Reaction Engineering: The supercritical water hydrothermal synthesis of nano-particles

Edward Lester[a*], Paul Blood[a,b], Joanne Denyer[a], Donald Giddings[c], Barry Azzopardi[a] and Martyn Poliakoff[a]

[a]School of Chemical, Environmental and Mining Engineering (SChEME), The University of Nottingham, University Park, Nottingham, NG7 2RD, UK.

[b]Clean Technology Research Group, School of Chemistry, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK.

[c]School of Mechanical, Materials, Manufacturing Engineering and Management University of Nottingham, University Park, Nottingham

Email[*]: edward.lester@nottingham.ac.uk

Tel[*]: +44-115-951-4974

Fax[*]: +44-115-951-4115

[*]Corresponding Author

Abstract

Supercritical Water Hydrothermal Synthesis (scWHS) is a relatively simple and environmentally friendly process for the production of potentially valuable metal oxide nanoparticles. However, it has never found industrial application to date due to poor process reliability, reproducibility and control. This paper presents the conclusions of collaborative work between chemical engineers and chemists that attempts to optimise the reaction engineering of this process, with the goal of reducing or even eliminating these fundamental process flaws. Initial investigations highlighted that the mixing environment within the scWHS reactor is highly unusual in terms of conventional reaction engineering because the Reynolds numbers are very low, furthermore, they illustrated that the current reactor designs were inefficient. This led to the development of an optimised reactor, termed the *Nozzle Reactor*, which was designed on the basis of Light Adsorption Imaging (L.A.I.) and Computational Fluid Dynamics (C.F.D.) modeling, both of which show excellent mixing mechanics. Initial scWHS experimental results using the Nozzle Reactor are presented. These show a dramatic improvement in process reproducibility and reliability that, given further investigation, will lead to process optimisation. Preliminary evidence suggests that the reactor could eventually lead to the ability to control particle properties, such as size, composition and shape, through the manipulation of process variables.

Keywords: Supercritical Water, Reaction Engineering, Mixing, Nano-particulates, Visualisation, Imaging.

Introduction

In recent years, both scope of application and demand for nano-scale metal and metal oxides have greatly expanded. Nano-sized materials exhibit many desirable properties and the efficient production of these materials is likely to play a key role in the future of the specialty chemical industry. The range for applications of metal (e.g. Ag) or metal oxide (e.g. CeO_2) nanoparticles is greatly expanding; current and potential applications include colloid science, environmental remediation, catalysis and photo-catalysis, electronics, medicinal applications, separations, thin films, inks, and disinfection. However, many of the industrial synthetic routes in use today are generally not easily scalable, involving relatively noxious chemicals and expensive precursors, and a complex and time-consuming sequence of steps. Supercritical Water Hydrothermal Synthesis (scWHS) offers a relatively simple route which is inherently scalable and chemically much more benign than current technology. As a result, this continuous process has been investigated extensively by several research groups[1-11], but has yet to be applied industrially due to problems of reliability, reproducibility and process control.

The scWHS process is relatively straightforward; it involves the mixing of an aqueous metal salt stream with a supercritical water stream within a continuous reactor to produce nano-size metal oxide particles. When water is heated towards its critical point (P_c = 374 °C, T_c = 218 atm), it changes from a polar liquid to a fluid with a low dielectric constant and low pH. K_w also increases, giving rise to correspondingly increased concentrations of H^+ and OH^-. These enhanced levels of OH^- were first exploited for nano-particle synthesis by Adschiri and Arai[5], who showed that, under these conditions, hydrolysis of the metal salts was immediately followed by a dehydration step.

$$\text{Hydrolysis: } ML_x + x\,OH^- \rightarrow M(OH)_x + xL^-$$

$$\text{Dehydration: } M(OH)_x \rightarrow MOx/_2 + x/_2\,H_2O$$

For the past six years[12-17], the Clean Technology Research Group at the University of Nottingham has been carrying out research into the development and eventual optimisation of the scWHS process with the goal of making the process industrially viable. Recently, our group expanded this approach to the synthesis of single-phase mixed metal oxides[12-14]. There have also been investigations, with limited success, into the effects of pH, metal salt concentration, temperature, pressure etc., on the morphology and size distribution of fine metal oxide particles.

The flowsheet for the Nottingham scWHS process[12-15, 18] is given in **Figure 1**. Until recently, the reactor used was a vertically up-right Swagelok® T-piece (0.71 cm internal diameter). Supercritical water entered the reactor via the side arm, whilst the aqueous metal salt was introduced through the top arm. Almost every scWHS investigation conducted in this apparatus was hindered by the unreliability of the process and poor product reproducibility. The root of the problem was particle accumulation and agglomeration within the reactor and its two inlets, which caused a narrowing and eventual blockage of the process pipes. As a result, the apparatus usually required extensive cleaning between runs, and in many cases, the experiments had to be shutdown prematurely because of blockages within the metal salt inlet. Experiments under various process conditions suggested that the key to eliminating these problems lay in the engineering of the reactor. The resulting investigation into reaction engineering and reactor modeling involved the collaboration of chemical engineers and chemists at the University of Nottingham.

Two techniques were used to model the scWHS reactor. The first technique (LAI modeling) involved performing 'simulations' of the scWHS mixing environment at ambient conditions in a pseudo-reactor, using an approach described recently[15] The results of LAI modeling were then complemented by Computational Fluid Dynamics (CFD) simulations of the reactor under similar conditions. The LAI experiments[15], which examined the efficiency of a T-piece reactor at different flowrates and reactor/inlet orientations, produced some very interesting conclusions. The flow regime within the scWHS reactor was found to be highly unusual in the terms of conventional reactor engineering. Firstly, the Reynolds number (Re) for each of the reactant streams was found to be extremely low (Re_{FW} = 148, Re_{FS} = 20), suggesting that both feed streams were highly laminar in nature.

However, throughout all these initial modeling experiments, highly turbulent macro-mixing could be clearly observed as the two streams converged in the reactor. This was unexpected when considering the highly laminar nature of the reactor feeds; further investigation highlighted that the driving force behind this turbulent macro-mixing phenomenon was not the inertial forces produced by the process pumps, but the strong buoyancy forces present in the reactor. The two feed streams have significantly different fluid densities (ρ_{scW} = 371 kg m^{-3}, $\rho_{M(aq)} \approx$ 998 kg m^{-3}) such that, when these fluids interact, relatively large natural convection or buoyancy forces are induced. The extent to which these buoyancy forces dominate in these reactor systems was calculated using dimensional analysis[15] i.e. Grashof Number (Gr) and Reynolds Number. The results of analysis showed that the natural convection forces within the scWHS system were relatively large enough to induce turbulent flow/mixing (Gr = $9.5x10^9$) which dominate over the much smaller inertial forces produced by the pumps ($Gr/Re^2 > 1$). Thus, the main conclusion was that a T-piece scWHS reactor is very inefficient at handling such an atypical mixing system. This paper presents a new reactor design that has been specifically developed to: a) handle this unusual mixing environment efficiently b) exhibits flow properties that have an increased ability to handle the particulate product c) be capable of producing a greatly improved heat transfer profile.

Experimental

This optimal scWHS reactor was assessed using modelling techniques (LAI and CFD) identical to those presented in a previous publication [15]. Direct observation of fluids under supercritical water conditions is highly impractical due to the engineering restrictions at the high pressures and with the small pipe diameters used in this process. Therefore, to assess the nature of the mixing mechanism within each reactor design, work was carried out to physically recreate the mixing scenario in a scaled-up ambient model. This was achieved using two carefully-selected fluids that exhibit a similar ratio of inertial to viscous forces at ambient conditions to that present in the actual scWHS reactor under operating conditions. Data and fluid properties from the actual scWHS rig were also used to calculate the inlet Reynolds Numbers for the scH_2O and aqueous metal salt streams entering the scWHS reactor. The corresponding flowrates in the pseudo-reactor were then adjusted so that the Reynolds numbers of the feed streams were similar to those exhibited in the scWHS system. The mixing dynamics observed were enhanced and quantified using a two-dimensional image analysis technique known as Light Adsorption Imaging (LAI)[15]. This technique is based on the adsorption of light by a dyed fluid, the output being an accurate and quantitative ‘concentration map’.

The resultant steady state ‘concentration map’ created using this technique, besides giving quantitative data, has several advantages over the original digital image. The map has essentially been filtered, eliminating the effects of changing chord length across the pipe diameter as well as any errors induced from non-homogeneous light distribution across the image. Of course, the steady state images that are presented in this paper do not illustrate fully the processes that occur in these pseudo-reactors. Much more information was provided by creating real-time animations of the concentration maps produced at 30 frames per second. This was done by bulk processing each digital video frame by frame and subsequently binding them into an animation. The animations associated with this research can be viewed at www.nottingham.ac.uk/supercritical.

Quantifying how 'ideal' each reactor configuration is, although complex, highly desirable. Therefore, an analysis system was devised, that reduces each modeling experiment down to a single 'idealisation' or efficiency rating. This allows each reactor variant to be compared directly to every other variable. This technique, known as 'Idealisation Analysis' in previous publications[15] takes advantage of the more quantifiable data produced by the LAI technique to compare the mixing scenario under examination with a theoretically 'ideal' scenario – the result is a single number from 0 to 1 (0 being ideal, 1 being non-ideal). Throughout this research, the rating system has proved very useful in identifying improved reactor geometries.

Design Criteria

The LAI and CFD modeling illustrated the effect and, therefore the importance, of the density difference between the two reactant fluids[15]. This suggested that the key to optimising the reactor was to exploit the density difference between the two fluids. An 'ideal' scWHS reactor should be able to satisfy the following criteria:

- *Instantaneous strong and uniform mixing of two reactant streams* - to aid in the formation of many small metal oxide nuclei which is desirable for small particle formation;
- *Short average residence time combined with a narrow residence time distribution* - to minimise the subsequent particle growth and to narrow particle size distribution;

- *Minimal heating of the aqueous metal salt stream prior to the reactor, followed by immediate and rapid heating of the salt solution within the reactor* – to prevent premature precipitation/deposition of metal salts in the pipes prior to the reactor.
- *Strong net downstream flow/eddies for the rapid transport of product particles out of the reactor* – to prevent particle accumulation within the reactor and to minimise subsequent particle growth.

These criteria led to the invention of a new reactor design for scWHS – known hereafter as the *Nozzle Reactor*[19]. **Figure 2** illustrates our patented reactor; it is a pipe-in-pipe concentric arrangement in which the internal pipe has an open-ended nozzle with a cone attached. The supercritical water is fed downwards through the internal pipe and out the end of the 'Nozzle'; the aqueous metal salt steam is fed counter-currently upwards through the outer pipe. The reactor outlet is situated upwards through the outer pipe.

LAI and CFD Modelling

The steady state concentration map and its equivalent CFD simulation for the Nozzle Reactor are shown in **Figures 3a and 3b** respectively. The reactor takes advantage of the density difference between the two reactants so that the resultant mixing pattern satisfies all four of the criteria above. As the two reactant fluids are introduced, the mixing is instantaneous and strong. The resultant turbulent macro-mixing eddies are streamlined downstream to the outlet of the reactor. No contamination and, therefore, reaction occurs within the reactor inlets, nor are there any areas of poor net flow ('stagnant zones'). Both major contamination and stagnation were in all of the previous reactor configurations tested[15, 16, 20]. The strong downstream macro-eddies in the Nozzle Reactor are advantageous for two reasons: i) they result in uniform and high net flow through the reactor to its outlet and, therefore, a relatively short residence time; ii) the strong downstream eddies also aid in transporting of the particles out of the reactor. Both of these advantages prevent accumulation in the reactor and minimise particle growth.

This design can be adapted to give an ideal heating/cooling scenario for the scWHS reaction; as shown in **Figure 2**. Ideally, the metal stream should be kept below 50°C up until it is contacted with the supercritical water stream within the reactor; hereby preventing precipitation of the metal salt prior to the reactor, a common problem regularly observed in the previous reactors used for scWHS[21]. In these old reactors, the large density difference between the reactants allows the supercritical water stream to flow upstream counter-current to the metal salt flow; this prematurely heats the inlet stream to a temperature were hydrothermal synthesis can only occur at very low yields, but precipitation of the metal salt can readily occur. In some cases, this effect was so severe that the rig required shutting-down and the inlet pipes cleaning. In an attempt to prevent this from occurring, cooling jackets were attached to the metal salt inlet pipe, but only a small improvement was observed[21]. In the Nozzle Reactor, there is no upstream mixing inside either inlet since the density difference between the two reactants can only induce eddies streamed one-way, towards the reactor outlet. Therefore, the metal salt stream will remain ‘cold’ until it is mixed with the supercritical water within the reactor; the resultant mixing is almost instantaneous, resulting in rapid heating of the metal salt. This fast heating/fast mixing scenario, may have potential in many other supercritical water processes. The efficiency of this heat transfer profile can be increased with the addition of extra cooling and heating. A cooling jacket can be attached to the metal salt inlet to prevent the conduction of heat down the pipes from the reactor and a band heater to the area surrounding the nozzle to maintain and control the reaction temperature, see **Figure 2**

The cone section was added so that it would act in the same manner as a thin film reactor, spinning disc or spinning cone reactors[22-24]. In the Nozzle reactor, however, the centrifugal forces are replaced by natural convection forces.

The Idealisation rating system, briefly described earlier, was used to assess the *Nozzle Reactor* LAI models. The lowest rating, or most ideal, achieved by the other reactor geometries (T-piece, Y-Piece, + Piece, x Piece) was 0.15. In all, a total of 74 simulations have been completed. In the case of the *Nozzle Reactor*, the results were highly encouraging giving values as low as 0.05. Overall, throughout the LAI and CFD modelling process, the Nozzle Reactor exhibited all of the desired attributes required by the scWHS process. The next stage was to test the design on the actual scWHS rig shown schematically in **Figure 1**.

Testing at supercritical conditions

The Nozzle Reactor was constructed used Swaglok® high pressure fittings; the outer tube consisted of a 3/8” tube (316 Stainless Steel, 0.065” wall thickness) and the inner tube was constructed from a 1/8” tube (316 Stainless Steel, 0.035” wall thickness). The construction of this reactor is shown schematically in **Figure 4**. The ‘nozzle’ was omitted for these initial tests as a precaution due to the large reduction in available flow area it would have produced. **Table 1** summarises the size of different metal oxides generated using the nozzle reactor.

Process Reliability and Reproducibility

Experiments were performed to generate CeO_2 to test the reliability and the reproducibility of the new optimised reactor design. The initial test was to run the process for prolonged periods (up to 9 hrs) to assess the process reliability.

The following process conditions were used:

- Cerium ammonium nitrate (0.2M) set at 5 mL min^{-1} flowrate
- Supercritical water set at 10 mL min^{-1} flowrate
- Supercritical water temperature 410°C
- System pressure was set at 3600 p.s.i.
- Water cooling coils were added the reactor outlet and metal salt reactor inlet
- A 1kW Watlow band-heater was added to the reactor section of piping to heat the section to 370°C
- A 0.5 μm filter was used downstream of the reactor in order to protect the Tescom BPR from potentially damaging large particles.

Over five prolonged runs, only minimal particle accumulation was observed, no pipe blockages occurred and the system pressure remained constant and highly controllable. This is in contrast to the previous experiments performed using the T-piece arrangement in which pipe blockages were a regular occurrence, and pressure fluctuations were expected. The efficiency of this reactor configuration in producing an ideal heating profile was highlighted by the installed thermocouples - T1 and T2 (See **Figure 4**). The internal thermocouple T1, situated just 2 cm upstream of the reactor in the metal salt inlet, routinely logs a steady temperature of 24 ºC. Thus, indicating that the metal salt stream remains 'cold' until it is contacted with the supercritical water stream within the reactor. Furthermore, the Thermocouple T2, just 4cm downstream of the reactor, was recording a stable temperature of 370 ºC at steady state. This high and stable downstream temperature gives further evidence of the fast mixing and heat transfer mechanism occurring between the two reactant streams.

The resulting CeO_2 powders were dried out in an oven at 90 deg C and degassed at 130 ºC for up to 8 hours. These dry powders were then analysed using BET to determine each surface area. The isotherms produced by all samples were Type 2, indicating non-porous particles, with calculated surface areas within the region 90 ± 5 m^2g^{-1}; demonstrating excellent sample reproducibility, see **Figure 5**. Previously, using the T-piece reactor, the surface area of CeO_2 powders were found to fluctuate unpredictably between 52 and 104 m^2g^{-1} [12, 21].

Product Tunability

The reliability and reproducibility of the experiments with the Nozzle Reactor mena that better and more accurate experimental control can be achieved in future experiments. For example, **Figure 6** shows the change in surface area, determined by BET analysis, of CeO_2 as the flowrate of the aqueous metal salt feed flowrate was changed. A peak surface area of $100m^2/g$ was obtained at 8 ml/min, giving the optimal ratio of supercritical water to aqueous metal salt for small particle formation.

Conclusions

The dominant driving force behind the mixing of supercritical water and aqueous metal salts streams in a scWHS reactor appears to be the bouyancy forces induced by the large density difference between the two reactants. This realisation means that the orientation of the reactor, as well as the relative positions of the inlets and outlets, become key properties in the design of the reactor. Subsequent investigation in alternative reactors suggested that the key to generating an optimal reactor design was to take advantage of the bouyancy forces produced by these density gradients i.e. use them to induce mixing, to prevent inlet-mixing and to transport the mixture/particles to the outlet.

The *Nozzle Reactor* is a customised design that uses the bouyancy induced eddies to produce an 'ideal' mixing scenario. The strong downstream eddies produced reduce residence time and subsequent particle growth, improve particle transportation and induce an ideal heating/cooling profile. The initial scWHS experimental results highlight the possibility that the improved reproducibility and reliability, given further investigation, will lead to eventual process optimisation. Furthermore, it could lead to the eventual ability to control particle size, composition and shape through the manipulation of process variables.

We thank the EPSRC and ICI Strategic Technologies for financial support. We Thank Dr P. A. Hamley, Mr M. Guyler, Mr P. Fields and Mr R. Wilson for their help.

[1] T. Adschiri, in *2nd International Conference on Processing Materials for Properties*, San Francisco, USA, **2000**.
[2] T. Adschiri, Y. Hakuta, K. Arai, in *5th International Symposium on Supercritical Fluids*, Atlanta, USA, **2000**.
[3] T. Adschiri, Y. Hakuta, K. Arai, *Ind. Eng. Chem. Res.* **2000**, *39*, 4901.
[4] T. Adschiri, Y. Hakuta, K. Sue, K. Arai, *J. Nanoparticle Res.* **2001**, *3*, 227.
[5] T. Adschiri, K. Kanazawa, K. Arai, *J. Am. Ceram. Soc.* **1992**, *75*, 1019.
[6] T. Adschiri, S. Yamane, S. Onai, K. Arai, in *Proc. 3rd Int. Symp. on Supercritical Fluids, Vol. T 3*, Strasbourg, France, **1994**, p. 241.
[7] F. Cansell, B. Chevalier, A. Demourgues, J. Etourneau, C. Even, Y. Garrabos, V. Pessey, S. Petit, A. Tressaud, F. Weill, *J. Mater. Chem.* **1998**, *9*, 67.
[8] L. Cote, A. S. Teja, A. P. Wilkinson, Z. Zhang, *J. Mater. Res.* **2002**, *17*, 2410.
[9] L. Cote, A. S. Teja, A. P. Wilkinson, Z. Zhang, *Fluid Phase Equilibria* **2003**, *210*, 307.
[10] L. J. Holm, A. S. Teja, in *Proc. 5th International Symposium on Supercritical Fluids*, Atlanta, USA, **2000**.
[11] V. Pessey, R. Garriga, F. Weill, B. Chevalier, J. Etourneau, F. Cansell, *High Pressure Res.* **2001**, *20*, 289.
[12] A. Cabañas, J. A. Darr, T. Ilkenhans, E. Lester, M. Poliakoff, in *Hydrothermal Synthesis*, Osaka, Japan., **2000**.
[13] A. Cabañas, J. A. Darr, E. Lester, M. Poliakoff, *Chem. Commun.* **2000**, 901.
[14] A. Cabañas, J. A. Darr, E. Lester, M. Poliakoff, *J. Mater. Chem.* **2001**, *11*, 561.
[15] P. J. Blood, J. P. Denyer, B. J. Azzopardi, M. Poliakoff, E. Lester, *Chem. Eng. Sci.* **2004**, *59*, 2853.
[16] E. Lester, P. J. Blood, M. Poliakoff, in *Symposium on Supercritical Fluids and the Future*, Birmingham, UK, **2004**.

[17] J. P. Denyer, E. Lester, P. A. Hamley, M. Poliakoff, D. Giddings, P. J. Blood, F. He, in *Proc. 8th Meeting on Supercritical Fluids, Vol. 1*, ISASF, Bordeaux, **2002**, p. 385.
[18] A. Cabañas, M. Poliakoff, *J. Mater. Chem.* **2001**, *11*, 1408.
[19] E. Lester, B. J. Azzopardi, UK, **2004** International Patent Application PCT/GB2005/000483.
[20] E. Lester, P. J. Blood, M. Poliakoff, in *7th International Conference on Nanostructured Materials*, Wiesbaden, Germany, **2004**.
[21] J. P. Denyer, Ph.D. Thesis, University of Nottingham (Nottingham, UK), **2003**.
[22] K. V. K. Boodhoo, W. A. E. Dunk, R. J. J. Jachuck, *Abstracts of Papers of the American Chemical Society* **2001**, *222*, 520.
[23] C. Brechtelsbauer, N. Lewis, P. Oxley, F. Ricard, C. Ramshaw, *Organic Process Research & Development* **2001**, *5*, 65.
[24] H. C. Yatmaz, C. Wallis, C. R. Howarth, *Chemosphere* **2001**, *42*, 397.