Measurements and Modeling of Binary Adsorption for Separating Refrigerant R-410A

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Mitigating anthropogenic greenhouse gas (GHG) emissions is the most pressing environmental issue facing the scientific community in the 21st century. According to a report published by the United Nations in 2021, global temperatures must decrease by 1.5-2.0 K within the early 21st century to prevent irreversible, global, and catastrophic weather patterns such as severe drought and flooding. Substantial research efforts focused on mitigating and capturing CO_2 are ongoing; however, focus must also be placed on decreasing other atmospheric GHGs including CH_4, NO_2, and fluorocarbons. The heating, ventilation, air-conditioning, and refrigeration (HVACR) industry is among the largest GHG-producing sectors worldwide, producing both direct emissions of fluorocarbon refrigerants and indirect CO_2 emissions from energy demand; therefore, HVACR applications present a promising opportunity for decreasing global GHG emissions. Presently, over 80% of the global refrigerant supply consists of high global warming potential (GWP) fluorocarbon refrigerants, 46% of which is refrigerant R-410A (50/50 wt% HFC-32 (CH_2F_2)/HFC-125 (CF_3CHF_2)).

Hydrofluorocarbons (HFCs) have up to 4,000 times the impact on global warming per mass compared with CO_2; therefore, global legislation is currently phasing out HFCs. The United States (U.S.) American Innovation and Manufacturing (A.I.M) Act in 2020 and the European Union (E.U.) protocol 517/2014 are among the strictest legislative steps implemented to phase down HFCs. The former imposes an 85% reduction of high-GWP HFCs by 2035, whereas the latter was implemented in 2014 and requires a 66% reduction in all fluorinated GHGs by 2030. Approximately 2,800 ktonnes of HFCs are currently in global circulation and will need to be handled responsibly once reclaimed and replaced with next-generation, low-GWP refrigerants. Ideally, the refrigerants are recycled and repurposed; however, the most prevalent refrigerants are either azeotropic or near-azeotropic blends that must first be separated. Refrigerant R-410A has a GWP of 2,256 and must be replaced, but the near-azeotropic blend must first be separated into HFC-32 (GWP=771) and HFC-125 (GWP=3,740). HFC-32 has a low enough GWP to be directly recycled into next-generation HFC/Hydrofluoroolefin (HFO) refrigerant blends, whereas HFC-125 could be catalytically converted into a high-value fluorinated feedstock.

Since R-410A and other HFC refrigerant blends cannot be separated by conventional distillation, other methods are currently being explored, including extractive distillation using ionic liquids, fluoropolymer membranes, and adsorbents. Extensive process design is needed to implement any industrial separation processes, which requires accurate thermodynamic and transport property measurements and modeling. The following presentation focuses on adsorption-based separation of HFC-32 and HFC-125. Both experimental measurements and thermodynamic modeling of binary adsorption have been performed. Vapor-adsorption equilibrium (VAE) data were measured using the Integral Mass Balance (IMB) Method with a new Hiden Isochema XEMIS-003-MC. The experimental methods and results for various zeolites with HFC-32/HFC-125 will be presented and discussed. VAE modeling was performed using Real Adsorbed Solution Theory (RAST) with an adsorbed phase activity coefficient model recently developed by our group, the Spreading Pressure Explicit with Local Interactions (SPLINT) model. The SPLINT model will be presented while emphasizing model behavior consistent with adsorption thermodynamics. The thermodynamic consistency of experimental VAE data will additionally be discussed while presenting RAST model results for binary adsorption of HFC-32/HFC-125.