16th European Symposium on Computer Aided Process Engineering
and 9th International Symposium on Process Systems Engineering
W. Marquardt, C. Pantelides (Editors)

Application of particulate models for industrial processes

George Skillas,[a] Catrin Becker,[a] Marcel Verduyn,[a] Johannes Vorholz[a]

[a]Process Technology & Engineering, Degussa AG 1024-319, D-63457 Hanau/Wolfgang, Germany

Abstract

Two approaches for modeling and simulating gas phase processes with varying degrees of detail and computational effort are presented. The first example involves a single reactor used in the production of nanoscale particles, the second example deals with an entire spray granulation process producing particles in the millimeter range. In both cases particle size is an important measure for product quality. The aim of the work is to predict particle size distribution (PSD) and flows as a function of process and operation parameters.

The reactor is simulated by means of computational fluid dynamics (CFD). Hereby, the computed flow and chemical species fields are used as input for a simulation of particle inception, growth and aggregation. Due to the complexity of the system quantitative results are prone to errors. However, the method is robust and the results for the particle field help understanding and explaining different aspects of the reactor and the aggregate particles produced.

In spray granulation processes the PSD depends, very often in a complex manner, on process and/or material parameters. Moreover, process dynamics can also play an important role. Furthermore, the interaction and interconnection of different unit operations (granulators, mills, classifiers) is in the scope of interest, when the application of sophisticated models (as in the first case) is restricted or impossible due to computational limits. In this second example, a literature model for growth and abrasion (Heinrich et al. (2002)) is extended to breakage and implemented into Aspen Custom Modeler. In order to ensure a high flexibility of the model, the process is divided into several unit operations which can be arbitrarily combined within a flowsheet. The model is parameterized using plant measurements combined with suitable estimates and applied to industrial granulation processes. It can be utilized for process conception as well as for process optimization.

Keywords: spray granulation, nanoparticles, particle dynamics, particle size distribution, cfd.

1. Carbon black reactor modelling

1.1. Introduction

Most carbon black is produced by the furnace black process, Kühner 2000. In this process natural gas and preheated air are burnt in a combustion chamber and then feedstock, i.e. liquid aromatic oil, is injected into the hot gases. The oil decomposes mainly to carbon and hydrogen while carbon black is formed. When the desired particle size and morphology are achieved reactions are stopped by quenching with water. Subsequently the gas is led through a heat exchanger to preheat the process air. Bag-house filters separate gas and carbon black agglomerates. In this paper we will discuss

the part of the process described above, where oil is injected and carbon black particles are formed.

1.2. The Model

For the results presented here Navier-Stokes equations for turbulent flow, energy and chemical composition, coupled with a monodisperse particle model which included inception aggregation and surface growth were solved. Turbulence is computed by the realizable k-ε model. Convective and radiative heat losses are accounted for. Radiation is modelled with the discrete ordinates model. We consider CO_2, H_2O and carbon black absorption to compute the absorption coefficient.

The particle model is monodisperse. The aggregate number N, volume V and area A concentration are transported through the computational domain. Model aggregates consist of monodisperse primary particles. These are modelled as hard spheres i.e. no overlap is allowed.

Nucleation, oxidation and growth rates are modelled by Arrhenius expressions each with two parameters (R_i, T_i), while the particle collision coefficient is computed by taking into account expressions for both free molecular and continuum regimes. The Arrhenius form of the nucleation rate was derived by simplifying the classical nucleation theory expression, see Skillas et al. 2005 for details.

Atomisation of the liquid oil with detailed droplet break-up mechanisms is not considered in the calculation, instead experimental data is used for droplet diameter and velocity to partially account for these limitations.

We considered species mixing and not reacting to be rate limiting, i.e. the composition of the species in the gas is determined under the assumption that the chemical reactions are so fast that chemical equilibrium is achieved locally.

The geometry of the simulated reactor can be seen in Figure 1. The computational domain is three-dimensional starting at the end of the combustion chamber and encompasses a narrow tube and the reactor tunnel.

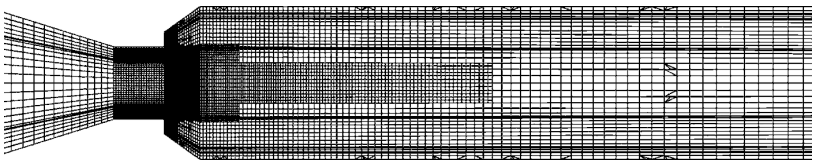

Figure 1: Reactor geometry and discretisation of the computational domain.

1.3. Model application and discussion

Mass flow data calculated by simulation and measured mass ow data, taken from Skillas et al. 2005, are shown in Figure 2. Inlet gas oxygen concentration is shown as a λ value for natural gas combustion in the combustion chamber. The trends are in qualitative agreement with experiment for both λ values. The slope value is over-predicted by the model, nevertheless steepness is similar to experiment. The pronounced difference between calculated and experimental value at an oil flow of 430 kg/h, found for the SSA as well Skillas et al. 2005, can be attributed to the performance of the chemical model. The CFD chemical model is assuming equilibrium. Comparison of reactor gas chromatography measurements with equilibrium calculations show a consistent under-prediction of CO_2 concentration and an over-prediction of CO, i.e. at equilibrium conditions more carbon is consumed by oxygen than in reality. The more O_2 present, the lower the calculated carbon black mass compared to reality, leading in the extreme to differences like the one at 430 kg/h. In part this effect is compensated for in the particle

model through the fit parameters. Considering that this prediction is an extrapolation of the fit the performance is good.

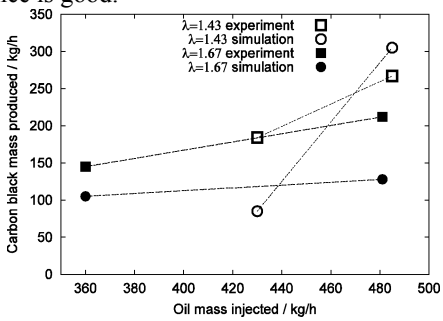

Figure 2: Carbon black mass flow produced by, vs. oil mass ow injected into, the reactor for simulation and experiment. The set of four model parameters R_n, T_n, R_g and T_g are adjusted by comparing the measured and calculated data for the two rhs pairs of points. The two left hand side (lhs) pairs are predicted with the model using the best parameter set found.

As mentioned above, residual oxygen burns oil vapour, raising the temperature in the vicinity of the oil droplets, c.f. Figure 3a. Temperature reaches a peak in this region and approaches the adiabatic flame temperature in the order of 2300 °C, as the chemical model assumes chemical equilibrium in each computational cell. Temperatures in the vicinity of the walls are accurate within 100 °C, when compared with experimental data

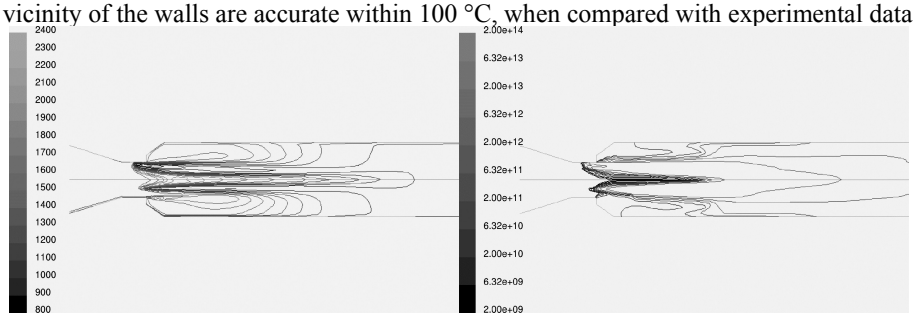

Figure 3: From left to right (a) reactor temperature in K and (b) aggregate number concentration in #/mg. The upper portion is a cut through an oil nozzle containing plane, while the lower portion shows a cut through a plane between two oil nozzles. The oil injection region can be seen.

obtained by pyrometry measurements. The low temperature region is caused by energy needed for oil evaporation.

Number concentration data are shown in Figure 3b. Particles form on the envelope of the oil droplet evaporation region, where high temperatures needed for particle formation are present.

Due to high velocities (low residence time) in the core flow aggregates at the end of the computational domain consist on average of only 7 primary particles (c.f. Figure 4a), while the aggregate concentration drops about an order of magnitude.

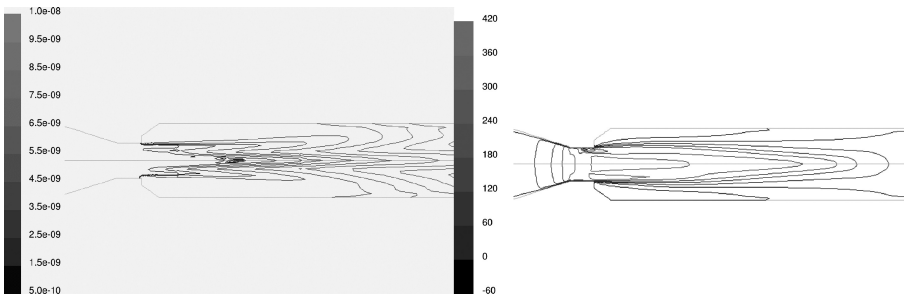

Figure 4: From left to right (a) primary particle diameter in m and (b) axial velocity in m/s. The upper portion is a cut through an oil nozzle containing plane, while the lower portion shows a cut through a plane between two oil nozzles. The core flow residence time is short, resulting in particles with an diameter of about 10 nm. A recirculation zone can be seen, near the reactor walls.

The inhomogeneity in the $N\psi$field, due to oil injection almost vanishes after about 40% of the reactor tunnel length.

To understand the primary particles per aggregate field one has to consider flow velocities, c.f. Figure 4b. Recirculation zones resulting in longer residence times, which promote aggregation, exist in both planes. The lowest aggregate number concentration occurs in the recirculation region and it is lowest between oil nozzles. This is consistent with high temperatures and concentration of growth species locally available, which in reality are needed to promote aggregation through neck-forming between primary particles.

The shape of the fields in Figures 3-4 does not vary with process conditions, while the actual numbers follow empirical laws. For example, decreasing the reactor temperature lowers aggregate concentration N and increases primary particle diameter d_p. Good agreement between simulation and experiments is found at conditions where the equilibrium assumption holds.

2. Modelling a plant producing particulate products

2.1. Introduction

The particle size distribution (PSD) of particulate products, as e.g. granulates, is an important measure for the product quality as it influences properties like solubility, dust formation or dispersibility. In turn, the PSD is influenced by process parameters as for example the hydrodynamic conditions inside a granulator as well as by the design of the whole plant.

Especially in the case, where the influence of variations in the interconnection of different unit operations (granulators, mills, classifiers) is in the scope of interest, the application of sophisticated models as discussed in the previous sections is restricted or impossible due to computational limits. Instead, it is desirable to work with models of "moderate" accuracy that, on the other hand, enable the modeling of a larger network of unit operations or even a whole plant.

2.2. The model

In the present work a literature model of a spray granulation process (Heinrich et al. (2002)) is extended and implemented in Aspen Custom Modeler (ACM), a part of the industrial standard simulator Aspen Engineering Suite (AES). In order to ensure a high flexibility of the model, the process is divided into several unit operations (granulator, separators as sieves or cyclones, and mills) which can be arbitrarily combined on a

flowsheet. The utilization of ACM has the additional advantage, that thermophysical property databases (Aspen Properties) can be accessed and/or that user developed unit operations can be combined with "off-the-shelf"-models for "standard" unit operations available in Aspen Plus or Aspen Dynamics.

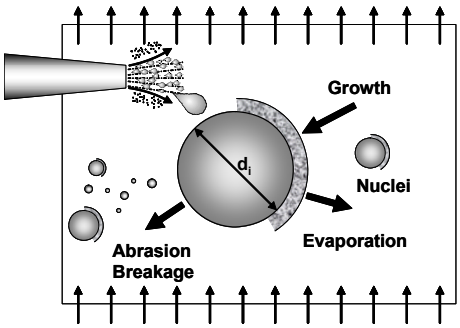

Figure 5: Granulator unit

In a spray granulation process a fluid product, e.g. a suspension, is sprayed onto particles in a fluidized bed. A part of the drops is deposited on the particles, the solvent evaporates in the hot, unsaturated fluidization air, and the solid matter remains on the particle, resulting in an onion-like growth. At the same time the particle is also subjected to mechanical stress causing abrasion or even breakage resulting in a diameter decrease or the birth of new smaller particles (figure 5).

For the granulator unit the population balance account considering growth, abrasion and breakage is solved. The expressions for effective growth and abrasion are based on a model by Heinrich et al. (2002), in addition, breakage terms are introduced. Mills and separators are modeled using short cut methods, e.g. by fixed PSD of the bed spectrum and separation functions.

2.3. Application of the model to industrial spray granulation processes

The model is applied for the simulation of the start up behavior of a newly built spray granulation process which was built up by the unit operations shown in figure 5. In the first step the model parameters are determined from plant measurements of an already existing (but smaller and partly designed differently) plant for the same product or estimated by suitable assumptions. After that, the parameters are adopted for the simulation of the new plant.

By the simulation of the start up procedure an instability of the new process, i.e. process runaway by accumulation of fines in recycle streams and product quality decrease, was detected, which was confirmed during the start up of the plant. This situation is shown qualitatively in figure 6 on the left hand side. The flexibility in combination of the unit operations enabled the simulation of different scenarios for the stabilization of the process which finally resulted in the introduction of corrective measures that led to stable behavior (figure 6 (rhs)).

Another application of the model is the examination of the influence of the change of process parameters (e.g. grinding intensity, suspension flow, or variations in the interconnection of separators) on the product quality, for example the particle size distribution. Whereas in the case when stability problems are considered, qualitatively correct trends might be sufficient, the accuracy of the results needs to be higher, when the PSD is predicted. Typical results (made anonymous) are shown in figure 8. In this case the above mentioned parameters are again fitted to the results of plant measurements. In the second step the model is extrapolated to different operating situations of the *same* plant (figure 7).

Although there are still some quantitative deficiencies the agreement between simulation and experiment can be considered as good.

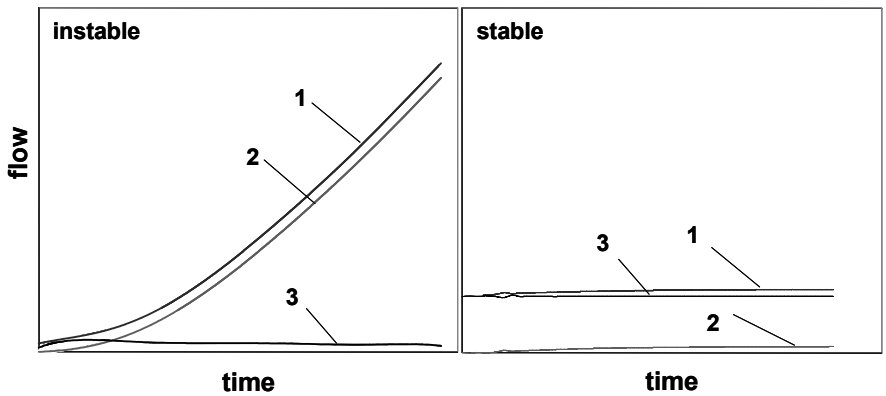

Figure 6: Stable (lhs) and instable (rhs) behavior of a plant during start up

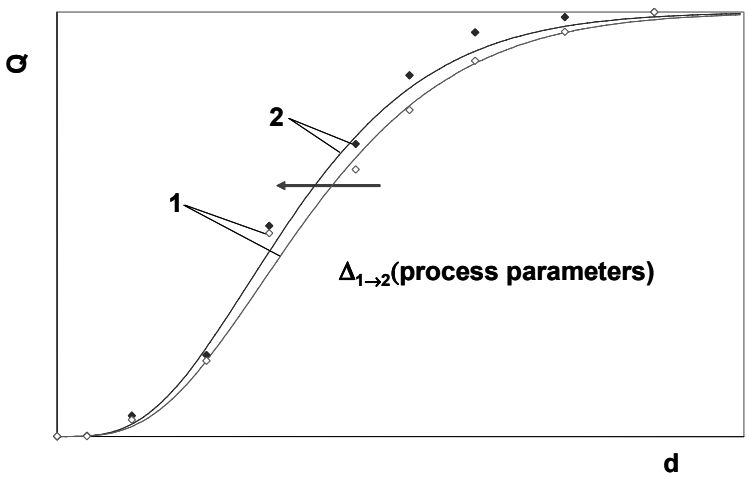

Figure 7: Prediction of the PSD of a granulate product as a function of the process parameters (symbols denote experimental data, lines represent simulation results)

References

S. Heinrich et al., 2002, Analysis of the start-up process in continuous fluidized bed spray granulation by population balance modelling, Chem. Eng. Sci. 57, 4369-4390

G. Kühner, 2000, What is carbon black?, Degussa AG, Inorganic Chemical Products Division, P.O. Box 110533, D-60000 Frankfurt 11, Germany.

G. Skillas et al., 2005, Simulation of particulates in a carbon black reactor, J. Nanop. Res. 7, 15-27.