NDnano
Notre Dame Nanoscience and Technology

NDnano Summer Undergraduate Research
2021 Project Summary

1. Student name & home university: Tipton Lichtenstein from University of Florida

2. ND faculty name & department: Professor Alexander Dowling, Chemical and Biomolecular Engineering

3. Summer project title: Molecular and process design framework for the separation, recycling, and reuse of hydrofluorocarbon mixtures

4. Briefly describe new skills you acquired during your summer research:
Through my summer research, I expanded on my programming abilities. For example, I learned to effectively use the terminal, GitHub and other applications related to coding within a team environment. Additionally, it was my first experience with process modeling and simulation, so it helped me learn more about the academic approaches to these types of problems.

5. Briefly share a practical application/end use of your research:
The research I conducted could have large implications for the future of the battle against global warming as it seeks to find a way to reduce the emissions of high global warming potential HFCs.

6. 50- to 75-word abstract of your project:

An increasing amount of attention has been placed on HFC refrigerants due to their ozone depletion potentials and global warming potentials. Addressing this concern, we seek to create a framework to optimize HFC separation processes and develop methods for screening ILs for HFC separations allowing recycling and reuse of HFCs. We utilize experimental data and molecular simulations to model and optimize a process system for the separation of R-410A at scale while remaining economically viable.

7. References for papers, posters, or presentations of your research:

[1] United Nations Environment Programme. Ozone Secretariat. (2006). The Montreal Protocol on Substances that Deplete the Ozone Layer. UNEP/Earthprint.
[2] American Innovation and Manufacturing Act of 2020. Environmental Protection Agency. (2020). Consolidated Appropriations Act, 2021. H.R.133.
[3] The Kyoto Protocol. UNFCCC. (2005). Greenhouse Gas Data.
[4] Lei, Z.; Dai, C.; Zhu, J.; Chen, B. Extractive distillation with ionic liquids: a review, *AIChE J.* **2014**, *60*, 3312–3329.
[5] Pereiro, A.; Araujo, J.; Esperança, J.; Marrucho, I.; Rebelo, L. Ionic liquids in separations of azeotropic systems - a review. *J. Chem. Thermodyn.* **2012**, *46*, 2–28.
[6] Morais, A.; Harders A.; Baca K.; Olsen G.; Befort B.; Dowling A.; Maginn E.; Shiflett, M.B. Phase Equilibria, Diffusivities, and Equation of State Modeling of HFC-32 and HFC-125 in Imidazolium-Based Ionic Liquids for the Separation of R-410A. *Ind. Eng. Chem. Res. AIChE J.* **2020,** *59, 40,* 18222-18235. doi: 10.1021/acs.iecr.0c02820
[7] Shiflett, M.B.; Yokozeki, A. Solubility and diffusivity of hydrofluorocarbons in room-temperature ionic liquids. *AIChE J.* **2006,** *52*, 1205-1219. doi:10.1002/aic.10685
[8] Befort, B.; DeFever, R.; Tow, G.; Dowling, A.; Maginn, E. Machine Learning Directed Optimization of Classical Molecular Modeling Force Fields. **2021,** arXiv:2103.03208

One-page project summary that describes problem, project goal and your activities / results:

In recent years, an increasing amount of attention has been placed on CFC and HFC refrigerants due to their ozone depletion potentials (ODP) and global warming potentials (GWP). Due to the risks posed by their continued use, there have been international attempts to curtail the usage of specific CFCs with high ODPs, such as the phase-out of R-22 (Freon) as laid out within the Montreal Protocol [1]. Additionally, the EPA has plans to reduce the overall HFC production and imports by 85% within the next 15 years [2]. This presents an issue as there are thousands of tons of HFC compounds in use that are set to be phased out in the foreseeable future. Furthermore, although HFCs do not have high ODPs like their CFC counterparts, many have high GWPs. For example, R-410A, a commonly used ternary near-azeotropic HFC mixture of R-32 and R-125 with a GWP of 2088 [3], is scheduled for phase-out under current environmental regulations. Thus, the need for separating azeotropic HFC mixtures into their components is apparent as these separations would reduce the emissions and waste from HFCs. In the case of R-410A, the components could be recycled.

However, there are currently no methods to feasibly achieve azeotropic separation of HFCs due to either unrealistically high energy requirements or lack of adequate separating agents. Through experimental trials, it has been demonstrated that ionic liquid (IL) entrainers have the potential to selectively separate certain azeotropic mixtures into their components [4,5]. Furthermore, Shifflett and coworkers collected experimental data for the solubility of HFC compounds within ILs and have created an ASPEN simulation demonstrating an IL-enabled extractive distillation process that selectively separates an HFC mixture [6, 7]. However, the study primarily focused on a single IL and HFC. To make these results applicable to a wider range of HFC mixtures, the next step is to evaluate the ability of custom IL entrainers to break azeotropic HFC mixtures.

To address this gap, we seek to create a framework to optimize HFC separation processes and develop a method for screening ILs for HFC separations. This framework would help avoid the trial-and-error process that might otherwise be required to determine which IL entrainer is best suited to each HFC mixture. In this context, my NDnano summer research project has focused on establishing tests for the heat integration network to ensure the process is operating with the lowest possible heat input and number of exchangers. This has enabled us to verify the process is accurately reporting the cost for utilities and to evaluate the economic impact of these separations.

As ongoing work, we utilize experimental data and molecular simulations [8] to model and optimize a process system for the separation of R-410A at scale while remaining economically viable. Through this work, we model the VLE of R-410A with IL entrainers and then predict the ternary phase behavior of R-32 and R-125 from binary solubility data to within 10% error of the compositions. By using binary data, we avoid expensive experiments with ternary mixtures in favor of relatively inexpensive solubility experiments. Then, I compared the volatilities of four custom ILs based on binary/ternary phase data, which was another focal point of my NDnano research. This volatility study will serve as one of many methods for screening ILs for HFC separations in the future.