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Modeling Frameworks of Complex Separation Systems

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4.1

Introduction

Process modeling has always been an important component of process design, from the conceptual synthesis of the process flow sheet, to the detailed design of specialized processing equipment such as advanced reaction and separation devices, and the design of their control systems. Recent years have witnessed the traditional modeling approach being extended to the design of complex processes such as fuels cells, hybrid separation systems, distributed systems, etc. Inevitably the process modeling technology needed to fulfil the demands posed by such a diverse range of applications on different scales of complexity (Marquardt et al. 2000; Pantelides 2001). Years ago at the Foundations of Computer Aided Process Design Conference 1994, Pantelides and Britt (1995) presented a comprehensive review of some of the early developments in the area of multipurpose process modeling environments, i.e., software tools aiming at supporting multiple activities based on a common model. Recently, Pantelides and Urban (2004) presented a critical review of the progress achieved over the past decade and identified the key challenges for the next decade (Pantelides and Urban 2004).

In recent years, complex processing systems such as periodic pressure-swing adsorption processes, zeolite membranes and hybrid separations processes have been finding increasing applications as energy efficient alternatives to other traditional separation techniques (such as cryogenic separation), and much progress has already achieved in improving their performance with respect to both the process economics and the attainable purity of the products (see, for instance, Ruthven et al. 1994). The performance of these processes is critically affected by a number of design and operating parameters (design of the processes, duration of the various processing steps, operating levels at each step, etc.). Therefore, their accurate modeling in a compact and robust way is a necessity so as to minimize the capital and operating costs of the process while ensuring that minimum purity and throughput specifications are met.

This chapter presents a review of modeling frameworks for complex processing systems with an emphasis not only on the models themselves but also on specialized solution techniques related to these models. More specifically, due to their increased industrial interest, a general modeling framework for adsorption-diffusion-based gas separation processes is presented in Section 4.2 with a focus on pressure-swing adsorption and membrane-based processes for gas separations. The subsequent sections present a critical review of models and specialized solution techniques for crystallization and grinding processes. Finally, concluding remarks are drawn in the Section 4.4.

4.2

A Modeling Framework for Adsorption-Diffusion-based Gas Separation Processes

4.2.1

General

Gas separation is important in many industries ranging from the development of natural gas and oil resources to petrochemicals and foodstuffs. Moreover, separation and recovery from gaseous industrial effluents are issues of considerable environmental significance to a world-wide level and constitute a major problem demanding efficient solutions. It is generally accepted that the greatest energy consumption generally derives from the separation sections of the processes, which may also account for in excess of 50% of the total capital costs. The principal gas separation technologies include absorption, fractional distillation and adsorption-diffusion-based processes. The market leaders are absorption and distillation, both of which are capital and energy intensive. Adsorption-diffusion-based processes, compared with the other two processes, possess several advantages:

- low energy requirements,
- small, easily operated, low cost units,
- compactness and light weight,
- non-labor-intensive,
- modular design allowing easy expansion or operation at partial capacity.

The selection of separation techniques depends primarily on the process scale. Distillation and, to a lesser extent, absorption exhibit large economies of scale. Conversely, adsorption-diffusion-based separation techniques are modular with relatively fixed capital/throughput ratios for a given separation and hence are favored for smaller scale operations (Yang 1987; Ruthven et al. 1994).

The basic requirement in an adsorption separation process is the existence of an appropriate material (adsorbent) that preferentially adsorbs one component from a gas mixture. The selectivity of each adsorbent depends on a difference in adsorption equilibrium or kinetics (diffusion through the pore space of the adsorbent). All adsorption separation processes involve two major steps: (1) adsorption, during which the preferentially adsorbed species are captured from a feed mixture by the

adsorbent, and (2) desorption during which the adsorbed species are removed from the adsorbent in order to regenerate the material. It is evident that the effluent during the adsorption step corresponds to the light (weakly adsorbed) product of the separation process (often called the raffinate), while the effluent during desorption corresponds to the heavy (strongly adsorbed) product of the process.

The need for process commercialization has led to the use of cyclic or periodic adsorption separation processes where fixed beds packed with adsorbent operate at a certain sequence and are periodically regenerated by total or partial pressure decrease (pressure-swing adsorption (PSA), vacuum-swing adsorption (VSA)), or less often by temperature increase (temperature-swing adsorption (TSA)). Periodic adsorption processes are thus dynamic in nature and operate in a periodic mode having fixed adsorption and desorption cycle times. The periodic excitation is achieved by regular periodic variation of the boundary conditions of certain properties of the gas mixture (temperature, pressure, concentration, velocity) at the two ends of each bed and the connectivity between two or more beds that operate in a certain sequence depending on the complexity of the process. After a certain number of cycles each bed approaches a so-called "cyclic steady state" in which the conditions at the beginning and at end of each cycle are identical to each other. Over the last two decades PSA-VSA processes have gained increasing commercial acceptance over TSA, which is preferred only if the preferentially adsorbed species is too strongly adsorbed imposing high vacuum demands for adequate adsorbent regeneration (Ruthven et al. 1994).

An alternative technology employed in adsorption-desorption processes for gas separations is membrane technology. Membranes are thin films ranging from a few micrometers down to the order of several nanometers, which are made of organic (polymers) or inorganic materials and can be nonporous (dense) or porous. Inorganic membranes have considerable advantages in many gas separation processes, which are required to operate under demanding conditions, such as high temperatures and in corrosive environments. Recently there has been considerable interest in the potential of microporous zeolite membranes because of their regular and controlled pore size and geometry. Commercialization of membrane technology has prompted the growth of coherent, crack-free membrane films on top of planar or cylindrical macroporous supports (pore size of the order of 0.1–10 μm) that provide mechanical strength and do not significantly affect the separation performance of the membrane (Burggraaf 1996; Baker et al. 1997; Strathman 2001). Consequently a membrane unit or module is made using standard geometric arrangements (hollow fiber, spiral wound, etc.). The simple design of a membrane enables straightforward expansion of capacity compared to periodic adsorption processes.

The concept of a membrane process is straightforward: the separation is achieved through preferential permeation of a species from a gas mixture through the membrane. The key parameters that determine membrane performance are the selectivity towards the gas to be separated and permeate flux or permeability. The former is related to product purity and recovery while the latter is related to throughput or productivity and determines the membrane area required.

4.2.2

Process Description

4.2.2.1

The PSA Processes

A typical PSA-VSA process consists of a high pressure, adsorption step during which the gas is fed through the bed co-currently and separation is achieved followed by the recovery of the light product (raffinate), and a low pressure, desorption step, where the bed is regenerated (usually in counter-current fashion) with the possible simultaneous recovery of the heavy product (extract). These two basic steps are interconnected through the necessary depressurization (blow down) and pressurization steps that are employed either co-currently or counter-currently in the respective beds, depending on the specific needs of each particular application. These four basic steps constitute a single PSA or VSA cycle, which is repeated until cyclic steady conditions are achieved. Note that the desorption step is achieved by purging the bed with a fraction of the light product at low pressure (PSA) or by evacuation of the bed using pumps (VSA). The former method is favored in terms of energy-savings since the use of a pump is avoided, but on the other hand it produces a light product with significantly reduced recovery. The basic four-step cycle described above requires the use of only two beds and is shown schematically in Fig. 4.1. In practice more beds

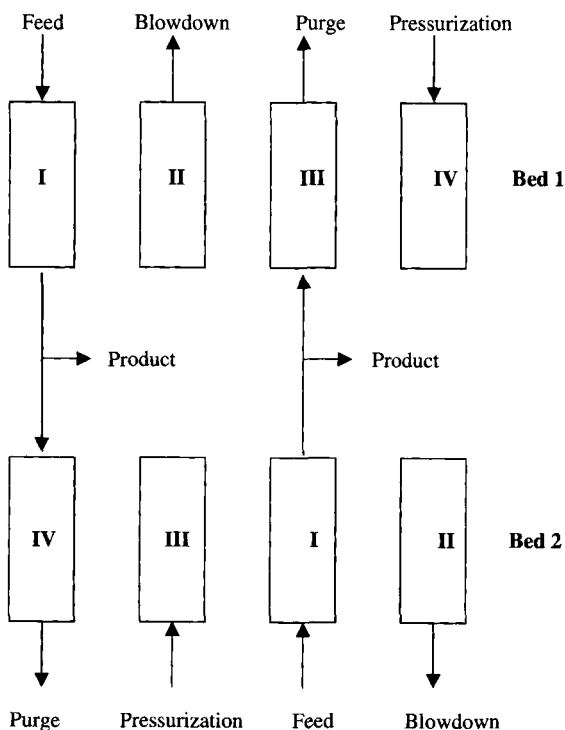


Figure 4.1 A typical four-step two-bed (Skarstrom) PSA cycle

are normally employed in typical industrial applications, based once again on the specifications of each application and the economics of the process.

The performance of a PSA process is assessed on the basis of several important output quantities. These are, the (light) product purity collected during the adsorption step, the (light) product recovery defined as the amount of light product collected in the adsorption step minus the amount of product used to purge the bed in the desorption step normalized by the amount of the light product in the feed. If this amount is normalized on the basis of the amount of adsorbent used in the bed then one defines the (light) product productivity per unit time. Although in most cases PSA processes involve the recovery of the light product in a gas mixture there have been a few theoretical and experimental studies in the literature that deal with the additional recovery of the heavy product from the exhaust, during the blow down and purge steps (Ritter and Yang 1989; Kikkinides and Yang 1991, 1993; Kikkinides et al. 1993, 1995).

The performance of the PSA process is critically affected by a number of design and operating parameters. The first category includes the size of the bed(s) in the process and the physical characteristics (e.g., particle size) of the adsorbent. On the other hand, important operating parameters include the duration of the various steps and the overall cycle and the pressure and/or temperature levels in each step. The process designer is therefore confronted with an optimization problem typically aiming to minimize the capital and/or operating costs of the process while ensuring that minimum purity and throughput specifications are met. In view of the large number of degrees of freedom, a mathematical programming approach to the optimization of PSA appears to be highly desirable, but this has to address the intrinsic complexity of the processes being studied and in particular the complications arising from their periodic nature. To this end, the optimization of periodic PSA systems has received some attention by the process systems engineering community. Smith and Westerberg (1991) presented a mixed-integer nonlinear program (MINLP) to determine the optimal design of PSA separation systems (operating configuration, size and operating conditions) using simple models and simple time-integrated balances to describe the initial and final concentrations and temperature profiles for each stage. The work of Nilchan and Pantelides (1998) is a key contribution to the optimization of periodic adsorption processes. They presented a rigorous mathematical programming-based approach to the optimization of general periodic adsorption processes. Detailed dynamic models taking account of the spatial variations of properties within the adsorption bed(s) are used. A new numerical method was proposed for the solution of the optimization problem and the calculation of the cyclic steady state, employing simultaneous discretization of both spatial and temporal variations to handle the complex boundary conditions. The approach is capable of handling interactions between multiple beds. Bechaud et al. (2001) investigated stability during cyclic gas flow with dispersion and adsorption in a porous column, as encountered during PSA. Ko et al. (2003) presented a mathematical model and optimization procedure of a PSA process using zeolite 13X as an adsorbent. Serbezov and Sotirchos (2003) investigated a semianalytical solution of the local equilibrium PSA model for multi-component mixtures. The solution involves simple algebraic and ordinary differential equations and can provide the basis for quick evaluation of different design alter-

natives and optimization studies. Recently, Cruz et al. (2004) presented a strategy for the evaluation, design, and optimization of cyclic adsorption processes. Jiang et al. (2003) developed a direct determination approach using a Newton-based method to achieve fast and robust convergence to cyclic steady state of PSA processes. An efficient, flexible and reliable optimization strategy that incorporates realistic detailed process models and rigorous solution procedures was investigated.

4.2.2.2

Membrane Processes for Gas Separations

Contrary to the PSA–VSA process where there is a certain degree of complexity in synchronizing the cyclic operation of two or more fixed beds, the case of a membrane separation process is much simpler. In the latter case the membrane unit has a simple geometrical arrangement operating at steady state conditions. In this arrangement there are two main compartments: the retentate at high pressure where the feed is introduced, and the permeate at low pressure where the product is collected. The two compartments are separated by the membrane layer, which controls the separation performance of the process and the production rate of the product. Since the driving force for permeation is the difference between the partial pressures of the product in the two compartments, it is obvious that there will be a back-pressure effect that deteriorates the separation performance of the membrane. In order to reduce the back-diffusion effect one needs to reduce the partial pressure of the product in the permeate side as much as possible. This is once again achieved by either evacuating the permeate section with the use of a pump or by sweeping the product away with the use of a sweep or purge inert gas that lowers the partial pressure of the permeate product. In most commercial applications the sweeping is done counter-currently to the feeding achieving the maximum possible separation performance for the membrane unit. A typical single-stage membrane unit for separation is shown in Fig. 4.2. Again practice has prompted the use of more complex configurations using recycle streams or membrane cascades depending on the specifications and the economics of each application.

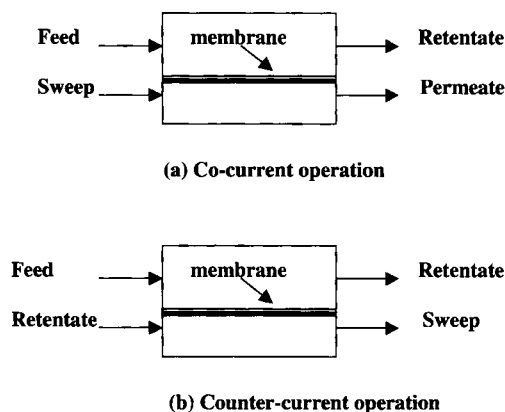


Figure 4.2 Single stage (a) co-current and (b) counter-current membrane processes

The optimization of membrane-based gas separation systems has received limited attention. This can be mainly attributed to the complexity of the underlying mathematical models. Tessendorf et al. (1999) presented various aspects of modeling, simulation, design and optimization of these processes. A membrane module model was developed capable of handling multicomponent mixtures and considering effects of pressure drop and energy balance. The module has implemented and tested in an external process simulators. Kookos (2002) proposed a superstructure representation of the membrane-based gas separation network along with a targeting approach to the synthesis of membrane networks. Using simple models, the membrane material is optimized together with the structure and the parameters of the network. Varelziz et al. (2003) presented a mathematical programming approach to optimize complex structures of zeolite membranes using detailed models. Various tradeoffs between different optimization objectives were systematically revealed. The impact of detailed modeling on the optimization results was investigated through a comparison with corresponding results obtained using simple models.

4.2.3

A General Model of Adsorption-Diffusion-based Gas Separation Processes

In modeling the separation performance of each process we will assume for the sake of generality that the same material is used to develop the microporous adsorbent particles and the membrane layer. Furthermore, we will assume that essentially the same material is used to make the macroporous binder of the adsorbent particles and the macroporous support on top of which the thin membrane layer is formed. This assumption will enable us to uncouple any effects that depend on the physicochemical characteristics of the materials used in the two separation processes from the effect of the inherent process characteristics of each process. Of course this assumption is often difficult to hold in practice since there are materials that are easier to make in the form of adsorbent particles than coherent membrane layers and vice versa.

Mass Balance in the Fixed Bed and/or the Membrane Compartments

For the sake of simplicity we will consider 1D transport along the axial direction neglecting any radial variations. This assumption is seen to be valid for the majority of theoretical and experimental cases found in the open literature. Thus, the mass balance for component i in the interstitial fluid is given by the following equation:

$$\varepsilon_b \frac{\partial C_i}{\partial t} + \frac{\partial(uC_i)}{\partial z} - D_{i,z} \frac{\partial^2 C_i}{\partial z^2} + k_{f,i}(C_i - C_{R_p,i}) = 0 \quad (1)$$

For $i = 1, N$ where N is the total number of species. Alternatively it is equivalent to write the above equation for the first $N - 1$ species and include an overall material balance.

The total concentration of the gas mixture C is related to the temperature T and total pressure P from an equation through an equation of state, which in most cases is represented by the ideal gas law:

$$C = \sum_{j=1}^N C_j = \frac{P}{RT} \quad (2)$$

The flux term $k_{fi}(C_i - C_{R_p,i})$ in the above equations accounts for interparticle (film) diffusion in the gas phase of component i , transported from the interstitial fluid to the surface of the adsorbent particles or the membrane layer.

For a membrane process, Eqs. (1) and (2) hold for the case of gas transport through the retentate and permeate units by simply neglecting the accumulation term, $\frac{\partial C_i}{\partial t}$, due to the steady state operation of the process, and by putting $\varepsilon_b = 1$ since in this case the compartments are completely empty. Also in this case the values of the mass transfer coefficients $D_{i,z}$ and k_{fi} will be different for the same reason.

Equilibrium Adsorption Behavior at the Particle or Membrane Surface

In many cases the adsorption equilibrium behavior of a multicomponent gas mixture at the surface of the adsorbent is adequately represented by the Langmuir isotherm:

$$\theta_i^* = \frac{q_i^*}{q_i^{\text{sat}}} = \frac{b_i C_{R_p,i}}{1 + \sum_{j=1}^N b_j C_{R_p,j}} \quad (3)$$

The advantage of the Langmuir equation is that it is relatively simple and can be easily inverted and solved for the gas phase concentrations, while the parameters q_i^{sat} and b_i can be evaluated from the respective simple component equilibrium isotherm data. The main drawback of the above equation is that it predicts a constant separation factor an assumption that is often violated especially for the case of nonideal gas mixtures (Krishna 2001; Karger and Ruthven 1992). In the latter case more involved modes based on the ideal adsorption solution theory (IAST) should be employed.

Mass Balance in the Microporous Particle or Membrane Surface

$$\frac{\partial q_i}{\partial t} = q_i^{\text{sat}} \frac{\partial \theta_i}{\partial t} = -\nabla N_i \quad (4)$$

Where N_i is the flux of component i transported through the pore space of the particle.

It is straightforward to show that:

$$\frac{\partial \bar{q}_i}{\partial t} = -N_i(\bar{q}_i) \quad (5)$$

Where \bar{q}_i denotes the volume-averaged adsorbed phase concentration.

For a membrane process, Eqs. (4) and (5) hold after neglecting the respective accumulation terms, due to steady state operation.

Evaluation of the Flux Terms

Evaluation of the flux terms N_i in Eqs. (4) and (5) requires the identification and description of the major transport mechanisms that take place in the pore space of the adsorbent particles. Transport in the pores can take place through various mechanisms, depending on the strength of the interaction of the gas molecules of one species with the molecules of the other species and with the pore walls, and by the relative magnitude of three different length scales characterizing, the size of the molecules, the distance between the pore walls and the fluid density in the pores, respectively. In many cases the adsorbent particle consists of two interpenetrating networks of pores, one representing the pore structure of the particle crystallites (e.g., zeolites, silica gel, etc.) and consists of micropores (0.1–1.0 nm) according to the IUPAC classification and another one that represents the structure of the binder or support and consists of meso- (1–50 nm) and macropores (50–5000 nm) in the IUPAC classification (Gregg and Sing 1982). It is evident that different mass transfer mechanisms prevail at each pore network, with the micropores providing the necessary features for gas separation by selective diffusion through the micropores and/or adsorption at pore surface. The effect of the binder or support, on the other hand, is an additional resistance to the mass transfer of the species with no selective features in either adsorption or diffusion through the macropores of the material. Thus it is desirable to minimize as much as possible the effect of transport through the support in order to achieve a better separation performance. Fortunately, in many cases the resistance to mass transport through the micropores of the crystallites is much stronger compared to that through the support and thus the latter can be either completely ignored or approximated through a linear driving force expression assuming fast diffusion or permeation kinetics in the pore space of the support. In this case the additional diffusion resistance is incorporated into the film diffusion coefficient $k_{f,i}$.

The generalized Maxwell-Stefan (GMS) equations provide an adequate basis for the accurate description of multicomponent mass transfer in porous media with minimum unary data (Krishna and Wesselingh 1997; Kapteijn et al. 2000; Krishna 2001; Karger and Ruthven 1992). The basis of the Maxwell-Stefan theory is that the driving force for movement, acting on a species, is balanced by the friction experienced by that species and each friction contribution is considered to be proportional to the difference in the corresponding diffusion velocities. The application of this theory on microporous or surface diffusion yields:

$$-\frac{\theta_i}{R \cdot T} \nabla \mu_i = \sum_{j=1}^N \frac{\theta_j N_i - \theta_i N_j}{q_i^{\text{sat}} q_j^{\text{sat}} D_{ij}} + \frac{N_i}{q_i^{\text{sat}} D_i} \quad (6)$$

The driving force for diffusion is the chemical potential gradient ($\nabla \mu_i$). Parameters D_{ij} and D_i are the Maxwell-Stefan surface diffusivities and represent inverse friction factors between molecules and the solid surface, respectively. In of a binary mixture with adsorption equilibrium behavior represented by the Langmuir isotherm and after some algebraic manipulations the surface flux N_i is given by the following expression:

$$N_i = -\frac{N_{i0}}{(1 - \theta_i - \theta_j)} \frac{\left[(1 - \theta_j) + \theta_i \frac{D_j}{D_{ij}} \right] \nabla \theta_i + \left[\theta_i + \theta_j \frac{D_j}{D_{ij}} \right] \nabla \theta_j}{1 + \theta_i \frac{D_j}{D_{ij}} + \theta_j \frac{D_i}{D_{ij}}} \quad (7a)$$

$$N_{i0} = -q_i^{\text{sat}} D_i \quad (7b)$$

Note that if we assume $D_{ij} \rightarrow \infty$ the above equation becomes:

$$N_i = -N_{i0} \frac{[(1 - \theta_j)] \nabla \theta_i + \theta_i \nabla \theta_j}{(1 - \theta_i - \theta_j)} \quad (8)$$

The above equations correspond to the GMS ($D_{ij} \rightarrow \infty$) model, which basically assumes negligible diffusional adsorbate-adsorbate interactions and has been frequently employed to describe diffusion of binary mixtures in zeolites (Ruthven et al. 1994).

Finally, in the limit of dilute systems ($\phi_i \ll 1$), Eq. (8) becomes:

$$N_i = -N_{i0} \nabla \theta_i \quad (9)$$

which is the classic Fick's law applied in the microporous adsorbent.

For the case of fast diffusion kinetics in the pore space of the microporous particle it has been shown that the adsorbed phase concentration has a parabolic profile in space. Combining this assumption with Eqs. (3), (5), and (7) we come up with the linear driving force approximation (LDF) often employed to describe diffusion kinetics in the adsorbed phase:

$$\frac{\partial \bar{q}_i}{\partial t} = k_i (q_i^* - \bar{q}_i) \quad (10)$$

Heat Effects

The exothermic nature of the adsorption process can result, under certain conditions and system sizes, in significant temperature variations resulting in the heating and freezing of the bed during adsorption and desorption, respectively. Considering 1D adiabatic heat transport along the axis and assuming negligible variation between the temperature in the solid and fluid phase the following heat balance equation holds in the bed:

$$(\varepsilon_b \rho_g c_{p,g} + (1 - \varepsilon_b) \rho_s c_{p,s}) \frac{\partial T}{\partial t} + \varepsilon_p \rho_g c_{p,g} \frac{\partial T}{\partial z} - \lambda_z \frac{\partial^2 T}{\partial z^2} - \sum_{i=1}^N (-\Delta H_i) N_i = 0 \quad (11)$$

Where ρ_g and $c_{p,g}$ are the total density and heat capacity of the mixture in the gas phase and ρ_s and $c_{p,s}$ are the density and heat capacity of the adsorbent. Note that several alternative heat balance models with different levels of complexity can be developed, depending on the available degree of information for the above quantities.

For the case of a membrane unit the heat effects are in most cases negligible and the process can be safely considered as an isothermal one. In the rest of the manuscript and without loss of generality we will consider isothermal operation in order to

have a better comparison between the two types of processes. Inclusion of the heat balance is straightforward and only adds more unknown parameters without significant changes in the solution approach during the simulation and optimization procedures.

Pressure Drop Effects

In many applications the use of long beds and/or small adsorbent particles can induce a pressure drop of appreciable magnitude that results in certain changes in the propagation of the concentration and temperature waves through the bed. The pressure drop along the axial direction of the adsorption bed is usually determined by the Ergun equation:

$$\frac{\partial P}{\partial z} = \frac{150 \mu u (1 - \varepsilon_b)^2}{d_p^2 \varepsilon_b^3} + \frac{1.75 \mu u^2 (1 - \varepsilon_b)}{d_p \varepsilon_b^3} \quad (12)$$

Where μ is the viscosity of the gas mixture and d_p is the diameter of the adsorbent particles.

For the case of a membrane unit the simpler Hagen-Poiseuille equation for parallel laminar flow is used to calculate the pressure drop through the axial direction of each section (Pan 1983, Giglia et al. 1991). Nevertheless, the pressure drop effects are many cases negligible and can be safely ignored.

Boundary Conditions

The appropriate boundary conditions for the solution of the problem are described by the following set of equations:

1. Adsorption step or retentate compartment

$$\begin{aligned} u_f C_{i,f} &= u C_i + \left(-D_{z,i} \frac{\partial C_i}{\partial z} \right) & \text{at } z = 0 \\ \frac{\partial C_i}{\partial z} &= 0 & \text{at } z = L \\ u(0) &= u_f & \text{at } z = 0 \\ P(0) &= P_H & \text{at } z = 0 \end{aligned} \quad (13a) - (13d)$$

2. Desorption step or permeate compartment

$$\begin{aligned} u_p C_{i,p} &= u C_i + \left(-D_{z,i} \frac{\partial C_i}{\partial z} \right) & \text{at } z = L \\ \frac{\partial C_i}{\partial z} &= 0 & \text{at } z = 0 \\ u(L) &= u_p & \text{at } z = L \\ P(L) &= P_L & \text{at } z = L \end{aligned} \quad (14a) - (14d)$$

3. Blow down step

$$\begin{aligned} \frac{\partial C_i}{\partial z} &= 0 && \text{at } z = 0 \text{ and } z = L \\ u(L) &= 0 && \text{at } z = L \\ P(0) &= P_b(t) && \text{at } z = 0 \end{aligned} \quad (15a)-(15d)$$

4. Pressurization step

$$\begin{aligned} uC_{i,f} &= uC_i + \left(-D_{z,i} \frac{\partial C_i}{\partial z}\right) && \text{at } z = 0 \\ \frac{\partial C_i}{\partial z} &= 0 && \text{at } z = L \\ u(L) &= 0 && \text{at } z = L \\ P(0) &= P_p(t) && \text{at } z = 0 \end{aligned} \quad (16a)-(16d)$$

Note that the pressure histories at the feed end of bed during the pressurization and blow down steps, respectively, are known functions of time.

4.3

Modeling of PSA Processes in gPROMS

The advanced distributed process modeling capabilities of gPROMS (trademark of Process Systems Enterprise Ltd.) permit a detailed description of the complex phenomena taking place inside adsorption columns. A major advantage of gPROMS is its ability to describe detailed operating procedures and to handle discontinuities arising from major changes in the structure of the underlying models. In the context of PSA processes this is particularly important since the boundary conditions depend on the operating stage. Furthermore, the entire operation involves successive transitions between the various operating stages thus introducing extra discontinuities in the model. For the simple case of one PSA column but with no loss of generality boundary conditions can be efficiently implemented in gPROMS as seen in Fig. 4.3.

The implementation of the PSA operating schedule is also a complex simulation task given the transition between the various processing steps. Figure 4.4 illustrates the process scheduling task for a specified number of cycles (one PSA column).

```

SELECTOR
  OperationMode AS (Pressurization, Depressurisation)

BOUNDARY

#At the feed end
CASE OperationMode OF

  #Pressurization Step

  WHEN Pressurization
    FOR i:=1 TO NoComp DO
      Pfeed * Yfeed(i) = C(i,0) * R * Tfeed;
    END #FOR

    P(0) = Pfeed;

  #Depressurisation Step

  WHEN Depressurisation

    FOR i:=1 TO NoComp DO
      PARTIAL(C(i,0), Axial) = 0;
    END #FOR

    P(0) = Pwaste;
  END # Case

#At the product end
# Pressurization / Depressurisation step

PARTIAL(C, BedLength), Axial) = 0;
U(BedLength) = (Qvol*Patm) / (BedArea*P(BedLength));

```

Figure 4.3 Boundary conditions of a single PSA column in gPROMS

4.4 Efficient Modeling of Crystallization Processes

4.4.1 General

Crystallization from solution is one of the oldest and economically most important industrial separation processes. It is applied both as a large-scale continuous process for the production of inorganic (e.g., ammonium sulphate) and organic (e.g., adipic acid) material and as small-scale batch processes for the production of high purity pharmaceuticals or fine chemicals (e.g., aspartame). In order to optimize and control the crystallization process, reliable mathematical models are necessary. Detailed modeling of the crystallization process requires knowledge of phenomena on a microscopic as well as on a macroscopic scale. On the microscopic scale the basic phenomena are the primary (heterogeneous or homogeneous) nucleation, secondary

```

SCHEDULE

SEQUENCE
  Cycle := 1 ;

  WHILE Cycle <= NoCycles DO

    SEQUENCE

      CONTINUE FOR CycleTime/2

      SWITCH
        Column.OperationMode := Column.Depressurisation ;
      END # Switch

      CONTINUE FOR CycleTime/2

      SWITCH
        Column.OperationMode := Column.Pressurisation ;
      END # Switch

      RESET
        # Oxygen product purity
        Column.Purity := OLD(Column.M_product(2)) / SIGMA(OLD(Column.M_product)) ;
        # Oxygen product recovery
        Column.Recovery := OLD(Column.M_product(2)) / OLD(Column.M_fed(2)) ;
      END # Reset
      Cycle := Cycle + 1 ;
      REINITIAL
        Column.M_fed, Column.M_product, Column.M_waste
      WITH
        Column.M_fed    = 1E-6 ;
        Column.M_product = 1E-6 ;
        Column.M_waste  = 1E-6 ;
      END # Reinitial

    END # Sequence

  END # While
END # Sequence
END # Task OperateColum

```

Figure 4.4 Operating schedule of a single PSA column in gPROMS

nucleation, crystal growth, coagulation between crystals, and crystal fragmentation. A great variety of models with different degrees of complexity have been presented in the literature for the above processes. On the macroscale, the macromixing in the crystallizer is very important. Coagulation and fragmentation phenomena depend on local energy dissipation, which can be varied by orders of magnitude in a stirred tank.

The modeling of crystallization processes poses special problems not encountered in more conventional process operations. The state of such systems is usually characterized by particle size distribution functions instead of, or in addition to, standard point properties such as concentrations. Moreover, the steady state and dynamic behavior of these systems is described by population balance equations rather than simple mass balances. Finally, the physical properties of solids encountered in crystallization processes are generally much less well characterized than those of fluids.

Traditionally, most process modeling and simulation tools have been aimed primarily at the mainstream chemical and petrochemical industry. Commercial steady state simulation packages have now reached a high degree of sophistication, encompassing extensive libraries of unit operation models, as well as large compilations of physical property data and calculation techniques. However, given the differences outlined above, it is hardly surprising that the area of crystallization and grinding processes has not been served well by tools now used routinely by process engineers in other areas. It has been long realized that even with relatively sophisticated general process modeling tools, the modeling and simulation of particulate processes still presents serious difficulties. One key problem is the mathematical complexity of the models: population balances invariably lead to partial differential equations, and these are often coupled with other equations describing the evolution of properties in the fluid surrounding the particles through integral terms. This results in systems of integral-partial differential equations, which may be very difficult to solve. In fact most current equation-oriented modeling frameworks cannot even describe directly such distributed parameter systems (Pantelides and Oh 1996). To this end the rest of this part of the chapter will focus on presenting state-of-the-art techniques for reducing the modeling complexity of crystallization and grinding processes, without any loss of accuracy and generality, to a level where standard modeling tools can be used for simulation and optimization purposes.

4.4.2

A Comprehensive Modeling Framework of Crystallization Processes

A generally accepted concept for the modeling of dispersed phase systems is the population balance approach introduced for the particular problem of crystallization by Randolph and Larson (1971). Each crystal in the system is described by a vector of properties x (internal coordinates) and its position in the crystallizer r (external coordinates). A very detailed model of the process would require as much internal coordinates as possible (which can be supported by experimental findings) and must be spatially distributed. The most extensively used crystallization model until today is based on a spatially homogeneous population balance (zero external variables) with one internal variable (crystal volume or linear size). Recently, several efforts have been made towards an increase of the number of internal or external variables to describe more accurately the process. Here, this relatively simple model will serve as the basis for a comprehensive discussion of the difficulties, existing solutions techniques and possible extensions of current crystallization process models.

Apart for the common variables used for modeling of any chemical reactor (temperature, concentrations, etc.) an additional variable used for the crystallizer is the crystal size distribution (CSD), which is described by the differential crystal volume distribution function $f(x, t)$ where x is the crystal volume and $f(x, t)dx$ is the number concentration of crystals with volumes between x and $x + dx$. The evolution of the CSD ($f(x, t)$) is determined by the following population balance equation:

$$\begin{aligned} \frac{\partial f(x, t)}{\partial t} + \frac{\partial G(x, \mathbf{c})f(x, t)}{\partial x} = & \frac{1}{2} \int_0^x K(\gamma, x - \gamma; \mathbf{c})f(\gamma, t)f(x - \gamma, t) d\gamma \\ & - f(x, t) \int_0^\infty K(x, \gamma; \mathbf{c})f(\gamma, t) d\gamma + \int_x^\infty p(x, \gamma)b(\gamma)f(\gamma, t) d\gamma \\ & - b(x)f(x, t) + B(\mathbf{c})\delta(x - a(\mathbf{c})) + \frac{f_{in}(x) - f(x, t)}{\tau} \end{aligned} \quad (17)$$

where the vector \mathbf{c} contains composition and temperature of the liquid phase and is used to denote dependence of the undergoing phenomena on this. The function $G(x, \mathbf{c})$ is the volumetric growth rate of a crystal with volume x . The function $K(x, \gamma; \mathbf{c})$ is the so-called coagulation kernel defined such that the expression $K(x, \gamma; \mathbf{c})f(x, t)f(\gamma, t)dx d\gamma$ is the rate of coagulation events per unit fluid of volume between a crystal with volume in $[x, x + dx]$ and a crystal with volume in $[\gamma, \gamma + d\gamma]$. This is in general a symmetric function with respect to x and γ .

The function $b(x)$ is the fragmentation frequency for a crystal of volume x while $B(\mathbf{c})$ is the nucleation rate (i.e., the rate of generation of nucleus which are crystals with size $a(\mathbf{c})$). The function $p(x, \gamma)$ is called the fragmentation kernel and is such that $p(x, \gamma)dx$ is the probability for having a fragment of volume in $[x, x + dx]$ as a result of fragmentation of a crystal with volume γ . Finally τ is the residence time in the system and $f_{in}(x)$ is the inlet particle size distribution function. The initial condition for the solution of the Eq. (17) is $f(x, 0) = f_0(x)$.

The above equation is rather comprehensive in the sense that includes processes with different features and different computational requirements (continuous versus batch system, precipitation versus crystallization). For the sake of clarity of our discussion it would be useful to discriminate between the process of crystallization (Mullin 1993) and precipitation (Sohnel and Garside 1992). Although the physical phenomena are the same (precipitation is a type of crystallization) the features exhibiting by the two processes (e.g., crystal sizes, supersaturation, etc.) are quite different requiring a different modeling approach. From the practical point of view precipitation is the crystallization of sparingly soluble substances (mainly salts). The mass of the active species in precipitation is small and thus the final volume fraction of the solid phase is also small and the crystal radius does not usually exceed 1 μm . On the other hand in crystallization the mass fraction of the solid phase can be large and the size of crystals is of the order of millimeters. We can now focus our attention on the modeling of the different phenomena described in generic Eq. (17).

Generally, the nucleation rate is the sum of the primary nucleation rate (given by the theory of homogeneous nucleation) and the secondary nucleation rate (production of small crystals from the fragmentation of the large ones) (Dirksen and Ring 1991). In case of precipitation there is no crystal fragmentation and secondary nucle-

ation so $B(c)$, $a(c)$ can be directly computed from the homogeneous nucleation theory (a slight modification is needed for heterogeneous nucleation which is usually the case). In the case of crystallization, the nucleus size is extremely small in comparison with the mean crystal size in the system so it can be assumed equal to zero and the nucleation term in Eq. (17) can be replaced by the following boundary condition on particle size distribution (PSD).

$$G(0, c)f(0, t) = B(c) \quad (18)$$

From the mathematical point of view this is an important simplification which weakens the problem of multiple crystal size scales existing in Eq. (17). Although the secondary nucleation can be rigorously simulated using an appropriate fragmentation kernel (of attrition type), it is more convenient to be included in $B(c)$ as a term proportional to total solid mass concentration (Mahoney and Ramkrishna 2003).

The coagulation rate is the product of the collision frequency and the collision efficiency. For the case of precipitation the collision between the crystals is due to their Brownian motion and the carrier fluid flow field. The collision efficiency is the result of the microscopic interaction between the crystals (given by the DLVO theory) and does not depend on concentration c . Rigorous models based on first principles can be derived for the above phenomena (Elimelech et al. 1995). On the other hand, in case of crystallization the coagulation phenomenon is included in a purely phenomenological manner to achieve a fit of the model to the experimental data. The collision rate is usually assumed constant and the coagulation efficiency is associated with the creation of solid bridges between the collided particles so it depends on growth rate and thus on c .

The growth rate for the case of precipitation is computed rigorously taking into account the bulk diffusion and surface reaction steps for each substance participating to the crystal growth (e.g., Kostoglou and Karabelas 1998). The growth rate used for the case of crystallization is of empirical nature and several expressions can be found in the literature (Abegg et al. 1968). In many cases a surface reaction dominated growth rate is assumed in combination with a diffusive (in crystal size coordinate) term to account for the stochastic nature of the crystal growth phenomenon (Tavare 1985). Regarding the fragmentation kernel and rate several empirical functions have been used for crystallization modeling, whereas the phenomenon does not exist in precipitation processes.

Several attempts to increase the number of internal coordinates of the model for a better description of the crystals have been made. To mention but a few are the use of the intrinsic crystal growth rate as the second internal coordinate (Janse and de Jong 1976) and the case of different growth rates for different faces of the crystal (Ma et al. 2003). The heterogeneity in the crystallizer may be very important and must be modeled in some way. In case of crystallization (usually a continuous process) the compartmental modeling is the appropriate compromise between accuracy and computational efficiency. The crystallizer is approximated with a few well-mixed regions interconnected with material streams. The flow rate of the streams can be found by CFD calculations. For the case of crystallization there may be two-way coupling of

the CFD since the extent of crystallization influences the flow properties of the fluid. In case of precipitation (usually a batch process) a one-way coupling is always enough (due to small solid mass fraction). The nature of the process is such that the compartmental model is not appropriate and a fine grid, similar to that used by the CFD module is needed. So the direct implementation of the Eq. (18) in a CFD framework is necessary (Seckler et al. 1995). Furthermore, in the presence of strong nucleation the extremely strong nonlinearity of the nucleation term makes the usual averaging procedures for turbulent flows inapplicable, calling for the use of the complete probability density function (PDF) approach (Marchisio et al. 2002).

It is worth noting the existence of a user-friendly software package (PARSIVAL: particle size evaluation) designed for solving general integral-differential equations with one internal and zero external variables (Wulkov et al. 2001). The main application of the package is the simulation of crystallization processes. The algorithm behind the package is fully adaptive in both particle size and time coordinates. The size discretization is based on the Galerkin h-p method and the time discretization is of Rothe type. The package is not capable to handle control aspects.

4.4.3

Efficient Solution Approaches

In the general case Eq. (17) does not have an analytical solution and therefore it must be solved numerically. Its numerical solution is by no means a trivial task since the problem combines the following features:

- an extraordinarily wide range for the independent variable x (particle volume) since the particle radius can be from the order of nanometers (nucleus) to order of millimeters;
- highly localized in the x variable domain nucleus size distribution imposing difficulties to the use of polynomials for approximation of PSD;
- convolution type integral and the associated nonlinearity imposed by the coagulation term;
- The hyperbolic form of the growth term and its ability to move discontinuities in the x domain makes its discretization difficult.

In the literature there are well known techniques to face each of the above problems but their simultaneous consideration is still a very challenging task.

The conventional finite difference discretization it is not even capable to conserve integral properties of the system (e.g., total particulate mass), which are of paramount importance for crystallization application so special techniques must be developed.

In general the available methods for solving Eq. (17) can be divided into the following six categories: (1) analytical solutions, (2) finite element methods, (3) higher order methods, (4) Monte Carlo methods, (5) sectional (zero order) methods, and (6) methods of moments. A brief overview of each of these methods is presented below.

Analytical solutions of Eq. (17) have been derived for certain simple forms of the growth rate (constant and linear) and coagulation kernel (constant and sum) certain combinations of the phenomena described by Eq. (17) and batch or steady state conditions. A special reference will be made in the work of Ramabhadran et al. (1976) deriving an analytical solution for combined nucleation growth and coagulation in batch conditions, and the work of Saleeby and Lee (1995) for the case of nucleation, growth and stochastic crystal growth dispersion in case of Continuous stirred Reactors (CSTR). Although the value of analytical solutions for the simulation of realistic crystallization processes is limited, they have been extensively used as tools for the assessment of numerical techniques for the solution of Eq. (17).

The finite element approach (for x discretization) to the solution of Eq. (17) is not a usual choice but some particular versions of the technique have been used over the last years. In particular Gelbard and Seinfeld (1978) used collocation on finite elements using third order polynomials with continuous first derivatives along the element boundaries, as basis functions. Tsang and Huang (1990) used Petrov-Galerkin finite elements to account for the hyperbolic character of the growth term. More recently, Nicmanis and Hounslow (1998) used a finite element Galerkin approach with Lagrangian third order polynomials for the steady state case. Rigopoulos and Jones (2003) developed a collocation finite element technique using linear basis functions. Finally, Mahoney and Ramkrishna (2002) used the Galerkin finite element techniques with linear basis functions to solve the linear size-based edition of the Eq. (17). Special care is taken to capture and follow discontinuities appearing in the PSD. In all the above approaches a geometric grid based on particle volume is used, except in the final one where the grid is linear and based on particle diameter.

The higher order methods imply the global approximation of the PSD with a polynomial multiplied by a proper function. Lacatos et al. (1984) used a collocation procedure employing Laguerre polynomials. Recently, Hamilton et al. (2003) developed a collocation method based on Hermite polynomials defined on a grid moving in order to fulfill some integral conditions. Also collocation with wavelets as basis functions has been used. The higher order methods offer very high accuracy (on the cost of large computational effort and complex code implementation) but they have the drawback of requiring special treatment of singularities (e.g., a monodisperse initial distribution).

The Monte Carlo method has a long history as a tool for the simulation of the particulate processes. Van Peborgh Gooch and Hounslow (1996), developed a stochastic approach for the particular process of crystallization with an arbitrary number of internal variables. Falope et al. (2001) also used another variant of the Monte Carlo method for crystallization with two internal variables. The significance of the Monte Carlo method increases sharply as the number of internal variables increases making the solution of the deterministic problem from difficult to impossible. On the other hand there is not a simple and efficient way to use the Monte Carlo method for the spatially distributed case.

The sectional methods and the methods of moments are capable to transform Eq. (17) in a conventional ODE-DAE system that can be readily solved by existing integrators, and can be easily incorporated into existing modeling tools for flow sheet

simulation including crystallization processes. Due to their practical importance both methods will be discussed in further details.

4.4.3.1

Sectional Methods

According to the sectional methods (equivalent to finite volumes) the particle volume coordinate is partitioned using a number of points v_i ($i = 0, 1, 2 \dots L$). Particles with volume between v_{i-1} and v_i belongs to the i th class and their number concentration is denoted as N_i (i.e., $\int_{v_{i-1}}^{v_i} f(x, t) dx$). Until the 1990s the most widely used schemes for the discretization of Eq. (17) were those of Gelbard et al. (1980) and Gelbard and Seinfeld (1980). The corresponding codes, although developed for aerosol processes, were extensively applied to crystallization processes. As regards to the coagulation terms, the particle number-based approach of the discretization scheme does not conserve the total particle mass and the grid must be geometric with ratio larger than 2 for an efficient implementation. To overcome this deficiency Hounslow et al. (1988) developed a discretization method for crystallization applications conserving both particle number and mass having the disadvantage that the only choice for the grid is geometric with ratio 2. The method of Hounslow et al. (1988) was extended for a geometric grid with ratio the q th root of 2 (q is an integer) permitting grid densification (Litster et al. 1995). The most general discretization scheme is that of Kumar and Ramkrishna (1996), which conserves also particle number and mass but admits a completely arbitrary grid.

The crystal growth term in Eq. (17) makes it of hyperbolic form. The inability of fixed grid (Eulerian) discretization to handle properly this type of problem is well known. The direct finite volume discretization does not conserve particle mass. Kostoglou and Karabelas (1995) developed first and second order schemes that conserves particle number and mass simultaneously. Their first order scheme (of upwind type) is unconditionally stable but suffers from numerical diffusion. The second order scheme shows much less diffusion but numerical dispersion appears (source for instability). An efficient treatment of the crystal growth terms requires a grid moving along the characteristics of the hyperbolic Eq. (17) (Lagrangian approach). The implementation of the moving grid approach is easy in the absence of coagulation and fragmentation (Gelbard 1990) but for the numerical solution of the complete Eq. (17) the moving grid must be compatible with the discretization of the coagulation or fragmentation terms. This compatibility can be achieved only using the Kumar and Ramkrishna (1996) discretization scheme. Their method made for the first time possible the use of a sectional approach with moving grid for the solution of Eq. (17) (Kumar and Ramkrishna 1997). The generation of new particles by nucleation makes necessary the addition of more and more sections during a particular simulation. This is not a desirable feature for any kind of numerical algorithm. The advantage of having a fixed number of ODEs instead of a variable (possibly uncontrolled one) is very important and it is strongly believed that a fixed grid (Eulerian) approach is preferable than the Lagrangian one. The increase of computing efficiency made possible the use of a large number of sections (few hundredths versus few decades as seen ten

years ago) leading to a great reduction of the numerical diffusion error of the Eulerian methods. The proposed discretized form of Eq. (17) is (the fragmentation terms are not shown since they can be found in the corresponding Section 4.4):

$$\begin{aligned}
 \frac{dN_i}{dt} = & \sum_{\substack{j \geq k \\ j, k \\ x_{i-1} \leq x_j + x_k < x_{i+1}}} (1 - 0.5\delta_{jk}) h K(x_j, x_k, \mathbf{c}) N_j N_k \\
 & - N_i \sum_{k=1}^L K(x_i, x_k, \mathbf{c}) N_k + (1 - \delta_{i1}) A_{i-1} N_{i-1} - (1 - \delta_{iL}) A_i N_i \\
 & + B(\mathbf{c}) \delta_{im} + \frac{N_{i, \text{in}} - N_i}{\tau}
 \end{aligned} \tag{19}$$

where the x_i are such that $v_{i-1} = (x_{i-1} + x_i)/2$, δ_{ij} is the Kronecker delta in L-dimensional space, the integer m is such that $v_{m-1} a(\mathbf{c}) \leq v_m$ and

$$A_i = \frac{2}{(v_{i+1} - v_{i-1})(v_i - v_{i-1})} \int_{v_{i-1}}^{v_i} G(\mathbf{x}, \mathbf{c}) d\mathbf{x}$$

$$h = \begin{cases} \frac{x_{i+1} - x_j - x_k}{x_{i+1} - x_i}, & x_i \leq x_j + x_k \leq x_{i+1} \\ \frac{x_j + x_k - x_{i-1}}{x_i - x_{i-1}}, & x_{i-1} \leq x_j + x_k \leq x_i \end{cases}$$

4.4.3.2

Methods of Moments

A proper discretization of Eq. (17) with the sectional method leads to a model with at least 50 degrees of freedom (number of ODEs). This renders the sectional method computationally intractable for the case of spatially distributed problems. The handling of complex spatially distributed problems imposes the need for low degrees of freedom approaches to the solution of Eq. (17). This made the method of moments a necessity to efficiently solve the population balance equation. These methods have a longer history than the sectional ones and they are based on the transformation of the Eq. (17) in a system of equations for some moments of the unknown distribution. The system is getting closed by defining a closure relation, relating the moments appearing in the right hand side of the system to those of the left hand side. The method of moments achieves an enormous reduction of the computational effort (typically 3–8 degrees of freedom) sacrificing the information content and the accuracy of the solution. Only some moments of the PSD can be computed with accuracy less than that of the sectional method but they are considered adequate for practical applications.

There is a great variety of method of moments. The older variants were used only for the case of very simple rate and kernel functions. Other methods assume a particular shape for the PSD (e.g., log-normal, gamma, Weibull, see Williams and Loyalka 1991) and the results are reliable only if the actual solution resembles the assumed form (e.g., problems with bimodal PSD cannot be attacked by these methods).

Recently, a quite general method of moments (generalized method of moments) was developed by Marchisio et al. (2003) and applied in crystallization systems. This method can be used without a restriction to the sophistication of the models for the occurring phenomena (i.e., rates and kernels) and to the actual shape of the PSD. The evolution equations for the moments of index a_i of the PSD

$$\begin{aligned} \frac{dM_{a_i}}{dt} = & \frac{1}{2} \sum_{j=1}^{P/2} \sum_{k=1}^{P/2} [(x_j + x_k)^{a_i} - x_j^{a_i} - x_k^{a_i}] K(x_j, x_k, c) w_j w_k \\ & + (1 - \delta(a_i)) \sum_{j=1}^{P/2} x_j^{a_i-1} G(x_j, c) w_j + B(c) a^{a_i}(c) \end{aligned} \quad (20)$$

The evolution of x_j, w_j ($j = 1, 2, \dots, P/2$) is given implicitly from the following nonlinear algebraic system:

$$\sum_{j=1}^{P/2} w_j x_j^{a_i} = M_{a_i} \quad i = 1, 2, 3, \dots, P \quad (21)$$

The system of Eqs. (20) and (21) can be easily solved with a traditional ODE-DAE integrator. To derive the full crystallization model Eqs. (20) and (21) must be coupled with other equations describing the behavior of the crystallization process (component mass balances, energy balances, physical property models, etc.). For example, assuming a three-phase continuous mixed suspension mixed product removal crystallizer, by appropriate heating or cooling, a product is generated in the form of crystals. A vapor phase is also formed because of the evaporation of part of the liquid which comes into the crystallizer. The contents of the crystallizer are removed by means of the top outlet stream (vapor) and the bottom outlet stream (slurry with product crystals and solution). The material balance of each component is mathematically expressed as follows:

$$\frac{dM_i}{dt} = q_{in} C_{i,in} - q_{out} C_{i,out} - q_v \rho_v \gamma_i \quad \forall i = 1, \dots, \text{NoComp}$$

The energy balance has the following general form:

$$\frac{dU}{dt} = q_{in} \rho_L h_{L,in} - q_{out} [\varepsilon_L \rho_L h_{L,out} + (1 - \varepsilon_L) \rho_s h_{s,out}] - Q_{jacket}$$

Supplementary relations for the mass balance equation involve calculation of the total amount of the solute in the crystallizer, the combined concentrations of the other components, the volume of the crystallizer, the mass fractions in the liquid and vapor phase, the total amount in the solid phase, vapor-liquid equilibrium relations, etc. In regards to the energy balance supplementary relations serve to calculate the specific internal energies for each phase, the fraction of the suspension volume and the rate of heat removal of the crystallizer. Due to space limitations details of these relations are not presented here.

4.4.4

Modeling and Optimization of Crystallizers

The selection of the optimal method for solving the population balance equation strongly depends on the particular features of the mathematical problem under question. Some general guidelines for the selection of the appropriate method are given in Table 4.1. It is important to emphasize that the efficient solution of the population balance equation can provide the basis for model-based design, control and optimization studies of large-scale crystallizers. The presence of very little work in this area can be attributed not only to the lack of rigorous models but also, and perhaps more importantly, to the lack of techniques for efficient solving the population balance equation without loss of accuracy. It is clear that the population balance equation constitute the basic component of the overall crystallization modeling framework. Component mass balances, energy balance and auxiliary algebraic equations describing the physical properties complement the model.

The design and optimization of crystallizers is a very challenging problem. There is a lack of systematic procedures for developing optimal operating policies and design options for complex crystallization systems. Kramer et al. (1999) presented a formal approach of design guidelines considering the influence of crystallizer geometry, scale, operating conditions and process actuators on the process behaviour and product quality. Kramer et al. (2000) developed a compartmental modeling framework to describe the crystallization process of evaporative and cooling suspension crystallizers. The framework has been implemented in the SPEEDUP environment and is capable of predicting a large supersaturation profile in a large-scale crystallizer. Ma et al. (2002) presented a rigorous compartmental crystallization model to achieve optimal control. Ge et al. (2000) have illustrated the application of mathematical optimization to the problem of batch crystallization. A targeting approach to the optimization of multistage crystallization networks has been investigated by Sheikh and Jones (1998). Bermingham et al. (2003) presented a formal optimization approach for the design of solution crystallization processes using rigorous models. A large-scale industrial case study was used to illustrate the applicability and usefulness of the overall optimization methodology. Recently, Choong and Smith (2004a,b) proposed an optimization framework based on a stochastic optimization algorithm for

Table 4.1 Optimal method of solution for the crystallization model versus number of external and internal coordinates of the model

Internal coordinates number	External coordinates number		
	0	1	More
1	Sectional	Sectional, Moments	Moments
2	Monte Carlo, Moments	Moments	Moments
More	Monte Carlo	Not available	Not available

optimizing batch cooling and batch, semi-batch and nonisothermal evaporative crystallization operations. The results demonstrate significant improvements over conventional approaches and heuristic rules.

The deviation of the well-mixed behavior in a crystallizer is primarily caused by the hydrodynamic conditions, which lead to temperature, supersaturation and participle concentration profiles in the crystallizer. An approach which can overcome the shortage of the well-mixed models is the employment of a multizonal representation which divides the equipment volume into a network of interconnected zones where the idealized mixing pattern is assumed for each zone. Urban and Liberis (1999) used a hybrid multizonal/CFD modeling approach for the modeling of an industrial crystallizer. Each zone incorporates a detailed description of the crystallization phenomena in terms of population balance equations. Both homogenous and heterogeneous crystal nucleation are taken into account, the latter being a strong function of the turbulence energy dissipation. A CFD model of the process is used to determine the directionality and rate of flow between adjacent zones, and the mean energy dissipation rate within each zone. Zauner and Jones (2002) adopted a compartment mixing model to predict the mixing on crystal precipitation. The population balance is solved simultaneously with the mass balance using data obtained by CFD calculations. Recently, Bezzo et al. (2004) presented a formal multi-scale framework based on a hybrid multizonal/CFD model. The framework is applicable to 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) homogenous fluid, the physical properties of which are relatively weak functions of intensive properties. A crystallization process was used to illustrate the overall modeling approach.

4.5 Modeling of Grinding Processes

4.5.1 A General Modeling Framework of Grinding Processes

Fine grinding of solid materials is of prime importance in many industrial applications. In addition to mineral processing, it is also widely used in the manufacture of paints, ceramics, pharmaceuticals etc. The grinding process can be performed under wet or dry conditions using a large variety of equipment. In general, the grinding of the feed material is made by mobile pieces (e.g., spheres, cylinders) or by large fixed in space elements (e.g., rollers) made from hard material. Irrespective of the details of the particular grinding process, the scope is always the reduction of the particle size (the range can be from millimeters to micrometers) and the simulation approach is the same. Traditionally, the simulation of processes associated with the grinding of solids is based on the solution of a particular and rather simplified form of the population balance equation known as fragmentation equation. The main feature of grinding modeling is the application of a population balance, and the selec-

tion of appropriate independent variables. Hence, the usual approach taken in the literature is based on solution through the use of population balance equations to produce models which can simulate grinding. Today, a significant challenge which faces those who model grinding is the lack of a modeling tool which allows the easy implementation of the many different forms and evolutionary changes in the grinding models. This is coupled with the need for robust solution techniques for the various integral-partial-differential equations found in utilizing the population balance approach.

Recent simulation examples in the literature include grinding of coal in ring-roller mills (Sato et al. 1996), the wet stirred ball attrition of alumina and synthetic diamond (Shinohara et al. 1999), the attrition of alumina hydrate in a tumbling mill (Frances and Laguerie, 1998), the dry stirred ball attrition of quartz (Ma et al. 1998) and the wet stirred bead attrition of carbon (Varinot et al. 1999). According to the particular formalism, the evolution of the particle size distribution (PSD) as it is described by the differential particle volume distribution function $f(x, t)$ can be calculated from the solution of the following linear integral-differential equation:

$$\frac{\partial f(x, t)}{\partial t} = \int_x^\infty b(\gamma)p(x, \gamma)f(\gamma, t) d\gamma - b(x)f(x, t) \quad (22)$$

The first part of the right hand side of the above equation stands for the generation of particles of size x by fragmentation of larger than x particles and the second term for the loss of size x particles due to their fragmentation. The function $b(x)$ is the fragmentation frequency for a particle of volume x (the term rate is also used instead of frequency). The function $p(x, \gamma)$ is called fragmentation kernel and is such that $p(x, \gamma)dx$ is the probability for having a fragment of volume in $[x, x + dx]$ as a result of fragmentation of a particle with volume γ . The grinding equipment usually operates under batch conditions so the corresponding form of the fragmentation equation (which can also be directly used for plug flow continuous operation) is examined here.

The above formalism is purely phenomenological so there is not space for considerable improvements. The extension of the formalism using external coordinates is meaningless since the equation cannot be considered to describe a local phenomenon in the physical space. An axial external coordinate has been used in a purely phenomenological manner by Mihalyko et al. (1998) to account for the partial mixing (axial dispersion) during plug flow grinding process. Also attempts to add more internal variables for the characterization of the particles have not been made. In generally Eq. (22) is considered adequate to describe the grinding process. The challenge for the development of efficient techniques for its solution is coming not from the need to incorporate it (describing the "local" phenomenon) in CFD codes but for the need to incorporate efficient grinding equipment submodels to the large flow sheet simulators.

The fragmentation functions $b(x)$, $p(x, \gamma)$ should satisfy the following requirements in order to give physically meaningful results:

1. $\lim_{x \rightarrow 0} b(x) = 0$ to avoid the generation of smaller and smaller particles without limit.

2. $\int_0^{\gamma} xp(x, \gamma)dx = \gamma$ this is the mass conservation condition and stipulates that the total volume of particles resulting from the breakup of a particle of volume γ must be equal to γ .
3. $v(\gamma) = \int_0^{\gamma} p(x, \gamma)d\gamma$, where $v(\gamma)$ is the number of fragments generated during the breakup of a particle with volume γ . In all cases, it should be $v(\gamma) \geq 2$.
4. $\int_0^k xp(x, \gamma)dx \geq \int_{\gamma-k}^{\gamma} (\gamma - x) p(x, \gamma)d\gamma$ for $k < \gamma/2$. This condition is usually overlooked having as consequence the use of fragmentation kernels without physical meaning for fitting experimental data.

The fragmentation frequency used in the grinding literature (Varinot et al. 1997, 1999) has the following form

$$b(x) = C \frac{x^b}{1 + (x/x_a)^a} \quad (23)$$

This is a composite law resulting from the matching of the two asymptotes (power laws) $b(x) = x^{b-a}$ ($x \gg x_a$) and $b(x) = x^b$ ($x \ll x_a$) at the region of $x = x_a$. Usually $b-a$ is a small number implying an almost size independent fragmentation rate for large particles. As the particle size decreases the relatively large exponent b dominates prevailing further fragmentation of the smaller particles.

The most general fragmentation kernel employed for grinding simulation (Eyre et al. 1998) is

$$p(x, \gamma) = \frac{1}{\gamma} \left[C_1 \left(\frac{x}{\gamma} \right)^{\alpha_1} + C_2 \left(\frac{x}{\gamma} \right)^{\alpha_2} \right] \quad (24)$$

The values of the parameters C_1 , C_2 , α_1 , α_2 should be carefully chosen in order to satisfy the above-mentioned requirements 2 through 4. This kernel exhibits the very important property of homogeneity. A breakage kernel is called homogeneous if the shape of the fragment size distribution does not depend explicitly on the parent particle size γ but only on the ratio x/γ . An homogeneous kernel can be written as $p(x, \gamma) = \frac{1}{\gamma} p\left(\frac{x}{\gamma}\right)$.

4.5.2

Solution Approaches

4.5.2.1

Sectional Methods

The solution methods for the Eq. (22) with frequency in Eq. (23) and kernel in Eq. (25) can be organized in five categories as follows:

- a) Analytical (Ziff and McGrady, 1986) and large time asymptotic solutions (Ziff, 1991) exist only for the particular case $a = C_1 = 0$ in Eqs. (24) and (25).

- b) Stochastic (Monte Carlo) methods (Mishra 2000). In the case of grinding simulation the addition of extra internal variables is not an option so stochastic methods are of little importance.
- c) Higher order (polynomial approximation) methods. In particular the Galerkin weighted residual formulation using as basis functions B-splines (Everson et al. 1997) and wavelets (Liu and Tade 2004) have been used.
- d) Sectional (zero order) methods.
- e) Moment methods.

The last two categories include methods which allow direct and unconditionally stable transformation of Eq. (22) to a system of ODEs that can be solved and further processed by existing integration codes. For this reason these methods will be discussed in detail.

According to the sectional method the particle volume coordinate is partitioned using the points v_i ($i = 0, 1, 2 \dots L$). The particles with volume between v_{i-1} and v_i belongs to the i th class and their number concentration denoted as N_i (i.e., $\int_{v_{i-1}}^{v_i} f(x, t) dx$). The characteristic particle size for the class i is taken to be $x_i = \frac{v_{i-1} + v_i}{2}$. The direct sectional (finite volume) equivalent of (22) is ($i = 1, 2, \dots L$):

$$\frac{dN_i}{dt} = \sum_{j=i+1}^L n_{ij} b_j N_j - b_i N_i \quad (25)$$

$$b_i = b(x_i) \quad (26)$$

$$n_{ij} = \int_{v_{i-1}}^{v_i} p(x, x_j) dx \quad (27)$$

This system of ODEs can be solved analytically (Reid, 1965) and has been extensively used in the grinding literature as the fundamental equation and not a simplification of the continuous form of Eq. (22). Experimental values of N_i can be directly supplied from sieve analysis and n_{ij} can be found by fitting the model in Eq. (25) to the experimental N_i sequentially. The problem arises from the fact that the discretized form of Eq. (26) does not conserve integral properties of the PSD and in particular total particle mass. This problem was considered by Hill and Ng (1995) who used two sets of unknown constants multiplied by both terms of the right hand side of Eq. (25). These constants were computed by the requirement of internal consistency with respect to the total particle mass and total particle number. The term "internal consistency" of a characteristic scheme with respect to a particular moment of the PSD refers to the ability of the discretized system to reproduce the discretized form of the evolution equation for the particular moment. Although this is a highly desired property (i.e., for the total particle mass, this is equivalent to the total mass conservation), it cannot guarantee the exact computation of the moment.

The procedure developed by Hill and Ng (1995) may require complex analytical derivations that depend on the particular form of the fragmentation kernel and on the particular grid used for the characteristic. The above authors made these deriva-

tions for three forms of the fragmentation kernel, two forms of the grid (equidistant and geometric) and exclusively for power law fragmentation rate. The major drawback of their procedure is that it cannot be directly generalized for arbitrary parameters and implemented in a computer code. Vanni (1999) improved the situation by replacing the requirement of internal consistency with respect to the total particle number, with a better handling of the second term of right hand side of Eq. (25) (death term). This new version (slightly less accurate than its predecessor) can be fully automated, i.e., computed numerically regardless of the fragmentation rate and kernel.

A different approach for the development of a quite general sectional method with arbitrary fragmentation functions, arbitrary grid, exhibiting internally consistency with respect to two arbitrary moments has been investigated by Kumar and Ramkrishna (1996). In this case the internally consistency is achieved by the proper sharing of the fragments resulting from a fragmentation event to the respective sections. The coefficients n_{ij} for the particular case of internal consistency with respect to total particle mass are:

$$n_{ij} = (1 - \delta_{ij})Z(x_i, x_{i+1}, x_k) - (1 - \delta_{1j})Z(x_i, x_{i-1}, x_k) \quad (28)$$

$$Z(a, b, c) = \int_a^b \frac{b-y}{b-y} p(y, c) dy$$

where δ is the Dirac delta function.

Several improvements have been proposed for the above sectional approach. As an example, Attarakih et al. (2003) developed a method where the pivot (characteristic) size for each class is free to move between the boundaries of the class and in addition the grid is moving as a whole to capture better the features of the PSD. The improved methods of this type can be implemented only through custom codes and cannot cast the problem to the form of system of ODEs directly solvable by commercial integrators.

4.5.2.2

Methods of Moments

The idea led to the development of the method of moments is that in some cases the amount of information on the PSD given by a sectional method can be sacrificed in favor of the reduction in the computational requirements. For example, in a large plant simulator the grinding submodel has to be solved as efficiently as possible even in the expense of having as the only output the total particle number concentration and the mean particle size. From the technical point of view the method of moments is a generalization of the methods of weighted residual having a trial function more general than a linear superposition of basis function, i.e., $f(x, t) = F(x, t; \mathbf{c})$ where the function F has a known form and the vector $\mathbf{c} = (c_1, c_2, \dots, c_P)$ contains P unknown time dependent parameters which can be found in the following way. The Eq. (22) is multiplied by the P power law test functions x^{a_i} ($i = 1, 2, \dots, P$) and then is integrated for x between 0 and ∞ to give the system of equations (assuming an homogeneous fragmentation kernel):

$$\frac{dM_{a_i}}{dt} = (J_{a_i} - 1) \int_0^\infty b(x)F(x, t; c) dx \tag{29}$$

$$\int_0^\infty x^{a_i} F(x, t; c) dx = M_{a_i} \tag{30}$$

where $J_{a_i} = \int_0^\infty x^{a_i} p(x) dx$. The most widely used forms of the distribution F are the lognormal distribution $f(x, t) = \frac{c_1}{\sqrt{2\pi c_2 x}} \exp\left[-\frac{1}{2c_2} \ln^2\left(\frac{x}{c_3}\right)\right]$ the gamma distribution $f(x, t) = \frac{c_1}{\Gamma(c_2 + 1)} \left(\frac{x}{c_3}\right)^{c_2} e^{-x/c_3}$ with $(a_1, a_2, a_3) = (0, 1, 2)$ and Γ is the gamma function (Kostoglou and Karabelas 2002; Madras and McCoy 1998). For the case of a power law fragmentation rate $b(x)$, the integrations in equations can be performed in closed form leading to a simple system of ODEs with respect to the a_i . If $b(x)$ is not of power law form, the integral in equation (29) must be computed numerically. The Hermite and Laguerre quadratures are ideally suited for the case of lognormal and gamma distribution respectively.

A systematic way to improve the log-normal method is the so called interpolation between the moments method (Kostoglou and Karabelas 2002). This method can be applied only for power law breakage rate using the following set of a_i (a_1, a_2, \dots, a_P) = (0, 1, 2 ... $P-1$). An explicit form of F is not assumed and each moment z appearing in the right hand side can be calculated from the integer moments of the PSD by the following interpolation rule:

$$M_z = \exp \left[\sum_{k=0}^{P-1} \log(M_k) \frac{\prod_{j=0, j \neq k}^{P-1} (z - j)}{\prod_{j=0, j \neq k}^{P-1} (k - j)} \right] \tag{31}$$

For $P = 3$ the log-normal method is recovered while improved results can be found using $P = 4$ and $P = 5$. Larger values of P cannot improve the solution because the amount of information contained in the higher moments of the distribution is limited.

According to the generalized method of moments the PSD is approximated by a set of Dirac delta functions with unknown strength and location; i.e., (P is an even number)

$$F(x, t) = \sum_{j=1}^{P/2} w_j \delta(x - x_j) \tag{32}$$

Substituting Eqs. (29) and (30) leads to the following system of ODEs-DAEs:

$$\frac{dM_{a_i}}{dt} = (J_{a_i} - 1) \sum_{j=1}^{P/2} w_j x_j^{a_i} b(x_j) \tag{33}$$

$$\frac{dM_{a_i}}{dt} = (J_{a_i} - 1) \sum_{j=1}^{P/2} w_j x_j^{a_i} b(x_j) \quad (34)$$

This method is quite general and can be used for any fragmentation rate and kernel. It is developed for the solution of the aerosol growth equation (quadrature method of moments; McGraw 1997) and aerosol coagulation equation (generalized approximation method; Piskunov and Golubev 1999) independently. Kostoglou and Karabelas (2002) used it for the solution of the fragmentation equation (generalized method of moments). Typical values of P are 4 (Kostoglou and Karabelas 2004) and 6 (Marchisio et al. 2003), and the best choice for a_i seems to be $(a_1, a_2, \dots, a_P) = (0, 1/3, 2/3, \dots, (P-1)/3)$. The system of Eqs. (33) and (34) can be solved directly using an ODE-DAE solver (Kostoglou and Karabelas 2002, 2004) or using an ODE solver for (33) simultaneously with special procedures from the theory of Gaussian integration to find the weights w_j and abscissas x_j (Marchisio et al. 2003).

4.5

Concluding Remarks

Compared to the traditional tools and approaches for modeling and simulation of complex separation systems significant progress has been achieved the last decade. Today's modeling tools provide advanced modeling languages and frameworks, either based on process engineering concepts or on mathematical perspectives that are suited to represent complex structural and phenomenological aspects of process systems engineering. However, a number of issues must be considered open still today.

Significant challenges remain in all of the specific processing systems reviewed and these have been identified in the corresponding sections. A more general challenge is how to allow the incorporation of ideas originated from academic research into tools for industrial use. The emergence of open software architectures now provides reasonable straightforward routes for academic developments in some areas, such as physical properties and numerical solvers, to be directly used in process modeling tools. However, the situation is more problematic in areas of research that are related to the fundamentals of process modeling as reviewed in this chapter for specific processes. Arguably, the task of testing academic ideas and, ultimately, transferring them to commercial use has become more difficult in recent years due to the complexity of modern process modeling software and the degree of advanced software engineering that it entails (Pantelides and Urban 2004).

Von Wedel et al. (2003) emphasized that the development of complex chemical process models can be improved towards a formal theory to automatically generate, manipulate, and reason about these models. Such a theory will have a strong impact on the capabilities of future modeling tools for complex chemical processing systems, but it constitutes an on-going open research issues. It will enable inexperienced researchers to effectively use model-based techniques for a wide range of

applications such as parameter estimation, process control and optimization. The excellent book by Hangos and Cameron (2001) provides the basic principles towards this direction.

As mentioned in the excellent review by Pantelides and Urban (2004) the increasing power of process modeling technology brings new perspectives to the development and deployment of model-based solutions throughout the process lifecycle, from the initial process development to the detailed design of individual items of processing equipment and entire plants, and their control systems. To a large extent, this has been a natural evolution of earlier trends in this area and it is particularly true for the processes reviewed in this chapter. For example, a very interesting development in recent years has been the increasing permeability of the boundary between “off-line” and “on-line” applications for crystallization processes. This permeability has two distinct but related positive aspects. First, the process models themselves are re-used for both design and operational tasks, although in many cases some simpler models may be required in view of the special efficiency and robustness requirements posed by real-time and other applications, as illustrated in the review of crystallization and grinding processes. Secondly, standard process modeling software tools such as gPROMS are employed for tasks on both sides of the boundary.

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