

O3-2 Versatility of Maillard Products in the Formulation of Spray-dried Microcapsules containing Nutritional Ingredients

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INTRODUCTION

A major challenge in the functional food industry is to deliver health benefits to the consumer while maintaining, or improving the taste and aroma of the final food product. Incorporation of bioactive/nutritional ingredients into food products for enrichment is challenging as many bioactive components are not soluble in aqueous systems and exhibit limited stability against chemical or physical degradation once isolated from their natural source. These bioactive components also need to be bioavailable to exert their desired health benefit in the body. Encapsulation strategies may be used to address some of the issues relating to the incorporation of functional nutritional ingredients into foods. A limiting factor in the design and formulation of microcapsules intended for food applications is the limited availability of food grade encapsulants. All encapsulants used in formulations for food applications need to have generally regarded as safe (GRAS) status.

We have previously used Maillard reaction products formed in aqueous-based systems for encapsulation of omega-3 oils, delivered as spray-dried emulsions (Augustin et al. 2006). In this presentation, we examine the effects of order of processing, namely formation of Maillard complexes before or after emulsification, on oil microcapsule properties. We also provide examples of the use of Maillard reaction products for stabilisation and delivery of a fat-soluble vitamin (tocopherol). The versatility of protein-carbohydrate Maillard reaction products as encapsulants is further demonstrated in the application of these encapsulants for the delivery of probiotics.

MATERIALS AND METHODS

Preparation of microcapsules

Two basic methods of preparation of microcapsules were used (Augustin & Sanguansri 2001). In one method, the protein [Na caseinate (NaCas) or whey protein isolate (WPI)] and carbohydrate (CHO), chosen from a range including glucose (glc), dried glucose syrup (DGS) and a modified resistant starch (RS) (Augustin et al. 2005) were dispersed in water and heated prior to addition of oil or tocopherol dissolved in medium chain triglyceride oil, emulsified using a homogeniser (350/100 bar) and spray dried (Method 1, **Fig 1**). Alternatively, an oil-in-water emulsion stabilised by a protein-CHO mixture was heated and spray-dried (Method 2, **Fig 1**). For the encapsulation of probiotics, either an extensively hydrolysed casein-CHO mixture was heated, sunflower oil was added and the mixture homogenised or a hydrolysed whey protein-CHO-oil mixture was homogenised and heated, and these emulsion preparations were cooled to 20°C prior to addition of probiotic and spray-drying (Sanguansri et al. 2005).

Analyses of microcapsules

Analyses of oil microcapsules were based on methods previously used for assessment of microencapsulation efficiency and headspace propanal (Augustin et al. 2006) and lipolysis *in-vitro* in simulated gastric and intestinal fluids (Oliver et al. 2009). The extent of lipolysis during *in-vitro* digestion was quantified by GC. Tocopherol was extracted from the microcapsules and analysed using GC (AOAC 1989). The survival of LGG probiotics during storage were analysed by a standard plate count method after incubation in MRS (de Man, Rogosa and Sharpe) media (Crittenden et al 2006).

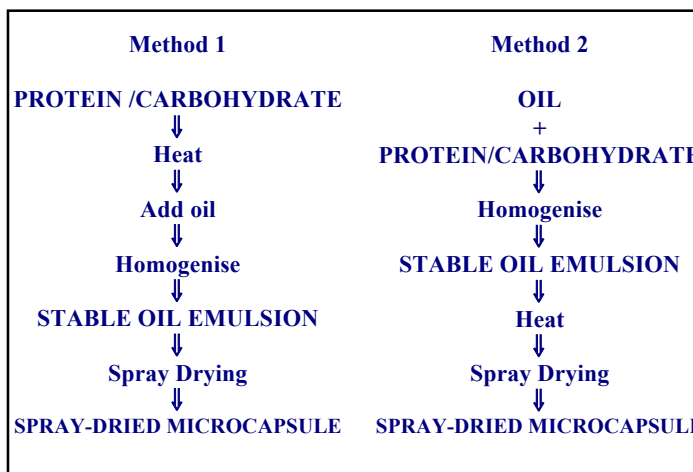


Figure 1. Basic process used for preparation of spray-dried oil microcapsules

RESULTS

Maillard Reaction Products for Oil Encapsulation – Effects of Order of Processing

When a different order of processing is used (Methods 1 or 2) for preparation of microcapsules with the same gross composition, there will be differences in the interfacial composition and structure. When an aqueous protein-CHO mixture is heated the surface active species that are capable of stabilising the interface are the intact protein, Maillard reaction products and proteins degraded by heat, and all these compete for the oil-water interface during homogenisation of the heated protein-CHO/oil dispersion (Method 1). Where the oil is added to the protein-CHO mixture prior to homogenisation, the interface will be stabilised by intact protein and on subsequent heating a different interface will be formed (Method 2).

Storage stability of fish oil microcapsules: **Fig. 2** shows that formation of the emulsion followed by heating (Method 2) is more effective for arresting oxidation than formation of Maillard complexes prior to emulsification (Method 1), despite the heat treatment applied to fish oil emulsion.

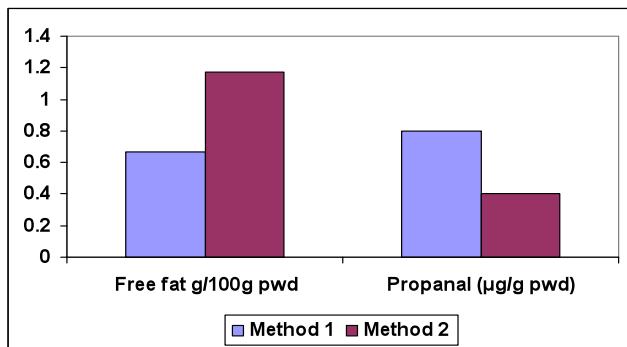


Figure 2. Properties of tuna oil powders (50% oil, 16.7% Na-Cas, 16.7% glc, 16.7% DGS) (Data from patent WO 01/74175 A1)

Lipolysis of canola oil microcapsules: Fig 3 shows that the resistance of canola oil microcapsules to lipolysis *in-vitro* is enhanced when microcapsules are prepared from heated emulsions (Method 2) compared to when they are prepared from heated protein-carbohydrate mixtures prior to emulsification (Method 1).

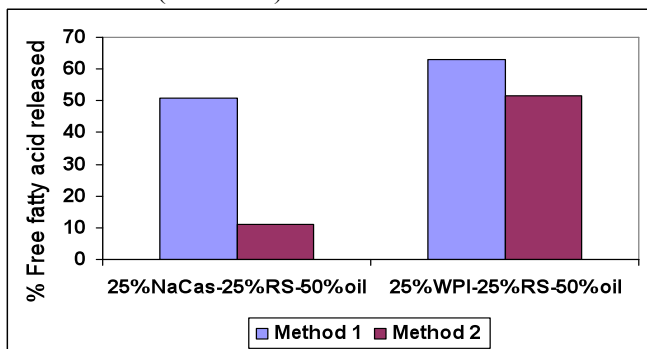


Figure 3. In-vitro lipolysis (% free fatty acid released) of canola oil powders (50% oil, 25% protein, 25% RS)

Interface effects on lipid oxidation and lipolysis degradation: The interface of oil globules in an emulsion is known to influence both oxidation and lipolysis (McClements & Decker, 2000; Chung et al., 2011). The reduced susceptibility of microcapsules to oxidation and lipolysis when Method 2 is used for preparation of oil microcapsules suggest that a more robust interface is formed when a homogenised emulsion is heated.

Maillard Reaction Products for Encapsulation of Oil Soluble Vitamin (Tocopherol)

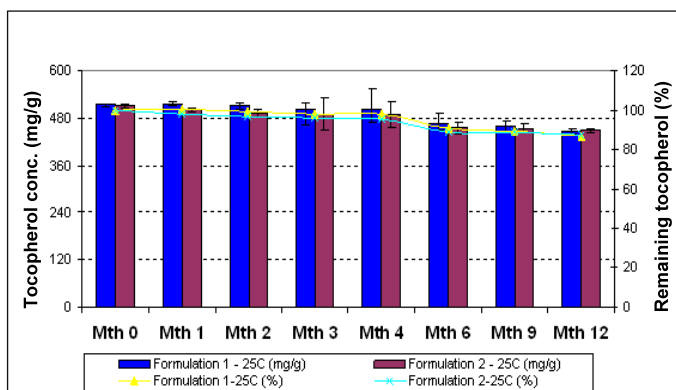


Figure 4. Stability of microencapsulated tocopherol (vacuum packed in aluminium foil bags) over 12 months storage at 25°C. Formulation 1 (50% tocopherol in oil: 16.7%NaCas: 16.7%glc: 16.7%DGS); Formulation 2 (50% tocopherol in oil, 16.7%NaCas, 16.7%glc, 16.7%RS)

Maillard complexes are effective for protecting tocopherol against degradation during storage (Fig 4). Less than 10% loss in activity is required for shelf stable commercial products during storage at 25°C (ICH-Q1A R2, 2003).

Maillard Reaction Products for Encapsulation of Probiotics

Maillard complexes are effective for protecting probiotics during storage at elevated temperature and humidity (Fig 5). There is greater protection afforded to probiotics (Lactobacillus rhamnosus, LGG) during storage at 40°C for 5 weeks when the encapsulant material contains heated hydrolysed protein-CHO mixtures compared to commercial freeze dried LGG. This is even though the microencapsulated LGG was exposed to an extra rehydration step and heat during the encapsulation process.

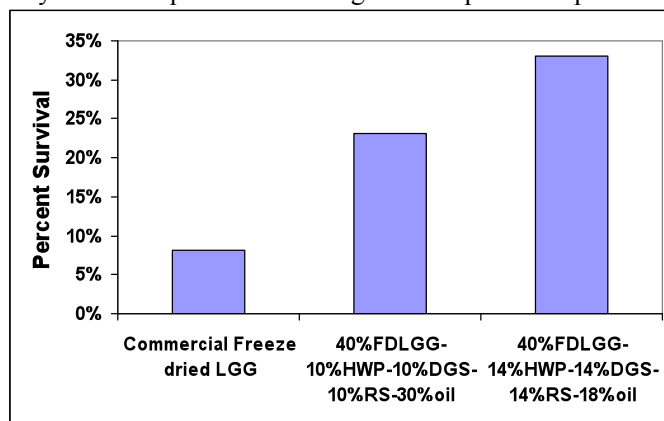


Figure 5. Survival of spray-dried probiotics (LGG) encapsulated with hydrolysed proteins after 5 weeks storage at 40°C, compared to commercial freeze dried LGG (FDLGG) which are stabilised by 45% sugars.

CONCLUSION

Maillard complexes are versatile encapsulants that are effective for protecting and delivering bioactives. Altering the protein-carbohydrate combination and order of processing allows manipulation of the properties of the microcapsules.

ACKNOWLEDGEMENTS

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REFERENCES

- AOAC 989.09 α -Tocopherol Acetate in Supplemental Vitamin E Concentrates, Gas Chromatographic Method (First Action 1989)
- Augustin MA & Sanguansri L (2001) WO 01/74175 A1
- Chung C, Sanguansri L and Augustin MA. (2011) Food Chem 124, 1480-1489
- Sanguansri, L., Augustin, M.A. and Crittenden, R. (2005) WO 2005/030229 A1
- ICH Q1A (R2) (2003) Stability Testing of New Drug Substances and Products
- Crittenden R, Weerakkody R, Sanguansri L, Augustin MA (2006) App Envi Microbiol 72 (3) 2280-2282.
- McClements, D.J.; Decker, E.A. (2000). J Food Sci, 65, 1270-1282.