CHEMICAL ENGINEERING TRANSACTIONS
VOL. 43, 2015
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-34-1; **ISSN** 2283-9216
DOI: 10.3303/CET1543127

CFD Model of a Spinning Disk Reactor for Nanoparticle Production

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The use of a spinning disk reactor (SDR) was investigated for the continuous production of nanoparticles of hydroxyapatite. SDR is an effective apparatus for the production of nanoparticles by wet chemical synthesis. Rotation of the disc surface at high speed creates high centrifugal fields, which promote thin film flow with a thickness in the range 50 – 500 μm. Films are highly sheared and have numerous unstable surface ripples, giving rise to intense mixing. SDR performances are strongly affected by the adopted operating conditions such as the influence of rotation speed that determines the attainment of micro-mixing and the feeding point location that has a great influence on the particle size distribution of the product. The experimental device consists of a cylindrical vessel with an inner disk, 8.5 cm in diameter, made by PVC coated by an acrylic layer. The rotational velocity of the disc is controlled and ranges from 0 to 147 rad/s. The reagent solutions are fed over the disk at a distance of 5 mm from the disc surface through tubes, 1 mm in diameter.
A computational fluid dynamic model, validated in a previous work, was used to optimize the operative conditions of SDR. Through the CFD model it is possible to analyse the hydrodynamic of the thin liquid film formed on the disk at different speed rotations and to individuate the best mixing conditions between the reagents varying the feeding point positions. The production of hydroxyapatite was also investigated adding the reaction kinetic to model the product formation in the liquid phase and the population balance equation to predict particle size distribution. The simulation results were compared with available experimental data showing that the CFD model is fully capable to describe the process and qualifies as a suitable engineering tool to perform the SDR process design.

1. Introduction

In previous works, the use of a spinning disk reactor (SDR) for the continuous production of nanoparticles of several compounds such as titania (Stoller et al., 2009) and hydroxyapatite (HAP) was reported (Parisi et al., 2011). The so produced nanoparticles were successively applied in several processes with success (Vaiano et al, 2014), such as those reported in some works concerning the photocatalysis of different wastewater streams for purification purposes (Stoller et al., 2011) in particular for the purification of olive mill wastewater (Ruzmanova et al., 2013a; Ruzmanova et al., 2013b). The SDR has many advantages when compared with other mixing devices used for precipitation process: i) a small liquid residence time, limiting the growth rate after nucleation, that leads to the production of narrow PDSs of nanoparticles at a specific target size; ii) micro-mixing conditions attained by means of a limited energy consumption; iii) continuous operation, compatible to industrial practice, can be performed.
SDR performances are strongly affected by the adopted operating conditions such as the rotation speed that determines the attainment of micro-mixing and the feeding point location that has a great influence on the particle size distribution of the product, as recently shown by de Caprariis et al. (2012). As a consequence, a fine description of the thin film hydrodynamics is needed in order to optimize the operating conditions of the SDR.

Please cite this article as: De Caprariis B., Stoller M., Chianese A., Verdone N., 2015, Cfd model of a spinning disk reactor for nanoparticle production, Chemical Engineering Transactions, 43, 757-762 DOI: 10.3303/CET1543127

Some simplified descriptions of the film hydrodynamics were proposed beforehand. Burns et al. (2005) reported that, in case of high Ekman numbers, the Nusselt model may be used for a rough description of the film thickness, with an average overprediction around 10 %. The experimental results reported by the latter authors were recently used by Bhatelia et al. (2009) for the implementation and the successful validation of a CFD model. However, the implemented model did not consider the liquid film turbulence and thus does not result enough accurate to grasp the true film hydraulics.
In this work, a CFD model, already validated (de Caprariis et al., 2012), was further developed in order to investigate the use of a SDR for the production of hydroxyapatite nanoparticles by chemical reaction and precipitation. The hydroxyapatite production was studied with the aim to predict the SDR performances varying the operative conditions. The population balance was implemented in order to obtain a nanoparticle diameter estimate which was compared with the available experimental data.

2. Experimental set-up

A spinning disc reactor (SDR) was used to produce nanoparticles of hydroxyapatite (HAP) by chemical precipitation reaction. The SDR, schematized in Figure 1, is composed of a static external cylinder and an inner rotating disc of 8.5 cm in diameter, where the reaction takes place. The product is continuously removed from the bottom of the reactor. The three reagent solutions are injected over the disc at a distance of 1 mm. These solutions are fed in two steps: first only the central flow rate, composed by a 10 % aqueous solution of NH_4OH at a flow rate of 80 mL/min, is injected to create the liquid film all over the disc. Once the film is created, the two aqueous reagent solutions, both at the same flow rate of 100 ml/min and with a mass fraction of 5.6 % of $CaCl_2$ and 3.5 % of $(NH_4)_2HPO_4$, respectively, are injected at 2 cm from the centre of the disk. In order to obtain nanoparticles of HAP of high quality and purity, the calcium/phosphate (Ca/P) ratio of 1.67, corresponding to the stoichiometric conditions, was adopted. The rotational velocity was fixed at 146.5 rad/s. These operative conditions were found to be the optimal ones by de Caprariis et al. (2012).
The reaction takes place between calcium chloride and ammonium phosphate, in presence of ammonium hydroxide:

$$10CaCl_2 + 6(NH_4)_2HPO_4 + 8NH_4OH \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 20(NH_4)Cl + 6H_2O$$

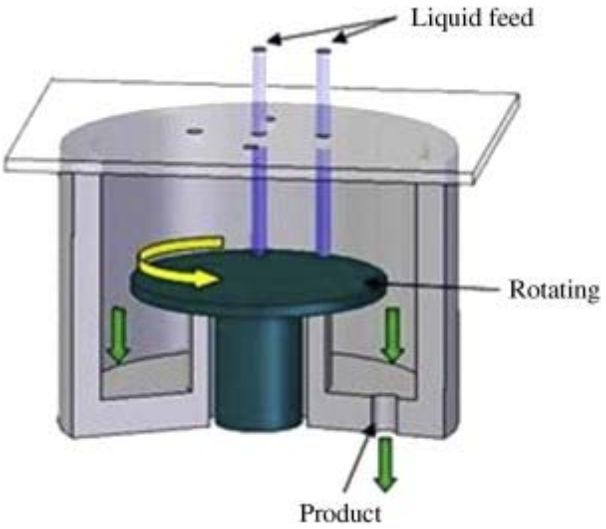

Figure 1: Schematization of the spinning disk reactor.

3. Model description

3.1 Model geometry

The computational grid necessary to resolve the CFD model was built in the Gambit environment. The computational domain considers only the liquid phase where the reaction takes place and a 70 μm grid height was selected representing the film thickness calculated by de Caprariis et al. (2012) for the same operative

conditions. The film thickness can be assumed constant according to the profiles reported in Figure 2a and considering that the reagents are injected 2 cm away from center of the disc. Therefore the grid consists in a cylinder 8.5 cm in diameter and 70 μm height, composed by 260,000 cells. The mesh is structured and made of hexahedral cells; in this way the flux is orthogonal to the faces of the cells limiting the errors due to the numerical diffusion, especially in the presence of convective fluxes.

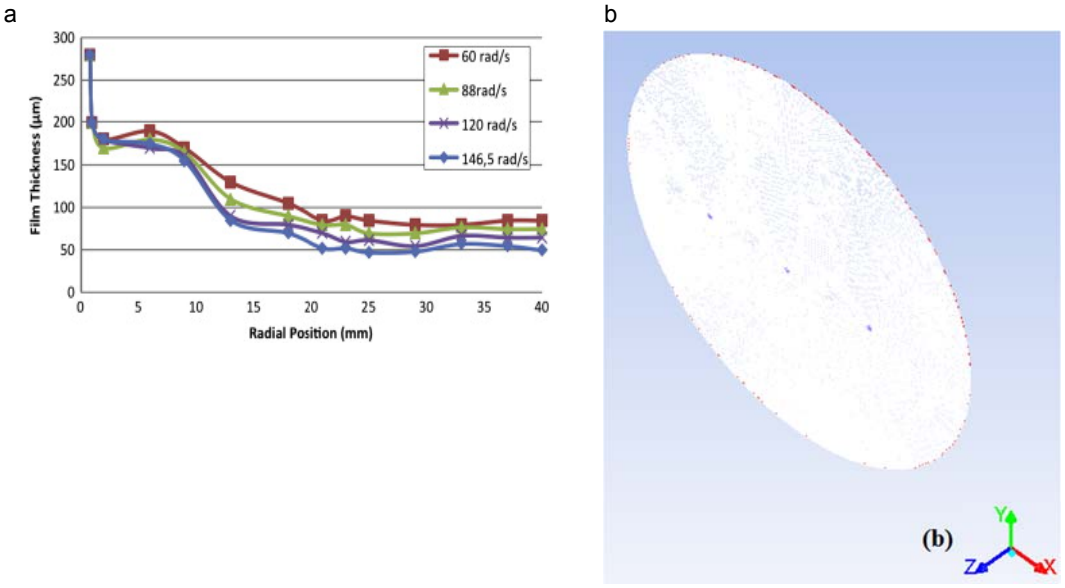

Figure 2: a-Film thickness profile (de Caprariis et al., 2012); b- Particular of the grid.

3.2 Model geometry

The numerical simulations were performed using ANSYS Fluent 14.5, a commercial CFD package based on finite volume resolution method.
The Eulerian multiphase model was adopted to model the reaction. This model is particularly recommended when the length of the interface between the phases is shorter than the considered computational domain, as in this case where the interface crystal-liquid is almost infinitesimal. Two phases were considered, one liquid phase containing all the reactants and a solid one constituted by the solid hydroxyapatite nanoparticles. The Eulerian model solves a set of n continuity and momentum equations for each phase, coupled through the interphase and pressure exchange coefficients. The reaction was modelled with the Finite Rate model using literature kinetic data (Changsheng et al., 2001). To take into account the size distribution of the particles, the population balance equation (PBE) was introduced to describe the changes in the particle population, in addition to momentum, mass, and energy balances.
The population balance equation in terms of density function n(V,t) is:

$$\frac{\partial}{\partial t}[n(V,t)] + \nabla[\vec{u}n(V,t)] + G = A_B + A_D + B_B + B_D \qquad (1)$$

The boundary and initial conditions are given by:
- BC: $n(V=0,t)=\dot{n}_0$
- IC: $n(V,t=0)=n_v$

where $\dot{n}_0$ is is the nucleation rate (#/m^{3}s). In the PBE G is the growth term, A_B and A_D are the birth and death due to aggregation terms, respectively, while B_B and B_D are the birth and death due to breakage terms, respectively. In this process all the terms, except for the growth term, can be considered negligible because of the nature of the reaction. In fact, in the precipitation reaction, the main part of the supersaturation ratio is consumed by the nucleation leaving a reduced driving force for the remaining phenomena. These observations suggest that only the nucleation step should be taken into account. This process was considered to behave at a constant rate.
As PBE can be solved by different methods, in this work the Quadrature Methods of Moments (QMOM) was adopted (Marchisio et al., 2003). Its application requires a relatively small number of scalar equations to track the moments of population with small errors. The method has the main advantage of basing on few variables

(typically six or eight moments) and incorporates a dynamic calculation of the size bins, requiring however longer computing time.
The turbulence was modelled according to the k-epsilon model.

4. Results and discussion

The use of the SDR is aimed to promote the mixing among the reagents with low contact times in order to maximize the product concentration, to have high nucleation rates and very low particles growth. The efficiency of the precipitation reaction depends on the mixing within the system. If the mixing is not adequate, the reagent streams penetrate the aqueous bulk formed on the disc creating three segregated phases. Due to this stratification, the reaction takes place without the optimal pH, leading to the formation of bigger and unstable particles with a higher tendency to agglomerate. Therefore the optimal conditions are obtained with a rapid mixing of the streams, low contact times of the reagents, high nucleation rate and low supersaturation available for the particle growth. All these aspects are favoured by a high rotational velocity of the disc in the overall film thickness. In Figure 3 the velocity profile of the liquid phase is reported showing a almost constant velocity along all the film height.

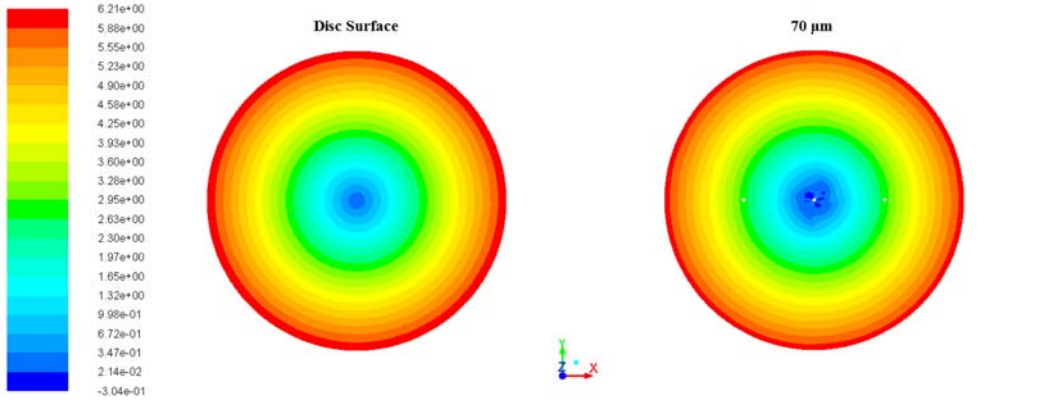

Figure 3: Velocity profile of the liquid phase at the disk surface and at the maximum film height (70 µm).

The contours of the two reagent streams are reported in Figure 4, showing the reagents profiles computed at the middle of the film (35 µm). These profiles confirm the goodness of the mixing, being the average stoichiometric ratio between them almost 1.67.

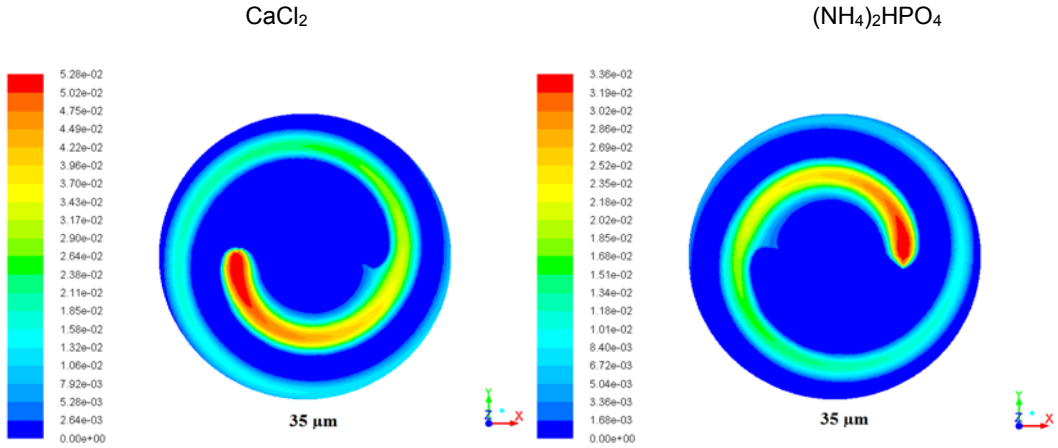

Figure 4: Reagent concentration profiles at a film height of 35 µm.

Since the precipitation reaction is nearly instantaneous, it takes place as soon as the reagent streams get in contact. Hence the maximum reaction rate is located in the contact points, as clearly shown in Figure 5.

In Figure 5a the HAP mass fraction contour confirms that the maximum concentration of the product is found in the contact regions between the reactants where the calculated reaction rate shows the highest values (Figure 5b).

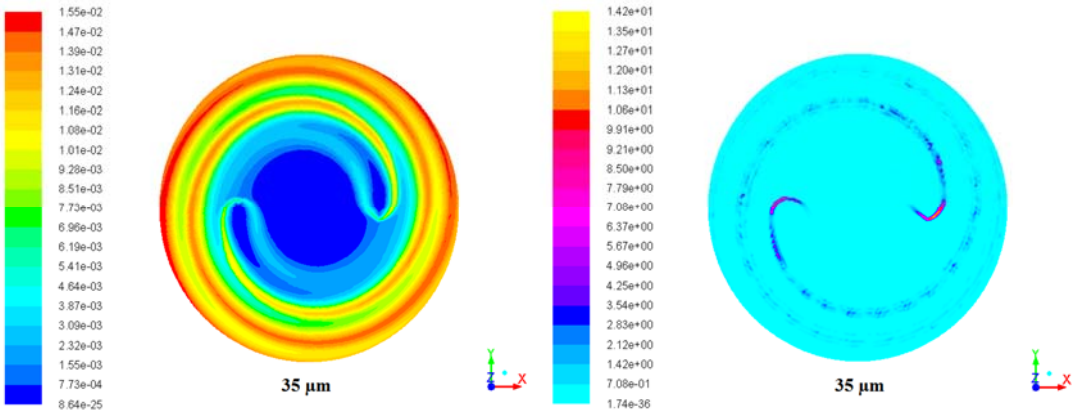

Figure 5: a-Hydroxyapatite concentration profile in the liquid phase at a film height of 35 µm; b-Reaction rate contour.

Once the liquid products were formed, the PBE equation was activated in the model in order to calculate the crystallite dimension to be compared with the experimental data.
The results of the PBE equation of concern are the moments of different orders that are directly related with the particle diameters, in particular the moments of order from 0 to 3 linked to the representative diameters by Eq (2) and (3):

$$d_{10} = \frac{m_1}{m_0} \quad (2)$$

$$d_{32} = \frac{m_3}{m_2} \quad (3)$$

d_{32} gives more accurate results since it takes into account the volume and surface shape factors of the particles. In Table 1 the values of the moments obtained at the periphery of the disc are reported, giving a dimension of the particle of d_{10}= 2.19 nm and d_{23} = 4.8 nm. It must be considered that these results refer to the dimension of the crystallyte since no crystal growth and agglomeration phenomenon were taken into account in the simulations.
The dimension of the crystallyte of hydroxyapatite were measured in a previous work (D'Intino et al., 2014) with X-ray diffraction technique and calculating the value of the diameter applying the Sherrer's fromula. The result indicates that the crystallyte diameter is about 5 nm, a value very similar to d_{23} obtained from the CFD simulations.

Table 1: Values of the moments obtained from the simulations.

Moments	
m_0	$4.12.10^{7}$
m_1	$9.04.10^{-2}$
m_2	$1.63.10^{-11}$
m_3	$7.82.10^{-20}$

5. Conclusions

A CFD model was developed in order to describe hydrodynamics and the reaction-precipitation process on the disk surface of a SDR$_T$ used for the production of hydroxyapatite nanoparticles. The interest in developing such a tool relies in the possibility to predict the outcome of the reaction conversion of the reagents and it is a prerequisite to estimate the particle size distribution of the product.
To model the interphase between the solid nanoparticles and the liquid phase the Eulerian model was used. First the reaction in the liquid phase was investigated, the results showing that the SDR is an effective device performing this class of reaction where the mixing of the reagents is of fundamental importance. The hydroxyapatite, indeed, is produced in the liquid phase instantaneously as soon as the reagents enter in contact.

In the second step of the simulations, the population balance equation was added to the model in order to predict the particle diameters. In the work only the nucleation was taken into consideration and so the crystallite dimensions were obtained. These values were compared with experimental data showing a very good agreement.
The obtained results show that the CFD model is fully capable to describe the process and qualifies as a suitable engineering tool to optimize the SDR process and equipment design.

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