

Leveraging Competitive Sorption in Microporous Polymer Membranes to Enhance Gas Separation Performance

By Pablo A. Dean

Chemical separations account for roughly half of the United States' industrial energy consumption, 49% of which is attributed to distillation alone. Membrane-based systems, on the other hand, offer a more energy-efficient alternative to conventional separation processes because they do not require thermally intensive phase changes to operate. Specifically, polymer membranes with a more permanent porosity (termed "microporous") have gained attention due to their impressive combination of permeability (throughput) and permselectivity (separation efficiency) relative to the empirically defined "upper bound" for membrane materials.

Traditionally, the permeability of a membrane for a gas is defined by the product of the gas's diffusivity and sorption coefficient in the material. By extension, a membrane's permselectivity can be broken down into the product of its diffusion selectivity and sorption selectivity. Microporous polymer membranes exhibit impressive diffusion selectivity due to their small free volume elements (< 2 nm) and rigid backbones. However, separating gases based primarily on size can become exceedingly difficult given that some gases differ in kinetic diameter by less than an angstrom. Instead, recent advancements in the design of microporous polymers have indicated that a phenomenon known as competitive sorption can be used to enhance separation performance by leveraging gas-polymer interactions instead of differences in gas diffusivity. This thesis investigates how the increase of sorption selectivity through competition between gases can be exploited to enhance the permselectivity of microporous polymer membranes. Specific focus is placed on the archetypal polymer of intrinsic microporosity (PIM-1) and its amine-functional analog (PIM-NH₂) to study how enhanced acid-gas (CO₂ and H₂S) sorption brought on by amine functionality positively impacts separation performance. To confirm the generalizability of these trends, competition effects in the microporous poly(arylene ether) (PAE) backbone were studied as well. To investigate more industrially viable membranes while retaining strong gas-polymer interactions afforded by the amine group, this PAE backbone was also used to develop 8 solution-processable tertiary-amine-functional analogs. Lastly, in an effort to study the effects of water vapor on CO₂-focused separations in amine-functional microporous polymer membranes, a humidified gas permeation apparatus was developed and used to measure dry and humidified CO₂ transport in PIM-1, PIM-NH₂, and a novel secondary-amine-functional analog, PIM-NHiPr. Taken together, this thesis focuses on the fundamentals and practical implications of leveraging competitive sorption to enhance performance in application-relevant and multi-component gas mixtures. More specifically, this work provides valuable insight regarding amine functionalization and its strong effects on sorption energetics and humidified gas transport that will help to inform future design of polymer membranes for gas separations.

Thesis supervisor: Zachary P. Smith

Title: Robert N. Noyce Career Development Professor of Chemical Engineering