THE PARTICLE TECHNOLOGY FORUM (PTF) NEWSLETTER

An American Institute of Chemical Engineers (AIChE) Forum

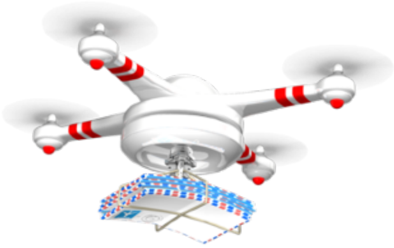
A Glance at the Newsletter

Editorial

Dear Fellow PTF Members,

I hope you and your families are doing well. What a summer we have had so far with the seesaw trend of global COVID-19 cases! The

Message from the Chair



Greetings!

I hope all of you are being safe and staying healthy. Last newsletter I had hoped we were rounding the corner to better times than the pandemic. Despite the outstanding innovations in nanoparticle engineering supporting highly effective vaccines, apparently there are social issues that still must be addressed to get our society past this disease.

Some things are returning toward normal and others are not. We do have a dual in-person and virtual AIChE Annual Meeting in Boston this November and I and many of us will plan to be in attendance if it is not stymied by the progress of COVID-19. Submissions to Area 3 are down across the board, as they are in several other areas of AIChE, and one of the critical issues is the inability for international and some industrial researchers to travel to Boston. Other regular attendees have wisely chosen not to attend in person in order to protect young ones and others who are not able to be properly vaccinated.

In any event, after careful consideration we have decided ***not*** to host a PTF Awards Dinner. The decision is both driven by the uncertainty of attendance, variability in people's interest with regard to dining in a bustling metropolis, and the fact that I wrote in the Spring 2021 newsletter about *"an end in sight to the global pandemic"* and *"hope that the next newsletter will come in the waning days of the pandemic"* clearly shows my lack of understanding of the human behavior. In addition, I would never have imagined when I wrote an article on COVID-19 in the Spring 2020 newsletter that we will be reaching yet another grim milestone by entering the 4th calendar year of the pandemic in under 4 months. However, I still strongly believe that we can slow down the spread of COVID-19 by doing the right things. My personal view remains that it is our responsibility to continue following the public health guidelines pertaining to COVID-19 from reliable health officials and sources. I would also urge everyone who is eligible to get vaccinated to take the jab. We are still far from reaching herd immunity, so the right things we do now will most certainly help to keep vulnerable population, especially young unvaccinated kids, safe.

"The time is always right to do what is right." **– Martin Luther King, Jr.**

Now, in regards to the "actual" PTF related business, the 2021 AIChE Annual financial burden it would be to plan a dinner that very well could be canceled without the ability to recover the costs associated with holding a space. In lieu of hosting a formal dinner, we will be reaching out to all members to see if an informal get together on Wednesday night is of interest. Please fill out this form (whether you plan on attending or not) to help us gauge interest in participating in an informal PTF social get-together:

https://forms.gle/QCurKoV6dDaj8LwY6

My continued gratitude to this newsletter's editor, Dr. Mayank Kashyap, for creating another informative newsletter and all members of the executive committee who keep programming and events running smoothly. Likewise, Reddy Karri for running the awards selection committees (whose work will be complete in the next few weeks).

Hope to see you in person (or virtually) in Boston this November!

Regards,

James Gilchrist, Professor, Lehigh University

Chair, The Particle Technology Forum of AIChE

Email, Website, Twitter: @Gilchrist_Lab, LinkedIn

Our Commitment on Diversity and Inclusion

Approved at 2019 AIChE Annual Meeting

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

Meeting will be hybrid, i.e. one-week in-person in Boston, followed by a week, virtually. This newsletter covers announcement about the meeting. The newsletter also includes technical articles, job postings, new books, and more.

Please feel free to reach out to me if you would like to contribute to the 2021 Fall newsletter by October 1, 2021 with an original/ unpublished technical article or other PTF related material that does not violate any copyrights.

***"Act as if what you do makes a difference. It does."* – William James**

Stay safe!! Stay healthy!! Stay strong!! Stay positive!!

Mayank Kashyap, SABIC

Editor - PTF Newsletter

AIChE PTF

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.

2021 AIChE Annual Meeting - Hybrid

Boston (November 7-11, 2021) and Virtual (November 15-19, 2021)

Message from AIChE Sent on March 29, 2021

Dear Colleague,

We are holding our upcoming 2021 AIChE® Annual Meeting in Boston at the John B. Hynes Convention Center, the Marriott Boston Copley Place, and Sheraton Boston, as well as in the virtual world for those unable to attend in person. After the

2021 AIChE ANNUAL MEETING

past year, bringing together our engineering community has never been so critical. This hybrid meeting is being designed to bring you the best of both worlds, and will take place over a two-week period, from November 7-11 in person and from November 15-19 virtually.

As everyone knows, nothing beats a live experience and we look forward to offering an excellent program in Boston. But it's important to us that we provide a virtual experience too. Our in-person sessions will be recorded and made available for viewing on the virtual platform for all attendees. So whether you "fly, drive or click in," we are building a great conference.

The program's theme "Building the Bridge in 21st Century Education: Chemical Engineering Industry + Academia" applies now more than ever! Our program includes a special discussion on new learning paradigms and will also encompass AIChE's highest lectures presented by Arup Chakraborty (MIT), Eric Shaqfeh (Stanford) and David Schaffer (UC Berkeley), 700+ sessions programmed by our divisions and forums and topical conferences, including the new program on Material Interfaces as Energy Solutions.

For attendees joining us in Boston, please note that your safety is our primary concern. AIChE is working with the venues to adhere to all local and national directives for social distancing and sanitizing protocols.

For now, keep an eye out for updates by email, social media and our [conference website](). We are happy to answer any questions—just email us at [programming@aiche.org]().

We are excited to see you all in Boston or virtually!

June C Wispelwey

June C. Wispelwey

Executive Director and CEO, AIChE

2020 AIChE Particle Technology Forum Awards

Young Professional Award Sponsored by SABIC

The Multi-Faceted Role of Particle Technology in Advancing Innovation for Sustainable Energy In Response To A Changing Climate

Greeshma Gadikota

School of Civil and Environmental Engineering,

Smith School of Chemical and Biological Engineering

Cornell University

Meeting our rising energy needs while limiting detrimental impacts on climate and environment is crucial for a sustainable future. Innovative, scalable and realizable technologies are needed to achieve congruence in our societal mission of lifting hundreds of millions of people out of energy poverty globally[1] while limiting the rise of global temperatures.[2] Removing legacy greenhouse gas emissions (GHG) from our air and water resources, capturing and storing current GHG emissions from existing energy conversion processes, and advancing the use of new renewable energy resources is crucial for meeting our energy needs in an environmentally sustainable manner. Innovations grounded in the science and engineering of particle technology are essential for translating this vision into a reality.

In this context, we will discuss three examples from the perspective of multiphase chemical interactions and particle technology. First, we discuss the role of fluid-particle interactions in innovative chemical pathways to rapidly remove CO_2 from air via a process known as enhanced weathering. Second, we discuss the role of chemo-morphological coupling during integrated CO_2 capture and removal technologies. Third, we discuss approaches to tune multiphase chemical interactions involved in recovering H_2 from renewable natural gas with inherent carbon removal.

(i) CO_2 removal from air via enhanced weathering – CO_2 is an acid gas and needs a base for capture and removal. Enhanced weathering is one scalable approach to remove CO_2 from air. This approach involves distributing fine particles of Mg- or Ca-bearing silicate minerals in soils and dissolving them to release Mg^{2+} or Ca^{2+} ions into the water present in the soils. Each Mg^{2+} or Ca^{2+} ion captures two molecules of CO_2 from air to produce bicarbonate ions. Distributing these finely ground silicates in soils is known to enhance soil productivity. However, quantifying the rates of cation release, which is directly related to the rates of CO_2 removal is challenged by the formation of silica passivation layers. Since investments in CO_2 removal technologies are closely tied to quantification of carbon and its fate, accelerating dissolution of silicates and developing predictive controls is crucial.

Approaches to address this challenge include developing hybrid technologies to dissolve silicates in ex-situ processes in a tunable manner and distributing these Mg^{2+} or Ca^{2+}-rich fluids in working farmlands (see **Figure 1**). Several advances in our understanding of reactive fluid-particle interactions now facilitate the deployment of this approach. Specific examples include insights into initial rapid release of Mg^{2+} and Ca^{2+} ions followed by slower dissolution rates due to mass transfer limitations,[3] dynamic reorganization of the silica matrix which contributes to these anomalous reactivities,[4] and direct electrosynthesis of acids and bases[5] (as reagents) from brine for on farm deployment.

Role of particle technology in enabling scalable deployment: Smaller particle sizes and higher surface areas are crucial for the rapid dissolution of minerals. Solar-powered milling is a less explored but highly promising approach for grinding silicates in an on-demand distributed manner. New fluid-particle contacting systems (e.g., fixed or differential bed reactors[3]) need to be developed to ensure that the fluid contacting the minerals is undersaturated with respect to the concentration of dissolved Ca^{2+} or Mg^{2+} ions to drive silicate dissolution. Advanced manufacturing strategies are needed for designing the next generation of reactors for the direct electrosynthesis of acids and bases from waste brine.

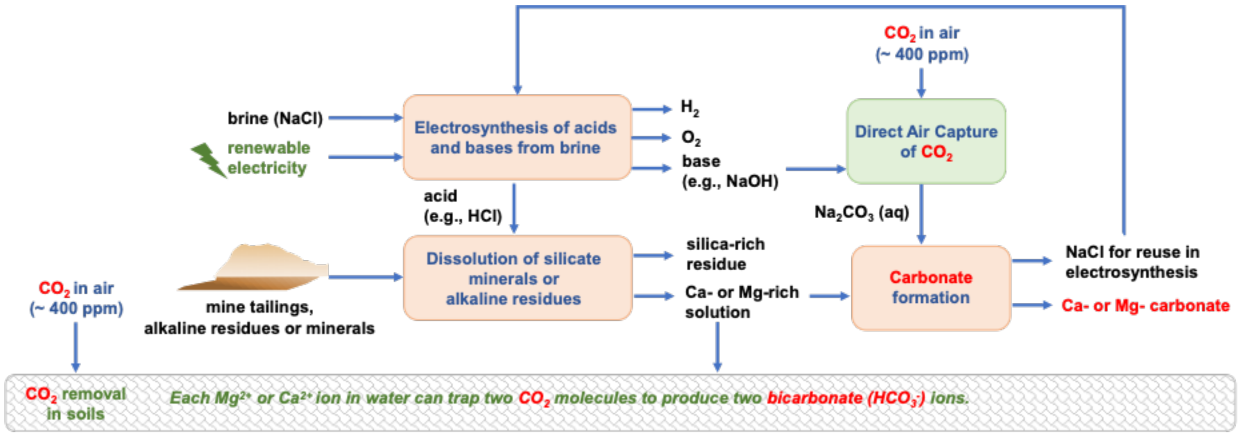


Figure 1. Synergistic integration of CO_2 removal via integrated enhanced weathering and direct air capture of CO_2

(ii) Integrated CO_2 capture and removal via inorganic carbonate formation – Rapid decarbonization of power plants and industries is now possible due to significant investments made in technologies for CO_2 capture and storage (CCS). CCS technologies involve capturing CO_2 via absorption,[6] adsorption,[7] and membrane separations[8] followed by storage in subsurface geologic reservoirs. The availability of suitable geologic reservoirs is crucial for scalable deployment. One less explored alternative is the capture and removal of CO_2 as inorganic carbonates at temperatures < 100°C by harnessing waste heat in a power plant or industrial process and using flue gas concentrations of CO_2. The limiting condition is the low solubility of CO_2 in water. To address this challenge, aqueous solvents are used to capture CO_2. Higher concentrations of bicarbonate and carbonate ions resulting from CO_2 capture facilitate the formation of Ca- or Mg-carbonates and inherent chemical regeneration of solvents.

Our recent studies exploring the feasibility of coupling CO_2 capture and inorganic carbonate formation (also known as carbon mineralization) with inherent solvent regeneration showed very promising results. Near complete conversion of calcium oxide (CaO) and about 70% conversion of magnesium oxide (MgO) to inorganic carbonates was noted using CO_2 capture solvents such as sodium glycinate (0.5 – 2 M), temperatures of 50-75°C, CO_2 partial pressure of 1 atm and a reaction time of 3 hours is a stirred reaction environment.[9-13] In contrast, less than 50% conversion of CaO or MgO is noted when reacted in deionized water. CaO is abundant in slags and more than 80% conversion of MgO abundant in the solid waste in ductile iron industry. Further, Ca- or Mg-hydroxides recovered from earth abundant silicates can be harnessed as alkaline sources. **Figure 2 (A)** is a schematic representation of this approach.

Several factors need to be considered when evaluating the scale-up of these integrated processes for CO2 capture and carbonate formation with inherent solvent regeneration. First, CO_2 mass transfer into the aqueous phase is dynamically linked to the availability of solvents without CO_2 loading. Solvent availability is in turn linked to carbonate conversions. Developing quantitative relationships between CO_2 capture, carbonate formation, and solvent regeneration is essential for advancing prediction and scale-up. Second, appropriate pH conditions are essential to facilitate CaO and MgO dissolution and carbonate conversions. Third, temperature may have a non-monotonic impact on CO_2 capture and carbonate conversion. Ambient temperature favors CO_2 capture, while higher temperatures favor CaO and MgO dissolution and the precipitation of Ca- and Mg-carbonates. Achieving tunable controls over these multiphase chemical interactions is crucial for the scalable realization of these technologies.

Role of particle technology in enabling scalable deployment: As an alternative to conventional absorbers and regeneration units for CO_2 capture using solvents, new multiphase fluid-solid contacting reactors are needed for integrated CO_2 capture and carbonate conversion pathways. As shown in **Figure 2 (A)**, the three steps of CO_2 capture, carbonate conversion, and solvent regeneration can be integrated into a single process. Alternatively, carbonate conversion and solvent regeneration can be decoupled and the regenerated solvent is recycled for CO_2 capture (**Figure 2 (B)**). Effective reactor designs are crucial for the scalable realization of these integrated technologies.

(iii) Enhanced H_2 with inherent carbon removal – Harnessing renewable energy feedstocks with inherent carbon removal is an emerging approach for carbon-negative energy generation. In this context, producing hydrogen with inherent carbon removal can meet our objective of achieving carbon-negative energy generation. H_2 production via steam methane reforming currently meets more 85% of the demand for H_2. However, every molecule of H_2 generated is accompanied by the evolution of one CO_2 molecule from a stoichiometric standpoint. The inherent capture of CO_2 using Mg- or Ca-silicate minerals to produce inorganic solid carbonates while enhancing high purity H_2 generation is a less explored but highly transformative approach.

The water-gas-shift reaction (WGSR) is the key step involved in H_2 evolution as shown here: $CO + H_2O \quad CO_2 + H_2$. Coupling this catalytic reaction which occurs at 200-250°C and pressures of 10-20 bar with the carbon mineralization of Ca- or Mg-silicates accelerates H_2 evolution while capturing and converting CO_2 as inorganic carbonates.[9] These innovative chemical pathways are built on our prior work demonstrating that Ca- or Mg-silicates can be successfully converted into inorganic carbonates at conditions relevant to the WGSR. **Figure 3** is a schematic representation of this approach and evidence of enhanced H_2 evolution with CO_2 suppression.

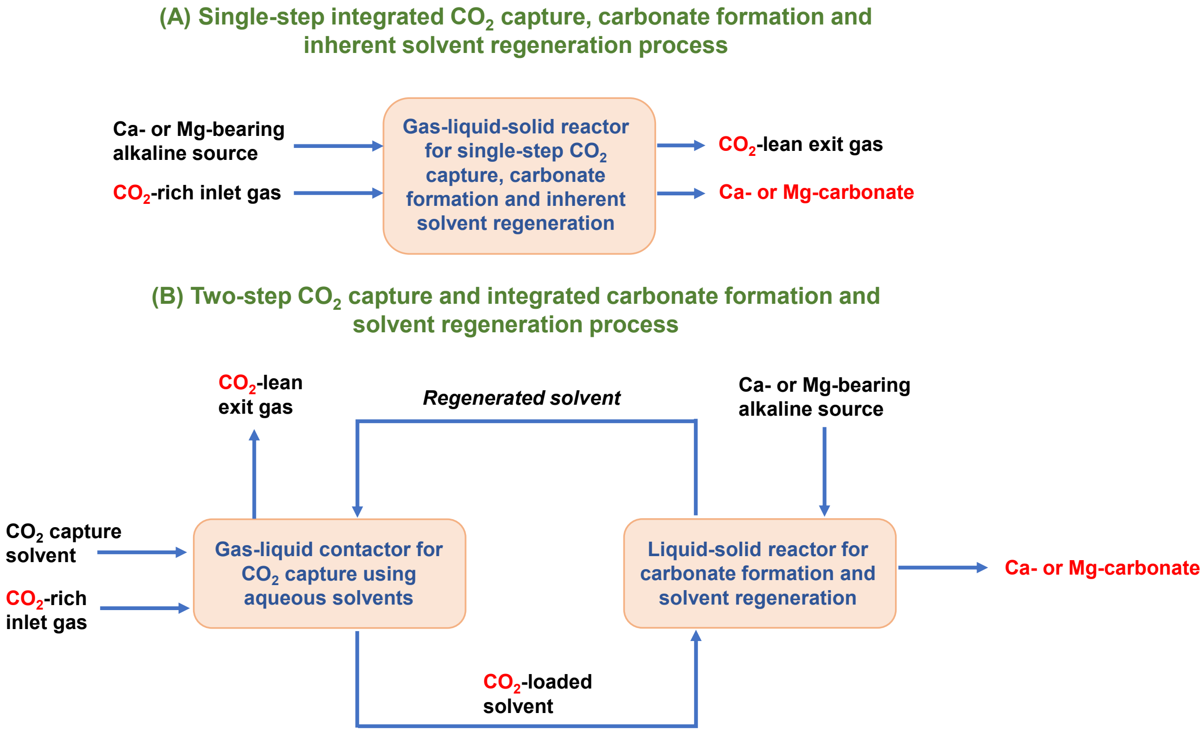


Figure 2. Integrated approaches to capture and convert CO_2 into Ca- or Mg-carbonates

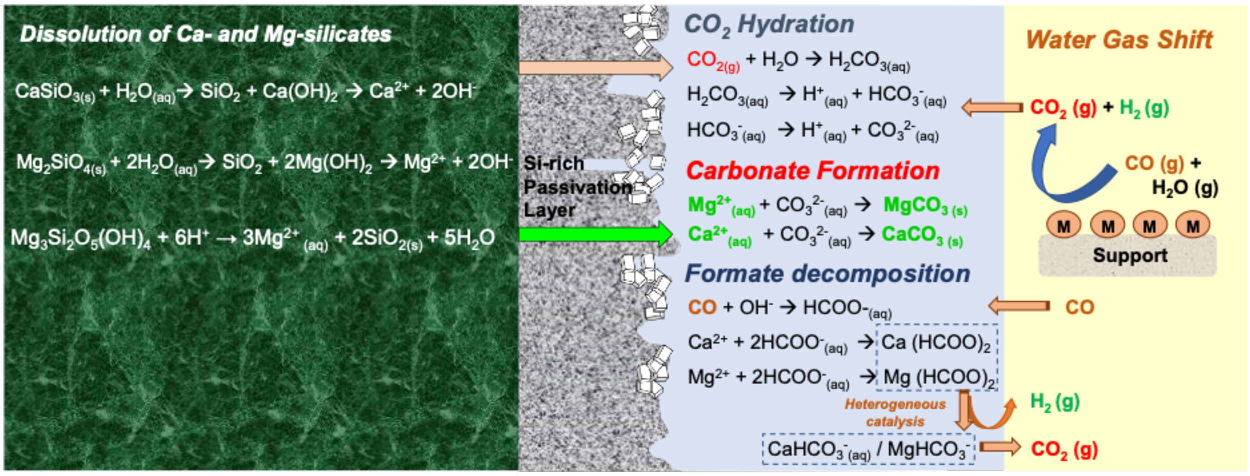


Figure 3. Schematic representation of the integrated approach to produce H2 with inherent CO2 removal via carbon mineralization (as published in reference [9])

Role of particle technology in enabling scalable deployment: As shown in **Figure 3**, several dynamic multiphase chemical reactions occur in tandem including the gas phase catalytic reforming of CO and water vapor to produce CO_2 and H_2, dissolution of silicates and partitioning of CO_2 into the liquid phase to produce inorganic carbonates, and if needed, the breakdown of formates to release H_2. Advances in *operando* characterization of these chemical transformations using advanced scattering and spectroscopy[14,15] now enable us to develop the mechanistic basis underlying these transformations and the conditions leading to high conversions of H_2 with inherent CO_2 removal. This information is essential for developing the next generation of reactive fluid-particle contacting systems for scalable implementation.

The inspiration for these advances emerges from the important contributions made to the science and engineering of reactive fluid-particle interactions within the particle technology community. Specific examples include innovations in chemical looping combustion (CLC) by the late Prof. John Grace[16] and Prof. L. S. Fan[17], and carbon mineralization by tuning fluid chemical compositions by Prof. Alissa Park.[4,18]

As we look to the future, meeting the rising demand for energy is inextricably linked to our ability to harness earth abundant materials. In this article, we discuss the use of earth abundant materials such as magnesium- and calcium-bearing silicates for producing carbon-negative energy carriers, and carbon capture, storage and removal. These technologies for clean energy conversion are highly congruent with energy storage technologies (e.g., batteries) that have a high demand for metals. Thus, advances in efficient, scalable and realizable energy and resource recovery and conversion technologies are inextricably linked to the foundations of particle technology and multiphase chemical interactions.

Acknowledgements

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George Klinzing Best PhD Award Sponsored by University of Pittsburgh On the Development of Microstructure-Based Constitutive Models for Particulate Suspensions

Paul Mwasame

Core R&D, Collegeville, Pennsylvania, Dow Inc.

Overview

Many of the constitutive equations describing the non-Newtonian flow of particle-laden fluids are phenomenological. Leveraging such models for predictive design and material discovery where rheology is a key requirement is difficult because the model parameters lack a clear connection to microscopic variables accessible to formulation scientists. To improve upon this situation, it is necessary to adopt systematic approaches towards realizing microstructure-based constitutive models. Relating the macroscopic stress to features at the microscopic level was a key element of my graduate research efforts under the guidance Dr. Antony Beris and Dr. Norman Wagner at the University of Delaware. Those efforts advanced new approaches, some for the first time, towards developing improved class of models for the rheology of particulate suspensions. The examples highlighted in the material that follows can be found in associated journals articles [1, 2] and the PhD thesis.

Introduction

Particulate suspensions are frequently encountered in a variety of industrial processes and are prominent in many consumer products. Their extensive use can be partly attributed to their unique rheological properties, e.g., yield stress, time-dependent viscosity and shear thinning, that have consequences for end-use consumer applications. Many industrial manufacturing steps also involve the use of process suspensions, further justifying research efforts to understand material flow and rheology through numerical, simulation and modeling studies. The empirical relationships that dominate continuum modeling of suspension rheology are typically specialized to shear flows, involve numerous/unphysical parameters, and/or are inadequate to describe rheological phenomena such as normal stresses. On the other hand, purely microscopic approaches to improve upon these deficiencies have primarily been successful in addressing idealized cases and/or small length/time scales because they are computationally expensive. Therefore, the aim of article is to outline some approaches that can be useful towards developing new and improved constitutive equations with a focus on thixotropic suspensions and emulsions.

Continuum description of material flow

Advances in computational power over the last few decades means that many industrial processes are designed using computer simulations. For flow modeling, computational fluid dynamics is routinely employed. The governing equation underlying this method is the Cauchy momentum balance. The most well-known version of this equation is the Navier-Stokes equation that describes the limit of Newtonian fluids where the extra-stress tensor is proportional to the rate of strain tensor, where the constant of proportionality is the viscosity, $\sigma_{\alpha\beta} = \mu\left(\nabla_\alpha v_\beta + \nabla_\beta v_\alpha\right)$. The presence of nano and micron sized particles in a fluid imparts additional microstructure that requires us to move beyond a constant viscosity as the appropriate transport coefficient. This necessitated the development of a class of models known as generalized Newtonian viscosity models where the viscosity is typically expressed as a function of the shear rate to impart non-Newtonian character to the flow properties, i.e. $\mu \equiv \mu(\dot{\gamma})$. The direct use of a kinematic variable does not allow for a distinction between different types of suspensions that may display the same non-Newtonian flow behavior but for very different reasons. Additionally, the stress tensor in generalized Newtonian models seldom provides correct predictions of normal-stress differences even in simple shear flows. These are only a few of the reasons that necessitate the development of improved constitutive models for the particulate suspensions. Two examples will be discussed in the following to illustrate how to move beyond some of these shortcomings.

Bottom-up approach for a thixotropic suspension with a yield stress

At the heart of the complex flow behavior of thixotropic colloidal suspensions is the buildup and breakup of aggregates under flow[3]. Common thixotropic materials include paint, toothpaste, and ketchup. The non-Newtonian phenomena typically observed in these suspensions may include yield stress, shear-thinning, time-dependent viscosity and viscoelasticity. The flow of ideal thixotropic materials, in the absence of viscoelasticity, is typically modeled using visco-plastic constitutive models infused with a dynamic variable that describes the structural evolution. A generic example of a so-called structure kinetic model is adapted from Mewis and Wagner[4] as

$$\begin{aligned}
&(a)\ \sigma = \lambda(t)\sigma + \lambda(t)\eta\dot{\gamma} + \eta_{\lambda=0}\dot{\gamma} \\
&(b)\ \frac{d\lambda}{dt} = -k_{-}\dot{\gamma}\lambda + k_{+}(1-\lambda)
\end{aligned} \tag{1}$$

The expression for the shear stress reduces to the Bingham model for *lambda = 1*. In addition, *lambda = (0,1)* accounts for structural change due to the impact of shear breakup and Brownian build up. While this model is useful to describe ideal thixotropy, its phenomenological explanation of the underlying structure evolution through *lambda* prevents a clear connection to the underlying microscopic picture. To improve upon this shortcoming, we need a more fundamental development of the microstructure evolution equation that is relevant to the phenomena underlying the time-evolving microstructure. In the case of thixotropic suspensions, this problem is perfectly suited for applying the framework of population balances to describe the evolution of the aggregate size distribution *n(m)* as[5]

$$\begin{aligned}
\frac{\partial n(\mathrm{m},\mathrm{t})}{\partial t} &= \frac{1}{2}\int_0^m \left[a(m-m',m';\dot{\gamma}) + c(m-m',m')\right] n(m-m')n(m')dm' \\
&-\int_0^\infty \left[a(m',m;\dot{\gamma}) + c(m',m)\right] n(m')n(m)dm' + \int_m^\infty b(m';\dot{\gamma})P(m\,|\,m')n(m')dm' - b(m)n(m)
\end{aligned} \tag{2}$$

where *m* is the number of primary particles in an aggregate, *a* and *b* are size and shear-dependent aggregation and breakage kernels respectively, and *c* is a Brownian kernel.

To specialize this approach to thixotropic suspensions with yield stress, aggregation must cease due to dynamic arrest when a space filling network forms. Additionally, a minimum particle size below which breakage is not feasible must be enforced to ensure the result is physically meaningful. Imposing these two requirements as well as the appropriate physics for the rate processes and invoking a monodisperse closure rule allows for the structure evolution equation for the zeroth moment (which is the reciprocal of the aggregation number) as[1]

$$\frac{d\mu_0}{dt} = \underbrace{-\beta\left(\frac{kT\phi_p}{2\mu_s\eta_r^h W\pi a_p^3}\right)\left(\mu_0^2+\mu_{-1/d_f}\mu_{1/d_f}\right)}_{\text{Brownian aggregation}} \underbrace{-\beta\alpha|\dot{\gamma}|\left(\frac{\phi_p}{\pi}\right)\left(\mu_0\mu_{3/d_f}+3\mu_{2/d_f}\mu_{1/d_f}\right)}_{\text{Shear aggregation}} + \underbrace{b_o|\dot{\gamma}|^2\left(\mu_{1/d_f}-m_p^{1/d_f}\mu_0\right)(\theta_0-1)}_{\text{Shear breakage}} \tag{3}$$

All the parameters have a clear physical meaning, relatable to measurable attributes of the system including *W*=Fuchs stability ratio, *a*=primary particle size, *alpha*=collision efficiency, *phi_p*=particle volume fraction, *mu_s*=medium viscosity and d_f=fractal dimension. *Beta* on the other hand, expresses dynamic arrest and the breakage term proportional to m_p expresses the minimum allowable aggregate size. This structure evolution equation can be applied to thixotropic suspension rheology by coupling this to an expression for the shear stress of the form $\sigma=\sigma_y(\mu_0)+\eta(\mu_0)\dot{\gamma}$. Mwasame *et al.*[1] adopted a specific form of this expression and showed good agreement with steady-state and transient experimental data on a model thixotropic suspension. In principle, the aggregation number computed from Eq. (3) can be compared against scattering measurements for further validation. It is also worth noting that the monodisperse closure rule used in developing Eq. (3) is taken for convenience, and more involved closure rules can be invoked to gain deeper insights into evolution of the particle size distribution. This highlights another advantage of the framework.

When compared to the structure kinetic approach, the result in Eq. (3) is shown to be distinct, emphasizing the novelty of utilizing population balances as a basis for thixotropic suspension modeling. The model parameters can be related to physicochemical attributes of the suspension particles implying potential use in inverse design. The immediate utility of this work is the availability of a microscopically inspired evolution equation for microstructure that can be used in constitutive equations for thixotropic suspensions that admit a structural variable.

Top-down approach for a macroscopic model of emulsion rheology

A Non-Equilibrium Thermodynamics (NET) framework is a robust and scalable approach for developing constitutive equations for a number of reasons: (1) the resultant relationships are applicable to general flows, (2) a single unifying framework provides both the structural evolution equation and expression for macroscopic stress, (3) the resultant model can be parameterized by enforcing consistency to know microscopic theory and (4) additional effects such as microinertia that are typically ignored can be incorporated into flow models.

The details of applying the NET formalism are somewhat involved but the principles are relatively straightforward. The first step is to describe the state variables of the system, which for structured fluids are the momentum field, the density field, and the conformation tensor field. For emulsions, the droplet shape is prescribed to be ellipsoidal in which case its principle axes are related to the eigenvalues of the conformation tensor. Next is to define a system Hamiltonian, expressing the total energy of the system, that is a function of the given state variables. For emulsion droplets, the free energy can be represented generically as[2]

$$H = \int \left(\frac{\underline{u}^2}{\rho} + g\left(I_1, I_2\right) + h_s\left(T\right) s_m\left(\phi\right) \right) d\underline{r} \tag{4}$$

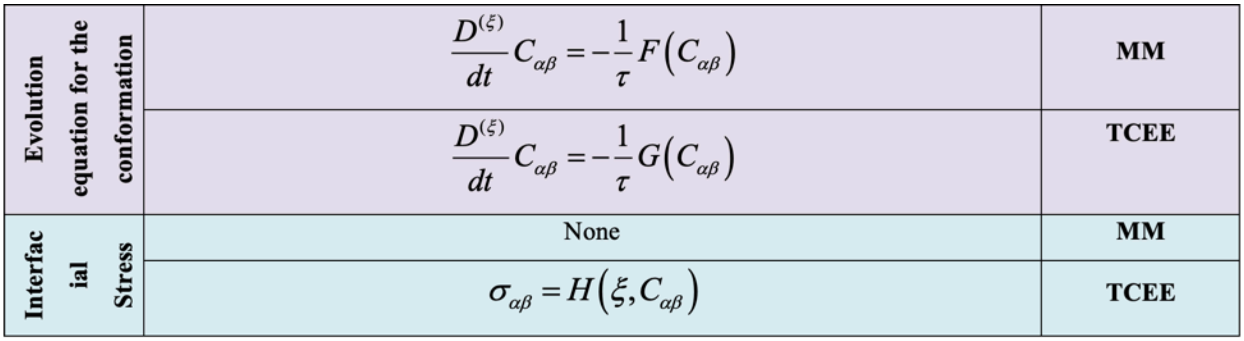
where the first term in the functional is the kinetic energy, the second term is the internal energy arising from droplet deformation out of equilibrium and the third term is an entropic term that will be neglected for the purpose of this discussion. In the interfacial energy term, and are first two invariants of the conformation tensor and depend on the state of droplet deformation. The last step is to generate the dynamic equations through the Poisson and dissipation brackets, expressing the reversible and irreversible dynamics, respectively. The brackets are functions of *F* and *H* and they obey specific symmetry/antisymmetry properties[6] with *H* representing the Hamiltonian (extended free energy) of the system whose form is provided by Eq. (4). Subsequently, the time evolution of an arbitrary function, *F* , is given by

$$\frac{dF}{dt} = \left\{F, H\right\} + \left[F, H\right] = \int \left(\frac{\partial \rho}{\partial t}\frac{\partial F}{\partial \rho} + \frac{\partial C_{\alpha\beta}}{\partial t}\frac{\partial F}{\partial C_{\alpha\beta}} + \frac{\partial u_\alpha}{\partial t}\frac{\partial F}{\partial u_\alpha} \right) d^3 r \tag{5}$$

The second equality above is derived following the standard chain rule of differentiation and provides the connection between the evolution equations for the system state variables and the structure of the brackets. This allows for the conformation tensor evolution equation and the expression of the extra stress tensor to be derived[2]. The latter emerging from the evolution equation of the momentum density field. In general, the Poisson bracket is always well known and exact once the state variables are decided. In contrast, the dissipation bracket is always approximate, requiring modeling of the irreversible dynamics in the system. Its mathematical expression involves phenomenological matrices that express dissipative effects including viscous dissipation, structural relaxation and non-affine effects[6]. Non-equilibrium thermodynamics and continuum mechanics principles (such as the requirement of a local non-negative entropy production rate, the Onsager/Casimir symmetry relations and the principle of material objectivity) can be profitably used to place restrictions on the phenomenological matrices entering the dissipation bracket. In this work, additional restrictions were also placed by leveraging known asymptotic theories for emulsion rheology[2].

To illustrate the power of the result that emerges, a phenomenological model for emulsion droplet dynamics (Maffetone-Minale (MM) model[7]) and the corresponding final result from the NET framework (referred to as TCEE model[2]) are compared superficially in Table 1. Both models predict the evolution equation for the conformation tensor with the only difference being the relaxation term on the right-hand side. The key advantage of the TCEE model, and thermodynamically consistent models in general, over phenomenological, solely structural, models like the MM model is that an accurate expression for the stress tensor arises simultaneously from the NET framework. In contrast, to predict the extra stress tensor using the MM model, one has to apply a separately expression for the stress tensor obtained by Batchelor[8, 9]. This limits its application to cases where the viscosity ratio between the droplet phase and matrix phase is unity. It should also be noted that the NET framework allows for natural extensions to account for additional complexity, for example, the impact of microinertia[10] and Ostwald ripening[11] in emulsions. This further highlights the robustness and versatility of the approach.

Table 1: Overview of functional forms of the MM model[7] and TCEE model[2]. The parameter *Tau* is a relaxation time and *Xi* is the non-affine parameter $\underline{\underline{C}}$. Note that $F\left(\underline{\underline{C}}\right)$ and $G\left(\underline{\underline{C}}\right)$ are distinct



Evolution equation for the conformation	$\frac{D^{(\xi)}}{dt}C_{\alpha\beta} = -\frac{1}{\tau}F\left(C_{\alpha\beta}\right)$	**MM**
	$\frac{D^{(\xi)}}{dt}C_{\alpha\beta} = -\frac{1}{\tau}G\left(C_{\alpha\beta}\right)$	**TCEE**
Interfacial Stress	None	**MM**
	$\sigma_{\alpha\beta} = H\left(\xi, C_{\alpha\beta}\right)$	**TCEE**

Summary

This article has presented a high-level description of two examples that highlight systematic constitutive model development in particulate suspensions. The NET framework is particularly ripe for further innovations, especially in applications where an accurate description of the full stress tensor is required. A key theme is the realization of constitutive relationships for particulate suspensions that incorporate microscopic variables such as the particle size distribution, particle deformation, viscosity ratio and kinetic parameters describing aggregation and breakage processes. Consequently, the models in this work have physically meaningful parameters that can be translated to processing and formulation variables that can be controlled to realize desired performance. Another advantage of microstructural based models is that they help bridge the gap between independent structural and rheological measurements that are now routinely carried out on particulate systems.

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Special Recognition - 2021 Process Development Division Practice Award

Shrikant Dhodapkar, Fellow in Plastics Process R&D at Dow Inc., won the 2021 Process Development Practice Award from the Process Development Division. This award recognizes individuals with outstanding industrial contributions in the practice or application of chemical engineering to process development. He was recognized for innovations, development and implementation of key enabling process technologies for the large-scale production of elastomeric polymers.

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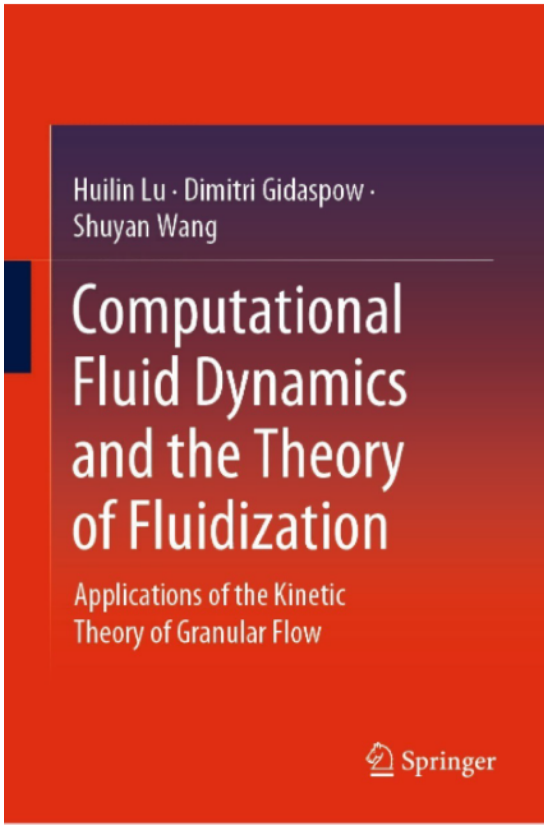

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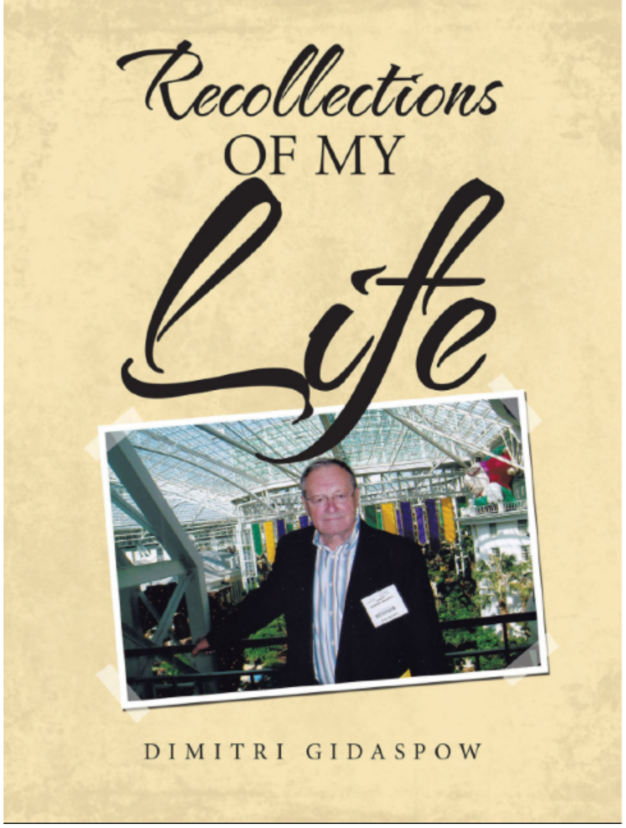

Recollections OF MY Life

DIMITRI GIDASPOW

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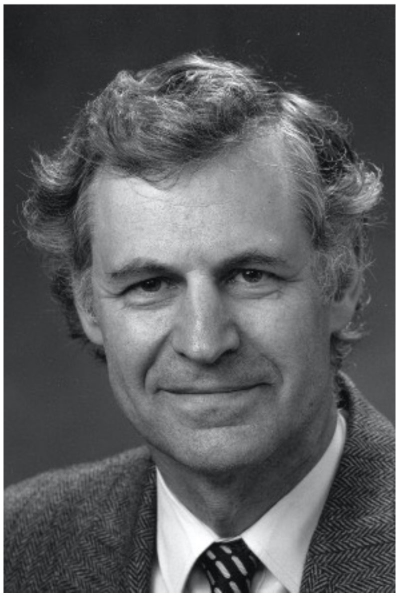
In Memoriam - John R. Grace (1943-2021)



John Ross Grace, one of the leading chemical engineers in Canada and an international figure in fluidization and fluid-particle systems, died in Vancouver on May 26th, 2021, after a long fight with Multiple System Atrophy.

John received his B.E.Sc in Chemical Engineering from the University of Western Ontario in 1965, ranked first in the class. Supported by an Athlone Fellowship, he completed a PhD at Cambridge University, working on the behaviour of bubbles in baffled fluidized beds, supervised by David Harrison and John Davidson. On graduation in 1968, he joined the Chemical Engineering Department at McGill University (Montreal), where he continued research framed by the two-phase model of fluidisation that he had encountered at Cambridge, to investigate bubble coalescence and splitting, particle attrition and entrainment, gas jetting, and reactor modelling incorporating interphase transport. He also developed the wider interest in multiphase phenomena that led to his first book, "Bubbles, Drops and Particles" (1978).

Following a year spent working with SNC, he became Head of the Department of Chemical and Biological Engineering at the University of British Columbia (UBC), a position he filled from 1979 to 1987. He was Dean of Graduate Studies from 1990 to 1996, and oversaw the planning of Green College and St. John's College, as well as a number of interdisciplinary centres/institutes including the Fisheries Centre and the Sustainable Development Research Institute. He was President of the Canadian Society for Chemical Engineering from 1989 to 1990. From 2001 to 2014, he was a Canada Research Chair in Clean Energy Processes at UBC. At UBC, John's research covered broad areas of fluidization and fluid-particle systems. He studied turbulent fluidized beds, circulating fluidized beds, spouted beds, liquid-solid and gas-liquid-solid fluidized beds and membrane reactors, and contributed in topics including choking, reactor modelling and simulation, scaling and scale-up, electrostatic phenomena, heat transfer and gas/solids mixing, particle attrition, tube erosion, coal combustion, biomass gasification, natural gas steam reforming, CO_2 capture by adsorption, and remediation of contaminated soil.

Throughout his career, John pursued comprehensive systematic studies on fluid-particle systems, combining theoretical insights with carefully designed experimental work. He made major contributions to understanding of fluidization (from bubbling through turbulent and fast fluidized beds to dense suspension upflow systems) and spouted beds. He published more than 700 papers, many regarded as classics in fluidization, and trained more than 100 graduate students and postdocs, as well as mentoring numerous visiting researchers. His work contributed tremendously to the advancement of fundamentals and applications of fluidization and particle technology over more than half a century. It has been recognized by numerous awards including the most prestigious International Fluidization Achievement Award (1998), AIChE PTF Lectureship Award (1991) and Thomas Baron Award (2007). John was elected as a fellow of the Canadian Academy of Engineering

(2001) and the Royal Society of Canada (2001), and invested as an Officer of the Order of Canada in 2014.

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The last years of his life were dogged by ill-health, but he kept working productively to the end. His last major work - "Essentials of Fluidization Technology", edited with Xiaotao Bi and Naoko Ellis – was published in 2020. In early 2021, John was inducted into the UBC Chemical and Biological Engineering Hall of Fame – actually the first person to receive this honour - for his outstanding contribution to society. In May 10-14th, 2021, he participated in the virtual CFB-13 Conference and, as chair of the Award Committee, presented the Fluidization Achievement Awards to three outstanding researchers. At the time of his death, he was still co-supervising a PhD student on electrostatic phenomena in fluidized beds with binary particle mixtures.

Listing someone's professional work rarely captures their significance or why they leave a unique hole. Without being assertive, John set standards for personal and professional performance. The messages received since his death emphasize his generosity and supportive approach - his intellectual and ethical standards made him a role model for younger academics throughout Canada and more widely. Some of the indigenous people of the Pacific North-West hold that you die twice: once when your body dies, and finally when your name is spoken for the last time. John's final death is a long way off.

Xiaotao Bi, Professor at UBC

Roland Clift, Adjust Professor at UBC and Professor Emeritus at University of Surrey

Naoko Ellis, Professor at UBC

Introducing Recently Elected AIChE Fellow from PTF

Ah-Hyung (Alissa) Park is the Lenfest Earth Institute Professor of Climate Change in the Department of Earth and Environmental Engineering, and the Department of Chemical Engineering, at Columbia University, where she also directs the Lenfest Center for Sustainable Energy. Her research focuses on Sustainable energy and materials conversion pathways, with an emphasis on integrated carbon capture, utilization, and storage technologies to address climate change. Park's group is also working on direct air capture of carbon dioxide and negative emission technologies. She has chaired AIChE's Area 3 (Particle Technology) program group, and is a director of the Chemical Engineering Technology Operating Council.

The Next Evolution of Multidisciplinary Collaborations between Industry and Academia

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Abstract

Particle technology is the science and technology related to the production, handling, modification, and use of a wide variety of particulate materials, both wet and dry, in sizes ranging from nanometers to centimeters. New technology drivers demand new materials and new processes that must be better, i.e., faster, cheaper, and sustainable. However, the science related to the handling and processing of particles and powders is far from well understood. Therefore, strong industry-academic collaboration is both a pressing and enduring need. This article highlights the accomplishments of such a collaboration between the Center for Multiphase Flow Research and Education (CoMFRE) at Iowa State University and AbbVie Inc. Several important factors distinguish this model of collaboration from industrial and academic partnerships of the past. CoMFRE focuses on multiphase flow science and is a highly multidisciplinary group, consisting of faculty with a variety engineering and science backgrounds and equipped with many experimental and computational techniques across scales. Focus is also given primarily to problems generic to the chemical industry

and pharmaceutical companies, specifically the drying of potent compounds including Active Pharmaceutical Ingredients (API) in agitated filter-dryers. Finally, the collaboration's utilization of open-source tools has greatly impacted the speed at which the products of research have begun to yield tools ready to impact process engineering decisions.

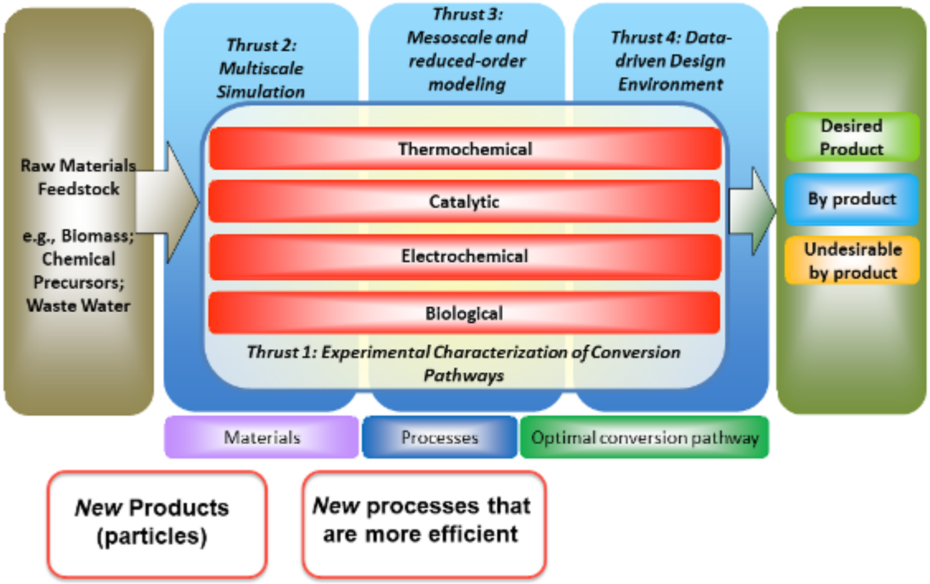


Figure 1. Approach to developing new technology

Challenges posed by technology drivers in particle-based industries

A generic industrial process can be conceptualized as the transformation of raw material feedstock through mechanical and chemical processes into a desired product (see Figure 1). Such processes could rely on biological, electrochemical, catalytic, or thermochemical conversion pathways, and encompass a wide range of multiphase flows. Examples of such processes are thermochemical transformation of biomass into bio-oil [1] [2], synthesis of ammonia from chemical precursors through electrochemical processes [3], algae bioreactors [4] [5] [6] [7], recovery of volatile fatty acids from waste water using specialized particles [8], etc. The processes are designed to obtain desired products and by-products that have to be separated from undesirable products. The design and selection of an optimal conversion pathway could involve the design of new materials or processes. At CoMFRE, several researchers are actively engaged in optimization and design of such pathways.

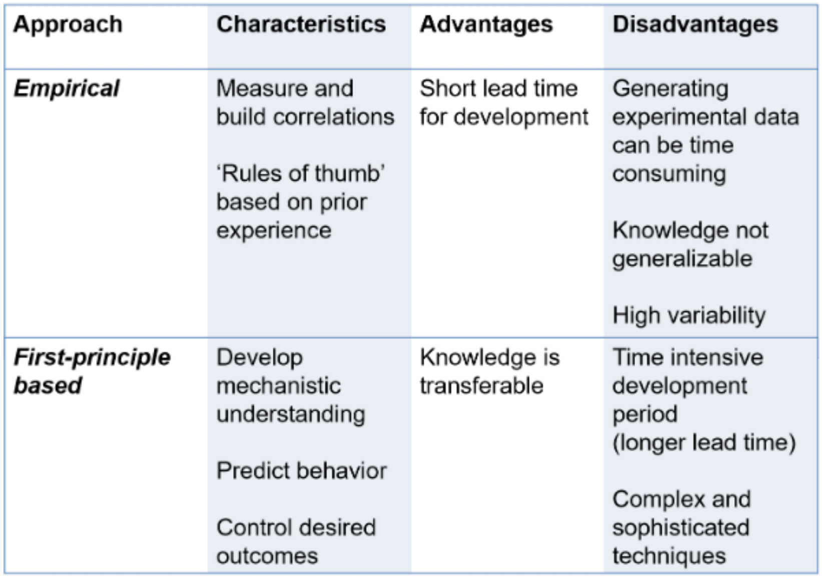
Approaches to addressing these challenges

The principal approaches used to tackle the challenges faced in developing new technologies are generally of two types (see Table 1):

1. Empirical approach,
2. First-principle based approach.

The empirical approach is data driven and endeavors to build correlations and models based on measurements and prior knowledge. These correlations can be generated in a short amount of time, after time intensive experimental data collection. However, the empirical approach is problem-specific. Knowledge transfer can be challenging and variability in the results can be high. The first-principle based approach develops mechanistic understanding and predicts the behavior of the processes. This approach can also be utilized to control desired outcomes of the process. Another advantage of using the first-principle based approach is that knowledge transfer can be effected through rational principles and procedures. However, the development of technology using first-principles is a time-intensive process (longer lead time), and involves complex and sophisticated techniques that can make this approach less desirable. A hybrid approach that combined both approaches in tandem may also be used.

Table 1. Approaches to address challenges posed by technology drivers in particle-based industries



Approach	Characteristics	Advantages	Disadvantages
Empirical	Measure and build correlations 'Rules of thumb' based on prior experience	Short lead time for development	Generating experimental data can be time consuming Knowledge not generalizable High variability
First-principle based	Develop mechanistic understanding Predict behavior Control desired outcomes	Knowledge is transferable	Time intensive development period (longer lead time) Complex and sophisticated techniques

First-principle based approach: Given the complexity of the physicochemical processes (laminar or turbulent, multiphase, multicomponent, reacting flows), multiscale simulations can play a critical role in better understanding and predicting of process performance. However, such simulations are typically very computationally demanding, and mesoscale and reduced-order models (ROM) based on the high-fidelity multiscale simulation database are needed to provide rapid cost-effective predictions. These ROM packages can then be integrated with experimental data into a data-driven design environment (e.g. with Machine Learning) to evaluate the performance of different material and process combinations, and thus select the optimal conversion pathway.

Industries, in general, have a short timeline for development of new materials and processes. On the other hand, academic institutions are encouraged to engage in fundamental research based on first principles that has a longer lead time. Despite these differences, opportunities for fruitful, mutually beneficial collaborations can be identified. Researchers working in industry can formulate the objective of the problem using their expertise and provide necessary guidance and resources to researchers at academic institutions. In return, academia can obtain accurate, first-principle based solutions to industry problems and facilitate synergy of bi-directional technology and knowledge exchange. Here we describe a specific example of this synergy in solving a problem in the pharmaceutical industry.

Problem example: the agitated filter-dryer

Agitated filter dryers (AFDs) are one of the most widely used dryer technologies in the pharmaceutical industry to dry potent compounds including active pharmaceutical ingredients (API). It is used to carry out filtration, washing and drying operations under containment and thus minimizes operator exposure to potent compounds. Drying of potent crystalline and/or amorphous APIs in AFDs is usually one of the longest and most challenging unit operations. The process of drying solvent from the wet cake has to be optimized to control the physical properties of APIs – a critical requirement for most of the downstream drug product processes. Engineers developing drying process in AFDs need tools that can augment process assessment and understanding from laboratory scale experimentation to enable reliable scale-up, especially in AFDs with significantly different agitator designs. Experimental process understanding has been difficult due to a lack of appropriate process analytical techniques (PATs) to understand the dynamics of wet and dry powder as a function of not only the process equipment design but also as a function of operating parameters such as temperature, pressure and mixing. Obviously, a need of larger quantities of highly expensive materials to carry out such experiments at scale also makes it prohibitive. To this end, modeling can provide a viable alternative to reduce experimentation at scale.

Industry needs: One of the pressing needs in the pharmaceutical industry for AFD operation is better control of physical properties during the drying process. Some of the central challenges in the drying process have been predicting and controlling particle agglomeration and/or particle attrition, which exhibit complex dependence on evolving physical properties of the compounds to be dried along with its interaction with solvent(s). In most cases, an intermittent agitation protocol is followed to minimize any impact on particle size distribution (PSD) while improving homogeneity during agitation. Central to the formulation of a drying protocol is understanding the temperature and solvent(s) concentration evolution as a function of various operational parameters. In other words, a model is needed that takes as input particle properties values (APIs or a compound under consideration), solvent properties, agitator geometric design, operating volume and operational parameters, namely the temperature, pressure and mixing profiles. The model then predicts wet cake heating and drying time, as well as particle size distribution, as output (see Figure 2).

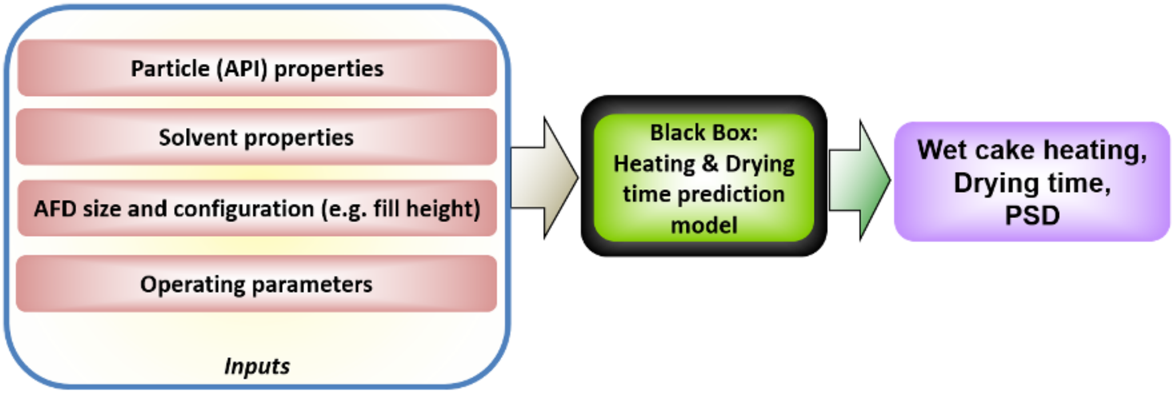
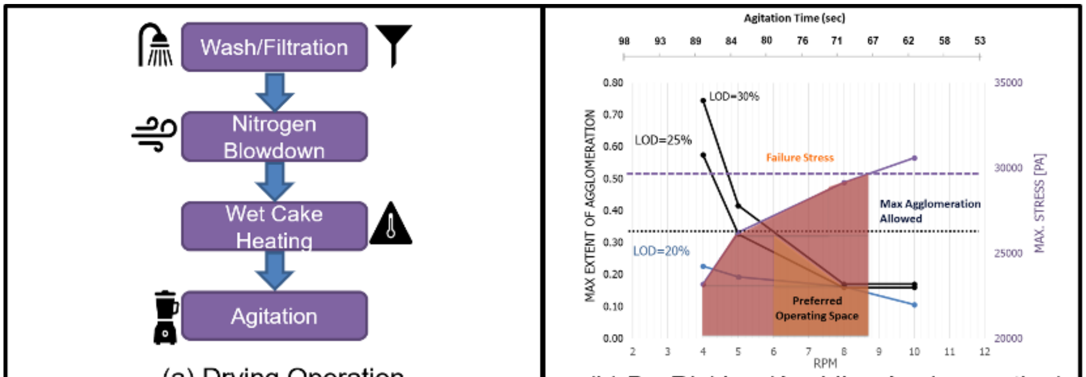
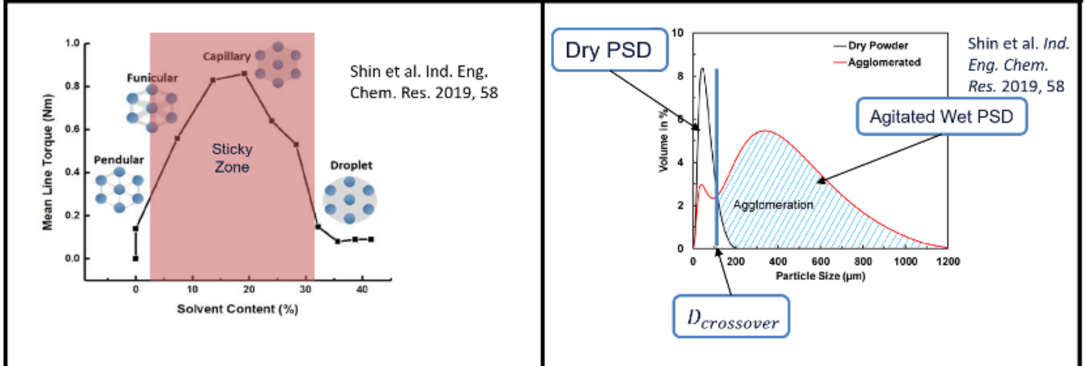


Figure 2. Industry needs describing the influence of design parameter inputs and the need for a drying protocol

Scientific challenges underlying the problem: Figure 3 gives an overview of the drying operation in agitated filter dryers and sheds light on the different scientific challenges faced during the drying process [9]. Initially, the wet cake is washed using a solvent or solvent mixture to remove any mother liquor containing impurities present in the wet cake. The wash solvent retained in the wet cake is in turn removed by the process of nitrogen blowdown. The temperature of heat transfer surfaces (jacketed AFD walls, heated agitator and filter plate as applicable) is gradually increased to facilitate the evaporation of unbound solvent and is called wet cake heating (Figure 3a) . Finally, the dried wet cake is agitated (once the minimum acceptable level of solvent is left in the mixture) intermittently to promote the heat transfer while ensuring homogeneity. Following are some of the challenges commonly encountered during the drying process design in AFDs [10]:



(a) Drying Operation (b) De-Risking (Avoiding Agglomeration)



(c) Sticky Zone (d) Risk of Agitating

Figure 3. The agitated filter dryer problem [9] and the underlying scientific challenges: (a) overview of the drying operation, (b) de-risking (avoiding agglomeration), (c) sticky zone characteristics, and (d) risk of agitating

1. It is very important to avoid agglomeration in order to maintain particle size distribution. This ensures consistent bulk physical properties. Defining target PSD (e.g., maximum allowed extent of agglomeration, see Figure 3b) and understanding crucial information in terms of local solvent content, temperature, and shear is critical. Minimization of agglomeration is also important to speed up the solvent(s) drying by avoiding solvent entrapment.

2. A sticky zone (Figure 3c) characterizes conditions where particles are likely to agglomerate over a range of Loss-On Drying (LOD) or solvent mass fraction. Commonly, instrumentation such as a mixer torque rheometer may be used to quickly characterize the LOD values where particles are more prone to agglomeration as adjudged by torque measurements. It is advised to refrain from any agitation of the wet cake before exiting the sticky zone. While the sticky zone, as developed from laboratory scale torque measurements, does provide qualitative guidance on when to start agitation, it does not provide quantitative assessment of the extent of agglomeration one could encountered at scale. Determination of the agglomeration and/or attrition kinetics as a function of particle dynamics and operational conditions is expected to help with the quantitative prediction of PSD. The sticky zone characteristics together with the extent of agglomeration must be analyzed to make a decision on agitation. While agitation is a key to achieve product homogeneity and accelerate drying, one needs to choose the right mixing intensity to minimize attrition. Understanding the relationship between the particle breakage and the agitation parameters is a key to select appropriate agitator speed and mixing duration.

Evolution of computational approaches:

1. Experiments or Discrete Element Modeling (DEM) simulations can provide data to be used with Machine Learning to create response curves of stresses, mixing time, PSD, temperature, and LOD. These response curves can be used to develop heating and drying time prediction models that will act as a black box.

2. Particle count in industrial sized AFDs is in the trillions or more. While experimentation could be highly expensive, DEM could also become infeasible. On the other hand, continuum models can accurately predict the flow and handle design changes to geometry and operating conditions at significantly reduced computational time and cost enabling the modeling of large scale AFDs.

3. Continuum modeling can add tremendous value for interrogating multiphase systems, because they tend to be cheaper than DEM at production scales and do not require time-consuming calibration. The open-source continuum modeling software OpenFOAM [11] [12] can be used to perform 3D simulations of cohesive granular flow with heat and mass transfer considerations. Multiple 3D OpenFOAM simulations along with a modest number of experiments/DEM can be used to generate data. Experimental measurements can be leveraged to provide the necessary transport closures. The other way is to approach the problem as a scale-up from individual particle scale information to the continuum, informed largely by DEM. These data can be used for Machine Learning to create a response curve to understand the dependence of wet cake heating and drying times on wet cake and particle properties. The response curve can be used to develop the black box for heating and drying time predictions (see Figure 4).

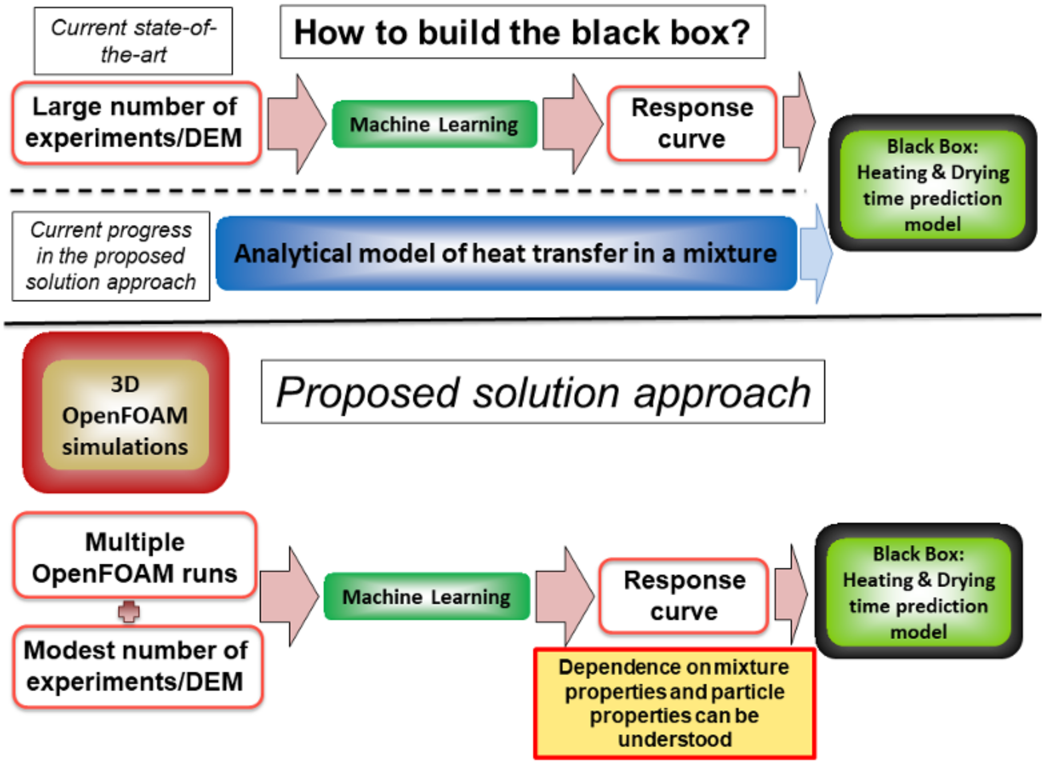


Figure 4. Different approaches to building the black box

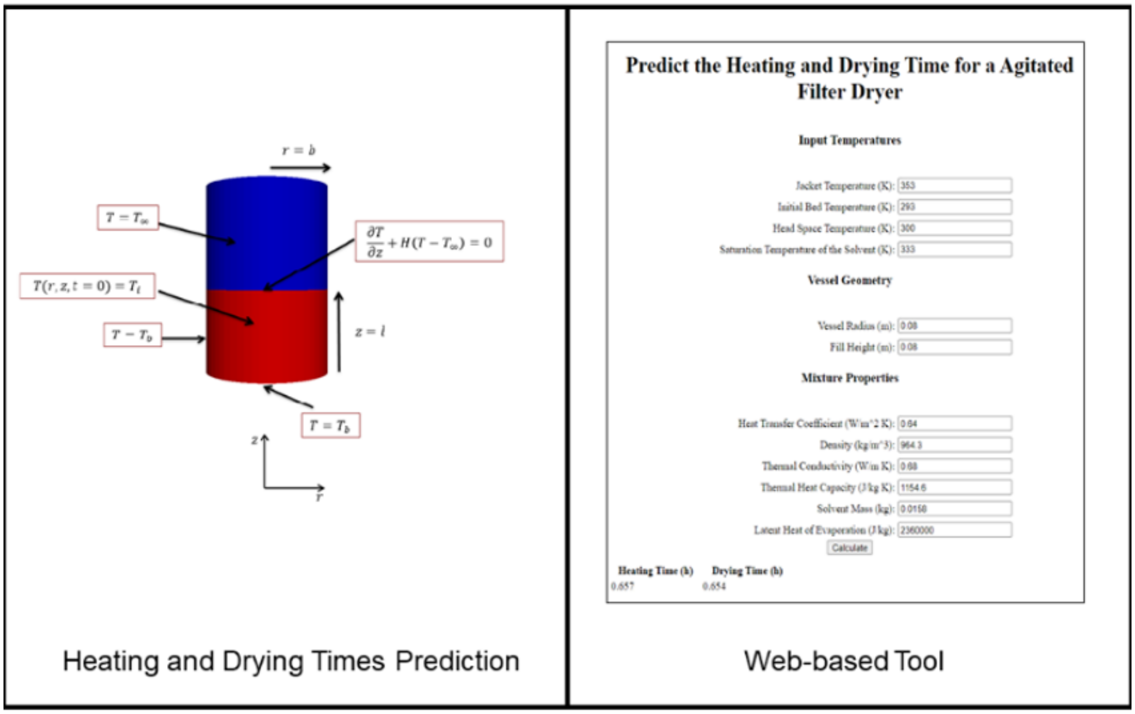
4. In order to verify the OpenFOAM code, an analytical model of heat transfer in a mixture has been developed to predict the evolution of temperature and solvent content. As a preliminary solution, this axisymmetric 2D analytical model in cylindrical coordinates can serve as the black box. However, it lacks intricate details such as location of hotspots (if any), and spatial distribution of the solvent. A homogeneous time-dependent separated phase model has also been developed, which can account for phase properties.

AbbVie and CoMFRE are working together to develop low cost, web-based tools to aid process engineers in exploring the bounds of operation to thoroughly understand the risk of agglomeration and attrition. CoMFRE has provided an analytical solution to heat and mass transfer in AFDs that has been deployed to engineers at AbbVie as a web-based tool to design a drying protocol. 3D multiphase heat and mass transfer simulations are required to understand sticky zone characteristics where particles are likely to agglomerate as a function of LOD or solvent mass fraction. Researchers at CoMFRE are also working on 3D multiphase continuum heat and mass transfer simulations so that drying process details are well-understood.

Web-based tool

An analytical model [13] to estimate time to escape the sticky zone has been developed by CoMFRE at Iowa State University (see Figure 5). The drying process in AFDs was divided into two stages: heating with no evaporation and phase change at constant temperature. The model predicts time to dry unbound solvent and provides transient and spatial information such as temperature and

LOD distribution. The analytical model for drying is deployed internally at AbbVie as a web-based model to provide democratized access to predictions. The web-based tool requires small scale measurements of material properties like heat capacity and thermal conductivity. The predictions can be further improved through Machine Learning by training on device-specific CFD campaign data.



Heating and Drying Times Prediction

Predict the Heating and Drying Time for a Agitated Filter Dryer

Input Temperatures

Jacket Temperature (K): 353
Initial Bed Temperature (K): 293
Head Space Temperature (K): 300
Saturation Temperature of the Solvent (K): 333

Vessel Geometry

Vessel Radius (m): 0.08
Fill Height (m): 0.08

Mixture Properties

Heat Transfer Coefficient (W/m^2 K): 0.64
Density (kg/m^3): 964.3
Thermal Conductivity (W/m K): 0.68
Thermal Heat Capacity (J/kg K): 1154.6
Solvent Mass (kg): 0.0158
Latent Heat of Evaporation (J/kg): 2360000

Heating Time (h)	Drying Time (h)
0.657	0.654

Web-based Tool

Figure 5. Web-based tool for heating and drying times prediction

Industry-academia multidisciplinary collaboration

The continual introduction of new materials and processes drives the production of new products that are manufactured in faster, cheaper, and more sustainable ways, but the science related to the handling and processing of particles and powders is far from well understood. This gap can be filled with a proactive collaboration between industry and academia.

Industries need a decision environment that can be achieved by integration of simulation software and data inputs to develop sustainable materials and efficient processes. They also need design tools to solve more difficult inverse problems that provide the necessary engineering insight from terabytes of information (Information to Insight – I2I). Academic research provides theories, mechanisms, models, and algorithms that can be used to integrate simulation software and data inputs to make decisions. It also provides analysis tools including experimental protocols to solve challenging inverse problems [14] [15]. Academic research can also help with dealing with information explosion (Big Data). Therefore, industry and academic institutions have to work together to address the challenges in developing new particle technology solutions.

It must be stressed that an additional important development has greatly impacted such collaborations: an explosion in access to high quality open-source software and tools. Open-source software underlays much of what has been discussed in this newsletter, from CFD, to Python-based webservers, to quickly deployable Machine Learning packages, and even the version control systems used in development and deployment. Such tools are indispensable for delivering cost effective, scalable, and maintainable solutions, where enterprise tools fall short.

The AbbVie-CoMFRE collaboration for solving the difficulties that pharmaceutical companies face in the drying operation of potent compounds including various APIs in agitated filter-dryers is a great example of this new multidisciplinary collaboration. The problem was introduced to CoMFRE because it has over 25 faculty working in some aspect of multiphase flows, including particle technology, with a wide range of computational and experimental expertise. The problem also has applications in other industries, and the solution procedure can easily be applied to other problem types, which is an industry-academia win-win.

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