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Synthesis of TiO₂ nanoparticles in a Spinning Disc Reactor

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Abstract

Reactive precipitation of TiO₂ in a spinning disc reactor (SDR) has been performed. Physical parameters such as rotational speed, disc surface texture, and operating parameters such as flowrate, ratio of water to precursor and location of feed introduction points have been studied in terms of their effects on TiO₂ particle size, particle size distribution (PSD) and particle yield. Smaller particles of less than 1 nm mean diameter with narrower PSDs are generally formed at higher yields at higher disc speeds, higher flowrates and on grooved disc surfaces, all of which provide the best hydrodynamic conditions for intense micromixing and near ideal plug flow regime in the fluid film travelling across the disc surface. Similar observations are made for particle characteristics at higher water/TTIP ratios which are attributed to the increased rate of the hydrolysis reaction favouring nucleation over growth. The introduction of the TTIP feed stream into the water stream away from the centre of the disc is also conducive to the generation of smaller and more uniformly sized particles due to the greater energy dissipation for improved micromixing at these locations. Comparisons with reactive-precipitation of TiO₂ in a conventional stirred tank reactor (STR) also demonstrate that the SDR performs better in terms of much improved particle characteristics and higher TiO₂ yields per unit processing time. This is attributed to more uniform and intense mixing conditions in the smaller volume, continuous SDR than in the STR.

Key words: spinning disc reactor, TiO₂, particle size, particle size distribution, mixing, yield

1. Introduction

Nano titanium dioxide (TiO_2) is widely used commercially in a variety of products such as white pigment, white food colouring, pharmaceutical and cosmetic products, skin care products, surface coatings and UV-irradiated photocatalysts for the decomposition of pollutants and air purification [1-4]. Due to their large surface area and strong interactions with metal catalysts, mesoporous nano TiO_2 particles have also found application as catalyst supports in metal catalysed oxidation [5-7] and hydrogenation [8] processes of significant importance. The industrial manufacture of titanium dioxide is generally based on either the chloride process or the sulphate process involving the naturally occurring rutile or ilmenite ores [9-11]. The chloride process consists of an initial reaction step between rutile and chlorine gas to form titanium tetrachloride which on heating in the presence of air or oxygen produces TiO_2 . In the sulphate process, concentrated sulphuric acid converts iron titanium oxide or ilmenite into titanium sulphate solution, which upon hydrolysis, forms a precipitate of TiO_2 particles [12]. Both processes are highly environmentally unfriendly as they result in large amounts of toxic waste by-products such as acidic ferrous sulphate [12]. On the other hand, the synthetic production of TiO_2 nanoparticles typically proceeds via a relatively more benign sol-gel process involving hydrolysis of a titanium (IV) alkoxide precursor in the presence of acidified water or alcohol (sol process) and thereafter polycondensation to remove the water molecules from the titanium hydroxide molecules to form a gel [2, 13]. The hydrolysis step has been documented to be so fast that it can lead to widespread inhomogeneity in particle characteristics if it is not adequately controlled when conducted in conventional stirred equipment [14]. In practice, methods used to deliberately slow down the hydrolysis step include diluting the precursor in alcohol and dropwise addition of the diluted precursor stream to the water stream [15, 16].

Process intensification has emerged over the last decade as one of the most promising development tools in the chemical process industry. It offers several potential benefits in process improvement, the primary ones being enhancement of production efficiency and process safety

considerations, lower cost, and minimisation of waste at source leading to reduced environmental pollution [17, 18]. In recent years, spinning disc reactors (SDRs) have been developed as a process intensification technology, where rapid mass and heat transfer rates can be obtained in the thin film of liquid produced due to centrifugal acceleration created by the rotation action [19]. In developing these characteristics, the SDR is considered a tool of process intensification due to its compactness, flexibility as an inherently safe and continuous reactor technology and capability to deliver better product quality in a diverse range of applications such as crystallisation and polymerisation.

In reactive-precipitation processes, SDR processing has been shown to facilitate improved methods of precipitation of organic and inorganic nanomaterials [20]. For example, in the liquid/liquid precipitation of barium sulphate [21, 22] and gas-liquid precipitation of calcium carbonate [23], significantly smaller crystals with a narrower size distribution than the conventional stirred tank technique have been shown to be feasible. More recently, the production of titanium dioxide with favourable nanoparticle characteristics has been demonstrated in a smooth surface spinning disc reactor both at ambient temperature [24] and at very high temperatures of 400-550°C [25]. According to the authors, the added advantage of the latter process is the in-situ production of anatase TiO_2 suspended in polyethylene glycol (PEG) at the elevated temperatures without any further calcination. Nevertheless, the need for the post-processing, energy-intensive removal of the high boiling point PEG used in place of water to yield pure TiO_2 remains.

There are a number of salient characteristics of the SDR which make it the apparatus of choice for production of nanoparticles by precipitation, one of which is its ability to provide a uniform and rapid micromixing environment when two liquid streams are contacted on the rotating surface [26, 27]. The highest degree of micromixing is mostly accomplished under vigorous hydrodynamic conditions generally generated at high disc rotational speeds and high feed flow rates [27]. Micromixing in precipitation processes is critically important because it has a direct impact on both nucleation and crystal growth kinetics [28]. It controls the formation and local distribution of supersaturation in the medium, which directly influences the nucleation

process. The growth process, on the other hand, is determined by the rate of molecular diffusion to the growing crystals, which is also dependent on the prevailing level of micromixing albeit to a lesser extent than the distribution of supersaturation. Another aspect is the near ideal plug flow conditions achievable in a SDR under a wide range of disc speeds and flowrates [29] which should be beneficial for producing much more well-defined crystals in terms of their size, morphology and purity [30]. Moreover, Cafiero et al. demonstrated that the energy input in the spinning disc process was much lower than the use of a T-mixer arrangement, suggesting that operating costs would also be reduced along with better control of particle characteristics [22].

The main novelty of the present work lies in determining the effects of several SDR operating parameters on the synthesis of TiO_2 by precipitation via the sol-gel route at a relatively low processing temperature of 50°C and the optimisation of combinations of these parameters in order to control the size and yield of particles to the desired level. Although the SDR has previously been demonstrated for precipitation of TiO_2 by the acid-hydrolysed sol-gel route at similar temperatures used in this study (50°C) [24], not only has there been no systematic study of the hydrodynamic effects of SDR on TiO_2 quality and yield undertaken to date but the effect of textured disc surfaces on TiO_2 characteristics has also not been investigated. Disc topography has previously been shown to have a significant beneficial effect on micro and macromixing in the thin film [29, 31]. The present work therefore aims to determine the optimised operating conditions required in the SDR, with the type of disc surface included as a variable parameter, for the production of TiO_2 nanoparticles in order to enhance the production efficiency and quality of the products.

2. Materials and Methods

In this work the sol-gel process was employed in the formation of titanium dioxide according to the following reaction steps [32-34]:

Hydrolysis:

Poly-condensation:

Two simultaneous reactions involving hydrolysis of titanium tetra isopropoxide (TTIP) with acidified water of pH 1.5 and polycondensation of the resulting titanium tetrahydroxide occur to produce a colloidal suspension of particles, with nitric acid serving as an acid catalyst in hydrolysis step of the sol-gel process for TiO_2 [35]. The nucleation stage of the precipitation process is regarded to be very fast as evidenced by the typically short characteristic time of the primary hydrolysis-condensation reactions in sol-gel solutions, which, for the TTIP precursor, is in the range of tens of milliseconds [36, 37]. It is expected that not all the condensation steps leading to amorphous TiO_2 would be completed in one SDR pass as it is relatively slow compared to the primary hydrolysis-condensation step. Rather, it is anticipated that a mixture of hydrated TiO_2 and titanium hydroxide would be formed in the colloidal suspension obtained directly from the disc prior to heat treatment. In fact Soloviev et al.[38] even suggest that a structure of the form $\text{TiO}_a(\text{OH})_b(\text{OR})_{4-2a-b}$ (where R represents the alkoxide group C_3H_7 in this work) may exist at some stage in the process due to incomplete hydrolysis and condensation, whereby all the R groups would be eventually replaced on hydrolysis. It is therefore entirely conceivable that particle of a mixed nature would be present in the suspension. Whilst recognising the above, particles formed in the SDR prior to heat treatment will henceforth be referred to as amorphous TiO_2 particles for the sake of simplicity.

To characterize and predict the performance of the SDR, TiO_2 precipitation experiments were performed on a smooth and grooved 30 cm diameter stainless steel rotating discs. Beneath the disc is a chamber through which heating fluid circulates to maintain the disc at the desired temperature of 50°C. The chamber is supported on an electric motor driven double pipe rotating shaft. The grooved disc consists of 8 concentric grooves machined in the surface. The schematic set up of the rig is illustrated in Figure 1.

TTIP (the precursor) and acidified water ($\text{pH} = 1.5$) were introduced at desired flowrates to the surface of the disc via stationary single point distributors located at 5 mm from the disc surface. TTIP was injected into the water film at 3 different radial positions: at the centre (1) of the disc and at 5 cm (2) and 10 cm (3) radial distance from the centre as shown in Figure 2.

For each run, two samples of 2 mL volume each, were taken at constant time intervals from the disc collector and rapidly introduced into 20 mL of 0.02 wt% gelatine solution. This method was suggested by earlier studies to avoid agglomeration and settling of particles [22].

To benchmark the SDR data, a stirred tank reactor (STR) consisting of a water-jacketed 250 mL capacity 'Pyrex' glass vessel was employed at a reaction temperature of 50°C . The reaction mixture was agitated by a 3-blade propeller impeller of 4.4 cm diameter placed about 4 cm from the bottom of the vessel. TTIP was added to the acidified water ($\text{pH}=1.5$) in the reactor via an inlet tube positioned above the water surface and a syringe pump set to deliver various TTIP flowrates in the range 5-20 mL/min to get a final ratio of water to TTIP of 20. All the STR experiments were performed at a water:TTIP ratio of 20 in order to avoid excessive formation of particles that would cause blockage in the system. Product samples were taken one minute after the addition of the TTIP and analysed using a high performance particle sizer (Model HPPS-Malvern instruments, UK).

A E61M014 conductivity probe of 4 mm diameter and 103 mm length, linked to a CDM210 conductivity meter (Hach-Lange Ltd.), was used for measuring the conductivity of all collected samples in order to determine the TiO_2 yield. Stanely et al. also applied conductivity measurements to monitor concentration variations in semibatch precipitations of barium sulphate and showed that conductivity versus time profiles during the reaction are of strong interest as they reveal the kinetic complexities intrinsic in precipitation reactions [39]. Additionally, Ghiasy et al. recently demonstrated that in the precipitation reaction of barium sulphate, conductivity could be used as an online controlled variable in a control related study of the SDR [40].

A conductivity-reaction time profile was established in the STR by taking measurements every 200 millisecond which were logged on a computer with a DaqPro 5300 data logger. The

conductivity probe was calibrated prior to its use in these experiments against a gravimetric technique for one set of STR experiments, in which 10 mL samples were taken at regular intervals over a period of one minute and dried overnight in an oven for particle yield measurement. Based on the conductivity-yield linear relationship, the conductivity measurements can be directly used to obtain yields of different samples coming off the disc.

2.2. Characterisation of TiO₂ nanoparticles

Particle sizes in the sol were measured via dynamic light scattering (Model HPPS- Malvern instruments, UK) using a He-Ne laser as light source ($\lambda = 633$ nm). All size measurements were carried out at 25°C. This Non-Invasive Back-Scatter (NIBS) optical technique enabled high concentration and sensitivity measurements over a broad size range of 0.6 to 6000 nm diameter. Samples coated onto carbon grids were also characterised by Transmission Electron Microscopy (TEM) to investigate their morphology. Selected samples were also heated in a furnace up to 400°C for 1 hour prior to being subjected to Scanning Electron Microscopy (SEM), Energy-Dispersive X-Ray Spectroscopy (EDS) and X-ray diffraction (XRD) analysis to assess the morphology, constituent species and phase of titania after the heat treatment.

2.3. Design of Experiments

In this study the response surface method (RSM) [41] was applied for three significant factors and six replicates of the centre point runs. The five level factors with their coded and uncoded values are shown in Table 1. These parameters were selected on the basis of their potential hydrodynamic influence on the crystal properties, with the range of values chosen on the basis of available equipment capability. A total of 20 experimental runs, including the centre point replicates, were conducted for each disc texture in order to define the particle size and yield values. Design Expert 8.0 statistical software package (Stat-Ease, Inc., Minneapolis, USA) together with regression analysis was used to estimate the second order polynomial coefficients

whilst surface plots generated from the quadratic models obtained enabled visual depiction of the main and interaction effects for each variable.

3. Results and Discussion

3.1. Effect of rotational speed

Figure 3 shows the effect of rotational speed on particle size distribution, both on a % volume and % intensity basis to highlight the similarities between the data. Increasing the disc rotational speed from 400 to 1200 rpm results in a decrease of the particle size and a narrowing of the PSD. At higher disc speed, shear rate within the film is enhanced [42] and the intensity of film surface wave formation is also greatly increased [43]. Both of these disc speed effects are expected to lead to improved micromixing in the film, as has recently been demonstrated experimentally [26, 27]. The degree of micromixing attained under the range of hydrodynamic conditions in our study may be analysed in terms of a theoretical micromixing time, which on comparison with the experimental induction time of titanium dioxide precipitation process can give a useful insight into the relative impact of micromixing on the particle formation steps during the nucleation phase. This follows a similar approach implemented by Cafiero et al [22] and more recently by Ghiasy et al. [40]. Based on a Schmidt number ($Sc = \nu/D$) of 22851 (where ν , the kinematic viscosity of water at 50°C is $5.53 \times 10^{-7} \text{ m}^2/\text{s}$ and the Stokes-Einstein diffusion coefficient “D” for TiO_2 nanoparticles is estimated to be $2.42 \times 10^{-11} \text{ m}^2/\text{s}$ [44]), the micromixing time constant can be determined from Eq. (1) which is applicable when molecular diffusion is accelerated by shear deformation of the fluid) [45]:

$$t_{micro} \cong 2 \left(\frac{\nu}{\dot{\epsilon}} \right)^{\frac{1}{2}} \text{arcsinh}(0.05Sc) \quad (1)$$

The energy dissipation rate in liquid flowing on the disc has been estimated by Khan [46] and reproduced by Cafiero et al. [22] and Ghiasy et al. [40]:

$$\varepsilon = \frac{1}{2t_{res}} \{ (r^2\omega^2 + u^2)_o - (r^2\omega^2 + u^2)_i \} \quad (2)$$

The average velocity, u , and the residence time, t_{res} , of the liquid solution on the disc are estimated by Eq.3 and 4 respectively, following the Nusselt theory [40]:

$$u = \left(\frac{\rho_L Q^2 \omega^2}{12\pi^2 r \mu_L} \right)^{1/3} \quad (3)$$

$$t_{res} = \left(\frac{81\pi^2 \nu}{16\omega^2 Q^2} \right)^{1/3} \left(r_o^{4/3} - r_i^{4/3} \right) \quad (4)$$

As illustrated in Figure 4, the micromixing time for rotational speeds of 200-1200 rpm and total flow rate of 3.6, 10.8 and 18 mL/s and, range from around 0.3 ms to 6 ms. Figure 4 clearly shows that the shortest micromixing time is achieved at highest rotational speed of 1200 rpm and highest flowrate of 18 mL/s. It is noteworthy that a very recently completed modelling study of micromixing time, based on experimentally determined micromixing efficiencies in the SDR, suggests that micromixing time may in fact be up to 2 orders of magnitude smaller than the theoretically predicted time constant from Eq. 1 [47]. The induction time for the clustering of particles in the sol-gel precipitation process of TiO_2 critically depends on the TTIP concentration (C_{Ti}) and hydrolysis ratio $H = C_W / C_{Ti}$, where C_W is water concentration, as defined by Eq 5 [38]:

$$t_{ind} = 0.15 C_{Ti}^{-1.5} (C_W - 1.45 C_{Ti})^{-4.7} \quad (5)$$

Compared to the stated micromixing times, the estimated induction time is in the range 0.027 to 0.067 ms applicable to H values in the range 99 to 131. Due to the very short micromixing times, especially at the highest disc speeds, as highlighted above, nucleation would be favoured over growth resulting in the formation of smaller particles [48]. A similar effect of disc rotational speed on particle size has been reported in a number of reactive-precipitation processes [22, 23, 49, 50].

Whilst the micromixing rate is rapid enough to directly influence the rate of precipitation, macromixing, on the other hand, is generally a slower process which has negligible impact on the reaction rate [45]. However, macromixing, which influences the residence time distribution of reagents, is important in establishing the distribution of reactants and consequently the supersaturation ratio in the reactor volume. Thus, significant spatial variations in supersaturation ratios in the reactor environment are often caused by slow macromixing, resulting in distinct regions with high nucleation rates (where supersaturation ratios are high) and those with comparatively higher growth rates (where supersaturation ratios are lower). Such non-uniform distribution of supersaturation ratios can therefore lead to significant widening of PSD and a deterioration of product quality [51]. Under conditions of higher disc speeds in the SDR, residence time distribution of the liquid film on the disc has been shown in an earlier study to become tighter [29]. This would give uniformly high supersaturation in the film as it travels over the disc surface which could account for the reduction in the particle size distribution observed at higher disc speeds in Figure 3.

3.2. Effect of Flowrate

Figure 5 shows that an increase in the flowrate from 3.6 to 18 mL/s induces a significant reduction in the mean particle size. In terms of the hydrodynamics phenomena taking place in the film, an increase in flowrate has a similar influence to an increase in disc speed, it causes higher shear in the film and more surface ripples and hence better mixing between the two reactant solutions, resulting in even and homogenous distribution of the reaction zones [27, 29]. As presented in Figure 4, the micromixing time constants for flow rates between 3.6 and 18 mL/s, are consistently below 1 ms at disc speeds beyond 800 rpm. Under such intense mixing conditions, nucleation would be favoured over growth. Furthermore, at higher flowrates, the lower residence time would reduce the potential for particle growth and agglomeration, as highlighted by corresponding TEM images shown in Figure 6 where a cluster of agglomerated particles can be observed at the lower flowrate in contrast to individual particles of much smaller sizes at the

higher flowrate. Similar influences of the residence time on the reduced potential for growth and agglomeration have been observed by Marchisio et al. in a TiO_2 precipitation process [52].

3.3. Effect of disc surface texture

The texture of the disc surface has been shown to govern the hydrodynamic characteristics of the film such as its residence time distribution and intensity of surface wave formation [29, 53], resulting in a marked enhancement of film transport properties [53]. In the present study, we have investigated the effect of a grooved and a smooth disc on particle characteristics. As shown in Figure 7 and Figure 8, the grooved disc results in smaller particle size and narrower particle size distribution as compared to smooth disc. A narrow particle size distribution for the production of silver nanoparticles was also achieved by Iyer et al. [54] using a grooved disc. Similar enhancement effects of grooved surfaces have also been reported for styrene polymerisation in the SDR [19]. Earlier studies on gravitational film flow on inclined surfaces have indicated that rivulet flow may be effectively overcome on textured surfaces, thus proving the opportunity for more continuous films to form and propagate across such surfaces and resulting in generally thinner films with better surface coverage [55]. Thus, the intensifying effects of the grooved disc in this investigation may be related to the ability of the grooves to encourage more steady, continuous film flow than the smooth disc at a given set of operating conditions, with film breakdown leading to rivulet flow occurring, if at all, at much lower flowrates than on the smooth disc. This hypothesis has indeed been validated in a recent residence time distribution study involving grooved and smooth disc surfaces in a SDR [29].

3.4. Effect of water/TTIP ratio

Figure 9 shows the effect of the ratio of water to TTIP on particle size distribution. A decrease in the mean particle size is observed when the ratio of water/TTIP is increased from 6 to 20. Lower initial concentrations of TTIP compared to water have been shown in an earlier study to favour nucleation rather than growth [56] and our results conform to these findings. The

concentration of TTIP also has a significant influence on the morphology of the prepared TiO_2 . Small spherical TiO_2 particles with narrow size distributions can be prepared when the precursor ratio is low (Figure 10(a)). In contrast, as shown in Figure 10(b), when the water-to-TTIP ratio is low, the prepared TiO_2 sample exhibit irregular morphologies, agglomeration, and a wider size distribution.

The effect of the water/TTIP ratio may be explained in terms of the extent to which the concentration of water affects the rate of hydrolysis. Soloviev et al [57] report that initial hydrolysis reaction is very fast and its time duration is much shorter compared to the whole induction period and the limiting processes determining the induction time are the reactions of additional hydrolysis and condensation reactions. Thus, Baros et al [58] used the amount of water remaining after the nucleation, instead of the amount of water put initially in the system, to define the kinetics of this process. The rate of nucleation may be estimated using following expression [58]:

$$\text{Rate of nucleation} = k(H - 1)^\beta \quad (6)$$

Where k is constant, H is the ratio of water to TTIP and β approximately is 2.12 corresponding to our experimental conditions. According to Eq. 6, the rate of nucleation increases when hydrolysis ratio increases. This behaviour has been attributed to facilitated release of R-OH group from active complex in reaction mixture at larger values of H . Oskam et al [59] also showed that at high water concentration, there is a significant increase in the rate of hydrolysis thereby producing ultrafine primary particles. The results were consistent with the findings of an earlier study which showed that when the precursor concentration was reduced (i.e H is increased), the length and the number of the aggregates decreased markedly [60].

3.5. Effect of feed input location

Several runs were carried out at constant flowrate and different rotational speeds at different radial distances of 0, 5 cm and 10 cm from the centre, to evaluate the effect of the feed injection point. In these experiments, the water stream was injected at the centre whilst the TTIP

stream was fed at the chosen radial positions. Figure 11 and Figure 12 show that by injecting the TTIP at increasing distances from the centre, there is a marked decrease in particle size and breadth of the PSD.

It is probable that there is significantly better mixing between the injected TTIP stream and the already established, more synchronised flow of water over the outer section of the disc in contrast to the inner zones of the disc close to the centre where the flow experiences a hydraulic jump before coupling properly with the rotating disc [61]. Furthermore, increased shear rate as the film thins out towards the edges would contribute to enhancing the mixing process between the two streams. Under these conditions, it is likely that nucleation rates are higher and more uniform throughout the film in this highly mixed environment, giving smaller particles with narrower PSDs. Moreover, with injection further way from the centre, the residence time of the mixed fluid stream is reduced (Table 2). This is also likely to contribute to reducing the extent of growth of the particles or agglomeration, resulting in smaller particles and yield. These results are consistent with a recent study on the production of hydroxyapatite nanoparticles in a spinning disc reactor, where the authors also observed that the mean size of the produced particles was decreased for a feed point of 3 cm from the centre [62].

As presented in Table 2, the calculated residence time of the mixed feed streams reduced with increasing distance of the TTIP injection point from the centre, resulting in a higher specific dispersion energy and even shorter micromixing time, which may be responsible for more homogenous nucleation producing smaller particles.

3.6. Optimisation of results by Response Surface Methodology

The surface plots in Figure 13a-f show that higher rotational speeds, higher flowrates and higher water/TTIP ratio all reduce the particle size. It is expected that film breakdown is likely to occur at very low flowrates and low disc speeds in the SDR, leading to a marked reduction in micromixing within the film, as has been highlighted in our earlier investigations on micromixing and residence time distribution on spinning discs [27, 29]. In contrast, higher flowrates and disc

speeds have been shown not only to encourage more continuous film formation across the whole of the disc surface but also to lead to more intense film surface ripples [43, 63] which further contribute to the enhancement of micromixing in the liquid.

The analysis of variance (ANOVA) for mean particle size on the smooth disc (Supplementary 1) shows that the interaction of rotational speed and flow rate is significant (p -value < 0.05). This is clearly evident in the interaction plot in Figure 14 which suggests that the higher rotational speed of 1200 rpm could effectively overcome the detrimental effect of film breakdown at low flow rates, and statistically result in similar small particle size as at higher flowrates. Operating at higher disc speeds is therefore clearly an advantage in achieving smaller particles in this particular process.

These surface plots also show that, at similar operating conditions, the grooved disc (Figure 13e-f) can produce smaller particles than the smooth disc over a wider set of operating conditions. Thus, by simply texturing a surface, there is more opportunity to produce the desired characteristics without incurring a large energy penalty, as lower rotational speeds can yield similar particle characteristics as those obtained on an untreated surface.

Whilst variations in the disc speed, liquid flowrate and surface texture give rise to physical hydrodynamic effects in the thin films as described above, the water/TTIP ratio contribute to the chemical effects in the precipitation process. In particular the nucleation rate increases proportionally with the water/TTIP ratio as highlighted in section 3.4, implying the formation of smaller particles. This effect is clearly evident in the surface plots shown in Figures 13 b,c, e and f which also highlight that both physical effects of the film hydrodynamics and the chemical effect of hydrolysis ratio have to be jointly maximised to obtain the smallest particle sizes.

The ANOVA for the mean particle size in grooved disc (Supplementary 2) shows that all the main effects are dominant and statistically significant. In contrast to the smooth disc analysis, the combination of factors for the grooved disc is not significant. One reason for this difference may be due to the grooves in the surface significantly altering the hydrodynamics of the film so that, for example, film breakdown is suppressed at even at low disc speeds and low flowrates.

Figure 15a-f shows the combinational effect of rotational speed, flow rate and ratio of reagents on the yield. The influence of the hydrodynamic parameters of the SDR on yield is dictated by whether the reaction is kinetically or mixing limited. If reaction is kinetically limited, the implication is that a reduction in yield is brought about by lower residence times of the film on the rotating disc surface and therefore higher rotational speeds and high flowrates. If, on the other hand, reaction is mixing limited, then higher values of these parameters will give an improvement in the yield due to enhanced micromixing under these operating conditions. An optimal range of rotational speeds and flowrates would therefore be expected to prevail whereby a balance between good mixing and sufficient residence time is achieved to maximize the yield. In this study, the process appears to be mixing limited at lower rotational speeds and lower flowrates (up to ~1000 rpm and 14.4 mL/s respectively), but at much higher speeds, the shorter residence time has negligible influence on the yield. Thus, at the very high speeds, kinetic limitations are apparently absent indicating that even within the greatly shortened residence time, the reaction is fast enough to proceed to a high yield. In contrast to particle size, the effect of water/TTIP ratio on TiO_2 yield is reversed, that is, lower ratio gives higher yield, according to Figures 15 b, c, e and f, which would suggest that higher yield is influenced primarily by the enhanced growth rates and agglomeration rather than nucleation rate. Overall, considering the influences of these three independent variables, it would be sensible to operate at the highest disc speed and flowrate achievable in practice in the SDR in combination with a moderate water/TTIP ratio in order to minimise the particle size for the best product quality and optimise the particle yield for a reasonably high productivity. The ANOVA for both the smooth and grooved discs also confirm that all the main effect are statistically significant (p-value <0.05) and there are no significant interactions between the variables.

Figure 15a-f also shows that the grooved disc gives nominally higher yield than the smooth disc under identical conditions of flow rate, rotational speed and water/TTIP ratio. The presence of grooves on the disc is likely to increase the surface wettability as well as liquid turbulence and

micromixing as discussed earlier, all of which contribute to enhancing the rate of precipitation and therefore the yield of TiO_2 particles.

The scatter plots (Figure 16) show a reasonably good correlation of 68.9 % between mean particle size and yield in both smooth and grooved disc. The scatter plot generally indicates that the highest yield and smallest particle size are achieved as the rotational speed is increased for both disc types.

3.7. TiO_2 Crystal Structure

The crystal structure of TiO_2 develops upon calcination at 400 °C for 1 hour of the amorphous material generated during the primary hydrolysis-condensation reaction in the SDR. The calcined samples were subjected to SEM, XRD and EDS analysis. Additionally, we have carried out XRD analysis on the as formed samples from the SDR, without heat treatment. Figure 17 clearly shows the effect of heat treatment on particles. In Figure 17a, the TEM analysis of the as-formed amorphous TiO_2 particles shows that these are significantly smaller than the size of the calcined particles shown in the SEM image of Figure 17b. Similar observations have been made in the literature [64]. It has been suggested that this effect may be due to thermally promoted crystallite growth and formation of agglomerated particles [65].

Figure 18 compares the XRD plot for as prepared TiO_2 hydrate or hydroxide and TiO_2 crystals after heat treatment. The XRD plot confirms the presence of amorphous species before the heat treatment and the formation of anatase phase after heat treatment.

EDS analysis shows in Figure 19 that only oxygen and Ti are present (33.29 % $\pm$ 7.17 of oxygen and 66.71 % $\pm$ 10.43 of titanium) indicating that the nature of the heat treated sample is TiO_2 .

3.8. SDR and STR comparison

Figure 20a shows that at similar power consumption, the SDR can produce more uniform, less agglomerated and smaller particles, with improved particle size distribution. The particle sizes are markedly different, with the particles produced by SDR being in the nano-size range

whereas the STR produced particles in micron-size range. Such differences may be accounted for by significant agglomeration in the STR due to poorer mixing conditions. Furthermore, applying SDR favours higher yield per second of processing time at similar power dissipation compared with the STR as presented in Figure 20b. It is to be noted that SDR residence times are between 0.2 -0.5 s for the range of operating parameters used in this work, as estimated from Eq 4, but in calculating the yield per unit processing time, a more conservative residence time of 1 s was applied. On the other hand, the reactant residence time in the STR was fixed at 60 s. Therefore, it is apparent from data in Figures 20 that the SDR generates not only better quality of product but also higher throughput of TiO_2 particles in a more economical, safer and continuous process.

4. Conclusions

The production of titanium dioxide nanoparticles via a sol-gel route on a Spinning Disc Reactor (SDR) was investigated for a wide range of parameters, with a view to determining the set of conditions required to minimise particle size and PSD and optimise particle yield.

Mixing plays a major role in controlling the size and size distribution of particles. The more intense the mixing, the smaller the particles. Here, the mixing quality was demonstrated to be strongly influenced by rotational speed, flowrate of reactants, type of disc surface and location of feed input on the reactor surface. It is therefore possible to control particle size and size distribution by varying the operating parameters of the SDR. The best operating conditions for obtaining smaller particles with narrower distributions are high rotational speeds, high flowrates and high water/TTIP ratio. Interaction effects particularly between the disc speed and flowrate on particle size have been demonstrated, which highlight the advantages of operating at the highest disc speed of 1200 rpm in this study. A grooved disc was also shown to be even more effective in producing smaller particles over a wider range of operating conditions, most likely due to the altered hydrodynamics which ensure that film breakdown is minimised. Improved particle characteristics were also achieved by introducing the titanium tetra isopropoxide (TTIP) precursor

into the water film away from the centre, as the micromixing of the TTIP into the water is enhanced in a more highly sheared, thinner water film.

In comparison with a conventional STR, the SDR can produce nano-sized particles with much narrower particle size distributions and also much higher yield of product per unit processing time on a similar power consumption basis.

The present work clearly demonstrates the beneficial use of SDRs for controlled TiO_2 nanoparticle synthesis at an economical throughput.

Acknowledgments

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Nomenclature

C_{Ti}	TTIP concentration [mol L ⁻¹ or kmol.m ⁻³]
C_w	Water concentration [mol L ⁻¹ or kmol.m ⁻³]
D	Dispersion coefficient [m ² s ⁻¹]
H	Hydrolysis ratio
Q	Liquid flowrate [m ³ s ⁻¹]
r	Radial position from disc centre [m]
Sc	Schmidt number
t_{res}	liquid residence time on the disc [s]
t_{ind}	Induction time [s]
t_{mic}	Micromixing time [s]
u	Average velocity [m.s ⁻¹]

Greek alphabets

ν	Kinematic viscosity of fluid [m ² s ⁻¹]
μ	Dynamic viscosity [Pa.s]
τ	Micromixing time [s]
$\mathcal{E}$	Energy dissipation [W/kg]
ρ	Density [kg.m ⁻³]
ω	Angular velocity [rad.s ⁻¹]

Superscripts

i	inner radius of the disc
o	outer radius of the disc
L	liquid

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Table Caption

Table 1. Factors and levels used for CCD optimisation study

Table 2. The Effect of TTIP feed location on energy dissipation, micromixing time and particle diameter (flowrate of 10.8 mL/s rotational speed of 1200 rpm and ratio of 20)

Figure Caption

Figure 1. Scheme of set up used for TiO₂ precipitation experiments

Figure 2. Scheme of injection point of TTIP feed

Figure 3.(a) Effect of disc speed on particle size and PSD (water/TTIP ratio 12, flowrate 10.8 mL/s) (b) Comparison of volume% and intensity% PSD data at 400 rpm disc speed , (c) 1200 rpm

Figure 4. Influence of disc speed on micromixing time constant at different flowrate

Figure 3. Effect of flowrate on particle size distribution at rotational speed of 800 rpm

Figure 4. TEM images at (a) flowrate of 3.6 mL/s (b) flowrate of 18 mL/s

Figure 5. Effect of disc surface on particle size distribution at flow rate of 12 mL/s and ratio of 12

Figure 6. TEM images of TiO₂ at 1200 rpm, ratio of 12 and flowrate of 10.8 mL/s (a) grooved disc (b) smooth disc

Figure 7. Effect of water/TTIP ratio on particle size distribution at flowrate of 10.8 and rotational speed of 800 rpm

Figure 8. TEM images at (flowrate of 10.8 mL/s and 800 rpm) different ratio (a) ratio of 6 (b) ratio of 20

Figure 9. Effect of feed input location on particle size distribution (flowrate of 10.8 mL/s, rotational speed of 1200 rpm and ratio of 20)

Figure 10. TEM images of TiO₂ (1200 rpm, ratio of 20 and flowrate of 10.8 mL/s) at different feed input point (a) 10 cm, (b) centre

Figure 11. Surface plot for particle size at various combinations of flowrate, rotational speed, ratio on smooth disc (a, b, c) and grooved disc (d, e, f)

Figure 14. Interaction effect of flowrate and rotational speed on smooth disc (The green dots on the centre are the six repeated centre points. The green dots on left and right of the plot are axial runs at similar conditions of ratio and rotational speed but different flowrate).

Figure 15. Surface plot of yield at various combinations of flowrate, rotational speed, ratio on smooth disc (a, b, c) and grooved disc (d, e, f)

Figure 16. Scatter plot of yield % vs. mean particle size(a) smooth (b) grooved (The plots are coloured by rotational speed; the red dots are for data at 1200 rpm and the blue dots at 400 rpm and the green dots at centre point (800 rpm)

Figure 17. Effect of heat treatment on particle size (a) TEM image for as-formed amorphous TiO_2 particles and (b) SEM image of particles after calcination at 400°C for 1 hour

Figure 18. XRD plot before and after heat treatment

Figure 19. EDS spectrum of TiO_2 crystals

Figure 20(a). Comparison of effect of SDR and STR processing on mean particle size at ratio of

20(b). Comparison of effect of SDR and STR processing on particle yield

The figure illustrates the experimental setup for the synthesis of poly(2,2,5-trimethyl-1,3-dioxane-5-thione) (PTMD). It includes a schematic diagram of the reactor and two photographs of the disc surfaces.

Schematic Diagram:

- Reactor Housing:** A central vertical chamber containing a **Disc surface**.
- Inputs:**
 - Nitrogen inlet:** A tube entering the top of the reactor housing.
 - TTIP:** A tube entering the top of the reactor housing.
 - Acidified water (pH=1.5):** A tube entering the top of the reactor housing.
- Outputs:**
 - Product outlet:** A tube exiting the bottom of the reactor housing.
 - Water outlet:** A tube exiting the bottom of the reactor housing, connected to a **Temperature control bath**.
 - Water inlet:** A tube entering the bottom of the reactor housing, connected to a **Temperature control bath**.
- Temperature Control Bath:** A reservoir at the bottom of the setup, containing a heating element (indicated by a wavy line).
- Flow Indicators:** Blue arrows indicate the flow of water, and red arrows indicate the flow of the reaction mixture.

Photographs:

- (a) smooth:** A photograph of a smooth, circular metal disc.
- (b) grooved:** A photograph of a circular metal disc with concentric grooves.

Figure2

Figure3

Figure4

Figure5

Figure6

Figure7

Figure8

Figure9

Figure10

Figure11

Figure12

Figure 13

Design-Expert® Software
Factor Coding: Actual
mean particle size (nm), smooth disc
15.0 15.21
X1 = C: Rotational speed (rpm)
X2 = A: Flow rate (mL/s)
Actual Factor
B: Ratio of water/TTP = 12

a

Design-Expert® Software
Factor Coding: Actual
mean particle size (nm), smooth disc
15.0 15.21
X1 = B: Ratio of water/TTP
X2 = C: Rotational speed (rpm)
Actual Factor
A: Flow rate (mL/s) = 10.8

b

Design-Expert® Software
Factor Coding: Actual
mean particle size (nm), smooth disc
15.0 15.21
X1 = B: Ratio of water/TTP
X2 = A: Flow rate (mL/s)
Actual Factor
C: Rotational speed (rpm) = 800

c

Design-Expert® Software
Factor Coding: Actual
mean particle size (nm), grooved disc
15.0 15.21
X1 = A: Flow rate (mL/s)
X2 = C: Rotational speed (rpm)
Actual Factor
B: Ratio of water/TTP = 12

d

Design-Expert® Software
Factor Coding: Actual
mean particle size (nm), grooved disc
15.0 15.21
X1 = B: Ratio of water/TTP
X2 = C: Rotational speed (rpm)
Actual Factor
A: Flow rate (mL/s) = 10.8

e

Design-Expert® Software
Factor Coding: Actual
mean particle size (nm), grooved disc
15.0 15.21
X1 = B: Ratio of water/TTP
X2 = A: Flow rate (mL/s)
Actual Factor
C: Rotational speed (rpm) = 800

f

Figure14

Factor Coding: Actual
Yield %, smooth disc

Figure16

Design-Expert® Software
Correlation: -0.689
Color points by value of
C:Rotational speed (rpm)
1200 400

Design-Expert® Software
Correlation: -0.689
Color points by value of
C:Rotational speed (rpm)
1200 400

Figure17

Figure18

Figure19

Figure20

Table1

Factors	-1.63	-1	0	1	1.63
Rotational speed (rpm) (X1)	400	600	800	1000	1200
Total Flowrate (ml/s) (X2)	3.6	7.2	10.8	14.4	18
Ratio of water/ TTIP (X3)	6	8	12	16	20

TTIP feed location	Residence	Energy	$t_{\text{micromixing}}$	Particle
on the disc	time (ms)	dissipation	(ms)	diameter
(30 cm in Diameter)		rate (W/Kg)		(nm)
centre	191	906	0.38	2.5
5 cm	151	1045	0.35	1.7
10 cm	81	1202	0.33	0.87

- Significant impact of SDR hydrodynamic conditions on particle size, PSD and yield
- A grooved disc gives further improvement in particle size, PSD and yield
- SDR achieves a higher yield, smaller particles and narrower PSD than in a STR

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