HYDROTHERMAL MANUFACTURING OF NANOMATERIALS. REACTOR COMPUTATIONAL FLUID DYNAMIC MODELING

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Abstract. The SHYMAN (Sustainable Hydrothermal Manufacturing of Nanomaterials) project address scale up, formulation, weight loading, cost and sustainability of nanomaterials hydrothermal synthesis processes. Final outcome will be a 100 tons per annum continuous plant built at Solvay's site in Warrington, UK. The University of Valladolid High Pressure Processes Group leads the Process Dynamics and Modeling Work Package, whose objective is the generation of an integrated kinetics model that can predict particle size and particle size distribution of a range of different nanomaterials (including TiO2, Fe2O3, hydroxyapatite, Ag, Co3O4, ZrO2, ZnS and CuO) with the continuous system at production scales of 1, 10 and 100 tons per annum. CFD simulations based and validated on bench and pilot scale reactors data had been used to determine the limits of the existing design in terms of flow dynamics and to assess confidence on scaling up to the final plant, two orders of magnitude away. Variables explored include pipe diameter, flow rate, flows ratio and internal to external pipe diameters. The combined thermodynamics/kinetics/fluids model is used to predict the mixing dynamics, fluid variables profiles (temperature, pressure, velocity, age of the fluid...) inside the reactors, Residence Time Distributions at the outlet, an estimation of the shape of the Particle Size Distribution and average particle size at the outlet. The Peng-Robinson equation of state with translated volume and transport properties models integrated in a CFD code are used.

Keywords. Computational Fluid Dynamics; Nanoparticles synthesis; Nanomaterials synthesis; Scale up

1. Introduction

Nanomaterials form the building block for any successful application of nanotechnology. Global market for nanotechnology was valued at nearly $20.1 billion in 2011. In 2009 the largest nanotechnology segment was in nanomaterials with $9 billion in sales, with a predicted rise to $37.3 billion by 2017 [1]. Figure 1 shows the predicted market structure divided mainly in nanomaterials, nanotools and nanodevices.

The production technologies for nanomaterials are therefore critical in the success of nanotechnology as a whole. Many wet and dry methods for manufacturing nanomaterials, have been developed, the latter being more visible in today's market. Inhalation of nanoparticles is the main route of human exposure based on how easily can they be suspended in air[2]. Hence, wet processing methods can prevent a large part of emissions. Therefore, for economic and environmental reasons it is vital that manufacturing routes that will facilitate the forecasted increase in production are:

1. Green – using reduced levels of solvents, sourcing the most environmentally friendly feed materials
2. Sustainable – with efficient energy recovery, low temperature processing and recycling
3. Low cost – through process optimisation to minimise the number of downstream processes prior to use
4. High Quality – the process should be capable of generating high quality materials with superior control over particle size, size distribution, formulation, etc.

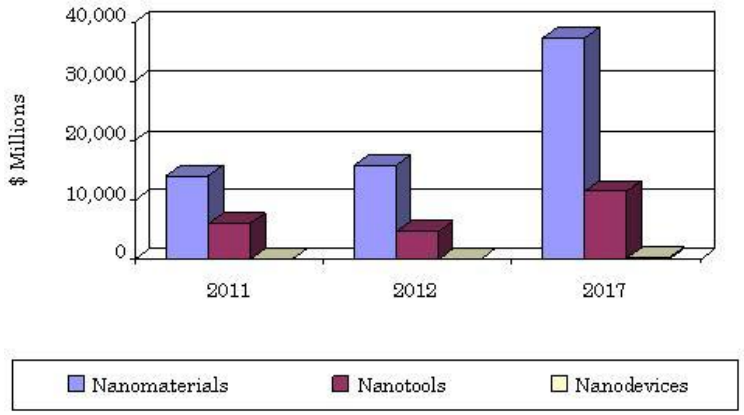

Figure 1. Global nanotechnology market 2009-2017[1].

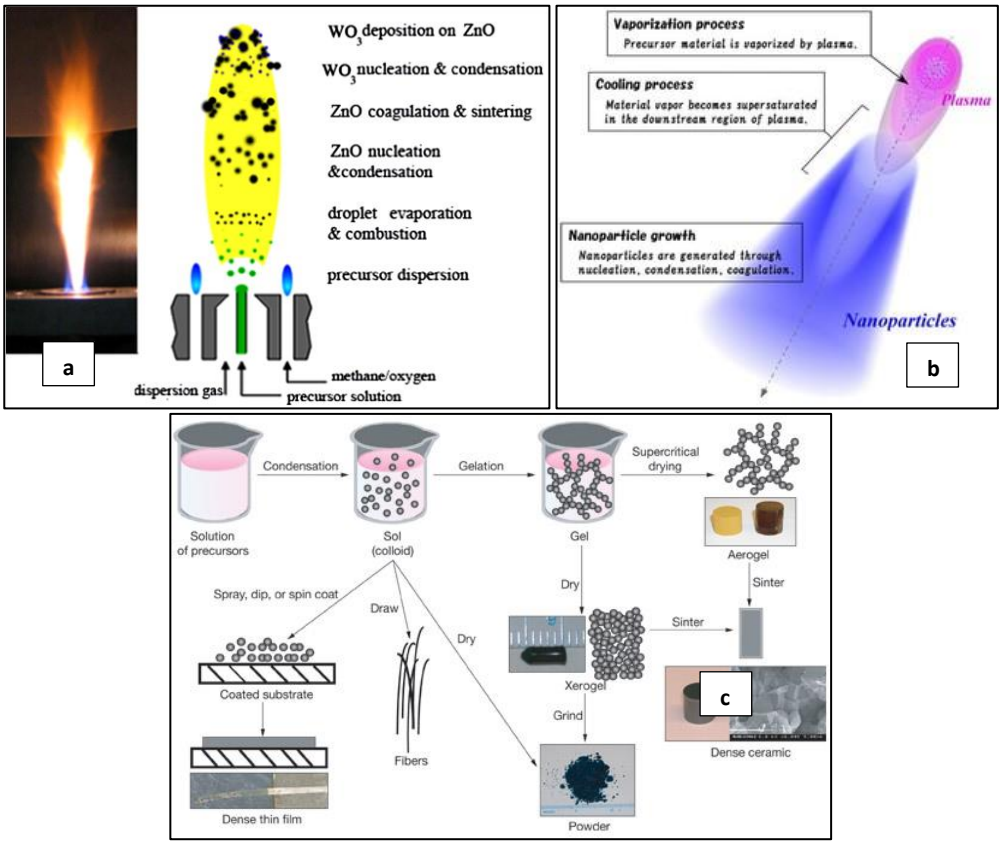

Figure 2. a) Flame pyrolysis[3],b) plasma synthesis[4] and c) sol-gel[5] synthesis of nanoparticles.

Hydrothermal synthesis is an alternative route to manufacture that offers unique opportunities for the synthesis of high quality nanoparticles and their formulation.

In contrast to other technologies, hydrothermal synthesis;

- Does not tend to use noxious chemicals – with water soluble precursors and water as a solvent
- Uses relatively simple chemistry – generally following hydrolysis and dehydration stages
- Allows straightforward downstream processing - the process is dispersion based
- Uses relatively cheap chemical precursors – acetates, nitrates and phosphates
- Can produce stoichiometric compounds like YAG [6] or BaTiO3 [7].
- Can produce non-stoichiometric materials where precise alloying [8] or doping [9] can be achieved.

- Can avoid agglomeration - the dispersed materials can be stabilised with additives, in situ.
- Size and shape distribution can be narrow and well controlled.

Continuous hydrothermal synthesis produces nanoparticulate materials by mixing superheated/supercritical water with a solution of a metal salt. i.e. rather than slowly heating the entire contents of a batch vessel, two fluids are continuously mixed together [10-13]. When water is heated towards its critical point (374ºC, 218 atm.)[14], the ionic product [H+][OH-] increases and the superheated fluid is technically supercritical, rather than near-critical. The enhanced levels of OH- were first exploited for continuous nanoparticle production by Adschiri and Arai, in 1992, who showed that under these conditions hydrolysis of metal salts (MLx) is immediately followed by a dehydration step[10].

Hydrolysis: $ML_x + xOH^- \rightarrow M(OH)_x + xL^-$ (1)

Dehydration: $M(OH)_x \rightarrow MO_{\frac{x}{2}} + \frac{x}{2} H_2O$ (2)

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The step from batch to continuous hydrothermal synthesis has been held back by engineering issues around mixing the heated fluid and the aqueous metal salt flow. One of the key factors that determines the success of such a reactor is how well it can mix the superheated water with the metal-salt solution. Blockages quickly form with T piece reactors [15] due to fluid partitioning, roping[16] and back mixing [17] where uncontrolled particle growth occurs.

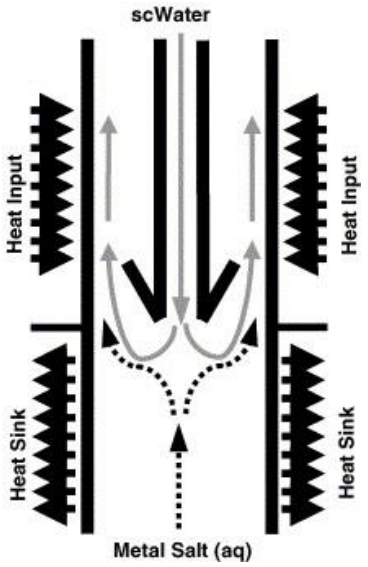

Figure 3. Mixing of the precursor solution and supercritical water during the continuous hydrothermal nanoparticle synthesis.

The experimental evaluation of each and every one of the possibilities to improve the performance of the reactor is not pragmatic, hence numerical simulations are being used to obtain an optimized configuration of the reactor for the levels of production that the Shyman projects aims for. The University of Valladolid High Pressure Processes, as acting part of the Process Dynamics and Modeling Work Package, is on charge of the development and application of a complete model that can predict particle size and particle size distribution of a range of different nanomaterials under selected flow conditions.

Here we aim to present the ongoing results of the modeling tasks in the Shyman project. CFD simulations have been performed on bench and pilot scale reactors to assess the limits of available design. Variables explored include pipe diameter, flow rate, flows ratio and internal to external pipe diameters.

2. Model Development

The model proposed for the Shyman project includes the description of the synthesis of nanoparticles using three stages:

a. Correct description of fluid-dynamic behaviour inside the equipment
b. Kinetic models, following Equations 1 and 2, including turbulence - chemistry interaction.
c. The description of the behaviour of the particle size distribution along the reactor, and the turbulence interaction with nucleation and growth.

The representation of such stages in the model requires the mathematical description of the following elements:

2.1 Thermodynamic properties

The use of the Volume Translated Peng-Robinson (VTPR) equation of state (Equation 3) improves the density calculation of saturated liquids and Vapor-Liquid equilibrium (VLE). It describes reliably supercritical fluids[18], thus it is applied here.

$$p = \frac{RT}{v + c - b} - \frac{a}{(v + c)(v + c + b) + b(v + c - b)} \tag{3}$$

2.2 Transport properties

Behaviour of the fluids close to their supercritical point may change suddenly. This makes it critical to obtain properties of the fluid as close to reality as possible. Therefore, here use the values provided by NIST [19] .

2.3 Fluid dynamics model

Here, fundamental conservation equations for mass, momentum and energy were used as described by Sierra-Pallares et al. in [20]. The system was solved using Reynolds Averaged Navier-Stokes (RANS) equations. The turbulence model used was realizable k-epsilon. The Residence Time Distribution (RTD) was described inside the geometry and at the exit point, suing the following transport equations[21]:

$$\frac{\partial}{\partial x_j}\left(\bar{\rho}\tilde{u}\bar{\tau} - \bar{\rho}D^T\frac{\partial\bar{\tau}}{\partial x_j}\right) = \bar{\rho} \tag{4}$$

$$\frac{\partial\bar{\rho}\tilde{f}}{\partial t} + \frac{\partial}{\partial x_j}\left(\bar{\rho}\tilde{u}\tilde{f} - \bar{\rho}D^T\frac{\partial\tilde{f}}{\partial x_j}\right) = 0 \tag{5}$$

2.4 Chemical kinetics and population balance model

The chemistry of the nanoparticle synthesis is represented by the reaction system in Equations 1 and 2. As suggested by Tsantilis et al. a pseudo-first order is assumed to calculate the kinetics of the consumption of chemical precursor [22]. To describe the evolution of nanoparticle synthesis the population balance model as described in [23] was applied. The monodisperse model (Equations 6 – 9) considers a first order kinetic and a Brownian collision frequency.

$$\frac{DC_p}{Dt} = -kC_p = -A\,exp\left(\frac{-E_a}{RT}\right)C_p \tag{6}$$

$$\frac{DC_{Ox}}{Dt} = -kC_p \tag{7}$$

$$\frac{Dm_0}{Dt} = \frac{DC_{Ox}}{Dt}N_a - \frac{\beta}{2}m_0^2 \tag{8}$$

$$\frac{Dm_1}{Dt} = \frac{DC_{Ox}}{Dt} N_a V_1 \quad (9)$$

2.5 Boundary conditions

The boundary conditions are as follows:

- Similar flow conditions (Reynolds and Grashof numbers) to those included in Aksomaityte et al. [24] are used.
- During the Shyman project the experimental data are obtained in the reactor available in The University of Nottingham. Therefore the geometry used here resembles that configuration (3/4").
- Operating pressure is 230 bar.

2.6 Numerical solution

In order to solve the 3D system of equations a relatively coarse mesh (≈300 000 cells) was used as a first approximation to the problem. The transport properties were taken from the NIST database. The ANSYS FLUENT v.13.0 software was used to solve the equations system.

3. Results

As mentioned above, the transport properties of the fluids close to their critical point may change suddenly. Therefore the distribution of variables such as temperature and density, and the resulting particle size distribution is represented (Figure 4). The smaller particle sizes are found in the mixing zone. The nanoparticle size increases with the path of the fluid along the reactor. As the pressure is constant the density variations are ruled by the changes in temperature throughout the fluid path in the geometry.

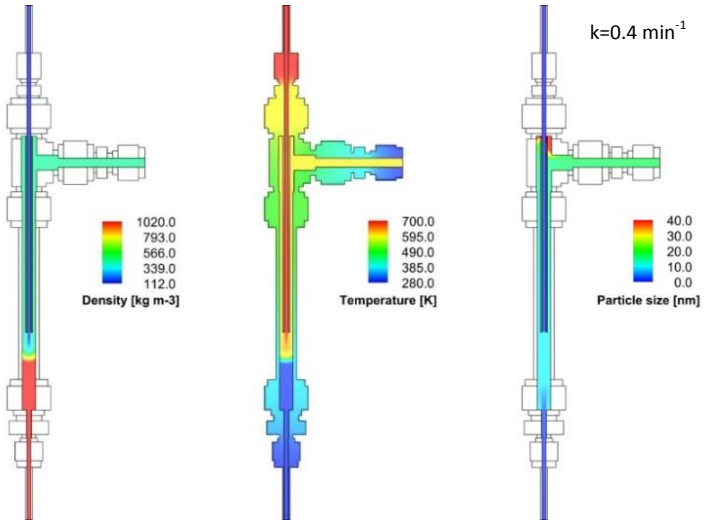

Figure 4. Density, temperature and size distributions

In the dead volume region in the superior part of the mixing chamber the particle size increases (red), which in the end produces a wider particle size distribution. A tracer pulse experiment shows that this effect is owed to the increase in the residence time in the dead volume (Figure 5).

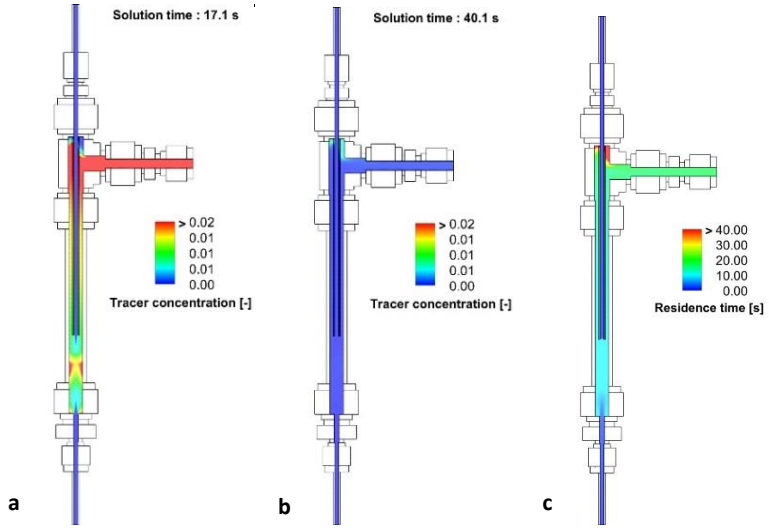

Figure 5 Tracer distribution at 17.1s a) 40.1s b) and residence time distribution c) in the geometry.

The RTD graph at the exit point (Figure 6) is characteristic of axial dispersion. As previously reported, residence time is related to the particle size thus this is a parameter variable to watch during the scale up of the process [23]. The size of the nanoparticles carried by the flow increases with the age of the fluid as more time for the stage of growth is allowed.

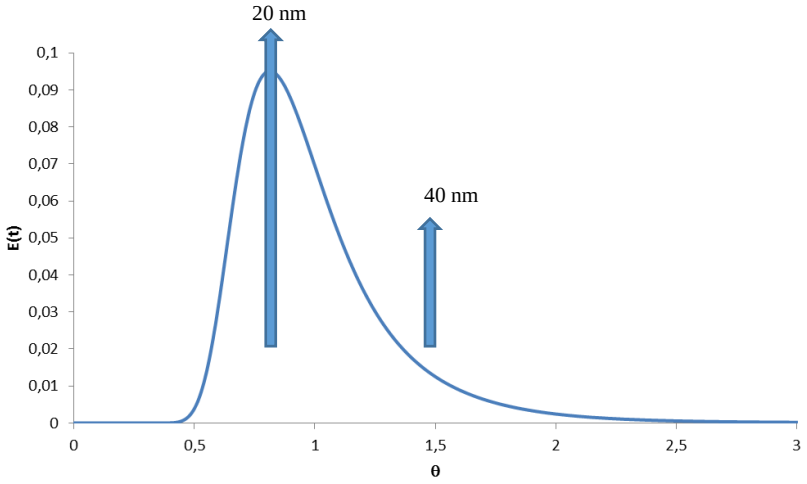

Figure 6. RTD curve at the exit point.

4. Conclusions

A model to describe and study the formation of nanoparticles during hydrothermal synthesis was implemented. It uses a 3D systems of equations based on the RANS approach and realizable k-epsilon to describe turbulence. Thermodynamic properties of water were described with data from NIST.

Density, temperature and particle size were conveniently represented in terms of the process geometry. Calculations show evidence that the particle size is a function of the rate of reaction. Thus reaction conditions such as temperature are crucial. As different temperature distribution in the reactor was observed, it is possible to control the reaction with different operating conditions (changes in heating, cooling, etc.) along the fluid path.

Residence time pattern described by tracer pulse agrees with that of an axial dispersion model and a transport equation for the residence time. In order to diminish the particle size the reduction of axial dispersion is important together with the removal of dead volumes. Thus, physical RTD experiments are needed in order to have a validated the model.

Acknowledgements

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Nomenclature

A	pre-exponential factor (1/s)
a	Attraction parameter (Pa m^6 /mol^2)
b	Co-volume (m^3/mol)
c	Volume translation term (m^3/mol)
C_{Ox}	Concentration of oxide (mol/ m^3)
C_p	Precursor concentration (mol/m^3)
D^T	Turbulent diffusivity (m^2/s)
E_a	Activation energy (J/mol)
$\tilde{f}$	Tracer concentration (mol/m^3)
k	kinetic constant (1/s)
m_0	Particles concentration (particles/m^3)
m_1	Particles volume (m^3/ m^3)
N_a	Avogadro's constant
p	Pressure (Pa)
R	Universal gas constant (J/mol K)
T	Temperature (K)
t	Time (s)
V_1	Monomer volume (m^3/molecule)
v	Molar volume (m^3/mol)
x_j	Space coordinate (m)

Greek Letters

β	collision frequency function (m^3/s)
$\bar{\rho}$	Average density (kg/m^3)
$\bar{\tau}$	Average age of the fluid (s)
$\tilde{u}$	Average velocity (m/s)

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