IFPRI Project Abstract

Model Assisted Design of Granular Products: Linking Process and Product Models for Wet Granulation

Rachel Smith
The University of Sheffield
Project Start Date: 1st October, 2019
Abstract Date: 25th May, 2020

Project Objective:

The objective of this project is to develop multi-dimensional process models of binder agglomeration that have as their output the appropriate particle properties (likely distributed) that are linked to associated product models to predict product performance. The project scope is constrained to high-shear and/or fluid bed granulation, however the choice of formulation(s) and modeling approach(es) are open.

Approach:

The aim of this research project is to develop a modeling framework for product performance driven process design which is deployable to industry, and demonstrate the potential of this strategy with two case studies: fluidised bed spray granulation and high shear granulation. This will involve the development and linking of population balance models for fluidised bed and high shear granulation with a mechanistically-based product model.

Recent Results:

Since the start of the project last year, the following key progress has been made:

- PhD student Peyman Mostafei has been recruited, and started his PhD in November 2019.
- Significant progress has been made in reviewing the literature.
- A population balance approach has been chosen to develop a dissolution/disintegration product model. This model will act as the case study product model for the project.
- Key mechanisms involved in the dissolution/disintegration process have been identified.
- Progress has been made towards identifying and modifying mechanistic expressions for hydration, swelling and dissolution.

Next Steps:

In the next year, focus will be placed on further developing expressions for the product model. In addition to implementing, modifying and developing expressions for each of the mechanisms, key decisions will be made about the inclusion/exclusion of mechanisms from the model, and the development of complementary experimental systems for model validation. We also plan to complete the literature survey. We will initiate both process model modification and overall framework development.

Modeling of screw feeder performance

Prabhu R Nott, Indian Institute of Science

Abstract

Screw feeders or conveyors are widely employed in industry for the bulk transport of particulate materials. Several studies have attempted to relate the discharge rate with the rotation speed of the screw via experiments and particle dynamics simulations. However, a detailed mechanics-based model that would assist in optimal design of screw feeders has not been attempted. In this work we consider a single-screw feeder, as the first step to modeling powder flow in a twin-screw feeder that is widely used in industry. We first construct a mechanics-based model by enforcing the balances of linear and angular momentum on a suitably chosen continuum element. With the simplifying assumptions that the granular medium moves as a rigid body that slips along the surfaces of the screw and barrel, and neglecting the effect of gravity, we show that under certain limiting conditions the discharge rate for a given angular velocity and screw geometry can be obtained. Further, we show that the discharge can be maximized by setting the ratio of the pitch to barrel radius to a specific value.

We then study the detailed flow within the conveyor by particle dynamics simulations using the Discrete Element Method. Our simulations show that a significant fraction of the material does indeed exhibit solid body motion, in agreement with the assumption of the simple model. We assess the effect of relaxing the limiting conditions employed in the model, thereby determining the connection between the friction at the walls and the kinematics. The variation of the volumetric flow rate with the ratio of pitch to barrel radius in the presence of gravity is finally compared with that from our model and simulations in the absence of gravity. We observe that both exhibit the same qualitative trends, indicating that the dependence of the volumetric discharge rate on the geometry of the conveyor is not altered by the introduction of gravity.

Our study thus provides useful information for the design of screw feeders, and provides insight into the mechanics of the flow of the powder in a screw conveyor. Moreover it lays the foundation for a more thorough analysis that is to follow, where we will use a robust constitutive relation for the stress to determine the flow and stresses developed in single and twin screw conveyors.

IFPRI UPDATE: SIMPLIFIED INDUSTRIAL FORMULATIONS DESIGN CHALLENGES

JAN VERMANT AND LUCIO ISA,
DEPARTMENT OF MATERIALS, ETH ZURICH

1. Goals

The goal of our work at ETH Zürich represents a combined effort of the labs of Profs. Lucio Isa and Jan Vermant. Our goals within the IFPRI project and more globally within our groups are threefold

(1) To explore how, moving away from model systems containing spherical colloids with near hard interactions, we can widen the range of rheological responses by changing the properties of the building blocks of the suspensions, so that even in simple formulations a wide range of behaviors can be 'built in", i.e. obtaining formulation guidelines to do "more with less" or simplifying formulations from within.

(2) To further develop a limited number of tools to interrogate the rheological response of the such dispersions by advanced rheological methods and methods to probe structural development in situ during flow using high resolution confocal microscopy.

(3) Apply these methods to simplified industrial dispersion by industrial partners and compare with the formulation guidelines obtained from (1).

2. Practical

Three PhD students were working in this general area and graduated in the course of the last 12 months. Gabriele Colombo (Vermant group) group defended his thesis 12.2019, and Chiao-Peng Hsu (Isa group) defended 05.2020 and R. Massaro (a long term visiting student from KU Leuven) defended 05.2020. The thesises can be obtained on request. We obtained additional funding through a Swiss national foundation grant and the ETH Zurich for 3 new PhD students, Vincent Nigel (started 05.2019, Isa group) will work on imaging the relative motion of rough and non-spherical particles in suspensions in relation to their rheology, Florence Müller (03.2020, Vermant group) will work on gels made with rough and non-spherical particles, and Pierre Lehéricey (08.2020, Vermant group) will focus on the elastic properties and yielding events. Additionally a postdoc will work (as of 06.2020) on the image processing routines. The Corona virus crisis had severe impact on the momentum of the group and transfer of know how between students. Due to the Corona virus crisis Activities were completely suspended as of 15.03 and partially restarted as of 27.04 with a full restart of experimental work 08.06.

We had also foreseen to have a visit of one of Prof. Lilian C. Hsiao students (Shravan Pradeep), but this exchange is postponed (The plan was to perform shear reversal with the ultra fast confocal, along with fast crystallization kinetics of rough PMMA particles)

We had some exchanges with IFPRI partners to identify suitable industrial systems to be studied, but discussions were not yet finalized and now would be a good time to do so. The new students are around and trained to run the experiments and protocols are in place.

3. Results

The focus of this work is on rheological phenomena which arise because of particles being in close contact, i.e. continuous and discontinuous shear thickening in stable dispersions, and thixotropic effects in colloidal gels.

3.1. **Stable dispersions.** The effect of **nanoscale surface roughness** on the dilatant discontinuous shear thickening of dense silica suspensions was investigated, to establish a link between the single particle properties and the bulk rheology. Nanotribological measurements of the interparticle contacts of model rough colloids were carried out along with macroscopic rheological studies. Rough particles exhibit discontinuous shear thickening over a broader range of shear rates and for volume fractions much lower than smooth colloids, possibly due to interlocking of surface asperities. One can increase the solid loading to postpone undesired shear thickening by mixing a small amount of low-friction particles into the system, and we suggest an engineering-tribology approach to control the macroscopic rheology of shear-thickening suspensions. Second the **role of reversible, short-range chemical bonds** in determining the frictional and adhesive interactions between particles was studied. Urea molecules were used as a tool to partially or fully screen hydrogen bonding between particles and therefore influence their contact properties. Time-dependent urea sorption reduces friction and adhesion, inducing a reduction in the high-shear viscosity of dense suspensions. Finally, we use **stimuli-responsive polymer brushes**, synthesized to a precise length by controlled radical polymerization, for the in situ, selective tuning of interparticle friction and adhesion, and for the modulation of surface roughness.

N. M. James*, C. P. Hsu*, N. D. Spencer, H. M. Jaeger, L. Isa, Tuning Interparticle Hydrogen Bonding in Shear-Jamming Suspensions: Kinetic Effects and Consequences for Tribology and Rheology. J Phys Chem Lett 10, 1663-1668 (2019)

B. Schroyen, C. P. Hsu, L. Isa, P. Van Puyvelde, J. Vermant, Stress Contributions in Colloidal Suspensions: The Smooth, the Rough, and the Hairy. Phys Rev Lett 122, 218002 (2019)

C. P. Hsu, J. Mandel, S. N. Ramakrishna, N. D. Spencer, L. Isa, Disentangling the roles of roughness, friction and adhesion in discontinuous shear thickening by means of thermo- responsive particles. Submitted, arXiv preprint: arXiv:2004.05970

Exploiting roughness and adhesion: Further work will focus on visualizing relative particle motions using the high speed confocal rheometer to understand what happens when particles are in 'contact' and how this should be engineered. High frequency rheology or superposition rheology may be exploited to interrogate this link further.

3.2. **Flocculated dispersions.** Here the main focus was on establishing the link between the microstructure and flow properties of colloidal gels. First,we systematically investigated the effects of interparticle attraction strength and steady shear deformations on the microstructure of a model depletion gel of PMMA spheres in CHB/Decalin at intermediate volume fraction $\phi = 0.2$. Particular care was taken to ensure reproducible initial structures, by using either a diffusion step of screening salt into a charge stabilized colloid–polymer mixture, or well-defined pre-shear protocols. By applying these procedures, we could observe the initial stages of gel formation across a wide range of depletant concentrations (polystyrene), ranging from shallow quenches close to the spinodal to high attraction strengths, where early arrest and fine particle strands were observed. Using a recently developed rheoconfocal setup, we investigated the shear-induced rearrangements occurring in the gels, by live imaging of the microstructure under steady flow at a stagnation plane. Dramatic variations in **gel heterogeneity** were observed as a function of the shear rate, far outweighing the influence of the depletant concentration and we obtained good scaling relations for the evolution of the microstructurehis work is being prepared for publication, pending comparison with simulations by the group of Jim Swan at MIT. However, the rheological signatures of these weak depletion gels were too small to warrant further detailed rheologiczal studies.

To compare rheological with structural data, matrices with higher viscosities were used and model flocculated suspension in both a Newtonian and a also viscoelastic medium was studied by combined rheological and rheo-confocal methods. To this extent model micrometer sized fluorescent PMMA particles were dispersed in polymeric matrices (PDMS). The effect of fluid viscoelasticity is studied by comparing the results for a linear and a branched polymer. Stress jump experiments on the suspensions were used to de-convolute the rate dependence of the viscous and elastic stress contributions in both systems. These results were compared to a qualitative and quantitative analysis of the microstructure during flow as studied by fast structured illumination confocal microscopy, using a counter-rotating rheometer. At equal viscous strength (comparable Pe numbers) but different stress ratios, the microstructural analysis showed that **denser clusters are developed in a viscoelastic matrix**. Furthermore, from the evolution of the viscous stresses at high shear rates, cluster densification in a viscoelastic matrix could be inferred from a lowered effective volume fraction.

R Massaro, G Colombo, P Van Puyvelde, J Vermant Viscoelastic cluster densification in sheared colloidal gels Soft Matter 16 (10), 2437-2447

Thixotropic systems: We now propose to focus on the role of roughness and shape effects in flocculated suspensions and elucidate how yield stresses and thixotropy can be better controlled.

4. Analysis methodology

- A stress-controlled rheometer was coupled to a fast scanning, instant structured illumination confocal microscope and a focus-tunable lens was incorporated in the setup to acquire 3D image volumes at video rates. The work was published:
  G Colombo, R Massaro, S Coleman, J Läuger, P Van Puyvelde, J. Vermant, Ultrafast imaging of soft materials during shear flow, Korea-Australia Rheology Journal 31 (4), 229-240 (2019).
- A high frequency rheometer setup is available and is being modified for combined steady shear and HF rheometry studied. A review on the use of high frequency rheology was published:

B Schroyen, D Vlassopoulos, P Van Puyvelde, J Vermant Bulk rheometry at high frequencies: a review of experimental approaches Rheologica Acta 59, 1-22 (2020)

- New setup for superposition rheometry, as a prime method to interrogate how rheology emerges from the contributions to viscous and elastic stress contributions for the different formulations strategies has been developed.
- Particles down to 500nm characterized at the single particle level using colloidal probe AFM (friction and adhesion)

5. Work plan - expected outcomes

We proposed a staged approach.

(1) Inventory of potential particulate samples should be identified with IFPRI members (D.1). A discussion has been started but not been finalized. It would be good to have this overview after the virtual AGM - to be ready by September 2020

(2) Inventory of desired benchmark rheological properties and profiles, with request for feedback (D.2). Feedback from iFPRI members is urgently requested. It would be good to have this overview ready by September 2020

(3) Report on the characterization of the particle systems (size, stability and initial rheological results) (D.3, month 6) This report is available, particles have been characterized using electron microscopies, AFM nanotribology and initial rheological results.

(4) Basic rheological characterization of the linear viscoelastic behaviour and the flow curves of the stable suspensions (D.4, year 1) This report will be delivered with the annual report.

(5) Full rheological characterization including high Frequency rheological characterization to rationalize the behaviour (D.5, month 18) Most likely this will be delayed by 8-12 months. A setup is being developed to do high frequency rheology with pre-shear or during flow.

(6) Rheological characterisation of selected thixotropic suspensions, combined with some rheo-confocal studies (D.6. month 30) This has been partially achieved.

(7) Responding DESIGN challenge by IFPRI members (MO30-36)

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IFPRI Project Abstract

A Systems Engineering Approach to Dry-Milling with Grinding Aid Additives

Principle Investigator(s): Arno Kwade, Sandra Breitung-Faes
PhD-Student: Anderson Chagas
Affiliation(s): Institute of Particle Technology (iPAT) – TU Braunschweig
Project Start Date: 01.09.2019
Abstract Date: 28.05.2020

Project Objective:

1. Develop a system engineering approach for optimizing and scaling industrial dry fine grinding processes with a special focus on grinding aid application.
2. Obtain deep knowledge and numerical relations about the effect of grinding aid additives and humidity on material behaviour, process aspects and energy transfer.

Material and Methods:

- ✓ **Material:** Calcinated alumina from the company Almatis Inc. and Calcium Carbonate from the company IMERYS Minéraux Belgique SA.
- ✓ **Grinding aid additives:** Diethylene glycol (DEG), Heptanoic acid (HepAc) and 1-Hexanol (HexOH).
- ❖ **Test equipment:** For the first project period a 4 liters batch ball mill as well as a 47 liters continuous ball mill and an ATP 100 Air classifier from Hosokawa Alpine, which can be operated alone or in a circuit, were employed.
- ❖ **Approach:** The current process models, adopted at the iPAT, will be modified to quantitatively include the effect of grinding aid additives on breakage mechanisms, material transport, energy dissipation and air classification during batch and closed circuit operations. The final process model will be able to predict product size distributions, throughput and energy consumption.

Recent Results:

Previous studies indicate that grinding aid additives mainly affect the product in terms of powder flowability and tendency to agglomeration of particles. The powder flowability influences directly the grinding mechanism, such as mass of particles captured between balls and, thus, stress intensity and energy dissipation during collisions: A higher flowability reduces the captured mass and increases the stress intensity and, therefore, the specific energy transfer within one collision to the product particles. Moreover, it will also impact the material transport through a continuous operated mill and, by consequence, mill holdup and process efficiency.

A preliminary flowability measurement in relation to additive type was conducted as shown in Figure 1. The feed material was pre-mixed with the additive using a Turbula mixer for 20 minutes and ground within the batch ball mill for 240 minutes in order to reach median size in the scale of a closed circuit product. In a first glance, this results indicate that the additives influence the powder flowability very differently, such as found for glycol and acid, and additives such as glycol may have a very small effect on the grinding efficiency.

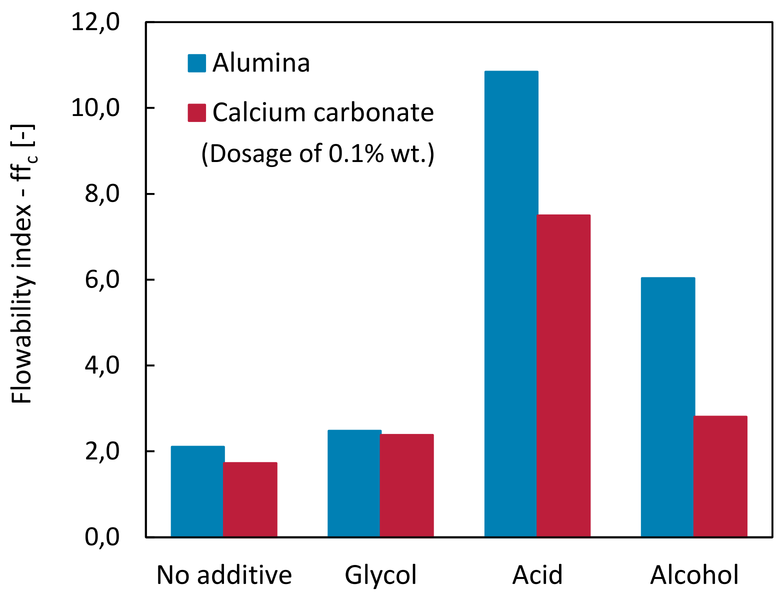


Figure 1: Flowability index of ground product in relation to additive type, measured with a ring shear tester with pre-consolidation at 1.0 kPa.

In parallel a batch grinding test with additives at same dosage are conducted. Figure 2 compares the grinding results (fineness as function of specific energy). The advantage of the batch test is that material transport can be ignored, so that effect of flowability on grinding itself is more evident. In the case of the alumina additives providing a medium flowability are best (alcohol), whereas the acid with the best flowability results in a relatively poor result. The reason is that with rising flowability the stress intensity increases but the stressing frequency decreases. On the other hand, for the calcium carbonate, the additives improve the result in a similar manner compared to no additive. However, the stress intensity provided by the small laboratory ball mill seems to be not high enough to produce a finer product without removing the fine particles. These two results demonstrate necessity of understanding separately the influence the additive type on the, above cited, many mechanisms of a grinding process. Additionally, the effect of dosage and moisture content should also be accounted quantitatively.

Potentially, the modelling of the ball motion and of the material capture between the balls under influence of different product flowabilities in combination with a population balance model shall provide a useful tool for optimization of product quality and energy efficiency.

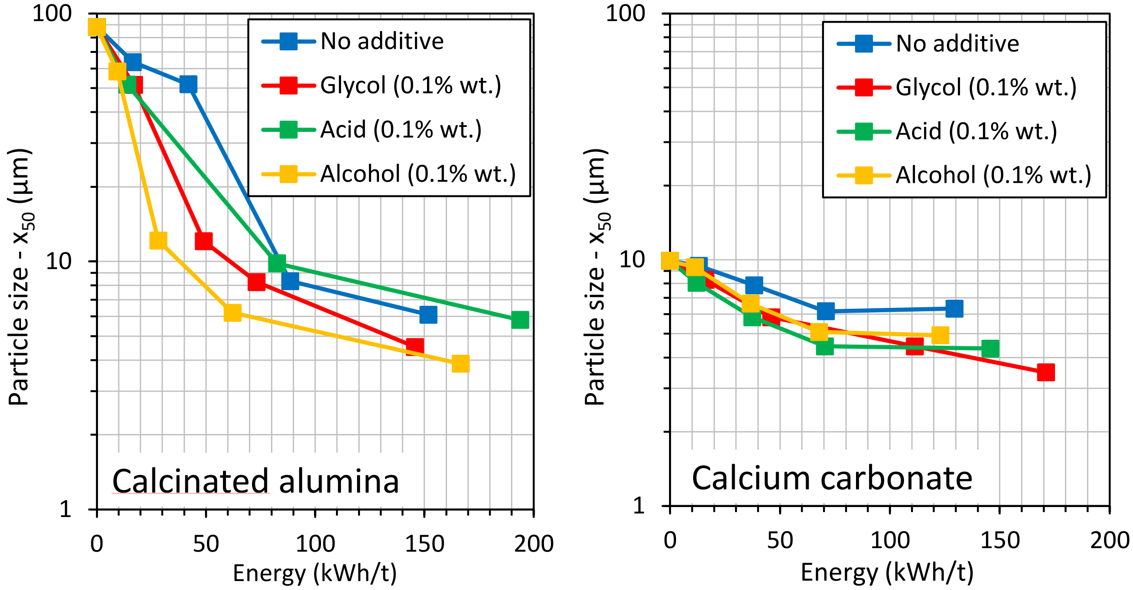


Figure 2: Impact of additive type on the batch grinding results at 70% of critical speed, 30% media filling and 100% media void filling by product.

Next Steps:

Quantitative description of additive effects on stress intensity, powder size reduction and energy dissipation by drop-weight-test, slow compression and hardgrove test, in all cases with grinding media and product, as well as characterization of bulk properties by a powder rheometer and rotating drum (dynamic angle of repose) beside shear tests.

In terms of grinding, additional batch grinding tests, in both 4 and 47 liters' mills as well as open and closed circuit milling tests with air classifier.

IFPRI Project Abstract

A multi-scale study of powder reconstitution phenomena

Claire GAIANI & Jeremy PETIT
University of Lorraine, LIBio (Laboratoire d'Ingénierie des Biomolécules), France
Project Start Date: January 1, 2019
Abstract Date: May 1, 2020

Project Objective:

Organic and biologically-derived materials in powder form are involved in the manufacturing of many products available in the industry (e.g., cosmetics, food, pharmaceutics). Their reconstitution is of upmost importance for the industry considering that most powdered ingredients are dissolved or infused before use. Therefore, deeper mechanistic understanding and global approaches are needed regarding the great variety of powders industrially available. Also, fundamental understanding enabling improvement of the reconstitution of these powders is still lacking with a focus on the particle surface.

Approach:

This project approach aims at:
(1) Developing a reconstitutability index to draw a predictive criterion for the classification of unknown industrial powders according to their reconstitution behavior from the knowledge of their physical and chemical characteristics.
(2) Bringing new knowledge in the reconstituability of industrial powders with a focus on the particle surface.

Recent Results:

(year#1) Reconstitution kinetics were monitored simultaneously for fifty industrial powders in order to be able to develop predictive models. Statistical correlations between the numerous powder characteristics and their reconstitutability were established. Powders were classified into four groups depending on their wetting and reconstitution ability (i.e. Green group: short wetting and reconstitution times, Yellow group: long wetting time and short reconstitution time, Orange group: short wetting time and long reconstitution time, Red group: long wetting and reconstitution times).
(year#2) It is well known that some reconstitution steps strongly depend on particle surface. Poorly wettable particles were coated with various sugars in order to establish correlations between powder reconstitution behavior and surface properties (i.e. hydrophobicity/hydrophilicity, hardness).

Next Steps:

The work of year 2 is ongoing. Various formulations will be done by coating whey powder with sugars (i.e. lactose, sucrose, fructose, glucose and saccharose). These sugars present different wetting behavior, ability to cover the particle surface, chain length, glass transition temperature… These new powders are characterized with a focus on the surface: stiffness, hydrophily, rugosity. The minimal sugar proportion necessary to improve whey powder wettability will be determined for each sugar and compared.
From year 3, we will start soon to work on empirical models able to predict reconstitution times as well as the definition of a reconstitutability index reflecting powder reconstitution behavior independently from reconstitution conditions in agitated vessels.

IFPRI Project Abstract

Dynamic and thermodynamic structural investigation of capillary suspensions

Jens Allard and Erin Koos
KU Leuven
Project Start Date: 25 September 2018
Abstract Date: 23 May 2020

Project Objective:

Structure and function and inherently related. Using a model system for dense and capillary suspensions, we will investigate the microstructural changes during interesting rheological transitions, e.g. yield, using confocal microscopy. Capillary suspensions, particles suspended in a bulk fluid with a small amount of immiscible secondary fluid added to form a percolating network of capillary bridges between the particles are of particular interest as they show a wide range of rheological behavior.

Approach:

Changes to the microstructure of a suspension of fluorescently labelled silica particles are investigated using a confocal microscope equipped with a linear shear cell. The same shear profiles are repeated on a commercial rheometer to obtain force measurement data. The particle positions and radii are determined using a combination of edge detection with Hough transform.

Recent Results:

We demonstrated (and validated) the approach with an experiment showing the change in the secondary fluid volume. The semi-local measures captured the changes in structure and rheology. An experiment with different volume fractions showed a transition from capillary-dominated behavior to granular-like behavior with particle loading. During the shutdown, we improved the measurement protocols and particle detection software.

Next Steps:

We observed a curious behavior this year where the roughness of the behavior influenced the bridge type that could be formed. This will be investigated next year. We will also use non-porous particles to repeat the experiments at different solid fractions and, by including the detection of the secondary fluid bridges to create weighted graphs, we should hopefully link this to the forces between particles and clusters. Finally, using a fast confocal rheoscope, we can get more information about the changes during the shear, more closely linking the stress measurements with the structure.

IFPRI Project Abstract

Characterization of Spray Drying Nozzles at Industrially Relevant Conditions

Nasser Ashgriz, Siyu (Jerry) Chen, Isaac Jackiw

Department of Mechanical and Industrial Engineering
University of Toronto, ON, Canada

Project Start Date: [1, October, 2018]
Abstract Date: 25 May 2020

Project Objective:

Spray drying is an industrial process used in the production of powdered products such as many pharmaceuticals. Pilot scale experiments are used to determine the optimal operating conditions of the sprays for complex fluids, and correlations are used to extrapolate to the production scale. Current correlations lack validation across a wide range of nozzle sizes and for highly viscous fluids which are relevant to the pharmaceutical industry. This study aims to develop these correlations and scaling relationships for a wide range of nozzle sizes and fluid viscosities by focusing on the near-nozzle breakup behaviour. Additionally, the formation and breakup of fluid ligaments will be quantified and analyzed.

Approach:

1. Develop benchmark data set for near-nozzle spray characteristics (Phase 1)
   a. Complex fluids: High viscosity, Polymeric
   b. Pilot and production nozzle sizes
2. Determine correlations for nozzle scaling and ligament formation and breakup (Phase 2)
3. Develop correlations for the effect of ambient temperature (Phase 3)

Recent Results:

For pressure swirl nozzles, multiple experiments with different operating conditions have been completed. Different fluids with different viscosities and at high injection pressures (500 to 900 psi), using nozzles with a wide range of orifice diameters (0.02” to 0.129”) are tested. An imaging technique is used for spray characterization. A larger number of images are collected at several axial and radial locations in each spray. The measurements not only provide the global SMD and distributions, but also the local SMD to study the spray patterns for different operating conditions. The particle size distributions have a unimodal distribution for some operating conditions, while show bimodal distribution for other operating conditions. Near nozzle images taken for the sprays show that at high pressures, fluids accumulates on the wave crests and troughs of the surface waves, which will generate thick, spanwise ligaments. The thin liquid sheet in between the wave crests and troughs perforates forming thin streamwise ligaments. These ligaments then generate small droplets further downstream. A new atomization model is proposed based on the sheet perforation mechanism, which well predicts the spray droplet sizes. The spray size distribution is also predicted using a summation of two gamma distributions.

In two-fluid atomization, the simultaneous existence of multiple breakup modes were identified; one in which surface waves on the liquid jet break, and one in which the bulk of the liquid core breaks. The presence of these two modes of breakup result in multi-modal particle size distributions (PSD). We have related each breakup size and the relative frequency between them to the PSD, and have developed models for the characteristic size of each breakup mechanism. The underlying mechanism of interest for high viscosity fluids is the membrane or bag-type breakup. We have performed experiments on the breakup of single suspended droplets, to determine the characteristic sizes that are generated, and to quantify the breakup process. The breakup process consists of three stages: deformation, formation of the initiation structure, and growth to breakup. We have developed a model for the first two stages, with the third in progress. Initial findings using empiricisms for the final stage show good agreement with our experimental results for the breakup sizes.

Next Steps:

For pressure swirl nozzles, more experiments with polymeric solutions such as HPMCAS/acetone solutions and maltodextrin/water solutions will be performed. Image analysis algorithm for characterizing the ligaments will be completed and used to find the thickness of the ligaments. This information will be used to determine the mass accumulated in the wave crests and troughs to complete the correlation for the proposed model for the atomization by pressure swirl nozzle.

For two-fluid atomization, the single droplet breakup experiments will be extended to high viscosity fluids to complete the breakup model. Experiments will provide the required information on the surface and core breakup modes and the relative frequency between them to describe the PSDs of sprays. The spray database will be further developed with production scale nozzles as well as higher wt.% glycerin mixes and HPCMS mixtures.

IFPRI Project Abstract

Self-Assembled Monolayers as Nucleating Surfaces to Study Early Formation Pathways of Crystal Polymorphs

Ulrich Wiesner
Materials Science and Engineering, Cornell University
Project Start Date: 15 September, 2015
Abstract Date: 18 May, 2020

Project Objective:

IFPRI is interested in understanding and controlling crystallinity, polymorphism, and particle morphology in the early formation stages of crystals. High level objective of this project is therefore to identify appropriate model systems to study, adapt, and apply characterization techniques to describe early particle formation states, and to collect data that is relevant for the development of molecular dynamics simulations or other models of assembly of molecules into nascent crystals. Focus should be on identifying possible early non-classical crystallization pathways, including amorphous states and oriented attachment of clusters to growing particles.

Approach:

Self-assembled monolayers (SAMs) are used to identify model systems for studies of the relationship between surface chemistry, solution conditions, and nucleation and growth of particular crystal polymorphs. These arrays of SAMs will provide nucleating surfaces for the organic model system 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophene carbonitrile (ROY). It was earlier shown that both solvent and SAM surface chemistry work together to control polymorphism of acetaminophen (ACM). However, the effect of supersaturation on polymorph selection was not addressed. To that end, work will now be performed by direct solution crystallization in a “closed” environment instead of the solvent evaporation crystallization in past studies of ACM. The new studies will allow exact control over the degree of supersaturation. To that end, temperature jump experiments will be performed in order to generate enough supersaturation to nucleate a crystal on the surface of the SAM. Different ROY polymorphs will be identified using a combination of Raman spectroscopy and wide-angle X-ray scattering (WAXS) available at facilities of the Cornell Center for Materials Research (CCMR). Possible work at Cornell’s High Synchrotron Source (CHESS) may allow the study of crystallographic details and early formation stages. Crystal morphology in the films will be studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Recent Results:

In the first part of this project, working with the model compound acetaminophen (ACM), we have established that both self-assembled monolayer (SAM) surface chemistry and solvent work together to control crystal polymorph, and that for a given solvent, surface chemistry dictates crystal orientation. Early formation stages were studied by means of *in-situ* wide-angle x-ray scattering (WAXS) at Cornell's High Energy Synchrotron Source (CHESS). We concluded from experiments of seeded nucleation of ACM Form II in water/dioxane that crystals nucleate at the SAM-solution interface and that they propagate faster at the substrate-solution interface than in the bulk. Studies of spontaneous nucleation and crystal growth of ACM Form 1 in water suggested that early structural transformations take place on the way to the final crystal, similar to what has been observed in inorganic crystallization.

In the last funding period, instead of studying ACM, we moved to a more complex system, ROY, that has 11 discovered polymorphs. Since SAM surface chemistry, solvent and supersaturation are all responsible for polymorph selection during nucleation, this time, supersaturation was considered explicitly. To control the degree of supersaturation, direct solution crystallization by cooling was applied in a small vial with SAM substrates placed vertically. Solvents were selected with high boiling points and high ROY solubility to induce supersaturation by few degrees of temperature jumps. As a first step, solubility curves of ROY in DMSO and benzyl alcohol were constructed, and entropy and enthalpy of dissolution were calculated using the van't Hoff equation. Subsequently, three parallel experiments of ROY in benzyl alcohol nucleated on a cover glass (i.e. without a SAM) were first performed with different degrees of supersaturation (S) of 1.5, 2 and 2.5. It was noticed that at different supersaturation levels, the dominant polymorph changed from Y for S=1.5, to ON for S=2.5. ROY in benzyl alcohol crystallized on octyltrichlorosilane (OTS) modified gold surfaces (SAM) at different supersaturation levels was also investigated. However, little to no crystallization on such SAM surfaces occurred over a 2 day period for all supersaturation levels studied, while lots of crystal clusters appeared in solution suggesting, that either homogeneous nucleation is preferred compared to heterogeneous nucleation on the SAM or that heterogeneous nucleation had appeared on the container walls. The main reason could be the repulsion between polar solvent molecules around ROY and the hydrophobic SAM surface, preventing the formation of crystals on the SAM surface. From here, we moved to the system of -OH modified hydrophilic SAM surfaces with a polar solvent (benzyl alcohol), as well as hydrophobic surfaces in combination with a nonpolar solvent (toluene) to study crystallization as well as polymorph selection at the same degree of supersaturation. The former experiments resulted in cubic shaped crystals while the latter produced rhombic shaped crystals. These shape differences suggested a different polymorph selection. From the crystal morphology, possible polymorphs were monoclinic Y or YT04 and triclinic R, respectively. Unfortunately, as a result of the Covid-19 shut-down, crystal polymorphs could not be verified by thorough characterization, *e.g.* using WAXS. Nevertheless, these sets of proof-of-principle experiments established that (i) polymorph selection for ROY is possible as a function of the degree of supersaturation, and (ii) similar to ACM, for ROY the combination of SAM + solvent dictates specific polymorph selection.

Next Steps:

As indicated, as next steps we will use a combination of wide-angle x-ray scattering and Raman spectroscopy in order to study the exact polymorphs formed under the conditions described above. In particular Raman spectroscopy, applied by using a Raman microscope to distinguish individual crystals, has been found to be a powerful tool in order to identify different ROY polymorphs which all have well distinguished bands in Raman spectroscopy. Furthermore, in future experiments we will pay closer attention to the cooling rate in order to identify with more precision at what exact temperature nucleation and growth of ROY crystals are initiated. For example, it might be possible to use *in-situ* FTIR to track the nucleation process and determine the induction time. Finally, once exact sets of SAM+solvent+degree of supersaturation have been identified that lead to specific ROY polymorphs, we will again try to use, *e.g.* synchrotron experiments to tackle the question of earliest nucleation and growth steps in the crystallization of ROY.

IFPRI Project Abstract

Controlling Rheology via Boundary Conditions in Dense Granular Flows

Karen E. Daniels
Dept. of Physics, North Carolina State University
Project Start Date: 1 August 2018
Abstract Date: 25 May 2020

Project Objective:

In prior work, we have previously shown [1] that nonlocal rheologies [2,3,4] successfully model granular flows across different packing densities, particle sizes and shapes, and shear rates. This success is provided by the measurement and specification of a set of three material properties for a particular set of particles. However, the results of the model depend on *a priori* knowledge of the flow profile, limiting its predictive power. Here we aim to (Q4) understand how changing the roughness and/or compliance of a boundary changes the resulting flow. This will ultimately allow us to determine a set of general principles (Q5) which allow us to correctly set the boundary conditions in nonlinear rheological models, and test their generality in other geometries (Q6).

Approach:

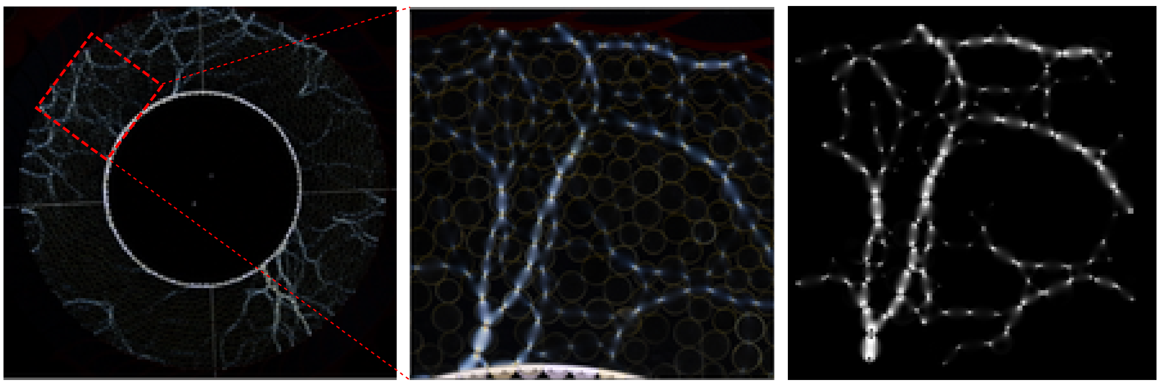
As for our work during the first funding period [1], we perform our experiments in an existing quasi-2D annular shear cell with a rotating inner wall and stationary outer wall. Both walls are laser-cut and are interchangeable to modify roughness, as shown at right. In each experiment, we aim to measure both the velocity (shear) profile and the bulk rheology (shear and normal stresses) in order to characterize the dependence of the boundary conditions on both the particle-shape and boundary-characteristics.

Recent Results:

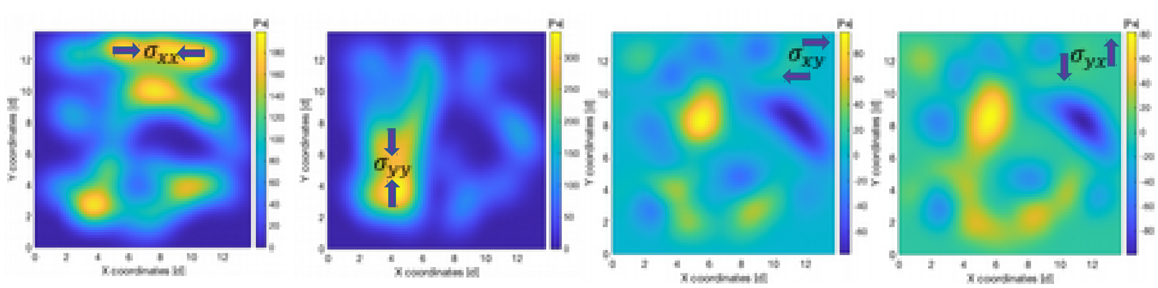
Graduate student Farnaz Fazelpour has been conducting experiments and data analysis using a variety of particle and boundary conditions, improving our ability to make quantitative measurements of the stress field, and its spatial and temporal fluctuations. These have focused on the use of photoelastic particles, which will allow for direct measurements in all geometries required for the project (different boundary conditions, and different flow geometries). This has required switching over to the use of soft particles, and making improvements to camera, lighting, and particle-tracking, force-inversion techniques that she will need for analyzing the experiments.

There are not new scientific results since December, since we have been out of the laboratory since mid-March, but we now have an improved data-analysis pipeline in place that will speed the analysis of experimental results once we are able to return.

The image series below shows a typical result from photoelastic inversion [1]. For a subregion (middle image) of the annular flow, chosen to allow ~100 pixels across the diameter of each particle) we obtain movies of the birefringence pattern within each disk. Once our image-processing algorithm has determined the best-fit value for each vector contact force, we can produce a reconstructed image for comparison; this is the image shown at the right, in excellent agreement with the original image.



The list of all particles, their contacts, and the interparticle forces are the complete set of data needed to determine the continuum stress tensor field, through a process of coarse-graining [2]. A sample such analysis is shown below, for this same image; note that the orientation of the force chains the magnitude and sign of its contributions to the various tensor components. These stress fields are calibrated in real units (Pa).



Next Steps:

Once the lab reopens, we will be able to collect long, statistically-independent series of images such as these, performed under a variety of packing densities and boundary conditions, and apply this data analysis pipeline. The results will be continuum stress fields for use in further testing the utility of rheological models (Q6). The improved quantification of the shear and normal stresses will allow us to quantitatively address Q4 and Q5 by performing additional runs.

References:

[1] Daniels, Karen E., Jonathan E. Kollmer, and James G. Puckett. "Photoelastic Force Measurements in Granular Materials." *Review of Scientific Instruments.* 88: 051808. (2017)

[2] Weinhart, Thomas, Remco Hartkamp, Anthony R. Thornton, and Stefan Luding. "Coarse-Grained Local and Objective Continuum Description of Three-Dimensional Granular Flows down an Inclined Surface." *Physics of Fluids.* 25: 070605 (2013)

IFPRI Project Abstract

A Holistic Approach for the Model-based Control of Crystal Size, Shape and Purity in Integrated Batch and Continuous Crystallization - Wet Milling Systems

Zoltan K. Nagy
Purdue University, Davidson School of Chemical Engineering, West Lafayette, US
Project Start Date: 11/30/2017
Abstract Date: 05 20, 2020

Project Objective:

[2-3 sentence summary of original project brief]
The main objective of this project is the design of novel, integrated crystallization systems, which are able to produce increased control of the properties of crystalline materials, in the context of crystal size and shape distribution. The attainable region of crystal size distribution (CSD) is widened by the application of recirculation stream and by integrating wet mill for batch, and multiple MSMPR units and downstream wet mill with recirculation stream(s) for the continuous operation. 2D PBM based modeling, design and model-based control approaches are in the focus of this project, where the *in-situ* imaging based monitoring tools inherently has special importance.

Approach:

[2-3 sentence summary of project proposal (experimental/theoretical approaches)]
In this project a model based approach is applied, based on the use of comprehensive population balance (PB) framework. 1D and 2D PBM-s will be developed for the batch and continuous integrated systems, involving the high resolution finite volume method (HR-FVM) for the solution of generated model-equations. Kinetic model parameter estimation procedure is developed and carried out for the crystallization of a representative model API forming high aspect ratio crystals. Nonlinear model predictive control, involving the full 2D PBM will be developed and implemented using crystal shape information from the *in-situ* imaging tools.

Recent Results:

[Short summary of past year's progress and its significance, including one or two illustrative graphics (if useful)]

The portable crystallization solvers were extended with agglomeration and breakage mechanisms, involving at this stage the standard breakage selection and fragmentation, as well as agglomeration functions from the crystallization modeling literature. Extending the list of kernels (i.e. the dependency of rates on the agglomerating and breaking particle sizes) is going to be carried out.

In the first step along the line of development of integrated continuous crystallizer-wet milling systems model with multiple recirculation streams, a flexible MSMPR crystallizer cascade model has been developed, involving nucleation, growth, dissolution, breakage and agglomeration of 1D crystals for cooling, antisolvent and combined cooling and antisolvent crystallization pocesses. The importance of this simulation goes beyond the simulation of simple MSMPR cascades: it enables to model tubular systems as tank-in-series compartmental model. Given that there is no upper limit for the number of crystallizers and each crystallizer can be fed with both solute and antisolvent streams, this flexible solver enables the simulation of integrated MSMPR-tubular crystallizer systems in various configurations with single-or multi point antisolvent addition. This also paws the way for the MSMPR network solver, where certain MSMPR crystallizers can be operated as wet-mills or agglomerators not only in series but also in parallel configurations, with recirculation streams.

2D population balance models inherently involves more kinetic parameters then their 1D counterparts, and effective de-coupling of the nucleation from the length and width growth rates becomes crucial as the length and width growth parameters are inherently correlated *via* the mass balance. A new method has been developed to use the evolution of relative number density information coming either from *in-situ* imaging tools, or from the routinely used FBRM, needing no backward or forward CSD to/from CLD transformations. In essence, we aim to maximize the correlation between the simulated number density and the measured relative number density. With another words, we want to force the simulations to show increasing particle number trends where the e.g. the FBRM count increases and *vice-versa*, with (not necessarily linearly) proportional rates. This method has successfully been applied for two model-APIs (paracetamol crystallization from ethanol and another API, called Compound A crystallization). Moreover, the parameter estimation of the Compound A has already been initiated using 2D PBMs, as Compound A forms high aspect ratio crystals, and the shape is sensitive on the crystallization conditions indicating that the length and width growth/dissolution rates are independent, hence, has to be modelled separately. In this 2D parameter estimation the FBRM count, using the correlation maximization method, solute concentration evolution, Mastersizer CSDs (both for product and intermediates) as well as length and width distributions, extracted from optical microscopy images (for products and select intermediates) are being used the infer the crystallization kinetics by solving minimization problems.

Next Steps:

[2-3 sentence summary of where the project is headed in the next year. If the project is in its last year, a short summary of open questions.]

Blaze Metrics' imaging tool will be purchases by the end of this year, which will enable to carry out detailed comparisons with the Mettler Toledo's newest *in-situ* imaging probe, the EasyViewer, which is already in our laboratory. Furthermore, the MSMPR cascade simulation will be extended to 2D case, with nucleation, growth, dissolution and breakage mechanisms. Both 1D and 2D flexible MSMPR cascade solvers will be extended to flexible tank crystallizer network systems, that will also allow recircullations. The agglomeration and breakage mechanisms will be enabled or disabled in every crystallizer individually, which will allow to dedicate some tanks systems of the network to wet-mills. The 2D parameter estimation of nucleation, length and width growth and dissolution of the model API will be finalized.

IFPRI Project Abstract

Investigating the Effect of Solvents and Impurities on Crystal Growth

Michael F. Doherty and Tobias Mazal
University of California Santa Barbara
Project Start Date: 1 September, 2017
Abstract Date: 25 May, 2020

Project Objective:

The goal of this research is to develop a practical engineering tool for predicting the relative growth rates (growth kinetics) and morphology of solution-grown faceted crystals, including the effects of solvent, and impurities/additives. The methodology will be tested on a variety of systems, including: paracetamol, olanzapine, ammonium acetate and a variety of drug substances, all grown from solution.

Approach:

Our approach is to leverage many years of research & development building our crystal design software tool called ADDICT. Our approach is to develop (fast) mechanistic models of crystal growth validated by experiments and both molecular simulations and KMC simulations.

Recent Results:

We have developed a Kinetic Monte Carlo simulation that is being used to test our mechanistic growth models for crystallization from solution. Testing is complete for the case of pure solvent with no impurity and results agree well the mechanistic models, which in turn agree well with morphology predictions for crystals with simple growth units (centrosymmetric growth units, such as naphthalene and rubrene solutes). The KMC simulations have been extended to include impurities in solution ("growth inhibitors") adsorbed onto the crystal terraces (crystal surface in front of the moving steps). We are in the finishing stages of testing conventional growth inhibition models relative to the KMC results.

Next Steps:

We will spend the next year completing our testing and making any appropriate modifications to the mechanistic models. These will then be incorporated into ADDICT.

IFPRI Project Abstract

Scale-up Rules for Mixing Mechanisms in Rotating Drum Flows

Indresan Govender[1,2] and Taswald Moodley[1]

[1]Chemical Engineering, University of KwaZulu-Natal, Glenwood, Durban, South Africa, 4041
[2]Chemical Engineering, University of Cape Town, Rondebosch, South Africa, 7701

Project Start Date: 02 February 2018
Abstract Date: 23 May 2020

Project Objectives:

1. Develop a continuum model of rotating flows that spans rolling-to-cascading flows.
2. Validate the model using PEPT.
3. Identify the energy proxies for discriminating between the dominant mixing mechanisms.
4. Extract dimensionless number that facilitates scale-up of the mixing mechanism.

Approach:

To evaluate mixing rules in rotating drum mixers using:

1. in-situ measurements via Positron Emission Particle Tracking (PEPT)
2. numerical simulation via DEM.
3. Continuum modelling with PEPT and DEM data as inputs to the continuum equations.

In the present work (phase 3) we formulate a continuum model for rotating drum flows and extract a suitable dimensionless number that facilitates scale-up of the dominant mixing mechanisms.

Recent Results:

A continuum model of rotating drum flows was formulated using the linearised form of the $\mu(I)$-rheology. The model velocity field and flow geometry were successfully validated against PEPT measurements. Energy proxies describing shear and advective mixing were identified from the differential energy balance of the model. The Entrainment number was shown to successfully scale-up the relative combinations of advection-to-shear mixing from bench scale to larger configurations consistent with industrial scale. The scale-up rule via the Entrainment number was shown to be valid across the rolling-to-fully-cascading flow regimes.

Next Steps: Test the scale-up rule beyond bi-disperse systems. A full tensorial analysis is currently being developed for the purpose of calculating the energy proxies directly from PEPT data. The extension to wet rheologies is also being pursued.

IFPRI Project Abstract

Detailed insight into microscopic phenomena using 3D-tomography data to develop a better model for dead-end filtration

Principle Investigator(s): Thomas Leißner, Urs A. Peuker
PhD-Student(s): Mashia Brockmann, Erik Löwer
Affiliation(s): TU Bergakademie Freiberg
Project Start Date: 01.10.2017
Abstract Date: 29.05.2020

Project Objective:

The project aims at the connection of the disperse particle properties with characteristics of the resulting filter cake structures. These include particle size, shape and wettability and the resulting particle-particle interactions. Finally, these investigated relationships will help to better understand the relevant process properties such as the dewatering behavior or the washability of these systems. For this purpose, mainly X-ray tomographic investigations of the filter cake structures are carried out.

Approach:

Material: Al_2O_3 (compact particles) and $CaSiO_3$ (fibres) were selected as particle systems, and for hydrophobization, we used silane as a coating agent.
Filtration approach: Using different vol.-% of ethanol to investigate the wettability effect on the filter cake in the VDI nutsche and in-situ cell. We carried out long-term scans for in-situ filter cakes which differed in ethanol vol.-%. We selected the 20, 40, 60, 80 and 100 vol.-%. This year we present mainly results using an aqueous phase to validate the data expoitation of the image processing.
Image processing approach: The main scope of the last year was on finalizing the data exploitation methods. This is due to the fact, that commercial software solutions did not deliver satisfying quantitative results. Therefore, individual models and algorithms have been implemented to extract much more information out of the X-ray images.

Recent Results:

For the analysis of the solid structure several self-developed methods are available, such as determination of particle size, shape, local void volume fraction, coordination number, pore size and pore connections as well as the determination of tortuosity. Going over to two fluid phases (describing de-saturation) within the void structure, the determination of the capillary length as well as the measurement of the local contact angle becomes a matter of additional interest. Furthermore, the size and shape of the hydraulically isolated liquid bridges can also be determined, quantifying local saturation.
In combination of both method steps, such as coordination number and fluid bridge formation or tortuosity and capillary length, conclusions on the dewatering behavior can be derived. For this purpose, a stepwise in-situ dewatering of a filter cake was carried out

within the µCT to determine the capillary pressure distribution in connection with the saturation. These results represent a capillary pressure curve.

By supportive conventional laboratory experiments these results are validated, as far as the individual local parameters are experimentally accessible by the macroscopic experiments. Otherwise the comparison with integral values is made.

In a parameter study with hydrophobized Al_2O_3 particles the influence on the internal cake structure was investigated. The approach was to change the mother liquid from a water-based suspension to an alcohol-based suspension by stepwise adding ethanol. Where the aqueous suspension stands for a non-wetted particle system. The addition of ethanol decreases step by step the wetting angle and finally the suspension with 100 % ethanol shows nearly perfect wetting ($\gamma = 10°$). We observed that filter cake porosity is a function of ethanol content within the suspension. It could be shown that with decreasing contact angle from $\gamma = 72°$ to 10° and thus better wettability the local porosity decreased significantly by 7 %-points, but the mean pore size and mean coordination number showed less change. The effect of the change in wetting, particle interactions respectively, seems to be more on the shape of the pore size distribution, where the span between the 25% and 75% quantile increased in a certain concentration range of the ethanol.
The decreased amount of the porosity is in strong relation to the change of the surface tension and wetting properties. To validate the wettability change on hydrophobic Al_2O_3 filter cakes, we compared experimental filtration data with tomographic extracted porosity data.

Next Steps:

Since now we have the methods for structural analysis in place and we are able to extend the previous experiments. Next, we will investigate plate-shaped or fibrous ($CaSiO_3$ - fibres) particle systems. For the renewal, we propose to extend the scope of the research and to add investigations on washing experiments of these particle systems and the resulting structural changes. The methods will also be applied to centrifuge sediments. To increase the resolution of the 3D-analysis, we will try to incorporate some FIB-analysis into our portfolio.

IFPRI Project Abstract

3D Printed "Perfect Particles"

Karen Hapgood (Academic Contractor) with Dr Jun Zhang & Dr Negin Amini (postdocs)
Deakin University, Geelong, Australia.
Project Start Date: 2015/2018
Abstract Date: June 2020

Project Objective:

Demonstrate multiple new ways 3D printing can be used to create controlled particles or agglomerate structures to advance our understanding of (a) Agglomerate breakage, (b) Agglomerate wetting, (c) Powder flow.

Approach:

A range of particles/granular matters with different material properties were 3D printed using different techniques and materials. Particle shape, size, structure, colour and infill/density were varied and controlled with accuracy, with experimental and simulation studies conducted in agglomerate breakage, stress visualization, liquid imbibition and powder flow etc.

Recent Results:

Agglomerate breakage: The strength distribution of a random sphere agglomerate as a function of orientation and compression rate has been plotted for the first time, demonstrating the unique fingerprint of the agglomerate structure. Real powder agglomerates with well-controlled strength and geometry from binder jetting have also been used in agglomerate breakage study. Two papers were generated with one published and one under review with APT.

Stress visualization: Stress visualization of 3D printed discs and 3D coffee bean model with orthotropic orientation was explored. The intensity field of the stress fringes were validated using FEA. Stress quantification of 2D and 3D particles were carried out using the gradient-squared method. We found that the method is more suited for 2D shapes and not complex 3D shapes.

Liquid imbibition: 3D printed lattice, voronoi and cement structure were used as powder bed analogues for liquid imbibition study. Effective surface coating was achieved to make the material surface hydrophilic/hydrophobic. Systematic analysis was carried out by comparing experimental results with theories and CFD simulations.

Particle flow and segregation: This study consists of multiple projects including 1. Coefficient of restitution of coffee bean geometry using EDEM. 2. Flow of irregular shaped particles/ particles with varying density using ROCKY. 3. Modify the surface roughness of the drum inner boundary. All DEM results will be validated against the comparative 3D printed experimental setup. These experiments in particular have been disrupted by lab closures since March at Deakin University due to Covid19. We hope to complete the experiments when the lab reopens, in time for the November final report.

IFPRI Project Abstract

Quantitative Prediction of Segregation at Process Scale

Joseph J. McCarthy
University of Pittsburgh
Project Start Date: 1 September 2015
Abstract Date: 25 May 2020

Project Objective:

This project is aimed at identifying critical material and process parameters that control the extent of powder segregation, such that we might develop quantitative models that predict segregation. These predictive models should be valid at full process scale and are to be validated against appropriate experiments.

Approach:

Segregation rate models hold promise for scale-up via continuum-level analysis using device-specific transport equations; however, experimental validation of dynamic models is extremely difficult and typical segregation models are not inherently built with scale-up in mind. Our approach overcomes the experimental limitation by exploiting a novel framework for segregation testing based on introducing a perturbation time-scale that establishes an "equilibrium" between mixing and segregation that is a function of the imposed (known) perturbations. With regard to the scale-up limitation, we have built – and continue to validate – segregation models that are written expressly in dimensionless form with an aim both to connect segregation modeling to flow rheology as well as to enable more transparent scale-up. We are using our experimental segregation validation framework both to benchmark existing segregation rate models as well as to test our new and developing models.

Recent Results:

Our most recent work has focused on archival publication of our previous work on model development and validation, as well as extension of our cohesive model beyond moisture-induced cohesion. As we transitioned the project to the oversight of a new graduation student, a DEM code was developed that can evaluate cohesion based on a more generic, surface energy (or van der Waals) mode. This simulation is being used to test the extensibility of our segregation rate modeling for cohesive materials.

Next Steps:

As the project wraps up, we intend to complete archival publication of all models, and set the stage for device-specific, applied modeling in the near future.

IFPRI Project Abstract

Flowability Assessment of Weakly Consolidated Powders

Colin Hare[1], Ali Hassanpour[2]
[1] Department of Chemical and Process Engineering, The University of Surrey, UK
[2] School of Chemical and Process Engineering, The University of Leeds, UK
Project Start Date: 01 March, 2015
Abstract Date: 24 May, 2020

Project Objective:

Measurement of unconfined yield strength of powders can be made with a variety of commercially available shear testing devices. Traditional flowability measurement devices have a number of short comings, e.g. reproducibility of unconfined yield strength is greatly reduced at low stresses, sometimes measurement is inconsistent with observed behaviour, or materials found to be cohesionless may still have practical differences. Generally the onset of flow is measured, which may not be a complete flow description. IFPRI seek to develop a theoretical understanding of flow of weakly consolidated and weakly cohesive powders and develop a practical means of making the measurement.

Approach:

We adopt the ball indentation method for determining powder flowability by measuring the resistance of a powder bed when penetrated by a sphere, which is quasi-statically introduced. It is necessary to determine the constraint factor of a powder in order to infer the yield stress from the indentation measurement. Indentation measurements are carried out on vertically consolidated beds at the same stress as uniaxial compression measurements, in order to compare flowability measurements and determine constraint factor. The influence of single particle properties and flow properties on constraint factor is explored in order to be able to predict its value so that indentation alone can be used to infer the yield stress. The shear cell method is also utilized as a comparative test.

Recent Results:

Ball indentation measurements were carried out on beds of titania prepared by sieve-filling prior to vertical consolidation, using the Freeman FT4 Powder Rheometer, to determine the influence of indenter size and position on the hardness measurement. Indents were carried out in the 50 mm diameter cell, with the centre of the radial indents (five indents for the 4 mm diameter indenter, four for the 6 mm indenter) at a radial distance of 14 mm. As shown in Figure 1, for both indenter sizes the hardness measured by the single indent in the centre is greater than the average of the radial indents[1]. This may indicate a greater packing fraction in the centre of the bed.

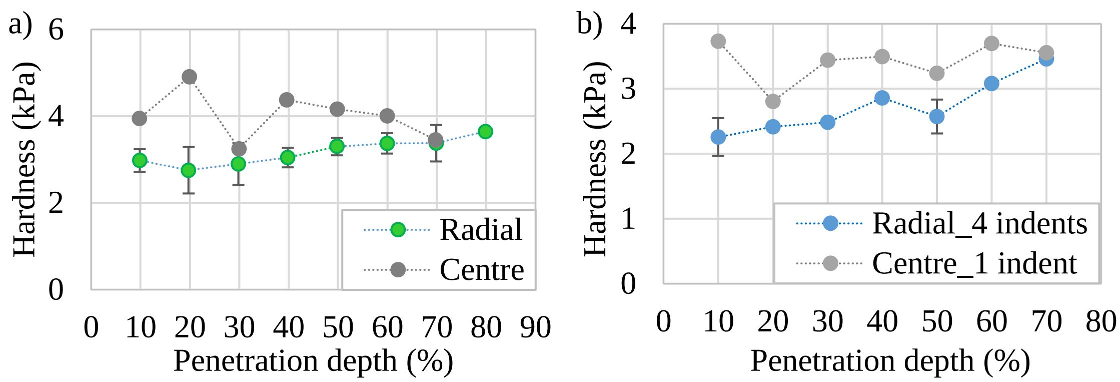


Figure 1. Hardness against dimensionless penetration depth at central and radial indentation positions (a) 4 mm indenter (b) 6 mm indenter

Indents were carried out in the central position of sieved, vertically consolidated beds using 4, 6 and 10 mm diameter indenters, with the hardness measurements shown in Figure 2. For the 10 mm indenter the hardness is relatively constant at penetration depths of 20 – 50% of the indenter radius, then increases beyond this. For the 4 and 6 mm indenter there is greater fluctuation in the hardness measurement with depth, particularly for the 4 mm indenter. Table 1 shows the maximum force measured for each indenter at all tested penetration depths. The force measurement increases as penetration depth and indenter size increase. The FT4 force sensor has a resolution of 0.1 mN and an accuracy better than the greater value of 1 % of the reading or 125 mN (0.25% of full-scale measurement). The results of Figure 2 and Table 1 suggest that as indenter size and penetration depth are reduced the hardness is overestimated due to the reduced accuracy of the force measurement.

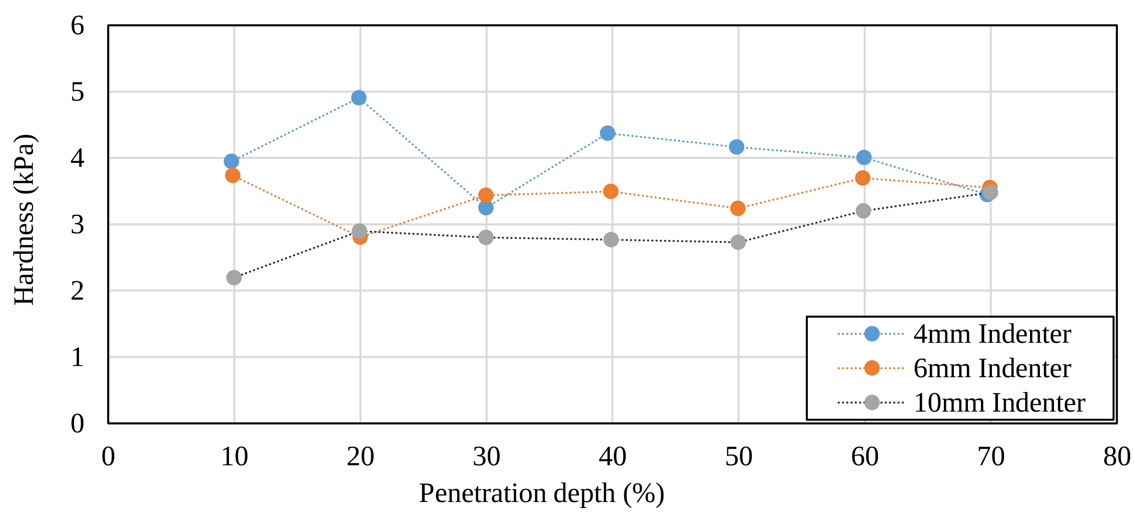


Figure 2. Hardness for various indenter sizes

[1] Note that due to lab closure in response to Covid-19, only 1 measurement has been carried out at each penetration depth for all centrally applied indents, as well as on only 1 bed for the 6 mm radial indents.

Table 1. Maximum indentation force (mN) for indenter sizes and penetration depths

Depth (%) / d_{Ind} (mm)	10	20	30	40	50	60	70
4	9.23	22.1	20.8	34.9	39.2	42.3	39.4
6	19.9	28.5	50	63	68.7	87.7	91.4
10	32.7	81.7	112.1	139	160	211	248.6

In the first 3-year IFPRI funded period the influences of individual particle properties on constraint factor were explored experimentally using silanised glass beads (size, size distribution) and by DEM simulations (surface energy, sliding and rolling friction coefficients). Individual relationships were found, though no relationship was determined for non-glass bead samples, the results have since been reanalysed based on flow properties, i.e. the flow function coefficient, ff_c (Figure 3). Since the indentation depth has been shown to influence the hardness measurement (Figure 2) and therefore the constraint factor, only materials indented to the same depth of 50% of the indenter radius are compared in Figure 3. The constraint factor increases approximately linearly with flow function for very cohesive materials ($1 \leq ff_c < 2$), then remains relatively stable around a value of 4 for cohesive ($2 \leq ff_c < 4$) materials. It should be noted that pea protein exhibited slip-stick behaviour, compromising the reliability of the constraint factor data for this material.

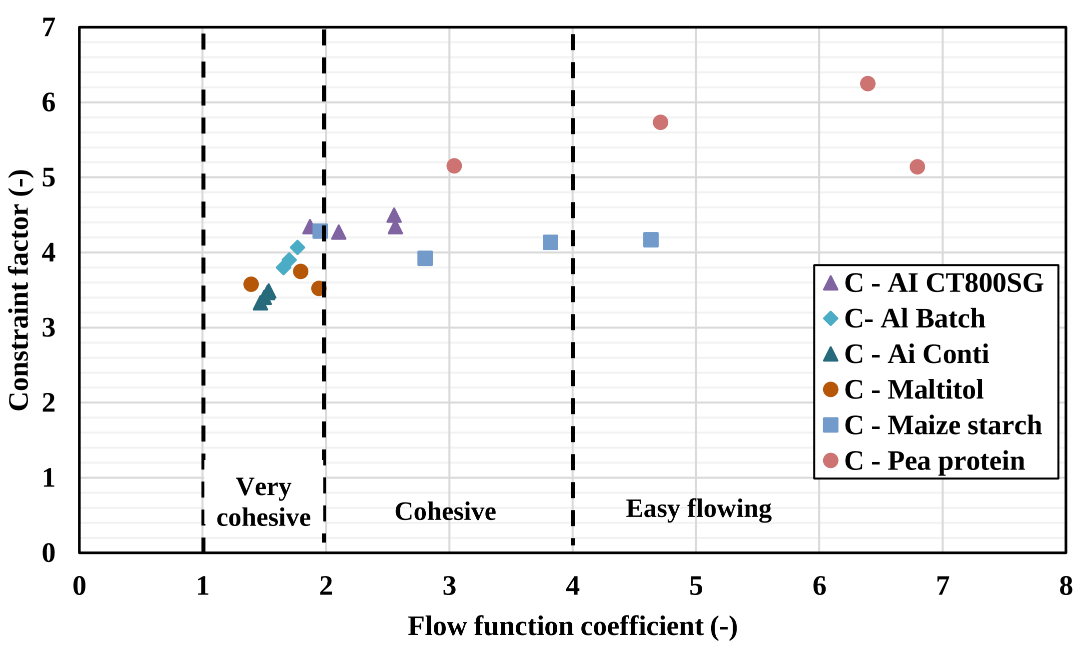


Figure 3. Relationship between constrain factor and flow function coefficient

It has previously been shown for titania that ball indentation onto sieve-filled, vertically consolidated beds and shear cell analysis using the Schulze RST XS.s with low stress cell can achieve unconfined yield stress measurements with coefficients of variation < 2% at an applied stress of 0.5 kPa, however the unconfined yield stress measurements do not agree between the techniques. In order to assess the accuracy of these two techniques, conical hoppers will be designed for mass flow based on each approach and the resulting flow behaviour will be assessed. The necessary measurements for design have been completed, resulting in a hopper angle of ~10^{o} and outlet diameters of 10 and 25 mm for flow functions determined by ball indentation and RST XS.s measurements, respectively.

Next Steps:

Reproducible measurements of unconfined yield stress are achievable with suitable bed preparation methods, i.e. by sieve-filling prior to ball indentation or by pre-shearing. An open question remains on the accuracy of these measurements and their consistency with observed flow behaviour. Furthermore, the homogeneity of the bed packing state in these two systems is unknown.

In the remainder of the project the flowability of various powders will be assessed using indentation, uniaxial compression and the shear cell method. The constraint factor will be determined for all materials, allowing the unconfined yield stress at low stresses to be determined from ball indentation measurements and compared to those from the shear cell method. The operability range and reproducibility of these techniques, in relation to particle and flow properties, will be assessed. Hopper flow measurements will be carried out to assess the accuracy of these two techniques. Additionally, the packing fraction distribution will be assessed by X-Ray tomography (Leeds. UK) for vertically consolidated beds to determine the flow field around the ball indenter.

Environmentally Responsive “Smart” Particles

Presented virtually/remotely, May 22, 2020.

By

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The International Fine Particle Research Institute (IFPRI) has commissioned a comprehensive critical literature review of “smart” particles that are responsive to their local chemical and/or physical environment. The initial focus is smart in-situ particles for process characterization, though the review is not limited to this application. Application examples include carbonless copy paper particles, particles for medical diagnostics, or thermally sensitive particles. Environmental forces to consider include, but are not limited to, mechanical force, electromagnetic radiation, temperature, pH, or other external triggers or stimuli. This presentation summarizes the scope of the review, highlighting examples related to the various triggers and stimuli from both commercial and academic examples. Smart particles used for commercial and experimental applications are also included. Each example, when applicable and information available, includes particle operating principles, detection, analysis, control methodologies, size range, response range, response sensitivity, and how they are synthesized/manufactured. This brief overview is offered as a supplement to the original outline supplied in January, and a chance for IFPRI feedback and guidance for the composition of the final review.