James R. Fair Process Science & Technology Center

TEXAS The University of Texas at Austin

Spring 2020 Newsletter

In This Issue:

Note from the Program Head

https://sites.utexas.edu/pstc/

Greetings from shelter in place. I'm currently sitting at the desk in my home office trying to keep up with my graduate students. Thank goodness for ZOOM. The next several months will be "interesting." We are teaching all summer course on-line which will include my summer offering of the separations processes course. If you know a college student who needs course credit for that course, let me know. One of the few advantages of on-line courses is their scalability and universal availability.

As you know, we cancelled the spring PSTC meeting (I have attached a picture of bluebonnets for those of you who sadly missed the April central Texas wildflowers). To enhance our communication with you during this unusual time, Lauren and I have expanded the newsletter content to promote access to on-going research efforts by our PIs. We have included a list of research group URLs which is always your best link to the PIs efforts. The PSTC/SRP is doing well so far. We anticipate that the fall will be a difficult time for our sponsors but we remain hopeful that companies will renew their support for 2021 / 2022. There will continue to be a need for talent and relevant industrial research after the current challenges go away.

One issue we will continue to face is age-related issues with our pilot plant support equipment. The engineering college generously supported a major rework of our cooling water system last summer and we will need to address the steam system piping shortly. To paraphrase my doctor, congratulations we've lived long enough to have age-related equipment problems. I was counting recently, and this is year 34 of the PSTC / SRP pilot operation so we are probably due some replacement parts and pieces.

I continue to be impressed with the students we attract to UT and the PSTC / SRP research program. Right after the first of the year, we conducted a dividing wall column experimental campaign, which required 24-hour coverage over 5 days of operation. We had a visiting scholar from the Technical University of Munich, two of my graduate students, and a senior undergraduate working all sorts of interesting hours. In each case, they volunteered so they could benefit from the unique experience our pilot scale equipment provides. As hiring levels tighten due to the economic slowdown, my sales pitch would be that our students have unique experience that gives them an advantage over the competition. Please contact me if you have specific hiring needs.

cont. →

Program Head Note cont.

We look forward to visiting with you once again in the fall. In closing, I will add a word of thanks to all the corporations, including some of our sponsors, who have responded to the pandemic. My wife is an ICU nurse so I was especially thankful for corporate innovation that supplied ventilators and PPE to the health care industry.

Best wishes – stay safe,

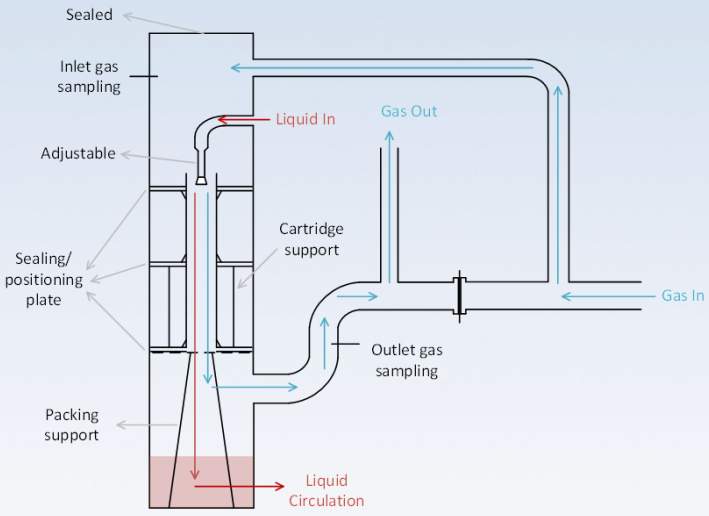
Bruce

SRP Update: Frank Seibert

As expected, the coronavirus has significantly impacted the SRP operations. Prior to the mid-March research shutdown, pilot activity was high. Insulation of the new stainless cooling water piping has been completed which insulation repairs throughout the plant.

The pilot plant was active with several distillation and air/water related packing studies. We are excited about the upcoming release of new high performance random packing data. The divided wall distillation column was also restarted and operated during February and March. The study was focused on the application of advanced control strategies.

Co-current gas film mass transfer controlled spray studies are resuming which include a significant amount of experimental variations. The study will use a modification of the air/water column to allow for co-current contacting (see figure below left). The Air/SO2/0.1 N NaOH test system will be used in these gas film mass transfer controlled studies. Three spray nozzle types (Full Cone, Flat Cone and Hollow Cone) and various contacting heights will be included.



Modified Air/Water Column for Co-Current Spray Studies

The capacity of a liquid-liquid extractor can be limited by poor drop coalescence at the main operating interface. This is especially true for many "wash" type extractors. In the 1990s, an SRP study was conducted to investigate the performance of Teflon and stainless structured packings in enhancing coalescence and increasing extractor capacity. In some cases, the coalescer addition increased the capacity by 60%. In recent years, new questions regarding coalescer designs have emerged which suggest that a larger study is needed. Such questions include:

- Can Teflon random packing provide a cost efficient alternative to Teflon structured packing?
- Are less expensive polypropylene packings as efficient as Teflon packings?
- What coalescer height is recommended?
- What capacity increase should be expected with a coalescer addition?
- What coalescer material of construction should be specified?

cont. →

SRP Update cont.

Many other related questions have been raised in the last ten years. Several PSTC sponsors have recently proposed that we explore the possibility of forming a group of PSTC sponsors which provide technical guidance and leveraging of their Tier II funds to support this study.

Interest in the SRP oil/water membrane separations process continues to increase with multiple projects planned in 2020. The studies involve a collaboration with Professors Lynn Katz and Kerry Kinney. A PhD graduate student, Carolyn Cooper, will also participate in these studies. A successful field test was completed in early December in treating produced water from an eagle ford site. The Kuwait Foundation of Science recently is currently funding a three-year study. The effects of differing oil concentrations (50-250 pm), surfactant types and micron and submicron solids handling are planned in the study. The study includes continued treatment of actual produced water.

A few days before the planned coronavirus-related shutdown at UT, T&R Chemicals of El Paso, Texas, made an emergency request that we recover three different chemicals (α-pinene, β-pinene and α-terpineol) in very high purity (>99%) from various pine oil derived feedstocks. Dr. Antonio Garcia of AMACS helped to facilitate the study. The pure chemical samples are needed by two Minnesota labs to determine their viability in killing several pathogens including Klebsiella Pneumoniae and Staphylococcus Aureus (MRSA), Pseudomonas Enterica, Hepadnaviruses (Hepatitis B), and Severe Acute Respiratory Syndrome (SARS CoV-2 Coronavirus that causes CORVID-19 disease). The applications will cover the uses for fabric cleaning and hard surface disinfection for Non-food Contact Sanitizers, water soluble powders/liquids and spray products. These chemicals will also be used to treat agricultural diseases affecting the US citrus and Italian olive industries. With the support of Dr. John Ekerdt, Associate Dean of Engineering, the UT Vice President for Research approved an exemption allowing the study to continue during current research shutdown. α-Pinene and β-Pinene are established antiviral, anti-fungal, and anti-microbial chemicals in the medicinal field. There are numerous NIH papers addressing their effectiveness. The α-terpineol is used to enhance the mixing and effectiveness of the pinenes in killing the pathogens.

Pure samples of α-pinene (99.4%), α-terpineol (99.8%), and β-pinene (99.2%) have just been obtained and have been shipped out on Tuesday, April 21, four weeks from the start of the project. Each of the chemicals were recovered from gum turpentine feedstocks obtained from Mexico and Georgia. The chemicals were purified using batch distillation from a complex mixture of 30 components. Many of these components have boiling points similar to desired chemicals.

These chemicals are not commercially produced in such high purity. T&R Chemicals is revamping their manufacturing facility to allow for their production and a new packed column will be installed this summer. Discussions are underway to assist T&R Chemicals with scale-up and demonstrating the optimum operation.

2020 SRP pilot plant and lab scale operations will include:

- Gas Film Controlled Spray Mass Transfer
- Dividing Wall Distillation
- Distillation Packing Characterization of Unique Structures
- Application of NIR to Obtain Fast Distillation Compositional Measurements
- Air/Water Packing Characterization
- Oil/Water Membrane Separations
- Batch Distillation to Obtain High Purity Chemicals from Pine Oil Feedstocks

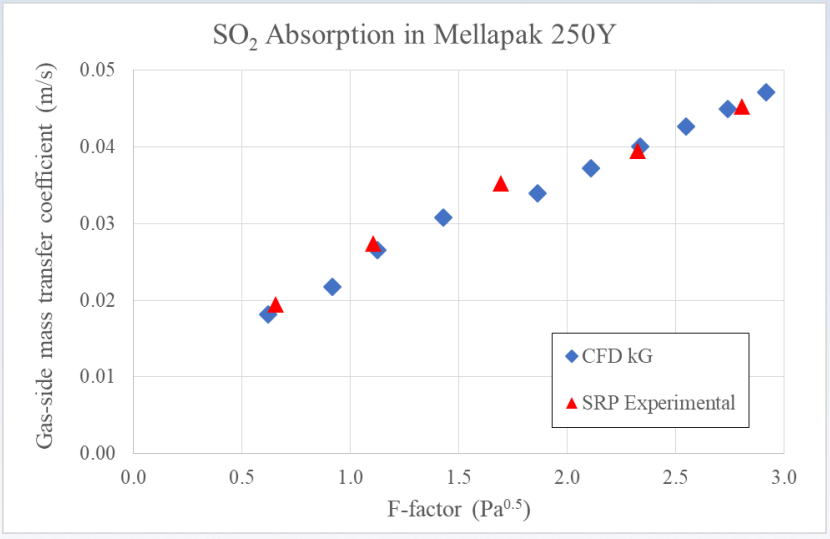
Research Updates from the Eldridge Group

Jeffrey Weinfeld

Reactive Dividing Wall Column: The reactive dividing wall column (RDWC) is an emerging chemical process technology that uses process intensification concepts to integrate chemical reaction and multicomponent separation into a single vessel with the goal of saving energy and money compared to traditional process. While other intensified processes such as dividing wall columns (DWCs) and reactive distillation columns (RDCs) have seen commercial success, a lack of open-literature experimental studies and validated models have prevented potential industrialization of RDWCs. In this research, the RDWC is being analyzed using the aldol condensation of propionaldehyde, a test chemical system with potential to be operated in an RDWC and displays many complex phenomena typical of industrial chemical systems. To ensure an accurate model, the phase equilibria of the chemical system was experimentally determined. Next, using batch and continuous reactors, the kinetics of the reaction system was investigated and modeled. Before experimenting on an RDWC, the system was first investigated in an RDC to validate a reactive distillation model and inform RDWC operation and design. The RDC was constructed at laboratory scale using Oldershaw distillation glassware. After a successful experimental campaign, the column was modified to an RDWC. Experimentation and modeling of the RDWC is in progress with initial success. Key contributions to the literature expected at the end of the project are an experimentally validated RDWC model, a large amount of experimental RDC and RDWC data, and a framework for transitioning a new process from an RDC to an RDWC using lab-scale experimentation and modeling to inform design.

Luke Macfarlan

Structured Packing Mass Transfer Predicted via CFD Simulation: This project is focused on predicting mass transfer for structured packings using computational fluid dynamics (CFD). Accurately modeling mass transfer is essential to predicting the performance of vapor-liquid contactors and developing superior packing designs. For Mellapak 250Y structured packing, CFD simulations predicted the gas-phase mass transfer coefficient for SO_2 absorption from air into caustic solution. This process was chosen because the SRP had historically performed experiments with the system and experimental data was available to validate the CFD simulations. Over F-factors ranging from around 0.5 to 3.0 $Pa^{0.5}$, the CFD simulations exhibited an average deviation of 2.9 percent from the SRP experimental values, showing excellent quantitative and qualitative agreement. Future work includes predicting the gas-phase mass transfer coefficients as well as liquid-phase mass transfer coefficients for a variety of packing geometries. These studies will advance efforts to improve and optimize structured packings, maximizing throughput for vapor-liquid contactors and minimizing operational costs.



Eldridge Group Research Update cont.

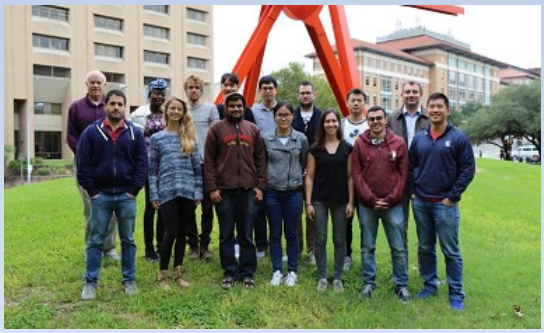
Mikey Phan

Structured Packing Hydraulic Performance Predicted via CFD: Semi-empirical models such as the Rocha-Bravo-Fair, Delft, and Billet-Schultes models represent the current state-of-the-art in predicting the hydraulic and separation performance of structured packings. However, these models are derived from experimental data that cover a limited range of operating conditions and chemical systems, thus precluding them from being truly predictive.

To develop a more robust and predictive hydraulic model for structured packings, computational fluid dynamic (CFD) modeling is being utilized to provide greater insight into the multiphase flow physics present inside these packings. Specifically, this study focuses on the observations of transitional and laminar flow structures inside simplified Representative Elementary Units (REUs) of structured packing predicted via CFD modeling of industrially relevant chemical systems. Consequently, the impact of these transitional and laminar flow observations on hydraulic model development will be elucidated.

Finally, CFD studies that analyze the ability of de facto standard turbulence models to capture transitional and laminar flow effects are currently underway. These turbulence models used extensively in the open literature to model flow physics inside structured packings may fail to capture transitional and laminar flow effects properly and thus potentially produce significant errors in predicted pressure drop values.

Baldea Group Research Update



While keeping at a safe distance, the Baldea Group at UT has been hard at work modeling the outbreak, and we may even have a few answers to pressing questions. Ever wondered how the evolution of the COVID-19 pandemic can be predicted? Or if the outbreak can be controlled? Head on to arXiv to read about the latest findings in Calvin and Fernando's paper (the link is here for reference: https://arxiv.org/abs/2004.06291).

We used the latest data from multiple countries to estimate the parameters of the epidemic model, Kalman filtering to estimate the number of exposed and asymptomatic people, and moving horizon optimal control to find the best social distancing policies for the US. Spoiler alert: "bang-bang" control seems to be the best policy for containing infections while minimizing social and economic disruption.

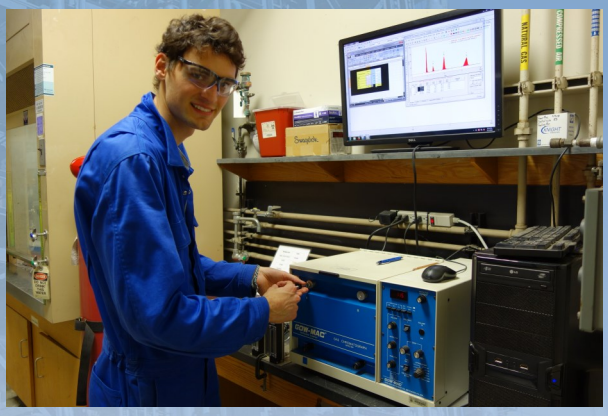
PI Research Websites

Stay up-to-date on each principal investigator's research by visiting their research websites here:

- Michael Baldea: http://sites.utexas.edu/baldea/
- Bruce Eldridge: https://sites.utexas.edu/eldridge/
- Mahmoud El-Halwagi: https://chenelhalwagi.engr.tamu.edu/
- Benny Freeman: https://membrane.ces.utexas.edu/
- James A. Ritter: https://sc.edu/study/colleges_schools/engineering_and_computing/faculty-staff/ritterjim.php
- Gary Rochelle: https://rochelle.che.utexas.edu/
- Frank Seibert: http://sites.utexas.edu/pstc/separations/

Student Spotlight: Johannes Hamacher

In this edition of our newsletter, we are focusing our spotlight on one of our visiting students, Johannes Hamacher, who has conducted research in the PSTC facilities this academic year. Johannes is originally from Garching, a small town north of Munich in Germany. He earned his bachelor's degree in chemical engineering at the Technical University of Munich in 2018 and is currently working towards his master's degree in chemical engineering.



Johannes chose to study chemical engineering because it was a mixture of the two fields he was most interested in—mechanical engineering and chemistry. In his undergraduate classes, he enjoy learning process design and thermal processes so he has focused his master's classes on those subjects. It was his undergraduate thesis and internship with Linde Engineering that directed him toward distillation columns.

While working as a visiting student at UT Austin, his major research project is to obtain dynamic data with PSTC's divided wall column. Johannes states, "This data is used to verify dynamic simulations and to test a new control structure to maintain the purity of the side product on a high level." He notes that control structures are an integral part of every process and the ability to model and work with control structures for such a complex model was a completely new area for him.

As part of his master's program at the Technical University of Munich, Johannes spends the third semester abroad doing a research stay at a university for five months. He was fascinated by the pictures and publications about the experiments at the PSTC. In his previous experiences, he had only worked with the system air/water and air separation and he could not pass up an opportunity to work on a pilot plant scale column and actual chemicals.

In looking at the outlook of this area of research, Johannes remembers a process designer at Linde Engineering who said that there are three rules for designing separation processes: the first is try distillation columns; the second is thinking about whether distillation columns could work; then third is asking yourself whether you're sure distillation columns don't work. Johannes says that as energy efficiency becomes more important, highly integrated processes such as dividing wall columns are needed to minimize energy costs, thus the need for a focus on those three rules as he progresses in his work.

When not focusing hard on his research in the lab, Johannes has enjoyed weekends at Zilker Park on the beach volleyball courts. The skill level of the pick-up games was very good and enjoyed improving his volleyball skills while here in Austin. He also had an opportunity to meet and join different Christian fellowship groups in the evenings. Johannes notes that the diversity of small Christian churches in Austin doesn't exist in Germany and he has really enjoyed the various discussions and interpretations of the Bible while meeting new friends in fellowship.

All in all, Johannes has had a memorable and impactful stay in Austin. The Process Science and Technology Center has been delighted to host Johannes and looks forward to his progress in his work and studies in Germany!

Publications

- J. Lu, H. Zhang, J. Hou, X. Li, X. Hu, Y. Hu, C. D. Easton, Q. Li, C. Sun, A. W. Thornton, M. R. Hill, X. Zhang, G. Jiang, J. Z. Liu, A. J. Hill, B. D. Freeman, L. Jiang, and H. Wang. "Efficient Metal Ion Sieving in Rectifying Subnanochannels Enabled by Metal-Organic Frameworks," *Nature Materials* (2020). DOI.

- G. Q. Chen, K. Wei, A. Hassanvand, B. D. Freeman, and S. E. Kentish. "Single and Binary Ion Sorption Equilibria of Monovalent and Divalent Ions in Commercial Ion Exchange Resins," *Water Research*, 175, 115681 (2020). https://doi.org/10.1016/j.watres.2020.115681
- J. Park, H. W. Yoon, D. R. Paul, and B.D. Freeman. "Gas Transport Properties of PDMS-coated Reverse Osmosis Membranes," *Journal of Membrane Science*, in press. https://doi.org/10.1016/j.memsci.2020.118009

- C. G. Rodriguez, M. Chwatko, J. Park, C. L. Bentley, B. D. Freeman, and N. A. Lynd. "Compositionally Controlled Polyether Membranes via Mono (μ-alkoxo) bis (alkylaluminum)-Initiated Chain-Growth Network Epoxide Polymerization: Synthesis and Transport Properties," *Macromolecules*, 53(4), 1191-1198 (2020). https://doi.org/10.1021/acs.macromol.9b02318

- B. D. Freeman. Editorial: "Polymer: Looking Forward," *Polymer*, 192, 122312 (2020). https://doi.org/10.1016/j.polymer.2020.122312

- H. W. Yoon, T. H. Lee, C. M. Doherty, T. H. Choi, J. S. Roh, H. W. Kim, Y. H. Cho, S.-H. Do, B. D. Freeman, and H. B. Park. "Origin of CO_2-philic sorption by Graphene Oxide Layered Nanosheets and Its Derivatives, *Journal of Chemical Physics Letters*, 11, 2356-2362 (2020). https://pubs.acs.org/doi/10.1021/acs.jpclett.0c00204

- E.-S. Jang, J. Kamcev, K. Kobayashi, N. Yan, R. Sujanani, T. J. Dilenschnieder, H. B. Park, D. R. Paul, and B. D. Freeman, "Influence of Water Content on Alkali Metal Chloride Transport in Cross-Linked Poly(ethylene glycol) Diacrylate. 2. Ion Diffusion," *Polymer*, 192, 122316 (2020). https://doi.org/10.1016/j.polymer.2020.122316

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- M. R. Landsman, R. Sujanani, S. H. Brodfuehrer, C. M. Cooper, A. G. Darr, R. J. Davis, K. Kim, S. Kum, L. K. Nalle, S. M. Nomaan, C. P. Oden, A. Paspureddi, K. K. Reimund, L. S. Rowles III, S. Yeo, D. F. Lawler, B. D. Freeman, and L. E. Katz, "Water Treatment: Are Membranes the Panacea?," *Annual Review of Chemical and Biomolecular Engineering*, in press.

- J. D. Moon, M. Galizia, H. Borjigin, R. Liu, J. S. Riffle, B. D. Freeman, and D. R. Paul, "Modeling Water Diffusion in Polybenzimidazole Membranes Using Partial Immobilization and Free Volume Theory," *Polymer*, 189, 122170 (2020). https://doi.org10.1016/j.polymer.2020.122170

- J. M. Pérez-Francisco, J. L. Santiago-García, M. I. Loría-Bastarrachea, D. R. Paul, B. D. Freeman, and M. Aguilar-Vega. "CMS Membranes from PBI/PI Blends: Temperature Effect on Gas Transport and Separation Performance," *Journal of Membrane Science,* 597, 117703 (2020). https://doi.org/10.1016/j.memsci.2019.117703

cont. →

Publications cont.

- A. J. Hill, A. W. Thornton, R. H. J. Hannink, J. D. Moon, and B. D. Freeman. "Role of Free Volume in Molecular Mobility and Performance of Glassy Polymers for Corrosion Protective Coatings," *Corrosion Engineering Science and Technology*, 55(20), 145-158 (2020). https://doi.org/10.1080/1478422X.2019.1701237

- K. A. Stevens, J. D. Moon, H. Borjigin, R. Liu, R. M. Joseph, J. S. Riffle, and B. D. Freeman. "Influence of Temperature on Gas Transport Properties of Tetraaminodiphenylsulfone (TADPS) based Polybenzimidazoles," *Journal of Membrane Science*, 593, 117427 (2020). https://doi.org/10.1016/j.memsci.2019.117427

- B. D. Freeman. "Reflecting on 12 Years as I&EC Research Associate Editor," *Industrial & Engineering Chemistry Research*, 58, 21171-21172 (2019). https://doi.org/10.1021/acs.iecr.9b06082

- C. Miguel Sanchez, T. Song, J. Brennecke, and B. Freeman. "Hydrogen Stable Supported Ionic Liquid Membranes with Silver Carriers: Propylene and Propane Permeability and Solubility," *Industrial & Engineering Chemistry Research*, in press. https://doi.org/10.1021/acs.iecr.9b04886

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