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Break up of Silica Nanoparticle Clusters Using Ultrasonication

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Abstract: This study is concerned with the deagglomeration of hydrophilic silica nanoparticle clusters (Aerosil® 200V) in water using an ultrasonicator operated in batch mode. An impeller was also present in the tank to ensure homogeneity. The effect of power input was studied in the range of 18 to 77 W (9 to 39 kW m⁻³) on the kinetics and mechanisms of deagglomeration and the dispersion fineness. The effect of particle concentration was also studied in the range of 1 to 15% wt.

The process was monitored through the evolution of particle size distribution (PSD), which indicated erosion as the dominant mechanism of breakup. The smallest attainable particle size was found to be independent of power input and solid concentration. Faster break up kinetics were noted as the power input was increased whereas increasing the solids concentration to 15% wt. slowed the process. It could also be shown that processing concentrated dispersions can be beneficial as the break up rate assessed on the basis of energy per unit mass of solids was faster for increased particle concentration.

Keywords: Deagglomeration, ultrasonication, Aerosil 200V, break up, nanoparticle clusters.

Introduction

Nanoparticles incorporated in novel formulations have been shown to improve product properties or achieve properties and performance that cannot be achieved otherwise. Abrasion resistant coatings, pharmaceuticals, catalysts, paints and coatings with increased colour brilliance and increased protection from sun creams are examples of such products ^[1].

When nanoparticle powders are incorporated into a liquid a hierarchy of structures forms: agglomerates, aggregates and primary particles. Agglomerates which are collections of aggregates or primary particles held together by weak bonds such as van-der-Waals forces and hydrogen bonds can be broken up in a processing environment. Aggregates, on the other hand, are held together by sintering bridges which cannot be broken in a processing environment. Deagglomeration can be achieved if the stresses acting on agglomerates exceed the tensile strength ^[2]: $\sigma_T = 1.1(1 - \varepsilon_a)/\varepsilon_a \times F_T/L_a^2$ where ε_a is the porosity of agglomerates, F_T is the sum of the attractive and repulsive forces and L_a is the agglomerate size.

There is limited published work with ultrasonicators on the deagglomeration of clusters of nanoparticles in a liquid ^[3,4,5,6]. These studies ^[3,4,6] assess the kinetics of deagglomeration using mean diameter for the whole dispersion, rather than the evolution of the Particle Size Distribution (PSD).

Pohl and Schubert^[3] investigated the deagglomeration of Aerosil® 90 and Aerosil® 200V in water with an ultrasonicator placed in a flow cell covering a power input range of 50 to 4000 W (specific energy of 10⁷ kJ m⁻³, or 10 GJ m⁻³). A comparison of their results with the ultrasonicator and a batch rotor-stator showed that the ultrasonicator produced a lower mean particle size for a given specific energy input. The effect of particle concentration was negligible in the range of 2 to 10 wt. %.

Sauter et al (2008)^[4] also performed experiments with Aerosil® 200V using an ultrasonicator in the recirculation loop of a stirred tank. The effects of processing time and power input from the ultrasonicator were studied over the specific energy input range of 10 to 3000 MJ m⁻³. They reported that the mean particle size decreased in time (investigated up to 20 min), with increases in power input.

Baldyga et al (2008)^[5] performed CFD to study the flow fields generated with an ultrasonicator and population balance modelling for the deagglomeration process, also for an ultrasonicator placed in a flow cell considering Aerosil® 200V in water. They reported that increased energy density resulted in a decrease in d_{30} of the whole dispersion.

Schilde et al^[6] compared an ultrasonicator in a flow cell to several other process devices, namely a sawtooth impeller, kneader, stirred media mill, 3 roller mill and disk mill, using Aerosil® 200V and Aeroxide® Alu C in water. The ultrasonicator was found to reduce the particle size to a smaller mean diameter than all other devices at a given energy input per unit mass.

This study made use of an ultrasonicator operated in batch mode to investigate the mechanism of break up which was not studied in previous work, as well as the kinetics of deagglomeration and how

fine a dispersion can be achieved with a given test system.

Experimental

Experiments were conducted in a jacketed glass tank of a diameter of 0.14 m. The liquid height was equal to the tank diameter, giving a dispersion volume of 2 litres. The ultrasonicator used, Hielscher UP200S, was operated in batch mode. The experimental set up also included an impeller to ensure homogeneity of the dispersion (Figure 1).

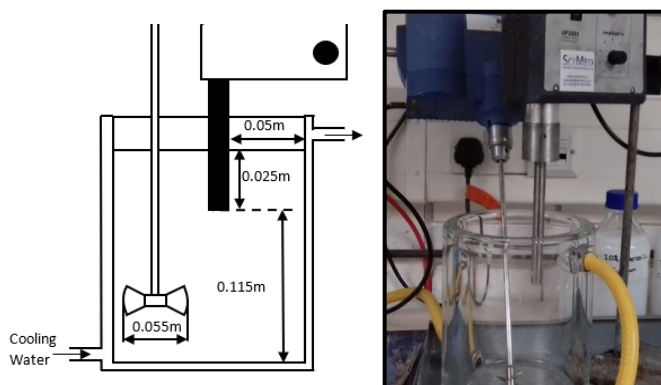


Figure 1 – Experimental set up

Table 1: Power input by the ultrasonicator

Amplitude (%)	Power Input (W)
25	17.91
50	33.83
75	61.64
100	76.75

The ultrasonicator operates at a fixed frequency of 24 kHz and the power input was changed by varying the amplitude. The power input was determined using the calorimetry technique. A power input range of 18 - 77 W covered (**Error! Reference source not found.**) corresponded to a specific power input range of 9-38 kW m⁻³. This was much higher than the power input by the impeller: 0.17 kW m⁻³. Hence, it can be assumed that break up was primarily due to the power input by the ultrasonicator.

The dispersed phase, Aerosil® 200V from Evonik Ind., was dispersed in water. Aerosil® 200V is a hydrophilic fumed silica, with a primary particle size of around 12 nm. It is widely used in industry as a rheology modifier, anti-settling, anti-sagging agent. The effect of solids concentration was also studied in the range of 1 to 15% wt.

The pre-dispersions were prepared by mixing the powder in water using only the impeller for around 30 mins, which corresponds to $t=0$, prior to starting the ultrasonicator.

The process was monitored by sizing samples taken during the process. The particle sizer used was Malvern Mastersizer 2000. The optical model used was $1.46 + 0.1i$, the continuous phase refractive index was set to 1.33.

The rheological properties of the final dispersions were measured using a Thermo Haake VT550 rheometer at 25°C. All were of Newtonian behaviour. The 1% wt. dispersion was found to be water-like. The viscosities of 10 and 15% wt. were found to be 6.4 and 9.9 mPa s respectively. These values are comparable to those reported in previous work^[8].

Results and Discussions

Bimodal PSDs were obtained under all processing conditions with fines (sub-micron material) increasing in volume and coarse material decreasing in both volume and size in time. An example is shown in Figure 2. This way of analysing data rather than using a mean diameter for the whole dispersion provides insight into the mechanism of break up. This evolution of the PSD is indicative of erosion being the dominant mechanism of deagglomeration, as described in previous work^[7]. It is also in line with findings using other processing devices (in line and batch rotor-stators and microfluidizer) with this test material reported in previous work^[5,7,8,9,10].

Figure 3 shows that the Sauter mean diameter of fines is around 200 nm, also regardless of the operating condition. This is much larger than the size of primary particles, therefore it can be concluded that the dispersion fineness is determined by the aggregate size. This agrees with findings from previous work with this particle-liquid pair using other process devices^[8,9,10].

PSDs of the pre-dispersions prepared using the same procedure were comparable (Figure 4) making it possible to study the effect of operating conditions on break up kinetics through the evolution of PSD during processing.

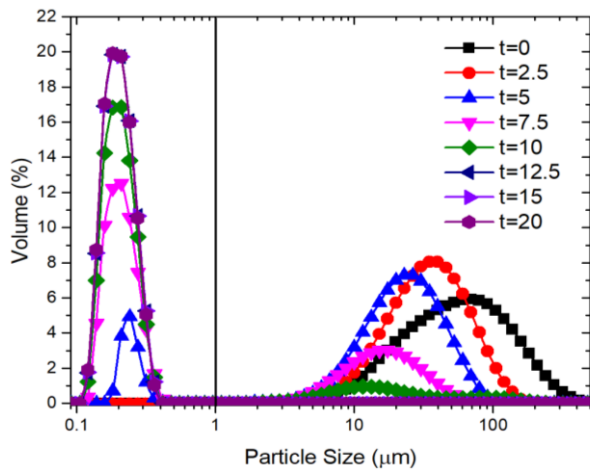


Figure 3: Evolution of PSD in time (min) during processing- 10% (w:w); 31 kW m⁻³

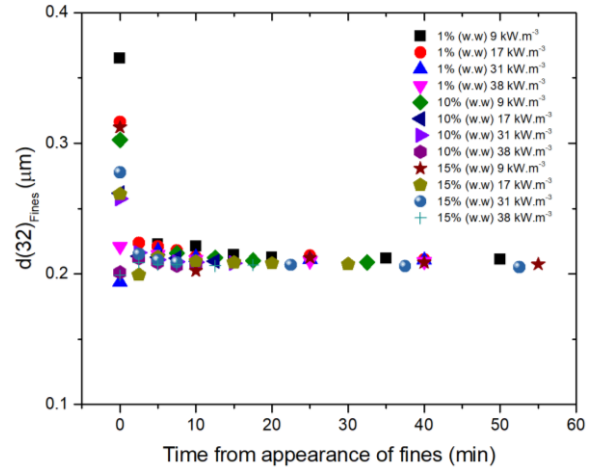


Figure 3: Sauter mean diameter of fines (All conditions)

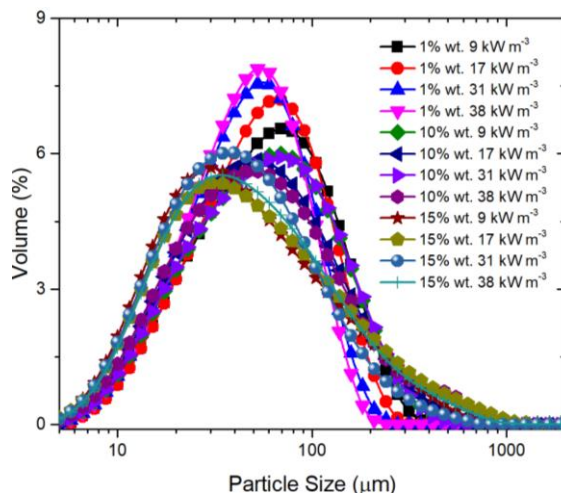


Figure 4: PSD of pre-dispersions

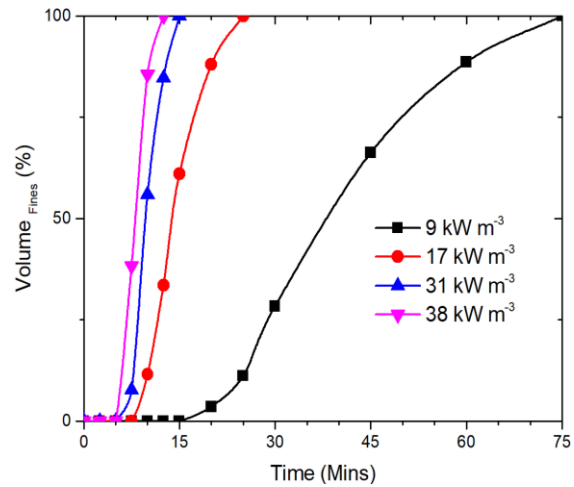


Figure 5: Effect of power input on fines generation rate (15% wt. Aerosil 200V in water)

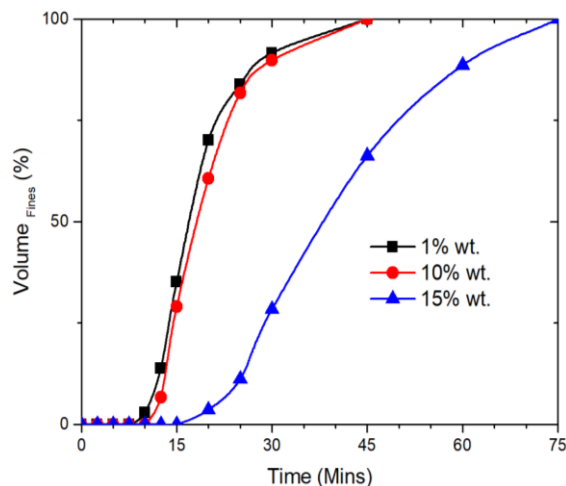


Figure 2: Effect of powder concentration on break up kinetics (9 kW m⁻³)

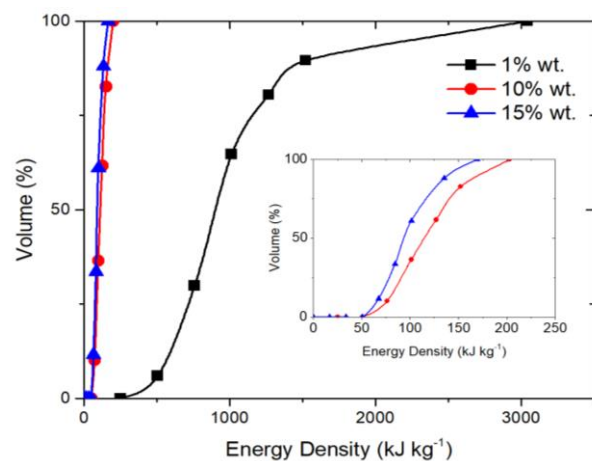


Figure 7: Effect of powder concentration on fines generation as a function of energy per mass of solids (17 kW m⁻³)

The evolution of the volume fraction of fines in time has shown that increasing the power input results in a faster break up at a given particle concentration as shown in Figure 5. On the other hand, increasing the solids concentration results in a slower break up kinetics which was particularly obvious when the concentration was increased from 10 to 15% wt. (Figure 6). Slower kinetics were also reported

using a microfluidic device in the 10-17% wt. range^[10] whilst little effect was found in other studies in particular up to 10% wt.^[3,8]. The effect of particle concentration would be related to the pre-dispersion rheology which would depend on both the method of preparation and how quickly the pre-dispersion was processed.

When evaluated in terms of energy per unit mass of solids, operating at higher solids concentrations proved to be more energy efficient (Figure 7). This is advantageous as concentrated masterbatches are often preferred for ease of transport and storage. Similar findings were reported with batch^[9] and in-line rotor-stators^[8].

Conclusions

The combined effects of particle concentration and power input on the deagglomeration of clusters of nanoscale silica powders (Aerosil® 200V) was investigated in water. The process was performed using an ultrasonicator operated in batch mode over a power input range of 18 to 77 W. The powder concentrations were 1, 10 and 15% wt.

The particle size distributions of the pre-dispersions prepared were comparable allowing the study of the effect of operating conditions on the deagglomeration process. Under all conditions the dominant mechanism of breakup was found to be erosion as was also reported for this particle-liquid pair with batch and in-line rotor-stators and a microfluidic device.

The Sauter mean diameter of the final dispersions was around 200 nm, also irrespective of the operating condition. This smallest attainable size is much larger than the primary particle size and hence it can be concluded that the dispersion fineness is limited by the size of the aggregates.

It could be shown that increasing the power input results in a faster deagglomeration process.

Increasing the solid concentration requires longer processing times and this effect was more prominent when the concentration was increased to 15% wt. and at the lower power input of 9 kW m⁻³. An analysis of the results on the basis of energy per unit mass of particles has shown that it is more energy efficient to process high concentration dispersions which presents advantages when making up master batches. It is worth bearing in mind that above a certain concentration, the rheology of the pre-dispersion can be too challenging to process.

Further work is underway with other process devices.

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