Facilitated Membrane for Natural Gas Sweetening

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Today, natural gas is sweetened, i.e., cleansed of acid gases – CO_2 and H_2S, primarily through the use aqueous solutions of alkanolamines (primary, secondary or tertiary amines) and of glycols. Absorption of the acid gas, particularly CO_2, into the lean solvent (reactant mixture) is relatively efficient because of the high binding energy. The reaction leads to the formation of both carbamates and bicarbonates. In contrast, considerable energy must be expended via pressure swing, or more commonly and more efficiently via temperature swing to desorb the absorbed and reacted gas. Reactive absorbents of this type present a variety of problems. Among these are (a) the production of corrosion by products because of the corrosive nature of the scrubbing solutions; (b) the relatively high volatility of alkanolamines resulting in vaporization losses; and (c) the high heats of dissolution resulting in energy intensive regeneration of the absorbent solutions. The use of tall gas-liquid contact columns also adds costs due to pumping.

We have developed an enzyme-based contained liquid membrane (EBCLM) design for the efficient separation of carbon dioxide (CO_2) from other gases including methane. This design has many advantages over existing technologies – the materials are not corrosive, evaporation is limited to water, and there is no need to use temperature swings to affect separation.

The initial step in this program was demonstration of adequate performance in a flat sheet design (FS-EBCLM – Table 1). The second step was conversion from a flat sheet design to a hollow fiber design (HF-EBCLM). We generated a cylindrical hollow fiber module consisting of spiral wound assembly of two sets of hollow fiber arrays (Celgard X30-240) separated by a high porosity spacer. One set of fibers is used for transport of the feed - retentate gas the other for the sweep – permeate. The shell side holds the liquid membrane, an aqueous solution containing salts, buffers and the enzyme carbonic anhydrase. The spacer material serves to ensure there is a known distance separating the feed as sweep fibers (i.e. a fixed minimum liquid membrane thickness). This thickness and the nature of the spacer material (porosity and hydrophobicity) affect performance and thus were the subject of considerable study.

Table 1 displays the permeance and selectivities for the first generation HF-EBCLM module containing a 100 µm thick, porous (63% open area), hydrophobic (nylon) mesh spacer. The total membrane area was 360 cm^2 with an area to volume ratio of 20 cm^2/cm^3. This is compared to a FS-EBCLM design having thickness of 330 µm with a annular hydrophilic spacer (100% open area). The total membrane area was 25 cm^2 with an area to volume ratio of 30.3 cm^2/cm^3. Both used the same liquid membrane chemistry. The permeance and selectivities of the HF design were lower than that of the FS design. These results suggested that the presence of the spacer affected performance.

Table 1. Performance comparison of first generation FS-EBCLM to HF-EBCLM.
(Liquid membrane: 3M cesium bicarbonate, 1M glycine buffer (pH=8.59) + 167µM CA)

Gas / Percentage	**Permeance (mol/m^2 s Pa)**	**Selectivity CO_2:N_2**	**Selectivity CO_2:CH_4**
Flat Sheet			
1%, non-flowing LM	$2.70*10^{-7}$	9254	
10%, non-flowing LM	$2.38*10^{-8}$	1879	
2.4% in CH_4, non-flowing LM	$3.22*10^{-8}$		203
Hollow Fiber			
10%, non-flowing LM	$3.10*10^{-9}$	301	
15%, non-flowing LM	$2.34*10^{-9}$	260	
15%, flowing LM	$5.30*10^{-9}$	227	

Table 2 provides the results of studies on the effect of spacer properties on performance as tested in the FS-EBCLM design. These illustrate the significant influence of the spacer. Based on these results we have selected cotton cheesecloth for further study of the effect of spacer thickness on performance in the HF-EBCLM. The results of these current studies will be presented.

Table 2. Effect of spacer properties on FS-EBCLM performance with 0.5 % CO_2 in N_2
(Liquid membrane: 0.075 M phosphate buffer (pH=8.0) + 167µM CA)

Material	**Thickness, (µm)**	**Porosity**	**Permeance (mol/m^2 s Pa)**	**Selectivity CO_2:N_2**
Annular	100	100%		
	330	100%	$1.37x10^{-8}$	301
Nylon tule	350	?? %	$8.00x10^{-9}$	202
Nylon mesh	100	???%	$6.25x10^{-9}$	225
Polyester cloth	330			
Cotton Cheesecloth				

The results to date demonstrate that both the flat sheet and hollow fiber designs based on the EBCLM platform effectively remove CO_2 from mixed gas streams using only a simple partial pressure differential as the driver. The EBCLM platform accomplishes this goal more efficiently than and without any of the adverse effects of amine-based systems. Initial estimates indicate that it also will be far more economical than is the case for amine-based designs.