Population Balance Modelling of Zirconia Nanoparticles in Supercritical Water Hydrothermal Synthesis

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ABSTRACT: Like any other precipitation process, in supercritical water hydrothermal synthesis (SWHS), the need to improve product quality and minimize production cost requires understanding and optimization of Particle Size Distribution (PSD). In this work, using Population Balance Equation (PBE) containing nucleation and growth terms, the reactive precipitation of zirconia nanoparticles prepared by SWHS in the batch reactor was modeled. An optimization method using genetic algorithm function in MATLAB environment was developed to find simultaneously the kinetic parameters of nucleation and crystal growth rates, used for predicting PSD in PBE. The methodology developed evaluated kinetic parameters at comparable order of magnitudes to those presented in the literature, indicating a reasonable validation of the modeling method adopted. PSD results, however, showed a weak convergence of experimental and those predicted, suggesting that here, aggregation most likely played a considerable role in the PBE modeling of SWHS preparation of the zirconia nanoparticles.

KEYWORDS: Zirconia; Supersaturation; Nucleation/growth rate; Supercritical hydrothermal synthesis.

INTRODUCTION
Zirconia systems have attracted much attention due to their extensive use in such a wide range of applications as ceramics, catalysis, chromatographic materials, fuel cell technology, and gas sensor applications [1] owing to their specific chemical and physical properties, including high chemical stability, high temperature insulation ability, and ionic conductivity [2]. Several techniques such as sol-gel [3], spray pyrolysis [4], thermal decomposition [5] and hydrothermal/solvothermal synthesis [6] have been proposed for producing zirconia nanoparticles. However, these methods require long reaction duration and employ considerable organic solvents, which impose additional
process costs necessary for the complete synthesis process [7]. During the last two decades, Supercritical Water Hydrothermal Synthesis (SWHS) has been shown to be an efficient method capable of producing metal oxide nanoparticles from metal salt aqueous solutions due to the widely low dielectric constant of the Super Critical Water (SCW) resulting in a high reaction rate and a low solubility of the metal oxides [8]. Other associated advantages to the hydrothermal process include high product purity, good environmental compatibility, efficient control of the morphological structure and Particle Size Distribution (PSD) by processing parameters such as reaction temperature, pressure, precursor concentration, and flow rate [8-10].

For practical use, the effective control of SWHS, like other precipitation processes, is required since the quality of the product has an important effect on the properties of the powders, such as its specific surface area, crystal size, purity and morphology. For various precipitation applications, PSD is of prime importance to product quality. Moreover, the ability to flow or the dissolution rate of the produced particles could also be directly related to the PSD [11]. During the precipitation process, the PSD is mainly controlled by a number of simultaneously occurring phenomena including primary nucleation and crystal growth [12]. Design and operation of continuous/batch precipitators face serious challenges in determining the appropriate PSD and considering the industrial potentials offered by such an approach, a more thorough understanding of the process, geared towards its mathematical modeling and numerical simulation could prove to be a valuable tool in the future development of this technique [13]. Furthermore, considering high operating pressures and temperatures involved, this approach could diminish the need for numerous experiments and costs associated with SWHS. However, as far as precipitation kinetics and consequently PSD determination of zirconia particles produced by SWHS are concerned, limited data have been reported to date in the literature. Becker et al. [1] prepared nanocrystalline zirconia in near and super critical water as well as supercritical isopropyl alcohol, using a broad range of temperatures, pressures, concentrations, and precursors, and investigated widely PSD, shape, aggregation and crystallinity. Matsui and Ohgai [14] worked on the formation rate and primary particle size of hydrous zirconia particles produced by the hydrolysis of various ZrOCl2 solutions, to investigate effects of H+ and Cl- ion concentrations on nucleation and crystal-growth of the primary particles.

Here, a mathematical model based on Population Balance Equation (PBE) is employed, to study nucleation and growth kinetics of zirconia produced by SWHS. Having established the equilibrium solubility of zirconia from our previous study, supersaturation, precipitation kinetics, and PSD were evaluated at different operating conditions as presented before [15].

MODELING FRAMEWORK

The modeling structure was established in two stages here. The first step was based on equilibrium calculation of ZrO2 system (as developed in our previous work [15]), followed by supersaturation values, calculated as [7]:

$$ S = \frac{Zr_0 - Zr}{Zr} $$

(1)

Where Zr and Zr0 denote the estimated and initial solubility of zirconium, respectively. The estimated solubility of zirconium at any given set of conditions is the sum of molalities for all stepwise hydrolysis species that are present in the solution, albeit at negligible concentrations [16]. Hence:

$$ Zr = [Zr^{4+}] + [ZrOH^{3+}] + [ZrO_2] + [Zr(OH)_2^{3+}] + [Zr(OH)_3] + [Zr(OH)_4] + [Zr(OH)_5] $$

(2)

The second step of the modeling which is the prime objective of this research involves the establishment of a nucleation-growth model based on a PBE to identify the kinetic parameters of nucleation and crystal growth of zirconia as well as the PSD using the previously developed thermodynamic model.

Population balance equation

Modeling with the PBE has been widely used in the last three decades to describe PSD in various chemical engineering processes as it provides a good account of parameter identification, operating conditions, process control and design of such processes as crystallization, polymerization, emulsion and microbial culture [17]. In crystallization, PBE describing the PSD is often solved in association with mass/energy balances and kinetics.
terms (including nucleation and crystal growth). For a perfectly mixed reactor, assuming no agglomeration and breakage, and with growth rate being independent of the crystal size, Randolph and Larson [12] proposed the PBE in a batch crystallizer as

$$\frac{\partial n(L,t)}{\partial t} + G \frac{\partial n(L,t)}{\partial L} = 0$$  \hspace{1cm} (3)

with

$$n(0,t) = \frac{r_N(t)}{G(t)}$$  \hspace{1cm} (4)

Where $n(L,t)$ denotes particle density at time $t$ within the size range $L$ to $L + dL$. $r_N$ is nucleation rate and $G$ is the isotropic growth rate. For crystallization by SCW, supersaturation is initially high; hence, primary nucleation becomes the predominant mechanism that controls the nucleation rate [18]. Therefore, in this work one may assume that it is safe to use the rate of primary nucleation in simulating the nucleation reaction. Based on nucleation and growth theory [19,20], nucleation rate $r_N$, representing the number of zirconia nuclei formed per time unit (s) and volume unit ($m^3$) is obtained using the general equation:

$$r_N = A \exp \left( \frac{-B}{(\ln S)^2} \right) \left( \text{particle/m}^3 \text{s} \right)$$  \hspace{1cm} (5)

and kinetics of the crystal growth is also expressed by:

$$G = k_g (S-1)^g \left( \text{m/s} \right)$$  \hspace{1cm} (6)

Where $A$, $B$, $k_g$ and $g$ are kinetic constants to be determined by solving the PBE.

Population balance resolution

In general, differential equations are presented to address the population density distribution when solving the PBE [11, 21-24]. However, analytical solutions to the PBE can only be attained for simple cases and for most other cases a numerical solution is required [25]. The numerical methods employed can be broadly classified into two main categories: the class of the methods that solve directly for the number density (e.g. the least square method [26], Monte Carlo methods [27], the Discrete Population Balance (DPB) methods [21,28, etc.) and the class of methods that solve for the moments of the number density [29] DPB is successfully employed for solving PBE [30] and involves discretisation of size domain into discrete intervals or classes and as such, they are capable of presenting directly the size distribution. Their main drawbacks are the required high computational resources and the obligation to define the DPB classes as a priori [31,32]. An alternative to the DPB is the Method of Moments (MOM), developed by Randolph and Larson [12] and Hulburt and Katz [33].

MOM involves the conversion of PBE to equations in terms of the moments of the number density and therefore, has better computational efficiency compared to DPB and other intensive computational approaches involving process flowsheet simulations, coupled with fluid flow equations [34]. However, it is worth noting that MOM solution for the moments which could be sufficient in applications involving comparative experimental data [29, 35]. Here, PSD had to be calculated from the moments provided by MOM.

The MOM is an established approach whereby PBE is transformed into a set of Ordinary Differential Equations (ODEs) by multiplying the PBE by $L^j$ (in a length based PBE) and integrating it, giving equations in terms of moments [12]. The $k$th moment, $m_k$, is defined as:

$$m_k(t) = \int_0^\infty L^k n(t,L) dL$$  \hspace{1cm} (7)

From these moments, four parameters describing the gross properties of the particle population can be derived as below namely, the total number of particles $N$, total length $L_t$, total area $A_t$, and total volume $V_t$ of solid particles per unit volume of mixture suspension [8],

$$n_1 = m_0$$  \hspace{1cm} (8)

$$L_1 = m_1$$  \hspace{1cm} (9)

$$A_1 = K_a m_2$$  \hspace{1cm} (10)

$$V_1 = K_v m_3$$  \hspace{1cm} (11)

Here, $K_a$ and $K_v$ refer to surface and volume shape factors, respectively. Having defined the moments as per Eq. (7) and using the PBE’s, (Eq.’s 3,4), a system of ODE’s can then be obtained [36-39] as expressed in a set of Eq. (12):
The resolution of Eq. (12) which includes nucleation and growth rates required determination of kinetic parameters such as A, B, k, g. This was achieved by minimizing the quadratic error function Eq. (13) for the ratio of the moments, y_i(t), as suggested by Barbier et al. [40]. A genetic algorithm function from MATLAB software was used for this optimization and “ode45 solver” was employed to solve the nonlinear set of Eqs. (12).

The algorithm iterates kinetic parameters until adequate convergence of the quadratic function of Eq. (13) was attained:

\[
F(A, B, k, g) = \sum_{k=0}^{5} \sum_{i=1}^{4} \left( \frac{y_{i,exp}^{k} - y_{i,thres}^{k}}{y_{i,thres}^{k}} \right)^2
\]

(13)

Where, \(y_{i,exp}^{k}\) and \(y_{i,thres}^{k}\) refer to the experimental and theoretical moment ratio, respectively.

The resolution of this optimization problem gave the kinetic parameters of nucleation/growth rate values for zirconia, with which the PBE was solved for moments at any desirable set of conditions. Finally, the number density was computed by inverting moments to obtain PSD [41].

**RESULTS AND DISCUSSION**

Evaluation of kinetics parameters identification and solution of the PBEs expressed above were carried out in MATLAB environment with a time step of 1 s to trim down computation time.

Optimal parameters identified are listed in Table 1 and compared with those reported in the literature. An average standard deviation of 1.45 (%) was achieved according to the optimized Eq. (13). Interestingly, these exhibit the same range as those presented in the literature, indicating perhaps a reasonable validation of the modeling adopted here.

The evolution of nucleation/growth rates and supersaturation with time could then be computed for different temperatures, pressures, pHs and precursor concentrations. Results indicate similar trends graphically; hence, representative samples are reported here for the sake of brevity. Fig. 1 illustrates one such graph of supersaturation of zirconium nitrate versus time, where initially no apparent reactant consumption occurred, despite high rate of primary nucleation (see also Fig. 2) contributing to very small nuclei being produced. As expected, when the total particle surface became large enough, zirconium nitrate in the liquid phase was consumed by particle growth, while in case zirconium nitrate concentration in the liquid phase was sufficiently close to its solubility, the concentration drop was brought to an end. However, the start of stable nuclei formation, the slope and the end point for the reaction do vary slightly in such diagrams prepared for various operational parameters.

It is worth mentioning that as expected, the nucleation rate (see Fig. 2) depended heavily on the supersaturation extent, where it reached its peak at the initial precipitation stage (with supersaturation being at its highest), and then decreased in line with supersaturation ratio following reactant consumption.

Following primary nuclei formation explained above, growth phenomena take place which changes with time in a similar pattern as supersaturation (see Fig. 3), as it relates to the latter according to Eq. (6) with the exponent \(g\) being of the order of 1.56.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A (m²/s)</th>
<th>B</th>
<th>(k_{g}) (m/s)</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>(10^{18.6})</td>
<td>4.6</td>
<td>(10^{12.8})</td>
<td>1.56</td>
</tr>
<tr>
<td>Reported value range</td>
<td>([10^{10} - 10^{15}]^g)</td>
<td>([1 - 8]^g)</td>
<td>([10^{-5} - 10^{-3}]^g)</td>
<td>([1 - 2]^g)</td>
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Variations of the first four moments (from zero to third moments representing the total number of particles, mean particle size, average particles surface and average density was computed by inverting moments to obtain PSD [41].

**Table 1: Results of the model parameter identification.**
Hounslow et al. [28] remodeled population balance for batch aggregation of particulate suspensions in a simply and accurately solvable form and suggested that in cases where growth occurs alone, the zero moment remains constant while the higher ones increase with time. This means there is no change in the number of particles, but there is an increase in the crystal volume. On the other hand, where aggregation alone takes place in a system, all three moments of zero, first, and the second decrease, while the third moment remains constant; i.e., the number of particles is reduced while the total volume remains constant. In this study, however, a different result to either of these is evident, where as a result of both primary nucleation and growth, all moment functions (zero to the third moment) increased with time where supersaturation was high and it then reached a constant value with no supersaturation, as reported by Marchisio et al. [44]. In other words, since aggregation is neglected here when the solution is no longer supersaturated, the moment functions should remain constant.

Reconstructing volume number density function into particle size number density indicates that the normal distribution of PSD does not agree with the experimental data (see Fig. 5). This may be due to the fact that in solving the PBE only nucleation and growth rates were considered. However, as noted by Zhao et al. [11] aggregation could influence the final product properties such as PSD, which might be the case here and as such is worth investigating further. Interestingly, this issue was confirmed by TEM graphs as presented in Fig. 6 [45], highlighting the need for aggregation term to be included for modeling purposes. Anyway, the contribution of the present study may be understood by this specific application of supersaturation calculation applied for PBE modeling to predict PSD of nano-sized metallic oxide particles produced by SWHS process, we have not only employed all synthesis reactions involved and in speciation calculation by dissociation constants (as opposed to a single main reaction [40, 46, 47]), but also in our solubility estimation, we have considered all zirconia species at high temperatures and pressures using R-HKF thermodynamic model. The fact that discrepancies were observed between the theoretical and empirical PSD in this work suggests that there is room for improvement in using this method.
CONCLUSIONS

In this work, an optimization method using PBE was developed to find kinetic parameters of nucleation and crystal growth rates, simultaneously, in SWHS of zirconia nanoparticles. The method was based on several laboratory experiments at different initial supersaturations in the batch reactor by minimization quadratic cost function. The zirconia nucleation and crystal growth functions by the parameters obtained were found to be:

\[ r_N = 10^{16.56} \exp \left[ -\frac{4.6}{\ln(S)} \right] \]

and

\[ G = 10^{12.6} (S - 1)^{1.56} \]

These kinetic parameters compare well with those presented in the literature, indicating a reasonable justification of the methodology implemented here.

PSD prediction, however, shows a weak convergence of experimental and predicted results, which suggests that aggregation may not be neglected in PBE modeling of zirconia precipitation here. Modeling and simulation method presented in this paper could be used to express the feeding stage of a reaction model, in conjunction with Computational Fluid Dynamics (CFD) and population balance modeling and for scale-up of the process to industrial production of similar nanomaterials using SWHS.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Pre-exponential factor, m³/s</td>
</tr>
<tr>
<td>A₀</td>
<td>Total surface of the particles, m²</td>
</tr>
<tr>
<td>B</td>
<td>Slope, dimensionless</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational fluid dynamics</td>
</tr>
<tr>
<td>g</td>
<td>Kinetic order, dimensionless</td>
</tr>
<tr>
<td>F()</td>
<td>Quadratic error function, dimensionless</td>
</tr>
</tbody>
</table>
Fig. 5: Comparison of calculated PSD of zirconia with experimental data at \( C = 0.125 \text{ M}, T = 500 ^\circ \text{C}, P = 586 \text{ bar and pH} = 1.0 \).  

![Graph showing comparison of calculated and experimental PSD of zirconia](image)

Fig. 6: TEM image of zirconia produced at \( C = 0.125 \text{ M}, T = 500 ^\circ \text{C}, P = 586 \text{ bar and pH} = 1.0 \) [45].  

![TEM image of zirconia](image)

Greek letters  
- \( \rho_c \) Crystal density, kg/m\(^3\)  
- \( \rho \) Crystal density, kg/m\(^3\)  
- \( V_t \) Total volume of particle, m\(^3\)  
- \( y_k(t) \) Moment ratio, m\(^{k-3}\)  
- \( y_k^{\text{exp}} \) Experimental moment ratio, m\(^{k-3}\)  
- \( y_k^{\text{theo}} \) Theoretical moment ratio, m\(^{k-3}\)  
- \( m_k(t) \) \( k \)th order moment of population density, m\(^{k-3}\)  
- \( M_e \) Molar weight, kg/mol  
- \( L_t \) Total length of particles, m  
- \( L \) Characteristic size, m  
- \( K_a \) Surface shape factor  
- \( K_v \) Volume shape factor  
- \( k \) Moment index, dimensionless  
- \( k_g \) Kinetic constant, m\(^4\)/s mol  
- \( G \) Crystal growth rate, m/s  
- \( S \) Relative supersaturation, dimensionless  
- \( SCW \) Supercritical water  
- \( SWHS \) Supercritical water hydrothermal synthesis  
- \( t \) Time, s  
- \( N_t \) Total number of particles  
- \( n(L, t) \) Number density of particles  
- \( PBE \) Population balance equation  
- \( PSD \) Particle size distribution  
- \( r_N \) Crystal nucleation rate, particle/m\(^3\)  

References  


