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## Synthetic Membranes

The level of R&D activity devoted to synthetic membranes has risen rapidly during the past several years. Great progress is being made both in separative capabilities and in the scope of practical applications.\* The trend is especially marked in the field of gas separations, in which at least 20 major companies worldwide are now active. Their membranes are being used in a host of important processes ranging from food preservation to natural-gas processing, refinery operations, and enhanced oil recovery.

A key event in the technology of gas separative membranes was the development by Monsanto of a method of producing tiny hollow polymer fibers, first used practically in 1979. Gases under pressure dissolve in the fiber walls and diffuse through the membrane at different rates. For example, the rates for methane and nitrogen are low, whereas those for moisture, oxygen, carbon dioxide, and hydrogen sulfide are rapid. There is an interesting contrast between barriers that have open tiny holes and those that present a continuous wall. The separation through a barrier with small holes is dependent on the ratio of the square roots of the masses. Thus the separation factor of nitrogen and oxygen is only about 1.07 through the holes, whereas some of the synthetic membranes have a separation factor of more than 7. The synthetic membranes are usually composed of such polymers as cellulosic derivatives, polysulfone, polyamide, or polyimide. The structure of the polymer chain has a dramatic effect on separating characteristics. Bulky side groups create excess free volume within the wall. Moreover, large improvements in separative capabilities are being achieved by altering polymer formulations. Between 1985 and 1988, separative capabilities were increased from 200 to 400%. A recent product announcement by Generon, a subsidiary of the Dow Chemical Company, indicates further substantial progress.

In many instances membrane technology is in competition with existing methods. For example, cryogenic equipment for separations of gases is well established. However, in comparison to other methods membrane equipment often has low capital costs, ease of operation, low energy consumption, operational cost effectiveness, and good weight and space efficiency.

Membranes alone cannot achieve perfect separation of gases, for example, nitrogen from the oxygen of air. However, in one pass through the fibers, the gas is changed from 21% oxygen to a gas containing 2 to 5% oxygen or less. This product is excellent for many applications such as preservation of fruit and grain and for safely blanketing highly inflammable liquids. In grain elevators, a low oxygen content safeguards the grain against rodents and other pests while eliminating danger of dust explosions. Fruit can be maintained in excellent condition much longer in the presence of a low oxygen content than with ordinary air present. At locations distant from a cryogenic plant membrane separation is the simplest, most cost-effective method of achieving the low oxygen content.

Installations of gas separative membranes are increasingly occurring in energy production activities. An initial application was to isolate hydrogen from other components in refinery streams. What may become more important is the processing of gas mixtures that contain methane, moisture, carbon dioxide, and hydrogen sulfide. Such mixtures are present in much of petroleum production, non-associated natural gases, and gas produced in connection with enhanced oil recovery attained through injection of carbon dioxide. Some natural gas contains a quite toxic level of hydrogen sulfide. Both this compound and carbon dioxide are corrosive to pipes, and their level and that of water must be reduced before injection into major pipelines. In the past, many discoveries of natural gas were capped because of excessive content of non-methane gases. Cheaper membrane technology is changing the economics. Carbon dioxide has become valuable in enhanced oil recovery so that gases that were worthless now have two useful components-carbon dioxide and methane. Another situation in which membrane technology is especially helpful is in offshore production of petroleum with its associated gases. The older technology for cleaning the gases is heavy, cumbersome, space demanding, and not entirely free of hazard. Membrane separation is preferable in many instances.

Prospects are excellent for further improvements in the selectivity and performance of membranes and for their energy and cost-effective use in a growing number of large-scale applications.—PHILIP H. ABELSON

<sup>\*</sup>A. S. Michaels, Chemtech 19, 162 (March 1989); R. W. Spillman, Chem. Eng. Prog. 85, 41 (January 1989).