Over the last three decades, operators across the chemical process industries (CPI) have employed membrane-based systems to carry out various types of separations. Because of their fundamental engineering and economic advantages over competing separation technologies, membranes are now being explored for CO₂ capture from power plant emissions and other fossil-fuel-based fluegas streams.*

The promise of system simplicity is a key driver of membrane R&D. While conventional solvent-based separation systems are both capital- and maintenance-intensive, “membrane systems have no moving parts and just let the gas streams simply pass through — so they are expected to be more reliable and less costly,” says Jeff Phillips, senior program manager of advanced generation, Electric Power Research Institute (EPRI; Charlotte, NC; www.epri.com). The unavoidable pressure and/or temperature cycling required for solvent regeneration adds complexity and imposes cost penalties, in terms of both the capital costs and parasitic energy losses. “All of these attributes make membrane systems a potentially cheaper alternative to absorption-based separation for capturing CO₂,” says Jared Ciferno, technology manager, existing plants, emissions and capture, at the U.S. Dept. of Energy’s (DOE) National Energy Technology Laboratory (NETL; Pittsburgh, PA; www.netl.doe.gov).

Membranes offer inherent advantages over absorption-based CO₂ capture from post-combustion fluegas and pre-combustion syngas, but numerous design and scale-up challenges remain.

However, the ability to parlay industry’s knowledge and experience into a standard membrane solution for capturing CO₂ has turned out to be a much more complex engineering challenge than many had anticipated. Rather, several critical distinctions will shape the ultimate solution, such as:

• The nature of the separation — separating CO₂ from nitrogen in the fluegas produced by conventional coal-fired power plants (Figure 1a), versus separating CO₂ from hydrogen in the syngas produced by integrated gasification combined cycle (IGCC) power plants (Figure 1b)

• The nature of the gas stream — the lower-pressure, larger-volume, relatively dilute post-combustion fluegas streams produced by coal-fired plants, versus the higher-pressure, smaller-volume, CO₂-enriched pre-combustion syngas streams produced by IGCC plants

• The anticipated location in the process — at the end of the process in a coal-fired plant for post-combustion CO₂ capture, versus further upstream, between other unit operations within an IGCC process, to separate CO₂ from the syngas before it is combusted in the gas turbines.

Pre-combustion vs. post-combustion capture

Currently, there are two fundamentally different approaches to coal-fired electric power generation. Traditional pulverized-coal (PC) plants rely on air-blown combustion of coal, whereas newer IGCC plants first react coal with oxygen (or air) in a gasification reactor, and fire the resulting synthesis gas (a mix of primarily H₂ and CO)

* Editor’s note: The author has written a white paper on this topic, which provides further details as well as additional sidebars, tables and figures. Click here to view the white paper.
in one or more gas or steam turbines.

Today, competing CO₂-separation membrane systems are being pursued to capture CO₂ from both the post-combustion fluegas stream (separating CO₂ from N₂), produced during coal combustion, and from the pre-combustion syngas (separating CO₂ from H₂) produced in an IGCC facility before the hydrogen enters the gas turbines.

Not only are these gas streams fundamentally different, but the available pressure differentials and CO₂ partial pressures of the streams are fundamentally different as well. This is a critical consideration during membrane design, because the inlet gas stream pressure and the net pressure differential across the membrane provide the driving force for any membrane-based separation.

For example, post-combustion fluegas streams typically have high volume (due to a high volume of N₂ in the combustion air passing through the combustor to the fluegas), yet the pressure and relative concentration of the resulting fluegas tend to be low (i.e., atmospheric pressure and CO₂ present at 10–15 vol.%).

By comparison, IGCC syngas is typically smaller in volume, and both the relative concentration and partial pressure of CO₂ are higher (with a partial pressure of 360–540 psi and CO₂ present at 40–50 vol.%) once the syngas has passed through a water-gas shift reactor (WGS).

Today, an array of membrane materials and engineering configurations is being developed for capturing CO₂. However, Phillips notes, “Aside from a few that are moving toward pilot-scale demonstration, most of today’s promising membrane developments for CO₂ separation are still being demonstrated in the laboratory, so they have a long way to go.” The good news, he says, is that “once they’ve been..."
adequately proven, these systems should scale up pretty easily (because membrane scaleup tends to be linear), so this should help to speed the eventual widespread commercial-scale use of membrane systems for CO\textsubscript{2} capture.”

**A pressing need**

“In terms of technical feasibility, the use of membrane systems for the pre-combustion removal of CO\textsubscript{2} from syngas in IGCC facilities is the most promising because of the higher pressures and concentrations that are available,” says John Marano, president of JM Energy Consulting, Inc. (Gibsonia, PA). However, Ciferno of NETL notes that “the need for a membrane-based retrofit option for post-combustion CO\textsubscript{2} capture from coal-fired power plants is perhaps even more urgent because of the severe operating and economic penalties imposed on the power plant by existing solvent-based absorption options.”

In general, the U.S. Dept. of Energy (DOE; Washington, D.C.; www.doe.gov) has set a target for CO\textsubscript{2}-capture technologies to achieve 90% CO\textsubscript{2} capture, incur less than 20% parasitic energy losses, and increase the overall cost of electricity (COE, a metric that is a function of the energy required for capture and the capital cost of the capture equipment) by no more than 10% for IGCC plants and by no more than 35% for conventional coal-fired plants.

Studies indicate that current absorption-based processes (i.e., the Selexol, Rectisol and monoethanolamine [MEA] processes) result in 10–30% parasitic energy losses, and increase the overall cost of electricity (COE, a metric that is a function of the energy required for capture and the capital cost of the capture equipment) by no more than 10% for IGCC plants and by no more than 35% for conventional coal-fired plants.

Solvent-based processes have numerous heat exchange requirements to cool the streams for treatment and to reheat them to meet temperature needs further downstream, says EPRI’s Phillips. “By comparison, there are many potential thermodynamic advantages and implied capital cost savings when a membrane system is able to handle syngas right out of the solids filter or WGS reactor and carry out the separation at, say, 300°C, to separate the CO\textsubscript{2} and send the H\textsubscript{2} straight to the gas turbine at the needed temperature,” he adds.

**Using a sweep gas to improve separation**

To improve membrane-separation efficiency in both pre-combustion and post-combustion settings, several membrane designers are investigating the use of a sweep gas on the downstream (low-pressure) permeate side of the membrane. Nitrogen is the sweep gas of choice for IGCC applications, while coal-fired power plants are more likely to use a slipstream of compressed combustion air.

In an IGCC facility, the ability to use a nitrogen stream to continuously remove product hydrogen from the permeate side of the membrane — a concept devised by NETL — helps to continuously boost the differential pressure (which creates a larger driving force) across the membrane, explains Marano. In addition, a nitrogen source is readily available in most IGCC facilities, because the enormous air separation units (ASUs) required to produce the needed oxygen for oxygen-blown coal gasification also produce large volumes of byproduct nitrogen.‡

Meanwhile, the use of a nitrogen sweep will serve another important purpose in an IGCC facility. “Hydrogen not only has a lower density and completely different flow geometries, but it has a broader flammability range and a flame speed that is an order of magnitude higher than hydrocarbon fuels,” explains Phillips. As a result, the advanced gas turbines being designed to burn hydrogen in IGCC plants are expected to require some fuel dilution — for example, via the addition of 40–60 vol.% N\textsubscript{2} — because the high firing temperature of H\textsubscript{2} would otherwise create excessive NO\textsubscript{2} emissions.

“If you add a nitrogen sweep on the permeate side of the H\textsubscript{2}/CO\textsubscript{2} separation membrane, you not only help the membrane to function better, but you help the downstream turbine meet its own hydrogen-nitrogen blending needs and lower the flame temperature in the gas turbine,” Phillips notes. “And, because the use of a sweep gas also allows the pressure of the product hydrogen stream to be kept at 350–450 psi or more, this could reduce the need for a booster compressor ahead of the hydrogen turbine.”

For coal-fired power plants, the use of air as the sweep gas (instead of nitrogen) is being investigated. A slipstream of air (which is already being produced to feed the boiler’s pulverized-coal combustion system) sweeping across the permeate side of the membrane would continuously remove product CO\textsubscript{2}, thereby increasing the pressure differential across the membrane and driving the CO\textsubscript{2}/N\textsubscript{2} separation further.

Once the air/CO\textsubscript{2} sweep mixture is returned to the combustor inlet, the oxygen is burned and the small recycled stream of CO\textsubscript{2} in the sweep helps to bring the partial pressure of the CO\textsubscript{2} in the boiler fluegas up from about 14 vol.% to 19 vol.%, improving the overall membrane separation, explains Tim Merkel, director of process R&D at Membrane Technology and Research (MTR; Menlo Park, CA; www.mtrinc.com).

Membrane systems for pre-combustion CO₂ capture

As IGCC deployment picks up speed, advanced IGCC facilities are expected to be routinely designed for carbon capture and storage (CCS). These state-of-the-art IGCC+CCS processes are expected to include a water-gas shift (WGS) reactor, in which the “unshifted” syngas stream (CO + H₂) is reacted with steam over a catalyst to convert CO to CO₂, producing a “shifted” syngas composed primarily of hydrogen and CO₂ (shown in Figure 1b).

This shift reaction serves two purposes. First, it yields an enriched hydrogen stream, which can be burned in specialized hydrogen turbines in the IGCC facility’s combined-cycle power plant. Second, it effectively concentrates the carbon in the syngas into an enriched CO₂ stream, making CO₂ capture for industrial use or enhanced oil recovery (EOR) applications or for long-term underground sequestration in a deep geological reservoir easier and more cost-effective.

IGCC systems provide an ideal environment for membrane separation. “When a membrane-based separation system is placed downstream of the WGS reactor, the shifted syngas not only has a higher concentration of CO₂, but the partial pressure of that CO₂ is also higher, providing the needed driving force across the membrane, minimizing the need for syngas compression,” says Phillips.

Specifically, syngas typically exits the gasifier at an elevated pressure of 600–800 psi or more. After the WGS step, the relative concentration of CO₂ in the shifted syngas is 40–50 vol.% CO₂, and its partial pressure is 240–400 psi. This provides enormous driving force for membrane separation compared to post-combustion fluegas, which typically contains just 15 vol.% CO₂ and is at atmospheric pressure.

For any CO₂-capture scenario, the ability to retain as much pressure as possible through the system is key not only to drive the separation, but also to meet the downstream pressure requirements. For instance, pipeline and subsurface sequestration require the CO₂ to be at pressures near 2,200 psi so that the CO₂ gas behaves like a supercritical fluid and takes up less space underground. Similarly, after syngas separation, the hydrogen stream will need to remain at a minimum pressure of 350–450 psi to meet downstream turbine requirements.

Eltron Research and Development (Boulder, CO; www.eltronresearch.com) has developed a three-layer H₂/CO₂ separation membrane that combines a proprietary, dense-phase metallic hydrogen-transport membrane with two catalyst layers, each just 300 nm thick. On the feed side of the membrane (which receives inlet syngas at 450–1,000 psi), the first catalyst layer dissociates the hydrogen gas into hydrogen atoms. On the permeate side, the other catalyst layer promotes the reassociation of the hydrogen atoms so that hydrogen gas exits the unit at pressures up to 400 psi. “Based on this atomic transport of hydrogen, this novel membrane design provides enhanced selectivity for hydrogen permeation — in the range of five or six nines purity,” adds Doug Jack, vice president of technology for Eltron.

DOE has set a 2010 target for pre-combustion CO₂/H₂ membrane-separation systems to achieve hydrogen flux rates of 200 std. ft³/h per square foot of membrane area (scfh/ft²) and a 2015 target of 300 scfh/ft². Jack notes that Eltron’s three-layer membrane/catalyst configuration has already demonstrated hydrogen flux rates of 450 scfh/ft².

To date, a pilot-scale unit of the Eltron process — which will lead to a bundled shell-and-tube vessel design (Figure 2) — has produced 5 lb/d of hydrogen as the product, and 85 lb/d of CO₂ as the retentate, under anticipated operating conditions. The company is seeking to partner with an existing coal-fired syngas facility to perform the next phase of scaleup, which will demonstrate a unit that produces 220 lb/d of hydrogen (1.9 tons/d of CO₂) using a slipstream of syngas from an actual coal gasifier.

When syngas is passed through the Eltron membrane system, roughly 95% of the hydrogen passes through as the product or permeate stream, while the CO₂ is captured on the upstream side of the membrane as the retentate stream. Because the CO₂ doesn’t pass through the membrane, it doesn’t experience a pressure drop, and “this helps the CO₂ stream to remain close to the gasifier pressure, minimizing the capital costs and energy requirements to recompress millions of tons of CO₂,” says Jack.

Meanwhile, using the concept of process intensifica-
The challenge of implementing membrane-based separation systems becomes even more acute for coal-fired power plants due to the nature of the fluegas stream. “Post-combustion membrane capture wasn’t even in the DOE project R&D portfolio until the last two or three years. But the need to retrofit existing coal-fired power plants is a big driver today,” says Ciferno of NETL.

“Post-combustion systems that rely on amine-based separation of CO₂ are already taking a pretty big hit, in terms of the cost penalty of the prevailing technique. So that provides a pretty big incentive for membrane designers to develop a system that can cost-effectively be retrofitted to existing power plants,” he adds.

To get around this fundamental engineering challenge of handling a large-volume, low-pressure, dilute stream, many of today’s membrane developers have been pursuing advanced membrane materials that provide increased flux rates and selectivity for CO₂. (Membrane materials are discussed in the white paper cited in the footnote on p. 42). Many are also designing their post-combustion membrane systems to pull a slight vacuum on the permeate side (as this is less costly than compressing the large volume of dilute fluegas at the inlet side), and pursuing designs that incorporate a sweep gas on the permeate side (discussed earlier) to increase the pressure differential across the membrane (shown in Figure 1a).

MTR has developed a new CO₂-selective polymeric membrane material and module — dubbed the MTR Polaris membrane — that provides higher CO₂ permeance for post-combustion fluegas applications than existing polymeric membranes, says Merkel. Permeance is a measure of pressure-normalized flux, an indication of how much gas is actually flowing across the membrane per unit of pressure differential.

Permeance equals permeability (an intrinsic material property) divided by the thickness of the selective layer, and is expressed in gas permeance units (GPU), with 1 GPU = $10^{-6}$ cm$^3$(STP)/cm$^2$(scmHg) = 3.3 $\times$ 10$^{-1}$ mol/(m$^2$.s.Pa).

With cellulose acetate membranes (the most common material used to remove CO₂ from methane during natural gas processing), flux rates “are so low, you’d need too much membrane surface area to effectively treat power plant fluegas, so this material is not economical for power plant applications,” Merkel says. By comparison, the spiral-wound MTR Polaris membrane (Figure 3) developed to separate CO₂ from nonpolar gases (such as methane or nitrogen) has a CO₂ permeance rate that is 10 times higher than that of cellulose acetate (1,000 GPU versus 100 GPU).

Because the MTR Polaris membranes are ten times more permeable to CO₂ than conventional materials (which reduces the required membrane area and capital costs), and use a slipstream of combustion air as a sweep gas, “we’ve been able to develop a system with reasonable membrane area requirements, reduced energy requirements, and reasonable capture costs for fluegas,” says Merkel.

To date, the MTR Polaris membrane has been demonstrated in 8-in.-dia. (incorporating 20 m$^2$ of membrane area) and 12-in.-dia. (50 m$^2$) modules in the field treating natural gas. In late 2009, the company will be working with the Arizona Public Service Co. (APS) Cholla power plant (Joseph City, AZ) to demonstrate a larger system that will handle actual coal-fired fluegas and produce 1 ton/d of CO₂. A commercial-scale system for a 600-MW power plant will eventually produce 10,000 ton/d of CO₂, says Merkel. To date, the air sweep system has been...
demonstrated at bench scale; larger-scale demonstration will take place at the APS Cholla site.

Facilitated transport membranes

Another class of membranes — facilitated transport membranes, or FTMs — “have been studied for over 40 years, and show tantalizingly good performance under ideal conditions,” says Merkel. “Unfortunately, they have never been used commercially, primarily because of carrier-instability problems.”

Today, Carbozyme, Inc. (Monmouth Junction, N.J.; www.carbozyme.us) is working to improve the basic FTM concept for CO₂ capture from post-combustion fluegas. Structurally, Carbozyme’s novel design consists of a series of hollow polymeric membrane fibers that are woven into a flat fabric, which provides a controlled mechanism for maintaining a flat liquid film (Figure 4). The liquid is trapped between the individual membrane strands in each woven sheet, and between the sheets that are layered and spiral-wound to fit into the process vessel. Alternating rows of the hollow polypropylene fibers in the fabric carry either the feed gas or the sweep gas. “This design combines membrane-based diffusion and liquid absorption for better overall separation,” says Michael Trachtenberg, chairman, CEO and CTO of Carbozyme.

Some earlier FTM designs rely on amines (which are corrosive and toxic) as the liquid phase to bind to CO₂ and promote absorption and desorption of CO₂ across the membrane-liquid interfaces in a single device. By contrast, Carbozyme’s FTM system relies on saltwater instead.

“Our spiral-wound units provide massive membrane surface area, helping to minimize residence time, and the gas runs axially in the bore of the hollow fibers, so there’s not much pressure drop across the system,” says Trachtenberg. “As CO₂ diffuses across the microporous, hydrophilic hollow fibers, it is catalyzed by an enzyme (carbonic anhydrase, or CA) that is immobilized at the gas-liquid interface. CA converts CO₂ to bicarbonate at the feed side, and following diffusion of the bicarbonate across a very thin film, the reverse reaction occurs via a second layer of CA at a second surface,” he explains (Figure 5).

CA is a very efficient catalyst for turning CO₂ into bicarbonate, whose solubility in water is several orders of magnitude higher than that of dissolved CO₂, and this enables high separation efficiencies, explains Trachtenberg. In addition, no heating or cooling of the inlet stream is required (fluegas enters the system at the adiabatic temperature of 52°C), and a mild vacuum pulled on the downstream side helps to increase the pressure differential across the membrane fibers. “The permeate stream has roughly 50 vol.% CO₂ with a comparable amount of water vapor, and when the water is taken out, the dry permeate stream is about 95 vol.% CO₂,” he says.

To date, a demonstration-scale unit with 0.5 m² of membrane surface area has operated for 250 h using artificial gas mixtures that simulate coal fluegas. The company is gearing up for a 40-m² demonstration system slated for startup later this year, which it hopes to operate for 2,000 hours using actual coal-combustion fluegas at DOE’s Energy and Environmental Research Center at the Univ. of North Dakota.

As competing membrane materials and system configurations continue to mature, the engineering community is confident that this technology will provide a more cost-effective option for CO₂ capture compared to the use of solvent-based absorption, which is the prevailing technology option available today.