

## Hydrogen Separation using Ternary Polymer Blend Compared with the Inorganic High Surface Area Zeolite Materials

Kal R. Sharma Ph.D. PE

Center for Computational Statistics, MS 4A7, Department of Applied and Engineering Statistics, George Mason University, Fairfax, VA 22030-4444

The gas separation of hydrogen by semi-permeable membrane technology can be achieved by the use of ternary, miscible polymer blend of tetramethylhexafluorobisphenol-A-polycarbonate, polyamide and aromatic polyether ketone. Simultaneous increases in permeability and permselectivity can be achieved. Mesoscopic simulations were performed to understand the permselectivity in porous inorganic high surface area materials such as zeolite. This was compared with the polymeric membrane technology. The inorganic materials has well controlled and tailored porosity. In situ separation of hydrogen can be used in fuel cells, underwater gill applications, chemical and biological sensing, neutralization devices, encapsulation applications, encryption of acoustic signature of structures. The permselectivity issues in zeolite material is discussed. Permeability as a function of pore size distribution and tortuosity, is presented for the inorganic high surface area material.

A robust design for membrane using polymeric system that acts as semipermeable membrane for purification of Hydrogen, Methane, Nitrogen and Carbon dioxide from process stream subsequent to cooling the gases was developed. The performance of the process for the purification using the membrane technology was appraised. A mathematical model is proposed for the permeability and permselectivity in polymeric membrane.

Systematic variations of the chemical structure can be used to achieve simultaneous increases in permeability and permselectivity. Systematic variations in the chemical structure and its effect on gas permeability and chain packing in substituted polycarbonates, for example, are proposed in the design of the membrane technology for separating hydrogen from a process stream. This process stream subsequent to cooling, may contain Hydrogen, Carbon Monoxide, Carbon Dioxide and Hydrocarbons. The membrane is proposed to be formulated from a ternary blend of miscible polymers or polymeric alloy. The permeability of Hydrogen can be written as a simple product of an average diffusivity,  $D$ , and an effective solubility,  $S$ , of the penetrant in the polymer matrix:

$$P = D * S \quad (1)$$

For conditions of negligible downstream pressure, the solubility coefficient,  $S$ , is equivalent to the secant slope of the gas sorption isotherm evaluated at upstream conditions. The average diffusivity,  $D$ , provides a measure of the effective mobility of the penetrant in the polymer matrix between the conditions at the upstream and downstream side of the film. The second key index of the performance of the membrane material is the separation factor, or permselectivity,

$$\alpha_{A/B...D} = P_A / \Sigma P_{A...D} \quad (2)$$

The ideal separation factor, by combining the two equations is,

$$\alpha_{A/B...D} = \{D_A S_A / \Sigma D_{A...D} S_{A...D}\} \quad (3)$$

where  $D_A / \Sigma D_{A...D}$  is the diffusivity selectivity, and  $S_A / S_{A...D}$  is the solubility selectivity. The solubility selectivity is determined by the differences in condensibility of the 5 penetrants and by their interactions with the membrane material. The diffusivity selectivity is based on the inherent ability of polymer matrices to function as size and shape selective media through segmental mobility and intersegmental packing factors. The glassy state of the polymeric system can have an influence on the porosity of the macrostructure. Typically there is a tradeoff between permeability and permselectivity. Exceptions are the polyimides, sulfonated aromatic polyether ketones, polyamides etc. Certain structural variations can substantially increase the permeability and permselectivity. Some of the design factors in material selection for the membrane technology include substitutions which inhibit chain packing, rotational mobility, miscibility, compatibility and compatibilizability.

Ternary miscible blends can increase the permeability and the glassy state can improve permselectivity. Chain packing inhibition can increase the permeability and decrease in permselectivity. Incompatibility can decrease the permselectivity and increase the permeability. An optimal can be found by simultaneously inhibiting chain packing and rotational mobility about flexible linkages which can lead to increases in both permeability and permselectivity. Decrease of mobile linkages can increase the permselectivity without decrease in permeability. Compatibilized alloy can improve the chemical stability of the membrane. Hydrophobicity can be increased to prevent the damage from condensibles by configurational manipulation of the polymer backbone. For example, Tetramethylhexafluorobisphenol-A polycarbonate blended with polyamide or with aromatic polyether ketone is an interesting system for the membrane material. When selecting a blend vs copolymer the commercial availability and molecular weight ranges of the products are to be considered carefully. Reversible sorption of the gas can be effected by alloying a salt into the system.

The morphologies of the miscible, immiscible and partially miscible polymer blends are another consideration in the membrane material selection. In a immiscible blend, two phases are present: 1) discrete phase (domain) which is lower in concentration and 2) continuous phase, which is higher in concentration. The miscible polymer blends exhibit single phase morphology. Partially miscible polymer blends may form completely miscible blend at a different concentration. The two phases in partially miscible blends may not have well-defined boundary. Each component of the blend penetrates the other phase at a molecular level. The molecular mixing that occurs at the interface of a partially miscible two-phase blend can stabilize the domains and improve interfacial adhesion.

A multicolumn membrane separator system is proposed for the separation and recovery of all of Hydrogen, Methane, Nitrogen and Carbon dioxide gases from process stream. A cooling stage is proposed to get the gases to temperatures where the polymeric membrane can withstand prior to the separation steps. Multiple sets of membrane separators are selected. For example six of them can be in parallel and may contain a membrane with a high permselectivity for Hydrogen and designated as A beds, B beds three in parallel that in a similar manner can remove the Methane, C beds, three in parallel to remove the Nitrogen and D beds, 2 in parallel to remove the Carbon di-oxide. Each bed of each set goes through a cyclic sequence of diffusion and concentration, adsorption/desorption and other complementary steps. Pressure and Temperature of these reactor systems are interesting variables and as a first approximation not considered as variables in the study.

The process performance was evaluated using design packages such as ECLIPSE and ASPEN. Different process scenarios were evaluated in this manner. The purity level, recovery (%), secondary product in each cycle are the parameters of interest. The waste gases generated has to be accounted for. Purge requirements is another process consideration. The optimization variable is cost. Flexibility of operation is also another salient consideration in this analysis. The number of beds in A, B, C and D were varied in the different scenarios.

The membrane can be formed by dissolution in dipolar aprotic solvents such N-Methyl-2-Pyrrolidone, Dimethyl Sulfoxide, Tetramethyl urea, Hexamethylphospharimide at elevated temperature. These solutions prepared at dilute concentrations of the polymers (about 5%) can be centrifuged and degassed and then the membranes cast onto glass plates. The membranes can be vacuum devolatilized and to remove the residual stress and defects. Thin membranes can be achieved by careful preparation. The permeability and permselectivity of the gases needs to be determined experimentally.

A model for the dependence of polymer structure on the permeability and permselectivity of the membrane is proposed. The different mechanisms such as substitution, miscibility, compatibility, morphology are modeled and the effects delineated. The models for miscibility in ternary blends are improved. The compositions of miscibility and conditions of phase separation can be calculated using the binary interaction model, and Equation of State such as the lattice fluid theory mentioned above. The interrelationships between permeability, permselectivity and polymer phase behavior is proposed to be captured in the model. The role of the morphology of the membrane in general and the glassy state, crystallinity and composition is proposed to be quantified.

The permeability in the inorganic high surface area material such as zeolite can be estimated from the diffusivity calculations. The diffusion through the solids with the macroporous microporous mesoporous distribution is given by;

$$D_{A, \text{tot}, \text{eff}} = D_{A, \text{tot}} \epsilon''/\tau \quad (4)$$

where the tortuosity factor is given by;

$$\tau = s'/\cos 2\phi \quad (5)$$

For example the tortuosity is 2 when  $\phi = 45^\circ$ ,  $s' = 1$ . The experimental range for tortuosity is 1.5-7. The  $\phi$  is the angle of the pores whereby the cylindrical molecules travel a  $\sec\phi$  greater distance. The shape factor  $s'$  is used to correct for the non-cylindrical pores. The average pore radius can be determined from the pores sized distribution. The Kelvin equation relates the capillary radius to vapor pressure at which condensation occurs:

$$P(r)/P_{sat} = \exp(-2\sigma\cos\theta/V_m/RT) \quad (6)$$

where  $\theta$  is the wetting angle

$$r = t + 2\sigma\cos\theta/(RT \ln(P_{sat}/P)) \quad (7)$$

The average pore radius can be determined from the PSD (Pore Size Distribution).

$$r_{psd} = \int r V(r) dr / \int V(r) dr \quad (8)$$

The number of saddle points in the pores size distribution is a measure of the presence of the macro pore, meso pore and micro pores. For pores of uniform size;

$$D_{A,tot,eff} = D_{g,tot} \epsilon^{1/\tau} \quad (9)$$

The total diffusion coefficient (bulk & Knudsen) in fluid phase and the porosity and tortuosity are the key parameters that affect the effective diffusivity. The porosity takes into account the fact that all of the material between the two faces of the solid is not entirely fluid phase. The zeolite material with tailored porosity can be used as a molecular sieve and thus be used in the process to separate the Hydrogen from the process stream. The tortuosity accounts for the case when the distance traveled by the fluid molecule in pore is much greater than distance between the two solid faces. For the trimodal distribution of macropores, mesopores and micropores;

$$D_{A,tot,eff} = \begin{aligned} & (\theta_{macro}^2/1/D_{AB} + 1/D_{A,K,macro}) & (10) \\ & \text{Flow through macropores} \\ & + (\theta_{meso}^2/(1/D_{AB} + 1/D_{A,K,meso})) \\ & \text{Flow through mesopores} \\ & + (\theta_{micro}^2 (1 + 3\theta_{macro})/(1 - \theta_{macro}) / (1 - (1 + N_B/N_A)\gamma_A) / D_{AB} + 1/D_{A,K,micro}) \\ & \text{Flow through micropores + macro/micro series} \end{aligned}$$

The micro-meso cutoff is 15 A and macro meso cutoff is 12.5 nm.

The multicomponent diffusivity was assumed to be the same as the binary diffusivities in the vapor phase with the predominant process being bulk and viscous diffusion. The Knudsen diffusion is accounted for by the collisions with the container walls. The collision integral for diffusion is a function of the Lennard Jones interaction potential parameter and is a simple arithmetic average of the pure component values. The temperature is a strong parameter for the bulk binary diffusion values and the molecular weight is key contributor.

#### Acknowledgments

Kal R. Sharma Ph.D. PE acknowledges Victoria F. Haynes Ph.D., Group Vice President and Chief Technical Officer, BF Goodrich, Brecksville, OH his mentor in industrial research, Richard Turton, Professor, Chemical Engineering, West Virginia University, Morgantown, WV his mentor in academic research, Prof. Nithiam T. Sivaneri, Professor and Associate Chair, Mechanical and Aerospace Engineering, West Virginia University, Morgantown, WV, Prof. Edward J. Wegman, Chair and Director, Center for Computational Statistics, George Mason University, Fairfax, VA, Prof. Eva Marand, Chemical Engineering at the Virginia Polytechnic and State University, Blacksburg, VA, Susan Meek, at the Virginia's Center for Innovative Technology, Hemdon, VA, Dr. Richard Shuford, Branch Chief, Polymers Research Branch at the Army Research Laboratory, Aberdeen Proving Ground, MD and his associates at Independent Institute of Technology.