Int Jr. of Mathematical Sciences & Applications
Vol. 7, No. 1, (January-June, 2017)
Copyright Mind Reader Publications
ISSN No: 2230-9888
www.ijmsa.yolasite.com

The Agitation Effects on the Batch Crystallization of the CAM

Enzo Bonacci
Department of Mathematics and Physics, Scientific High School "G.B. Grassi"
Latina (Italy)
E-mail: enzo.bonacci@liceograssilatina.org

Abstract

We discuss the influence of the agitation in the batch crystallization of the citric acid monohydrate (CAM), i.e., the role of the impeller for its shape (three-blade marine propeller) and speed as resulted from a pioneering experimental study accomplished at "La Sapienza" University of Rome in the '90s.

Key Words: crystallization, CAM, fluid dynamics, optimization theory, computer graphics

MSC(2010): 49-02, 65K10, 68U05, 76-02, 76-05, 97R60

INTRODUCTION:
Citric acid is an important organic substance with a vast market. Nevertheless, until 1997 the scientific literature reported little information about the process of crystallization by cooling through which the commercial product is obtained. In particular, the available studies were aimed to investigate only the kinetics of nucleation [1] and crystal growth [2] neglecting some effective aspects of the industrial crystallization in mechanically stirred tanks. In order to fill that sci-tech gap, the Department of Chemical Engineering at the University "La Sapienza" of Rome decided to conduct a long and meticulous experimental research on the crystallization in discontinuous (batch) of CAM (citric acid monohydrate) in the allotropic form that is stable at room temperature (Fig. 1). Among the graduate students involved in that pioneering experience there was the author [3-11] who, under the supervision of Prof. Barbara Mazzarotta [1, 2], had the specific task of assessing the effects on CAM of changing the crystallization conditions until their optimization. A series of 20 tests (15 of which useful for the dissertation purposes) led to the identification of the operating parameters ensuring large crystals whose size distribution was homogenous. These conditions can be summarized as follows: agitation speed 2% above the minimum value for solid suspension; seed crystals large 10% of the desired final size; seeding temperature 0.5 °C over that of spontaneous nucleation; tank crystallizer with a round (hemispherical) bottom (Fig. 2). The first achievement is briefly illustrated in this paper, i.e., we talk about the role of the agitation for the impeller's shape (three-blade marine propeller) and speed.

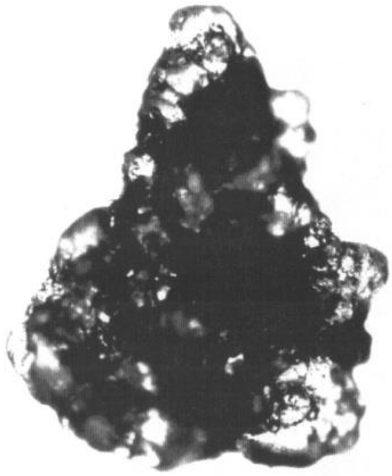

Figure 1. CAM crystal (grain size range 1.18-1.4 mm).

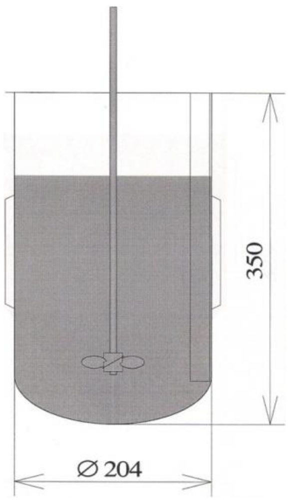

Figure 2. Project of the round bottomed tank.

BEST IMPELLER CHOICE:

We needed the just suspension condition (no precipitate particle remaining on the bottom more than one second) easily obtainable with the downward flow of an axial impeller. Therefore, we used a three-bladed impeller giving a predominantly axial motion to the solution (or suspension) in the tank. We chose the marine screw propeller instead of the radial impeller (Rushton turbine), also available in the laboratory (Table 1), after having compared their performances [4]. The stainless steel impellers, both with cylindrical rods as stems (height 50 cm; diameter 1 cm), were equally resistant to corrosion and mechanical stresses.

Table 1 Impellers available at “La Sapienza” University laboratory in the '90s

IMPELLER TYPE	DIAMETER	FLOW
Three-bladed impeller (marine screw propeller):	$\phi = 7.5\ cm$	*Axial*
Rushton turbine:	$\phi = 5.0\ cm$	*Radial*

The impeller choice according to the Zwietering equation.

After having measured all the necessary variables (Table 2 and 3), we estimated the just-suspension speed (Eq. 1) in rounds per minute (acronym rpm) of the two alternative impellers (Table 4) associated with each of our three tank crystallizers (flat, round and conical bottom), through the Zwietering correlation [12].

$$(1) \qquad N_{\mathrm{JS}} = 60\ S\ \frac{\nu^{0.1}\ d_p^{0.2}\ X^{0.13}\left(g\frac{\Delta\rho}{\rho_L}\right)^{0.45}}{D^{0.85}}$$

Table 2 Tank-independent variables

Kinematic viscosity of the liquid:	$\nu = 1.8 \times 10^{-5}\ m^2/s$
Maximum particle size:	$d_p = 1.7 \times 10^{-3}\ m$
Gravitational constant:	$g = 9.81\ m/s^2$
Liquid density:	$\rho_L = 1300\ kg/m^3$
Solid-liquid density difference:	$\Delta\rho = 1542 - 1300 = 242\ kg/m^3$
Weight percentage of suspended solid:	$X_{max} = 15\%\ (dimensionless)$
Diameter of the marine screw propeller:	$D = 7.5 \times 10^{-2}\ m$
Diameter of the Rushton turbine:	$D = 5 \times 10^{-2}\ m$

Table 3 Variables depending on the geometry of the impeller and tank

Bottom of the tank:	FLAT	ROUND	CONICAL
$\phi_{\mathrm{tank}} / \phi_{\mathrm{marine}}$: $T/D =$	3.03	2.77	2.93
$\phi_{\mathrm{tank}} / \phi_{\mathrm{Rushton}}$: $T/D =$	4.54	4.16	4.40
$\phi_{\mathrm{tank}} / \Delta_{\mathrm{marine-bottom}}$: $T/C =$	3.03	2.60	2.44

$\phi_{\text{tank}} / \Delta_{\text{turbine-bottom}}$: $T/C =$	4.54	2.97	2.59
Geometric factor of the marine impeller: $S =$	7.25	7.10	7.80
Geometric factor of the Rushton turbine: $S =$	15	13	14

Table 4 Just-suspension speeds from the Zwietering equation

Bottom of the tank:	FLAT	ROUND	CONICAL
Three-bladed marine impeller:	$713\ rpm$	$698\ rpm$	$739\ rpm$
Rushton turbine:	$2006\ rpm$	$1738\ rpm$	$1872\ rpm$

The high speed to achieve just-suspension via the Rushton turbine (Table 4) posed two problems: great energy consumption and huge instability of the rotating system. Vice versa, our three-blade marine impeller allowed a sustainable N_{JS} coupled with any tank. Hence, we assumed 740 rpm as minimum agitation speed ensuring the suspension of the precipitate particles [3].

The impeller choice according to the power consumption.
The Rushton turbine was definitely discarded after the approximate calculation of the power requirement for a given tank geometry, agitator speed and mixture properties (Table 5).

Table 5 Steps to determine the power requirement at different agitations

Level of agitation:	LOW	HIGH
Agitator speed: $N =$	$755\ rpm$	$1165\ rpm$
Agitator speed: $N/60 =$	$12.58\ rps$	$19.42\ rps$
Reynolds number: $Re = D^2 N \rho / \mu =$	3866	5967
Power number: $N_p = N_p(Re) =$	1.6	1.4
Power: $P = \rho N^3 D^5 N_p =$	$9.8\ W$	$31.6\ W$

We inferred that our tests would have required an agitation device delivering a power over 32 W. A small and light agitator, developing a rotational power of up to 130 W, was placed on top of the crystallizer. In addition to reading the rounds per minute ($0 - 2000$ rpm), its display measured the applied torque in a range between -0.9 and $+ 99.9$ N · cm. The stirring shaft could not be inserted directly in the gear box because it was an instability element with off-axis rotations and vibrations increasing in amplitude. In order to absorb the eccentricity of the rotation, avoiding structural failures and annoying noises, we prolonged the stem of the impeller connecting it to a short metal rod through a flexible and resistant portion of a vacuum hose [5].

CALCULATIONS AND SIMULATIONS:

We calculated that 2% above the minimum ($N_{\text{JS}} = 740$ rpm) kept the advantages of a supersaturated isotropic homogeneous mixture and the speed $N_{\text{C}} = 755$ rpm became standard in all tests [6]. Further fluid mechanics computations, enhanced by taking into account the CAM viscosity in the range $T = 19 - 22$ °C, led us to draw by hand the vortex flux lines within the three different shapes (Figs. 3, 5 and 7). All of them were substantially confirmed by outputs (Figs. 4, 6 and 8) from the VisiMix software (www.visimix.com). The tests were simulated through a QuickBASIC program (www.qbasic.net or www.qb64.net) written with particular care of the subroutines relative to the nucleation and secondary agglomeration by collision [8] because the microscopic analysis of various sized CAM crystals [10] had pointed out their strong tendency to agglomerate (Fig. 1). The experimental data (Figs. 9, 11 and 13) were in good agreement with the predictions (Figs. 10, 12 and 14) and it was possible to reproduce faithfully the influence of the cooling profile on the crystal granulometric properties and the effects of all the operating variables, except with heavy seed crystals. In this paper all the computer graphs come from the original dissertation in Italian [9] being partially translated in the new English captions and explained in the relative paragraphs. We however remark that the Italian word *prova* means test, *fondo* is bottom, *tondo* is round, *piano* is flat, *conico* is conical, *agitazione* is agitation, *alta* is high, *bassa* is low, *semina* is seed, *leggera* is light and *pesante* translates to heavy.

MAIN RESULT:

All the collected data showed that a low agitation was preferable to a high speed which, instead, gave bad results with a high percentage of fine-grained crystals, a decrease of the coarse-grained classes and a significantly reduced average size. A too high stirring rate favored the secondary nucleation with its absolutely negative effects on the crystal size distribution (dispersion). The attrition slowed down the crystal growth by splitting agglomerations and we noticed another phenomenon: the secondary nucleation by collision, recognized for its quadratic growth with respect to the impeller speed [2]. The side effects of other impacting parameters, such as light/heavy seeding and flat/round geometry [7, 11], did not affect the conclusions on the agitation effect because they caused, respectively, a major/minor divergence between the curves or an up/down shift of them.

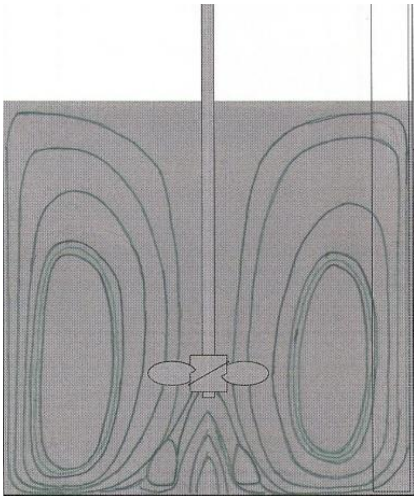

Figure 3. Calculated flux lines in a flat tank.

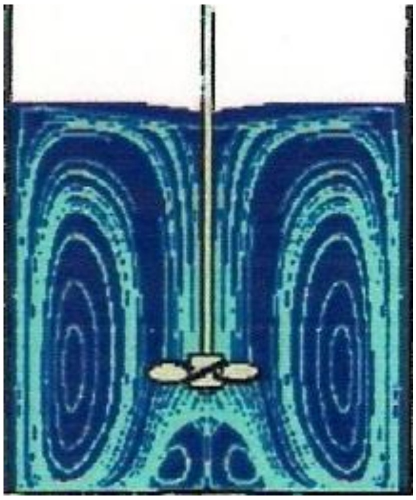

Figure 4. Simulated flux lines in a flat tank.

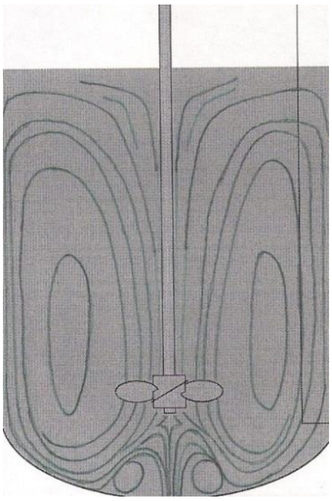

Figure 5. Calculated flux lines in a round tank.

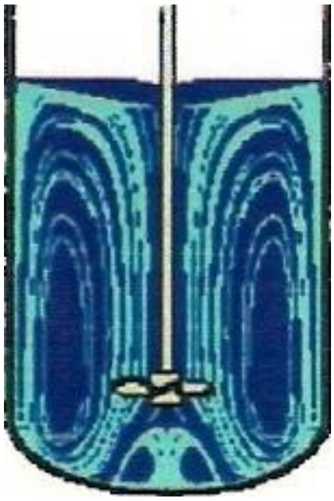

Figure 6. Simulated flux lines in a round tank.

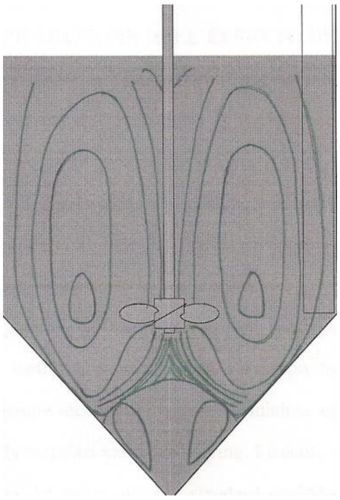

Figure 7. Calculated flux lines in a conical tank.

Figure 8. Simulated flux lines in a conical tank.

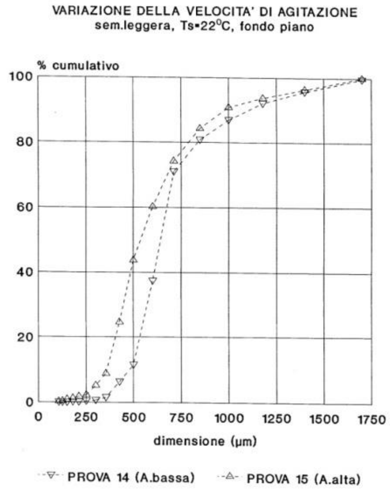

Figure 9. Crystal size distributions with the flat tank.

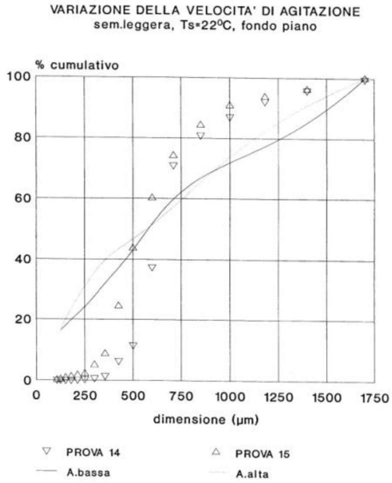

Figure 10. Simulations for the flat tank.

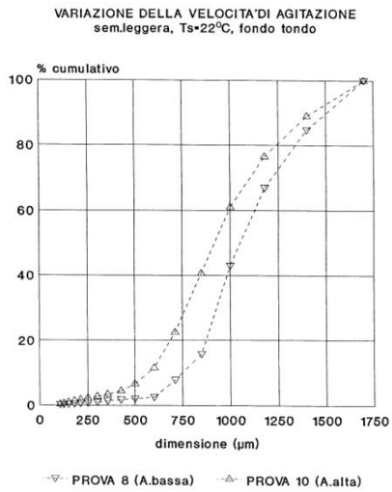

Figure 11. Crystal size distributions with the round tank.

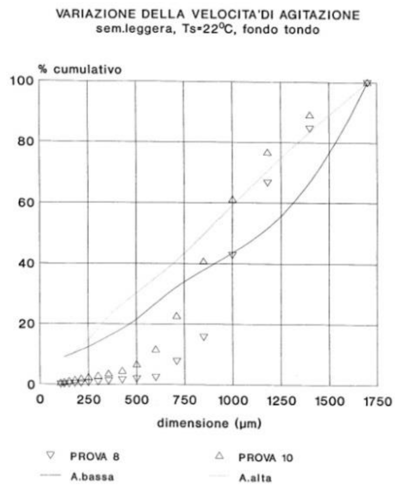

Figure 12. Simulations for the round tank.

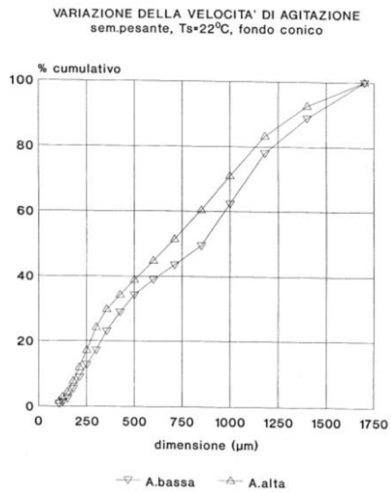

Figure 13. Crystal size distributions with the conical tank.

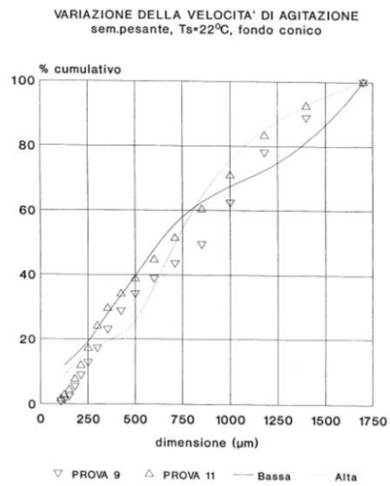

Figure 14. Simulations for the conical tank.

CONCLUSIONS:

This paper focuses on a part of the Chemical Engineering M.Sc. thesis written by the author in the years 1997-1998 and supervised by Prof. Barbara Mazzarotta. In the historic laboratories of the University "La Sapienza" of Rome (Faculty of Engineering) we analyzed the batch cooling crystallization of the CAM from aqueous solutions in differently shaped containers for evaluating the effects of variables such as the tank geometry (Fig. 15), the intensity of agitation (Fig. 16) and the conditions of seeding. Among the factors optimizing the process, the choice of a three-bladed impeller (marine screw propeller) allowed: energy savings, stability of the rotating system and low background noises. Then we found that an agitation ($N_C = 755$ rpm) slightly above the just-suspension speed established by the Zwietering correlation ($N_{JS} = 740$ rpm) was the most effective to reduce the negative incidences of attrition and secondary nucleation without renouncing to the benefits of a good mixing. The experimental work was supplemented by a QBasic program to simulate the crystal size distribution and by the VisiMix software to replicate the fluid dynamics inside each crystallizer.

Figure 15. The best tank (round bottomed).

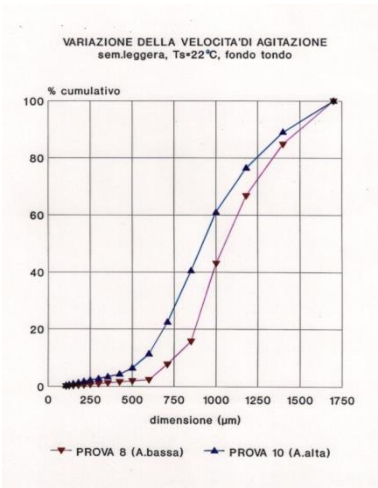

Figure 16. The best agitation (755 rpm).

ACKNOWLEDGMENTS:

I'm grateful to the Organizing Committee of the ICMCS 2016 for having given me the chance to present a pioneering Italian experimental survey in the magnificent scenario of the Oasis Hotel Chiang Mai in Thailand.

My thanks to the IYC-Latina Chairman Francesco Giuliano for both the invitation to lecture in the 2011 International Year of Chemistry and the nomination to the Sapio Prize for the Italian research.

I also wish to thank the Academy of the Sapio Prize for the invitations to the XIII, XIV and XV awarding ceremonies.

REFERENCES:

1. M. Bravi, B. Mazzarotta, "Primary Nucleation of Citric Acid Monohydrate: Influence of Selected Impurities," Chem. Eng. Journal 70(3) (1998) 197-202.
2. M. Bravi, B. Mazzarotta, "Size Dependency of Citric Acid Monohydrate Growth Kinetics," Chem. Eng. Journal 70(3) (1998) 203-207.
3. E. Bonacci, "Experimental Survey on the Batch Crystallization of CAM," In: 96th National Congress of the Italian Physical Society, Bologna (September 20-24, 2010), Atticon5594 Va-C-2.
4. E. Bonacci, "Experimental Survey on the Batch Crystallization of CAM," In: Proceedings of the International Year of Chemistry (IYC2011). DOI: 10.13140/RG.2.1.1812.1761.
5. E. Bonacci, *Experimental Study on the Crystallization of the Citric Acid*, Rome, Aracne Editrice, 2013 (ISBN 9788854857674).
6. E. Bonacci, "A Pioneering Experimental Study on the Batch Crystallization of the Citric Acid Monohydrate," Journal of Chem. and Chem. Eng. Vol.8 No.6(79) (2014) 611-620. DOI: 10.17265/1934-7375/2014.06.010.
7. E. Bonacci, "The Geometry Effect in a Pioneering Experimental Study on the Batch Crystallization of the CAM," Journal of Chem. and Chem. Eng. Vol.8 No.7(79) (2014) 727-735. DOI: 10.17265/1934-7375/2014.07.012.
8. E. Bonacci, "QB Program Simulating the Batch Crystallization of the CAM," ResearchGate Dataset (2015). DOI: 10.13140/RG.2.1.3082.7683.
9. E. Bonacci, "Summary of the Findings About the Batch Crystallization of the CAM," ResearchGate Dataset (2015). DOI: 10.13140/RG.2.1.2646.6409.
10. E. Bonacci, "Photo Gallery of CAM Crystals from Aqueous Solutions," ResearchGate Dataset (2015). DOI: 10.13140/RG.2.1.2673.2647.
11. E. Bonacci, "The Geometry Effects on the Batch Crystallization of the CAM," In: 101st National Congress of the Italian Physical Society, Rome (September 21-25, 2015), Atticon8991 V-C-11. DOI: 10.13140/RG.2.1.1868.0806.
12. N.T. Zwietering, "Suspending of Solid Particles in Liquid by Agitators," Chem. Eng. Sci. Vol.8 No.3-4 (1958) 244-253.