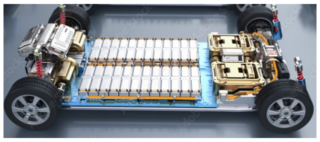
THE PARTICLE TECHNOLOGY FORUM (PTF) NEWSLETTER

An American Institute of Chemical Engineers (AIChE) Forum

Message From The Chair

Greetings and Excitement About Emerging Particle Technologies



As we move into spring season with the promise of most of the things returning to normal, I hope you and your families and friends are enjoying new beginnings and fresh starts.

These are exciting times for particle technology members playing a pivotal role in both old and new emerging technologies. We need to attract more of the graduates in chemical engineering proficient in particle technology. The energy paradigm shift needs more of these graduates by the industry. Not all academic institutions are offering courses in this field. Particle Technology Forum (PTF) leadership initiating new webinar series to expose the current undergraduate and graduate students to these exciting new areas of particle technology and how they can be part of the new emerging and transformative technologies. The goal is to get them interested in this field and offer the tools (AIChE online courses) for them to prepare for the future jobs in the new energy sector.

These sub-micron and nano particles are playing a major role in the emerging sustainable technologies:

- Hydrogen production via chemical looping, pyrolysis of natural gas, dehydrogenation of methane,
- Production of solar grade polysilicon using FBR,
- Dehydrogenation of propane and ethane,
- CO_2 capture from atmospheric air and flue gases for sequestration,
- Biomass pyrolysis using heat carrying inert particles or catalyst particles,
- Biomass gasification,
- Plastic pyrolysis using catalyst particles,
- Decarbonization of the conventional travel with fossil fuels

As you all know, we initiated special PTF Webinar series addressing some of the new emerging technology fields utilizing particle technology. First two talks were well attended. I am looking for an exciting speaker for the next webinar in the emerging technologies area. If you have recommendations, please reach out to me.

A Peek At The Contents

11th International Conference on Conveying and Handling of Particulate Solids

September 2 – 4 , 2024

Based on input from the PTF community, we have launched a new initiatives including increasing diversity, equity, and inclusion efforts. PTF community is now more diverse and talented team.

My gratitude to this newsletter's editor, Dr. Shrikant Dhodapkar, for creating informative newsletters, Dr. Ben Freireich for planning all PTF sessions, and all members of the executive committee who keep programming and events running smoothly. Prof. Maria Tomassone, Vice-Chair, is taking care of award nominations. Please take a lead in nominating well deserved nominees for various PTF awards. The deadline, **May 31, 2024**, is approaching fast. Please nominate.

Hope to see you in person at AIChE Annual Meeting - October 27- October 31, 2024, San Diego Convention Center, Hilton San Diego Bayfront, USA.

S.B. Reddy Karri, PhD, President &. CEO, PSRI
Chair, The Particle Technology Forum of AIChE
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FROM THE EDITOR'S DESK

In concurrence with the message from the PTF Chair, the focus of our Summer 2024 issue will be ***Emerging and Transformative Particle Technologies To Address Decarbonization & Sustainability Challenges***. The consensus of the scientific community is that the anthropogenic CO_2 emissions must be reduced to NetZero by 2050 to avert a climate crisis. Most major chemical and petrochemical companies have publicly committed to NetZero targets which will require groundbreaking and transformative technologies. Particle Technology has a role to play on many fronts.

I am inviting contributions (1-5 pages) from **all PTF members**. These could be technology overviews, perspectives, technology highlights of your research or that of your research group. The deadline for submission is **July 31st**. I hope that upcoming issue jumpstarts the interest and nucleates ideas for future research.

Shrikant Dhodapkar, PhD

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PTF Membership

To continue receiving the PTF newsletters (3 issues per year) and stay current with particle technology events and news, please make sure to renew/ start your membership by either:

- Checking Particle Technology Forum when renewing your AIChE membership annually,
- Becoming a PTF lifetime member so that you don't have to your renew membership every year

Become a PTF only member (Annually $15, Lifetime $150)

If you don't see the PT membership in your renewal screen, you can choose "Update Membership Options" and add PTF to your order.

You can also contact AIChE customer service at 800-242-4363 (US); 203-702-7660 (Outside the US); or email customerservice@aiche.org for membership questions and help.

PTF Membership Committee

PTF Award Winner 2023

Elsevier Life Time Achievement Award

Dr. Raymond Cocco

President

Particles in Motion, LLC

B.S. in Ch.E. at University of Florida in 1982

Ph.D. in Ch.E. at Auburn University in 1989

Citation: For his innovative technology development focusing on multiphase fluid dynamics and for his outstanding mentorship and service to Particle Technology Forum

Ray is president of Particles in Motion, LLC, a consulting company focusing on complex granular-fluid hydrodynamics in commercial applications. Before his current role, Ray Cocco was with PSRI for 16 years, where he was President and CEO. Before PSRI, Ray spent 17 years with The Dow Chemical Company, where he led research and development efforts in numerous particle technology platforms, including the production of WoodStalkTM (a particleboard made of straw) for Dow BioProducts, the production of vinyl chloride monomer, and RCl oxidation using fluidized beds, the production of hydrocarbon using circulating fluidized beds, the development of polyolefin catalyst for fluidized beds, and in the production of aluminum nitride and silicon carbide ceramic powders using moving bed reactors. Today, he is a member of the University of Florida Chemical Engineering Advisory Board, Auburn University Chemical Engineering Alumni Committee, and University College at London's board. He is also on the editorial boards for Powder and Bulk Engineering, Powder Technology, and Frontiers in Chemical Engineering: Mixing and Particle Technology. Ray was the past chair of the AIChE Particle Technology Forum (Group 3), a past member of the AIChE Chemical Technology Operating Council (CTOC), and an AIChE Fellow. Ray was also the chairman of the World Congress in Particle Technology VIII in April 2018. He has over 90 publications, three book chapters, several patents, numerous invited presentations, and consults for industry, national labs, and universities regularly.

Award Lecture: Evolution and Prospects of Scale-Up Tools for Fluidized Bed Technology

Abstract

Fluidized bed technology has garnered significant attention across various industries due to its versatile nature, efficient heat transfer capabilities, and in-situ particle mobility. This paper delves into the history and future of scale-up tools for fluidized bed applications, presenting a comprehensive overview of the advancements and challenges encountered with this technology.

The historical perspective encompasses the early applications of fluidized beds, tracing their roots from the gasification industry to their widespread adoption in chemical production, energy production, pharmaceuticals, and materials engineering sectors. Notably, the evolution of scale-up methodologies from Edisonian exploration with empirical correlations to more sophisticated computational techniques to artificial intelligence is explored, shedding light on the pivotal role of interdisciplinary collaborations in driving innovation.

ELSEVIER

Sponsor of the Lifetime Achievement Award

Scaling Up Tomorrow's Fluidized Bed Reactors

Dr. Ray A. Cocco
Particles in Motion, LLC

I have been working with fluidized bed reactors for over 30 years. In that time, I have seen five common pitfalls that have resulted in the termination of a scale-up project or, worse, the premature shutdown of a commercial operation. These five pitfalls are as follows:

1. Limited project management of resources and tools for an accelerated scale-up path,
2. Not considering particle size and size distribution and the change in that distribution early in the scale-up path,
3. Late consideration of the reactor type or the fluidization flow regime best suited for the economic feasibility of the commercial operation,
4. Low priority on modeling, limited understanding of the modeling, and low consideration of the modeling results, and
5. Delayed consideration of the complete economy associated with the fluidized bed reactor's operations.

These pitfalls can be mitigated early in the scale-up process, often well before development efforts. Additionally, such efforts can significantly accelerate the scale-up and/or reduce the scale-up costs [1]. This article focuses on how and when these pitfalls should be addressed.

Technical Project Management

The petrochemical, chemical, energy, and materials industries have made significant inroads in project management. For decades, scale-up and project management followed the Waterfall management style, where tasks followed a linear and sequential path while being managed from a top-to-down structure. This leaves little room for innovation and change. In the 1950s, Taichi Ohno and Shigeo Shingo of the Toyota Production System changed all that. They developed a new management philosophy focused on Value Stream Mapping, Just-in-Time inventories, and Continuous Improvements (Kaizen). More importantly, they implemented a bottom-to-top structure to empower teams. In the 1990s, this project management style, labeled "LEAN," had a global impact across most industries [2]. At the same time, Bill Smith of Motorola developed a defect reduction methodology, which was later termed Six Sigma. Six Sigma consists of five sequential steps: Define, Measure, Analyze, Improve, and Control (DMAIC) [3]. In the mid-1990s, under Jack Welch, GE made Six Sigma a mainstream project management tool. Today, these industries are using a combination of LEAN and Six Sigma called Lean Six Sigma. The statistics, defect reduction, and data-driven disciplines of Six Sigma are combined with LEAN's customer-focus and team management tools (e.g., Kanban, VSM, VOC, SMED, PDCA, Kaizen) [4].

A constraint of Six Sigma and Lean Six Sigma is the highly structured and linear methodology. The rigid structure works well with defect reduction but limits R&D efforts associated with a new fluidized bed design. It limits innovation and the "re" in research. Design for Six Sigma (DFSS) does help with these limitations to some extent by adding more research-focused steps such as Design, Verify, Optimize, and Validate [5]. The Design and Optimize steps provide room for innovation. The Verify and Validate steps offer a checks and balances that reduce missteps and rework while providing greater stakeholder confidence. However, DFSS still has a fairly linear path. While the Verify and Validate steps help with the overall process, they do not help with smaller tasks such as formalized verification and validation of each data set, model, and design.

Better project management for the scale-up of a fluidized bed reactor process is something my colleague, Prof. Jia-Wei Chew of Chalmers University of Technology, and I have contemplated about. If we are to reduce the time and costs for fluidized bed scale-ups, we need to have more verification and validation of each data set, model, and design throughout the whole scale-up process, and such steps need to be formalized. Indeed, Rober Synder of Innovation Elegance, LLC proposes frequent verification and validation with his Five Verbs® concept [6], where each task is broken down into Scrum Sprint-like steps [7] termed Draft, Review, Revise, Approve, Distribute, with each step using team members not associated with the previous step for each task (i.e., deliverable).

We proposed [1] that data and models should go through this formalized verification and validation step not only to ensure accuracy (i.e., and thereby less rework) but to permeate higher levels of trust within the team and the stakeholders. These data and models are essential to the economic, circular economy, and risk assessment. They need to be accurate and trusted to be accurate.

Particle Size and Size Distributions

Particle Size

The particle size and size distribution are key parameters to a fluidized bed hydrodynamic behavior [8, 9] and, therefore, key scale-up parameters. They should also be a key factor in many of the models used for scale-up. Figure 1, with its comparison of the Sauter mean particle size and the density difference (ρ_p-ρ_f), illustrates the importance of managing the particle size. A fluidized bed of smaller particles typically results in a less dense bed (i.e., lower bed density), longer jet penetration, and smaller bubble sizes. Indeed, the difference in fluidization behavior between Geldart Group A and B particles is remarkable. Bubbles in a bed of Geldart Group A powders are smaller and typically grow not larger than a few centimeters (10 cm). They have an equilibrium bubble size. Geldart Group B powders have bubbles that continue to grow, much larger than 10 cm, maybe even larger than meters. As a result, fluidized beds of Geldart Group B are prone to slugging, especially laboratory and pilot units with smaller diameters. At the very least, the larger bubbles contribute to a reduced mass transfer, which is detrimental to heterogeneous, diffusion-limited reaction pathways. Geldart Group A beds have concerns, too. A tall or dense bed of Geldart Group A may be prone to gas bypassing, whereas beds of Geldart Group B particles are not [10]. Gas bypassing is a phenomenon whereby a chain of fast-moving bubbles or voids dominate the bed hydrodynamics, much like channeling [11]. As a result, most of the fluidization gas escapes the bed, leaving large regions of nearly defluidized zones.

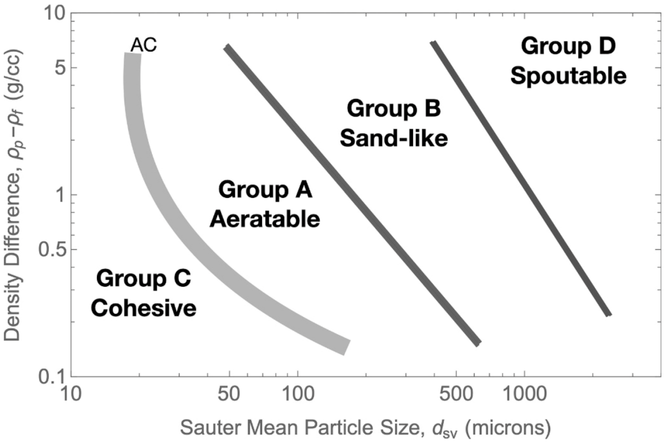

Figure 1: Interpretation of Geldart group classifications. Reproduced with permission from Elsevier [9].

Geldart Group C particles have an even more extreme behavior in fluidized beds. These particles are smaller than Group A particles and more influenced by interparticle forces (i.e., van der Waals, Coulombic, and capillary “bridging”). As a result, Group C particles are difficult to fluidize and often result in a channeling bed. If it is fully fluidized, typically with microjets or pulsing, the bed expansion is significant [12].

Indeed, the hydrodynamics differences between all the Geldart Classification groups can be profound and remain under study [9]. We can get some insight into the hydrodynamics data by looking at the axial pressure drop across the bed at the onset of fluidization and bubble formation or the minimum fluidization and bubbling velocities. For Geldart Group A particles, there is a flow regime of smooth or homogeneous fluidization where the bed is fluidized, but there are no apparent bubbles or voids. As the superficial gas velocity increases, bubbles appear. For Geldart Group B particles, bubbles are evident at the onset of fluidization. In other words, the minimum fluidization velocity is similar to the minimum bubbling velocity.

Such contrast in fluidization behavior is also apparent with bed defluidization [13]. A fluidized bed of Geldart Group B particles collapses in short order once the gas flow is discontinued (including the plenum being depressurized). For Geldart Group A powders, the bed defluidization takes longer, and for a fully fluidized bed of Group C powders, defluidization takes even longer than Group A beds.

The dynamics at the onset of fluidization or defluidization illustrate how bed permeability and particle mobility influence the behavior of packed and fluidized beds. In a packed bed, Group B particles have the highest permeability. It takes more gas to fluidize Group B particles because of the larger size and/or particle density, but with enough gas, the bed will fluidize with bubbles. For immobile particles in a paced bed, Group A and C particles have a lower static permeability than Group B particles. As a result, Group C particles are prone to channeling, and Group A particles may exhibit gas bypassing if the bed is high enough or the particles are dense enough (i.e., resulting in a higher bed density).

Smaller particles have higher mobility in fluidized beds. They move more gas into the emulsion due to a higher surface-area-to-volume ratio, (ii) drag more gas due to this higher surface area on the particles, and (iii) are more mobile in a fluidized bed. As a result, once these particles become mobile, the fluidization behavior of Group A and C particles results in smaller bubbles and a lower bed density than the Group B particles. The larger Group B, with its slower-moving particles and smaller surface-area-to volume-ratio, cannot drag as much gas into the emulsion as Group A or C particles. This is why adding fines to a fluidized bed that is not well fluidized or experiencing gas bypassing can often alleviate the maldistribution or gas bypassing [14]. Fluidized beds need to be designed to handle fines (i.e., cyclone design), especially for Geldart Group A and C powders. For existing cases that do not have that capability, adding horizontal internal can alleviate such issues by breaking up the bubbles to reduce their size, slowing them down and thus allowing for more gas to permeate the emulsion.

In short, the design and operation of a fluidized bed for these particle classifications are different and rarely interchangeable. So, is the Geldart particle classification chart a good scale-up tool? Well, that depends. Group C particles could behave like Group A particles at elevated temperatures. Similarly, Group B particles could behave like Group A particles. The issue is that the Geldart particle classification chart only considers particle size and the density difference between the particle and gas, which is often a 1000-fold difference. Changes in the gas density and viscosity are not considered.

In addition, changes in the C-A and A-B boundaries in the Geldart particle classification chart (Figure 1) are sensitive to particle shape [15, 16], cohesion [17-21], and fines levels [22]. Several investigators [17, 23-25] have suggested that the Archimedes number and possibly the Reynolds number need to be independent variables of a particle classification chart. At least with one or both dimensionless numbers, the impacts of the viscosity and sphericity can be captured [9].

The choice of an optimum particle size is typically an easy one with most fluidized bed reactor scale-ups. When it is not, emphasis is needed early in the research part of the program using well-defined experiments and validated models.

Particle Size Distributions

As noted above, the particle size distribution can affect the fluidized bed performance. Similarly, the change in the particle size distribution can result in changes in the fluidization behavior. Such changes in a fluidized bed are commonly evident when you don't want it and absent when you do. As a result, attrition and/or agglomeration need to be considered or, more specifically, modeled. It is recommended that a population balance model (PBM) be considered early in any scale-up process [1]. Arguably, not all the parameters will be available early on, but such a model is still valuable in assessing the economic and environmental impacts.

PBMs are systems of simultaneous ODEs that describe changes in the particle size distribution. I have seen too many projects where particle attrition or the formation of agglomerates was not considered early in the scale-up process. These need to be a priority in the research phase, maybe even in the discovery phase [1]. There are many incidences where the solids loss rates could compromise the economic viability of the commercial plant. A PBM is a predictive tool that can provide more realistic attrition (or agglomeration) rate estimates well before the commercial design has been finalized. Ghadiri [26-28], Werther and Hartge [29], and Werther and Reppenhagen [30] provide PBM models for fluidized bed attrition associated with jets and cyclones. However, the attrition rate models for fragmentation and abrasion are based on empirical expressions, and the fragmentation distribution captured by the fragmentation matrix is also unknown.

Without mechanistic models for particle attrition (and agglomeration), a PBM is limited to comparative, qualitative analysis and parametric studies. It is still a valuable scale-up tool, but mechanistic attrition rate model(s) can provide earlier economics associated with attrition and agglomeration early in the scale-up process. Indeed, particle attrition or agglomeration should be considered a high-risk scale-up concern. I have seen particle attrition add tens of millions of dollars to the operating costs via catalyst losses, and many projects fail to move forward due to the economic risk associated with attrition. So, a fluidized bed attrition mechanism and a corresponding attrition test procedure would be value-added to the process design.

However, this is not a simple request. Indeed, the hydrodynamics responsible for attrition is complex, as suggested by the two-dimensional particle tracking with imaging analysis of particle collisions in an attrition jet cup, as shown in Figure 2 [31]. Most of the particle collisions were with other particles and not with the wall, despite the small scale of the experiment and the tangential gas jet being used. Localized recirculation zones suggest that some particles will experience more repeated attrition than others. Amblard et al. [32] found that attrition rates depend on the amount of sample used, suggesting even further complications.

All is not lost, however. Effective PBM models can be obtained starting with the attrition test unit and subsequent fitting to lab, pilot, and market development scale data as a continuous improvement process. Fitting is through the rate expression parameters (k,n) and a selection of various fragmentation matrices. It is not a perfect model, but it is still a useful model.

Particle Clusters

Particle clustering typically involves Group A or C particles where interparticle forces have more influence. It is not as common with fluidized beds of Group B particles unless influenced by wetting, chemistry, or the addition of fine particles. Particle clustering in fluidized beds was first postulated by Wilhelm and Kwauk [33] and later expanded on by Kaye and Boardman [34], Yerushalmi et al. [35], Geldart and Wong [36], Baeyens et al. [37], Liu et al. [38], and many others. Image analysis of the clusters in a fluidized bed suggests that a significant amount of particles may behave as loosely adhered clusters in a fluidized bed [39]. For a bed of Geldart Group A particles of polyethylene, 75% of the bed consisted of particle clusters instead of individual particles, as shown in Figure 3.

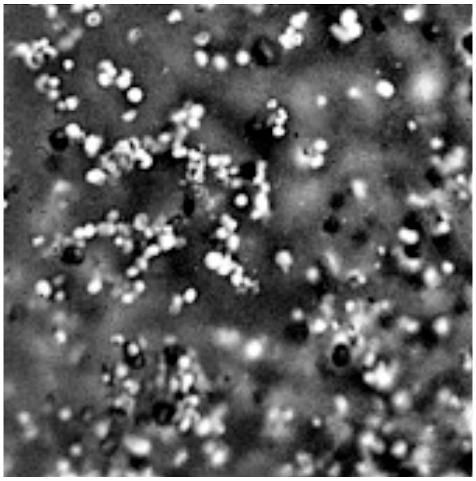

Figure 3: High-speed video frame of FCC catalyst in the bed region of a 6-inch (16-cm) diameter fluidized bed at a superficial gas velocity of 2 ft/sec (0.61 m/sec). Images were collected at 4000 frames per second with a 20 µs exposure time. Reproduced with permission from Elsevier [39].

Interestingly, Royer et al. [40] found that particle clustering was linked to surface roughness. The smoother the particle surface, the more likely particles were to cluster. Hypothetically, the higher coefficient of friction associated with the rougher surface results in a higher transfer of rotational to translation momentum, making clustering less likely [41]. The higher particle-to-particle friction led to higher momentum transfer. Lee et al. [42] captured this effect with spherical and slightly less spherical particles.

For most empirical correlations on fluidized beds, particle clustering is inherent to the measurements. The correlations are not universal but are typically accurate for similar particles and conditions. However, the problem with particle clustering is in calculating the entrainment rates. For example, particle clustering can reduce the entrainment rates by as much as 1000 fold of that for free-flowing Geldart Group A particles (i.e., no particle clustering). This can be detrimental to sizing the primary cyclone diplegs. With particle clustering not accounted for, the dipleg diameter will be too large and prone to plugging during normal operations. To further complicate the scale-up, cold flow experiments may also be a poor substitute as particle clustering, due to interparticle forces, is strongly linked to the temperature, pressure, moisture levels, and chemical composition of the fluidization gas. Even a tiny change in the water concentration can have a significant effect.

A mechanistic model of the role of these interparticle forces and particle clustering is needed, but it is also a complex problem. Some work is being done to get a characteristic parameter tied to clustering and interparticle forces. Ideally, this could be included in an entrainment correlation or CFD model to provide an empirical correction for clustering. There has been some progress here. Studies using an FT4 Powder Rheometer showed that particle clustering correlates to the consolidation index and the basic flowability energy determined from powder rheometer measurements [43]. Similarly, Mishra et al. [44] found that the characteristic velocities obtained from powder rheometry provided a relative gauge to particle-level cohesion. Affleck et al. [45] used the over- and under-shoot with the pressure drop and bed voidage curves obtained from fluidization and defluidization experiments to determine the granular Bond number. Soleimani et al. [46] could quantify the degree of interparticle forces with a dynamic Hausner ratio, which is an extension of the work of Valverde et al. [47].

Until all this is worked out, however, emphasis on measuring entrainment rates from a pilot unit could not have a higher priority. It should be on a large enough scale, at operating conditions, and with the intended bed material.

Fluidization Regimes

In 1986, Grace [23] developed a fluidization regime map that uses the dimensionless gas velocity and diameter proposed originally by Zenz and Othmer [48]. The map shows the minimum fluidization velocity and the terminal velocity, along with discernment of the Geldart Group classifications. Kunii and Levenspiel [49] adapted Grace's map to reflect fluidization regimes instead of fluidization equipment. It is still one of the most used tools in designing and operating fluidized beds. One representation of that fluidization regime map is shown in Figure 4.

All too often, the first design concept of a fluidized bed reactor is for operations in the bubbling fluidized bed regime. Compared to a turbulent or fast fluidized bed, the gas residence time is longer, on the order of 10 to 20 seconds (assuming no back-mixing, and the entrainment rates are lower. The lower gas velocity reduces particle attrition, which means lower solid loss rates. Both are effective for lab-scale studies. The extrinsic kinetics can be better captured in the more documented bubbling fluidized bed reactor, and fewer considerations are needed for capturing entrained particles and the bed depletion that may come with it.

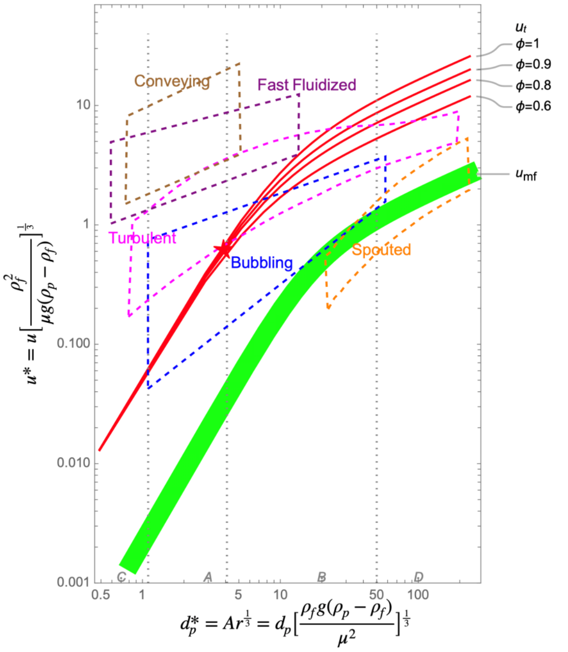

Figure 4: Fluidization regime map based on Grace [23] and Kunii and Levenspiel [49].

However, what needs to be considered in the early design stage is that mass transfer (or gas-solid contacting) and heat transfer are much higher in a turbulent fluidized bed regime. Cui et al. [50] found that as the gas velocity exceeded the onset of turbulent fluidization, excess gas entered the emulsion rather than forming additional bubbles. In other words, more of the gas was in the denser or emulsion regions of the fluidized bed. Thus, the productivity is higher for diffusion-limited reaction pathways in a turbulent fluidized bed. Indeed, most commercial fluidized beds operate in the turbulent regime, including the FCC regenerators, where the gains from improved mass transfer far exceed the costs associated with higher entrainment rates.

Unfortunately, the consideration of fluidization regime mirrors that used for the lab unit, which is typically the bubbling fluidized bed regime. It worked before, so it should work again, right? However, if the pilot unit mirrors the operation of the lab-scale unit, the unit productivity may not scale. The pilot units' larger diameter and taller bed add different hydrodynamics (i.e., backmixing, dispersion, etc.), which is better managed in a turbulent fluidized bed. For most scale-up projects, that realization comes too late.

It is essential to discuss the amount of time gas spends in a fluidized bed and the conditions required for fluidization. Using bubbling fluidized lab units is necessary for research and development. However, these units should not be the basis for considering the scale-up of key factors such as height, diameter, velocity, and internals. Models such as ROM, CFD, CPFD, CFD-DEM, AI-NN, etc., can help bridge the gap between lab-scale results and predicting pilot-to-commercial scale designs and operations. In short, modeling efforts need to be implemented early and often, even during the early stages of developing kinetic expressions. At the very least, kinetic and hydrodynamic time constants can go a long way in designing a fluidized bed reactor.

Modeling Edge

Sir Karl Popper once said, “A theory is just a mathematical model describing your observations.” As noted above, most scale-up efforts with fluidized bed reactors involve modeling (i.e., statistical models, ROM, HOM, AI, etc.); they do not involve modeling early and frequently enough [1]. Most scale-up teams do not have the critical mass to develop practical tools. Suppose a team consists of one CFD expert in a room full of other engineers unfamiliar with CFD models. In that case, the team will either not fully embrace the model as a primary scale-up tool or be unable to discern that the modeling results are incorrect. Stakeholders, who typically do not have a modeling background, tend to distrust modeling efforts, especially if the results are coming from a “separate” part of the team. A scale-up modeling program must integrate several skilled modelers into the team. That team needs to focus on not just developing models but verifying, validating, and approving each model. Perhaps a more formalized process is needed, such as the Five Verbs, where Develop, Review, Revise, and Approve are part of each data analysis and modeling task.

I understand that there may be some hesitation to increase scale-up modeling efforts. One of the main concerns is whether there is enough work for additional modelers and whether the higher upfront expenses can be justified against the project's net present value (NPV) or internal rate of return (IRR). However, the answer to both questions is usually yes, as long as we move away from traditional scale-up methods. To this end, we are exploring the possibility of expanding modeling efforts for fluidized bed reactor scale-up with integrated statistical ML, ROM, HOM, and AI models and comparing it to the 20-year net present value (NPV20) [1]. As shown in Figure 5, even minor improvements in modeling efficiency can positively impact the NPV20 and the process's start-up time.

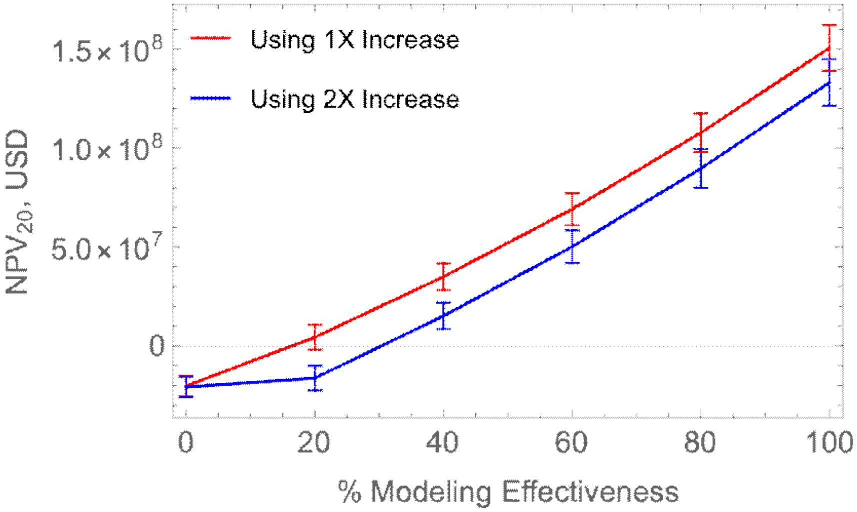

Figure 5: NPV_{20} estimates versus modeling effectiveness for new catalyst in a conceptual 2000 mTon/year acrylonitrile plant with the recommended increase (1X) and double the recommended increase (2X) in costs for additional modeling. Based on Ref [1].

Modeling efforts were found to shorten the delivery time of the scale-up process. That means the revenue stream starts sooner, and the costs incurred during scale-up can be recovered faster. The foundation of this assessment is that even today’s models can provide faster, more accurate, and less expensive scale-up data than expensive, time-consuming experiments. In many cases, the modeling results may be more accurate, as cold-flow experiments under ambient conditions with inert gases may not capture the bed hydrodynamics under operating conditions with reactive gases. Indeed, small-scale experiments that better represent the operating conditions of the proposed commercial plant may be better for tuning and vetting reactor models or models. Sundaresan noted in a previous PTF Newsletter [51] that

> *It is hoped that the confidence in our ability to model and simulate gas-particle flows will grow to the point where one can calibrate all the important physical properties of the gas-solid system of interest through a few well-defined and widely accepted measurements in small laboratory devices and then rely on simulations to probe the flow behavior in commercial-scale devices – at least, to screen various design options.*

With today’s new tools in data analysis and reactor modeling, I think we are approaching that reality, provided we are willing to take that path.

Data analysis

Data analysis is a crucial part of any research and development program. While it is helpful with data mining and statistical models, its real importance is validating the data within a confidence level. New tools that are much more powerful exist today. With the advent of machine learning (ML), data analysis of scale-up data can move beyond basic statistical models and principle component analysis. ML reveals multidimensional relationships with tools such as self-organizing maps (SOM), neural nets, and Gaussian process reduction [52]. For example, Patel et al. [53] used the ML tools of SOM and random forest (RF) methods to better understand factors tied to macroclusters and streamers in a riser. The data's multidimensional aspect precluded traditional statistical models from being useful. SOM results showed that broad particle size distributions or bimodal distributions reduced the growth of macroclusters and streams. In another study, the bubble hydrodynamics of a fluidized bed of Geldart Group B powders was found to be tied to the polydispersity [54]. Fu et al. [55] used a neural net model to predict optimum conditions for a fluidized bed reactor (i.e., pressure drop and expansion ratio). Kim et al. [56] used RF and ANN to optimize syngas production from a fluidized bed biomass gasifier. Lian et al. [57] used RF and ANN to analyze hydrogen production from a fluidized bed reactor. Indeed, ML methods for process monitoring, fault detection, and soft sensing are already being commercially implemented [58]. British Petroleum (BP) and General Electric monitor oil wells using ML to augment performance [59]. In short, ML tools can highlight key scale-up relationships missed by a more traditional data analysis process. All of which will reduce the time for scale-up and reduce economic risks.

Even the design of experiments (DOE) methodology is being advanced with AI. DOE procedures typically reduce the number of experiments while maintaining statistical significance at a predetermined confidence level, usually 95%. However, such DOE studies require most experiments to be performed before data analysis can be applied. With the advent of AI-directed DOEs, this is no longer the case. These AI-directed DOEs use deep learning to assess data as it is being collected. This results in the DOE being reorganized, varied, altered, and even reduced in size before all the experiments are completed [60, 61]. As a result, experiments can be done faster without compromising data integrity. Commercial software for AI-directed DOEs already exists as well [62, 63].

Using advanced data analysis, DOEs, and AI-DOEs is not a one-time event with scale-up. They need to be used throughout the scale-up process, even in the discovery phase [1]. From the assessment of the kinetics at the bench scale to process evaluations in the lab, pilot, and market development units, robust data analysis and DOE efforts can significantly impact the economic valuation associated with a fluidized bed reactor (and just about any other unit operations). Remember, the only thing worse than no data is bad data.

Reactor modeling

Reduced Order Models (ROM)

Reduced-order models (ROMs) have certainly taken a backseat to higher-order models (HOMs). ROMs tend to have one spatial dimension and one temporal dimension [29, 49, 64, 65]. They will not capture the radial dispersion (without an extension) and the extent of backmixing, but they can be quickly developed and implemented. For that reason, ROMs are still a valuable addition to the early stages of the scaling-up process. Such reactor models can help assess the (i) kinetics, (ii) dispersion/mass transfer [66, 67], (iii) particle attrition and solids loss rates (i.e., PBMs) [26-30], and (iii) concept of the reactor configuration early in the scale-up process. This is low-hanging fruit that should always be considered.

Higher Order Models (HOM)

Higher order models (HOMs) capture two- or three-dimensional spacial domains with options to capture the temporal dimension as well. These models are the CFD, CPFD, and CFD-DEM or Eulerian-Eulerian (two-fluid, TFM), Eulerian-Lagrangian (CFD-DEM), and a hybrid Eulerian-Lagrangian hybrid framework (CPFD or MP-PIC, Barracuda®). The most common commercial versions of these models are called Barracuda (www.cpfd.com), Star CCM+® (plm.sw.siemens.com), and Fluent® (www.ansys.com). There are also some open-source codes, such as OpenFOAM (www.openfoam.com) and MFIX (mfix.netl.doe.gov).

All these codes have been in development for decades and are valuable scale-up tools for commercial fluidized bed applications. What once took months to simulate, a full-scale commercial fluidized bed reactor can now be simulated in a few weeks thanks to faster and more robust solvers, parallelization, and GPUs. These models have gone through extensive validation through the software companies themselves and with other studies found in the literature. In short, these codes have been shown [68] to be accurate within the confines of the code's capabilities.

Yet, these tools may need some additional considerations [69]. Particle-fluid and particle-particle drag models are limited, especially for Geldart Group A and C powders, where interparticle forces are not captured [70]. Collisional stresses are often captured using the kinetic theory of granular fluids (KTGF) [71, 72], which requires the coefficient of restitution and the specularity coefficient, neither of which is easily measured.

Grid resolution is an additional challenge. According to Igci et al. [73] and Cloete et al. [74], the grid size needs to be on the order of 10 times that of the mean particle diameter. Hence, for Geldart Group A powders, the grid size needs to be about 1 mm, which is unrealistic for commercial applications where grid sizing is tens of centimeters. Thus, computational requirements also need to be considered with large-scale simulations, mainly by using subgrid models to accelerate solution times. For example, a filtered drag expression has been used where drag is first evaluated in a much smaller, more resolved computational domain gridded by this filtered size [75, 76]. A dynamic grid adjustment approach, whereby the impact of unresolved scales is predicted from the large resolved scales, has also been demonstrated [77]. However, for the most part, all this still remains academic.

Particle resolution also needs consideration for CFD-DEM and MP-PIC (CPFD) models. These models can simulate about 10^7 particles but require months on anything less than a massively parallel CPU platform. A commercial fluidized bed of Geldart Group A particles will have over 10^{14} particles. Thus, numerical coarse-graining is used to bridge this gap. In each cell, particles of similar size and density are treated as one parcel or cloud, thereby reducing the number of equations needed to resolve the hydrodynamics. It is an effective shortcut, but the parcel size needs to be resolved much like grid resolution as part of modeling development. Jurtz et al. [78] found that using a cluster-based drag model with coarse-graining can further reduce the simulation error.

None of these limitations should sway you from using these models as a primary component of your scale-up process. Unlike experimental data and the complexities of measuring that come with it, we know what is in these models, and even a model in poor agreement with data can highlight some of the underlying physics in understanding what is not being captured. Furthermore, these commercial codes were built for flexibility and allow for modifying existing constitutive equations or adding new ones. In short, they are tunable.

It is the tuning aspect of HOM that needs to be promoted. As noted above, there are still a lot of unknowns and constraints in these commercial codes that limit their usefulness in their initial state. However, these parameters are tunable and should be tuned to relevant data that mirrors the proposed operating conditions. As noted earlier by Sundaresan [51], “through a few well-defined and widely accepted measurements in small laboratory devices.” Experiments on a small scale allow for more precise measurements, providing the length scales are not conflicting. In other words, you need a well-instrumented laboratory reactor with a large bed diameter enough that the bubble hydrodynamics are not impeded. Key response variables from laboratory reactors should include bed density, transient pressure waveforms, gas and solid RTD curves, entrainment rates, and bubble hydrodynamics (i.e., pierce length, frequency, and rise velocity). It should be noted that the bed height needs to be high enough to (i) have fully developed bubbles and (ii) meet the kinetics time scale. For Geldart Group A powders, bed diameters should be at least 0.2 meters. For Group B particles, the bed diameters need to be large enough that fluidization remains smooth and slugging does not occur, which is usually larger than 0.2 meters.

Model tuning does not stop with small-scale experiments. It is a process that continues with each new unit (remember, Draft (Develop), Review, Revise, Approve, Distribute). These models should be returned with the pilot and market development units. The tuning parameters (i.e., coefficients to the constitutive equations or the constitutive equations themselves) should be similar. If not, some additional investigation may be needed to understand the discrepancies, but such investigation can now be done more in a timely manner.

Artificial Intelligence (AI)

It should be no surprise that I have AI on the list of recommended tools for fluidized bed scale-up. Even today, you can find commercial AI tools that would benefit any scale-up program. AI-driven optimizers coupled with CAD and CFD tools can be used for generative equipment design. One such tool is available from Siemens PLM® called, HEEDS (plm.sw.siements.com). It uses a hybrid-adaptive search algorithm (SHERPA) that can distinguish from local and global maxima or minima [79]. Generative equipment design has been applied to other unit operations [80, 81]. For fluidized bed reactors, CFD integrated with a HEEDS or similar optimizer could address the design of the gas distributor, liquid injection points, bed internals, and cyclone. For circulating fluidized beds, such efforts would be beneficial with aeration strategies, especially with standpipe design and operations.

Another area AI has made inroads in process scale-up is with flowsheet synthesis. Here, AI is used to develop process flow sheets and piping and instrumentation diagrams (P&ID) [82-84]. What traditionally takes weeks can be done in hours, allowing a flowsheet to be developed early in the scale-up process using minimal data. The Aspen Hybrid Modeler (www.aspentech.com) is a good example of this capability. HEEDS has also been used for flowsheet synthesis. In 2021, Dow and Siemens PLM coupled ASPEN Plus® with HEEDS to optimize condensation polymerization reactors that produce polydimethylsiloxanes [79]. Such an exercise is even more critical for fluidized bed processes, which can have less flexibility than more traditional reactors (e.g., superficial gas velocities, turn-downs, and particle emissions). In addition, detailed flow sheeting can be obtained even from process design efforts in the concept stage, and that flow sheet can continue to develop throughout the scale-up process [83].

AI has been shown to help address issues related to CFD, CPFD, and CFD-DEM modeling [69]. Gaps in some constitutive equations can be filled by tuning the models to well-defined, small-scale, relevant experiments directed by AI. Sundaresan et al. [85] suggested that deep learning methods can quantify the scale dependency of multiphase flows to improve constitutive models for momentum, species, and energy transfer. In a recent PTF Newsletter, Sundaresan [51] noted that modeling efforts could begin with the experimental measurements of the PSD and proxy experiments for the calibration of constitutive equations. Direct measurements of the actual particulate system may not be resource -effective. For example, drag models can be calibrated using fluidization and defluidization tests [86], whereas rheological and flow testing can be used to validate the collisional stress model [44, 87].

AI tools have also been applied to tuning filtered drag models, bridging the microscale to the mesoscale. Jiang et al. [88] gave an example using a neural network ML tool for tuning a filter drag constitutive model. Yang et al. [89] coupled a neural network with the EMMS drag model to determine the heterogeneity index. Similarly, Lu et al. [90] used AI in PyTorch coupled with MFiX to develop a filtered drag expression.

Even grid and parcel resolutions are getting help from AI. Lorsung and Fairimani [91] proposed that both the grid resolution as well as the time step can be made adaptive to selected gradients. Their Mesh Deep Q Network (MeshDQN) is designed as a general-purpose deep reinforcement learning framework to coarsen meshes while preserving target property calculation iteratively. A similar methodology could be applied to coarse graining efforts.

Physics-Informed Neural Networks (PINN)

Still, some engineers and scientists may be leery of AI models for scale-up design. AI models use regression of the input factors to an unspecified, hidden layer or layers of weights. The model results are only as good as the quantity and quality of the data used in the training and testing sets. In other words, you need lots of reactor data (with batching), which is a rare commodity early in the scale-up process. To address this shortcoming, a physics-informed neural network (PINN) may be beneficial. PINN regularizes a neural network to conform to physics by having both parts contribute to a loss function. An additional node layer is added to the AI architecture for consideration with the time gradient, the axial gradient, and the gradient of the axial gradient [92]. The approach has already been taken using the Navier-Stokes equation for flow around airfoils to maximize the lift-to-drag ratio [93] and the hydrodynamic tensors for Poiseuille, Couette, and lid-driven flows [94]. Eivazi et al. [95] used PINNs to model incompressible turbulent flow without a specific turbulence model. They only used the data from the boundary domain and reported good accuracy, even for the Reynolds stress component.

PINN has even been applied to two-phase flows. Ji et al. [96] and Weng and Zhou [97] used PINN to solve a set of stiff ODEs related to solution kinetics. Schiassi et al. [98] used the Physics-Informed Neural Network Theory of Functional Connections (PINN-TFC) based framework or Extreme Theory of Functional Connections (X-TFC) to model a compartment model consisting of ODEs. Qiu et al. [99] applied PINNs to two-phase flows using the Cahn−Hillard equation and Navier−Stokes equations. Also, Lu and Christov [100] used PINNs for modeling particle migration in a non-Brownian suspension from Couette flow, with results revealing that the inferred values of the empirical model's parameters vary with the shear Peclet Number as well as with the particle bulk volume fraction of the suspension.

Indeed, PINN may even have benefits with fluidized bed reactors as a self-contained model or a supporting model for the constitutive equations used in the HOMs (i.e., drag, collisional stresses, etc.). In addition, PINNs can offer accurate quantitative descriptions of the various fluidization phenomena and could supersede the current empirical correlations that have been previously too system-specific for general applications [101].

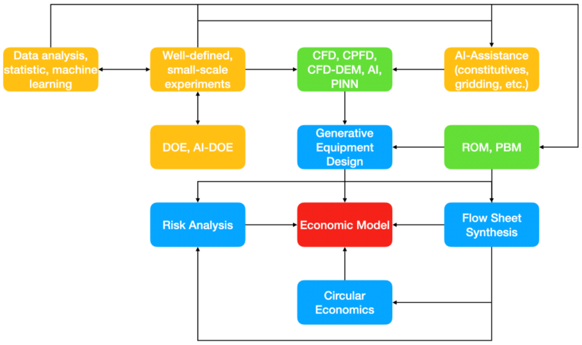

Figure 6: Proposed process flow diagram for the scale-up of a fluidized bed reactor process that relies strongly on modeling efforts.

Economics

The last, but not least, pitfall to avoid when scaling up fluidized bed reactors is not having a comprehensive economic model. It is crucial to develop and assess an economic model from the start of the scale-up project and continue refining it throughout the project. While most scale-up projects start with an economic model, these models are often limited to simple spreadsheet models. These models are often separate from the process flow sheet, equipment designs, and specifications, risk assessments, and circular economics. As a result, updating the economics can take days or weeks, limiting productivity and innovation. However, integrated advanced models provide updated economics in hours or less. For instance, an integrated network of models that includes Generative Equipment Design supported by ROMs, HOMs, AI, and Flowsheet Synthesis can transform the process design and scale-up methodology, as illustrated in Figure 6.

Adding in a risk assessment [102, 103] and circular economic [104, 105] models will allow the economic model to project the economic impact associated with variability in system integration, failure modes, volatility, and environmental impacts. Imagine having such a model in place when critical decisions are being considered.

Conclusions

Scaling up fluidized bed reactors tends to be a long and expensive process. Going from the test tube to commercial operation often takes 10 to 12 years. There have been some scale-ups that have gone faster. FCC technology took only three years, the SOHIO® process took four years, and the Unipol® process took eight years [106]. These cases are the exception, but they demonstrate that scaling up fluidized bed reactor processes can be done faster and cheaper. Indeed, in 30+ years with fluidized bed reactors, I have seen that more attention is needed towards:

1. Technical project management,
2. The particle size and size distribution, including the role of particle attrition and/or agglomeration,
3. The early consideration of the fluidization regime (i.e., bubbling, turbulent, fast-fluidization, conveying, moving bed, etc.),
4. The promotion and acceleration of modeling efforts, including data analysis, and
5. A fully encompassing and integrated economic model.

Specifically, project management is critical and needs to include steps where data, models, concepts, and designs go through independent verification and validation processes. Particle size and size distribution are key parameters in scaling up fluidized bed reactors. You need to understand how small changes in the size and distribution will affect the hydrodynamics and the economics. Similarly, the operating conditions of the fluidized bed need to be clear and defended by data and models, not from an incremental extension of a lab-scale concept. Far too many pilot units have moved forward with less than optimum design and operating conditions. When realized, it was often too late to change course.

Mitigating these three pitfalls will reduce rework and redos. Its impact on the scale-up time and economics is to limit the expansion of the original economics. The mitigations of the remaining two pitfalls are designed to reduce the scale-up time and economic costs below the original economics further.

Modeling, including data analysis, needs a greater emphasis and a higher priority. It needs to be implemented earlier and have a larger scope than what is typical in the industry. The additional resources and capital costs (i.e., licensing, CPUs, GPUs, networking, etc.) are unlikely to significantly impact the overall scale-up costs, primarily if the start-up time is delivered sooner and possibly eliminating a pilot or market development unit [1]. Although some models discussed here may not be available today as a useful scale-up tool, they will most likely be available in the next few years. Embracing early such technologies can have benefits later.

Finally, economic models need to go beyond the basic spreadsheet. These models are the key metric for stakeholder evaluations and approvals. These models need to be more extensive. An integrated network of models consisting of Generative Equipment Design that is supported with ROMs, HOMs, and AI, along with Flowsheet Synthesis, can transform the process design and scale-up methodology and be an invaluable tool throughout the whole scale-up project.

Other pitfalls exist in the design, scale-up, and operation of fluidized bed reactors [107]. However, based on my 30+ years of experience, these suggestions for avoiding these five pitfalls will significantly accelerate the start-up and lower the scale-up costs. With today's global challenges, some of which involve fluidized bed reactors as potential solutions (i.e., pyrolysis, decarbonization, carbon capture, battery stripping, waste to fuels, etc.), the urgency for faster scale-up with less risk is paramount.

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PTF Award Winner 2023

PSRI Fluidization and Fluid-Particle Systems Award

Dr. Bing Du

Principal Scientist, Process Reactor Development
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Citation: For contributions to fundamental understanding of choking phenomena and gas-solids mixing phenomena in turbulent fluidzation, and to fluidized bed reactor scale-up as a leader at ExxonMobil

Dr. Bing Du has been actively working in the area of fluidization and fluid-particle flow systems for more than 20 years and currently is the Principal Scientist for Process Reactor Development at ExxonMobil Technology and Engineering Company. He has actively participated in or led the development and scale-up of multiple processes related to fluidized bed reactors or fluid-solid systems. Applications cover Upstream, Downstream, and Chemicals in the oil/gas industry, and include FCC/Fluid Coking^{TM} process/hardware improvements, EMTAM^{TM} (Fluid bed Toluene Alkylation with Methanol) process development, Fluid Bed MTG (Methanol to Gasoline) technology development, and new chemical processes and waste recycling technology. Recently, the fluid bed MTG process has successfully demonstrated the production of eFuels from methanol synthesized from CO_2 and green hydrogen. Bing Du received his PhD in Chemical Engineering from the Ohio State University in 2005, MS and BS in Chemical Engineering from Tsinghua University. Before joining ExxonMobil, Bing worked at Dow Chemical for two years

PSRI
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Sponsor of the Lectureship in Fluidization Award

Fluidization: from Fundamentals to Commercialization

Dr. Bing Du

Principal Scientist, Process Reactor Development
ExxonMobil Technology and Engineering Company

Fluidization and particle technology have woven through most of my career, first dating back to the 1990s when I was in college. I first became aware of fluidization during my university graduation project and Master's Thesis (*Hydrodynamics and Mixing Behavior of Different Particles in a FCC Riser*) at the Fluidization Laboratory of Tsinghua University (FLOTU). Under the guidance of my advisor, Prof. Fei Wei, I learned about the crucial role of fluidization in reaction engineering and its wide application in various industries. This sparked my interest, and I made the decision to pursue a PhD in this field at the Ohio State University with Prof. L.-S. Fan, one of the world's most famous experts in fluidization and particle technology.

During my time at the Ohio State University, I had the privilege of studying under the guidance of Prof. Fan, a knowledgeable and dedicated advisor. Under his mentorship, I gained a thorough understanding of the principles behind fluidization and particle technology, with a focus on gas-solid fluidization. One aspect that I delved into in particular was the turbulent fluidization regime. This regime, sitting between the bubbling and fast fluidization regimes, is characterized by the vigorous movement of particles and irregularly-shaped bubbles. Despite its operational advantages, it has received less attention compared to other regimes due to the lack of accurate and real-time measurement techniques and its complex flow dynamics. Leveraging the innovative real-time Electrical Capacitance Tomography (ECT) technique developed in Prof. Fan's Lab, I conducted an in-depth investigation of the dynamic flow behavior in turbulent fluidized beds. Figure 1 visualizes the bubble dynamics in a gas-solid fluidized bed. With well-defined boundary conditions, the bubble size, bubble rise velocity, and solids holdup related to bubble flow were revealed [1]. Figure 2 illustrates both the radially symmetric time-averaged solids holdup distribution of the turbulent regime and the dynamic behavior of the bubble/void and emulsion phases, which have been scarcely reported in the literature [1]. Furthermore, my research also investigated how temperature, fines addition, and scale impact the dynamic flow behavior in turbulent fluidized beds, which is of great importance for commercial applications.

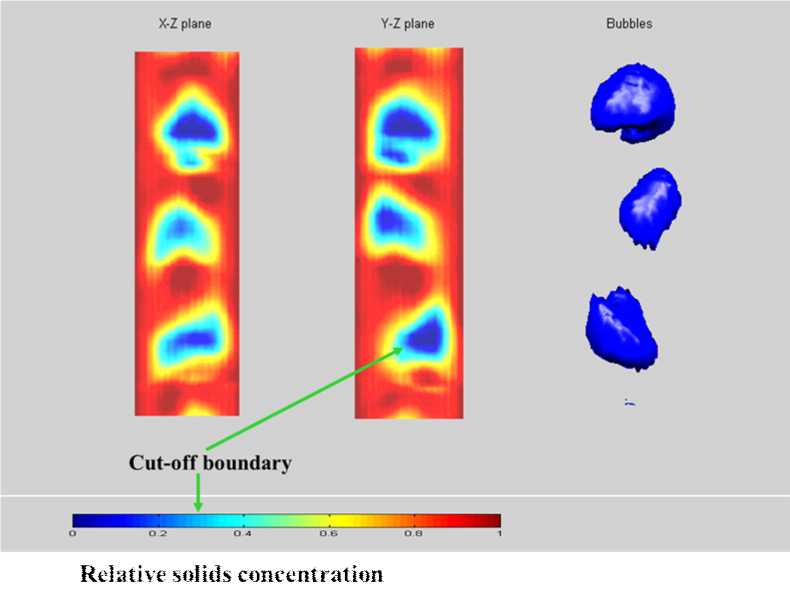

Figure 1 Visualization of Bubbles in a Gas-Solid Fluidized Bed [1]

Another area of research focus for me at the Ohio State University was discovering the fundamental principles and mechanisms behind the choking phenomenon in gas-solid circulating fluidized bed systems. "Choking" refers to a gas-solid fluidization phenomenon where a small change in gas or solids flow rate causes a significant shift in hydrodynamic behavior, such as pressure drop or solids holdup during gas-solid flow. Numerous efforts have been dedicated to exploring this phenomenon in the past few decades. However, the root cause of choking, the transition from dilute to dense fluidization, and the underlying mechanism have remained unclear. By applying electrical capacitance tomography (ECT) with the novel neural network multi-criteria optimization image reconstruction technique (NN-MOIRT), I have conducted extensive research into the dynamic flow structure and regime transition, and revealed the fundamentals and mechanism behind choking in gas-solid circulating fluidized bed systems. The research spanned a wide range of operating systems and conditions, such as bed diameter, particles with different Geldart Groups, gas humidity, and baffle/internals. Figure 3 displays the distinct flow structure variation that occurs during the choking transition as the gas velocity falls below the transport velocity [2, 3]. This variation is an intrinsic flow behavior and is not appreciably affected by gas/solids feeding patterns or electrostatics. This study was the first to reveal the presence

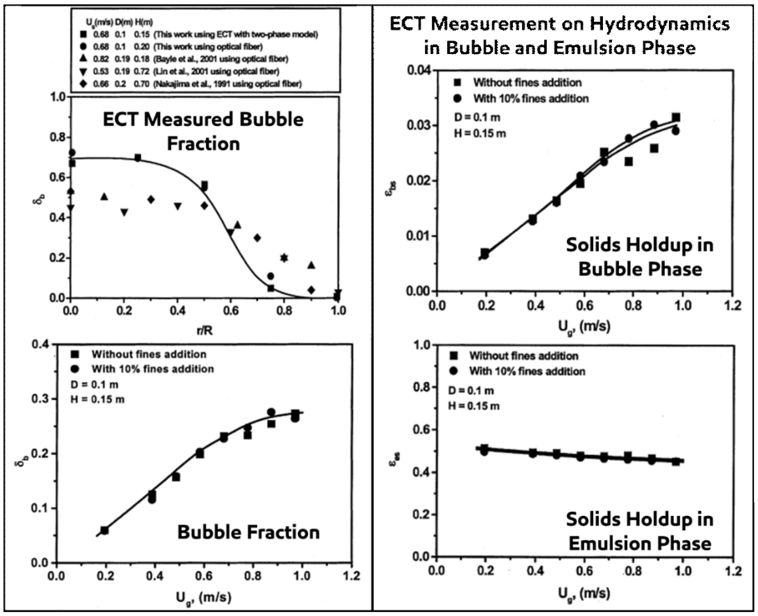

Figure 2 Bubble Dynamics in Turbulent Fluidized Bed [1]

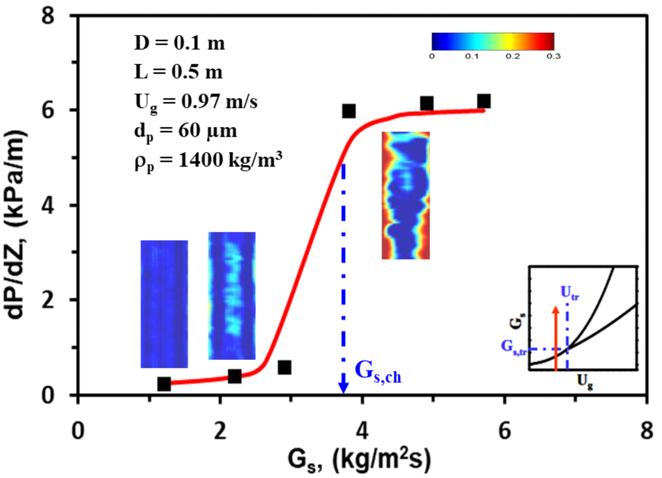

Figure 3 Choking Transition with Distinct Flow Structure Variation [2,3]

of solids ring flow structure and solids blobs at the center of the bed in circulating fluidized beds. The mechanism of coking transition initiation to the dense-phase fluidization regime can be explained by the disintegration of enlarged solids blobs and collapse of the solids suspension, which is a result of solids suspension instability. Based on the instability study, a criterion for the occurrence of choking transition for both Group A and Group B particles was developed.

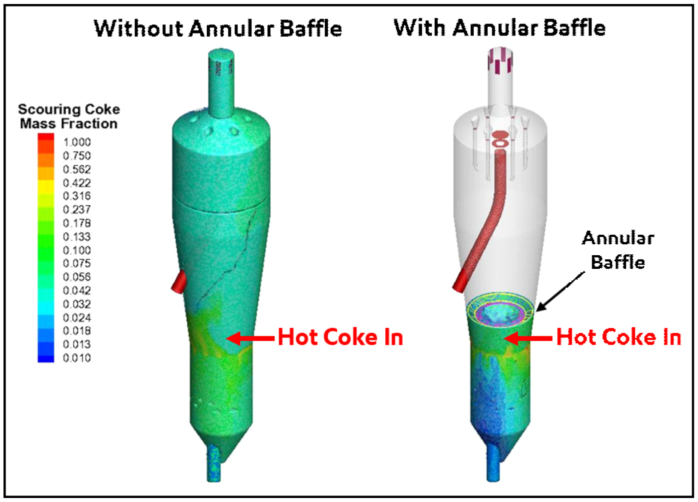

Figure 4 Enhanced FLK/FXK Reactor with Staging Baffle (Baffle to inhibit particle recirculation from stripping zone to coking zone) [4]

Following graduation from the Ohio State University, I joined The Dow Chemical Company for two years focusing on solids handling & conveying projects. Thereafter, I moved to ExxonMobil Corporation which has successfully commercialized the first Fluid Catalytic Cracking (FCC) and Fluid Coking/ FlexiCoking (FLK/FXK) technologies. FCC is a one of the most successful applications using fluidized bed technology. I feel fortunate to work for ExxonMobil to support and enhance the FCC and FLK/FXK technologies, including process optimization, hardware design, and improvement. One example was to develop a technology to improve the performance of the FLK/ FXK reactor by decoupling the reactor zone and stripping zone with a staging annular baffle. The optimal operating conditions for an FLK/EXK are to operate the reactor at a lower temperature to improve liquid yield and operate the stripper at higher temperatures to reduce fouling and hydrocarbon carryunder. However, for commercial FLK/FXK operation, the reactor and stripper are coupled to each other and operated at similar temperatures, which sets the liquid yield below the optimal under normal operation. To overcome this limitation, Figure 4 shows a solution of the improved fluid coking process to inhibit recirculation of the particles from the stripping zone to the coking zone by installing a centrally-apertured annular baffle [4]. Through computational fluid dynamics (CFD) and large-scale cold flow testing, the feasibility of this technology was successfully demonstrated.

I am currently the Principal Scientist for Process Reactor Development at ExxonMobil Technology and Engineering Company. As a well-recognized fluid bed process development and scale-up expert within ExxonMobil, I have actively participated in and led process development and scale-up for multiple processes related to fluidized bed reactor or fluid solid systems covering applications in the Upstream, Downstream and Chemicals. Figure 5 serves as an example to illustrate the approach used to scale up the fluid bed MTG (methanol to gasoline) process from pilot to “commercially ready” [5]. A model enabled scale-up methodology was applied to expedite the technology development while minimizing costs. The scale-up models, including computational fluid dynamics (CFD), phenomenological model, particle population balance model, etc, are built based heavily on fundamental understanding of intrinsic kinetics, bed hydrodynamics, heat and mass transfer, gas and solids mixing. Recently, this fluid bed MTG technology has been successfully demonstrated to produce eFuels from methanol synthesized by CO_2 and green hydrogen, which offers additional solutions for low carbon fuels. The Porsche announcement can be found from this link: Porsche is replacing gasoline with air and water (foxnews.com).

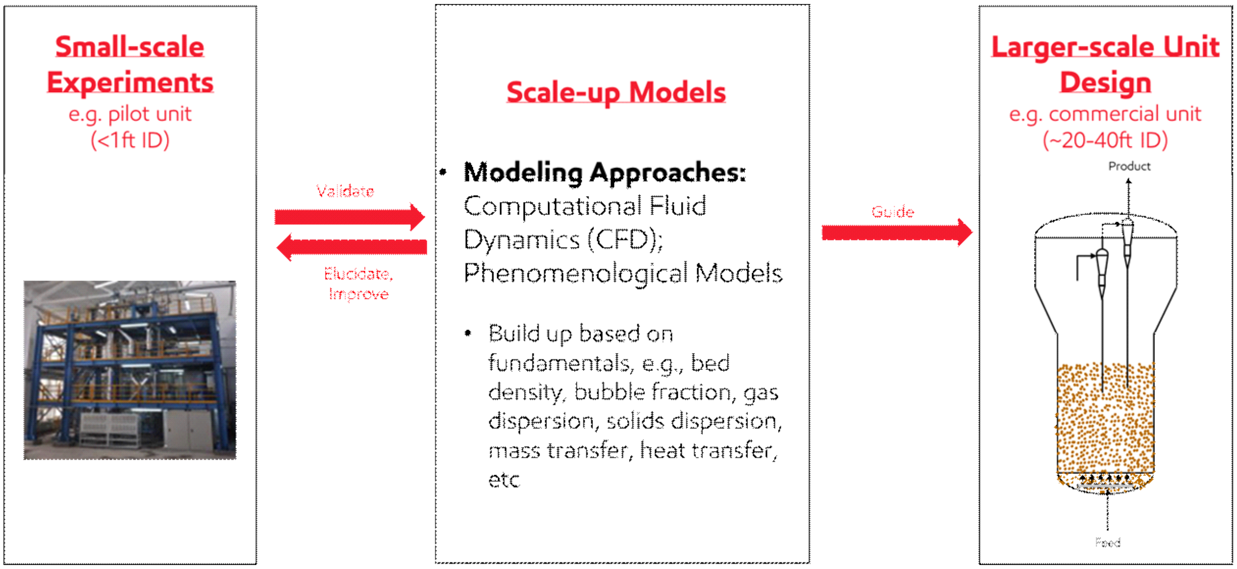

Figure 5 Fluid Bed MTG Process Development and Scale-up [5]

Fluidization and particle technology are filled with uncertainties and unknowns, which have always intrigued and motivated me. Not only do I seek to understand the fundamentals behind it, but I am also driven to utilize unique benefits to develop and commercialize new industrial applications. This technology played a crucial role in the previous energy revolution, as seen in the use of FCC technology to produce gasoline for the entire world. As we face the current energy transition in response to climate change, fluidization and particle technology will continue to play a critical role in almost every aspect of low carbon solutions and sustainability, e.g., carbon capture, blue hydrogen, low-emission fuels, and plastic recycling, etc.

I am grateful for the support and guidance of my advisors, mentors, friends, and colleagues in both academia and industry.

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PTF Award Winner 2023

Shell Thomas Baron Award In Fluid-Particle Systems

Dr. Mark Swihart

Distinguished Professor and Chair

Department of Chemical and Biological Engineering

University of Buffalo (SUNY)

swihart@buffalo.edu

Citation: For outstanding contributions and sustained innovation in the colloidal and aerosol synthesis of nanomaterials and their applications

Prof. Mark T. Swihart is SUNY Distinguished Professor and Chair of the Department of Chemical and Biological Engineering, and an Empire Innovation Professor in the RENEW Institute at The University at Buffalo (SUNY). His research interests and activities center on the synthesis and applications of inorganic nanomaterials, in fields ranging from sustainability to medicine. His research group develops and advances both gas-phase (aerosol) and solution-phase (colloidal) synthesis methods for producing novel nanomaterials and also conducts modeling and simulation work in support of material and process development. These materials have broad applications in bioimaging, catalysis, photo-catalysis, electrocatalysis, sensing, and photovoltaics. Swihart earned a B.S. in Chemical Engineering from Rice University in 1992, and a Ph.D. in Chemical Engineering in 1997 from the University of Minnesota under the advisement of Robert W. Carr, then spent one year as a postdoctoral researcher in the Particle Technology Laboratory in the Department of Mechanical Engineering at the University of Minnesota. He joined the Department of Chemical and Biological Engineering at the University at Buffalo (SUNY) in 1998, where he has remained for his entire faculty career. He was named department chair and Empire Innovation Professor in 2018 and SUNY Distinguished Professor in 2021. Swihart has co-authored the two most recent editions of Introduction to Chemical Engineering Thermodynamics (Smith, van Ness, Abbott, and Swihart), as well as over 300 peer-reviewed journal manuscripts. He has served as a research advisor to more than 95 current and former graduate students and 110 undergraduate researchers at UB. He is a co-founder of NanoHydroChem, LLC and ProOsseus, LLC.

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Thomas Baron Award

A Nanoscale Career Retrospective

Dr. Mark T. Swihart
SUNY Distinguished Professor and Chair of Chemical and Biological Engineering
University at Buffalo (SUNY)

I was deeply honored to receive the Shell Thomas Baron Award in Fluid-Particle Systems at the 2023 AIChE Annual meeting. This award is the result of the creative efforts of dozens of students over the past 25 years, who have carried out the work that was recognized. Guiding these students and watching them grow into independent researchers, faculty members, and CEOs, while in many cases following career paths that lead them far from the world of nanoparticles that they occupied in my research group has been a profound privilege. Thinking about them as I draft this brief newsletter article reminds me that, for those of us in academia, it is our students, not the research itself, that are the most important contribution we can make. With that in mind, I would like to tell a bit of the story of our research journey.

Nucleation

I entered the world of particle technology as a post-doc in the Particle Technology Laboratory at the University of Minnesota, under the guidance of Steven Girshick and Peter McMurry. We were working with folks from Advanced Silicon Materials, Inc. (ASiMI) to understand the undesirable formation of silicon particles during the growth of high-purity silicon rods. As a graduate student, I had worked on the kinetics of reactions of silanes and chlorosilanes, so I felt well-equipped to tackle the problem of silicon particle nucleation during the thermal decomposition of silane (SiH_4) to polycrystalline silicon and H_2 gas. The goal, whether growing giant rods or thin films by chemical vapor deposition, is generally to deposit silicon as fast as possible without nucleating particles in the gas phase. Intellectually, the question of how we go from molecules to solid particles without forming a supersaturated silicon vapor is both interesting and challenging. It is analogous to the nucleation of soot, but without the possibility of aromatic ring formation. Thus, instead of 2-dimensional polyaromatic hydrogens, the silicon nuclei are three-dimensional clusters with the cubic crystal structure of diamond.

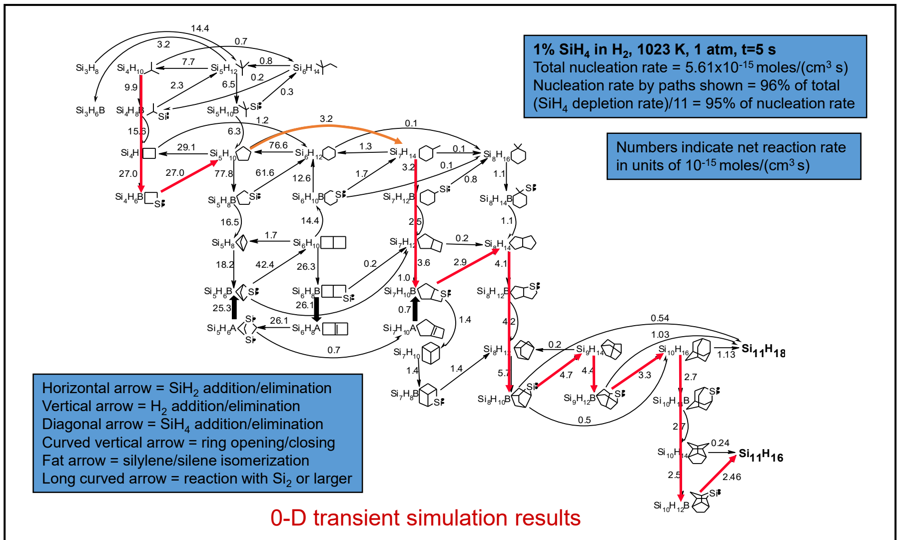

Figure 1: Analysis of particle nucleation pathways during pyrolysis of silane. Presented at the 1998 AIChE Annual meeting.

Figure 1 illustrates the sort of mechanisms and pathways we constructed leading from silane toward the silicon analog of adamantane, the fundamental building block of the diamond crystal lattice. [1-3] Soon after starting my first faculty position, I collaborated with Linda Broadbelt to apply the tools of automated reaction mechanism to this system. [4, 5] Students including Suddha Talukdar, [6] Yuanqing He, and Hongyi Dang, [7, 8] incorporated these nucleation models into increasingly sophisticated simulations of increasingly complex reactor configurations. Unfortunately, we were never fully successful in validating all this modeling effort. A fundamental challenge in this field is that under most conditions where one is generating nanoparticles intentionally, the influence of nucleation is washed out by subsequent aggregation and sintering. The lesson learned was that nucleation is most important when trying ***not*** to make nanoparticles. At the time, though, the scope for fundable research in making nanoparticles was much greater than for not making nanoparticles.

Growth

With initial hopes of validating our modeling of silicon nanoparticle formation, we constructed a laser pyrolysis reactor system that uses a CO_2 laser to heat a stream of silane-containing gas without heating the reactor or the surrounding gases, which do not absorb at the laser wavelength. This quickly led us to focus on the intentional synthesis of ultrasmall silicon particles. By the mid-1990's, Brus and coworkers had shown that aerosol-synthesized silicon nanoparticles below about 5 nm in diameter behaved as quantum dots, with efficient size-dependent photoluminescence, but they were only producing micrograms of material. [9] Our laser pyrolysis process, along with understanding of the role of hydrogen in suppressing silicon nucleation and growth, allowed us to produce ultrasmall silicon nanocrystals in macroscopic quantities. [10] The key to this is the extremely short reaction time accessible by laser heating. Particle aggregation limits the maximum number concentration that can remain after a given reaction time. By achieving reaction times before quenching of just a few microseconds, the laser pyrolysis method can reach number concentrations approaching 10^{14} cm^{-3}. Xuegeng Li led this effort, soon realizing that producing efficient emissions from our nanoparticles would require post-processing them in solution, to reduce their size, passivate surface defects, and attach molecules to their surface that would keep the surface passivated. [11] A series of students including Yuanqing He, Folarin Erogbogbo, and Parham Rohani continued producing silicon nanoparticles and various other materials by laser pyrolysis, while also advancing our work on surface modification of these materials. [12-19] Ultimately, we were able to make surface-functionalized silicon quantum dots with emission ranging from blue to the near infrared, as shown in Fig. 2. The most efficient emission is actually from the near-IR emitting material; they just look dim because of the low sensitivity of our eyes and cameras at those wavelengths.

Figure 2: Photograph of colloidal dispersions of silicon nanoparticles with emission from blue to the near infrared, under 365 nm UV illumination.

Branching

As our group developed broader expertise in nanomaterial synthesis and processing, we branched out into numerous material systems and applications. We developed a continuous thread of research in high-temperature colloidal synthesis of anisotropic and multicomponent nanomaterials that has continued for nearly two decades. In contrast to the aerosol synthesis methods that are governed by fast dynamics of heating, nucleation, growth, aggregation, sintering, and quenching, these colloidal synthesis methods are controlled by the thermodynamics and kinetics of growth of specific crystal facets, usually passivated with organic ligands of uncertain concentration and even identity. Controllably inducing heterogeneous nucleation of one material on another is essential for controllable growth of multicomponent nanostructures. Figure 3 provides an early representative example in which we control the shape and structure of 2- and 3-component nanostructures. Weili Shi, Ken-Tye Yong, Hongwang Zhang, and Sha Liu advanced this research direction in the group. [20-28]

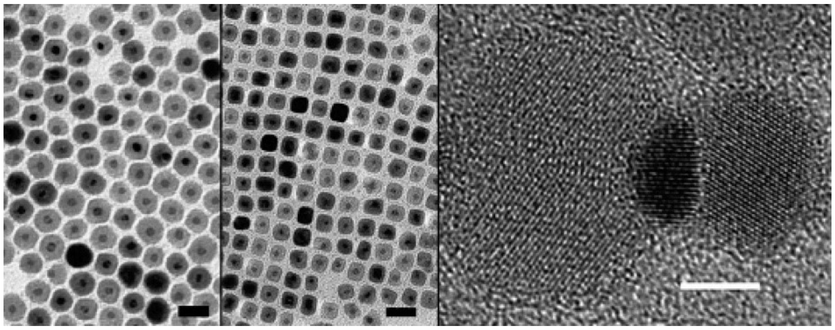

Figure 3: TEM images of multicomponent nanoparticles, left-to-right, gold core with spherical iron oxide shell, gold core with cubic iron oxide shell, and gold core with one iron oxide lobe and one lead sulfide lobe.

The next major branch of research in the group was our exploration of copper chalcogenide-based materials with composition and size-tunable localized surface plasmon resonance. Xin Liu launched us on this direction, followed by Xianliang Wang, Yang Liu, and Deqiang Yin. [29-50] For the sake of space, and because this is perhaps further from the interests of the PTF community, I will not describe these efforts in detail, but the work resulted in numerous publications, including those cited here and many others.

Around this same time, we began collaborations that explored the bioimaging applications of our silicon quantum dots and, ultimately, several other nanomaterials developed in the lab. The initial advances in this direction were by Folarin Erogbogbo and Ken-Tye Yong, with many collaborators. We produced numerous multi-functional (e.g., photoluminescence and magnetic image contrast) agents. [51-62] This culminated with *in vivo* studies like that illustrated in Figure 4. [63-67] For the silicon quantum dots, the idea was that the non-toxic and biodegradable nature of silicon would make these suitable for use in human applications like sentinel lymph node mapping. Unfortunately, by the time we had done all of the surface modification and packaging of the silicon quantum dots to maintain bright luminescence *in vivo*, the particles no longer degraded and remained in the livers of mice and monkeys for at least many months. Similarly, we applied the various nanoparticles with plasmon resonance for photoacoustic imaging and photodynamic therapy.[68-72] Ultimately, the lesson we learned from all of this work is that the use of inorganic nanomaterials as imaging agents would face nearly insurmountable regulatory challenges. Both the materials and the methods used to synthesize and characterize them are unfamiliar to regulatory agencies. While some of the imaging agents we developed would likely outperform the current agents used, *e.g.*, in sentinel lymph node mapping, the potential improvement is unlikely to be dramatic enough to attract the substantial investment that would be required to push these toward commercialization.

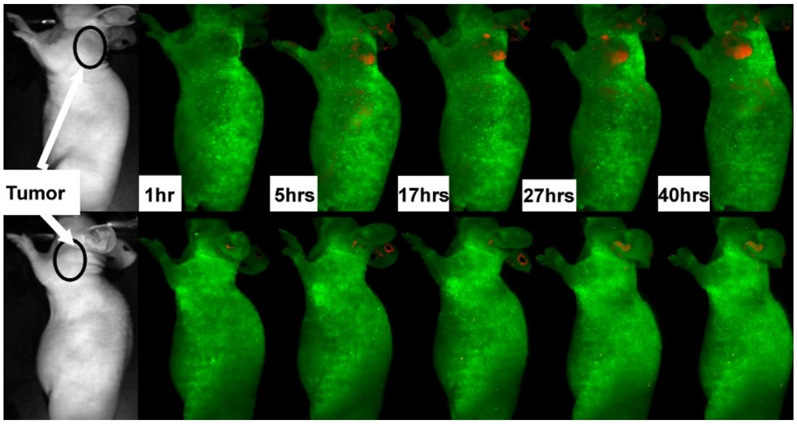

Figure 4: Targeted photoluminescence imaging of a mouse with targeted (top) and untargeted (bottom) micelle-encapsulated photoluminescent silicon quantum dots. Both mice have a tumor at the location indicated, which is selectively labeled by the silicon quantum dots.

What I am most excited about now

We have continued to dabble in an ever-wider range of research topics, far beyond the scope of this brief article. However, I wish to describe one final line of research that returns to aerosol synthesis of nanomaterials. Around 2007, in a meeting with colleagues at Praxair, Inc. (since merged with Linde), I learned about their “thermal nozzle” technology.[73] This method draws the hot products of combustion of a fuel through a converging nozzle to generate a hot, high-velocity jet of gases. Originally, it was applied in “hot oxygen” technology, in which fuel lean combustion left excess oxygen in the product stream. Introducing reactants into that hot oxidizing jet produced exceptionally fast heating and mixing that was useful, *e.g.*, for partial oxidation reactions. We immediately realized that it could also provide the extremely rapid heating that is required for high-throughput synthesis of nanomaterials. Moreover, we could use a hydrogen flame with excess fuel to produce a hot reducing jet. That would allow us to produce metallic nanoparticles of elements that can be reduced by hydrogen in the presence of water (*e.g.*, Fe, Co, Ni, Cu, Ag, and Pd) that cannot generally be produced in other flame aerosol reactors. The initial reactor system was constructed by William Scharmach, who named it the High Temperature Reducing Jet (HTRJ) reactor, in collaboration with folks from Praxair.[74] The current configuration, only slightly modified, is illustrated in Figure 5. Hot products of hydrogen combustion are drawn through a converging-diverging nozzle, as an aqueous precursor solution is injected into the throat of the nozzle. The precursor is sheared into tiny (few µm diameter) droplets that rapidly evaporate. The reactor section has a residence time of order 50 ms, and a typical temperature from 500 to 800 °C. A large flow of nitrogen quenches and dilutes the product particles at the reactor exit. In contrast to conventional flame aerosol reactors, this allows us to separate the combustion and particle formation processes. It also allows us to use water as the solvent and low-cost metal salt precursors, which are available for nearly every element. For the reducible metals that were the focus of our early research, led by William Scharmach, Munish Sharma, Shailesh Konda, and Moein Mohammadi, the metal nitrate precursors evaporate completely and particles nucleate from the gas phase, producing quite small nanoparticles.[74-79] More recently, we found that if we provide a pre-synthesized support material, such as graphene oxide, we can produce even smaller particles that nucleate heterogeneously on the support.[80] Current group members, led by Shuo Liu, have expanded the palette of materials further, focusing on metal oxides that form by droplet-to-particle conversion to produce hollow spheres, templating of pores in these materials, producing metastable mixed metal oxides, and applying these in catalysis and thermal insulation[81-87]. Some examples are illustrated in Figure 6. This is opening up a whole new range of composition space that has previously been inaccessible and that I expect will continue to produce fascinating materials and successful students for years to come.

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PTF Award Winner 2023

SABIC Young Professional Award

Dr. Kevin E. Buettner

Engineering Associate

Process Innovation and Scale-Up

ExxonMobil Technology and Engineering Company

kevin.buettner@outlook.com

Citation: For outstanding contributions in experimentation, CFD and DEM modeling, and industrial scale-up of fluid-particle processes.

Kevin E. Buettner is a lead pilot plant engineer within Process Innovation and Scale-Up at the ExxonMobil Technology and Engineering Company. He is a chemical engineering alumnus of the University of Oklahoma (2013) and the University of Florida (2018, Ph.D.), where he was a member of Professor Jennifer Sinclair Curtis' research group focused on model development for CFD simulations of granular flows. After joining ExxonMobil in 2018, he has made significant contributions in the process development and scale-up of "new-to-the-world" process technologies focused on complex fluidization systems. This has required the development and expansion of fluidization modeling capabilities to impact reactor design, and the operation of a new pilot plant to validate the reaction and hydrodynamic models required for novel process scale-up. Kevin currently serves as the Co-Chair for the Particle Technology Forum's (PTF) Area 3B, has over ten peer reviewed journal publications, and is an active referee for AIChE Journal, Chemical Engineering Science, and Powder Technology.

Sponsor of the
Young Professional Award

Thinking About The Future
A perspective From An Early Career Member Of The PTF

Dr. Kevin E. Buettner
ExxonMobil Technology and Engineering Company

In 2023, I was fortunate to be given the SABIC AIChE Young Professional Award from the PTF. This award was important to me for multiple reasons. First, it meant a lot to me that Prof. Jennifer Sinclair Curtis would be willing to use some of her time to nominate me for such an award. Second, it was inspirational to see the nomination letters from a variety of people who have been my mentors and peers helping me grow and improve. Lastly, it was another example of why the PTF has been such an important part of my professional growth and why I look forward to paying it forward in the future as a member. Overall, I would like to thank the committee for the selection and SABIC for sponsoring the award that highlights an early career member of the community.

I first became involved in particle technology as a member of Prof. Curtis' group while at the University of Florida. Her group has been using discrete element method (DEM) simulations to probe the impact of a variety of complex particle properties in hopes of developing improved constitutive/closure relationships. The research questions I was involved in revolved around understanding and improving models used to perform two-fluid method (i.e. Eulerian-Eulerian) simulations. The primary focus was on granular kinetic theory (GKT), which describes particle-particle interactions and was developed under the assumption that particles are rigid spheres. The goal of the research was to work past those assumptions, making GKT models applicable for particles that could be non-spherical, rough, or flexible. For this work, DEM simulations acted as the tool to create the data necessary for improving models, where Figure 1 is an example that shows the deviation between cylindrical particles with varying aspect ratio (AR) and the kinetic theory model with the spherical particle assumption. The benefit of these simulations is that they have the capability of measuring complex physics that are difficult, if not impossible, to measure experimentally. By the time I graduated, we had success in developing constitutive relationships that could expand the capabilities of two-fluid model simulations, but I did not appreciate that the approach we took to improve those models would be applicable in my future roles.

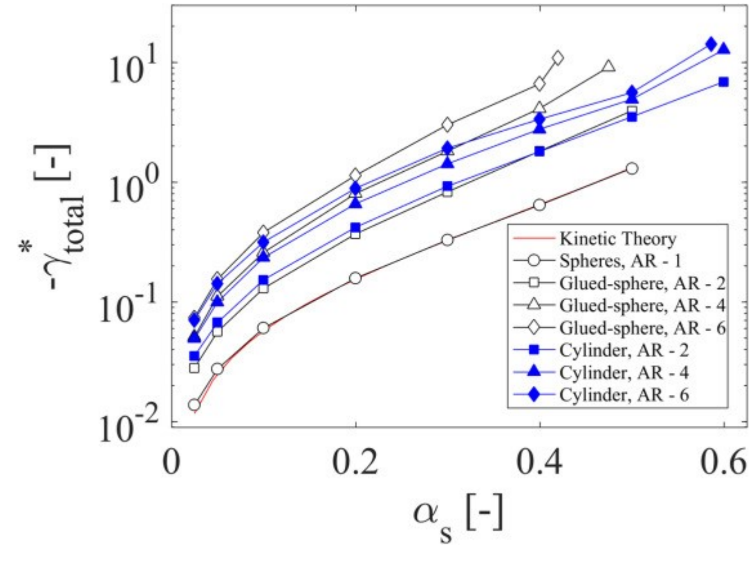

Figure 1. The magnitude of scaled total granular temperature change rate, $-\gamma^*_{total}$, varying with the solid volume fraction, α_s, for glued-sphere and true cylindrical particles. [1]

Fast forward to September 2018, where I was fortunate to join ExxonMobil's computational fluid dynamics (CFD) group. There are multiple novel technologies being developed in the gas-solids space, which makes it an exciting time for someone like me to be at ExxonMobil. I worked on projects that utilized my experiences in modeling gas-solids flows and I began to witness that just like in my Ph.D. studies, there were gaps in the available models that needed improvement. One common theme for many of these technologies is that the gas and particle physical properties for which the technology is being designed are outside the experience band for ExxonMobil. This makes scale-up a challenge because design correlations or models that have been reliable for other processes are not guaranteed to be applicable. Thus, these projects brought me back to the foundation of my thesis where we needed data to improve/ develop models past their original scope.

In each situation where we questioned the currently available correlation/model, we spent significant time making sure the range of applicability was fully understood. This would mean spending time in the literature deciphering assumptions made in the development of first principles models or conditions under which experimental data for fitting empirical models were collected. As an example, Rabinovich and Kalman [2] employed a diverse set of data to fit empirical models for a variety of important fluidization and pneumatic conveying correlations that are often the starting point for designing a new system. Those correlations can be contrasted with complex measurements like entrainment, where Chew et al. [3] provided a review that highlights the range of validity for available models in the literature. In many of these studies, the authors collect a variety of data, but the measurements rarely vary the gas density of the system. This is understandable, because of the challenges related to doing experiments at a relevant scale with a variation in gas density. With that said, with a clear description of the applicability of the model, we would then develop and design experiments to acquire the necessary data to expand the range of applicability to where we needed it.

The energy transition has the potential to require the development of new technologies and processes in the particle technology area. Thus, there will exist a set of risks that the new technologies being developed are designed using tools that are not applicable to the conditions of interest. I have gained a lot of appreciation for those who have spent the time putting together review articles to communicate the current state-of-the-art in a variety of areas. In these works, it is especially helpful to see authors clearly define assumptions or operating windows, allowing the reader to appreciate the gaps. These efforts aid researchers in clearly knowing where additional work is needed and reduce risk of poor model choice. Overall, we as a community should be sensitive to the fact that the acceleration of future technologies will be significantly aided just by clearly stating assumptions.

I have been very fortunate to transition from UF to ExxonMobil while still being connected to the particle technology community. In graduate school, the PTF was a place where I could present my research and network with academic and industrial leaders in the area. Because of that, I am thankful for the PTF and look forward to the future collaborations and friends I'll make through the rest of my career. Thank you again for the recognition.

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Job Postings At ExxonMobil

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PTF Award Winner 2023

George Klinzing Best PhD Award

Dr. Sara Hamilton

Department of Energy

Office of Fossil Energy and Carbon Management

sara.hamilton.triana@gmail.com

Citation: For her contributions to the advancement of new hybrid materials for electrochemical energy storage and reactive carbon capture integral to tackling the climate crisis.

Sara T. Hamilton received her M.Eng. in Chemical Engineering from Imperial College London in 2018 and her Ph.D. in Earth and Environmental Engineering from Columbia University in 2022 under the supervision of Ah-Hyung Alissa Park. During her Ph.D., she researched nanoscale hybrid electrolytes for electrochemical energy storage and combined CO_2 capture and conversion. She also received the SCGSR Fellowship from the Department of Energy's Office of Science, which supported her research at the National Renewable Energy Laboratory (NREL) on electrochemical interfaces in reactive carbon capture. Sara joined the Department of Energy’s Office of Fossil Energy and Carbon Management in 2023 as an ORISE Science, Technology and Policy Fellow.

This award recognizes an outstanding original dissertation by an individual who has earned a doctoral degree. The dissertation can be in any discipline in the physical, biomedical or engineering sciences, with particle science and engineering as its focus. The nominee must have received a doctoral degree within the last three calendar years prior to the year the award is given, and it is based only on the contributions made during the course of the PhD.

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Development of Nanoscale Hybrid Material-Based Electrolytes for Energy Storage and Tandem CO_2 Capture and Conversion

Dr. Sara Hamilton
Department of Energy
Office of Fossil Energy and Carbon Management

New materials are needed for improved electrochemical systems

The recent growth in worldwide installation of renewable energy and the need for CO_2 capture and utilization to meet climate targets requires large-scale electrochemical energy storage systems, including redox flow batteries (RFBs) and CO_2 electrolyzers. Electrolyte design and selection plays a critical role in the development of these electrochemical devices, dictating transport and solubility of the reactive species to ultimately deliver high energy, current and power density systems.

Nanoparticle Organic Hybrid Materials (NOHMs) as novel electrolyte components

Nanoparticle organic hybrid materials (NOHMs) are a new class of materials with promising properties for electrochemical energy applications, including high tunability, thermal oxidative stability and negligible vapor pressure. NOHMs consist of an inorganic core (typically nanometer sized) to which polymeric chains (the "canopy") are tethered ionically or covalently as shown in Figure 1(a). A wide range of nanocore-canopy combinations is possible for a variety of functionalities. To date, NOHMs have primarily been studied in the neat state, but their incorporation as electrolyte components requires an understanding of their behavior in the electrolyte solution and at the electrode/electrolyte interface. The work of this dissertation showed that NOHMs-based electrolytes can complex electroactive species and enable tandem CO_2 capture and conversion, offering improvements in electrolyte design of interest in electrochemical systems such as RFBs and CO_2 electrolyzers. Figure 1(b) shows a proposed scheme for the incorporation of NOHMs as electrolytes for tandem CO_2 capture and conversion and RFBs. The investigations of this dissertation revealed that NOHMs-based electrolytes are electrochemically stable, have tunable bulk physicochemical properties, and have interfacial effects that impact the reaction and transport of electroactive species.

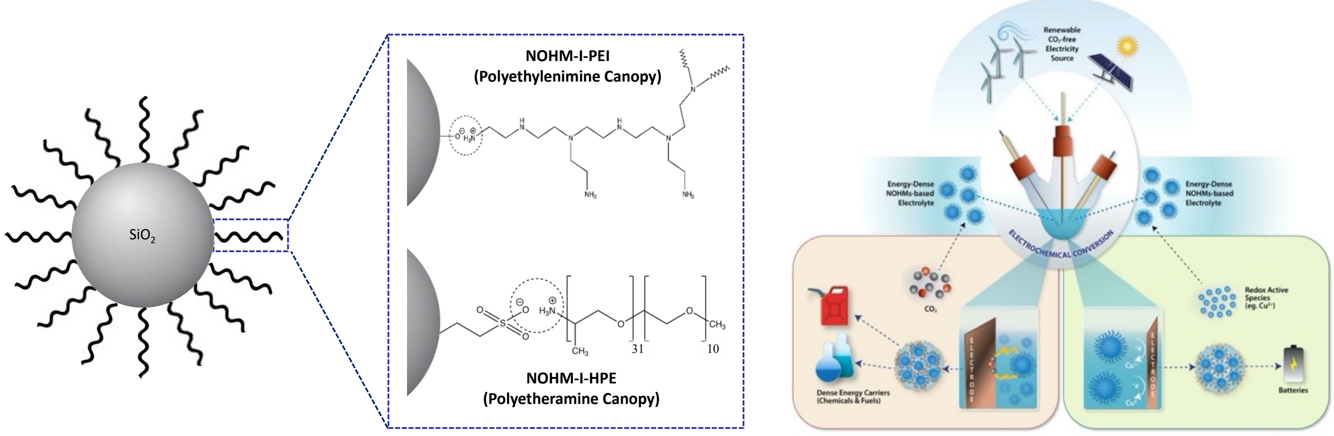

Figure 1: (a) Structure of NOHMs with different polymeric canopies: NOHM-I-PEI (polyethylenimine canopy) and NOHM-I-HPE (polyetheramine canopy). (b) NOHMs-based electrolytes for CO_2 capture and conversion and Redox Flow Battery applications.

NOHMs-based electrolytes are electrochemically stable in aqueous environments under both oxidative and reductive conditions

The first study in this dissertation focused on investigating electrochemical cycling of NOHMs-based electrolyte materials in oxidative and reductive environments and spectroscopic analyses to assess electrochemical stability. NOHMs-based electrolytes were found to have wider electrochemical voltage windows than water and to be robust to hours-long voltage holds, as discerned from electrochemical experiments followed by structural NMR and ATR FT-IR characterization. These findings, along with previous work on thermal stability[1], highlight the promise of NOHMs to be integrated in electrochemical devices with continuous operation for extended time periods, such as flow batteries and combined CO_2 capture and conversion systems including Direct Air Capture (DAC), where these materials could be continuously exposed to high oxidant concentrations.

Ionic stimulus enables control of the physicochemical properties of NOHMs-based electrolytes

The physicochemical properties of NOHMs-based electrolytes in solution, including conductivity and viscosity, were investigated in another study in this dissertation. Controlling transport properties is particularly important in NOHMs-based electrolytes mixtures, as they are challenged by inherently high viscosities, impacting charge transport critical in electrochemical performance. NOHMs were found to be highly responsive to ionic stimulus, with the addition of even low salt concentrations inducing large reductions of up to 90% in the viscosity of NOHMs-based electrolyte mixtures. Alterations in the intermolecular hydrogen bonding interactions, degree of polymer swelling, and the conformational structure of the NOHMs' polymer canopy with ionicity were discerned via light scattering and NMR techniques. Figure 2 provides a summary of the changes in polymeric canopy conformation that occur upon the addition of ionic stimulus in NOHMs-based electrolytes. These insights provide a mechanistic understanding of the effect of salt ions on measured bulk physicochemical properties and could be ultimately employed to tailor transport properties for a range of electrochemical applications. The findings from this study have been published in *JACS Au*.[2]

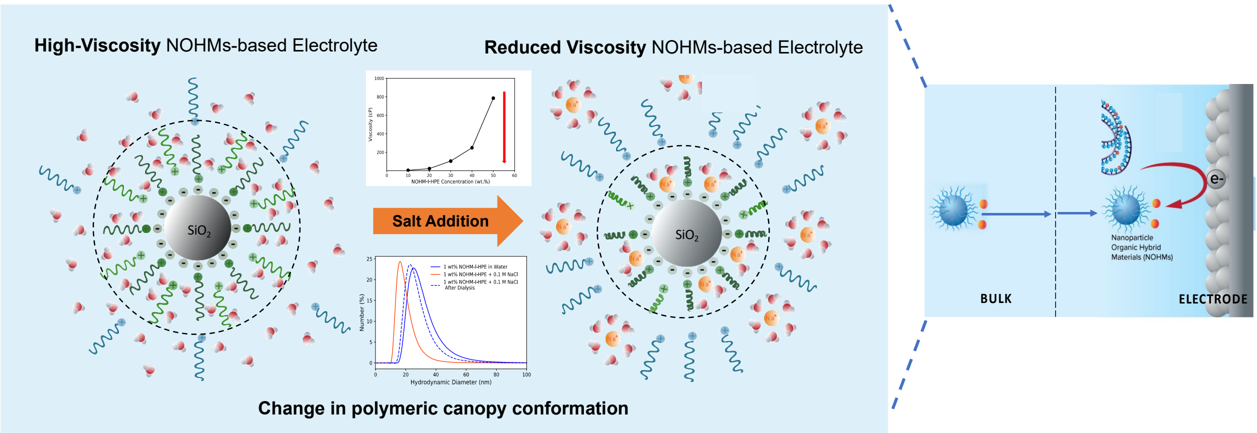

Figure 2: *Changes in polymeric canopy of NOHMs induced by salt ions reduce electrolyte viscosity.*

NOHMs can reversibly bind to electroactive species and their addition in the electrolyte alters diffusion and reaction pathways

Another study of this dissertation demonstrated the ability of NOHMs to reversibly bind electroactive species and revealed that their addition in the electrolyte alters diffusion and reaction pathways of interest in RFBs and other electrochemical devices. NOHM-I-HPE (NOHMs based on ether functional groups) were found to complex zinc and their addition in the electrolyte alters the diffusion and reaction of zinc ions, as discerned from electrochemical analyses. NOHMs were found to selectively adsorb at the electrode interface, impacting achievable current densities and the morphology of metal deposits (reducing dendrite formation) during the electrochemical deposition reaction of zinc, as revealed by XRD and SEM-EDX analysis. The interfacial adsorption of NOHMs was characterized with electrochemical and spectroscopic measurements and suggests differences in structuring of tethered and untethered polymer near the electrode surface, which may play a role in electrochemical conversion mechanisms. These findings are summarized in Figure 3. This study provides insights into how structured electrolyte additives such as NOHMs can allow for advancements in electrolyte design for controlled deposition of metal species from energy-dense electrolytes or for other electrochemical reactions. These findings have been published in *ACS Applied Materials and Interfaces*.[3]

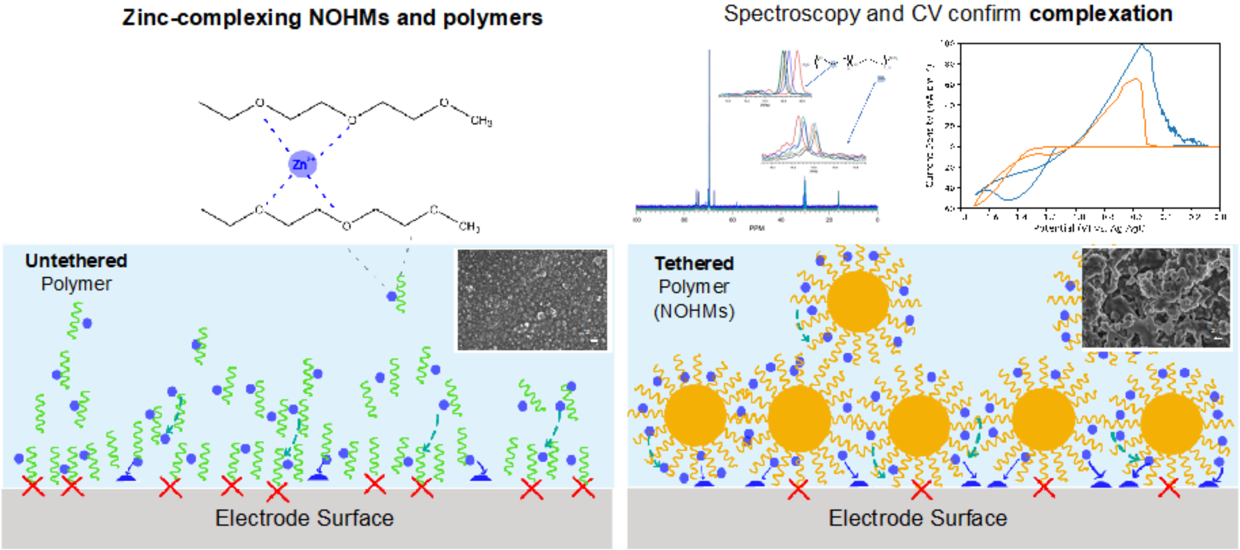

Figure 3: *NOHMs complex electrochemically active species and adsorb at the electrode/electrolyte interface, impacting diffusion and reaction pathways and electrodeposit morphologies.*

NOHMs effects at the electrode-electrolyte interface impact product distribution during the CO_2 reduction reaction and have been studied in operando using electrochemical AFM

The final study of this dissertation demonstrated the integration of NOHM-I-PEI (NOHMs based on amine functional groups) in tandem CO_2 capture and conversion schemes and investigated polymer/electrode interfaces *ex-situ* and *in operando*. NOHM-I-PEI and PEI-based electrolyte addition were found to impact product distributions during CO_2RR, which was partially attributed to possible polymer/catalyst interactions discerned by SEM-EDS analysis. *Operando* electrochemical atomic force microscopy (EC-AFM) measurements were performed at National Renewable Energy Laboratory (NREL) to probe these effects. These measurements revealed changes in PEI conformation at the interface under applied polarization during CO_2RR, aligning with the electrode due to electrostatic effects. This led to changes in interfacial morphology and nanomechanical properties of the surface. The addition of supporting electrolyte salt ions and carbamate bond formation upon CO_2 saturation of the solution were both found to impact the reconfiguration of polymeric chains on the electrode surface, as revealed by trends in surface modulus. Polyamines of higher molecular weight had different effects on the surface morphology, suggesting polymer architecture needs to be considered when designing ionomer/catalyst interfaces for CO_2RR and other electrochemical systems. These findings complement bulk electroreduction measurements and provide insights into the mechanisms of CO_2 capture and electrochemical conversion in polyamine-based electrolytes. Taken together, the findings from the last two studies both highlight the complex interfacial behavior of NOHMs-based electrolytes, which has important implications in next-generation electrochemical systems, impacting achievable current densities, morphology of electrodeposits, regeneration overpotentials, and product distribution in electrochemical processes including CO_2 capture and conversion. Figure 4 summarizes the findings from this study. The research on combined carbon capture and conversion has been published in *Advanced Functional Materials* and the work on operando characterization is currently under review.[4]

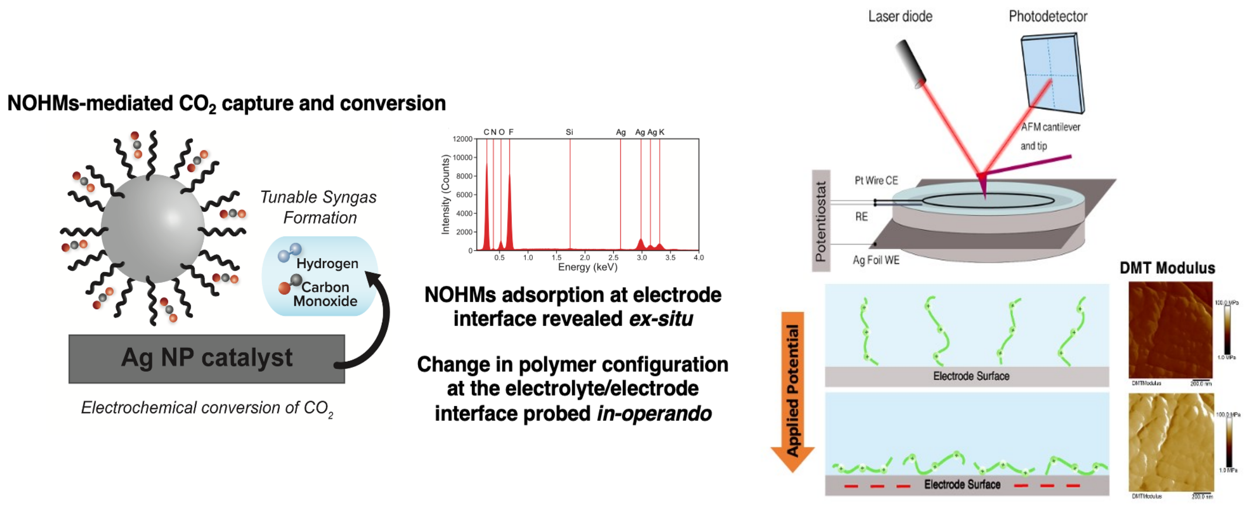

Figure 4: *NOHMs can enable combine CO_2 capture and conversion and adsorb at the electrode-electrolyte interface impacting product distribution. These interfacial effects have been*

NOHMs are promising materials for electrochemical systems important in energy and environment applications

The development of new electrolyte materials is necessary for the advancement of electrochemical devices for renewable energy storage and integrated CO_2 capture and electrochemical conversion. This dissertation presents discoveries of Nanoparticle Organic Hybrid Materials (NOHMs) as a new class of electrolyte materials. NOHMs with ether group and amine group functionalities (NOHM-I-HPE and NOHM-I-PEI), which have different binding affinities towards electrochemically reactive species, were the primary focus of this work. NOHMs-based electrolytes were found to have tunable bulk transport properties and the capability to bind electrochemically reactive species, including CO_2 and metal ions. This presents opportunities to integrate NOHMs in electrochemical devices such as Redox Flow Batteries, where solubility can improve device energy density, and tandem CO_2 capture and conversion schemes, where CO_2 capture and electrochemical reduction steps are integrated with the NOHMs as electrolyte additives. The impact of NOHMs addition on electrochemical reactions was evaluated and their effects at the electrode interface, of interest in various electrochemical reactions, were probed using both *ex-situ* and *operando* characterization techniques. Additionally, electrochemical stability of NOHMs-based electrolytes was assessed to determine their potential to be integrated in electrochemical devices with continuous long-term operation. Overall, the findings from this dissertation present new fundamental discoveries in the development of next-generation polymer-particle hybrid materials with applications in a wide range of energy and environment applications.

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Statement on Diversity

The AIChE Particle Technology Forum is committed to maintaining a diverse and inclusive community of highly skilled chemical engineering professionals within the environment of the Institute and profession in which all members, regardless of characteristics such as gender identity and expression, race, religion, age, physical condition, disability, sexual orientation, educational level, socioeconomic class, nationality or ethnicity, are valued and respected.”

As a global scientific and engineering society, we affirm the international principles that the responsible practice of science, free from discrimination in all of its forms, is fundamental to scientific advancement and human wellbeing, as outlined by the International Council for Science’s (ICSU) Statute 51. We also affirm our commitment to an engineering and scientific environment that facilitates the planning, execution, review and communication of engineering and scientific work with integrity, fairness, and transparency at all organizational levels. This extends to our general scientific endeavors—including our professional interactions and engagement with other engineers, scientists, students, trainees, and the general public. We recognize that harm to our profession, our scientific credibility, individual wellbeing, and society at large is caused by not doing so.

To this end, the PTF will implement the principles of diversity, inclusivity, and equity within PTF leadership and membership to build a community across the chemical enterprise. We are committed to quantifying and monitoring our diversity at least annually at the Executive Committee and reported at the general business meeting.