on the stability of essential oil-in-water emulsions. Creaming, measured by creaming index (CI), is a phenomenon represented by the separation of oil droplets where a layer is placed on the top of the emulsion and is attributed to the thermodynamic instability because all these systems are prone to phase separation from the interface tension (enthalpy/entropy) observed between the phases (McClements, 2004; Tadros, 2009). The decrease in the CI for all treatments that had ultrasound-assisted can be explained by emulsions produced using ultrasound are more stable and have submicron droplets with an extremely narrow particle

size distribution (Silva et al., 2015a; Jafari et al., 2008b). The size of the droplets produced during homogenization influences the tendency for creaming to occur, with smaller droplets moving more slowly (Ozturk & McClements, 2016). Consequently, emulsification processes that produce small droplets during homogenization will give better stability to gravitational separation. Moreover, in general, emulsion stability is affected by physicochemical parameters such as solvent conditions (pH, salts and temperature) and the biopolymers characteristics (e.g., mixing ratio, concentration, charge density, type, etc.) (Niu et al., 2016). The hydrophobic polypeptide chain of the gum Arabic is suggested to adsord the molecules to the droplet surface, while the hydrophilic arabino galactan blocks extend into the solution, providing stability against droplet aggregation through steric and electrostatic repulsion. Gum Arabic is an effective emulsifier due to its high water solubility, low solution viscosity, good surface activity, and ability to form a protective film around emulsion droplets (Niu et al., 2016; Bouyer et al., 2013; Harnsilawat et al., 2006). The addition of inulin contributed for a more stable emulsion. According Silva & Meireles (2015), inulin molecules do not exhibit surface activity, i.e. they do not have the ability to adsorb thereby reducing the interfacial tension and the total free energy of the system. However, the mechanism of stabilization is based on the thickening of the continuous phase which promote a physical barrier to coalescence of the emulsion droplets and avoid the increasing of its size.

3.2. Microparticle characterisation

Considering the lower yield of microencapsulation ginger essential oil when applying only the homogenization process and better results for the ultrasound-assisted emulsions, the characterisation of the particles was performed only for treatments assisted by ultrasound. The particle characterisation results are shown in Table 5. The moisture content of the

microcapsules ranged from 0.88 % to 1.76 % and did not differ ($p>0.05$) among the treatments. The moisture content values found were very similar to those reported in other studies of microencapsulated essential oils by spray drying, such as oregano essential oil using gum Arabic and modified starch as wall materials (1.12 %) (Toledo Hijo et al., 2015) and coriander essential oil using chitosan, alginate and inulin as wall materials (1.12-2.48 %) (Dima et al., 2016).

Table 5. Mean values and standard deviations for the moisture content, wettability, solubility and encapsulation efficiency of the particles produced.

Wall material	Variables			
	Moisture content (%)	**Wettability (s)**	**Solubility (%)**	**Encapsulation efficiency (%)**
GA	1.76 ± 0.93^{a}	288 ± 6^{a}	82.2 ± 3.5^{a}	86.5 ± 3.3^{b}
GA:MD	0.88 ± 0.28^{a}	245 ± 21^{b}	84.6 ± 3.7^{a}	93.0 ± 0.8^{a}
GA:IN	1.73 ± 0.11^{a}	248 ± 9^{b}	81.4 ± 7.1^{a}	48.0 ± 2.8^{c}

[a,b,c] Values with different letters in the same column differ significantly ($p<0.05$) by Duncan test. GA, gum arabic; MD, maltodextrin; IN, inulin.

Wettability is defined as the rehydration capacity of a powder in water and the capacity of the microcapsules to mix with water is one of the most important reconstitution properties. In the present study, the time needed for the powders to become completely wet ranged from 245 to 288 s. The type of wall material significantly affected this property. The shortest wettability time was observed when inulin and maltodextrin were used in the formulation together with gum Arabic, suggesting that these materials improved the instantisation, i.e., reconstitution characteristics of the particles. Fernandes et al. (2014b) found

the same behavior when inulin and maltodextrin were used as secondary wall materials in the microencapsulation of rosemary essential oil.

The powders used as ingredients for the food industry must exhibit good solubility in water. Solubility is the last particle dissolution step and is a decisive factor for the quality of these products (Jayasundera et al., 2011). All of the particles were relatively soluble despite the hydrophobic nature of the core material, yielding results ranging from 81.4 % to 84.6 %. Pure ginger essential oil is not soluble in pure water at room temperature, whereas encapsulating the essential oil resulted in better solubility. The type of encapsulant used did not affect this property.

The encapsulation efficiency values ranged between 48.0 % and 93.0 %. There was significant difference ($p<0.05$) by Duncan test among the oil retention capacity of samples and the treatment of GA:IN was less effective in retaining the oil. One of the most important quality parameters for the encapsulation of an essential oil is the microencapsulation efficiency, which is the percentage of the initial amount of essential oil that is encapsulated. The nature of the wall material is one of the main factors when considering the retention of volatile constituents. Among all of the encapsulants studied, gum Arabic is the most popular and commonly used ingredient for encapsulating essential oils by spray drying, due to its emulsifying properties and excellent retention of volatiles during drying (Jafari et al., 2008c). However, this wall material has a high cost and limited availability. Mixing gum Arabic with other materials or completely replacing it is an alternative strategy for encapsulating essential oils or other substances. The mixture containing maltodextrin proved to be an effective matrix for retaining ginger essential oil. It has the advantage of being relatively inexpensive and provides good protection of the encapsulated materials. Maltodextrin cannot be used as wall material without addition of a surface active wall constituent because of its lack of emulsification properties; however, the

incorporation of this carbohydrate into the wall improves drying properties of the wall matrix, most likely by enhancing the formation of a dry crust around the drying droplets, reduction of oxygen permeability (Sansone et al., 2011) and possibly filling the empty spaces in the encapsulating matrix. In the study carried out by Fernandes et al. (2014b) the same behavior was described, i.e., lower encapsulation efficiency values when inulin was applied with modified starch or gum Arabic in the microencapsulation of rosemary essential oil. Although the treatment GA:IN presented lower encapsulation efficiency than the others, the presence of inulin would be an alternative based on the prebiotic properties of this carbohydrate and on the consumer seeking for food with additional health benefits.

FT-IR spectroscopy was applied to show the charachteristics of the encapsulated ginger essential oil into different Arabic gum matrixes. Fig. 4 shows spectra of all components applied in microencapsulation process. Ginger essential oil (bulk oil) bands are associated to C=C and C=C-C=C stretching at 1740 and 1640 cm^{-1} respectively. Another important vibrational mode associated to $–CH_2-$ groups is presented in the essential oil spectrum at 2922 cm^{-1} (Dalonso et al., 2009; Schulz et al., 2005). Bands that characterize Arabic gum (a carbohydrate) are present at 1017 cm^{-1} (C-O stretching), at 1370 cm^{-1} (CH_3 bending), 1450 cm^{-1} (C-H bending) and 1600 cm^{-1} (C=O stretching).

Maltodextrin is a polymer consisting of β-D-glucose units connected by glycosidic bonds (1→4) and mainly is applied as a storage stabilizer by reduction of stickiness, agglomeration problems and difficulties to dry (Gabas et al., 2007). Inulin is a polymer assembled by fructose units with β(2-1) links ended by glucose monomers and, as the maltodextrin, presents encapsulating properties (Bakowska-Barczak & Kolodziejczyk, 2011). Inulin (IN) and maltodextrin (MD) present almost same spectrum profile, featuring the band assigned to C-O-C at 1015 cm^{-1}.

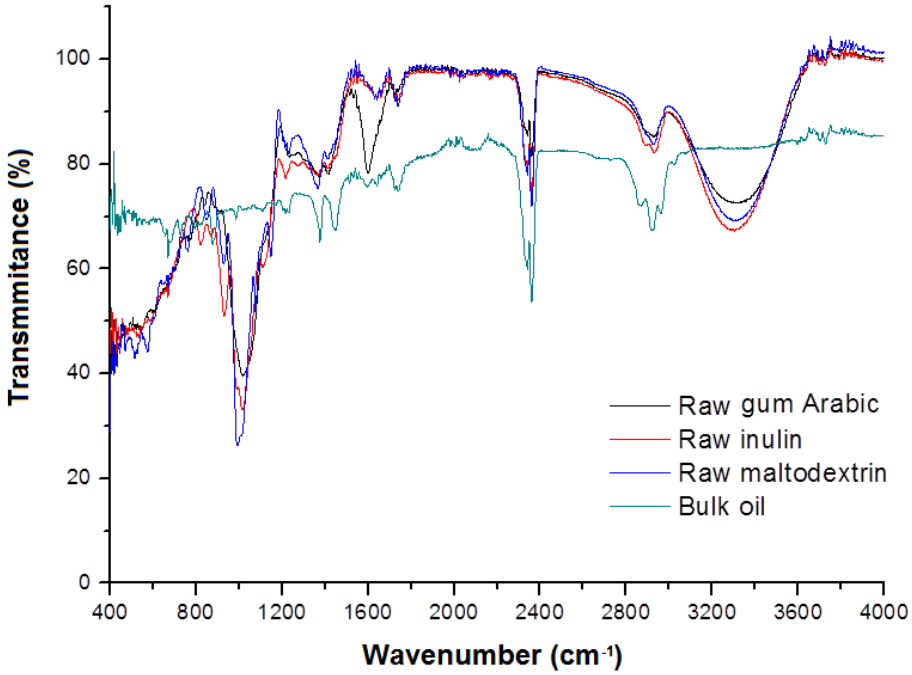

Fig. 4. FT-IR spectra of raw wall materials and ginger essential oil (bulk oil).

Fig.5 shows the FT-IR spectra dependence on composition of GA microparticles. Spectra of gum Arabic (GA), gum Arabic:inulin (GA:IN) and gum Arabic:maltodextrin (GA:MD) microparticles present very similar profiles. IN and MD incorporated to GA matrix are chemically stable due to the absence of wavenumber shifting. A reduction in transmittance of bands at 1015 cm^{-1} associated to C-O-C groups as well as an raise of intensity at 1600 cm^{-1} due to C=O stretching, are observed. These effects may be related to the change in wall composition after incorporation of IN and MD to GA matrix.

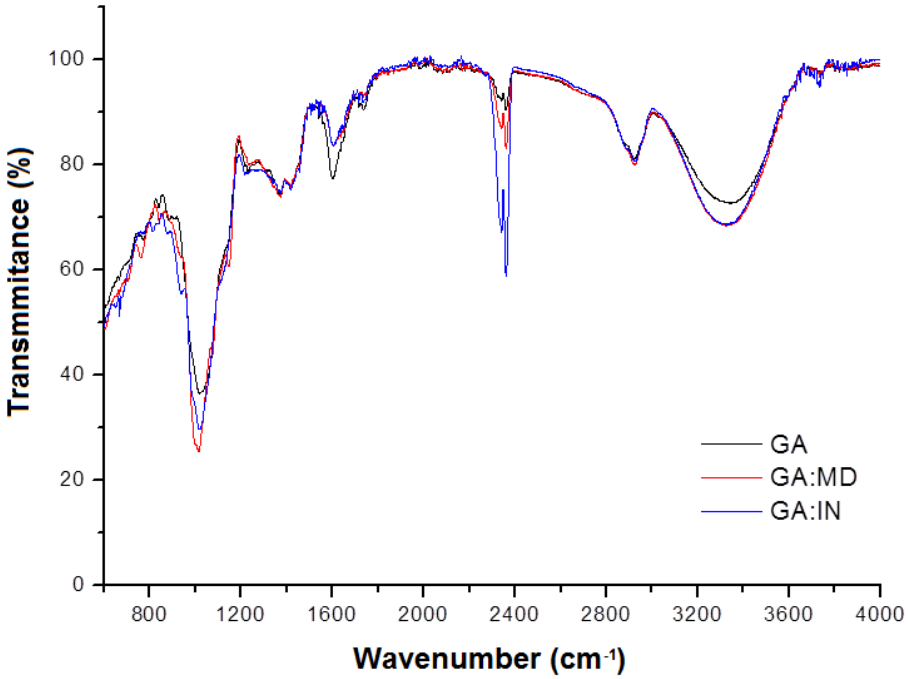

Fig. 5. FT-IR spectra of the microparticles produced using different wall materials composition. GA: gum Arabic, MD: maltodextrin, IN: inulin.

3.2. Moisture sorption isotherms

The estimated values of the coefficients and the statistical parameters used to evaluate the adequacy of the models for the moisture adsorption behaviour are shown in Table 6. Oswin and GAB models fitted well to the data in the isotherm curves for all the treatments, when considering the lowest value of the average relative deviation (E). The GAB model was chosen to describe the isoterms behavior (Fig. 6) because it also provides important information about food products based on the estimative of the moisture content of the monolayer (X_m) which is important to establish appropriate storage conditions for dehydrated foods. Regarding the GAB parameters, as shown in Table 6, the X_m of gum Arabic and gum Arabic plus inulin were higher when comparing to

treatment gum Arabic plus maltodextrin. The use of maltodextrin together with gum Arabic caused decrease of the hygroscopicity of the storage powders at different relative humidities (Fig. 6). The equilibrium moisture content in the treatments formulated with gum Arabic was greatly increased when exposed to relative humidity higher than 0.80. Toledo Hijo et al. (2015) also found that the water adsorption isotherm adjusted by the GAB model at 25 °C for oregano essential oil microparticles obtained by spray drying using gum Arabic and maltodextrin as wall materials.

Table 6. Estimated values of the coefficients and statistical parameters for the studied models GAB, Halsey, Henderson, Oswin and Smith for the different treatments.

Model (Equation)		**GA**	**GA:MD**	**GA:IN**
GAB $X_{eq} = \frac{X_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}$	X_m	0.039	0.031	0.037
	C	6.059	4.189	7.451
	K	0.964	0.968	0.962
	E	2.692	8.261	4.985
HALSEY $X_{eq} = \left(\frac{a}{ln\ a_w}\right)^{1/b}$	a	-0.001	-0.001	-0.001
	b	0.083	0.083	0.083
	E	57.535	51.255	58.957
HENSERSON $X_{eq} = \left[\frac{ln(1 - a_w)}{-a}\right]^{1/b}$	a	3.115	1.708	2.192
	b	2.037	4.421	3.154
	E	44.602	67.446	40.728
OSWIN $X_{eq} = a\left[\frac{a_w}{(1 - a_w)}\right]^b$	a	0.072	0.054	0.069
	b	0.579	0.612	0.567
	E	8.875	16.266	8.501
SMITH $X_{eq} = a + b\log(1 - a_w)$	a	-0.062	-0.062	-0.053
	b	-0.183	-0.158	-0.166
	E	64.618	105.278	57.259

GA: gum Arabic. MD: maltodextrin. IN: inulin. X_{eq}: equilibrium moisture content (g g^{-1} dry powder); X_m: monolayer moisture content (g g^{-1} dry powder); C.K: model constants related to the monolayer and monolayer properties; aw: water activity; a.b: model parameters; E: relative mean error; R^2: coefficient of determination.

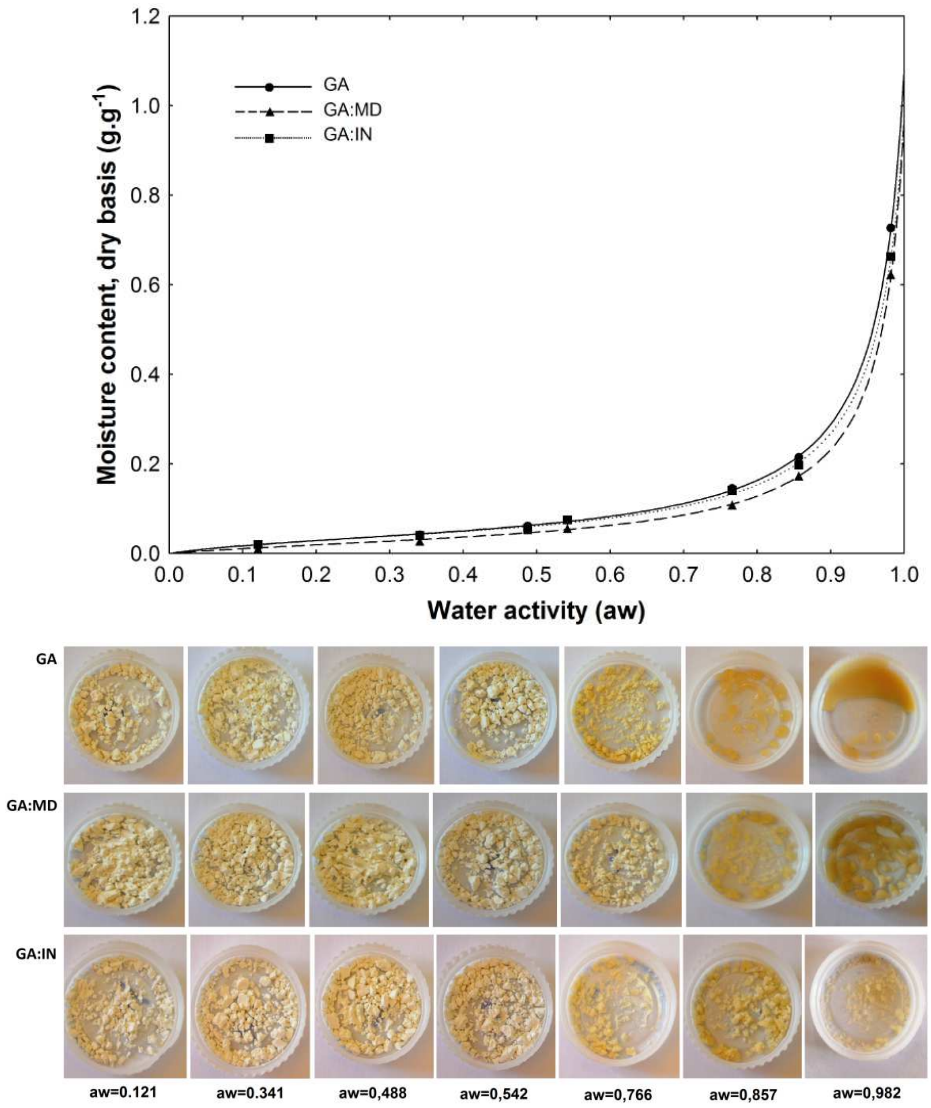

Fig. 6. Sorption isotherms of the ginger oil powders using different wall materials, adjusted by GAB model. Physical aspect of ginger oil powders produced with formulations of encapsulants at different relative humidities in the determination of the equilibrium moisture adsorption isotherms. GA: gum Arabic, MD: maltodextrin, IN: inulin.

The state of water plays a crucial role in food conservation. The quality of preserved food depends upon the moisture content, moisture migration or moisture uptake by the food material during storage. The physical characteristics of the powders subjected to different humidity levels demonstrated that there was minimal physical changes in the particles produced with inulin when compared to the other treatments (Fig. 6). The gum Arabic plus inulin was the only treatment in which the powders visibly remained in the glassy state. The other treatments underwent changes from a glassy state to a rubbery state, at a_w > 0,857 for GA and GA:MD microparticles. These results suggest that inulin presents interesting properties regarding the water affinity during storage and may be used as secondary encapsulation material mixed with some other types of polymers. Powder produced with only gum Arabic were considered the most hygroscopic material over the water activity range tested. The presence of maltodextrin produced powders with lower hygroscopicity when compared to the others treatments.

3.5. Morphology and particle size distribution

The scanning electron microscopic images (SEM) (Fig.7) showed no evidence of cracking in the particles produced using all the carbohydrates formulations, which is important to ensure low gas permeability and better protection to the ginger essential oil against oxidation. In the present study, the microcapsules prepared with inulin had a higher proportion of spherical particles, most likely because these matrices provided elasticity during the drying process, although the perceptible differences in the surface characteristics of each type of particle were observed. In general, the particles had a spherical shape. The occurrence of dents is probably due to shrinkage at the early stages of the drying process. Spray-dried materials are typically hollow spheres.

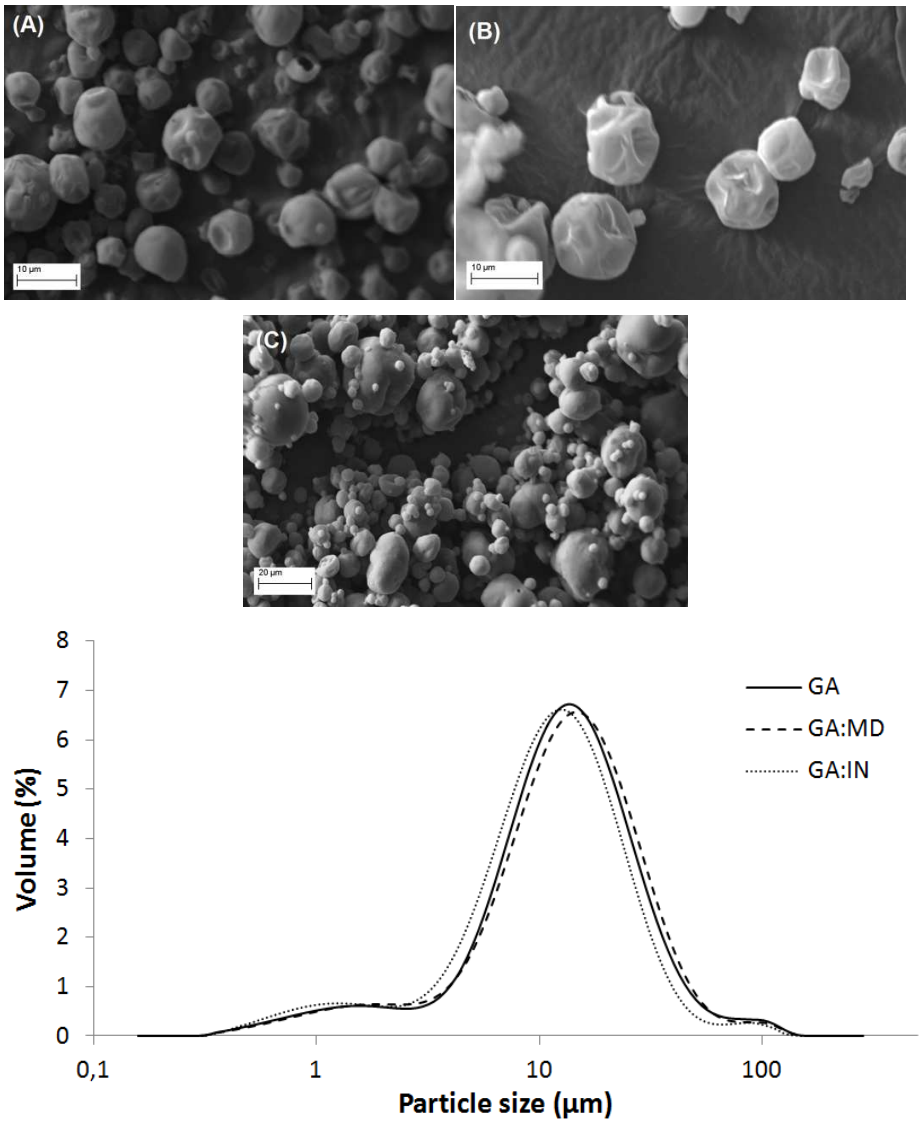

Fig. 7. Scanning electron micrographs of the particles containing ginger essential oil using the following wall materials (A) gum Arabic (GA); (B) gum Arabic/maltodextrin (GA:MD); and (C) gum Arabic/inulin (GA:IN) and particle size distribution of powders.

The particles produced using gum Arabic and maltodextrin presented the higher particle sizes, 6.35 μm, expressed as d_{32} (Table 7). When inulin was applied to formulation instead of maltodextrin, the particle size was decreased and an average value of 5.42 μm was obtained. The polydispersity index, calculated using the PDI equation was low (2.04-2.07) which indicate a homogeneous distribution. According to the literature (Bakry et al., 2016; Jafari et al., 2008c), the diameter of spray-dried particles depends on the atomisation method used, the properties of the material, the concentration and viscosity of the encapsulated material and the drying conditions. There are reports that larger particles have an increased encapsulation efficiency (Jafari et al., 2008c). The presence of inulin produced emulsion droplets with higher particles size, however, this trend was not followed by the dried particles containing inulin, which showed the smaller size.

Table 7. Particle size distribution of the ginger essential oil microparticles produced by using the different wall materials.

Treatment	**d_{43} (μm)**	**d_{32} (μm)**	**d_{10}**	**d_{50}**	**D_{90}**	**PDI**
GA	15.44 ± 0.13^{a}	6.18 ± 0.03^{b}	3.78	12.15	28.85	2.06
GA:MD	15.83 ± 0.14^{a}	6.35 ± 0.03^{a}	3.65	12.71	29.94	2.07
GA:IN	13.41 ± 0.21^{b}	5.42 ± 0.04^{c}	3.07	10.75	24.96	2.04

a,b,c Values with different letters in the same column differ significantly ($p<0.05$) by Duncan test. GA: gum Arabic, MD: maltodextrin, IN: inulin.

3.6 Thermogravimetric analysis (TGA)

TGA is a technique used to study the loss of sample weight as a function of temperature and to evaluate its thermal stability. It is an important technique for verification of the food properties when they are subjected to some kind of heat treatment at higher temperatures as cooking and pasteurization.The particles

containing ginger essential oil showed two or three stages of weight loss (Fig. 8). In all cases a relative thermal stability was observed up to 200 °C, with a weight loss of 4.56 %, 4.19 % and 4.34 % for GA, GA:MD and GA:IN respectively. On the other hand, at temperature of 200 °C, the weight loss observed for the bulk oil was 86.85 %. Above this range of temperature, the mass loss observed corresponded to material decomposition. The first event below 200 °C corresponds to the loss of free water in the materials and also some part of the unprotected volatile oil. The others events are related to the loss of mass because of thermal dehydroxylation/decomposition and volatilization of melted materials (Otálora et al., 2015). The second and third stages (GA-IN) or the second stage (other treatments), between 200 °C and 350 °C, involve reactions of wall material constituents, i.e., carbohydrates (Fritzen-Freire et al., 2012), which may be associated with carbohydrate ring dehydration, decomposition, and depolymerization (Hosseini et al., 2013). Temperatures that provide the greatest weight loss rate in each stage are normally considered as the degradation temperature (Td) (Yoksan et al., 2010). Based on the results, the particles added with maltodextrin and inulin presented lower thermal stability when compared with particles of GA, where inulin was responsible by the higher decrease in the thermal stability.

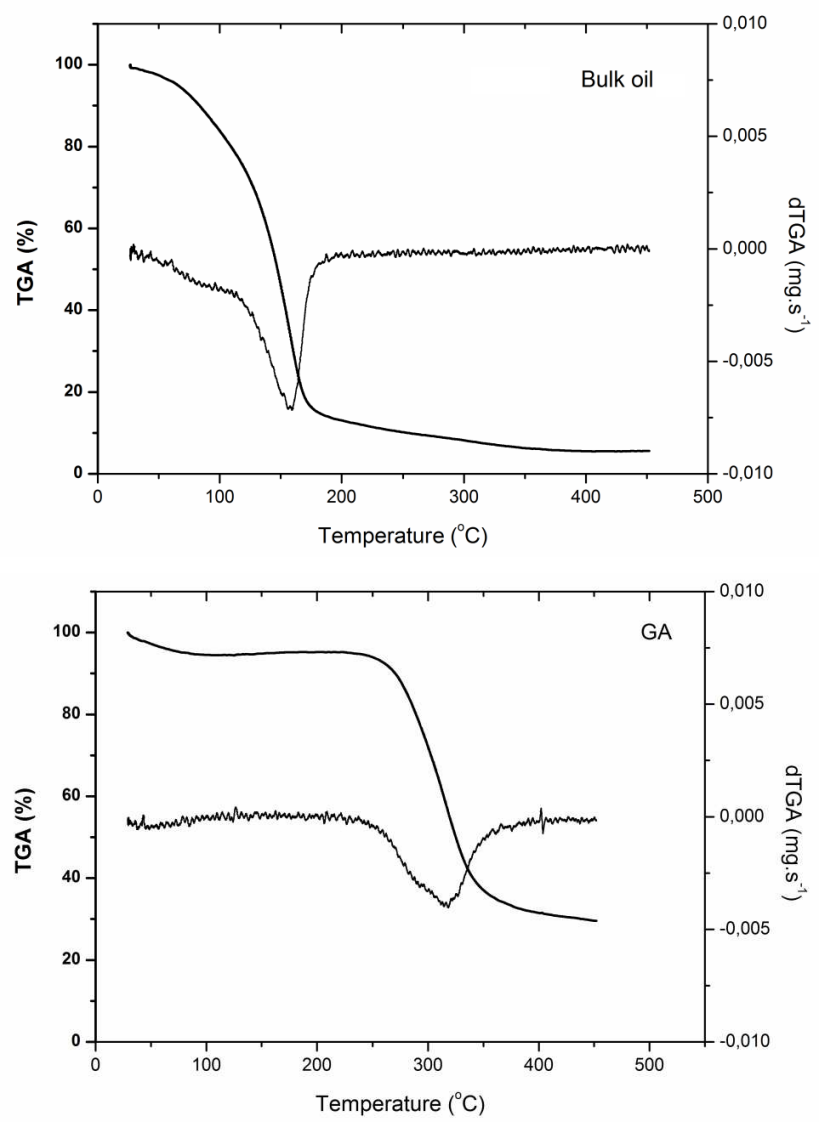

Fig. 8. TGA (A) and DTG (B) curves of the bulk oil and of the particles containing ginger essential oil produced with gum Arabic (GA), gum Arabic and maltodextrin (GA-MD), and gum Arabic and inulin (GA-IN) as wall materials, in a nitrogen atmosphere (…to be continued…).

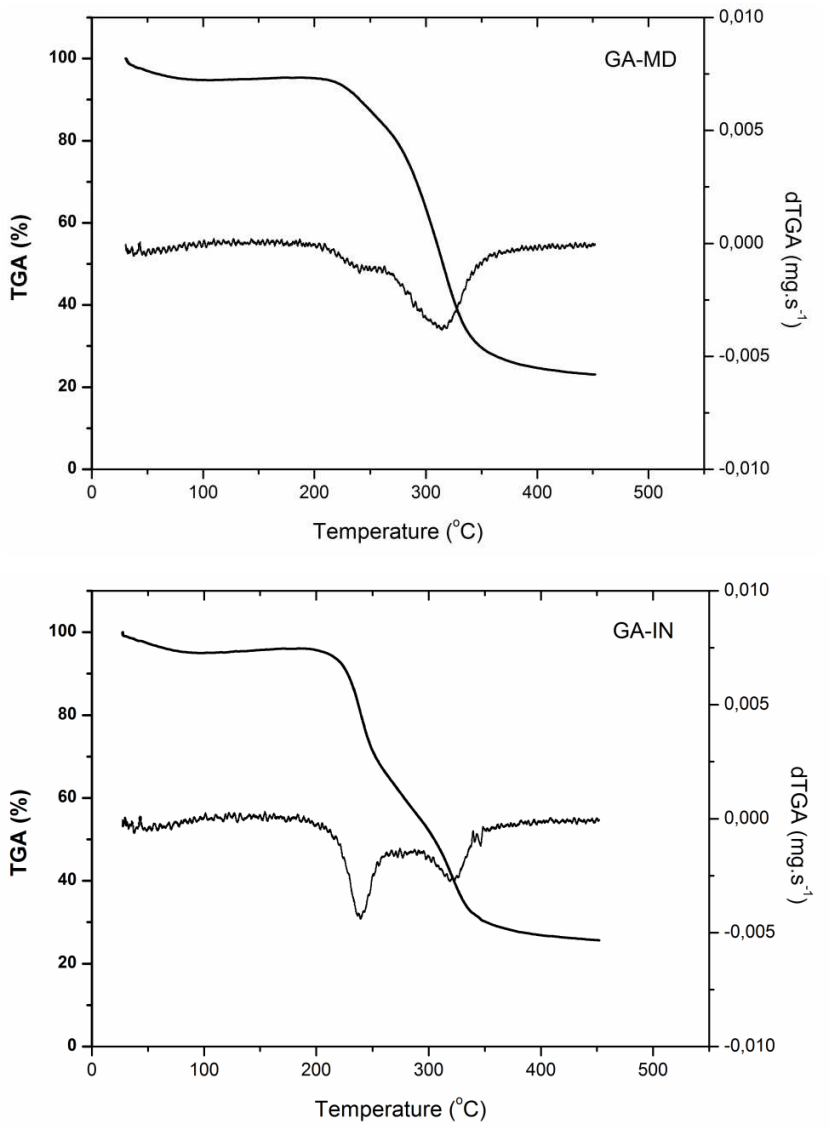

Fig. 8. TGA (A) and DTG (B) curves of the bulk oil and of the particles containing ginger essential oil produced with gum Arabic (GA), gum Arabic and maltodextrin (GA:MD), and gum Arabic and inulin (GA:IN) as wall materials, in a nitrogen atmosphere.

3.7. X-ray diffraction

The X-ray diffraction was used to identify the crystallinity of the samples. In general, a crystalline material presents sharp peaks while amorphous products provide a broader peak pattern (Caparino et al., 2012). Fig. 9 shows powder X-ray diffraction patterns obtained at different treatments of ginger essential oil microparticles and at raw materials used as wall materials. All the samples had an amorphous structure with a minimum of crystallinity, as indicated by diffuse and broad peaks in the diffractograms. The spray drying process did not affect the crystallinity of the wall materials tested.

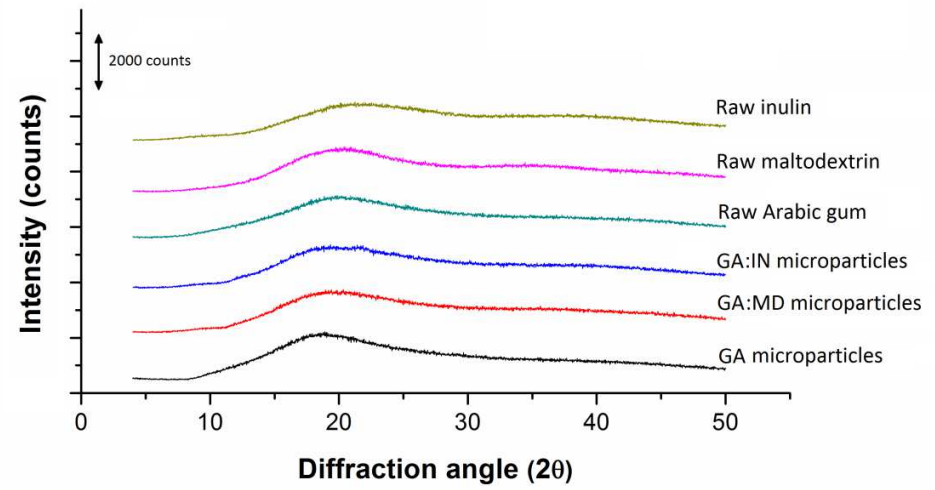

Fig. 9. X-ray diffraction patterns of the raw materials and the microparticles produced. GA: gum Arabic, MD: maltodextrin, IN: inulin.

It should be noticed that the materials produced by spray drying process, presented an amorphous structure, which is a characteristic of products subjected to this specific type of drying process, due to the fast moisture evaporation. It is important to know the physical condition of a dry food, because this condition will influence on powered food properties. Rehydration properties, such as

solubility, may be influenced by the physical state of the powder components. Products with crystalline components tend to dissolves slowly, since the dissolution of crystals occurs only on the outer surface, exposed to the solvent. On the other hand, powders containing amorphous components hydrates quickly because of the low energy levels of bonds between molecules ,when compared to the crystalline state (Marabi et al., 2007). It is known that amorphous solids are in general more soluble and more hygroscopic (Botrel et al., 2014). Data obtained indicate the preservation of biopolymers amorphous phase on produced particles.

4. Conclusions

The use of homogeneization followed by utrasonication was efficient in the emulsion formation when compared with homogeneization process alone. The importance of the use of carbohydrates with a high capacity for emulsification (i.e., gum Arabic) as wall material together with the more suitable secondary wall material was reaffirmed in this study, which showed that such blend materials are more efficient in retaining volatiles compounds. The mixture containing maltodextrin proved to be an effective matrix for retaining ginger essential oil. It has the advantage of being relatively inexpensive and provides excellent protection of the encapsulated materials. The presence of inulin and maltodextrin improved the wettability of the particles, however the presence of inulin decreased the encapsulation efficiency.

Acknowledgements

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ARTIGO 2 Associating whey protein isolate with inulin/maltodextrin for obtaining spray-dried ginger essential oil

Artigo redigido conforme norma da revista Food Hydrocolloids

ASSOCIATING WHEY PROTEIN ISOLATE WITH INULIN/MALTODEXTRIN FOR OBTAINING SPRAY-DRIED GINGER ESSENTIAL OIL

ABSTRACT

The aim of this study was evaluate the effects of associating whey protein isolate (WPI) with maltodextrin (MD) and inulin (IN) biopolymers on the ultrasound-assisted emulsification of ginger essential oil and producing spray-dried microparticles. The higher viscosity values were obtained for the emulsions prepared with WPI and IN. Moreover, the ginger essential oil emulsion stabilized by WPI and IN had the apparent viscosity increased when ultrasound-assisted was applied in the emulsification process. The emulsions obtained by using ultrasound were more stable according on the creaming index. The solubility and moisture content of the particles were not affected by the wall material. The wettability property of the powders was improved by the addition of IN. The lowest level of water absorption under conditions of high relative humidity was observed in treatments containing IN. The partial replacement of WPI by MD (1:1, w/w) significantly affect the efficiency of encapsulation. Larger particles were observed in the powders prepared with WPI. All of the powders obtained from these treatments exhibited an amorphous structure and did not present cracks in the surface. The use of IN and MD proved to be good alternative secondary wall materials for ginger oil together with WPI.

Keywords: Milk protein, prebiotic carbohydrate, ultrasound-assisted emulsification, microencapsulation

1. Introduction

Ginger belongs to the family *Zingiberaceae*. It is cultivated in many countries, and commercialized to other parts of the world (Jelled et al., 2015). It is among the oldest cultivated horticultural crops and is a common food additive in a number of foods and beverages (Unni et al., 2015). Ginger is well known for its nutraceutical value, which can be attribute to a variety of bioactive compounds, including the gingerols, zingiberene and the shogaols (Butt & Sultan, 2011; Semwal et al., 2015).

In encapsulation processes, a compact and continuous polymeric film encloses the core material, forming a microcapsule (Porras-Saavedra et al., 2015). Spray-drying is the most commonly used technique for the encapsulation of essential oils. It is a low-cost microencapsulation technology commonly used on an industrial scale, which has the attractive advantages of producing microcapsules in a relatively simple, continuous operation and inexpensive, compared to other microencapsulation techniques (Bakry et al., 2016). The solution homogenization is an important step which precedes the drying process and proteins have been widely used for stabilising food emulsions. The emulsion can be homogenized by high pressure or ultrasound to obtain the uniform and small oil droplets (Le & Le, 2015). Ultrasonic emulsification is an emerging technique used to produce stable emulsion (Ramisetty et al., 2015). It is of great interest for the food industry, to investigate methodologies that are capable to enhance the emulsifying properties of proteins (O'Sullivan et al., 2014). The ultrasonic emulsification process has been proposed as a two-step mechanism: in the first step, a combination of interfacial waves and instability leads to the eruption of dispersed phase droplets into the continuous phase, and the second step consists of breaking up of droplets through acoustic cavitation near the interface (Shanmugam & Ashokkumar, 2015).

Encapsulation efficiency may be increased by means of selecting wall materials that present different functional properties. Whey proteins, which make up 20 % of the milk proteins, are of considerable interest as an encapsulant in the food industry because of their high nutrition value (Khem et al., 2016) and the presence of hydrophobic and hydrophilic amino acids which makes this product excellent copolymers feasible for encapsulation of hydrophobic compounds (Liu et al., 2016). Carbohydrates with shorter chains e.g., maltodextrin and inulin, act as filling agents and matrix formers. The principal disadvantage of most carbohydrates as encapsulating materials is their low emulsifying capacity and lower volatile retention, but they are being increasingly studied for use in polymeric mixtures. Maltodextrin, a white glucose polymers, exhibits a neutral taste, is odorless and is easily digested by humans (Otálora et al., 2015). The inulin from chicory roots is commercialised as a purified food ingredient and due to its technical and nutritive properties, inulin may also be an interesting possible encapsulation agent (Turchiuli et al., 2014).

All the potential attributes of essential oils and the increasing demand for natural additives in the food industry have led to study the ginger powder as a potential food ingredient. The choice of wall material or the ideal mixture of wall materials for each system is of extreme importance, since the encapsulating material determines many of the physicochemical characteristics of the product in powdered form, as well as its behavior during storage. The partial replacement of whey protein isolate by carbohydrates could increase the volatiles retention in the encapsulation of ginger essential oil during spray drying. Thus, the objective of this study is to apply spray drying technique to produce microencapsulated ginger essential using WPI, WPI:MD and WPI:IN as wall systems. The effects of emulsification processes (with and without ultrasound emulsification) on stability parameters of emulsion were evaluated.

The influence of different wall material system was investigated based on properties and functionalities of microparticles in terms of stability and characteristics of the emulsion, encapsulation efficiency, reconstitution properties, chemical profile, microparticles stability, morphology, particle size distribution and crystallinity.

2. Materials and Methods

2.1. Materials

Ginger (*Zingiber officinale*) essential oil (Ferquima, Vargem Grande Paulista, Brazil) was used as the core material. Whey protein isolate (Hilmar Ingredients, Hilmar, USA), high-performance inulin (degree of polymerisation >10, Orafti®GR, BENEO-Orafti, Tienen, Belgium) and maltodextrin (Maltogil DE 10, Gargil, São Paulo, Brazil) were used as wall materials.

2.2. Preparation of ginger essential oil emulsion

The volume of each emulsion was set at 400 mL. The ratio between the ginger essential oil and each biopolymer was maintained at 1:4 (w/w) (Fernandes et al., 2014). Each hydrocolloid suspension (whey protein isolate (WPI), whey protein isolate + maltodextrin (1:1; w/w) (WPI:MD) and whey protein isolate + inulin (1:1; w/w) (WPI:IN)) was prepared by dissolving the material at 20 % (w/w) (Fernandes et al., 2013a,b) in distilled water. The solutions were prepared the day before emulsification and stored at room temperature for 12 h to ensure complete saturation of the molecules of the materials.

The ginger essential oil was slowly incorporated into each polysaccharide suspension by mechanical stirring at 1000 rpm for 5 min, using a rotor-stator blender (Ultra-Turrax IKA T18 basic, Wilmington, USA), to form emulsions (H). For the treatments where the ultrasound was applied (H/U), after

the homogenization process by mechanical stirring, the samples were submitted to ultrasonication at 160 W of nominal power (Branson Digital Sonifier®, Model S-450D, Branson Ultrasonics Corporation, Danbury, USA), 20 kHz, for 2 min. The height contact between the ultrasonic probe and the emulsions was standardized to 30 mm. The effect of the ultrasound was investigated and the emulsification experiments were performed in triplicate according to Table 1 with three replicates.

Table 1. Composition of the feed emulsions and emulsion processes used in the experiments

Feed emulsion ($g.100g^{-1}$)				**Emulsion step**	
WPI	**MD**	**IN**	**Oil**	**Homogenization (H)**	**Ultrasonication (U)**
20	-	-	5	x	
20	-	-	5	x	x
10	10	-	5	x	
10	10	-	5	x	x
10	-	10	5	x	
10	-	10	5	x	x

WPI: whey protein isolate; MD: maltodextrin; IN: inulina

2.3. Characterisation of the emulsions

2.3.1. Emulsions viscosity

Rheological measurements were conducted using a concentric cylinder viscosimeter (Brookfield DVIII Ultra, Brookfield Engineering Laboratories, Stoughton, MA, USA), assembled with a cylindrical sample chamber 13R/RP (19.05 mm of diameter and depth of 64.77 mm), and a spindle SC4-18 (17.48 mm of diameter and 35.53 mm length). For each test, the filled sample cup (6.7

mL) and spindle were temperature equilibrated (at 25 °C). Flow curves were obtained at shear rates of 0.1-171.7 s^{-1} for the emulsion submitted to homogenization and of 0.1-85.9 s^{-1} for the emulsion submitted to homogenization followed by ultrasonification. The power law model (Eq. 1) was used to analyze the flow properties of the emulsified samples, as follows.

$$\boldsymbol{\tau = k.\gamma^{n}} \qquad (\mathbf{1})$$

where τ = shear stress (Pa), γ = shear rate (s^{-1}), k = the consistency index ($Pa.s^{n}$), and n = the flow behaviour index (Silva et al., 2015). Apparent viscosity of the emulsion was calculated as the ratio between the shear stress and the shear rate at 40 s^{-1}.

2.3.2. Emulsion droplet size

The droplet size distribution of the emulsions was determined by light scattering using laser diffraction (Mastersizer 2000 Malvern Instruments Ltd., Malvern, UK). The average diameter was calculated based on the average diameter of an area of a similar sphere, the surface mean diameter (d_{32}), while the volume surface mean diameter (d_{43}) and the polydispersity index (PDI) were determined according Eq. (2), (3) and (4), respectively. The samples were analyzed in triplicate for each repetition of the evaluated emulsion by the wet method with dispersion in water and a refractive index of 1.52. The measurements were performed at 25 °C.

$$\mathbf{d_{32}} = \frac{\sum \mathbf{n_i d_i^3}}{\sum \mathbf{n_i d_i^2}} \quad (\mathbf{2})$$

$$\mathbf{d_{43}} = \frac{\sum \mathbf{n_i d_i^4}}{\sum \mathbf{n_i d_i^3}} \quad (\mathbf{3})$$

$$\mathbf{PDI} = \frac{\mathbf{d_{90} - d_{10}}}{\mathbf{d_{50}}} \quad (\mathbf{4})$$

where d_i is the average droplet diameter; n_i is the number of drops; and d_{10}, d_{50} and d_{90} are the diameters at 10 %, 50 % and 90 % cumulative volume, respectively.

2.3.3. Optical microscopy

The emulsions optical microscopy was performed immediately after their preparation. The samples were poured onto microscopes slides, covered with glass cover slips and observed using a Carl Zeiss Model MF-AKS 24 x 36 Expomet optical microscope (Zeiss, Germany).

2.3.4. Creaming stability

The creaming index (CI) of the ginger essential oil emulsions was analyzed as described by Silva & Meireles (2015). Immediately after emulsion preparation, 25 cm^3 aliquots of each emulsion were poured into a cylindrical graduated glass tube (internal diameter = 1.8 cm, height = 16.5 cm), sealed and stored at 25 °C for 30 h. The emulsion stability was measured by the height of the upper phase over the storage period. The CI was determined according to Eq. (5):

$$\mathbf{CI}\ (\%) = \left(\frac{\mathbf{Hc}}{\mathbf{Ht}}\right)\mathbf{x100} \quad (\mathbf{5})$$

where Ht represents the initial height of the emulsion and Hc is the upper phase height (cream phase).

2.4. Microencapsulation by spray drying

The spray drying process was conducted only for the emulsions obtained when applying the ultrasonication step (H/U). The feed emulsions were dried using a spray-dryer (model MSD 1.0; Labmaq do Brasil, Ribeirão Preto, Brazil) equipped with a two-fluid nozzle atomiser. The following operational conditions were used, as described in previous studies: inlet temperature of 170 ºC and feed rate of 0.8 Lh^{-1} (Fernandes et al., 2013a,b). The atomasing air flow was kept in 35 $L.min^{-1}$. The dried powder was collected and stored in opaque airtight containers at 4 °C until further analysis. The effects of the encapsulating systems were evaluated.

2.5. Characterisation of the microcapsules

2.5.1. Moisture content

The moisture content of the powder was determined gravimetrically by oven-drying at 105 °C to constant weight (Association of Official Analytical Chemists [AOAC], 2007).

2.5.2. Reconstitution properties

The wettability of the powders was determined using the method described by Fuchs et al. (2006). One gram of powder was sprinkled over the surface of 100 mL of distilled water at 20 °C without agitation. The time taken for the powder particles to sediment, sink, be submersed and disappear from the water's surface was recorded and used for a comparison of the extent of wettability of the samples.

The solubility of the powders was evaluated according to the method proposed by Cano-Chauca et al. (2005), with modifications. The powders were weighed (1 g) and stirred into 25 mL of distilled water for 5 min using a blender. The solution was then centrifuged at 760×g for 10 min. An aliquot of 20 mL of

the supernatant was transferred to a pre-weighed Petri dish and oven-dried at 105 °C overnight. The solubility (%) was calculated as the percentage of dried supernatant in relation to the amount of powder originally added (1 g).

2.5.3. Essential oil encapsulation efficiency

Ginger essential oil content in the microparticles was determined as described by Li & Lu (2016), with some modifications. 1000 mg sample was dissolved in 20 mL distillate water in glass tubes assisted by ultrasound (2 min), followed by 10 mL hexane addition and mixing for 1 min. Essential oil was extracted with hexane by heating the sample in glass tubes at 45 °C in a water bath with intermittent mixing. The tubes were cooled to room temperature and hexane was separated from the aqueous phase by centrifugation at 3000 rpm for 5 min. The extraction was performed four times. The amount of ginger essential oil in hexane was quantified by measuring absorbance at 270 nm in a UV-visible spectrophotometer (Bel Photonics, Piracicaba, Brazil) and its concentration was calculated using a calibration curve. Essential oil encapsulation efficiency (EE) was determined using Eq. (6):

$$\mathbf{EE}\ (\%) = \frac{\boldsymbol{M}}{\boldsymbol{M_0}} \boldsymbol{x}\ \mathbf{100} \qquad (\mathbf{6})$$

where M is the amount (mg) of oil in in microparticles and M_o is the initial oil amount (mg) added to the emulsion.

2.5.4. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy was performed on the pure essential oil, the wall materials and the powders. These measurements were taken at ambient temperature, in the range of 400–4000 cm^{-1}, using an Fourier transform infrared Jasco 4100 spectrometer.

2.5.5. Moisture sorption isotherms

The sorption isotherms for the treatments were determined using the gravimetric static method with a saturated saline solution at 25 °C. The seven saturated saline solutions (NaCl, K_2CO_3, $MgCl_2$, LiCl, $Mg(NO_3)_2$, KCl and K_2SO_4) had water activities ranging from 0.12 to 0.98. The moisture sorption isotherm data were correlated to the water activity (relative humidity) using the following mathematical models: GAB, Halsey, Henderson and Oswin and Smith (Toledo Hijo et al., 2015).

The parameters of these equations were estimated by correlating the mathematical models to the experimental data using a quasi-Newton nonlinear regression. The model that was considered most suitable was based on the low mean relative percentage deviation modulus (E), defined as follows in Eq. (7):

$$\mathbf{E} = \frac{\mathbf{100}}{\mathbf{N}} \sum_{\mathbf{i=1}}^{\mathbf{N}} \frac{\left|\mathbf{m_i} - \mathbf{m_{pi}}\right|}{\mathbf{m_i}} \qquad (\mathbf{7})$$

where m_i is the experimental value, m_{pi} is the predicted value and N is the population of experimental data.

2.5.6. Thermogravimetric analysis

Curves were obtained using TGA50H thermobalance (Coorporation Shimadzu, Kyoto, Japan) under the following operating conditions: alumina pan; dynamic nitrogen atmosphere with flow of 100 mL min^{-1}; heating rate: 10 °C min^{-1}; temperature range: 50-550 °C. Approximately 5 mg of sample were used.

2.5.7. X-ray diffraction

Samples of products were placed in a support for powder and covered with a glass sheet. Measurements were performed using a Shimadzu X-ray diffractometer (model XRD-6000) using Cu-Kα1 radiation with a wavelength of

1.54 Å at 30 kV and 30 mA. Samples were analyzed at angles from 4° to 40° in 2 h with an increment of 0.02° (1.2° min^{-1}).

2.5.8. Particle morphology and size distribution

The particle morphology of the samples was evaluated using scanning electron microscopy (SEM). The powders were attached to a double-sided adhesive tape mounted on SEM stubs with a diameter of 1cm and a height of 1 cm, coated with gold in a vacuum evaporator and examined using an MEV 1430 VP – LEO scanning electron microscope (Electron Microscopy Ltd., Cambridge, UK). The SEM was operated at 20 kV with magnification of 900–1200x.

The particle size distribution was determined for all of the samples using a Mastersizer 2000 laser light diffraction instrument (model Hydro 2000 MU, Malvern Instruments, Malvern, UK). A small sample of powder was suspended in ethanol with agitation and the particle size distribution was monitored during each measurement until successive readings were consistent. The area-weighted mean diameter (d_{32}), volume-weighted mean diameter (d_{43}) and the polydispersity index (PDI) were calculated using Eq. (2), (3) and (4).

2.6. Statistical analysis

Analysis of variance in factorial design was performed to evaluate the effect of ultrasound and the polymer composition on the emulsion parameters studied. One way analysis of variance was performed to evaluate the effect of encapsulating matrices composition on the properties of the microparticles. Significant differences ($p<0.05$) between the treatments mean values were examined by *Duncan* test. The experiments were performed in triplicate.

3. Results and discussion

3.1. Emulsion characterisation

The preparation of the emulsion to be processed is the first step involved into the process of encapsulation by spray drying. The ability of each encapsulating agent to produce small and uniform particle size is related with its ability to completely cover the oil drops during homogenization and prevents its coalescence after homogenization (Rascón et al., 2011). The rheological properties of foods are very important for product development and design in food processing and to know the exact behavior of food to produce a specific product (Yanjun et al., 2014). The formulation procedure may involve the incorporation of a hydrocolloid stabilizer during emulsification. Proteins generally stabilize emulsions by forming a coating over oil droplets and, thus, preventing agglomeration (Kaushik et al., 2016). Emulsions exhibit a wide variety of different rheological behaviors depending on their composition, structure, and droplet interactions (McClements et al., 2007). The viscosity of the liquid feeds to be spray dried should be lower than 300 mPa.s to ensure good atomization (Battista et al., 2015) and in the present study all the treatments were in the ideal range.

The relation between viscosity and shear rate for the emulsions produced with different composition and obtained using H (homogenization) and H/U (homogenization/ultrasound) processes are presented in Fig. 1. The higher viscosity values were obtained for the emulsions prepared with whey protein isolate and inulin. Moreover, the ginger essential oil emulsion stabilized by whey protein isolate and inulin had the apparent viscosity increased when ultrasonication was applied in the emulsification process (Table 2). Inulin is commonly used as a gelling agent in food because it forms a solution with high viscosity in water. On the other hand, the lowest viscosity values were obtained for the emulsions prepared with whey protein isolate and maltodextrin. Aqueous

solutions containing maltodextrin have commonly low viscosity (Santiago-Adame et al., 2015) and this carbohydrate can contribute to decrease the viscosity when applied with whey protein isolate.

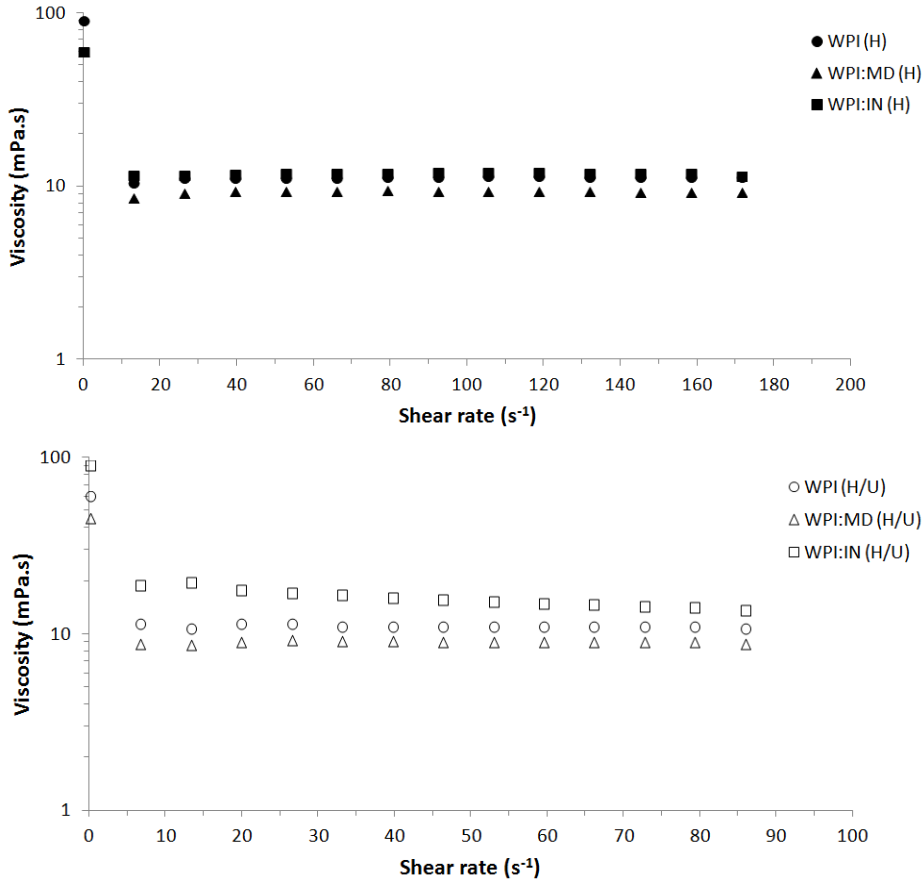


Fig 1. Rheological parameters obtained for the feed emulsions submitted to the homogenization (H) and homogenization followed by ultrasound (H/U) processes. GA: gum Arabic, MD: maltodextrin, IN: inulin.

Table 2. Valued for apparent viscosity (mPa.s) of the emulsions produced using different wall materials and by homogenization (H) and ultrasonication (H/U).

	Emulsification process	
Wall	**H**	**H/U**
material	**Apparent viscosity (mPa.s)**	
WPI	11.21 ± 0.14^{aA}	11.08 ± 0.26^{bA}
WPI:MD	9.44 ± 0.13^{cA}	9.06 ± 0.25^{cA}
WPI:IN	11.71 ± 0.37^{bB}	13.67 ± 0.29^{aA}

Values with different letters (lower case) for the same emulsification process and different letters (upper case) using the same wall material differ significantly ($p<0.05$) by Duncan test. WPI: whey protein isolate, MD: maltodextrin, IN: inulin.

Ultrasound treatment of the samples caused increase in apparent viscosity for the treatment WPI:IN. In such cases, the changes in flowing behaviour upon ultrasound treatment are a consequence of changes in binding capacity for water, i.e. hydrophilic parts of amino acids are opened toward water surroundings leading to higher binding of water molecules (Krešić et al., 2008; Phillips & Williams, 1995).

The emulsions were considered to present Newtonian fluid behavior characteristics with n values close to 1, except the emulsion produced using WPI and IN where was considered to have a non-Newtonian fluid behavior typically pseudoplastic (n <1). The Power law model was well fitted to the experimental data obtained high determination coefficient values and low average relative error values (Table 3).

Table 3. Rheological parameters for the emulsions produced using different wall materials and by homogenization (H) and ultrasonication (H/U).

Treatments					
Wall material	**Emulsification process**	**K (mPa.s^n)**	**n**	**R^2**	**E(%)**
WPI		0.01	1.00	0.99	7.05
WPI:MD	**H**	0.01	0.99	0.99	7.17
WPI:IN		0.01	0.98	0.99	6.35
WPI		0.01	0.97	0.99	6.00
WPI:MD	**H/U**	0.01	0.98	0.99	6.59
WPI:IN		0.03	0.81	0.99	6.13

WPI: whey protein isolate, MD: maltodextrin, IN: inulin. K: consistency index; n: flow behavior index; E: mean relative error.

The results of the average droplet size and polydispersity index of essential oil-polysaccharides emulsions are shown in Table 4, and their droplet size distribution is presented in Fig. 2. Diferences among emulsion droplet size and size distribution were observed depending on the carbohydrate used in the formulation of emulsions and the reduction in emulsion droplet size does not exclusively depend on the type of energy provided to the system (H or H/U). The emulsification processes of ginger essential oil and the different wall materials combinations resulted in emulsions with droplet diameter (d_{43}) ranging from 3.71 to 60.97 µm with higher values obtained for the whey protein isolate emulsificated by homogenization and lower values for whey protein isolate with the application of ultrasonication as an emulsification method. The processing of blends by ultrasonication after a previous homogenization rendered emulsions with a expanded droplet size only for the treatment with maltodextrin addition. This suggests possible overprocessing for the emulsification of these

biopolymers because too intense homogenization can increase the droplet size of the emulsion (Floury et al., 2003; Jafari et al., 2007; Silva et al., 2015). Higher degree of polydispersity in the distribution of droplet size can be observed for the emulsions prepared using WPI (H) and WPI:MD (H/U). For the treatment WPI, the acoustic cavitation phenomenon, due application of low frequency ultrasound, is what promotes the breaking of the droplets during emulsification using ultrasound (Silva et al., 2015), provided significantly smaller droplet sizes when the ultrasound was applied. Microscopy methods were used in order to investigate the size, shape and morphology (Xiang et al., 2016). Fig. 2 shows also the microstructure of the emulsions created by the different emulsification process and proteins/carbohydrates matrices. The micrographs confirm the results obtained in the droplet size distribution. It is observed that the processes result in different colloidal systems and that the benefits of the U/H process, independent of the biopolymer used in the emulsification of ginger essential oil. The presence of dispersed oil droplets contributes to higher values of the apparent viscosity of the emulsions (Petrovic et al., 2010).

Table 4. Particle size distribution of the emulsion droplets produced by homogenization (H) and ultrasound process (H/U) for the evaluated treatments.

Wall material	EP	d_{43} (µm)	d_{32} (µm)	d_{10}	d_{50}	d_{90}	PDI
WPI		$60.97^{aA} \pm 0.98$	$4.29^{bA} \pm 0.02$	1.16	4.32	9.74	1.98
WPI:MD	**H**	$5.70^{cB} \pm 0.05$	$2.19^{cA} \pm 0.01$	1.14	4.92	12.44	2.30
WPI:IN		$13.78^{bA} \pm 0.09$	$5.06^{aA} \pm 0.08$	1.48	6.85	16.96	2.26
WPI		$3.71^{bB} \pm 0.41$	$1.28^{bB} \pm 0.02$	0.68	1.57	5.68	3.19
WPI:MD	**H/U**	$8.64^{aA} \pm 0.72$	$1.32^{bB} \pm 0.04$	0.81	1.72	3.46	1.54
WPI:IN		$8.45^{aB} \pm 0.15$	$2.50^{aB} \pm 0.03$	0.92	2.63	14.24	5.06

Values with different letters (lower case) for the same emulsification process (EP) and different letters (upper case) using the same wall material differ significantly ($p<0.05$) by Duncan test. WPI: whey protein isolate, MD: maltodextrin, IN: inulin.

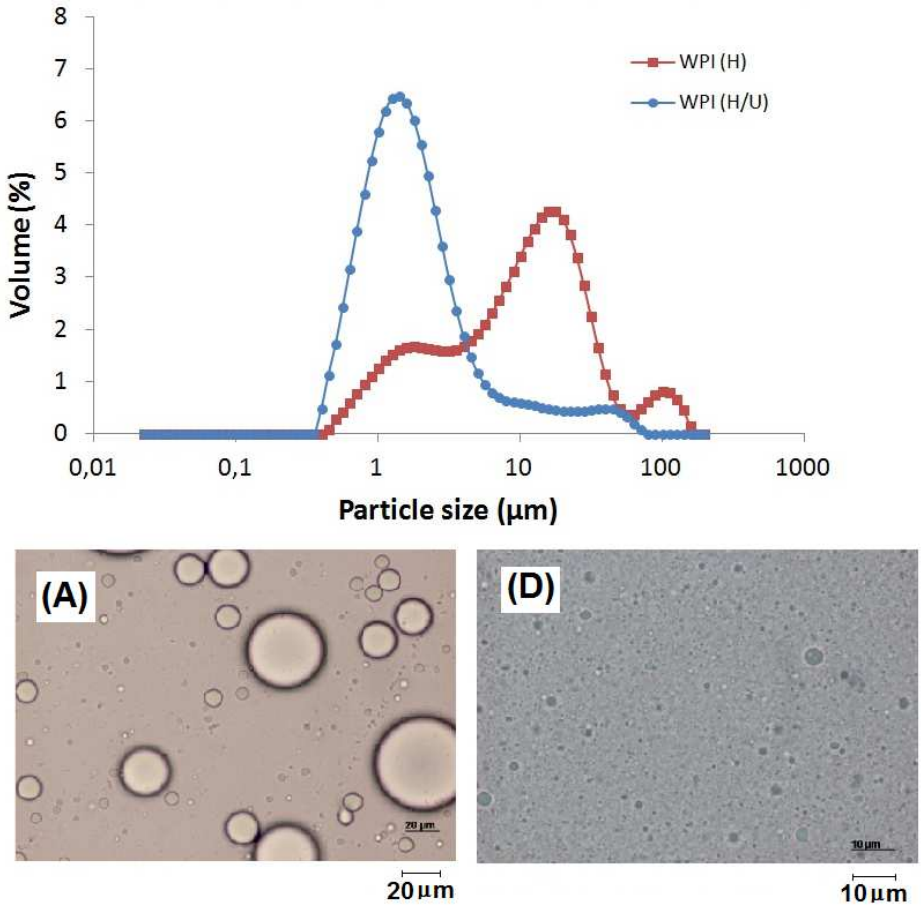
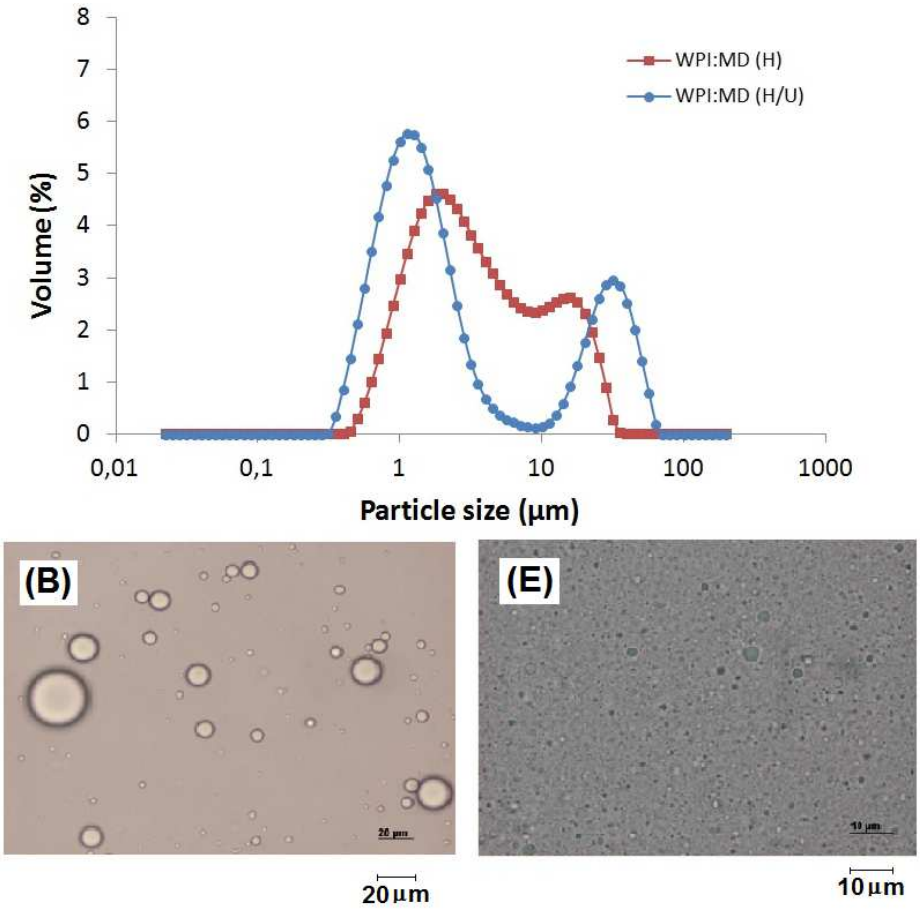


Fig. 2. Droplet size distribution curves of the ginger essential oil emulsions processed by homogenization (H) and homogenization plus ultrasound (H/U) and optical micrograph of the ginger essential oil emulsions processed by homogenization (U) (A,B, C) and homogenization plus ultrasound (H/U) (D,E, F). WPI: whey protein isolate, MD, maltodextrin, IN: inulin (…to be continued…).



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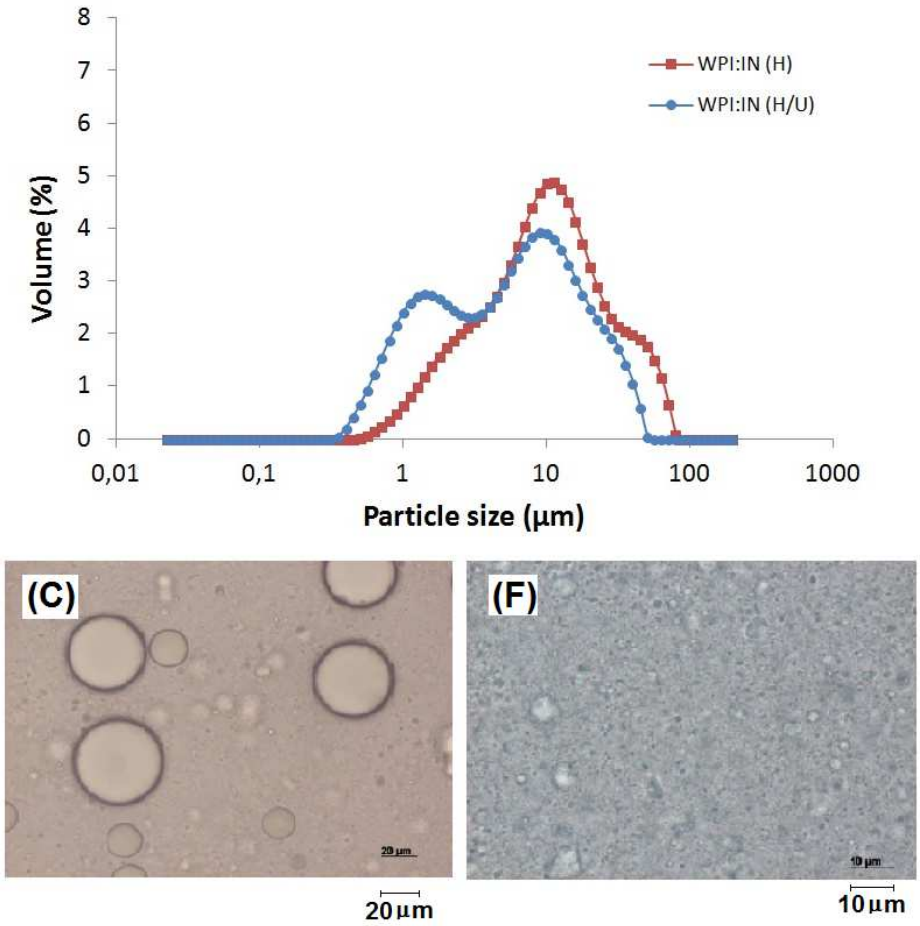

Fig. 2. Droplet size distribution curves of the ginger essential oil emulsions processed by homogenization (H) and homogenization plus ultrasound (H/U) and optical micrograph of the ginger essential oil emulsions processed by homogenization (U) (A,B, C) and homogenization plus ultrasound (H/U) (D,E, F). WPI: whey protein isolate, MD, maltodextrin, IN: inulin.

Under quiescent conditions, the most obvious manifestation of emulsion instability is creaming, and the rate of creaming is very sensitive to droplet size distribution (Bernard et al., 2011). Creaming is the upward movement of

droplets due to the fact that they have a lower density than the surrounding liquid, whereas sedimentation is the downward movement of droplets due to the fact that they have a higher density than the surrounding liquid (McClements et al., 2007). An emulsion with a stable core material into the wall material solution is a critical factor on microencapsulation and must be stable over a certain period of time, before spray drying step (Bakry et al., 2016). The stability of the emulsions to creaming was shown in Fig. 3. The decrease in the CI for WPI and WPI:MD treatments that had ultrasound-assisted can be explained by emulsions produced using ultrasound are more stable and have droplets with an homogeneousy particle size distribution. The decrease in CI can be explained by the more favorable orientation of proteins resulting from the influence of turbulent behavior produced by ultrasound (Yanjun et al., 2014). The emulsion stability improved with the addition of inulin and in both cases (H or H/U) with the addition of inulin the creaming phenomenon not occurred. This fact can be linked to the gelling of the colloidal system promoted by the high shear of inulin during ultrasonic emulsification. Inulin gel development is a dynamic process in which the amorphous inulin in contact with water starts a nucleation and crystallisation process (Alvarez-Sabatel et al., 2015; Glibowski and Pikus, 2011). The gel structure acted as a physical barrier to coalescence of the oil droplets and promoted stability in these systems (Silva & Meireles, 2015). Besides that physico-chemical properties of protein-polysaccharide complexes increase the entropy of mixing of biopolymers and their co-solubility contributing to more stable emulsions (Rodea-González et al., 2012; Tolstoguzov, 2003).

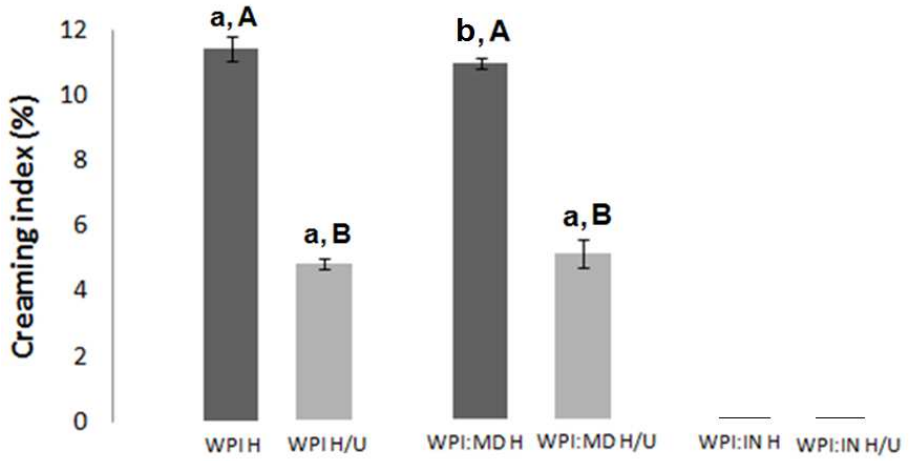

Fig. 3. Effect of the emulsification process and the wall material system on the creaming index (%) of the emulsions. Values with different letters (lower case) for the same emulsification process and different letters (upper case) using the same wall material differ significantly ($p<0.05$) by Duncan test. WPI: whey protein isolate, MD: maltodextrin, IN: inulin

3.2. Particle characterisation

Considering the lower yield of microencapsulation ginger essential oil when applying only the homogenization process and better results for the ultrasound-assisted emulsions, the characterisation of the particles was performed only for treatments assisted by ultrasound. The particle characterisation results are shown in Table 5. Long shelf life of dried product is closely related to low moisture content. Moisture contents of all spray-dried emulsions varied from 1.05 to 1.98 % and were not significantly different ($p>0.05$). In general, moisture content of 3–4 % is the minimum specification for most dried powders used in the food industry (Goyal et al., 2015). The moisture content values found were considered low and within a range that ensures a long shelf life.

Table 5. Mean values and standard deviations for the moisture content, wettability, solubility and oil retention of the particles produced.

Wall material	Variables			
	Moisture (%)	**Wettability (s)**	**Solubility (%)**	**Encapsulation efficiency (%)**
WPI	1.98 ± 0.52^{a}	435 ± 31^{a}	$76.94 \pm 1{,}49^{a}$	47.13 ± 1.39^{b}
WPI:MD	$1.05 \pm 0{,}62^{a}$	347 ± 17^{b}	78.62 ± 3.34^{a}	61.64 ± 5.60^{a}
WPI:IN	1.76 ± 0.69^{a}	316 ± 19^{b}	81.58 ± 7.47^{a}	48.14 ± 1.78^{b}

[a,b] Values with different letters in the same column differ significantly ($p < 0.05$) by Duncan test. WPI, whey protein isolate; MD, maltodextrin; IN, inulin.

Wettability describes the ability of a solid surface to be wetted by a liquid and, thus, the potential of the liquid continuous phase to stabilize and encapsulate the dispersed phase (Battista et al., 2015). In the present study, the time needed for the powders to become completely wet ranged from 316 s to 435 s. The type of wall material significantly affected this property. The shortest wettability time was observed when inulin and maltodextrin were used in the formulation, suggesting that these materials improved the instantising characteristics of the particles. The WPI:IN microcapsules adsorbed water faster due to the high number of hydrophilic groups (–OH) of inulin which increased the adherence capacity of water molecules on the surface of microcapsules. The same behavior was found by Dima et al. (2016) in the study of *Coriandrum sativum* L. essential oil from chitosan/alginate/inulin microcapsules which the shorter time was found for coriander essential oil microencapsulated by spray drying using chitosan and inulin as carrier agents. The whey protein isolate obtained the largest wettability values probably by the characteristic of the material that has larger hydrophobic chain in its structure.

Pure ginger essential oil is not soluble in pure water at room temperature, whereas encapsulating the essential oil resulted in better solubility and facilitated the incorporation in a food matrix. The powders used as ingredients for the food industry must exhibit good solubility. All of the particles were relatively soluble despite the hydrophobic nature of the core material, yielding results ranging from 76.94 % to 81.58 % and did not present significantly difference.

The principal challenge to producing powders by spray drying is developing powders with desirable properties and reduced costs. For the specific case of essential oils, research into microencapsulation by means of spray drying is concentrated on improving encapsulation efficiency and retaining volatiles, in addition to trying to extend the maximum product shelf life. Therefore, one of the most important quality parameters for the encapsulation of an essential oil is the microencapsulation efficiency, which is the percentage of the initial amount of essential oil that is encapsulated. The encapsulation efficiency values ranged between 48.14 % and 61.64 %. There was significant difference ($p<0.05$) among the oil retention capacity of samples and the treatment of WPI:MD was more effective in retaining the oil. Spray drying-microencapsulation of cinnamon infusions (*Cinnamomum zeylanicum*) showed high efficiency of encapsulation (>70 %) using maltodextrin (Santiago-Adame et al., 2015). In the study of Dima et al. (2016) the efficiency of encapsulation ranged from 51 % to 63 %, and it is lower when inulin was applied to the carrier matrix. The nature of the wall material is one of the main factors in the retention of volatile constituents.

FT-IR spectroscopy was applied to show the charachteristics of the encapsulated ginger essential oil into whey protein isolate different matrices. Fig. 4 shows spectra of all components applied in microencapsulation process. Ginger essential oil (bulk oil) bands are associated to C=C and C=C-C=C stretching at 1740 and 1640 cm^{-1}, respectively. Another important vibrational

mode associated to –CH2- groups is presented in the essential oil spectrum at 2922 cm^{-1} (Dalonso et al., 2009; Schulz et al., 2005). Isolated whey protein (WPI) spectrum provides bands associated to C=O stretching (amide I peptide bonds) at 1515 and 1630 cm^{-1} (Silverstein et al., 2006).

Maltodextrin is a polymer consisting of β-D-glucose units connected by glycosidic bonds (1→4) and mainly is applied as a storage stabilizer by reduction of stickiness, agglomeration problems and difficulties to dry (Gabas et al., 2007).

Inulin is a polymer assembled by fructose units with β(2-1) links ended by glucose monomers and, as the maltodextrin, presents encapsulating properties (Bakowska-Barczak & Kolodziejczyk, 2011). It can improve calcium bioavailability, being a dietary fibre which shows prebiotic effects (Robert et al., 2012). Inulin (IN) and maltodextrin (MD) present almost same spectrum profile, featuring the band assigned to C-O-C at 1015 cm^{-1}. Absorption bands associated to O-H bonds (3000-3600 cm^{-1}) are detected from WPI, IN and MD.

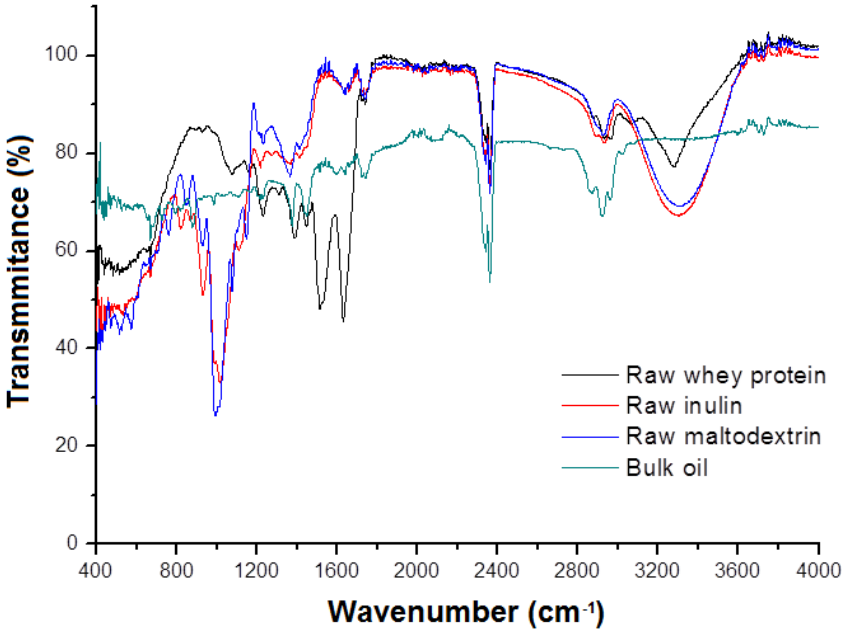

Fig. 4. FT-IR spectra of raw wall materials and ginger essential oil (bulk oil).

Fig. 5 shows the FT-IR spectra composition dependence of microparticles. When inulin (IN) and maltodextrin (MD) are incorporated to whey protein isolated (WPI), the FT-IR absorption bands present certain differences. Inulin and maltodextrin alter considerably the intensity of absorption in 1015 cm^{-1} due to C-O-C groups. The amide I bands assigned to C=O stretching (1515 cm^{-1} and 1630 cm^{-1}) had its intensity reduced due to the mixture with IN and MD witch chemical structures do not contain ketone groups.

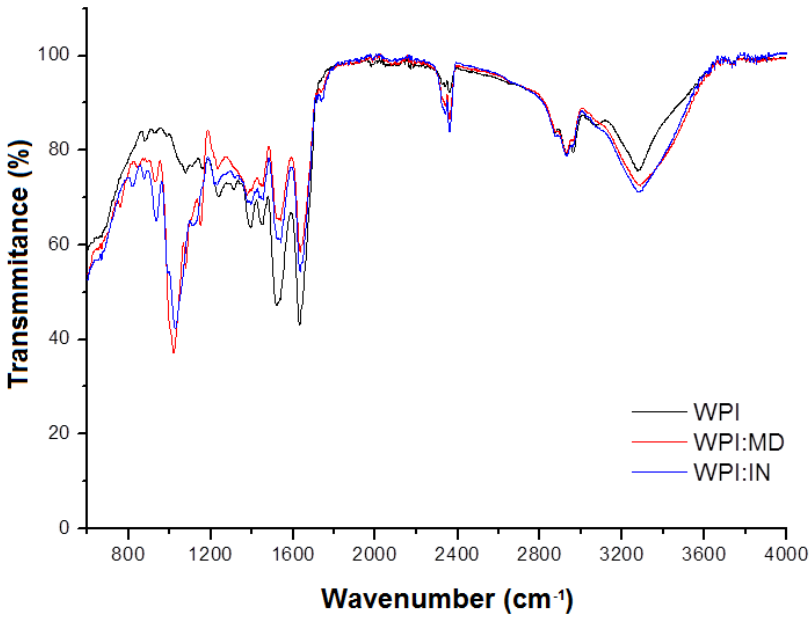

Fig. 5. FT-IR spectra of the microparticles produced using different wall materials composition. WPI: whey protein isolate, MD: maltodextrin, IN: inulin.

3.2. Moisture sorption isotherms

The moisture sorption isotherms is unique for each material and must be evaluated experimentally. The sorption isotherms can provide data about the shelf life stability of a given food commodity (Shrestha et al., 2007). The estimated values of the coefficients and the statistical parameters used to evaluate the adequacy of the models for the moisture adsorption behaviour are shown in Table 6. The model that best fit to the variations in isotherm data for all the treatments was the GAB model, when considering the lowest value of the average relative deviation (E). Fig. 6 illustrates the moisture sorption behavior of spray-dried ginger essential oil at 25 °C, as fitted by the GAB equation. The water adsorption isotherm of the oregano essential oil microparticles also was adjusted by the GAB model at 25 °C (Toledo Hijo et al., 2015). Regarding the

GAB parameters, as shown in Table 6, the X_m of WPI:MD and WPI:IN were smaller when comparing to treatment WPI.

Table 6. Estimated values of the coefficients and statistical parameters for the studied models GAB, Halsey, Henderson, Oswin and Smith for the different treatments for spray-dried ginger essential oil.

Model (Equation)		**WPI**	**WPI:MD**	**WPI:IN**
GAB $X_{eq} = \frac{X_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}$	X_m	0.048	0.038	0.041
	C	5.850	34.964	12.555
	K	0.916	0.948	0.923
	E	9.012	14.708	10.583
HALSEY $X_{eq} = \left(\frac{a}{ln\, a_w}\right)^{1/b}$	a	-0.001	-0.001	-0.001
	b	0.085	0.085	0.085
	E	70.758	67.256	71.191
HENSERSON $X_{eq} = \left[\frac{ln(1 - a_w)}{-a}\right]^{1/b}$	a	3.037	1.786	3.082
	b	2.862	4.381	3.109
	E	14.011	35.955	17.381
OSWIN $X_{eq} = a\left[\frac{a_w}{(1 - a_w)}\right]^b$	a	0.079	0.072	0.073
	b	0.449	0.508	0.444
	E	12.743	18.114	11.039
SMITH $X_{eq} = a + b \log(1 - a_w)$	a	-0.004	-0.021	-0.001
	b	-0.117	-0.136	-0.105
	E	15.287	27.293	17.580

WPI: whey protein isolate, MD: maltodextrin, IN: inulin. X_{eq}: equilibrium moisture content (g g^{-1} dry powder); X_m: monolayer moisture content (g g^{-1} dry powder); C,K: model constants related to the monolayer and monolayer properties; aw: water activity; a,b: model parameters; E: relative mean error.

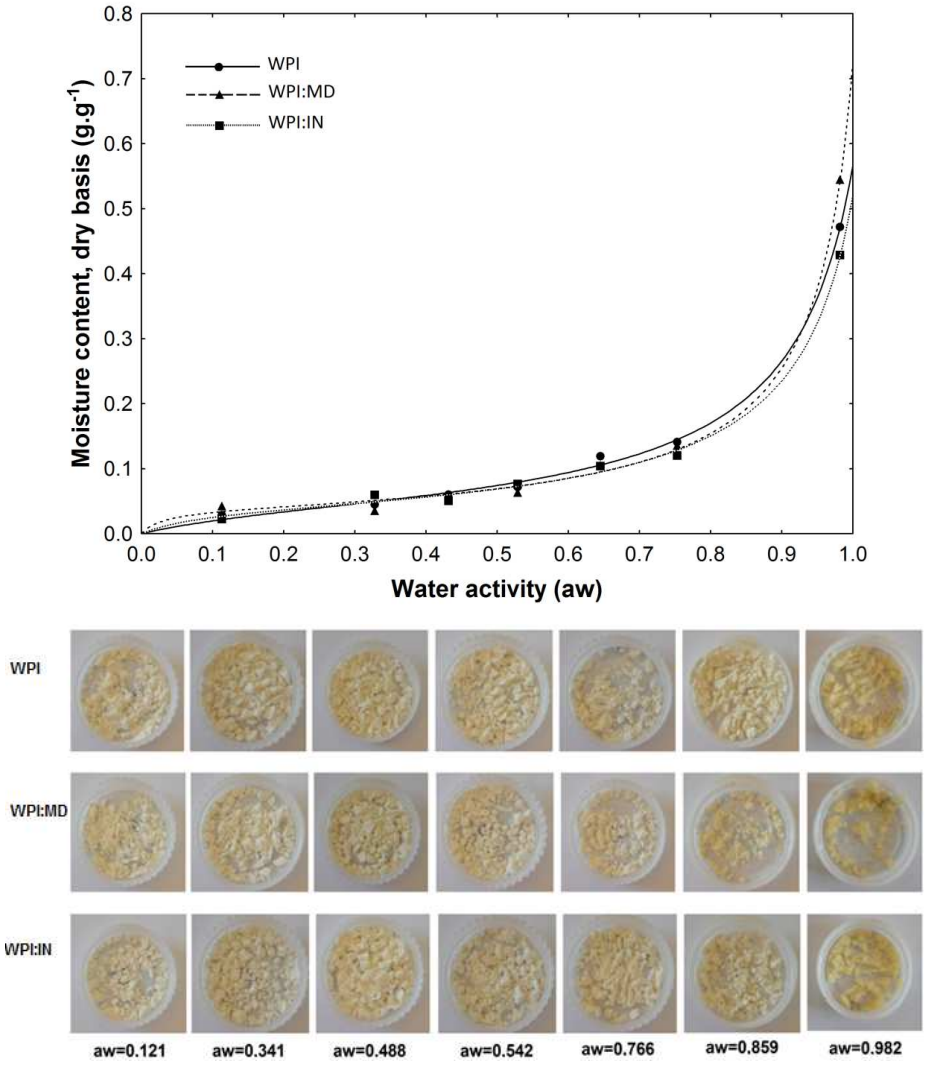

Fig. 6. Sorption isotherms of the ginger oil powders using different wall materials, adjusted by GAB model. Physical aspect of ginger oil powders produced with formulations of encapsulants at different relative humidities in the determination of the equilibrium moisture adsorption isotherms. WPI: whey protein isolate, MD: maltodextrin, IN: inulin.

With increases in a_w, the equilibrium moisture contents of the ginger essential oil microencapsulated also increased. It is known that the chemical and physical properties of a powder are significantly affected by water absorption or desorption. Storage of amorphous powders in a high RH environment can lead to agglomeration or crystallization (Shrestha et al., 2007). The physical characteristics of the powders subjected to different humidity levels demonstrated that there was no apparent phase change in the particles produced with inulin (Fig. 6). The whey protein isolate plus inulin was the only treatment in which the powders visibly remained in the glassy state. The other treatments underwent changes from glassy state to a rubbery state. These results suggest that inulin is an interesting additive for the encapsulation of spray dried active compounds.

3.5. Morphology and particle size distribution

According the scanning electron microscopic images (SEM) (Fig. 7), most of the microcapsules had spherical shape and smooth surface with no apparent fissure or crack, which is important to provide lower permeability to gases, better protection and ginger essential oil retention. In the present study the microcapsules prepared with whey protein isolate had a higher proportion of spherical particles, most likely because these matrices provided elasticity during the drying process. The encapsulating matrix for an unstable essential oil, limonene, using individual matrices, gum Arabic, whey protein concentrate and mixtures of gum Arabic–cassava starch, whey protein concentrate–cassava starch was investigated (Ordoñez & Herrera, 2014). All the microcapsules obtained in this study, regardless of the encapsulating matrix used, showed rounded external surfaces with some concavities; and holes and fractures in the external surface of the particle were not observed nor were broken microcapsules.

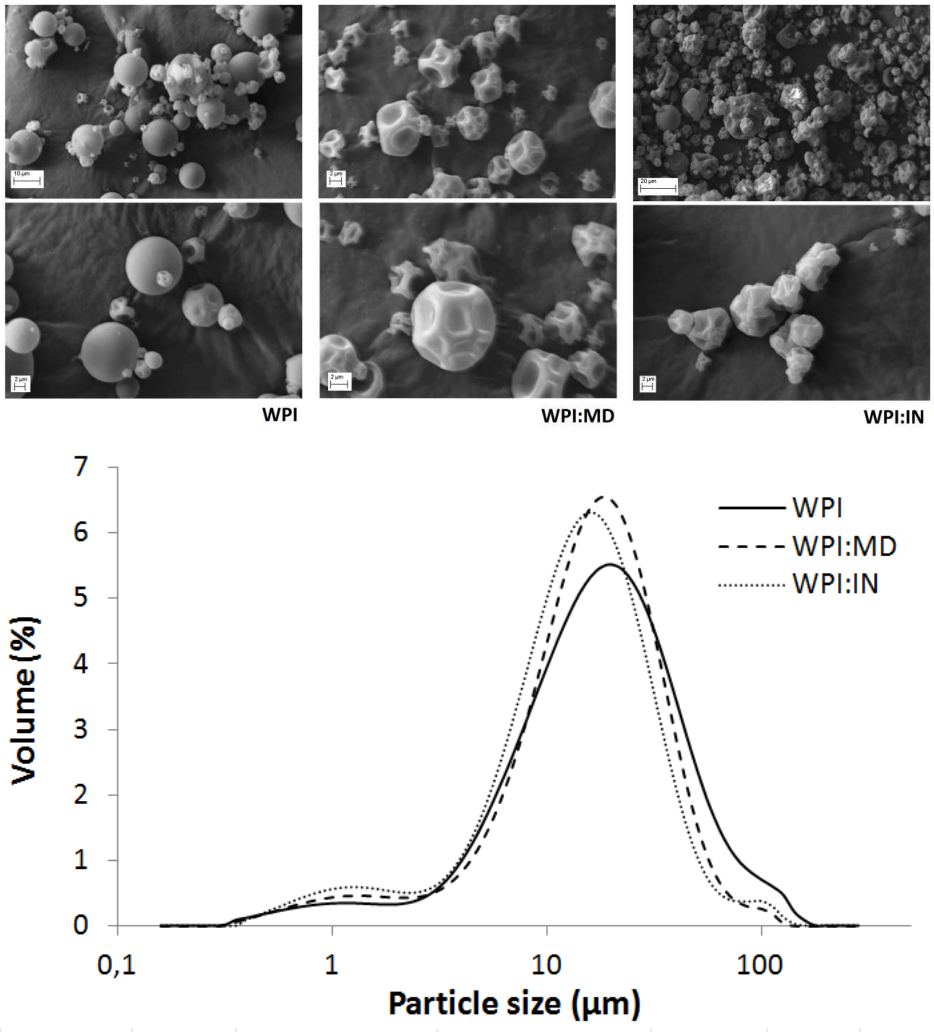

Fig.7. Scanning electron micrographs of the particles containing ginger essential oil using the following wall materials WPI; WPI:MD; and WPI:IN and particle size distribution of powders and particle size distribution of powders. WPI: whey protein isolate, MD: maltodextrin, IN: inulin.

The particles produced using WPI alone presented the higher particle sizes, 22.47 μm, expressed as d_{43} (De Brouckere mean diameter) (Table 7, Fig. 7). When inulin was applied to formulation, the particle size was decreased and an average value of 16.96 μm was obtained. The scattering of the particles, calculated using the PDI equation was low (2.00-2.50) which indicate a homogeneous distribution.

Table 7. Particle size distribution of the ginger essential oil microparticles produced by using the different wall materials.

Treatment	d_{43} (μm)	d_{32} (μm)	d_{10}	d_{50}	d_{90}	PDI
WPI	22.47 ± 0.73^{a}	7.67 ± 0.06^{a}	4.77	16.63	46.30	2.50
WPI:MD	18.56 ± 0.10^{b}	7.08 ± 0.03^{b}	4.51	15.40	35.40	2.00
WPI:IN	16.96 ± 0.06^{c}	6.37 ± 0.02^{c}	3.76	13.46	32.37	2.12

[a,b,c] Values with different letters in the same column differ significantly ($p < 0.05$) by Duncan test. WPI: whey protein isolate, MD: maltodextrin, IN: inulin

3.6 Thermogravimetric analysis (TG)

TG is a technique used to study the loss of sample mass as a function of temperature and to evaluate its thermal stability. It is an important technique for verification of the food properties when they are subjected to some kind of heat treatment at higher temperatures as cooking and pasteurization. The particles containing ginger essential oil showed three stages of weight loss. In all cases a relative thermal stability was observed up to 200 °C, with weight loss below 5 % (Fig. 8). Similar behavior was found by Oliveira et al. (2014) in the study of alginate/cashew gum nanoparticles for essential oil encapsulation. By the other hand, at temperature of 200 °C, the weight loss observed for the bulk oil was 86.85 %. The first stage may be attributed to moisture loss from the samples. Above this range of temperature, the mass loss observed corresponded to

material volatilization and decomposition. The second and third stages, between 200 °C and 400 °C, involve reactions of wall material constituents, i.e., proteins and carbohydrates (Fritzen-Freire et al., 2012), which may be associated with carbohydrate ring dehydration, decomposition, and despolymerization of polymer units (Hosseini et al., 2013). It can be also observed that the presence of maltodextrin in the blend, leads to greater thermal microparticle stability, based on the lower weight loss rate between 200 °C and 300 °C. Based on the results, all the wall material systems were able to increase thermal stability of the oil, where WPI:MD system proved to show higher protection with lower degradation rate.

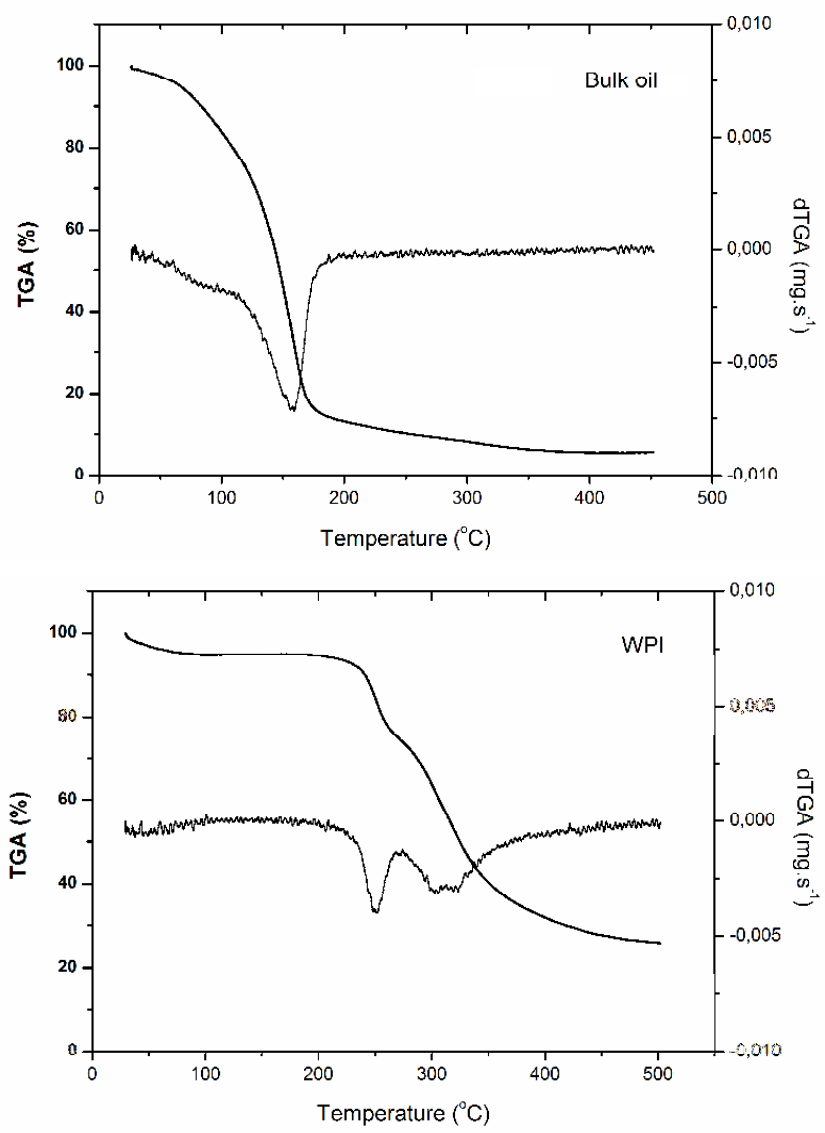

Fig. 8. TGA and DTG curves for the bulk oil and the particles containing ginger essential oil produced with differente matrix, in a nitrogen atmosphere. WPI: whey protein isolate, MD: maltodextrin, IN: inulin (…to be continued…).

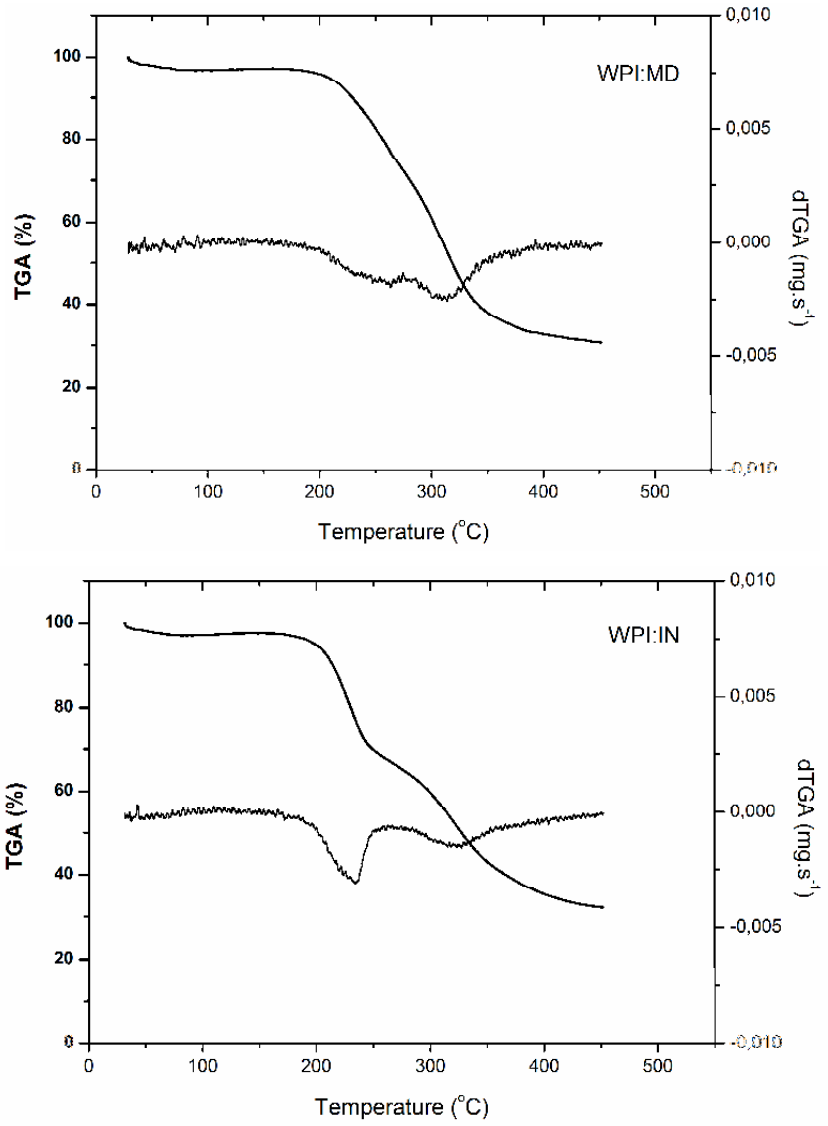

Fig. 8. TGA and DTG curves for the bulk oil and the particles containing ginger essential oil produced with differente matrix, in a nitrogen atmosphere. WPI: whey protein isolate, MD: maltodextrin, IN: inulin.

3.7. X-ray diffraction

The X-ray diffraction was used to identify the crystallinity of the samples. The determination of the dry products' structural properties through X-ray diffraction is an important analysis of microparticle stability (Silva et al., 2016). In general, X-ray diffractions patterns with broad bands, i.e., with a broader peak pattern, indicate amorphous structures because the molecules in the amorphous state are disordered and thus produce scattered bands (Silva & Meireles, 2015). Fig. 9 shows powder X-ray diffraction patterns obtained at different treatments of ginger essential oil microparticles and at raw materials used as wall materials. All the samples had an amorphous structure, as indicated by diffuse and broad peaks in the diffractograms with a minimum of organisation, based on the occurrence of large diffuse peaks. The spray drying process did not affect the crystallinity of the wall materials tested when comparing raw materials and microparticles produced. The liberation of volatile compounds encapsulated in amorphous matrices can occur when the amorphous matrix transforms from the vitreous state to the gum state, either through an increase in moisture content or at elevated temperatures, leading to a collapse of the system (Ordoñez & Herrera, 2014).

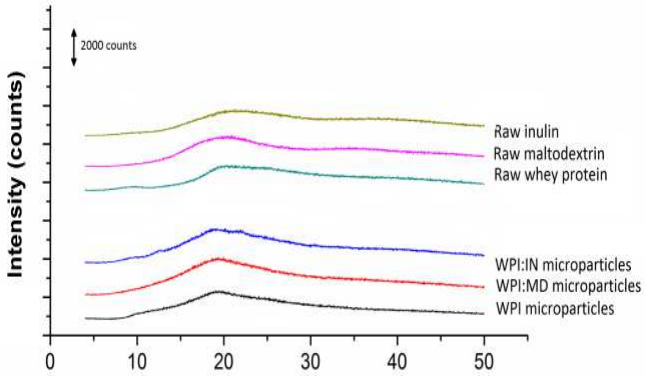

Fig.9. X-ray diffraction patterns of the raw materials and the microparticles produced. WPI: whey protein isolate, MD: maltodextrin, IN: inulin.

4. Conclusions

The importance of the use of whey protein isolate with a high capacity for emulsification as wall material was reaffirmed in this study. The emulsion with inulin demonstrated to be more effective in relation to stability. However, the presence of maltodextrin improved the encapsulation efficiency, which is the most important factor when microencapsulation of essential oil was studied. The presence of inulin contributes to improve the solubility and wettability, on the other hand the encapulation efficiency did not differ significantly when comparing to whey protein isolate as wall material. It can be also observed that the presence of maltodextrin in the blend, leads to greater thermal microparticle stability. The presence of inulin produced powders with lower water adsorption at high relative humidity. All the microcapsules showed rounded external surfaces with some concavities and fractures in the external surface of the particle were not observed; and had an amorphous structure. The partial substitution of whey protein isolate by inulin or maltodextrin produced particles with improved properties and support the importance of the evaluation of blends for the essential oils encapsulation process be spray drying.

Acknowledgements

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“VERSÃO PRELIMINAR”

ARTIGO 3 Goma do cajueiro e inulina: nova alternativa para microencapsulação de óleo essencial de gengibre

Artigo redigido conforme norma da revista Carbohydrate Polymers

GOMA DO CAJUEIRO E INULINA: NOVA ALTERNATIVA PARA MICROENCAPSULAÇÃO DE ÓLEO ESSENCIAL DE GENGIBRE

Resumo

Este trabalho teve como objetivo avaliar o efeito da substituição parcial de goma do cajueiro por inulina, utilizados como materiais de parede, nas características do óleo essencial de gengibre microencapsulado por *spray drying* a partir de emulsões assistidas por ultrassom. As variáveis umidade, molhabilidade, solubilidade, densidade de leito, densidade compactada, eficiência de encapsulação e tamanho de partícula foram avaliadas. Além disso, foram estudadas as propriedades das microcápsulas através da análise de FTIR, isotermas de adsorção, análise termogravimétrica, raio-X e microscopia eletrônica de varredura. A umidade dos pós diminuiu com a adição de inulina. O tempo de molhabilidade dos pós foi menor com o aumento do teor de inulina nos tratamentos avaliados. Verificou-se que a solubilidade dos tratamentos foi afetada pela composição do material de parede e alcançou valores superiores (89,80 %) quando a inulina foi aplicada em maiores concentrações. As amostras com goma do cajueiro pura adicionada à matriz apresentaram os menores valores de densidades de leito e compactada. A eficiência de encapsulação (15,8 %) foi menor na maior concentração de inulina. As partículas com goma do cajueiro e goma do cajueiro e inulina na proporção de 3:1 m/m, não apresentaram fissuras, ao contrário dos outros dois tratamentos. As partículas tiveram características amorfas e o tratamento com goma do cajueiro como encapsulante apresentou as maiores absorções de água em altas atividades de água. Apesar de obtidos valores baixos para a eficiência de encapsulação a goma do cajueiro e a inulina podem ser considerados alternativas no processo de encapsulação de óleos essenciais, no entanto a avaliação de novas misturas se faz necessário para melhora da retenção dos compostos voláteis do óleo de

gengibre. A matriz goma do cajueiro e inulina na proporção de 3:1 (m/m), apresentou as melhores características em relação à eficiência de encapsulação e à morfologia, não apresentando fissuras na sua estrutura.

Palavras-chave: carboidratos, *Spray drying*, óleo essencial, *Zingiber officinale*, eficiência de encapsulação

1. Introdução

Muitos estudos tem sido realizados com foco em compostos bioativos com novos mecanismos de ação e com efeitos antimicrobianos e antioxidantes. Os extratos naturais de plantas tem sido utilizados durante muitos anos para diferentes finalidades e recentemente com potencial aplicação como conservantes de alimentos. O gengibre é um rizoma de *Zingiber officinale* Rosco pertencente à família *Zingiberaceae*, comumente utilizado como tempero, suplemento dietético e fins medicinais (Yeh et al., 2014). O óleo essencial de gengibre possui odor característico e sabor picante e tem sido aplicado na indústria de alimentos, bebidas, higiene e cosméticos devido ao seu potencial antimicrobiano e antioxidante e consiste principalmente de monoterpenos e sesquiterpeno hidrocarbonetos (An et al., 2016; Huang et al., 2012).

A tecnologia de encapsulação é bastante utilizada na estabilização, solubilização e liberação de componentes ativos sensíveis a fatores externos. A utilização da microencapsulação por *spray drying* possibilita ainda a minimização de volume/massa e facilita os processos de estocagem e transporte quando comparados a partículas na forma líquidas ou gel (Keshani et al., 2015). A aplicação do processo de ultrassom contribui para a formação de emulsões mais estáveis que servirão de alimentação no processo de microencapsulação. Somado a esses fatores, o gengibre desidratado pode ser utilizado para a fabricação de especiarias a base de gengibre, fármacos e cosméticos, bem como alimentos com sabor de gengibre, como refrigerantes e doces (An et al., 2016).

O sistema de parede, em processos de microencapsulação de óleos essenciais, consiste de polímeros contendo grupos químicos com propriedades hidrofílicas e hidrofóbicas capazes de proporcionar características emulsificantes ao sistema. A goma de cajueiro é um polissacarídeo obtido através dos exsudados da casca do caule da planta *Anacardium occidentale* Linn (família, Anacardiaceae) (Bittencourt et al., 2016). O interesse tecnológico na goma de

cajueiro baseia-se nas suas características reológicas, sua biodegradabilidade e por se tratar de um polímero natural. Trata-se de uma possível alternativa para substituir a goma Arábica na indústria alimentos, uma vez que a utilização desta goma é restrita devido ao seu alto custo. A inulina tem atraído muita atenção dos diversos setores industriais devido aos relatos de seus vários benefícios, principalmente pela sua natureza prebiótica (Buriti et al., 2007). Devido à sua baixa capacidade de hidrólise, a inulina é utilizada em dieta rica em fibras e também na preparação de microcápsulas resistentes à variação do pH (Dima et al., 2016). Assim, o objetivo deste trabalho foi avaliar a influência dos encapsulantes, goma do cajueiro e inulina, nas propriedades dos pós produzidos por *spray drying* a partir de emulsões assistidas por ultrasonicação, visando a obtenção de produtos funcionais contendo óleo essencial de gengibre.

2. Material e Métodos

2.1. Materiais

O óleo essencial de gengibre adquirido da Ferquima Ind. e Com. Ltda, Vargem Grande Paulista, Brasil, foi utilizado como material ativo. A inulina (grau de polimerização > 10, Orafti®GR, BENEO-Orafti, Tienen, Bélgica) e a goma da árvore de cajueiro (isolado e purificado pela Universidade Federal do Ceará, Fortaleza, Brasil) foram utilizados como materiais de parede.

2.2. Métodos

2.2.1. Delineamento experimental

Os experimentos foram conduzidos em delineamento inteiramente casualizado com três repetições, conforme mostra a Tabela 1. Análise de variância foi realizada para avaliar os efeitos das quatro formulações encapsulantes nas características dos pós microencapsulados com óleo essencial

de gengibre. As diferenças entre os valores médios obtidos foram examinadas por meio de teste de médias *Duncan* em nível de 5 % de probabilidade ($p<0,05$).

Tabela 1. Composição da matriz encapsulante para cada tratamento utilizado como emulsão de alimentação no processo de secagem por atomização.

Tratamento	Material de parede (g.100 g^{-1} de emulsão)		Material encapsulado (g.100g^{-1} de emulsão)
	Goma do Cajueiro (CJ)	Inulina (IN)	Óleo essencial de gengibre
1:0	20,0	-	5,0
3:1	15,0	5,0	5,0
1:1	10,0	10,0	5,0
1:3	5,0	15,0	5,0

2.2.2. Preparo das emulsões

As soluções dos materiais de parede foram preparadas pela dissolução dos materiais de parede em água destilada, para cada formulação, preparadas um dia antes da emulsificação e mantidas a temperatura ambiente por 12 h para garantir a completa saturação das moléculas dos biopolímeros (Fernandes et al., 2013a,b). O óleo essencial foi progressivamente adicionado à solução de material de parede sob agitação a 1000 rpm durante 5 min usando um homogeneizador (Ultra-Turrax IKA T18 basic, Wilmington, EUA). As emulsões, após a homogeneização por agitação mecânica, foram imediatamente submetidas ao processo de ultrassonicação com 160 W de potência nominal (Sonifier® Branson Digital, Modelo S-450D, Branson Ultrasonics Corporation, Danbury, USA), 20 kHz, durante 2 min, para garantir a emulsificação completa de óleo essencial de gengibre. O contato entre a altura da sonda ultrassônica e as emulsões foram padronizadas a 30 mm.

As emulsões foram utilizadas como alimentação líquida no processo de secagem por atomização. Para cada tratamento, 400 mL de emulsão foi preparada para a produção das partículas. A razão da massa de óleo essencial para material de parede foi mantida em 1:4 (m/m) (Fernandes et al., 2014a). A porcentagem de sólidos (material de parede) utilizada como solução de alimentação foi de 20% (m/m) para todos os tratamentos (Fernandes et al., 2014b).

2.2.3. Microencapsulação através da secagem por atomização

As emulsões foram secas utilizando um secador por atomização (modelo MSD 1.0; Labmaq do Brasil, Ribeirão Preto, Brasil) equipado com bico atomizador de duplo fluido. As variáveis de processo aplicadas, estudadas previamente, foram: temperatura do ar de entrada de 170 °C, taxa de fluxo de alimentação 0,8 $L.h^{-1}$ (Fernandes et al., 2013a,b). O fluxo do ar de atomização foi mantido a 35 $L.min^{-1}$. Os pós resultantes foram coletados e estocados em contêineres opacos e fechados a 4 °C até a realização das análises.

2.2.4. Caracterização das partículas

2.2.4.1. Teor de umidade

O teor de umidade dos pós foi determinado pelo método da AOAC (ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS, AOAC, 2007). A porcentagem de perda de peso dos pós após a secagem em estufa a 105 °C até peso constante foi obtida, e o teor de umidade (%) em base úmida foi calculado.

2.2.4.2. Morfologia das partículas

A morfologia das partículas foi avaliada por meio de microscopia eletrônica de varredura (MEV). As partículas foram imobilizadas em uma fita adesiva dupla-face e montadas sobre *stubs* do microscópio com um diâmetro de

1 cm e altura de 1 cm. As amostras foram então cobertas com ouro em câmara a vácuo e examinadas com o microscópio eletrônico de varredura (MEV 1430 VP – LEO Electron Microscopy Ltd., Cambridge, UK). O MEV foi operado a 20 kV com magnitudes de 900x a 1200x.

2.2.4.3. Distribuição do tamanho de partículas

A distribuição do tamanho de partículas foi medida usando instrumento de espalhamento de laser (Mastersizer 2000, modelo Hydro 2000 UM, Malvern Instruments, Worcestshire, UK). Uma pequena amostra de pó foi suspensa em álcool etílico (índice de refração 1,36) sob agitação, e a distribuição do tamanho de partículas foi monitorada durante cada medida até que sucessivas leituras tornassem-se constantes. O diâmetro médio de volume, d_{43}, foi obtido (Eq. (1)) e índice de polidispersibilidade (PDI) foi calculado conforme Eq. (2):

$$\mathbf{d_{43}} = \frac{\sum \mathbf{n_i d_i^4}}{\sum \mathbf{n_i d_i^3}} \qquad (\mathbf{1})$$

$$\mathbf{PDI} = \frac{[\mathbf{d_{90}} - \mathbf{d_{10}}]}{\mathbf{d_{50}}} \qquad (\mathbf{2})$$

onde d_i é o diâmetro médio da partícula; n_i é o número das partículas; d_{90}, d_{50} e d_{10} são diâmetros médios de volume a 90 %, 50 % e 10 % do volume acumulado, respectivamente.

2.2.4.4. Molhabilidade

A molhabilidade dos pós foi determinada utilizando o método de Fuchs et al. (2006) com algumas modificações. As amostras do pó (0,1 g) foram espalhadas sobre a superfície de um béquer contendo 100 mL de água destilada a 20 °C sem agitação. O tempo necessário até que a última partícula de pó afundasse ou se molhasse foi usado para a comparação da extensão de molhabilidade entre as amostras.

2.2.4.5. Solubilidade

A solubilidade dos pós em água fria foi avaliada com base no método proposto por Cano-Chauca et al. (2005) com algumas modificações. 25 mL de água destilada foram transferidos para um béquer de 50 mL. Uma amostra de pó (1,0 g) foi pesada e adicionada ao béquer contendo água e sob agitação a baixa velocidade. Depois que toda a amostra havia sido adicionada, a agitação foi aumentada para alta velocidade por 2 min. O material foi então transferido para um tubo de centrífuga de 50 mL e centrifugado a 760 x g por 15 min. Uma alíquota de 20 mL do sobrenadante foi transferida para uma placa de Petri e seca em estufa a 105 °C por 4 h. A solubilidade em água fria foi calculada de acordo com a equação (3):

$$\textbf{Sol}\ (\%) = \frac{\textbf{gramas de sólidos no sobrenadante} \times \mathbf{1,25}}{\textbf{gramas de amostra}}\textbf{x100} \qquad (\mathbf{3})$$

2.2.4.6. Densidades de leito e compactada

O material em pó (aproximadamente) 10 mL foi cuidadosamente adicionado a uma proveta graduada de 50 mL, previamente tarada, e este valor foi pesado. O volume, lido diretamente na proveta, foi usado para calcular a densidade de leito (ρ_{leito}) de acordo com a relação massa/volume (Jinapong et al., 2008). Para a densidade compactada ($\rho_{compactada}$), aproximadamente 5 g de pó foi adicionado em uma proveta de 25 mL, sendo a amostra repetidamente batida manualmente levantando e abaixando a proveta sob seu próprio peso a uma distância vertical de 10 cm até não haver mais diferença observada no volume entre sucessivas medidas. A densidade compactada foi calculada pela razão da massa por volume aparente (compactado) dos pós (Goula and Adamopoulus, 2008).

2.2.4.7. Eficiência de encapsulação

A quantidade de óleo encapsulado foi determinada usando n-hexano como extrator (Li e Lu, 2016), com algumas modificações. O gengibre em pó (1,0 g) foi dissolvido em 20 mL de água destilada à 45 ºC e levado à agitação manual por 1 min. Em seguida, a amostra foi levada ao processo de ultrasonicação a 160 W de potência nominal (Sonifier® Branson Digital, Modelo S-450D, Branson Ultrasonics Corporation, Danbury, USA), 20 kHz, durante 1 min. Logo após, foram adicionados 10 mL de hexano com posterior agitação em vortex e em banho-maria a 45 °C por 30 min. Em seguida a amostra foi centrifugada a 3000 rpm por 5 min. Após a centrifugação, foi retirado o sobrenadante e adicionado em balão de 50 mL. Em seguida, foram adicionados mais 10 mL de hexano, agitado em vortex e centrifugado novamente por 5 min. Este procedimento foi repetido por quatro vezes. No final das lavagens, o balão de 50 mL foi completado com o solvente. A quantidade de óleo essencial de gengibre foi determinada medindo a absorbância à 270 nm com espectrofotômetro UV- VIS SP 2000 (Bel Photonics, Piracicaba, Brasil) e a sua concentração foi calculada usando uma curva analítica. A eficiência de encapsulação do óleo (EE) foi determinada usando a Eq. (4):

$$\mathbf{EE}\ (\%) = \frac{\mathbf{M}}{\mathbf{M_0}}\mathbf{x\ 100} \qquad (\mathbf{4})$$

em que M é a quantidade em mg de óleo na partícula e M_o é a quantidade de óleo teórico (mg) com base na emulsão inicial que originou as partículas em base seca.

2.2.4.8. Espectroscopia de infravermelho com transformada de Fourier

A espectroscopia de infravermelho com transformada de Fourier de (FTIR) foi realizada sobre o óleo essencial puro, os materiais da parede e os pós

produzidos. Estas medidas foram realizadas à temperatura ambiente, na faixa de 400-4000 cm^{-1}, utilizando-se um espectrômetro (Jasco 4100, Tóquio, Japão).

2.2.4.9. Isotermas de adsorção de umidade

As isotermas de adsorção foram determinadas por método gravimétrico estático usando soluções salinas saturadas a 25 °C. Sete soluções salinas saturadas (NaCl, K_2CO_3, $MgCl_2$, LiCl, $Mg(NO_3)_2$, KCl e K_2SO_4) foram utilizadas com atividade de água variando entre 0,12 a 0,98. Os dados da isoterma de adsorção de umidade foram correlacionados com a atividade de água usando os seguintes modelos matemáticos: GAB, Halsey, Henderson, Oswin e Smith (Toledo Hijo et al., 2015). Os parâmetros das equações foram estimados correlacionando os modelos matemáticos aos dados experimentais utilizando uma regressão não linear usando o método de Quasi-Newton com critério de convergência de 10^{-4}. O modelo foi considerado o mais adequado baseado nos menores valores para o módulo do desvio relativo médio (E), definido pela e Eq. (5):

$$\mathbf{E} = \frac{\mathbf{100}}{\mathbf{N}} \sum_{\mathbf{i=1}}^{\mathbf{N}} \frac{\left|\mathbf{m_i} - \mathbf{m_{pi}}\right|}{\mathbf{m_i}} \qquad (\mathbf{5})$$

onde m_i é o valor experimental, m_{pi} é o valor predito do teor de umidade em cada umidade relativa e N é a população dos dados experimentais.

2.2.4.10. Análise termogravimétrica (TGA)

As curvas TG/DTGA foram obtidas utilizando a termobalança TGA50H (Shimadzu Coorporation, Kyoto, Japão) nas seguintes condições operacionais: atmosfera dinâmica de nitrogênio com taxa de 100 mL min^{-1}; razão de aquecimento: 10 °C min^{-1}; faixa de temperatura: 50-550 ºC. Aproximadamente 5 mg de amostra foram utilizados e colocados em cadinho de alumina.

2.2.4.11. Difratometria de raio-X

Amostras dos produtos secos foram colocados em um suporte para pós cobertos com tampa de vidro. As medidas foram realizadas usando difratômetro de raio-X (modelos XDR-6000) usando radiação Cu-K α1 com um comprimento de onda de 1.54 Å a 30 kV e 30 mA. As amostras foram analisadas em ângulos de 4 a 40° em 2θ com um incremento de 0,02° (1,2°.min^{-1}).

3. Resultados e Discussão

3.1. Caracterização das partículas

As partículas produzidas utilizando os diferentes materiais de parede apresentaram formas relativamente esféricas (Figura 1). A formação de partículas ocas é característica do processo de secagem por atomização e ocorre pela formação de um vacúolo dentro das partículas após a formação da crosta e, a partir de então, a partículas se incham quando a temperatura excede o ponto de ebulição da água (Nijdam e Langrish, 2006). Não foram observadas rachaduras ou fissuras nas partículas com goma cajueiro e goma do cajueiro e inulina na proporção de 3:1, m/m, assim como no trabalho de Botrel et al. (2014) que avaliaram o uso de isolado proteico de soro e inulina como materiais de parede para óleo de peixe microencapsulado. Esse fato tem grande influência no processo encapsulação, proteção e manutenção das substâncias ativas dentro da matriz do carreador. Por outro lado, as partículas contendo quantidades maiores de inulina na formulação do material de parede (GC:IN, 1:1 e 1:3) apresentaram fissuras em sua estrutura (Figura 1), indicando que o aumento excessivo de inulina levou à formação de estutrutras menos resistentes ao processos de secagem por *spray*, provavelmente devido a menor capacidade viscoelástica da inulina em comparação à goma do cajueiro. Esta ocorrência de fissuras, pode ter como consequência uma diminuição da eficiência de encapsulação, já que o composto ativo está susceptível à volatilização e perdas. A aplicação de altas

temperaturas permitem a rápida formação da membrana semi-permeável na superfície das gotículas, no entanto, o uso de temperaturas muito altas pode causar danos devido à exposição ao calor excessivo e à formação excessiva de bolhas e rupturas na superfície das partículas, levando à perda de componentes voláteis do óleo essencial. Porém, todos esses fatores dependem da matriz encapsulante e do material encapsulado.

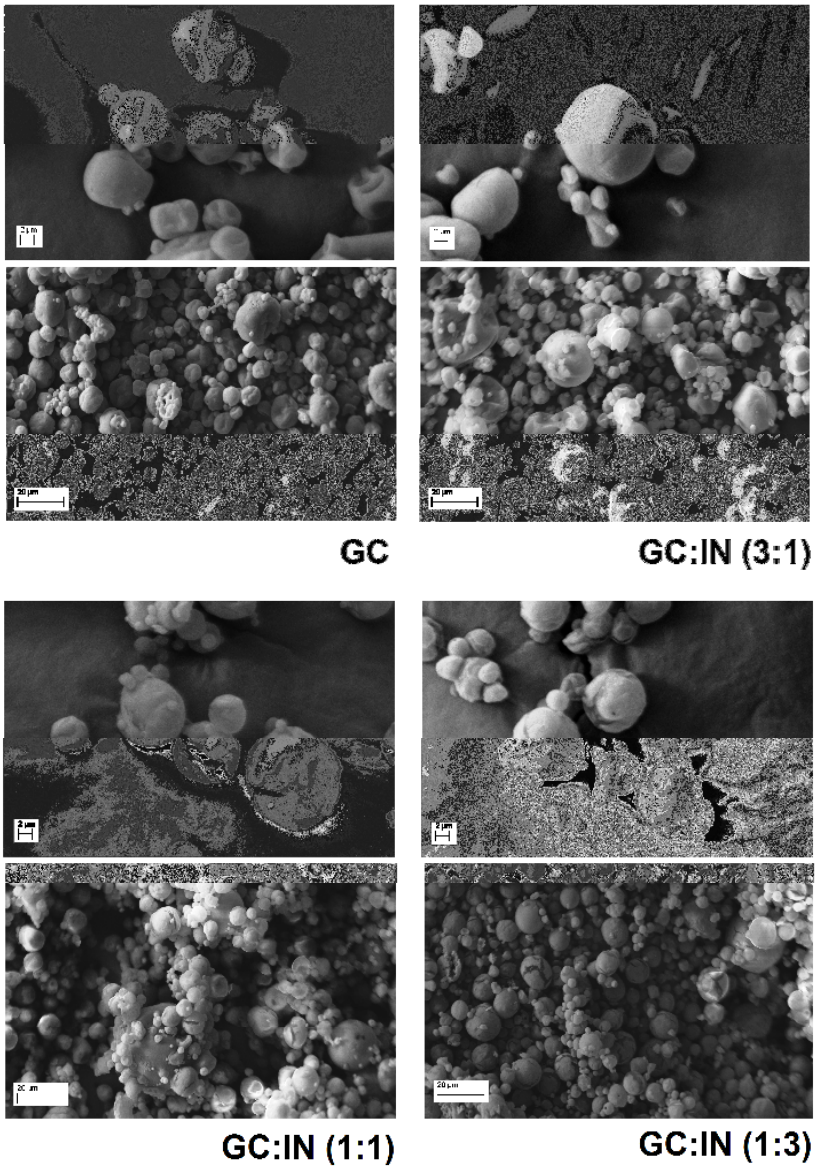

Figura 1. Micrografias eletrônicas de varredura obtidas para as partículas de óleo essencial de gengibre produzidas com os materiais de parede em diferentes proporções. GC = goma do cajueiro; IN = inulina.

Observou-se que o tamanho das partículas foi influenciado significativamente ($p < 0,05$) pelo tipo de material de parede, sendo os maiores valores de d_{43} (17,70 µm) obtidos para as partículas de óleo essencial de gengibre encapsuladas com goma de cajueiro e inulina em maior proporção (1:3, m/m) (Tabela 2). A distribuição das partículas foi considerada homogênea, com base nos valores de PDI (1,61-1,77) (Figura 2). Silva et al. (2016a) obtiveram valores entre 12,3 e 17,4 µm (d_{43}) para óleo de urucum microencapsulado por *spray drying* utilizando-se como materiais de parede isolado proteico de soro e amido modificado.

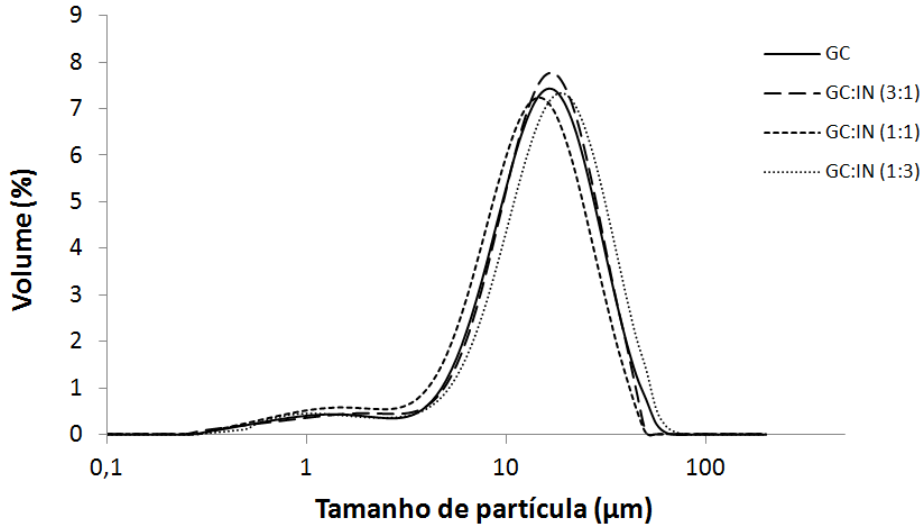

Figura 2. Distribuição do tamanho de partícula. GC: goma de cajueiro, IN: inulina.

Tabela 2. Distribuição do tamanho de partícula para as partículas produzidas com os diferentes materiais de parede.

Tratamento	$\mathbf{d_{43}}$	$\mathbf{d_{32}}$	$\mathbf{D_{10}}$	$\mathbf{d_{50}}$	$\mathbf{d_{90}}$	**PDI**
GC	$15,79 \pm 0,21^{b}$	$6,88 \pm 0,06^{b}$	5,08	14,09	30,00	1,70
GC:IN (3:1)	$15,52 \pm 017^{b}$	$6,90 \pm 0,04^{b}$	5,11	14,21	28,02	1,61
GC:IN (1:1)	$13,64 \pm 0,21^{c}$	$5,96 \pm 0,03^{c}$	3,76	12,24	25,41	1,77
GC:IN (1:3)	$17,70 \pm 0,82^{a}$	$7,57 \pm 0,81^{a}$	5,40	15,87	32,69	1,72

[a,b,c] Valores com letras diferentes na mesma coluna diferem entre si significativamente ($p<0,05$) pelo teste de *Duncan*. GC: goma de cajueiro, IN: inulina

O estudo das propriedades de reconstituição de particulados é necessário em produtos alimentícios a fim de se compreender o seu comportamento durante o processamento, comercialização e o consumo final do produto. Estas propriedades são influenciadas pelo tamanho, forma e morfologia das partículas, densidade e pela presença de óleo na superfície das microcápsulas (Dima et al., 2016). Os resultados da caracterização das partículas podem ser verificados na Tabela 3.

Tabela 3 Médias e desvios padrão para teor de umidade, molhabilidade, solubilidade, eficiência de encapsulação, densidade de leito e densidade compactada para as partículas produzidas.

	Variáveis					
Material de parede	**Teor de umidade (%)**	**Molhabilidade (s)**	**Solubilidade (%)**	**Eficiência de encapsulação (%)**	**Densidade de leito ($g\ mL^{-1}$)**	**Densidade compactada ($g\ mL^{-1}$)**
GC	$4,42 \pm 1,03^{a}$	328 ± 17^{a}	$70,65 \pm 4,86^{c}$	$28,05 \pm 0,44^{b}$	$0,27 \pm 0,005^{c}$	$0,46 \pm 0,010^{c}$
GC:IN (3:1)	$2,17 \pm 0,70^{b}$	252 ± 10^{b}	$78,35 \pm 4,42^{b}$	$30,42 \pm 1,02^{a,b}$	$0,28 \pm 0,009^{b,c}$	$0,50 \pm 0,006^{b}$
GC:IN (1:1)	$2,08 \pm 0.87^{b}$	229 ± 17^{c}	$82,81 \pm 3,01^{a,b}$	$31,19 \pm 2,91^{a}$	$0,31 \pm 0,008^{a}$	$0,53 \pm 0,013^{a}$
GC:IN (1:3)	$2,04 \pm 1,00^{b}$	91 ± 14^{d}	$89,80 \pm 7,15^{a}$	$15,81 \pm 1,38^{c}$	$0,29 \pm 0,016^{b}$	$0,51 \pm 0,018^{b}$

[a,b,c,d] Valores com letras diferentes na mesma coluna diferem entre si significativamente ($p<0,05$) pelo teste de *Duncan.*

GC = goma do cajueiro; IN = inulina

A umidade das microcápsulas variou entre 2,04 % e 4,42 %. Os valores de umidade encontrados foram similares a outros estudos como o *spray drying* de óleo de urucum utilizando amido modificado e isolado proteico de soro como materiais de parede (1,70 %-3,90 %) (Silva et al., 2016a). O teor de umidade das amostras adicionadas de inulina diferiram estatisticamente ($p<0,05$) da amostra contendo apenas goma do cajueiro pura. Foi verificado que a presença de inulina contribuiu com a redução da umidade dos pós. Para uma melhor conservação e estabilidade das partículas são desejáveis menores valores de umidade, que contribui também para a melhoria das propriedades de reconstituição. Menores valores de umidade em partículas evitam a formação de aglomerados, por outro lado altos teores de umidade provocam reduções significativas na temperatura de transição vítrea diminuindo a estabilidade do produto.

A molhabilidade é uma das propriedades físicas mais importantes relacionadas com a reconstituição dos pós em soluções aquosas, sendo diretamente afetada pela interação molecular entre as duas fases. No presente estudo, os tempos obtidos para que os pós tornassem completamente molhados variou entre 91 – 328 s. O tipo de material de parede influenciou os valores desta propriedade. Os menores tempos para a molhabilidade, ou seja, a obtenção de partículas com melhores características de instantaneização ocorreu quando a inulina foi utilizada na formulação em uma maior concentração. Este fato pode ser explicado devido à estrutura química da inulina, que provavelmente contribuiu para uma maior ocorrência de grupos hidrofílicos nas partículas, reduzindo o tempo de instantaneização pela maior interação com a água. Além disso, a inulina é muito solúvel em água, a 20 - 25 °C (Glibowski e Pikus, 2011), o que favoreceu os tratamentos com adição deste composto em maior concentração em sua formulação (GC:IN (1:3)). No trabalho de Dima et al. (2016) o tratamento com a aplicação de inulina também foi o que apresentou o menor valor para este parâmetro (112 s adicionada à quitosana).

Uma boa solubilidade é requisito fundamental para aplicação dos pós como ingredientes na indústria de alimentos. A solubilidade é a última etapa de dissolução de partículas na matriz alimentícia e é considerada essencial para a qualidade destes produtos. O consumidor não terá uma boa percepção do produto final caso este apresente aglomerados e grumos após a dissolução no meio desejado. O aumento no nível de substituição de goma de cajueiro por inulina teve efeito significativo ($p<0,05$) no aumento da solubilidade dos pós, tendo em vista a característica hidrofílica deste componente. Todas as partículas foram relativamente solúveis, apesar da natureza hidrofóbica do material do núcleo e os resultados variaram de 70,65 % a 89,80 %. O óleo essencial de gengibre puro não se solubiliza em água à temperatura ambiente, por outro lado, o processo de microencapsulação permitiu que o óleo seja usado em meios aquosos. A estrutura química mais complexa da goma do cajueiro, com regiões hidrofóbicas, pode ter contribuído para diminuir a solubilidade das partículas comparadas com o tratamento adicionado de inulina em maior concentração (GC:IN (1:3)).

Um produto seco de baixa densidade será armazenado em recipientes de maiores dimensões, em comparação com um produto de alta densidade e, dependendo da situação, produtos de baixas densidades não são interessantes para as indústrias, demandando maiores gastos com transporte e comercialização. Os valores de densidade de leito variaram de 0,27 a 0,31 $g.mL^{-1}$. Os resultados de densidade compactada variaram entre 0,46 e 0,53 $g.mL^{-1}$. A densidade mais baixa foi observada quando apenas a goma do cajueiro estava presente. No trabalho de Dima et al. (2016), os valores encontrados para a densidade de leito de microcápsulas contendo óleo essencial de coentro variaram entre 0,35 $g.mL^{-1}$ 0,42 $g.mL^{-1}$ e para a densidade compactada entre 0,50 $g.mL^{-1}$ e 0,62 $g.mL^{-1}$.

Para o caso específico do óleo essencial, a pesquisa de microencapsulação por meio da secagem por atomização tem-se concentrado em melhorar a eficiência de encapsulação e retenção de voláteis (Fernandes et al., 2014a), além de tentar prolongar ao máximo a vida útil do produto. A retenção dos componentes voláteis de óleos essenciais microencapsulados através de secagem por *spray* é uma variável de grande interesse pois indica a quantidade de óleo que está de fato presa dentro da matriz e consequentemente será liberada quando requisitada. Esta variável está fortemente relacionada ao tipo de material de parede utilizado, à concentração de sólidos da solução de alimentação e à temperatura aplicada ao processo. Para uma alta eficiência de encapsulação, as microcápsulas não devem, ao final do processo de secagem, apresentarem rupturas na parede, o que poderia ocasionar na perda de componentes, principalmente para materiais de núcleo que são voláteis. Os valores de eficiência de encapsulação variaram entre 15,81 % e 31,19 %. Houve diferença significativa entre as amostras ($p<0,05$) sendo o tratamento com maior concentração de inulina o menos efetivo para a retenção de óleo. A presença da inulina como material de parede secundário mostrou afetar significativamente a eficiência de encapsulação, sendo que existe um valor ótimo onde a eficiência é maior. Neste caso a mistura de goma de cajueiro e inulina (1:1) apresentou as maiores valores. No trabalho de Oliveira et al. (2014) os valores de eficiência de encapsulação por *spray drying* de óleo essencial de *Lippia sidoides* foram entre 21 e 48 %. Neste estudo, os autores avaliaram o sistema encapsulante de alginato e goma do cajueiro, concluindo que a concentração de 1:1 m/m desses materiais de parede resultou no maior valor de eficiência. A eficiência de encapsulação pode ser aumentada pela seleção de materiais de parede que apresentem diferentes propriedades funcionais. A substituição parcial de goma do cajueiro por inulina não alterou a retenção de voláteis na encapsulação de óleo essencial de gengibre até a proporção de 1:1 m/m. A adição de inulina é

uma opção interessante para a atual demanda por alimentos benéficos à saúde humana com alegações funcionais.

A goma de cajueiro é potencial substituta da goma Arábica em muitos fins, devido principalmente às suas propriedades emulsificantes. Os principais componentes desta goma são rabinose, ramose e também glicose e ácido glucurônico, organizados em uma estrutura de heteropolissacarídeo ramificada (Bittencourt et al., 2016; Silva et al., 2016b). A espectroscopia de infravermelho com transformada de Fourier (FT-IR) permite mostrar as bandas espectrais de absorção do óleo essencial de gengibre microencapsulado em diferentes matrizes, destacando as possíveis mudanças associadas à estabilidade química do óleo. A Figura 3 mostra que o óleo essencial de gengibre se encontra encapsulado na matriz de goma de cajueiro devido às bandas de absorção de grupos –CH2- (2922 cm^{-1}) e de estiramentos de ligações C-H (877 cm^{-1}), típicas do óleo essencial e que são identificadas no espectro das micropartículas de óleo em matriz da goma de cajueiro. Além disso, as bandas de sacarídeos (estiramento C-O) estão presentes com forte intensidade em 1015 cm^{-1}. Bandas associadas a flexões de grupos CH_3 (1370 cm^{-1}) e de ligações C-H (1450 cm^{-1}) do óleo essencial estão provavelmente sobrepostas pelas mesmas bandas na goma de cajueiro da matriz de encapsulamento (Dalonso et al., 2009; Schulz et al., 2005). Bandas associadas a estiramento assimétrico de grupos –COO- e –OH são observadas para goma de cajueiro em 1640 cm^{-1} e 3300 cm^{-1}, respectivamente (Oliveira et al., 2014). As bandas de absorção relativas ao óleo essencial não apresentam mudança de número de onda, quando identificadas na matriz das micropartículas, após encapsulamento, sugerindo que há relativa estabilidade química do material encapsulado.

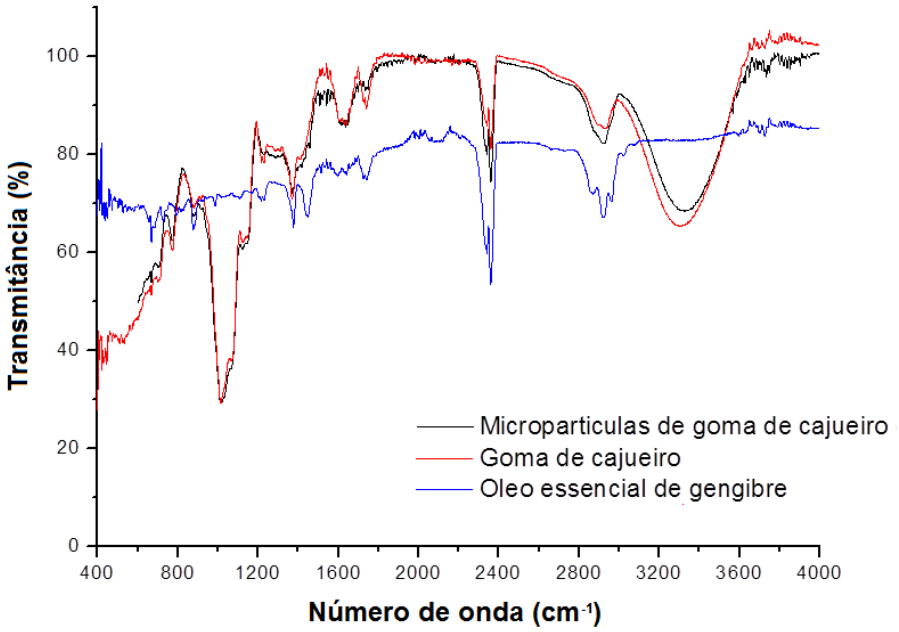

Figura 3. Espectros de FT-IR de micropartículas de óleo essencial de gengibre encapsulado em goma de cajueiro, goma de cajueiro pura e óleo essencial de gengibre puro.

A Figura 4 mostra a comparação entre três diferentes proporções de goma de cajueiro e inulina e o tratamento com apenas goma do cajueiro. O perfil apresentado para os quatro espectros é o mesmo, embora se observa que o aumento da proporção de inulina no material de parede provoca uma redução na transmitância associada à banda de –OH em torno de 3300 cm^{-1}. Como o grupo –OH é característico da inulina, uma proporção aumentada é diretamente relacionada à intensidade de suas bandas espectrais.

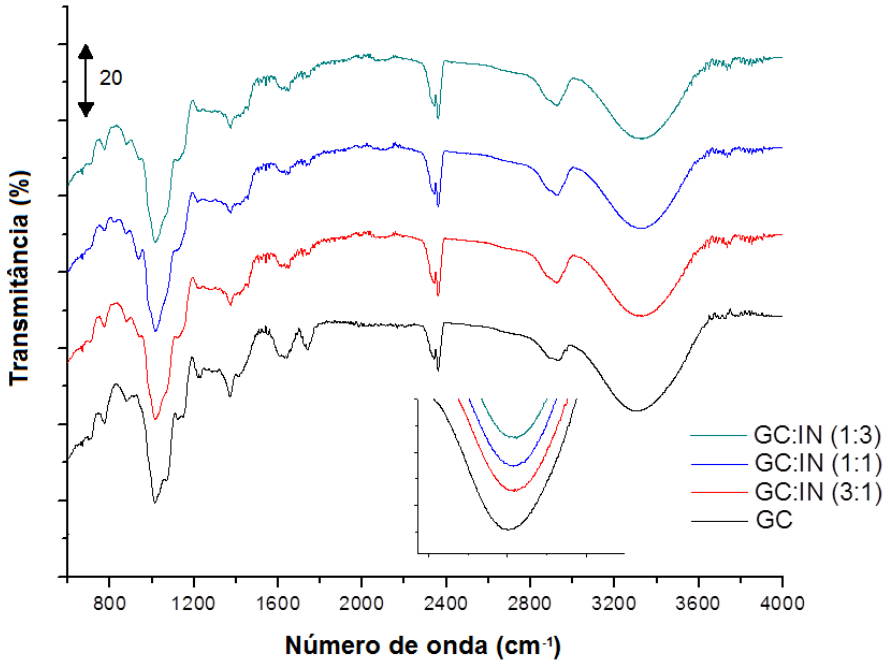

Figura 4. Espectros de FT-IR de óleo essencial de gengibre encapsulado em diferentes proporções de goma de cajueiro (GC) e inulina (IN).

3.2. Isotermas de adsorção de umidade

Os valores estimados dos coeficientes e dos parâmetros estatísticos utilizados para avaliar a adequação dos modelos para o comportamento de adsorção de umidade das partículas contendo óleo essencial de gengibre nos quatro diferentes tratamentos estão na Tabela 4.

Tabela 4. Valores estimados dos coeficientes e parâmetros estatísticos de ajuste dos modelos GAB, Halsey, Henderson, Oswin e Smith para o óleo essencial de gengibre microencapsulado nos diferentes tratamentos.

Model (Equation)		**GC**	**GC:IN (3:1)**	**GC:IN (1:1)**	**GC:IN (1:3)**
GAB $X_{eq} = \frac{X_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)}$	X_m	0,141	0,181	0,128	0,081
	C	0,931	0,599	0,820	2,196
	K	0,850	0,822	0,857	0,899
	E	11,485	13,679	8,612	8,890
HALSEY $X_{eq} = \left(\frac{a}{ln\ a_w}\right)^{1/b}$	a	-0,001	-0,001	-0,001	-0,001
	b	0,085	0,085	0,085	0,085
	E	67,876	68,395	61,522	69,145
HENSERSON $X_{eq} = \left[\frac{ln(1 - a_w)}{-a}\right]^{1/b}$	a	2,422	2,457	2,514	2,511
	b	2,393	2,484	2,497	2,496
	E	14,838	22,762	35,723	16,996
OSWIN $X_{eq} = a\left[\frac{a_w}{(1 - a_w)}\right]^b$	a	0,116	0,108	0,100	0,104
	b	0,454	0,458	0,474	0,461
	E	37,009	30,821	68,472	20,639
SMITH $X_{eq} = a + b\log(1 - a_w)$	a	-0,016	-0,016	-0,025	-0,014
	b	-0,179	-0,171	-0,169	-0,165
	E	18,309	21,475	27,614	16,389

GC: goma de cajueiro, IN: inulina. X_{eq}: teor de umidade no equilíbrio ($g.g^{-1}$ de material seco); X_m: teor de umidade da monocamada ($g.g^{-1}$ de material seco); C, K: constantes do modelo relacionadas à monocamada e às propriedades da monocamada; aw: atividade de água; a, b: parâmetros do modelo; E: módulo do desvio relativo médio.

O modelo que melhor se ajustou na descrição do comportamento isotérmico de adsorção dos quatro tratamentos foi o modelo de GAB (Figura 3),

quando considerado o menor valor do desvio relativo médio (E). O modelo de GAB também apresentou um bom ajuste ao comportamento das isotermas de adsorção de umidade de partículas de óleo de peixe microencapsulado em matriz proteína:inulina (Botrel et al., 2014).

O modelo de GAB fornece importantes informações para produtos alimentícios, na medida em que a estimativa do teor de umidade da monocamada (X_m) e sua respectiva atividade de água são importantes para definir as condições apropriadas de estocagem (Silva et al., 2014). O valor da monocamada é um teor de umidade crítico onde os alimentos desidratados são mais estáveis. Com relação aos parâmetros do modelo de GAB, observa-se que X_m, teor de umidade da monocamada, da goma do cajueiro e inulina em maior concentração foi menor, quando comparado aos demais tratamentos, indicando menor disponibilidade de sítios ativos de ligação com a água. Observou-se que a adsorção de umidade das amostras aumentou consideravelmente em atividades de água (a_w) acima de 0,8. A amostra contendo apenas o encapsulante goma do cajueiro foi que adsorveu maior quantidade de água no maior valor de a_w, indicando que é um material bastante higroscópico. As partículas produzidas utilizando-se goma de cajueiro como material encapsulante sofreram modificação física significativas, passando para o estado gomoso, em meio contendo a_w=0,982. Por outro lado, pôde-se verificar através das características físicas dos pós submetidos às diferentes umidades, que não houve transição de fase nas partículas produzidas quando se adicionou inulina à goma de cajueiro (Figura 5).

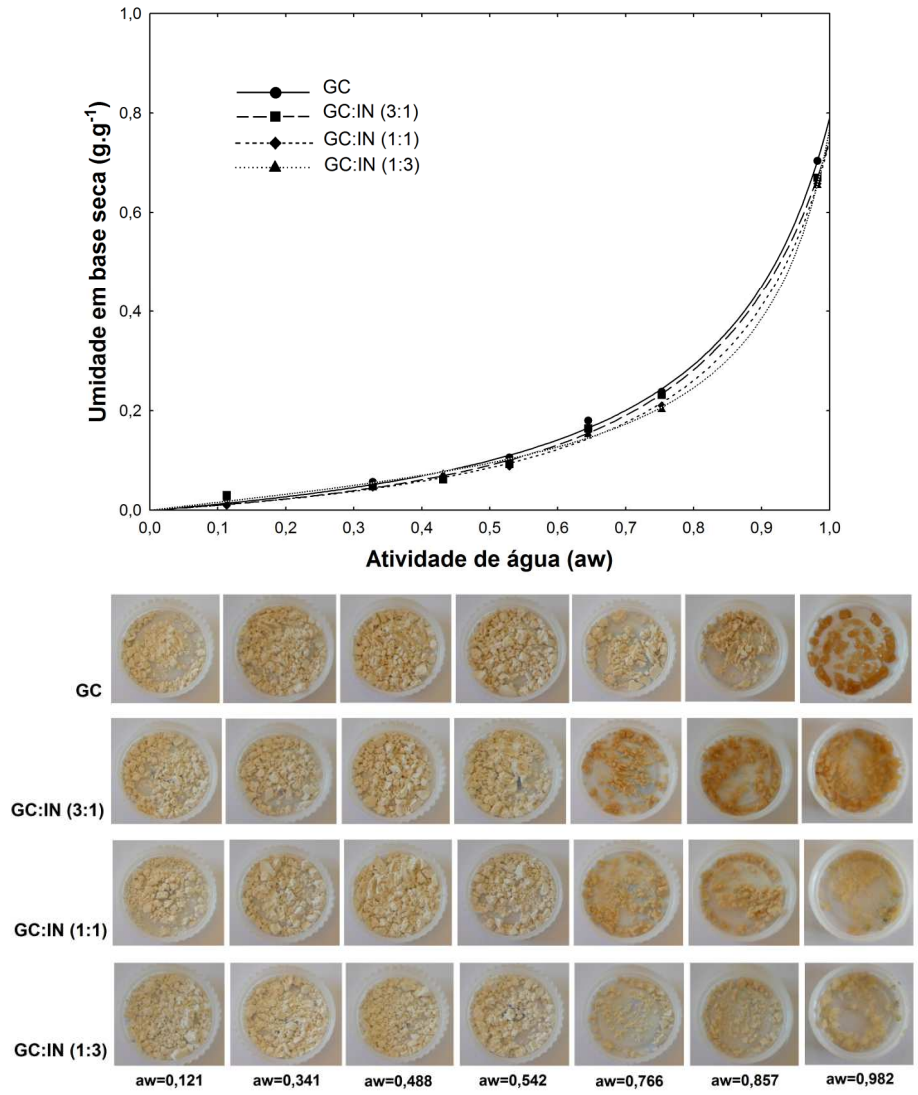

Figura 5. Isotermas de sorção das partículas produzidas utilizando diferentes materiais de parede e ajustadas pelo modelo de GAB. Aspecto físico dos pós produzidos com os encapsulantes estudados em diferentes atividades de água durante a determinação das isotermas de adsorção de umidade, no equilíbrio. GC= goma do cajueiro; IN = inulina.

3.3. Análise termogravimétrica (TGA)

A TGA é uma técnica para estudar a variação de peso de uma amostra em função da temperatura e avalia a estabilidade térmica da amostra. As partículas contendo óleo essencial de gengibre apresentaram três estágios de perda de massa. O primeiro estágio, até 110 °C, é atribuído à perda de umidade das amostras. Acima destas temperaturas, as perdas de massa observadas correspondem a processos de decomposição dos materiais. O segundo e terceiro passos se devem a ocorrência de reações dos constituintes dos materiais de parede, ou seja, carboidratos e proteínas (Fritzen-Freire et al., 2012; Silva et al., 2016a). Nesta etapa podem ocorrer reações relacionadas à desidratação de anéis de carboidratos, despolimerização e decomposição de unidades dos polímeros (Hosseini et al., 2013). As temperaturas correspondentes à inclinação máxima de cada passo de mudança de peso, observadas quando determina-se a primeira derivada da curva de TGA em relação à temperatura, chamada de termograma derivado da termogravimetria (DTGA), estão descritas na Figura 6.

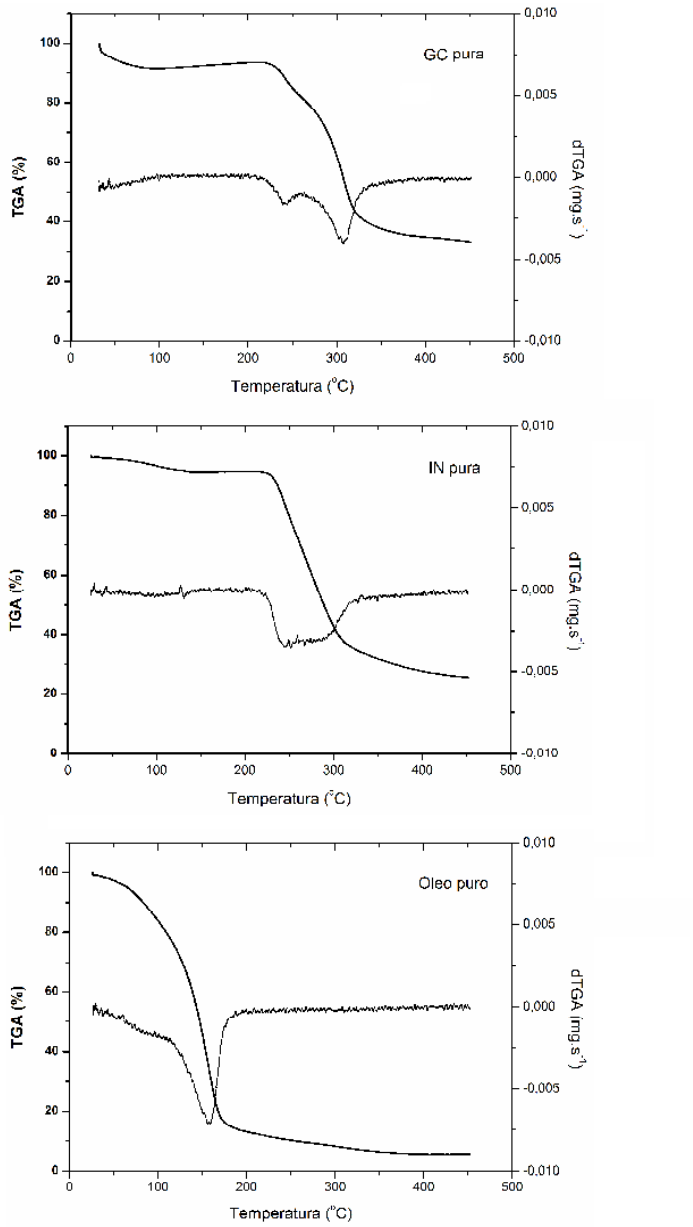

Figura 6. Termogramas TGA e dTGA obtidos para os materiais puros e micropartículas de óleo essencial de gengibre, em atmosfera de nitrogênio. GC = goma do cajueiro; IN = inulina (...continua...).

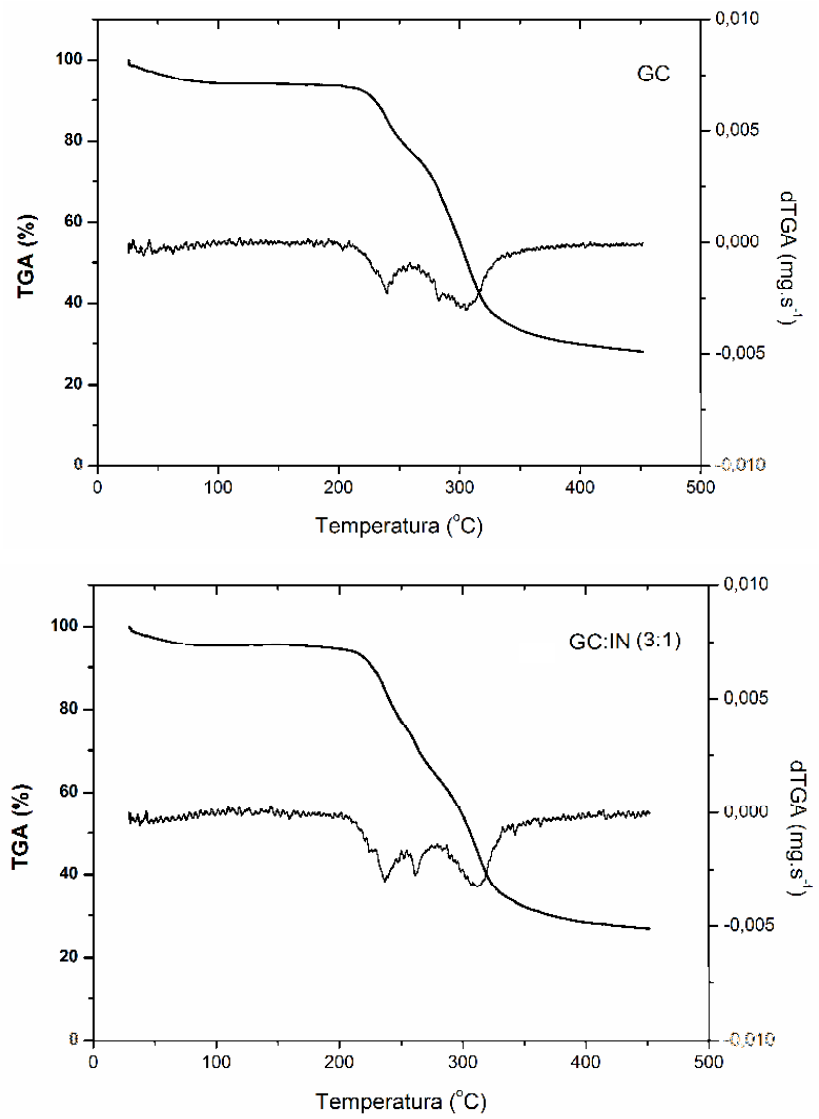

Figura 6. Termogramas TGA e dTGA obtidos para os materiais puros e micropartículas de óleo essencial de gengibre, em atmosfera de nitrogênio. GC = goma do cajueiro; IN = inulina (...continua...).

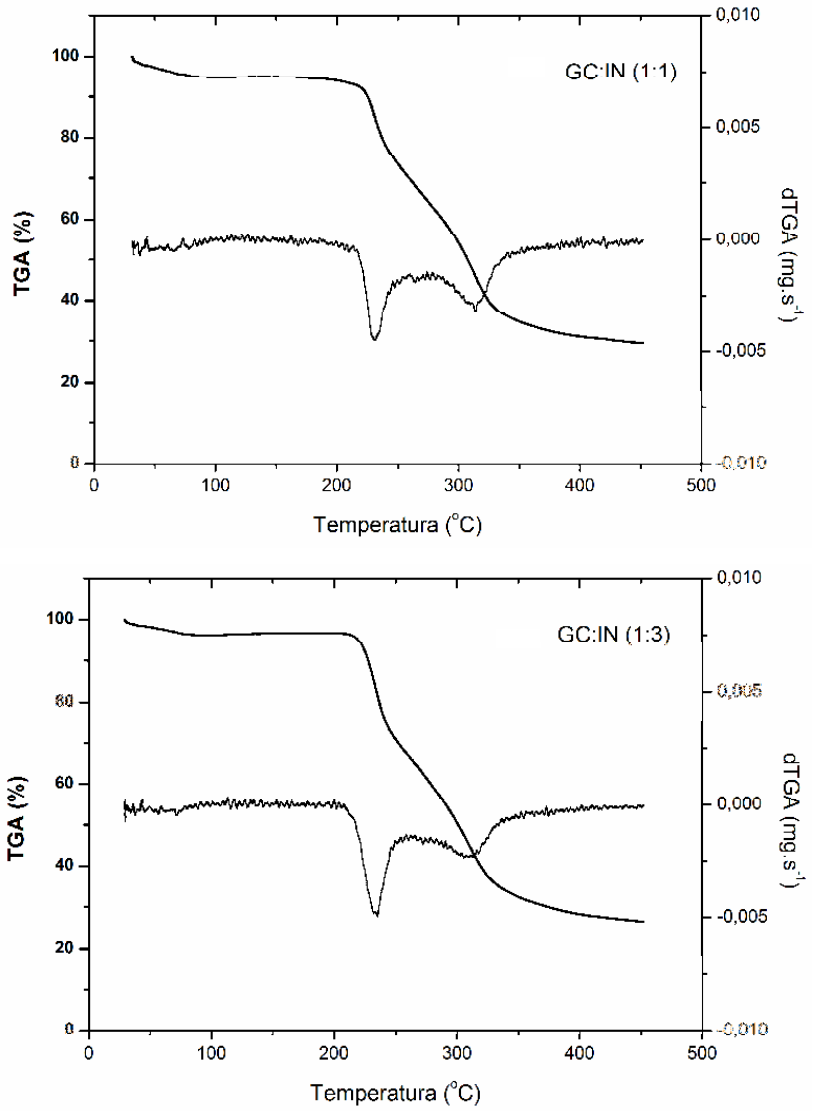

Figura 6. Termogramas TGA e dTGA obtidos para os materiais puros e micropartículas de óleo essencial de gengibre, em atmosfera de nitrogênio. GC = goma do cajueiro; IN = inulina.

Observou-se que, como na maioria dos óleos essenciais, 86,94 % do óleo essencial de gengibre foi evaporado a temperaturas inferiores a 200 ℃. Pode ser verificado que uma maior proporção de goma do cajueiro na mistura, levou a uma maior estabilidade térmica das microcápsulas. Por outro lado, no trabalho de Oliveira et al. (2014) verificou-se que uma proporção maior de alginato na mistura com goma do cajueiro, leva a uma maior estabilidade térmica de óleo essencial microencapsulado por *spray drying*.

3.4. Difração de Raio-X

A característica da estrutura física dos pós produzidos aplicando-se os materiais de parede goma de cajueiro e goma do cajueiro e inulina em diferentes proporções, foi avaliada através da metodologia de difração de raio-X. É possível verificar a ocorrência de pico difuso e largo característico de materiais com estruturas amorfas, com muito pouco grau de cristalinidade e organização (Figura 7). As partículas produzidas com o dois polímeros de carboidrato utilizados como materiais carreadores apresentaram comportamento semelhante, com exceção da amostra contendo maior concentração de inulina que apresentou características de um material amorfo com regiões cristalinas, evidenciado pela presença de picos. Silva e Meireles (2015) observaram resultado semelhante ao avaliar a utilização de inulinas de diferente grau de polimerização (DP’s de 10 e 23) na encapsulação do óleo de semente de urucum por freeze-drying. Os difratogramas de ambas inulinas revelaram que estes biopolímeros apresentavam características de materiais amorfos e após a secagem das emulsões as micropartículas foram caracterizadas como materiais amorfos com regiões cristalinas. O processo de secagem através da atomização tende a produzir produtos secos no estado amorfo metaestável devido ao tempo insuficiente para se cristalizar (Jayasundera et al., 2011).

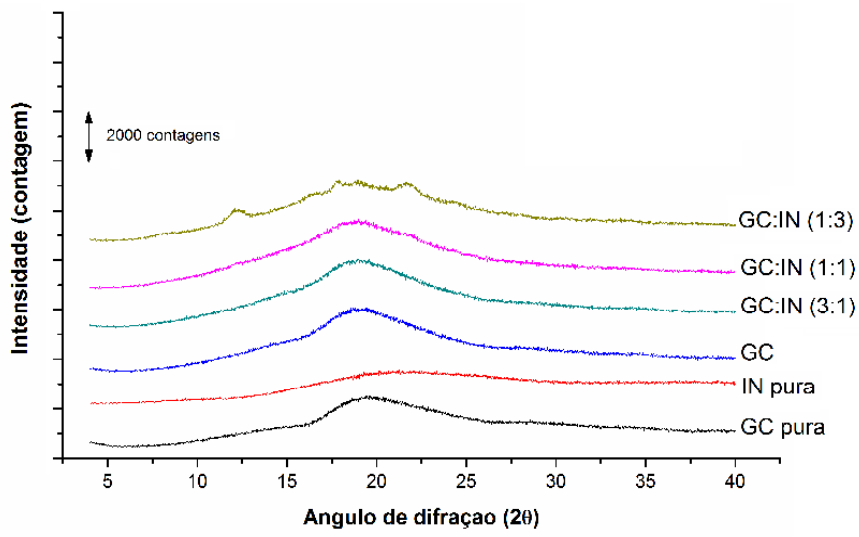

Figura 7. Difratogramas de raio-X para as partículas produzidas utilizando os carreadores estudados. GC = goma do cajueiro; IN = inulina.

4. Conclusões

As partículas obtidas utilizando a goma de cajueiro e inulina na proporção de 3:1 m/m, como material encapsulante, apresentaram características desejáveis no produto final quando analisadas em conjunto as variáveis estudadas neste trabalho. Este tratamento não apresentou fissuras, obteve uma boa estabilidade térmica, não apresentou mudança de fase em altas atividades de água e apresentou uma maior eficiência de encapsulação semelhante ao tratamentos 1:1 m/m e maior que o tratamentos contendo apenas GC. Apesar de obtidos valores baixos para a eficiência de encapsulação, a goma do cajueiro e a inulina podem ser considerados alternativas no processo de encapsulação de óleos essenciais em função de apresentar características tecnológicas de interesse. No entanto, a avaliação de novas misturas se faz necessária para a obtenção de maiores valores de eficiência de encapsulação do óleo de gengibre.

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“VERSÃO PRELIMINAR”

ARTIGO 4 Propriedades de óleo de gengibre microencapsulado: influência dos parâmetros operacionais na secagem por atomização de emulsões

Artigo redigido conforme norma da revista Drying Technology

PROPRIEDADES DE ÓLEO DE GENGIBRE MICROENCAPSULADO: INFLUÊNCIA DOS PARÂMETROS OPERACIONAIS NA SECAGEM POR ATOMIZAÇÃO DE EMULSÕES

Resumo

A secagem por atomização é um importante método utilizado pela indústria de alimentos na produção de aromas microencapsulados, melhorando suas propriedades de manuseio e dispersão. O objetivo deste estudo foi avaliar a influência das condições de processo nas propriedades de óleo essencial de gengibre microencapsulado por secagem por atomização, utilizando-se isolado proteico de soro (IPS) e inulina (IN) na proporção de 1:1, m/m como agente encapsulante. Os efeitos da concentração de material de parede (20 %, 25 % e 30 %) e da temperatura de entrada do ar (140 °C, 155 °C e 170 °C) na umidade, molhabilidade, densidades de leito e compactada, eficiência de encapsulação, tamanho de partícula e dispersibilidade foram avaliados através de um delineamento inteiramente casualizado em esquema fatorial com três repetições. Foi estudada também o comportamento reológico das emulsões e seu aspecto físico por meio de microscopia ótica. Verificou-se ainda as características morfológicas das partículas produzidas no tratamento otimizado nas variáveis respostas nas quais os modelos foram preditivos: eficiência de encapsulação, molhabilidade e PDI. O aumento na concentração de IPS:IN na solução de alimentação influenciou fortemente o aumento da viscosidade ($p<0,05$) das emulsões analisadas e o tratamento com a incorporação de 30 % de material de parede apresentou os maiores tamanhos de gotas na emulsão. A elevação do concentração de material de parede e da temperatura do ar de entrada diminuíram o teor de umidade das partículas. A molhabilidade, eficiência de encapsulação, tamanho de partícula e PDI foram afetados significativamente pelos dois fatores analisados e os modelos estatísticos se ajustaram as variações

dos dados. A densidade de leito e a densidade compactada foram influenciadas positivamente principalmente pelo termo linear da concentração de material de parede. Através do processo de otimização, considerando as variáveis molhabilidade, eficiência de encapsulação e dispersibilidade, os resultados indicaram que, uma moderada concentração de material de parede (22,34 %) e alta temperatura de entrada do ar (170 °C), foram as melhores condições para o processo de secagem por atomização de óleo essencial de gengibre. Nessas condições, a análise de microscopia eletrônica resultou em partículas relativamente esféricas, com cavidades e dobras na superfície e não foram observadas rachaduras ou fissuras na superfície.

Palavras-chave: *Spray drying*, *Zingiber officinale*, propriedades físicas, propriedades de reconstituição, ultrassonificação.

1. Introdução

Atualmente, os principais desafios na produção de pós são o desenvolvimento de partículas com propriedades desejadas e custos reduzidos. Para o caso específico do óleo essencial, a pesquisa de microencapsulação por meio da secagem por atomização tem-se concentrado em melhorar a eficiência de retenção de voláteis, além de tentar prolongar ao máximo a vida de prateleira do produto. O produto microencapsulado apresenta algumas vantagens em relação à sua forma original, no que diz respeito ao transporte, à manipulação e ao seu emprego em matrizes alimentícias. Além disso, componentes aromatizantes desempenham um papel importante na satisfação dos consumidores e influenciarão o consumo de alimentos.

As condições de secagem são muito importantes para definir a qualidade do processo de encapsulação. Devem ser considerados parâmetros como velocidade do ar de secagem, umidade do ar de entrada, temperatura do ar de entrada, vazão de alimentação, concentração da alimentação, formulação da alimentação, propriedades reológicas, propriedades termodinâmicas e especificação de atomização (Keshani et al., 2015). O aumento da concentração de material de parede tem efeito positivo no rendimento de produto encapsulado, no entanto, verifica-se que quantidades ótimas devem ser determinadas para cada processo e cada tipo de óleo essencial. Cada material de parede possui a sua concentração ideal que está relacionada à uma viscosidade ótima para a retenção de componentes voláteis. A influência das temperaturas do ar de entrada na retenção de voláteis também têm recebido bastante atenção.

As proteínas do leite, tais como isolado proteico de soro, concentrado proteico de soro, leite em pó desnatado e caseinatos, tem sido amplamente pesquisados no processo de encapsulação de óleos essenciais. Durante a etapa de emulsificação, estas proteínas mudam sua conformação e se posicionam na interface óleo-água além de contribuir com forças repulsivas que tornam as

emulsões significativamente mais estáveis (Jafari et al., 2008a). Devido à sua baixa capacidade de hidrólise, a inulina é utilizada como fibra dietética (Dima et al., 2016) e é uma alternativa como material encapsulante para a produção de alimentos com alegações funcionais, aumentando as possibilidades de desenvolvimento de novas formulações de encapsulantes.

O gengibre (*Zingiber officinale* Roscoe), uma importante especiaria pertencente à família das *Zingiberaceae*, é largamente utilizado nas formas seca e fresca (Chari et al., 2013) e possui eficientes atividades antioxidantes, anti-inflamatórias e antimicrobianas (Yeh et al., 2014). O gengibre seco pode ser utilizado para a fabricação de condimentos, medicamentos e cosméticos, bem como de alimentos com sabor de gengibre, como refrigerantes e doces (An et al., 2016). O óleo essencial de gengibre possui como principais componentes o α-zingibereno, o citral e o β-felandreno (Yamamoto-Ribeiro et al., 2013; Singh et al., 2008; Wohlmuth et al., 2006; Yu et al., 2008). As variações na composição química deste óleo podem estar relacionadas com as diferenças nas matérias-primas, localização geográfica, período da colheita e pela metodologia analítica de determinação aplicada (Wohlmuth et al., 2006).

Considerando as características promissoras do óleo essencial de gengibre e a ausência do estudo sobre a microencapsulação deste produto, este estudo avaliou o efeito da concentração de isolado proteico de soro e inulina nos parâmetros reológicos e no tamanho das gotas nas emulsões. Além disso, a influência conjunta da concentração de material de parede e da temperatura do ar de entrada do secador por *spray* foi avaliada nas propriedades das microcápsulas de óleo essencial de gengibre, tais como, eficiência de encapsulação, propriedades de reconstituição, tamanho das partículas e morfologia dos pós.

2. Material e Métodos

2.1. Materiais

O óleo essencial de gengibre adquirido da Ferquima Ind. e Com. Ltda, Vargem Grande Paulista, Brasil, foi utilizado como material encapsulado. A inulina (grau de polimerização > 10, Orafti®GR, BENEO-Orafti, Tienen, Bélgica) e isolado proteico de soro (Hilmar Ingredients, Hilmar, EUA) foram utilizados como materiais de parede.

2.2. Métodos

2.2.1. Delineamento experimental

Os experimentos foram conduzidos em delineamento inteiramente casualizado em esquema fatorial pela avaliação do efeitos dos fatores temperatura do ar de entrada, com três níveis (140 °C, 155 °C e 170 °C), e concentração de sólidos, com três níveis (20 $g.100g^{-1}$, 25 $g.100g^{-1}$ e 30 $g.100g^{-1}$) (Tabela 1) nas variáveis respostas teor de umidade, eficiência de encapsulação, molhabilidade, densidades de leito e compactada, tamanho de partícula (d_{43}) e índice de polidispersibilidade (PDI) relacionado à homogeneidade da distribuição no tamanho de partículas. Procedeu-se à análise de variância, com três repetições e com nível de significância de 5 %. As variáveis foram analisadas por meio da metodologia de superfície de resposta. Após a eliminação dos fatores não significativos, verificou-se a significância da regressão e da falta de ajuste a um nível de confiança de 95 %, através de análise de variância, utilizando-se o teste F para o planejamento estudado. O teste de médias Duncan foi aplicado para avaliação da diferença entre as médias para a variável viscosidade.

Tabela 1 Composição dos materiais de parede para cada tratamento utilizado como solução de alimentação no processo de secagem por atomização nas três diferentes temperaturas de entrada do ar do secador.

Tratamento	Material de parede (g.100 g^{-1})		Temperatura do ar de secagem (°C)
	Isolado Proteico de Soro (IPS)	Inulina (IN)	
1	10,0	10,0	140
2	12,5	12,5	
3	15,0	15,0	
4	10,0	10,0	155
5	12,5	12,5	
6	15,0	15,0	
7	10,0	10,0	170
8	12,5	12,5	
9	15,0	15,0	

As condições ótimas para a encapsulação de óleo essencial de gengibre, em função das variáveis independentes concentração de material de parede e temperatura do ar de entrada, foram obtidos utilizando-se o modelo polinomial "desirability" descrito por Derringer e Suich (1980). A validação do modelo foi determinada por comparação dos valores experimentais e dos valores preditos das variáveis dependentes consideradas no presente estudo, sendo os ensaios realizados em triplicata sob a condição otimizada.

2.2.2. Preparo das emulsões

As soluções dos materiais de parede foram preparadas pela dissolução dos materiais de parede em água destilada, para cada formulação, preparadas um

dia antes da emulsificação e mantidas a temperatura ambiente por 12 h para garantir a completa saturação das moléculas dos polímeros. O óleo essencial foi progressivamente adicionado à solução de material de parede sob agitação a 1000 rpm durante 5 min usando um homogeneizador (Ultra-Turrax IKA T18 basic, Wilmington, EUA). As emulsões, após a homogeneização por agitação mecânica, foram subsequentemente submetidas ao processo de ultrassonificação com 160 W de potência nominal (Sonifier® Branson Digital, Modelo S-450D, Branson Ultrasonics Corporation, Danbury, USA), 20 kHz, durante 2 min, para garantia da emulsificação completa de óleo essencial de gengibre. O contato entre a altura da sonda ultrassônica e as emulsões foram padronizadas a 30 mm.

A emulsão foi utilizada como alimentação líquida no processo de secagem por atomização. Para cada tratamento, 400 mL de emulsão foram preparadas para a produção das partículas. A razão da massa de óleo essencial para material de parede foi mantida em 1:4 (m/m) (Fernandes et al., 2014). A porcentagem de sólidos (material de parede) utilizada como solução de alimentação foi de 20 %, 25 % e 30 % (m/m).

2.2.2.1. Viscosidade da emulsão

As medidas reológicas foram conduzidas usando um viscosímetro de cilindro concêntrico (Brookfield DVIII Ultra, Brookfield Engineering Laboratories, Stoughton, MA, EUA), uma câmara cilíndrica 13R/RP (19,05 mm de diâmetro e profundidade de 64,77 mm), e um *spindle* SC4-18 (17,48 mm de diâmetro e 35,53 mm de comprimento). Para cada teste, o copo de amostragem e o *spindle* foram equilibrados a uma temperatura de 25 °C. As curvas de escoamento foram obtidas a uma taxa de cisalhamento de 0,1 s^{-1} a 86 s^{-1} para os tratamentos 20 % e 25 % e de 0,1 s^{-1} a 22 s^{-1} para o tratamento 30 %. O modelo da lei de potência (Equação 1) foi usada para analisar dos dados experimentais das emulsões.

$$\boldsymbol{\tau = k.\gamma^{n}} \qquad (\mathbf{1})$$

onde τ = tensão de cisalhamento (Pa), γ = taxa de cisalhamento (s^{-1}), k = índice de consistência ($Pa.s^{n}$), e n = índice de comportamento de escoamento (Silva et al., 2015a). A viscosidade aparente da emulsão foi calculada como a relação entre as tensão de cisalhamento e a taxa de deformação no ponto 20 s^{-1}.

2.2.2.2. Microscopia Óptica

A microestrutura das emulsões foi avaliada logo após o processo de homogeneização através de microscopia ótica. Para isso, alíquotas das amostras foram colocadas em lâminas cobertas com lamínulas e observadas em um microscópio ótico Carl Zeiss (MF-AKS 24 x 36 Expomet, Zeiss, Alemanha) com sistema de captura acoplado com câmera digital – Axio Cam ICc com aumento de 40 e 100 vezes. Foram obtidas cinco imagens de cada amostra, de modo a varrer toda a lâmina e se obter um resultado representativo.

2.2.3. Microencapsulação através da secagem por atomização.

As emulsões foram secas utilizando um secador por atomização (modelo MSD 1.0; Labmaq do Brasil, Ribeirão Preto, Brasil) equipado com bico atomizador de duplo fluido. As variáveis de processo aplicadas foram: temperatura do ar de entrada de 140 °C, 155 °C e 170 °C e taxa de fluxo de alimentação 0,8 $L.h^{-1}$ (Fernandes et al., 2013a,b) para todos os tratamentos. O fluxo do ar de atomização foi mantido a 35 $L.min^{-1}$. Os pós secos foram coletados e estocados em frascos opacos e fechados a 4 °C até a realização das análises.

2.2.4. Caracterização das partículas

2.2.4.1 Teor de umidade

O teor de umidade dos pós foi determinado pelo método da AOAC (ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS, AOAC, 2007). A porcentagem de perda de peso dos pós após a secagem em estufa a 105 °C até peso constante foi obtida, e o teor de umidade (%) foi calculado em base úmida.

2.2.4.2. Molhabilidade

A molhabilidade dos pós foi determinada utilizando o método de Fuchs et al. (2006) com algumas modificações. As amostras em pó (0,1 g) foram espalhadas sobre a superfície de um béquer contendo 100 mL de água destilada a 20 °C sem agitação. O tempo necessário até que a última partícula de pó afundasse ou se molhasse foi usado para a comparação da extensão de molhabilidade entre as amostras.

2.2.4.3. Densidade de leito e densidade compactada

O material em pó (aproximadamente) 10 mL foi cuidadosamente adicionado a uma proveta graduada de 50 mL, previamente tarada, e este valor foi pesado. O volume, lido diretamente na proveta, foi usado para calcular a densidade de leito (ρ_{leito}) de acordo com a relação massa/volume (Jinapong et al., 2008). Para a densidade compactada ($\rho_{compactada}$), aproximadamente 5 g de pó foi adicionado em uma proveta de 25mL, sendo a amostra repetidamente batida manualmente levantando e abaixando a proveta sob seu próprio peso a uma distância vertical de 10 cm até não haver mais diferença observada no volume entre sucessivas medidas. A densidade compactada foi calculada pela razão da massa por volume aparente (compactado) dos pós (Goula e Adamopoulus, 2008).

2.2.4.4. Eficiência de encapsulação

A quantidade de óleo encapsulado foi determinada usando n-hexano como solvente extrator conforme metodologia descrita por Li e Lu (2015), com algumas modificações. O pó seco por atomização (1,0 g) foi dissolvido em 20 mL de água destilada à 45 ºC e levado à agitação manual por 1 min. Em seguida, a amostra foi levada ao processo de ultrassom por 1 mim à 40 % de amplitude (160 W, 20 kHz). Logo após, foram adicionados 10 mL de hexano com posterior agitação em vortex e em banho-maria a 45 °C por 30 min. Em seguida, a amostra foi centrifugada a 3000 rpm por 5 min. Após a centrifugação, foi retirado o sobrenadante e adicionado em balão de 50 mL. Em seguida, foram adicionados mais 10 mL de hexano, agitado em vortex e centrifugado novamente por 5 min. Este procedimento foi repetido por quatro vezes. No final das lavagens, o balão de 50 mL foi completado com o solvente. A quantidade de óleo essencial de gengibre foi determinada medindo a absorbância à 270 nm com espectrofotômetro UV- VIS SP 2000 (Bel Photonics, Piracicaba, Brasil) e a sua concentração foi calculada usando uma curva de calibração. A eficiência de encapsulação do óleo (EE) foi determinada usando a Eq. (2):

$$\mathbf{EE}\ (\%) = \frac{\mathbf{M}}{\mathbf{M_0}}\mathbf{x\ 100} \qquad (\mathbf{2})$$

em que M é a quantidade em mg de óleo na partícula e M_o é a quantidade de óleo teórico (mg) com base na emulsão inicial que originou as partículas em base seca.

2.2.4.5. Distribuição do tamanho de partículas

A distribuição do tamanho de partículas foi medida usando instrumento de espalhamento de laser (Mastersizer 2000, modelo Hydro 2000 UM, Malvern Instruments, Worcestshire, UK). Uma pequena amostra de pó foi suspendida em álcool isopropílico (índice de refração 1,39) sob agitação, e a distribuição do

tamanho de partículas foi monitorada durante cada medida até que sucessivas leituras tornassem-se constantes. O diâmetro médio de volume, d_{43}, foi obtido (Eq. (3)) e o índice de polidispersibilidade (PDI) foi calculado conforme Eq. (4):

$$\mathbf{d_{43}} = \frac{\sum \mathbf{n_i d_i^4}}{\sum \mathbf{n_i d_i^3}} \quad (\mathbf{3})$$

$$\mathbf{PDI} = \frac{[\mathbf{d_{90}} - \mathbf{d_{10}}]}{\mathbf{d_{50}}} \quad (\mathbf{4})$$

onde d_i é o diâmetro médio da partícula; n_i é o número das partículas; d_{90}, d_{50} e d_{10} são diâmetros médios de volume a 90 %, 50 % e 10 % do volume acumulado, respectivamente.

2.2.4.6. Morfologia das partículas

A morfologia das partículas foi avaliada para o tratamento ótimo, considerando os parâmetros anteriores, por meio de microscopia eletrônica de varredura (MEV). As partículas foram imobilizadas em uma fita adesiva dupla-face e montadas sobre *stubs* do microscópio com um diâmetro de 1 cm e altura de 1 cm. As amostras foram então cobertas com ouro em câmara a vácuo e examinadas com o microscópio eletrônico de varredura (MEV 1430 VP – LEO Electron Microscopy Ltd., Cambridge, UK). O MEV foi operado a 20 kV com magnitudes de 900x a 1200x.

3. Resultados e Discussão

3.1. Caracterização das emulsões

As emulsões do tipo óleo em água (O/A) são amplamente utilizadas na indústria de alimentos porque permitem o aumento da retenção e a estabilidade dos compostos ativos. As aplicações de ultrassom nas emulsões fornecem grandes vantagens em relação a outras técnicas, principalmente devido à eficiência energética, baixo custo de produção, facilidade de manipulação do

sistema e melhor controle sobre variáveis de uso deste equipamento (Silva et al., 2015b). O aumento na concentração de IPS e inulina como sólidos da solução de alimentação influenciou fortemente o aumento da viscosidade ($p<0,05$) das emulsões analisadas. O maior valor de viscosidade foi observado quando se utilizou 30 % de material de parede na formulação, quando comparado aos outros tratamentos, os quais também se diferenciaram entre si (Tabela 2). A maior viscosidade observada neste tratamento está relacionada a uma maior quantidade de proteínas utilizado e concentração de sólidos. As dispersões contendo proteínas, de uma forma geral, estão associadas a uma alta capacidade de absorção e retenção de água o que contribui para aumentar a viscosidade do meio (Añón et al., 2001). Além disso, a inulina auxilia como barreira para a coalescência de gotículas através do espessamento na fase contínua, já que sua adição leva a um aumento da viscosidade, dificultando a mobilidade das gotículas e, assim, promovendo a estabilidade cinética essencialmente por um mecanismo físico (Silva e Meireles, 2015). As emulsões foram consideradas com características de comportamento de fluidos não-newtonianos tipicamente pseudoplásticos ($n<1$). O modelo da Lei de Potência foi bem ajustado aos dados experimentais obtendo altos valores de coeficiente de correlação e baixos valores de erro relativo médio.

Tabela 2 Parâmetros reológicos obtidos para as emulsões estudadas.

Tratamento	K (mPa.s^n)	n	R^2	E (%)	Viscosidade aparente (mPa.s)
IPS/IN (20%)	0,01	0,87	0,99	7,08	8,36 ± 0,29^a
IPS/IN (25%)	0,07	0,77	0,99	4,41	36,63 ± 7,49^b
IPS/IN (30%)	3,16	0,34	0,99	10,15	419,97 ± 48,95^c

K: índice de consistência; n: índice de comportamento de fluido; E: erro relativo médio.
^{a,b,c}Valores seguidos de letras diferentes na mesma coluna se diferem entre si ($p < 0,05$) pelo teste de *Duncan*.

As pequenas gotas de óleo geralmente são mais eficientemente incorporadas dentro da matriz de parede das microcápsulas produzidas, além da emulsão ser mais estável durante o processo de microencapsulação por *spray drying* sendo um dos parâmetros críticos para otimizar a eficiência de encapsulação (Jafari et al., 2008). De acordo com a Figura 1, o tratamento com a incorporação de 30 % de material de parede apresentou os maiores tamanhos das gotas na emulsão. Através desses resultados, os tratamentos com 20 % e 25 % mostraram ser mais eficientes na estabilização da emulsão com maiores chances de obterem maiores valores de eficiência de encapsulação. No trabalho de Silva et al. (2015b) esses autores observaram através da microscopia ótica, que os processos de homogeneização (dispersão em fase múltipla e ultrassom) resultaram em diferentes sistemas coloidais e que o processo de ultrassom, independente do biopolímero utilizado na emulsão de óleo de semente de urucum, foi o procedimento mais eficiente. Nesse trabalho, a aplicação de ultrassom como procedimento para emulsificação forneceu emulsões com menores tamanhos de gotículas de óleo para todos os tratamentos realizados (goma arábica, isolado proteico de soro, amido modificado e polietilenoglicol) para incorporação de óleo de urucum.

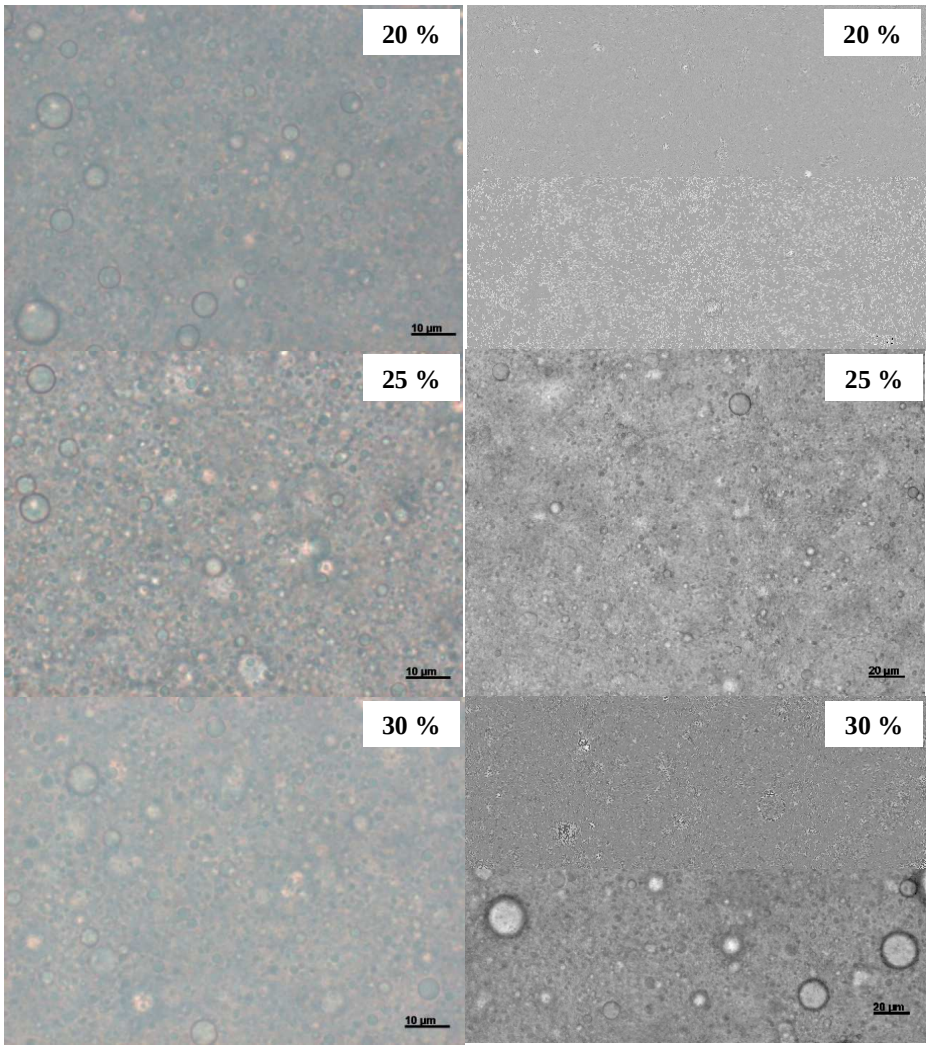

Figura 1 Fotomicrografia óptica das emulsões de óleo essencial de gengibre processadas com aplicação de homogeneização e ultrassom nas diferentes concentrações de sólidos totais estudadas (20 %, 25 % e 30 % de IPS:IN).

Caracterização das partículas

A caracterização das partículas foi realizada com base nas propriedades: teor de umidade, eficiência de encapsulação, molhabilidade, densidade de leito,

densidade compactada, tamanho de partícula e PDI. Deste modo, o comportamento das variáveis que apresentaram o modelo preditivo ($R^2 > 0,80$) foi apresentado por meio de gráfico de superfície de resposta. O teor de umidade é o principal fator que afeta a estabilidade e as propriedades físicas das partículas, desde que, um pequeno aumento no conteúdo de água é capaz de diminuir a temperatura de transição de vítrea (T_g) o suficiente para aumentar a mobilidade do material encapsulado na matriz encapsulante durante o armazenamento impactando negativamente nas principais propriedades físicas e tecnológicas destes materiais. O teor de umidade das partículas diminuiu com o aumento da temperatura de ar de entrada e concentração de sólidos na solução de alimentação (Figura 2). Este comportamento se deve em função de que em maiores temperaturas do ar de entrada, maior será a taxa de transferência de calor entre o ar de secagem e a partícula, proporcionando uma maior força motriz para a evaporação da água e por conseguinte, os pós com menores teores de umidade serão formados. Além disso, os baixos teores de umidade das microcápsulas de óleo essencial de gengibre foram obtidos em maiores concentrações do material de parede devido ao aumento dos sólidos totais na solução de alimentação antes do processo de secagem por atomização e, assim, reduzindo a quantidade de água a ser evaporada. Os resultados das análises das partículas podem ser verificados na Tabela 2. A umidade das microcápsulas variou entre 1,31 % e 5,55 %, sendo o maior valor para o tratamento com concentração de 20 % de IPS:IN e temperatura do ar de entrada de 140 °C e o menor para a amostra com 30 % de material de parede e 170 °C do ar de entrada do secador. No trabalho de Şahin-Nadeem et al. (2013) sálvia (*Salvia fruticosa* Miller) em pó foi produzida por *spray drying* e a influência da temperatura do ar de entrada (145 °C, 155 °C e 165 °C) e o tipo de material de parede (β-ciclodextrina, goma arábica e maltodextrina) foram avaliados. Assim como o presente trabalho, esses autores encontraram maiores valores do teor de umidade

em menores temperaturas do ar de secagem e concluíram que de fato maiores temperaturas levam ao um aumento da remoção de água dos materiais, resultando em uma secagem mais rápida destes produtos. Na secagem de extrato de gengibre por *spray drying*, o fator que mais afetou o variável resposta teor de umidade foi a temperatura de entrada do ar (Jangam e Thorat, 2010). Fernandes et al. (2013a) estudaram as condições operacionais do processo de secagem por atomização de óleo essencial de alecrim utilizado-se goma arábica como material encapsulante e observaram valores de umidade variando entre 0,26 % e 3,16 %. Neste estudo, as variáveis estudadas foram concentração de material de parede (10,00 %-30,00 %), temperatura de entrada do ar (135 °C -195 °C) e vazão de alimentação (1,00 $L.h^{-1}$-0,50 $L.h^{-1}$) sendo que a variável que apresentou maior influência na umidade das microcápsulas produzidas foi a temperatura de entrada do ar. Foi observado que, com aumento da temperatura do ar e com a diminuição da vazão de alimentação, a umidade das partículas diminuíram.

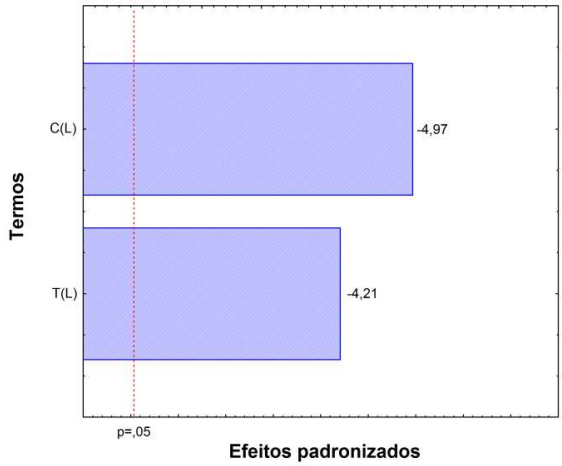

Figura 2 Diagrama de pareto para a variável resposta teor de umidade. C: concentração de material de parede, T: temperatura do ar de secagem, (L) efeito linear.

A molhabilidade é uma das propriedades físicas mais importantes relacionadas com a reconstituição dos pós em soluções aquosas, sendo diretamente afetada pela interação molecular entre as duas fases. Valores muito altos deste parâmetro não são desejáveis pela indústria de alimentos já que demandaria maiores tempos de reconstituição dos materiais em pó. No presente estudo, os tempos obtidos para que os pós tornassem completamente molhados variou entre 235 – 378 s. A concentração de IPS:IN foi o fator que mais influenciou os valores desta análise (Figura 3). Os menores tempos para a molhabilidade, ou seja, a obtenção de partículas com melhores características de instantaneização ocorreu quando a matriz IPS:IN foi utilizada na formulação em uma menor concentração. Isto se deve provavelmente porque a densidade aumentou em concentrações mais elevadas, tornando o pó mais compactado e dificultando a penetração da água nas partículas.

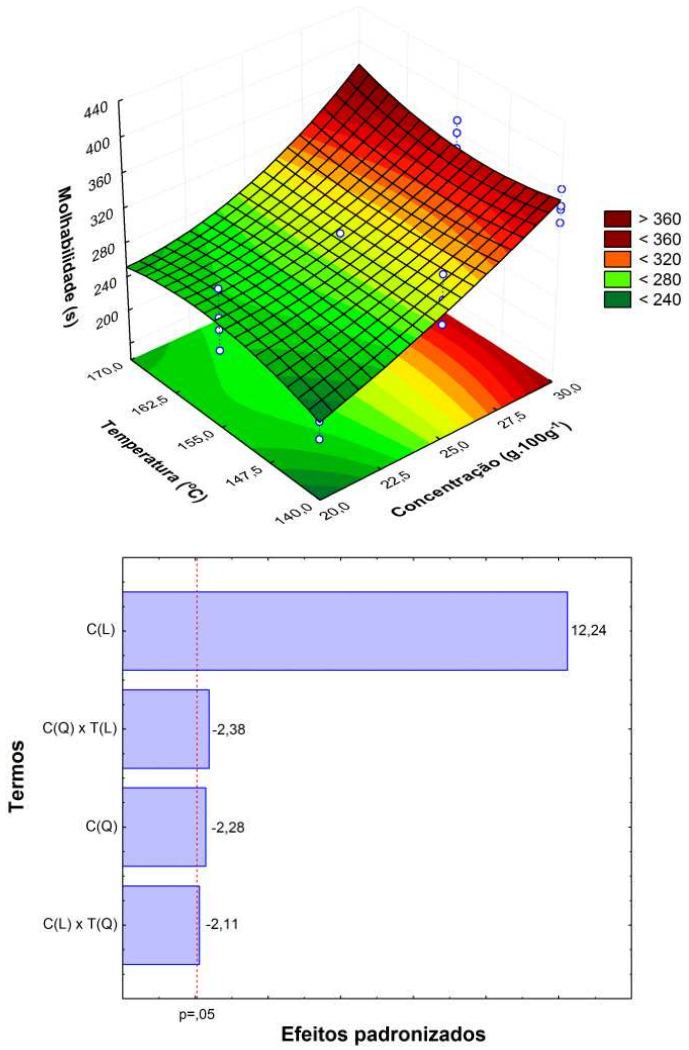

Figura 3 Superfície de resposta e diagrama de pareto para a variável resposta molhabilidade. C: concentração de material de parede, T: temperatura do ar de secagem, (L) efeito linear, (Q) efeito quadrático.

Um produto seco de baixa densidade será armazenado em recipientes de maiores dimensões, em comparação com um produto de alta densidade e,

dependendo da situação, produtos de baixas densidades não são interessantes para as indústrias, demandando maiores gastos com transporte e comercialização. A densidade de leito é a massa das partículas sólidas, incluindo a umidade, dividido pelo volume total ocupada pelas partículas, a umidade da superfície e todos os poros, sendo geralmente usado para caracterizar o produto final obtido por secagem (Shi et al., 2013). Os valores de densidade de leito variaram de 0,33 a 0,39 g mL^{-1}. Os resultados de densidade compactada, na qual o volume é compactado e o vazios formados por ar são eliminados, variaram entre 0,49 e 0,56 g mL^{-1}. As densidades mais baixas foram observadas para a microcápsula obtida com temperatura do ar de entrada de 155 °C e concentração de sólidos encapsulantes de 20 %. Conforme observado na Figura 4, o termo concentração de sólidos na alimentação linear afetou positivamente ambas as densidades analisadas e com maior influência comparado aos outros fatores significativos. Portanto, com o aumento de sólidos na solução houve uma aumento no valor das densidades. Şahin-Nadeem et al. (2011) ao estudarem a secagem por atomização de *Sideritis stricta* concluíram que a temperatura do ar de entrada não causou efeito significativo nas densidades de leito das partículas e que o aumento da concentração de material de parede aumentaram os valores desta variável. Esses autores encontraram, para a densidade de leito, valores bem similares ao presente estudo (0,34 g mL^{-1} a 0,38 g mL^{-1}). No trabalho de Shi et al. (2013), os valores da densidade de leito das microcápsulas de mel produzidas por *spray drying* aumentaram de 0,32 g mL^{-1} para 0,51 g mL^{-1} com o aumento da concentração da maltodextrina na solução de alimentação.

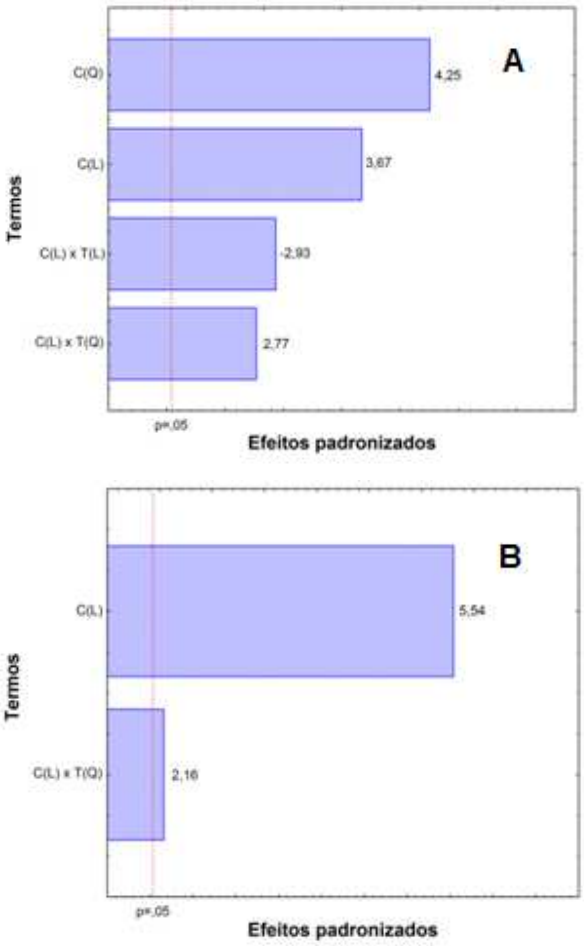

Figura 4 Diagrama de pareto para as variáveis respostas densidade de leito (A) e densidade compactada (B). C: concentração de material de parede, T: temperatura do ar de secagem, (L) efeito linear, (Q) efeito quadrático.

A retenção do óleo essencial microencapsulado através de secagem por *spray* é uma variável de grande interesse pois indica a quantidade de óleo que está de fato presa dentro da matriz e consequentemente será liberada quando requisitada. A eficiência de encapsulação pode ser aumentada pela seleção de

materiais de parede que apresentem diferentes propriedades funcionais. Esta variável está fortemente relacionada ao tipo de material de parede utilizado, à concentração de sólidos da solução de alimentação e à temperatura aplicada ao processo. Os valores de eficiência de encapsulação variaram entre 29,13 % e 47,32 %, sendo o menor valor obtido para o tratamento de 30 % de concentração de IPS:IN e temperatura de entrada do ar de 140 °C (Figura 5). Estes resultados podem estar relacionados com as propriedades de emulsão. Uma diminuição na concentração desta mistura induziu uma diminuição gradual na quantidade de óleo das partículas, que conduz a uma maior perda do óleo essencial por volatilização durante a secagem por atomização. Em contraste, um aumento excessivo da concentração de sólidos na emulsão levou a uma redução do rendimento de encapsulação de aromas. A concentração de materiais de parede na alimentação é diretamente relacionada com a viscosidade do meio, que por sua vez, interfere com a retenção de compostos voláteis; e cada tipo de material de parede possui a sua própria concentração ideal na solução de alimentação e existe ainda uma viscosidade otimizada para a retenção de partículas voláteis (Reineccius, 2004). Se a viscosidade da solução de alimentação é demasiadamente elevada, a formação das partículas é retardada durante a atomização, ao passo que uma baixa viscosidade atrasa a formação da crosta semi-permeável, aumentando a perda dos componentes voláteis. Botrel et al. (2012) encontraram valores de eficiência de encapsulação para óleo essencial de orégano microencapsulado em matriz de goma arábica, maltodextrina e amido modificado (1:1:1, m/m/m) variando entre 5,1 % e 33,9 %. No trabalho de Santhanam et al. (2015) utilizando ultrasonificação para emulsificação de óleo de peixe em matrizes de caseinato de sódio, maltodextrina e proteína de soja foi encontrado valores de eficiência de encapsulação entre 71,61 % e 77,28 %.

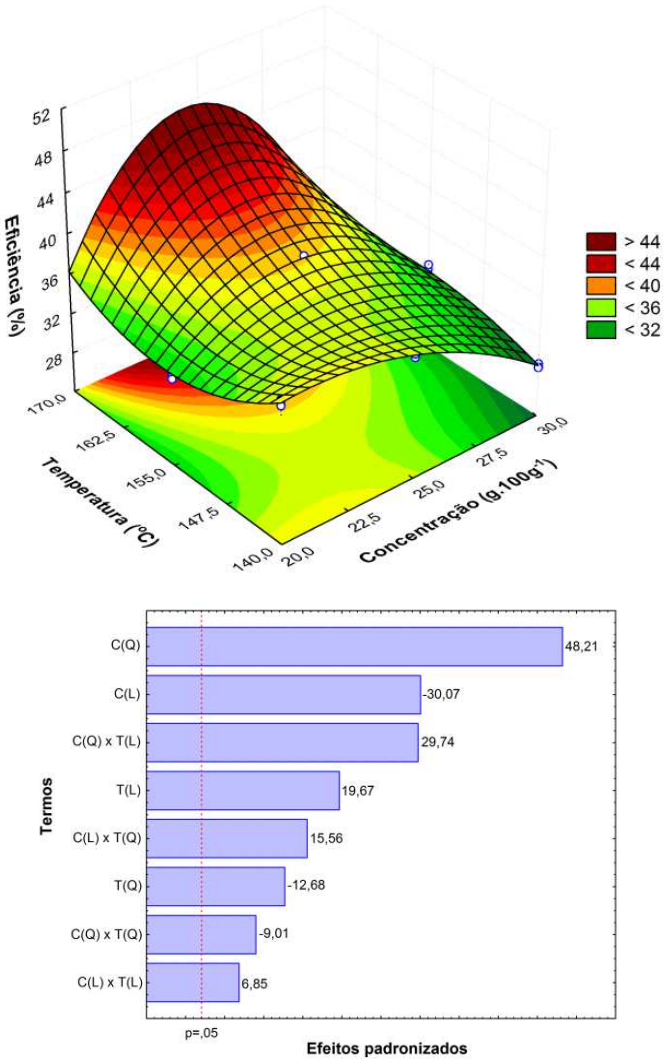

Figura 5 Superfície de resposta e diagrama de pareto para a variável resposta eficiência de encapsulação. C: concentração de material de parede, T: temperatura do ar de secagem, (L) efeito linear, (Q) efeito quadrático.

A viscosidade da emulsão aumentou em função da concentração de sólidos (IPS:IN), assim, em altos valores de viscosidades o tempo necessário

para formação da crosta é maior, aumentando os movimentos de circulação das gotículas no interior das microcápsulas e resultando em uma menor eficiência de encapsulação. Esse comportamento pode explicar os menores valores obtidos de eficiência de microencapsulação em altos valores de concentração de material de parede na solução. Já em concentrações muito baixas, a redução do conteúdo de sólidos ocasiona um aumento na quantidade de água disponível para evaporar o que leva a uma diminuição da viscosidade da solução e um maior tempo é necessário durante o processo de secagem, diminuindo também a retenção dos voláteis. Portanto, é de extrema importância encontrar o valor ótimo de concentração de encapsulante estudado para tornar o processo mais eficiente, reduzindo a perda do material encapsulado. A eficiência de encapsulação de oleoresina de alho foi mais elevada quando a concentração de maltodextrina foi aumentada de 40 % para 60 % (Balasubramani et al., 2015). Neste estudo, o aumento da temperatura do ar de entrada de 180 °C a 220 °C, aumentou inicialmente a eficiência da encapsulação com a temperatura, porém diminuiu drasticamente quando a temperatura atingiu 220 °C. Os autores explicaram que esse comportamento ocorreu devido ao rompimento de um equilíbrio entre a taxa de evaporação de água e formação de filme, o que poderia levar ao rompimento de microcápsulas e, assim, a uma baixa eficiência de encapsulação. Portanto, é desejável que uma elevada temperatura do ar de entrada seja utilizada no processo de secagem por atomização para permitir uma rápida formação da membrana semipermeável na superfície da partícula. Entretanto, essa temperatura não pode ser tão alta a ponto de causar danos térmicos ao produto seco ou de rupturas na superfície das microcápsulas, o que aumentaria as perdas dos componentes voláteis e a entrada de ar, ocasionando processos oxidativos.

A variação do tamanho de partícula pode ser explicada pelas propriedades físicas da matriz de alimentação, tais como a viscosidade, a

concentração de sólidos, entre outros (Díaz-Bandera et al., 2015). Observou-se que o tamanho das partículas foi influenciado principalmente pela concentração do material de parede e pela temperatura do ar de entrada, sendo os maiores valores de d_{43} obtidos para as partículas de óleo essencial de gengibre encapsuladas em maiores concentrações de sólidos totais na alimentação e em menores temperaturas do ar de entrada do secador (Figura 6). O maior tamanho médio das partículas produzidas com o uso de IPS:IN na concentração de 30 % pode ser explicado em razão da maior viscosidade observada para este tratamento. O aumento do tamanho das microcápsulas com o aumento da concentração de sólidos na alimentação também pode ser atribuído a um início do processo de aglomeração de partículas no secador, onde a formação de pontes de ligação entre partículas pode levar à produção de partículas com tamanho maiores (Shi et al., 2013). O controle no tamanho das partículas secas por atomização é um fator importante devido a sua grande influência na aparência, escoamento e dispersibilidade (Reineccius, 2004). Por outro lado, partículas muito pequenas produzidas implicam em maior área superficial, o que pode levar a uma maior quantidade de óleo não encapsulado (Anwar e Kunz, 2011).

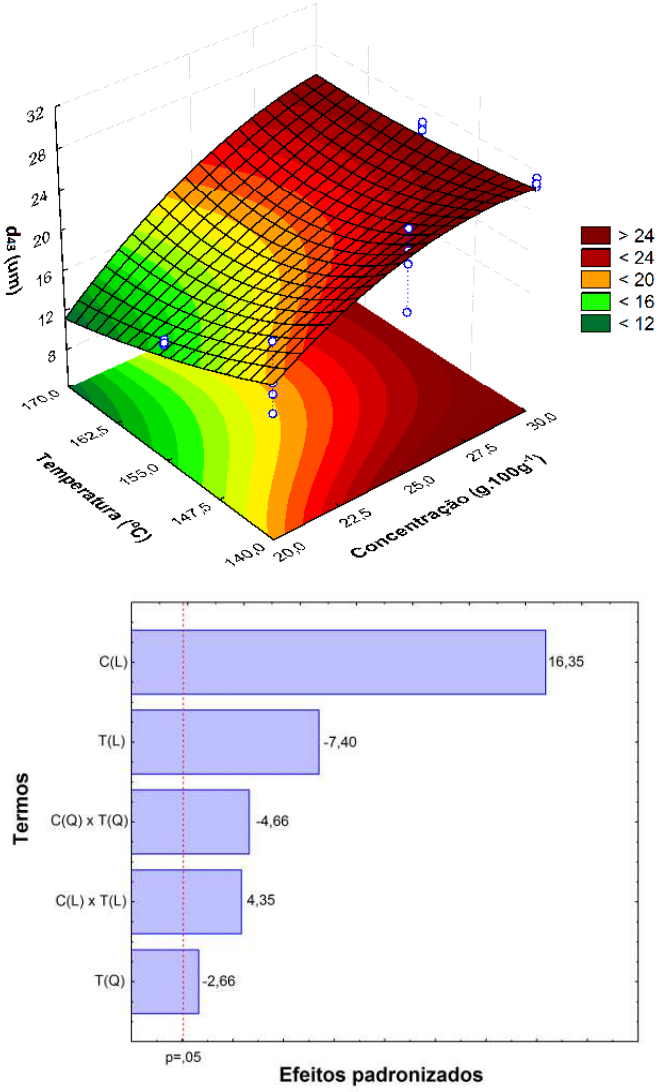

Figura 6 Superfície de resposta e diagrama de pareto para a variável resposta tamanho de partícula. C: concentração de material de parede, T: temperatura do ar de secagem, (L) efeito linear, (Q) efeito quadrático.

O valor de dispersibilidade se relaciona com o grau de uniformidade de distribuição de tamanho das partículas. Assim, quanto menor for o valor deste parâmetro menor é a dispersão da distribuição de tamanho de partícula, o que indica um sistema homogêneo que permite uma melhor padronização do produto e das propriedades das microcápsulas. A distribuição das partículas foi considerada homogênea, com base nos valores obtidos no presente estudo (Figura 7). O termo linear da concentração do material de parede influenciou positivamente este parâmetro, obtendo maiores valores de dispersibilidade e, por outro lado, o termo linear da temperatura do ar de entrada influenciou negativamente, diminuindo os valores desta variável resposta. Portanto, quanto maior a concentração de IPS:IN maior o valor de dispersibilidade e, consequentemente, mais heterogênea a distribuição de tamanhos de partículas.

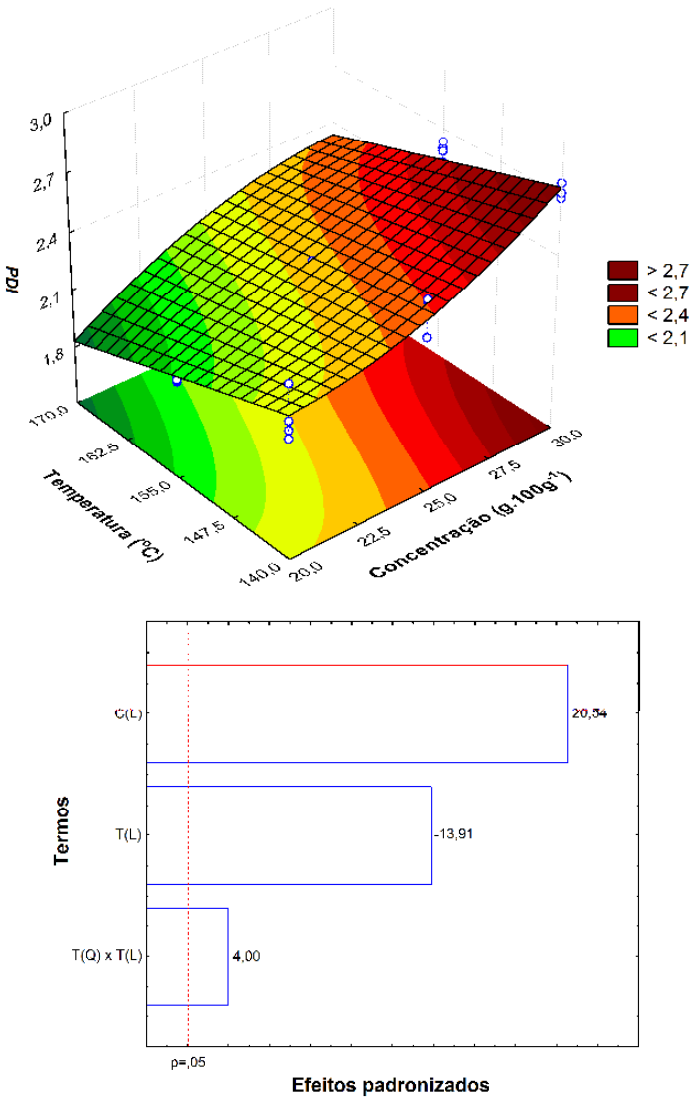

Figura 7 Superfície de resposta e diagrama de pareto para a variável resposta índice de polidispersibilidade. C: concentração de material de parede, T: temperatura do ar de secagem, (L) efeito linear, (Q) efeito quadrático.

Para a microencapsulação de óleo essencial de gengibre, a condição ótima foi obtida com base na maior eficiência de encapsulação e nos menores valores de molhabilidade e PDI. Estas variáveis foram significativamente afetadas pelas condições estudadas na secagem por atomização. De acordo com os resultados encontrados pela metodologia de superfície de resposta analisados na Figura 8, a combinação de 22,34 % de concentração de material da parede e de 170 °C da temperatura de entrada do ar foi verificada para proporcionar os melhores resultados do processo. Sob estas condições, os valores preditos para a eficiência de encapsulação foi de 44,9 %, 251 s para a molhabilidade e 2,05 de PDI para o tamanho de partícula (Figura 8).

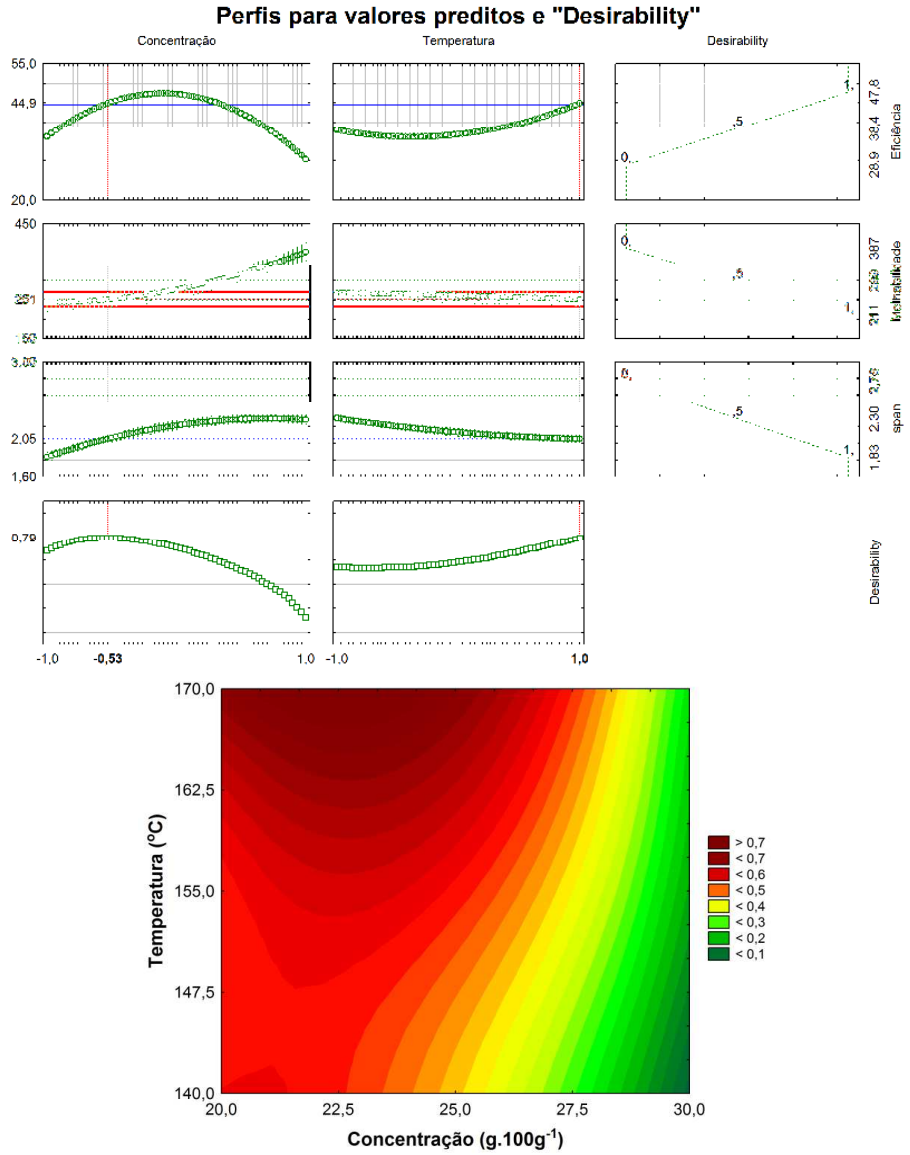

Figura 8 Gráficos que mostram os valores para as variáveis eficiência de encapsulação, molhabilidade e span que otimizam as condições de microencapsulação dentro das faixas de valores de temperatura e cpmcmetração estudadas.

As condições ótimas foram validadas experimentalmente e pelos valores das variáveis respostas, utilizando-se a equação polinomial e função "desirability", e os valores preditos são apresentados na Tabela 3. Os resultados mostram que foram encontrados baixos valores de erro médio relativo e o modelo pode ser considerado validado experimentalmente.

Tabela 3. Resultados da validação experimental para as condições ótimas de secagem estudades.

	Eficiência de encapsulação (%)		
	Valor Experimental	Valor Predito	E(%)
Concentração de material de parede (%) 22,3 %	49,5 46,7 46,5	44,9	5,56
	Molhabilidade (s)		
	Valor Experimental	Valor Predito	E(%)
Temperatura do ar de entrada (°C) 170 °C	228 262 246	251	5,44
	PDI		
	Valor Experimental	Valor Predito	E(%)
	1,98 1,81 2,13	2,05	6,85

Morfologia

As partículas produzidas na condição ótima apresentaram formas relativamente esféricas, com cavidades e dobras na superfície e não foram observadas rachaduras ou fissuras (Figura 9). Esse fato tem grande influência no processo encapsulação, proteção e manutenção das substâncias ativas dentro da matriz encapsulante. Nas condições otimizadas do estudo de Botrel et al. (2014) (temperatura do ar de entrada de 185 °C, fração de inulina na concentração de 40

% em relação ao IPS e 6 % de concentração de óleo de peixe), as partículas apresentaram formas esféricas e sem evidência de rachaduras ou fissuras. O óleo essencial de manjericão microencapsulado em goma arábica apresentou forma esférica com algumas dobras na superfície (Garcia et al., 2012).

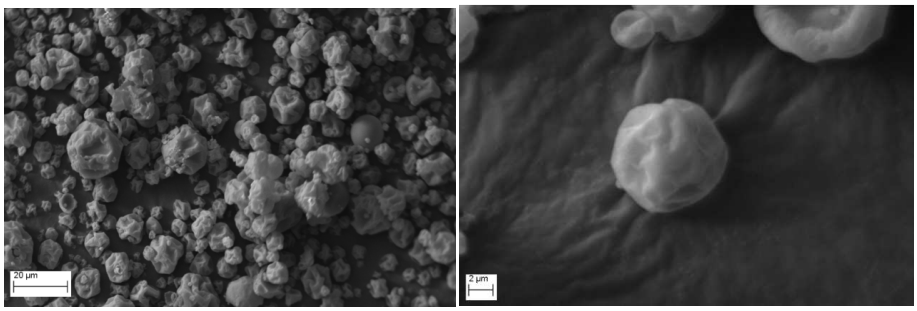

Figura 9 Imagens obtidas através de microscopia eletrônica de varredura para as partículas de óleo essencial de gengibre produzidas com os seguintes condições otimizadas: 22,34 % de material de parede (isolado e inulina 1:1; m/m) e 170 °C do ar de entrada do secador.

Conclusões

Verificou-se que as partículas obtidas utilizando 22,34 % de IPS:IN como material encapsulante e 170 °C como temperatura do ar de entrada do secador apresentaram maior eficiência de encapsulação, menor tempo de molhabilidade e maior homogeneidade na distribuição do tamanho de partículas. As micropartículas produzidas utilizando estas condições de secagem apresentaram-se sem fissuras na superfície das microcápsulas. O estudo evidencia a necessidade de determinação dos melhores parâmetros de processo, visto que pontos ótimos para variáveis pré-determinadas podem ser obtidos.

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CONCLUSÃO GERAL

O estudo de diferentes encapsulantes para melhorar as características das partículas e maximizar a retenção de óleo e componentes voláteis mostrou como possíveis e eficientes matrizes de encapsulação para o óleo essencial de gengibre a mistura de goma arábica e maltodextrina (1:1 m/m) e a mistura de isolado proteico de soro e maltodextrina (1:1 m/m). A goma arábica mostrou-se superior ao isolado proteico de soro em relação à eficiência de encapsulação. Porém, devido à escassez e ao alto valor no mercado, a substituição parcial da goma arábica pela maltodextrina ou total pelo isolado proteico de soro e maltodextrina, se torna facilmente justificável.

A goma do cajueiro e a inulina podem ser consideradas alternativas no processo de encapsulação de óleos essenciais e no desenvolvimento de novas formulações com alegações funcionais e com a utilização de biopolímeros naturais não convencionais. O óleo essencial microencapsulado na matriz de goma do cajueiro e inulina na proporção de 3:1, m/m, apresentou as melhores características, principalmente em relação à eficiência de encapsulação.

Através do processo de otimização da matriz isolado proteico de soro e inulina (1:1 m/m), considerando as variáveis molhabilidade, eficiência de encapsulação e dispersibilidade, os resultados indicaram que, uma moderada concentração de material de parede (22,34 %) e alta temperatura de entrada do ar (170 °C), foram as melhores condições para o processo de secagem por atomização de óleo essencial de gengibre.

A partir dos resultados obtidos, a goma do cajueiro e a inulina mostraram-se interessantes substitutos em alimentos por aumentarem as possibilidades de novas formulações de encapsulantes com biopolímeros naturais, da ampla extração no Brasil e por a inulina se tratar de uma fibra com atividades funcionais comprovadas, como uma alternativa de encapsulante na

produção de alimentos com alegações funcionais. Portanto, fazem-se necessários mais estudos sobre a aplicação desses novos encapsulantes e das novas formulações otimizadas em matrizes alimentícias e da aceitação pelos consumidores.