Theses of Doctoral (PhD) dissertation

Analysis of hydrodynamic effects on product quality in polymerization reactors

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1. History, objective

Population balance models have been used for describing the disperse systems for a long time (Hulburt and Katz, 1964; Valentas and Amundson, 1966). Most of these models are one- or two-dimensional ones, i.e. these models provide the changes of numbers of dispersed elements or apart from this the changes of their characteristic size. There are disperse systems, such as suspension polymerization, in which chemical reactions take place inside the dispersed elements. The volume, concentration of components and the temperature of dispersed elements may vary due to chemical reactions. This characterization reveals that for modelling these systems it is necessary to use multi-dimensional population balance models. The aim of this work was to develop a multi-dimensional population balance model which is suitable to model the interactions between the dispersed elements and the chemical reactions inside the dispersed elements simultaneously.

Solution methods of one- and two-dimensional population balance models have been developed in a wide range (Ramkrishna, 2000). The Monte Carlo method is suitable for solution of two- or multi-dimensional population balance models. The advantage of this method is that the population undergoes “real” physical processes, it can be programmed easily and it is reliable. Several Monte Carlo methods have been developed in the past years (Zhao et al., 2007). Based on the method employed for determination of the sampling time step, Monte Carlo simulations can be grouped into time-driven and event-driven ones. With regard to the total number of simulated particles, Monte Carlo methods can be further classified into constant number and constant volume methods. Monte Carlo methods have been applied for calculation of discrete events in a wide range, but there were only a few works dealing with such problems where time continuous processes, such as chemical reactions, took place inside the dispersed elements. Furthermore, in these publications it was assumed that conversion of the reaction was instantaneous after a discrete event (Irizzary, 2008). However
there are a lot of reactions, such as polymerization, which cannot be considered instantaneous. In the context of that, the aim of this work was to develop a Monte Carlo method, which is suitable to handle processes both discrete and continuous in time simultaneously.

In industry, most of the reactors are operated in a continuous manner since those have many advantages. Micromixing can influence the quality of products made in continuous reactors significantly. Coalescence/redispersion models can be applied for modelling such systems in a wide range. This model represents fluid as a population of large numbers of fluid elements which interact with each other (Lakatos, 2008). There are component and heat exchanges between the colliding fluid elements. The calculation of non-isothermal chemical reactions with moment method is very complex. The aim of this work was to develop also a Monte Carlo method, which is suitable to calculate non-isothermal chemical reactions in continuous reactors.

References

Irizarry R., 2008, Chemical Engineering Science, 63, 95-110 and 111-121.
2. Theses

1. I developed a multi-dimensional population balance model for modelling suspension polymerization reactors. The model is suitable to describe random interactions between the monomer droplets by collisions and the polymerization reactions inside the monomer droplets, simultaneously.

a) Polymerization reactions take place in the monomer droplets. The volume, the concentration of components and the temperature of droplets vary continuously in time due to the reactions. The model contains descriptions of these time continuous changes due to the chemical reactions.

b) The monomer droplets inside the suspension polymerization reactors collide with each other, with the agitator and the wall of the equipment due to the intensive mixing. Coalescence or coalescence/redispersion of droplets takes place because of the collisions of monomer droplets, depending on the energy of collisions. In the case of coalescence the energy of collision is high enough to drain out the liquid film between the two colliding droplets, and it results in aggregation of the two droplets. In this event equalization of concentrations and the temperature is complete. In the event of coalescence/redispersion between two colliding monomer droplets partial component and heat exchange takes place. The degree of exchange depends on the surface of contact, on the time of moving together and on the coefficients of component and heat transfers. Monomer droplets can collide with the energy eddies inside the turbulent flow field, and due to this process a monomer droplet can break up. As a result of breakage of droplets, the properties of new droplets remain of the same value as of the origin was. The developed model contains the changes of concentrations of components, as well of the volume and temperature of droplets due to the discrete time events outlined above.
c) Temperature rise in droplets occurs due to the exothermic polymerization reactions. The temperature change of monomer droplets affects the temperature of continuous phase due to the heat exchange between the monomer droplets and the continuous phase. The model contains the energy balance of the reactor of the macro-scale.

Major related publications: 1, 2, 3, 6

2. I developed a Monte Carlo method which is suitable to compute the time continuous processes inside the dispersed elements and the stochastic collisions induced discrete event processes between the dispersed elements in disperse systems, simultaneously. I determined the minimal size of population of dispersed elements suitable for simulating the properties of droplets, formed in industrial reactors, with acceptable accuracy.

a) Events continuous in time: It is possible to compute the changes of the volume, the concentration of components and the temperature of all elements inside the population, continuously in time.

b) Random events discrete in time: The collision and breakage processes are modelled as inhomogeneous Poisson processes independent from each other. Coalescence, breakage and coalescence/redispersion events, independent from each other, were calculated: These events can change the concentrations of components, and the volume, and temperature of dispersed elements. The next discrete event is calculated by the collision and breakage frequencies and probabilities characteristic for the given disperse system. The simulation program is suitable to calculate all these changes.

Major related publications: 1, 2, 3, 6
3. I improved the Monte Carlo method for analysing the effects of non-isothermal micromixing in continuously operated adiabatic chemical reactors. The developed method is suitable to model and simulate chemical reactors working under realistic operation conditions in which non-isothermal micromixing of fluids plays important role.

a) The continuous phase inside the reactor is described as a population of large number of fluid elements which interact with each other. Chemical reactions take place in the fluid elements if the elements contain all of the necessary components. Chemical reactions are computed continuously in time so that calculation of concentrations of components and the temperature of fluid elements is continuous in time.

b) Coalescence/redispersion processes between the fluid elements are taken into consideration. Component and heat transport takes place between the fluid elements due to the coalescence/redispersion. This process affects the concentration of components and the temperature of fluid elements discretely in time. Both the component and heat transfer coefficients can be defined, but those can be taken also of random nature. The stochastic character of the process revealed using the second case.

Major related publications: 4, 5
3. Utilisation opportunities

The developed population balance model is suitable to describe the phenomena in disperse systems. It is suitable to describe the changes of volume, concentration and temperature of dispersed elements due to the chemical reactions inside dispersed elements and the interactions between the dispersed elements. The developed Monte Carlo method is suitable to calculate the changes due to the discrete and continuous in time events simultaneously. The changes due to the interactions between the dispersed elements can be calculated from the collision and breakage frequencies and probabilities. The developed model and solution method have been used to analyse the suspension polymerization of vinyl chloride. But the developed technics is suitable to model and analyse such systems in which there are more phases let it be fluid-fluid or solid-liquid systems. For example it is suitable for modelling separation equipments such as liquid-liquid extractors and solid-liquid leaching, bioreactors and fluid-solid non-catalytic reactors, as well as crystallization processes. In these systems, there are some interactions between the dispersed elements and inside the elements diverse chemical processes take place. The method provides an opportunity to take into consideration interactions between the disperse elements and the wall or the mixer with especial regard for the temperature transport.

The developed simulation technique can be applied to design the optimal heating-cooling profile of reactors. The further developed Monte Carlo method is suitable to analyse non-isothermal, continuously operated chemical reactors. The temperature changes due to the chemical reactions can be calculated easily with the method. The effects of micromixing on the quality and quantity of products can be analysed. The applicability of method has been demonstrated on a simple reaction kinetic example, but the method is suitable to analyse reactions with complex kinetic such as consecutive-competitive reaction systems. These systems are really sensitive to micromixing.
4. Major publications related to Theses


