2. Membrane Separations and Energy Savings

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"Membrane Separations and Energy Savings"

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1. Introduction

It is the purpose of this paper to review the recent developments and future trends in various membrane processes, which will result in energy savings. Historically, there was a long period of academic curiosity in membrane research covering from gas separation to reverse osmosis. With advent of asymmetric membrane technology, many membrane processes proved to be energy efficient than the conventional separation methods. Thus, membrane technology has gained wide acceptance from many sectors of industry. The commercial sale of membranes is still modest compared to the major technologies, but it is one of the fastest growing industries.

Recently the U.S.Department of Energy conducted a study (1) to evaluate and prioritize research needs in the membrane separation industry in order to foster and better support the deveolpment of energy-efficient new technologies. The National Science Foundation (U.S.A.) did also do a similar investigation. Both agencies have arrived neary at the same conclusion, that is, membrane separations can offer many new and alternative methods of separations that are more energy efficient than existing processes. This paper is largely based on these findings.

2. World Energy Picture

It is estimated that the total energy cousumption in the world is in the order of 300 quads (quad is 10^{15}Btu). The population of the U.S.A. is only 5% of that of the entire globe but the energy consumption is about 27% of the world, which is approximately 80 quads. The consumption by the industrial sector in the U.S. is about 30 quads, out of which distillation alone consumes 2 quads.

These numbers are summaried in Table 1.

3. Energy Savings by Membrane Processes (Including Potential)

If membrane processes replace or augment some distillation operations (by pervaporation) the potential energy savings could amount to 0.2 to 1.0 quads, which is equivalent to $1 \sim 5x\ 10^5$ barrels of oil per day. Of course, there are other industrial separations where membrane might find its way to save more energy. A few examples are given below :

When oxygen enriched air is used in place of regular air, it is estimeted to save 0.06-0.36 quads per year. If membranes are used to upgrade sour natural gas an energy savings of 0.01 quads per year will result. The membranes used currently in reverse osmosis possess adeguate salt rejection and water flux. However, these membranes are easily degraded when sterilizing oxidants are present in the feed solution. If high-performance, oxidant-resistant membranes are developed, they could replace existing cellulose acetate membranes. These newly deveolped membranes can be employed in reverse asmosis to substitute evaporation processes yielding a potential energy savings of 0.04-0.05 quads. Another area of considerable energy savings is in the field of wastewater treatment. If the development of chemically sesistant reverse osmosis/ultrafiltration/microfiltration membranes is realized 0.25-0.5 quads of energy can be recovered from the hot streams of wastewater and recycled to the process. The total energy waste by various industries is estimated at 1-2 quads annually by discharging wastewater as hotstreams. The potential energy savings by membrane processes are summariged in Table 2.

4. Membrane Business

The total sale of worldwide membranes was estimated in 1990 to be about $1.6 billion with an annual increase rate of 15%. This means that the total sale of membrane based industry could amount to $5 billion annually. The worldwide membrane research expenditure was estimated to be approximately $127 million consisting of $76 million (60%) by industry and $51 million by governments. It is interesting to note that the United States spent $11 million while Japan and Europe expended $20 million each on research as shown in Table 3.

5. High Priority Areas of Membrane Research (Established Processes)

According to the U.S.Department of Energy, several high priority areas of mebrane research are needed to bring energy saving membrane processes to technical and commercial readiness within the next 5 to 20 years. Only the top priority items as shown in Table 4 are described here briefly :

A. Pervaporation

It is believed that pervaporation may supplement or replace many existing distillation processes. Since distillation is energy intensive separation process (annual energy consumption is 2 quads), a conservative 10% of this energy would represent 0.2 quads annually which could be saved by using membnares.

Pervaporation is a membrane separation process of liquid mixtures by permeation and evaporation. The driving force is the partial pressure difference across the membrane. The permeate stream is taken off either by a vacuum or by a sweep gas. Recovered organic vapors are condensed in a cold trap to be removed or recycled to the process.

Curently, pervaparation is used mainly for breaking the azeotropic mixtures of alcohol-water. However, future demands are in the areas of organic-organic sepasations and construction of solvent-resistant modules. The lack of membranes and modules which can operate in solvent medium at high temperatures is the major hindrance in the development of commercial pervaporation system. Research breakthroughs in this area seem imminent, then the applications of peraporation process will be widespread throughout separation industry.

B. Gas Separation

If high grade (larger than 75%) oxygen enriched air is produced using membranes at low cost, considerable energy savings (0.06-0.36 quads per year) would result throughout industry. Also, by removing acid gases (H_2S and CO_2) from the sour natural gas, it can be upgraded to yield energy savings of 0.01 quads per year.

Gas separation by membranes is an old concept (more than 100 years old), but its industrial applicutions became widespread only recently. Separation is achieved due to the difference in permeation rates of the feed components under a partial pressure difference across the membrane.

The newly demanded areas of gas separation membranes are the development of generally applicable method for producing very thin skinned or composite membranes. Another high priority asea is the oxygen separating membrane with high selectivity and high flux.

Membranes with no defects and a very thin permselective layers on the order of 500 Å or less must be mass produced in order to meet the demand. Some experimental materials exhibit high selectivity and high permeability but there are no generally applicable techniques developed to spin hollow fibers. The prospects of success seem to be very good.

C. Microfiltration

Microfiltration is widely used in all industries. Especially it is used in fuel processing, which is relevant in our consideration, this includes oil refinery, coal liguefaction, coal gasification, and removal of particulates from spent oil.

Microfiltration is a filtration process under a pressure gradient across the membrane. It is a well-developed large scale commercial process. It covers wide range of applications from semiconductor industry to waste treatment.

High priority areas are developments of low-cost membrane modules and high temperature and solvent-resistant membranes. When these membrane modules are available, new but significant markets could be opened up in the petrochemical industry, in the filtration of hot gas streams, and cold sterilization of foods, beverages and pharmaceutical products.

D. Reverse-Osmosis

If the new generation of oxidation-resistant reverse osmosis membranes are developed commercially, many evaporation processes in food industry will be replaced by reverse osmosis process, which will produce considerable energy savings. Also, reverse osmosis became more efficient than the low pressure distillation/evaporation processes for sea water desalination when the energy-saving, low-pressure, thin-film composite membranes were developed.

Revere osmosis is a membrane separation process in which a greater hydrostatic pressure than osmotic pressure is applied to reverse the flow of osmosis so that solvent is separated out from the feed solution. Since no phase change occurs during reverse osmosis, it is inherently a low-energy desalination process.

Some of the identified needs in reverse osmosis are membrane fouling, seawater desalination, energy recovery for large seawater desalination systems, low-pressure reverse osmosis desalination, ultra-low-pressure reverse osmosis desalination and optimization of spiral-wound element.

Thin film composite membranes made from aromatic polyamides offer better characteristics in reverse osmosis than traditional cellulose acetate membranes. However, these new membranes tend to be less oxidation-resistant. Therefore, it is highly desirable to develop a membrane resistant to oxidants, such as chlorine, ozone, and hydrogen peroxides. In reverse osmosis, membrane fouling is the major problem. Chlorination of reverse osmosis feed waters is mostly required to avoid bacterial fouling of the membranes. Improved pretreatment methods are also impostant problems to be solved.

E. Ultrafiltration

Ultrafiltration often finds no competing processes and in case where competing processes exist such as chromatography and precipitation, ultrafiltration is the most energy-efficient process as both of these competing processes involve an energy-intensive evaporation step. Ultrafiltration typically requires only 10% of the energy used by evaporation. Ultrafiltration also saves energy by reducing the degree of downstream waste treatment.

Ultrafiltration is a pressure driven membrane process to separate molecules or pasticles in solution on the basis of size. It separates polymers, proteins, colloidal materials, and enzymes to name a few.

The biggest problem in ultafiltration application is membrane fouling. Basic understanding of why and how fouling is taking place is needed. Another issue is low cost and long life membranes. These problems may be too large to overcome in the immediate future but the benefit will be tremendous to the producers, users, and the public.

6. Emerging Membrane Technology

The above described membrane separations are well-established industrial processes. Further development of these processes promise much wider applications in industry and the impact of energy savings will be significant. Besides these processes, there are many emerging membrane techniques that are less established and many are not commercial yet. Their applications may seem little to do with energy savings now but when these processes find their ways to practical applicatlons, the implication of energy savings would be tremendous. Thus, these new processes are being vigorously pursued by both academic and inustrial researchers.

A. Inorganic Membranes

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.

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 serilization.

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

B. 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 galssy polymers with high glass transition temperatures have high permeability, while keeping their high selectivity. A couple of examples would be Poly(vinyltrimethyl 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 permeabilbity.

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.

C. Membranes in Biotechnology

The recent growth of biotechnology has brought a need for efficient separation methods to isolate proteins and peptides form bioreactor broths. The affinity membrane process is based on the principles of affinity chromatography and membrane filtration. By overcoming diffusional limitations 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.

D. 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 heen 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.

E. 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.

F. 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.

7. Conclusion

Membrane separations offer many energy saving methods. The prospective applications are far reaching in every corner of industry. The potential to increase energy savings by developing more efficient membrane processes is tremendous.

8. Reference

1. Baker,R.W., Cussler, E.L.,Eykamp,W.,Koros,W.J., Riley,R.L., and Strathmann, H., "Membrane Separation Systems : Recent Developments and Future Directions", Volume I and Volume II, Final Report, U.S.Department of Energy, Washington,D.C.(1990)

Table 1

Annual Energy Consumptions

World	300	quadrillion	(300×10^{15} Btu)
U.S.A.	80	quads	(26.7% of World)
U.S. Industry	30	quads	(37.5% of U.S.A.)
Distillation	2	quads	

Table 2

Energy Savings by Membrane processes

Membrane process	Application	Energy Savings
Pervaporation	Distillation	0.2-1.0 quads
Gas Separations	O_2Enriched Air	0.06-0.36 quads
	Sour Gas	0.01 quads
Reverse Osmosis	Evaporation	0.04-0.05 quads
RO, UF, MF	Wastewater	0.25-0.5 quads

Table 3

Membrane Business (Worldwide)

Membrane sale		$1.6 billion
Membrane-based Industry		$5 billion
Research Expenditure		$127 million
	U.S.A.	$11 million
	Japan	$20 million
	Europe	$20 million

Table 4

High Priority Areas of Membrane Research

A. Pervaporation	Organic-organic separations
	Solvent-resisistant modules
B. Gas Separations	Thin skinned membranes
	High O_2/N_2 selectivity
	Thin composite
C. Microfiltration	High temperature & solvent-resistant
	Low cost
D. Reverse Osmosis	Oxidant-resistant
E. Ultrafiltration	Fouling-resistant