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A sub-zero crystallization process for the recovery of lactose

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ABSTRACT

In industry, lactose is generally produced by concentrating whey permeate by evaporation followed by a slow cooling process where lactose is crystallized. Here, an alternative method is presented whereby the concentration and crystallization steps are combined at sub-zero temperatures, so-called eutectic freeze crystallization. It was discovered that simultaneous crystallization of lactose and water (ice) is possible. The obtained lactose crystals had an average size of 10 μm and a thin triangular or tomahawk morphology.

The process was analyzed in detail in two steps: freeze concentration and lactose crystallization at sub-zero temperatures. Freeze concentration experiments showed that concentrating to supersaturation was possible without excessive lactose crystallization. In the second step, lactose was crystallized at temperatures below zero from a 30 wt% lactose solution, without observation of significant primary or secondary nucleation. The amount of seed material had a large influence on the final yield, crystal size and morphology. The optimum seed amount was found to be at 0.08% of the total lactose; the resulting crystals had an average size of 26 μm and a tomahawk morphology. Although highly supersaturated conditions are present in the sub-zero crystallization of lactose, crystal growth is found to be the predominant process rather than nucleation.

1. Introduction

Lactose has a wide range of applications ranging from additives in the food industry to products for the pharmaceutical industry. Lactose is the main sugary compound in human and mammalian milk where, among others, it acts as a source of energy. It is a key ingredient for the production of infant formula from cow milk where the amount of lactose in cow milk (4.6%) is increased to the concentration of human milk (7%) (McSweeney and Fox, 2009). Furthermore, lactose is used as a free-flowing or agglomerating agent to accentuate/enhance the flavor of some food applications (McSweeney and Fox, 2009). In the pharmaceutical industry, it is used as a filler for drugs in tablets, capsules and aerosols.

Industrially, lactose is sourced from whey, a side product from cheese and casein production. The lactose production process can be described in three stages: increasing concentration, crystallization of lactose and purification (Wong and Hartel, 2014). Proteins in whey are first removed by ultrafiltration; producing a whey protein concentrate and whey permeate. Whey permeate has a lactose concentration of 5%; in a second stage, it is concentrated by evaporation to 39%–56% (Wong and Hartel, 2014). The lactose in concentrated whey permeate is subsequently crystallized as α-lactose monohydrate; the supersaturated whey permeate leaves the evaporator at a temperature between 65 °C and 70 °C and is slowly cooled down to 20°C–25 °C. While the solution is cooled, supersaturation is created and so the driving force for crystallization is increased. Industrial crystallization by gradual cooling generally takes up to 14–18 h (Yuping et al., 2006). After crystallization, the lactose crystals are separated from the mother liquor by centrifugation and an additional washing and centrifugation step is used to remove any remaining impurities (Wong and Hartel, 2014). The liquid that is separated by centrifugation is called de-lactosed whey permeate. Any remaining water content in the lactose crystals is removed in a fluidized bed dryer.

1.1. Lactose crystallization

Fig. 1 shows part of the lactose–water phase diagram constructed from data published by different authors (Wong et al., 2011)(Vu et al., 2003)(Hudson, 1908). The rate of nucleation can be characterized by the induction time, i.e. the time elapsed between the initiation of

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supersaturation and the initial formation of nuclei (Karpinski and Wey, 2002). The induction time can be used to divide the graph into different regimes: an under saturated solution regime, a metastable regime and a labile zone. In the under saturated regime, no crystal growth or nucleation occurs and it is a transparent solution. In the labile zone, supersaturation is high, which results in a relatively short induction time of between 10 and 36 h (Herrington, 1934) (Wong and Hartel, 2014). In the metastable zone, crystallization without the addition of seeds will not occur quickly. The induction time reported for crystallization without stirring in the metastable zone was 136 h (Herrington, 1934) (Wong et al., 2011). When lactose crystals are present, crystal growth and secondary nucleation are possible in the metastable regime (Wong and Hartel, 2014).

For industrial crystallization processes, it is important to produce relatively large and uniform crystals because this makes further separation and handling of the crystals easier. The optimum size of lactose crystals is 200–300 μm with a tomahawk shape (Durham, 2009). The size, size distribution and shape of the crystals depends on the type of solution and the operating parameters. Furthermore, the size and size distribution of lactose seeds have a large influence on the nucleation and growth rate during crystallization. Ideally, seed material has a small crystal size distribution with a minimal amount of aggregation and is free of small crystals (<20 μm)(Wong et al., 2011). Yuping et al. (2006) studied the effect of seed amount for lactose crystallization and reported an optimum amount of nuclei (27 mg/100 g).

In industrial crystallization, generally a large amount of fines is produced due to secondary nucleation; this limits the separation efficiency, resulting in low recovery rates (Paterson, 2009). There is a trade-off between the amount of supersaturation, rate of crystallization and the amount of secondary nucleation. Operating close to the solubility of lactose reduces the amount of nucleation, however it results in a lower crystallization rate. Wong et al. (2012) compared an industrial crystallization process with an improved process based on the metastable limit. The authors found that in order to minimize secondary nucleation or the production of fines, a cooling profile needs to be selected such that the concentration profile of the crystallization process lies within the upper metastable zone. They found that using a cooling profile based on the medium metastable regime produced 28% less fines than an industrial process.

Supersaturation ratios of α-lactose solutions depend on temperature, concentration and mutarotation equilibrium of α-/β-lactose, Visser (1983) developed a method to determine the supersaturation ratio:

$$S = \frac{C}{C_s - FK_m(C - C_s)}$$

where F and K_m are factors to account for β-lactose in the solution. In an industrial process, a supersaturation ratio between 1.5 and 2 is generally used (Visser, 1983; Wong et al., 2012; Yuping et al., 2006).

1.2. Low-temperature crystallization

Industrial lactose crystallization from whey is an energy-intensive process because of the evaporation step. Furthermore, high temperatures and long residence times, up to 18 h, are needed during cooling crystallization. Evaporators and crystallizers can suffer from fouling. Whey permeate contains about 370 ppm calcium and 440 ppm phosphorus; at these concentrations whey permeate is already saturated with calcium and phosphate (Durham, 2009). When whey is heated above 60 °C, calcium and magnesium phosphates and residual proteins, fat, etc. precipitate and form scaling on the evaporators and heat exchangers; this leads to higher energy and maintenance costs (Bylund and Svensson, 2015).

Several studies have been performed involving methods for improving the lactose crystallization process. Ultrasound is known to lower the induction times for lactose nucleation due to cavitation of the (lactose) solutions, this results in an increase in crystallization rate (Dincer et al., 2014; Zisu et al., 2014). Similar, gas addition, like nitrogen or carbon dioxide, during lactose crystallization increases the nucleation rate and yield. A larger amount of gas will result in a decrease in crystal size (Adhikari et al., 2018; Xun et al., 2017). Antisolvents, like methanol, acetone or ethanol can lower the solubility of the solute thus increasing the supersaturation. MacFhionnghaile et al. (2017) studied the effect of different antisolvents in combination of lactose crystallization. Mixtures of α-lactose monohydrate and β-lactose were crystallized under most conditions with β-lactose content increasing with increasing amount of antisolvent. Patil et al. (2020) investigated the recovery of lactose with a combination of antisolvent and sonication. They found that the highest lactose recovery was obtained using a mixture of acetone and ethanol as antisolvent.

In this research, a new crystallization method is investigated to produce lactose at sub-zero temperatures: eutectic freeze crystallization (EFC). The eutectic point of a solution is the point at which both the solvent and the solute start to crystalize. Although EFC has been used for the separation of brine streams (Lewis et al., 2010; Randall and Nathoo, 2015, 2018), limited research has been found by the authors for the recovery of heat-sensitive products in the food industry. In a patent by Spronsen (2017) freeze concentration is used to concentrate a lactose solution well below the eutectic point. They found that it was possible to freeze concentrate a solution up to 27 wt% without crystallization of lactose. After this concentration step lactose is crystallized at a constant temperature of 10–20 °C, the remaining mother liquid could be recycled to the reactor. In our research it is investigated if it is possible to combine the concentration and crystallization step at sub-zero temperatures.

From Fig. 1, the eutectic point of an aqueous lactose solution can be determined at 11 wt% and −0.7 °C. Using this, in theory, the solution

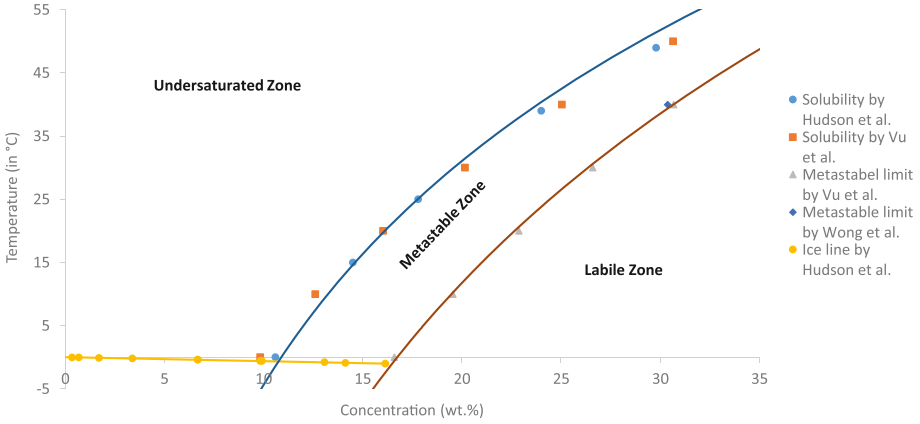

Fig. 1. Phase diagram of lactose–water solution (only α-lactose monohydrate). Data used from Hudson (1908), Vu et al. (2003) and Wong et al. (2011).

can be converted into pure ice and lactose (Fig. 2). Based on primary energy demands, converting water into ice is favorable over evaporation. The heat of solidification of ice produces 334 kJ/kg, whereas the heat of evaporation consumes 2265 kJ/kg. In practical operation, the energy consumption levels are closer. Fouling by calcium phosphate when using freeze concentration is limited because calcium phosphate precipitation is favored by higher temperatures (Durham, 2009).

Lactose crystallization at sub-zero temperatures is not unique, it does occur in ice-cream production as well, where lactose crystals can cause a sandy texture if they become too large. At temperatures below zero, lactose has greatly exceeded its solubility saturation and, from a thermodynamic point of view, could easily crystallize (McSweeney and Fox, 2009). However, nucleation is strongly dependent on temperature and viscosity. Where the higher supersaturation increases the driving force for crystallization, it is counter affected by the low nucleation rate due to the decreased temperature and increased viscosity of ice cream. Once nucleation has occurred, crystallization can proceed quickly (McSweeney and Fox, 2009). Nickerson (1954, 1956) investigated the effect of seeding on the rate and quantity of lactose crystallization in ice cream, they found that lactose crystallization is slow without the presence of initial nuclei (Nickerson, 1956). Furthermore, they found that if a small amount of lactose crystals was present initially, they caused the ice cream to become sandy more quickly than when a large number of nuclei were present. Livney et al. (1995) investigated the induction time and initial growth rate of lactose crystals in ice cream. They found that the induction time initially decreased when the temperature was lowered until a minimum time of 3 h was found between −10 °C and −12 °C. Further decrease of the storage temperature caused the induction time to increase again. The initial growth rate increased when the temperature was decreased from −5 °C to −10 °C. Further decrease would result in a lower initial growth rate.

The dependency on the amount of seed on crystal growth plus the slow nucleation kinetics found in ice-cream production provides an opportunity, it is an indication that crystallization of lactose from a solution, without excessive nucleation, is possible at sub-zero temperatures.

2. Materials and methods

2.1. Experimental setup

Experiments were performed using a crystallizer consisting of a double walled vessel with cooling fluid inside the vessel and cooling fluid circulating through the wall (Fig. 3). A glass beaker with a solution was placed inside the vessel. The cooling fluid between the vessel and glass beaker ensures good thermal contact between the wall of the vessel and the glass beaker. Essentially, liquid could be poured directly into the reactor, however, for experimental reasons, e.g. to look through and for easy removal of slurry, a glass beaker is used. The contact fluid was stirred with a magnetic stirrer at 200 rpm to ensure good heat transfer to the glass beaker. The cooling fluid in the jacket was cooled by a chiller with a flow of 10 L/min. Agitation of the lactose solution was done by an anchor stirrer inside the glass beaker. The use of an anchor mixer ensures that the area at the wall is well mixed and that a uniform temperature is created. The temperature inside the glass crystallizer beaker was measured using a precision temperature sensor (Tempcontrol PT 6180 with ASL F200 indicator), which has (calibrated) accuracy of 0.02K. Data acquisition and equipment control of the temperature indicator was done via an RS-232 connection and a program running in Python.

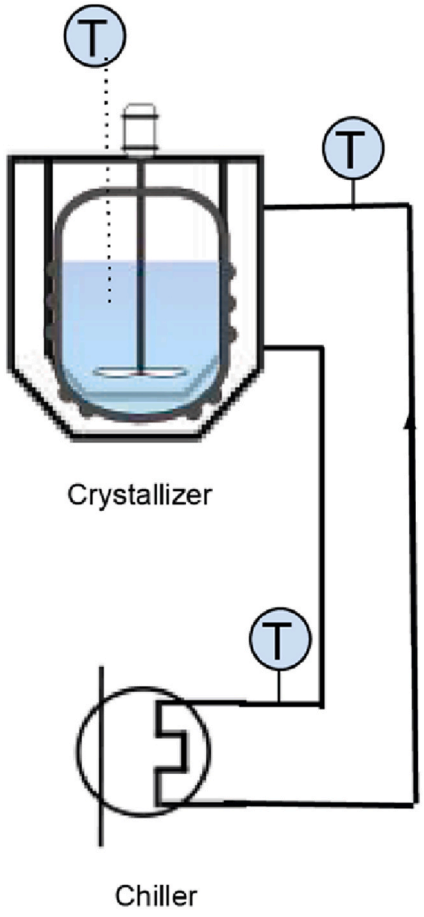

Fig. 3. Crystallization reactor for eutectic freeze crystallization.

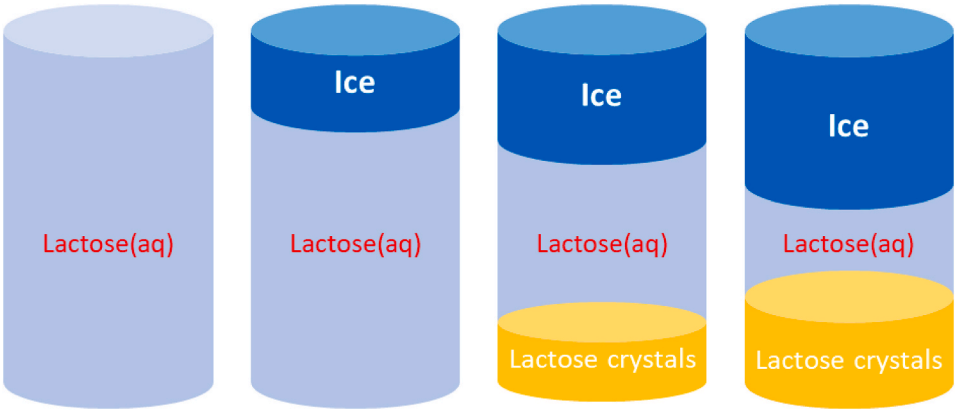

Fig. 2. An ideal development of an EFC process: 1. A lactose solution is cooled to temperatures below zero 2. The temperature drops below the freeze point and ice crystallizes, the concentration of lactose in the solution increases 3. Lactose crystallizes when the solution is saturated with respect to lactose, this is the eutectic point. Due to density differences ice floats to the top and lactose crystals sink to the bottom 4. The simultaneous crystallization of ice and lactose will continue until the process is stopped.

2.2. Materials

2.2.1. Lactose concentrate

Lactose solutions were prepared by dissolving analytical grade lactose monohydrate (≥99% α-lactose) in hot (60°C–80 °C) MilliQ water. During dissolution, the solution was stirred with a magnetic stirrer. The concentration of the solution was determined using a refractometer (Krüss AR4), and any evaporation was compensated by adding MilliQ water.

2.2.2. Seeds

Micronized lactose from DFE Pharma (Lactohale 300) was used as seed. Fifty percent of the particles are smaller than 5 μm and ninety percent of the particles are smaller than 10 μm. The material does not have a defined morphology. The seeds were produced by milling and fractionated by air classification. Fig. 4 shows the particle size distribution of the seed crystals.

2.3. Crystallization methods

The effect of low-temperature crystallization on the quality and quantity of lactose was investigated by two methods. First, a sub-EFC process whereby both ice and lactose are produced simultaneously, secondly, a freeze concentration process with removal of the ice and a low-temperature lactose crystallization step.

2.3.1. Eutectic freeze crystallization

A 900 ml solution of 30 wt% lactose was used to investigate EFC of a pure lactose–water system. The solution was cooled in ± 4h with a chiller temperature of −4.5 °C, resulting in a liquid temperature before ice nucleation of −3 °C. A lower temperature than the eutectic temperature was chosen as there would be no supersaturation of ice and lactose above the eutectic temperature and thus no driving force for crystallization. When the temperature dropped below −2.7 °C, 0.08% seed material based on the total amount of lactose (250 mg/kg solution) was added, and the operation was kept at constant temperature for ~22 h. This was chosen to exceed the time used in an industrial lactose crystallization process (14–18 h) to get more insight in the full development of the process. The low seed amount was based on the optimum amount reported by Yuping et al. (2006); due to the small crystal size of the seed, a relatively small amount resulted in a large number of crystals.

The concentration of the solution was measured by sampling a few millilitres and measuring the brix value using a refractometer (Krüss). After 22 h, the reactor was filed with ice/lactose and the operation was stopped. Continuing for a longer period was impossible because the stirrer would not be able to stir the thick slurry. For our 1-L batch process, the large volume of ice made it impossible to effectively separate the slurry into ice, lactose crystals and mother To still be able to separate the slurry, we took a step back and first melted the ice, leaving only lactose crystals and mother liquid. The final concentration of the mother liquid (after ice melting) was well above the solubility concentration; with no dissolution and, as crystallization occurs slowly, no addition of mass was expected.

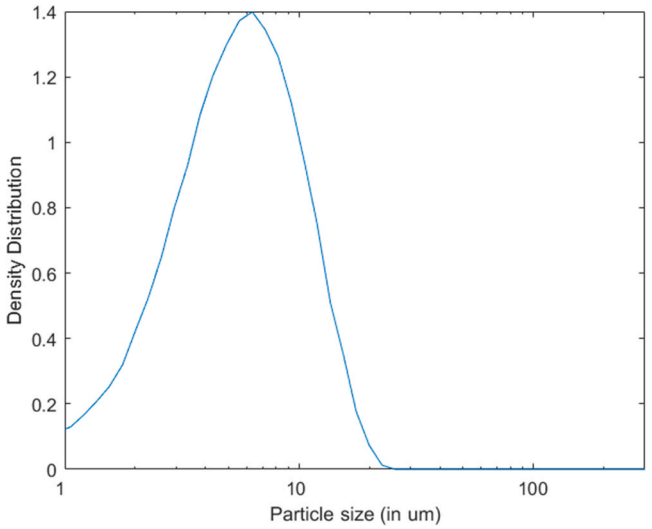

Fig. 4. Particle size distribution of seed (DFE Pharma, Lactohale 300).

With the ice melted, the slurry was allowed to settle and was filtered over a sintered glass filter with pore size 16–40 μm. The lactose was subsequently washed with 2-propanol to remove any moisture. The so washed lactose crystals were dried at 45 °C for 24 h to remove any remaining free water (not the hydrate). The overall mass balance was evaluated by determining the final concentration in the solution as well as the recovered lactose, enabling the calculation of the amount of ice. See appendix A for a detailed description of the mass balance. The lactose crystals were investigated under a microscope (Leica dm750 with polarized light) and a particle size analyser (Sympatec laser diffraction).

2.3.2. Uncoupled system: freeze concentration and sub-zero lactose crystallization

To investigate the process in more detail, the system was uncoupled into two steps: (1) freeze concentration and (2) crystallization at sub-zero temperatures without ice formation.

2.3.2.1. Freeze concentration. Before crystallization, a concentration step is generally used to produce a supersaturated liquid to create a driving force for crystallization. For this research, five different solutions with a lactose content ranging from 5 to 30 wt%, were investigated to check if it was possible to concentrate the solutions by freeze concentration without the development of lactose nuclei. A lactose solution (800 mL) was poured into the crystallizer, and the temperature of the chiller was set to −5.5 °C. The solution was agitated with an anchor stirrer at 70 rpm. When the temperature of the solution stabilized, ice spontaneously nucleated after 1–2 h. The experiment was stopped when the glass beaker was filled with ice. The slurry was filtered over a sintered glass filter with pore size 40–100 μm. Three washing steps with 50 mL of cooled (0 °C) MilliQ water were applied before removing the ice from the filter. Melting of ice by the washing fluid is expected to be neglectable as heat transfer from washing water of ±0 °C is low. A mass balance was made, and the final concentration of the solution, ice and wash water was determined using a refractometer (Krüss AR4). A sample of the concentrate was investigated under the microscope to check if there was spontaneous nucleation. The growth rate of ice at constant chiller temperature (−5.5 °C) was determined for different start concentrations; the growth rate was defined as the mass of pure ice divided by the residence time.

2.3.2.2. Crystallization of lactose at sub-zero temperatures without ice formation. A 30 wt% lactose solution was used to investigate crystallization of lactose after freeze concentration; 950 mL of lactose solution was added to the crystallizer. After dissolving the lactose at 50 °C the solution was cooled as fast as possible. The temperature of the chiller was set to −3 °C, resulting in a final temperature of the solution of −1.9 °C and a supersaturation ratio of 4.1 (determined by the method described by Visser, 1983). As crystallization proceeded, the supersaturation decreased because the temperature was constant. Different amounts of lactose seeds, namely 0.08, 0.2 and 5 wt% based on the total lactose content, were added when the temperature of the liquid reached −1.85 °C. The amount of 0.08 wt% was based on the optimum reported by Yuping et al. (2006). Seed was added from room temperature; the temperature increase for 5% was 0.19 °C, 0.04 °C for 0.2% and there was no effect observed for 0.08%. The temperature of the chiller was kept

stable for 22 h, which is relatively close to the residence time in an industrial process. The extent of crystallization was determined by sampling a few millilitres of solution and measuring the brix degree using a refractometer (Krüss).

The crystallized slurry was filtered over a sintered glass filter with pore size 16–40 μm. The filtrate was subsequently washed with 2-propanol to lower the water content. The lactose crystals were dried until constant weight at 45 °C in an incubator to remove any remaining water. An overall mass balance was evaluated by determining the final concentration and the amount of lactose recovered. The lactose crystals were investigated under a microscope (Leica dm 750 with polarized light) and a particle size analyser (Sympatec laser diffraction) to determine the shape and size of the particles.

2.3.3. Accuracy of experiments

Eutectic freeze crystallization, freeze concentration and sub-zero crystallization of lactose solution were investigated in a batch reactor. From initial experiments (not shown here) the optimum operating conditions were determined. During the experiments the chiller temperature and agitation rate was kept constant to ensure constant conditions. All crystallization experiment were done in duplicate and the freeze concentration experiments in triplicate to ensure that the results are reliable. The resulting standard deviations for the freeze concentration experiments were determined and added to the figure. Every sample was checked three times by manual refractometer to ensure that the same value was obtained. Refractive measurements with known amounts of lactose were used to make a calibration curve to relate the refractive index (°Brix) to the lactose concentration. Particle size analysis of the solid sample were performed in duplicate or triplicate, were applicable the standard deviations were given.

3. Results and discussion

3.1. Crystallization under sub-eutectic conditions

In two experiments, with the same operating conditions, 30 wt% lactose solutions were cooled to sub-eutectic conditions (−3 °C). At these conditions the solution is already supersaturated with respect to both lactose as ice. It was found that it was possible to crystallize lactose and water (i.e. ice) simultaneously. The final slurry was a mixture of lactose, ice and remaining liquid. Fig. 5 shows the two temperature profiles of the lactose solutions during an EFC experiment at a constant chiller temperature of −4.5 °C. Due to the stochastic nature of the process, the temperature profiles have slight differences although the same operating conditions were used. The point of ice nucleation of the two curves was chosen to overlap by shifting the second curve in time.

At −2.7 °C, lactose seeds were added (1). One could expect that the crystallization of lactose would start immediately after seeding, however, the temperature still drops after adding seed and the seed does not seems to have a pronounced effect. After seeding lactose, ice spontaneously nucleated (2). A rapid increase in temperature occurred due to the release of latent heat of ice crystallization (2). After ice nucleation, the temperature decreased slightly by 0.02 °C. After 2.5 h of ice nucleation, the temperature increased, indicating that lactose was being crystallized, latent heat was released and the concentration decreased (4). If only ice was being crystallized, then a decrease in temperature would be expected because the freeze point decreases with concentration. Nine hours after ice nucleation, the temperature of the solution decreased again, indicating that the concentration of the solution increased (5). The final concentration of the solution was found to be 29.5 wt% and 29 wt% lactose for experiments A and B, respectively, which is only slightly below the starting concentration of 30 wt%. Although steady state was not yet achieved, the experiment was stopped because the 1-L batch reactor was filled with ice, lactose and mother liquid, and the stirrer would not be able to stir the thick slurry.

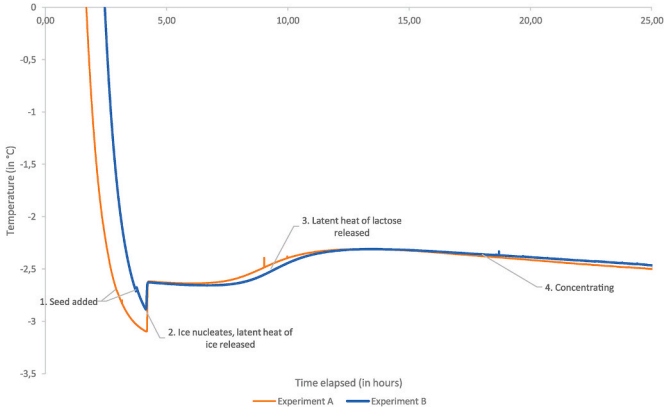

Fig. 5. Temperature profiles of the solutions during sub-eutectic freeze crystallization.

Fig. 6 shows a polarized light image of the lactose crystals extracted from the reactor from the first experiment. The seed material does not have a clear morphology, whereas the crystals produced by the process have a triangular or tomahawk shape. The particles are crystals because they alter part of the polarized light, but the polarized light is only slightly altered by the crystals, which indicates that they must be thin.

The volumetric mean diameter particle size of the crystals was for both experiments 18 μm; see Fig. 7 for the full particle size distributions. Although the filter has a pore size of 16–40 μm, it was able to separate the slurry properly; the final products were a clear solution and a solid cake. Due to the efficiency of the filter and the self-filtering effect of the solid cake, it was possible to separate particles smaller than 16 μm. When viewed under the microscope, only a few crystals were visible in the solution; in comparison with the lactose recovered (115 g), this is insignificant.

For our 1-L batch process, the large volume of ice made it impossible to effectively separate the slurry into ice, lactose crystals and mother liquid. The mass balances were therefore determined based on the description in Section 2.3.1. The total amount of solid lactose recovered was 42% and 41% of the initial lactose amount for experiments A and B, respectively. The ice fraction was calculated based on the initial mass of the solution and found to be 26% and 24%, respectively.

A possible solution for the difficult separation of ice/lactose and mother liquid would be to go from a batch process to a continuous process. Continuous removal of ice and lactose would make the separation easier, because a lower slurry density can be applied. Also, the residence time in the crystallizer and the amount and size of the lactose

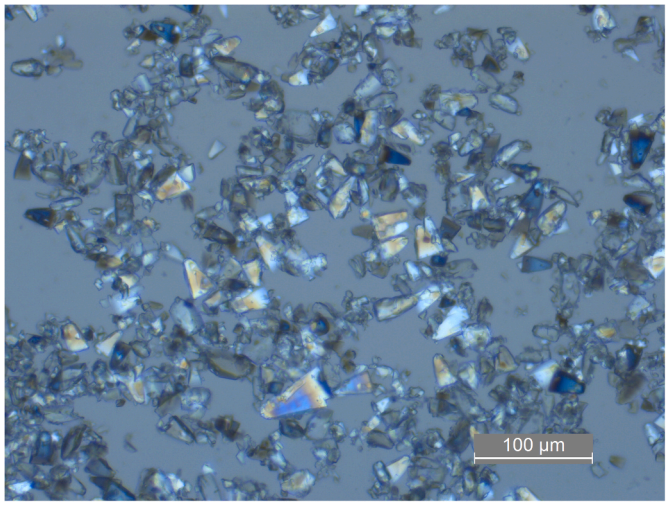

Fig. 6. Lactose crystals after 22 h produced under sub-eutectic conditions.

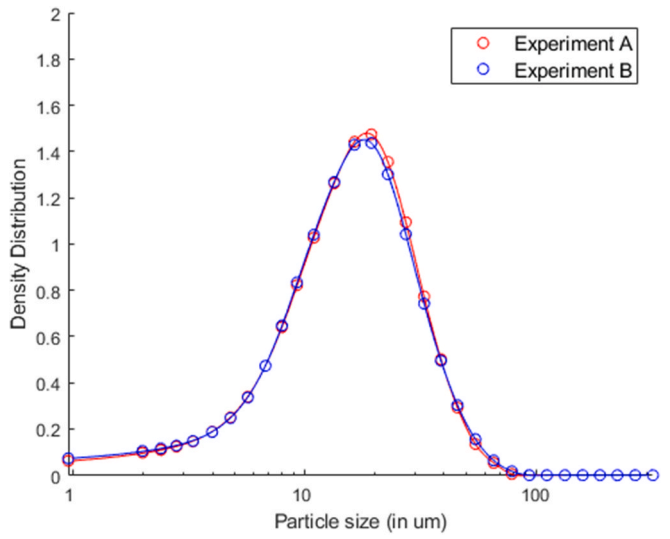

Fig. 7. Particle size distribution of the lactose crystals produced by eutectic freeze crystallization.

seeds could be optimized to create larger lactose crystals.

3.2. The uncoupled system: freeze concentration and sub-zero lactose crystallization

In Section 3.1, it was shown that simultaneous crystallization of lactose and ice is possible. However, separation of the different fractions in a batch system is difficult. To investigate EFC in more detail and to improve the lactose crystal quality (size and shape), the process was separated into two parts: freeze concentration and crystallization at sub-zero temperatures without ice formation.

3.2.1. Freeze concentration part

Five different solutions, with a lactose content ranging from 5 to 30 wt%, were investigated to check if it was possible to concentrate the solutions by freeze concentration without nucleation of lactose. The point of ice nucleation can be easily determined by the sudden increase of in the temperature due to the heat released by ice crystallization just after 1 h (Fig. 8). The temperature after initial ice nucleation is the freezing temperature of the solution. The Hudson's freeze line in Fig. 1 could be extended by our measurements as given in Fig. 9. The freeze line produced by Hudson et al. showed a close fit with these results.

In Fig. 9, the metastable limit reported by Vu et al. (2003) is extrapolated to make an intersection with the determined freeze point line; the intersection lies at −1.2 °C and 16 wt%. Although this

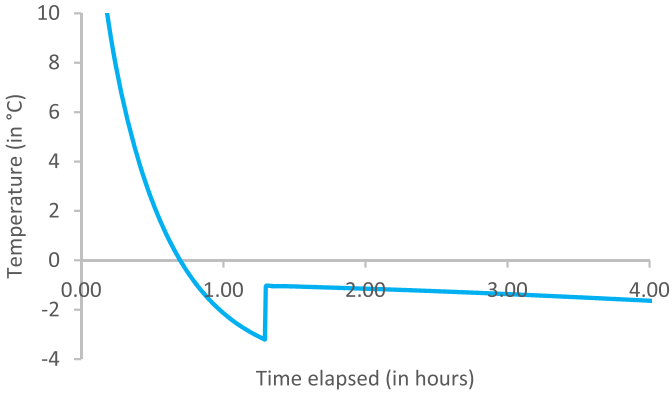

Fig. 8. Temperature profile of the freeze concentration batch operation of a 10 wt% lactose solution.

interpolation must be done with caution, because the exact shape of the metastable limit below zero is unknown, it is expected that lactose will spontaneously nucleate below this value. For a start concentration up to 15%, lactose did not crystallize during the freeze concentration experiments. However, when a start solution of 20 wt% and 30 wt% lactose was concentrated, a small amount of small lactose crystals (<10 μm) were visible when viewed under a microscope. This is in accordance with the extrapolated metastable limit. It is expected that the presence of a small amount of nuclei/crystals will not affect the overall process, because they can serve as initial nuclei in the lactose crystallization process.

In the different experiments, lactose solutions were concentrated 1.1–1.5 times the start concentration with an initial concentration between 5 and 30 wt% (Appendix B). For a low lactose concentration, a relatively large amount of water needs to be converted to slightly increase the concentration. To increase the lactose concentration from 5 to 7.5 wt%, 47% of water needs to be removed from the solution, whereas to increase the lactose concentration from 20 to 26 wt%, a similar 46% of water needs to be removed (Appendix B).

The growth rate of ice decreases with increasing concentration at constant temperature (Fig. 10). As the freeze point temperature decreases with increasing concentration, the driving force for ice crystallization decreases when a constant coolant temperature is used.

From the experiments, it can be concluded that an aqueous lactose solution can be concentrated to 30 wt% by freeze concentration without significant nucleation of lactose.

3.2.2. Sub-zero crystallization of lactose without ice formation

To study the sub-zero crystallization of a 30 wt% lactose solution, a chiller temperature of −3 °C was chosen so that only lactose will crystallize and no ice will be formed. Initial experiments showed that crystallization was possible; however, operating conditions, seed type and the amount had to be optimized to obtain large uniform crystals.

The influence of seeding was investigated by varying the seed amount from 0.08% up to 5% DFE Pharma lactose. Fig. 11 shows microscope images with polarized light of lactose crystals produced after 22 h for 5%, 0.2% and 0.08% seed, respectively. The influence of different amounts of seed can be clearly seen. Five percent seeds result in small crystals with a mixture of shapes: triangles and particles without a clear crystal structure. The particles are crystals because they alter part of the polarized light. Seeding with 0.2% DFE Pharma led to larger crystals with triangular morphology. The crystals are thin as they hardly change the polarization. When 0.08% seed is used, the crystals have a much larger and a clear tomahawk morphology and can be detected clearly under polarized light.

Fig. 12 shows the particle size distributions for the experiments above; all results are based on volumetric distributions. The second peak of the 0.08% graph in Fig. 12 was further investigated by dynamic image analysis. It was found that this peak in the volumetric distribution was due to the formation of aggregates. A two-term Gaussian distribution was used to determine the mean of the first peak of the 0.08% graph. Also, the difference in the height of the peaks can be explained by the presence of aggregates. From Figs. 12 and 13, an evident increase in particle size can be seen, from a volumetric mean diameter of 7 μm for 5% seed up to 26 μm for 0.08% seed. It can be concluded that lactose crystals produced with a low seed amount grow larger in size. This is in agreement with the results found by Nickerson (1954, 1956), where a small amount of nuclei caused ice cream to become sandy more quickly than with a large amount.

The differences in the shape and size of the crystals resulted in different filtration behavior. Filtration of the larger tomahawk crystals produced with 0.08% seed were easy to filter within a minute, and the final product was a wet powder. Filtration of the small crystals from the experiment with 5% seed was cumbersome, filtration took a long time and removing the filtrate was difficult because it was a hard paste.

During the experiments, the concentration of lactose in the solution

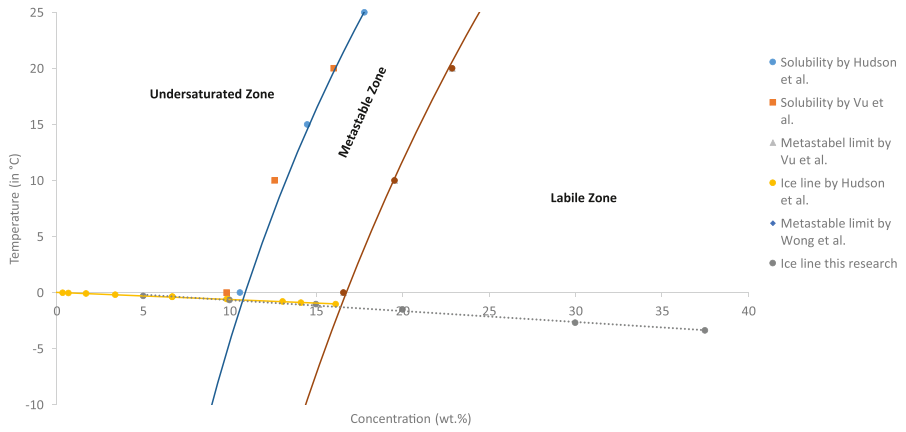

Fig. 9. Extended and zoomed in version of the phase diagram of lactose. Data used from Hudson (1908), Vu et al. (2003) and Wong et al. (2011).

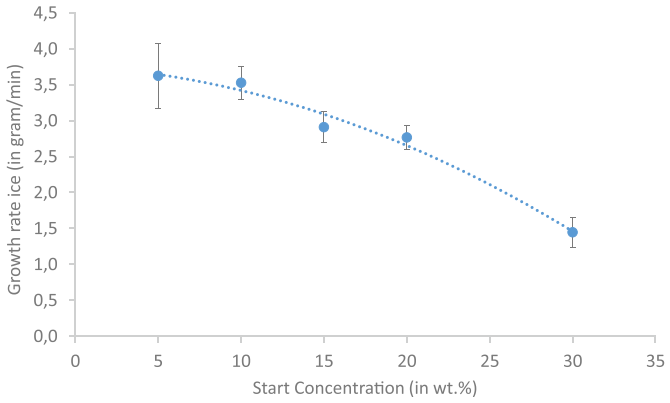

Fig. 10. Growth rate of ice as a function of the start concentration of lactose at a chiller temperature of −5.5 °C.

was continuously monitored. In Fig. 14 the concentration is given as a function of the elapsed time; the missing data points between 5 and 20 h are because the concentration was not measured overnight. When the temperature of the solution was −1.85 °C, seeds were added to initiate the crystallization process. For 5% seed, the concentration decreases fast after adding seed, indicating a high crystallization rate. When the concentration decreases, i.e. supersaturation decreases, the crystallization rate also decreases. For 0.08 wt% seed, the concentration initially does not change; after 2 h there is a slight decrease in concentration. The concentration decrease is slower and constant over time, indicating a slow crystallization rate. The influence of the amount of initial surface area can be clearly seen in Fig. 12; a higher seed surface area resulted in a higher mass deposition rate.

In an industrial process, the temperature profile is selected such that supersaturation is small, generally 1.5–2. This to minimize the amount of (secondary) nucleation resulting in a process that is governed by crystal growth producing large uniform crystals. If a higher supersaturation is used, it would result in excessive nucleation and thus many small crystals. At sub-zero crystallization of lactose, the start concentration is 30 wt% at a temperature of −1.85 °C, resulting in a supersaturation ratio of 4.1. The final concentration of the mother liquid after crystallization increases from 21% up to 22.8% for 5% and 0.08% seed, respectively; under these conditions, the final supersaturation ratios are still 2.7 and 3, respectively. When the crystallization is allowed to run longer, the concentration still decreases until ice nucleates as the concentration drops below the freezing point (see Appendix C, Fig. 2, experiment 2). In comparison with an industrial process, the initial and final supersaturation are extremely high. Under these conditions, it would be expected that nucleation will govern the crystallization process. However, similar to an industrial process, the crystallization at sub-zero temperatures is controlled by the available surface area rather than the amount of supersaturation. Apparently, the effect on the nucleation rate with high supersaturation is counter affected by the low temperature used. Furthermore, the final size of the crystals is dependent on the amount of crystals present initially, e.g. with less particles, every particle can growth bigger in size. From this, we can conclude that for sub-zero crystallization of lactose, although high supersaturations are used, crystal growth is the predominant process rather than nucleation.

The overall yield of the process, based on recovered material versus the initial amount of lactose, was 32%, 35% and 42% for 0.08%, 0.2% and 5% seed, respectively. Paterson (2009) reported a theoretical yield for a slow cooling crystallization process of 82.6%. In practice, however, there are losses during separation and washing of the crystals; industrial yields are reported to be around 60%–65% (Paterson, 2009). The yield for the batch system in this paper is relatively low, however the system is

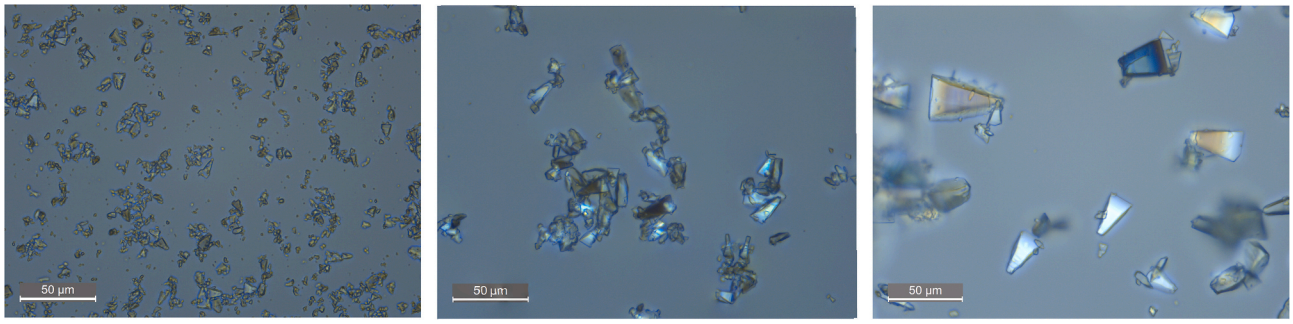

Fig. 11. Lactose crystals produced with 5%, 0.2% and 0.08% seeds (left to right). The second and third images were created by focus stacking different pictures from a microscope with polarized light.

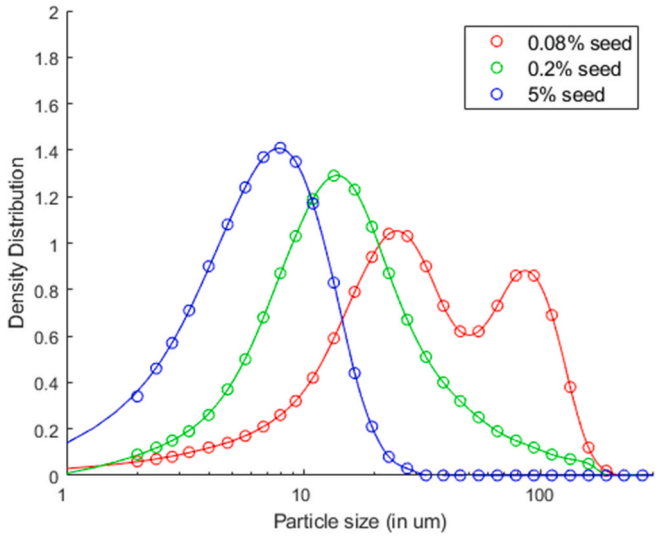

Fig. 12. Particle size distribution for crystallization below zero with 0.08%–5% seed.

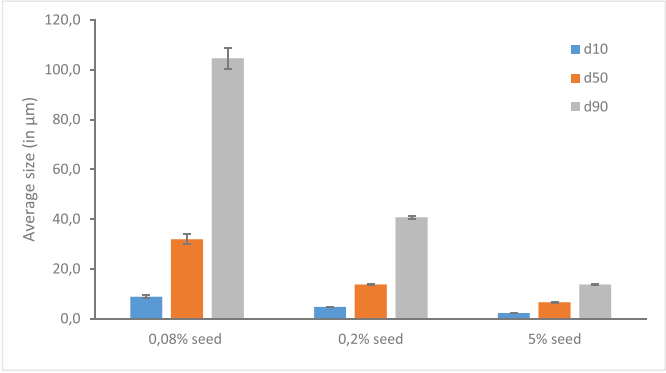

Fig. 13. Particle size d10, d50 and d90 as function of seed amount.

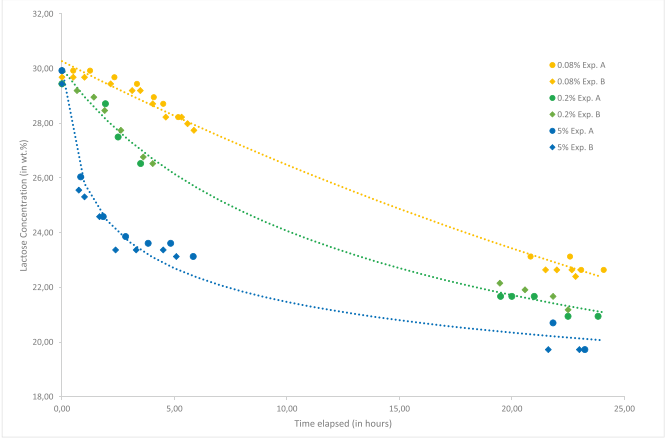

Fig. 14. Concentration profiles during low-temperature crystallization, t = 0 is the time of seeding. The lines between the points was added for guiding the readers eye, the regression was based on the general expression for crystal growth $\left(G = \frac{d\Delta c}{dt} = K_g \Delta c^g\right)$.

not optimized. One way for optimizing the yield would be to treat the mother liquor again in a second batch process. Furthermore, if the process would be made continuously and part of the liquid after crystallization would be recycled, then the yield is expected to increase.

4. Conclusion

This study presents a low-temperature crystallization method for the separation of lactose. Two methods were presented: (1) a sub-eutectic process where simultaneous ice and lactose is formed and (2) concentrating by freeze concentration and subsequently a low-temperature crystallization process.

It was found that simultaneous crystallization of lactose and water (ice) was possible under sub-eutectic conditions. The lactose crystals had an average size of 18 µm and they had a thin triangular or tomahawk morphology.

Experiments show that it is possible to concentrate a lactose solution up to 30 wt% without significant nucleation. The freeze points determined in these experiments were added to the phase diagram of lactose–water. For the lactose crystallization step, it was found that the amount of seed has a large influence on the final morphology, crystal size and yield. Seeding with a larger amount of 5% led to a small amount of crystal growth with tomahawk crystals as well as particles without a clear structure. Seeding with a small amount (0.08%) ensured more crystal growth leading to crystals with an average size of 26 µm and a tomahawk shape. Although the supersaturation was large at sub-zero temperatures, no excessive primary or secondary nucleation was apparent during the process. A larger available surface area increased the crystallization rate substantially. From this, it can be concluded that, although highly supersaturated conditions are used in sub-zero crystallization of lactose, crystal growth is the predominant process rather than nucleation. The yield found for the batch system used in this paper was 32%–42%.

Credit author statement

Ruben Halfwerk, Conceptualization, Investigation, Formal analysis, Writing – original draft, Visualization, Project administration. Doekle Yntema, Supervision, Project administration, Funding acquisition, Writing – review & editing. Jaap Van Spronsen, Conceptualization, Writing – review & editing. Albert Van der Padt, Supervision, Conceptualization, Project administration, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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