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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 °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™ ($M = 1650\,g\,mol^{-1}$ (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 ($M_n = 1031\,g\,mol^{-1}$), 10DE ($M_n = 1505\,g\,mol^{-1}$) and 5DE ($M_n = 2446\,g\,mol^{-1}$) were purchased from Cargill (Hammond, IN). Crystalline sucrose ($M = 342\,g\,mol^{-1}$) was obtained from Domino Imperial Sugar (Miami, FL). Glucose syrup solid 25DE ($M_n = 730\,g\,mol^{-1}$) and 20DE ($M_n = 886\,g\,mol^{-1}$) 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 $3.0 \pm 0.5\%$ (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 $60\,\mu \times 1$ 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 $0.32\,mm \times 30\,m \times 1\,\mu m$ 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 $500 mOsmkg_{H_2O}{}^{-1}$ 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).

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

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

$$DE_{app} = \frac{16,200}{M_n - 18} \quad (2)$$

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 $T_g = 25$ °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

Tzero aluminium hermetic pan. The pan was crimp sealed. The following run conditions were used: hold at −20 °C for 5 min, ramp at 10 °C min^{-1} to 100 °C (scan 1), quench cool back to −20 °C and repeat ramp (scan 2). The T_g was taken as the inflection point on the second scan of the thermogram.

3. Results

3.1. Accelerated shelf life test

At each time point during the experiments under accelerated test conditions (35 °C, 3.5 bars O_2), the products of limonene oxidation were summed. The measured value at day 1 for our measurements (or at day 7 for the data from the literature) was subtracted from subsequent measurements to erase the influence of the history of the sample (initial conditions). The increase in oxidation products with time showed a linear trend with the square root of the corrected time (Fig. 1). This is typical of a Brownian diffusive process where the displacement of a Brownian molecule (O_2) is proportional to the square root of time. As a result, the slope of the trend (oxidation product concentration versus square root of time) is related to the apparent oxygen diffusion coefficient

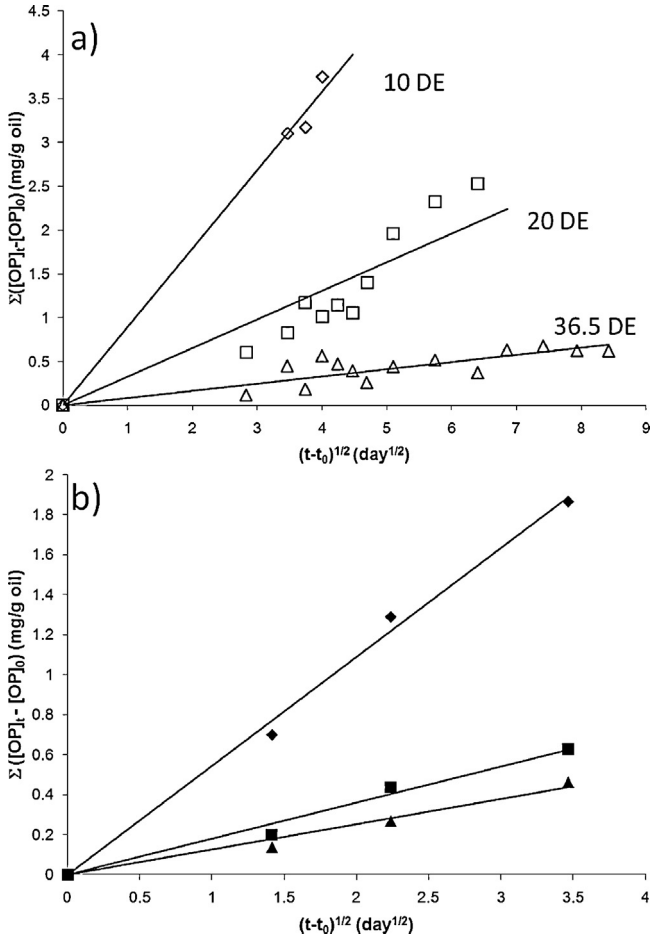

Fig. 1. (a) Data from Anandaraman and Reineccius (1986) at 32 °C, example given for the determination of the limiting step in the mechanism of limonene oxidation in spray dry samples of various molecular weights. (b) Data from this study, sum of oxidation products of limonene at 35 °C as a function of the square root of time. Diamonds are for orange oil oxidation in carrier molecular weight 1081 g mol^{-1} obtained by mixing 18DE and low molecular weight OSS, squares are for oxidation of orange oil in carrier molecular weight 655 g mol^{-1} made of 38% (w/w) sucrose and 62% (w/w) 10DE maltodextrin, and triangles are for orange oil oxidation in carrier molecular weight 557 g mol^{-1} made of 50% (w/w) sucrose and 50% (w/w) 10DE maltodextrin.

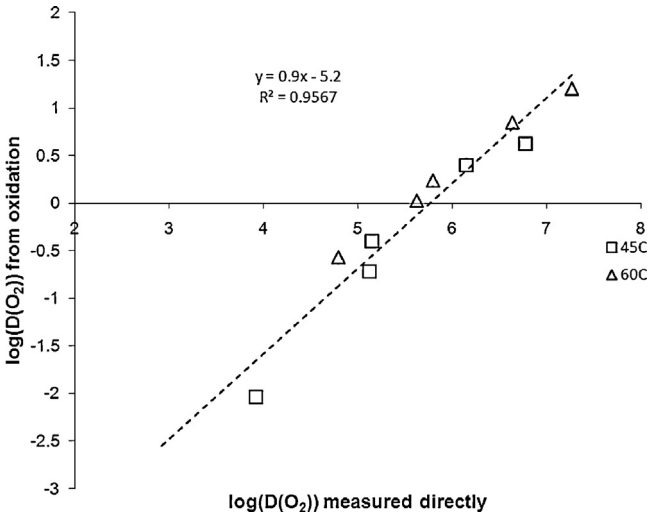

Fig. 2. Relationship between generation of oxidation products and oxygen penetration in the matrix. The slope of the log-log representation is close to 1 with a high regression coefficient.

$(2D_{app})^{1/2}$ (Crank, 1975; Einstein, 1956), see Eq. (3) where OP stands for oxidation products.

$$\sum([OP]_t - [OP]_0) \propto \sqrt{2D_{app}(t - t_0)} \quad (3)$$

The results presented in Fig. 1 are well corroborated with those from the literature (Anandaraman & Reineccius, 1986; Baisier & Reineccius, 1989; Subramaniam, 1984), where oxidation was measured at 3 different temperatures (32, 45 and 60 °C) under ambient air atmosphere and for up to 78 days. Fig. 1a is a representation of published data measured at 32 °C (using Eq. (3)). The loading was 13% (w/w) orange oil for all samples. Pure maltodextrins and glucose syrups of increasing DE were used with no emulsifier. The products of oxidation (OP in Eq. (3)) were measured using a GC-internal standard method on an extract of the samples. The data at various temperatures were easily fitted with an Arrhenius relationship, where the logarithm of the sum of the products of oxidation was plotted linearly with the reciprocal of the absolute temperature (results not shown).

According to Fickian diffusion theory, the slope of the representation in Fig. 1 is proportional to the square root of an apparent diffusion coefficient assuming that the surface area of the powder is not formulation dependent.

3.2. Oxidation product generation and oxygen penetration

Although the apparent diffusion coefficient calculated from Fig. 1 could be linked to the diffusion of oxygen, a direct relationship between the development of oxidation products and the penetration of oxygen through the matrix is lacking. However, using the literature data (Anandaraman & Reineccius, 1986), this missing relationship can be approximated using storage at 45 °C and 60 °C and measured values of oxygen in the reported matrices and oxidation product generation (see Fig. 2). A log-log representation of the data looks more appropriate, due to the large range in the measured values on both axes. The slope corresponds to the power-law of the direct relationship between the two quantities.

According to Fig. 2, measuring the oxidation product concentration corresponds to indirectly measuring the penetration of oxygen into the matrix. Also, the square root relationship in Fig. 1 demonstrates that the oxidation of encapsulated orange oil is limited by the diffusion of oxygen into the matrix.

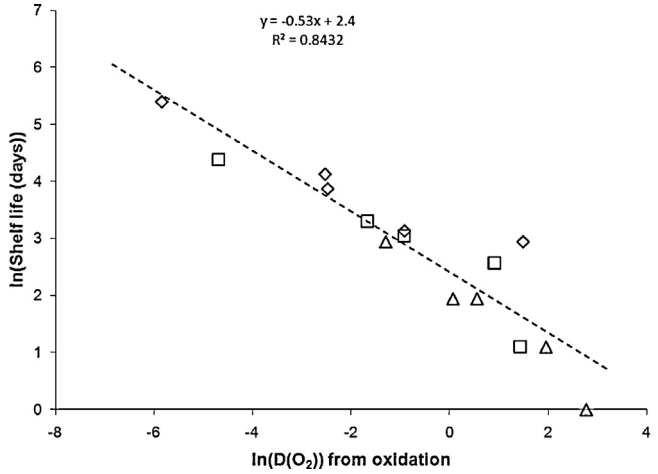

Fig. 3. Relationship between shelf life and the apparent oxygen diffusion coefficient derived from the measurement of oxidation product for 3 temperatures (32 °C: diamonds; 45 °C: squares; 60 °C: triangles). The shelf life of the delivery system is linked to the reciprocal of the square root of the diffusion of oxygen with a relatively high confidence (R^2 = 0.84) considering that the data have been generated by a sensory panel.

3.3. Oxidation product generation and shelf life

Another relationship is necessary to link the oxidation product generation to the shelf life of the delivery systems. Again, using literature data (Anandaraman & Reineccius, 1986; Subramaniam, 1984), a direct relationship between the log(shelf life), as measured by trained panellists, and log(diffusion coefficient), as obtained from the analysis of the oxidation product generation, can be observed. The relationship is depicted in Fig. 3, where the three storage temperatures (32 °C, 45 °C and 60 °C) are reported.

From Fig. 3 and the embedded relationship, the shelf life is a measure of oxidation product concentration rather than its evolution per se. The shelf life – oxygen diffusion coefficient relationship is neither temperature nor molecular weight distribution dependent, since one measurement of oxygen diffusion coefficient corresponds to one shelf life period and only one. This analysis of the data has not been previously presented in this way and allows for determination of the absolute performance of delivery systems against oxidation.

Extrapolation of the literature data (Anandaraman & Reineccius, 1986; Subramaniam, 1984) to obtain the oxygen diffusion coefficient at 35 °C was successfully realized for maltopolymers using an Arrhenius representation. In the following sections, those calculated oxygen diffusion coefficients for carbohydrates of homologous structures are compared to experimental values for matrices based on carbohydrates of non-homologous structures.

3.4. Effect of matrix molecular weight distribution on oxidation product generation

The apparent oxygen diffusion coefficient was determined as a function of the number average molecular weight of all species present in the matrix, assuming that all matrices were in a glassy state. Apparent diffusion coefficients at 35 °C were determined for compositions reported in Table 1, with the results for all samples presented in Fig. 4. The open triangles are extrapolated values at 35 °C from the Arrhenius representation of values at 32 °C, 45 °C and 60 °C (Anandaraman & Reineccius, 1986; Subramaniam, 1984).

In Fig. 4, a satisfactory negative correlation exists between the logarithm of the diffusion coefficient and the reciprocal of the number average molecular weight of the matrix. The diffusion of oxygen increases with increasing molecular weight. Data from the literature (Anandaraman & Reineccius, 1986; Subramaniam, 1984) are included with the results from the current study.

Table 1
Composition of spray dry samples represented in Fig. 4 (a = Anandaraman & Reineccius, 1986) (b = Sillick & Gregson, 2010).

Symbol	Matrix	Emulsifier	(orange oil)	Samples	Source
△	Maltodextrins	–	13% (w/w)	5	a
■	Maltodextrins	OSS	16.6% (w/w)	2	This study
♦	Maltodextrin–sucrose	Saponin	30% (w/w)	19	This study
*	Glucose syrups	Saponin	30% (w/w)	4	This study
●	Maltose	Gum Arabic	20% (w/w)	2	This study
◊	Maltodextrin–sucrose	–	0% (w/w)	4	b

3.5. Absolute shelf life values

The representation of Fig. 4 can be translated into absolute shelf life stability using the relationship expressed in Fig. 3 after a slight transformation.

The oxygen diffusion is measured at 35 °C, but a shelf life prediction at 25 °C will be more useful for stability under realistic industrial storage conditions. Again, extrapolating data measured at 3 different temperatures (Anandaraman & Reineccius, 1986; Subramaniam, 1984) generates a direct relationship between the oxygen diffusion coefficient estimated at 35 °C and the one predicted at 25 °C (see Fig. 5).

From the linear relationship expressed in Fig. 5, the diffusion coefficient at 25 °C can be estimated from the diffusion coefficient measured at 35 °C. Then, from the linear regression shown in Fig. 3, the shelf life at 25 °C or at any other temperature can be estimated.

It is useful to express absolute shelf life stability period as a function of M_n^{-1} at temperatures relevant for product storage or application. The resulting relationship for shelf life at 20 °C *vs* M_n (Fig. 6a) allows for the formulation of a carbohydrate matrix with the desired 'absolute' shelf life.

According to the Arrhenius dependence of shelf life and oxidation product generation, the shelf life data at 20 °C can be extrapolated to other temperatures. A simplification is to represent the diffusion coefficient as measured from the oxidation product formation at 35 °C against the extrapolated values obtained at another temperature from the Arrhenius dependency. The shelf life is decreased consistently by a factor of 1.6 if the temperature of storage is 25 °C rather than 20 °C, which leads to the representation in

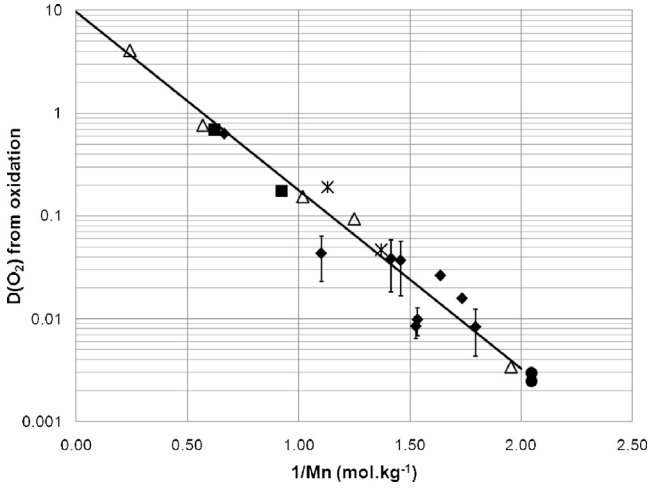

Fig. 4. Effect of number average molecular weight on the apparent diffusion coefficient of oxygen at 35 °C in spray dry powders loaded with various amounts of orange oil, and containing various amounts of sucrose, different DE maltodextrins and emulsifier quantity and nature. Refer to Table 1 for the legend.

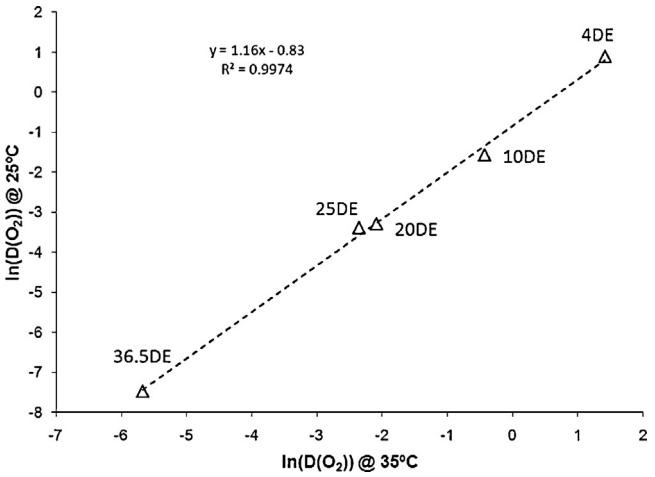

Fig. 5. Determination of the relationship between the estimated oxygen coefficients of diffusion at 2 different temperatures for the 5 matrices reported in Anandaraman and Reineccius (1986).

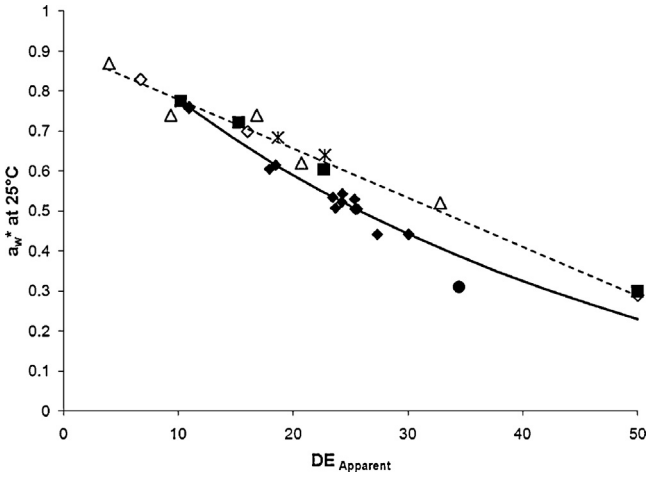

Fig. 7. Physical stability to humid air conditions at 25 °C for compositions corresponding to Table 1 and taken from the literature. Open diamonds are data from Sillick and Gregson (2010), dotted line is the extrapolation for maltose, solid curve is the calculation for a_w^* using the model in Sillick and Gregson (2010) for sucrose-containing formulations with a k parameter of 1.5.

Fig. 6b where the accelerated shelf life test at 35 °C is used to predict the shelf life upon storage at 20 °C.

Using the prediction in Fig. 6a, a 2 year shelf lifeshelf life at 20 °C can be achieved for glucose syrup carrier systems having a DE of 25–30.

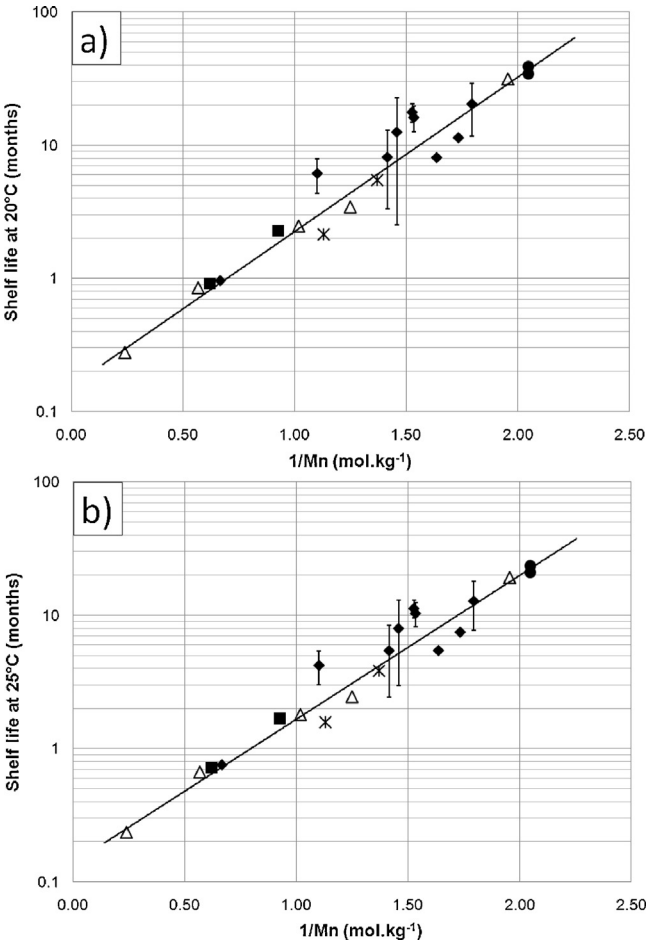

Fig. 6. (a) Shelf life stability at 20 °C and (b) at 25 °C for spray dry delivery systems produced using pure maltodextrins (open triangles), combination of maltodextrin and sucrose (diamonds), conventional carrier systems (squares), pure glucose syrups (asterisks) and maltose Gum Arabic (circles).

3.6. Consequence for improved stability to oxidation

A strong relationship between the molecular weight of the carrier and the stability to humid air conditions has been previously reported in literature using the experimental determination of the critical water activity (Sillick & Gregson, 2010). This reported study dealt with mixtures of various disaccharides and maltodextrins and critical water activity data was expressed as a function of disaccharides added to the maltodextrin. Representing the critical water activity data as a function of an apparent DE reveals a linear relationship over the entire range of apparent DE investigated. The apparent DE is in fact directly related to the degree of polymerization of the sugar residues (DE = 100/DP), or to the number average molecular weight (M_n = 162DP + 18) (Avaltroni et al., 2004). The term "apparent DE" is used, because "true DE" cannot be measured in mixtures of maltodextrins and sucrose using the standard copper(II) sulphate titration procedure, as sucrose does not possess any titratable reducing end. As reported, the slope of the relationship is dependent on the matrix composition. The a_w^* decreases rapidly if sucrose is added to the maltodextrin, whereas the mixture of maltodextrin and maltose shows a less dramatic effect, demonstrating an improved resistance to humid conditions. The apparent DE has the advantage of allowing selection of the best maltopolymer molecular weight distribution to achieve both an improved resistance to oxidation and an acceptable behaviour under humid conditions.

As shown in Fig. 7, 25DE corn syrup showed stability at 60.4% RH whereas a mixture of 10DE:sucrose 2:1 showed stability at 53% RH for a similar average molecular weight. It was shown in Fig. 6 that the sample made of maltose and Gum Arabic was most stable to oxidation. This sample was only physically stable in an exceptionally dry and cold environment. According to our measurements, the Gum Arabic-containing sample, even though it was used at 30% (w/w) in the matrix (70% (w/w) maltose), did not have improved physical stability compared to pure maltose. The presence of orange oil did not affect the moisture sorption properties of the carrier.

As a final remark, within the duration of the project (around 6 months) none of the samples prepared have shown caking when stored in conventional packaging at room temperature, except for the sample made of maltose and Gum Arabic (see Table 1). This sample formed aggregates in a period of less than 1 month. Also, samples made of the highest apparent DE have shown little to no

discolouration compared to the samples made of the lowest apparent DE, showing a visual improved resistance to oxidation.

4. Conclusions

A model has been developed for the prediction of shelf life of oxidation-sensitive spray-dried flavours. The M_n of the matrix was found to be the main factors affecting oxygen permeation, and thus, oxidative stability. The oxidative stability increased with increasing apparent DE, but led to a decreased resistance to humidity. Therefore, a compromise has to be found to produce an acceptable shelf-stable product.

A suitable surfactant (Q-Naturale™) has been selected that was efficient at very low concentrations and allowed for the matrix properties to be preserved and predictable. Citrus spray dry powders can be formulated using a simple combination of matrix ingredients without antioxidant to give a product with a predicted absolute shelf life of 2 years.

The approach described here can likely be extended to other carbohydrate based encapsulation systems with larger particle size. Especially, when combined with a model that can account for spatial variations in moisture and glass transition temperature (van Sleeuwen, Zhang, & Normand, 2012). This could lead to a practical prediction of the actual shelf life of an encapsulated flavour under realistic storage conditions.

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