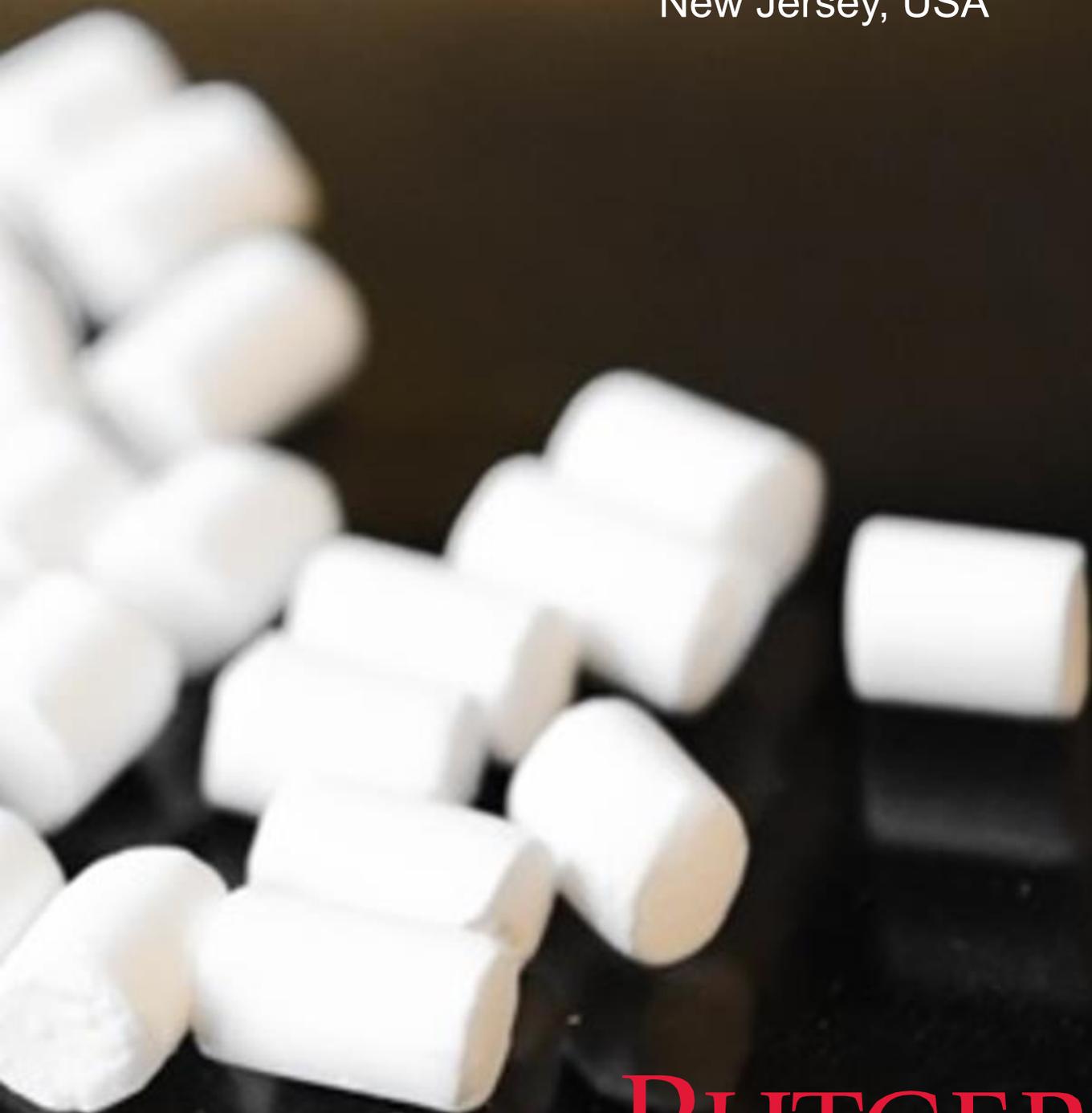# Rutgers Catalyst Manufacturing Consortium

Rutgers University
New Jersey, USA

RUTGERS

# Rutgers Catalysts Manufacturing Consortium (CMC)

While a large segment of the US industry, including the petroleum, chemical, pharmaceutical, automotive, and energy industries makes and/or uses catalysts, there has not been an academic program focused on the operations required to make catalytic materials. Thus, catalyst manufacturing processes are often designed relying on empiricism, leading to uncertain/sub-optimal processes, decreased quality, and increased costs.

Our Missions

At Rutgers, we are combining a high level of expertise in the fields of particle technology, optimization, multi-scale simulation, catalysis and molecular modeling to develop and promote science-based methods for designing and optimizing catalyst manufacturing methods. Our objective is to improve manufacturing processes, such as impregnation, drying, slurry mixing, extrusion, calcination, etc. An integral part of the project is educational activities, including research training of undergraduate students, graduate students and postdoctoral fellows in the area of Catalyst Manufacturing.

Our Goals

A combination of experiments and computer models have been used to improve the understanding and performance of the unit
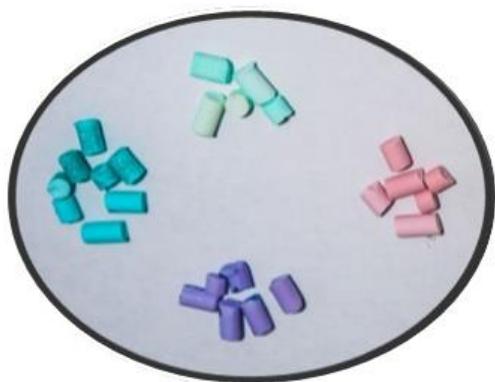
operations used to make catalysts. This knowledge, and the resulting methods and practices developed, have been transferred to industrial partners to help transform this important segment of the global economy into a science-driven enterprise. The specific goals of the consortium are:

- To create a world-wide prime center of excellence in catalyst manufacturing research.
- To enhance fundamental understanding of catalyst manufacturing operations.
- To develop new technology for efficient catalyst manufacturing.
- To provide a research, development, and education resource for industry.

Our Faculty

The consortium was founded on October 1, 2003. The Rutgers faculty that are currently participating in the consortium and their areas of expertise are: Benjamin J. Glasser (drying, fluidized beds), Fernando J. Muzzio (particle technology, powder flow), William Borghard (calcination, catalyst preparation), Silvina Tomassone (impregnation, interfaces), Alberto Cuitino (calcination, compaction), and Nina Shapley (particle technology, filtration).

Expertise Operations

A list of possible manufacturing operations of interest to the consortium is given below: Powder blending, Powder sampling, Calcination, Slurry mixing, Pellet compaction, Roller compaction, Powder segregation, Catalyst drying, Non-Newtonian liquid mixing, Powder flow/handling, Multiphase flow/CFD, Dispersion of solids, Impregnation, Mulling, Extrusion , Nano-templating, Fluidized bed coating, Granulation, Catalysis, Spray drying, Atomization, Flash/Rotary Drying/Calcination, Plow-shear mixing, Liquid-Solid separation (Filtration/Flocculation), Precipitation catalysts.

Our Projects

Projects that are currently funded by CMC are:

- Impregnation of Catalysts
- Drying of Supported Catalysts
- Scale-up in Rotary Calciners
- Powder Flow, Handling and Characterization
- Catalyst Filtration

Projects that have been funded by CMC in the past include:

- Powder Segregation
- Mulling/Extrusion of Catalyst Supports
- Slurry Mixing
- Continuous Powder Blending
- Sensing of Mulling Operations

To Join

The annual fee for membership in the consortium is $38,000. These are unrestricted funds for research. The consortium members (companies and faculty) meet every 6 months (October and March) for project reviews. In the October meeting, the consortium decides on continuing with current projects or starting new projects. Where consensus is not possible, a vote is taken, with each company getting one vote. Copies of the slides from the talks at the consortium meeting are made available to the consortium members. In addition, each project provides a written report on progress every six months.

A description of the projects follows. Further information on the CMC can be found at: http://cbe.rutgers.edu/catalyst/

Current Member Companies

- Exxon-Mobil
- Evonik
- Euro Support Manufacturing
- Clariant
- Sabic
- Haldor Topsoe
- Powder Processing & Technology
- Criterion Catalysts
- BASF

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Impregnation of Catalysts

Background

Catalyst impregnation is a crucial process in the preparation of industrial catalysts. In this process, metal salts or complexes are dissolved in an aqueous solution and contacted with a porous oxide catalyst support such as alumina (Al_2O_3) or silica (SiO_2). During a contact time of typically 30-60 minutes the metal is adsorbed from the solution onto the high surface area support. The catalyst is dried and further pretreated to transform the metal from its precursor state into its active form. Generally,
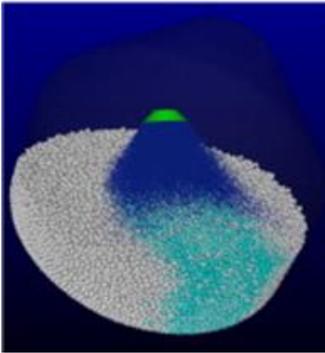

Figure A1: Particle dynamic simulation of double cone impregnator. A fan shaped spray pattern is shown.

the process of impregnation is performed in rotating vessels with one or more nozzles that distribute the solution with the metal precursor into the catalyst support. This process is also referred to as dry impregnation as the amount of liquid sprayed onto the catalyst bed is kept at a minimum, and thus, the bed continues to operate as a granular bed. The ability to control dry impregnations and establish effective models for large batches can significantly reduce the amount of time required per batch while simultaneously achieving a more homogeneous distribution of solution, i.e. similar metal loading in each catalyst particle/pellet after the impregnation step.

Project Goals

The main goals of this project are: 1) to understand how mixing and flow are affected when the particles have a certain degree of moisture or are saturated with liquid, 2) to
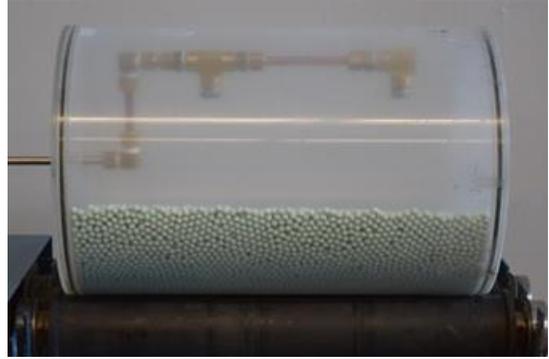

Figure A2: Impregnation set up in a cylindrical vessel with 2 spraying nozzles.

ensure that the liquid is homogeneously distributed into the entire particle bed, 3) to minimize the extent and distribution of dead zones for a given impregnator configuration and 4) to establish a scalable model that can be quickly applied to impregnation processes for optimal mixing and liquid distribution.

Summary of Studies

In this work, a combination study incorporating a series of experiments as well as particle dynamic simulations are performed in order to obtain a deeper understanding of the mixing and impregnation mechanisms. Various impregnator shapes are used, such as double cone blender and cylindrical vessel. A computational study is performed using the discrete element method (DEM). Commercial software (EDEM, DEMSolutions Inc.) is used to facilitate technology transfer. Algorithms are being used to allow for the spraying of water droplets on a flowing particle bed and the allowance of catalyst support particles to absorb the water, thus increasing weight and density. Figure A1 shows an example of fluid spraying

Impregnated (left) and bare (right) alumina particles

onto a particle bed in a double cone blender.

Experimental techniques are used to validate computational models by measuring metal content as a function of time in specific spray zones. Different spraying configurations are implemented in the rotating cylinder to determine the effect of this parameter on impregnation and validate simulation results (see Figure A2). In addition, mixing experiments are performed to better understand the relationship between spray flow rate and its effect on the axial dispersion of particle bed; an example is shown in Figure A3.
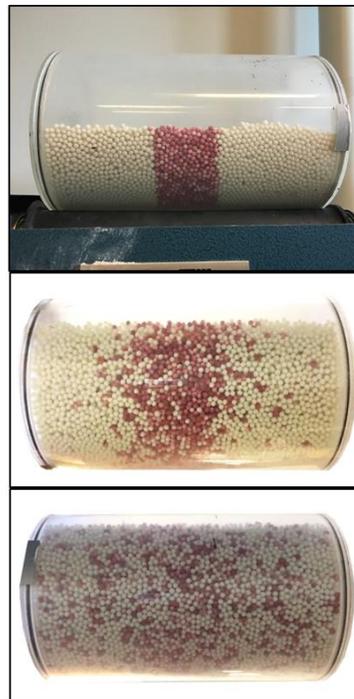

Figure A3: Experimental study on axial dispersion using 5 mm dyed alumina particles in a rotating drum.

A rotating drum impregnator

Drying of Supported Catalysts

Background

Supported catalysts are essential components in a variety of industrial processes, ranging from catalytic converters to production of new drugs. The performance of a catalytic process is intimately related to the catalyst design - uniform, egg-yolk, egg-shell and egg-white metal profiles. It is generally believed that the metal profile is controlled by the conditions that are applied during impregnation where the metal contacts the solid support for the first time. However, experiments have shown that drying may also significantly impact the metal distribution within the support. Therefore, to achieve a desired metal profile we need to understand both impregnation and drying. Controlling the drying conditions can enhance catalyst performance.

Project Goals

The goal of this project is to develop a fundamental understanding of unit operations during catalyst preparation, so we can predict, control and optimize metal distribution and dispersion in supported catalysts. Therefore, we can provide our partners with efficient tools to monitor and control the final quality of supported catalysts.
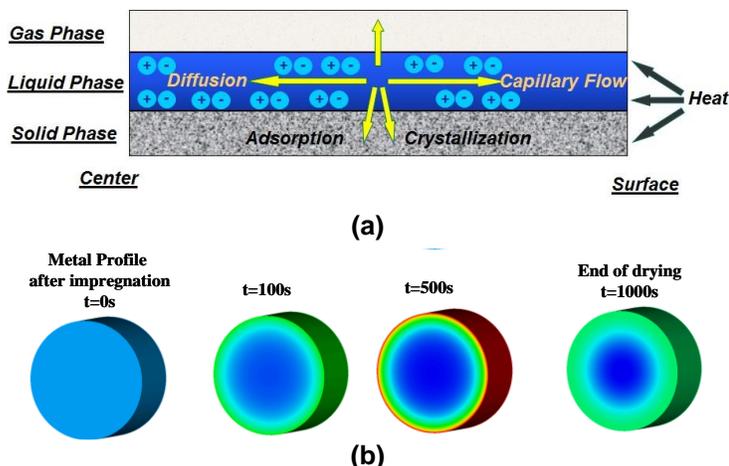
Summary of Studies

In this work we have developed a theoretical model for drying which we have validated experimentally. In this model, we have taken into account heat transfer from the hot air to the wet support, solvent evaporation in the support, convective flow towards the support external surface due to the capillary force, as well as metal diffusion and deposition due to adsorption and crystallization (see Figure B1a). In general, the convective flow is the main driving force to transport the metal component and the solvent towards the supports external surface (t=500s in Figure B1b), while the back-diffusion causes metal to transport towards the support center (t=1000s in Figure B1b).

We also developed a theoretical model to predict the drying process for high metal load conditions; this was accomplished by building upon a model that was established for low metal loadings. It is found that the drying mechanisms for low metal loading conditions and high metal loading conditions are quite different. This model is applicable for higher concentrations of nickel nitrate (above 0.1 M). It included the effects of the metal concentration on the solution density, viscosity, surface tension, vapor pressure and the volume ratio of metal. Good agreement was found between experimental and simulation post-

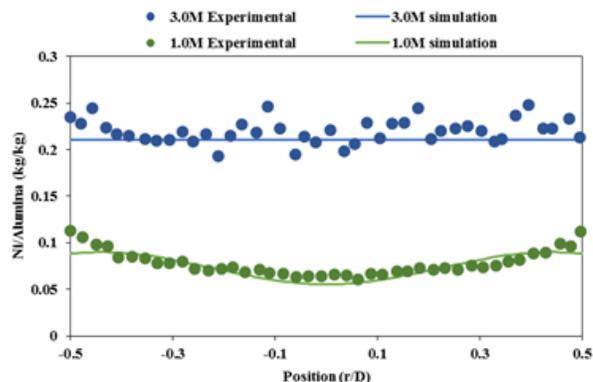Figure B1: (a) drying mechanism, (b) simulation of the evolution of the metal distribution during drying.

Figure B2: Experimental results compared to post drying metal distributions using simulation for two different metal loadings (1.0 M and 3.0 M). (T=800C, uniform initial condition)

Figure B3: L-R: Porous alumina supports before impregnation, during impregnation and after impregnation followed by drying at 80ºC.

drying metal distributions for this model using nickel nitrate. (see Figure B2).

In our work, we are interested in investigating the importance of the physical properties of the solid support (porosity, pore size distribution, particle size) and liquid solution (pH, ionic strength, initial metal precursor concentration), the nature of interactions that exist between the dissolved metal and the solid support (physical adsorption, crystallization, ion exchange, film-breakage, pore-blockage), and their effects on the distribution and dispersion of the active metal. We have examined the distribution of various metals such as Nickel, Copper, Barium, and/or Palladium on Alumina (see Figure B3).

Impregnation of alumina pellets

Scale-up in Rotary Calciner

Background and Goals

Calcination is one of the crucial operations in catalyst manufacturing. In calcination processes, heat is applied to ores and other solid materials in order to bring about a thermal decomposition, phase transition, or facilitate removal of a volatile fraction. Developing better process level understanding of this operation can significantly improve the quality of the end product as well as save on energy and material costs. For a good product quality and efficient process, it is necessary to raise the temperature of the particles uniformly with a minimum

High thermal conductivity

Low density

Low speed of rotation

⇨ Heated in layers

Intermediate thermal conductivity

Intermediate density

⇨ Cooler core

Low thermal conductivity

High density

⇨ Well mixed

Figure C1: Heat transfer DEM simulations.

processing time. In rotary calciners, which are the most common devices used for calcination processes, the calcination process highly depends on the heat transfer in the radial direction and on the axial dispersion of the particles. The heat transfer and the dispersion of particles depend on the properties of the particles and the calciner operating conditions, such as speed of rotation and size of calciner. Usually, the appropriate process parameters are determined based on laboratory or pilot scale experiments. However, the technology transfer to larger manufacturing scale productions is not well understood, which prohibits efficient production. In this project, we use carefully designed experiments and numerical simulations to better understand the effect of material properties and operating conditions of calciners on the calcination process with a particular interest in understanding the scale-up in rotary calciners.
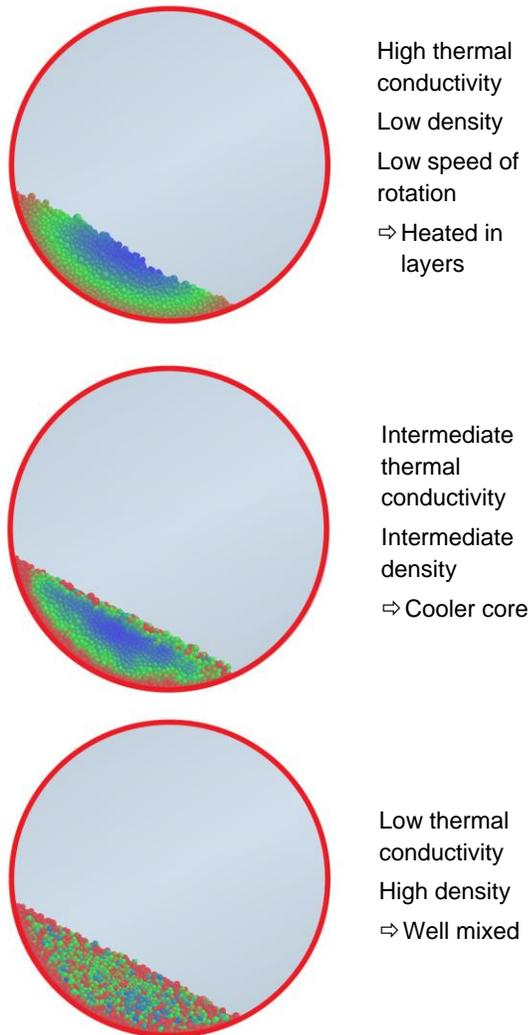
Summary of Studies

We use the discrete element method (DEM) to simulate the heat transfer and flow of particles in rotary calciners. The DEM is an idealistic tool as it can directly represent heterogeneity in the processed materials and the interaction among individual particles. Using these simulations, we have investigated effects of thermal properties, mechanical properties, and material properties, such as size and density of particles, on the heat transfer process in rotary calciners. We have also studied the effect of operating conditions, such as calciner size, speed of rotation, and fill level on the scaling of the heat transfer process (Figure C1 shows simulation results for various process parameters.)

In collaboration with consortium member companies, we also experimentally investigate the flow and dispersion of powders in pilot scale calciners. The main goal of these experiments is to understand the mean residence time and

Figure C2: Colorimeter to analyze concentration of tracer particles.

axial dispersion of common catalyst powders. We have investigated the effects of various operating conditions, such as feed rate, speed of rotation, baffles, and calciner incline, on the residence time distribution. (Figure C2 shows the colorimeter test for measuring concentration of tracer particles used to measure the residence time distribution). Along with these, we use small scale laboratory experiments to investigate thermal properties of catalyst powders and to validate our DEM simulations. (Figure C3 shows the laboratory experimental set-up for heat transfer.)

Based on the simulations and experiments the following key observations are found:

1) Based on hundreds of DEM simulations, we developed a quantitative scale-up equation in rotary calciners for heat transfer via conduction. Using this scale-up equation, the appropriate operating conditions required to raise or lower the temperature of powders can be determined. If the thermal properties of the powders are known, the operating conditions can be determined without any experiment. If the thermal properties are not known (which is usually the case), the appropriate operating conditions can be determined by measuring the temperature increase time scale in a single experiment and utilizing the scale-up model.

2) We have developed an online graphic user interface (GUI), so that consortium members can accesses and use the model. In the GUI, we have combined the heat transfer with expected powder flow in calciners.

3) We have found that the heat transfer rate has very low dependence on speed of rotation and fill level, but highly depends on the size of the calciner. The heat transfer also highly depends on the thermal conductivity and heat capacity of the particles, but the effect of particle size on heat transfer is negligible.
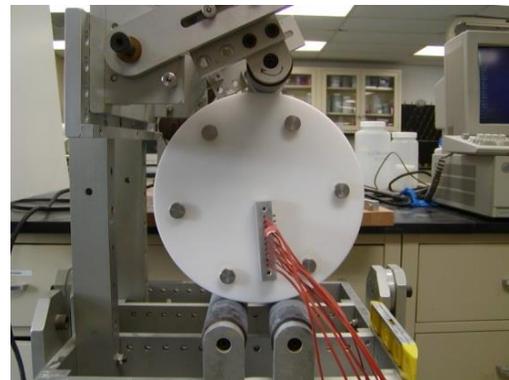

Figure C3: Side view of the aluminum calciner. 10 thermocouples were inserted within the calciner through the Teflon made side-wall. The calciner rests on the computer controlled rollers.

4) In addition to the scale-up model, we have developed a model to predict the particles' temperature distribution. We found that particles with higher density, low thermal conductivity, in high speed of rotation and low fill level processes, tend to have uniform temperature.

5) Baffles enhance the mixing, the heat transfer rate, and the uniformity of particles' temperature.

6) Based on experiments, we found that the mean residence time is indirectly proportional to the speed of rotation and angle of incline, but is only slightly affected by the feed rate. On the other hand the axial dispersion coefficient increases with speed of rotation and angle of incline.

We continue to study the scale up and effects of various parameters on the calcination process using these experiments and numerical simulations. In particular, we are studying the radiative heat transfer using numerical simulations and the effect of dams on the powder flow using experiments in rotary calciners.

Alumina powder in a rotating drum

Measuring the moisture content of alumina powder using a moisture balance

Powder Flow, Handling and Characterization

Background

Powders and granular materials can be found in many processing steps in catalyst manufacturing; they exhibit a variety of flow patterns, and their state and behavior differs from application to application. Since there is a lack of fundamental understanding of powder behavior, multiple problems can be encountered during production, such as jamming of hoppers, sub-standard blending performance, and weight variability of final products due to segregation and/or agglomeration. Scale-up can also be a challenge, since the lack of constitutive equations for granular materials forces most scale-up efforts to follow the trial-and-error route. There are numerous methods to characterize the flow properties of granular materials, such as avalanching testers, fluidizers, shear cells, indicizers, density methods, angle of repose, etc.; however, most of them are application-specific, and it is not clear, how they correlate with each other or with process performance. For this reason, the use of most of these testers is restricted to a specific application, for which they were designed, and any attempts to apply the results of such experiments to a different application frequently result in process problems.

Goals

The goal of this project is to develop a fundamental understanding of granular and powder flow and shear properties, so that the behavior of intermediate and final catalyst products during manufacturing and processing can be predicted and controlled. The techniques and methods investigated in this project could provide our partners with valuable tools and ideas to efficiently design and scale catalyst manufacturing processes.

Figure D1: Alumina powders with different water content.

Summary of Studies

In this work, we have created a family of standard catalyst materials, spanning a wide range of flow properties from very cohesive to free-flowing. Figure D1 shows the appearance of alumina powders after adding deionized water at various weight percentages. We then used the characterization equipment to investigate the flow properties of these materials and to determine the correlations between the techniques. Then multivariate analysis, principle component analysis (PCA) was

applied to the material properties library and partial least square regression (PLS) was used to correlate material's flow properties to the process performance. A cubic score plot was used to visualize how each material is projected into the reduced dimension space (shown in Figure D2). The study has found that loss-in-weight feeder's feeding performance is highly related to material's flow properties, its relative standard deviation (RSD), and the relative deviation between the mean (RDM). The target feed rate is predictable by material flow properties library set up with PCA. We have also confirmed that the feed rate deviation caused by hopper refill is predictable based on material flow properties. We are currently working on improving the model's prediction, testing for scale-up and also applying our model to other unit operations.
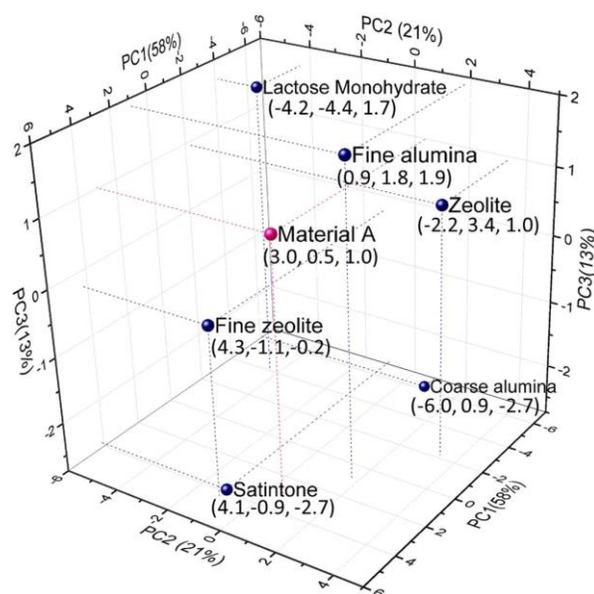

Figure D2: A cubic score plot was used to visualize how different materials are distributed in the projected spaces. The coordinates of each material are shown as the scores of each principal component. The similarity score based on weighted Euclidean distance can be calculated to further quantify similarity or dissimilarity between different materials.

Measuring the thermal properties of powders in a water bath

Filtration for Catalyst Manufacturing

Background

Filtration is widely used in catalyst production. It combines the collection and washing processes for precipitated or crystallized catalytic particles. In cake filtration, pressure-driven or vacuum-driven, flow of the particulate suspension through a filter membrane or filter cloth causes the separation. A filter cake formed from the solid particles builds up over time on the filter medium. In general, it has fairly large openings and most of the filtration is performed by the cake itself, which is ideally porous, where the pores are the gaps between particles. Usually, subsequent washing of the filter cake is performed in order to eliminate residual electrolytes.

However, this traditional process is still largely empirical. It can often be plagued by several challenges which make it difficult to predict the actual rate of filter cake formation and the required pressure drop or flow rate and thus their evolution over time. Therefore, a laboratory scale test that can provide insight into how a particulate material of interest would behave in a manufacturing scale filtration process would be very useful.

Goals

The goals of this study are to:

- Characterize the dependence of the Darcy permeability coefficient on the applied pressure drop, for relevant catalytic materials.
- Identify key variables or dimensionless parameters (e.g. particle Reynolds number, Peclet number, Stokes number) and explore experimentally relevant ranges of these parameters.
- Use continuum modeling to generalize the results to new materials or new operating conditions.

- Map the filter cake microstructure and the variation in particle size distribution at different axial locations along the filter cake.

Figure E1: Benchtop Nutsche filter purchased from Pope Scientific. The vessel has a 1 liter capacity with a 4 inch diameter.

Summary of Studies

In this work, we have developed tools and protocols for filtration experiments using a benchtop Nutsche filter device (shown in Figure E1) and model materials such as 5 & 30 micron diameter glass beads. The glass beads are nonporous and generally result in a simple filtration, allowing the filtration process to be studied. The slurry volume is varied along with the applied pressure and the screen mesh size. Cake permeability, filter media resistance, and the bulk density are calculated for each experiment. The FT-4 powder rheometer is used to find the air permeability of beds of glass beads in order to compare them to the water permeability of the filter cakes. Micro-CT images (shown in Figure E2) are compiled from filter cakes generated by the Nutsche filtration experiments in order to study the porosity and

voids of the filter cakes. The tendency of particles to aggregate is likely a key physical property that affects filterability and zeta potential may be a direct indicator of this tendency. Also, the particle size distribution varies at different heights in the cake, in the case of large particles (GB30) with rapid settling.

In ongoing work, we intend to: extend Nutsche filter experiments to catalytic materials and small glass beads at higher pressures, measure the particle size distribution at different heights in the resulting cake, examine the effect of pH on the tendency of particles to aggregate and therefore their filterability, and investigate the effect of small-bead fraction on permeability and filterability in large/small bead mixtures.
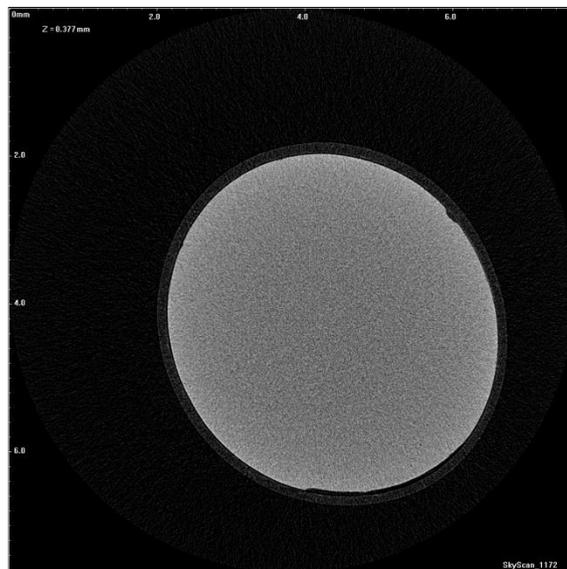

Figure E2: Micro-CT image of glass bead filter cake sample formed at 6 psi applied pressure on the 1 μm filter screen.

Benchtop filtration