



Trade Science Inc.

December 2007

Volume 2 Issue 3

CHEMICAL TECHNOLOGY

An Indian Journal

Full Paper

CTAIJ 2(3) 2007 [114-118]

The effect of glucose on the sucrose crystallization: modelling and experiments

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Received: 26th October, 2007 ; Accepted: 1st November, 2007

ABSTRACT

This work is devoted to study the effect of glucose on the the quality of sucrose crystallization in batch crystallizer. The liquid phase concentration in crystallizer and a supersaturation profiles was measured by using a refractometer. The logiciel LUCIA "Laboratory Universal Computer Analysis Image" was used to determine the Crystal Size Distribution (CSD) by analysing the obtained image by optical microscope and Scanning Electron Microscopic (SEM). A non-linear optimization method is applied to estimate the growth and nucleation rate parameters from batch cooling crystallization experiments. The calculated results are in agreement with those observed and determined by LUCIA. The effect of glucose on the mean particle size of the final product is discussed.

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KEYWORDS

Nucleation;
Secondary nucleation;
Crystallization;
Sucrose;
Modeling.

INTRODUCTION

Crystallization is a solid-liquid separation process, where molecules are transferred from a solute dissolved in a liquid phase to a solid phase. The molecule is governed by nucleation and growth rates. This is known as crystallization kinetics. In sugar manufacturing, crystallization is a crucial step upon which the rate of sugar extraction depends.

Crystallization in sucrose solutions involves both nucleation and crystal growth. According to the classical theories of nucleation^[1] Secondary nucleation is the main pathway followed industrial crystallization processes. The formation of nuclei is unwanted in many crystallizations, especially sugar crystallization, because

it widens the range of the crystal size distribution. A broader size distribution range means the product of the crystallizer is out of specification and the flow properties of the product are unsatisfactory. It is to the industry's benefit to avoid the occurrence of nucleation. Nucleation in the presence of other crystals does not occur below the secondary nucleation threshold (SNT). Thus, the position of the SNT should be identified and the variables that affect the nucleation above the SNT should be investigated. The nucleation can be a major determinant of quality in sugar-based products. The kinetics of nucleation and crystal growth require supersaturation, which is obtained by temperature changes and can be affected by impurities.

For a better understanding the role of oversaturation

ration and the nucleation phenomenon, several models have been developed in the literature^[1,2,3]. All models are based on the population balance equation. These works are treated the crystallization of sucrose without studying the effect of impurities on the nucleation and growth rates. Indeed, the effects of impurities in the secondary nucleation have little attention in the literature.

The object of the present work is aiming to investigate the effect of glucose on the growth and nucleation rates. This is achieved by comparing the measured concentration profile in solution and the profile predicted by a dynamic mathematical model.

EXPERIMENT

The sugar contains 99% of sucrose, was provided by the Belgian company of sugar refinery (Tirelemeont). Glucose(99%) was supplied by Sigma. Distilled water was used for the preparation of the treated solutions. The experimental apparatus used in this study consisted of a Crystallizer with contenance 2 L, the solution is agitated using an agitator provided with a propeller Mixel TT equipped with 2 against-blades, the output engine is 0,37 kw. The stirring velocity is selected so as to ensure a good homogeneity of the solution; the speed is kept constant at 250 rpm. The temperature in the crystallizer was controlled by means of a heating bath equipped with an external temperature Pt1000 sensor which was set in the solution, the accuracy is $\pm 0.01^\circ\text{C}$. For water-sucrose mixture, a saturated solution was prepared by dissolving 761.15g of sucrose in 233.82g of distilled water at 70°C . These mass are measured by using the KERN FOB 1.5K0.5 balance with accuracy of 0.0001g. In the case of impure solutions, a saturated solution was prepared by dissolving 754.52g of sucrose in solution contains 233.82g of water + 22.19g of glucose.

Initially the saturated solution is prepared by dissolving sucrose in distilled water. The temperature was kept constant at 70°C for 30min while agitating. The experiment continues by lowering the temperature inside the solution following a controlled temperature linear profile. The terminal temperature reached is 40°C . The kinetic measurements were obtained using the samples as the time function. Samples of the solution

are periodically removed from the crystallizer and placed under the microscope for image capture. Solution concentration was measured with an Abbe5 refractometer, the accuracy is 0,1. Each data point presented is an average of three experiments.

The microscopic analysis was carried out by a binocular Nikon microscope provided with an objective of a maximum enlargement of $30 \times 50 \times 2.5$. The lighting of the sample is ensured by optical fibres providing a cold light favorable to the maintenance of the sample in its state initial. A camera Nikon DXM 1200 F is connected to a system of frame grabbing on PC. The images are acquired and are analyzed by the software of images analysis LUCIA "Laboratory Universal Computer Analysis Image". The accuracy of the method does not exceed 1% in the concentrations of sugars.

Model formulation and solution

For a perfectly mixed batch crystallizer of constant volume, in which crystal breakage and agglomeration are assumed to be negligible, the population balances equation PBE is a partial differential equation in time, t and crystal size, L :

$$\frac{\partial n(L,t)}{\partial t} = -G \frac{\partial n(L,t)}{\partial L} \quad (1)$$

where n is the population density and G is the size-independent crystal growth rate.

Subject to the boundary and initial conditions:

$$n(0,t) = n^0 = \frac{B_0}{G} \quad (2)$$

$$n(L,0) = 0 \quad (3)$$

where n_0 is the population density at the initial size of nuclei, $L=0$, B_0 is the nucleation rate.

The solution phase concentration in the crystallizer is described by a mass balance of the crystallizing solute:

$$\frac{dC}{dt} = -3\rho_c k_v h \int_0^\infty G n(L,t) L^2 dL \quad (4)$$

In which C is the concentration (mass of solute per total mass of the mother liquor), ρ_c is the crystal density, k_v is the volume shape factor converting L^3 into crystal volume and h converts solvent mass to slurry volume.

In this work, the temperature $T(t)$ recorded experimentally will be used instead of the energy balance equa-

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tion. This is done to avoid the error in estimating the overall heat transfer coefficient and to avoid estimating the heat of crystallization and its dependency on concentration.

The driving force for the nucleation and growth rates is the difference between the bulk concentration and the saturation concentration calculated at the bulk temperature. The kinetic expressions for nucleation and growth are taken to be empirical power-laws in supersaturation.

The nucleation kinetics are described by the following empirical expression.

$$B_0 = k_b S^b \quad (5)$$

The growth kinetics are described by :

$$G = k_g S^g \quad (6)$$

Where the saturation S is defined as:

$$S = \frac{C - C_{sat}(T(t))}{C_{sat}(T(t))} \quad (7)$$

$C_{sat}(T(t))$ is the concentration of saturation of sucrose in solution. The saturation concentration of sucrose in water is done as:

$$C_{sat}(T(t)) = 64.47 + 0.1033 (T(t)) + 14.24 \cdot 10^{-4} (T(t))^2 - 70.2 \cdot 10^{-7} (T(t))^3 \quad (8)$$

For the saturation limit of sucrose in solution phase with the presence of impurity, the $C_{sat}(T(t))$ is obtained from:

$$K_{sat} = \frac{C_{sat}^*(T(t))}{C_{sat}(T(t))} \quad (9)$$

With these equations the model is completely defined. The parameters k_b , b , k_g , and g are inferred from the experimental data.

The PBE Eq. (1) is solved using the method of moments. The i th moment of the PBE is defined as:

$$\mu_j = \int_0^\infty n(L,t) L^j dL \quad (10)$$

The first four moments are required for the general batch crystallizer model

$$\frac{d\mu_0}{dt} = B_0 \quad (11)$$

$$\frac{d\mu_j}{dt} = j G \mu_{j-1} \text{ for } j = 1, 2, 3, 4 \quad (12)$$

The initial conditions are:

$$\mu_j(0) = 0 \text{ for } j = 1, 2, 3, 4 \quad (13)$$

$$C(0) = C_0 \quad (14)$$

The Eqs. (4), (11) and (12) will be solved using a fourth-order Runge–Kutta.

Parameters estimation

The calculation of the best parameters in the representation of experimental data was performed either by the Marquardt–Levenberg's algorithm for current minimization process (W.Marquardt, 1963). The minimization is carried out on sums of squares of deviations between calculated and experimental quantities. The objective function in terms of the least square estimations takes the form:

$$\phi(k_g, g, k_b, b) = \sum_{i=1}^{N_{data}} (C_i^{cal} - C_i^{exp})^2 \quad (15)$$

The approach uses a nonlinear optimization routine to generate successive guesses of the kinetic parameters. For each guess, the dynamic model equations describing the process are solved and the resulting measurement predictions are compared with the data according to an optimization criterion. Generally, the criterion is a measure of the prediction errors. The model equations are solved implicitly each time the optimizer provides a parameter guess. The iterative optimization process ends when the specified tolerance has been achieved.

RESULTS AND DISCUSSION

In the parameters optimization process, the concentration phase in the crystallizer, at each time, is simultaneously calculated for the studied system by using a fourth-order Runge-Kutta. Four kinetic parameters (k_g, g, k_b, b) are fitted from the experimental data relative to the measured concentration phase in the crystallizer v.s times. According to the BCF theory, the lower growth exponent is unity. The parameters K_g and K_b are known to be only positive. Most of the kinetic parameter estimation studies on sucrose performed have been investigated in MSMPR Crystallizers^[3,5]. The nucleation rate is expressed in terms of growth rate and not in terms of supersaturation due to the difficulty in measuring the driving force accurately. However, in crystallization systems, b and g are of the order of zero to three. Typical values of b lie between 0.5 and 2.5^[1].

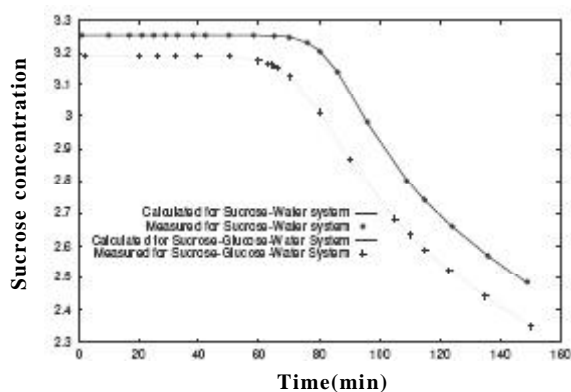


Figure 1: Sucrose concentration profile in the crystallizer

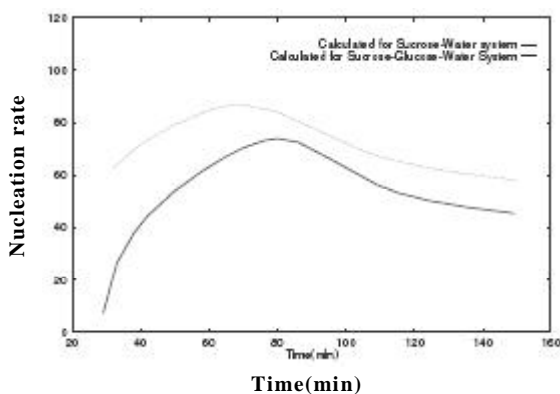
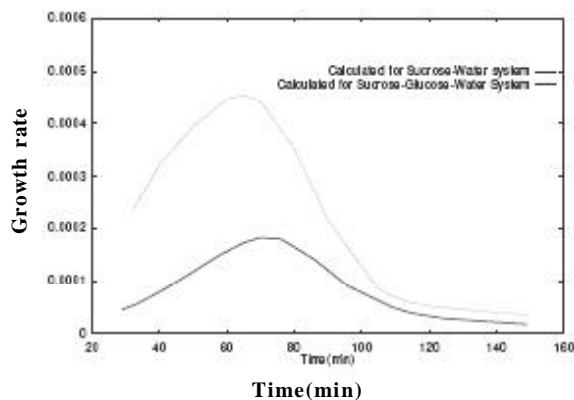
Figure 2: Nucleation rate (B_0) profileFigure 3: Growth rate (G) profile

TABLE 1: Optimum kinetics parameters for sucrose crystallization

System	g	b	kg (m/s) (g/g water) ^{-b}	kb (No./g/s) (g/g water) ^{-b}
1*	1.830	0.3915	0.041	162.84
2*	1.929	0.3557	0.042	166.73

The estimated parameters are shown in TABLE 1 for the two studied systems. It appears from this TABLE that the obtained parameters are physically realistic and comparable with the other parameters in the literature.

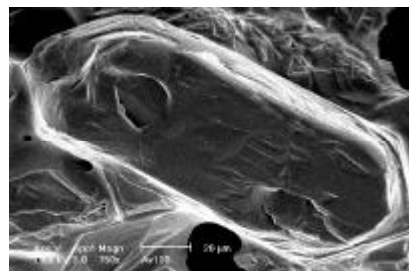


Figure 4: (SEM) typical after a peak of supersaturation

TABLE 2: Crystal average size as function of times for different system

Sucrose-water			Sucrose-glucose-water		
Time (min)	L_{max}^{exp} (μm)	L_{max}^{cal} (μm)	Time (min)	L_{max}^{exp} (μm)	L_{max}^{cal} (μm)
50	20	15.72	50.	80.	71.51
58	-	40.10	60.	-	116.68
65.	80.	74.96	66.	200.	151.42
80.	200.	193.00	80.	-	236.00
150	-	420.02	150.	-	366.94

Figure 1 illustrates the calculated concentration profiles in the crystallizer plotted against time. For comparison, we include the experimental data obtained by refractometric analysis. This figure shows the quality of the adjustment of the kinetic parameters. It can be seen that the deviation standard for concentration is less than 0.1% for the sucrose-water system, 0.03% for the sucrose-glucose-water system. Concerning the effect of glucose on the crystallization of sucrose, one concludes from these two figures that the addition of impurities permits a reduction in the solubility of sucrose in the solution phase of the crystallizer, as mentioned in the literature^[7]. This suggests that these impurities are in competition with sucrose. Consequently, an increase in solution phase supersaturation was obtained in the crystallizer and the time of crystallization of sucrose was decreased.

Figures 2 and 3 show the profiles of nucleation rate and growth rate plotted against time for the two systems studied. It appears from these figures that the effect of glucose allows to an increase in the nucleation rate B_0 and to a decrease in the growth rate G of the sucrose crystals.

The crystals formed in these experiments exhibit the occurrence of a secondary nucleation phenomenon. Figure 4 was taken using a field emission scanning electron microscope (SEM). It illustrates an example of the

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needle-like crystal(s) formed after a peak of supersaturation. The observation of the aspect of the crystals before and after the peak gives more insight. Before the peak, crystals show regular surfaces. After the peak, crystals show imperfect surfaces with many fine that seem to have grown on the surface. From the SEM image, it can be observed that the crystal adopts long needle shaped structures: it shows that secondary nucleation has occurred.

The TABLE presents the estimated mean dimension sizes at different times for the two studied system. For comparison, the experimental data were included in this TABLE. Indeed, one observes that the calculated results are in agreement with the maximal measured sizes. By comparing the obtained sizes of the particle for the sucrose-water and sucrose-glucose-water systems, one notes that the presence of glucose causes a reduction in length of the obtained final product.

CONCLUSION

Secondary nucleation and growth of sucrose crystallization was investigated at supersaturated conditions. The liquid phase concentration containing in batch crystallizer was measured as function of time by using a refractometer. The parameters of the growth and nucleation rates have been successfully estimated for sucrose crystallization by using the non-linear optimization method and for a linear cooling profile. The obtained kinetic parameters are physically realistic and comparable with the other parameters in the literature. The estimated results are in agreement with the experimental data. It has been shown that the presence of impurities in liquid phase in batch crystallizer of sucrose permit to produce the smallest mean particle sizes of the final product.

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