Consolidating nanoparticles in micron-sized granules using spray drying

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Abstract. Suspensions of nanoparticles (SiO$_2$, SiC, TiO$_2$, CNT, Nanoclay and Hydroxyapatite) were spray dried to produce dry granulated products. The nanoparticles were consolidated in granules making them more convenient and safer to use in further processing compared to handling of nanopowders.

1. Introduction
Vast amount of products are expected to emerge utilising the special properties offered by nanoscale building blocks. New production facilities are needed, designed to handle the nanoscale ingredients in the processing of the new products. The nanoscaled ingredients need to be controlled to ensure safety of the operators by avoiding nanoscale ingredients being released to the environment. This sets new challenges for production equipment and also sets requirements to the engineering of the nanoscaled ingredients such that they become convenient to control and safer to use in the production process. The nanoscale ingredients can be suspended in a liquid and consolidated to micron-size granules using a granulation process like spray drying. Being an intermediate product micron-sized granules of the nanoscale ingredients offer a way to ease the use of nanoscale ingredients in a subsequent production process. Further, micron-sized nanostructured granules can be engineered in such a way that after re-suspending the granules they decompose into individual nanosize particles [1]. Hence, micron-size granules of the nanoscale particles may produce an important link between producers of nanoparticles and their customers using nanoscaled ingredients in their products.

One of the main objectives of the EU co-founded research project SAPHIR (www.saphir-project.eu) has been on developing safe processes covering the entire production line from the nanoparticle synthesis through to the production of final products. Together with the 22 partners in the project GEA Niro has been working on different steps of the production line to develop new technologies to ensure safety and control over the entire process. GEA Niro has been using its spray drying capabilities to produce micron-size granules of a large range of different nanoparticles. Spray drying is a quick and relatively low temperature process and the promising features of the nanocomponents are preserved. As part of the SAPHIR project GEA Niro has developed ways to ensure that the granulation process can occur without release of nanoingredients to the environment preventing that operators become exposed to the nanoscale ingredients [2]. This makes the use of spray drying in a nanoparticle production line a viable solution for producing an intermediate product. This intermediate product can be traded for further use in the production of final products utilizing the more convenient properties of micron-sized granules ensuring easier handling and safer production.
It is the aim of this article to present selected results obtained during the SAPHIR project on producing micron-sized granules of different nanoparticles by use of the spray drying process.

2. Materials and Methods

2.1. Materials

Nanoparticles were supplied by SAPHIR partners (SiC, SiC + CNT) or commercial suppliers (SiO$_2$, TiO$_2$, CNT, Nanoclay and Hydroxyapatite) as suspensions or as dry nanopowders. Pumpable and sprayable suspensions were realized by addition of solvent and dispersants. Sieving of the suspensions was conducted to ensure that the suspensions did not contain lumps. The suspensions were continuously stirred until spray drying.

2.2. Spray drying

Spray drying was performed in a size Mobile Minor™ spray dryer having a capacity up to 5 kg/h. Different configurations of the spray dryer were used as shown in Figure 1. The Mobile Minor™ plant has a diameter of 0.8 meters with a cylindrical height of 0.65 meters and a 40° cone angle. Co-current drying was conducted with the two fluid atomization nozzle positioned in the centre of the hot gas disperser. A pneumatic hammer was mounted on the conical part of the chamber and was in operation during the experiments. Different means of separating the granules from the air stream has been performed as indicated in Figure 1. In all cases the exhaust gas was filtered by a HEPA filter before emission.

2.3. Granule characterisation

Residual moisture content was measured using a Halogen Moisture Analyser (HR73, Mettler Toledo) at 105°C. The granule size was measured using a Mastersizer 2000 (Malvern Instruments) equipped with a dry feeding unit (Scirocco) dispersing the sample at 0.5 bar. Three size values are reported: d10 is the size where 90% (volume) of the population are larger, d50 is the median size and d90 is the size where 10% of the population is larger. Granule morphology was investigated at Danish Technological Institute, Center for Micro Technology and Surface Analysis using a scanning electron microscope (Ultra55, Zeiss).
3. Results and discussions

Experiments were conducted using the methodology and facilities available at GEA Niro’s Test Center. In the planning of experiments safety aspects of handling the materials were investigated based on available information sources. In each case a safety evaluation was conducted detailing which precautions should be taken in all stages of the experiments. With nanomaterials having health aspects which are either not available or not fully determined safety precautions were implemented to ensure that experiments were conducted without exposing operators and environment to unknown risks.

Suspensions were prepared using high shear mixing (combined with ultrasonic treatment if needed) to ensure that atomization would be efficient during the spray drying operation. If needed dilution of the suspensions was done to reduce viscosity such that it became sprayable. Finally sieving was done to ensure removal of large aggregates that would otherwise block the atomization nozzle. In preparation of the spray drying experiments the equipment was assembled and safety devices checked. The spray dryer was heated and stable process parameters were obtained while running on pure solvent. When the plant was thoroughly heated and running stable spray drying of the suspensions was initiated. Process parameters were continuously recorded during the tests and if needed process parameters were adjusted to ensure stable operation. Dry granules were obtained in special containers connected to the product outlet of the spray dryer. Yield, residual moisture content and granule size distribution was measured and morphology determined. Finally, granules were sent for further processing by other SAPHIR partners. Table 1 shows results from selected experiments conducted during the SAPHIR project using the spray drying process to produce micron-size granules from nanoparticle suspensions. In the duration of the project experiments were done on a large range of nanomaterials and Table 1 is merely a selection of obtained results.

| Nano-material | SiO₂ | SiC | TiO₂ | CNT | Nanoclay | Hydroxyapatite |
|---------------|------|-----|------|-----|----------|----------------|
| Surface area, Sₙₑₐ | 220 | 59 | 50 | - | - | - |
| Particle size nm | - | 33 | 30 | - | <200 | 10 |
| Solvent | Water | Ethanol | Water | Water | Water | Water |
| Dispersant/Binder | PVA | PEI | Dispex N40 | PP | Dispex N40 | - |
| Concentration % TS | 40 | 5 | 36 | 15 | 10 | 6 |
| Plant setup (Figure 1) | B | A | C | A | B | A |
| Nozzle | NTF-EP | NTF-E | NTF-EP | NTF-EP | NTF-EP | NTF-E |
| Temperatures in/out °C | 180/90 | 115/60 | 171/82 | 200/81 | 180/90 | 200/100 |
| Drying gas kg/h | 80 | 79 | 79 | 80 | 80 | 64 |
| Feed kg/h | 2.9 | 2.8 | 3.6 | 3.2 | 3.7 | 1.7 |
| Atomization gas kg/h | 8 | 6 | 3 | 7 | 9 | |
| Amount g | 330 | 42 | 650 | 68 | 190 | 110 |
| Residual moisture % | 4.6 | 1.5 | 1.8 | 3.6 | 4.7 | 2.6 |
| Particles size d₁₀ µm | 14 | 13 | 10 | 9 | 11 | ND |
| | d₅₀ µm | 43 | 12 | 29 | 16 | 20 | ND |
| | d₉₀ µm | 103 | 39 | 77 | 59 | 50 | ND |
| Morphology | Cenospherical | Cenospherical | Sherical | Cenospherical | Sherical | Sherical |

ND: Not determined

3.1. SiO₂
Nanosilica is commercial available at a relatively low cost and was obtained as a concentrated suspension (40% total solids). Nanosilica was selected as a model material in experiments designed to compare two granulation methods used in the SAPHIR project. Those were Spray Freeze Drying and
Spray Drying. The spray drying produced an interesting result as the granules had a relatively high residual moisture content. That the residual moisture content consistently is higher for granules produced from nanoparticle suspensions than from granules produced from submicron-sized particle suspensions are believed to be caused by the large surface area of the nanoparticles giving a larger binding of solvents. Figure 2 shows a microscope picture of the granules.

Figure 2. Microscope picture of SiO$_2$ granules (SEM by Danish Technological Institute)

3.2. SiC
SiC was supplied by a SAPHIR partner as a suspension using ethanol as solvent to protect the nanomaterial from oxidation. Spray drying was conducted using inert gas and product containers were sealed to avoid exposing product to atmospheric air. The aim was to produce a superior pressing powder which could be used in the production of advanced ceramic components. At a solids content of 5% the suspensions had a high viscosity. Vigorous agitation and ultrasonic treatment was implemented in order to ensure that viscosity would not limit atomization in the spray drying process. Granule morphology was ceno-spherical.

3.3. TiO$_2$
During the SAPHIR project vast amount of TiO$_2$ granules was produced using spray drying as this was used by another SAPHIR partner in production of self cleaning coated surfaces utilising the photocatalytic behaviour of titanium oxide [3]. Commercial available TiO$_2$ ((Degussa P25) was applied, suspensions prepared and spray dried. TiO$_2$ was also used as a model product in the experiments conducted with the aim of finding the optimal spray drying configuration for safe granulation of nanomaterials [2]. Furthermore, extensive work was done on the suspensions preparation with the aim of finding a dispersant that would ensure that the spray dried granules would re-disperse completely in water [1].
3.4. CNT
Carbon nanotubes (CNT) have attracted much interest due to its interesting characteristics. However, CNT health effects in humans have still not been fully determined. A spray drying experiment was conducted with the aim of producing CNT consolidated into micron-sized granules as a mean of increasing the safety during handling of this product. CNT was obtained from a commercial supplier. Atomizable suspensions could only be realized at relatively low concentrations. Spray drying was conducted with ease and a very black granulated product was obtained having a relatively good flowability.

3.5. Nanoclay
Nanoclay is another nanomaterial which is receiving much interest from science. Being available commercially it was used to test whether spray dried granules could be produced from nanoclay suspensions such that the granules would be dispersible. The shear thinning behaviour of nanoclay suspensions was utilised to ensure a low apparent viscosity of the suspensions for atomization. Spray drying was conducted and nice spherical granules were produced. Redispersability was good but further research into different dispersant systems could improve redispersability even further.

3.6. Hydroxyapatite
Hydroxyapatite nanoparticles have important dental and medical applications. Spray drying has been conducted and spherical granules were obtained. Detailed studies into its drying behaviour showed that size reduction continued during the entire drying process producing solid granules of high density.

4. Conclusions
GEA Niro has during the SAPHIR project consolidated nanoparticles into micron-size granules using the spray drying process. This has been performed on a large range of nanomaterials and in all cases micron-size granules were produced which were easy to handle compared to a nanopowder.

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