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Isothermal study of nonenzymatic browning kinetics in spray-dried and freeze-dried systems at different relative vapor pressure environments

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Abstract

Nonenzymatic browning (NEB) in freeze-dried and spray-dried lactose, trehalose, and lactose/trehalose-based food model systems containing L-lysine and D-xylose (2% w/w) as reactants was investigated at four different relative vapor pressure (RVP) (33.2%, 44.1%, 54.5%, 65.6%) environments at room temperature. Sorption isotherms of model systems were determined gravimetrically and data were modelled using the Brunauer–Emmett–Teller (BET) and Guggenheim–Anderson–deBoer (GAB) models. Glass transition, T_g, was measured by DSC. Physical structure of model systems was observed by SEM. NEB was followed spectrophotometrically. Freeze-dried and spray-dried systems had different physical structures and sorption properties, but similar glass transition behavior. NEB kinetics seemed to be affected not only by the matrix composition but also by the physical properties of the materials obtained by different drying methods. Crystallization of the component sugars seemed to have direct relation to the NEB reaction. The results indicated that different physical properties of the materials by different drying methods should be considered in controlling the NEB reaction in real low-moisture food systems.

Keywords: Spray-drying; Freeze-drying; Nonenzymatic browning; Lactose; Trehalose

Industrial relevance: Nonenzymatic browning, as a model of a possibly diffusion-controlled binary reaction between amino acids and reducing sugars, produces flavours and colors but may also cause detrimental changes during processing and storage of foods. The objective of this study was to determine nonenzymatic browning kinetics and the effects of different drying methods on the nonenzymatic browning behaviour of food models. According to the study presented application of the results to real food systems should take into account differences in physical properties of dried, low-moisture, food systems.

1. Introduction

Drying is the most common method in production of stable food ingredients and food products. Amorphous materials can be produced from a solution by rapid cooling or removal of solvent water, e.g. by freeze-drying and spray-drying (Cohen & Yang, 1995; Roos, 1995a; White & Cakebread, 1966). Different drying methods produce amorphous materials with various physical properties, for example, particle size, structure, surface area, and porosity may differ (Aguilera, Chiralt, & Fito, 2003; Fäldt & Bergenståhl, 1996; Kim Suk & Bhowmik Santi, 1994; Kitabatake, Indo, & Doi, 1989; Lloyd, Chen, & Hargreaves, 1996; Saito, 1985) and their thermal behaviour (Kim Suk & Bhowmik Santi, 1994; Miao & Roos, 2004b) may also differ. Freeze-dried amorphous materials exhibit higher porosity while the materials obtained by spray-drying more easily shrink to form dense particles. Consequently, the functional properties of the materials might also be affected (Chinprahast, Jantawat, & Kristavee, 1995; Otegui et al., 1997). The physical state of an amorphous matrix greatly influences stability and affects rates of both physical and chemical changes during processing and storage (Buera & Karel, 1995; Champion, Le Meste, & Simatos, 2000; Eichner, 1981; Karmas, Buera, & Karel, 1992; Kim, Saltmarch, & Labuza, 1981; Roos, Karel, & Kokini, 1996; Roudaut, Simatos, Champion, Contreras-Lopez, & Le Meste, 2004; Slade & Levine, 1991).

Nonenzymatic browning, as a model of a possibly diffusion-controlled binary reaction (Buera & Karel, 1995) between an amino acid and a reducing sugar, is a very important chemical reaction in foods. It produces flavors and colours, but it may also cause detrimental quality changes during processing and

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storage (Labuza & Baisier, 1992; van Boekel, 2001). Therefore, the control of the reaction has been given much attention. Many researches have carried out studies of relationships between reaction rates and the physical state aiming at relating the glass transition using different model systems with observed reaction rates (Bell, 1996; Bell, White, & Chen, 1998; Karmas et al., 1992; Karmas & Karel, 1994; Lievonen, Laaksonen, & Roos, 1998; Lievonen & Roos, 2002a; Miao & Roos, 2004a, 2005a; Schebor, Buera, Karel, & Chirife, 1999; Roos & Himberg, 1994). Karmas et al. (1992) related glass transition temperature with nonenzymatic browning kinetics and Karmas and Karel (1994) suggested that NEB was affected by water activity, glass transition, and crystallization of the matrix, while Buera and Karel (1995) showed that NEB was also influenced by collapse. Bell (1996) distinguished the effects of water activity and the glass transition on the NEB kinetics. NEB was also found to be affected by structural properties of the matrix materials, such as porosity (White & Bell, 1999) and density (Burin, Jouppila, Roos, Kansikas, & Buera, 2000). Recent work by Miao and Roos (2005a) revealed that NEB was related to matrix composition and crystallization of component sugars. In the previous studies, NEB reaction rate was clearly demonstrated to be affected by water content, water activity, temperature, pH, and concentration and the type of reactants. It was also found that coinciding with the glass transition, physical changes of the matrix materials affected the NEB rate. It should be noted that most of the previous studies of NEB kinetics used freeze-dried model systems, but most dairy powders, which often undergo browning, are produced by spray-drying. To evaluate the NEB kinetics in real food systems, we presumed that there may be differences in the NEB kinetics between freeze-dried and spray-dried model systems because of their different physical properties.

Our previous study (Miao & Roos, 2004b) compared the nonenzymatic browning kinetics in spray-dried and freeze-dried food model systems at different temperatures applicable to spray-drying. Results indicated that NEB activation energies were different in freeze-dried and spray-dried systems and NEB kinetics seemed to be affected in different matrix by different drying methods. The objective of the present study was to determine nonenzymatic browning kinetics in freeze-dried and spray-dried lactose, trehalose, and lactose/trehalose matrices at isothermal conditions and to observe effects of glass transition and storage RVP on NEB kinetics. Furthermore, effects of different drying methods and physical changes of materials on the nonenzymatic browning behaviour were evaluated.

2. Materials and methods

2.1. Preparation of model systems

2.1.1. Materials

Three amorphous food model systems were prepared. The models consisted of lactose (Sigma Chemical Co., St. Louis, Mo., U.S.A), D-(+)-trehalose (British sugar company, UK), and lactose/trehalose (1 : 1) as matrix materials, and they contained L-lysine (Sigma Chemical Co., St. Louis, Mo., U.S.A) and D-xylose (Sigma Chemical Co., St. Louis, Mo., U.S.A) as nonenzymatic browning reactants, because of their high reactivity (Karmas et al., 1992). According to the results of previous studies (Lievonen & Roos, 2002b; Miao & Roos, 2004a) and pre-experiments carried out in the present study, the exact amounts of the reactants, 1 : 1, were adjusted to 2% (w/w) of the total solids. P_2O_5 was used as a desiccant and LiCl, CH_3COOK, $MgCl_2$, $Mg(NO_3)_2$, $NaNO_2$, and NaCl were used to prepare saturated salt solutions with different RVPs. All chemicals were purchased from Sigma Chemical Co. (St. Louis, Mo., U.S.A).

2.1.2. Spray-drying

Three aqueous 20% (w/w solids) clear solutions were prepared from the matrix materials, the reactants, and distilled water. The solution was spray-dried using a Niro Atomizer spray-drier (Niro Production Minor with centrifugal rotary atomisation, Single stage dryer, Copenhagen, Denmark) with an inlet temperature of 170–175 °C and outlet temperature of 70–75 °C. Two particle sizes of spray-dried powders were collected through two different outlets of the drier. Particle sizes, measured using a microscope (Leica, Wild MPS46/52, Heerbrugg, Switzerland) were (1) fine powder, size 7–16 μm (from outlet of cyclone), and (2) coarse powder, size 16–28 μm (from outlet of drying chamber). Coarse powder was used for the kinetics study. Spray-dried materials were immediately cooled down to room temperature and kept in vacuum desiccators over P_2O_5 at room temperature for at least 10 days, and every second day the P_2O_5 was changed to dry the powders. Samples were further dried in a vacuum oven at 25 °C for 24 h before experiments.

2.1.3. Freeze-drying

Three 20% (w/w solids) clear solutions were prepared from the matrix materials, the reactants, and distilled water. Solutions in 20–22 ml aliquots were frozen on Petri dishes immediately after preparation (24 h at -20 °C, followed by 24 h at -80 °C) and freeze-dried (>48 h, $p<0.1$ mbar) (Lyovac GT 2; Amsco Finn-Aqua GmbH, Hürth, Germany) to produce a completely amorphous glassy state of the food model (Roos & Karel, 1991). The freeze-dried materials were ground using a mortar and pestle immediately after freeze-drying and stored subsequently in evacuated desiccators over P_2O_5.

2.2. Water sorption

Sorption isotherms for the six food models were determined gravimetrically. Triplicate samples of about 0.5 g of the freeze-dried and spray-dried food models, prepared in 20-ml glass vials, were stored in a vacuum desiccator over P_2O_5 for at least one week. After storage the samples were considered "anhydrous" (Lievonen et al., 1998). The dehydrated triplicate samples were subsequently kept at 22–23 °C over saturated solutions of LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$, and NaCl with RVP of 11.4%, 23.1%, 33.2%, 44.1%, 54.5%, 65.6%, and 76.1% respectively, giving a water activity, a_w of 0.01× RVP at equilibrium (Greenspan, 1977; Labuza, Kaanane, & Chen,