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ORIGINAL PAPER

Impact of the spray drying conditions and residence time distribution on lysine loss in spray dried infant formula

Iris Schmitz-Schug · Petra Foerst · Ulrich Kulozik

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Abstract The essential amino acid lysine plays an important role for the nutritional quality of infant formula. Unfortunately, it is easily damaged during spray drying which is usually used to produce infant formula powders. In this study, we showed that the extent of lysine loss can be controlled by adjusting the air inlet temperature and the air-to-liquid ratio. Depending on the spray drying conditions, 10.4±2.9% lysine loss down to no lysine loss was determined after spray drying in laboratory scale and in pilot scale. A main impact on lysine loss could be attributed to the particle residence time which was shown to be longer for the short-form, pilot-scale spray dryer than for the tall-form, laboratory-scale spray dryer. Median particle residence time was 6 s in the laboratory scale dryer and 17 s in the pilot scale dryer. The air-to-liquid ratio of the spray dryer proved to be a good parameter to compare different types of spray dryers. The extent of lysine loss during storage of the spray dried powders was independent of the extent of lysine loss during spray drying. Lysine loss during storage can be reduced by low storage temperatures and low water contents of the powder. Coupling kinetics of lysine loss that take into account the physical state of lactose, i.e., glassy, rubbery, or crystalline, with the processing conditions and particle residence time during spray drying was shown to be a promising tool to improve the nutritional quality of spray dried infant formula.

Keywords Spray drying · Residence time distribution · Scale-up · Infant formula · Available lysine · Nutritional quality

1 Introduction

For the production of high-quality milk products, it is important that sensitive ingredients are not damaged during processing. Infant formula belongs to the class

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of products which requires a very good quality and availability of the nutrients contained in it because it is often the only nutrient source for infants. Consequently, it must be guaranteed that infant formula contains, in sufficient quantity, all nutrients that are necessary for a healthy growth. The essential amino acid lysine is one of the decisive nutrients that determine the nutritive value of infant formula. Lysine is only available for the human metabolism if its ε-amino group is free (Meade et al. 2005; Moughan and Rutherfurd 2008; van Boekel 1998). Lysine loss in infant formula is mainly caused by the early Maillard reaction between the ε-amino group of lysine and lactose. Advanced Maillard reaction, formation of isopeptides or lysinoalanine, and reactions with oxidized phenols can also lead to lysine loss.

Cow's-milk-based powdered infant formula is usually produced by reconstituting and mixing the ingredients followed by a thermal treatment for microbial safety and an evaporation step to increase the concentration before finally spray drying the concentrate. Spray drying was identified to be the critical production step concerning lysine loss in infant formula (Ferrer et al. 2000; Finot 1983). This can be explained by the fact that the rate of lysine loss is higher in the dry state than in the liquid state with a maximum at low or intermediate water activities (a_w=0.2–0.5) depending on the experimental conditions (Malec et al. 2002; Morgan et al. 1999; Schmitz et al. 2011b). Thus, the extent of lysine loss during spray drying is influenced by drying kinetics and particle flow inside the spray dryer. These two factors determine the temperature–concentration–time–history of a particle and, consequently, the extent of lysine loss.

Several authors have studied drying kinetics and how they can be applied to spray drying. Usually, drying kinetics models are integrated in computational fluid dynamics (CFD) simulations in order to characterize the spray drying behavior of various products (Patel and Chen 2005; Woo et al. 2008). Accurate experimental data to fit the model parameters is necessary to predict the drying kinetics, e.g., in a CFD simulation.

Apart from drying kinetics, residence time is an important factor with regard to product quality. On the one hand, particle residence time has to be long enough to ensure dehydration to the desired residual water content. On the other hand, long residence times lead to longer exposure times to high temperature when the particles are already in dry state. This can result not only in the loss of lysine but also in denaturation of proteins, for example. Gianfrancesco (2009) measured median particle residence times of 2–3 min in a pilot-scale spray dryer equipped with a rotary atomizer. Kieviet and Kerkhof (1995) obtained a median residence time of τ_{50}=58.5 s for a co-current pilot-scale spray dryer with a pressure nozzle. Jeantet et al. (2008) determined mean particle residence times of 9–12 min for a pilot-scale spray dryer with a pressure nozzle as atomization device, a fines return system, and an internal fluid bed. These results show on the one hand that there is a wide range of residence times according to the dryer configuration and on the other hand that particle residence times can be quite long during spray drying.

Despite the principle awareness that sensitive compounds can be damaged during spray drying, there are only few studies that investigate the spray drying process with the aim of reducing the damage of sensitive food, pharmaceutical, or biological products. For this class of products, the drying process not only has to fulfill the

basic requirement to obtain a dry powder but also to preserve sensitive compounds. Menshutina et al. (2010) studied spray drying of probiotics and showed that the drying process can be optimized with regard to microorganism inactivation by taking into account the drying kinetics together with the inactivation kinetics. Similarly, Mestry et al. (2011) employed the response surface methodology to improve the nutritional quality of a fermented juice of carrot and watermelon powders. In addition, a good knowledge and control of the spray drying process makes it possible to combine two processing steps in one. Reinhold et al. (2001) showed that a targeted conversion of ingredients during spray drying is possible if the reaction is faster than drying.

The aim of this study therefore is to characterize the spray drying process of model infant formula in a first step and to correlate the process characteristics with the extent of lysine loss in a second step. Model infant formula was spray dried in laboratory scale and in pilot scale with the air-to-liquid ratio as scale-up parameter. Powder characteristics and lysine loss were determined as a function of the spray drying conditions. Additionally, particle residence time distribution was measured for laboratory scale as well as for pilot scale. Lysine loss during storage of the spray dried powders was included in the investigations. Thus, a comprehensive and differentiated analysis of the spray drying process is obtained, and it can be optimized with regard to the nutritional quality, i.e., the availability of lysine.

2 Materials and methods

2.1 Preparation of the model infant formula

In this study, an infant formula model system with a protein/lactose ratio of 1:5 and a whey protein/casein ratio of 60:40 was used. The composition of the model infant formula is based on the typical composition of commercial infant formulas except the lipid phase which was excluded to avoid difficulties in handling and masking of effects in the water phase. The dry matter is composed of skim milk powder (22.2%), whey protein isolate (8.4%), lactose (68.3%), potassium citrate (1.0%), and disodium phosphate (0.1%). Before spray drying, the dry matter was reconstituted in deionized water to a concentration of 20% dry matter which is the upper limit of solubility at room temperature.

2.2 Spray drying in laboratory and pilot scale

The model infant formula was spray dried in laboratory scale as well as in pilot scale. The laboratory scale spray dryer (B-290; BÜCHI Labortechnik AG, Flawil, Switzerland) was a tall-form co-current spray dryer equipped with a two-fluid nozzle working with compressed air. Air inlet temperature (T_{in}) was set at 152–208 °C and product mass flow rate at 0.8–1.3 $kg.h^{-1}$. The temperature of the concentrate before spray drying was kept constant at 30 °C. The air volume flow rate was 35 $m^3.h^{-1}$. The dried powders were recuperated and analyzed as described in the following.

Spray drying in pilot scale was performed in a short-form co-current spray dryer (PRODUCTION MINOR™; GEA Niro, Søborg, Denmark) with a two-fluid nozzle

that works with compressed air as atomizing device. Air inlet temperatures were in the range of 160–200 °C, the air volume flow rate was 411 $m^3.h^{-1}$, and product mass flow rates were in the range of 11.0–18.7 $kg.h^{-1}$. The produced powders were analyzed in the same way as the samples of laboratory-scale spray drying.

Scale-up from laboratory scale to pilot scale was done by maintaining the air-to-liquid ratio of the nozzle (ALR_{nozzle}). The air inlet temperatures in pilot scale were in the same range as in laboratory scale. Additionally, the air-to-liquid ratio of both spray dryers (ALR_{dryer}) was calculated according to Eq. 1 where $\dot{m}_{air}$ is the air mass flow rate and $\dot{m}_{water}$ is the mass flow rate of water contained in the concentrate.

$$ALR_{dryer} = \frac{\dot{m}_{air}}{\dot{m}_{water}} \tag{1}$$

By using the air-to-liquid ratio of the dryer (ALR_{dryer}), it becomes possible to compare the process characteristics of spray drying in pilot scale and in laboratory despite the differences in geometry and consequently in the air flow pattern. In laboratory scale, ALR_{dryer} of 36–118 were used whereas in pilot scale ALR_{dryer} were in the range of 25–47. The different ALR_{dryer} ranges are due to the different geometries of the dryers and to the different drying efficiencies.

2.3 Water content and water activity

Karl-Fischer Titration (Karl-Fischer Titrator; Titro Line KF, Schott, Mainz, Germany) was used to measure the water content *X*. Analyses were carried out at 40 °C in a 1:1 mixture of Hydranal®–Formamid dry and Hydranal®–Methanol Rapid (Sigma-Aldrich, Steinheim, Germany). Samples were stirred for 5 min to equilibrate the system and then titration was done with Hydranal®–Composite 5 (Sigma-Aldrich). The titrator was calibrated with Hydranal®–Water Standard (Sigma-Aldrich). Analyses were carried out in triplicate.

The water activity was determined at 25 °C using a Novasina Sprint (Novasina AG, Lachen, Switzerland). The measurements were carried out in triplicate.

2.4 Determination of available lysine

Available lysine was measured using the *o*-phthaldialdeyhde method described by Ferrer et al. (2003). At alkaline conditions and in the presence of β-mercaptoethanol, *o*-phthaldialdehyde (OPA) reacts with free amino groups, e.g., the ε-amino group of lysine and a fluorescent isoindole is formed. The detected fluorescence intensity is directly related to the amount of free amino groups, i.e., available lysine.

Powder samples were reconstituted at 10% dry matter in deionized water and a 50-μL aliquot was mixed with 950 μL water and 1 mL 12% sodium dodecyl sulfate (SDS; Serva, Heidelberg, Germany) solution. After storage at 4 °C overnight, the samples were sonicated at 25 °C for 15 min in an ultrasonic bath (Sonorex Super RK 100H; Bandelin, Berlin, Germany). The OPA reagent was prepared daily out of 80 mg OPA (OPA; Merck Darmstadt, Germany), 2 mL ethanol (Merck Darmstadt, Germany), 0.2 mL β-mercaptoethanol

(Merck), 5 mL 20% SDS solution, and 50 mL 0.1 M sodium tetraborate (Sigma-Aldrich) buffer (pH 9.7–10), and diluted to 100 mL with water. To start the fluorescence reaction, 150 μL of the OPA reagent was added to 5 μL of the pretreated sample in a 96-well black microtiter plate (Greiner Bio-One, Frickenhausen, Germany). Fluorescence was measured at $\lambda_{excitation}$=340 nm and $\lambda_{emission}$=455 nm in a microtiter plate reader (Genios Plus; Tecan, Crailsheim, Germany). Possible interferences from small peptides, free amino acids, and amines were measured after precipitation of 2 mL reconstituted sample with 2 mL of 10% trichloroacetic acid (TCA; Scharlau, Barcelona, Spain) and centrifugation at 3,000 rpm for 15 min. Analyses were carried out in triplicate.

2.5 Particle residence time distribution

Particle residence time distribution was determined for both spray dryers at the spray drying conditions described above. Sodium chloride NaCl (neoLab, Heidelberg, Germany) at a concentration of 0.1 mol.L^{-1} and Cochineal Red A (E124; Brauns-Heitmann, Warburg, Germany) at a concentration of 0.125 mg.g^{-1} were added as markers to the model infant formula that was prepared as described above. Step marking was realized by switching the product supply from standard model infant formula to model infant formula supplemented with the markers. Samples were collected at the bottom of the cyclone in regular time steps. Time was set to zero when the product reached the atomizer. In laboratory scale, sampling time was 5 s, 10 s, 20 s, 30 s, 40 s, 50 s, 60 s, 70 s, 80 s, 120 s, 160 s, and 220 s. In pilot scale, samples were taken after 20 s, 40 s, 60 s, 2 min, 4 min, 7 min, 15 min, 20 min, 30 min, and 40 min. Samples were reconstituted in deionized water for further analyses. NaCl concentration was determined with a flame photometer (ELEX 6361; Eppendorf, Hamburg, Germany). The color was measured with a spectrophotometer (SP68; X-Rite, Köln, Germany). The CIE $L^*a^*b^*$ color system with the coordinate lightness L^*, red/green value a^*, and yellow/blue value b^* was used to express the samples' color. The color saturation index C^* (chroma) can be calculated according to Eq. 2:

$$C* = \sqrt{a*^2 + b*^2} \tag{2}$$

The NaCl concentration and the color saturation index C^* at the different time steps were used to calculate the particle residence time distribution. In order to obtain the non-dimensional cumulative residence time distribution $F(t)$, the tracer concentration $C(t)$ at time t was normalized with C_0 being the concentration in the model infant formula without added tracer and C_∞ the concentration in the model infant formula supplemented with the tracer:

$$F(t) = \frac{C(t) - C_0}{C_\infty - C_0} \tag{3}$$

Particle residence time distributions were characterized by the median residence time τ_{50} and the 10% and 90% percentiles τ_{10} and τ_{90}, respectively. To compare the particle residence time with the air residence time, the mean residence time of the

particles $\bar{t}$ was calculated according to Eq. 4 where $\bar{t}_i$ denotes the mean time of interval i and ΔC_i the concentration difference in interval i:

$$\bar{t} = \sum_{i=1}^{n} \bar{t}_i \cdot \Delta C_i \tag{4}$$

The mean residence time of the air $\bar{t}_{\text{air}}$ was estimated assuming plug flow inside the spray dryer based on the volume of the spray dryer V_{dryer} and the air volume flow rate $\dot{V}_{\text{air}}$:

$$\bar{t}_{\text{air}} = \frac{V_{\text{dryer}}}{\dot{V}_{\text{air}}} \tag{5}$$

2.6 Sorption isotherm

The sorption isotherm was obtained by storing freeze-dried samples over saturated salt solutions [P_2O_5 (0% RH), LiBr (6.4% RH), NaOH (8.2% RH), LiCl (11% RH), CH_3COOK (23% RH), $MgCl_2$ (33% RH), K_2CO_3 (43% RH), $MgNO_3$ (53% RH), NaBr (58% RH), KJ (69% RH), NaCl (75% RH), KCl (84% RH), and K_2SO_4 (97% RH)] at 25 °C to adjust water activity to 0, 0.064, 0.082, 0.11, 0.23, 0.33, 0.43, 0.53, 0.58, 0.69, 0.75, 0.84, and 0.97, respectively (Greenspan 1977). The samples were weighed regularly until equilibrium was attained. The water content was deduced from difference in weight. Samples with a water activity of 0.53 and above crystallized during adjustment of the water activity which could be observed by a weight loss and which leads to a step in the sorption isotherm. The sorption isotherm was fitted with the Guggenheim–Anderson–de Boer (GAB) model where X denotes the water content, X_m the monolayer water content, a_w the water activity, and K' and C constants (van den Berg and Bruin 1981):

$$\frac{X}{X_m} = \frac{K' \cdot C \cdot a_w}{(1 - C \cdot a_w) \cdot (1 + (K' - 1) \cdot C \cdot a_w)} \tag{6}$$

2.7 Statistical analysis

For spray drying in laboratory scale, a 2^2 central composite factorial experimental design was drawn up with eight center points in total so that a rotatable and orthogonal design is obtained. The experiments were run in six blocks, three blocks for the square which included five center points each and three blocks for the star which included three center points each, and the order of the experiments was randomized. Three replicates of each factor combination were run. Response surfaces were built with the results.

Similarly, a 2^2 central factorial experimental design was chosen for pilot-scale drying. Three replicates were run in three blocks with one center point each, and response surfaces were established.

All experiments and analyses were run in triplicate. Mean values ±95% confidence levels are reported. The Student t test was applied to estimate differences between mean values at a confidence level of 95%.

3 Results

3.1 Impact of the spray drying conditions on the powder characteristics

The model infant formula was spray dried in laboratory scale as well as in pilot scale. In laboratory scale, air inlet temperatures of 160–200 °C led to air outlet temperatures of 49.5±8.1 °C to 106.7±12.7 °C (Fig. 1). Air outlet temperature increased with increasing air inlet temperature and decreasing product mass flow rate. The temperature profile inside the spray dryer is an important factor regarding the quality of thermally sensitive products. The air temperature determines together with the drying kinetics the temperature of the product to be dried (Gianfrancesco 2009; Mezhericher et al. 2010). At the beginning of the drying process, as long as the water activity at the droplet surface stays close to a_w=1, the product temperature equates to the wet bulb temperature. This corresponds to the first drying stage or constant rate drying. Once the critical moisture content is attained, humidity cannot anymore be transported as fast from the droplet center to the surface as evaporation takes place at the droplet surface. During this second drying stage, the drying rate is not constant but falling, the water activity decreases, and the product temperature starts to rise. The product temperature is limited by the air temperature, i.e., a droplet or particle can maximally reach air temperature. Thus, the product temperature is determined by the drying kinetics, the air temperature profile, and the particle residence time.

The water content of the powders that were produced in laboratory scale was between 9.9±1.1% wb and 3.7±0.6% wb (Fig. 2), corresponding to water activities of 0.85±0.04 to 0.10±0.01. Water content increased with increasing product mass flow rate and decreasing air inlet temperature. Spray drying conditions that led to high residual water contents in the powder were also characterized by low air outlet

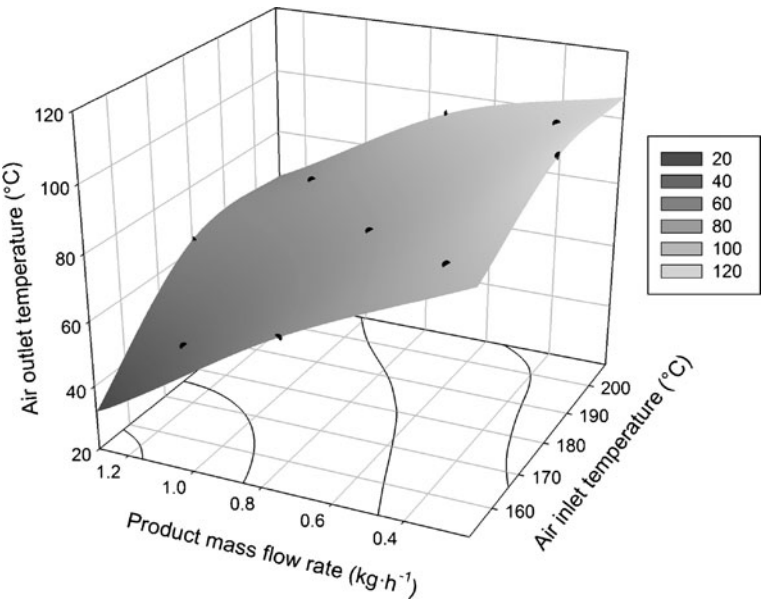

Fig. 1 Air outlet temperature depending on the drying conditions in laboratory scale

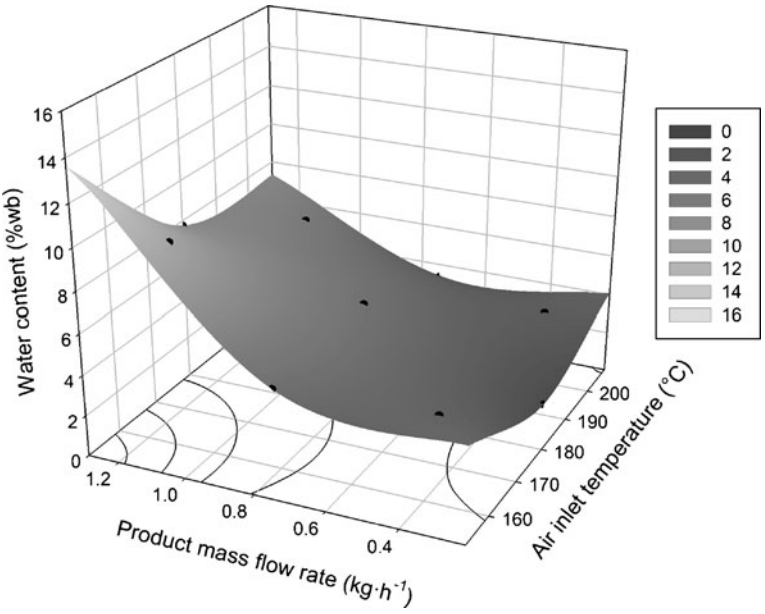

Fig. 2 Water content of the spray dried powders produced in laboratory scale

temperatures. These findings are in accordance with results for whole milk powder reported by Birchal et al. (2005). At a water content of 9.9±1.1% wb (a_w=0.85± 0.04), drying was not completed and the powder was still humid. Moreover, in this case lactose was in the crystalline state contrary to the other spray drying conditions that led to amorphous powders as shown in Fig. 3 and explained below. In Fig. 3, the sorption isotherm of the model infant formula at 25 °C is plotted with the

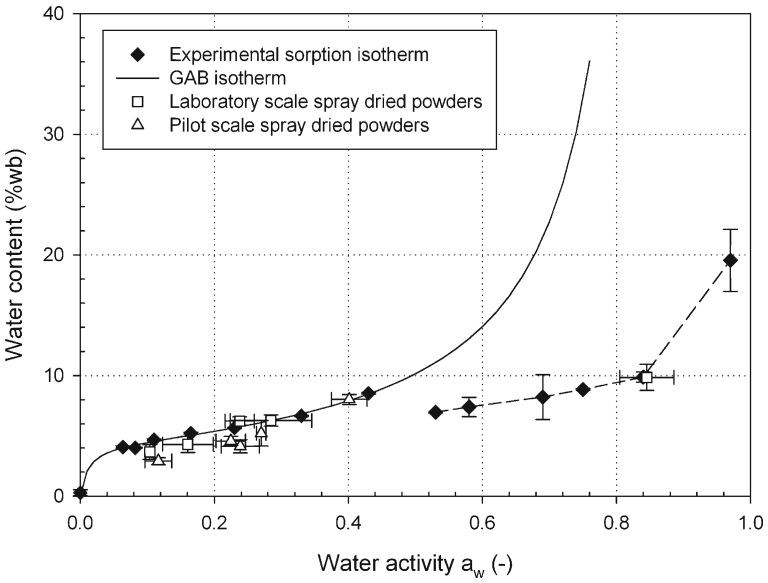

Fig. 3 Sorption isotherm of the model infant formula in comparison with the spray dried powders

experimental values of Schmitz et al. (2011b). Two different parts can be distinguished: at a water activity of 0.43 and below, the lactose of the model infant formula is in the amorphous state. Between a water activity of 0.43 and 0.53, a rupture in the sorption isotherm can be observed that corresponds to the crystallization of lactose. At a water activity of 0.53 and above, lactose is in the crystalline state at 25 °C. The amorphous part of the sorption isotherm was fitted with the GAB isotherm (van den Berg and Bruin 1981).

Pilot-scale spray drying gave similar results. The air outlet temperature was between 60.1±4.1 °C and 105.7±4.0 °C (Fig. 4). The measured water contents of the produced powders were between 8.0±0.4% wb and 2.9±0.3% wb, and the corresponding water activities between 0.40±0.03 and 0.12±0.02 (Fig. 5). Comparison of the powder characteristics with the sorption isotherm shows a good analogy (Fig. 3). In pilot scale, no humid samples were obtained and samples were in the amorphous state. However, the drying condition that led to a powder with a water content of 8.0±0.4% wb represents the upper limit of drying capacity, and the process is unstable. In the pilot-scale spray dryer, it was possible to measure the humidity of the outlet air. In Fig. 6, the relative humidity of the outlet air is correlated with the water activity of the spray dried powders. At all conditions, the water activity of the powder is only slightly higher than the relative humidity of the outlet air. Consequently, the particles are almost in equilibrium with the drying air at the spray dryer outlet. The importance of the relative humidity of the outlet air was elaborated by Schuck et al. (2008). They demonstrated that it was necessary to control the relative humidity of outlet air to regulate the water activity and moisture content of dairy powders. Similarly, Ozmen and Langrish (2003) concluded that dried powder particles were almost in equilibrium with the drying gas during spray drying of skim milk in pilot scale.

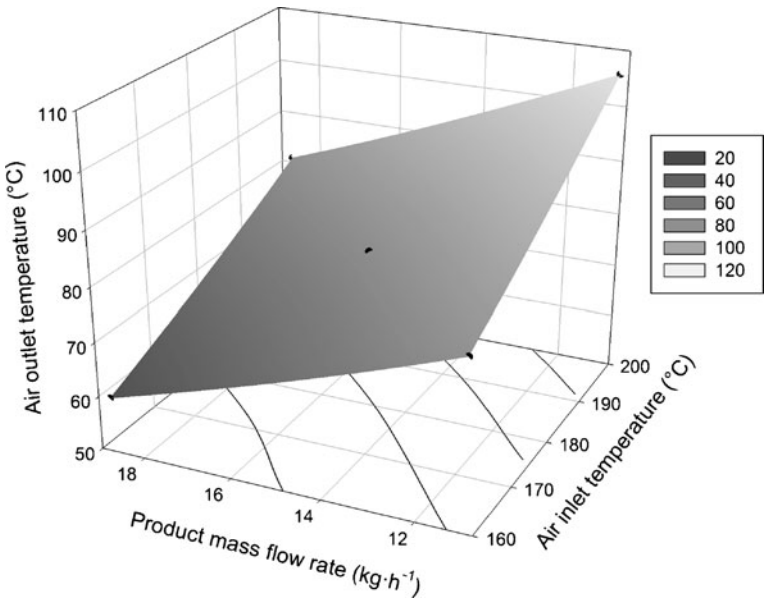

Fig. 4 Air outlet temperature as a function of the spray drying conditions in pilot scale

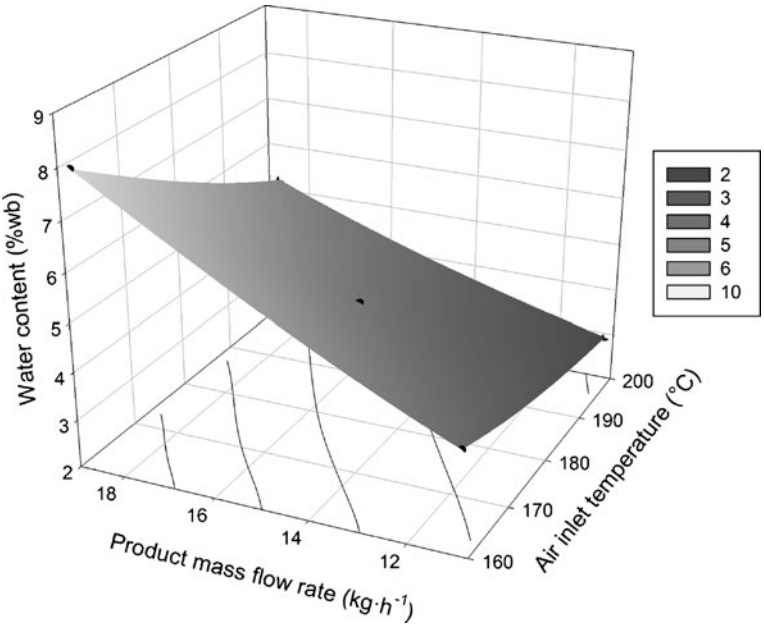

Fig. 5 Water content of the powders that were spray dried in pilot scale

3.2 Particle residence time distribution

Particle residence time distribution is an important parameter of the spray drying process. On the one hand, particle residence time has to be long enough to ensure drying of the particles. On the other hand, long residence times can lead to the

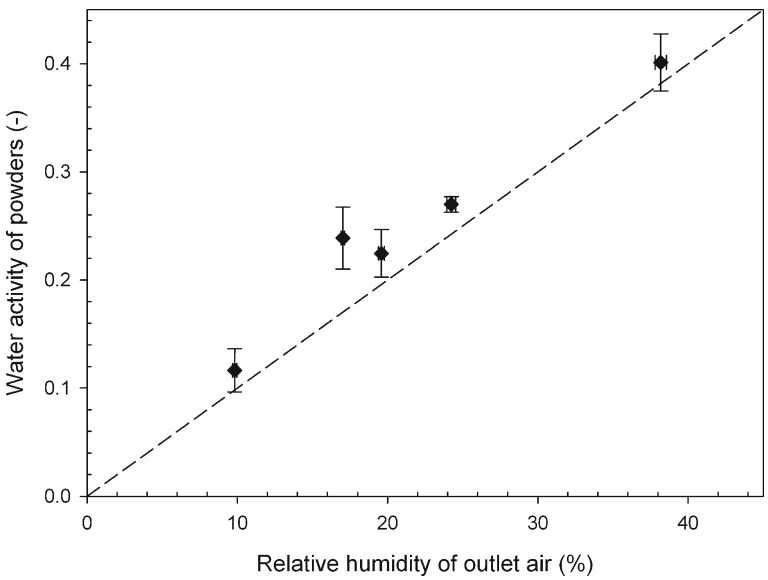

Fig. 6 Relation between the water activity of the spray dried powders and the relative humidity of outlet air in pilot-scale drying

deterioration of sensitive products. As explained in the previous paragraph, particle temperature rises when the particle concentration increases. Consequently, longer residence times result in longer times at high concentration and high temperature which is harmful to thermally sensitive ingredients, as for example lysine. In order to assess the differences between laboratory-scale spray drying and pilot-scale spray drying, particle residence time distribution was measured in the range of the experimental conditions.

The particle residence time distribution of the laboratory-scale spray dryer (Fig. 7) is characterized by a median residence time τ_{50} of 6 s as well as by τ_{10} and τ_{90} values of 0.2 s and 55 s, respectively. In contrast, longer particle residence times were measured in the pilot-scale dryer (Fig. 8). Here, a median particle residence time τ_{50} of 17 s was obtained, the τ_{10} and τ_{90} values being 4 s and 1 min 22 s, respectively. The last particles left the dryer after about 6 min. These long particle residence times indicate recirculation flows inside the drying chamber and possible wall deposition of particles. This hypothesis is confirmed by the comparison of the mean residence time of air with the mean residence time of particles. Assuming plug flow inside the spray dryer, the mean residence time of the air can be estimated by dividing the volume of the spray dryer by the air volume flow rate. Using this approach, the calculated mean residence time of air is 1.1 s for the laboratory-scale spray dryer and 12 s for the pilot-scale dryer. In contrast to that, the mean particle residence times are 24.8 s for the laboratory-scale dryer and 90.2 s for the pilot-scale spray dryer, respectively. Consequently, the particle mean residence time is longer than the mean residence time of air. This divergence can be explained by the presence of recirculation zones and powder backflow inside the drying chamber as well as by temporary particle deposition on the dryer walls.

In conclusion, particle residence time distribution in the laboratory-scale dryer differs significantly from particle residence time distribution in the

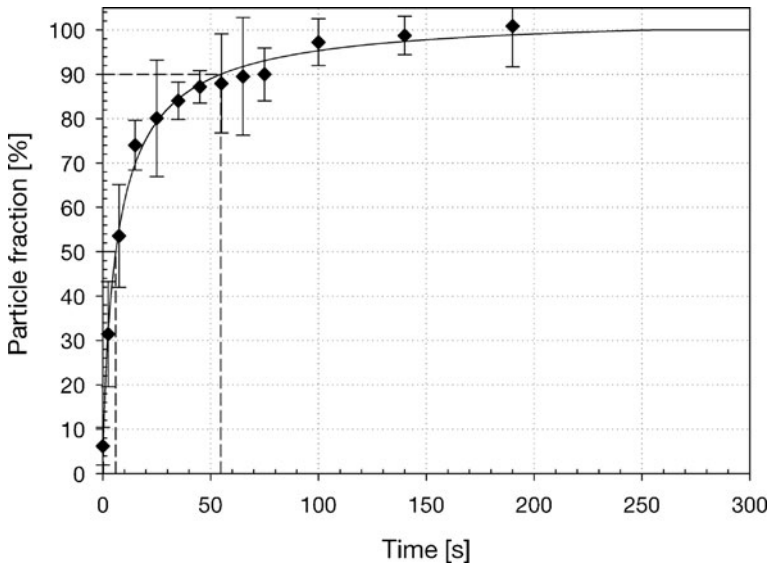

Fig. 7 Particle residence time distribution of the laboratory-scale spray dryer

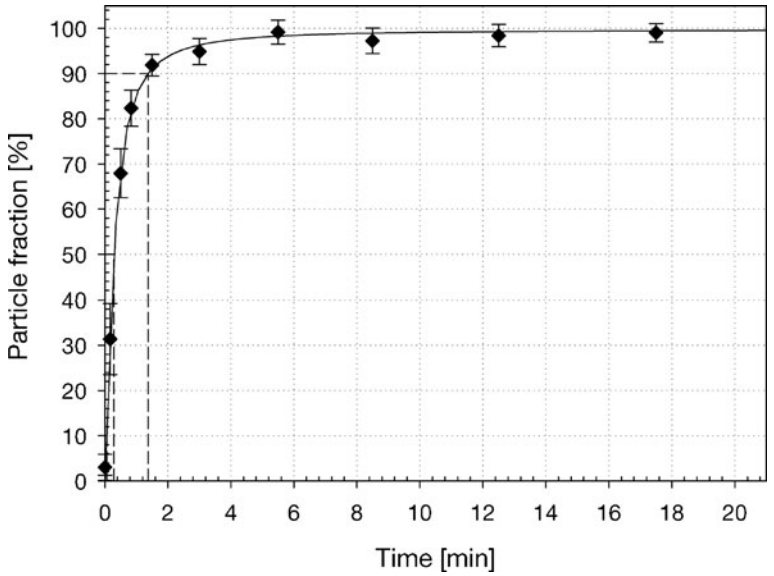

Fig. 8 Particle residence time distribution of the pilot-scale spray dryer

pilot-scale spray dryer. As a consequence, the temperature–concentration–time–history of the particles is not equal in both dryers, which has an impact on the thermal stress and on lysine loss as will be shown in the following. It was confirmed that particle residence time distributions can assume considerable values. Thus, they cannot be neglected in attempts to minimize product damage of thermally sensitive components. This, in practical applications, seems the case however.

3.3 Impact of the spray drying conditions on lysine loss

The model infant formula was spray dried in laboratory scale as well as in pilot scale, and available lysine was measured as a function of the spray drying conditions (Figs. 9 and 10). Lysine loss is reported as a function of the air-to-liquid ratio (ALR_{dryer}) of the respective spray dryer and not as a function of the product mass flow rate so that laboratory-scale conditions can be compared with pilot-scale conditions. Despite the partly rather high air outlet temperatures and low particle water contents (X) reported for laboratory-scale spray drying in previous paragraphs, insignificant lysine loss was detected in the model infant formula after spray drying in laboratory scale (Fig. 9). At maximum, lysine loss ≤3% was measured.

Regarding lysine loss due to spray drying in pilot scale, a quite different pattern than in laboratory scale was determined (Fig. 10). Here, lysine loss of up to 10.4± 2.9% was measured after spray drying. Lysine loss increased with increasing air inlet temperatures and increasing air-to-liquid ratio (ALR_{dryer}). This means that more severe drying conditions, i.e., conditions that lead to higher air outlet temperatures and consequently also to higher product temperatures and to lower residual water contents of the powders, cause higher lysine losses.

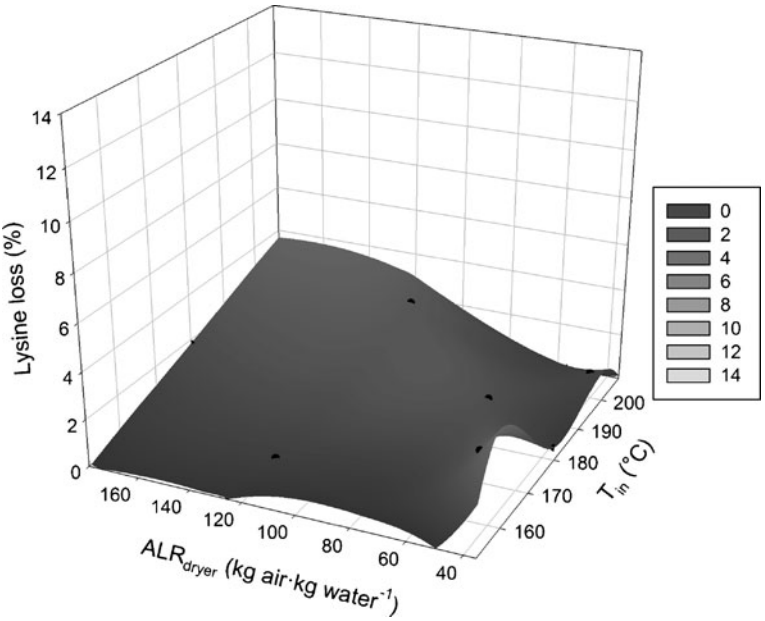

Fig. 9 Lysine loss due to spray drying in laboratory scale

3.4 Lysine loss during storage of the spray dried powders

The spray dried powders were stored at 25 °C and 37 °C for 6 months, and lysine loss was monitored throughout the storage period in order to assess the relative impact of storage versus the drying stage. Lysine loss was expressed as percent of the initially

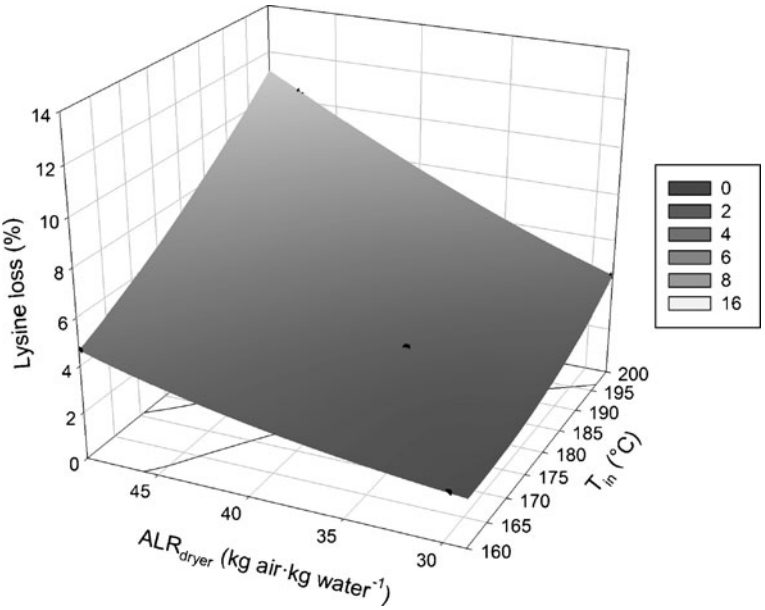

Fig. 10 Lysine loss due to spray drying in pilot scale

available lysine (before spray drying), but only the fraction of lysine loss occurring during storage is considered in Figs. 11, 12, 13, and 14. During storage at 25 °C in powders produced by laboratory-scale spray drying, no significant lysine loss occurred with the exception of one drying condition (Fig. 11). Lysine loss in samples that were spray dried in laboratory scale at T_{in}=180 °C and $\dot{m}_{product}$ = 1.3 kg.h^{-1} (X=7.8±0.5% wb) increased during storage at 25 °C and reached about 35% after 24 weeks. At 37 °C, higher losses than at 25 °C were found (Fig. 12). Again, the highest losses (88.9±2.2% after 24 weeks) were measured in the powders that were spray dried at T_{in}=160 °C and $\dot{m}_{product}$ = 1.1 kg.h^{-1} (X=7.8±0.5% wet basis).

A similar trend was observed in the powders produced by pilot-scale spray drying. Here, at a storage temperature of 25 °C, no significant lysine loss was measured during the first 20 weeks of the storage period except in the powders spray dried at T_{in}=160 °C and $\dot{m}_{product}$ = 18.7 kg.h^{-1} (X=8.0±0.4% wb) where lysine loss of about 30% occurred within 24 weeks (Fig. 13), which will be discussed further below. The water content of this powder is in the same range as the water content of the laboratory-scale powder with the highest lysine loss during storage (T_{in}=180 °C and $\dot{m}_{product}$ = 1.3 kg.h^{-1}, X=7.8± 0.5% wb). After 24 weeks, lysine loss reached about 35% in the laboratory-scale powder

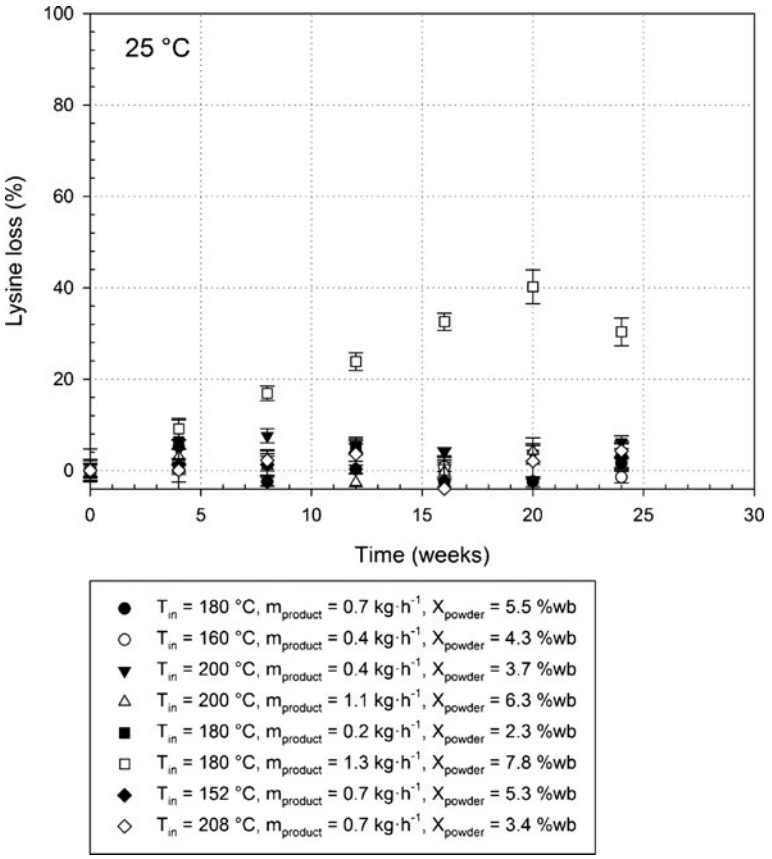

Fig. 11 Progress of lysine loss in the powder samples of laboratory-scale spray drying during storage at 25 °C

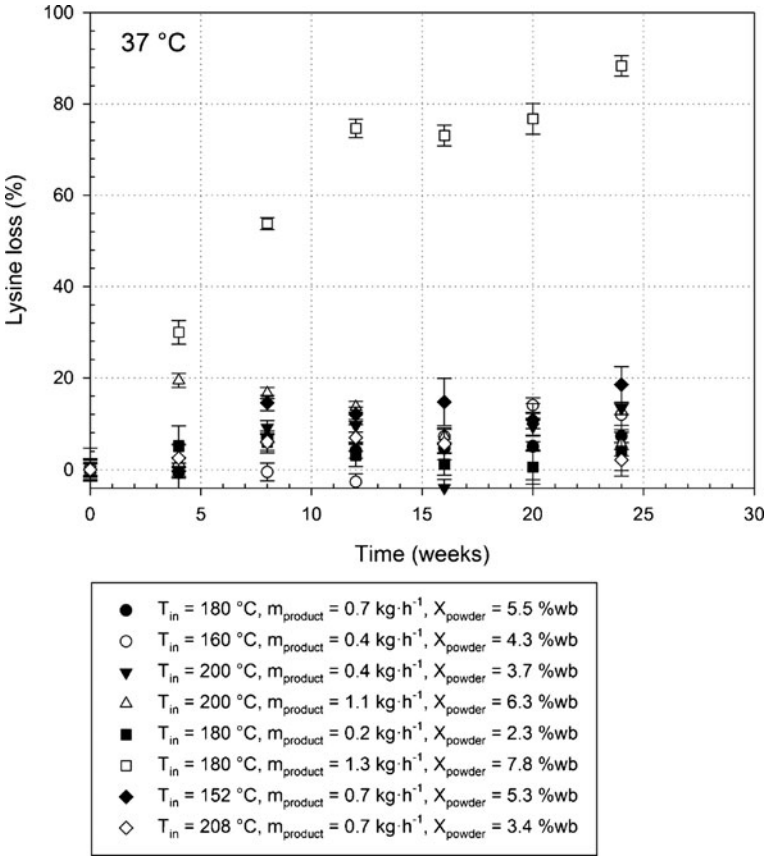

Fig. 12 Increase of lysine loss in the powder samples of laboratory-scale spray drying at 37 °C

and about 30% in the pilot-scale powder. After spray drying, no significant lysine loss was measured in both powders, and the air outlet temperatures were in the same range with 63.3±7.4 °C in laboratory-scale and 60.1±4.1 °C in pilot-scale spray drying. In conclusion, lysine loss during storage at a given temperature seems to be governed by the powder's water content independent of the spray dryer scale, particle residence time, and air inlet temperature.

During storage of the pilot-scale powders at 37 °C (Fig. 14), the highest losses of 89.0±1.8% were observed in the samples of the same drying condition (T_{in}=180 °C and $\dot{m}_{product}$ = 1.3 kg.h^{-1}, X=7.8±0.5% wb) as at 25 °C. Comparison with the corresponding laboratory-scale powder (T_{in}=180 °C and $\dot{m}_{product}$ = 1.3 kg.h^{-1}, X=7.8±0.5% wb) shows that the extent of lysine loss was similar. In the storage period, the extent of lysine loss was less pronounced with decreasing water content of the pilot-scale powders. During pilot-scale spray drying (Fig. 10), the maximum of lysine loss (10.4±2.4%) occurred at T_{in}=200 °C and $\dot{m}_{product}$ = 11.0 kg.h^{-1} with a water content of 2.9±0.3% wb in the produced powder and T_{out}=105.7±4.0 °C. During storage of this powder at 25 °C and 37 °C, no significant lysine loss took place (Figs. 13 and 14). The same is true for a powder with a similar water content X=2.3±0.3% (Figs. 11 and 12) which was spray dried in laboratory scale (T_{in}=180 °C,

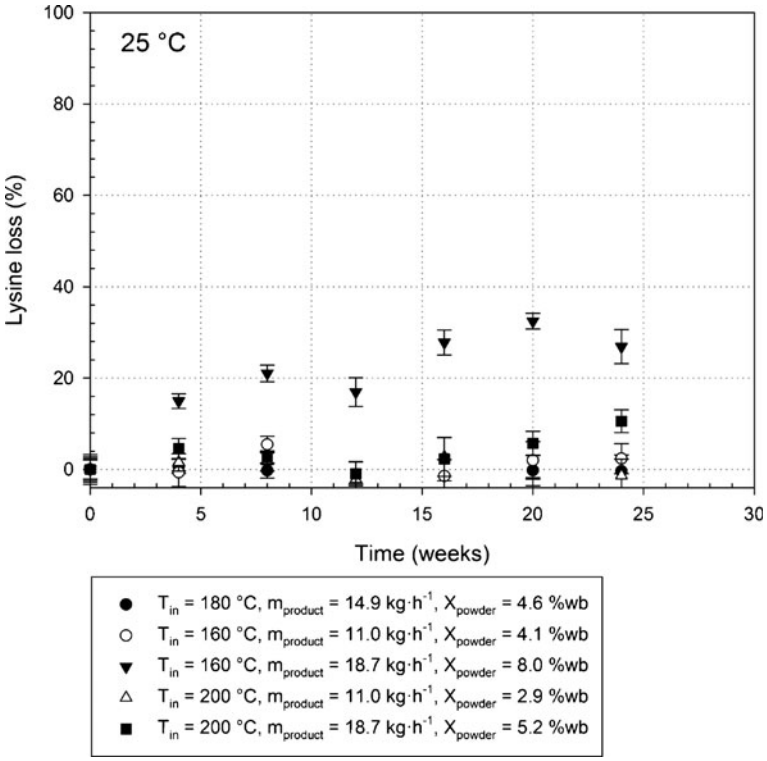

Fig. 13 Lysine loss occurring in the spray dried powders during storage at 25 °C

T_{out}=106.7±12.7 °C, $\dot{m}_{product}$ = 0.2 kg.h^{-1}) without any significant lysine loss due to spray drying (Fig. 9). These observations support the assumption that the water content during storage at a given temperature is the decisive factor concerning lysine loss during storage. Furthermore, it is important to control the storage temperature because a temperature increase from 25 °C to 37 °C more than doubled lysine loss. To optimize spray drying with regard to the overall lysine loss in the final product, it is consequently necessary to minimize lysine loss during spray drying and to ensure low residual water contents in the powder at the same time in order to minimize lysine loss during storage.

4 Discussion

The results presented in the previous section demonstrate that significant differences exist between pilot- and laboratory-scale drying, but depending on the aim of the spray drying application, for example lysine loss during storage, both spray drying scales give similar results. In pilot-scale spray drying, the powder characteristics and air outlet temperatures were similar to the laboratory-scale experiments. However, comparing the air-to-liquid ratios (ALR_{dryer}) in Figs. 9 and 10, it becomes obvious that higher ALR_{dryer} were needed in laboratory scale (ALR_{dryer}=36–180) than in pilot scale (ALR_{dryer}=30–49) to obtain the same drying result. This was probably due to

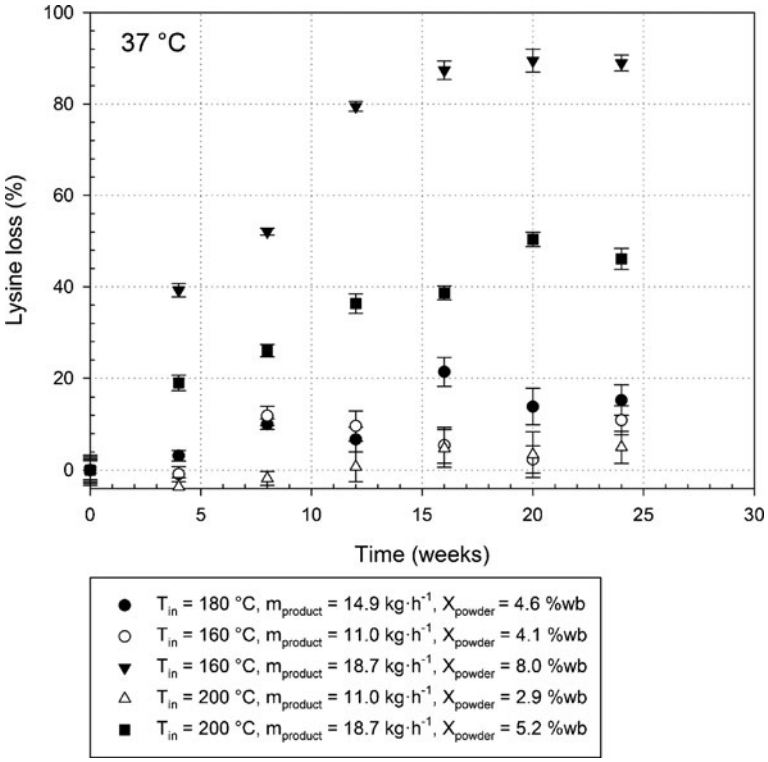

Fig. 14 Lysine loss in the pilot-scale spray dried powders during storage at 37 °C

the different form of the two dryers. The laboratory-scale dryer resembled a tall-form dryer (height/diameter≈3.2:1). It was characterized by relatively short residence times in the spray dryer as was shown before. As a consequence, a high energy input, i.e., a high air mass flow rate, is needed to obtain the same drying result as in pilot-scale drying. The pilot-scale dryer was a short-form dryer (height/diameter≈ 1.6:1) in which recirculation and backflow of air and, consequently, powder particles might occur (Fletcher et al. 2006), and it was larger than the laboratory-scale dryer. As was shown before, this led to longer residence times. Particle residence times measured in this study are in the same range as residence times reported in literature (Gianfrancesco 2009; Jeantet et al. 2008; Kieviet and Kerkhof 1995). In accordance with our observations, all of these authors noticed that mean particle residence time is longer than the mean residence time of air. Gianfrancesco (2009) attributed this divergence to the wrong assumption of plug flow and to powder inertia, recirculation, and interaction with the dryer walls.

Longer residence times do not only mean longer reaction times but also higher particle temperatures. The residence time in laboratory scale was probably not long enough for the particles to reach air temperature whereas in pilot scale the longer residence times would also lead to higher particle temperatures. This explains why no or little lysine loss was detected in powders that were spray dried in laboratory scale but lysine loss of up to 10.4±2.9% was measured in powders that were spray dried in pilot scale. These results are consistent with values that can be found in literature.

In order to highlight the importance of the particle history during spray drying, the impact on lysine loss of temperature, concentration, and time has to be discussed. Schmitz et al. (2011a, b) studied the kinetics of lysine loss at conditions relevant for spray drying as a function of concentration, temperature, and physical state. They did not only show that lysine loss increased with increasing temperature and time following second-order reaction kinetics but most of all they highlighted the role of the physical state. The physical state of the system, glassy, rubbery, or crystalline, is mainly determined by the physical state of the lactose contained in the model infant formula. From their results, it becomes obvious that the maximum of lysine loss coincides with the transition zone from the rubbery to the crystalline state. The rubbery state as well as the crystalline state is characterized by a high mobility in the system which might favor lysine loss to occur. However, the availability of lactose for the early Maillard reaction between lactose and the amino group of lysine is, as expected, obviously higher in the rubbery state than in the crystalline state resulting in a maximum of lysine loss in the transition zone. In summary, lysine loss due to spray drying can only be understood and controlled by taking the physical state as well as the particles' temperature and concentration into account. Moreover, the particle residence time plays a major role as it determines the possible reaction time. As dehydration of small droplets is fast, particles will have high concentrations and temperatures in the case of long residence times. These are critical conditions regarding lysine loss and, consequently, high lysine loss will arise.

The results on lysine loss during storage showed that the extent of lysine loss is controlled by the storage temperature and the powders' water content independent of the type of spray drying used in this study. Literature values for lysine loss during storage are quite scattered. Malec et al. (2002) found higher lysine loss than in this study. They observed lysine loss of about 65% after storage at 37 °C of a lactose–casein model system for 16 days for a water activity of 0.52 and after 50 days for a water activity of 0.33. Chavez-Servin et al. (2008) measured lysine loss of 7.98% in infant formula stored at 25 °C for 6 months. These results are in good accordance with our study in contrast to the results of Ferrer et al. (2000) who did not determine significant lysine loss in adapted infant formula stored at 20 and 37 °C for 6 months. An explanation for these differences is probably the variations in composition, water content, and physical state of the studied powders.

5 Conclusion

This paper shows that lysine loss in spray dried infant formula can be controlled by the correct choice of the spray drying parameters. During spray drying, the temperature profile inside the spray dryer and the particle residence time are important factors concerning lysine loss. Higher particle temperatures caused by higher air outlet temperatures or by recirculation to zones with higher air temperatures will entrain higher lysine loss because of the strong temperature dependence of lysine loss. This is especially true for conditions at which the particles are in the rubbery state. As was shown, the physical state plays a major role concerning lysine loss with the highest lysine loss occurring in the rubbery state. Combining the kinetics of lysine loss with lysine loss measured in the spray dried powders allows drawing conclusions on possible process optimizations.

Special attention should be paid to the particle residence time. The longer a particle remains in the spray dryer, due to recirculation or because it sticks to a wall, the longer the time it is at elevated temperature and, thus, probably at critical concentration and physical state. Here, further optimization regarding air flow and particle deposition on the dryer walls would be needed. Atomization nozzles that create a controlled particle size distribution could be a tool to modify particle residence time in the spray dryer. Another factor that has to be reviewed is the fines return system. The fines are powder particles that have already passed the spray drying cycle and that will be exposed again to conditions that provoke lysine loss.

The aim of the drying process should not only be to minimize lysine loss during spray drying but also to produce powders that are stable during storage with the focus on their nutritional quality. The importance of the water content in this context was shown. To sum up, it is possible to improve the nutritional quality of powdered infant formula when the results of this study are considered.

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