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# Effect of galacto-oligosaccharide concentration on the kinetics of lactose crystallisation

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## ABSTRACT

Galacto-oligosaccharides (GOS) are said to have a retarding effect on the nucleation and growth of α-lactose monohydrate crystallisation. Studies regarding the kinetic parameters for crystal growth and nucleation were conducted utilising gravimetric analysis and laser light scattering to follow the lactose crystallisation. A statistically significant retarding effect of GOS on lactose crystal growth at concentrations between 0.8 and 3% (w/w) GOS of total solution was observed. A significant nucleation suppressing effect was confirmed further. Studies concerning the change in crystal morphology revealed that as GOS concentration was increased, a transition from the common tomahawk shape to a shape with shortened crystal faces away from the apex to a needle like appearance occurred, strongly suggesting a growth retardation effect on the (010) face. Crystals subjected to high pressure liquid chromatography (HPLC) analysis did confirm an incorporation or inclusion of GOS into the crystal lattice.

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## 1. Introduction

Galacto-oligosaccharides (GOS), a product of lactose hydrolysis and transglycosylation by β-galactosidases (Sako, Matsumoto, & Tanaka, 1999), are suspected to be one of the reasons for the decrease in crystal yield observed in α-lactose monohydrate crystallisation from batches of whey that have been known to have undergone some fermentation. This is because GOS have a similar structure to lactose, allowing the GOS to directly interfere with the incorporation of further lactose molecules into the preexisting crystal lattice. Conditions for structural interaction with α-lactose monohydrate crystal lattice structures were determined first by van Kreveld (1969). Further studies by Visser and Bennema (1983) and Dincer, Parkinson, Rohl, and Ogden (1999) confirmed those conditions indirectly. These conditions are an identical conformation at the β-4 galactosyl moiety and or at $C_4$ of the glucose moiety. As shown in Fig. 1, GOS, represented by 6′galactosyl lactose, present both of the configurations. This makes them possible crystallisation retarders.

The only paper that studied the effect of GOS on lactose crystallisation behaviour (Smart & Smith, 1991) found that galactosyl lactose, a galacto-oligosaccharide, showed a remarkable retarding effect on lactose crystallisation. The aim of this work is to qualify and quantify the effects GOS have on the crystallisation kinetics of α-lactose monohydrate. In addition, it was desired to establish an understanding of the specific type of inhibitor GOS represent and their effect on α-lactose monohydrate morphology.

## 2. Materials and methods

### 2.1. Materials

Pharmaceutical grade hydrous lactose (Wyndale, Kapune, New Zealand) was used in the experiments. GOS were supplied by Friesland Campina Ingredients North America, Inc. (Paramus, NJ, USA) in the form of Vivinal-GOS (GOS syrup with 57% GOS on a dry basis consisting to at least 67% of trisaccharides and further containing ~23% (w/w) lactose, ~20% (w/w) glucose, and ~0.5% (w/w) galactose). The “impurity” glucose present in the Vivinal-GOS has been reported to have no effect on α-lactose crystal morphology at concentrations levels encountered in this study, i.e., <5% (w/w) of the final solution (Michaels & van Kreveld, 1966).

Standard analytical grade methanol was used in particle size distributions analysis throughout the growth experiments. Edetate calcium disodium (CaEDTA) concentrated solution (50 mg $L^{-1}$) was

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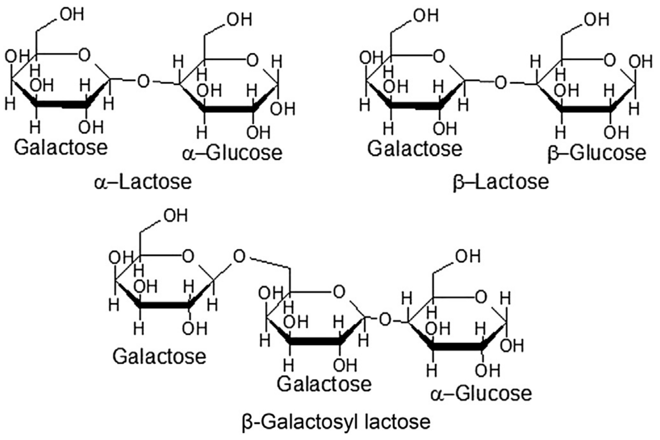

**Fig. 1.** Chemical structure of α-lactose, β-lactose, and 6′-galactosyl lactose.

used as the mobile phase for high performance liquid chromatography (HPLC) analysis.

### 2.2. *Preparation of lactose solutions*

Preparation of supersaturated solutions was achieved by adding a calculated amount of α-lactose monohydrate and GOS liquor to a preheated amount of distilled water and stirred under appropriate temperatures till all visible material had dissolved. This was followed by a short heating phase to over 90 °C for around 10 min in covered beakers, to dissolve possible ghost nuclei still inhabiting the solution. Cooling of the solutions was initiated by placing the beakers in a temperature controlled water bath at 30 °C. Solutions were then filtered through a Wattman Number 100 filter paper (100 μm) to remove any insoluble impurities present in the solution and transferred into the crystallisation beakers.

### 2.3. *Refractive index of lactose solutions*

For an optimal particle size distribution (PSD) analysis, the Mastersizer 2000S (Malvern Instruments Ltd, Malvern, UK.) that was used for analysis needs correct and precise information about the optical properties of the material subjected to analysis and the dispersion medium used. The refractive index of the circulated solution was estimated by using the equation developed by Butler (1998) as 1.3300. The refractive index of α-lactose monohydrate crystals was taken as 1.533 and the specific density as1.54 (Westhoff, Kuster, Heslinga, Pluim, & Verhage, 2000).

### 2.4. *Growth studies*

Crystal growth rates were measured by recording weight change of uni-sized seed crystals in different supersaturated and GOS concentrated solutions, after a growth period of four hours under constant stirring (400 rpm) and temperature (30 °C). The uni-sized α-lactose monohydrate seed crystals were obtained through mechanical sieving in an electronic sieve shaker (EMS-8, Electrolab, Mumbai, India) for 20 min. The chosen sieve size fraction used for the seeding material was 106–125 μm. The range of absolute α-lactose supersaturation ($S_{abs}$) levels used in growth studies [0.8–8.6 $C_\alpha - C_{\alpha s}$, (g α-lactose 100 g water$^{-1}$)] was chosen to prevent nucleation during the experiments resulting in misleading observations. $C_\alpha$ being the initial concentration of α-lactose present in solution upon preparation with $C_{\alpha s}$ the equilibrium/solubility concentration of α-lactose monohydrated. An example calculation for determining the amount of α-lactose monohydrate that needs to be added to produce a solution with the correct supersaturation, defined in terms of the absolute supersaturation, is shown in the on-line Supplementary Material. The degree of GOS (0–3%) added was to simulate the natural range of GOS present in industrial crystallisation processes.

Growth solutions were prepared according to the description given above in 250 mL Schott bottles, before transferring the solutions into 1000 mL glass beakers equipped with baffles. A known amount of seed crystal was added into the beakers before placement into the 30 °C water bath where the stirrers were started. After completion, the beakers were retrieved and their contents vacuum filtered through a pre-weighted filtration unit equipped with a 0.45 μm pore size filter paper. Washing with a slightly supersaturated lactose solution (23 g lactose 100 g water$^{-1}$) guaranteed that all crystalline material had been transferred from the crystallisation beakers into the filtration units. The filtration units were placed into a drying oven for approximately 180 min at 85 °C. After the initial drying period the filter crucibles were placed into a desiccator, where they were allowed to cool down to room temperature and then weighted. “Total” free water removal was ensured by using additional drying/weighting cycles for approximately 45 min until a weight difference of less than 0.02 g was observed.

Laser light scattering analysis was used to measure the volume mean diameter of the initial seed crystals using a Malvern Mastersizer 2000S (Malvern Instruments Ltd) using a small sample unit. Conversion of the mass based growth rate obtained from the measured weight difference, to the more common form of size related increase over time, was carried out using the conversion method formulated by (Thurlby, 1976) assuming a constant specific growth rate of all crystal faces.

All data were subjected to a single analysis of variance (95%), proving a significant difference between the means. A post applied Tukey test (95%) confirmed the difference in all cases except were the reference values were compared against the 0.4% (w/w) GOS containing solutions. This was probably due to the variance of the applied measuring method, i.e., imprecision associated with the gravimetric weight determination.

### 2.5. *Nucleation studies*

Nucleation studies were carried out using an abbreviated method based on that of Kauter (2003) for studying the effect of lactose impurities on secondary nucleation. Kauter (2003) used a laser light scattering apparatus to obtain, at different stages during experimental runs, the volume percentage occupied by crystals in the sample container and used their particle size characteristic values to calculate the actual number of particles generated in the system by secondary nucleation. A linearisation of numbers delivered the secondary nucleation rate.

The studies performed here extend this approach, studying the changes in overall nucleation behaviour with increasing levels of supersaturation and GOS concentrations in solution over a set time of180 min. The main difference was that in these experiments no seed crystals were added into the highly supersaturated lactose solution; supersaturated solutions [(12–18 $C_\alpha - C_{\alpha s}$, g α-lactose 100 g water$^{-1}$)] were placed into a temperature controlled water bath set to 25 °C. Agitation was generated through a multi impeller system set to 400 rpm. Sample aliquots were withdrawn from the solutions at different stages of the experiment and transferred for analysis into the Mastersizer previously aligned with saturated lactose solution (23 g lactose 100 g water$^{-1}$). This allowed the extraction of PSD and fractional volume percentages given a particular size range. The sample size taken for analysis was

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