Milling of Nanoparticle Clusters for New Formulation Lubricants

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ABSTRACT

This paper comes from a large project aiming to develop new lubricants for the automotive industry, containing nanoparticles in their formulation. The paper details a part of the process chain relating to the preparation of an intermediate product which is a concentrated (23 wt.%) dispersion in a base oil. The stirred bead mill could succesfully be used to prepare these dispersions and results will be shown on the effect of operating conditions during a study undertaken to scale up the dispersion volume. The mill was operated in first the batch mode with a small chamber (300 ml), then in re-circulation mode with a larger chamber (600 ml) to process a higher quantity of 2500 ml dipsersion.. The use of two grinding bead sizes in conjunction with a higher agitator tip speed dramatically increased the de-agglomeration rate for the large volume dispersion allowing us to obtain similar degree of fineness as in small scale. Dispersion rheology and selected CFD will also be presented.

Keywords: stirred bead mill, nanoparticle dispersion, novel lubricants with nanoparticles, de-agglomeration, MoS_2

1 INTRODUCTION

This paper comes from a large project developing novel lubricants, which contain nanoparticles in their formulation, for the automotive industry. Fluid lubricants are used in almost every field of human technological activity and their purpose is multi-fold: they reduce frictional resistance, protect the engine against wear between contacting surfaces, remove wear debris, reduce heating and contribute to cooling, improve fuel economy, improve emissions. Nanoscale particles as additives have shown promising indications that they can contribute to friction reduction and enhance protection against wear [1].

The process involves several steps as shown in Figure 1 starting with the production of an intermediate product which has a high particle content and can therefore be easily transported and stored. During the pre-dispersion stage all the additives including nanoparticles are incorporated into a base oil. Whilst nanoparticles are referred to by their primary particle size, they often exist in the form of clusters, i.e. agglomerates which can be broken down to smaller fragments or aggregates which are held by stronger bonds and cannot be broken down in a process device [2]. The pre-dispersion is processed in an energy intensive device to break up the nanoparticle clusters and obtain a fine concentrated dispersion, the intermediate product. This is subsequently diluted in a different oil as required to obtain the final formulated product.

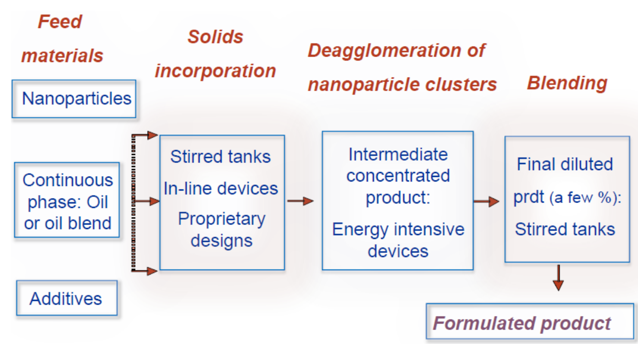

Figure 1: Process stages for the production of lubricants with nanoparticles in their formulation

This paper is concerned with the deagglomeration stage during which nanoparticle clusters are broken down to achieve a stable, concentrated intermediate product. Selected results from the study are presented for the case of molybdenum disulphide (MoS_2) particles which are known to be lubricious even in dry form. Of the several process devices considered, data obtained using a stired bead mill are presented, emphasising the importance of operating conditions and processing time when increasing the product volume to achieve dispersions of comparable properties. Some results from CFD simulations, carried out to gain a better understanding of the flow patterns inside the mill are also included.

2 EXPERIMENTAL

2.1 Process equipment and operating conditions

The pre-dispersions containing 23% (w:w) MoS_2 nanoparticles in polyalpha olefin (PAO6) and two types of dispersants were prepared by using a stirred tank equipped with a pitched blade turbine run at 250 rpm.

For the dispersion stage, the stirred bead mill was chosen on account of its intensive energy input and ability to handle high solid concentrations. The specific mill used in this study is a WAB Multi-Lab Mill (Figure 2). It was operated in batch or re-circulation mode with chamber sizes of 300 and 600 ml respectively. The agitators used are made of yttrium stabilized zirconia and of a diameter of 0.064 m (Figure 3).

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In the batch mode, the milling chamber was filled with 0.8 mm zirconia grinding bead (Tosho YTZ) with a bulk filling volume of 65%. The agitator was run at a tip speed of 8 m/s and the milling was carried out for 240 minutes.

In the re-circulation mode, the milling was initially performed at the same conditions as that in the batch mode for 180 minutes. The dispersion obtained was further milled using a smaller bead size of 0.5 mm for another 120 minutes at a higher agitator tip speed of 14 m/s.

Figure 2: WAB Multi-Lab Mill

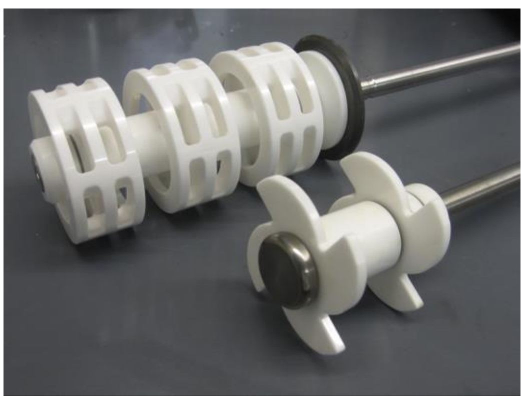

Figure 3: Agitator geometries of WAB Multi-Lab Mill used in the batch mode (below) and re-circulation mode (above).

2.2 Particle Size Measurement s

Beckman Coulter LS230 was used to obtain the particle size distributions of samples taken during dispersion. The instrument uses a combination of laser diffraction and PIDS (Polarization Intensity Differential Scaning) techniques to measure particle between 0.4 and 2000 μm and between 40 and 400 nm, respectively.

2.3 Rheology Measurements

The rheology of the dispersions was measured by using Anton Paar Rheolab QC with a concentric cylinder geometry.

2.4 CFD Simulations

The CFD simulations were carried out in a three dimensional domain by using the commercial CFD code FLUENT 13. The geometry for the CFD model is shown in Figure 4 and consists of about 700 thousand computational cells (hybrid hexagonal – tetrahedral cells).

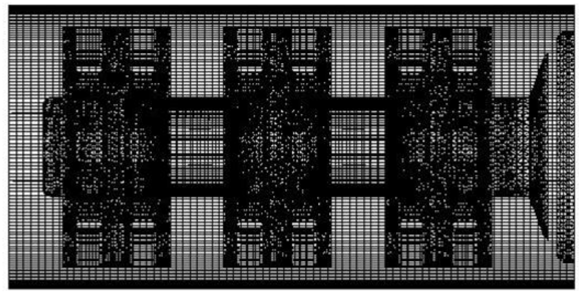

Figure 4: Geometry of the stirred media mill for CFD simulations

The flow field inside the milling chamber was calculated by using an Eulerian-Eulerian multiphase model in conjuction with standard k-ε turbulence model. The simulation was carried out in a steady-state mode and the rotation of the agitators was modelled by using a multiple reference frame (MRF) approach. The inlet and outlet of the milling chamber were modelled as velocity inlet and pressure outlet, respectively, while the agitators and milling chamber walls were modelled as no-slip boundary condition.

According to Eskin [3], the energy supplied by the rotor dissipated due to viscous friction between the grinding beads and fluid (ε_{visc}) and inelastic collisions between grinding beads (ε_{coll}) can be described as follows

$$\varepsilon_{visc} = 9\pi\mu d_b n_b \Theta R_{diss} \tag{1}$$

$$\varepsilon_{coll} = \frac{12(1-k^2)}{d_b\sqrt{\pi}}\alpha_b^2 \rho_b g_o \Theta^{3/2} \tag{2}$$

where μ, d_b, n_b, Θ, R_{diss} are liquid viscosity, bead diameter, bead numerical concentration, granular temperature and dissipation coefficient, respectively, while k, α, ρ, g_o are restitution coefficient for bead-bead collisions, bead volumetric concentration, bead density and radial distribution function. These parameters were taken into account by using a user-defined function.

3 RESULTS AND DISCUSSIONS

3.1 Break up process

The pre-dispersions prepared in a stirred tank contained large agglomerates of the order of microns or tens of microns: data for t= 0 min in Figures 5 and 6.

During the first 15 minutes of milling in batch mode, these large agglomerates were broken up into smaller fragments of 100 nm and 3 µm (Figure 5). Further milling up to 60 minutes increased the volume fraction of sub-micron fragments while that of the micron sized material decreased. Further milling resulted in the generation of fine material below 100 nm and agglomerates above 1µm were completely broken up by 120 min. The final particle size distribution after 240 milling was bimodal with peaks around 60 and 170 nm.

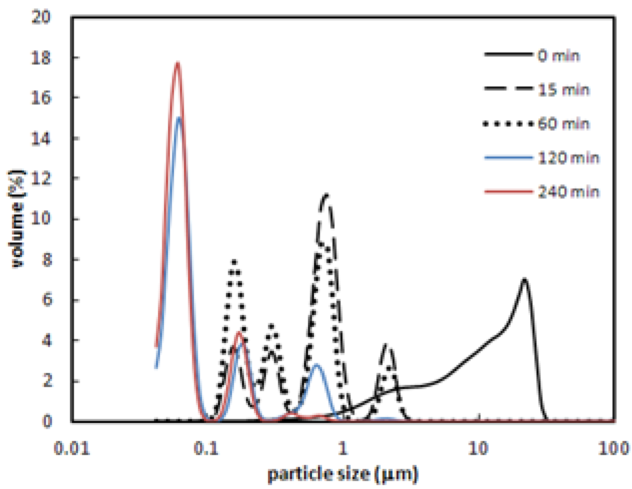

Figure 5: Evolution of particle sizes during batch milling

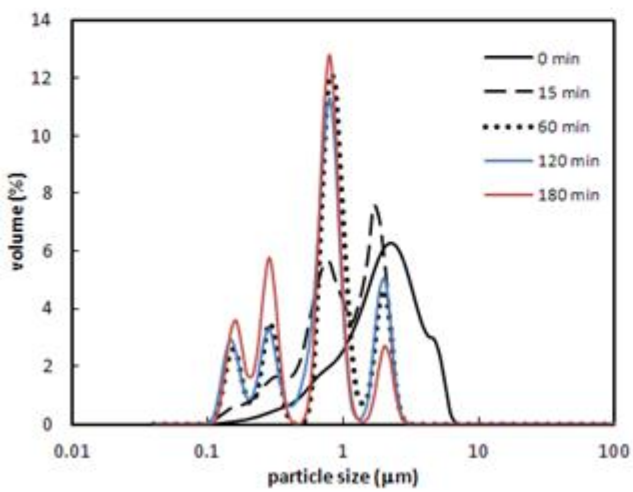

Figure 6: Evolution of particle size distribution during milling in the re-circulation mode with 0.8 mm beads

When operated in re-circulation mode under the same operating conditions, within the first 15 minutes of milling, a multi-modal particle size distribution was obtained in the range of 100 nm and 3 µm and although the volume of larger agglomerates decreased and finer ones increased in time, this was a very slow process (Figure 6). Milling up to 180 minutes did not produce a dispersion as fine as that obtained under batch conditions. The size range was similar to that prepared by milling in the batch mode for 15 minutes. Since the volume of dispersion processed in the re-circulation mode is about 10 times larger than that in the batch mode, the specific energy (energy per unit volume per unit time) supplied by the mill operated in the batch mode for 15 minutes is similar to that in the re-circulation mode for 180 minutes. Based on this, it would take more than 50 hours of milling in re-circulation mode.

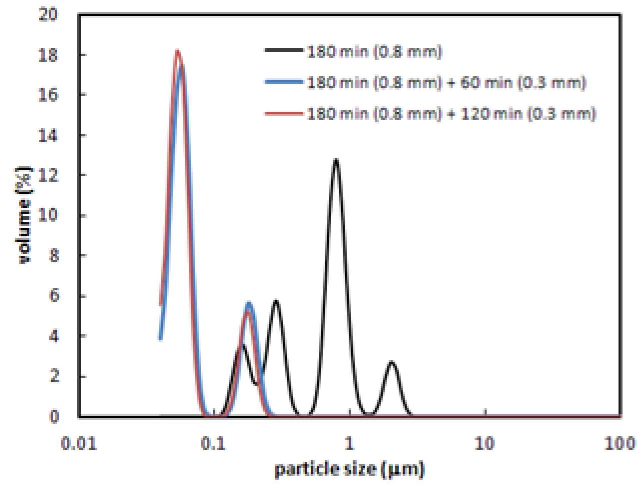

Figure 7: Evolution of particle sizes during milling in re-circulation mode with 0.3 mm grinding bead.

Such long processing times and thereby high energy input is not acceptable for manufcature and would increase the product price. Therefore, different solutions to shorten the processing time was investigated and both the grinding bead size and stirrer speed were changed. The dispersion prepared with 0.8 mm grinding beads was milled further using smaller 0.3 mm grinding beads. In addition, the agitator tip speed was increased from 8 to 14 m/s. This proved to be a highly effective solution reducing the aggregate size to less than 200 nm after just 60 minutes (Figure 7)- similar to that obtained in the batch mode after 240 minutes of milling.

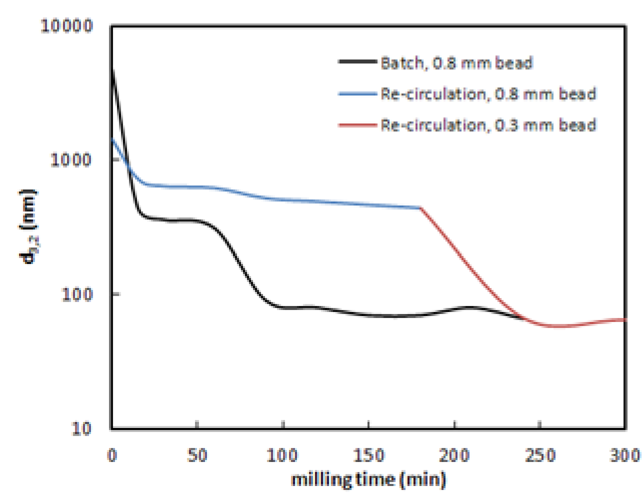

Figure 8: Evolution of Sauter mean diameters (d_{32}) during milling in batch and re-circulation modes

Figure 8 shows a comparison of the results obtained under different operating conditions in the form of mean diameters which of the same range for the two cases. It can be seen that if a change from large to smaller diameter beads is implemented after 15 minutes of milling with large beads the overall processing time can be further reduced significantly.

In all cases, PSDs obtained point towards breakage through progressive shattering.

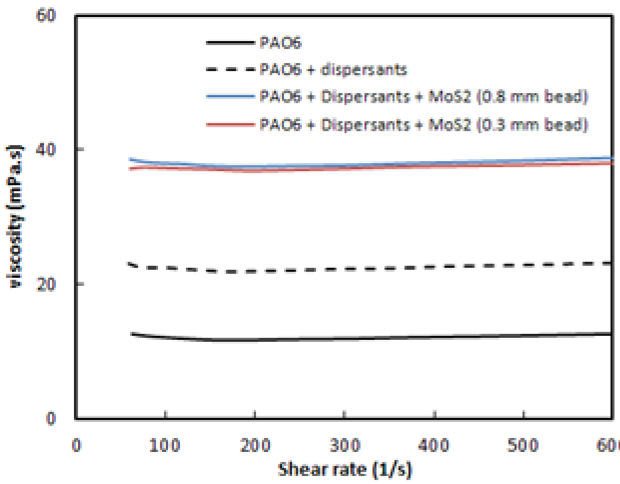

Figure 9: Rheology of base oil and dispersions at 60 ^{o}C

In addition to particle sizes, the rheology of the base oil, PAO6 and final dispersions was studied (Figure 9). Allm materials were of Newtonian behaviour. The addition of dispersants increased the oil viscosity (from 12 mPa.s to 22.5 mPa.s at 60 ^{o}C) and a further addition was noted with the addition of particles. The viscosity of final dispersions prepared in the re-circulation mode with 0.8 and 0.3 mm grinding beads are very similar, i.e. 38 and 37 mPa.s, respectively. This is further confirmation of the dispersion properties being consistent in both cases.

3.2 CFD Simulations

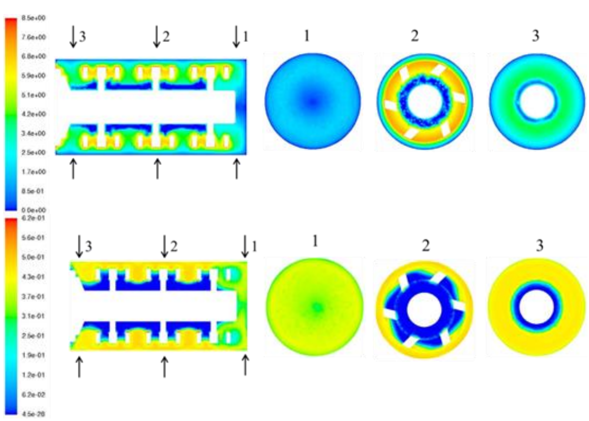

Figure 10: Predictions of (a) velocity profiles, (b) beads concentration in the stirred bead mill with PAO6 as the continuous phase

Selected results from CFD simulations are shown in Figure 10. Consistent with velocity profiles, the grinding beads were observed to accumulate close to chamber walls under these turbukent flow conditions due to centrifugal force. These are in agreement with results reported by Jayasundara [4]. In line with this finding, the highest energy dissipation rates was found to occur close to chamber walls.

4 CONCLUSIONS

The operation of a stirred bead mill was investigated to produce different volumes of a concentrated intermediate product to be used in automotive applications. The dispersion process was monitored through particle size measurements on the samples taken. Dispersion rheology was also determined. CFD simulations provided a good insight in terms of the flow within the mill.

The effects of operating mode, grinding bead size and stirrer speed on the performance of a stirred media mill to prepare concentrated dispersions (23 wt.%) of MoS_2 in PAO6 for the formulation of a novel nanoparticle based lubricants have been investigated. Break up occurred through progressive shattering in all cases. The properties of the dispersion produced in a small quantity in batch mode could be replicated when operated in re-circulation mode at a higher quantity by changing the bead size and increasing the stirred speed. The process could thus be optimised and successfully scaled up.

5 ACKNOWLEDGEMENT

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