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An Overview of Membrane Separations

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ABSTRACT

The field of membrane separations is discussed. The major membrane types and applications are outlined. The outlook with respect to research activities and commercial applications is surveyed. The advantages and disadvantages of this separation process are discussed. Certain applications where membranes may save energy and improve productivity are also discussed.

BACKGROUND

Membrane separations have evolved into an expanding and diverse field. There are now numerous types of membranes, various applications, and certain uses which have attained commercial success. It would be impossible to provide a thorough review of all aspects of membrane separations in a paper such as this. Therefore, an overview of this field will be provided here.

Many reviews, books, and reports provide additional detail on the various topics discussed in this paper (1-13). Lonsdale (1) provides an interesting look at the growth and evolution of membrane technology. He divides his discussion between pre and post 1950. He discusses the major applications and membrane types. Strathmann's article (2) is a very complete and well done description of membrane separation processes. He discusses membrane structure and properties as well as various applications. The topic of gas membrane separations is well documented in an article by Matson et al. (3). Topics such as transport theory, membrane materials, membrane geometries, and permeator design are all covered. Schell (4) discusses various commercial gas separation processes and compares membranes to conventional processes. He also compares two different membranes for nitrogen enrichment to demonstrate how membrane performance affects economics. A recent report (5) provides 650 titles and abstracts on membrane gas separation covering the years 1975 to 1983. Way et al. (6) provide a good overview of the liquid membrane field. Noble et al. (7) recently completed a more complete and thorough review of liquid membranes. Danesi (8) has recently written an article which covers metal extraction using supported liquid membranes. He covers both the modeling and experimental work performed at Argonne National Laboratory. Hwang and Kammermeyer (9) recently reissued their classic text on membrane separations. Meares (10) edited a text on membrane separations. The various chapters cover a wide range of applications. Scott (11) edited a text which covers the patent literature between 1978-80. Lloyd (12) edited a text on material science of synthetic membranes. The material in the text is based on a symposium held at an ACS meeting and covers many aspects of membrane materials as well as usage. Flett (13) edited a text devoted to ion-exchange membranes. An assessment of membrane technology and it's applications was done for the U.S. Department of energy (14). The text covers a wide range of membrane types, equipment, and uses. There is also a large number of references listed. The reader should refer to these recommendations for a more detailed discussion of topics of interest.

The historical evolution of membrane technology is a subject in itself. From the first mention of membranes as a separation device in 1854 to the present, this area provides some interesting reading. Two excellent sources are Lonsdale's article (1) and Sollner's prologue in Hwang and Kammermeyer's text (9).

MEMBRANE DEFINITION

A membrane can be viewed as a semi-permeable barrier between two phases. This barrier can restrict the movement of molecules across it in a very specific manner. The membrane must act as a barrier between phases to prevent intimate contact. This barrier can be solid, liquid, or even a gas. The semi-permeable nature is essential to insuring that a separation takes place. If all species present could move through the membrane at the same rate, no separation would occur. The manner in which the membrane restricts molecular motion can take many forms. Size exclusion, differences in diffusion coefficients, electrical charge, and differences in solubility are some examples.

There are two points to note concerning this definition. First, a membrane is defined based on what it does, not what it is (2). Secondly, a membrane separation is a rate process. The separation is accomplished by a driving force, not by equilibrium between phases.

With this definition in mind, we can now look at various membrane types and applications. The following discussion is not meant to look at every membrane type or application. Rather, it is an attempt to cover the major uses.

MEMBRANE TYPES

Membranes can be classified by their structure. There are other ways of classifying, such as function, but structure or membrane material is probably a good overall grouping.

1. Polymer Membranes

This is probably the most common form of synthetic membranes and the one that first comes to mind when thinking of membrane structure. Within this classification, there are the following:

a) asymmetric skin. The work of Loeb and Sourirajan (15) to develop these membranes led to the first large scale use of membranes in reverse osmosis.

b) homogeneous films. These films are widely used in the food and consumer packaging industries to provide barriers to contaminants.

c) amorphous.

d) composites. This group includes polymer blends and actual layered membranes.

2. Liquid Membranes

a) supported films. These films can be supported by either sheets or hollow fiber materials. Both liquid phase and gas phase separations can be accomplished with these membranes.

b) emulsions. These membranes are actually double emulsions. Li (16) pioneered their use as a separation process. They can be used for liquid phase separations.

c) bulk. Bulk liquid membranes are useful for laboratory research. They are too thick to be useful commercially.

3. Solids

a) ceramics. Current research in ceramic membranes may dramatically expand the range of applicability of membrane separations, especially in high temperature and corrosive environments.

b) glass.

c) metals.

4. Ion Exchange

These membranes have a polymeric backbone with fixed charge sites. The counter ion has mobility within the membrane and this configuration gives these membranes their unique properties for ionic separations. These membranes have recently found use as supports for carrier-impregnated liquid membranes (17).

a) cationic.

b) anionic.

MEMBRANE CONFIGURATIONS

1. Sheets
   a) continuous column (18)
   b) supported liquid
   c) polymer film

2. Spiral Wound

3. Hollow Fiber
   a) coated fibers
   b) supported liquid

4. Emulsion

MEMBRANE APPLICATIONS

Ultrafiltration

Ultrafiltration membranes are sometimes described as microfiltration, hyperfiltration, or reverse osmosis membranes. The distinction is usually based on the size of the molecules being excluded by the membrane. Reverse osmosis operates in the range of approximately 0.1 to 1 nm. The range is 1 to 100 nm for ultrafiltration and 100 to 1000 nm for microfiltration (2).

The driving force for separation in this application is a hydrostatic pressure gradient. The pressure gradient applied needs to be larger than any osmotic pressure gradient opposing the molecular motion. A feed solution flows to the membrane surface where small molecules are allowed to pass through the membrane and large molecules are excluded. Typical pressure drops are 10 to 100 kPa (0.1 to 1.0 atm) for microfiltration, 50 to 500 kPa (0.5 to 5.0 atm) for ultrafiltration, and 2000 to 10,000 kPa (20 to 100 atm) for reverse osmosis (2).

The uses of these membranes are varied. Reverse osmosis membranes are used to separate salts and microsolutes from solution. The largest use is in removing salts from water. Ultrafiltration membranes are used to separate macromolecular solutions. These solutions can include fruit juices and protein mixtures. Microfiltration can sterilize solutions by removing bacteria and other cellular material. Sourirajan (19) provides an excellent reference for reverse osmosis.

Dialysis

Dialysis employs a concentration gradient as a driving force for separation. A feed solution is fed to the dialyzer. A receiving phase called the dialysate flows on the opposite side of the membrane. A concentration gradient is set up across the membrane and the solute of interest flows from the feed to the dialysate.

Dialysis membranes are mainly used to separate salts and microsolutes from macromolecular solutions. The major use is as an artificial kidney in blood purification.

Electrodialysis

Electrodialysis uses an electrical potential gradient to affect a separation. Ion-exchange membranes are used in conjunction with the electric field to selectively remove ionic species. By alternately stacking cationic and anionic ion-exchange membranes and imposing the electric field across the stack, alternate streams with enriched and depleted ionic content can be formed.

The major use of electrodialysis is desalting ionic solutions. Fuel cells containing ion-exchange membranes use this same driving force.

Gas Separations

The applications described above normally apply to liquid solutions. Gases can also be separated using a pressure or concentration gradient. A concentration gradient is used with carrier-mediated liquid membranes described below.

The major uses of membranes for gas separation are nitrogen recovery from air for inert atmospheres, carbon dioxide recovery from gas wells, and hydrogen recovery from ammonia and refinery plants. Polymer membranes are utilized for these uses. At this point, there are no large scale gas separations using carrier-mediated liquid membranes.

Carrier-Mediated Transport

Carrier-mediated transport makes use of diffusion across the membrane combined with a reversible reaction to provide both a larger and more selective flux. A liquid phase containing a non-volatile carrier is used as the membrane. There are two basic mechanisms for this enhanced transport.

In coupled transport, the reversible reaction is an ion exchange and the solute flux is linked (coupled) to the exchanged ion flux. The carrier is normally an ion exchange reagent. This reaction normally occurs at the liquid-liquid interface since the ions are not soluble in an organic phase (liquid membrane). One example of this process are the ion-exchange extraction reagents for copper recovery. These reagents exchange copper and hydrogen ions. Another recent example is ionizable crown ethers. These compounds solubilize the metal ion and provide the counter ion. Ionizable crown ethers exchange metal ions and hydrogen ions. These examples illustrate counter transport. In this mode, the transport of the metal ion and hydrogen ion are in opposite directions. The use of neutral crown ethers as carriers is an example of co-transport. In this mode, the metal ion and the counter ion are both transported in the same direction.

Facilitated transport is concerned with the reversible reaction between the carrier and the solute and is not coupled to other components. This reaction normally can take place throughout the liquid membrane phase. One example is oxygen transport using hemoglobin. Separation of acid gases (carbon dioxide and hydrogen sulfide) using amine carriers is another example. See (7) for further examples.

Cussler (20) provides a good description of carrier-mediated transport in liquid membranes. Variations on these reaction schemes are possible. A recent paper by Goddard (21) illustrates these variations.

Carrier-mediated transport is possible using either supported or emulsion liquid membranes. Both supported or emulsion liquid membranes can be used for liquid phase separations while supported liquid membranes are used for gas separations.

There is only one large scale use of this technology at this time. An emulsion liquid membrane system for zinc removal from wastewater is now being used in Austria (22).

Controlled Release

The purpose of this technology is to provide a constant or at least minimum amount of delivery of a chemical over an extended period of time. Some examples are drug delivery and pesticide release.

This release is accomplished in three ways. The release rate is zero-order if the active agent is maintained as a pure material in a reservoir. The release rate is usually first order if the active agent is dissolved within the membrane matrix and becomes diluted with time. A third case is one where the active agent is present as a pure phase in the interior of the device but becomes dissolved in the membrane matrix near the surface. This third case follows time to the negative 0.5 kinetics.

Other factors which are important are membrane shape and external mass transfer resistances (boundary layer effects).

This technology is finding wide application in the drug and pharmacutical industry. Some examples are drug delivery through the skin for motion sickness and implants for birth control. One familiar example for pest control are the strips which can be hung in a room to repel insects.

Membrane Electrodes

Membrane electrodes are ion specific membranes which are used as one electrode with a reference electrode and a counterelectrode also present. The measurement of ionic current can be related to the amount of a specific ion present since only that ion can pass through the membrane electrode. The membranes can be classified as glass, crystalline, heterogeneous, and liquid (1).

An additional application of this approach is in sensor development. By constructing a membrane which is very selective for the compound of interest, the membrane could become the basis for sensing and quantifying this compound.

This sensing can be accomplished in different ways. A conductivity or other probe could be placed on the sweep (permeate) side of the membrane to measure only those compounds which pass through the membrane. The membrane can contain very specific complexing agents for the compound of interest. Then the membrane could be the sensor as the conductivity or other membrane property changed as a function of complexation.

Pervaporation

This process involves the contact of a liquid mixture on one side of the membrane. Selective diffusion of solutes across the membrane occurs and the solutes are released to a gas phase. Both diffusion and evaporation are used as separating mechanisms.

Difficult liquid phase separations, such as azeotropic mixtures or closely boiling components, can be accomplished using this technique. One example is ethanol-water separation.

MEMBRANE PROCESSES

Advantages

1. Low Energy Requirements.

The only energy normally required is to move the fluids on each side of the membrane. Some membrane operations also require a pressure drop. No heat is required as in distillation. This last point is especially important when processing heat degradable materials such as food products and biochemicals.

2. Simplicity.

Membrane units are simple in design. They are modular. They can be easily expanded by adding additional modules. There are few additional components, such as pumps and instrumentation, needed. Scale-up is easy as it only requires additional modules and/or an additional unit. This compact design leads to low space requirements. This point can be very important when space is at a premium. Installation is usually simple and inexpensive. Many units are skid-mounted or fit onto existing equipment to make it easy to incorporate into existing processes. Operation is simple since it is essentially an on-off process and does not usually exhibit long start-up times.

Disadvantages

1. Flux vs. Selectivity

In many applications, obtaining a highly selective separation means a low solute flux and vice-versa. Some progress has been made in making very thin films which can be selective. But, in general, this trade-off remains a problem.

2. Economy of Scale

Because membrane units are modular, they do not have the economy of scale that other separation processes, such as distillation, possess. Scaling up to a larger capacity does not significantly reduce the cost of the membrane separation based on feed volume processed.

3. Reliability

Many companies are reluctant to install large scale membrane separation units until their useful lifetime and general reliability have been demonstrated. This conservative approach causes a slow implementation of membrane or any other new technology.

A second aspect of this point is predictibility. While single membrane performance can be predicted and verified very well on the laboratory scale, good design of modular units to minimize pressure drop, mass transfer resistances, and contamination problems is going to be required so that actual plant performance can be accurately estimated.

4. Fouling.

Fouling is any unwanted coating of the membrane surface which reduces flux or separation performance. This problem includes concentration polarization, solids deposition, and gel formation.

5. Material Sensitivity

Traditional polymer membrane materials are sensitive to temperature, pH, and chemical environment.

OUTLOOK

I believe that the outlook for membrane separation separations looks very promising. There are many commercial ventures and various research activities which will continue to move this technology forward. Some of these activities are:

1. Add-ons to existing plants. For the short term, most membrane installations will be as an add-on to existing processes to perform a specific function. These membrane units will be used mainly for gas separations and filters.

2. Applications where the following features are important:

   a) space. Because of their compact modular design, membrane units can be accommodated in less space than alternate separation techniques. This can be critical in nuclear facilities, submarines, space vehicles, etc.

   b) purity. Membranes work very well in applications where purity, sterility, and contamination prevention are important. Also, very selective separations can be obtained if high yield is not critical. Food and biochemical applications have this obvious need.

   c) ease of operation. Membrane units are simple to operate. This can be important where the system runs intermittently, in remote locations, and in locations where operating personnel are at a minimum.

3. Development of specific complexing agents. There is research activity to obtain complexing agents for metals, gases, and proteins.

4. New materials. Research is continuing on new polymers, ceramics, carbon, and liquids for various applications.

5. Thin films. Very thin films (1 micron or less) will be required to obtain large enough fluxes to be economically attractive in many applications.

6. Improved modularization. Minimizing pressure drop and mass transfer resistances will lead to improved performance under plant conditions.

7. Improved prediction of performance. Complete and accurate models of membrane separations will aid in design and scale-up of

these processes. Good models also identify the variables and properties which affect system performance.

There are certain applications where membrane technology can compete in terms of energy conservation and improved productivity.

1. Replace energy-intensive separations. Certain separation processes require a phase change. These processes include distillation, evaporation, and absorption. Feed streams also need to be heated to the phase change temperature. Membrane separations normally do not require a phase change and can operate at ambient conditions. This can result in large energy savings.

2. Sensible heat recovery. There are various processes where water or air streams are discharged at elevated temperatures. These processes include drying operations and hot process water. It would be advantageous to recover and reuse this sensible heat. This requires solvent removal from air streams and clean up of water streams to produce a clean fluid which can be recycled and/or reused. Membrane units are currently being tested for these applications.

3. Solute concentration. Dilute solutes, normally in aqueous streams, are difficult and energy-intensive to concentrate. Environmental considerations require removal of solutes, such as heavy metals or organics, before discharge. If these materials could be concentrated and recovered or recycled, the process economics would improve as well as meeting environmental standards. Membranes, such as reverse osmosis and ultrafiltration, can be used to remove water and concentrate these streams. Liquid membranes can be used to remove the solute and produce a clear aqueous stream.

4. Energy conversion. Fuel cells, batteries, and photoelectric converters use membranes as components. These and other energy conversion systems are being studied as replacements for conventional systems. Replacing conventional systems could lead to increased energy savings and more efficient operation.

5. Chemical reactors. Catalysts and other reagents can be bound into a membrane to produce a reactor. Enzymes immobilized in polymer membranes and carriers bound in liquid membranes are two examples. Expensive catalysts or carriers can be bound in the membrane saving on replacement or recovery costs. Products can be continuously removed, driving the reaction to completion.

There are various industries where membrane technology can have an impact.

1. Metals industry
   a) metal recovery
   b) pollution control
   c) enriched air for combustion

2. Food and biochemical industry
   a) purification
   b) concentration
   c) sterilization
   d) product enhancement
   e) evaporation replacement
   f) by-product recovery

3. Textile and leather industry
   a) sensible heat recovery
   b) pollution control
   c) chemical recovery

4. Pulp and paper industry
   a) evaporation replacement
   b) pollution control
   c) fiber and chemical recovery

5. Chemical process industry
   a) organics removal and/or recovery
   b) pollution control
   c) gas separation
   d) chemical recovery and reuse

6. Medical and health care
   a) artificial organs
   b) controlled release
   c) blood fractionation
   d) sterilization
   e) water purification

7. Wastewater treatment
   a) salt removal
   b) deionization

CONCLUSIONS

Membrane separations have evolved from a research activity to a varied field with many commercial applications. The specified advantages of membrane separations have provided uses in many industrial processes. As the disadvantages continue to be overcome with continuing research activity, membranes should become a separation process on equal footing with more traditional processes such as solvent extraction, distillation, and absorption.

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