

Hydrogen Separation Membranes

HYDROGEN SEPARATION MEMBRANES

The Problem

Coproduction of power, fuels, chemicals, and hydrogen through coal gasification coupled with carbon capture and storage will undoubtedly play a large role in the future energy generation of the United States. Hydrogen production technologies have the potential to nearly eliminate carbon emissions and dependency on oil. However, current technology options for hydrogen production and CO₂ separation are typically more expensive than traditional energy production.

Hydrogen separation membranes represent a potential pathway for economical hydrogen production and CO₂ separation. Hydrogen separation membranes are commercially available, but most developments have sprung from advancements in hydrogen separation from steam methane-reforming plants or refineries. Most membranes used today are susceptible to contaminants commonly found in coal-derived syngas, such as sulfur, ammonia, mercury, and trace metals. Gas cleanup technologies will minimize many of these contaminants, but trace amounts will break through, and system upsets will inevitably occur. Considering that most membrane materials are very expensive, optimizing and demonstrating resistance to common contaminants is needed.

The Solution

The development and deployment of hydrogen separation membrane technologies are vital to energy sustainability in a carbon-constrained world. Coal gasification technologies combined with advanced gas cleanup and carbon capture technologies will enable the production of hydrogen from coal with near-zero emissions. Hydrogen separation membrane technologies have the potential to play an important role in near-zero-emission plants because membranes can produce hydrogen economically, at large scale, and with very low levels of impurities.

How It Works

Conventionally, cold-gas cleanup methods have been employed to remove contaminants from coal gasification syngas streams. Methods such as Rectisol® or Selexol® are commercially available and are very effective at removing contaminants but also have high capital and operational costs.

Significant economic benefits can be realized by utilizing warm- or hot-gas-cleaning techniques. The Department of Energy (DOE) has reported that thermal efficiency increases of 8% over conventional techniques can be realized by integrating warm-gas cleanup technologies (1) into integrated gasification combined-cycle (IGCC) plants. Hydrogen separation membranes typically operate at warm-gas cleanup temperatures, so they are a good match for IGCC projects employing warm-gas cleanup and carbon capture.

Conventional Hydrogen Separation Processes

- Pressure swing adsorption (PSA) is the most common method used today for hydrogen separation. PSA is based on an adsorbent bed that captures the impurities in the syngas stream at higher pressure and then releases the impurities at low pressure. Multiple beds are utilized simultaneously so that a continuous stream of hydrogen at purities up to 99.9% may be produced (2).
- Temperature swing adsorption is a variation on PSA, but it is not widely used because of the relatively long time it takes to heat and cool sorbents.
- Electrical swing adsorption has been proposed as well, but it is currently in the development stage.
- Cryogenic processes also exist to purify hydrogen, but they require extremely low temperatures and are, therefore, relatively expensive (3).

Principles of Hydrogen Separation Membranes

Most hydrogen separation membranes operate on the principle that only hydrogen can penetrate through the membrane because of the inherent properties of the material. The mechanism for hydrogen penetration through the membrane depends on the type of membrane in question. Most membranes rely on the partial pressure of hydrogen in the feed stream as the driving force for permeation, which is balanced with the partial pressure of hydrogen in the product (permeate) stream.

Figure 1 illustrates the basic operating principles of hydrogen separation membranes for use in coal-derived syngas. This figure

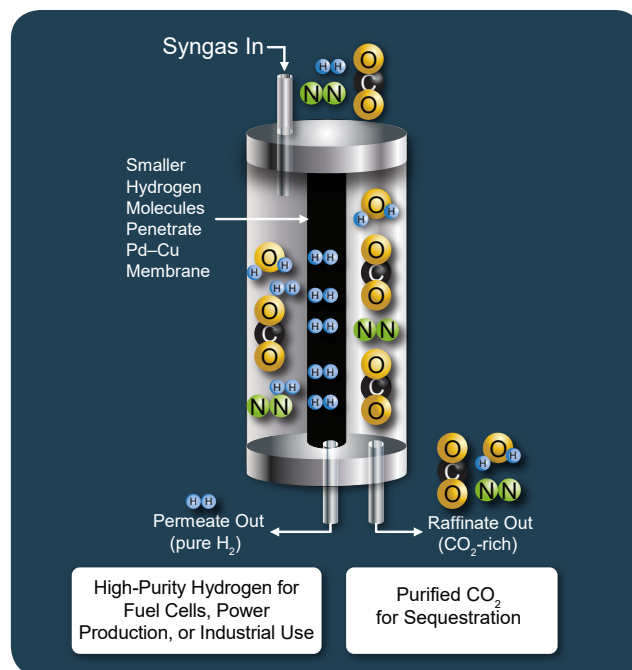


Figure 1. Illustration of the operating principle of hydrogen separation membranes (4).

shows a tubular membrane, but plate and frame-style membranes have also been developed. The “syngas in” stream refers to the feed gas into the membrane module. The permeate stream, which in this case is made up of mostly hydrogen, has permeated through the membrane wall. The remaining gases (raffinate stream) are what is left of the feed stream once the permeate is separated. A sweep gas such as nitrogen may be used on the permeate side to lower the partial pressure and enable more hydrogen to pass through the membrane.

Types of Membranes

Table 1 compares, in general, the relative operational performance of five membrane types. Each membrane type has advantages and disadvantages, and research organizations and companies continue to work to develop better versions of each.

Table 1. Properties of Five Hydrogen-Selective Membranes (3, 5, 6)

	Dense Polymer	Microporous Ceramic	Dense Ceramic	Porous Carbon	Dense Metallic
Temperature Range	<100°C	200°–600°C	600°–900°C	500°–900°C	300°–600°C
H ₂ Selectivity	Low	Moderate	Very high	Low	Very high
H ₂ Flux	Low	High	Moderate	Moderate	High
Known Poisoning Issues	HCl, SO _x , CO ₂		H ₂ S	Strong vapors, organics	H ₂ S, HCl, CO
Example Materials	Polymers	Silica, alumina, zirconia, titania, zeolites	SrCeO _{3-δ} , BaCeO _{3-δ}	Carbon	Palladium alloys, Pd–Cu, Pd–Au
Transport Mechanism	Solution/diffusion	Molecular sieving	Solution/diffusion	Surface diffusion, molecular sieving	Solution/diffusion

Commercially Available Membranes

- Air Liquide has technology called MEDAL™ that is typically used in refinery applications for hydrotreating. The membrane is selective to components other than hydrogen, including H₂O, NH₃, and CO₂ and, therefore, would probably not be a good fit in most coal gasification applications (7).
- Air Products offers a line of hydrogen recovery membranes referred to as PRISM® membrane systems (8). The PRISM membrane is intended for separations in hydrocracker and hydrotreater systems or for CO purification in reformer gases. The systems are low-temperature and not intended for processing on coal-derived syngas.
- Wah-Chang offers small-scale Pd–Cu membranes for commercial sale that are capable of producing an ultrapure stream of hydrogen from syngas. The one drawback of the membrane (like many Pd-based membranes) is that it has a very low tolerance to H₂S and HCl, both of which are commonly found contaminants in coal-derived syngas.

Development of New Membranes

Many companies and organizations are actively researching new hydrogen separation materials that have the potential to meet DOE performance goals (9–21). Most of the initial testing of these membranes has been performed using gases mixed in the labs. The next step in the DOE plan is to test the membrane systems using hydrogen-rich syngas produced in coal gasification systems to ensure that the membranes are effective in the presence of components typically found in commercial applications. The Energy & Environmental Research Center’s (EERC’s) National Center for Hydrogen Technology (NCHT) has successfully performed initial work in this area, using a commercially available hydrogen separation membrane, and is in the planning stages for testing several of the new hydrogen separation membranes that are being developed in the DOE program.

The EERC’s NCHT has multiple bench- and pilot-scale gasification systems capable of gasifying coal, biomass, and other solid or liquid feedstocks. Each system has the capability to be coupled with a bench-scale warm-gas cleanup train capable of reducing contaminants to levels that are suitable for hydrogen separation membranes. Water–gas shift reactors, including sour and high- and low-temperature shift, can be inserted at any location in the cleanup train. Hydrogen separation using membranes can be performed at elevated temperatures without the need to quench the syngas because of the capability of the warm-gas cleanup train. The hydrogen membrane can be inserted into any point in the cleanup train to simulate the desired operating conditions but would normally be installed after the sulfur removal and shift reactors, depending on the sensitivity of the membrane to sulfur. If needed, a small slipstream of the syngas from any gasifier can be pulled for hydrogen separation testing.

Testing has been performed at the EERC’s NCHT in conjunction with DOE to develop methods to remove contaminants from syngas to levels suitable for a hydrogen separation membrane. The warm-gas cleanup train is capable of removing sulfur, particulate, chlorine, and trace metals including mercury at temperatures above 400°F. A recent test involved gasification of Texas lignite in the EERC’s transport reactor development unit, with a slipstream of gas being sent to the warm-gas cleanup train. The test demonstrated that hydrogen with purity greater than 99.9%+ could be produced from Texas lignite without reducing the temperature of the syngas below 400°F.

What Comes Next?

The next step for several of these membranes is testing on a bench- or pilot-scale coal gasification unit, where the syngas is cleaned to levels that would mimic a typical commercial-scale gasification operation. Successful demonstration at the pilot scale would include demonstrating that high hydrogen flux can be maintained over long durations, little or no performance degradation due to impurities, high hydrogen recovery rates, and low operating cost. Membranes that successfully meet these criteria and the 2015 criteria listed by DOE may be candidates for scale-up to a demonstration-scale facility, followed by potential inclusion in a FutureGen-style facility.

About NCHT

The NCHT is located at the EERC at the University of North Dakota. The EERC was designated as the NCHT in 2004 in recognition of over 50 years of hydrogen research involving fossil and renewable energy. With its 85 commercial partners, NCHT is focused on the production, storage, transport, and end use of hydrogen.

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