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Modelling and simulation of continuous hydrothermal flow synthesis process for nano-materials manufacture

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ABSTRACT

Continuous hydrothermal flow synthesis (CHFS) technology has shown great advantages in nanomaterial formulation compared with other synthesis methods. CHFS uses a flow of supercritical water as a reagent that reacts with a flow of metal salts to produce nanoparticles in a reactor. The process uses no organic solvent, therefore is green, and has good controllability due to being in continuous operational mode. Experimental studies have shown that very high quality nanoceramics can be made in minutes rather than days. This paper describes simulation studies of the reaction and precipitation in a CHFS process using population balance modelling technique. Models for reaction kinetics, thermodynamics and nucleation are presented. Particle surface growth mechanism and particle aggregation effects have also been taken into consideration in the population balance models. System kinetics and the dynamic evolution of particle size distribution under supercritical conditions were simulated. The effects of temperature, aggregation and growth rate on particle size distribution were also investigated.

1. Introduction

Nanomaterials (particles <100 nm) are at the leading edge of nanotechnology. Their unique size-dependent properties make these materials superior and indispensable in many technological applications. Traditional nanomaterial synthesis methods such as sol–gel, micelle and inverse micelle, and co-precipitation synthesis, require expensive starting materials and are very time consuming. From the green chemistry point of view, the development of nanomaterial synthesis processes with low cost and low environmental impact is becoming increasingly important for many industries [1]. In an attempt to develop more environmentally friendly processes, supercritical fluids such as supercritical carbon dioxide [2–5] and supercritical water [6–17] have been used as greener alternatives to toxic organic solvents.

Hydrothermal synthesis of inorganic materials has been investigated since the end of the 19th century. It was designed for the precipitation of materials from aqueous solutions at temperatures above boiling point and pressures greater than atmospheric pressure [18]. Traditional hydrothermal synthesis is usually carried out in a batch type reactor. Aqueous phase solutions are fed into the reactor and heated up to a certain temperature slowly and aged for several hours or days. During the heating-up period, it is believed that homogeneous nucleation and grain growth processes occur in the reactor, which result in the production of fine microstructure crystals [19]. However, long operational times are a drawback for the traditional hydrothermal synthesis methods [18]. Continuous hydrothermal flow synthesis (CHFS) technology is considered as an advancement of traditional batch type hydrothermal method, which involves the mixing of one aqueous metal salt solution with a supercritical water (SCW) stream within a continuous reactor to produce nano-size metal oxide particles. Compared to the batch type hydrothermal synthesis, CHFS has shown advantages of fast reaction rate therefore short residence time, independent parameter control (pressure, temperature, etc.), avoidance of batch to batch variations and improved controllability and process particle characteristics. As a result, the CHFS process fulfils many of the ideals of the principles of green chemistry [20].

To date, CHFS technology has largely been carried out at laboratory scales (<1 kg/day) due to the extreme system operation conditions and high cost of a larger process. More recently, high throughput processes have been developed to make multiple unique products daily [21–23]. The CHFS processes of nano-products pose problems such as pipe blockage, pool mixing and overheating during laboratory or scale-up attempts. Mixing of salt solutions with SCW is a key feature of the CHFS process. Controlling particle size, flow rate and altering reactor configuration can help enhance mixing performance. Also, the particle sizes are vital as they are closely related with the product quality and function [20]. An important step in size control is the evaluation of particle size distribution (PSD). While most research work so far has focused on improving preparation methods and testing final

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product features, only a few researchers have attempted the mathematical simulation of CHFS processes. Among those, Thompson and Dyer [24] and Sheikh et al. [25] both developed population balance (PB) models for predicting the size distribution of zeolite particles produced in low temperature hydrothermal synthesis. Lummen and Kvamme [26] and Nahtigal et al. [27] used molecular dynamic modelling for simulating the nucleus size distribution after nucleation in a CHFS process. Some other modelling studies have been carried out on the CHFS process including computational fluid dynamic (CFD) modelling of mixing behaviour study and reactor design, and numerical modelling on particle size versus time [1,20,28,29]. Erriguible et al. [30] and Sierra-Pallares et al. [31] used a mono-disperse model to predict particle diameters in supercritical nanoparticle synthesis. These two studies are so far the only attempts for evaluating particle size characteristics in CHFS. However, the actual PSD cannot be obtained from this modelling strategy as the particles were assumed to be mono-dispersed, hence only particles mean sizes being obtained. It should be noted that selected authors also recently used in situ X-ray methods to evaluate the particle size via high energy X-ray radiation diffraction methods [32].

The purpose of the work herein is to develop PB models for the CHFS process, which can be used to investigate particle formation mechanisms and to study the effect of changes in reactor design and operational conditions with the aim of reactor design optimisation at laboratory scale as well as pilot plant. This manuscript is structured as follows. Firstly the modelling equations and essential parameters for nanoparticle evolution are presented and discussed. Then a case study of simulating the production of nano-size TiO_2 particle in a continuous mixed solution mixed product removal (MSMPR) reactor using CHFS method is described. The modelling results are then presented and some relevant conclusions are drawn.

2. Model equations and kinetic parameter estimation

2.1. Precipitation kinetics

In order to predict particle size distribution using population balance (PB) modelling, it is important to understand the system kinetics of the target process. In a CHFS process, it is believed that particles precipitate through a reaction crystallization process as it involves solution mixing, chemical reaction and crystallization processes such as supersaturation generation, nucleation and crystal growth [33].

Inside the reactor, aqueous phase metal oxides are formed after fast reaction between a metal salt solution and supercritical water. Due to the high system temperature, the solubility of metal oxide reduced to a great extent, which generates a high degree of supersaturation within the system. The enhanced solution supersaturation then becomes the driving force for a rapid nucleation and eventually leads to the formation of nanoparticle nuclei. The produced nuclei then go through growth and coalescence to form fine particles and aggregates. A schematic presentation of CHFS precipitation mechanism is shown in Fig. 1.

The PB based modelling framework for the simulation of the production of nano-materials is given in Fig. 2. Four models are involved in the simulation:

(a) A reaction model for the chemical reactions is required for determinations of the reaction rate constant of the CHFS process under various feed solution temperatures. The concentration of produced TiO_2 in the aqueous phase (before nucleation) is also determined by this model.
(b) Thermodynamic model is used to determine the system solubility profile and the level of supersaturation in the reactor. This is achieved by modelling the solution thermodynamic equilibrium constant at various conditions (temperature and pressure) and using the relationship between equilibrium constant and saturation concentration to calculate particle solubility at the given conditions.
(c) Nucleation model simulates the nucleation process. Initial nucleation rate is estimated as a function of system supersaturation properties together with critical nuclei size and other thermodynamic and physics properties.
(d) The final model is the PB model, which integrates the above three models with particle growth and aggregation mechanism to form system PB equations and predicts product PSD.

2.2. The reaction model

Traditionally, it is understood that like conventional hydrothermal synthesis, two reaction steps are involved in CHFS, namely hydrolysis and dehydration [18]:

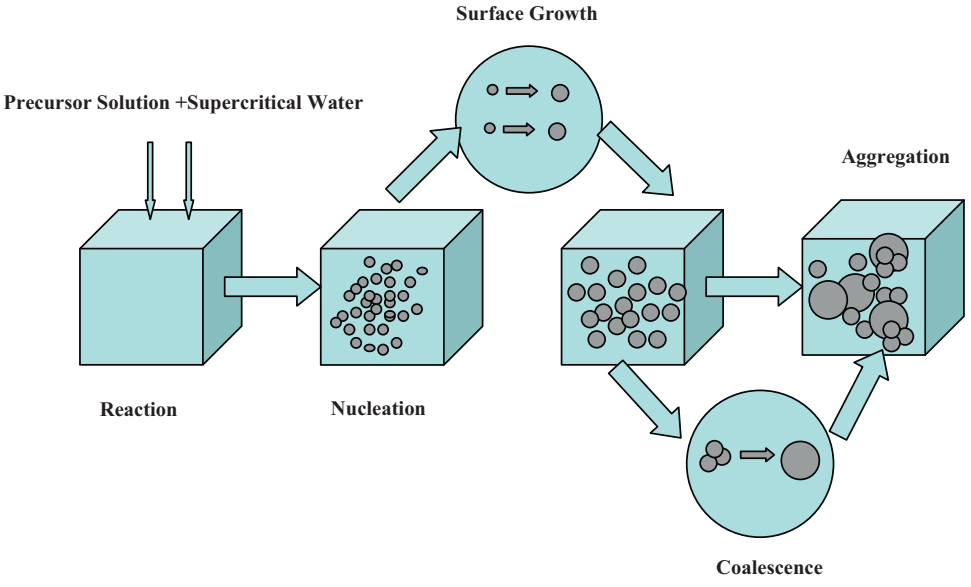

Fig. 1. Schematic presentation of precipitation mechanism.