

Abstract

Spray Drying is a widely applied industrial process, in which granular material is obtained from a liquid feed. The idea of performing polymerisation reactions within a spray in order to integrate several process steps (polymerisation, drying of a solvent, generation of a spherical product) into one apparatus has been discussed for a long time and has frequently been subject to experimental investigations. A mathematical model of droplet polymerisation, which accounts for transport processes inside the drop and predicts polymer properties, has not been published so far. A second matter in spray drying is the evolution of a product's morphology. Established quasi-homogeneous, spherically symmetric single droplet models presuppose a certain morphology and do not allow for structure simulation on a detailed scale. Both questions are addressed by new numerical models, in the first part by an enhancement of established one-dimensional droplet models for reactive drying, in the second part by a novel approach for the simulation of structure generation using a meshfree method.

Single Droplet Modelling of Spray Polymerisation

Free radical polymerisation within a droplet is considered by both lumped and one-dimensionally resolved models of solution drying with additional chemical reactions. Drying leads to an inhomogeneous distribution of the reactants' mixture and affects chemical reactions. Polymer properties are calculated using the method of moments. Its molecular weight depends on reaction conditions and varies through time and space. A sound mathematical description of the reaction-diffusion system is derived and accounts for density changing reactions and the varying specific volume of the polymer component. Moreover, a new approach of polymer moments' diffusion is introduced, which - in contrast to the literature approach - preserves spatial inhomogeneities of polymer properties.

Numerical simulations reveal that drying and chemical reactions are not simultaneous, but mostly sequential mechanisms. After solvent vaporisation, polymerisation is performed at a high monomer content, practically as bulk polymerisation. Evaporation of a volatile monomer will decrease the polymer yield tremendously. Further investigations are conducted on various process and model parameters. Several process variants are discussed by means of numerical DoEs. Polymerisation in solvent is scarcely applicable under most reasonable parameter settings. Bulk polymerisation can provide a feasible yield at elevated monomer saturations of the gas phase. Depending on non-ideal thermodynamics, reactive absorption appears as the main driver for increased polymer production. Slight pre-polymerisation before atomisation may provide an additional, yet limited gain in yield. Comparison between the lumped and the one-dimensional model shows that a simple 0D approximation is only feasible in the simple case of a non-volatile monomer.

Simulation of Structure Development within a Droplet by the Meshfree SPH Method

Structure evolution is a complicated process involving interactions of different phases, various physical effects and different time-scales. The meshfree SPH approach represents the continuum by irregularly distributed interpolation points, which move according to a Lagrangian point of view. When such points belong to different physical phases, the method can describe evolving interfaces and structure evolution efficiently. A novel approach for drying of a slurry is introduced. As SPH has not been applied to droplet drying yet, fundamental effects need to be derived. This involves free surface heat and mass transfer according to linear driving forces and an efficient, implicit solution of the energy equation and various approaches for crust formation in the second drying period. Moreover, a new approach for modelling surface tension by pairwise forces is introduced. By adjustment of model parameters, formation of dense, compact structures as well as hollow granules of different crust porosity can be simulated. These parameters can be interpreted in the sense of the binder content. Finally, a new SPH-grid coupled model is presented, which directly computes diffusion in the gas via an underlying mesh. Through this, the receding of water within a porous structure by drying is calculated.

Zusammenfassung

Die Sprühtrocknung ist ein verbreiteter industrieller Prozess, um granuläres Pulver aus einer flüssigen Vorlage zu erzeugen. Die Grundidee der Polymerisation in einem Spray, um mehrere Prozessschritte in einem Apparat zu vereinen (Polymerisation, Abtrennung des Lösungsmittels, Herstellung sphärischer Partikel aus dem Polymer), wird seit langer Zeit diskutiert und immer wieder experimentell untersucht. Ein mathematisches Modell, welches Transportprozesse innerhalb der Tropfen berücksichtigt und Polymereigenschaften vorhersagt, wurde jedoch bisher nicht veröffentlicht. Eine zweite Fragestellung der Sprühtrocknung betrifft die Ausbildung der Morphologie des finalen Produkts. Etablierte quasi-homogene, auf Kugelsymmetrie basierende Einzeltropfenmodelle setzen eine spezifische Struktur des Produkts voraus und ermöglichen nicht die Simulation der Morphogenese auf einer Detailskala. Beide Fragestellungen werden mit Hilfe neuer numerischer Modelle adressiert, im ersten Teil über die Erweiterung etablierter eindimensionaler Tropfenmodelle für reaktive Trocknungsprozesse, im zweiten Teil mit Hilfe eines neuartigen Ansatzes zur Simulation der Strukturausbildung basierend auf einer gitterfreien Methode.

Einzeltropfenmodellierung der Sprühpolymerisation

Freie radikalische Polymerisation innerhalb eines Tropfens wird als konzentriertes und als ortsverteilt Modell der Lösungstrocknung mit chemischen Reaktionen berücksichtigt. Trocknung beeinflusst die Verteilung der Edukte und die Polymerisationsreaktionen. Polymereigenschaften werden mit Hilfe der Momentenmethode berechnet. Das Molekulargewicht des Polymers hängt von den Reaktionsbedingungen ab und variiert örtlich und zeitlich. Eine konsistente Beschreibung des Reaktions-Diffusions-Systems wird hergeleitet und berücksichtigt dichteverändernde Reaktionen und veränderliche spezifische Volumina des

Polymers. Ein neuer Ansatz zur Diffusion statistischer Momente erhält - anders als der Literaturansatz - örtliche Inhomogenitäten von Polymereigenschaften.

Trocknung und chemische Reaktionen erfolgen nicht gleichzeitig. Nach Verdampfung des Lösungsmittel findet die Polymerisation bei hohen Monomergehalten statt, die praktisch einer Massepolymerisation entsprechen. Durch Verdampfung flüchtiger Monomere nimmt die Ausbeute drastisch ab. Prozess- und Modellparameter der Tropfenpolymerisation werden eingehender untersucht und verschiedene Prozessvarianten mit Hilfe numerischer DoEs diskutiert. Das Prozessfenster zur Lösungspolymerisation ist sehr begrenzt. Massepolymerisation ermöglicht bei erhöhtem Monomergehalt im Gas eine hinreichende Ausbeute, die infolge reaktiver Absorption in Abhängigkeit von der nicht-idealen Thermodynamik auftritt. Eine vorgeschaltete Teil-Polymerisation vor Zerstäubung der Vorlage kann in Grenzen die Ausbeute erhöhen. Ein konzentriertes Modell beschreibt nur den einfachen Fall eines nichtflüchtigen Monomers korrekt.

Simulation der Strukturentwicklung über die gitterfreie SPH-Methode

Strukturausbildung ist ein komplexer Vorgang, der die Interaktion verschiedener Phasen, diverse physikalische Effekte und unterschiedliche Zeitskalen betrifft. Der gitterfreie SPH-Ansatz beschreibt das Kontinuum durch unregelmäßig verteilte Interpolationspunkte, die sich gemäß einer Lagrange-Betrachtungsweise bewegen. Werden derartige Punkte verschiedenen physikalischen Phasen zugeordnet, lassen sich verändernde Grenzflächen und strukturbildende Prozesse effizient beschreiben. Da SPH bisher nicht in Bezug auf Tropfentrocknung eingesetzt wurde, werden grundlegende Ansätze hergeleitet. Dies betrifft Wärme- und Stofftransport über die Tropfenoberfläche mit Hilfe linearer Triebkraftansätze, die effiziente, implizite Lösung der Energiebilanz und diverse Konzepte zur Krustenbildung im zweiten Trocknungsabschnitt. Zudem wird ein neuer Ansatz zur Berechnung von Oberflächenspannungskräften auf Basis paarweiser Kräfte vorgestellt. Durch Anpassung von Modellparametern lassen sich sowohl die Ausbildung dichter, kompakter Strukturen als auch von Hohlgranalien mit unterschiedlicher Mikroporosität simulieren. Diese Parameter können in physikalischer Weise als Bindergehalt interpretiert werden. Abschließend wird ein neuer Ansatz von SPH-Gitter-Kopplung vorgestellt, der Diffusion in der Gasphase direkt über ein unterlegtes Gitter abbildet. Berechnungen zeigen das Zurückweichen von Wasser innerhalb einer porösen Struktur infolge von Trocknung.

1. INTRODUCTION: SPRAY DRYING AND REACTIVE DRYING PROCESSES

Spray drying is a basic, common operation in the process industry in order to obtain powder from a liquid feed. It is applied in food and pharmaceutical processes as well as in the chemical industry. The feed - a solution, a slurry or an emulsion - is atomised into hot gas. Due to the intensive heat and mass transfer, drying takes place within seconds. The final product properties depend on many parameters like process conditions, operation mode and properties of the feed material. Production of tailored products demands extensive experiments. The question of predictively modelling the product properties has been addressed in different ways. Current state of the art are single droplet models, which typically assume spherical symmetry of the droplet and - at least in sections - a quasi-homogeneous material. Detailed simulation of structure generating processes is however not possible with these approaches. Whereas sole drying is widely applied, reactive spray drying processes are rare. Spray polymerisation has been discussed to some extent in the literature, but can still be considered as a "promising process", which offers desired properties in theory, but lacks practical applications and a theoretical model.

Both questions, the matter of structure evolution within a droplet and modelling and process evaluation of spray polymerisation will be addressed within this work by single droplet models. In the first part, droplet polymerisation will be evaluated by an extension of established, one-dimensional single droplet models of solution drying to a reactive drying model. The second part will consider structure evolution within the drop by a novel approach based on the meshfree SPH method. Focus of this work lies in the derivation and application of these new models. Especially the development of the SPH drying model concerns many implementational aspects in order to achieve the desired applica-

bility. Drying applications will therefore not be treated in detail and the reader is referred to the respective literature (e.g. Mujumdar 2007).

1.1 Spray Polymerisation

The basic idea of spray polymerisation utilises the combination of several process steps within one apparatus. This appears attractive for several reasons. Concerning process intensification and an efficient use of resources, the reduction of process steps is favourable, especially, when small spherical polymer particles need to be obtained. Assuming that chemical reactions take place during evaporation of the solvent (Biedasek 2009, p. 15), the combination of an energy demanding (drying) process with the heat release of chemical reactions is appealing. Moreover, batch processes demand a high solvent content in order to reduce the viscosity. Heat release due to chemical reactions needs to be dissipated efficiently, whereas a small droplet provides very intensive heat and mass transfer with the surrounding gas. Despite these attractive features and a series of patents on this process (for an extensive study see Krüger 2004), these considerations have mostly been theoretical. Only very fast reactions can be carried out within the gas because of the little residence time. Especially acrylic acid and its salts appear attractive as possible applications, which has been considered experimentally on a lab scale by Franke, Moritz, and Pauer (2017). The process control within a droplet is limited to the adaption of feed composition and adjustment of drying gas properties, which may, however vary significantly throughout a dryer. A model, which takes all relevant chemical reactions into account and predicts product properties, is therefore highly desirable. So far, Walag (2011) provides the only mathematical model of this process. By assuming the droplet as ideally mixed, he derives equations for emulsion polymerisation within a drop. A spatially resolved description, which takes inhomogeneities and transport processes within the droplet into account, is lacking yet.

1.2 Single Droplet Models for Spray Drying

Mezhericher, Levy, and Borde (2010) distinguish between three basic concepts of droplet drying models. Semi-empirical approaches are based on a characteristic drying curve, with process prediction being largely based on experimental experience. The reaction engineering approach does not take the complete processes within a droplet into account, but only solves the equations for the droplet as a whole. Its efficiency makes it interesting for the incorporation in large scale simulations of a complete spray dryer, in which more resolved models would be too costly. If the model is assumed in a lumped approximation, the model must be fitted well to experiments or previously been tuned by the third class of single droplet models, deterministic drying models. These models take all relevant processes within the drop into account and typically solve the underlying equations on a one-dimensional scale in radial direction. Azimuthal or polar effects are typically neglected under the assumption of spherical symmetry. The reactive drying model, which is derived throughout this work, falls into the last category.

Nesic and Vodnik (1991) provide a principle model of the different process periods during drying, from initial heating, to a quasi-steady-state in which heat transfer is directly converted into evaporation up to the formation of a crust, which hinders further evaporation and provokes heat up, followed by boiling and final drying. The process of crust formation has been addressed in several ways like treatment of the solid phase by population balance models (Seydel 2005; Handscomb, Kraft, and Bayly 2009) or by representation of a crust with approximate, regular (pore)geometries (Mezhericher, Levy, and Borde 2009). If solution drying is involved, the transport of a solute in radial direction is modelled (Sloth et al. 2006; Czaputa and Brenn 2012).

Concerning reactive drying processes, in particular spray polymerisation, a lumped approximation of the droplet may fall short, as spatially inhomogeneous educt concentrations change the local reaction conditions and hence polymer properties. The spray polymerisation model will therefore follow the one-dimensional models of solution drying and enhance this approach with special regard to polymerisation reactions. A different approach will be laid out concerning structure evolution. With the long term aim of predictively modelling how a structure is formed on a detailed scale, a two-dimensional model will be employed, which accounts for all underlying physical effects.

1.3 Meshfree Methods and Simulation of Structure Evolution

Meshfree methods discretise the continuum by interpolation points, so-called particles, which are moving according to a Lagrangian point of view. The term particle is not to be mistaken as a solid granular mass, aside from special approaches like the Discrete Element Method (Cundall 1971). Particles mean truly interpolation points, which are employed in order to discretise continuum equations. In this sense, implementation of physical effects can be undertaken based on first principles. Particles may bear additional properties or variables. Therefore, these methods are not bound to the equations of motion, but can be used for the solution of additional physical effects by using the meshfree discretisation operators.

The Lagrangian nature of meshfree approaches offers natural advantages over grid-based methods. When evolving interfaces are modelled by grid-based methods, the mesh has to adapted continuously and interfaces need to be tracked by approaches like Level Set (Sethian 1999) or Volume of Fluid (Hirt and Nichols 1981). This may become very costly, especially when a large number of interfaces is to be tracked and strong deformations occur. Due to particle motion, meshfree methods are self-adapting. Particle classes of various kind can be employed in order to represent different physical phases. Phase boundaries are therefore intrinsically represented by co-occurrence of particles of different nature. Interface tracking is in the best case done automatically due to particle motion. The evolution of material bridges, break-up and merging can also be treated in a natural way. On the downside, there is little standard simulation software for meshfree methods, which also involves a lack of standard workflows and an increased user effort for pre- and post-processing. Furthermore, the advantage of a flexible particle distribution needs to be paid by a high computational load, as discretisation operators typically involve a much larger number of neighbouring points than in grid-based methods. Besides, meshfree methods partly lack a mathematical foundation, when an analysis can only be conducted for regular particle alignment, whereas particles are allowed to be distributed irregularly throughout a simulation. Hence, such approaches can be considered as special methods suitable for special problems, which cannot compete with highly developed mesh-based methods in their typical applications. For non-standard cases, in which established methods are challenged, meshfree methods

provide an alternative. Structure evolution can be considered as one of these particular problems.

Throughout this work, the Smoothed Particle Hydrodynamics method (SPH) will be used, which can be considered as the first completely meshfree method in computational fluid dynamics. SPH was developed at the same time independently by Lucy (1977) and Gingold and Monaghan (1977) for the simulation of astrophysical problems. In this field it became one of the standard approaches within the next decades. In the 1990s, SPH was extended to problems concerning incompressible liquids (Monaghan 1994; Cummins and Rudman 1999), which made it interesting for engineering problems as well. Reviews of the method have been provided by Monaghan (1992, 2005, 2012), one of its original inventors. SPH applications are often found in problems involving sloshing or violent flows, which for instance concerns coastal engineering. The method proved to be suitable to calculation of large material deformations like the impact of projectiles (Stellingwerf and Wingate 1994) and for calculating the evolution of cracks (Das and Cleary 2013). Its capability of treating problems of structure evolution was shown by Keller (2015), who modelled the generation of a porous structure, determined by a considerable number of interacting physical effects.

1.3.1 Previous Applications of SPH to Drying

Drying models employing SPH are very rare, but the little number of contributions is indeed concerned with the matter of structure evolution, which underlines the special ability of SPH in this respect. Ito and Yukawa (2012) modelled the evolution of cracks within a flat drying paste by SPH. Due to the drying process, the mechanical stress inside the paste increases. If, locally, the stress exceeds the yield stress, the material will be damaged there, resulting in the initiation of a crack. Subsequently, this fracture grows further and takes up the mechanical stress within its surrounding. The process of drying itself has not been taken into account directly. Ito and Yukawa rather considered a constant increase of mechanical stress over time as a result of drying without accounting for heat and mass transfer. The model therefore provides an insight into the fracturing of a drying material, but crack initiation and growth in this approach could be linked to any physical effect with continuously increasing mechanical stress and not just drying in particular.

Karunasena, Senadeera, Gu, et al. (2014) and Karunasena, Senadeera, Brown, et al. (2014a,b) examined the drying of plant cells and studied the impact of the drying process on the deformation of single cells as well as on cell clusters. The morphological behaviour was captured by an SPH-DEM hybrid model, in which the cell walls are represented as linked DEM particles and the cell interior is modelled as a highly viscous Newtonian liquid using SPH. The drying kinetics rely on the differences in osmotic pressure over the cell walls with the mass loss due to drying being dedicated to all SPH particles within a cell in equal measure. With the mass of the particles being diminished, their volume is reduced as well, resulting in cell shrinkage. The structural behaviour is determined by the parameterisation of several attractive and repulsive forces between DEM particles and according to their interactions with SPH particles.

Detailed, spatially resolved simulations of drying kinetics have not been conducted in SPH so far.

2. THEORETICAL PRINCIPLES

In the following, the underlying principles being fundamental for the derivation of drying models will be laid out. Typically, one would be short on this topic when presenting a classic single droplet drying model. However, this work is also concerned with an appropriate and sound representation of the polymer phase and a consistent derivation of balance equations. Indeed, there are still drying models being published, in which transport equations are not mass-conservative. Such approaches are neither sufficient for more complicated applications like spray polymerisation nor are the underlying simplifications reasonable in general. Therefore, the principles of diffusion and reaction driven convection and their consideration in transport equations will be discussed to a longer extend.

2.1 Transport Equations

Transport of an entity can be modelled mathematically via a partial differential equation in differential or integral form. In the following only differential formulations will be used. In general, transport of an arbitrary entity ψ can be expressed as

$$\frac{\partial \psi}{\partial t} + \nabla (\psi \vec{v}^*) + \nabla \phi_\psi = \sigma_\psi. \quad (2.1)$$

The temporal change of the respective entity, $\frac{\partial \psi}{\partial t}$, is called the accumulation term. The second term denotes convective transport with the continuum velocity \vec{v}^* , whereas ϕ_ψ indicates the molecular flux of the property ψ (Bird, Stewart, and Lightfoot 2002, p. 588). Sources and sinks are denoted as σ_ψ . Table 2.1 gives an overview of the most common properties with their respective fluxes and sinks/sources. \vec{v}^* is an average fluid velocity, where the base for averaging can in general be arbitrarily chosen (Taylor and Krishna 1993, p. 3ff). Most commonly

Table 2.1: Transport properties.

equation	property ψ	velocity v^*	flux ϕ_ψ	sources σ_ψ
continuity eq.	ρ	\vec{v}		
momentum eq.	$\rho\vec{v}$	\vec{v}	$-\Pi$	$\rho\vec{f}$
mass bal. species j	ρ_j	\vec{v}	\vec{j}_j	$r_j^F MW_j$
energy balance	ρu	\vec{v}	$\vec{q} + \sum_j \vec{j}_j h_j + p\vec{v}$	$-\tau : \nabla\vec{v} + \vec{v} \cdot \nabla p$
continuity eq. molar	c	\vec{v}^N		$\sum_j r_j^F$
molar bal. species j	c_j	\vec{v}^N	\vec{J}_j^N	r_j^F

the mass average velocity \vec{v} and the molar average velocity \vec{v}^N are employed for modelling transport of mass based properties such as (partial) densities and mass fractions or molar values as concentrations and mole fractions, respectively.

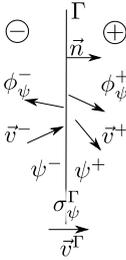


Figure 2.1: Transport across a phase boundary Γ .

Equation 2.1 is the conservation equation of a property in a continuum, where a smooth distribution of the respective values can be assumed. In contrast, a property may change discontinuously at a phase transition, with an abrupt change in physical behaviour. Mathematically the interface between two phases – and + is assumed to be infinitesimally thin without storage capacity, at which the respective properties may change jumpwise between both phases (see Figure 2.1). In- and outgoing

fluxes and sinks/sources need to add up to zero. A general balance equation at an interface Γ is (comp. Taylor and Krishna 1993, p. 9f)

$$(\psi^+ \vec{v}^+ + \phi_\psi^+ - \psi^- \vec{v}^- - \phi_\psi^- + \psi^- \vec{v}^\Gamma) \cdot \vec{n} - \sigma_\psi^\Gamma = 0. \quad (2.2)$$

Superscripts – and + denote the phases on both sides of the interface, where the interface normal \vec{n} is directing from – to +. Additionally to convective and diffusive transport the motion of the phase boundary Γ itself with the interface velocity \vec{v}^Γ needs to be taken into account. Equation 2.2 is the basis for the derivation of boundary conditions in mathematical models. These will be considered in detail, when the equations for reactive drying models of single droplets are derived in chapter 3.

2.1.1 Transport in a Mass Averaged System

Mass and Momentum Balance Equations

Due to the basic principles of mass conservation and the connection of momentum with the mass or density of a fluid element, it is straightforward to model the laws of hydrodynamics in a mass averaged notation with the velocity \vec{v} . $\psi = \rho$ yields the mass balance or continuity equation

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \vec{v}). \quad (2.3)$$

With $\psi = \rho \vec{v}$ the momentum balance (Navier-Stokes equations) in conservative form can be obtained to

$$\frac{\partial \rho \vec{v}}{\partial t} = -\nabla \cdot (\rho \vec{v} \vec{v} - \Pi) + \rho \vec{f}, \quad (2.4)$$

in which Π denotes the Cauchy stress tensor and \vec{f} is a vector of external forces (as force per unit mass - in unit of an acceleration) such as gravity and surface tension. Applying the product rule on equation 2.4 and subtracting the continuity equation the non-conservative momentum balance can be obtained (Ferziger and Peric 2007, p. 10)

$$\rho \frac{\partial \vec{v}}{\partial t} = -\rho \vec{v} \nabla \cdot \vec{v} + \nabla \Pi + \rho \vec{f}. \quad (2.5)$$

Whereas in simulations both formulations yield similar results on very fine meshes, for coarse discretisations the non-conservative form is prone to additional errors (Ferziger and Peric 2007, p. 10). The Cauchy stress tensor is usually split into a diagonal tensor corresponding to the fluid pressure p and the deviatoric stress tensor τ

$$\Pi = -pI + \tau \quad (2.6)$$

$$\frac{\partial \vec{v}}{\partial t} = -\vec{v} \nabla \cdot \vec{v} - \frac{\nabla p}{\rho} + \frac{\nabla \tau}{\rho} + \vec{f}. \quad (2.7)$$

The Navier-Stokes equations and the mass balance provide a set of $d + 1$ equations (d being the spatial dimensionality of the problem), but contain $d + 2$ unknowns - the density, d components of the velocity vector and the pressure. In compressible flows the pressure is dependent on the density and can be evaluated by an equation of state (EOS). Fluid density and pressure are not coupled in