Scale-up of Perfluoro(butenyl vinyl ether) (PBVE) and Perfluoro(2,2-dimethyl-1,3-dioxole) (PDD) Copolymers for the Separation of R-410A

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Efficient separation methods are needed for azeotropic hydrofluorocarbon (HFC) refrigerant mixtures that are being phased out by recent legislation. R-410A is an azeotropic mixture consisting of 50 wt% (69.8 mol%) difluoromethane (HFC-32, CH_2F_2) and 50 wt% (30.2 mol%) pentafluoroethane (HFC-125, CHF_2CF_3) that is widely used in air-conditioning applications and will be phased out of use over the next two decades. Membrane technology has been explored in the literature to separate R-410A and other refrigerant mixtures. Amorphous perfluoropolymers have been demonstrated to provide a selective separation for refrigerant mixtures. In this study, copolymers of perfluoro(butenyl vinyl ether) (PBVE) and perfluoro(2,2-dimethyl-1,3-dioxole) (PDD) are used to separate the components of R-410A. Pure gas permeability of HFC-32 and HFC-125 are obtained via the pressure-rise method in a static membrane apparatus. Solubility of HFC-32 and HFC-125 in PDD-PBVE copolymers is obtained with a Hiden Gravimetric Microbalance and is modeled with the Dual Mode Sorption model. Diffusion coefficients for HFC-32 and HFC-125 are calculated by modeling the time-dependent absorption for HFC-32 and HFC-125 into a polymer film and using a one-dimensional Fickian model. A calculated permeability is found from the solubility and diffusivity, as described by the solution-diffusion model and compared with the measured gas permeability. Ideal selectivity was calculated using the pure gas permeability and compared with mixed gas selectivity. To demonstrate the separation on a larger scale, the selective perfluoropolymers are also coated on hollow fiber supports and assembled in a hollow fiber module for mixed-gas selectivity measurements. Correlations for coating thickness as a function of coating velocity were developed via the Navier-Stokes Equation and Landua's Law. SEM imaging was used to obtain experimental values for the coating thicknesses. Results indicate that high ideal selectivity of approximately 20 can be obtained with a 30 mol% PBVE and 70 mol% PDD film. The coating methodologies yield evenly coated fibers with sub-micron coatings well described by Landua's Law. Preliminary results of the scaled-up hollow fiber module show HFC-32 purity of greater than 85 mol%.