Title: **Seeding optimization in the batch crystallization of CAM**

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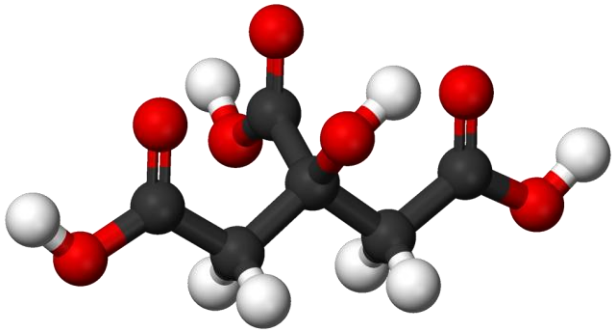
The state of art in 1997

Citric acid **[8]** is an important organic substance but, until 1997, the scientific literature reported little information about the crystallization by cooling in stirred-tank reactors (STRs), i.e., the process by which the commercial product is obtained.

The studies then available were focused mostly on the kinetics of nucleation **[15]** and on the crystal growth **[16]** rather than on the industrial aspects of the crystallization in STRs.

Formula: $C_6H_8O_7$



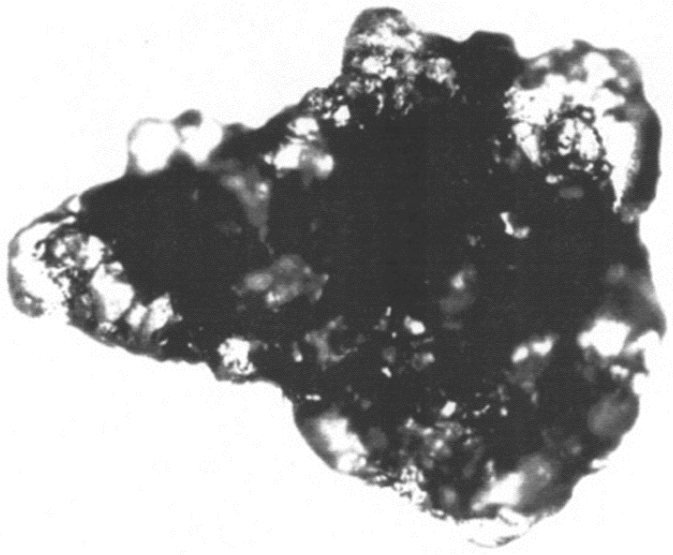
Structure: monoclinic

Producing CAM at La Sapienza's lab

The Department of Chemical Engineering at the University "La Sapienza" of Rome decided to fill that sci-tech gap through a detailed investigation on the crystallization in discontinuous (batch) of the citric acid monohydrate (CAM) at San Pietro in Vincoli's lab (DICMA). The author participated in that cutting edge experience, under the supervision of Prof. Barbara Mazzarotta, in the years 1997-1998.

Crystal size 150-180 μm

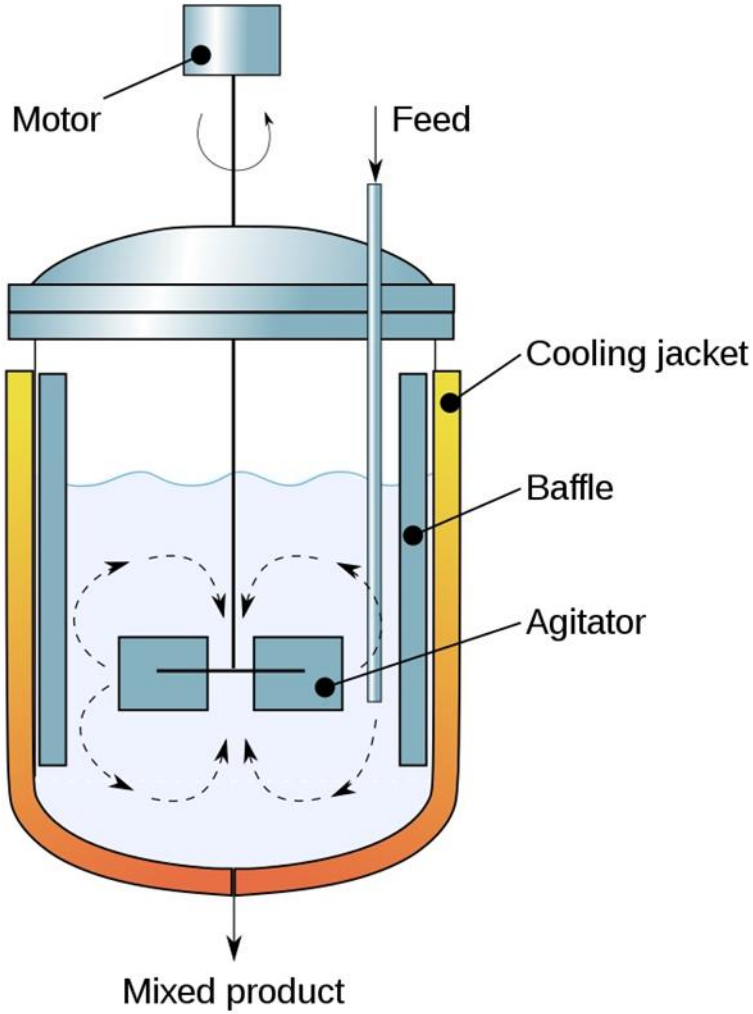
Crystal size 1.18-1.4 mm



Seeking for an optimal CSD of CAM

We spotted the main operating conditions in batch reactors, we modified them until an *optimal* crystal size distribution (CSD) of CAM **[7]**, confirmed also via computational fluid-dynamics (CFD), and we wrote a QBasic program predicting the outcomes of any test **[6]**.

The resulting M.Sc. thesis **[3]** and the related research papers **[4,5,11]** were acknowledged as *pioneering* achievements more than a decade later **[1,2,10,12]**.



A strict test protocol

All tests were executed via the following eight steps:
1)Preparation of an aqueous solution of citric acid in the volume of 8 L, saturated at a temperature of 25 °C, i.e., 3.39 kg of water and 7.09 kg of citric acid;
2)Solubilization by heating;
3)Crystallization by cooling: we descended from 30 °C to a final temperature between 19 °C and 20 °C, i.e., 5 °C or 6 °C lower than the saturation temperature, to attain the desired precipitation;
4)Separation by filtration *under vacuum*;
5)Drying on exposure to air;
6)Classification of the crystalline product;
7)Analysis through the optical microscope;
8)Pictures of some crystal specimens.

The best STR geometry

The optimal STR's bottom has a *round* shape because the flux lines, constantly tangent to its inner surface, assure the best dispersion for the suspended CAM particles **[5,9,13]**.

Being scarcely affected by other factors (e.g., the *mixing* and the *viscosity*), this geometric result seems valid in general, for *any* batch crystallization.

The best STR mixing

The optimal mixing is in a baffled STR with a three-blade marine impeller (axial flow) at an agitation speed ~2% above the minimum value for solid suspension **[10,11,14]**.

The *VisiMix* software, computing the fluid dynamics of the low viscosity aqueous solution of citric acid inside a vertical round-bottomed small batch crystallizer, corroborates the choice of a 3-blade marine impeller.

Best simulated flux lines

The best seeding conditions

A series of 20 batch tests let us identify the operating parameters ensuring an optimal CSD of CAM.

These conditions can be summarized as follows:

1.Three-blade marine propeller as agitator.
2.Agitation speed ~2% above the minimum value for solid suspension.
3.Seed crystals large ~10% of the desired final size.
4.Seeding temperature ~0.5 °C over that of spontaneous nucleation.
5.Tank crystallizer with a round (hemispherical) bottom.

Here we illustrate the second and third achievement, i.e., the role of the *seed crystal size* & *seeding temperature*.

Finding the optimal seeding

In this talk we expound only the influence of the seeding.

We show that the best CSD, i.e., a homogeneous distribution of large crystals, comes from *small* size seed and *low* seeding temperature.

Namely, the seed crystals should be large one tenth of the desired CAM final average size and the seeding temperature slightly above that of spontaneous nucleation.

Such conclusions are supported by experimental tests and computer simulations.

Influence on the crystallization of various factors

Dipping CAM crystal seed

Tests at varying temperatures and sizes of the seed

Light seed and low seeding temperature

The optimal seeding temperature

Experimental evidence has indicated that seeding at a *low* temperature, but *before* nucleation occurred, results in a marked improvement in the crystalline product.

The optimal temperature for seeding crystalline germs is right next to the spontaneous nucleation temperature (T≈22°C); the further away from this threshold, the worse it is **[1–4,6,7,12]**.

However, it makes no sense to dip seed crystals once nucleation has already taken place, which is why the tests performed in this manner were stopped at an early stage.

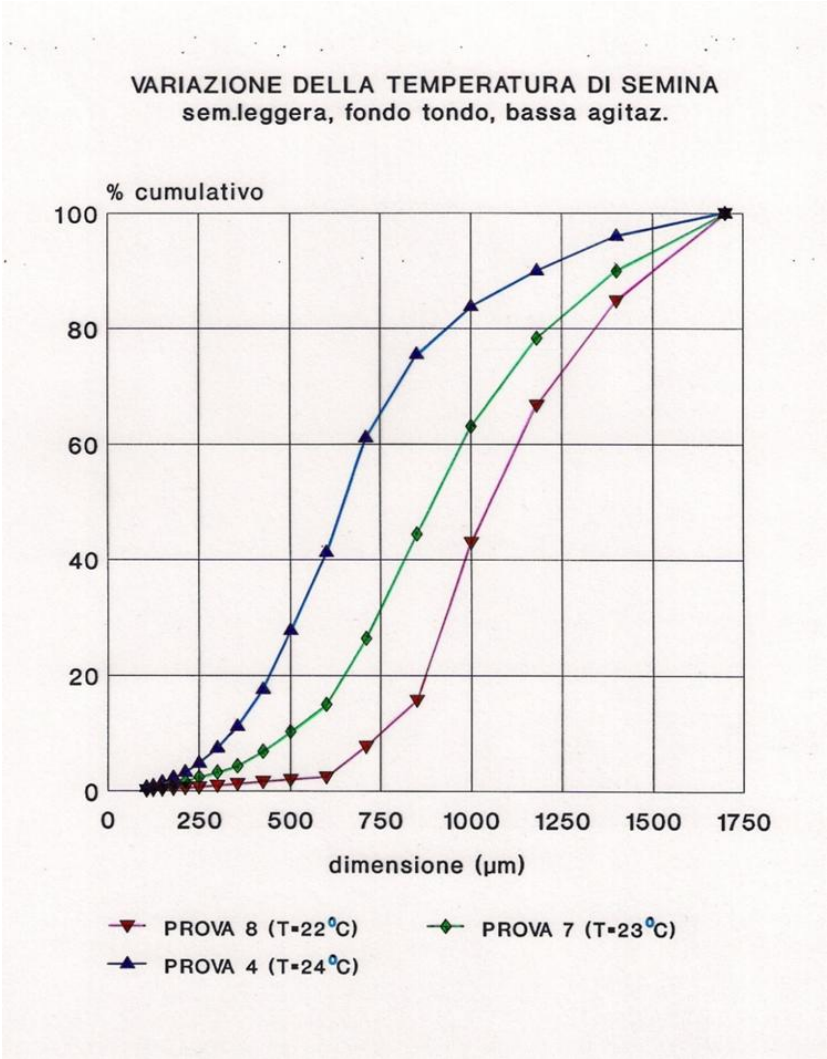
Temperature choice from the CSD

Three successive seeding temperatures were tested: **22°C**, **23°C**, and **24°C**.

The best product was obtained at the lowest temperature (**T=22°C**), while the worst result was obtained at the highest temperature (**T=24°C**).

The optimum value of *22°C* is the lower integer limit before spontaneous nucleation (between *21.4°C* and *21.7°C*).

Low temperature (T=22°C)



Interpreting our temperature tests

The effect of seeding is stronger as the closer the dipping of germination crystals is to the spontaneous nucleation wave (standard T=22°C).

In fact, if the seed is added at too high a temperature, its presence shifts the delicate meta-equilibrium, accelerating its end.

Therefore, the nucleation wave would occur at a higher thermal level (with a low initial supersaturation and a tiny remaining seed) originating a worse crystalline product, affected by a wide granulometric distribution, poor homogeneity, and small average size.

The optimal seed crystals' size

Seeding always has a positive effect but, among the different types of seed, the *light* one ($L_{seed} \approx 1/10$ $L_{product}$) is better than the heavy one ($L_{seed} \approx 1/3$ $L_{product}$) which, in turn, is more effective than the heavier one ($L_{seed} \approx 1/2$ $L_{product}$).

The risk of a ruinous second wave of nucleation increases with the *heaviness* of the seed.

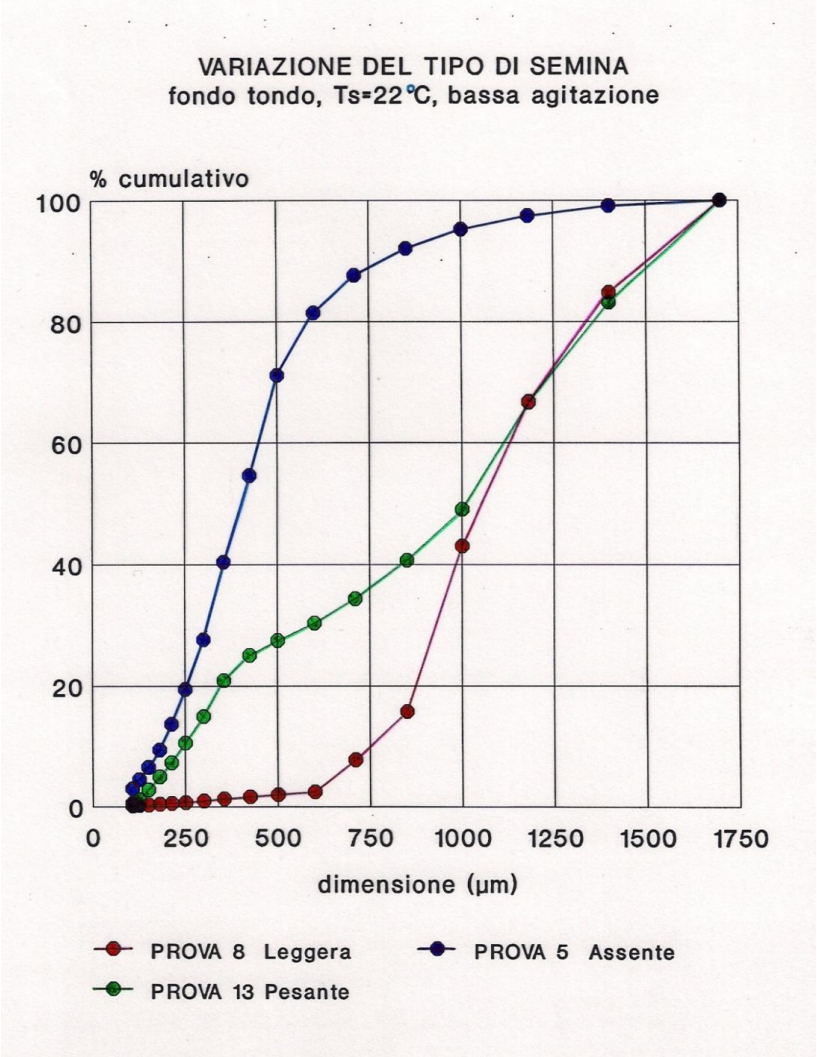
Furthermore, during growth the heavy seed crystals (with a low surface/volume ratio) are disadvantaged in energy supply, in favor of smaller crystalline conformations, and this penalizes the final average size of the distribution **[1–4,6,7,12]**.

Size choice from the CSD

The ***heavy seed***'s diagram is worse than the CSD obtained with ***light seed*** but, in any case, better than the test in ***absence of seed***, which produces tiny crystals.

The duration and intensity of any subsequent nucleation, to be avoided, would be directly proportional to the quantity and average size of the seed crystals.

Light seed ($L_{seed} \approx 1/10\ L_{product}$)



Interpreting our size tests

A *light* seed is optimal because, during the first nucleation, it removes only a minimal part of the supersaturation and, in the competitive mechanism of growth, *small* seed crystals (with a big surface/volume ratio) absorb a considerable share of the residual *driving force* (i.e., the difference between the solute's chemical potentials in, respectively, the supersaturated and saturated solution) increasing the average size of the product and avoiding further nucleation.

On the contrary, a *heavy seed* diverts a significant portion of the available supersaturation for its own growth (inhibiting the generation of other crystals), and the residual *driving force* is excessive, with an elevated risk of subsequent nucleation.

A simulation program in QBasic

In order to simulate the CAM tests, we wrote a QBasic program *ad hoc* (see, e.g., **www.qbasic.net**) starting from previous work about the batch crystallization of potassium sulfate.

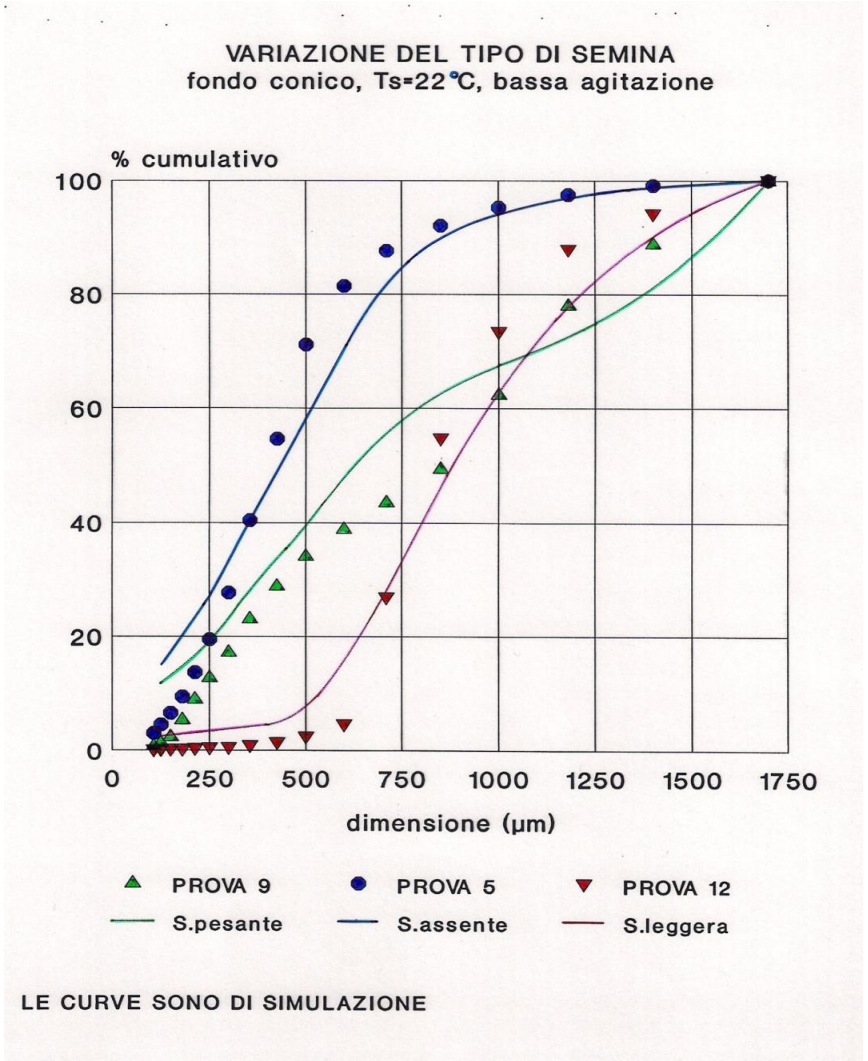
The CAM peculiarities, inferred via the microscopic analysis of its grains **[8]**, were coded through subroutines specific to the agglomeration and the secondary nucleation by collision **[6]** of the discontinuous phase.

Eventually, the experimental data were in good agreement with the predictions 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.

Data & simulations for the conical tank

Conical-bottomed STR

Simulation curves



Conclusions

In the years 1997-1998, at DICMA-lab of La Sapienza University we analyzed the batch cooling crystallization of the citric acid monohydrate (CAM) from aqueous solutions.

The choice of a *light* seed optimized the process, by avoiding subsequent nucleation and increasing the average size of the crystalline product.

Looking for a homogeneous distribution of large crystals, we found that a temperature slightly above the spontaneous nucleation (T=21.4°C–21.7°C), namely T=22°C, was the most effective to reduce the negative incidences of a low initial supersaturation and a negligible surplus seed.

The experimental work was supplemented by a QBasic program to predict the CSD.

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- *Aracne Editrice*, for the 2013 "Diritto di Stampa" **[3]**;
- *SIF 101st Congress in Rome*, for the 2015 talk **[9]**;
- *Ettore Majorana 40th Gran Gala*, for the 2015 invitation;
- *ICMCS 5th Conference*, for the 2016 appreciation **[10]**;
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- *AGMA 8th Conference in Odesa*, for the 2024 talk **[14]**;
- *AGMA 9th Conference in Odesa*, for the 2025 talk.

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