

초청강연 I

1990 \$1.6B/y
Increase 15%
Mem. Tech. 5B/y

CURRENT AND FUTURE TRENDS OF MEMBRANE RESEARCH

GPA: 1.5M/y
DOE 4.5M/y

* SC1-702

class instead
polymer
desal -> SP.3/6/84 reject 2ndF

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Membrane technology has gained tremendous acceptance by industry in recent years. A long dormant period of laboratory research in academia and industry has evolved into a new era of commercial growth. The total sale of membranes is still modest compared to the major technologies, yet it is one of the fastest growing industries. This can be best illustrated by inspecting the market place. In 1990, the total sales of worldwide membranes was estimated to be approximately \$1.6 billion with an annual increase rate of 15%. This means that the estimated total sales of membrane based industry is nearly \$5 billion annually.

Equally important evidence is an increase in research activities, as demonstrated by the explosion of publications and proliferation of membrane meetings. A number of research centers have sprung up around the world in addition to newly emerging membrane companies and membrane research groups within large corporations. All of these research activities can be eventually translated into some form of publication. As an example of the rapid growth in membrane research, the number of papers submitted to the Journal of Membrane Science alone was almost 2000 and the number of papers accepted was over 1300 in 1990.

The worldwide membrane research expenditure in 1990 was estimated to be around \$127 million consisting of \$76 million (60%) by industry and \$51 million by governments, which can be broken down to \$11 million in the U.S.A., \$20 million in Japan, and \$20 million in Europe.

I. Established Membrane Technology

In a recent study by the U.S. Department of Energy summarized several areas of membrane research as potential priority topics. Most of these processes are already developed and industrialized technologies. Here, a brief overview will be presented.

1. Pervaporation (LeCarbone Lorraine Group) *France*

If solvent-resistant pervaporation modules can be made, there will be lots of industrial applications avoiding expensive and energy consuming distillation process. Pervaporation for organic/organic mixtures is highly touted. Also, separation of organic/water system and dehydration of acidic, basic, and concentrated aqueous solvent streams can be candidates for industrial pervaporation.

(glycol, trace organic, solvent.)
↓
water vapor removal.

2. Gas Separations

Development of thin film techniques will be important for new gas separation membranes with high selectivity and flux. Especially oxygen/nitrogen separation will be practical with improved membrane performance. Other systems include CO₂, H₂, CH₄, H₂S, NO_x, SO_x, and H₂O vapor.

3. Reverse Osmosis

The development of ~~oxidation-resistant~~ reverse osmosis membranes is desirable. The performance of polyamide membranes is much superior than that of cellulose acetate. However, the drawback of these membranes is the susceptibility to degradation in the presence of oxidizing agents, such as chlorine, ozone, or hydrogen peroxide. In many applications of reverse osmosis the membrane is brought to contact these oxidizing agents. Another area of important research is anti-fouling of membrane, especially, to prevent the bacterial attachment to the membrane.

4. Microfiltration

The market of microfiltration is already very large and still growing. Nevertheless, many problem areas remain to be solved. They include low cost high temperature resistant, solvent resistant, non-fouling and cleanable membranes.

5. Ultrafiltration → (solvent resistant)

protein adsorption
The priority research areas are very similar to those for microfiltration.

6. Electrodialysis

This well-established process requires further development of engineering problems, such as temperature stability, better flow design to avoid the concentration polarization, and anti-fouling.

II. Emerging Membrane Technology

Less established, and certainly not commercial yet, are the following membrane processes. They are being vigorously pursued by academic and industrial researchers.

1. Inorganic Membranes 40A

It is quite desirable to have thermally and chemically resistant membranes. There are several different types of inorganic membrane materials that are currently being investigated, such as polymerized phosphorous compounds, silica or glass, alumina, carbon, silicon-carbide and other refractory materials. Metalized membranes are also being studied.

phenomenological → (mechanistic analysis)

10/10/5
10/10/5
10/10/5

OSW 16-278

In many cases, organic precursors are carefully selected and manipulated before pyrolysis to form the inorganic membrane. Sol-gel techniques, aerosol methods, chemical vapor deposition, anodizing methods and plasma techniques have all been employed.

Inorganic membranes offer several technological advantages. They are resistant to high temperatures, chemically inert, autoclavable, and provide a high flux. Inorganic membranes have minimal adsorption, suffer from no membrane compaction and no swelling, and can withstand high-pressure back flushing and steam sterilization.

In spite of the above mentioned advantages for inorganic membranes, there are some disadvantages, such as brittleness, difficulty of fabricating, and high cost.

2. New Polymeric Membranes

Although the permeability is high for rubbery polymeric membranes, selectivity is generally poor for these materials. On the other hand, glassy polymers are known to exhibit high selectivity, but poor permeability. Recent trends in polymeric membrane research show that glassy polymers with high glass-transition temperatures have high permeability, while keeping their high selectivity. A couple of examples would be Poly(vinyl trimethyl silane) and Poly(1-trimethyl silyl-1-propyne), which were developed by Japanese and Russian investigators. A large free volume can be introduced into the glassy polymer by quickly quenching it, thus permitting high permeability.

Liquid crystal polymers also offer high selectivity and are being pursued actively. Block-copolymers of various kinds are being developed to achieve high permeability and high selectivity.

3. Membranes in Biotechnology

高

The recent growth of biotechnology has brought a need for efficient separation methods to isolate proteins and peptides from bioreactor broths. The affinity membrane process is based on the principles of affinity chromatography and membrane filtration. By overcoming diffusional imitations found in the traditional chromatographic beds, the processing time is shortened considerably, thus the capacity for total fluid handling increases without an additional increase in operating pressure.

Ion exchange membranes can be used on a similar principle. Many protein and peptide molecules can be separated and concentrated in large quantities. This area of membrane applications is predicted to have the largest growth among all membrane fields in the next decade. Practical applications will be in the food and beverage industry, the agricultural industry, the pharmaceutical industry, and the biomedical industry.

High pure water

TOC	(PPb)
APCO	< 500
AC	< 20
PC	< 5

- heavy water recovery

4. Membrane Reactors

Tremendous amounts of research have been carried out in dealing with enzyme bioreactors. Immobilized enzymes have been utilized to combine the enzyme reactivity with the membrane selectivity. By combining two functions effectively, a synergistic effect can be accomplished. The overall yield can be improved without losing the expensive enzymes on a continuous basis.

For non-biological reactions, chemical reactions involving hydrogen (either hydrogenation or dehydrogenation reactions) have been successfully carried out in membrane reactors to show the advantages of using the membrane reactor configuration.

As inorganic membranes become available, membrane reactors will become much more popular and practical. Industrial applications will be numerous in chemical and petroleum processes.

5. Membrane Sensors

There are already several membrane sensors on the market. These are either ion specific or gas specific types. The current emphasis in research has been in developing microsensors using permselective membrane tips. With the advent of the microelectronics industry, this area will receive a lot of attention. Either a bottleneck or a breakthrough in future integrated electronics systems will be made in this area.

6. Barrier Membranes

The packaging industry is using more and more membrane materials. There has been some research on the barrier properties of various membrane materials. The market share is believed to be bigger than that of the ordinary membrane processes. Development of oxygen, carbon dioxide, and moisture barriers is in great demand. Also, some organic solvent and pharmaceutical barriers are of interest.

III. Conclusion

Membrane technology is rapidly replacing and/or augmenting the traditional separation processes in many industries. In some cases, it opens new markets. Research and development in academia and industry have proven that the new technology is cost effective and viable. The future of membrane technology looks bright.

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