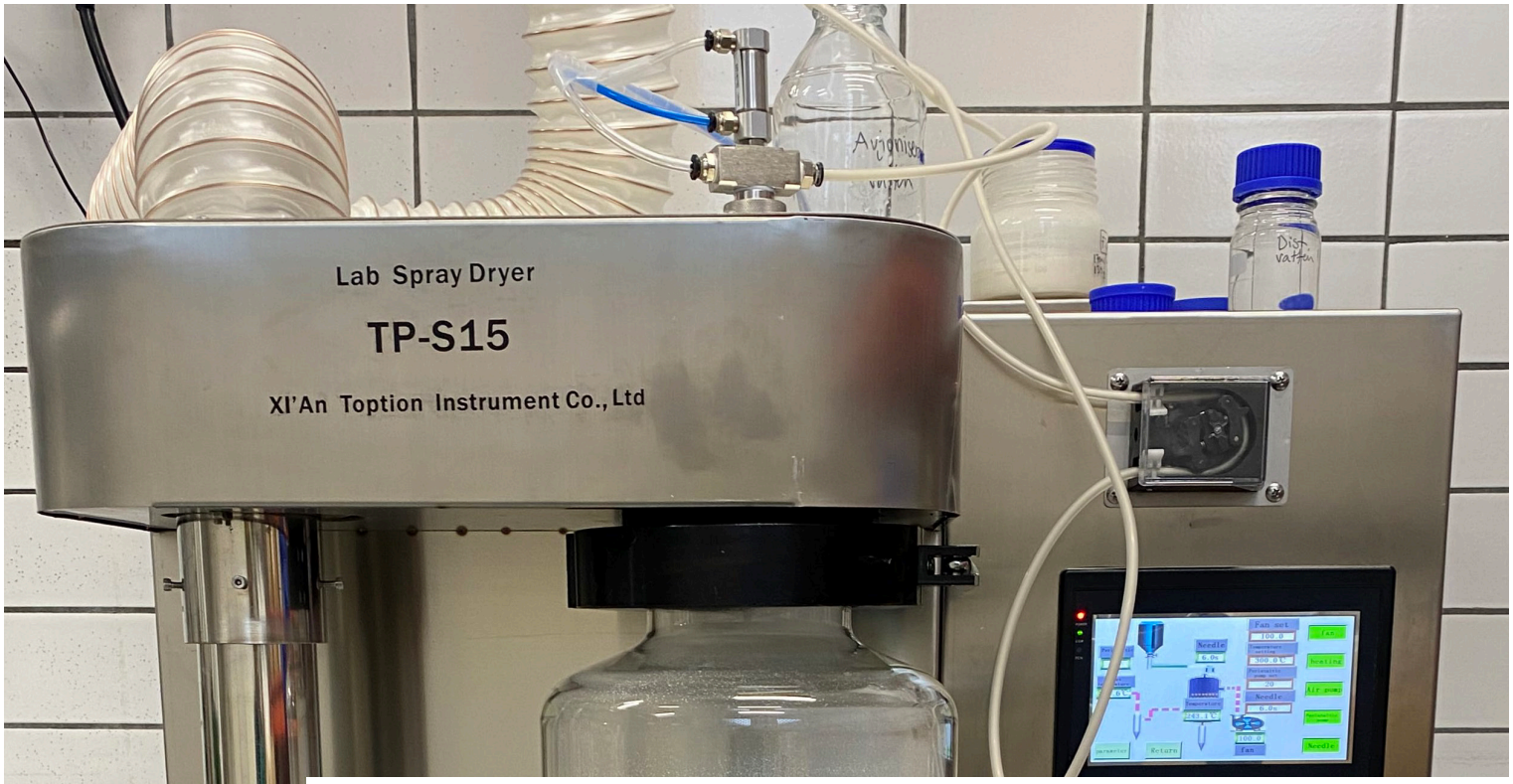

Effect of powder spray drying on catalyst formulation in tablet form

DEPARTMENT OF CHEMICAL ENGINEERING | LUND UNIVERSITY
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Effect of powder spray drying on catalyst formulation in tablet form

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Preface

This master thesis project was conducted at Hulteberg Chemistry & Engineering AB during spring 2023. The project focused on investigating the impact of powder spray drying on catalyst tablet formulation, and it involved extensive experimental work.

I would like to thank my supervisor, Christian Hulteberg, for granting me the opportunity to pursue my master thesis at the company, and your invaluable support throughout the project. Thank you for teaching me to embrace hands-on problem-solving when faced with unexpected challenges and the reality that things don't always go as planned.

I would also express my appreciation to Josephine Digné, my co-supervisor, for her unwavering assistance, prompt responses to my questions, and valuable guidance.

Furthermore, I give my heartfelt thanks to all my colleagues at Hulteberg C&E for their continuous support, encouragement, and inclusion within the company's community.

Kajsa Wahlgren, May 2023, Malmö

Abstract

Heterogenous catalysts consist of a large surface area support material applied with the catalytic active phase, and the activity of a catalyst is often correlated to the surface area per volume. Support materials often need to be processed further to be optimal for specific processes. For example, powders can be suitable for minireactors or fluidized-bed reactors. However, in a fixed-bed reactor, powder increases the pressure drop, and in gas-phase reactions, it risks being blown out. Therefore, the support material needs to be processed further in order to maintain the structure or better suit the reactor. The final form is called the carrier and can for example be tablets, extrudates or encapsulated powder.

The behaviour of powder is, however, more difficult to predict than fluids or gases. This is because powder behaviour is dependent on the degree of heterogeneity of the particles, the packing history of the powder, and the influence of the environment. To tablet a powder, the flowability of the powder needs to be sufficiently good for the powder to fall down the small holes in the tablet machine. Good flowability of a powder is correlated to spherical particles with sizes above 100μm.

This report examines the effect of spray drying on a Y-zeolite powder to increase its flowability and thereby improve the tabletting process of the powder. The best result was also applied to a CeZr powder. The Y-zeolite and CeZr powder have an approximate particle size of 4μm and the objective of utilizing the spray dryer was to generate droplets containing several powder particles, which, upon drying, form larger particles that enhances the flowability of the powder. The flowability was evaluated by calculating the ratio of large particles produced from the spray dryer, along with measuring the angle of repose of the collected powders. The experiments were designed to examine the impact of various settings on the spray dryer and the preparatory steps preceding it. First, the influence of nozzle size was tested, followed by assessing the significance of adding binder to the slurry. Lastly a trial matrix was created, testing the impact of dry content and the feed rate of the slurry.

The results were, in most cases, that the flowability of the powder decreased after spray drying. However, there were two exceptions where the flowability of the Y-zeolite powder actually improved, namely for the samples with highest dry-matter content in the slurry (54wt%). As a result, the combination of a dry weight of 5wt% and a feed rate of 1200 ml/h was determined to yield the best results, and these conditions were used for testing the CeZr powder. However, the flowability of the CeZr powder decreased when subjected to spray drying with these settings. Therefore, it was concluded that every powder requires its own investigation to determine the most suitable settings to increase flowability.

The influence of the spray dryer settings was assessed using graphs in Excel and statistical analysis software. It was observed that a larger nozzle, and exclusion of binder in the slurry, led to a greater extent of large particles. The statistical software revealed significant impact of dry weight in the slurry for the mass ratio of large particles and flowability of the powder. Specifically, a higher dry-matter content yielded more favourable outcomes. On the other hand, the feed rate showed, in almost all cases, no statistical impact on the results.

The spray dried powder was then tableted, and the tabletting performance was compared to that of the original powder. The large particles obtained from the best results of the spray-dried Y-zeolite, which showed enhanced flowability in comparison to the original powder, also improved the tabletting process and more tablets were obtained than from the original Y-zeolite powder. The large particles from the spray-dried CeZr powder, however, showed decreased performance in flowability, and the tabletting process also worked better for the original CeZr powder than the spray dried. It is evident that improved flowability plays a crucial role in enhancing the tabletting process.

For future experiments, the impact of the inlet air stream and inlet air temperature would be of interest to examine. Furthermore, better methods to measure flowability should be considered. The method of measuring the angle of repose has many drawbacks where one of them is that it is very sensitive to the operator and another one is low precision.

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1. Introduction

In today's society, a substantial number of technological elements in the industry are dependent on chemical reactions. Raw materials with low value can be converted via chemical reactions to compounds with a much higher degree of utility. To make the industrial processes more economical and environmentally favourable the reactions need to be as effective as possible. Up to 90% of all chemical processes use heterogenous catalysts to increase the reaction rate, or even enable a reaction to occur at all (Ertl et al., 2008). Heterogenous catalysts consist of a solid material with a large surface area where the catalysing active site is dispersed (Hulteberg, 2017). It can be of various forms, sizes, shapes, densities, porosities etc., and its suitability depends on the application.

When producing the catalyst in industry, the first step is to create the catalyst support material. Thereafter, the active phase is applied to the surface. Specific support material can therefore be used to produce different catalysts. A common shape of support materials is powders, which can be further processed in different ways depending on the desired catalyst form. It can, for example, be encapsulated, tableted or extruded to solids of larger form.

Hulteberg Chemistry & Engineering AB conducts, among other things, a business where catalysts for specific processes are characterized and synthesized. Support material is purchased as a powder, which is used for fluidized-bed catalytic processes. In order to improve the utility of the powder, the goal is to also tablet the powder by using a tabletting machine. However, poor flowability of some powders impair the tabletting process. The reason for the poor flowability is presumably due to the powder particles being too small and not spherical enough, which makes them attach to each other rather than subjugate to gravitational forces. As a solution to the problem, the company has purchased a spray dryer. The purpose of the spray dryer is to spray a liquid slurry of the powder into larger and more spherical particles, which hopefully will enable better flow, and thereby improving tabletting of the powder.

1.1 Aim

The aim of this master thesis is to examine the preparational steps and spray-drying effect of the powder to enable tabletting of poorly flowing powder. The effect of the spray dryer will be of large focus, and the most suitable parameter settings obtained from the evaluation will be presented. The powder obtained from the spray-drying process will be examined by flowability and tabletting performance ability.

1.2 Research questions

- Is spray drying a potential solution for poorly flowable powder in order to increase the flowing properties of the powder?
- Is the composition of the slurry fed to the spray dryer of importance to obtain good flowability of the powder? And if yes, what is the best composition?
- How do the different settings of the spray dryer affect the flowability of the powder?
- Is it possible to produce tablets of the powder obtained from the spray dryer?

1.3 Scope of report

The project was conducted in the following steps. First, a literature study was made to collect valuable information within the area and regarding similar experiments. Subsequently, the experimental phase was initiated. First a Y-zeolite powder was tested in the spray dryer, and the results were analysed. The settings providing the best flowability of the powder were determined and used for spray drying a Cerium Zirconia powder. Lastly, the powders were processed through the tabletting machine and the performances were observed. The results and conclusions are summarized and presented in this report.

1.3.1 Disposition

In the report, background information is presented about catalysts, powder characteristics, the spray-drying process and equipment, and tabletting. Then the material and method of each part of the experiment is explained. The results in flowability of the powders run through the spray dryer are then presented, first an overview of all experiments, and later more detailed results from specific changes in the experiments. The water content of the spray-dried powder, and the results from tabletting the power, is also presented. Additionally, the results are

discussed in similar order as they are presented in the results part. Lastly, conclusions are drawn from the results and discussion.

2. Background

2.1 Catalysts

Catalysts are compounds that, when in contact with a specific reaction, increase the reaction rate without getting consumed during the process. The kinetics is changed by the catalysts, but the thermodynamics of the reaction remains the same (Ertl et al., 2008). The reason for the increase in reaction rate in the presence of a catalyst is due to the catalyst lowering the activation energy that is required for the reaction to take place. Thus, when the reactants collide, the energy will more often be enough to reach the transition state and, thereby, for the reaction to occur. The Gibbs free energy of the overall reaction remains unchanged; however, it is easier to activate the reaction. A schematic graph of the reaction states can be seen in Figure 1 (García-Suárez, 2007).

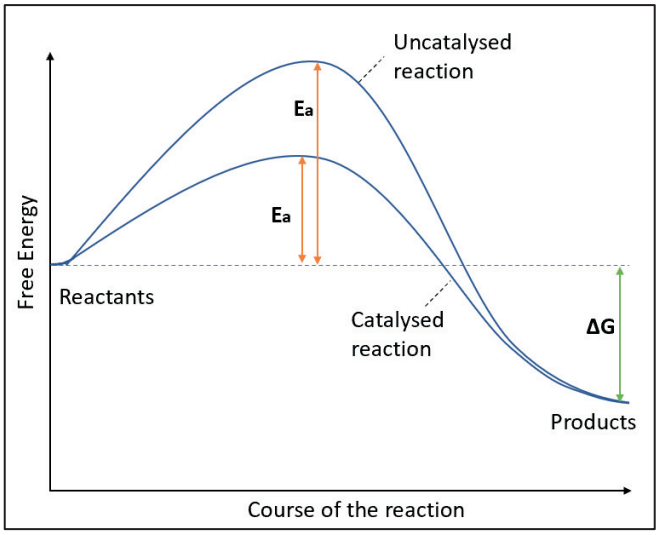


Figure 1: Free energy of a reaction with and without the presence of a catalyst.

The understanding of catalysis started to develop in the late 18th century, and at the beginning of the 19th century, many metals had been characterized with catalytic effects. In the year of 1835, Jöns Jakob Berzelius (1779-1848) proposed the name for the phenomenon of catalysis, and in 1909 and 1912, the Nobel Prize was awarded to important developments within the area (Wisniak, 2010). Today approximately 90% of all industrial chemical processes utilizes catalysts, especially heterogeneous catalysts, in some way to increase the reaction rate and make the processes more effective (Ertl et al., 2008).

Catalysts can be both chemical and biological. Chemical catalysts often consist of metals, and biological catalysis is performed by cells or enzymes (Dill & Bromberg, 2011). Chemical catalysts can be either homogeneous or heterogeneous. Homogeneous catalysts are dissolved in the reaction fluids, while the heterogenous catalysts are solids interacting with the reaction fluid/fluids of different aggregational state/states (Roberts, 2009). The kinetics of the two variants work the same, but the advantages are quite different. One advantage with homogenous catalysts compared to heterogenous catalysts is the reduced limitations by diffusion. From the differences in aggregational state arises a stagnant layer between the phases where particles can only pass by diffusion. To reach the active phase in a heterogenous catalysts the product must also be transported through the pores of the catalysts, which is also limited by diffusion. Homogenous catalysts have less mass transport of this kind (Roberts, 2009). The greatest advantage of heterogenous catalysts is that it is easily separated from the product and thereby have a greater ability to be reused (Emergen research, 2022; Ertl et al., 2008). Due to this, heterogenous catalysts accounted for 73% of the market share of catalysts in 2021 (Precedence research, 2022).

Solid catalysts are often constituted by three structural layers: the active phase, the support, and the carrier. Each layer plays an important role in the different functions the catalyst must fulfil. The **active phase** consists of a catalytic material that executes the catalytic effect on the reaction. The transition group metals in the periodic table are commonly used as active phase materials since they can easily accept and donate electrons from other molecules. Catalysts can be of the unsupported form, but mostly the active phase is applied to a **support material**. The support material is a high surface area material where the active phase is dispersed in order to increase the

exposure to the reactants. A high surface area per volume is often correlated to the high activity of the solid catalyst. Therefore, the support material plays a major role in the performance of the catalyst. The support material can also be modified in terms of thermostability, shape, mechanical strength, and porous structure. Commonly used materials for support are γ-alumina, silica and activated carbon. Zeolites are hydrated aluminosilicates with a crystalline, microporous structure, easily accessible for small molecules, which makes them perfect as catalyst support material. (Ertl et al., 2008)

Support materials often need to be processed further to be optimal for specific processes. For example, powders can be suitable for minireactors or fluidized-bed reactors. However, in a fixed-bed reactor, powder increases the pressure drop, and in gas phase reactions, it risks being blown out (He et al., 2020). Therefore, the support material needs to be processed further in order to maintain the structure or better suit the reactor. The final form is called the **carrier**. The carrier can be obtained in two ways. either the support material is encapsulated by another material, or the support material is tableted or extruded into larger solid particles. The result becomes the carrier. The carrier influences the reactant and product transport between the active phase and bulk due to diffusion limitations. Heat transfer and pressure drop of the reactor also relate to carrier shape and material (Hulteberg, 2017).

2.2 Powders

Powder is a common form of product manufactured all over the world. The behaviour of powder is, however, more difficult to predict than fluids or gases. This is because powder behaviour is dependent on the degree of heterogeneity of the particles, the packing history of the powder, and the influence of the environment. Consequently, this can be a big challenge when designing relevant processes handling the powder and scale-up of existing ones. (Hassanpour et al., 2019)

Powder characteristics can be measured in three ways: *flowability*, *compressibility*, and *compactability*. *Flowability* is when the powder particles flow like fluids. *Compressibility* is when the powder particles are applied to stress resulting in closer packing and interactions, and like a gas, the volume of the powder decreases. When compressed to a great extent some powders can form dense, strong compacts which have behaviours similar to solids, called *compactability*. (Hassanpour et al., 2019)

The flowability of powder is dependent on particle size distribution, morphology, the density of particles and the ability to build bridges (Rosén, 2023). For large particles, gravitational forces are stronger than internal interaction, leading to better flowability of the powder. Small particles, however, have a larger surface-to-mass ratio, and the internal interactions can therefore be dominant compared to the gravitational forces. Morphology also affects the surface-to-mass ratio, where non spherical, or asymmetric, particles have a larger surface-to-mass ratio. Powders with small and asymmetric particles are often more difficult to handle. The powder particle size that becomes easy to handle depends on the internal interactions for the specific powder. However, a rule of thumb is that particle sizes above 100μm have good flowability. If the powder is wet with, e.g. by water or oil, the internal interaction can increase due to the creation of liquid bridges. Furthermore, the flowability of a powder is influenced by the packing history of the powder. If the powder is compressed before poured, the flowability will be worse. (Rosén, 2023)

2.2.1 Flowability measurements

There are a few ways to measure the flowability of a powder. One example of a static method is to measure the angle of repose, and one example of a dynamic method is to pour the powder through an orifice and measure the time.

To measure the angle of repose, the powder is poured through a funnel onto a horizontal base. The pile that arises on the base is controlled by either fixing the size of the base; controlling the base diameter, or fixing the height from the base to the funnel orifice (Hassanpour et al., 2019). Measuring the angle of repose is an easy and traditional method. However, it has a few drawbacks. The result can be very influenced by the operator. The emerged pile can appear different depending on the height at which the powder is poured, or if it is vibrated while poured. The method also has low precision, and if the slope of the pile is not completely straight, variation in measurement points can occur, which decreases the repeatability of the method. (Stimpson, 2023)

The dynamic method mentioned, pouring the powder through an orifice, measures the ability, and the time it takes, for a powder to flow freely through a hole. The geometry of the funnel is of great importance, especially the

diameter of the orifice. Two results can be obtained from this test. One result is millimetre diameter of the smallest orifice the powder can flow through for at least three successful attempts. The other result is the time is takes per powder mass (or volume) to flow through the orifice of a specific size. The test is simple to accomplish and only 50-100g of powder is needed. (Hassanpour et al., 2019)

2.3 Spray dryer

A spray dryer can be used for the creation of catalyst powder, or any powder, that is additionally processed with another shaping process. Contrariwise, catalysts can be prepared with completely different steps and then shaped using a spray dryer. More precisely, it is the support material of the catalyst being prepared in these ways. The active phase of the catalyst is applied after the desired shape of the support material is formed (Ertl et al., 2008). Spray drying used for *shaping* the catalysts support material will be examined further in this report.

A spray dryer is a process where a liquid slurry is fed to a drying chamber through an atomizer. The atomizer disperses the slurry into small droplets that meet a hot air flow inside the drying chamber. Heat transfer from the air to the droplet evaporates the liquid from the droplets, which ends up as dry powder particles, granules particles or agglomerates. Most particles end up at the bottom of the drying chamber and is collected in a vessel. Fine particles follow the exhaust air to the cyclone, where the flow pattern separates the solids from the gas. The fines are collected in a vessel at the bottom of the cyclone, and the exhaust air exits the spray dryer from the top of the cyclone to the atmosphere. Spray dryers are used a lot in the food industry, producing powder of for example, coffee, milk, soup, dried eggs and baby food, but also to produce other products such as household detergents, cosmetics and pharmaceuticals (Masters, 1979). An overview of the spray dryer process can be seen in Figure 2.

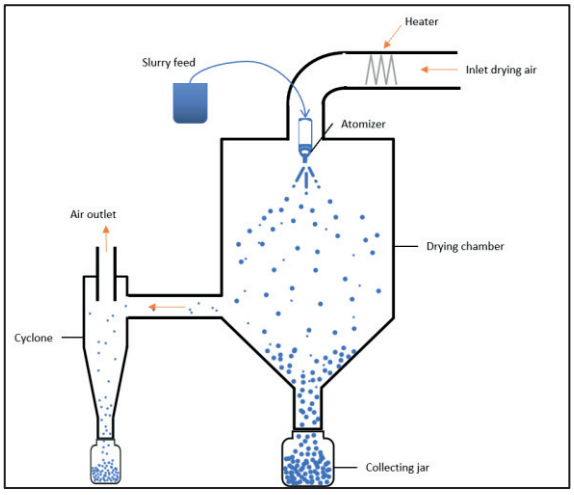


Figure 2: Schematic overview of a spray dryer

2.3.1 History

The first spray drying process implemented in the industry was in operation in 1920 producing milk powder and detergents. However, the concept of spray drying was already presented in detail in 1872 by Samuel Percy, who applied for a patent with the title “Improvements in Drying and Concentrating Liquid Substances by Atomizing”. (Masters, 1979)

2.3.2 Atomization

The purpose of the atomization step is to disperse the fluid into small droplets with a high surface-to-mass ratio to make the drying process more effective. Energy in the atomizer is used to break up the liquid bulk and create new surfaces of individual droplets. The energy used is commonly centrifugal energy, pressure, or kinetic energy. However, sonic and vibrational energy can also sometimes be used. Different atomizer types use different energies to disperse the fluid. (Masters, 1979)

In *rotary atomizers* the fluid is dispersed by centrifugal force since the atomizer consists of a spinning wheel or disc. The fluid enters the wheel or disc in the middle, and the rotation of the wheel or disc causes the centrifugal force that disperses the fluid into the drying chamber, Figure 3. (Masters, 1979)

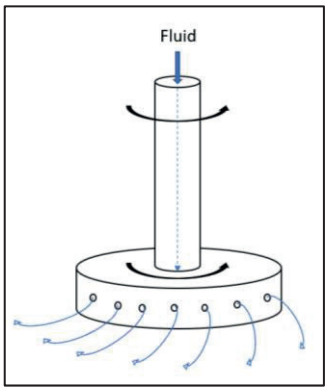


Figure 3: Pictures showing the performance of a rotary atomizer.

Nozzle atomizers instead use pressure or kinetic energy to disperse the fluid. In a *pressure nozzle*, the feed is pressed through the small orifice of the nozzle reaching high speed. When the liquid film enters the drying chamber the pressure difference and instability of the film causes the liquid to disintegrate into a spray. Upstream of the nozzle orifice, the liquid is imparted to rotate, which causes the cone-shaped geometry of the spray to the drying chamber. In *two-fluid nozzles*, however, high-velocity air enters the nozzle as well. Instead of pressure, this nozzle uses kinetic energy from the air to disintegrate the liquid feed into spray droplets. The air and feed are mixed either internally or externally depending on if the air and feed come in contact before or after the nozzle orifice. Pressure nozzles operate with a pressure of up to 680 atm, but the two-fluid nozzles use a pressure of a maximum 7 atm. (Masters, 1979) Schematic figures of the nozzle principles, as well as the spray pattern exposed to the drying chamber, can be seen in Figure 4.

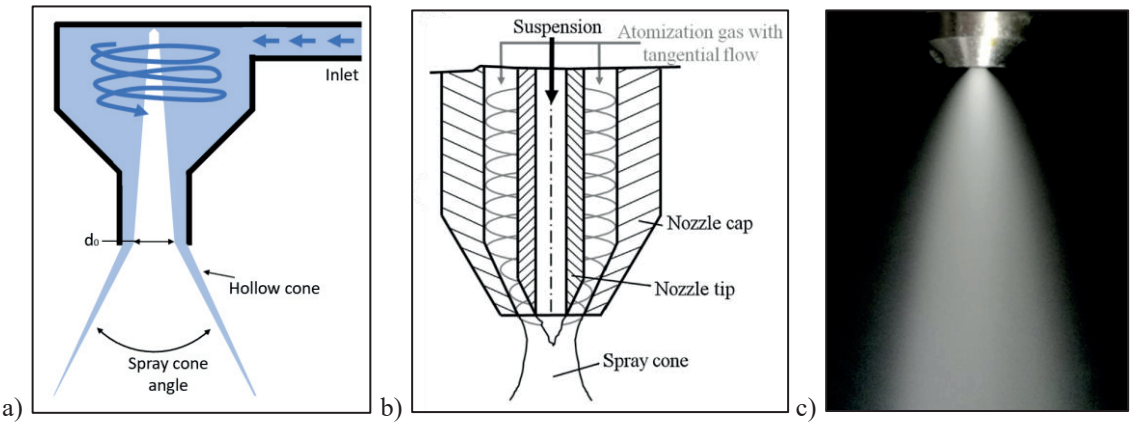


*Figure 4: Pictures showing **a)** the inside of a pressure nozzle **b)** the inside of a two-fluid nozzle with external mixing. Reproduced with permission. (Bremerstein et al., 2014) (Fig. 2b) and **c)** the shape of the spray when entering the drying chamber from a nozzle atomizer with a water supply pressure of 0.5 MPa. Reproduced with permission. (Han et al., 2020)(Fig. 12c).*

The decision of which atomizer to use must be considered according to feed properties and the desired characteristics of the product powder. Using rotary atomizers usually produce particles with mean sizes of 30-120µm whilst nozzles produce more coarse particles with a mean size of 120-150µm (Masters, 1979). When talking about mean size and size distribution, D50 is an expression often used. This means the size that at least 50% of the particles share (Overgaard, 2023). The mean size of the particles from a spray dryer is proportional to feed rate and feed viscosity but inversely proportional to wheel/disc speed, wheel/disc diameter and nozzle pressure, thus inversely proportional to the exposure of energy. (Masters, 1979)

2.3.3 Spray-air contact

As soon as the droplets leave the atomizer, it encounters the hot air stream and is expected to dry. However, the movement of the air and spray as they encounter is of great importance for the characteristics of the drying and is determined by the design of the spray dryer. It can be designed as co-current, counter-current, or mixed. The hot air flow can be dispersed into the drying chamber in different ways. For rotary atomizers, the hot air flow is also designed to rotate throughout the drying chamber. The inlet of the air stream can, for example, be placed in the ceiling above the atomizer wheel, on the top corner of the spray dryer, or vertically upwards underneath the wheel,

with circular motion. Depending on whether the design is co-current or counter-current, the air stream and atomizer spray rotates in the same or opposite direction. For co-current spray dryers with nozzle atomizers the hot air stream often enters the drying chamber at the ceiling above the atomizer. In counter-current designs, the inlet of the hot air stream is located at the bottom of the drying chamber. The air stream enters the chamber in a circular movement upwards towards the spray. To utilize the heat most effectively, counter-current designs are desirable. (Masters, 1979)

Theoretically, spray drying is a rather gentle process. The inlet air temperature is very high, however, initially the heat is used to evaporate the water inside the spray droplets. The drying of a particle only takes up to a few seconds. Dry particles then travel with the air stream to the collection vessel, and the particle itself is not exposed to temperatures higher than the outlet temperature of the air, usually below 100°C. (Rosén, 2023) However, the occurrence of *wall deposition* can increase the particle residence time. Wall deposition is when particles stick to the wall for different reasons: the particles still being wet, swirling particles interacting with the particles already stuck to the wall, or surface dusting on the wall by dry particles. Wall deposit re-entrainment to the air flow is a problem for heat-sensitive products because the quality of the food decreases when exposed to heat. Wall deposit is a larger problem with smaller spray dryers where the radial distance between the atomizer and the wall is shorter. (Masters, 1979; Zhou et al., 2022)

2.3.4 Drying of droplets

How the droplet dries influences the characteristics of the particle, especially the particle size and shape. Higher dry-substance content in the feed and slow drying lead to less and more isotropic shrinkage of the particle. (Qomariyah et al., 2019; Rosén, 2023) Isotropic shrinkage maintains the sphericity to a greater extent due to high internal surface energy. During fast drying, droplet stability is decreased, and droplet deformation can occur, resulting in donut-shaped or other non-spherical particles. This is also affected by the extent of dry matter in the feed. The different types of shrinkage and the resulting shape can be seen in Figure 5. (Qomariyah et al., 2019)

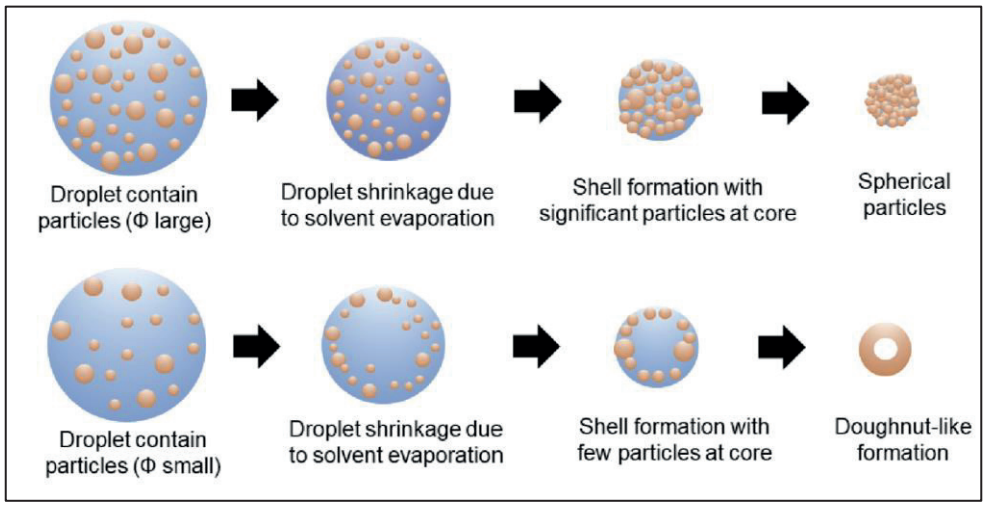


Figure 5: Shrinkage of droplets with high and low volume fractions of dry substance. Reproduced with permission. (Qomariyah et al., 2019)

Choice of atomizer, type of dryer and formulation of slurry can also affect particle size and shape. A design with two nozzle atomizers directed towards each other increases the *agglomeration* of particles. (Rosén, 2023) Agglomeration is when particles adhere to each other and are often desired during spay-drying. (Masters, 1979)

2.3.5 Separation of powder

As mentioned before, large particles will fall down the drying chamber to the collecting vessel to the bottom. However, there will still be a large number of powder particles in the airstream leaving the drying chamber. Therefore, further separation is needed. In cyclone separators, the air containing particles enters the top corner of a cylinder and circulates down the cyclone at the walls. In the middle of the cyclone, a spiral vortex is formed, similar to what happens in a tornado. The air molecules are lighter than the powder particles. Thus, they have less inertia and are more easily influenced by the vortex travelling upwards. The powder particles follow the circular flow downwards and are collected in a vessel underneath the cyclone. The flow pattern of the cyclone can be seen in Figure 6. (University of Calgary, 2023) Except for cyclones, the powder and air can be separated with different

equipment, for example, bag filters. A bag filter separates the powder particles from the air using a textile filter. (Ciobanu et al., 2021)

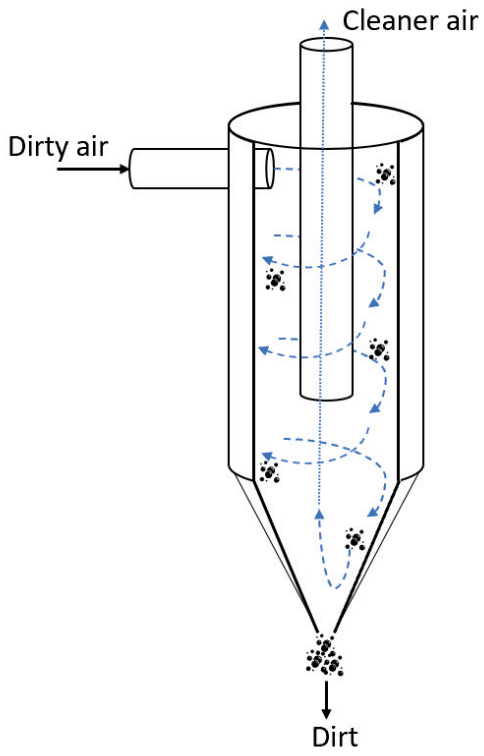


Figure 6: Cyclone separator flow pattern.

2.4 Tabletting

Powder can be further processed into tablets when applied to high-stress motion. A tablet machine consists of receptacles, called *dies*, each with several small holes of only a few millimetres that are filled up with powder. The powder in the die holes is compressed by *punches* entering the hole from both the top and the bottom, exposing the powder to high pressure. Different settings on the machine determine the amount of powder volume in each hole and the pressure applied to the tablets resulting in different tablet characteristics such as strength, density and mass. The main interest in industrial applications using tablets are tablet tensile strength and tablet disintegration/dissolution behaviour. (Emady et al., 2016)

To increase the flowability of the powder and the ability to control it, the powder is often pre-processed into granulates before tableted. This also decreases the risk of segregation between the formulation ingredients. Granulation can be done both as wet and dry, and the idea is to make the particles attach to each other into larger clusters or agglomerates. In wet granulation, a liquid binder is used to agglomerate the particles, and in dry granulation, the powder is compressed into a large ribbon and then milled into granulates. (Emady et al., 2016)

3. Material and methods

3.1 Powders

The powder of interest to tablet was a Cerium-Zirconia (CeZr) powder with a particle size of about 3.5µm. However, the cost of this powder was high. Therefore, a Y-zeolite powder with the size of 4µm was used for the experiments instead. The best result from the Y-zeolite experiments was then tested using the CeZr powder and compared. As a reference, the powder Puralox SSCa-150/120 was used, an alumina oxide powder, since its flowability was good enough for tabletting without major disruption. The particle size of this powder was 149µm. As a binder, the boehmite powder Disperal was used, and graphite was used as a lubricant.

3.2 Instruments

A “Lab Spray Dryer TP-S15” from Toption Lab was used for the spray drying step, and a “10 STN-“D” Tooling-Pre Compression Mini Press-II” from Pankaj Industries was used as the tablet press instrument. The specific spray drier used consists of a two-fluid pressure nozzle, and the powder is separated from the gas passing through a cyclone.

3.3 Methods

A mixture of slurry was blended and subsequently fed to the spray dryer. From the spray dryer, the resultant powder mass was measured, and the powder was either calcinated or dried in an oven. To assess the flowability of the spray-dried and further calcinated/dried powder, the angle of repose was measured and compared to that of the original powder. The mass of the powder collected from the spray dryer was measured for every run, and the angle of repose was measured. The powder was then tableted, and the mass of tablets produced was measured.

Initially, multiple spray drying experiments were conducted to verify and better learn the spray dryer installation effects, after which three experimental studies were conducted. For the first test, various nozzles were tested to evaluate the impact of nozzle size and the preferred size was determined. Secondly, experiments were conducted regarding the significance of adding a binder to the slurry. Thirdly, a trial matrix was constituted to evaluate the significance of the powder and water composition in the slurry, as well as the dependence on feed rate. The results of the trial matrix also present the combined significance of these two parameters.

3.3.1 Mixing slurry

A known volume of water was measured with a graduated flask and cylinder for adequate volume precision. The water was added to a vessel which was placed on a magnetic stirrer. Powder and binder mass was measured and added to the stirring water successively. The planned composition of each test is presented in Table 1, Table 2, and Table 3 below, and Table 11 in the appendix presents the exact masses of the compounds of every sample.

When testing the tabletting machine, 100g of powder was decided to be sufficient for initial tests to obtain a few acceptable tablets. Therefore, the slurries for the trial matrix contained at least 110g of powder since some of the powder exits the ventilation system during the run of the spray dryer.

3.3.2 Spray dryer

The parts of the spray dryer were installed, and the fan and heat were started. When the heat of the inlet air stream reached a pre-determined value, the slurry was fed to the spray dryer. The spray dryer then continued for a certain amount of time, and the temperature of the outlet and inlet stream was measured every other minute to track the process performance. When the run was finished, water was fed to the spray dryer for a few minutes to clean the hoses. The feed and heat were then turned off, and the temperature started to decrease. When the temperature reached below 50°C, the fan was also turned off. During further self-cooling of the spray dryer, the powder in the collection vessels was transferred to plastic storage vessel. If the spray dryer were to be used again the same day, the glass chamber was emptied from powder using a brush. Otherwise, the chamber was taken down and cleaned with water.

The powder from the spray dryer was collected in two vessels. According to the literature, the vessel below the glass chamber collects powder with larger particle sizes. Therefore, this powder will be referred to as “large particles powder” or just “large”, and the powder collected from the vessel below the cyclone as “fine particles

powder" or "fines". The mass ratio between large particle powder and fine particles powder was calculated according to Equation 1, and the powders were kept separate during the following analysing and tabletting steps.

$$mass\ ratio = \frac{m_{large}}{m_{large} + m_{fines}} \quad (1)$$

3.3.3 Calcination and drying

After the spray drying process, the powder was heat treated. In the presence of a binder in the slurry, the powder was calcinated, and if not, the powder was only dried. Calcination was performed by increasing the temperature in the oven with 120°C per hour up to 500°C, where the temperature was kept constant for 4 hours before cooling. For drying, the temperature was instead kept constant at 120°C for 15 hours before cooling.

The powder mass was measured before and after calcination or drying. The assumption was made that the powder was completely dry afterwards, and thereby the water content before heat treatment could be calculated using Equation 2.

$$w_{\%} = \frac{m_{after} - m_{before}}{m_{before}} \quad (2)$$

3.3.4 Angle of repose

To examine the flowability of the powder, the angle of repose was measured. A funnel was held by a stand at a height where the outlet of the funnel was 4cm above the table. The outlet diameter of the funnel used was 2cm. A paper was placed under the funnel, and the powder was poured carefully through the funnel creating a pile on top of the paper. When the top of the pile reached the outlet of the funnel, the edges of the pile on the paper were marked with a pencil. The set-up can be seen in Figure 7.

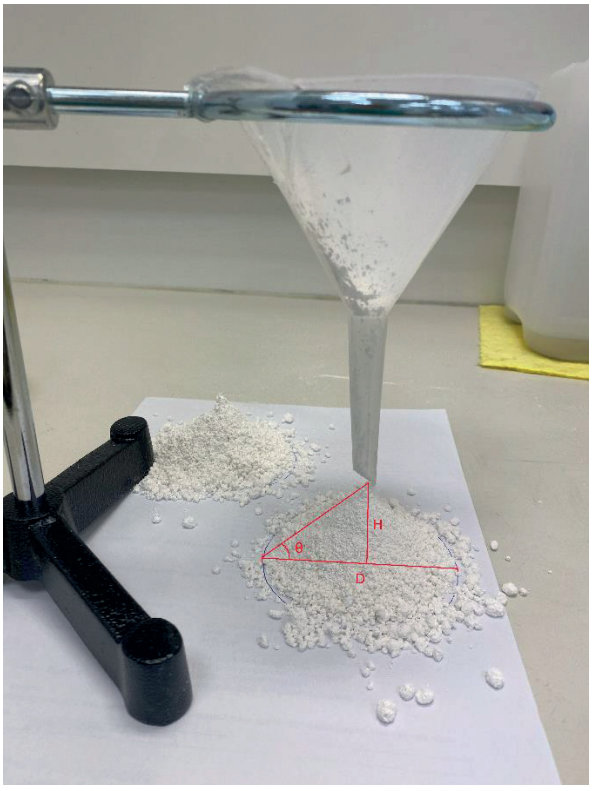


Figure 7: The set-up of the angle of repose measurements of a powder

The diameter of the pile circle on the paper was measured at four different angles, and the average value was used to calculate the angle of repose, Θ, using Equation 3 below.

$$tan(\theta) = \frac{2H}{D} \quad (3)$$

The angle of repose was measured for both the large and the fine particles powder from the spray-drying experiments. A smaller angle of repose corresponds to better flowability, which was therefore desired. To reduce the variability in the experimental results, the angle of repose measurement was performed four times for every powder.

3.3.5 Tabletting

At the end, a few samples were tabletted. The tabletting machine and its parts were assembled according to the instructions of the tabletting machine. The size of the dies used was 3x3mm. The powder was poured into the feed vessel, and the machine was put on. From the beginning of each run the main thickness, the weight adjustment, and the tamping thickness was set equally to all tests. However, during each run, this was adjusted a bit as an attempt to improve the tabletting process for each powder. Since not much time was devoted to the tabletting machine, the best pressure and speed were unknown and not of interest in this report.

The samples tableted were original Y-zeolite powder, original CeZr powder, original Puralox, the best result of Y-zeolite from the trial matrix and spray-dried CeZr powder. A mix of each powder was prepared according to the recipe of the CeZr tablets purchased by Hulteberg Chemistry & Engineering AB, consisting of Dispersal binder and graphite. The same amount of powder, 50 g, was added to each preparation mix, and with the additives, 63 g of preparation mix was obtained.

3.3.6 Execution of spray drying experiments

Three tests were performed and analysed. First, the nozzle size of the spray dryer was examined, secondly the significance of the binder added to the slurry, and lastly, a trial matrix examining slurry composition and spray drying feed rate. The flow and temperature of the inlet air stream could also be changed, but these were kept constant for each experiment.

For the nozzle test, the inlet air temperature settings were kept constant at 250°C and the fan at maximum capacity creating an air flow of 336 m^3/h. The composition of the slurry was 40wt% powder with 3.4% binder. The feed rate was set to 900 ml/h. The nozzle sizes tested were 0.1mm, 2mm and 2.5mm. The data is summarized in Table 1.

Table 1: Nozzle test set values for the different parameters. Nozzles size is the only parameter varied.

Sample name	Powder in slurry [%]	Binder in powder [%]	Inlet air temp[°C]	Airflow [m^3/h]	Feed rate [ml/h]	Nozzle size [mm]
N1	40	3.4	250	336	900	0.1
N2	40	3.4	250	336	900	2
N3	40	3.4	250	336	900	2.5

For the binder test, the temperature of the inlet air stream was changed to 300°C instead of the maximum temperature settings of the air stream. A nozzle size of 2.5 mm was used, and the composition of the binder was, of course, varied. Otherwise, the set values were the same as in the nozzle test. The data for the binder test is summarized in Table 2.

Table 2: Binder test set value for the different parameters. The binder amount is the only parameter varied.

Sample name	Powder in slurry [%]	Binder in powder [%]	Inlet air temp [°C]	Airflow [m3/h]	Feed rate [ml/h]	Nozzle size [mm]
C1	40	0	300	336	900	2.5
C2	40	3	300	336	900	2.5
C3	40	10	300	336	900	2.5

Lastly, the trial matrix was performed. The inlet air temperature was 300°C here as well, the nozzle size was 2.5 mm, and no binder was present in the slurry, while the powder composition and feed rate were changed. A triplet of one of the setting combinations was also made to test the standard deviation of a run. The data is summarized in Table 3.

Table 3:Trial matrix set values for the different parameters. Powder amount and feed rate are the only parameters that was varied.

Sample name	Powder in slurry [%]	Binder in powder [%]	Inlet air temp [°C]	Airflow [m^3/h]	Feed rate [ml/h]	Nozzle size [mm]
F11	20	0	300	336	400	2.5
F12	20	0	300	336	1200	2.5
FX1	37	0	300	336	400	2.5
FX2	37	0	300	336	1200	2.5
F21	45	0	300	336	400	2.5
F22-A	45	0	300	336	1200	2.5
F22-B	45	0	300	336	1200	2.5
F22-C	45	0	300	336	1200	2.5
F31	54	0	300	336	400	2.5
F32	54	0	300	336	1200	2.5

For the nozzle and binder test, the results were compared and analysed in graphs in Excel. The trial matrix had two input parameters, unlike the nozzle and binder tests which only had one input parameter each. To analyse the statistical significance of both parameters, a multifactor *analysis of variance table* (ANOVA table) was created in Statgraphics, with 2 as the maximum order of interaction. The dry weight and feed rate were set as input parameters, and the mass ratio as response variable. When creating the ANOVA table for the mass ratio, every sample was inserted once since only one mass ratio was obtained from each sample. However, four angles of repose were obtained from each sample. Therefore, each sample was inserted four times to create the ANOVA table for the angle of repose.

A full factorial *design of experiment* (DOE) was also created for the trial matrix in the statistical program JMP. To be able to insert the four angles of repose and the mass ratios for each test, every test was inserted four times and added with the same mass ratio every time but with different angles of repose.

4. Results

4.1 Performance of methods

The performance of spray drying varied a lot while conducting the tests. With the fan at maximum performance combined with the existing ventilation system, the temperature of the inlet air stream almost never reached values above 240°C. When using a set value of 300°C, the slurry was fed to the spray dryer when the temperature reached above 230°C. The reason for this was that the inlet airstream temperature increased very slowly at this level. During the spray drying performance, usually around 10-20 minutes, the temperature increased further a few degrees but almost never above 235°C.

Additionally, according to the literature, most particles were expected to end up in the collection vessel at the bottom of the drying chamber, corresponding to the powder of large particles being of greater mass than the powder of fine particles. However, this was not obtained in any case from the experiments with this spray dryer. The mass of the fine particles powders was always greater than the large particle powders.

The performance of the chosen methods for measurements also showed variations in results. The angle of repose is a traditional method to measure the flowability of powders, and the equipment and set-up was easily arranged. Therefore, this method was chosen to analyse flowability. To increase the reliability, the angle of repose measurements was performed on four piles of every powder. However, as executing the measurements the observation was made that the result is very sensitive to how it is operated. For example, it appeared to be different pile sizes if the powder was poured in the middle of the funnel directly through the hole or if the powder was poured at the side of the funnel to let it flow down the funnel slope itself before entering the hole down to the base. Slowly vibrating down the powder also showed different results from pouring it all at once. Large scoops of powder destroyed the created tension of the pile sides, causing the pile to flatten itself to the ground. Vibration movements allowed only small portions of powder to flow down the funnel and onto the pile at the same time, enabling better build-up of the pile apex.

4.2 The angle of repose – all tests in summary

The angles of repose of all tests can be seen in Figure 8 for fine particles and Figure 9 for large particles. The result is presented as a box and whisker diagram. A smaller value corresponds to better flowability.

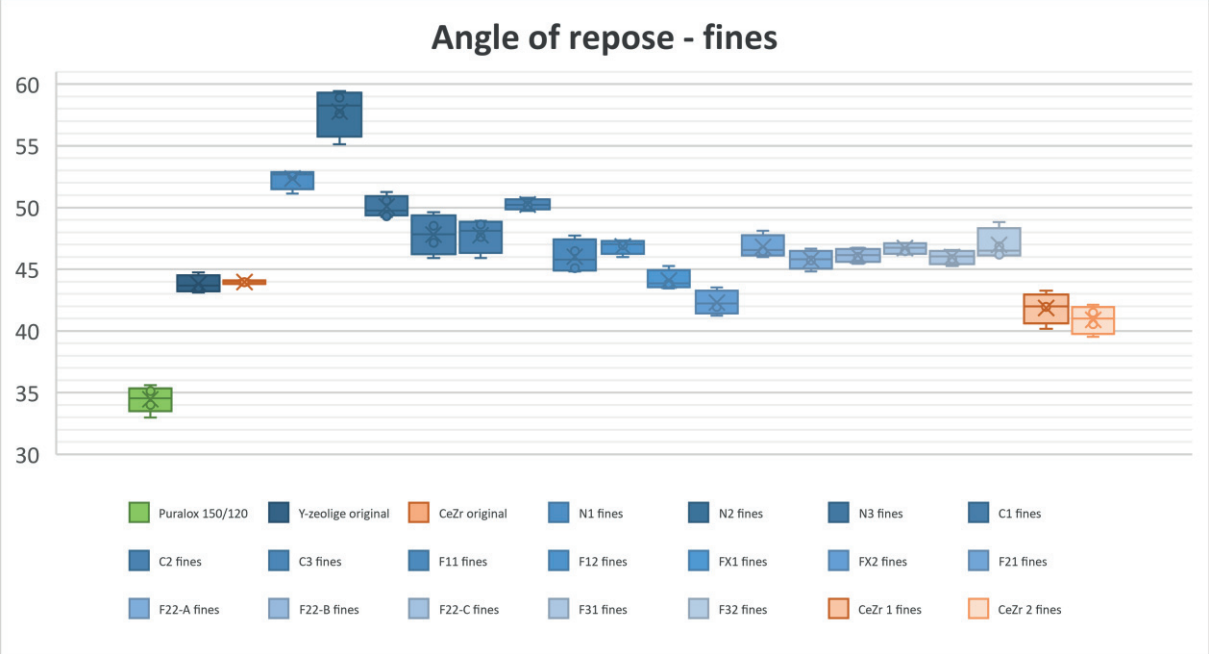


*Figure 8: A box and whisker diagram of the angles of repose for the **fine** particles obtained from all tests, together with the angles of repose for the original powders. Green is the reference Puralox powder, blue boxes are the Y-zeolite powder, and orange boxes the CeZr-powder.*

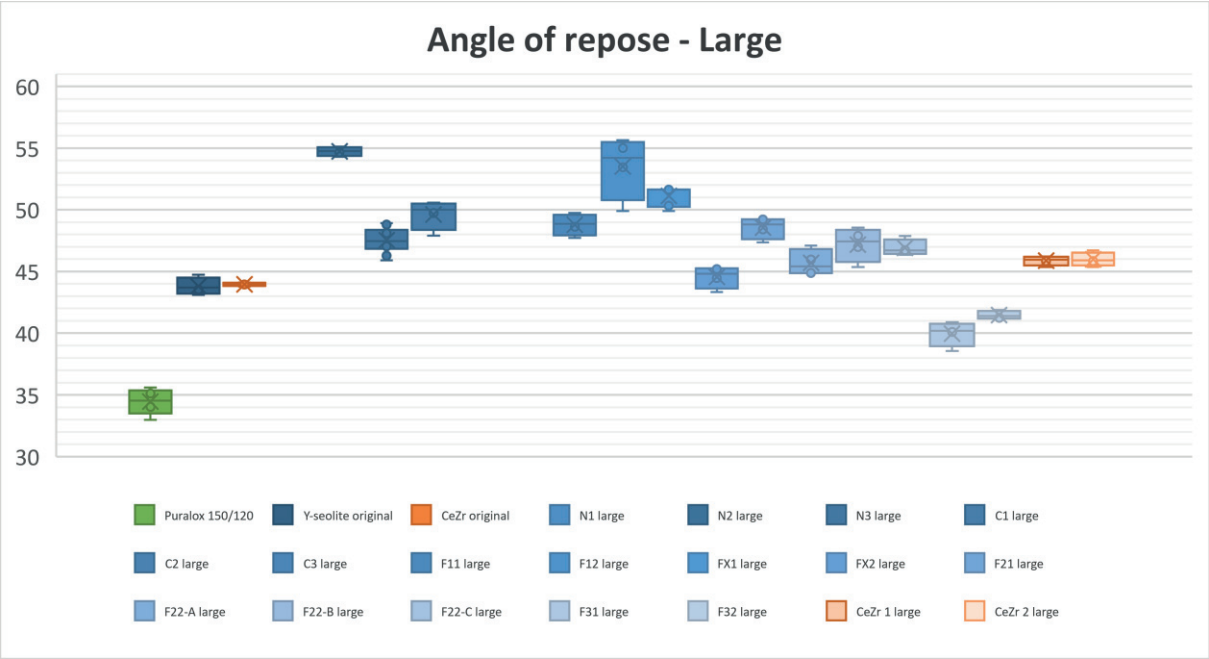


*Figure 9: A box and whisker diagram of the angles of repose for the **large** particles obtain from all tests, together with the angles of repose for the original powders. Green is the reference Puralox powder, blue boxes are the Y-zeolite powder, and orange boxes the CeZr-powder.*

According to Figure 8, fine particles collected from spray drying Y-zeolite powder has a larger angle of repose than the original Y-zeolite powder. Contradictory, CeZr powder seems to decrease in angle of repose while spray dried. Puralox powder still has the smallest angle of repose. The result from the large particles seems, however, to be different, according to Figure 9. Most spray-dried Y-zeolite powders still have a larger angle of repose compared to the original powder, except for FX1 and FX2. CeZr shows larger angles of repose after spray drying. Puralox powder has the smallest angle of repose also here.

4.3 Nozzle size test

A slurry of 40% dry weight was prepared and used for the nozzle test. Combining this dry weight with the smallest nozzle size, 0.1 mm, the slurry became clogged inside the nozzle, resulting in a flow blockage. Therefore, the run was terminated quickly, before all slurry was fed to the spray-dryer, and only a small amount of powder was obtained. The mass ratio was anyways measured and inserted into an Excel sheet, Figure 10. No significance-analysis was made for this test. However, observing the results, the trend shows that a larger nozzle gives higher mass ratios.

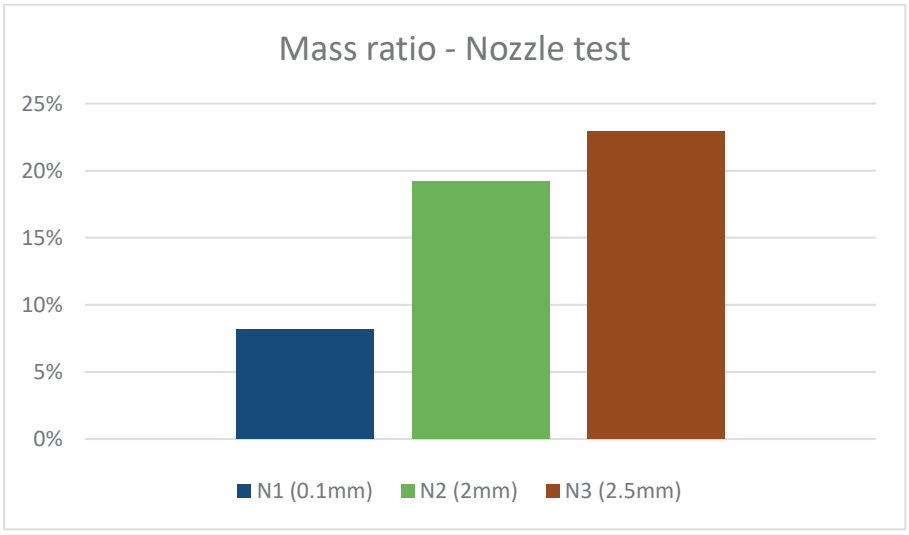


Figure 10: Mass ratio of large particles for each of the nozzle test runs.

From the four measurements of the angle of repose, a box and whisker plot was created in excel, Figure 11, for both the fine and large particle powders collected from the spray dryer.

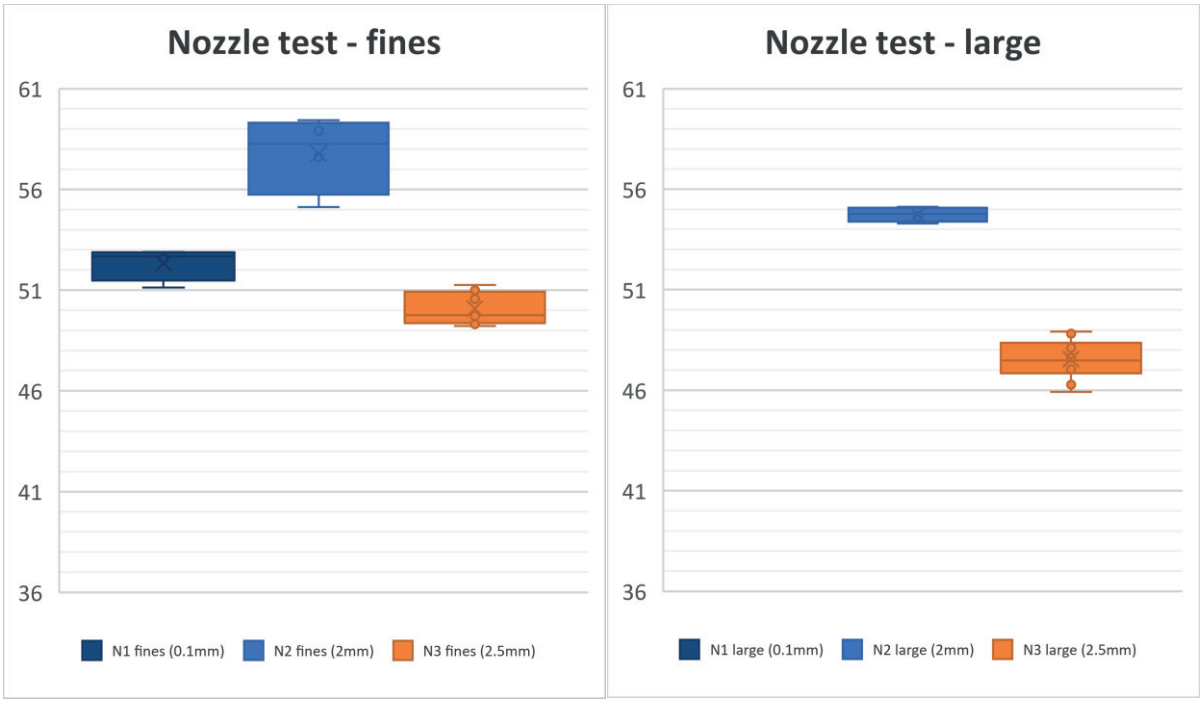


Figure 11: Box and whisker plot from the four replicated of angle of repose measurements for the nozzle test. A comparison between the fine particles can be seen to the left and the large particles to the right. The amount of large particle powder when using the 0,1mm nozzle was too small to be able to measure the angle of repose.

As mentioned before, only a small amount of powder was obtained from the 0.1mm nozzle run. The amount of collected large particles was thus too small to measure the angle of repose. Looking at the fine particle results of the three nozzle sizes, no linear trend can be observed. No significant difference can be seen between the smallest and the largest nozzle sizes; however, the 2mm nozzle seems to give the worst flowability. For the large particles, the largest nozzle seems to give the best flowability comparing only the two sizes from which the powder's angle could be measured. It was decided to continue with the largest nozzle size for further testing.

4.4 Binder composition test

In the same way as the nozzle test, the binder composition test mass ratios were inserted into an Excel sheet, and the results can be seen as a staple diagram in Figure 12. The results of the angle of repose from this test can be seen in Figure 13.

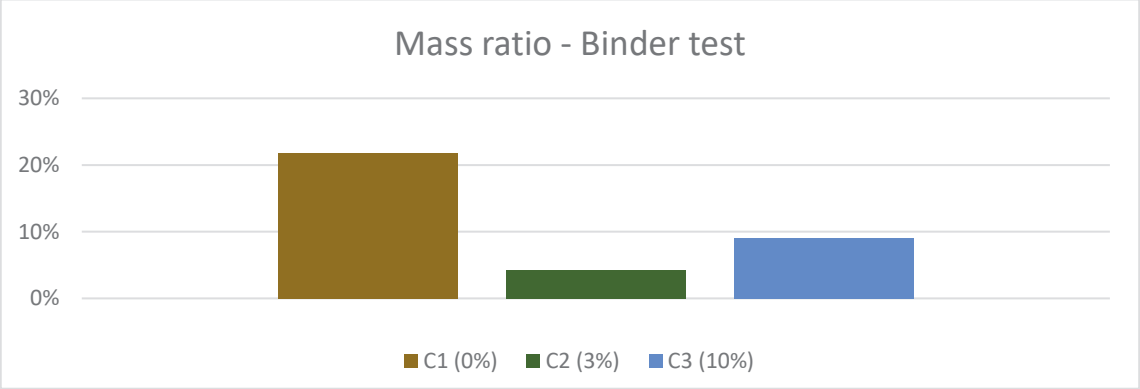


Figure 12: Mass ratio of large particles for each of the binder composition test runs

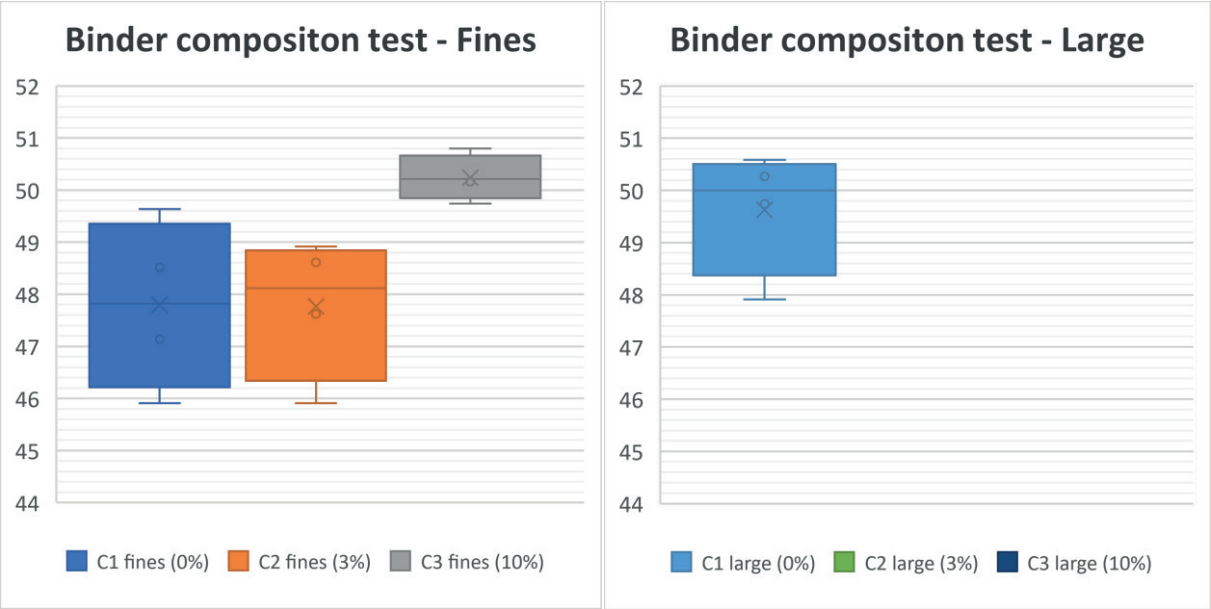


Figure 13: Box and whisker plot from the four replicated of angle of repose measurements for the binder composition test. A comparison between the fine particles can be seen to the left and the large particles to the right. The amount of large particle powder when using 3% and 10% binder composition was too small to be able to measure the angle of repose.

Contradictory to the nozzle test, no linear trend can be seen for the mass ratios in this test. However, when using no binder in the slurry, it seems that the amount of collected large particles increased a lot. For the fine particles, the angle of repose seems smaller when using less binder, but no significant difference can be seen between 0% and 3%. Too small an amount of large particles were collected while using 3% and 10% binder for it to be possible to measure the angle of repose, thus, nothing can be said about any trend here. It was decided to continue with 0% binder for the coming tests.

4.5 Trial matrix

The original plan was to make a trial matrix where the dry weight was changed between three levels: 20%, 45% and 70%. However, while adding the powder to the water when making the slurry, it became more and more difficult to suspend the powder as the dry weight increased. The maximum value of dry weight achieved was 54%. When the maximum value changed, the middle value also changed, from 45% to 37%, but results were anyways obtained for both these values. All four values of dry weight could be included in both the ANOVA tables from Statgraphics as well as the DOE from JMP.

4.5.1 Mass ratio

The trial matrix mass ratios were also measured and summarized in a table plot in Excel, Figure 14.

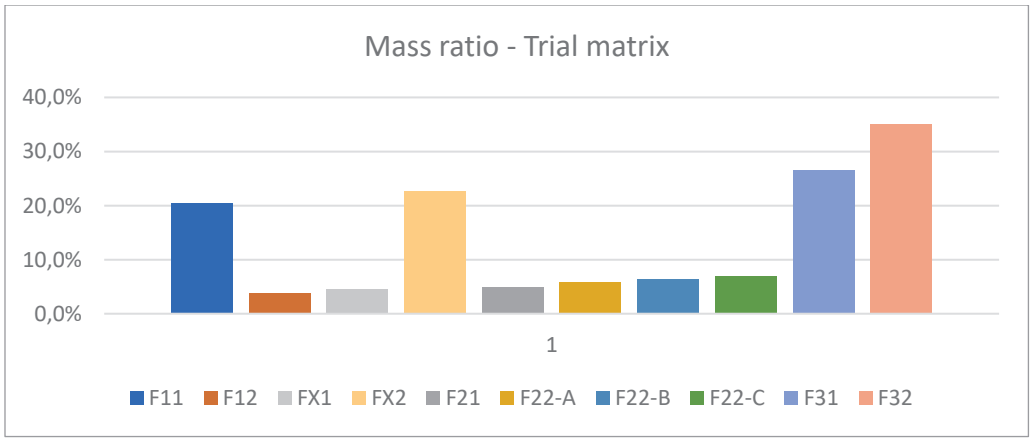


Figure 14: Mass ratio of large particles for each of the runs in the trial matrix

The ANOVA table created from the trial matrix results can be seen in Table 4. To visualize the results better a means plot was created from the ANOVA table, which can be seen in Figure 15 for both the dry weight and the feed rate.

Table 4: Multifactor ANOVA table for Mass ratio for the large particle powders - Type III Sums of Squares. All F-ratios are based on the residual mean square error. Created in Statgraphics.

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Feed rate (400,1200)	0.0018	1	0.0018	53.8	0.0181
Dry weight (20,54)	0.0777	3	0.0259	766.3	0.0013
Feed rate*Dry weight	0.0327	3	0.0109	322.2	0.0031

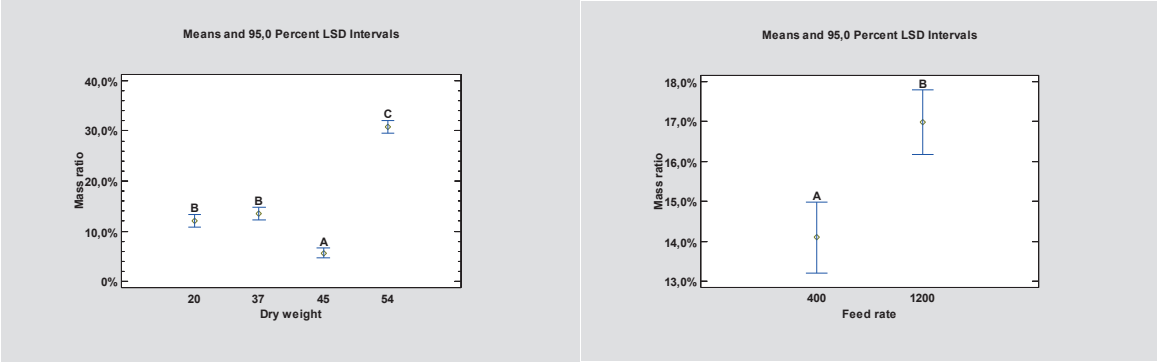


Figure 15: Multifactor ANOVA for mass ratio for large particle powders depending on dry weight to the left and feed rate to the right.

Upon examining the P-values in Table 4, it becomes evident that both the dry weight and the feed rate have a significant impact on mass ratio when spray drying at a confidence level of 95%. Moreover, the combined effect of the two input parameters is statistically significant. Figure 15 shows that the mass ratio results do not display significant disparities between dry weight percentages of 20% and 37%, as they belong to a shared group, namely group B. Conversely, dry weights of 45% and 54% constitute distinct groups, indicating significant differences between them and group B. Furthermore, there exists a significant difference in mass ratio between the two different feed rates, owing to the same rationale.

4.5.2 Angle of repose

The angles of repose from the trial matrix are presented as a box and whisker plot for the fine particles and the large particles as Figure 16 and Figure 17, respectively.

*Figure 16: Box and whisker plot from the four replicated of angle of repose measurements for the **fine** particles from the trial matrix test.*

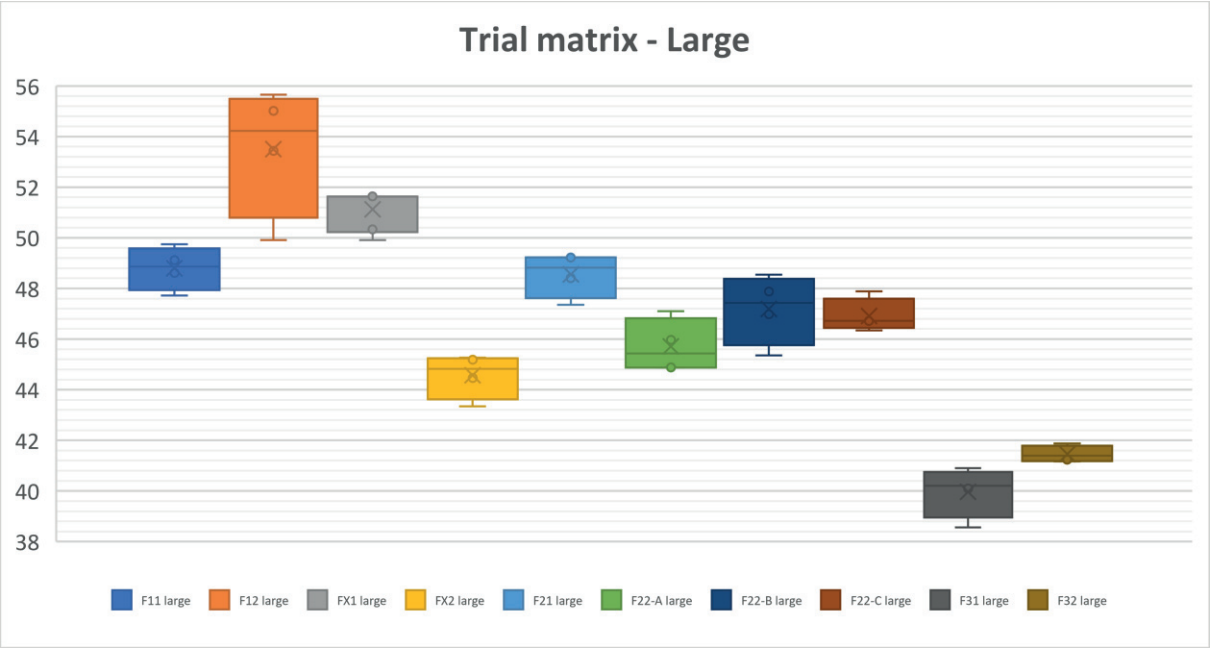


*Figure 17: Box and whisker plot from the four replicated of angle of repose measurements for the **large** particles from the trial matrix test.*

It is difficult to say something about any trend appearing for the angle of repose dependent on mass ratio and feed rate from Figure 16 and Figure 17. However, from the fine particle results, it appears that FX2 (37% dry weight, 1200 ml/h feed rate) has the best flowability. This is not in accordance with the large particle results where F31 (54% dry weight, 400 ml/h feed rate) appears to have the best flowability. Furthermore, F31 large does not overlap any other test, but FX2 fines are not significantly different from FX1 fines.

An ANOVA table was created also here. The P-values can be seen in Table 5, and the difference between the dry weight can be seen in Figure 18.

Table 5: Analysis of Variance for the angle of repose - Type III Sums of Squares.
All F-ratios are based on the residual mean square error. Created in Statgraphics.

Source	P-Value fines	P-Value large
Feed rate (400,1200)	0.6297	0.2207
Dry weight (20,54)	0.0000	0.0000
Feed rate*Dry weight	0.0083	0.0000

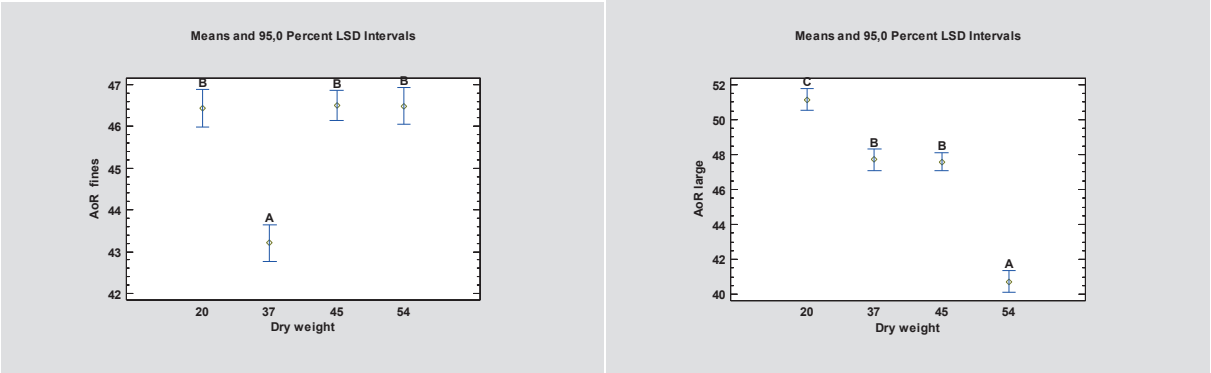


Figure 18: Multifactor ANOVA for the angle of repose depending on dry weight. Fine particles result to the left and large particles to the right.

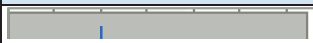
Table 5 shows that the dry weight is statistically significant for the angle of repose, but the feed rate is not. However, the combined effect is still valid. This is valid both for the fine and the large particles. Figure 18 shows that 37% dry weight is the only value being different from the other in angle of repose for fine particles since it belongs to group A and all the other dry weight belongs to group B. More diversity can thus be seen for the large

particles. Since feed rate did not have a significant impact on the angle of repose there was no difference between the angles of repose between the feed rates.

4.5.3 Design of experiment

In the statistical program JMP, a *design of experiment*, DOE, was created. For the DOE all dry weight were used, but not the triplicate of 45% dry weight. The average value of those three values were instead used. The effect summary from the DOE can be seen in Table 6. The P-values show that the dry weight has a significant impact on the results. The combined effect is significant but not the feed rate itself.

Table 6: Effect summary of DOE Trial matrix created in JMP.

Source	LogWorth		P-value
Dry weight (20,54)	6.439		0.0000
Feed rate (400,1200)	0.175		0.6677
Feed rate*Dry weight	1.614		0.0243

An effect test and parameter estimate of each of the response variables were created and is presented in Table 7 for the mass ratio, Table 8 for the angle of repose of large particles and Table 9 for the angle of repose of fine particles.

*Table 7: Effect test and parameter estimates for response variable **Mass ratio** from DOE created in JMP.*

Source	Estimate	Std Error	DF	Sum of Squares	F Ratio	Prob > F
Feed rate (400,1200)	0.0077	0.0178	1	0.0019	0.1883	0.6677
Dry weight (20,54)	0.0649	0.0239	1	0.0730	7.3659	0.0112
Feed rate*Dry weight	0.0569	0.0239	1	0.0562	5.6661	0.0243

Table 7 shows that the mass ratio is affected by the dry weight and the combined effect, but not only the feed rate, with a confidence level of 95%. The positive sign of the estimates indicated that the trend is positive, meaning that the mass ratio increases with increasing dry weight.

*Table 8: Effect test and parameter estimates for the response variable **Angle of repose** of **large particle powders** from DOE created in JMP.*

Source	Estimate	Std Error	DF	Sum of Squares	F Ratio	Prob > F
Feed rate (400,1200)	-0.1525	0.5242	1	0.7258	0.0847	0.7732
Dry weight (20,54)	-4.6471	0.7034	1	374.2218	43.6457	<.0001
Feed rate*Dry weight	-0.8981	0.7034	1	13.9764	1.6301	0.2122

Table 8 shows that the angle of repose of large particles is affected by the dry weight alone. No combined effect or feed rate effect is significant, with a confidence level of 95%. The negative sign of the estimate indicated that the angle of repose decreases with increasing dry weight.

*Table 9: Effect test and parameter estimates for the response variable **Angle of repose** of **fine particle powders** from DOE created in JMP.*

Source	Estimate	Std Error	DF	Sum of Squares	F Ratio	Prob > F
Feed rate (400,1200)	-0.0707	0.3270	1	0.1560	0.0468	0.8303
Dry weight (20,54)	0.2055	0.4387	1	0.7318	0.2194	0.6431
Feed rate*Dry weight	-0.0098	0.4387	1	0.0017	0.0005	0.9823

Table 9 shows that no input parameter is significant for the result of angle of repose for fine particles. No trend can be observed on a confidence level of 95%.

A prediction profiler from the DOE was also created in JMP and can be seen in Figure 19 below, which is a visualization of the DOE results. The feed rate has very little or no impact on the mass ratio and angles of repose. The impact of the dry weight is more distinct and is seen to be positive for the mass ratio and angle of repose - fines but negative for the angle of repose - large. Since a high mass ratio and low angle of repose are desired, these results seem to conclude that high dry weight is advantageous, at least if observing the collected large particles.

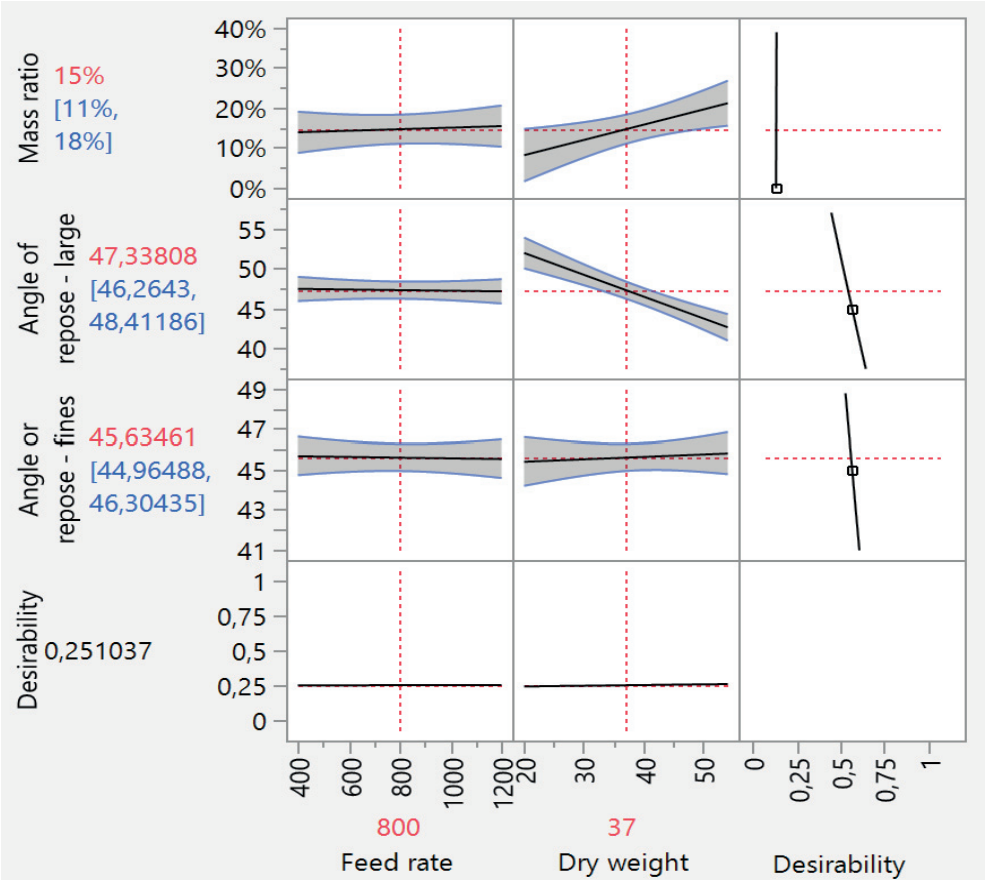


Figure 19: Prediction profiler from DOE in JMP

4.6 Water content after spray drying

After each run through the spray dryer the water content of both the fine and large particles was measured. The water content of all the test runs and official runs is presented in Figure 20. The average water content after all runs was 14.7%.

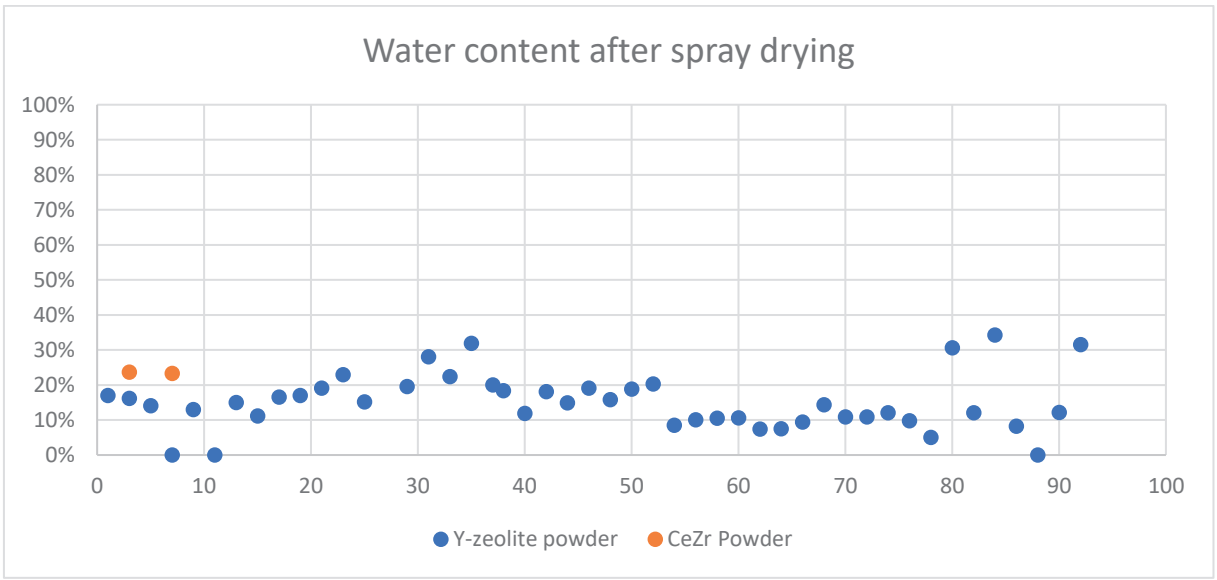


Figure 20: Water content of each powder after running through the spray dryer

4.7 Tabletting

As a result of the trial matrix, large particles collected from spray-dried FX1 and FX2 were mixed and used as "spray-dried Y-zeolite powder" for the tabletting process. The large particles from the spray-dried CeZr were also used as "spray-dried CeZr" for the tabletting process.

During the process of tablet formation, 63 g of powder preparation mix was used for each run. A higher quantity of tablets was obtained using the initial CeZr powder compared to the spray-dried CeZr powder. In contrast, the original Y-zeolite powder generated minimal tablet formation, whereas the spray-dried Y-zeolite powder yielded 7.86 g of tablets. Puralox, included as a reference powder, yielded many tablets but not more than the original CeZr powder. The specific tablet masses obtained for each powder can be observed in Table 9.

Table 10: Total mass of the tablets generated from the tabletting machine for each powder preparation.

Powder	Puralox	Y-zeolite original	Y-zeolite spray dried	CeZr original	CeZr spray dried
Tablet mass [g]	19.97	-	7.86	11.25	31.91

It must be considered when examining the tablet masses that it was the initial attempt on the tablet machine, and only one attempt was made for each powder. Additionally, despite the settings being set to the same values at the beginning of each run, they were adjusted differently throughout each process.

The original powders can be seen in Figure 21 and pictures of the tablets can be seen in Figure 22 and Figure 23. The puralox powder is originally smoother than the other two, and the CeZr powder has a more yellow colour. The same amount of graphite was added to all preparation mixes; however, the powder behaviour differs thus the colour is different for all tablets. No visual difference can be seen between the original and the spray-dried CeZr powder. The spray-dried Y-zeolite can, on the other hand, be distinguished from the other tablets by the visible presence of large particles within them.

Figure 21: Original powder of Puralox to the left, CeZr in the middle and Y-zeolite to the right.

Figure 22: Tablets of Puralox powder to the left and spray-dried Y-zeolite to the right.

Figure 23:Tablets of original CeZr powder to the left and spray-dried CeZr powder to the right.

5. Discussion

5.1 Performance of methods

In Table 12 in the appendix, each spray drying run is presented and includes the actual inlet temperature and outlet temperature of the hot air stream. It can be noticed from the inlet air temperature that the temperature varies a much between each test but also along each run, even though the inlet temperature is set to the maximum value of 300°C. Therefore, it would be interesting to examine how differences in inlet air temperature affect the mass ratio and angle of repose of the collected powder.

The methods used to examine the powders collected from the spray dryer also have some uncertainties, concluded from the performance of the method presented in the results part. As mentioned in the background, measuring the angle of repose has many drawbacks. The pouring is manually made; therefore, it is very difficult to control the vibration while pouring. It is also very difficult to make sure that the compressibility history of each powder is the same before every measurement. However, the measurements were conducted by the same person for every sample, which may increase the consistency. Different methods for measurements should be considered for further testing, for example, a powder rheometer.

5.2 Angle of repose – all tests in summary

The first question to answer was if spray drying is a potential method to increase the flowability of a powder in order to improve the tabletting process. According to Figure 8 and Figure 9, the angle of repose seems to increase after spray drying the powder. As a larger angle of repose is connected to worse flowability, it seems that the flowability mostly decreases after spray drying. However, this was not the case for the large particles collected from samples FX1 and FX2. These were also used for the tabletting process showing improved performance of tabletting compared to the original Y-zeolite powder.

The original Y-zeolite and CeZr powders are compared to both the fine particle powders and the large particle powders. It is presented at the beginning of the results part that the result from the fine and large particles should not be compared with each other due to considerable differences in behaviour when poured. Original Y-zeolite and CeZr are probably more similar to fine particles than large particles due to their small particle size. It can therefore be questioned whether the large particles can be compared to the original powders using the angle of repose method.

When handling the powders, the large particle powders were perceived to have better flowability. However, the fine particles attached to a great extent to each other into larger lumps of several mm in diameter. When pouring the powder through the funnel to measure the angle of repose, the lumps rolled down the pile and made the bottom area of the pile larger. The flowability of the fine particles of powder, therefore, usually seems to be the same, or even better, than the large particles powders according to the angle of repose. Since this is against the perception when handling the powder, the decision was made not to compare the results from the fine and large particle powders with each other, but only to compare the results between the powders of each category. This observation also implies that achieving a higher mass ratio is desirable, as it leads to more large particles being obtained. Contradictory, as mentioned above, when considering the angle of repose, a smaller value is desired.

The perception that the collected large particles' flowability is better than the fine particles has not been proven by any measurement. However, this statement is in accordance with the literature saying that large particle powders generally have better flowability than small particle powders due to the larger impact of gravitational forces and less impact of internal forces between the particles. Additionally, it is also not proven that the particles collected from the vessel below the large drying chamber are of larger size than the particles collected from the vessel below the cyclone. However, this assumption is validated with literature; therefore, the assumption was, and will be, valid throughout the report.

5.3 Nozzle size test

As the nozzle size affects the size of the particles created from the spray dryer, a large nozzle size reasonably creates larger particles. Larger particles are connected to better flowability; therefore, a large nozzle should theoretically conduce to better flowability. This was somewhat proven by the results from the nozzle test. The largest nozzle generated a larger mass ratio, and the flowability was better with a larger nozzle. However, the

flowability of the fine particles of powder produced with the smallest nozzle also showed good flowability. The combined result from the mass ratio and the angle of repose says, though, that the largest nozzle is preferred with the objectives of this report.

The choice of atomizer was also stated to affect the morphology and size of the powder particles. A pressure nozzle generally produces larger particles than a rotary atomizer. A spray dryer with two nozzle atomizers directed towards each other additionally increases the agglomeration of particles, leading to larger end-product particles and better flowability of the powder. A two-nozzle atomizer should be considered for further testing.

5.4 Binder composition test

The results from the binder composition test show that the mass ratio was considerably higher when no binder was used. However, the flowability of the fine particles collected when 0% and 3% binder was used showed no significant difference. According to the flowability, both 0% and 3% binder could be chosen to continue with. Previous experiments with spray dryers in literature use both slurries where the binder is present (Grigoriev et al., 2022; Singlard et al., 2022) and where the binder is not (Machoke et al., 2023; Moejes et al., 2018; Shang et al., 2021). No indication of whether a binder should be used could therefore be concluded from this. Since the mass ratio was considerably higher when no binder was used, this was the composition chosen to continue with in further experiments. However, it would be interesting to do further testing on binder composition to strengthen the results. The flowability measurements were made only a short time after calcination, which excludes testing of the durability of the spray drying impact on the powder. If the powder agglomeration decomposes after time, perhaps a binder can reduce that effect.

5.5 Trial matrix

Table 4 shows that the obtained ANOVA results from Statgraphics predict that dry weight, feed rate and the combined effect are statistically significant for the response factor mass ratio. However, the analysis made using JMP shows that only dry weight and the combined effect are of importance for the mass ratio and not feed rate by itself. It is interesting that the programs give different predictions. The reason for this can be how the data is added to the program. In Statgraphics, the ANOVA table for the mass ratio was made separately from the angle of repose data. Each sample was added once since only one value of mass ratio was obtained per sample. However, in JMP all samples were added four times to be able to insert all four values of the angles of repose. Therefore, the same mass ratio was added four times. This could affect the standard deviation of the test and somehow also affect the significance predictions for the input variables.

Comparing the ANOVA table and DOE results for the angles of repose (Table 5, Table 8 and Table 9), they also show different conclusions. The ANOVA table shows that dry weight and the combined effect are statistically significant at 95% confidence level. However, DOE says that only dry weight is significant for the angle of repose of large particles, and none of the parameters is significant for the angle of repose of fine particles. To analyse the angle of repose the samples were added equally for the two programs, each sample was added four times both in the ANOVA table and the DOE. Therefore, how the results was added to the programs cannot be the explanation for why they give different analysis results. The explanation can instead be that the ANOVA and DOE methods calculate their predictions in different ways and therefore end up with different results. More research about it is necessary to better understand the programs, and the settings for each method should be done in order to increase the understanding of the results and compare them more righteously.

The methods, however, agree on the high significance of dry weight in all situations except for the angle of repose of fine particles.

5.6 Water content after spray drying

Mediani et al. (2014) present a study where the moisture content after the different drying methods, air drying, freeze-drying and oven drying (Table 1) were 8.5-9.4%. In a report by Farshchi et al. (2019) the effect of spray-drying detergent granulates was examined, and the moisture content after spray-drying was between 0.5 to 2.0wt% (Farshchi et al., 2019)(Table 4). Comparing the moisture content after the spray drying runs in this report, 14.7% seems a bit high. Since moisture can increase the internal forces between the particles in the powder and decrease the flowability, as explained in the background, this was solved by oven drying the powder afterwards. However,

a spray dryer able to decrease the moisture content further to an accepted moisture content level would be desired since that would decrease the total energy demand and residence time.

5.7 Tabletting

During the tabletting process, it seemed like the spray-dried Y-zeolite powder with the best flowability, a mix of sample FX1 and FX2, showed improved performance compared to the non-spray-dried Y-zeolite powder. This did not correspond to the tabletting performance of the original and the spray-dried CeZr powder. However, CeZr was only run through the spray dryer once using the settings concluded to be best for the Y-zeolite powder. Even though the powders have similar particle sizes, the internal forces could be different, leading to different behaviours. Therefore, another array of settings might be desired in order to obtain better flowability of the CeZr powder and perhaps improve the performance of tabletting the powder.

As stated in the results, this was the first and only trial of each powder in the tabletting machine. The settings were, additionally, changed differently for each powder, which could result in a different number of tablets being created. More trials should have been made in order to proper evaluate the tabletting results. In addition, it would be interesting to estimate the hardness of each tablet by testing the crush strength of the different tablets. The time for this project was not enough to test the crush strength. However, in further studies, this should be considered.

No difference could be seen between original and spray-dried CeZr tablets. However, the large particles of spray-dried Y-zeolite powder were clearly visible within its tablets. Reasonably, this is why the powder flowability had been increased. On the other hand, heterogeneity within the tablet might cause troubles for mass transfer.

6. Conclusion

In conclusion, it seems that spray drying is a potential solution for increasing the flowability properties of a powder. However, much effort is needed to find the best slurry composition and spray drying setting for each powder desired to increase flowability. Every powder behaves differently even though the particle size distribution is equal, and therefore different settings may be suitable for different powders. The slurry composition is of great importance for the powder obtained from the spray dryer. Higher dry weights in the slurry seem to increase the mass ratio and decrease the angle of repose, thus increasing the flowability of a powder. No, or little binder, is preferred, at least for the Y-zeolite powder examined in this report.

The settings of the spray dryer also seem to affect the flowability of the spray-dried powder. A larger nozzle size is desired to increase the particle size of the powder, which is highly connected to better flowability, according to the literature. High feed rate did, in some cases, show to give larger particle sizes, and in some cases, it did not. High feed rate combined with high dry weight in slurry, however, seemed to give more evident positive results in flowability. The influence of the inlet air temperature and of the inlet air flow on the powder was not included in this report and would be interesting to examine further.

It is possible to tablet powder that has been run through the spray dryer, and for the Y-zeolite, this seemed to increase the performance of the tabletting process when choosing the spray-dried powder with better flowability than the original Y-zeolite powder. The CeZr powder run through the spray dryer with the best settings derived from the Y-zeolite experiments did not improve in flowability. This could be the reason of why the spray-dried CeZr showed no improvements while tabletting. Spray-dried CeZr could, presumably, also improve the tabletting process, but more experiments then need to be done in order to find the best spray drying conditions for this specific powder and increase its flowability.

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8. Appendix

Table 11 and Table 12 show the exact composition of each slurry and the conditions for the spray dryer during spray drying. The sample numbers here are the original sample numbers when starting testing. The results were then rearranged to organize and simplify the results for the reader. Sample N2 in Table 11 and Table 12 later became N3 in this report since the largest nozzle size was used. An average of K1, K2, K3, K4 and K5 instead became N2 above in the report, since a nozzle size of 2mm was used for these tries. T1, FMT1 and FTM2 were never used in any of the tests but were a help in the process of learning the spray dryer performance. When spray drying C2, the nozzle of size 2.5mm showed problems in spraying, and a nozzle size of 1.5mm was used instead. Later the nozzle of size 2.5mm was fixed, and C2 was run again, now called C2-2. Therefore, C2-1 was also not used in any of the tests.

Table 11: Composition and comments on every slurry created for every test.

			Slurry					
Sample nr	Substances	Date of making	Water content [ml]	Powder amount [g]	Binder [g]	Powder %	Binder %	Comments on slurry
T1	Y-zeolit & Disperal	24-feb	500	122.27	14.77	22%	10.8%	Ca 50:50 volym solid/water
K1	Y-zeolit & Disperal	28-feb	400	258.91	9.18	40%	3.4%	Always start with water and then add powder!!
K2								
K3								
K4	Y-zeolit & Disperal	02-mar	200	129.5	4.593	40%	3.4%	I was extra careful with the amount of water! Continue with that!
K5								
N1	Y-zeolit & Disperal	10-mar	450	290.92	9	40%	3.0%	Added water first. Used magnetic stirrer when added powder. Works really good.
N2								
FMT1								
FMT2								
C1	Y-zeolit & Disperal	16-mar	200	133.388	0	40%	0.0%	
C2-1	Y-zeolit & Disperal	31-mar	200	129.3	4	40%	3.0%	
C2-2	Y-zeolit & Disperal	31-mar	200	129.36	4.023	40%	3.0%	
C3	Y-zeolit & Disperal	31-mar	200	120.1	13.3	40%	10.0%	
F11	Y-zeolit & Disperal	04-apr	500	125.87	0	20%	0.0%	
F12	Y-zeolit & Disperal	04-apr	500	125.14	0	20%	0.0%	
F21	Y-zeolit & Disperal	11-apr	170	139.08	0	45%	0.0%	
F22-A	Y-zeolit & Disperal	11-apr	170	139.25	0	45%	0.0%	
F22-B	Y-zeolit & Disperal	12-apr	170	138.97	0	45%	0.0%	
F22-C	Y-zeolit & Disperal	12-apr	170	139.11	0	45%	0.0%	
F31	Y-zeolit & Disperal	12-apr	100	117	0	54%	0.0%	Very difficult to add the whole amount of powder (70%). Only managed to 54%.
F32	Y-zeolit & Disperal	12-apr	100	116	0	54%	0.0%	
FX1	Y-zeolit & Disperal	18-apr	200	117.52	0	37%	0.0%	
FX2	Y-zeolit & Disperal	18-apr	200	117.58	0	37%	0.0%	

Table 12: Results and comments of every test run through the spray dryer.

	Spray dryer

Sample nr	Date for run	Inlet air temperature [°C]	FAN	Air flow [m3/h]	Feed rate [0-100]	Feed rate [ml/h]	Nozzle size [mm]	Time [min]	Inlet temp - actual (*C)	Outlet Temp (*C)	Comments on Spray dryer
T1	24-feb	200-250	100	336	15-50	1000	2				Test round! – Was trying different settings along the run.
K1	28-feb	250	100	336	45	900	2	10:00	235	96.7	
K2	01-mar	250	100	336	45	900	2	10:00	226-232		After 7 minutes, it became wet in the dry chamber collecting vessel. Collected everything anyways at the end.
K3	02-mar	250	100	336	45	900	2	09:30	223-227	89.5	Slurry empty after 9:30 minutes
K4	02-mar	250	100	336	45	900	2	09:30	221	87	Half the slurry empty so the run was ended. Slurry must be enough for K5 as well.
K5	03-mar	250	100	336	45	900	2	07:00	223-226	90-97	Not very mixed slurry. sediment at the bottom. Added water in the end to dilute the sediment. Everything empty after 7 minutes.
N1	10-mar	250	100	336	40	800	0.1	02:00			The slurry clogged the nozzle pretty fast even though “needle” were decreased to 4s. 40%dw with 0.1mm nozzle is probably too much... Gave up after clogging many times in only 2 minutes.
N2	14-mar	250	100	336	45	900	2.5	15:00	238-247	96.8-101.4	Forgot to put on the fan at first, therefore the temperature increased very much in the beginning
FMT1	14-mar	200-250	100 / 60	#VALUE!	20	400	2.5		Same as set value	92-106	
FMT2	14-mar	300	100	336	40	800	2.5		233-239	105	Run until slurry got empty
C1	16-mar	300	100	336	45	900	2.5	15:00	230-234	90	Problem with a powder cake on the side of the drying chamber. Tried to turn the nozzle another direction, it was clear that the nozzle is not completely straight, and the spray is concentrated on one side.
C2-1	03-apr	300	100	336	45	900	1.5	10:00	229	96	Problem with nozzle 2.5. Run with 1.5 instead.
C2-2	03-apr	300	100	336	45	900	2.5	13:00	229	97	
C3	03-apr	300	100	336	45	900	2.5	12:30	232	96	
F11	05-apr	300	100	336	20	400	2.5	78:00	241-247	109	Took a very long time compared to previous runs…
F12	05-apr	300	100	336	60	1200	2.5	09:30	230-241	83	
F21	11-apr	300	100	336	20	400	2.5	33:30	233-247	100-112	
F22-A	11-apr	300	100	336	60	1200	2.5	08:00	240-244	90-100	
F22-B	12-apr	300	100	336	60	1200	2.5	07:30	236-239	85-100	
F22-C	12-apr	300	100	336	60	1200	2.5	07:30	236-239	86-101	
F31	13-apr	300	100	336	20	400	2.5	23	232-247	95-112	Splashed wet big white drops on the sides of the drying chamber
F32	13-apr	300	100	336	60	1200	2.5	05:30	235-238	90-95	Splashed wet big white drops on the sides of the drying chamber
FX1	18-apr	300	100	336	20	400	2.5	36	225-238	98-108	
FX2	18-apr	300	100	336	60	1200	2.5	08:30	232235	84-86	

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