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Oxidation kinetics and thermodynamic analysis of chia oil microencapsulated in a whey protein concentrate-polysaccharide matrix

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ABSTRACT

The oxidation kinetics of chia oil (CO) in bulk and microencapsulated by spray-drying in a biopolymer matrix of whey protein concentrate (WPC) with mesquite gum (MG) (67:33 w/w ratio) stored at 25, 35 and 40 °C at different water activities (a_w) were determined. Oxidation was described by a zero-order kinetic equation of the autocatalytic type in all cases. The oxidation of CO within microcapsules was slower than in bulk, independently of the storage temperature. The kinetics parameters, rate constant and activation energy, decreased as a_w increased. In the a_w range between 0.614 and 0.654 both kinetic parameters presented the lowest values, which corresponded to the minimum integral entropy $(\Delta S_{int})_T$ zone. The $(\Delta S_{int})_T$ zone is considered as the zone of maximum stability as less water is available to participate in degradation reactions, acting as plasticizer in the polymeric matrix and hindering oxygen diffusion through the pores, retarding the oxidation process.

1. Introduction

Chia (*Salvia hispanica* L.) is an ancient plant native of Mexico and Guatemala whose oil has received much attention for being a rich source of polyunsaturated fatty acids (PUFA), containing mainly α-linolenic and linoleic acids (Álvarez-Chávez et al., 2008; Muñoz et al., 2013; Ramírez-Jaramillo and Lozano-Contreras, 2015). Chia oil is used for diabetes, high blood pressure, and for generally reducing the risk of heart disease and stroke (cardiovascular disease), and serves as precursor for a vast number of signal molecules like prostaglandins (Chapkin, 2008; Kaur et al., 2014). Despite the nutritional value of chia oil, its high degree of unsaturation makes it prone to oxidation, which is carried out by a free radical process where three steps are involved: initiation, propagation, and termination (Kamal-Eldin et al., 2003). These steps involve the formation of hydroperoxides, which in turn react to form secondary or tertiary lipid oxidation products, leading to the decomposition of the fatty acids that are part of the oil. Hence, lipid oxidation leads to the formation of off-flavours and degradation products that could be harmful to health, in addition to alteration of the oil sensory characteristics (Tonon et al., 2011). One alternative to preserve chia oil properties is to microencapsulate it by spray-drying, which is a widely used technique in the food industry for protecting sensitive compounds. Spray-drying offers several advantages over other techniques: for instance, equipment availability, production capacity and costs, and capacity for treating heat sensitive products

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(Estevinho et al., 2013). There are four main factors that might affect microencapsulated unsaturated lipids oxidation during manufacturing and storage: temperature, water activity (a_w), moisture content (M) and glass transition temperature (Tg).

An aspect of considerable interest is the effect of the water activity on the physical changes of the solid matrix entrapping the oils, which may affect the oil distribution and, consequently, the accessibility of oxygen to the oil. After drying, a highly viscous solid matrix in the glassy amorphous state is obtained; when moisture content or temperature increases, the solid changes from the amorphous glassy state to the rubbery state with a high molecular mobility. Temperature at the state change, called the glass transition temperature, depends on the solid matrix nature and decreases as moisture content increases (Roos et al., 1996). Because molecular mobility is increased by the plasticizing effect of water or by temperature, the so-called collapse may occur (Levine and Slade, 1990). These physical changes are associated with partial release of encapsulated lipids, and the released oil may then be more exposed and undergo rapid oxidation.

Water activity and glass transition temperature are interrelated, and together provoke structural changes on the matrix of the microcapsule, eventually leading to its collapse, stickiness, and shrinkage, so both of them have bearing on the stability of a food system (Roos, 2007). Hence, state diagrams can be established to obtain critical storage conditions, where it is assumed that an increase in molecular mobility enhances structural transformations and diffusion that accelerate deteriorative changes.

The thermodynamics of water vapour sorption provide a reliable criterion for predicting the storage stability and shelf-life of spray-dried food products (Sánchez-Sáenz et al., 2011). Thermodynamic analysis of sorption needs the knowledge of isotherms behaviour as a function of temperature. The Guggenheim–Anderson–de Boer (GAB) equation is a localized multilayer sorption and condensed film model. The minimum integral entropy can be interpreted as the required moisture content for forming a monolayer, where the water activity at which a dry food product is most stable (Pérez-Alonso et al., 2006), and strong bondings occurs between the water (adsorbate) and the food (adsorbent) that corresponds to less water being available for chemical and spoilage reactions (Nunes and Rotstein, 1991).

In this context, many authors have studied the lipid oxidation of diverse oils from different botanical origin, but in depth studies of the oxidation of microencapsulated chia oil are lacking. Ixtaina et al. (2015) microencapsulated chia oil using lactose and sodium caseinate as wall materials, finding that the microencapsulated chia oil oxidized more rapidly at 170 °C than 135 °C during spray-drying. They also reported that when higher homogenization pressure (600 bar compared with 400 bar) was applied during the emulsion preparation, the smaller droplet size of the emulsion produced a larger contact area between the prooxidant compounds and lipid hydroperoxides during the drying process. Nevertheless, microencapsulated chia oil oxidized significantly less than bulk chia oil. Martínez et al. (2015) produced spray-dried chia oil microcapsules using 2:1 hydroxypropyl methylcellulose-to-maltodextrin DE-15, and core-to-wall ratios, finding that the peroxide value of the microencapsulated oil was higher than that of the bulk oil, without offering plausible explanation for these results.

The aim of this work was to: i) produce chia oil microcapsules by spray-drying using a whey protein concentrate-mesquite gum matrix blend as wall material; ii) determine the minimum integral entropy zone for establishing the most suitable microcapsules storage conditions (water activity and temperature) by; iii) to interrelate the physical state of the amorphous matrix with the glass transition temperature at the critical storage conditions; and iv) determine the extent of the peroxidation of the microencapsulated chia oil in comparison to the bulk chia oil.

2. Materials and methods

2.1. Materials

Chia (*S. hispanica* L.) seeds were obtained from local farmers of the Atlixco region, State of Puebla, Mexico. Whey protein concentrate (WPC; 80% protein in dry basis (d.b.)) was acquired from Hilmar Ingredients (Hilmar, CA, USA). Powdered mesquite gum (MG) from *Prosopis laevigata* trees, was provided by Universidad Autonoma Metropolitana-Iztapalapa (Dr. E. J. Vernon-Carter). MG is a highly branched complex heteropolyelectrolyte formed principally by L-arabinose and D-galactose, and minor proportions of 4-O-methyl-D-glucuronate, and L-rhamnose, in a 2:4:1:1 ratio, and a protein content of around 4.8% d.b., which is responsible for the excellent emulsifying properties of MG (Román-Guerrero et al., 2009).

Deionised water was used in all experiments. All the chemical reagents used were purchased from Sigma Aldrich, S. A. de C. V. (Toluca, State of Mexico, Mexico).

2.2. Methods

2.2.1. Chia oil extraction and composition

CO extraction was accomplished by cold pressing following the procedure described by Rodea-González et al. (2012), with slight modifications. In short, 300 g of chia seeds were placed in the press chamber of a Tamer hydraulic press (model PHT-20, Shangai, China) and pressure was applied by means of a 40 cm long and 10 cm diameter plunger that gradually exerted a pressure up to 9 tons at room temperature. Trace amounts of seed were removed from CO using a cloth filter, and filtered CO was stored in amber bottles at 5 °C in darkness until required.

A gas chromatograph (Agilent 6890, model G1530A, CA, USA) equipped with an auto sampler (model 7683B), a flame ionization detector (FID) and a CP-Sil 88 column (100 m × 0.25 mm × 0.39 mm) was used for determining CO composition. Initial column temperature was 90 °C, and a heating ramp of 1.5 °C/min was used until 225 °C was achieved. Helium was used as carrier gas at a flow rate of 0.7 mL/min. CO composition was as follows: 7.6% oleic acid, 18.9% linoleic acid, 58.2% α-linolenic acid, and the balance to 100% was made up by minor compounds in concentrations lower than 3.2%. This composition is similar to those reported by Álvarez-Chávez et al. (2008) and Rodea-González et al. (2012).

2.2.2. Oil-in-water (O/W) emulsion formulation

Biopolymer blend selection for formulating the oil-in-water emulsions was done based on the studies made by Rodea-González et al. (2012) who emulsified CO with WPC:MG blends obtaining oil-in-water emulsions with high encapsulation efficiency and stability; by Matsuno and Adachi (1993) who stated that best protection against lipid oxidation is provided by protective colloids that exhibit drying curves that are characterized by an early decreasing drying rate where water evaporation is controlled by diffusion mechanisms; and by Rodríguez-Huezo et al. (2007) who found that WPC and MG blends significantly lowered the effective diffusivity of water during drying than either biopolymer on its own.

Briefly, an aqueous solution (25% w/w) of WPC-MG in 2:1 ratio with 0.3% w/w sodium azide for preventing the proliferation of microorganisms was prepared, and kept overnight in a shaking water bath at room temperature (~20 °C) to warrant a full hydration of the biopolymer molecules. The requisite amount of CO was