

Crystallization kinetics of amorphous lactose, whey-permeate and whey powders

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Abstract—Amorphous lactose, whey-permeate and whey powders have been converted to their crystalline forms by exposure to air at various temperatures and relative humidities. The total time required for sorption, induction and crystallization of these powders was observed by following the time-dependent mass change of the powders during treatment. These experiments have shown that higher temperatures and relative humidities lead to shorter crystallization times. Lactose crystallizes within 1 min at an air temperature of 100 °C and relative air humidity of 80%, whereas whey-permeate and whey powders requires up to 5 min at the same set of conditions. Thus, as previously described, the presence of proteins and salts in the whey-permeate and whey powders reduces the crystallization rate. The rate constants and activation energies have been determined over a range of temperatures and humidities to enable the calculation of crystallization times for the design of an industrial process that crystallizes whey and whey-permeate powders. Finally, the crystallization rates found in this work are sufficiently fast to be applicable in an industrial process that crystallizes whey and whey-permeate powders.

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1. Introduction

The handling of whey powder products is often difficult due to the lactose component in the powder. Lactose solidifies in an amorphous state during rapid drying in a spray dryer.¹ Amorphous lactose is thermodynamically unstable and hygroscopic, absorbing moisture from the surrounding and subsequently plasticizing. This causes the individual whey powder particles to become sticky.² The temperature at which this transition from an amorphous solid-state to a viscous rubbery state occurs is known as the glass transition temperature.³ The glass transition temperature can fall below ambient temperature when the powder absorbs sufficient moisture during storage, leading to caking of the powder. This presents a problem during subsequent handling processes, such as pneumatic conveying. A further decrease in the glass

transition temperature is accompanied by a higher molecular mobility of the lactose. At this point, the lactose begins to crystallize after an initial induction period.⁴ The crystalline modification is thermodynamically stable and significantly less hygroscopic.

The aim of this work is to develop a practical method for reducing the caking tendency of lactose in whey powder by introducing a controlled crystallization step following the spray-drying process. The resulting powder should thus be more free-flowing and easier to handle,⁵ even when it is exposed to humid conditions.⁶ Knowledge of the effect of various parameters, such as temperature and humidity, on the rate of crystallization is therefore necessary. The focus of the current investigation is the determination of the kinetic parameters associated with the crystallization of amorphous lactose in pure lactose, whey-permeate and whey powders.

Various authors have investigated the crystallization kinetics of lactose at low temperatures.^{7–9} These workers have found that amorphous and crystalline lactose have different sorption isotherms; the amorphous form has a

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much higher moisture content at a given humidity than the crystalline form. During crystallization, the amorphous lactose will initially absorb moisture from the surroundings due to its hygroscopic nature, and subsequently release moisture as it crystallizes. The crystallization kinetics can be determined from the mass change of the powder. Jouppila and Roos¹⁰ have investigated the crystallization of amorphous lactose in milk powders and have shown that lactose crystallization in milk powder is delayed compared with the crystallization of pure lactose powders. Haque and Roos¹¹ have suggested that the crystallization of lactose in spray-dried lactose–protein mixtures at room temperature is delayed by the presence of whey-protein isolate, Na-caseinate, albumin and gelatine.

A reduced form of the Johnson–Mehl–Avrami (JMA) theory^{12–15} can be used for modelling the lactose crystallization kinetics. This theory describes many solid-state reactions that occur through a process of nucleation and growth, and is given by the following equations:^{16,17}

$$\theta = 1 - \exp\{-[k \cdot (t - t_{\text{Ind}})]^n\} \quad (1)$$

$$k(T) = k_0 \cdot \exp\left\{-\frac{E_A}{\tilde{R} \cdot T}\right\} \quad (2)$$

θ is the fraction crystallized, k is the crystallization rate constant, t is the time, t_{Ind} is the induction time, n is the reaction order, k_0 is the pre-exponential factor, E_A the activation energy of the crystallization and \tilde{R} is the ideal gas constant. These parameters are determined experimentally in this work so that Eqs. 1 and 2 can be used in future calculations when designing a whey powder crystallization process.

2. Results and discussion

Figure 1 shows the change in moisture content with time of pure lactose samples exposed to 60 °C and various relative humidities. All measurements were conducted

twice to check for reproducibility. Initially, the moisture content of the samples increases to about 6%. After a short induction time at this moisture content, the amorphous lactose begins to crystallize, and some of the moisture is released to the surrounding air. Thus, sorption, induction and crystallization can be tracked ‘on-line’ by observing the mass change of the sample. The crystallization times determined in this work can be used for designing an industrial process that produces stable crystalline lactose powders.

Assuming that the lactose crystallizes completely as α -lactose-monohydrate, the final moisture content of the sample must be at least 5% to account for the bound hydrate water. However, Figure 1 shows that the moisture content of the lactose at the end of a 60 °C conversion is between 1% and 1.5%. This suggests that the amorphous lactose crystallizes not only to a hydrate, but also to different anhydrous forms, including possibly β -anhydrous lactose, α -anhydrous lactose and mixed anhydrous forms of α - and β -lactose in molar ratios of 5:3, 3:2 and 4:1.¹⁸ The types of crystals that form depend on the relative humidity and temperature of crystallization, the powder composition, and the time of exposure.^{19,20} The experiments show that less α -lactose-monohydrate forms at higher crystallization temperatures. The compositions of the powders produced in this work have been investigated by Nijdam and co-workers.²¹ Figure 2 shows measurements of the overall-crystallization times required for amorphous lactose powder at different temperatures and relative humidities. Higher temperatures and relative humidities result in shorter crystallization times. At the highest temperature and relative humidity tested, the time for crystallization is only 1 min. In this case, diffusion of water into the particles is likely to limit the crystallization process.

Figure 3 shows the change in moisture content of whey-permeate samples exposed to 60 °C and various relative humidities with time. The moisture content increases initially in the same manner as for lactose.

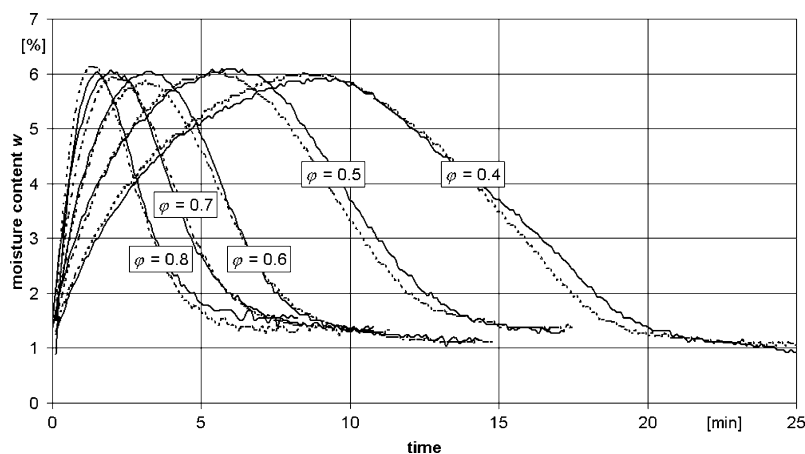


Figure 1. Sorption- and crystallization behaviour of amorphous lactose at 60 °C.

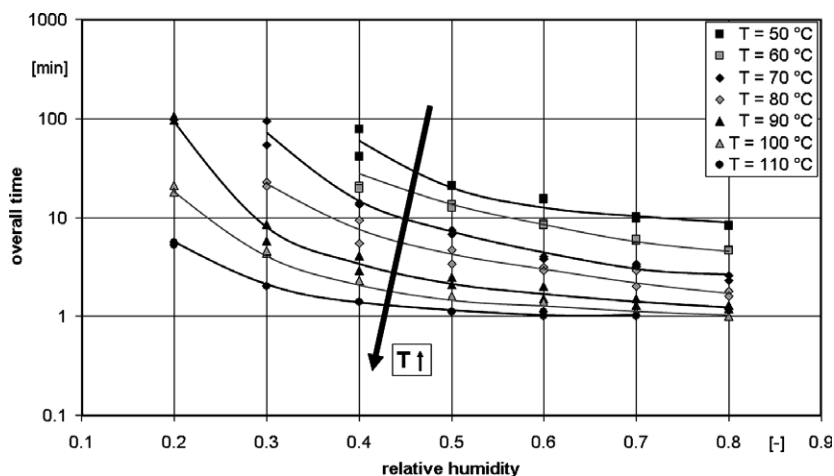


Figure 2. Overall times for sorption, induction and crystallization of amorphous lactose powder at various temperatures and relative humidities.

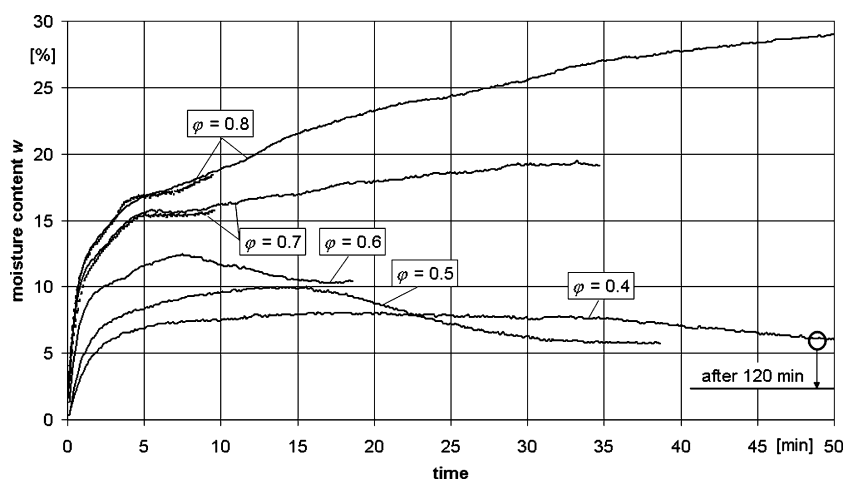


Figure 3. Sorption- and crystallization behaviour of amorphous whey-permeate powder at 60 °C.

However, in this case, the moisture content increases to a much higher value. Clearly, the salts and proteins present in the whey-permeate powder contribute to the hygroscopicity of the powder. At relative humidities between 40% and 60%, the moisture content decreases after a brief induction period. This decrease in moisture content is caused by the crystallization of the amorphous lactose. At relative humidities between 70% and 80%, the moisture content increases up to a certain value, remains at this level for a certain time, and then increases further towards a higher equilibrium value. Under these conditions the crystallization is so fast that the release of water through the crystallization overlaps the absorption process. Therefore, the crystallization is already complete before the sorption equilibrium moisture content is reached. Note that the higher moisture content at these conditions for whey-permeate in comparison to lactose powder may be affected by a solubilization process of substances like salts or proteins. The

end of crystallization corresponds to a point just after the 'shoulder' in the moisture content profile.

Figure 4 shows measurements of the overall-crystallization times required for amorphous whey-permeate powder at different temperatures and relative humidities. The crystallization time of amorphous whey-permeate powder is longer than that of pure lactose. As reported in literature,^{11,22–24} the crystallization is delayed by the presence of salts and proteins, which effectively lowers the concentration of lactose, and hence lengthens the mean path length required for lactose molecules to migrate in order to bond with other lactose molecules.

Figure 5 shows that amorphous whey powder crystallizes in a similar manner to amorphous whey-permeate powder. At 80% humidity, a similar 'shoulder' appears in the moisture content profile.

Figure 6 shows measurements of the overall-crystallization times required for amorphous whey powder at different temperatures and relative humidities. Once

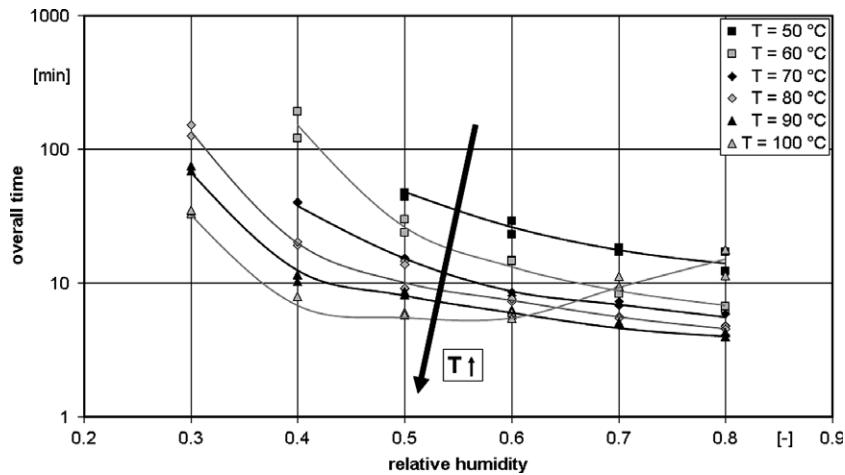


Figure 4. Overall times for sorption, induction and crystallization of amorphous whey-permeate powder at various temperatures and relative humidities.

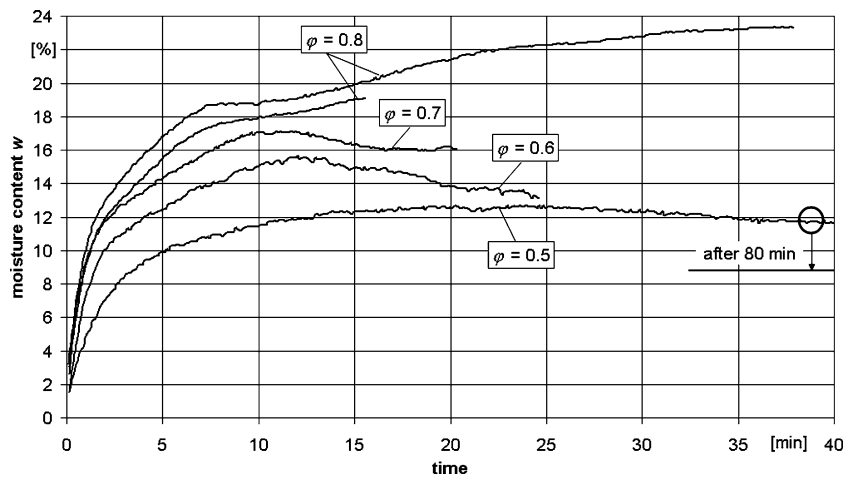


Figure 5. Sorption- and crystallization behaviour of amorphous whey powder at 50 °C.

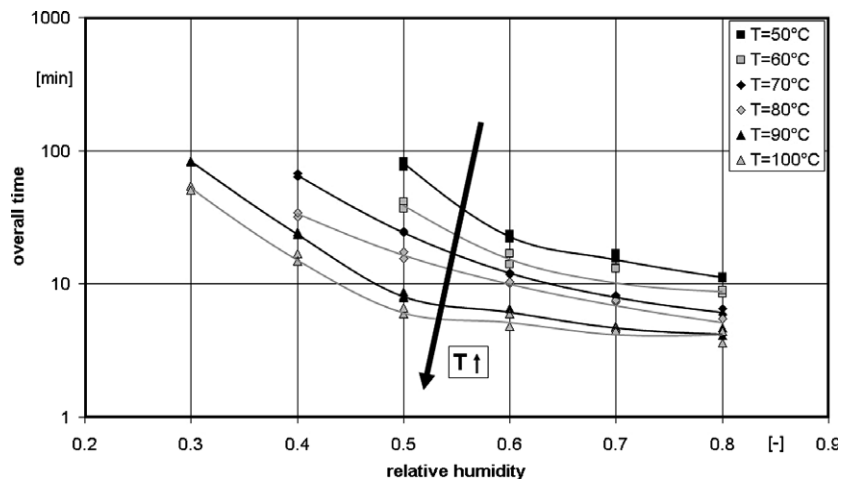


Figure 6. Overall times for sorption, induction and crystallization of amorphous whey powder at various temperatures and relative humidities.

again, this figure shows that amorphous whey behaves similarly to amorphous whey-permeate powder.

The required residence times for the crystallization of amorphous whey and whey-permeate powders are of the

same order of magnitude, although the concentration of proteins in whey is slightly higher, or equivalently, the concentration of lactose is slightly lower. The raw data obtained can be transformed into a crystalline fraction θ versus $(t - t_{\text{Ind}})$, as follows:

$$\theta = \frac{w_{\text{max}} - w}{w_{\text{max}} - w_{\text{final}}} \quad (3)$$

θ is the fraction of the lactose that has been crystallized. w_{max} and w_{final} are the maximum moisture content at time t_{Ind} and the moisture content at the end of the crystallization, respectively. Eq. 1 can be rearranged as follows:

$$\ln[-\ln(1 - \theta)] = n \cdot \ln(t - t_{\text{Ind}}) + n \cdot \ln(k) \quad (4)$$

A plot of $\ln[-\ln(1 - \theta)]$ versus $\ln(t - t_{\text{Ind}})$ gives a straight line with a slope of n and an intercept of $n \cdot \ln(k)$. Figure 7 shows such a plot for lactose crystalli-

zation at 50 °C and various relative humidities. The crystallization rate constants k for lactose, whey-permeate and whey powder, calculated using the slope and intercept in Eq. 4, are shown in Figures 8–10.

In the case of whey-permeate and whey powder, the reaction order n and the crystallization rate constants k could only be determined properly at relative humidities less than 70%, because the form of the curve differs from Eq. 4 at higher relative humidities. Values for the reaction order n at various temperatures and relative humidities are given in Tables 1–3.

Figures 8–10 show that the rate constant increases markedly with increasing relative humidity and temperature, which indicates that the mass change of the sample is controlled by crystallization rather than mass transfer of moisture within the particles or at the surfaces of the particles. However, at a high temperature of 110 °C and a relative humidity of 70%, the rate

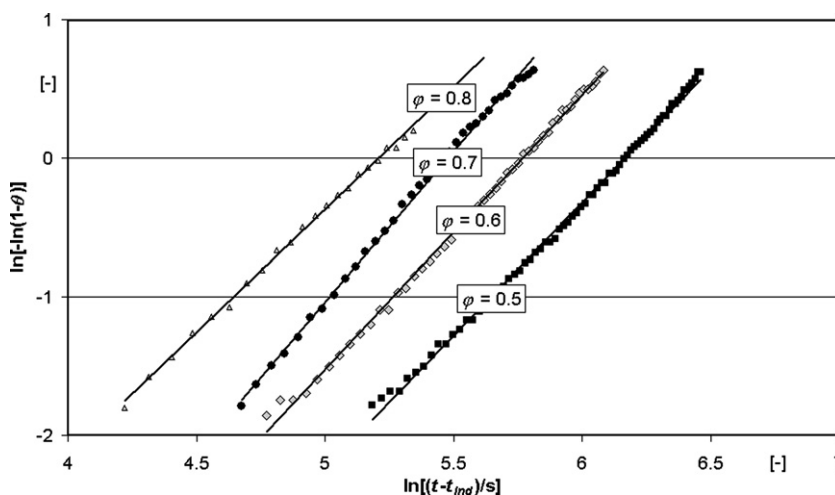


Figure 7. Transformed crystallization time for lactose powder at 50 °C and diverse relative humidities.

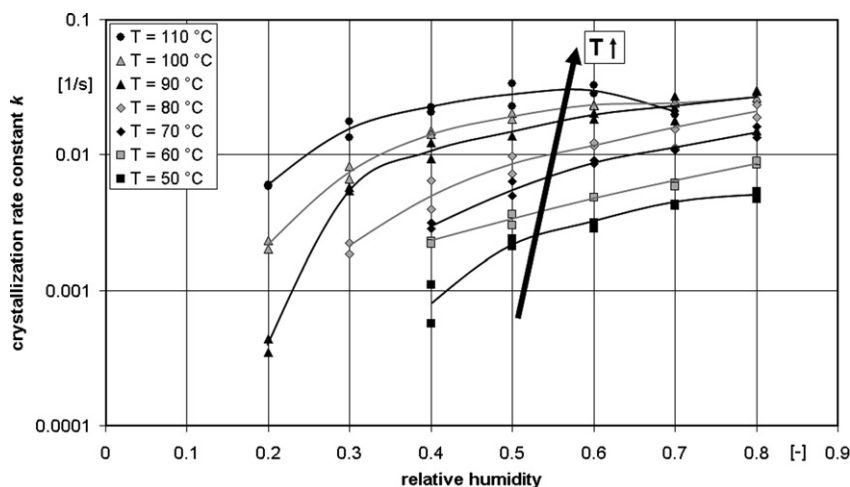


Figure 8. Crystallization rate constants k of lactose powder at various temperatures and relative humidities.

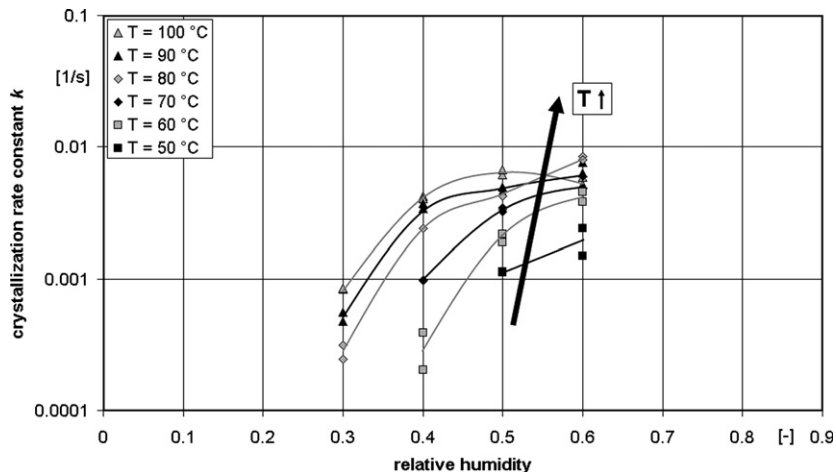


Figure 9. Crystallization rate constants *k* of whey-permeate powder at various temperatures and relative humidities.

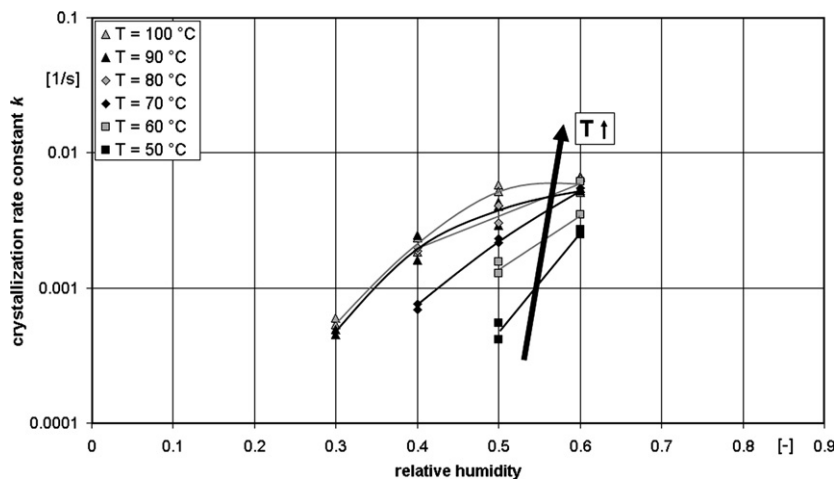


Figure 10. Crystallization rate constants *k* of whey powder at various temperatures and relative humidities.

Table 1. Reaction order *n* for the crystallization of amorphous lactose powder

φ (-)	<i>n</i> (-)						
	<i>T</i> = 50 °C	<i>T</i> = 60 °C	<i>T</i> = 70 °C	<i>T</i> = 80 °C	<i>T</i> = 90 °C	<i>T</i> = 100 °C	<i>T</i> = 110 °C
0.8	2.1	1.7	1.5	1.6	0.8	0.2	
0.8	1.7	1.6	1.7	1.5	1.5	1.0	
0.7	2.0	1.9	1.9	1.8	1.4	1.4	0.8
0.7	2.2	2.0	2.0	1.5	1.7	1.4	1.6
0.6	2.0	2.2	1.9	1.9	1.4	1.4	0.8
0.6	2.3	1.9	1.9	1.7	2.0	1.2	1.3
0.5	1.7	2.4	2.3	2.0	1.6	1.5	1.6
0.5	1.9	2.0	1.8	2.2	2.1	1.3	0.9
0.4	1.4	1.7	2.2	1.6	1.6	1.4	1.5
0.4	2.0	2.3	2.1	1.6	1.6	1.6	1.5
0.3				1.9	2.0	1.8	1.9
0.3				1.8	2.1	1.9	1.6
0.2					1.0	1.6	1.4
0.2					1.1	1.8	2.1

constant decreases. An XRD analysis of the samples has shown that, at these conditions, lactose powder

crystallizes solely as β -lactose, which could explain this break in the trend. Figures 8–10 confirm that the

Table 2. Reaction order n for the crystallization of amorphous whey-permeate powder

φ (-)	n (-)					
	$T = 50\text{ }^\circ\text{C}$	$T = 60\text{ }^\circ\text{C}$	$T = 70\text{ }^\circ\text{C}$	$T = 80\text{ }^\circ\text{C}$	$T = 90\text{ }^\circ\text{C}$	$T = 100\text{ }^\circ\text{C}$
0.6	2.1	0.6	1.7	1.5	1.7	1.3
0.6	1.2	0.6	2.0	1.7	1.2	1.0
0.5	1.5	0.5	1.8	1.4	1.7	1.3
0.5	1.6	0.5	1.8	1.4	1.6	1.3
0.4		0.4	1.4		1.8	1.6
0.4		0.4	1.5	1.3	1.5	1.5
0.3				0.9	1.2	1.2
0.3				1.5	1.3	1.5

Table 3. Reaction order n for the crystallization of amorphous whey powder

φ (-)	n (-)					
	$T = 50\text{ }^\circ\text{C}$	$T = 60\text{ }^\circ\text{C}$	$T = 70\text{ }^\circ\text{C}$	$T = 80\text{ }^\circ\text{C}$	$T = 90\text{ }^\circ\text{C}$	$T = 100\text{ }^\circ\text{C}$
0.6	1.0	1.5	1.5	1.6	1.6	0.8
0.6	1.0	1.2	1.3	1.3	1.3	1.3
0.5	1.2	1.4	1.0	1.5	1.5	1.4
0.5	1.1	1.2	1.3	1.6	1.3	1.5
0.5					1.7	
0.4			1.2	1.3	1.5	1.4
0.4			1.3	1.2	1.1	1.6
0.3					1.5	1.3
0.3					1.6	1.5

crystallization of whey-permeate and whey powder is slower than that of pure lactose powder, which we have explained above is due to the presence of salts and proteins.

Eq. 2 can be rearranged to give the following equation:

$$\ln(k) = \ln(k_0) - \frac{E_A}{R} \cdot \frac{1}{T} \quad (5)$$

A plot of $\ln(k)$ versus $\frac{1}{T}$ results in a straight line with slope $-\frac{E_A}{R}$ and intercept $\ln(k_0)$. Figure 11 shows such a plot for lactose powder crystallization at various relative humidities. The pre-exponential factors k_0 of the Arrhenius-equation are given in Table 4.

Table 4. Pre-exponential factors of the Arrhenius-equation for the crystallization of lactose, whey-permeate and whey powder at various relative humidities

φ (-)	Lactose powder k_0 (1/s)	Whey-permeate powder k_0 (1/s)	Whey powder k_0 (1/s)
0.8	1.9E+04		
0.7	1.1E+04		
0.6	2.5E+04	8.46E+00	5.40E-01
0.5	1.9E+04	1.92E+01	1.03E+04
0.4	1.0E+06	2.94E+07	1.80E+02
0.3	1.2E+08	3.55E+05	5.09E-01
0.2	1.9E+20		

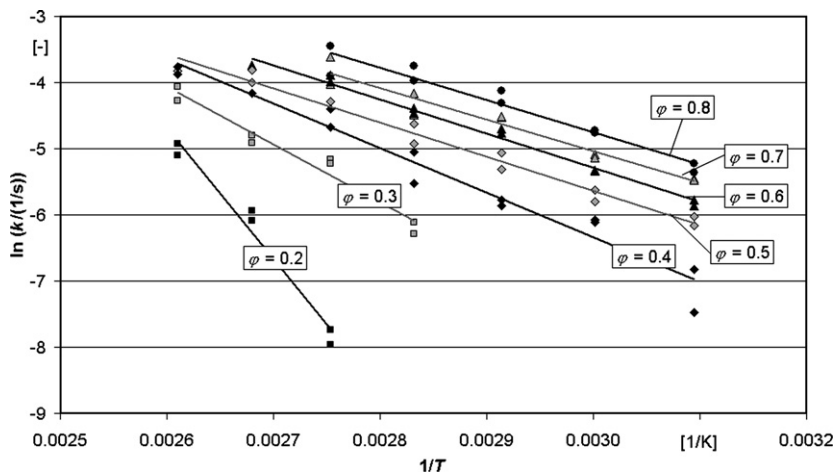


Figure 11. Arrhenius-plots JMA rate constants for lactose powder determined gravimetrically at various relative humidities.

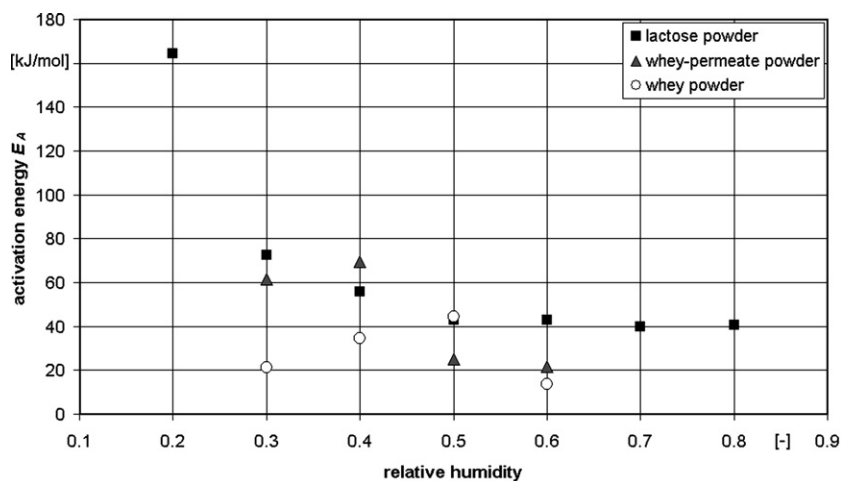


Figure 12. Activation energies for the crystallization of amorphous lactose, whey-permeate and whey powder at various relative humidities.

Figure 12 shows that the activation energies for the crystallization of amorphous lactose, whey-permeate and whey powders are dependant on the relative humidity. This can be seen most clearly in the case of lactose, for which the activation energy decreases from 164 kJ/mol to approximately 40 kJ/mol as the relative humidity is increased from 20% to 50%. At higher relative humidities, the activation energy of crystallization assumes a constant value. The activation energy for the whey powders could not be measured at lower relative humidities, due to prohibitively long crystallization times, which prevented measurements at these relative humidities. Note that the rate constants k , induction times t_{Ind} , reaction order n , pre-exponential factors k_0 and the activation energies E_A determined in this work can be used in future calculations for designing a whey powder crystallization process.

3. Experimental

3.1. Materials

Amorphous lactose, whey-permeate and whey powders were provided by the German producers *Uelzena*, *Meggle* and *Lactoprot*. The compositions of the whey-permeate and whey powders are given in Table 5. The amorphous nature of these products was confirmed by X-ray powder diffraction (XRPD) and differential scanning calorimetry (DSC).

Table 5. Composition of amorphous lactose, whey-permeate and whey powders

	Lactose (wt %)	Protein (wt %)	Salt (wt %)
Lactose powder	99.7	n.a.	n.a.
Whey-permeate powder	≈78–80	≈3–4	≈10
Whey powder	≈73	≈12	≈3

3.2. Experimental equipment

The crystallization kinetics were determined gravimetrically at various temperatures and humidities using a balance to follow the mass change of the amorphous powders, while they absorbed and desorbed moisture from the surroundings (Fig. 13). The sample was exposed to defined conditions in a custom made wind tunnel, where hot humid air with a velocity of 0.2 m/s flowed over the sample. The tunnel had an external heating jacket with recirculating oil, whose temperature was controlled at the dry-bulb temperature of the airflow in order to avoid any condensation on the walls.

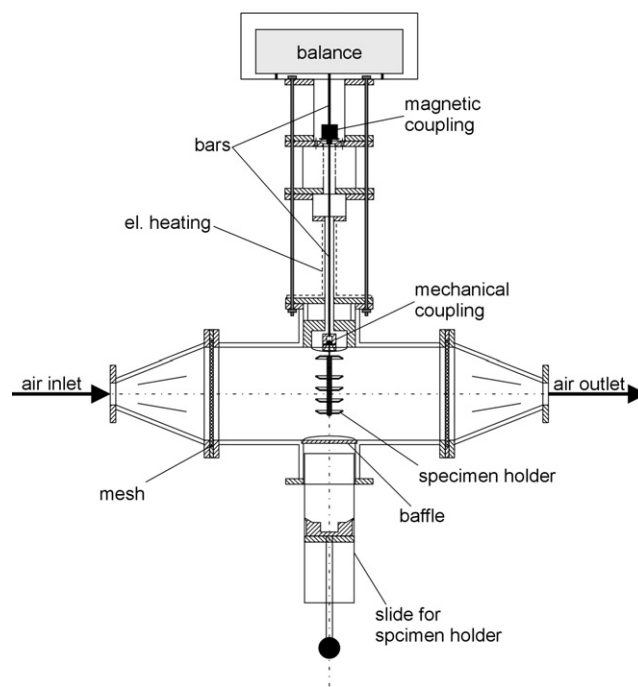


Figure 13. Layout of the balance and the cylindrical wind tunnel (inner diameter $d_i=210$ mm).

The sample was dispersed on a specimen holder, which consisted of four dishes, one above the other, each with a diameter of 62 mm. The holder was inserted into the tunnel through a port at the bottom, and attached to the balance (Type E 2000 D, Sartorius, Göttingen) via a magnetic-coupling device. A slight overpressure was set in the box containing the balance, so that hot, humid air could not rise upwards towards the balance. The resultant airflow into the wind tunnel was negligible compared with the flow of hot humid air within the wind tunnel. The coupling devices and connections were heated electrically to prevent water condensation on these parts. The mass change of a sample was continually recorded to track the crystallization process.

3.3. Sample preparation

The lactose and whey powder samples were sieved onto the dishes using a mesh in order to form a mono-layered particle bed with particles of 150 μm or smaller. The powders were then dried under vacuum at 40 °C for 10 h. Before starting the experiment, the sample was heated for 1 h in an oven at a temperature that was 10 °C higher than the intended process temperature within the wind tunnel. Thus, moisture condensation onto the sample when it was inserted in the wind tunnel was prevented. To ensure that no lactose has crystallized while heating in the oven, samples were analyzed with differential scanning calorimeter and X-ray diffraction (XRD) measurements in preexaminations.

The dry weight of each lactose sample was determined after the crystallization process by drying a portion of the sample for 24 h under vacuum at 105 °C. At these conditions, the bound hydration water in α -lactose-monohydrate was released completely. The dry weights of the whey-permeate and whey powders could not be determined in this manner, because Maillard reactions, due to the presence of the proteins, would have resulted in a progressive mass loss of the sample as the lactose and protein reacted to form water. Therefore, these samples were dried for 10 h under vacuum at 70 °C. These samples were subsequently put into a desiccator with P_2O_5 as the drying agent, and the air within the desiccator was purged with N_2 . The samples were then allowed to cool down to ambient temperature, after which the dry weights were determined.

4. Conclusions

Time-dependent crystallization of amorphous lactose in pure lactose, whey-permeate and whey powders was investigated. Higher temperatures and relative humidities result in faster lactose crystallization. At the crystallization conditions used in this work, the required crystallization time for pure amorphous lactose powder ranged from 1 to 100 min. Whey-permeate and whey

powders required more time to crystallize than pure lactose powder; the quickest crystallization for these powders could be achieved in only 5 min. Clearly, the presence of proteins and salts in the whey-permeate and whey powders hinder the crystallization rate. The rate constants and activation energies have been determined over a range of temperatures and humidities to enable the calculation of crystallization times for the design of an industrial process that crystallizes whey and whey-permeate powders. Finally, the crystallization rates are sufficiently fast so that an industrial process that crystallizes whey and whey-permeate powders in the range of minutes is feasible.

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