

Modeling and simulation of counter-current reactors for continuous hydrothermal flow synthesis of nanoparticles

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Abstract: Numerical simulation using computational fluid dynamics is carried out to study the performance of a counter-current reactor in a continuous hydrothermal system for nanomaterial synthesis that is operated under supercritical water condition. Inlet flowrate and temperature are the key process variables and vary in the simulation. The predicted temperatures are in good agreement with measurements taken from a laboratory rig of identical design and under the same operating conditions. It is found that fast mixing in the reactor can be achieved by high inlet temperature, high inlet flowrate of the supercritical water and using unbalanced flow conditions, i. e. the supercritical water flowrate should not be equal to that of the precursor. The comparative simulation also reveals that the insertion length of the inner tube is a key factor dictating the reactor performance, and it needs to be less than 72.5 mm in order to achieve satisfactory mixing under the current reactor configuration.

Key words: counter-current reactor; hydrothermal synthesis of nanomaterials; computational fluid dynamics; supercritical water; mixing; reactor design

0 Introduction

Numerous metal oxide particles in the nano-size range have been manufactured in both batch and continuous modes (see Lits. [1-8]) using supercritical water hydrothermal synthesis which is relatively green due to the use of water rather than organic solvents. These materials have a wide range of applications in various areas such as colloid science, environmental remediation, catalysis and photo-catalysis,

electronics, medicinal applications, separations, thin films, inks, and disinfection^[9]. Compared with batch processes, continuous hydrothermal flow synthesis (CHFS) process has advantages because it is easier to control and can avoid batch to batch variation in product quality^[10-12]. In a CHFS process, reactions between supercritical water and metal salt can take place in impinging jet type of reactors in milliseconds. The detailed mechanisms of nano-particle formation were considered to involve the combination of complex

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nucleation, growth and aggregation processes with further research needed in order to gain full understanding. As a result, optimisation of the mixing, temperature and velocity profiles is critical to reactor design, hence production of desired nano-particles. Obviously, it is difficult and costly to achieve the goal of optimum reactor design through experimentally testing various design alternatives^[13]. Computational fluid dynamics (CFD) modeling^[14] offers a powerful tool to evaluate the performance of different reactor designs, such as stirred tank reactors^[15-16] and impinging jet crystallisers^[17] under ambient conditions, and has been used to study supercritical water oxidation processes including hydrothermal flame study^[18] and hazardous organic waste treatment^[2, 19]. The application of CFD modeling to supercritical water hydrothermal synthesis for the production of nano-particles is, however, still limited. Lester, *et al.*^[9] used CFD to simulate the velocity distributions inside a nozzle reactor, but methanol and sucrose were used as model materials of supercritical water and metal salt. A reactor with X-shaped geometry was simulated by Aimable, *et al.*^[8] to predict the temperature and velocity distributions in the reactor, but without validation against experimental measurements. Kawasaki, *et al.*^[20] studied a T-shaped mixer for continuous supercritical hydrothermal synthesis of TiO₂ nanoparticles. Simulations with different experimental conditions were performed using CFD in order to understand the mixing behaviour. However, validations of velocity, temperature distributions against experimental data were not presented. The mixing behaviours in turbulent supercritical water hydrothermal reactors including a T-shaped mixer and a counter-current reactor^[9] were numerically studied^[21] attempting to quantify the mixing efficiency in the reactors. However, only the simulated velocity and dye concentration contours in the counter-current reactor were compared with the experimental

observations from the literatures. Sierra-Pallares, *et al.*^[22] used CFD to simulate a submerged nitrogen jet and a supercritical carbon dioxide reactor, but only the density, temperature and residence time distributions from the nitrogen jet were compared with the measured data from the literatures. A reactor operating under supercritical water conditions for nanomaterial formation was also simulated by Demoisson, *et al.*^[23], but the experimental study only placed one thermocouple in the reaction zone, hence only the measured temperature at this point was compared with the simulated value. Antisolvent precipitation processes in ethanol solution using supercritical carbon dioxide as an antisolvent were simulated^[24-25] to predict crystal size distributions of paracetamol and nicotinic acid but without validations against velocity, temperature and concentration distributions.

In this paper, the synthesis processes in a counter-current reactor of a CHFS system^[13, 26] were simulated using the ANSYS Fluent package^[27]. The temperature profiles in the reactors obtained from simulations were compared with the available experimental data and the mixing between supercritical water and precursor streams in the reactor was examined in details. The simulation identified the insertion length of the supercritical pipe as one of the key factors that affects the reactor performance. The effect of insertion length of the supercritical water pipe into the reactor on the reactor performance was also investigated to produce an optimal reactor configuration in terms of the length. The governing equations for mass, momentum, species concentration and turbulence, together with the supercritical water properties are briefly described in Section 1. It is followed by Section 2 in which the processes in the counter-current reactor and the experimental procedure to obtain temperature profiles are presented. The computational details and solution methods are introduced in Section 3,

and simulated results are analysed and discussed in Section 4, which is followed by concluding remarks in the final section.

1 Mathematical formulation

1.1 Hydrodynamic and concentration models

The three-dimensional continuity, momentum and enthalpy equations based on time-averaged quantities obtained from Reynolds averaging of the instantaneous equations are numerically solved to obtain hydrodynamic and heat transfer profiles. There exist many turbulence models in which the most commonly-used one is the two-equation $k-\epsilon$ model^[28] where the turbulent kinetic energy k and its dissipation rate ϵ are the two quantities for which two additional transport equations are solved with standard empirical constants^[29].

Simulation of mixing was carried out by introducing in the calculation a secondary liquid as an inert tracer into the primary liquid in the counter-current reactor. The temporal and spatial distributions of the tracer concentration were obtained from the solution of the Reynolds-averaged species transport equation. This equation for a non-reacting mixture can be expressed as follows:

$$\frac{\partial \rho Y_i}{\partial t} + \frac{\partial \rho u_j Y_i}{\partial x_j} = \frac{\partial}{\partial x_i} \left(\Gamma_{i,\text{eff}} \frac{\partial Y_i}{\partial x_j} \right) \quad (1)$$

where the effective diffusion coefficient of specie i , $\Gamma_{i,\text{eff}} = \Gamma_i + \mu_t / \text{Sc}_t$, ρ is the mixture density, u_j is the mixture velocity, Y_i represents the species mass fraction, Γ_i the species diffusion coefficient, μ_t the turbulent eddy viscosity, and Sc_t the turbulent Schmidt number.

1.2 Thermodynamic properties

The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use can be used to calculate the thermo-physical properties of water^[30]. However, a large number of special functions were used in the formulation to fit a large amount of experimental data. Therefore, it would be computationally very costly to solve

the formulated equations for each iteration of CFD simulation. Although model-based methods can be used to calculate water properties, such as density, viscosity, thermal conductivity and diffusion coefficient in this study, the water properties obtained from National Institute of Standard and Technology^[31] using the IAPWS formulation 1995^[30] were piece-wise curve-fitted in polynomial forms over several temperature ranges at a fixed pressure of 24.1 MPa^[32], and used to calculate the thermodynamic properties efficiently and accurately. For diffusion coefficients in the mixing study, the water diffusivity was estimated using the correlation from Liu, *et al.*^[33].

2 Experimental studies

Fig. 1 shows the flow diagram of the CHFS system using a counter-current reactor^[13]. Deionised water was pumped through a heated, helical coil using pump P1 with a fixed pressure of 24.1 MPa and a constant flowrate in the range of 10 to 25 mL/min. An electrical heater was used to heat the deionised water to a required temperature of 350 °C to 450 °C. An aqueous precursor and an aqueous base were pumped using Pumps P2 and P3, respectively, at 24.1 MPa with a fixed flowrate in the range of 5 to 10 mL/min from each pump. The fluid streams from P2 and P3 were then mixed before entering the reactor where the mixture stream from P2 and P3 was mixed with the stream from P1, to react and generate nano-particles. The slurry containing nano-particles then went upwards in the annular section and left the reactor to enter a heat exchanger for rapid cooling before being collected as the product. In order to concentrate the study on fluid flow and heat transfer, the mixture stream from P2 and P3 (Fig. 1) was mimicked by deionised water during temperature profiling experiments and CFD modeling. Tab. 1 lists the operating conditions used in the experimental studies and CFD modeling. Note that in this study all volumetric flowrates quoted

as inlet conditions of supercritical water and precursor streams are based on the density of water at atmospheric pressure and at a temperature of 20 °C.

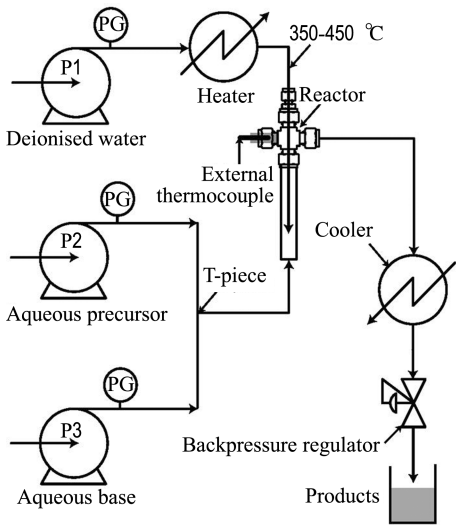


Fig. 1 Flow diagram of a counter-current CHFS system^[13]

Tab. 1 Operating conditions for experiments and simulations (inlet temperature of precursor stream fixed at 20 °C, and pressures of supercritical water and precursor streams fixed at 24.1 MPa)

Run number	Supercritical water temperature/°C	Supercritical water flowrate/(mL · min ⁻¹)	Precursor flowrate/(mL · min ⁻¹)
CCR-1	350	10	10
CCR-2	350	20	20
CCR-3	350	25	10
CCR-4	400	10	10
CCR-5	400	20	20
CCR-6	400	25	10
CCR-7	450	10	10
CCR-8	450	20	20
CCR-9	450	25	10

The detailed schematic diagram of the counter-current reactor shown in Fig. 1 is illustrated in Fig. 2(a). The reactor consists of an inner tube ($D_i = 1.75$ mm in diameter) inserting downward into a larger outer tube. The superheated water flows downwards in the inner tube to the mixing point to mix with the metal salt solution flowing upwards (Fig. 2(a)). The

generated product stream flows upwards in the annular section, then a 90° bend and a horizontal tube to leave the reactor. Some long, fine J-type thermocouples were inserted into the reactor at different locations along the z direction as shown in Fig. 2(a). The tips of the thermocouples were floated in the bulk flow due to the purpose of measuring bulk temperatures and also the difficulty to fix them onto a wall. The estimated tip position variations are within 2 mm across the tube cross-section (x - y plane).

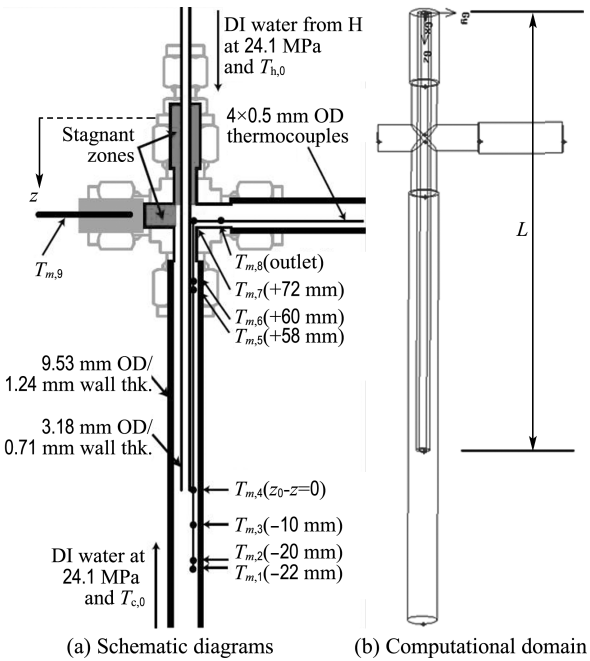


Fig. 2 A counter-current reactor schematic diagram and computational domain ($z_0 = L = 0, 103$ m)

3 Simulation details

3.1 Computational details

Fig. 2(b) shows the computational domain of the reactor which includes a stainless steel inner tube with an insertion length of L for introducing supercritical water to the mixing point, an outer tube with precursor stream flowing upwards, an annular channel formed between the outer tube and the inner tube for mixture/product stream to flow upwards, and an exit arm. GAMBIT software was used to discretise the three-dimensional domain and produced 6.26×10^5 mesh cells. The operating

conditions used for the computational studies were taken directly from the experiments, which are listed in Tab. 1. A tracer with the same operating temperature, pressure and properties as the supercritical water was introduced into the supercritical water stream for mixing studies. The flowrates of the tracer and supercritical water streams were 1% and 99%, respectively, of the total flowrate used.

3.2 Solution method

ANSYS Fluent software^[27] was used to solve the mass, momentum and energy conservation equations and species transport equation, together with the equations for turbulent quantities, k and ϵ , for the velocity, temperature and species distributions in the reactor. The obtained steady-state flow and temperature profiles were used as the initial values to solve the transient species equations. Standard SIMPLE pressure-velocity coupling was used with a second-order upwind scheme being employed for the discretisation of the convection terms in the governing equations. Standard k - ϵ model equations with standard wall functions were used. The insulation of the system has led to the assumption that the heat loss through the outer wall of the reactor is negligible, i.e. adiabatic boundary condition. Constant inlet temperatures for the inlet fluids were specified. The mass inlet flow mode was used to calculate the inlet velocities of both supercritical water and precursor streams. A turbulent intensity of 5% and the corresponding hydrodynamic diameters were used for the inlet conditions for turbulence. The outlet flow mode was used for their corresponding exit boundaries, which specify fully-developed outlet flow conditions. Standard non-slip wall boundary conditions were applied in the studies with the standard turbulent wall function being used. Different mesh sizes and convergence tolerances were tested to eliminate their effects on simulated results.

4 Results and discussion

In this section, the simulation results of fluid flow and heat transfer characterised by velocity and temperature profiles are presented with the mixing behaviour being investigated by analysing tracer concentration profiles. The effect of various operating conditions on the fluid flow, mixing and heat transfer is also discussed.

4.1 Fluid flow and temperature profiles

Fig. 3 shows the velocity vectors, contours of temperature and density distributions around the supercritical exit region in the reactor. The reactor (Fig. 2(a)) has an inlet supercritical water temperature of 450 °C with a flowrate of 20 mL/min, and an inlet precursor temperature of 20 °C with a flowrate of 20 mL/min as listed as CCR-8 in Tab. 1. The supercritical water

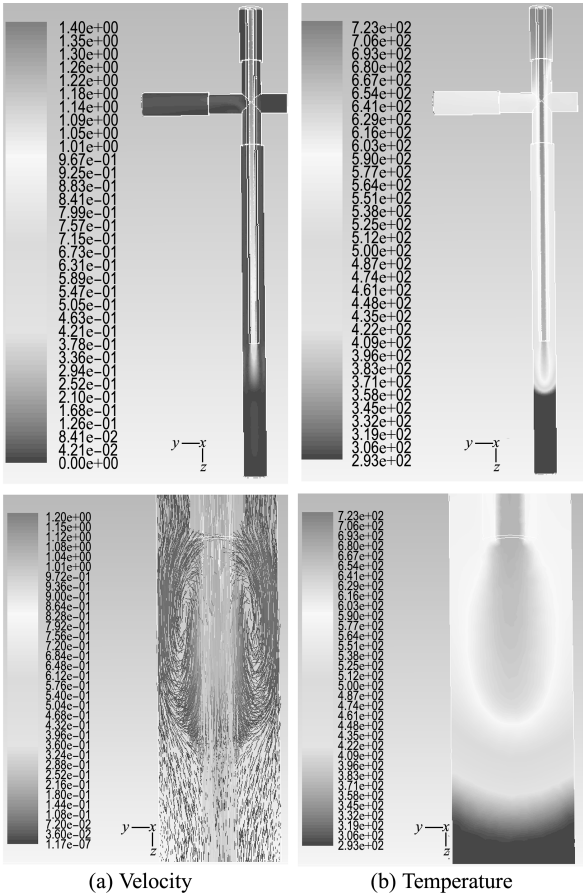


Fig. 3 Velocity and temperature distributions for case CCR-8 in the whole reactor (top) and the exit region of supercritical water jet

stream ejected from the inner tube and flew downwards to meet with the up-coming precursor stream and form a recirculation zone surrounding the jet (Fig. 3(a)), which led to the mixing between the supercritical water and precursor streams. The mixture then went upwards through the annular section to the reactor exit. The hydrodynamic penetration distance, defined as the distance along central line between the exit point of the supercritical water and the point where the central line velocity in the z direction becomes zero, is about 7.2 times of the inner tube diameter ($D_i = 1.75$ mm).

By examining the axial velocity, temperature and tracer concentration along the central line ($x = 0, y = 0$) of the reactor, it is clear that from the supercritical water inlet to the exit along the inner tube, the supercritical water stream was cooled down from the inlet temperature of 450 °C to 396 °C, which led to the axial velocity at the exit being only 60% of its inlet value. This can cause slow mixing between the supercritical water and the precursor streams, hence affecting nanoparticle product quality. The mixing distance, defined as the tracer core length along the reactor central line from the supercritical water exit to a central line point with a tracer concentration of 0.005 in mass fraction (fully mixing level at the reactor outlet), was estimated to be 2.8 times of the inner tube diameter (D_i) in this case (CCR-8 in Tab. 1).

As the locations of the thermocouple tips can vary within 2 mm on the x - y plane in the annular section, i. e. $y = 1.587$ –3.5 mm for the reactor, the predicted results at $y = 1.7$ and 2.9 mm are plotted in Fig. 4, together with the measured temperature profiles for comparisons. It can be seen that the predicted results are in good agreement with measurements. The reactor outlet temperature of 337 °C, determined in the previous study^[13] and shown as a thick solid line in Fig. 4, is close to the simulated

value of 335 °C in this investigation. In fact, by comparing the results from the previous study^[13] with the simulated ones in this study, the corresponding reactor outlet temperatures are in good agreement with each other.

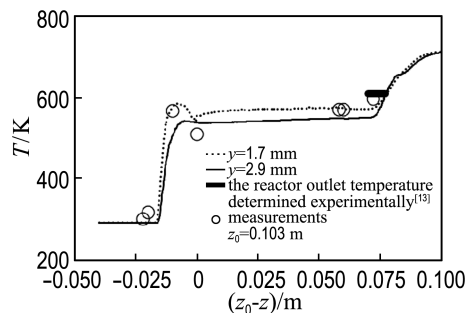


Fig. 4 Predicted and measured temperature distributions along the z direction in a counter-current reactor — CCR-8

4.2 Effect of the inlet temperatures of supercritical water

4.2.1 Balanced inlet flowrates Balanced flowrates condition is defined as an operation, in which the flowrate of supercritical water is equal to the flowrate of the precursor stream, as listed as CCR-1, CCR-2, CCR-4, CCR-5, CCR-7 and CCR-8 in Tab. 1. Fig. 5 shows the temperature variations along the z direction in the reactor between different inlet temperatures of supercritical water stream with balanced flowrates (CCR-2, CCR-5 and CCR-8). The simulated temperatures along the z direction at $y = 1.7$ mm showed the temperature bump feature near the exit region of the inner pipe, while the predicted temperatures at $y = 1.9$ mm reproduced experimental data for other regions. Taking into account of the possible variation of the thermocouples tips in x - y plane being about 2 mm, the simulated temperatures are in a fair agreement with measurements.

By examining the temperature variations along the central line under three inlet temperatures of supercritical water with balanced flowrates, it was found that the simulated temperatures at the exit of the supercritical water jet along central line were

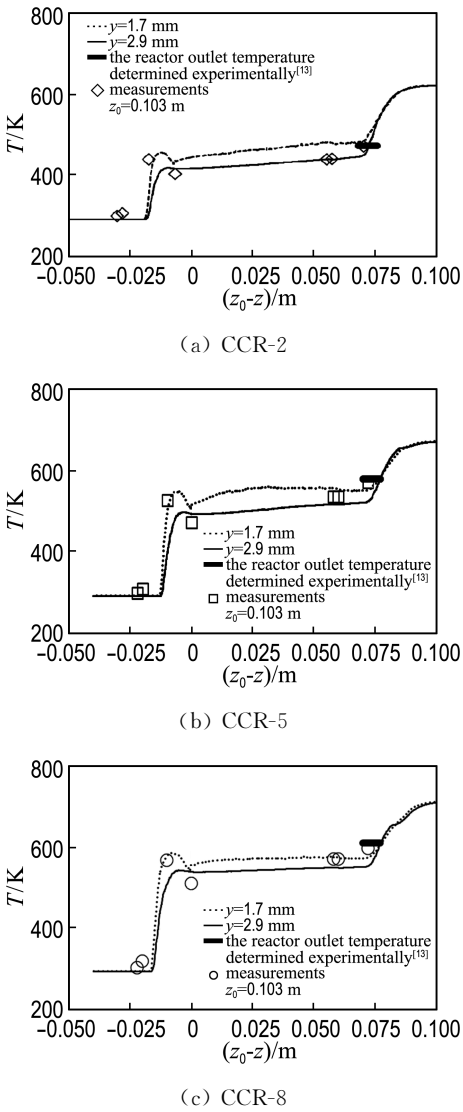


Fig. 5 Comparisons of temperature variations along the z direction between different inlet temperatures of supercritical water stream with balanced flowrate in a counter-current reactor

much lower than their corresponding inlet temperatures. With an inlet temperature of 350 °C (CCR-2), the exit temperature from the inner pipe is 256 °C, indicating a decrease of 94 °C. Similarly, the exit temperatures for the inlet temperatures of 400 °C (CCR-5) and 450 °C (CCR-8) were about 20 °C and 53 °C, respectively, lower than their inlet temperatures of the supercritical water stream. This is due to that the reactor has a long insertion length of the inner pipe, 73.5 mm from central line of the outlet flow to the exit of the inner pipe. The long inner tube inserted into the reactor

produced large heat transfer area between the supercritical water stream and the product mixture, hence more heat was transferred from the supercritical water in the inner pipe to the product mixture in the annular section, thus resulting in large temperature reduction of the supercritical water in the inner pipe. Accordingly, the axial velocities at the exit of the inner pipe were reduced to less than 76%, 41% and 60% of their inlet axial velocities for supercritical water inlet temperatures of 350, 400 and 450 °C, respectively. The lower temperature and lower axial velocity at the exit of the inner pipe led to slower decay of the tracer concentrations, hence weaker mixing.

4.2.2 Unbalanced inlet flowrates If the supercritical water flowrate is not equal to that of the precursor stream, it is called an unbalanced flowrates condition, such as CCR-3, CCR-6 and CCR-9 in Tab. 1. Fig. 6 shows the temperature variations along the z direction in the reactor between three different inlet temperatures of supercritical water stream with unbalanced flowrates (CCR-3, CCR-6 and CCR-9). For three different inlet temperatures of supercritical water under unbalanced inlet flowrate, the predicted temperature along the z direction well duplicated the measured data, which is due to that the flowrate of supercritical water is 2.5 times of the precursor stream, hence the effect of heat loss through the annular wall becoming less important and the recirculation zone maintaining strong. As the supercritical water jet has 2.5 times flowrate comparing to the precursor stream, the jet momentum dominates the performance near the exit region of the inner tube, hence the recirculation zone surrounding the exit.

4.3 Effect of inlet flowrates of supercritical water stream with balanced flowrates

Fig. 7 shows the comparisons of temperature variations along the z direction between different balanced flowrates with supercritical water inlet temperature of 450 °C.

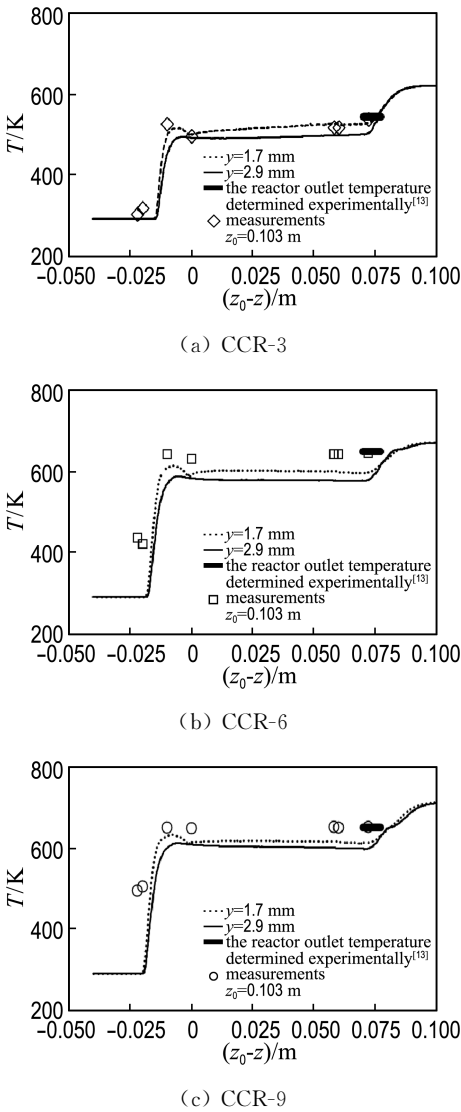


Fig. 6 Comparisons of temperature variations along the z direction between different inlet temperatures of supercritical water stream with unbalanced flowrate in a counter-current reactor

It can be seen that the predicted and measured temperatures at the exit region have a temperature dip which shows a very similar trend of temperature distributions to that shown in Fig. 5. The simulated temperatures along the z direction for the reactor reproduced the experimental data well. Temperature differences in the annular section (between $z = 0$ and 73.5 mm) are about 7 °C for CCR-7 and 2 °C for CCR-8.

The lower inlet flowrate of supercritical water in CCR-7 produced about 5 °C lower exit

temperature at the supercritical water exit, comparing to CCR-8. The corresponding axial velocity of supercritical water at the exit for CCR-7 is reduced to 97.7% of the inlet axial velocity, comparing to a value of 99.8% for CCR-8. Therefore, the recirculation zone generated with CCR-7 is smaller than that with CCR-8. Accordingly, the simulated tracer concentration along the central line for CCR-8 reduced faster than that for CCR-7, indicating that CCR-8 has faster mixing.

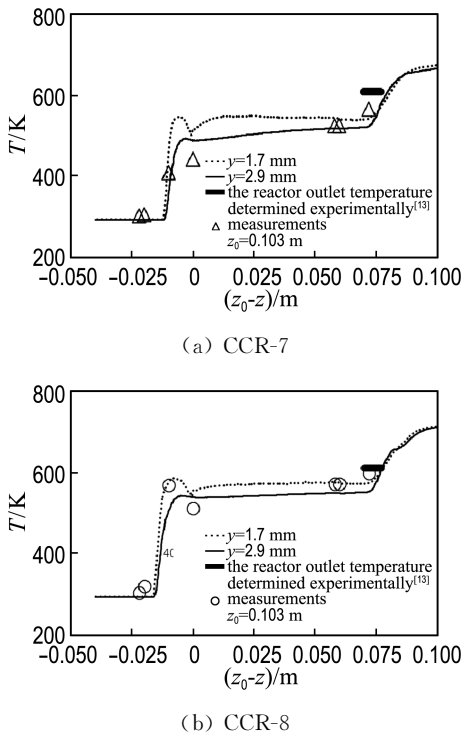


Fig. 7 Comparisons of temperature variations along the z direction between different balanced flowrates with supercritical water inlet temperature of 450 °C in a counter-current reactor

4.4 Comparisons between balanced and unbalanced flowrates

Fig. 8 shows the temperature variations along the z direction between balanced flowrates (CCR-7) and unbalanced flowrates (CCR-9) with an inlet temperature of supercritical water stream being 450 °C. It can be seen that the runs with unbalanced inlet flowrates generate good agreement between prediction and measurement. With 2.5 times of balanced supercritical water

flowrate, the unbalanced flowrates produce higher exit temperatures of about 6 °C at the exit point of the supercritical water stream. The axial exit velocity at the exit point with unbalanced flowrate for the reactor (CCR-9) is about 61% higher than that with the balanced flowrate (CCR-7) which roughly corresponds to the increase of the supercritical water flowrate from 10 mL/min (CCR-7) to 25 mL/min (CCR-9). The similar findings can be observed for other inlet temperatures of supercritical water (400 and 350 °C). However, due to the axial exit velocity at the exit point with unbalanced flowrate (CCR-9) being about 2.56 times of the balanced case (CCR-7), the formed recirculation in CCR-9 is much stronger than that for CCR-7, hence much faster mixing in case CCR-9.

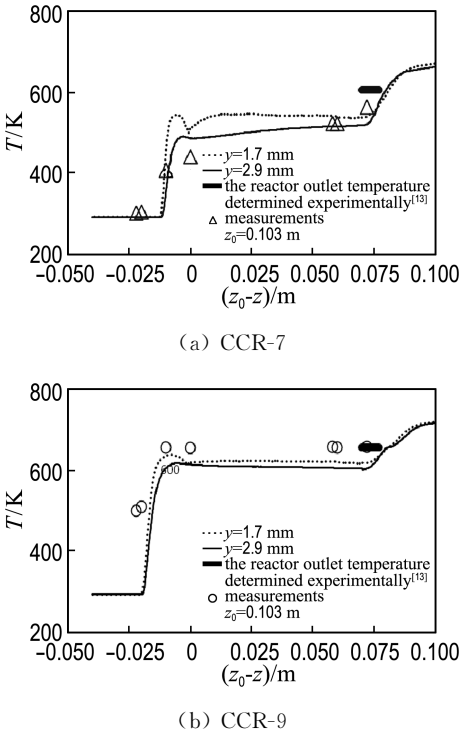


Fig. 8 Comparisons of temperature variations along the z direction between balanced and unbalanced flowrates with supercritical water inlet temperatures of 450 °C in a counter-current reactor

4.5 Mixing behaviours

Contour of tracer mass fraction at 15 s after starting the transient simulations for CCR-8 is

plotted in Fig. 9. The circle points are the monitoring locations along the central line of the reactor, where the tracer mass fractions were recorded during the transient simulations. The variations of tracer mass fraction at the four monitoring points, $A_1(z = 103.0$ mm), $A_2(z = 103.875$ mm), $A_3(z = 106.5$ mm), $A_4(z = 110.0$ mm), as shown in Fig. 9, over the time period of 15 s are plotted in Fig. 10(a). A normalised distance for a monitoring point, $\Delta L/D_i$, is defined as the distance between the monitoring point and the supercritical water jet exit along the central line of the reactor, ΔL , divided by the inner tube diameter (D_i). The monitored distributions of tracer mass fraction were normalised by the fully mixed mass fraction, c_∞ , at each point. The mixing time, defined as the time required for the local tracer mass fraction to reach 99% of c_∞ , for the four monitoring points of A_1 - A_4 ($\Delta L/D_i = 0, 0.5, 2$ and 4) were estimated from the predicted tracer mass fractions with values of 0.8, 2.5, 3.4 and 3.9 s, respectively. The fully mixed tracer mass fraction is 0.005 under the current operating conditions (CCR-8 in Tab. 1). Along the central line of the reactor, this tracer mass fraction was reached at the normalised distance ($\Delta L/D_i$) of 4, the monitoring point A_4 in Fig. 9. Fig. 10(b) shows the residence time distributions (RTD) in the counter-current reactor (CCR-8) at four monitoring locations (A_1 - A_4 in Fig. 9) and the reactor outlet. The corresponding mean RTDs obtained are 0.18, 0.20, 0.22, 0.24 and 5.00 s, respectively. The tailored parts of the RTDs, in particular, the RTD at the reactor outlet, were caused by the recirculation in the reactor, including the one near the exit of the supercritical water stream and also the recirculation regions near the 90° joint for the RTD at the reactor outlet.

The Reynolds number, Re , is defined as the relative magnitude between the momentum of a supercritical water jet and the viscous drag force at the jet exit ($z = 0$) and the Froude number,

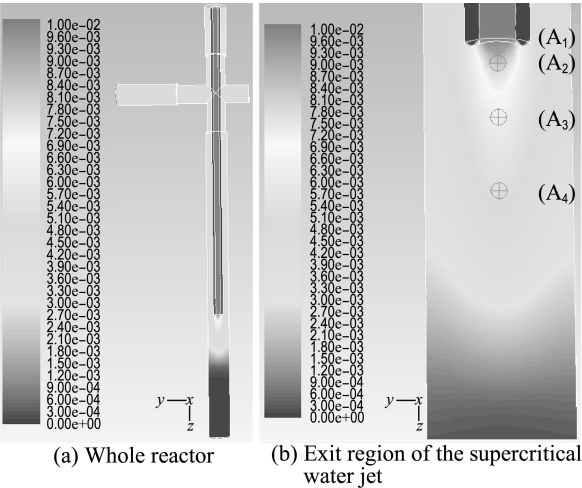


Fig. 9 Contours of tracer mass fraction after 15 s in a counter-current reactor — CCR-8

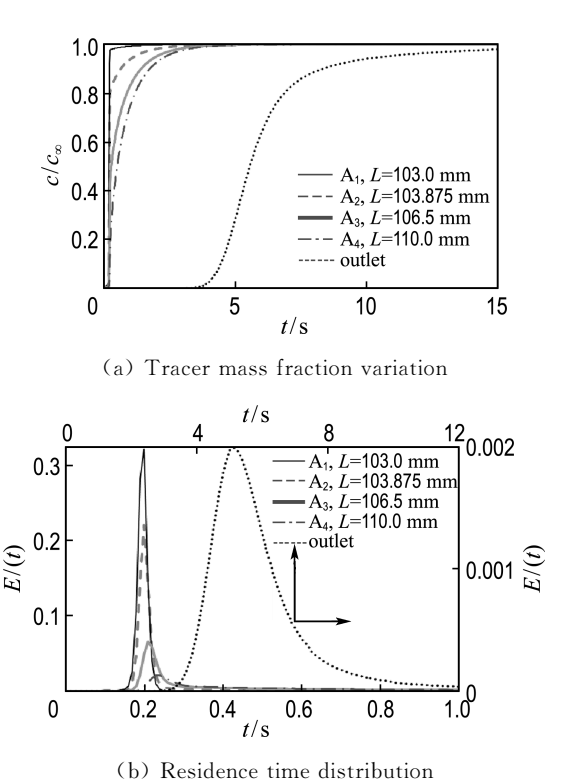


Fig. 10 Tracer mass fraction variations and residence time distributions vs. time in the counter-current reactor — CCR-8 at different locations

Fr^2 , at $z = 0$, can be estimated by the relative magnitude of the momentum of the jet against the buoyancy force^[13]. The experimentally estimated^[13] and numerically predicted Re and Fr^2 for the cases listed in Tab. 1 are plotted in Fig. 11 with very good agreement being observed. With higher inlet flowrates of the supercritical water stream, the Reynolds number

and Froude number were increased for all three inlet temperatures of the supercritical water, indicating that the flow behaviours at the exit of the inner tube ($z = 0$) were dominated more by the momentum of the supercritical water jet. This case may lead to stronger recirculation around the jet exit region and also better mixing between the supercritical water and the up-coming precursor stream. With higher inlet temperatures of the supercritical water, the reactor flow characteristics in the jet exit region became more turbulent and less buoyancy affected.

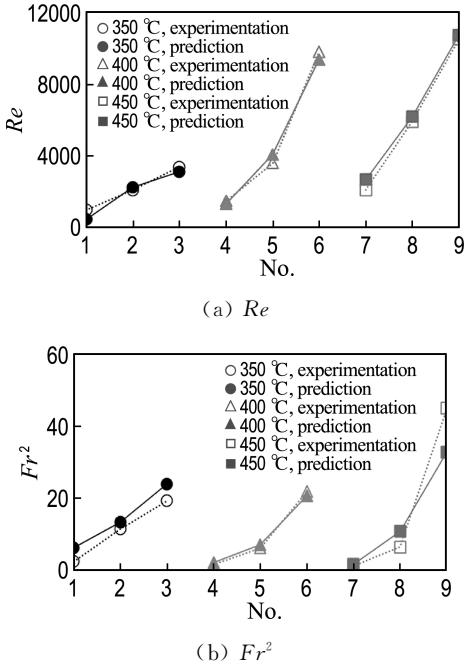
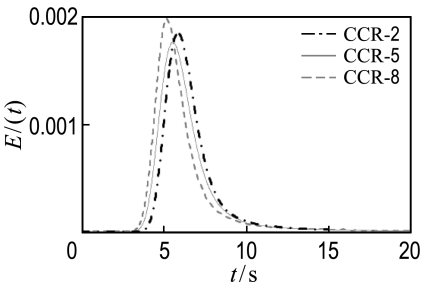
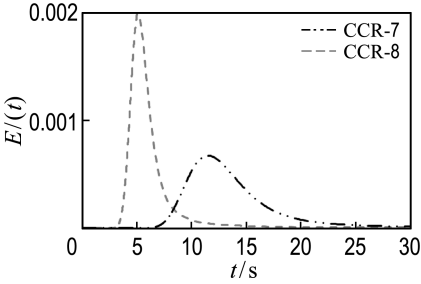


Fig. 11 Reynolds number and Froude number at the exit point of supercritical water jet under different operating conditions as listed in Tab. 1

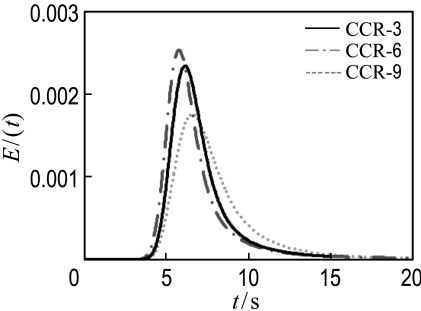
The comparisons of RTDs at the reactor outlet under different operating conditions are plotted in Fig. 12. With a balanced inlet flowrates at different inlet temperatures (CCR-2, CCR-5, CCR-8), higher inlet temperature of the supercritical water led to shorter mean residence time (Fig. 12(a)). It may be caused by a higher temperature, hence higher velocity, of the supercritical water stream at the exit point, which is supported by the



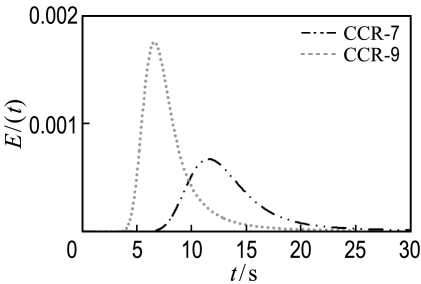
(a) Balanced inlet flowrates at different inlet temperatures



(b) Different balanced flowrates at an inlet temperature of 450 °C



(c) Unbalanced flowrates at different inlet temperatures



(d) Balanced and unbalanced flowrates at an inlet temperature of 450 °C

Fig. 12 Residence time distributions at the reactor outlet

longer mean residence time (Fig. 12(b)) than the higher balanced flowrate case (CCR-8), hence slower mixing in the reactor under the operating conditions of lower balanced flowrates. Similarly, the unbalanced flowrate case (CCR-9) has a much shorter residence time and narrower RTD (Fig. 12 (d)) than CCR-7. With unbalanced flowrates (Fig. 12(c)), an inlet temperature of 450 °C for the supercritical water stream (CCR-9) produced slightly weaker mixing when comparing with other two cases (CCR-3 and CCR-6).

4.6 Optimisation of reactor configuration

With the current reactor configuration, in addition to the flowrates and inlet temperatures, the insertion length of the supercritical water stream, defined as the distance between the inlet and exit of supercritical water stream, is a major factor affecting the reactor performance under the same operating conditions as discussed in Section 4.2.1. In order to investigate the effect of insertion length of the supercritical water stream, it was reduced from the original length of 103.0 mm to 85.5, 72.5, 52.5, 45.5 mm. Simulations were carried out under the five reactor configurations using the operating conditions of case CCR-5. The locations of the monitoring point A_4 for the five reactor configurations are 110.0, 92.5, 79.5, 59.5, 52.5 mm, respectively, along central line in the z direction. With a shorter insertion length, L , the hump near the exit of supercritical water stream (Fig. 13) is smaller and the exit temperature of supercritical water becomes higher. By monitoring the tracer mass fractions at point A_4 (as shown in Fig. 9) and the reactor outlet, the mixing time at point A_4 and the mean residence time at the outlet for the five insertion lengths ($L = 103.0, 85.5, 72.5, 52.5, 45.5$ mm) are illustrated in Fig. 14 (a). It is demonstrated that mixing was more intensive with an insertion length $L \leq 72.5$ mm. The reason can be attributed to that the supercritical water stream loses more heat to the product

predicted temperatures and velocities. At an inlet temperature of 450 °C for the supercritical water stream, the lower balanced flowrate case (CCR-7) produced much wider RTD and also

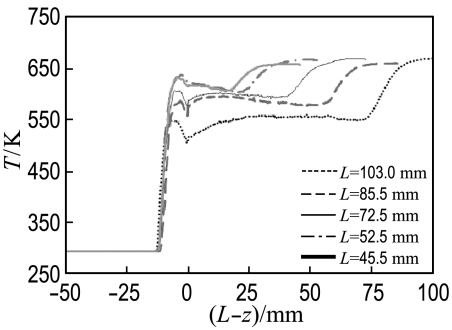


Fig. 13 Predicted temperatures along the z direction ($y = 1.7$ mm) under five insertion lengths of the supercritical water pipe with the same operating conditions

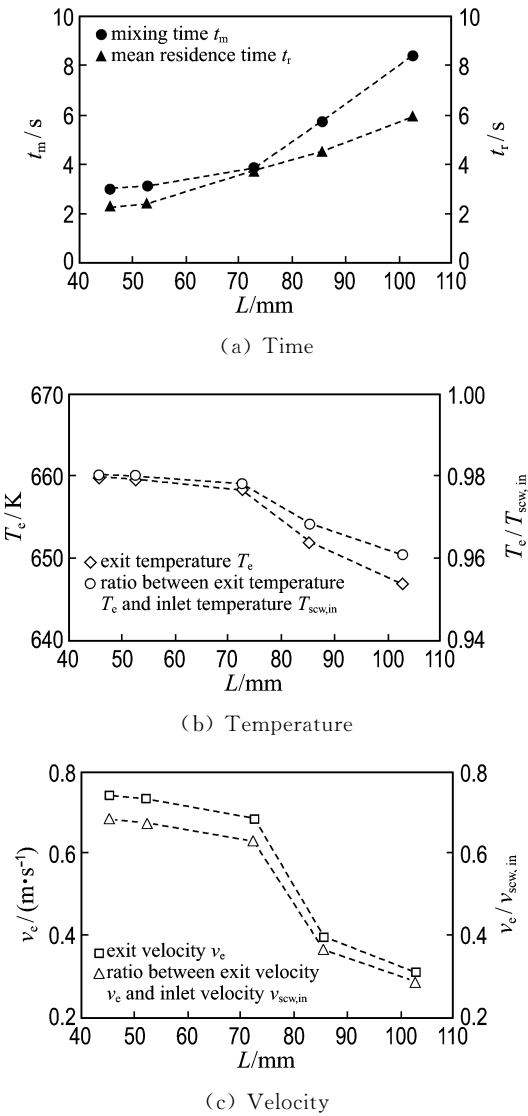


Fig. 14 Mixing and mean residence time at the reactor outlet and temperatures and velocities at the exit point (A_1) of supercritical water under fine insertion length

stream in the annular channel with longer insertion lengths. Therefore, the temperatures of supercritical water at the exit point (A_1) for cases of $L \leq 72.5$ mm are much higher than those for $L > 72.5$ mm (see Fig. 14 (b)). Accordingly, much lower exit temperatures for cases of $L > 72.5$ mm led to much lower exit velocities (see Fig. 14 (c)), hence resulting in weaker mixing. This study shows that the insertion length for this reactor configuration should not be longer than 72.5 mm in order to achieve good mixing.

5 Concluding remarks

The fluid flow and heat transfer patterns, as well as the mixing behaviour in the counter-current reactor used for continuous hydrothermal synthesis of nanomaterials are investigated. The distributions of velocity, temperature and tracer concentration were compared under varied conditions of inlet flowrate as well as inlet temperature of supercritical water, and inlet flowrate of precursor streams. Higher inlet temperatures and higher inlet flowrates of the supercritical water stream, and also unbalanced flowrate conditions are found to produce faster mixing. The predicted temperatures along the z direction under different operating conditions were in good agreement with experimental data. The study identified the major factors that affect the reactor performance, hence providing useful information for improvement of the reactor design. For the current reactor configuration, the much lower exit temperatures, hence lower exit axial velocities, at the exit of the supercritical water tube due to the heat loss through the tube wall into the annular section were identified as one of the major factors affecting the reactor performance. Optimising the insertion length of the supercritical water pipe based on the existing reactor configuration indicated that the insertion length should be shorter than 72.5 mm.

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逆流反应器中纳米材料连续热液流动合成过程建模与仿真

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摘要: 利用计算流体动力学的数值模拟来研究超临界水操作条件下, 用于纳米材料合成的连续热液系统中的逆流反应器的性能. 入口流量和温度是关键过程变量并在仿真过程中发生变化. 预测的温度与取自相同的设计和在相同操作条件下的实验室测量数据相吻合. 研究发现反应器中物料的快速混合可以通过超临界水的高流量与高入口温度, 和使用非平衡的入口流量条件即超临界水的流量不等于反应物流量来实现. 对比仿真还显示内管插入长度是一个反应器性能的关键控制因素, 当前反应器配置下其必须小于 72.5 mm, 以达到令人满意的混合效果.

关键词: 逆流反应器; 纳米材料热液合成; 计算流体动力学; 超临界水; 混合; 反应器设计

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