Hybrid CFD-Multizonal Modelling of Polymorphs and Agglomeration Phenomena in Crystallisation Processes

Sean K. Bermingham[1], Stefania Trivellato[1,2], Maddalena Vernier[1,2], Fabrizio Bezzo[2,*]
[1]Process Systems Enterprise Ltd., Bridge Studios, 107a Hammersmith Bridge Road, London W6 9DA (United Kingdom)
[2]DIPIC – University of Padova, via Marzolo 9, 35131 Padova, (Italy)
[*]fabrizio.bezzo@unipd.it, tel. +39 0498275468, fax +39 0498275461

The capability to simulate crystallisation systems is of paramount importance for the design and operation of crystallisation processes with the aim of controlling the product quality and yield. Crystallisation phenomena are affected by the chemical and physical behaviour of the system being considered as well as by the fluid flow and mixing pattern in the vessel. Here, a comprehensive description of crystallisation processes is achieved by coupling a general process modelling tool with a computational fluid dynamics (CFD) tool. This hybrid model allows an accurate description of the product quality. The approach is assessed by simulating a polymorphic system and a system exhibiting agglomeration.

1. Introduction

Crystallisation is a separation, purification and recovery process employed to produce a wide variety of solid materials. It is a phase change in which a crystalline product is obtained from a solution or a melt. The economic value of the product derives from the quality aspects of the crystals, such as the crystal size distribution (CSD), morphology and kind of polymorph; therefore it would be very advantageous if accurate prediction methods were available for a product quality estimate.

The crystallisation processes are described through the combination of mass, energy and population (PBE) balances; the PBE accounts for the various mechanisms which determine the final qualities of the crystals: nucleation, growth, agglomeration and breakage; the latter will not be taken into account during this work. These phenomena can be implemented by using state-of-the-art process modelling tools like the gPROMS® software (Process Systems Enterprise, Ltd.) adopted in this work.

However, basically all crystallisation phenomena are strongly influenced by the flow turbulence and the mixing pattern of the system under investigation. The hydrodynamics can be described by means of CFD codes such as the Fluent® software (Fluent, Inc.) used here. In particular, a hybrid Multizonal/CFD approach (Bezzo *et al.,* 2004) is carried out. As it will be described in Section 3, thanks to this method it is possible to address both the solution of a full PBE and the representation of the fluid flow dynamics, which is described by the CFD model. The crystalliser is divided in a network of homogeneous and well-mixed zones, each of them is described within the gPROMS modelling environment. On the other hand Fluent® solves the momentum

balance and passes the updated flow-related parameters to gPROMS; the iterative sequence is repeated until convergence.
The goal of this paper is to investigate the potential of this hybrid approach to describe polymorphic systems, which require separate PBEs for each dispersed phase in every zone, and to model the complex agglomeration phenomenon.

2. Theory

The population balance equation considers both the size and the number of particles, describing the evolution of the population density function *n(L,t)*:

$$\frac{\partial\left[n(L,t)V(t)\right]}{\partial t} = -V(t)\frac{\partial\left[n(L,t)G(L,t)\right]}{\partial L} + V(t)\left[B(L,t) - D(L,t)\right] + \phi_{in}(t)n_{in}(L,t) - \phi_{out}(t)n_{out}(L,t) \tag{2.1}$$

where L is the crystal size, V the volume, G the growth, (B-D) the agglomeration term and ($\phi_{in} - \phi_{out}$) accounts for the convective transport into and out of the volume.
The following systems are taken as case studies: Case 1: an unseeded fed-batch antisolvent crystallisation producing two polymorphs, α-L-Histidine and β-L-Histidine (ter Horst *et al.,* ,2006 and Roelands, 2005); Case 2: a seeded batch precipitation producing Vaterite (Andreassen and Hounslow, 2004).
Polymorphism is the possibility for a substance to crystallise in different structural arrangements each of them having the same chemical structure; in order to predict the polymorphic fraction one PBE has to be written for each polymorph. The supersaturation-dependent expressions for the nucleation, and for the growth of the polymorph L-Histidine are based on the paper by ter Horst *et al.,* (2006): it is shown that the growth depends on the mass transfer coefficient k_d:

$$k_d = D_m / L\left[2 + 0.8\left(\varepsilon L^4 \rho^3 / \mu^3\right)^{1/5} Sc^{1/3}\right] \tag{2.2}$$

where D_m is the diffusion coefficient, ρ and μ are the density and the dynamic viscosity of the liquid, Sc is the Schmidt number and ε is the turbulent energy dissipation rate.
Agglomeration is a process in which particles collide, adhere one to the other and form a new larger particle. The agglomeration rate is characterised by a rate constant β, termed the agglomeration kernel, which is the product of two factors: β_0, which depends on operating conditions and $f(L_1,L_2)$, which is some function of the two agglomerating particles sizes L_1 and L_2. In this work the supersaturation-dependent growth rate and the size-independent kernel developed by Liew *et al*., (2003), have been chosen:

$$\beta_0 = \left[A_{50}G/\left(\rho d_{3.0}^2 \varepsilon\right)\right] / \left[1 + A_{50}G/\left(\rho d_{3.0}^2 \varepsilon\right)\right] \cdot d_{3.0}^3 \sqrt{8\pi\varepsilon/15\nu} \tag{2.3}$$

where $d_{3,0}$ is the 3.0 mean particle size, A_{50} is a substance specific parameter (in this case vaterite) and ν is the fluid kinematic viscosity. Note that both correlations (2.2) and (2.3) depend on the fluid flow behaviour through the turbulent energy dissipation rate ε.

3. Hybrid gPROMS/CFD model

Crystallisation processes are described in gPROMS using the *Advanced Model Library for Solution Crystallisation* (AML:SC®; Bermingham *et al*., 2005), which contains predefined models describing conservation laws, kinetics and sensors.

The interaction between the fluid flow behaviour and the other phenomena is a critical aspect in those processes (e.g. crystallisation) where such interactions significantly affect product quality and process performance (e.g. effect of fouling on uptime). Hybrid gPROMS/CFD modelling can be applied to those systems where the fluid dynamics operate on a much faster time-scale than other phenomena, and can be described in terms of steady-state CFD computations involving a pseudo-homogeneous fluid, which takes account of the presence of a solid phase through the density and viscosity. A CFD model of the process is used to determine the flow pattern and the fluid-related properties inside the equipment, dividing the space into a relatively large number of cells; it focuses only on hydrodynamic prediction.

The gPROMS Multizonal (MZ) representation divides the equipment volume into a network of interconnected zones where an idealised mixing pattern is assumed for each zone. The correspondence between the two geometric representations is auto-generated by the MZ Interface. The crystalliser is divided into a grid of zones, specified by the user. The zones created in such a way are called internal zones, as shown in Figure 1. The gPROMS model needs also to specify the interaction between the system and the environment; this is done by defining environment zones, which correspond to FLUENT® inlets and/or outlets.

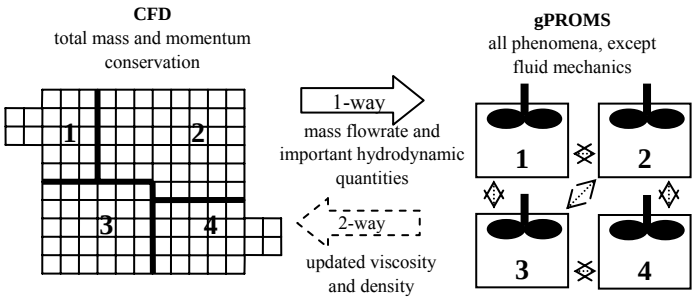

Figure 1 Exchange of information in the Multizonal model.

It is possible to choose between two different schemes of the MZ mode: 'one-way' and 'two-way'. In the 'two-way' mode the CFD is not only used to create a hydrodynamic model, but it is also used during the simulation; this MZ mode takes into account changes in the hydrodynamics, calculated by the CFD, as a result of the predicted changes in density and viscosity, calculated by gPROMS. In this work the 'one-way' approach is used (see Figure 1).

4. Simulations results

In order to assess the effects of the use of a hybrid MZ/CFD model the crystalliser has been divided in 4 regions. A lab scale 4L baffled crystalliser with a centred impeller has been taken into account. The rotation speed has been set equal to 500 rpm. The results are illustrated through Figures 2-7. Figures 2 and 3 show the average growth and agglomeration rates for the two case studies: a single zone model is compared to a four zone model. Particularly in Case 1, it can be seen that the non-homogeneous distribution of ε determines significant differences in the description of the kinetics of crystallisation phenomena. This is confirmed by the results of Figures 4 and 5: clearly both growth and agglomeration can exhibit large differences between different region of the vessel, even when a relatively small piece of equipment is described.

Figures 6 and 7 compare the effect of a multizonal approach in terms of the crystal volume density. The effect is quite remarkable in Case 1: if a local representation is not adopted the simulation cannot grasp the effect of the hydrodynamics on the yield and polymorphs distribution. On the contrary, in Case 2, the differences in volume density in the agglomeration case study are not significant. This is not surprising since the agglomeration term does not influence the CSD, as the growth does.

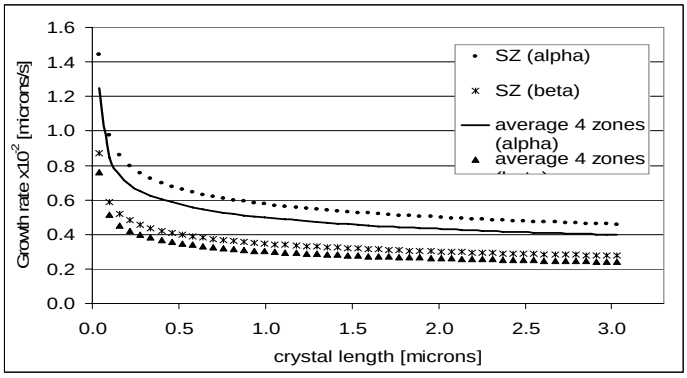

Figure 2. Case 1: growth rate trends of both polymorphs α and β, for the simulations with a single and four zone model (end of the batch).

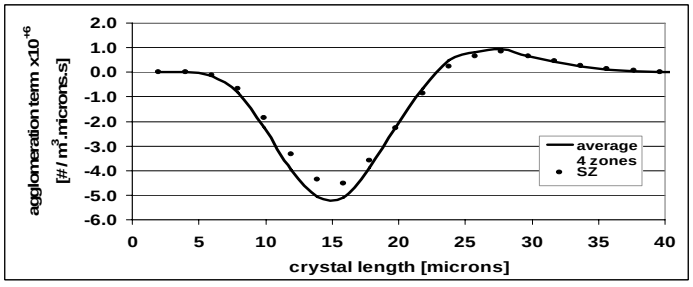

Figure 3. Case 2: Averaged agglomeration rate for the simulations with a single and four zone model (end of the batch).

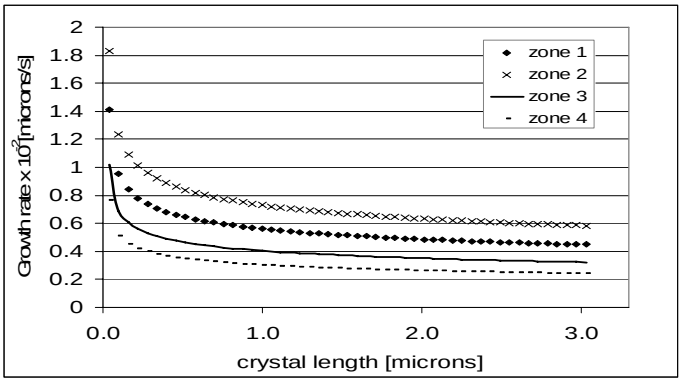

Figure 4. Case 1: Growth rates of polymorph α in the four zone model (end of the batch).

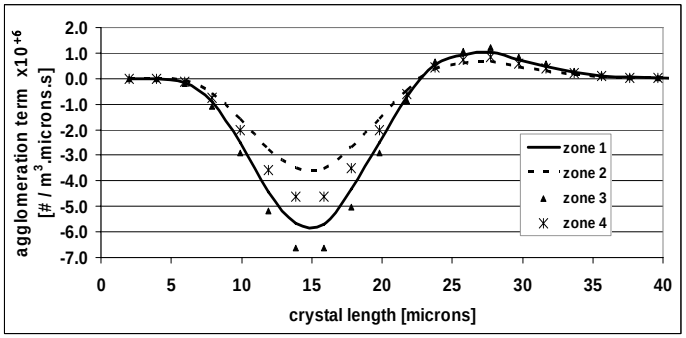

Figure 5. Case 2: Agglomeration rate in the four zone model (end of the batch).

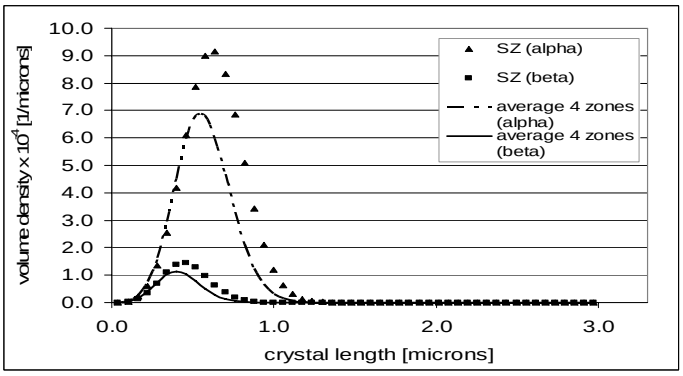

Figure 6 Case 1: volume density function of both polymorphs for the simulations with the one and four zone model (end of the batch).

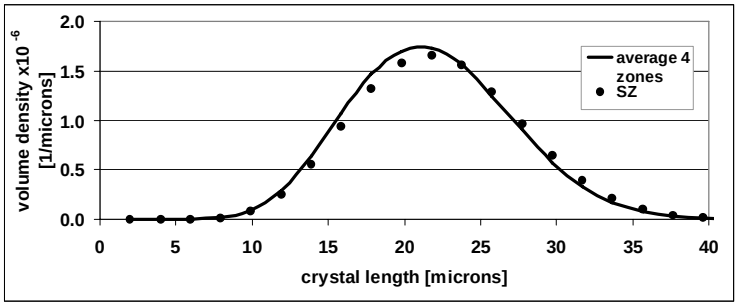

Figure 7 Case 2: crystals volume density for the simulations with the one and four zone model (end of the batch)

5. Conclusions

This work demonstrate how a precise description of the hydrodynamics is needed to correctly describe the evolution of crystallisation phenomena modelled through a full PBE. All the crystallisation mechanisms which affect the final qualities of the crystals are influenced by the flow turbulence and the mixing pattern. The effectiveness of a hybrid multizonal/CFD model, which takes advantage of state-of-the-art general process modelling tools and CFD codes, has been proved by means of two case studies. It is shown that the single zone model cannot properly describe the effect of the interaction between the hydrodynamics and the other chemical and physical phenomena affecting crystallisation. A local representation is needed.

Future work will consider a methodology to assess the effect of the number of zones on the final solution.

6. References

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