Optimisation of nanomaterials synthesis at industrial scale

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1. Introduction

Continuous hydrothermal synthesis (CHS) is a relatively straightforward concept and, in principle, it is scalable, economic and versatile. CHS has shown significant promise since its inception by Adschiri in the early 1990s[1]. Figure 1 shows the basic elements of the process. A preheated flow (often supercritical) mixes with a cold aqueous flow containing dissolved metal salts. The reaction engineering was the key to taking this technology forwards. Particles (on the whole) form within milliseconds and it was found that poor mixing could lead to blockages or a poor-quality product[2]. We found that if the superheated fluid was passed down an inner nozzle pipe against an up flow of cold metal salt. Nanoparticles form at the interface of the two fluids and the buoyancy of the heated flow causes the nanoparticle slurry to be carried upwards (downstream) for cooling and collection[3].

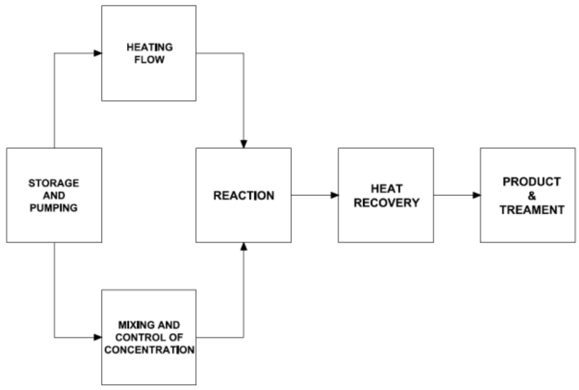

Figure 1 : flowsheet for continuous hydrothermal synthesis

The mixing geometry at bench scale was found to be vital because of the narrowness of the pipework (which tended to be 1/8 to 3/8''). The research work at the University of Nottingham led to a new reactor design and this was commercialized through the formation of a spin out company called Promethean Particles. The main drivers from this point were scale up, enhancing product quality and improvement in process economics. Over recent years this process has been scaled up 4 times from bench scale (g/hr) to pilot scale (100's and 1000's g/hr) to full scale (at tons per day - with a total of 75,000x from the original bench scale system[4]). At full scale all the processing stages in Figure 1 (particularly heat recovery) became critical in making the process viable. From a sustainability perspective, production rate was a critical denominator in dictating cost/kg and sustainability impact.

Nucleation and growth kinetics were considered to be critical, particularly when using faster flow rates, wider pipes and changes in mixing dynamics incumbent in non-Newtonian fluids. CFD models were created to validate pseudo fluid modelling and empirical work. Various process conditions were the simulated using the CFD and available kinetics data to create a predicted particle size distribution. These results can be seen in Figure 2[5]. This work underpinned the work towards a production rate of 1000tn/year. The plant has a supercritical water flow rate of 3m^3/hr and a metal precursor flow of 1.5m^3/hr to create a total reaction outflow at supercritical conditions (400°C and 240 bar) of 4.5m^3/hr.

2. Materials and Methods

To validate the process, ZrO_2 was manufactured and compared with bench and pilot scale products. The plant was operated at 400°C and 240 bar with an 0.25M aqueous solution of Zirconium Acetate, $Zr(CH_3COO)_2$.

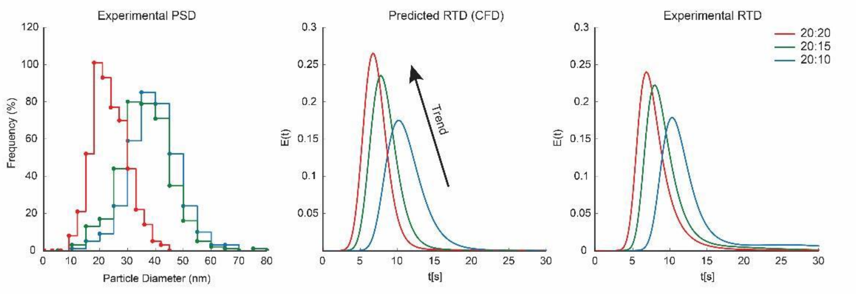

Figure 2 : Size distributions obtained for the production of nanoparticles along with experimentally and predicted RTDs

3. Results and discussion

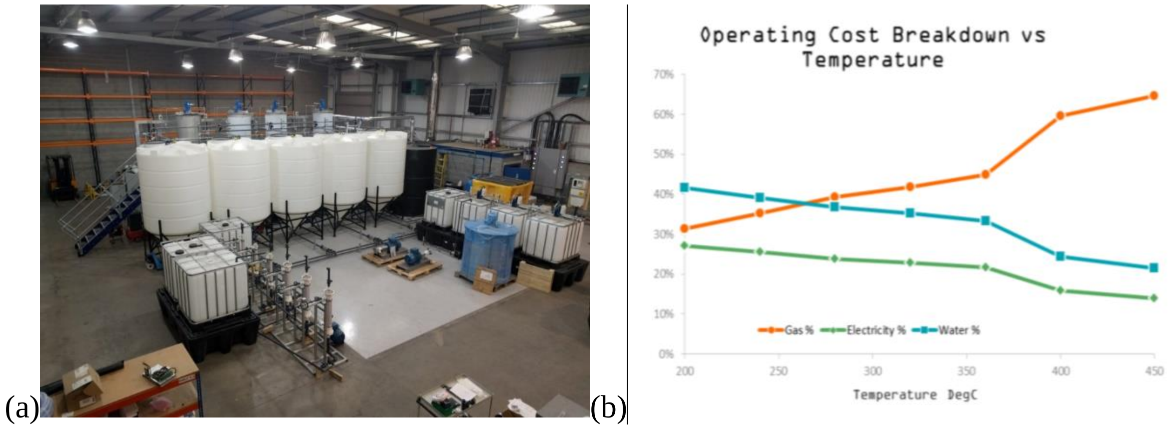

Figure 3: The full scale supercritical water plant (a) with cost analysis vs operating conditions (b).

The ZrO_2 particles were found to be quite uniform in size (Figure 4) with no evidence of particles larger than 10nm. The particles themselves appear to be 6-8nm ± 2nm and highly crystalline.

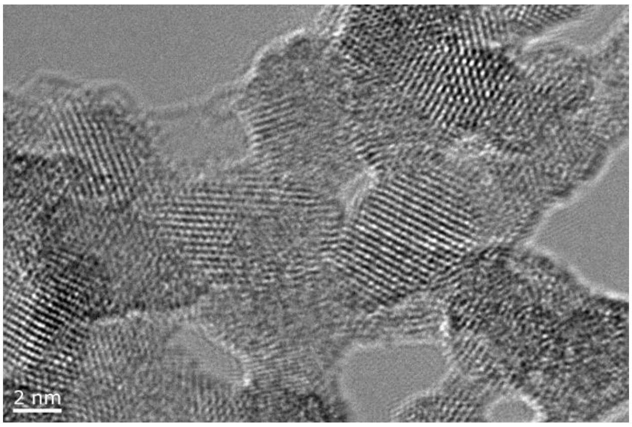

Figure 4: ZrO_2 particles from the full scale plant magnified at 1,000,000x magnification.

A “cradle to grave” LCA showed that the cumulative energy demand (CED) and global warming potential (GWP) for continuous hydrothermal synthesis (at scale) was relatively against other technologies[6]. However, some low variable technologies (e.g. sulphate and chloride process) were found to have a lower CED than CHS but, in comparison with technologies with similar product flexibility (e.g. HT plasma, sol-gel…), CHS was lower in of CED, GWP but with a higher product quality.

4. Conclusions

Continuous hydrothermal synthesis is scalable and commercially viable. The plant has been shown to be capable of making materials at supercritical conditions, and the ZrO_2 produced on the plant was the highest purity and highest crystallinity, with highest rate of conversion seen, of all the ZrO_2 samples produced at any previous scale. The surface area was found to be in excess of $200m^2/g$. TEM images showed the ZrO_2 sample to have a primary particle size of 6nm which was comparable to particles produced at pilot and bench scale. LCA analysis was carried out to compare CHS with other technologies with favourable results. Over a dozen materials have since been made on the full scale plant as the company continues to make and sell to clients around the world.

References

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