Investigation of Crystallization Process of Lactose in Milk Serum Permeate

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Abstract. One of the main factors determining physicochemical and structural properties of the dry permeate of spray drying is lactose which is present in permeate as a basic phase. If lactose is in the β-form in a dry powder, the powder easily absorbs moisture from the atmosphere during storage, causing agglutination, clumping, and caking of the product. Prevention of negative consequences associated with increased hygroscopicity, is ensured by the directed crystallization of lactose in a condensed product before spray drying. The purpose of this investigation was to study the crystallization process of lactose in permeate under industrial conditions when using various seed materials. Results of the studies showed that the type of a crystal forming agent does not affect the size and shape of lactose crystals and the level of lactose crystallization. Seed material is of critical significance as it will ensure both a high level of crystallization and homogenous crystals which, in general, leads to an increase in melting temperature, due to a decrease in the proportion of amorphous lactose, as well as improves the drying process.

1. Introduction

Concentrates of milk and serum are becoming increasingly demanded on the modern market of food supplements [1]. The technology for their production is based on the fractioning of milk raw materials by means of ultrafiltration. As a result, two streams are formed: protein concentrate (retentate) and filtrate (permeate). The use of such product as permeate is possible during the organization of lactose (milk sugar) production with the quality of finished product of different categories. This is ensured by the fact that more than 80% of the mass of permeate dry residue is lactose.

The industrial production of lactose (milk sugar) requires the organization of a multistage process, which entails the need for the enterprise to provide large scale expenditure of resources. In this regard, feasibility of implementation of lactose (milk sugar) production is confirmed provided that there are significant volumes of processed raw materials integrated with a high market potential.

The alternative approach to the above decision can be the production of spray-dried permeate, in which a number of technological operations and side streams can be excluded from the processing [2]. If the equipment and operations used in the production line ensure the quality of the dry product at a level approximated to the characteristics of food lactose, the spray-dried permeate can be successfully used in various areas of food industry, such as confectionery, bakery and others.
Lactose is one of the main factors determining physicochemical and structural properties of dry permeate and a basic permeate phase. When lactose is a vitreous / amorphous state (β-form) in the dry product, a highly viscous liquid is likely to form since the powder absorbs moisture from the atmosphere during storage. This process leads to caking, clumping, agglutination of the product, in particular cases monolith is likely to form, due to this the resulting product is impossible to be used further [3].

To prevent the increased hygroscopicity of the dry permeate and reduce its negative consequences, a number of measures can be taken, in order to specially crystallize lactose in the thickened product before spray drying [2, 4].

In the original permeate with about 5 % of a lactose mass fraction, lactose is in the state of a true solution. During thickening a mass fraction of dry substances increases, the solution becomes saturated, and the spontaneous crystallization of α-lactose begins. At this stage, forming nuclei of α-lactose crystals can be destroyed since they possess sufficient kinetic energy. With a decreasing temperature kinetic energy decreases, crystal aggregates become more stable, the saturated solution turns supersaturated, and the growth of lactose crystals begins [5]. Thus, the intensive crystallization is achieved by concentrating the permeate to the highest possible content of dry substances and the concentrate cooling. After the crystallization, the concentrated permeate must contain not less than 70 % of the crystallized lactose with homogeneous small crystals [4]. This can be achieved by using a directed crystallization which makes it possible to control a number of parameters: cooling rate, stirring intensity, as well as the introduction of seed material (crystal forming agents).

The introduction of a crystal forming agent is one of the simplest methods for supersaturation control, which allows launching the crystallization process at a required level of supersaturation, providing the sufficient surface of particles for controlled consumption of supersaturated solution, obtaining crystals with the required parameters [6].

Fine crystalline milk or beet sugar can be used as seed materials in dry or suspension form stabilized by surfactant materials approved for use in the food industry [7].

The purpose of this research is to study seed materials for the lactose crystallization.

2. Research materials and methods
For the research we used the ultrafiltration permeate of milk serum concentrated using an industrial nanofiltration installation to a mass fraction of dry substances (18–20) %.

The crystallization in industrial conditions was studied using the modes for permeate production by spray drying system installed at one of dairy plants of the Russian Federation. Permeate with a mass fraction of dry substances (18–20) % was condensed using a film evaporator to a mass fraction of dry substances (55–60) %. Then it was directed to a crystallizer to carry out the periodic process of crystallization of lactose under the following modes: cooling during the filling of the crystallizer at slow stirring to 30–32 °C, introduction of the seed material and further cooling at a rate of 2,0–2,5 °C/h to 10–12 °C.

The modes of laboratory tests were close to industrial conditions as much as possible: a permeate sample was condensed to a mass fraction of dry matters (55–60%) using a RV 06-ML 2-B, IKA laboratory rotary evaporator at a temperature of 65 °C and with a flask rotation frequency equal to 50 rpm with help of a MM 2 A Laboratorní pristroje Praha magnetic stirrer. The condensed product was quickly cooled to a temperature of 38,0–40,0 °C, then it was cooled to 30–32 °C during slow stirring at a rate of 2,5–3,0 °C/h. At this temperature the seed material was introduced and the cooling was carried out further to a temperature of 10–12 °C at a rate of 2,0–2,5 °C/h.

Fine crystalline lactose (K1), fine crystalline sucrose (K2), and a suspension of fine crystalline sucrose (K3) were used as seed materials (crystal forming agents).

During the crystallization samples were selected at predetermined intervals. For each test the value of the mass fraction of dry substances (GOST (State Standard) P 54668-2011 and GOST 33957-2016) and the microstructure of the samples were recorded using a Levenhuk D740T digital microscope. Linear dimensions of lactose crystals in the studied samples were determined by microscopy at 600 and 150 times magnification [8].
The degree of lactose crystallization was calculated by counting the mass fraction of dry matters in the crystallisate by the percentage of crystallized lactose:

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C = \frac{(S_1 - S_2) \times 9500 \times 100}{L \times S_1 \times (95 - S_2)}
\]

where: 
C is the degree of lactose crystallization;

S₁ is percentage of dry substances at the outlet of the vacuum-evaporator apparatus by refractometer;

S₂ is percentage of dry substances in the crystallized concentrate by refractometer;

L is percentage of lactose.

3. Research results and their discussion

The laboratory studies showed that during the crystallization of the condensed permeate without seeding, the variation in crystal size ranged from 10 µm to 450 µm. In this case, small crystals (10.00–20.00 µm) prevailed, the size of large crystals reached 300.00 µm. The crystallization level was 75–80%. The use of any of investigated crystal forming agent (K₁, K₂, K₃) led to less variation in crystal size and enlargement of the fraction including crystals of size from 35.00 to 140.00 µm, though the sizes of particular crystals could reach 250 µm. The crystallization degree was 80–84%. At the first stage, the laboratory studies were carried out and the dosages of crystal forming agents introduced per 1 ton of dry substances of the condensed product were selected: K₁ – 0.22 kg / t, K₂ – 0.44 kg / t, K₃ – 10 ml / t. These dosages were used in the study of the crystallization process under industrial conditions.

The results of experiments carried out in industrial conditions showed that the dynamics of crystallization when using all types of seed material was identical. As an example, figure 1 shows a process diagram for a K₃ Crystal forming agent.

The process control began at the moment of filling the crystallizer. Since during the filling there is a simultaneous cooling of condensed permeate, the product temperature decreases sharply at the inlet to the crystallizer. Thus, both conditions for reaching the supersaturation point of lactose in the solution are satisfied: high concentration of dry matters and cooling to a temperature at which α-lactose becomes less soluble [5, 6]. The process of spontaneous crystallization is launched, and, correspondingly, the mass fraction of dry matters in the intercrystalline liquid begins decreasing, while the degree of crystallization increases and amounts to 30–35 % in the first hour of the filling, then it heightens to 50–55% for the second hour.

Figure 1. Dynamics of degree of lactose crystallization when using K₃ crystal forming agent.
By the end of filling the crystallizer the level of crystallization rises to 10–15% and reaches 60–70%, i.e. the significant part of lactose crystallizes within 4 hours. This is likely to be facilitated by the fact that, as the crystallizer is filled and portions of hot product enter, the rate of cooling slows down and the temperature of the product can vary within 2–3 °C. In supersaturated solutions lactose is in α- and β-isomeric forms in the reversible equilibrium which significantly depends on temperature. Increased temperatures contribute to a fast mutarotation of β-lactose into α-lactose which is less soluble than β-lactose, therefore it reaches the supersaturation point faster and begins crystallizing [9]. So, the crystallization level increases despite the temperature fluctuations (figure 1, Crystallization level line).

![Figure 2](image.jpg)

**Figure 2.** Microstructure of condensed product during crystallization, seed - K3, (a) – after 2 hours of filling the crystallizer, (b) – after 4 hours of filling the crystallizer, (c) – after 10 hours of cooling.

![Figure 3](image.jpg)

**Figure 3.** Permeate microstructure during crystallization without seed material.

The introduction of seed material at a temperature of 30–32 °C initiates secondary heterogeneous nucleation which can be triggered at low supersaturation levels. After seeding, the crystallization level slowly increased and amounted to 80–84% by the end of cooling.

The examination of crystal morphology showed that the general dynamics of crystal forming agent is the same when using any seed material. Crystal forming agent starts from the moment the crystallizer is filled (figure 2 a). The active growth of crystals continues within the first hours of filling the crystallizer till the seed material is introduced.

After seeding, there is a noticeable increase in the number of crystals in the view field of the microscope (figure 2 b). When passing to the crystallization mode, the slow growth of crystals starts, but, as a rule, the size of crystals does not enlarge radically (figure 2 c).

The process which was carried out without introducing the seed material differ (Figure 3). Despite the high level of crystallization the sizes of individual crystals were more than 400 µm in the absence.

The shape of lactose crystals is determined, first of all, by the degree of supersaturation of the solution, the crystallization rate, the presence of impurities, and a number of other parameters [6, 7, 9]. Since, in addition to lactose, the condensed permeate includes a number of impurities (non-protein nitrogen, protein, mineral substances), the microstructure of the crystallized permeate included, primarily, lactose crystals in the shape of a prism or a needle (figure 2 a). As the rate of crystal growth slowed down, the crystals acquired the shape of a tomahawk or diamond-shaped plates.
4. Conclusion
So, according to the data obtained, the type of crystal forming agent does not significantly affect the size and shape of lactose crystals. The use of a seed material is of critical significance as it will ensure homogeneity of crystals in addition to a high level of crystallization, which, in general, leads to elevated melting temperature due to the decreased portion of amorphous lactose, as well as improved drying [10].

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References
[1] Melnikova E I, Bogdanova E V and Pavelyeva D A 2020 World and Russian market of whey ingredients Dairy industry 8 56–58
[2] Volodin D N et al 2018 Efficient technology for processing lactose-containing raw materials: ways to improve the quality of spray-dried permeate Milk processing 8 14–17
[3] Phosanam A, Chandrapala J, Adhikari B and Zisu B 2021 Storage stability of powdered dairy ingredients: a review Drying Technology 99 (8) 6842–51
[4] Píseký J 1997 Handbook of Milk Powder Manufacture (Niro A/S : Copenhagen, Jk)
[5] Pandalaneni K and Amamcharla J K 2018 Evaluating the crystallization of lactose at different cooling rates from milk and whey permeates in terms of crystal yield and purity Journal of Dairy Science 101 10 8805–21
[6] Wong S and Hartel R 2014 Crystallization in Lactose Refining-A Review Journal of Food Science. 79 3 R257–R272
[7] Zadow J G 1992 Whey and lactose processing (London and New York: Elsevier Applied Sciences) 489 p
[8] Ryabova A E, Galstyan A G, Malova T I, Radaeva I A and Turovskaya S N 2014 On the issue of heterogeneous crystallization of lactose in the technologies of condensed milk products with sugar Technique and technology of food production 1 32 78–83
[9] Portnoy M and Barbano D M 2021 Lactose: Use, measurement, and expression of results Journal of dairy science S0022-0302 (21) 00468-9 DOI: 10.3168/jds.2020-18706
[10] Arissara P, Jayani C, Bogdan Z and Benu A 2021 Storage stability of powdered dairy ingredients: a review Drying Technology DOI: 10.1080/07373937.2021.1910955