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Spray Drying for Processing of Nanomaterials

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Abstract. Consolidation of nano-particles into micron-sized granules reduces the potential risks associated with handling nano-powders in dry form. Spray drying is a one step granulation technique which can be designed for safe production of free flowing low dusty granules from suspensions of nano-particles. Spray dried granules are well suited for subsequent processing into final products where the superior properties given by the nano-particles are retained. A spray drier with bag filters inside the drying chamber and recycling of drying gas combined with containment valves are proposed as a safe process for granulation of potential hazardous nano-particles.

1. Introduction
Production of high-tech materials using nanoparticles is of great scientific interest as they are expected to yield products with superior characteristics. Turning a product produced on a laboratory scale into a commercial product means that process equipment needs to be available at the required capacity using suitable technologies for handling nanomaterials and their special properties. As long as health and environmental effects of nanomaterials are not fully understood the process technologies used should ensure the highest protection of operators and environment. A well established method of processing is to have the nanomaterials dispersed in a suspension. This significantly reduces the risks, however having the nanomaterials in suspension has implications due to higher transport costs of the often relatively diluted suspension and for aqueous suspensions containing perishable components the durability may restrict this method. Further, in order to produce solid materials it is required that the nanomaterials are transformed into a dry form. Spray drying produce a micronized product from suspensions of nanoparticles, nanocapsules and other components having dimensions in the nanometer range. Hence, the spray drying technology may establish a link between the nanomaterial synthesis and the traditional processes which can produce the actual end products using micronsized materials.

Spray drying is a one step process where a liquid is atomized to micronized droplets and dried by hot gas. The drying occurs in an insulated chamber consisting of a cylindrical chamber with a conical bottom. The hot drying gas is introduced through an air dispenser situated in the chamber roof. Atomization is performed using different techniques. Centrifugal atomizers, pressure nozzles and air blast nozzles are the techniques most frequently used but others are available. Drying time is from 1 to 5 seconds depending on the initial droplet size. Due to the energy consumption used for evaporating solvent the drying gas is cooled to an outlet temperature typically between 50°C and 120°C depending on product and application. The evaporative cooling means that the heat exposure of the product is relatively low and the final product temperature is often lower than the outlet temperature of the gas. The separation of dried product from the drying gas is done using a cyclone, a bag filter or both. Spray drying is a quick and relatively low temperature process and the promising features of the
nanocomponents are preserved. By formulating the suspensions prior to spray drying re-dispersibility of the granules can be obtained.

GEA Niro is specialized in the development, design and engineering of liquid and powder processing equipments for the manufacture of products in powder, granular or agglomerated form. GEA Niro is recognized as the leading supplier of spray drying technologies for the food and pharmaceutical industry. For the past two years GEA Niro has worked on developing safe processing routes for production of non-dusty micronsized granules from formulated suspensions of nanoparticles. Through the EU founded SAPHIR (Safe, integrated & controlled Production of High-tech multifunctional materials and their Recycling) project GEA Niro has been collaborating with its 21 project partners in optimizing all processes involved in the nanoparticles synthesis through to the production of final materials of ceramic nature for use in many different applications. GEA Niro’s aim in this project is to utilize the spray drying technology for production of nanostructured granules which can be handled in its dry form or redispersed. As part of this project and through other experiments performed in GEA Niro’s Test Centre in Copenhagen experience in handling a range of different nanomaterials (e.g. SiC, SiO$_2$, TiO$_2$, Hydroxyapatite and carbon nanotubes) has been obtained using the spray drying process. Generally, results indicate that most suspensions of nanoparticles are easily dryable. In fact, results using the Drying Kinetic Analyzer™ (novel instrument for determining drying behaviour) have shown that the suspensions of ceramic nanoparticles tested have drying rates which are higher than other products dried in a spray drying system due to a longer constant rate drying period. This means that one stage drying can be utilized which makes up for a relative simple spray drying system. Micronsized granules may still produce dust if not treated with consideration. An area where accidental release of dust can occur from the spray drying is during changing of product containers. This risk can be removed by use of containment solutions. Buck® containment systems produced by GEA Pharma Systems are utilized in combination with the spray drying system for safe processing of nanomaterials. GEA Niro’s pharmaceutical test plants are equipped with the Buck valve system to eliminate the risk of dust being released to the production environment. Especially the Buck Hicoflex® system is a containment interface for safe transfer of granules with a suitable containment level for use in nanomaterial processing systems.

This paper presents results obtained during the SAPHIR project where spray drying has been utilized for production of a non-dusty product from a suspension of nano titanium dioxide. The purpose has been to produce granules which can be used for coatings where the photo catalytic behaviour of the anatase phase of the titanium can be utilized. To ensure easy handling of the coating equipment a mean granule size below 50 µm was required and the product should be free flowing. Different spray drying configuration and drying parameters have been tested to find the optimum conditions for continued production of the product.

2. Materials and Methods

2.1. Materials
Titanium dioxide (Degussa Aerioxide TiO$_2$ P25) having a specific surface area of 50 m$^2$/g was dispersed in an aqueous solution of Dispex N40 (Ciba). Through vigorous stirring a suspension containing 37% dry matter was obtained. 2-Octanone was used as foam reducer. Sieving of the suspension was conducted to remove lumps which otherwise would block the atomization nozzle. The suspension was continuously stirred until spray drying.

2.2. Nozzle characterisation
The nozzle used for atomizing the suspension was a GEA Niro two fluid nozzle. Nozzle characterization was done using a Malvern Spraytec (Malvern Instruments) with a setup shown in Figure 1.
Results of droplet size were recorded during atomizing water at a flow rate of 1.5; 2.5 and 4.0 kg/h using atomization gas flow rates between 1 and 20 kg/h. Knowledge of the spraying behaviour of the nozzle was used in selecting atomization conditions during spray drying.

2.3. Spray drying

A Mobile Minor™ (GEA Niro) spray dryer was used in four different configurations as illustrated in Figure 2.

The plant has a 0.8 m chamber diameter with a cylindrical height of 0.65 and a 40° cone angle. Co-current drying was conducted with the atomization nozzle positioned in the centre of the hot gas dispenser. A pneumatic hammer was mounted on the conical part of the chamber and was in operation during the experiments. Nitrogen was used as drying gas. The inlet drying gas rate was 80 kg/h at temperatures between 155°C and 195°C, and the outlet temperature was between 70°C and 90°C giving a feed rate between 2 and 5 kg/h. In using the IFD-MM configuration the inlet temperature to the fluid bed was 60°C at a rate sufficient to fluidize the granules. The bag filters were cleaned during
operation by back flush purging using nitrogen gas at 2 bar(g). Process parameters were continuously recorded during operation.

2.4. Granule characterisation
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.

Residual moisture content was measured using a Halogen Moisture Analyser (HR73, Mettler Toledo) at 105°C.

Granule morphology was investigated at Technological Institute, Center for Micro Technology and Surface Analysis using a scanning electron microscope (Ultra55, Zeiss).

3. Results and discussions
Initial test using the Drying Kinetic Analyzer™ (DKA) was performed. The DKA is a novel instrument enabling real time drying kinetic measurements and morphology development observations on a levitated drop drying at carefully controlled conditions. The drying behaviour determination of the nano-TiO$_2$ suspensions at 37% solids showed that the drying rate was relatively high (data not shown) and that a spherical granule was produced. The volume reduction during drying of the suspension droplets was 45%. The final size of non-agglomerated granules produced by spray drying is determined by the droplet size obtained in the atomization process and the volume reduction occurring during drying. The volume reduction is often dependent on the drying temperatures. Hence, the drying behaviour determination should be done at the same temperature as during spray drying.

Knowledge on the performance of the atomization system is important for control of granule size. Figure 3 shows the spraying performance of the two fluid nozzle atomization water at three different flow rates. The droplet size is dependent on the liquid flow rate and the atomization gas flow rate. The ratio between the atomization mass flow rate and the liquid mass flow rate (ALR) is normally used to illustrate the performance of two fluid nozzles. Knowledge of nozzles performance can be utilized in adjusting atomization conditions during spray drying experiments as suspensions will be influenced by changing liquid flow rates and ALR in a similar way as found for water.

![Figure 3](image-url)

**Figure 3.** Graph shows droplet sizes produced by the GEA Niro two fluid nozzle operating at three different water flow rates and granule size produced in the Mobile Minor spray dryer (using the A configuration as show in Figure 2) at two different suspension flow rates. Suspension droplet sizes are calculated from the measured granule sizes using the volumetric reduction determined using the Drying Kinetic Analyzer™. Absissa is the Ratio between Atomization gas mass flow rate and the Liquid mass flow rate (ALR).
The size of spray dried granules obtained at a feed capacity of 2.0 kg/h and 3.0 kg/h are shown in Figure 3. The calculated droplet sizes of the suspensions follow the same tendency as that found for water atomization. In producing a non-dusty product the granules should be as large as possible. In this case, however, the mean size (D50) should not exceed 50 µm. Different spray drying configurations have been utilized in producing a product which has a D10 (granules size where 10 % (volume) of the population having a smaller size: i.e. dusty part of the population) as high as possible while keeping the D50 under the 50 µm. Table 1 shows process parameters, granule size and residual moisture content from spray drying experiments using the four different configurations.

| Description                  | Unit | Plant configuration (see figure 2) |
|------------------------------|------|------------------------------------|
| Feed rate                    | kg/h | A  3.1  B  2.9  C  2.8  D  5.0 |
| ALR                          |      | A  1.4  B  1.3  C  2.6  D  3.5 |
| Inlet gas temperature        | °C   | A  154  B  182  C  160  D  195 |
| Outlet gas temperature       | °C   | A  82   B  79   C  84   D  71  |
| Granule size                 | µm   | D(10; V) 91  B  11  C  142  D  17 |
|                              |      | D(50; V) 261  B  32  C  392  D  43 |
|                              |      | D(90; V) 751  B  87  C  912  D  120 |
| Residual moisture            | %    | A  0.91  B  0.5  C  0.42  D  0.3 |

1 Data from cyclone fraction
2 Data from chamber fraction

By using spray drying configuration A the finest part of the population is not collected by the cyclone. Hence, two fractions are obtained. The cyclone fraction has a suitable granule size but the bag filter fraction contains a very dusty product with a D50 of only 5 µm. However, only 5% of the total mass produced was collected under the bag filter. Having two fractions of a product always gives rise to questions on what to do with the non-spec fraction. Often it can be redispersed and mixed with the next production; however, avoiding two fractions is preferable. Figure 4 shows SEM pictures of the granule morphology obtained using the four different configurations. In plant configuration A individual spherical granules were produced as expected from the drying behaviour analysis. Slightly higher tendency for agglomerated granules was obtained for plant configuration B. The reason is that the fine part of the population will stay in the SD-IF chamber until agglomerated with bigger wet droplets and become sufficiently heavy to fall to the product container at the bottom. Agglomeration is an efficient way to remove the finest granules from a population by agglomerating them to bigger granules. This agglomeration process is forced using plant configuration C where the granules collected by the cyclone were returned to the atomization zone. Examples of such agglomerated particles are seen in Figure 4 C. Table 1 also shows that even though atomization has occurred at a higher ALR in the plant configuration C compared to configuration B the mean granule size was larger. Again, using configuration C gives rise to a non-spec fraction collected under the bag filter containing very dusty product and this is not optimal even though that the amount was limited. Agglomeration is very distinct for granules produced using configuration D. The agglomeration occurred in a random way as in the B configuration but, the fluid bed function as a classifier by blowing off the finest granules. Control of the granule size using configuration D was very difficult and having a mean granule size below 50 µm was only obtained for a relatively short time.

Figure 5 shows a SEM picture of granules produced using configuration A. One of the granules has become damaged in the process by either high shear or impact with the production equipment. No binders were used in the suspension preparation, and this limits the granule resistance to shear and impact that may occur especially in the cyclone or in the duct from the chamber. In the cases where binders need to be avoided a low shear process should be considered to ensure that granule damage is kept at a minimum.
With the four different configurations tested, configuration B appears to be the most attractive solution as it is a simple low shear system, it produces only one fraction, it is easy to control and it confines all granules inside the chamber. This configuration has been utilized on other suspensions of nanomaterials where it also proved to be a suitable configuration utilising that the suspensions of nanoparticles dry relatively easily.

Safety issues in spray drying involves a number of individual risks which need to be tackled, e.g. dust explosion, solvent explosion, hot surfaces and emission of granules to the production
environment. These risks are to be considered both with the plant in operation and during cleaning. The risks relating to explosions and hot surfaces is relatively trivial and are routinely tackled doing GEA Niro’s design of spray drying equipment. Also risk of emission of granules is routinely tackled, however with the health concerns associated by dealing with nanostructured granules special emphasis should be laid on this risk. The atomization step produces micronsized droplets which dry to granules still in the micronsize range. This means that the granules produced during spray drying are much easier to control compared to nanopowders as they will remain in the area of where emission has occurred. Even though, release of granules from the spray drying plant should be avoided. This risk can be eliminated using a closed circuit plant as the one shown in Figure 6. This plant operates as the plant configuration B, but with a HEPA filter placed after the bag filters to ensure complete confinement of the nanomaterials. Further, a condenser is used to condense the vapours in the outlet drying gas which means that the gas can be reused after reheating it to the inlet temperature. The exhaust flow is very small compared to a normal open plant. Loss of granules during change of product container is eliminated through the use of the Hicoflex® system from Buck® (Figure 6 b, c). The proposed plant is a Mobile Minor sized plant having a capacity up to 5 kg/h. The plant can be scaled to the full size range that GEA Niro supplies, but in each case the design and level of safety should be selected on the basis of a risk evaluation based on the environmental and health implications with the products to process.

4. Conclusions
This study demonstrates that spray drying can successfully produce a non-dusty, micronsized granulated product from suspensions of nanomaterials. Four different configurations were tested for spray drying a suspension of nano-TiO$_2$. It was concluded that the SD-IF-MM configuration was the optimal configuration for this particular product. A closed circuit configuration of this plant equipped with the Hicoflex® system would enable safe processing of nanomaterials.

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