FROM BEER DEBLOOD MEMBRANE SEPARATION TECHNOLOGY MAKES A BIG

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USING A COLANDER TO SEPARATE PASTA FROM THE WATER IN WHICH IT WAS COOKED IS A COM-MONPLACE KITCHEN EXPERIENCE. But what about the cooking water that usually disappears down the drain? Suppose you had a colander with holes that could not only separate pasta and water, but just as easily remove the salt and starch added to the water in the cooking process — making the water so pure that it would taste great at the dinner table. In principle, this is exactly what can be done with membrane separation, a valuable technology whose commercial potential continues to grow through the efforts of NJIT researchers.

Membrane separation has secured niches in a wide range of industries over the past few decades, from brewing beer to manufacturing pharmaceuticals. (See sidebar on page 12.) This technology is also integral to meeting stringent standards for the purity of the water we drink and the air we breathe. It is key to preventing explosions in aircraft fuel tanks and helping people contend with kidney disease through hemodialysis. In short, membrane separation is becoming the technology of choice for numerous applications that require separating components in a liquid or gas and achieving the highest levels of purity at costs lower than those of alternative processes. Reflective of this technology's value, NJIT researchers have received some \$6 million in support to date from sources such as the National Science Foundation (NSF), the U.S. Environmental Protection Agency, Department of the Interior, Department of Energy, Department of Agriculture and Office of Naval Research.

Making the desert bloom

"The basic principles of membrane separation have been known for a long time," explains Kamalesh Sirkar, distinguished professor of chemical engineering at NJIT and one of the investigators named on more than a dozen patents stemming from membrane separation research. "Intestines in animals and humans are semipermeable membranes, and early experiments to study the process of separation were performed by chemists using samples of animal intestine," says Sirkar, who is also an NJIT Foundation Professor of Membrane Separation and director of the university's Center for Membrane Technologies.

GROWING MARKETS FOR PURITY

Industry observers predict that the current \$4 billion-plus market for membrane separation technology will grow 7.4 percent annually for the foreseeable future. This growth is being driven by the expanding use of membranes for water treatment and in a growing range of industries, such as the food and beverage industries.

In addition to increasingly stringent regulations affecting the treatment of drinking water and wastewater, factors shaping the membrane market include the separation requirements of the high-tech pharmaceutical and semiconductor segments. Membrane technology makes it economically attractive to reclaim valuable process components and recycle water used in these and other industrial areas.

While the greatest demand will be for polymeric membranes, there will be a growing market for membranes fabricated from nonpolymeric materials, such as ceramics. Nonpolymeric membranes have the potential to extend the use of this technology in high-temperature and corrosive environments such as those encountered in petrochemical processing.

Currently, less-selective microfiltration membranes account for the largest share of the market. These are widely used for pretreatment ahead of other separation processes and for applications that do not require exceptionally high purity. However, the demand for reverse osmosis membranes is expected to increase by virtue of their ability to provide much higher levels of purity economically and efficiently.

> However, it wasn't until the early 1960s that the use of membranes for separation applications turned the corner toward practicality. That was after Samuel Yuster, Sidney Loeb and Srinivasa Sourirajan at UCLA fabricated a functional synthetic membrane from cellulose acetate polymer. It is widely held today that this pioneering innovation launched the membrane separation revolution.

The UCLA researchers demonstrated that reverse osmosis achieved with their membrane could reject salt and produce fresh water at a rate sufficient for real-world use, an accomplishment with important international implications at the time. Desalinating seawater to stimulate economic development in arid parts of the globe was a technological priority for the administration of President John F. Kennedy. "Go to the moon and make the desert bloom" was a catchphrase of the era. Today, desalination plants based on membrane technology are commonplace in regions such as the Middle East and North Africa, where they produce millions of gallons of fresh water daily. Plants of this type are also beginning to appear in coastal areas as well as in arid regions of the United States.

"The advantages of membrane separation were immediately apparent," Sirkar says. "It's a compact technology with relatively low energy consumption that can operate at room temperature for many different applications." It's also an environmentally friendly technology that does not require potentially harmful additives to effect separation.

After the UCLA breakthrough, a key advance was the development of spiral-wound membranes. In discussing this engineering innovation, Sirkar shows visitors to his NJIT office a cylinder approximately 18 inches long and 2 inches in diameter,

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Professor Kamalesh Sirkar, director of NJIT's Center for Membrane Technologies

explaining that the spiral-wound design allows some three hundred square feet of polymeric membrane surface to be contained in a cubic foot.

Membrane devices for hemodialysis provide even more separation power in a very compact form. Employing tiny hollow-fiber membranes, these devices pack as much as sixteen hundred square feet of membrane surface area in a cubic foot. So much separation power available so compactly has led to the use of membrane technology for a burgeoning range of applications, and there are many innovative uses under investigation.

At Sirkar's NJIT lab, recent groundbreaking work in the field has included a membrane distillation technique that promises to be considerably less expensive than reverse osmosis; a selective protein ultrafiltration method that could rival chromatography as a process for protein purification; and gas permeation membranes that facilitate the separation of carbon dioxide from air by allowing the carbon dioxide to pass through the membrane ten thousand to eighteen thousand times faster than oxygen and nitrogen. The technique for protein ultrafiltration has major significance for the production of pharmaceuticals and nutritionally enriched foods, and the work with gas permeation membranes could be an important step forward in sustaining environments such as those needed for manned space flight.

A matter of holes

Essentially, membrane separation depends on creating minute holes, or pores, in the membrane material by means of very sophisticated manufacturing processes. The size of the pores is key to determining which molecular components in a liquid or gas will pass though the membrane from a region of high concentration to a region of much lower concentration, even blocking the passage of particular molecules almost entirely. Typically, pressure or concentration differences on the two sides of the membrane cause separation to occur, with the potential separation efficiency and selectivity of the membrane increasing as the size of the pores decreases.

The approximate diameters of the pores in microfilter, ultrafilter and nanofilter membranes are, respectively, .02 to 10 microns, 1 to 100 nanometers, and 0.5 to 2 nanometers. A micron is one millionth of a meter, and it would take some 1000 microns to equal the thickness of a U.S. dime.

A nanometer is a billionth of a meter, or the equivalent of ten hydrogen atoms in a row.

In reverse osmosis and other membrane separation processes, pore size is 1 nanometer and smaller. For separation of gas mixtures, the polymeric membranes used do not have pores in the conventional sense. Gas molecules dissolve in the polymer membrane and diffuse through what are known as interchain gaps in the material.

The M stands for membrane

In recent years, at least a dozen students who have earned PhDs at NJIT have specialized in the membrane separation field. One of these is Uttam Shanbhag, who was awarded his doctorate in chemical engineering in 1997. Today, Shanbhag is a research engineer at MEDAL[™], L.P., a company based in Newport, Delaware. MEDAL, whose name is derived from Membrane Systems DuPont Air Liquide, began in 1988 as a joint venture between Air Liquide and DuPont. The company has been a wholly owned subsidiary of Air Liquide since 1992.

MEDAL is a good example of how the commercial potential of membrane technology is being realized, in this case for gas separation. Shanbhag says that the company offers advanced polymeric membrane systems for nitrogen generation, carbon dioxide removal from natural gas streams, and purification of hydrogen for chemical, petrochemical and fuel-cell applications. In addition, among various other applications, he says that this technology is proving effective for cleaning the emissions produced by landfills before release to the atmosphere.

MEDAL also supplies membrane modules for Air Liquide's OBIGGS units, now used primarily on military aircraft to minimize the possibility that vapors in an aircraft's fuel tanks will ignite and cause disastrous explosions. OBIGGS is an acronym for On-board Inert Gas Generator System.



Graduate student Chen Wan (right) with Professor Marino Xanthos, who has participated in groundbreaking membrane work as director of research at the NJIT Polymer Processing Institute.

As an aircraft's fuel is consumed, the accumulation of explosive vapors in its fuel tanks is prevented by injecting inert nitrogen-enriched air into the tanks. Consisting of more than 95 percent nitrogen, the air introduced into the tanks displaces the flammable fuel/air mixture and protectively blankets any fuel remaining. The nitrogen-rich air is produced during flight by using membrane separation to remove the requisite amount of oxygen in air from the atmosphere as it is routed to the fuel tanks via the OBIGGS unit.

Shanbhag says that the civilian air transport industry is looking closely at this technology because it could help to prevent tragedies such as the crash of TWA Flight 800 in 1996. There is considerable evidence indicating that the destruction of the Boeing 747, and the loss of 230 lives, resulted from the explosive ignition of vapors in the plane's center fuel tank. "This may not have happened if an OBIGGS unit had been in place on the aircraft," Shanbhag says.

Solid intellectual assets

The number of patents issued to NJIT researchers and cooperative research with industry are also clear indicators of the commercial importance of membrane technology — and of the university's prominent role in the field. "NJIT has tremendous expertise and a solid base of IP assets that we can leverage for commercialization and sponsored research," says Judith Sheft, assistant vice president for technology development at NJIT.

Sheft points out that NJIT faculty have been named on many patents involving membrane separation that have been granted over the past few years, with more patents pending. Cooperative development of technological breakthroughs employing membrane separation is also under way in the commercial arena. For example, NJIT is exploring a potential business relationship with a manufacturer of polymeric membranes as a follow-up to collaborative R&D work. In the area of industry-sponsored research, NJIT recently entered into an agreement with a large international firm to study how systems to deliver surgical anesthesia can be improved by using membrane separation to remove carbon dioxide from the mixture of anesthetic gases.

Out on the leading edge

Building on their substantial success in the field, NJIT researchers are continuing efforts to enlarge the potential of membrane separation technology. "There are still exciting developments ahead," says Professor of Chemistry Somenath Mitra. Those developments include Mitra's research into combining microfluidics and membrane separation to create tiny sensing devices that could be used for a multitude of applications, among them continuous monitoring of drinking water supplies.

Mitra explains that an analytical device on this scale — in essence, a "lab on a chip" — would be an economical and considerably more efficient alternative to other testing methods. "This is a highly flexible technology that could be easily incorporated in a testing system," Mitra says. "Doing so would allow some analyses of water that now require several days to be done in hours, perhaps minutes."

Distinguished Professor of Physics Roland Levy is a pioneer in other regions of the membrane separation frontier. A focus of Levy's work has been gas separation using ceramic membranes, specifically tubular membranes of porous borosilicate glass. Ceramic membranes offer various advantages, including mechanical strength, chemical stability and the capacity to withstand high-temperature environments, on the order of 1000 degrees centigrade.

Levy has also researched and patented techniques for creating membranes with pores that are uniform in size and distribution, and with pore dimensions measured in angstroms. An angstrom is one ten billionth of a meter — the size equivalent of a single hydrogen atom. Such control over the uniformity and distribution of pores, and the ability to create pores at the angstrom level, promise to increase the utility of a technology that is already very useful. While membranes with angstrom-size pores are still relatively distant on

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PATENTED ACCOMPLISHMENTS

A sample of the membrane separation patents (including patent numbers) on which NJIT researchers are named clearly indicates the extent and success of their work, and the utility of this technology —

- Membrane Separation of Carbon Dioxide (6,635,103)
- Method and Apparatus for Isolation Purification of Biomolecules (6,022,477)
- Apparatus and Process for Selectively Removing a Component from a Multicomponent Aqueous Solution by Pervaporation (5,993,515)
- Method and Apparatus for Gas Removal by Cyclic Flow Swing Membrane Permeation (5,928,409)
- Method and Apparatus for Extraction and Recovery of Ions from Solutions (5,868,935)
- Subnanoscale Composite, N2-permselective Membrane for Separation of Volatile Organic Compounds (5,789,024)
- Method and Apparatus for Selectively Removing a Component from a Multicomponent Gas/Vapor Mixture (5,753,009)
- Hollow Fiber Contained Liquid Membrane Pervaporation for Removal of Volatile Organic Compounds from Aqueous Solutions (5,637,224)

the commercial horizon, Levy says that the "infinite selectivity" of such membranes would make membrane separation an even more powerful industrial tool.

Marino Xanthos is another NJIT investigator working to expand the utility of membrane separation technology. In addition to being a professor of chemical engineering, Xanthos is director of research at NJIT's Polymer Processing Institute.

The many achievements of Xanthos and his colleagues include groundbreaking membrane research supported by funding from the New Jersey Commission on Science and Technology for which Xanthos was the principal investigator (PI), and NSF-supported work that involved Sirkar and Xanthos as co-PI's. Recently, these two researchers were also named on a patent application covering the virtually solvent-free production of polymeric membranes. Environmentally friendly manufacture of this type of membrane material can thus complement the inherently benign nature of membrane separation processes. Xanthos has also participated in the quest to improve the production of highly efficient polymeric membranes, with significant results impacting pore size and the capacity to operate at higher temperatures.

"We discovered that the right polymer blend in combination with a process that can be called 'stretching' facilitates producing membranes with nanometer-size pores," he says. "This is the range needed for, say, practical separation of a greater variety of pollutants in liquid and gas streams. Our current research in polymeric membranes focuses on the use of functional inorganic and organic fillers of appropriate shape and size to promote porosity at the nano level." Commenting on the critical role of pore size in the ongoing membrane research at NJIT, Xanthos adds, with a smile, "You might say we're competing to see how low we can go."