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OPTIMAL FEED LOCATION IN A SPINNING DISC REACTOR FOR THE PRODUCTION OF TiO2 NANOPARTICLES

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In this work the influence of feed location over a rotating spinning disc reactor is investigated. 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 configuration which provides a good quality of the produced titania nanoparticles by minimizing the reactor scaling. It was found that a multiple reagent injector system get this target, allowing a production of titania particles under 100 nm in size and a negligible scaling over the disc surface.

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 for industrial applications since it involves a much smaller specific energy consumption (Baffi 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 negligible growth of the originated particles and decrease of agglomeration phenomena.
Micromixing conditions over the SDR surface is more easily achieved when 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 critical concentration values are locally 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 solution is required (Hintz et al., 2004).
The agglomeration phenomena are enhanced by the particles collisions and reduced by the potential of the electric double layer surrounding each particle in suspension, due to the presence of ions in solution. This electric potential is expressed by the Z-potential value of the suspension. Agglomeration rate is increased at low absolute Z-potential values, since, in this case, the collision energy of two particles overcomes 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 an SDR on titania nanoparticles agglomeration was experimentally investigated, with reference to the precipitation of titania nanoparticles. Different feeding configurations were examined: the traditional two points injection system (TIS) and different configuartions of multiple injector systems (MIS).

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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 separately feeding on the disc surface the two reagent solutions, respectively titanium tetraisopropoxide (TTIP) and 0.1 M nitric acid (NAS). All the runs were performed 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 reaction steps:

Hydrolysis: $Ti(OC_3H_7)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_3H_7OH$
Polycondensation: $Ti(OH)_4 \rightarrow TiO_2\,(\text{agglomerated})\downarrow + 2H_2O$

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 titanium dioxide was produced by both SDR and stirred batch reactor and used to reduce by photocatalysis the organic matter of an olive vegetation wastewater (Stoller et al., 2007).
In this work, two different reagent injection systems were used as shown in Figure 1.

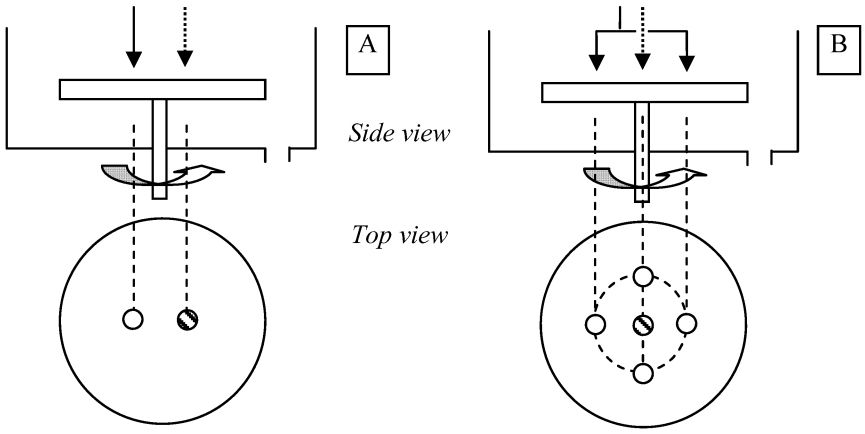

Figure 1: Scheme of the used feeding distribution systems (A. TIS; B. MIS)

Both systems use 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 an internal 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 solid 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), in the range size 1-6000 nm, 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.

3. RESULTS AND DISCUSSION

The objective of the work was, primarily, to investigate the effect of the reagents feeding mode on both the nanoparticles size and suspension stability. The particle size decreases by increasing nucleation rate and increases at higher agglomeration conditions. In order to induce the maximum value of nucleation rate micromixing has to be attained, since it allows to maximize the product concentration and the local supersaturation, as well. Unfortunately, in such case there is also a very high density of the local solid mass slurry, which gives rise to a strong agglomeration of the produced particles. Thus the objective of producing very small nanoparticles by fostering the reagents mixing, 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 related 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, that is

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

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

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

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

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

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, whereas when there is a splitting of the overall flow rate of one of the TTIP in several points of a circumference at the feeding point the ratio TTIP/water decreases. For the analysis of the experiments results, it is useful to adopt a local point dimensionless ratio TTIP/water ratio, W^*_d, equal to:

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

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):

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

The average velocity of the liquid on the disc, u, and the residence time of the liquid, t_{res} , may be calculated by the expressions:

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

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

where r^* is the radial distance from the center of the disc, ω the angular velocity of 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:

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

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, 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.
The scaling is due by the agglomerated particles, which have a micronic size and are segregated over the disc surface, whereas the particles collected in the outlet stream from the disc case concern only those ones only partially agglomerated. Therefore, looking at the results reported in Table 1 concerning the particle size it is clear that adopting a TIS configuration we have a very high mixing of the reagents leading to a very small size of the particles, but at the same time we have a very high local mass slurry, which enhances agglomeration and scaling. If a MIS asset is adopted the lower expected local product concentration does not allow the production of very small particles, but, due to a reduced slurry value, agglomeration is decreased and scaling as well. For all the MIS runs the stability of the suspension is quite high, as shown by values of Z-potential around or higher 100 mV. For TIS configuration the smaller particles size is obtained for the case with the feeding point at 5 cm from the disc center, corresponding at the highest value of the local dispersed energy. Among the runs performed with a MIS configuration, the best results, in terms of low particle size and low scaling, were obtained for the case MIS-8 with feed point at 7 cm.
A more deep investigation on the achieved performances is allowed by looking at the PSDs, on volume basis, for the two best runs with TIS and MIS system, reported in Figs. 2 and 3, respectively.

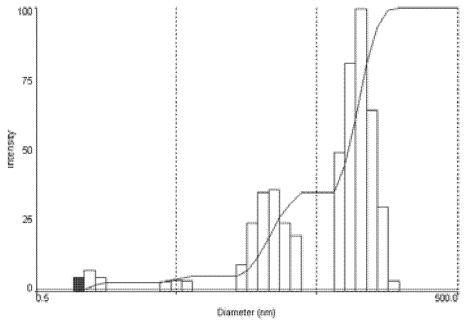

Fig. 2: PSD for TIS (feed point at 5 cm)

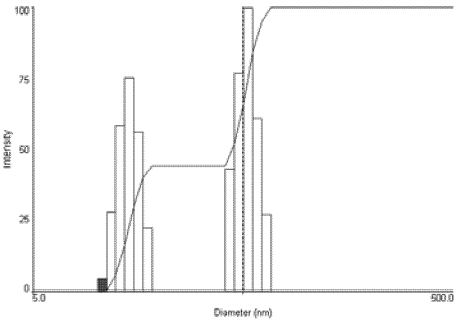

Fig. 3: PSD for MIS-8 (feed point at 7 cm)

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 a higher charge density over their surface. 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 configuration 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 the MIS configuration 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. The minimum size of the obtained nanoparticles obtained, for the configuration MIS-8 with the TTIP feed point at 7 cm from the disc center may be justified on the light of the W^*_d. By increasing the value of the dimensionless ratio W^*_d the local ratio between the concentrations of TTIP and water is decreased. At a value of W^*_d equal to 3,7 the ratio between TTIP and water is still higher than the stechiometric one, thus TTIP is still the limiting reagent. In this case the operating supersaturation is, in principle the maximum achievable, and very small nanoparticles are generated. By increasing the W^*_d value the ratio TTIP/water becomes lower than the stechiometric one and the local product concentration is smaller than the maximum one, entailing lower values of the nucleation rate.

4. ACKNOWLEDGMENTS

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5. REFERENCES

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.