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Orange oil stability in spray dry delivery systems

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ABSTRACT

The oxidation stability of orange oil flavours encapsulated in carbohydrate based spray dry delivery systems is assessed through accelerated shelf life testing, compatible with the physical state of the delivery system. It is demonstrated here that the oxidative shelf life stability is limited by the diffusion of oxygen through the carbohydrate matrix. Determination of the evolution of orange oil oxidation products with time and correlations with simple but accurate sensory data allows for prediction of absolute shelf life. The oxidative shelf life appears to be dependent only on the number average molecular weight of carbohydrates in the matrix and is not affected by the substitution of small sugars (e.g., maltose for sucrose). A maximum of 2 years shelf life at 25 °C is predicted if sugar dimers are the predominant species in the matrix. The drawback to extended oxidative stability is a low physical stability under humid conditions promoting local softening in the sample. Maltose, having low hygroscopicity, improves the physical stability compared to sucrose. The best compromise between physical (caking) and chemical (oxidation) stability is obtained for carbohydrate compositions with number average molecular weight of 560 g mol^{-1} that do not contain sucrose (stability against oxidation: 20 months at 25 °C and stability against humidity: 50% RH at 25 °C).

1. Introduction

Spray drying is the most profitable technology for flavour encapsulation (Gouin, 2004) and represents more than 85% of the delivery systems used in the flavour industry (Bouquerand, Dardelle, Erni, & Normand, 2013; Porzio, 2012). The glassy matrices and the process of drying transform the liquid flavour into a solid powder that is easier to transport and handle for incorporation into final applications. Some other benefits are associated with the "structured flavour": those are mainly linked to the protection against external stresses (e.g. light, oxygen). Ultimately, the delivery system provides stability and integrity of the flavour composition for some time, until it is used and consumed.

Despite its longevity, spray drying is still a technology that can show improvement, especially in the domain of shelf life (Ubbink & Schoonman, 2005). The shelf life of conventional products based on octenyl succinated starches and maltodextrin matrices is not more than 18 months, due to loss or oxidation of the flavour. For citrus flavours, which are especially sensitive to oxygen, the shelf life does not exceed 12 months (Ubbink & Schoonman, 2005).

Spray dried particles are commonly made using polymeric emulsifiers (e.g. octenyl succinylated starches (OSS) and Gum Arabic) (Porzio, 2012). These are high molecular weight emulsifiers that are detrimental to the density of the glassy system by promoting free volume (Benczedi, Tomka, & Escher, 1998; Limbach & Ubbink, 2008). The benefit associated with high molecular weight molecules in the matrix is that they bring physical stability under humid air conditions (Aeberhardt, Bui, & Normand, 2007; Bouquerand, Maio, Meyer, & Normand, 2008). Finished spray dried powders have a relatively high glass transition temperature ($T_g > 30\,^\circ\text{C}$) due to their low water content. Caking, or physical stability, is therefore not an issue with spray dried flavours except for fruit juice powders as low molecular weight sugars and acids are present in fruit juice compositions (Adhikari, Howes, Bhandari, & Truong, 2001; Bhandari & Howes, 1999).

If one excludes the caking issue, the shelf life of spray dried powders is limited by the oxidative stability of the oil and/or by the loss of oil during storage. There is a need to understand and control the oxygen barrier properties of spray dried products to provide the desired stability in application. Stability control is possible by including anti-oxidant ingredients in the formulation or by physically reducing the oxygen permeability. One way to accomplish the latter is to increase the density of the glass by lowering the molecular weight of the carrier system while still maintaining good protection against humidity (Anandaraman & Reineccius, 1986; Baisier & Reineccius, 1989).

The idea of lowering the molecular weight of the carrier to reduce the oxygen permeation is not new (Subramaniam, 1984).

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One of the most common ways of achieving a low molecular weight matrix while still remaining cost effective is to add sucrose to maltodextrin (cf. Durarome® (Bohn, Cadwallader, & Schmidt, 2005)).

The molecular weight can also be lowered by eliminating the polymeric emulsifier or replacing it with one that does not interfere with the basic properties of the matrix. One such emulsifier is Q-Naturale™. An aqueous extract of the bark of the soap bark tree (*Quillaja saponaria*), Q-Naturale™ is an example of a natural saponin-containing emulsifier (Mitra & Dungan, 1997; Stanimirova et al., 2011). Saponins are powerful emulsifiers that can be used at very low concentrations to make spray dry pre-emulsions that are stable under high shear generated at the spray dry nozzle (Bouquerand et al., 2011).

This article is based on careful analysis of published data on oxidation of orange oil in spray dried powders. Our investigation has led to the construction of a comprehensive model that links the shelf life (determined by a sensory panel and GC–MS measurements of oxidation products) and the number average molecular weight of the carrier carbohydrate used to encapsulate the flavour.

2. Materials and methods

2.1. Materials

The number average molar mass (M_n) was measured using freezing point osmometry (Rong, Sillick, & Gregson, 2009) for pure maltodextrins, modified starches and glucose syrup. Q-Naturale™ ($M = 1650\,\mathrm{g\,mol^{-1}}$ (Stanimirova et al., 2011) and octenyl succinated starches of different M_n (4443 and 1916 g mol^{-1}) were purchased from Ingredion™ (Bridgewater, NJ). Maltodextrins 18DE ($M_n = 1031\,\mathrm{g\,mol^{-1}}$), 10DE ($M_n = 1505\,\mathrm{g\,mol^{-1}}$) and 5DE ($M_n = 2446\,\mathrm{g\,mol^{-1}}$) were purchased from Cargill (Hammond, IN). Crystalline sucrose ($M = 342\,\mathrm{g\,mol^{-1}}$) was obtained from Domino Imperial Sugar (Miami, FL). Glucose syrup solid 25DE ($M_n = 730\,\mathrm{g\,mol^{-1}}$) and 20DE ($M_n = 886\,\mathrm{g\,mol^{-1}}$) were purchased from Grain Processing Corporation (Muscatine, IA).

The orange oil used in all course of this study was a Valencia Orange Peels manufactured by cold pressing process and dewaxed by winterization. No antioxidant was added to the oil.

2.2. Sample preparation

A horizontal box dryer (Ernest D. Menold Inc., Lester, PA) equipped with high pressure homogenization and high pressure nozzle atomization was used to produce the prototypes. Carbohydrates (maltodextrin, glucose syrup and sucrose) were incorporated in water. Q-Naturale™ was introduced as a liquid solution (22% w/w dry) and ranged from 0.06% to 0.66% (w/w) solid concentration in the final product (Bouquerand et al., 2011). Orange oil was added and the solution was stirred using a Lightnin® mixer (Lightnin, Rochester, NY). The feed was homogenized at 70 bars and atomization pressure was maintained at 70 bars. Inlet and outlet temperatures of the dryer were maintained at 170 °C and 72 °C respectively. Powders were characterized by an average particle size of 90 ± 10 microns (sieve analysis) and a water content of 3.0 ± 0.5% (w/w) (Karl Fischer).

2.3. Accelerated shelf life test

An accelerated shelf life test for oxidation was developed and used for evaluating the prototypes. It is based on the assumption that oxidation of the encapsulated oil is limited by the diffusion of oxygen through the carbohydrate barrier rather than the oxidation reaction itself. Products of the oxidation reaction were quantified after defined periods of time from 0 to 13 days. Samples were placed in 15 ml glass vials with no cap. These were then placed in a Parr reactor (Parr Instrument Co., Moline, IL). The reactor was sealed and flushed with oxygen four times, then pressurized to 3.5 bars, closed and placed in an oven at 35 °C.

On days 1, 3, 6 and 13, samples were taken for analysis and the reactor refilled with oxygen to continue to the next time point. For analysis, 0.5 g of sample, 12.5 μl of internal standard solution (50 mg ml^{-1} chlorocyclohexane in acetone) and 1.5 ml water were placed in a 20 ml headspace vial, sealed and mixed to dissolve sample. The headspace was sampled using a purple 60 μ × 1 cm PEG SPME fibre (Sigma–Aldrich) for 20 min after equilibrating at 40 °C for 20 min. Desorption of the fibre in a 220 °C GC inlet for 5 min was followed by chromatography on a 0.32 mm × 30 m × 1 μm Restek Stabilwax column (Bellefonte, PA) with MS detection (Agilent 5975B, Santa Clara, CA). The GC oven (Agilent 6890) was programmed from 50 °C to 240 °C at 6 °C min^{-1} after a 3 min initial hold, and held at final temperature for 10.3 min. Cis and trans limonene oxides, carvone, and cis and trans carveol were quantified by comparison to the internal standard.

The accelerated test required the powder sample to have a T_g higher than 50 °C. DSC-measured glass transition temperatures ranged between 55 °C and 65 °C. A high oxygen pressure is used in the headspace to remove competition for diffusion within the glass and to increase the amount of oxygen diffusing into the matrix. This enhances the sensitivity of the test by maximizing the amount of oxidation products. Tests were carried out at 35 °C to accelerate oxygen diffusion.

2.4. Molecular weight in number

Measurement of the number average molecular weight of maltodextrins was performed by osmometry using a μ-Osmette 5400 freezing point osmometer (Precision Systems Inc., Natick, MA, USA) (Rong et al., 2009). Measurements were made following the manufacturers recommendations for calibration using 100 and 500mOsmkg$_{\mathrm{H_2O}}{}^{-1}$ calibration fluids (Precision Systems Inc.). Fifty microliter samples were measured into specially designed sample vials. The instrument automatically determined osmolality *via* freezing point depression measurement.

The number average molecular weight of the carbohydrate matrix systems was calculated from individual ingredients using Eq. (1).

$$M_n = \left(\sum_i w_i\right)\left(\sum_i \frac{w_i}{M_{n_i}}\right)^{-1} \tag{1}$$

An apparent DE was calculated for all samples using Eq. (2) (Avaltroni, Bouquerand, & Normand, 2004).

$$\mathrm{DE}_{app} = \frac{16,200}{M_n - 18} \tag{2}$$

2.5. Resistance to humidity

The resistance to humidity was assessed by the measurement of a_w^* at 25 °C (Sillick & Gregson, 2010) for glucose syrups and formulations containing a mixture of sucrose and maltodextrins. The a_w^* is the value of the equilibrated water activity (a_w) for $T_g = 25\,°\mathrm{C}$. Samples were equilibrated for 1 week at 25 °C in desiccators under controlled relative humidity conditions ranging from 10% to 80% relative humidity.

2.6. Glass transition temperature (T_g) measurements

Glass transition (Tg) measurements were conducted on these samples using a TA Instruments Q2000 DSC previously calibrated with indium. Between 3 and 8 mg of sample was loaded into a