Chemical Engineering Journal 299 (2016) 373–385

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Prediction of residence time distributions in supercritical hydrothermal reactors working at low Reynolds numbers

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HIGHLIGHTS

- Prediction of trans-critical fluid flow reactors working at low Reynolds numbers.
- Residence time distributions obtained in a novel experimental rig.
- Complete validation of CFD code using residence time distributions.
- Relevant flow structures for nanoparticle production methods are discussed.

ARTICLE INFO

Article history:
Received 27 November 2015
Received in revised form 19 February 2016
Accepted 13 April 2016
Available online 22 April 2016

Keywords:
CFD
Hydrothermal synthesis
RTD
Turbulence models

ABSTRACT

Supercritical water has been demonstrated as a suitable reaction media for the generation of nanomaterials. Many single and complex metal oxides can be obtained using hydrothermal synthesis techniques. This work presents a methodology to characterise continuous hydrothermal flow systems both experimentally and numerically, working at low Reynolds numbers. Under these conditions traditional computational approaches in the field are of limited use, so new tools are in demand. Residence time distributions (RTD) experiments are carried out using a purpose built continuous flow rig featuring an injection loop on the metal salt feed line, allowing injection of a chromophoric tracer. Computational fluid dynamics (CFD) calculations are also conducted using modelled geometry to represent the experimental apparatus, using a specialised approach for modelling turbulence. The performance of the CFD model is tested against the experimental data provided, verifying that the CFD model is able to predict the main flow features with good accuracy. The results indicate that the RTD profile is affected strongly by the mixing step and turbulent diffusion in the annulus section of the reactor. Different mixing regions are identified based on a mixing scale analysis. The internal RTD and its relation to the synthesis of nanomaterials is also investigated.

1. Introduction

Designing efficient mixing devices for the supercritical synthesis of nanoparticles is a key factor in obtaining particles of small size and with a narrow particle size distribution (PSD) [1]. Normally, mixing in these types of devices occurs in a turbulent manner. Turbulent mixing is the ability of turbulent flows to effectively mix entrained fluids on a molecular scale. It is a vital aspect of the dynamics of such flows, with wide-ranging consequences in nature and engineering [2].

Several techniques for generating inorganic nanoparticles using a supercritical fluid (SCF) as the reaction medium have been proposed in literature [3]. 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, through hydrothermal synthesis [4,5]. Supercritical fluids (SCFs) have also been used to deposit thin metal films onto a wide range of surfaces and incorporate metallic nanoparticles into a wide variety of inorganic and organic substrates by the reduction of metal precursors in supercritical CO_2, by employing a reducing agent and suitable stabilizer [6].

While the experimental aspects of such technologies are well known, modelling has received relatively little attention. Few

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http://dx.doi.org/10.1016/j.cej.2016.04.073
1385-8947/

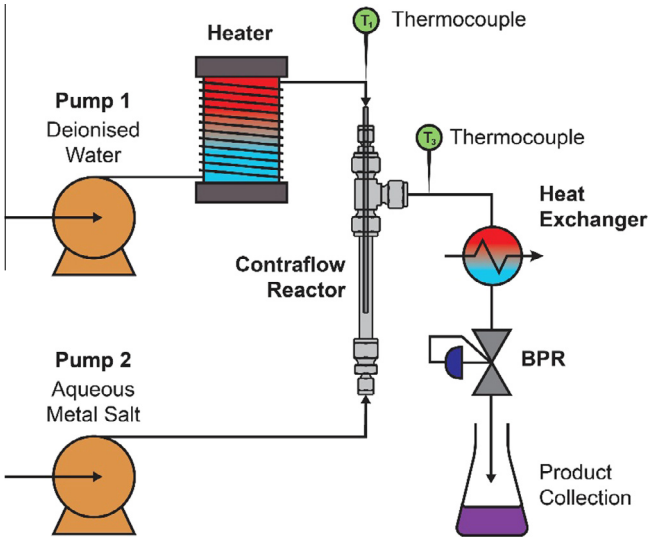

Fig. 1. Schematic of a typical apparatus configuration used for the continuous synthesis of nanomaterials. Process monitoring and safety features such as pressure transducers and pressure relief valves are omitted.

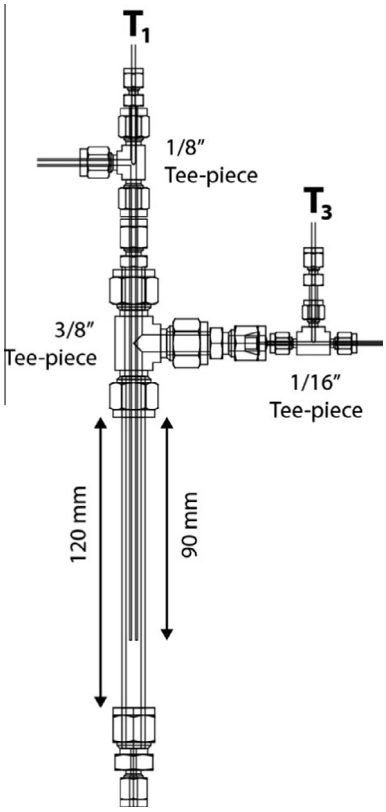

Fig. 3. Diagram of the contraflow reactor used for residence time distribution studies, indicating lengths of the inner and outer tube. Apparatus following the reactor outlet was selected so as to minimise internal volumes; during nanoparticle synthesis this would not be possible due to the potential for blockages.

attempts have been made to model such complex systems and those which have are far from providing detailed insight. Blood et al. [7] examined the process through physical simulation. They used methanol and sucrose solutions to emulate the flow behaviour in hydrothermal reactors in an attempt to observe mixing patterns resulting from the different densities of the fluids involved. They concluded that natural convection can cause significant turbulence and that resulting flow patterns are highly dependent on the geometry and orientation of the mixer. Following these insights, Lester et al. [8,9] designed a mixer which exploits natural convection in order to obtain narrower size distributions. Kawasaki et al. [10] demonstrate an important application of a computational model to tee-shaped and swirling mixers. In their studies they indicate a relationship between average particle size and heating, concluding that the trend of particle size was strongly correlated to the heating rate of the initial solution and final reaction temperature, which was estimated from computational fluid dynamics (CFD) simulations. Ma et al. [11] developed a computational model to predict fluid flow and heat transfer processes in a

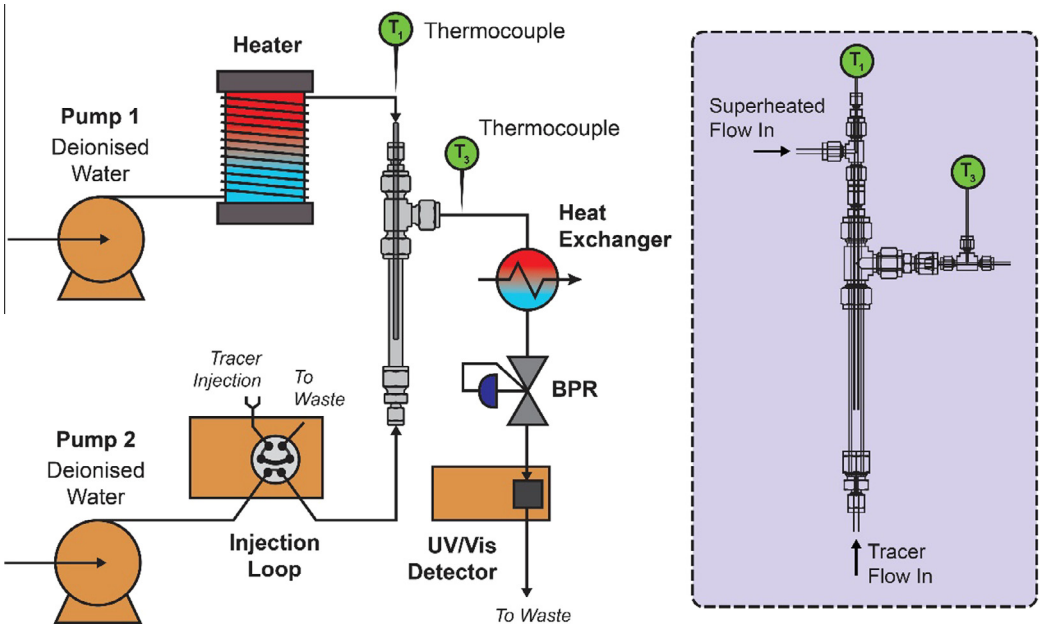

Fig. 2. Schematic illustrating the modified apparatus configuration used to map reactor residence time distributions, using injections of chromophoric tracers and UV/Vis detection.