

Advancements in the Supercritical Water Hydrothermal Synthesis (scWHS) of Metal Oxide Nanoparticles

Edward Lester^{*a}, Paul Blood^{a,b}, Jun Li^{a,b} and Martyn Poliakoff^b

^aSchool of Chemical Environmental and Mining Engineering (SChEME)

^bClean Technology Research Group, School of Chemistry

University of Nottingham, University Park, Nottingham, NG7 2RD, UK

Edward.Lester@nottingham.ac.uk

ABSTRACT

Supercritical Water Hydrothermal Synthesis (scWHS) is a relatively simple and environmentally friendly process for the production of potentially valuable metal oxide nanoparticles. Previous problems with blockages forming in the original T piece reactor were overcome by redesigning the reactor using image analysis and computational fluid dynamics. An optimised reactor, termed the *Nozzle Reactor*, has been developed which can be run continuously and is able to produce a range of different metal particles including titania, ceria, zirconia, copper oxide, YAG, hematite, magnetite and silver. The reactor also shows a dramatic improvement in process reproducibility ($\pm 5\text{m}^2/\text{g}$ for BET surface area) and in control of particle size. Preliminary evidence suggests that the reactor could eventually lead to the ability to good control of particle properties, such as size, composition and shape, through the manipulation of process variables.

Keywords: supercritical water, metal oxides, image analysis, reactor design.

1 INTRODUCTION

Nanoparticulate metal oxides and metals are finding increasing applications in areas as diverse as sun blocks, electro-conductive printing inks, electronic displays, pigments and catalysts. Many of the routes to such particles involve relatively noxious chemicals, are not easily scalable, have a complex and time-consuming sequence of stages, or may require expensive precursors. These methods include sol-gel[1] (aerogels and xerogels), metal-atom aggregation in cryogenic inert gas matrices[2], thermal or ultrasonic decomposition of metal carbonyls, reduction of metal ions[3] semiconductor particles, zeolites and inverse micelles[4]. By contrast, Supercritical Water Hydrothermal Synthesis (scWHS) offers a relatively simple route which is inherently scalable and chemically much more benign. Mixing supercritical water with a metal salt causes precipitation of a metal

oxide after a hydrolysis and then a dehydration stage. The difficulty with continuous operation of the scWHS process is in the maintaining of complete control over mixing, in order to prevent blockages, and over product quality, in terms of particle size and size range. Experiments to visualise fluid mixing were undertaken in order to understand this mixing process more fully, and also to explain why the T-Piece reactor originally used at Nottingham was prone to blockages[5].

2 MODEL MIXING

The two fluids were carefully selected to model the properties of the two streams in the continuous scH₂O reactor. Methanol (Pseudo-scH₂O) was chosen to represent scH₂O whereas the aqueous metal salt stream was modelled by a 40 % w/w aqueous sucrose solution (Pseudo-metal salt). The density and viscosity ratios between these two fluids are similar to those between scH₂O and the pressurized aqueous metal solution stream in the actual supercritical system. Methylene Blue dye was used at a near-saturation concentration of 12 ppm to colour the sucrose solution. All modelling experiments were initiated by feeding the blue sucrose solution into a flowing MeOH environment thus recreating the scenario in the supercritical reactor (the metal salt is introduced into a flowing scH₂O environment).

The results illustrate the path taken by the pseudo-metal salt and highlight any zones of strong mixing/turbulence within the supercritical water reactor. The reactor model of the T-piece reactor was constructed out of polished transparent acrylic resin, with a constant internal tube diameter of 3.8 cm. Corresponding flow rates in the pseudo-reactor were calculated so that the inlet Reynolds numbers of the Methanol and Sucrose streams were close to those exhibited in the actual scH₂O system.

Figure 1 shows how the system was arranged and Figure 2 shows the mixing in a T piece that approximated to the actual supercritical water reactor.

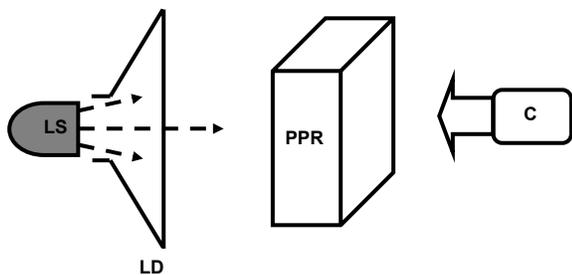


Figure 1: The modeling setup used to video fluid mixing in the pseudo reactor: Key: LS – light source (500W), LD – light diffuser, PPR – Perspex pseudo reactor, C – camera.

- operation and to aid in the instantaneous formation of many small metal oxide nuclei which is desirable for small particle formation
- *Very short average residence time combined with a narrow residence time distribution* - to minimise the subsequent particle growth and narrow particle size distribution
- *Minimal heating of aqueous metal salt stream prior to the reactor, followed by immediate and rapid heating within the reactor* – to prevent 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

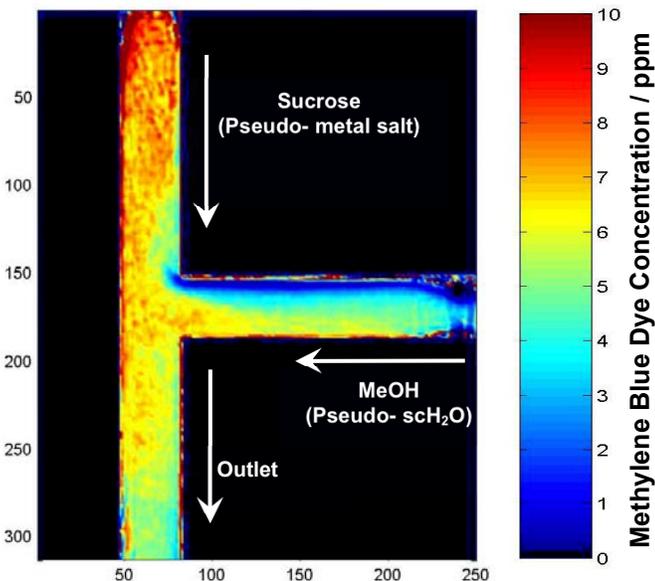


Figure 2: The mixing regime inside the T piece reactor

This experiment demonstrated clearly why blockages were occurring readily in the T piece system. Note fluid partitioning in the side arm where the supercritical water is introduced and the pre-mixing in the metal salt inlet.

Many other experiments were carried out on different geometries and different flow rates including T piece, Y piece, tangential side swirl and countercurrent tangential swirl reactors. Each reactor had numerous orientations and flow arrangements. Each experiment highlighted the difficulties of mixing two fluids with significant differences in density and therefore buoyancy. The optimal mixing geometry would clearly need

- *Instantaneous strong and uniform mixing of two reactant streams* – to give steady state

3 THE NOZZLE REACTOR

Figure 3 illustrates the nozzle reactor [6,7]; with its 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.

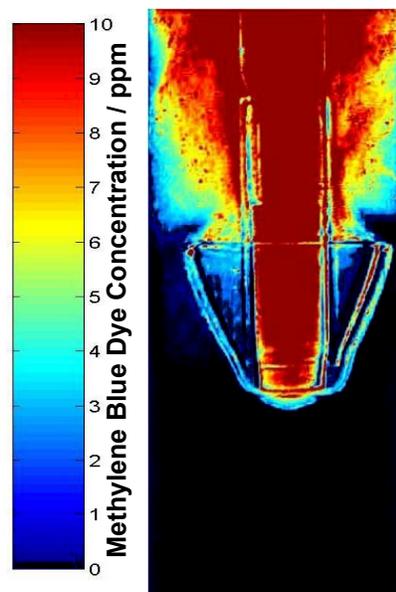


Figure 3: The nozzle reactor mixing supercritical water (down the inner pipe) with metal salt (up the outer pipe)

4 NANOPARTICLES FROM THE NOZZLE REACTOR

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'). 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.

The metal stream can also be kept below 40°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, which is a common problem during scWHS. 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.

4.1 Iron Oxide

Hematite (Fe_2O_3) nanoparticles can exhibit superparamagnetic behaviour and improved coercivity. Their potential applications include M.R.I. contrast agents, recording media, catalysts, pigments, targeted drug delivery and sensors. With iron nitrate as the metal salt precursor at a concentration of 0.05M, the size of product can be controlled between 5nm to 50nm by adjusting the water feed temperature. Figure 4 shows the relationship between particle size and operating temperature.

4.2 Copper Oxide

Copper oxide (mixed CuO and Cu_2O) particles can be used as an antimicrobial agent, in wood preservation, conductive inkjet printing and in pigments. By using copper formate as the metal salt precursor at a concentration of 0.01M, nanoparticles around 50nm can be produced continuously (see Figure 5).

4.3 Cobalt Oxide

Co_3O_4 has potential application in biomedicine, catalysis and recording media[8]. Operating at 415°C using cobalt acetate tetrahydrate as the organic metal salt precursor. Figure 6 shows a TEM image of the particles around 20-30nm.

4.4 Cadmium Sulfide

CdS has potential applications in photochemical catalysis, non-linear optics, infrared detectors, and photosensitizing sensors. Using cadmium nitrate and thiocarbonyl as the two precursors and operating at 200°C, 10nm particles can be produced (Figure 7)

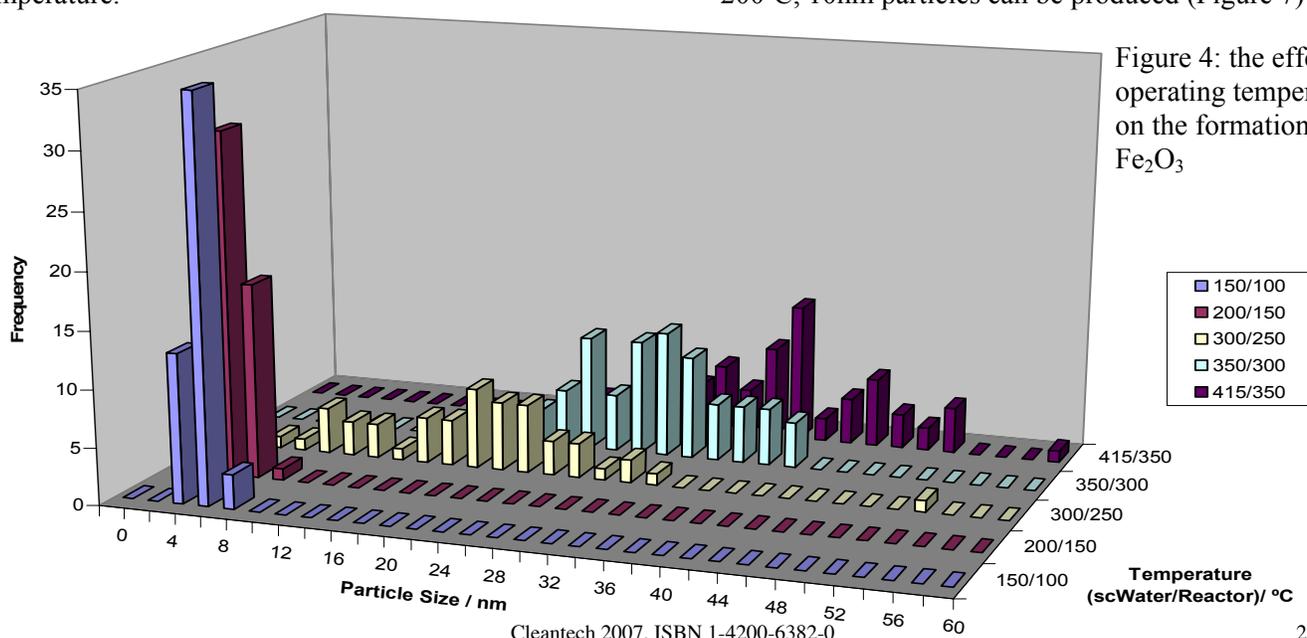


Figure 4: the effect of operating temperature on the formation of Fe_2O_3

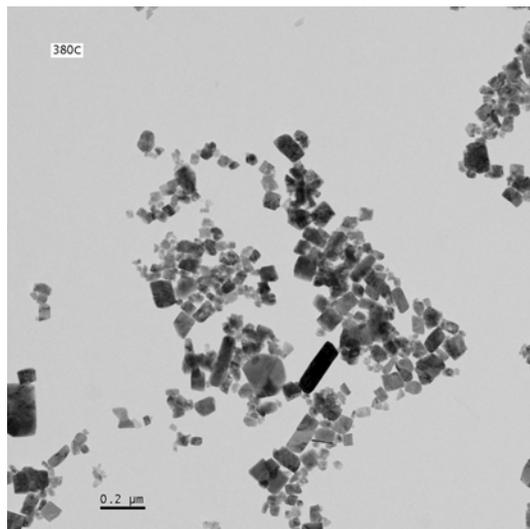


Figure 5: copper oxide nanoparticles. Note lower concentrations can be used to reduce particle size.

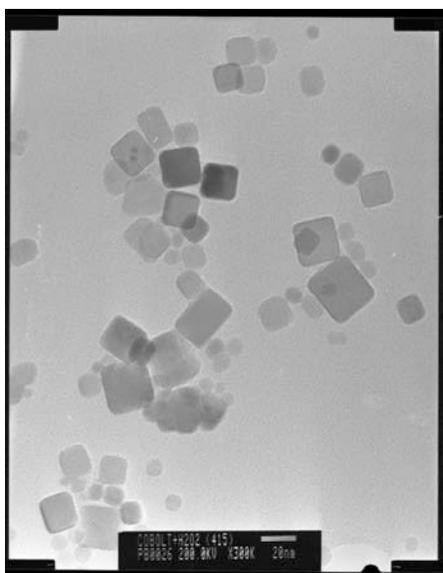


Figure 6: Co₃O₄ particles (around 20-30nm)

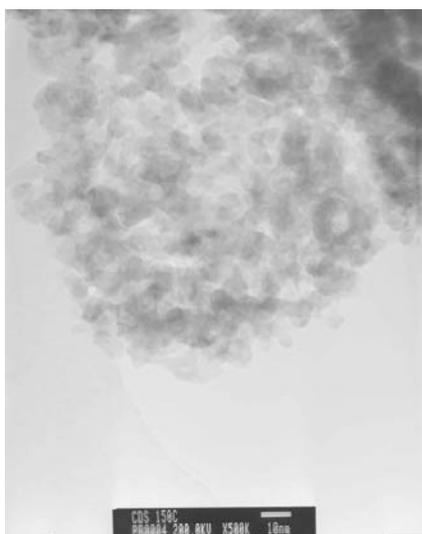


Figure 7: CdS particles (around 10nm)

5 CONCLUSIONS

The Nozzle Reactor is an optimised design specifically developed for the supercritical water hydrothermal synthesis of nanoparticles. The nozzle reactor takes advantage of differential buoyancy forces to produce an ideal steady-state mixing profile.

The application of the nozzle design on the actual scWHS rig has resulted in a significant improvement in both product reproducibility and process reliability. We are in the position where we can investigate the process chemistry and the influence of process variables effectively. It is capable of producing highly useful and valuable nanoparticles such as silver, copper oxide, cobalt oxide, YAG, CdS and iron oxide in a clean, flexible and relatively cheap process.

The large selection of particles produced since the implementation of the nozzle design is perhaps a hint of this process's commercial potential. Further work is required into the real application, treatment and capping of these particles.

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7 REFERENCES

- [1] I. Kartini, P. Meredith, X. S. Zhao, J. C. D. da Costa, G. Q. Lu, *Journal of Nanoscience and Nanotechnology* 2004, 4, 270
- [2] K. J. Klabunde, C. Mohs, *Chemistry of Advanced Materials*, Wiley, New York, 1998.
- [3] P. Mulvaney, H. A., *J. Phys. Chem.* 1990, 94, 4183.
- [4] Y. Wang, N. Herron, *J. Phys. Chem.* 1988, 92, 4988.
- [5] P. J. Blood, J. P. Denyer, B. J. Azzopardi, M. Poliakoff, E. Lester, *Chem. Eng. Sci.* 2004, 59, 2853.
- [6] E. Lester, P. Blood, J. Denyer, D. Giddings, B. Azzopardi, M. Poliakoff accepted for publication in *J. Supercritical Fluids* [doi:10.1016/j.supflu.2005.08.011](https://doi.org/10.1016/j.supflu.2005.08.011)
- [7] E. Lester, B. Azzopardi, Countercurrent mixing device, World Patent WO2005077505 - 2005-08-25
- [8] L. Cote, A. S. Teja, A. P. Wilkinson, Z. Zhang, *J. Mater. Res.* 2002, 17, 2410