International scientific online conference

Algebraic and Geometric Methods of Analysis

- Title: **Shape optimization in the batch crystallization of CAM**
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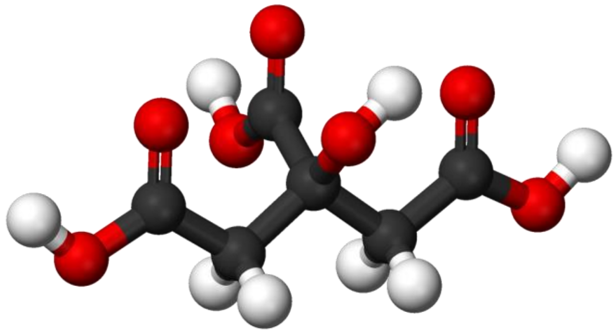
The state of art in 1997

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 **[13]** and on the crystal growth **[14]** rather than on the industrial aspects of the crystallization in STRs.

Formula: $C_6H_8O_7$



Structure: monoclinic

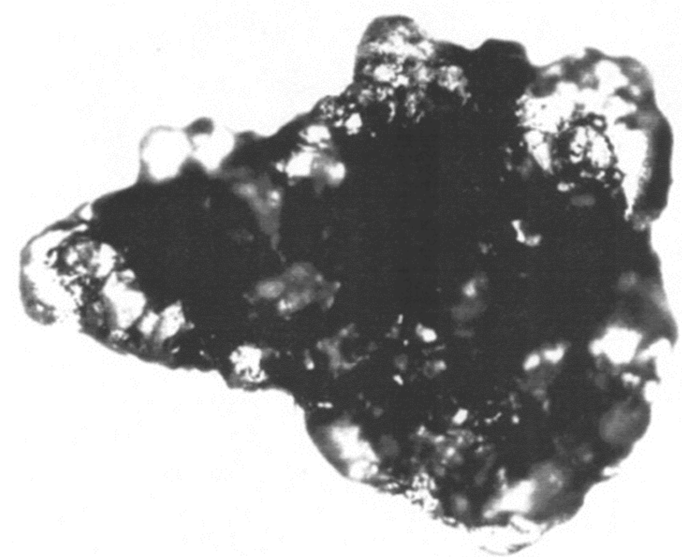
Producing CAM at La Sapienza's lab

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

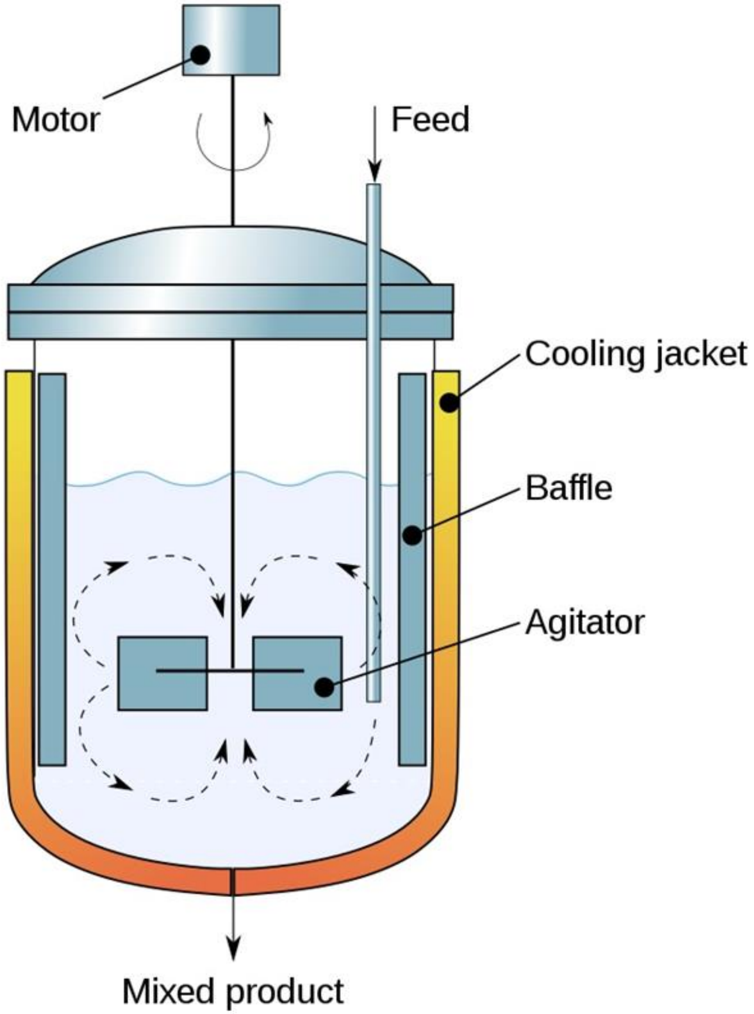
Crystal size 1.18-1.4 mm



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]**.



Finding the optimal shape of STRs

Here we expound only the influence of the STRs' geometry.

We show that the best CSD, i.e., a homogenous distribution of large crystals, always comes from round-bottomed tanks.

Hemispherical tanks perform slightly better than conical and much better than flat (discarded in industrial practices).

Based on experimental tests and computer simulations, such conclusions seem valid beyond the limits of our survey on CAM.

Influence on the crystallization of various factors

Geometry of the stirred-tank reactor's bottom

Experimental tests in differently shaped STRs

Round bottom better than conical and flat

Results of a meticulous testing

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 impeller.
2. Agitation speed ~2% above the minimum value for solid suspension **[15]**.
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.

In this talk we illustrate the last achievement, i.e., the role played by the STRs in crystallizing the CAM thanks to their differently shaped bottoms **[9]**.

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, in order 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;

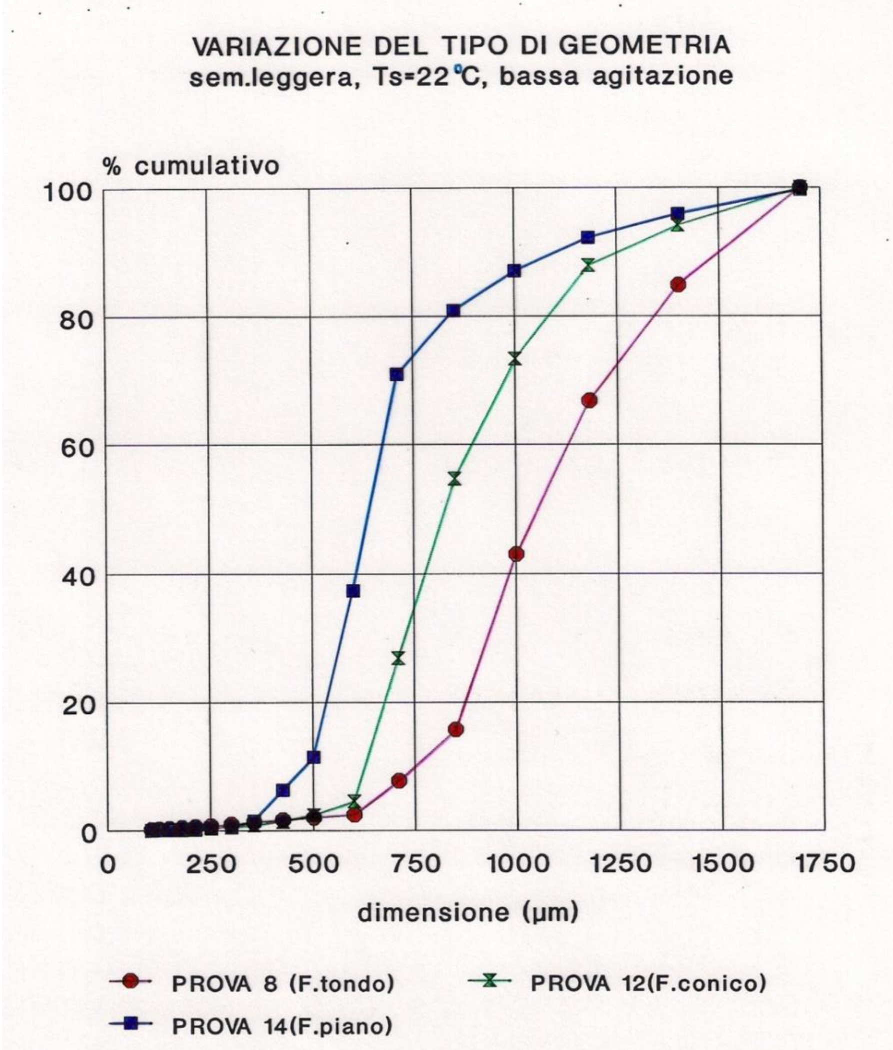
8)Pictures of some crystal specimens.

Comparing our three STRs' shapes

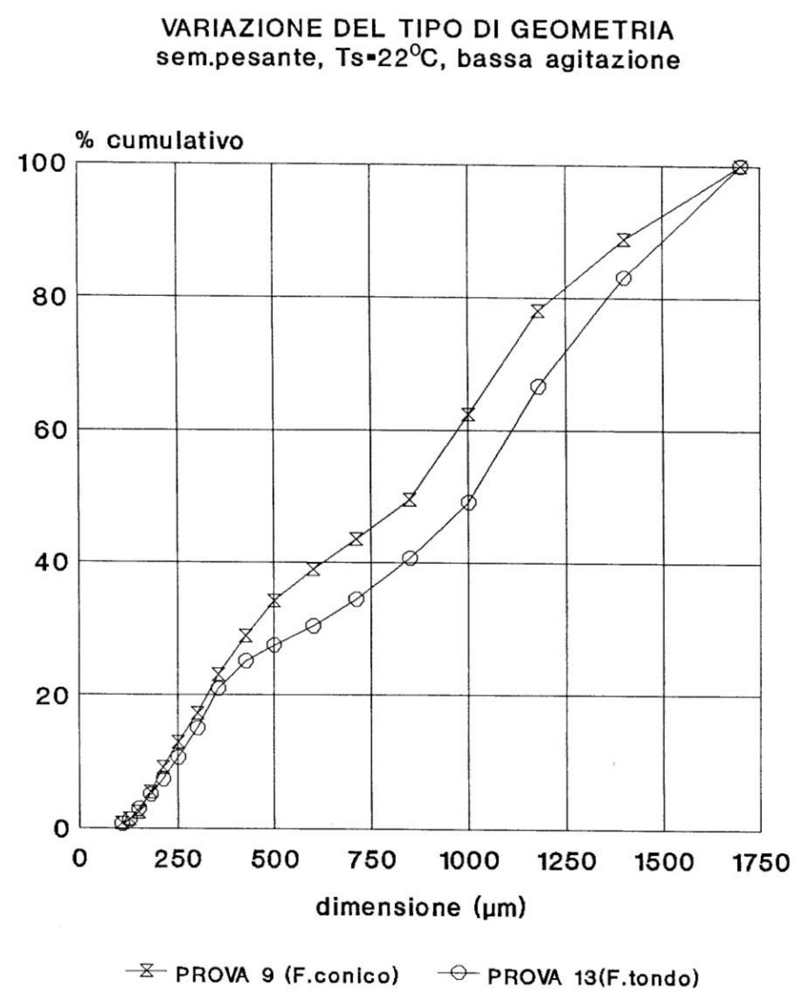
Geometric features of our STRs:	**FLAT**	**ROUND**	**CONICAL**
TANK's volume (L):	*10.1*	*9.9*	*9.8*
TANK's total height (mm):	*265*	*350*	*325*
TANK's height of the body (mm):	*265*	*255*	*205*
TANK's height of the bottom (mm):	*0*	*95*	*120*
TANK's outer diameter (mm):	*230*	*214*	*230*
TANK's inner diameter (mm):	*220*	*204*	*220*
JACKET's height (mm):	*120*	*120*	*120*
JACKET's outer diameter (mm):	*270*	*254*	*270*
JACKET's inner diameter (mm):	*260*	*244*	*260*
JACKET's distance from the top (mm):	*80*	*100*	*50*
JACKET's distance to the bottom (mm):	*65*	*35*	*35*
BAFFLES' height (mm):	*260*	*250*	*200*
BAFFLES' width (mm):	*20*	*20*	*20*
BAFFLES' thickness (mm):	*5*	*5*	*5*

Comparison among tests

Comparing our three STRs



The best two STRs



The best STRs according to our tests

1st) Round-bottomed STR **2nd) Conical-bottomed STR**

Interpreting our tests

All the collected data indicated that a stirred-tank reactor with a *hemispherical bottom* was preferable to any other differently shaped STR, producing large-sized homogeneous CAM crystals.

On the opposite, the flat-bottomed STR gave bad results in terms of CSD, with a high percentage of fine-grained crystals and a significantly reduced average size.

The best performance of the round-bottomed tank was surely due to its *optimal shape* and not to other parameters, such as the different thermal profile induced by the cooling jackets or the mixing efficacy.

To corroborate our conclusion, we measured the *heat exchange* in each STR: maximum for the vessel with a conical base, followed by the round and, eventually, the flat-bottomed tank.

We established also the *agitation* efficiency in each STR: maximum for the vessel with a flat base, followed by the conical and, finally, the round-bottomed tank.

Computational fluid dynamics

The experimental evidences were supported by the VisiMix software (**www.visimix.com**) computing the fluid dynamics inside each crystallizer for CAM viscosity in the range T=19-22 °C and for the tests' standard speed N_C=755 rpm.

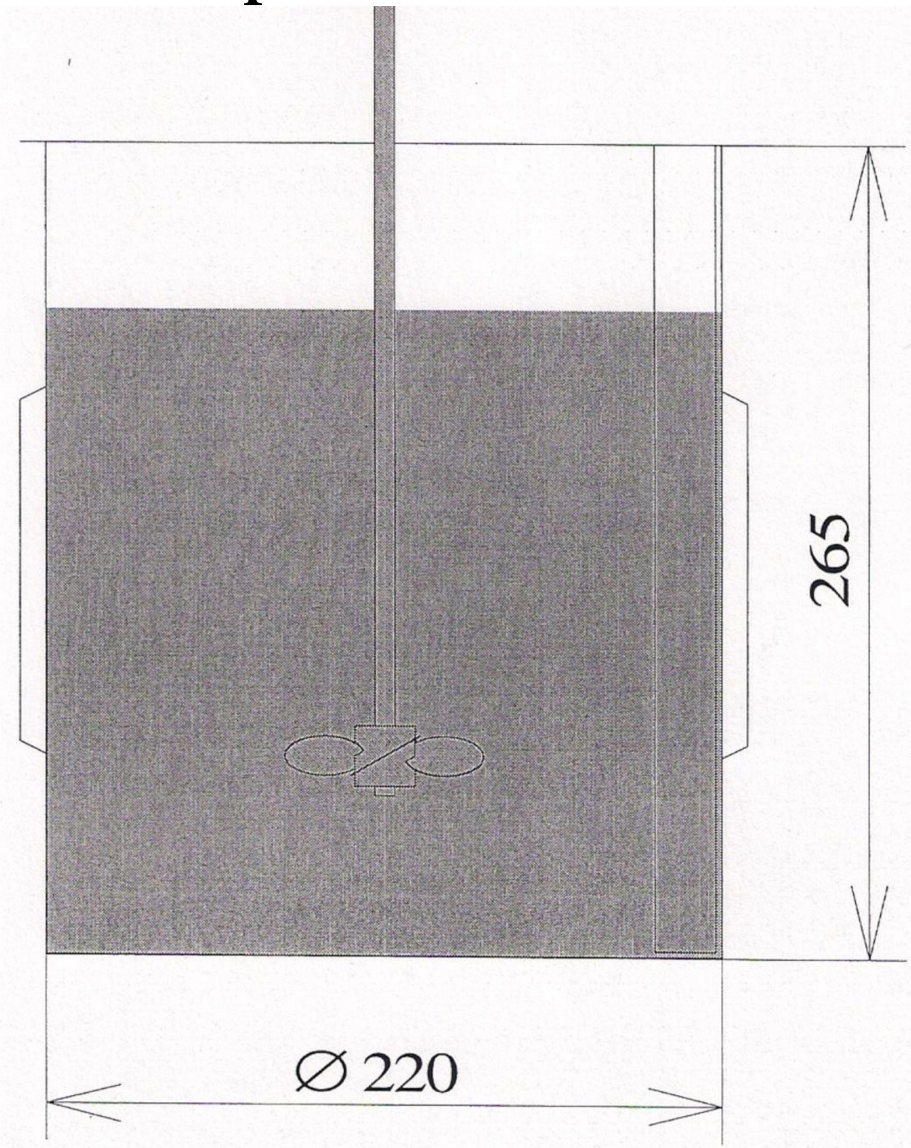
The *round* shape was confirmed as the best STR's bottom because the flux lines, constantly tangent to its inner surface, assured the best dispersion for the suspended CAM particles.

The *conical* shape did not fully comply the dispersed phase's motion lines given by the impeller, whereas the *flat-bottomed* STR's deformed flux lines generated the worst suspension state.

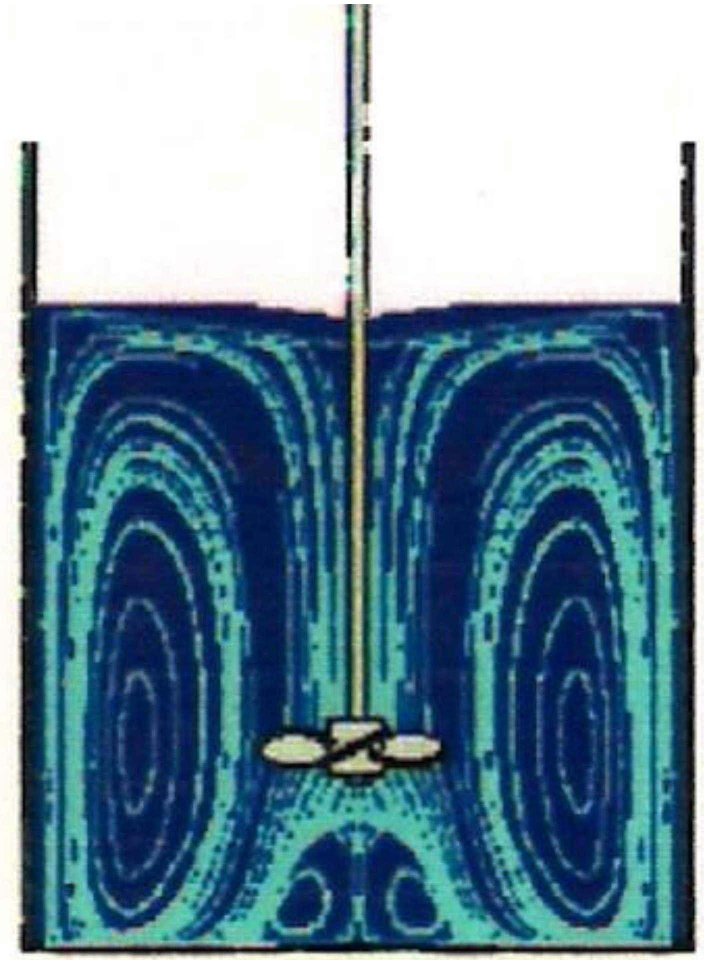
Being scarcely affected by *mixing* (choice of the impeller and/or the stirring rate) and by *viscosity* (choice of the substance and/or the temperature for the cooling process), such conclusions seem valid in general, for *any* batch crystallization.

The flat-bottomed crystallizer

A shape to be avoided

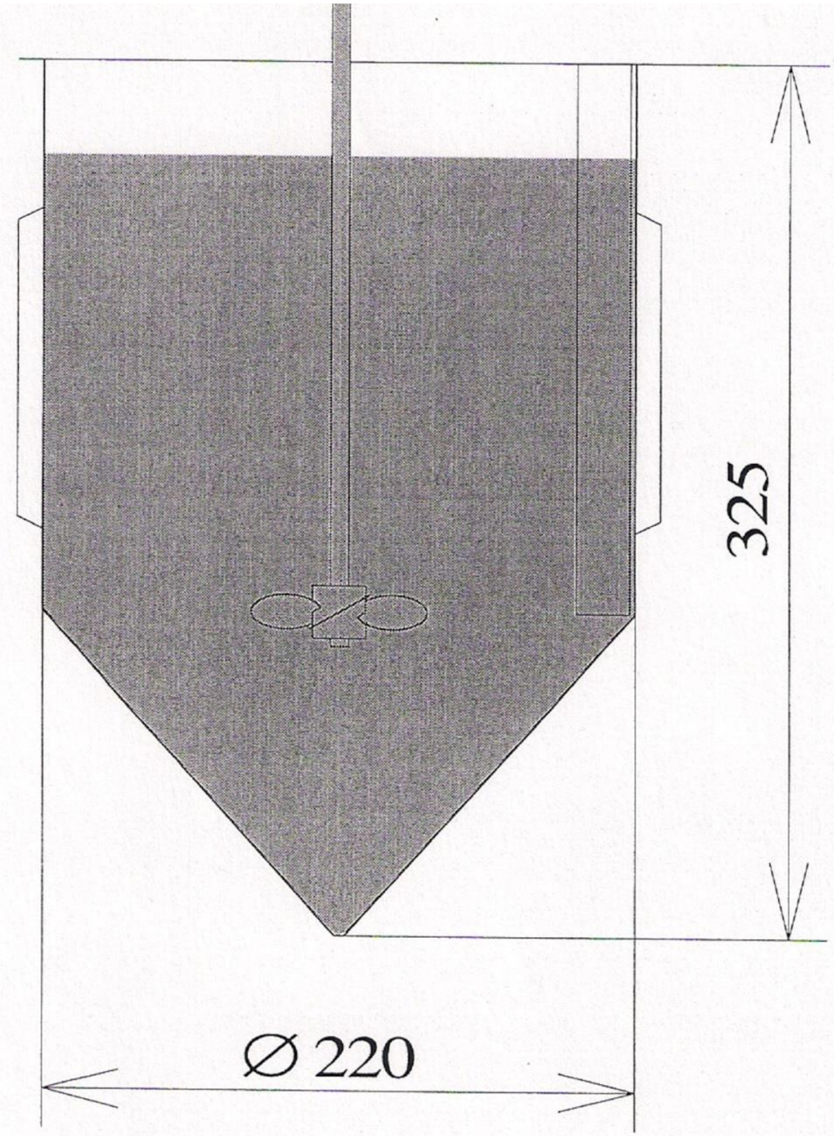


An ineffective flux



The conical-bottomed crystallizer

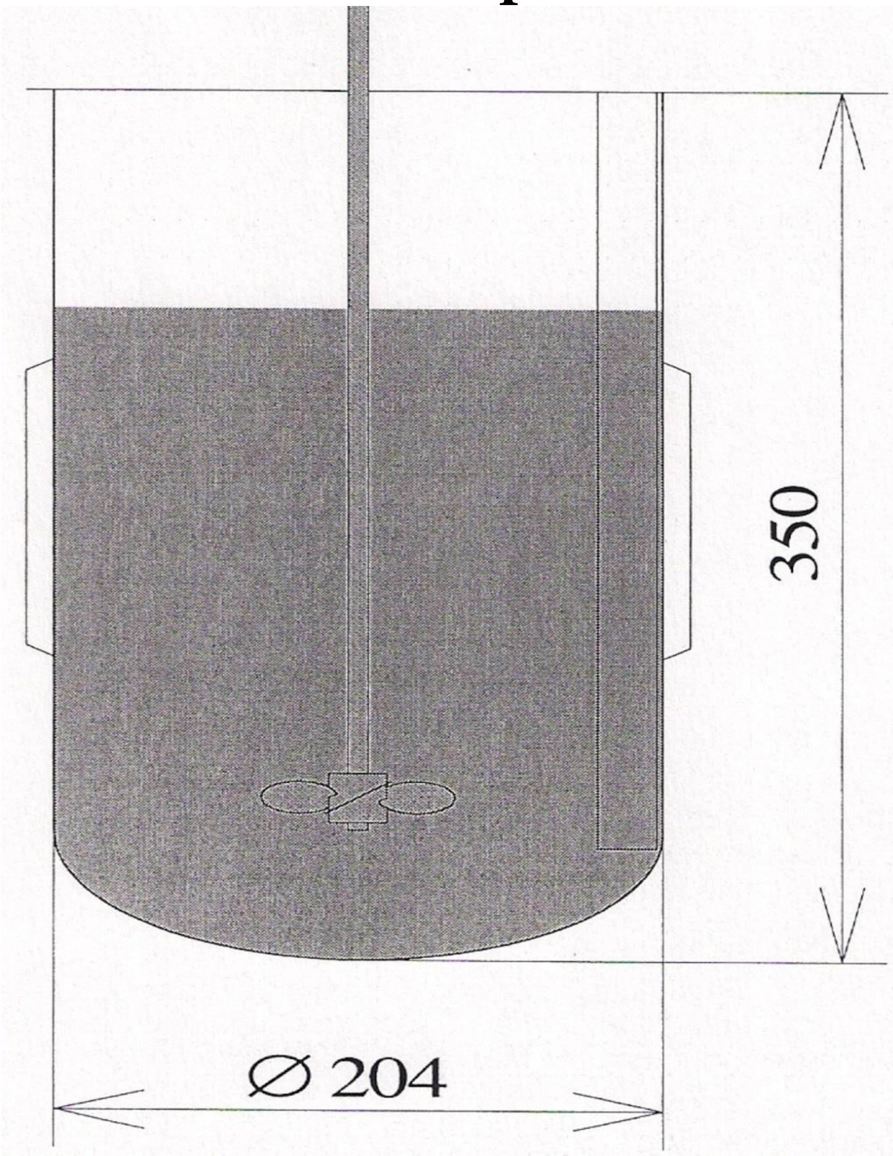
A possible shape



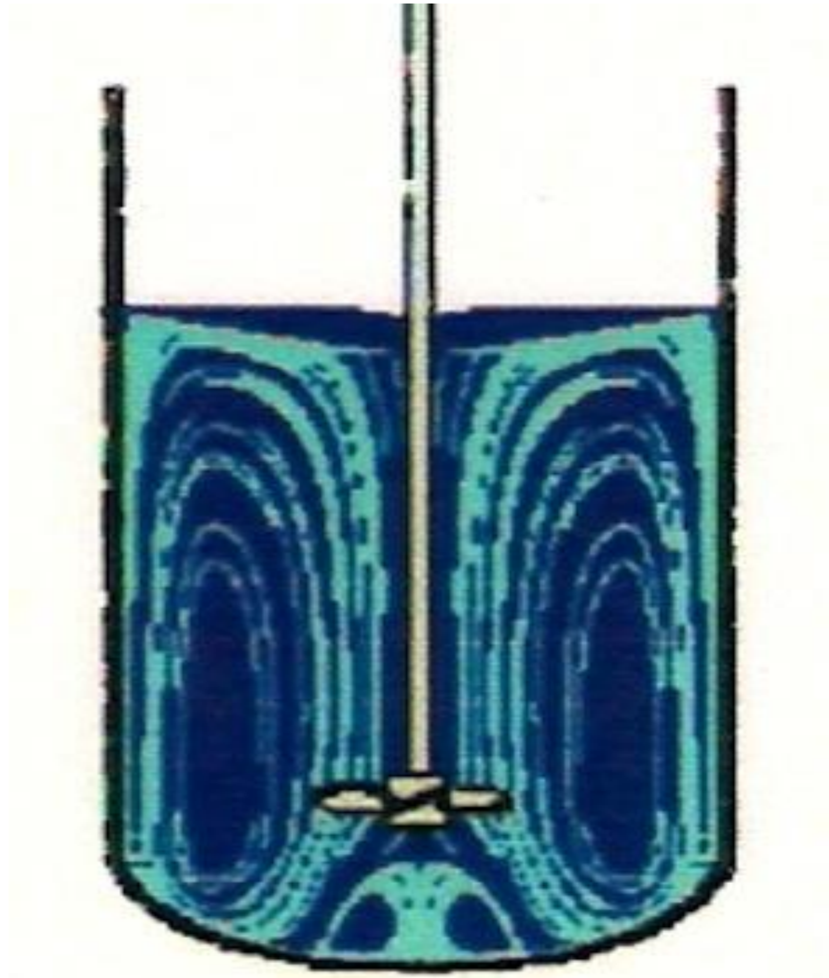
An acceptable flux

The round-bottomed crystallizer

The best shape



The optimal flux



The best STRs according to CFD

Best STR
(round bottom)

Second best STR
(conical bottom)

A simulation program in QBasic

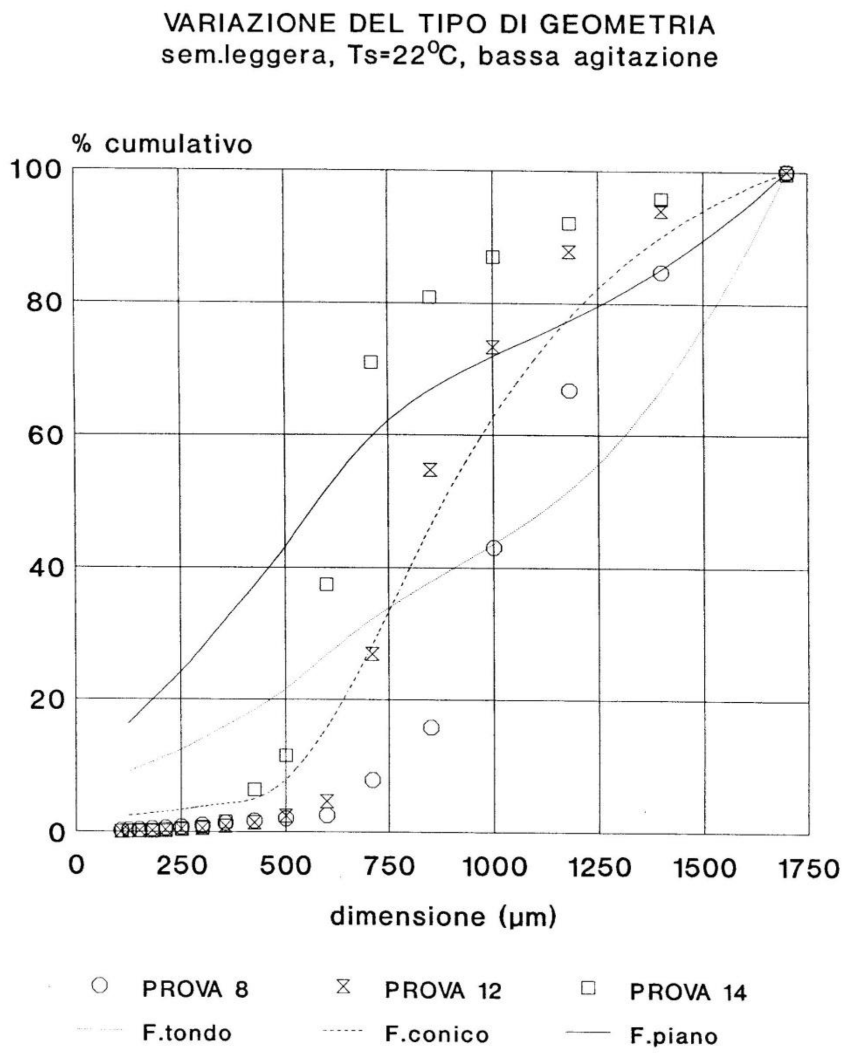
In order to simulate the CAM tests, we wrote a QBasic program *ad hoc* (see, e.g., **www.qbasic.net**) starting from a previous work about the batch crystallization of the potassium sulfate.

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

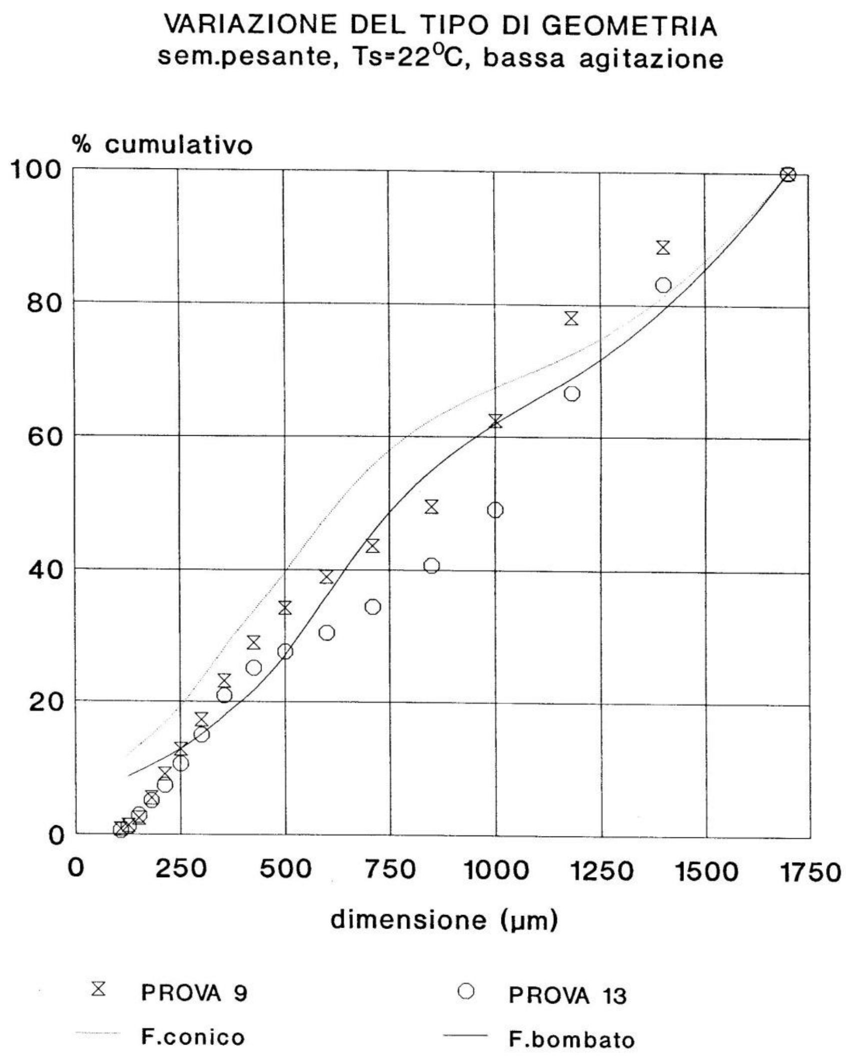
Eventually, the experimental data were in good agreement with the predictions and it was possible to reproduce faithfully the influence of the cooling profile on the crystal granulometric properties and the effects of all the operating variables, except with *heavy seed* crystals.

Comparing simulations with real data

Comparing our three STRs



The best two STRs



The best STRs according to simulations

1st) Round-bottomed STR

2nd) Conical-bottomed STR

Conclusions

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

The choice of a stirred-tank reactor (STR) with a hemispherical bottom *optimized* the process, allowing the best suspension state for CAM particles.

Looking for a homogenous distribution of large crystals, we found that the conical-bottomed STR was in second place for efficiency, whereas the flat-bottom shape performed rather poorly, providing the lowest crystalline quality.

The experimental work was supplemented by a QBasic program to predict the CSD and by the VisiMix software to simulate the fluid dynamics inside each crystallizer.

Acknowledgements

As far as the study on CAM is concerned, we wish to thank the Organizing and Scientific Committees of the:

- *SIF 96th Congress in Bologna*, for the 2010 talk **[1]**;
- *International Year of Chemistry*, for the 2011 lecture **[2]**;
- *Magna Graecia 15th Prize*, for the 2012 Science Award;
- *Sapio Prize*, for the 2012-2018 award nominations;
- *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]**;
- *Frascati Scienza*, for the ERN 2019 invited lecture **[12]**;
- *AGMA 7th Conference in Odesa*, for the 2023 talk.

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Slide 1.

www.imath.kiev.ua/~topology/conf/agma2018/images/bg.jpg

Slide 2.

https://en.wikipedia.org/wiki/Citric_acid#/media/File:Citric-acid-3D-balls.png

https://en.wikipedia.org/wiki/Citric_acid#/media/File:Zitronens%C3%A4ure_Kristallzucht.jpg

Slide 3.

www.researchgate.net/publication/279193084_Photo_gallery_of_CAM_crystals_from_aqueous_solutions

Slide 4.

https://en.wikipedia.org/wiki/Baffle_(heat_transfer)#/media/File:Agitated_vessel.svg