SimDOME

User Story: coprecipitation of NMC hydroxides

Aims	• Provide models for crystallization & coprecipitation • Emphasis on the coprecipitation of NMC hydroxides
Methodology	• CFD models based on OpenFOAM and Ansys CFD • Compartment model for fast calculations
Results	• CFD is accurate but computationally expensive • Compartment model ideal for process optimization

Summary

The focus here is on reactive crystallization or coprecipitation, where a solid phase is formed in a liquid, thanks to a chemical reaction. Solid particles are formed by nucleation and subsequently grow, aggregate and break, interacting with the continuous liquid phase. Two models are described here: a full CFD model and a simplified compartment model. Both approaches are built upon the open-source CFD code OpenFOAM and the commercial code Ansys CFD Fluent. The methodology is eventually demonstrated for a real practical case: the coprecipitation of Ni, Mn, Co hydroxides to produce NMC cathodes for lithium ions batteries.

Case Description

Reactive crystallization or coprecipitation is a very popular process employed to produce solid particles from a mother solution. The process is driven by supersaturation, a thermodynamic variable stating the excess of a specific compound, formed by a fast chemical reaction, with respect to its solubility. Because the reaction is fast and the reactants need to be mixed, fluid flow and mixing play a very important role. Particles are formed within the liquid solution due to nucleation (primary and secondary, homogeneous and heterogeneous) and then interact with the continuous liquid phase, by growing into larger particles and by exchanging momentum. Particles also interact with each other by aggregating and might break into smaller particles due to the impact on the walls and moving parts of the reactors, in which the process is conducted. Results focus here on the coprecipitation of Ni, Mn, Co hydroxides to produce NMC cathodes for lithium ions batteries but the framework can be applied also to other systems.

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Models description

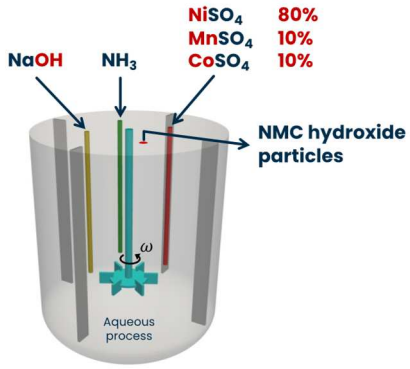

Figure 1: Sketch of the reactive crystallization process.

Figure 1 describes the reactive crystallization process considered. This is typically conducted in a large stirred tank, where reactants are feed with different feeding tubes. Metal ions are first complexed by ammonia and then due to the mixing with sodium hydroxide, and the increase in pH, the NMC hydroxide is then formed. The driving force for the process is the supersaturation defined as the ratio between the product of the Ni, Mn, Co and hydroxyl ions concentrations and the solubility products, corrected by the activity coefficients. Supersaturation defines the rates with which solid NMC particles nucleate and growth and influences also the aggregation and breakage rates.

The modelling framework is summarized in Fig. 2.

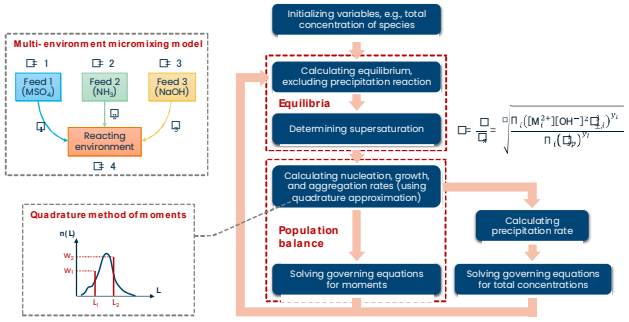

Figure 2: Summary of the modelling framework.

Incomplete mixing between the reactants is described via a multi-environment micromixing model, whereas the effect of nucleation, growth, aggregation and breakage on the particle size distribution (PSD) is described via a population balance, in turn solved with the quadrature method of moments (QMOM). A complete description of the framework is reported in our previous work (Para et al, 2022).

The modelling framework has been validated with experimental data by Shiea at al. (2022). As mentioned, the fluid dynamic of this reactive solid-liquid system is described by resorting to two approaches: (1) a full CFD model in which the stirred tank is described with all its geometrical details and (2) a simplified compartment model in which the tank is divided into a finite small number of compartments.

Results

Figure 3 shows results obtained from one of our typical simulations run with the full CFD model. The CFD model describes the transient startup of the process and predicts the PSD of the obtained NMC particles exiting the reactor.

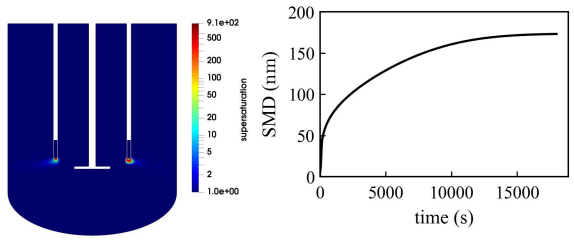

Figure 3: Contour plot of supersaturation (left) and time evolution of the Sauter mean diameter (SMD) of the particles exiting the reactor (right).

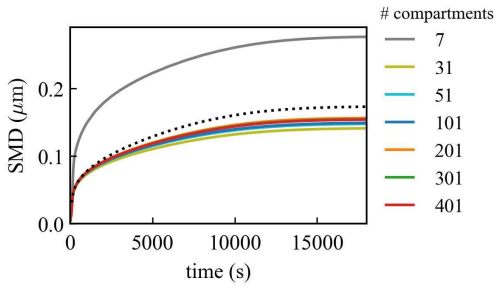

Figure 4: Comparison between the Sauter mean diameter (SMD) of the NMC particles exiting the reactor predicted by the full CFD model (dotted line) and the compartment model with different compartments.

Contact us:
emanuele.ghedini@unibo.it

A similar result can be obtained with the compartment model, as reported in Fig. 4. As it is seen by increasing the number of compartments the prediction of the compartment model gets closer and closer to the full CFD model. It is interesting to point out that similar results are obtained with very different computational costs. By using 42 cores the full CFD simulation requires more than 14 days to run, whereas the same simulation is run with the compartment model (with 51 compartments) with 26 cores in 4.5 hrs. The computational cost of the full CFD model can be further reduced by employing operator-splitting, that allows to increase the time-step size, and by resorting to a hybrid parallelization, using MPI and OpenMP. This reduces the load-balance issue related to the use of the operator-splitting method. With this approach the spatial domain is divided into zones and the calculation of each zone is assigned to a small number of processors using MPI. Simultaneously for each of this zone a second parallelization, adopting this time OpenMP is employed, using a large number of cores to perform the source integration, significantly decreasing the time required by the solver to perform a time-step.

Link to download the software: https://github.com/mulmopro/wet-synthesis-route

References

Para, M.L., Alidoost, M., Shiea, M., Boccardo, G., Buffo, A., Barresi, A.A., Marchisio, D. A modelling and experimental study on the co-precipitation of Ni0.8Mn0.1Co0.1(OH)2 as precursor for battery cathodes (2022) Chemical Engineering Science, 254, art. no. 117634.

Shiea, M., Querio, A., Buffo, A., Boccardo, G., Marchisio, D. CFD-PBE modelling of continuous Ni-Mn-Co hydroxide co-precipitation for Li-ion batteries (2022) Chemical Engineering Research and Design, 177, pp. 461-472.

Contact us:

emanuele.ghedini@unibo.it