Chemical Engineering Science 65 (2010) 5676–5686

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Modeling of crystal morphology distributions. Towards crystals with preferred asymmetry

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ARTICLE INFO

Article history:
Received 29 January 2010
Received in revised form
16 March 2010
Accepted 17 March 2010
Available online 27 March 2010

Keywords:
Population balance modeling
Crystal growth
Crystal symmetry
Crystallization
Group theory

ABSTRACT

Exploitation of crystal symmetry is very important in formulation and efficient simulation of population balance models for crystal morphology. This work presents the first population balance model for morphology distribution considering the diversity of symmetry. In this model, we analyze the symmetry of a population of crystals using group theory and divide the population into various symmetry classes, which, in turn, is subdivided into various morphological forms. The internal coordinate vector for any given crystal can be symmetry reduced and can be grouped into various sets characterized by identical growth rates. It has been shown that the internal coordinate vector can be represented in such a way that only one internal coordinate needs to be treated dynamically for each set while all other coordinates remains invariant during growth. This leads to a very small number of dynamic internal coordinates and the effective dimensionality of the problem becomes very small, allowing simulation of a population of asymmetric crystals with minimal computational effort. It has been shown using this model that the concentration of more symmetric crystals invariably increases during the growth process. However, this natural gravitation of the crystal population towards more symmetric forms can be controlled by manipulating the supersaturation which has been shown using numerical examples.

1. Introduction

We focus in this paper on cultivating, in a well-stirred crystallizer, geometrically asymmetric crystals with a preponderance of faces having properties of specific interest. The properties are linked to an application as, for example, in the promotion of bioavailability in pharmaceutical products, higher chemical activity of particles in synthetic catalysts, and so on. Asymmetric crystals, however, are constantly gravitating towards symmetry so that sustenance of asymmetry calls for ways to forestall this migration. We rely for this navigational effort only on the manipulation of supersaturation although other avenues have existed at least on an empirical basis particularly in industrial practice. However, the methodology we adopt will set the trail for more comprehensive approaches in a rational manner when quantitative understanding of other effects becomes available.

There is currently in the literature good understanding of the required mathematical framework for analyzing the behavior of a population of crystals growing in a stirred crystallizer (Dirksen and Ring, 1991; Zhang and Doherty, 2004; Ma et al., 2008; Borchert et al., 2009). However, such efforts have relied on the boons of symmetry so that the description of morphology requires only a very limited number of variables. The objective that we have set forth cannot, however, be met by imposing such constraints. We seek in this paper an approach built on exploiting basic features of an asymmetric crystal that serve to minimize the computational effort involved for cultivating asymmetric crystals. The strategy for this is built on minimizing the number of crystal dimensions that vary during growth. The appreciation of how such a minimization is actually accomplished requires geometrical insight of a faceted crystal.

It has been shown that a faceted crystal may be interpreted as the intersection of convex polyhedra, each bounded by a "family" of faces characterized by the same growth rate (in a common supersaturation environment), viz., the rate at which each face advances from an arbitrary reference point in a direction normal to itself. As the orientation of each crystal face remains fixed relative to crystal coordinates during growth, the interior angles between faces of the polyhedron representing a particular family is invariant with time. Since frequently some faces are slow growing relative to others, allowing the crystals to be viewed as two dimensional objects, we restrict our demonstrations to such

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doi:10.1016/j.ces.2010.03.026

crystals for visual clarity. However, the methodology discussed in this article is not restricted to the two dimensional crystals alone and can readily be extended to three dimensional crystals by replacing polygons by polyhedra.

Our methodology consists in exploiting the symmetry properties of the polygons by elucidating the maximum number of distinct time varying crystal dimensions. Towards this end, we provide a theoretical development that begins with defining a crystal state vector comprising all crystal faces and progress towards its description in terms of the minimum number of distinct time varying components in the vector. In what follows, various recent efforts for modeling crystal shape and morphology is recalled before attending to the issues of main concern in the paper.

2. Previous work

Control of crystal shape can be realized by changing the properties of the solution, namely by using additives (Weissbuch et al., 1991; Sangwal, 2007), changing the solvent (Davey et al., 1982) or in the simplest way by manipulating supersaturation (Liu and Bennema, 1994; Liu et al., 1995; Boerrigter, 2002). Thus the control of supersaturation presents an avenue for manipulating crystal shape towards a desired direction. However, a quantitative model based understanding of crystal growth is essential in order to achieve desired control in commercial applications.

Crystallizers are usually modeled using the population balance equation (Randolph and Larson, 1971; Myerson, 1993; Ramkrishna, 1985, 2000) considering only one internal variable. Often readily measurable quantities like volume, mass or diameter of the particle is used as an internal variable depending on the method of measurement used in the experiments. While such a simplistic one dimensional model is useful in predicting the size distribution of crystals, it has no means to predict crystal shape. Clearly, a multi-dimensional population balance model is required to describe the distribution of shape and size of a population of crystals.

Multidimensional model of a crystal population often recognizes crystals in terms of more than one characteristic dimension without invoking a faceted structure (Ma et al., 2002; Puel et al., 2003). However, recognition as a faceted structure is essential for applications like catalysis where it is advantageous to promote a specific face. Following the early work of Cardew (1985), Gadewar and Doherty (2004) considered crystals as faceted objects and a single crystal model was formulated considering appearance and disappearance of faces. Zhang and Doherty (2004) used this multidimensional description of a single crystal in a population balance model with the assumption that crystals of the same size must have the same shape. This assumption reduced the multidimensional description into a uni-dimensional PBE. Subsequently, Zhang et al. (2006) have explored many interesting features of the three dimensional single crystal model. Briesen (2006) described another technique for reduction of the two dimensional crystal population balance into a series of one dimensional PBEs.

Although the detailed morphological population balance model was formulated and solved (Ma et al., 2008; Wan et al., 2009; Borchert et al., 2009), quantitative modeling of real crystallizers could not be achieved as an essential property of particulate solid, asymmetry was ignored. Asymmetry is an important attribute of a particulate solid because along with size, it determines the specific surface for a given solid. The specific area of a symmetric shape is always less than the specific area of a corresponding asymmetric shape. Modeling of asymmetry using population balance has not been ventured so far as it is believed that considering asymmetry will lead to an unmanageable number of dimensions in the model. For example, Ma et al. (2008) considered symmetric crystals of potash alum which have 26 faces. They remarked that all 26 dimensions are needed if symmetry is not considered.

In this study, we model the growth process of asymmetric crystals using a population balance model. We demonstrate that the dimensionality of the population balance equation for growth does not necessarily increase by considering a population of asymmetric crystals. In order to formulate such a population balance model, we define and quantify the symmetry of a given crystal. Subsequently crystals are classified into various classes according to their symmetry. For each class, a separate population balance equation is written. It is shown that with this approach the dimensionality of the population balance equation does not exceed the number of independently growing faces.

This modeling effort also brings out the notion of evolution of symmetry of a population of crystals. It also shows that due to growth, a population of crystals always travels towards a more symmetric form. In the next section we shall discuss the model in detail, demonstrate the ideas using a numerical example, and present our conclusions.

3. Theory

Crystals are polyhedral objects which can have faces of more than one kind. Each kind is characterized by a distinct arrangement of atoms/molecules which leads to a specific growth rate. The faces that have identical arrangement of atoms grow at the same velocity and we shall refer to them as *faces of the same family*. Faces of different families grow at different rates and this difference in growth rates leads to morphological evolution.

Crystals are usually modeled in terms of a set of distances from an origin, the choice of which is closely related to the symmetry of the crystal. Symmetry of an object refers to the existence of one or more lines of symmetry about which rotation and/or reflection leaves the object unchanged. Maximum symmetry usually has a center of symmetry which can be chosen as the origin. For the less symmetric form, the choice of the origin depends on the extent of symmetry and will be discussed subsequently.

Now, consider a crystal comprising m families of faces with the ith family having f_i faces, then the total number of faces of the crystal, denoted n, is given by

$$n = \sum_{i=1}^{m} f_i \tag{1}$$

so that the vector of distances of all faces from a suitably chosen center, $\mathbf{h} \in \Re^n$, may be written as a partitioned vector $\mathbf{h} \equiv [\mathbf{h}_1, \mathbf{h}_2, \ldots, \mathbf{h}_m]$. Where $\mathbf{h}_i$ represents the distances of faces of the ith family from the center and can be written as: $\mathbf{h}_i \equiv [h_{1,i}, h_{2,i}, \ldots, h_{f_i,i}] \in \Re^{f_i}$, $i = 1,2,\ldots,m$. If the growth rate of the kth face of the ith family is denoted $\dot{H}_{k,i}$, then from the definition of the family, we have $\dot{H}_{1,i} = \dot{H}_{2,i} = \cdots = \dot{H}_{f_i,i} \equiv \dot{Z}_i$. If further the crystal is symmetric, with the origin at the symmetry center, we would have $h_{1,i} = h_{2,i} = \cdots = h_{f_i,i} \equiv z_i$, $i = 1,2,\ldots,m$. In this case, the crystal state vector $\mathbf{h}$ may be replaced by the vector $\mathbf{z} \in \Re^m$. Hence, there is a reduction of dimensionality of the crystal state vector from n, which can be very large, to m which could be substantially smaller. We show below that this reduction in dimension is also enjoyed by asymmetric crystals, with a left-over time-invariant state vector whose dimension would depend on the extent of symmetry of the crystal.

Consider a *completely* asymmetric crystal with the ith family having f_i faces whose distances from some origin to be specified