Numerical Investigation of Particles Breakage and Growth in Gas-Solid Processes: Spiral Jet Milling and Polyolefin Polymerization in Fluidized Bed Reactors

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This thesis aims at studying the spiral jet milling process of active pharmaceutical ingredients (APIs) and the polyolefins polymerization process by means of Eulerian-Eulerian simulations.

The micronization of pharmaceutical powders via spiral jet milling is an industrial process that uses high-energy gas to realize collisions between particles, which eventually break down into smaller size components.
The physics behind the process is complex and its understanding is not trivial. Particles are moved by a high-velocity compressible gas flow and impacts force powders to undergo a fragmentation process that reduces the particle size by order of magnitudes, making the spiral jet milling description really challenging.
A well-known problem of the APIs processing is the formation of large solid aggregates that stick on the spiral jet mill walls and reduce the micronization chamber volume, compromising the process effectiveness and taking the final size of particles out of target. This phenomen, called caking, requires the apparatus stoppage to mechanically remove the formed crusts that have to be wasted. The large cost associated to many pharmaceutical powders and the time needed to clean the system cause a huge economic loss.
This work is focused at numerically studying the caking mechanism to understand the effect that the chamber diameter reduction has on the gas velocity fields for standard operating conditions of the spiral jet mill. A simple mimic strategy is proposed to emulate the chamber volume reduction due to crusts formation and the system fluid-dynamics is studied by means of single-phase CFD simulations to determine the causes that takes the final particles size out of specific.
Simulations show that caking causes the deterioration of the classification capabilities of the system if the gas mass-flow rate is kept constant, especially near the spiral jet

mill upper and lower walls, allowing larger particles to escape the micronization chamber. In order to avoid the forced transport of massive particles towards the system outlet, the nozzle absolute pressure has to remain constant to keep the fluid spin ratio and the classification characteristic unchanged while caking is building up.
Spiral jet milling still lacks of a solid theoretical ground able to properly describe the physics behind the process and the determination of substance-specific operating conditions is usually based on expensive experimental campaigns driven by the technicians' experience. This, together with the impossibility of experimentally characterize the system to avoid the multiphase flow field corruption, put big constraints on the experimental study of the process and problems that may affect it, such as caking, are not studied in detail.
In this framework, the work reported in this thesis also describes the construction of a novel uncoupled quasi-3D model able to study the spiral jet milling at process scales and times.
The gas velocity fields computed through 3D single-phase CFD simulations are provided as input in a 1D compartmentalized model to calculate solid velocities along the micronization chamber radial direction. Mass and momentum balance equations are used to build a computational model in which the solids velocities are calculated availing of simple algebraic relationships developed for pneumatic transport. The particles size reduction is taken into account through a breakage kernel that is function of gas energy and solid holdup. A set of parameters is tuned through *ad hoc* experiments to consider the substance-specific breakage behaviour and the characteristics of the inlet particle size distribution.
The model performance are evaluated for lactose and paracetamol by validating the predictions for D10, D50 and D90 against design of expert data taken as reference.
In good agreement with the assumptions made at the beginning of the derivation, model predictions are better if an high-specific energy process is considered, *i.e.,* high pressure and low solid feed-rate (dilute flow conditions). The best results are obtained if small particles are processed (low Stokes number) and if the inlet particle size distribution is narrow.
It is shown that simulation predictions can be improved if a specific-pressure parameters set is calculated, especially when treating fragile materials with wide inlet distributions.
Finally, suggestions on some possible model formulation enhancements and future works are given.

The second topic studied in this thesis is the simulation of polydisperse Eulerian-Eulerian gas-solid flows for analyzing the polymerization process of polyolefins in fluidized bed reactors (FBRs).
In order to study such a process, modelling tools represents a valid and necessary option to design the operating conditions and ensure the desired product quality in terms of final particle sizes and molecular properties.
Two modelling approaches are usually employed to this end, multiscale kinetic models and detailed CFD-based models. The first type of framework, usually involving compartmentalized models, has the major advantage to be computationally affordable,

offering the possibility of implementing detailed single particle models. On the other hand, the reactor fluid-dynamics is usually described through semi-empirical relationships that makes them suitable for a narrow range of applications.
CFD models, instead, provide the fully detailed calculation of the multiphase flow field but at computational cost that is not always sustainable, especially if applied to real-scale systems.
This study focuses on the calculation of the fluidization properties of FBRs by comparing the results obtained through a simplified 1D compartmentalized model and those coming from detailed 2D multiphase CFD model with the kinetic theory of granular flows to account for the granular nature of solid particles.
The behaviour of a bed composed by Geldart A-B type particles is analyzed for different operating conditions in a system without reaction and solid injection or withdrawal, focusing on the steady-state fluid dynamic behaviour of monodisperse and polydisperse particles populations.
Results show that the simplified compartmentalized approach is capable to predict the solid mixing in the bubbling fluidization regime for high-density polyethylene particles. Average volume fractions are close to the values predicted by the CFD model along the whole cylindrical part of the reactor, especially for monodisperse particles. Predictions are in good agreement also for broad size distributions, especially in terms of average diameters. Considering the negligible computational cost associated to compartmentalized models if compared to CFD and their versatility to implement complex kinetic schemes, such multiscale approaches represent an effective tool for industrial process design.
Anyway, the detailed description of the polymerization process during time can be extremely helpful in predicting the flow rates and the particle sizes of the final product. In this context, CFD approaches constitute a reliable tool for determining the operating conditions needed to obtain given output particles properties.
The scientific literature does not offer any mature modelling set-up able to study FBRs in continuous operating mode since large production plants require a huge computational effort to correctly discretize the system in space and time.
The last part of the thesis aims, therefore, at understanding if a 2D scaled geometry can effectively describe the continuous polymerization process by correctly predicting average particles size and solid hold-ups.
Starting from a desired particles residence time and typical operating conditions, simple material balances are used to calculate the scaled-down reactor volume and a CFD-PBM model is implemented to simulate the multiphase fluid dynamics inside the reactor. The polymerization process is modeled through the DQMOM approach and a simple particle growth model is validated against an analytical solution. Different solid withdrawal positions along the reactor axis and inlet flow rates are studied to determine their influence on the final solid holdup and average particle sizes within the reactor.
The results show that the solid holdup does not change remarkably if the outlet position is varied along the reactor height but it increases if the catalyst feed-rate is increased. The reactor is well-mixed at any height and, as for the non-reactive cases, the particles average size does not change remarkably along the reactor axis. Large

particles are found only in the very bottom part of the reactor.
Calculations show that the computational approach proposed allows the description of a steady-state operation by simulating a limited physical time (order of 10^2 s). On the other hand, it is not possible to correctly calculate the reactor holdup since the system tends to empty itself for every condition and solid outlet topology tested.