CHEMICAL ENGINEERING TRANSACTIONS Volume 17, 2009
Editor Sauro Pierucci
 ISBN 978-88-95608-01-3 ISSN 1974-9791
DOI: 10.3303/CET0917166

Optimal Feed Location In A Spinning Disc Reactor For The Production Of Tio2 Nanoparticles

Marco Stoller *, Luci Miranda, Angelo Chianese
Chemical Engineering Dept., University of Rome "La Sapienza", 00184 Rome, Italy
* corresponding author: stoller@ingchim.ing.uniroma1.it

In this work different feeding location points over a rotating spinning disc reactors are compared. The examined system was the production of titanium dioxide nanoparticles by chemical reaction-precipitation. The reaction is the hydrolysis of tetraisopropoxide by 0.1 M nitric acid aqueous solution at ambient temperature. The goal was to identify the feeding system which enables to produce titania nanoparticles by minimizing the reactor scaling. It was found that a multiple reagent injector system allows the production of titania nanoparticles by minimization of scaling.

1. Introduction

The production of nanoparticles by chemical reaction-precipitation requires the attainment of local micromixing conditions in the reaction volume.Two process intensification apparatuses assure such a condition: T-mixer and rotating spinning disc. However, the spinning disc reactor (SDR) appears to be more suitable since it involves a much smaller specific energy consumption (Bffi et al. 2002, Stoller and Chianese, 2005). Further advantages of this technique is to allow a continuous production of nanoparticles at high flow rate and very short residence time. This latter characteristic leads to a reactor cost saving and a reduction of agglomeration phenomena.
Micromixing conditions over the SDR surface is more easily achieved vhen the feed location is near the center of the disc, and for this reason the feeding point of the two reagent solutions is usually located at a smmetrical and short radial distance from the center of the disc by a two point injection system (TIS) (Baffi et al., 2002). If locally critical concentrations values are exceeded, nanoparticles, once formed, tend to form agglomerates (Cao, 2004), which induce scaling over the disc surface and the external case's walls. This fact greatly reduces the operation time of the SDR, with the consequence of frequent cicles of shut down and cleaning.
In case of production of titanium dioxide nanoparticles, that is the system examined in this work, agglomeration phenomena lead to the production of micronic particles. In order to restore the original nanoparticles size a long time re-dispersion of the agglomerates in an acid solutions is required (Hintz et al., 2004).
An important factor enhancing the agglomeration phenomena is the particles suspension stability, usually expressed by the Z-potential value of the suspension.

Please cite this article as: Stoller M., Miranda L. and Chianese A., (2009), Optimal feed location in a spinning disc reactor for the production of tio2 nanoparticles, Chemical Engineering Transactions, 17, 993-998 DOI: 10.3303/CET0917166

Agglomeration rate is increased at low absolute Z-potential values, since the collision energy of two particles may overcome the repulsive forces given by their electrostatic double layer. As a rule of thumb, a value less than |30|mV is sufficient to lead to agglomeration if the suspension is calm. In case of flowing suspensions, due to the high kinetic energies of the particles in the stream, this limit is increased (Altman and Agranovski, 2005).
In this work the effect of the location feed configurations over a SDR on titania nanoparticles agglomeration was experimentally investigated. Different feeding configurations were examined like as the traditional two points injection system (TIS) and some multiple injector systems (MIS).

2. Experimental setup

The SDR used in this work consists of a disc, made by brass, 0,30 m in diameter. The case, hosting the rotating disc, has an internal diameter of 0,40 m. The rotational speed of the disc can be controlled, however the maximum value of 1500 rpm was always adopted. The reaction was carried out by feeding on the disc surface titanium tetraisopropoxide (TTIP) and 0.1 M nitric acid solution (NAS) at ambient temperature.
The reaction leads to a quick precipitation of titanium dioxide, which is slightly soluble in water. The overall reaction system consists of the following reactions:

Hydrolysis: $Ti(OC_3H_7)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_3H_7OH$

Polycondensation: $Ti(OH)_4 \rightarrow TiO_2\,(agglomerated)\downarrow + 2H_2O$

Disaggregation: $TiO_2(agglomerated) \rightarrow TiO_2$

The volumetric ratio between the two reagent solutions, W = [TTIP]/[NAS], was maintained equal to 2/15, as suggested by Hintz (Hintz et al., 2004). This indication was successfully checked by the Authors in previous works, where several titanium dioxide samples were produced by both SDR and stirred batch reactor and used to reduce by photocatalysis the organic matter of an olive vegetation wastewater stream (Stoller et al., 2007).
In this work, two different reagent injection systems were used as shown in Figure 1.

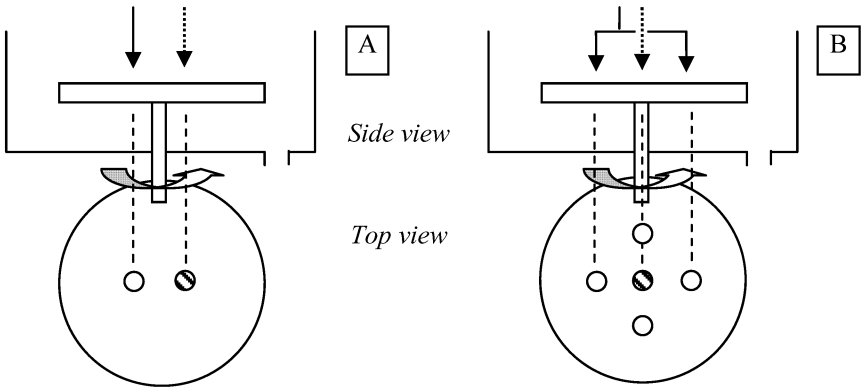

Figure 1: Scheme of the used feeding distribution systems (A. TIS; B. MIS)

Both systems uses the contemporary feeding of the reagent solutions over the disc. In case A, the injection points were placed at the same distance from the radial

centre of the system, thus at 180° each other (TIS). In case B, the aqueous solution was fed at the center of the disc, whereas the TTIP was fed into the liquid film, by a multiple injection system (MIS), at different points placed symmetrically along a circumference. In this study, the effects of both the radial distance of the injection points, r*, (7 cm up to 14 cm from the center) and the number of injectors, n*, (1 to 8) were investigated. The adopted injectors have a diameter, d*, equal to 2 mm.
The flow rate of TTIP, Q_{TTIP}, and that one of the acidified water, Q_w, was 53,3 ml/min and 400 ml/min, respectively, corresponding to a reagent ratio equal to 2/15, and the feeding operation lasted around 1 minute. The adopted amount of the reagents leads theoretically to the production of an overall titania mass $m_{overall}$ of 13,75 g of titanium dioxide. The performances of the precipitation process were evaluated by measuring the produced particle size distribution (PSD) and the stability of the suspension (Z-potential) by means of the instrument Plus 90 supplied by Brookhaven.
In order to evaluate the scaling degree, at the end of each run the titanium dioxide mass deposited over the disc surface and the reactor case walls was collected, dried and weighed. It has to be noticed that in some cases the deposited particles are much larger than those ones collected in the outlet slurry stream, whose size measurement is hereafter reported.

3. Results and Discussion

The objective of the work was, firstly, to investigate the effect of the reagents feeding mode on both the nanoparticles size and suspension stability. The particle size is decreased by increasing nucleation rate and at conditions of low agglomeration. In order to induce a high nucleation rate a huge supersaturation ratio of the limiting reagent and a very high mixing, due to a high turbulence, has to be attained in the reaction volume. Unfortunately, a local very high concentration of reagents gives rise, after the reaction-precipitation process, to a high local particles concentration, which may cause agglomeration. Thus the objective of producing very small nanoparticles by fostering both reagents supersaturation and local turbulence, as for the traditional two feeding point system, TIS, may be in contrast with the purpose of minimizing agglomeration between the produced particles. For this reason, multiple injectors systems, MIS, were considered in this work. For this latter system the water stream, flowing from the center to the periphery of the disc, sweeps away the nanoparticles suspension as soon as precipitation takes place, reducing the number of particles collisions. Moreover, splitting the overall TTIP solution flow in several streams the local produced particles concentration is reduced and the particles collisions as well. In this case, the particles concentration is strictly correlated to the local ratio, W*, between the flow rate of the injected TTIP stream, Q^*_{TTIP}, and that one of the acidic aqueous solution stream crossing the area projected under the injection point, Q^*_W:

$$W^* = Q^*_{TTIP} / Q^*_w \quad (1)$$

The local flow rate of TTIP exiting a single injector is given by:

$$Q^*_{TTIP} = Q_{TTIP} / n^* \quad (2)$$

If we assume that the fraction of the aqueous stream crossing the reaction volume is proportional to the radial chord under the injection tube, assumed on first approximation equal to d*, we have

$Q^*_w = Q_w (d^* / 2\pi r^*)$ (3)

Combining eqs.1, 2 and 3, the following relationship is obtained:

$W^* = (Q_{TTIP} / Q_w) (2\pi r^* / d^* n^*)$ (4)

If the feeding of TTIP is continuously distributed along a disc circumference, the "ideal" flow rate ratio between TTIP and water, is equal to the two feedstream flow rate, W. It is useful to adopt a local point dimensionless TTIP/water ratio, W^*_d, by assuming:

$W^*_d = W^* / W$ (5)

The local turbulence may be expressed as the specific dispersed power ε , determined by the hydrodynamic of the two reagent solutions at the mixing point. In case of TIS, both the two reagent solutions are assumed to have a tangential velocity and the specific energy can be calculated as follows (Moore, 1996):

$$\varepsilon = \frac{1}{2t_{res}} \left\{ \left(r^2\omega^2 + u^2\right)\Big|_R - \left(r^2\omega^2 + u^2\right)\Big|_{r^*} \right\} \quad (6)$$

$u = (\rho_L Q_L^2 \omega^2 / 12\pi^2 \mu_L r)^{1/3}$ (7)

$$t_{res} = \frac{3}{4}(12\pi^2)^{1/3} \left[\frac{\mu_L (R^4 - r^{*4})}{\rho_L \omega^2 Q_L^2} \right]^{1/3} \quad (8)$$

where t_{res} denotes the residence time of the liquid solution on the spinning disc, r the radial distance from the center of the disc, ω the angular velocity of the disc, u the average velocity of the liquid solution on the disc, Q_L the flow rate on the disc, ρ_L the density of the solution and μ_L the viscosity of the solvent.The results obtained for both injection systems are reported in Table 1.

Table 1: Operating parameters and experimental results

System	r* [cm]	n*	L_P [nm]	L_C [nm]	W^*_d	Z potential [mV]	ε [mW/g]	m% [%]
TIS	5	-	1	21	1,0	31	711,4	> 90,0
TIS	10	-	2	75	1,0	30	219,1	> 90,0
TIS	14	-	5	112	1,0	35	49,6	> 90,0
MIS-1	7	1	55	146	20,9	184	-	> 90,0
MIS-1	10	1	90	197	41,8	158	-	76,9
MIS-1	12	1	136	313	58,6	106	-	56,8
MIS-1	14	1	188	422	58,6	122	-	54,6
MIS-2	7	2	44	119	14,6	142	-	88,9
MIS-2	10	2	142	144	20,9	101	-	68,7
MIS-2	12	2	155	304	25,1	123	-	54,8
MIS-2	14	2	201	478	29,3	144	-	53,1
MIS-8	7	8	12	41	3,7	99	-	22,4
MIS-8	10	8	22	65	5,2	121	-	15,4
MIS-8	12	8	26	89	6,3	101	-	0
MIS-8	14	8	28	115	7,3	104	-	0

In Table 1 L_P is the most frequent size and L_C is the mean particle size on the crystal number basis and the mass of scaling has been reported as the ratio between the experimental value $m_{scaling}$ and the overall predicted precipitated mass, $m_{overall}$ that is:

$m\% = 100\ m_{scaling} / m_{overall}$ (9)

In case of MIS, the specific energy at the mixing point of the two solutions is expected to be much reduced with respect to the TIS case since the tangential component of the aqueous stream velocity is only a small portion of the overall velocity. Accordingly, both the values of the velocity u and the specific energy ε should be strongly decreased.
The specific energy was calculated only for TIS arrangement, since eq. (6) refers only to this configuration. Among the different feeding point configurations the best ones seem to be: the TIS with feed point at 5 cm and the MIS-8 with feed point at 7 cm. In fact, the first configuration assures the minimum size generated crystals, due to the highest specific energy involved, whereas the second feeding system allows to obtain a suitable size of the produced nanocrystals together with a high particle stability shown by a Z-potential value around 100 mV.
A more deep investigation on the achieved performances is allowed by the PSDs, on volume basis, for the two best runs, reported in Figs. 2 and 3, respectively.

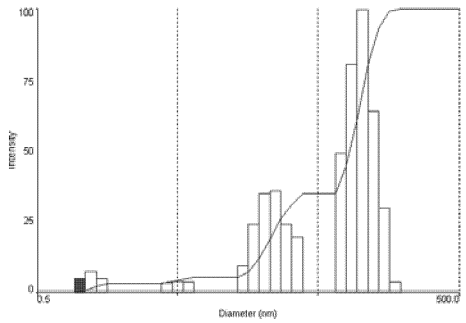

Fig. 2: PSD for TIS (feed point at 5 cm)

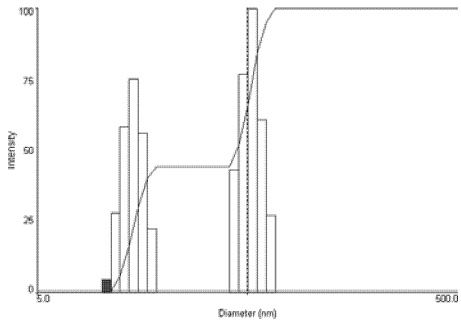

Fig. 3: PSD for MIS-8 (feed point at 7 cm)

An interpretation of the obtained size distributions is as follows. When we produce very small crystals of 1 nm, i.e. in the TIS case, each of them is relatively poorly charged by the ions of the added acid in solution, as shown by a low Z-potential, and is very prone to agglomeration, in particular in presence of high turbulence. On the contrary, the larger crystals, generated in the MIS-8 run, have a smaller overall total area and are more charged for unit surface at a constancy amount of acid cations in solution, and as a consequence, they are more stable and have a lower tendency to agglomeration.
It is possible, thus, to conclude that:

- The lowest value of particle size may be obtained for the application of the TIS at the minimum radial distance from the center. This is because of the maximum specific energy attained at the mixing point which determines micromixing conditions (Baffi et al. 2002). The generated nanoparticles, probably 1 nm in size, give rise to a high agglomeration and, as a consequence, big particles are formed. They segregate and a large scaling over the disc surface takes place.
- When MIS is applied a significant increase of the mean particle size occurs if one or two TTIP feeding point are adopted. On the contrary, when the overall TTIP solution is split in 8 streams we have a slight crystal size increase with respect to the TIS series of runs, but scaling, due to particles agglomeration, is strongly decreased. These results of the run MIS-8 with the TTIP feed point at 7 cm from the disc center may be justified on the light of the W^*_d and Z-potential values. A value of W^*_d

equal to 3.7 means to have a higher ratio between TTIP and water, with respect to the suggested value of 1, but still enough high to assure a number of water molecule equal or higher than those one of TTIP. In this case TTIP is still the limiting reagent and the operating supersaturation is high enough to generate low nanoparticles, but at the same time the particle concentration is reduced with respect to the TIS case. This fact together with a low Z-potential entails a smaller agglomeration.

4. Acknowledgments

Authors gratefully acknowledge the financial support received by LABOR Srl (Rome, Italy).

5. Acknowledgments

Altman I.S., Agranovski I.E., "Mechanism of nanoparticle agglomeration during the combustion synthesis", 2005, Applied Physics Letters 87

Baffi G., Cafiero M.L., Chianese A., Jachuck J., "Process Intensification: Precipitation of Barium Sulphate Using a Spinning Disc Reactor (SDR)", Industrial Engineering Chemistry Research 41 (2002) 5240-46

Cao G., "Nanostructures and Synthesis: Properties and Applications", Imperial College Press, 2004.

Helz D.R., Zepp R.G., Crosby D.G. (Eds.), "Aquatic and Surface Photo-Chemistry", Lewis Publishers, Boca Raton, 1994.

Hintz W., Nikolov T., Yordanova V., Tomas J., "Generation of titania nanopowder via sol gel synthesis", 2004, CHISA 2004 Proceedings.

Lesheva I., Peev G., "Film flow on a horizontal rotating disc", 2003, Chemical Engineering and Processing Volume 42, Issue 11 925-929

Moore S. R., "Mass Transfer to Thin Liquid Films on Rotating Surfaces, with and without Chemical Reaction", Ph.D. Dissertation, University of Newcastle upon Tyne, Newcastle upon Tyne, U.K., 1996.

Stoller M., Mescia M., Valencia Peroni C., Chianese A., "Control of the crystal size distribution of titanium dioxide particles using a spinning disc reactor", 2007, AIDIC Conference Series 311-316.

Stoller M., Chianese A., "Process Intensification techniques for the production of undermicronic particles by precipitation", 2005, Compositi e Nanotecnologie 1 45-49, ISSN 1826-4697.

Stoller M., Miranda L., Chianese A., "Organic matter reduction in an olive vegetation waste water by photocatalysis with titanium dioxide nanoparticles", 2007, Ecomondo 2007 Proceedings.