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Quantification of mixing efficiency in turbulent supercritical water hydrothermal reactors

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ABSTRACT

This paper presents a mathematical model able to quantify mixing efficiency in Supercritical Water Hydrothermal Reactors (SWHR) for the production of different types of nanoparticles. In fact, mixing plays a crucial role in determining the final particle size distribution and therefore the final product quality. In this work, mixing of supercritical water streams is studied with Computational Fluid Dynamics (CFD) by using the Reynolds Averaged Navier Stokes (RANS) approach coupled with an equation of state and a micromixing model, to take into account the effect of molecular mixing. The performance of the model is investigated in three different scenarios, corresponding to very different values of the Richardson number and very different mixer configurations. The main results show how mixing can be quantified by means of a global mixing time and how turbulence enhances the process, leading to better final product characteristics, especially in terms of lower mean particle size and narrower particle size distributions. This confirms previous research on this topic, highlighting the fact that both the mean particle size and the particle size distribution are strongly dependent on the mixing features of the SWHR.

1. Introduction

The proper design of mixing devices in the supercritical synthesis of nanoparticles is a key parameter to obtain particles characterized by small size and narrow particle size distributions (PSDs). Several supercritical-based techniques have been proposed in the literature (Byrappa et al., 2008), where nanoparticles are a product of a reaction in which a supercritical fluid (SCF) is used as reaction medium. Supercritical water has been used for the production of several single and complex metal oxides such as, AlOOH, Fe_3O_4, NiO, $CoFe_2O_4$, ZrO_2, CeO_2 and TiO_2 by hydrothermal synthesis (Adschiri et al., 2001; Cote et al., 2002; Cabañas and Poliakoff, 2001). Metallic nanoparticles of Cu (Blackburn et al., 2001), Ag and Pd (McLeod et al., 2004) have also been obtained by the reduction of metal precursors in supercritical CO_2 by using a reducing agent and a convenient stabilizer.

A good design of the mixer for faster heating and homogenization of the mixture is a key task for obtaining nanoparticles having a narrow size distribution. It is possible to find different designs in the literature, such as mixers with movable needles (Mae et al., 2007), swirl type mixers (Wakashima et al., 2007), classical tee mixers (Adschiri et al., 2003) and nozzle-type mixers (Blood et al., 2004; Lester et al., 2006). But, although this process is experimentally well known, modelling has received little attention. Attempts to model such systems are few and far from supplying a complete insight. Adschiri et al. (2003) have tackled this problem via Computational Fluid Dynamics (CFD) calculations. In their work, the flow and the reaction of an organometallic precursor dissolved in supercritical water were analyzed. The methodology included the use of the standard method of moments for modelling the evolution of the PSD. Results showed that the PSD was very much affected by the flow pattern in the mixer, however the effects of heat transfer across the walls were not considered. A different approach to the problem was investigated by Blood et al. (2004). The mixing system was examined by employing methanol and sucrose solutions to mimic the behavior of the mixture in the SWHR, the attempt was to observe mixing patterns thank to the different densities of the fluids involved. They concluded that natural convection can cause significant turbulence in the reactor, and the resulting flow patterns are highly dependent on the geometry and orientation

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of the mixer. Based on these ideas, Lester et al. (2006) designed a mixer that takes advantage of the natural convection, resulting in particles with narrow size distributions.

A different approach was used by Wakashima et al. (2007) who tried to use the effect of forced convection to enhance mixing. In their work, the performance of a swirling micromixer was compared to a classical tee mixer. Due to its larger turbulence intensity, the swirling micromixer is capable of faster homogenization of the mixture. As a result, smaller particles with narrow size distributions were obtained.

Most of the studies described thus far have been limited to mixing at the macroscale. However, mixing at the microscale is also proven to be very important in many cases, as a matter of fact it is well known that micromixing can influence particle size (Baldyga et al., 2005). And these effects are also observed in supercritical fluids (Henczka et al., 2005).

The purpose of the research presented in this paper is to develop a mathematical model capable of predicting the mixing dynamics in hydrothermal synthesis reactors. In this way, the role of mixing in the process of formation of nanoparticles can be elucidated. A complete methodology, based on the use of both macro and micromixing models, capable of estimating mixing efficiency by means of global mixing time calculations, is here presented and thoroughly discussed.

The remainder of this article is organized as follows: Section 2 presents the complete development of the model, emphasizing the mixing modelling. Section 3 deals with the test cases employed to validate the model. In Section 4, the validation of the model and the main results are presented and discussed.

2. Development of the model

In this section, the main features of the model are described. First, thermodynamic modelling is commented, secondly the governing equations, concerning mass, momentum, and energy balances are discussed, including the turbulence closure employed. Eventually, a micromixing model, suitable to deal with supercritical fluids, is presented.

2.1. Thermodynamic model and transport properties

Close to the critical point, the properties of water are very variable with temperature and pressure. To account for this variability, an equation of state in reference quality has been employed (Wagner and Pruss, 2002). This means that the mathematical structure of the equation and special functional forms are suited for an improved description of the critical region, leading to represent even the most accurate data within their experimental uncertainty. These equations of state are explicit in the Helmholtz energy $\mathcal{A}$ depending on the local density and temperature:

$$\mathcal{A}=f(\rho,T), \tag{1}$$

and is often made dimensionless by using the gas constant R and the temperature, T:

$$\Phi=f(\rho,T)/(RT). \tag{2}$$

The dimensionless Helmholtz energy is divided into two parts, the ideal gas part ϕ^0 and the residual part ϕ^R, so that the following equation is obtained:

$$\Phi\left(\frac{\rho}{\rho_C},\frac{T}{T_C}\right)=\Phi^0\left(\frac{\rho}{\rho_C},\frac{T}{T_C}\right)+\Phi^R\left(\frac{\rho}{\rho_C},\frac{T}{T_C}\right), \tag{3}$$

where subscript C indicates the critical point. Pressure and entropy can be obtained by using the following expressions:

$$p=\rho^2\left(\frac{\partial\mathcal{A}}{\partial\rho}\right)_T, \tag{4}$$

$$s=-\left(\frac{\partial\mathcal{A}}{\partial T}\right)_\rho. \tag{5}$$

The other thermodynamic properties can be obtained with the aid of Maxwell's relations and the first law of thermodynamics. The transport properties are calculated with an extended corresponding states method (IAPWS, 1997, 1998). All the calculations have been integrated into the code with the REFPROP(C) (Lemmon et al., 2002) library of properties. The uncertainty obtained with this database is about 0.05% for the thermodynamic calculations and 2% for the transport properties calculations. In this work, it is considered that the overall flow properties are not affected by the presence of the particles or their precursors. Water self-diffusion coefficients have been calculated using the Mathur–Thodos equation, as it is recommended in the literature (Kutney, 2005).

2.2. Fluid dynamic model

The flow and mixing of fluids under supercritical conditions are governed by fundamental conservation equations for mass, momentum and energy (Meng and Yang, 2003). When dealing with turbulent flows with strong fluctuations of temperature, a suitable averaging method must be used. The density averaging technique or Favre average (Anderson et al., 1984) derives a time-averaged solution by decomposing actual flow properties into an average value and a fluctuating one. The conservation equations for mass, momentum, energy and scalars read as follows:

$$\frac{\partial\overline{\rho}}{\partial t}+\frac{\partial\rho\widetilde{u}_j}{\partial x_j}=0, \tag{6}$$

$$\frac{\partial\overline{\rho}\widetilde{u}_i}{\partial t}+\frac{\partial}{\partial x_j}(\overline{\rho}\widetilde{u}_j\widetilde{u}_i)=-\frac{\partial\widetilde{p}}{\partial x_i}+\frac{\partial}{\partial x_j}(\widetilde{\sigma}_{ij}-\overline{\rho}\widetilde{u_i''u_j''})+\overline{\rho}g_i, \tag{7}$$

$$\frac{\partial\overline{\rho}\widetilde{e}}{\partial t}+\frac{\partial}{\partial x_j}\left(\overline{\rho}\widetilde{u}_j\left[\widetilde{e}+\frac{\widetilde{p}}{\overline{\rho}}\right]\right)=\frac{\partial}{\partial x_j}\left[\lambda\frac{\partial\widetilde{T}}{\partial x_j}+\widetilde{u}_j\left(\widetilde{\sigma}_{ij}-\overline{\rho}\widetilde{u_i''u_j''}\right)-\overline{\rho}\widetilde{e''u_j''}\right], \tag{8}$$

$$\frac{\partial\overline{\rho}\widetilde{Y}}{\partial t}+\frac{\partial}{\partial x_j}(\overline{\rho}\widetilde{u}_j\widetilde{Y})=\frac{\partial}{\partial x_j}\left[\overline{\rho}\mathcal{D}\frac{\partial\widetilde{Y}}{\partial x_j}-\overline{\rho}\widetilde{Y''u_j''}\right], \tag{9}$$

where u_j is the velocity component in the x_j direction; ρ is the density; e is the internal energy; λ is the thermal conductivity; Y is a passive scalar; $\mathcal{D}$ is the scalar diffusion coefficient and g_i is the gravitational acceleration in the x_i direction. The viscous stress tensor, σ_{ij}, reads as follows:

$$\widetilde{\sigma}_{ij}=\eta\left[\left(\frac{\partial\widetilde{u}_i}{\partial x_j}+\frac{\partial\widetilde{u}_j}{\partial x_i}\right)-\frac{2}{3}\delta_{ij}\frac{\partial\widetilde{u}_k}{\partial x_k}\right], \tag{10}$$

where η is the molecular viscosity. In this work, the Reynolds stress tensor $-\overline{\rho}\widetilde{u_i''u_j''}$ is calculated with the V2F model of Durbin (1993), that has been employed successfully in predicting supercritical pressure heat transfer (He et al., 2008). The four-equation V2F model gives improved results for separated flows, in comparison with two equation models, at almost the same computational cost. In the above set of equations, the unclosed terms calculated by means of the V2F model read as follows:

$$-\widetilde{Y''u_j''}=\mathcal{D}^T\frac{\partial\widetilde{Y}}{\partial x_j}\quad\text{with } \mathcal{D}^T=\frac{\eta^T}{\overline{\rho}\mathrm{Sc}^T}, \tag{11}$$