

## Cooling Profile of Potassium Hydrogen Tartrate Batch Crystallization

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**ABSTRACT:** Batch crystallization is an important chemical unit operation. So, large numbers of published works were focused on batch crystallization modelization, simulation, optimization, and control and parameter estimation. In this work, an optimization is made with the objective to obtain the optimal cooling temperature strategy of a batch crystallizer realized in our laboratory. The potassium hydrogenotartarate (cream of tartar) subject of our study is recovered from wine tartar, a solid byproduct of winemaking, using batch cooling crystallization. To determine the optimum cooling temperature profile with a maximum yield of cream of tartar, we used coupled population, material and energy balance model. This model can describe the dynamics of the batch crystallization process. Based on this model, an optimal cooling temperature profile is calculated, using method of moments and the solubility data of cream tartar in water.

**KEYWORDS:** Cooling crystallization, batch, optimization, temperature profile, potassium hydrogen tartrate, moment's method.

### 1. INTRODUCTION

The crystallization plays an important role in many chemical industries. In this process the temperature of the solution in the crystallizer has a direct effect on the supersaturation. And the supersaturation is the driving force of the crystallization process. The temperature is used for the crystallization monitoring and controls [1-5]. Also, cooling batch crystallization is studied, to find the kinetics of crystallization [6-8]. To study the effect of the parameters on the final particle size distribution as well as the purity and the yield of crystallized product [8, 9]. Without forgetting, to find the optimal cooling strategies [11-16]. However, it should be noted that, one of the crucial points in the crystallization process is the cooling strategy. The aim of

our work is an optimization to find the cooling temperature profile of our crystallizer to maximize the total volume of the final crystalline product, during the recovery of cream of tartar (potassium hydrogen tartrate). The recovery of cream of tartar is carried out using cooling crystallization and water is used as solvent. In our work a temperature profile is calculated and compared to different cooling modes obtained depending on the constraints of our crystallizer. The population balance coupled with the material and energy balances allows the modeling of the crystallization process. And often the nucleation and growth mechanisms are modeled empirically [2, 17-19].

When one characteristic size is considered, for a batch crystallizer the population balance equation is [2, 20]:

$$\frac{\partial n(x,t)}{\partial t} + \frac{\partial G(x,t)n(x,t)}{\partial x} = 0 \quad (1)$$

$n(x,t)$  represent the population density and  $G(x,t)$  is the growth kinetic. Mc. Cabe's hypothesis simplifies the modeling of this kinetics with  $G(x,t) = G(t)$  and equation (1) becomes:

$$\frac{\partial n(x,t)}{\partial t} + G(t) \frac{\partial n(x,t)}{\partial x} = 0 \quad (2)$$

$n(x,t)$  is the number of moles of crystals of size  $x$  per unit volume at time  $t$ . with  $x \in [X_{\min}, X_{\max}]$ ,  $X_{\min}$  represents the size of the smallest stable crystal which does not dissolve and cannot that grow, and  $X_{\max}$  is equal to or greater than the maximum crystal size in the solution. For modeling reasons, it is chosen so as never to be reached by the process.

The solute concentration balance describing the mass transfer from the liquid to the solid

Phase(material balance) is represented by equation (3):

$$\frac{d(V_l(t)C(t))}{dt} + \frac{d(V_T(t)C_s(t))}{dt} = 0 \quad (3)$$

C(t) represents the solute concentration mol/m<sup>3</sup>; C<sub>s</sub>(t) is the concentration of the solid phase mol/m<sup>3</sup>; V<sub>T</sub>(t) is the suspension volume (total volume) (m<sup>3</sup>), the variation of this volume du to the mass transfer is very small, this variation

can be neglected. V<sub>l</sub>(t): The solution volume or of the liquid phase (m<sup>3</sup>).

The expression of V<sub>l</sub>(t) represents the difference between the total volume of the solution and the volume occupied by the solid phase (crystals) (equation 4):

$$V_l(t) = V_T(t) \left(1 - \frac{M_s}{r_s} C_s(t)\right) \quad (4)$$

M<sub>s</sub> is the molar mass kg / mol and ρ<sub>s</sub>: The density Kg / m<sup>3</sup>. The solid phase concentration is deduced from the moment

of order 3 (method of moments) which represents the total volume of the crystals (equation 5):

$$C_s(t) = \frac{K_v r_s}{M_s} \int_{X_{\min}}^{X_{\max}} x^3 n(x,t) dx \quad (5)$$

K<sub>v</sub> is a shape factor equal to π / 6 for sphere.

The crystallizer temperature is described by the energy balance around the jacket wall(6) :

$$\sum_{i=1}^3 C_{p_i} n_i \frac{dT_{cr}}{dt} = - \Delta H_c V_T \frac{dC_s(t)}{dt} + UA(T_{cr}(t) - T_{de}(t)) \quad (6)$$

C<sub>pi</sub> (i = 1, 2, 3), C<sub>pref</sub>: Molar thermal capacity of solid, solute, solvent and cooling liquid respectively in J K<sup>-1</sup>mol<sup>-1</sup>. n<sub>i</sub> (i = 1, 2, 3), n<sub>ref</sub>: Number of moles of solid, solute, solvent and cooling liquid respectively in mol; T<sub>Cr</sub> is the

Temperature in the crystallizer (°K); ΔH<sub>c</sub>: is the enthalpy of crystallization in J mol<sup>-1</sup>; U is the heat transfer coefficient (J m<sup>-2</sup>K<sup>-1</sup>s<sup>-1</sup>); A is the heat transfer area (m<sup>2</sup>). T<sub>de</sub> is the temperature of the jacket wall (°K).

## 2. RESULTS AND DISCUSSIONS

The initial condition for the population balance is given by the following and we assume that nucleation R<sub>n</sub>(t) occurs at negligible size.

$$n(x, t = 0) = n_0(x)$$

$$R_n(t) = \frac{d}{dt} \left( \int_{X_{\min}}^{X_{\max}} n(x,t) dx \right)$$

The distribution beyond maximum size X<sub>max</sub> is zero. We obtain the following border condition:

$$n(X_{\min}, t) = \frac{R_n(t)}{G(X_{\min}, t)} \quad (7) \quad ; \quad n(X_{\max}, t) = 0 \quad (8)$$

The moments of the system are defined by the following integrations:

$$m_i(t) = \int_0^{\infty} x^i n(x,t) dx, i = 0, 1, 2, \dots \quad (9)$$

Using the definition of a moment of order i (expressions 9), and the information provided by the population balance

(equation 2) as well as the Mc Cabe hypothesis and the boundary condition (7) and (8) we have:

$$\frac{dm_i(t)}{dt} = iG(t)m_{i-1}(t) \tag{10}$$

$$\frac{dm_3(t)}{dt} = 3G(t)m_2(t)$$

$$\frac{dm_2(t)}{dt} = 2G(t)m_1(t)$$

$$\frac{dm_1(t)}{dt} = G(t)m_0(t)$$

$$\frac{dm_0(t)}{dt} = R_n(t)$$

With  $C_s(t) = \frac{K_v r_s}{M_s} m_3(t)$

$C_s(t)$  is measurable and proportional to  $\mu_3(t)$ , we can calculate the evolution of the variables  $\mu_i(t)$ ,  $C_s(t)$ ,  $C(t)$  and  $T_{Cr}(t)$  which are controlled by the temperature of the jacket

$T_{de}(t)$ . Equation (11) represents a material balance over the amount of material remaining in the liquid phase.

$$C(t) = C_{Sat}(0) - \frac{K_v r_s}{M_s} m_3(t) \tag{11}$$

To induce the crystallization phenomenon, the instantaneous solute concentration at time t must be at least equal to the

saturation concentration (solubility) at an adequate temperature  $T_{Cr}$ :

$$C(t) \gg C_{Sat}(T_{Cr}(t))$$

$$C_{Sat}(T_{Cr}(t)) = A \exp(B.T_{Cr})$$

$$T_{Cr}(t) = \frac{1}{B} \ln \frac{C_{Sat}(T(t))}{A}$$

With A in mol / kg of solvent and B in 1 / ° C. The initial concentration C(t) is assumed to be saturated for the initial temperature (The expression of C(t) is the instantaneous solute concentration). These values as well as the parameters

used in the simulation are given in table 2. On the other hand, starting from equation (10) and accepting a constant growth rate, This iterative relation is used to arrive at an expression of the moment of order 3.

$$R_n(t) = 0, \quad \frac{dm_0(t)}{dt} = 0, \quad m_0(t) = C_0$$

$$m_1(t) = C_0 G(t) + C_1$$

$$m_2(t) = G^2 C_0 t^2 + 2GC_1 t + C_2$$

$$m_3(t) = G^3 C_0 t^3 + 3G^2 C_1 t^2 + 3GC_2 t + C_3$$

$$m_3(t) = N_T L^3 \left[ \frac{G^3 t^3}{6} + 3 \frac{G^2 C_1 t^2}{2} + 3 \frac{G C_2 t}{1} + 1 \frac{C_3}{1} \right]$$

And 
$$T_{Cr}(t) = \frac{1}{B} \ln \frac{C_{Sat}(0) - n_T \left[ \frac{G^3 t^3}{6} + 3 \frac{G^2 C_1 t^2}{2} + 3 \frac{G C_2 t}{1} + 1 \frac{C_3}{1} \right]}{A} \tag{11}$$

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By considering (L): Size of crystals.  $C_0 = N_T$ ;  $C_1 = L_1 N_T$ ;  $C_2 = L_2 N_T$ ;  $C_3 = L_3 N_T$ .

$$\text{With : } \frac{K_S r_S}{M_S} N_T L^3 = n_T$$

$n_T$  : The number of total moles of cream of tartar crystals.

The parameters A and B are those of the exponential model of the solubility of cream of tartar as a function of temperature (Table 1, Figure 1).

In the crystallization process of cream tartar experiments using our crystallizer, the temperature of the crystallizer was lowered by 58° C for 30 min through a cooling jacket. Indeed the initial temperature of the crystallizer at 70° C is cooled in several modes up to 12° C for 30 minutes according to different cooling modes [26], these cooling temperature strategies are determined arbitrarily, without

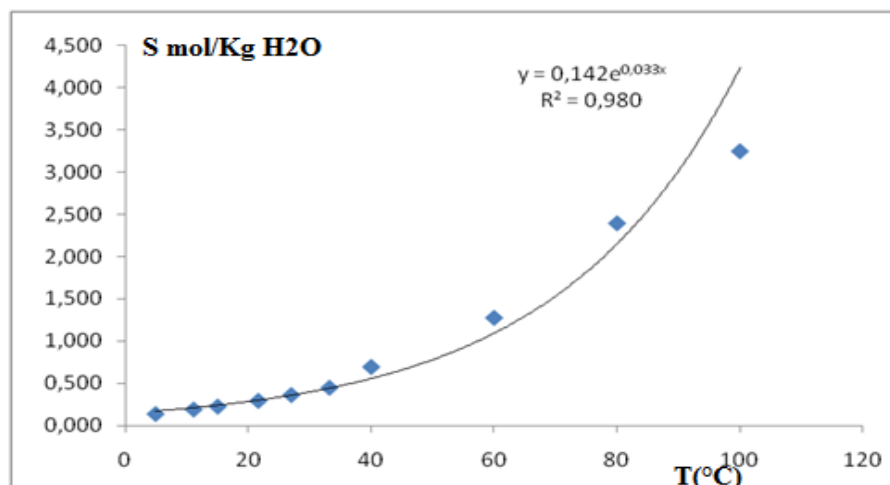
taking into account the solubility data of hydrogen tartrate in water.

In a work published in 2001 by Sousa P. and Lopes Ana MC [27] and using the polythermal method, the solubility of cream of tartar was determined in a temperature range from 4.9 to 47.2 °C. The consideration of the solubility values for T= 60, 80 and 100 °C according to the technical data of the company Faure (Table 1) gives an acceptable correlation coefficient  $R^2 = 0.98$  (Figure 1).

**Table 1: Solubility of cream of tartar in water at different temperatures.**

[\* (Sousa Paula and Lopes Ana M. C., [27]); \*\* technical data (Faure)]

T(°C)	Solubilité g/100g H <sub>2</sub> O*	Solubilité g/100g H <sub>2</sub> O**
0		3,2
4,9	2,65	
11,1	3,64	
15	4,29	
20		5,7
21,6	5,56	
27	6,86	
33,2	8,47	
40		13,1
47,2	9,75	
60		24
80		45
100		61



**FIGURE 1: Cream of tartar solubility (  $Y = 0.142 e^{0.033x}$ ,  $R^2 = 0.980$  )**

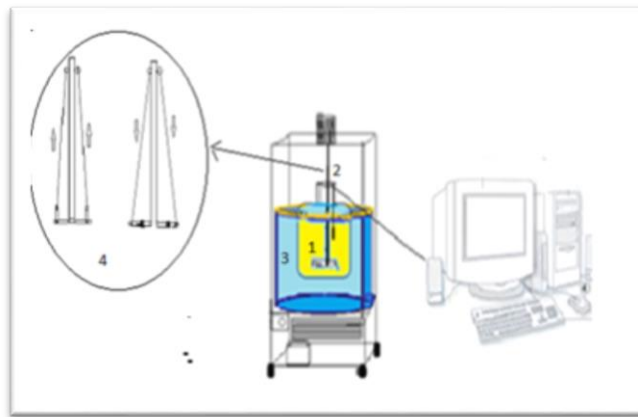
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A cooling profile for the batch crystallization of hydrogen tartrate is calculated from equation (11). On the other hand in previous work, the size distribution of different samples of Cream of tartar was measured by Malvern Mastersizer 2000 using ethanol / tween-20 (1/6 vv) as the dispersant

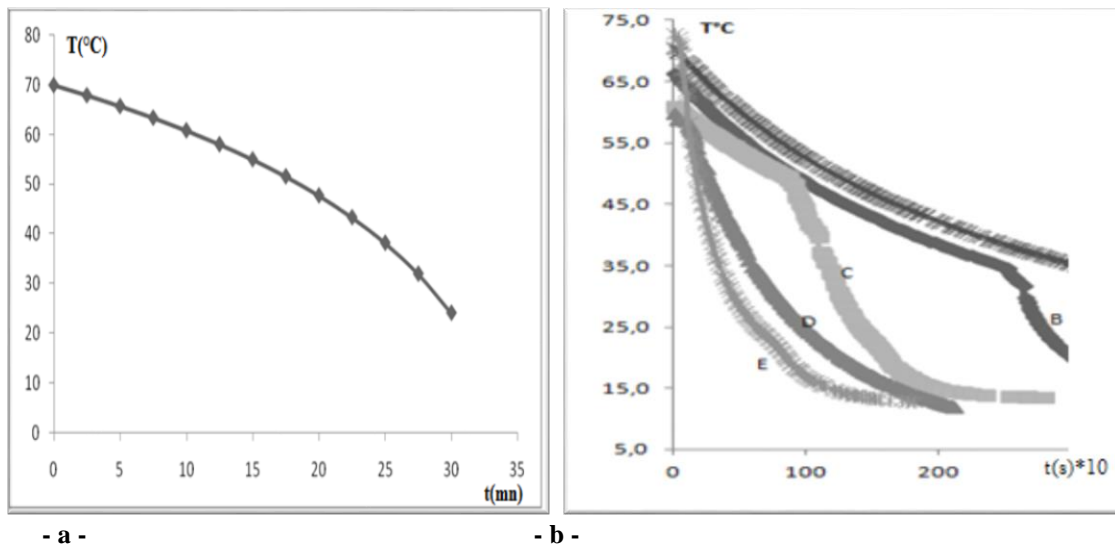
solvent. These different samples correspond to different temperature profiles produced using the device shown in figure 2 [26]. Possible cooling strategies (modes A, B, C, D, E) were applied according to the constraints of our crystallizer.

**Table 2: The parameters of the cooling profile.**

Paramètres	Unité	Valeur
$C_{sat}(0)$	Mol/Kg de solvant	1.43 ( $T_{cr} = 70\text{ }^{\circ}\text{C}$ )
$n_T$	Mol/Kg de solvant	0 ( $T_{cr} = 70$ ; $t = 0$ ) 1.1154 ( $T_{cr}$ finale $12^{\circ}\text{C}$ ; $t = 30$ mn ; $R=78\%$ )
L	$\mu\text{m}$	320
$M_s$	Kg/mol	$188 \cdot 10^{-3}$
G	m/s	$3.67 \cdot 10^{-5}$
A	Mol/Kg de solvant	0,142
B	$1/^{\circ}\text{C}$	0.033



**FIGURE 2: Cream of tartar crystallization [26].**



**FIGURE 3: a - Approximation of the cooling profile calculated from equation 11; b- Temperature profiles in the crystallizer according to different cooling strategies [26].**

#### 4. CONCLUSION

In our study, we did not aim only to solve an environmental problem: Elimination of solid waste from winemaking by recovering a valuable product: The cream of tartar. But also to study an important unit operation which is the batch cooling crystallization. Based on the solubility data, the population balance coupled with the material balance we have calculated a cream of tartar crystallization cooling profile. The calculated profile is close to the cooling mode represented by curve C (Figure3b) this mode is derived from a cooling strategy consisted in cooling with stirring at room temperature do 50°C then at 12°C in the cooling bath with continuous refrigeration.

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