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The influence of drying methods on the stabilization of fish oil microcapsules: Comparison of spray granulation, spray drying, and freeze drying

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ABSTRACT

The stability of microencapsulated fish oil prepared using various drying methods is investigated. The fish oil with ratio of 33/22, eicosapentaenoic acid (EPA):docosahexaenoic acid (DHA), is emulsified with four combinations of matrices, and emulsions are dried by spray granulation (SG), spray drying (SD), and freeze drying (FD) to produce 25% oil powders. The objective is to identify the most critical factors to determine powder stability and to further examine the superiority of the SG process compared to other drying processes. The stability is examined by measurement of peroxide values (PV) and GC-headspace propanal after 8-week's storage at room temperature (±21 °C)

The best matrices are a combination of 10% soybean soluble polysaccharide (SSPS) and 65% octenyl succinic anhydride (OSA-starch). Microencapsulation of 620 mg/g omega−3 fish oil with these matrices then dried by SG is able to produce powder having a very low propanal content and with a shelf life of 5 weeks at ±21 °C. The results indicate that microcapsules produced by SG are actually formed firstly by agglomeration of seed particles. These agglomerated particles are then covered by successive layers. The particle enlargement is determined by mechanism of the layer growth. Therefore, the SG process produces "multiple encapsulations" granules which provide maximum protection to the oil droplets.

Comparison of the SG, SD, and FD processes confirms that combination of matrices, drying temperature, microcapsule morphology, and processing time are among the most critical factors governing stability. Exposure to heat is proved to be a limiting factor for drying unstable emulsion.

1. Introduction

Selection of the best coating materials and microencapsulation process are crucial steps in food microencapsulation. Previous works have underlined that the best way to emulsify fish oil is to combine coating materials that function as a carrier matrix and as an emulsifier (Sheu and Rosenberg, 1998). Literature review indicates that even the best combination of biopolymers for microencapsulating fish oil used with different drying techniques can produce both stable and unstable products. It is necessary to determine which combinations are the best for microencapsulating the right amount of polyunsaturated fatty acids (PUFAs) in fish oil.

In an earlier publication, Anwar et al. (2010), underline that spray granulation (SG) is a good method to produce fish oil powder. SG offers low drying temperature (max. 70 °C) to dry an emulsion and this method is suitable for microcapsule production containing sensitive cores such as fish oil. To date, there are data gaps in the field of fish oil microencapsulation that need to be filled. There are no studies where various production methods are compared especially to evaluate SG in comparison with other drying techniques, i.e., spray drying (SD), and freeze drying (FD).

Previous research usually investigated microencapsulation by a commonly used method such as spray drying or only by freeze drying. Unsatisfied outcomes obtained by a certain method might be different if produced by other processes. Each drying method offers advantages and disadvantages and so does each coating material. By carefully examining these two factors, this research is designed to answer the questions associated with the stability of fish oil microcapsules against oxidation in relation to how they are produced.

Abbreviations: SG, spray granulation; SD, spray drying; FD, freeze drying; EPA, eicosapentaenoic acid; DHA, docosahexaenoic acid; PUFAs, polyunsaturated fatty acids; SSPS, soybean soluble polysaccharide; OSA-starch, octenyl succinic anhydrate-starch; HPBCD, hydroxypropyl betacyclodextrin; PV, peroxide value; GC-headspace, gas chromatography-headspace; SEM, scanning electron microscope; FEG-SEM, field emission gun-scanning electron microscope; MC-1, matrix combination-1; MC-2, matrix combination-2; MC-3, matrix combination-3; MC-4, matrix combination-4; ME, microencapsulation efficiency.

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Hence, in this research, four biopolymers (maltodextrin, soybean soluble polysaccharide (SSPS), hydroxypropyl betacyclodextrin (Kleptose® HPBCD), and modified starch or OSA-starch (Hi-Cap® 100)) are evaluated in combination as coating materials for fish oil. The selection is based on their superiority as reported in literature.

Maltodextrin is a filler matrix (Rosenberg et al., 1993), which is cheap, highly soluble in water and able to form stable emulsion (Anandaraman and Reineccius, 1986). Soybean soluble polysaccharide (SSPS) is claimed to have excellent emulsifying properties and is better than gum acacia (gum arabic) (Matsumura et al., 2003). Hydroxypropyl betacyclodextrin (HPBCD) offers advantage by encapsulation in the molecular form (nanoencapsulation) (Choi et al., 2010). It has a unique molecular cavity for entrapping guest molecules, including fatty acids (Duchene et al., 2003; Yu et al., 2001). Modified starch has replaced the ordinary starch due to its better emulsifying capacity (Singh et al., 2007).

Spray drying is a common technique used for microencapsulation of food ingredients (Desobry et al., 1997). It is a simple inexpensive method in which either proteins or polysaccharides or a combination of both can be used to create the shell. However, SD has some drawbacks, e.g., high drying temperature (can be more than 200 °C) and that it is only suitable for matrices that are highly soluble in water (Gharsallaoui et al., 2007). Spray drying an emulsion containing sensitive ingredients such as fish oil is risky. Because of the high drying temperature used in spray drying, deterioration of sensitive ingredients caused by oxidation has been reported (Hogan et al., 2003; Kolanowski et al., 2006).

Unlike SD, FD has been shown to be an attractive method for extending the shelf life of foods. Drying is carried out at temperatures lower than ambient temperatures, and the absence of air prevents product deterioration caused by oxidation or chemical modification. This method can minimize the product damage due to decomposition or changes in structure, texture, appearance and flavor, which can occur as a consequence of the high drying temperature used in spray drying (Longmore, 1971).

For spray granulation (SG), low drying temperature and the formation of granules with the "onion-skin" structure has distinguished this method from the commonly used ones. As heat may trigger the oxidation, production where this factor is eliminated should increase powder stability (Anwar et al., 2010).

Therefore, this research characterizes and compares the effect of (1) low to medium drying temperature but longer residence time of spray granulation, (2) high drying temperature but very short residence time of spray drying, and (3) no heating but very long drying time of freeze drying on microcapsule stability. Several combinations of walls to encapsulate fish oil will be used in each drying process. The results are compared based on product stability against oxidation, microencapsulation efficiency and microcapsule physical properties by particle size analysis, and scanning electron microscope (SEM) examinations. The oxidative stability is evaluated based on two indicators: peroxide values (PVs) and detection of volatile propanal measured by headspace gas chromatography upon storage at room temperature (±21 °C) for 8 weeks.

2. Materials and methods

Fish oil 33/22 (EPA:DHA) ultra refined (kindly provided by Cognis Deutschland, Illertissen, Germany) was used as a core. The coating materials were combination of SSPS (Soyafibe-S-EN100, Fuji Oil, Osaka, Japan) with maltodextrin (Granadex M 20, Biesterfeld Spezialchemie, Hamburg), hydroxypropyl betacyclodextrin (Kleptose® HPBCD which was kindly provided by Roquette Freres, Frankfurt, Germany), and octenyl succinic anhydride or OSA-starch (HI-CAP® 100, which was a gift from National Starch Food Innovation, Hamburg, Germany). All chemicals used in this study were of analytical grade. Purified water was used for the preparation of all solution. All experiments and analysis were carried out in duplicate.

2.1. Preparation of emulsions

Coating materials or wall were dissolved in purified water, in a 3 L plastic jar, using Ultra-Turrax (T50, IKA Labortechnik, Staufen, Germany) at 10,000 rpm. The emulsions were prepared at 50% (w/w) total solids with an oil load of 25% (dry basis). Combination of matrices (MC-1, MC-2, MC-3, and MC-4) and their compositions are summarized in Table 1.

The MC-2 formula consists of 10% SSPS and 65% maltodextrin. Previous study indicated that this combination has proved to be a good wall mixture for encapsulating fish oil by giving enough protection to fish oil in the emulsion form. Oxidation prevention was particularly obvious when this mixture used to encapsulate 18/12 fish oil (ratio of EPA:DHA) (Anwar et al., 2010). To further evaluate the role of SSPS in stabilizing fish oil emulsion, the percentage of SSPS is increased to 12.5% in the MC-1 formula, and accordingly the amount of maltodextrin is reduced (62.5%). To compare the outstanding properties of SSPS and maltodextrin, the role of modified starch (65%) in combination with SSPS (10%) is investigated in MC-3. Finally, the ability of hydroxypropyl betacyclodextrin (HPBCD) to reduce oxidation is tested in MC-4, not as a secondary matrix, but as one of the main matrices (15%) along with SSPS (10%) and maltodextrin (50%).

Following complete dissolution of coating materials, the plastic jar was immersed in a cold water bath with ice and cooled for 10–20 min until a temperature of 10–12 °C was reached. Fish oil in the ratio of 1:4 (core:wall) was added and mixing continued at 8000 rpm for 2–3 min. There was no addition of antioxidant during preparation of emulsion. The coarse emulsions were then further homogenized using a laboratory homogenizer (Panda 1K, NS1001L, GEA Niro Soavi S.p.A., Parma, Italy) at 270/40 bar and using Gann homogenizer (Gann Apparate und Machinenbau GmbH, Stuttgart, Germany) at 200 bar.

2.2. Spray granulation

The homogenized emulsion was collected in plastic jars that were covered with plastic sheets to avoid contact with oxygen, and immersed in an ice water bath. Before spraying the emulsion, 250 g maltodextrin were inserted into Spouted Bed, ProCell 5 Lab-System (Glatt Ingenieurtechnik GmbH, Weimar, Germany) as the seed particles. When the spray granulation (SG) process started, the seeds were suspended by the fluidized gas into which the

Table 1
Combination of coating materials used to emulsify fish oil.

Combination code	Drying process	Matrix combinations (%)				Fish oil (25%)
		SSPS	Maltodextrin	OSA-starch	HPBCD	
MC-1	SG	12.5	62.5	–	–	33/22 ultrarefined
	SD	12.5	62.5	–	–	
	FD	12.5	62.5	–	–	
MC-2	SG	10	65	–	–	
	SD	10	65	–	–	
	FD	10	65	–	–	
MC-3	SG	10	–	65	–	
	SD	10	–	65	–	
	FD	10	–	65	–	
MC-4	SG	10	50	–	15	
	SD	10	50	–	15	
	FD	10	50	–	15	