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Notre Dame Nanoscience and Technology

NDnano Summer Undergraduate Research
2020 Project Summary

1. Student name & home university:

Erick J. Mendez Rios – University of Puerto Rico at Mayaguez

2. ND faculty name & department:

Edward J. Maginn Chemical and Biomolecular Engineering
Alexander Dowling Chemical and Biomolecular Engineering

3. Summer project title:

"Integration of 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:

Over the summer I learned how to use the Cassandra software package for molecular simulations. I also learned how to use Jupyter notebooks to visualize and analyze data. I also familiarized myself with Python programming. In addition to these technical skills, I refined my time management, organizational, and project management skills since my project was composed of other small projects that had a set timeline.
I also gained an insight into how refrigerant technology changes over time and how the market is impacted by this.

5. Briefly share a practical application/end use of your research:

This research can result in the development of novel methods to separate refrigerants with low global warming potential from refrigerants with high global warming potential. This can lead to the widespread use of refrigerants with low global warming potential and may lead to the adoption of novel refrigerants in the market.

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

The goal of this project is to develop tools and processes that enable the separation of high and low global warming potential HFCs. To achieve this, we conducted molecular simulations to compute the density of four different ionic liquids and compared them to experimental data. Next, we optimized solubility simulations to allow us to simulate the solubility of ionic liquids mixed with HFCs. Finally, we are attempting to predict the vapor-liquid-equilibrium curve of an R-125/R-32 azeotropic mixture.

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

References:

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16: Budhathoki, S., Shah, J. K., & Maginn, E. J. (2015). Molecular Simulation Study of the Solubility, Diffusivity and Permselectivity of Pure and Binary Mixtures of CO2 and CH4 in the Ionic Liquid 1-n-Butyl-3- methylimidazolium bis (trifluoromethylsulfonyl) imide. *Industrial & Engineering Chemistry Research*, 54(35), 8821-8828.
19: Raabe, G. (2013). Molecular simulation studies on the vapor–liquid phase equilibria of binary mixtures of R-1234yf and R-1234ze (E) with R-32 and CO2. *Journal of Chemical & Engineering Data*, *58*(6), 1867-1873.
20: GasServei (2019). R-32 Technical Data Sheet.
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One-page project summary that describes problem, project goal and your activities / results:

Refrigerators and heat pumps use refrigerant as a medium to transfer heat between two spaces. Prior to the late 1980s, refrigerants often contained chlorofluorocarbons, but these materials were phased out due to their high ozone depletion potential. This led to the development of hydrofluorocarbon mixtures, which were released to the market as a replacement. These mixtures do not deplete the Earth's ozone layer, but many are potent greenhouse gases with much higher global warming potentials than CO_2 and since 2016 are in the process of being phased out of the market. However, this phase out of is complicated because there are thousands of tons of refrigerant mixtures that contain both low and high global warming potential compounds and many of these mixtures form azeotropes which make them challenging to separate. **The goal of this project is to develop tools and processes that enable the separation of high and low global warming potential HFCs, allowing the recovery and reuse of the low global warming potential HFCs.**

R-125

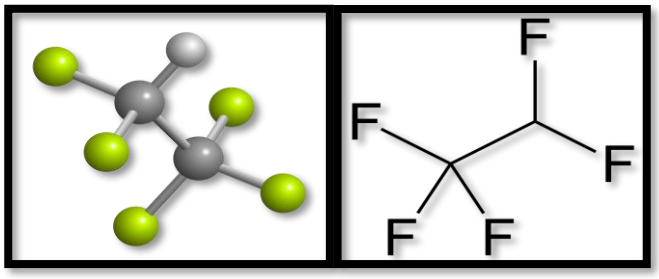

Figure 1: **Pentafluoroethane molecular structure**

R-32

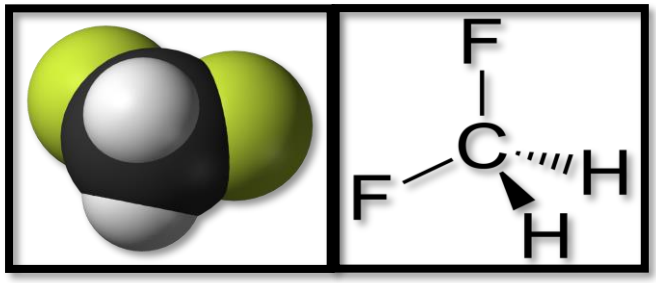

Figure 2: **Difluoromethane molecular structure**

Gibbs Ensemble Monte Carlo Simulation

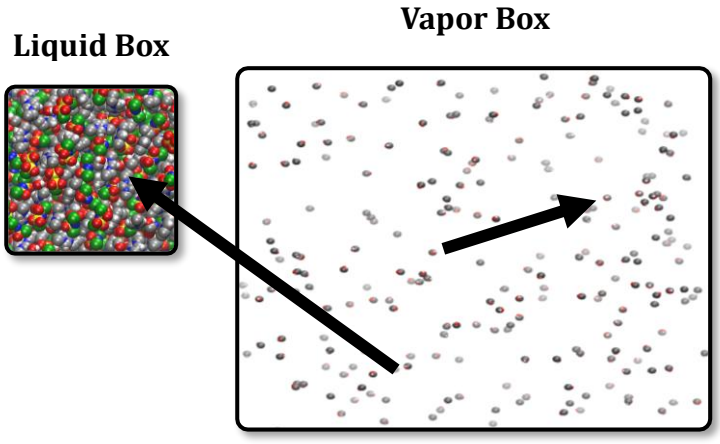

Figure 3: **Simulation schematic**

Initially I used the Cassandra software package to simulate four pure ionic liquids to determine their density and compare the results to the experimental data that was available. This was done to validate the forcefield and decide if we could move on to simulate ionic liquids mixed with hydrofluorocarbons to determine solubility of HFCs in ionic liquids. Since simulating HFC/IL mixtures is computationally expensive, it was necessary to optimize the simulations by minimizing simulation time. For this, multiple combinations of number of simulation parameters, including particle insertion trial moves and intermolecular interaction cutoff values were evaluated by conducting short simulations and observing which of these parameter combinations was most efficient. After this I conducted multiple solubility simulations for mixtures of refrigerants with the ionic liquids at different pressures. This allows us to determine solubility change with pressure change. The solubility simulations were running for about 6 weeks and some finished entirely, however others need more time to equilibrate. Schematics of the efficiency tests and the results for R32-BmimBF4system are provided below.

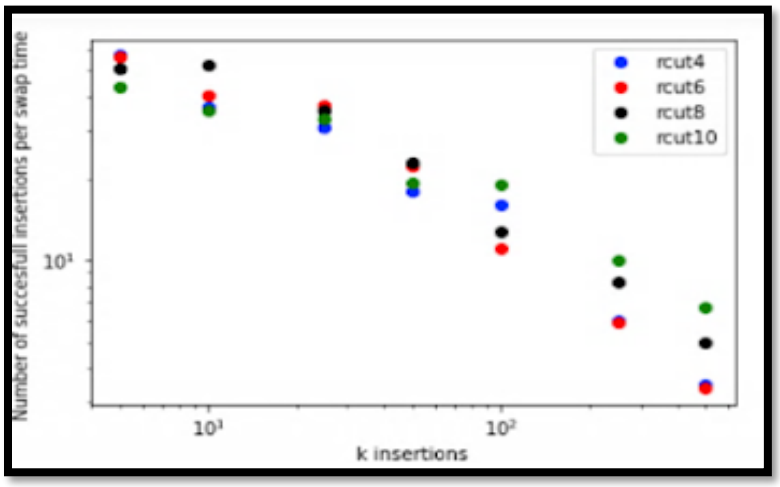

Figure 4: Efficiency results for R-32 / Bmimbf4 mixture.

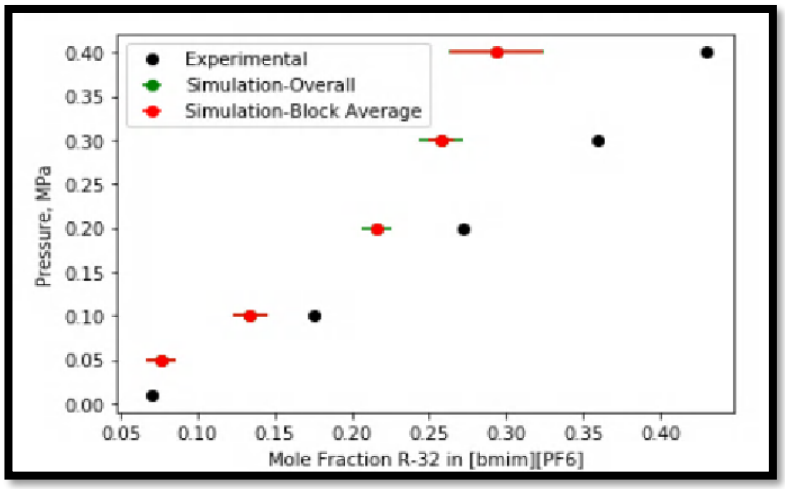

Figure 5: Solubility of R-32 in [bmim] [pf6] ionic liquid

In addition to this we attempted to simulate a vapor liquid equilibrium curve for a system of R-32 and R-125. This was done by running multiple simulations at pressures from 9.0 bar to 11.50 bar from 50% to 90% R-32 composition. A vapor liquid split was identified from the simulations, but future work must be done to ensure proper VLE curve modeling.

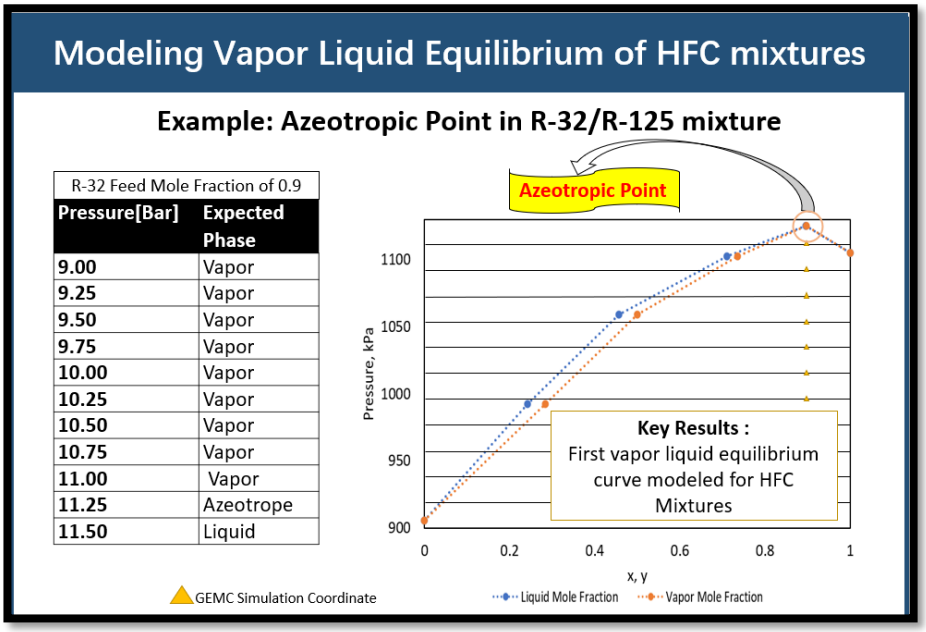

Figure 6: R-32/R-125 vapor liquid equilibrium model

Next steps for this project would be to allow the solubility simulations to run for more time so they can finish equilibrating and then compare these results to the experimental data. For the vapor liquid equilibrium, additional compositions from 10% to 40% R-32 compositions at the specified pressure range must be modeled to determine how effective this method is.