

Hydrogen from Coal Program



Securing Our Future

Research, Development,
and Demonstration Plan

For the Period 2010 through 2016

External Draft

September 2010



U.S. DEPARTMENT OF

ENERGY

Fossil
Energy

National Energy Technology Laboratory

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Executive Summary

Hydrogen has the potential to play a significant role in the nation's energy future, particularly for the production of clean electric power from coal. Production and use of hydrogen in a gasification combined cycle system for stationary power applications will complement the development of next generation hydrogen turbine technology that enables the plant to achieve near-zero pollutant emissions and increased plant efficiency. The Hydrogen from Coal Program's Research, Development, and Demonstration (RD&D) activities include development of hydrogen separation membranes and other advanced technologies that efficiently produce high purity hydrogen for stationary power production. When combined with carbon management technologies such as carbon capture and storage (CCS) and coal-biomass co-utilization, these next generation power plants will achieve significant reductions in greenhouse gas (GHG) emissions with low electricity costs.

The Hydrogen from Coal RD&D Plan

This multi-year RD&D Plan addresses the strategies, goals, milestones and progress of the program, and defines the research areas needed to support the other Office of Clean Coal (OCC) programs and the overall DOE Hydrogen activity.

This RD&D Plan is organized by section, as follows:

- Section 1. Introduction
- Section 2. Hydrogen from Coal Program Mission and Goals
- Section 3. Technical Discussion
- Section 4. Technical Plan
- Section 5. Implementation Plan

Detailed activities and technical targets are provided in the Technical Plan in Section 4. Implementation of the Program's activities will be coordinated closely with the related activities supported by the Office of Fossil Energy (FE) and other organizations both inside and outside the government.

The FE Hydrogen from Coal Program was initiated in fiscal year 2004 (FY 2004). The Program is transitioning from hydrogen production for transportation applications to electric power applications by reducing technological market barriers for the reliable, efficient, and environmentally friendly conversion of coal to hydrogen with carbon capture and storage and other carbon reduction techniques. This Hydrogen from Coal RD&D Plan focuses on those hydrogen activities necessary to support the goals of FE's Office of Clean Coal in development and demonstration of advanced, near-zero emission coal-based power plants. The outcome of this strategy will be the deployment of advanced hydrogen separation membrane modules and other advanced concepts such as process intensification that provide high purity hydrogen for use in a stationary turbine using integrated gasification combined cycle (IGCC) technology. Collectively, these technologies will enhance plant efficiency and in combination with CCS and displacement of a portion of the coal with biomass, provide significantly reduced GHG emissions.

Goals: The goals of the Hydrogen from Coal Program RD&D activities are:

- Prove the feasibility of a 40 percent efficient, near-zero emissions power facility that uses membrane separation technology as well as other advanced technologies to reduce the cost of electricity by at least 35 percent (relative to a base case IGCC with CCS using currently available technologies).

- Develop hydrogen production and processing technologies that will contribute approximately 2.9 percent in improved efficiency and 12 percent reduction in cost of electricity to the 40 percent efficient near-zero emissions power facility.

Overview of Technology in the RD&D Plan

RD&D will be directed toward hydrogen production and separation from coal gasification for stationary power applications by:

- Performing research on:
 - Hydrogen membrane separation, and
 - New strategies for process intensification and other advanced concepts such as co-production and chemical looping.

Advanced hydrogen membranes integrated with other advanced IGCC technologies can improve overall power generation efficiency and reduce costs. Process intensification involves developing novel technologies that combine multiple processes into one step, use new control methods, or integrate alternative energy technologies with hydrogen from coal technologies. Chemical looping offers the potential for hydrogen production with near-100 percent carbon capture and increased plant efficiency. Novel co-production concepts may allow more effective plant operation or further reduce costs for clean electric power production.

- Pursuing technical targets for the program including the following:
 - Develop hydrogen membranes by 2015 that can provide hydrogen fuel that meets gas turbine specifications from syngas under warm gas cleanup conditions at a flux level of 300 standard cubic feet per hour per square foot (SCFH/ft²) of membrane area, at pressures that will reduce compression costs for H₂ and CO₂, and at a membrane cost of less than \$100 per ft².
 - Develop advanced concepts for syngas processing in gasification-based electric power generation systems that will significantly reduce complexity and cost, improve plant and fuel utilization and/or improve efficiency, to produce H₂ for gas turbine fuel and CO₂ for sequestration.

Accomplishments and Progress

The Hydrogen from Coal Program has successfully transitioned from its initial start-up in FY 2004 to full operations. The Program has been actively soliciting proposals from industry, universities, and other organizations to help the program achieve its goals. Currently, the program has projects to develop advanced technologies targeted toward higher efficiency and reduced cost of electricity from IGCC plants that produce hydrogen and use it to generate electricity.

Research progress is periodically reviewed to update the RD&D Plan with respect to goals, technical targets, milestones, and program schedules. This FY 2010 update reflects the focus on close coordination with the Office of Clean Coal power generation programs and activities to achieve lower cost, improved plant efficiency, reduced GHG emissions, and creation of jobs.

Technical

Ongoing research activities are aimed at development and scale-up of precious-metal-based hydrogen separation membranes and other membrane concepts. Several of the hydrogen membrane developers' test results have shown that, in the absence of sulfur, their membranes can exceed the 2015 flux technical target noted above. Notably:

- Eltron Research, Inc. is developing alloy-based membranes and has developed a separator unit rated to produce 1.5 lbs/day of hydrogen. Eltron's best alloy membrane has demonstrated a H₂ flux rate of 411 SCFH/ft² at specified pressure and gas compositions.
- Worcester Polytechnic Institute (WPI) is developing Pd-based membranes on tubular stainless steel or alloy supports. WPI achieved a H₂ flux of 359 SCFH/ft² in pure gases at 442°C and 100 psi ΔP with a 3–5 micron (μm) thick palladium(Pd) membrane with an Inconel base. WPI has also built an engineering-scale prototype membrane.
- Praxair is building a Pd-alloy based prototype multi-tube hydrogen purifier and will use the unit to demonstrate prototype performance. A Pd-Au membrane (5 percent Au, 9μm thickness) showed H₂ flux in pure gas of 384 SCFH/ft² and the H₂/N₂ selectivity was 495 at 200 psi.
- United Technologies Research Center (UTRC) is developing two types of membrane separators using metallic supports: one based on a commercial tube design with a Pd-based alloy; the other using a novel nano-composite material. UTRC's current membrane flux performance is approximately 45 SCFH/ft² at a temperature of 450°C and feed pressure of 200 psi. Anticipated performance for the nano-oxide membrane is H₂ flux of 400 SCFH/ft².
- Southwest Research Institute (SwRI) is developing Pd-foil-based membrane separators. SwRI has tested 70 percent Pd, 20 percent Au, 10 percent Pt foils under the DOE Test Protocol gas composition, with flux levels of approximately 30 SCFH/ft².

Precious metals are effective materials for hydrogen separation membranes. However, they are expensive and present a potential security risk, given that some supplies are imported. The National Energy Technology Laboratory (NETL) completed a comprehensive assessment of the production of precious metals currently used in hydrogen membrane fabrication. The assessment showed:

- Commercial deployment using precious metals has potential global economic and environmental impacts.
- Global deposits are primarily located in South Africa and Russia.
- Less than 10 significant mining companies currently exist in the world; production is declining.

Collectively, these factors could restrain the ability to provide for affordable and environmentally acceptable hydrogen production via membrane separation technologies. To address these concerns, a competitive Funding Opportunity Announcement (FOA) was released soliciting research projects that would conduct both fundamental and applied research on novel, non-precious metal hydrogen separation technologies. The projects were selected in September 2009 and are shown in Table ES-1.

Table ES-1: Non-precious Metal Membrane Projects

| Project Performer | Project Title/Description | DOE Funding | Participant Funding |
|---------------------------------|--|-------------|---------------------|
| Colorado School of Mines | Nanoporous metal carbide surface diffusion membranes | \$998,543 | \$250,628 |
| Ceramatec | Ceramic or ceramic composite proton conducting membranes | \$924,549 | \$253,637 |
| Worcester Polytechnic Institute | Supported molten metal membranes | \$996,567 | \$249,857 |
| Southwest Research Institute | Amorphous Zr-Ni alloy membranes for hydrogen separations | \$799,786 | \$199,950 |
| University of Florida | Novel magnetically assisted fluidized bed reactor development for chemical looping | \$999,920 | \$249,980 |
| University of Nevada-Reno | Amorphous alloy membranes prepared by melt-spin methods | \$1,163,596 | \$290,899 |
| University of Texas at Dallas | Non-precious metal mixed matrix membranes | \$1,000,000 | \$250,000 |

Based on its earlier research work, the Hydrogen from Coal Program issued a FOA in March 2010 seeking innovative projects that could be scaled up for eventual pre-commercial demonstration. The FOA was closed in May 2010 and four projects were selected: Praxair, Inc.; United Technologies Research Center; Western Research Institute; and Worcester Polytechnic Institute.

Activity

Hydrogen production from coal activities are closely linked with the system’s up-front gasification technologies, downstream turbine combustion, and CO₂ capture and sequestration. Therefore, these four DOE programs are coordinated within the Office of Clean Coal to enhance integration of the separate programs. Additionally, the Hydrogen from Coal Program continues to coordinate with other DOE offices by participating in the development of various planning documents and in the DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review of the sponsored projects.

Benefits

The technologies being developed by the Hydrogen from Coal Program offer a variety of important technical, economic, and environmental benefits. These benefits include a reduced carbon footprint, reduced cost of electricity, increased energy security through reduced imports, and the creation of high-tech domestic jobs.

Reduced Carbon Footprint

Gasification technologies have shown the potential to produce clean hydrogen and electricity from coal and coal/biomass mixtures with virtually zero criteria pollutant emissions. Hydrogen turbines utilized in combined cycle power production systems using hydrogen from gasification can provide electricity at higher efficiency and lower cost than conventional systems, while facilitating the capture of carbon dioxide for storage. Carbon sequestration technologies are being developed to provide the capability to cost-effectively use the concentrated CO₂ streams from gasification in enhanced oil recovery, geological storage, and accelerated biomass growth processes for fuel production¹.

¹ DOE/NETL, *Affordable, Low-Carbon Diesel Fuel from Domestic Coal and Biomass*, January 2009

Substitution of a portion of the coal feedstock with biomass can provide an added benefit in carbon reduction. NETL systems studies show that the combination of CCS and substitution of a portion of the coal feedstock with biomass of several types will provide substantially lower life-cycle carbon emissions, while allowing operators to use regional non-food biomass resources in large efficient coal-based plants.

Reduced Cost of Electricity

When compared to the reference IGCC case with CCS using current technology, an advanced IGCC plant with CCS using warm gas cleanup, hydrogen separation membranes and an advanced hydrogen turbine offers a significant improvement in plant efficiency and capital costs, leading to reduced cost of electricity to consumers. The membranes are less expensive than the technology they replace, and provide the added benefit of producing CO₂ at a higher pressure, leading to reduced compression costs for sequestration. Overall, NETL studies estimate that use of hydrogen separation membranes in conjunction with warm gas cleanup instead of the current Selexol technology for separation of CO₂ and H₂ will improve plant efficiency by 2.9 percent and reduce the overall cost of electricity by 12 percent.²

Co-production of electricity with hydrogen, other fuels, or chemicals for export could also reduce electricity costs. Hydrogen could be exported and sold to reduce the cost of electric power, improve gasifier utilization, and help build hydrogen infrastructure. Production and storage of hydrogen at the plant site during periods when electricity is not needed (e.g., night) would allow higher capacity electric power production when electricity demand is high (e.g., peak daytime hours) or allow better integration with intermittent sources such as solar or wind.

Creation of High-Tech Domestic Jobs

The development of hydrogen production and separation technologies that provide high purity hydrogen will complement the development of advanced hydrogen turbines. This will result in the United States becoming a key leader in these technologies and creation of new high paying domestic jobs to manufacture and oversee the deployment and operation of next generation gasification and turbines technology.

Increased Energy Security

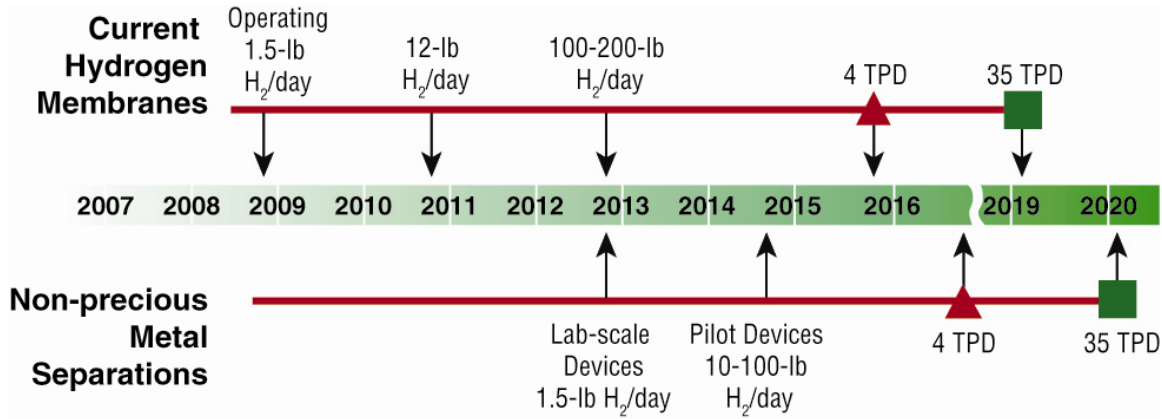
The technologies developed by the Hydrogen from Coal Program offer the potential to improve domestic energy security in two ways. The electrification of the nation's energy sectors using clean, highly efficient, low carbon coal power production systems to supply surface transportation vehicles (e.g., plug-in hybrids) will over time reduce the need for insecure imported crude oil. Additionally, while offering reduced cost of electricity benefits noted above, co-production technology provides the potential to domestically produce a variety of fuel and chemical products which are currently imported.

² DOE/NETL, *Current and Future Technologies for Gasification-Based Power Generation*, November 2009

Technical Activity Gantt Chart Summary

The specific sub-element activities and their associated timelines are shown in the chart in Figure ES-1, which summarizes the activities and technologies associated with hydrogen production from large-scale IGCC plants.

Figure ES-1. Hydrogen from Coal RD&D Program Milestones



Current Hydrogen Membranes

- End of 2008: Operating at 1.5 lb H₂/day
- End of 2010: Operating at 12 lb H₂/day
- End of 2012: Operating at 100–200 lb H₂/day
- End of 2015: Scale-up membrane module to 4 tons H₂/day production for component testing
- Beginning of 2019: Scale-up membrane module to 35 tons H₂/day production for integrated testing

Non-precious Metal Separations

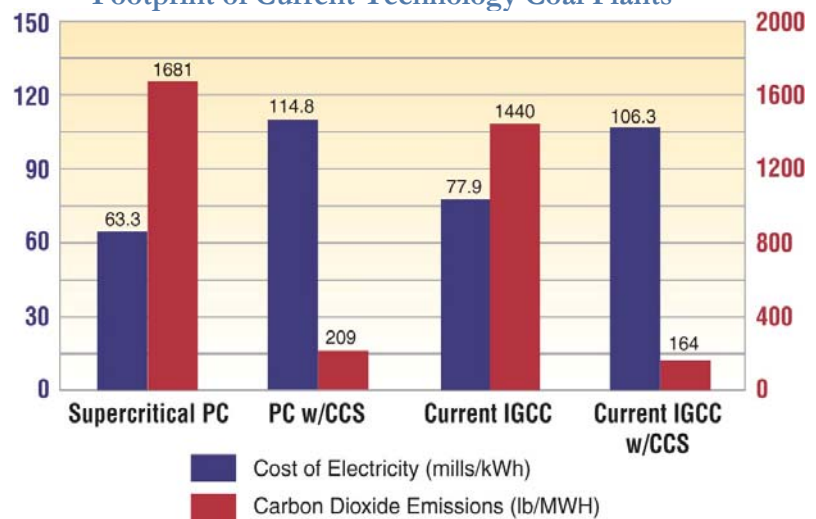
- End of 2012: Operating lab-scale devices at 1.5 lb H₂/day
- End of 2014: Operating pilot-scale devices at 10–100 lb H₂/day
- End of 2016: Scale-up non-precious metal membrane module to 4 tons H₂/day for component testing
- Beginning of 2020: Scale-up non-precious metal membrane module to 35 tons H₂/day for integrated testing

1. Introduction

As a preeminent primary source of energy, coal is an abundant domestic resource, with the United States boasting hundreds of years of supply at current demand levels. Today coal represents over 50 percent of the nation's electricity supply, but contributes over 40 percent to the nation's total carbon dioxide emissions. Continued use of coal-supplied electricity will require the significant reduction of the carbon footprint of coal-fired power plants. As seen in Figure 1, the gasification of coal to produce hydrogen and its use in turbines in an IGCC system provides a pathway to produce clean electricity from coal with higher efficiency, lower carbon footprint and lower cost when compared to other coal power generation technologies. In combination with co-feeding of biomass and carbon management techniques including carbon capture and sequestration and advanced re-use such as algae production, these technologies could provide electric power with near-zero emissions.

The Hydrogen from Coal Program RD&D Plan provides a roadmap that the program will pursue to develop the technologies necessary for coal to meet the overall OCC goals of reduced GHG emissions, favorable economics, new clean energy jobs, and improved energy security. The advanced power generation program goals for OCC are to achieve 90 percent carbon capture while maintaining less than 10 percent increase in cost of electricity (COE) over a 2003 reference IGCC plant having no carbon capture. The COE of that plant is 9.3¢/kWh, so the cost target for carbon capture is no more than 10 percent greater, or 10.2¢/kWh. The IGCC case in Figure 1 represents technology progress as of 2007. Integration of technologies being researched under the Hydrogen from Coal Program will play a key role in achieving the cost reduction goal.

Figure 1. Cost of Electricity and Environmental Footprint of Current Technology Coal Plants



Source: DOE/NETL, *Cost and Performance Baseline for Fossil Energy Plants*, 2007

Note: 1 mill = 1/10th of one cent

The Plan discusses current and future technologies for the production of hydrogen from coal, its use for producing clean electricity, and its potential for the co-production of hydrogen and power with near-zero emissions. The Plan will serve as a resource document for the hydrogen activities, emphasizing close coordination with OCC goals, milestones, and targets.

2. Hydrogen from Coal Program – Mission and Goals

The mission of the Hydrogen from Coal Program is to develop advanced and novel hydrogen production technologies that will ensure the use of our nation's abundant coal and biomass resources to produce affordable electricity in a safe and environmentally clean manner. The RD&D activities will provide the pathways to produce affordable hydrogen from coal in an environmentally clean manner. These technologies can provide reduced carbon footprint and lower cost of electricity. When compared to stand-alone electricity, fuels, or chemical facilities, the coproduction of electricity and hydrogen from coal or coal/biomass mixtures offers a variety of important technical, economic, and environmental benefits.

The goals for the Hydrogen from Coal Program are:

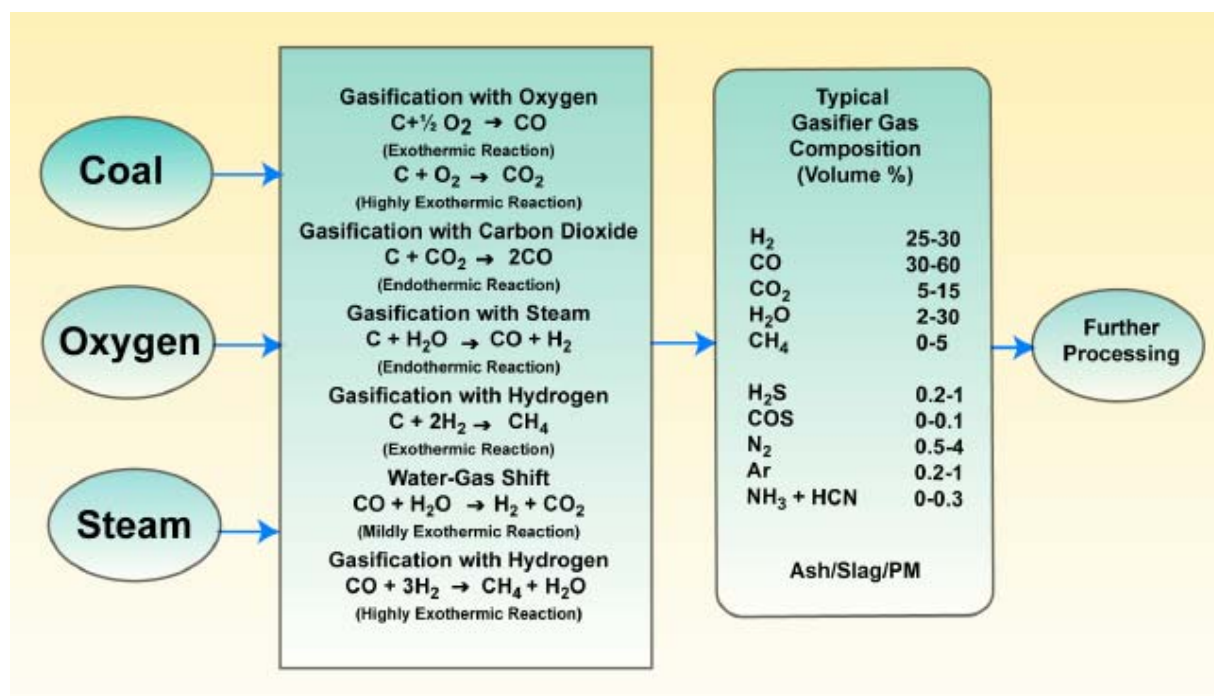
- Prove the feasibility of a 40 percent efficient, near-zero emissions power facility that uses membrane separation technology as well as other advanced technologies to reduce the cost of electricity by at least 35 percent (relative to a base case IGCC with CCS using currently available technologies).
- Develop hydrogen production and processing technologies that will contribute approximately 2.9 percent in improved efficiency and 12 percent reduction in cost of electricity for the 40 percent efficient near-zero emissions power facility.

3. Technical Discussion

3.1. Current Gasification Technology

Hydrogen can be produced from coal by gasification followed by processing the resulting synthesis gas using currently available technologies. The coal is first gasified with oxygen and steam to produce a synthesis gas consisting mainly of carbon monoxide (CO) and hydrogen (H₂), with some CO₂, sulfur, particulates, and trace elements. Oxygen (O₂) is added in less than stoichiometric quantities so that complete combustion does not occur. This process is highly exothermic, with temperatures controlled by the addition of steam. Increasing the temperature in the gasifier initiates devolatilization and breaking of weaker chemical bonds to yield tars, oils, phenols, and hydrocarbon gases. These products generally further react to form H₂, CO, and CO₂. The fixed carbon that remains after devolatilization is gasified through reactions with O₂, steam, and CO₂ to form additional amounts of H₂ and CO. These gasification reactions are shown in Figure 2.

Figure 2. Major Gasification Reactions



The minor and trace components of coal also are transformed in the gasification reactor. Under the sub-stoichiometric reducing conditions of gasification, most of the fuel's sulfur converts to hydrogen sulfide (H₂S), but some (3–10 percent) also converts to carbonyl sulfide (COS). Nitrogen bound with the fuel generally converts to gaseous nitrogen (N₂), with some ammonia (NH₃) and a small amount of hydrogen cyanide (HCN) also being formed. Most of the chlorine content of the fuel is converted to hydrogen chloride (HCl) gas and some particulate-phase chlorides.

Minerals in the feedstock (ash) separate and leave the bottom of the gasifier as an inert slag (or bottom ash), a potentially marketable solid product. The fraction of the ash entrained with the syngas, which is dependent upon the type of gasifier employed, requires removal downstream in particulate control equipment, such as filters and water scrubbers. This particulate is typically recycled to the gasifier to ensure high carbon conversion. Some gasifiers also yield devolatilization or pyrolysis products (e.g., coal tars, oils, phenols), some of which can be sold. The remaining products can and must be controlled to eliminate any potential environmental impacts.

Trace elements associated with both organic and inorganic components of the coal, such as mercury and arsenic, are released during gasification and settle in different ash fractions (e.g., fly ash, bottom ash, slag) and gaseous emissions. The particular chemical species and physical forms of condensed-phase and vapor-phase trace elements are functions of gasifier design and operating conditions.

The temperature of the synthesis gas as it leaves the gasifier is generally in the range of 1,000°F to 1,900°F, depending upon the type of gasifier selected. With current technology, the gas has to be cooled to ambient temperatures to remove contaminants, although with some designs, steam is generated as the synthesis gas is cooled. Depending on the system design, a scrubbing process is used to remove HCN, NH₃, HCl, H₂S, and particulates, and operates at low temperatures with synthesis gas leaving the process at about 72°F. The H₂S and COS, once hydrolyzed, are removed by dissolution in, or reaction with, an organic solvent and converted to valuable by-products, such as elemental sulfur or sulfuric acid with 99.8

percent sulfur recovery. The residual gas from this separation can be combusted to satisfy process-heating requirements.

The raw clean synthesis gas must be re-heated to 600–700°F for the first of two water-gas shift (WGS) reactors that produce additional hydrogen from water through the catalytically assisted equilibrium reaction of CO with H₂O to form CO₂ and H₂. The exothermic reaction in the WGS reactor increases the temperature to about 800°F, which must be cooled to the required inlet temperature for the second WGS reactor in the range of 250–650°F, depending on design. The WGS reaction increases the amount of product H₂ in the final mixture, as well as the concentration of carbon in a single product (CO₂), which allows for easier capture. Hydrogen must be separated from the shifted gas containing CO₂, CO, and other contaminants, and may need to undergo a polishing step that removes any remaining sulfur, CO, and other trace contaminants in order to meet the requirements for various end-uses (e.g., turbines or fuel cells). The resulting hydrogen can provide excellent fuel for advanced gas turbines with no carbon emissions, while the captured CO₂ can be routed to compression and sent to sequestration facilities. The specifications for fuel gas for advanced gas turbines are shown in Table 1. The available information shows that there is the need for more data to determine the purity requirements for hydrogen separation membranes for gas turbines and other relevant applications.

Hydrogen could also be exported to improve gasifier utilization and potentially reduce the cost of electric power, depending upon product prices. Production and storage of hydrogen at the plant site during periods when electricity demand is low would allow higher capacity electric power production when electricity demand is high (e.g., peak daytime hours) or allow better integration with intermittent sources such as solar or wind.

Table 1. Fuel Gas Specifications for Gas Turbines

| Contaminant | Gas Turbine |
|--|---|
| Total non-particulates | Not available |
| Total sulfur (H ₂ S, COS, etc.) | 750 ppmv fuel gas 20 ppmv for Selective Catalytic Reduction (SCR) |
| Total halides (Cl, F, Br) | 5 ppmv fuel gas |
| Total fuel-nitrogen (NH ₃ , HCN) | Fuel-bound nitrogen 200–400 ppmv |
| Total alkali metals (Na, K, Li vapor and solid phases) | 100 ppbv fuel gas |
| Volatile Metals (V, Ni, Fe, Pb, Ca, Ba, Mn, P) | 20 ppbw Pb ^a 10 ppbw V ^a 40 ppbw Ca ^a 40 ppbw Mg ^a |
| Water | Not available |
| Total hydrocarbons (C ₁ basis) | Not available |
| Oxygen | Not available |
| Carbon dioxide | Determined by required carbon capture |
| Carbon monoxide | Determined by required carbon capture |
| Formaldehyde | Not available |
| Formic acid | Not available |
| Particulates | 0.1–0.5 ppmw fuel gas |

^a *Specification for Fuel Gases for Combustion in Heavy-Duty Gas Turbines*, GEI 41040G, GE Power Systems, Gas Turbines, January 2002. <http://www.netl.doe.gov/technologies/coalpower/turbines/refshelf/GE%20Turbine%20Fuel%20Specs.pdf>

3.2. Comparison of Current and Future Technology

At the present time, only a small number of IGCC plants operate on a commercial scale worldwide, and none use membrane separation technology. IGCC plants using current technology without CCS have not flourished due to higher capital costs than pulverized coal (PC) plants, leading to a higher cost of electricity. However, IGCC plants have lower costs to capture CO₂, leading to lower costs of electricity than PC when CCS is incorporated.³ NETL has also conducted further analysis which shows the technical, environmental, and economic benefits of incorporating advanced technologies (including membrane separation, warm gas cleanup (WGPU), advanced turbines, advanced coal pumps, and advanced oxygen separation) into IGCC plants with CCS. Select results from this analysis can be seen in Table 2. All of these IGCC cases involve capture and sequestration of 90 percent of total CO₂.

NETL's analysis shows that integration of advanced hydrogen separation membranes offers the single biggest cost savings and incremental improvement in efficiency of any single advanced IGCC technology under development. This efficiency improvement is nearly equal to the incremental improvement from moving two generations forward in turbine technology, from the current 7FA turbine to one generation past the advanced F-series turbines.

Table 2. Summary of IGCC Cases with CCS

| | Units | CASE 1 – Reference | CASE 2 – WGPU/Selexol | CASE 3 – WGPU/ Hydrogen Membrane | CASE 4 – Hydrogen Membrane/ Advanced Turbine |
|-------------------------------|-----------|--------------------|-----------------------|----------------------------------|--|
| Technology readiness goal | – | Current | N/A | 2015 ^a | N/A |
| Efficiency | % | 30.4 | 33.3 | 36.2 | 40.0 |
| Total Plant Cost | \$/kW | 2,718 | 2,425 | 2,047 | 1,683 |
| Levelized Cost of Electricity | cents/kWh | 11.48 | 10.00 | 8.80 | 7.36 |

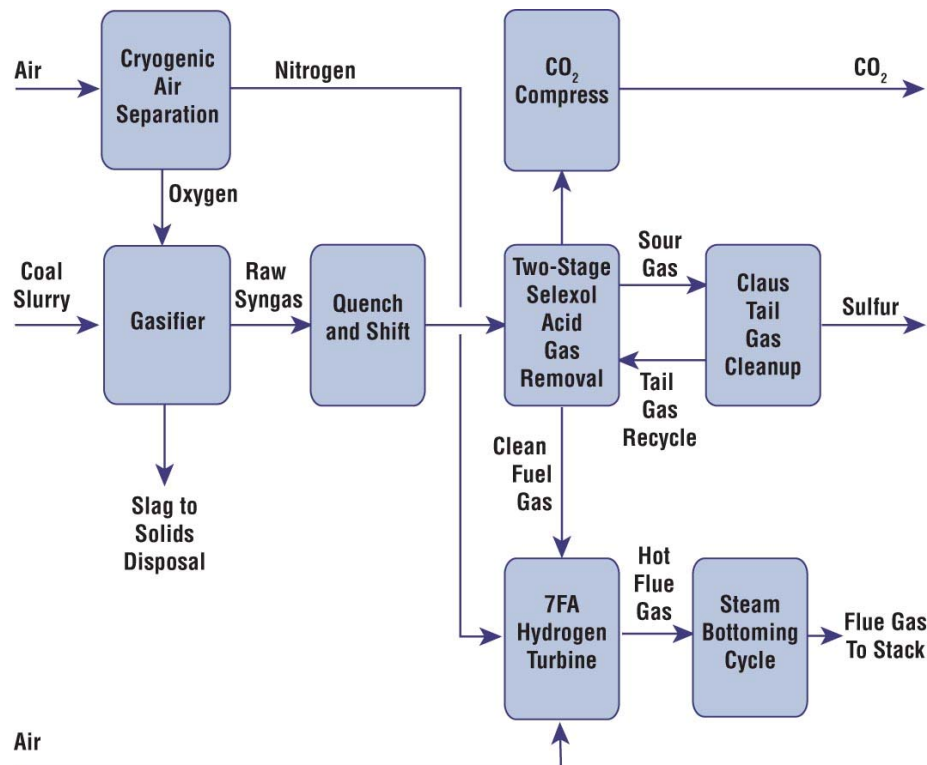
Source: DOE/NETL, *Current and Future Technologies for Gasification-Based Power Generation: Volume 2*, November 2009

^a See Section 4 for additional hydrogen membrane goals, milestones, and technical targets.

NETL's IGCC reference case, shown schematically in Figure 3, produces electric power and sequesters CO₂ using gasification and separation technologies considered state-of-the-art in 2003. The plant has an 80 percent capacity factor, and uses cryogenic air separation to produce oxygen, which is fed to single-stage slurry feed gasifiers with radiant-only syngas coolers. The plant uses two trains of water quench and a sour water gas shift to produce extra hydrogen, followed by a two-stage Selexol process to remove CO₂ and acid gases. Sulfur is then recovered using Claus technology, and the hydrogen is burned in a 7FA hydrogen turbine. CO₂ is compressed and transported offsite for subsequent sequestration. This plant configuration leads to a total plant cost of \$2,718/kW and has an efficiency of 30.4 percent, leading to a 20-year levelized cost of electricity of 11.48 cents/kWh.

³ DOE/NETL, *Cost and Performance Baseline for Fossil Energy Plants*, May 2007

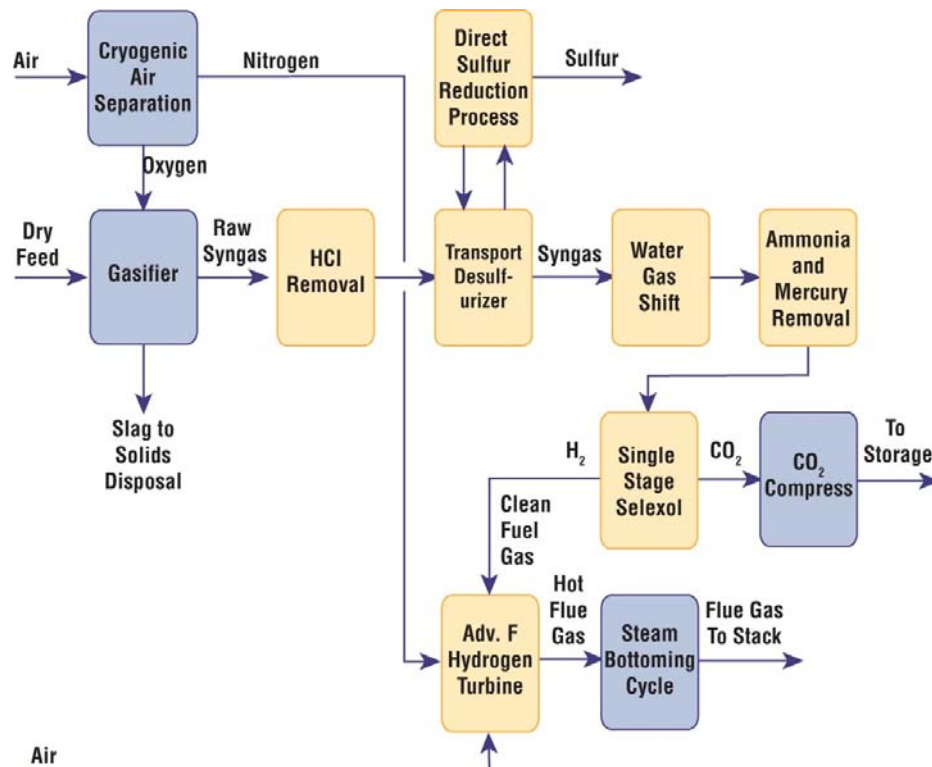
Figure 3. Case 1: Reference Case for Carbon Capture Plant, 80% Capacity Factor



Source: DOE/NETL, *Current and Future Technologies for Gasification-Based Power Generation: Volume 2*, November 2009

To show the incremental benefits of each advanced IGCC technology, NETL developed a series of cases based on this reference plant which added new technologies one at a time. The first incremental case (Case 2) has a higher capacity factor than the reference case at 85 percent, and as seen in Figure 4, utilizes similar air separation and gasification equipment to produce syngas. The cold gas cleanup and two-stage Selexol acid gas removal system is replaced with a warm gas cleanup system and uses only a single-stage Selexol system to remove CO₂. This advanced cleanup system includes removal of sulfur, hydrochloric acid, ammonia and mercury. The clean fuel gas is then sent to an advanced F-class turbine for power generation. This plant configuration leads to a total plant cost of \$2,425/kW and has an efficiency of 33.3 percent, leading to a 20-year levelized cost of electricity of 10.00 cents/kWh.

Figure 4. Case 2: Reference Case Plus Advanced F Turbine, 85% Capacity Factor, WGPU and Selexol Separation



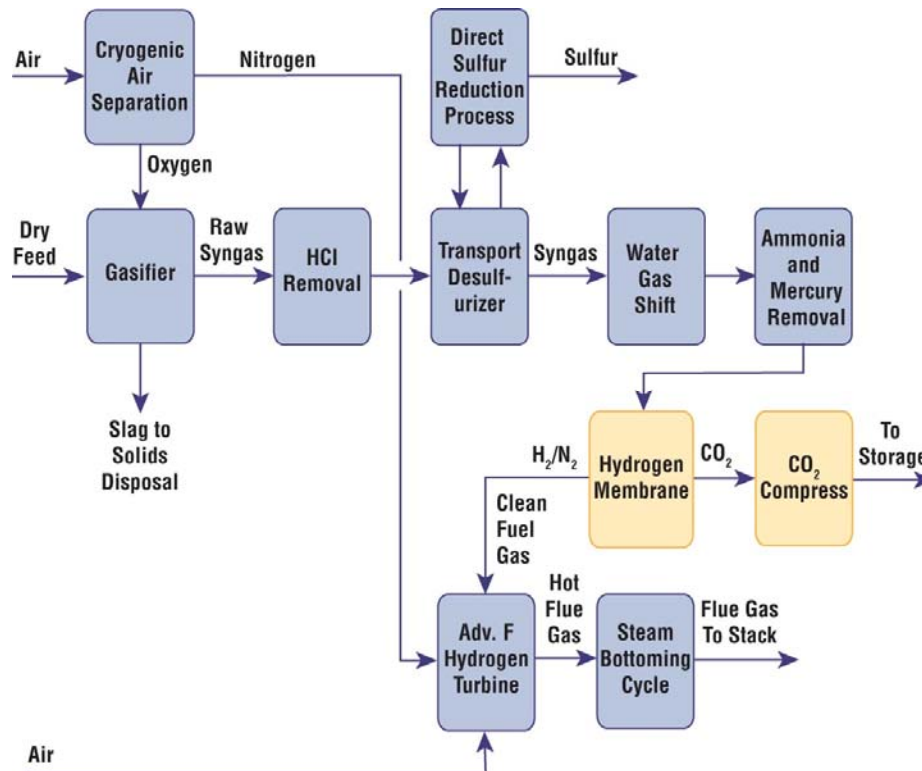
Source: DOE/NETL, *Current and Future Technologies for Gasification-Based Power Generation: Volume 2*, November 2009

Case 3, shown in Figure 5, incorporates advanced hydrogen separation membranes, currently under development by the Hydrogen from Coal RD&D Program. In this case, the single-stage Selexol CO₂ separation is replaced by a hydrogen membrane, while other upstream and downstream processes, including the use of warm gas cleanup, remain the same. The membrane concept used for this analysis is assumed to meet the Program's 2015 Technical Target for hydrogen flux, hydrogen purity, operational flexibility, and cost (see Section 4 for details). When using hydrogen separation membranes, hydrogen gas permeates through the membrane and is then swept with nitrogen gas from the air separation unit to keep a low partial pressure of hydrogen, which enhances the hydrogen flux in the membrane. The CO₂ remains on the non-permeate side, which allows it to remain at a high pressure and reduces the amount of energy required to compress it to the pressures required for sequestration applications. Additionally, efficiency improvements are seen due to reduction of extra equipment associated with the Selexol process. Overall, replacing the one-stage Selexol separation system of Case 2 with a hydrogen separation membrane system improves plant efficiency by 2.9 percent.

This plant configuration leads to a total plant cost of \$2,047/kW and has an efficiency of 36.2 percent, leading to a 20-year levelized cost of electricity of 8.80 cents/kWh. This overall capital cost for the plant using WGPU and membrane separation is \$378/kW lower than the WGPU and Selexol separation plant, with \$189/kW being from the reduced cost of the hydrogen separation unit, and \$49/kW due to decreased compression requirements for CO₂. There is also a reduction in turbine operating costs due to elimination of the syngas expander. The remaining savings are primarily due to the increased efficiency of the plant.

When combining the effects of improved efficiency and lower capital costs, using a hydrogen membrane system lowers the overall cost of electricity by 12 percent compared to the one-stage Selexol system in Case 2.

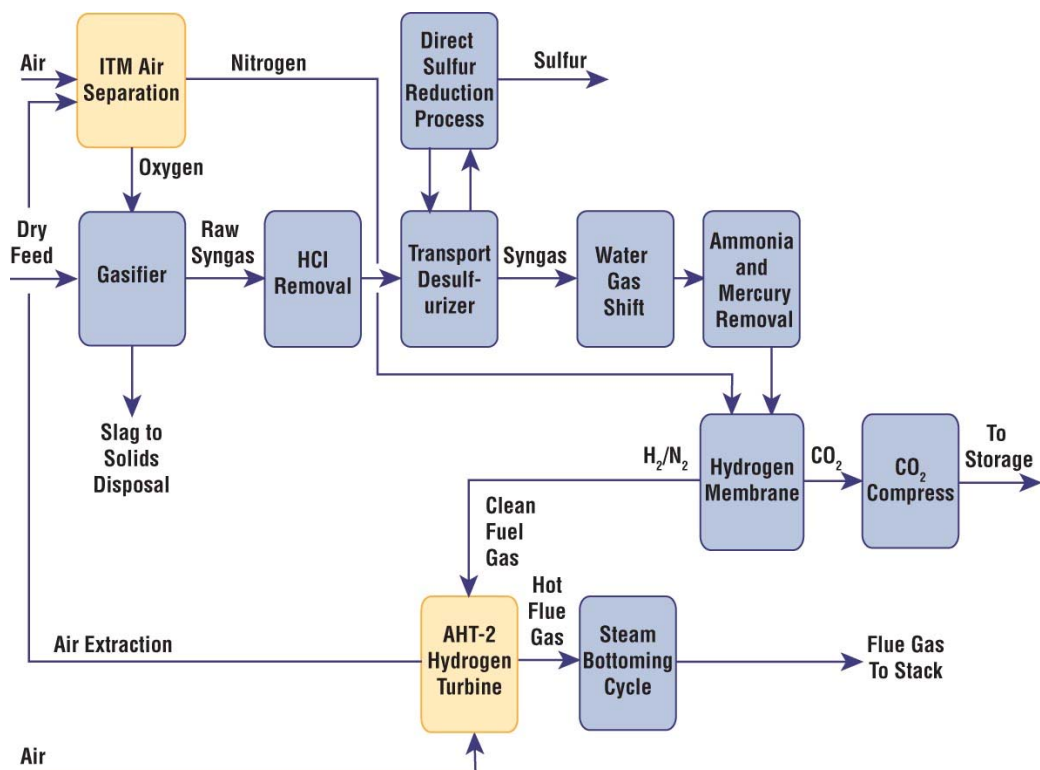
Figure 5. Case 3: Reference Case Plus Advanced F Turbine, 85% Capacity Factor, WGPU, and Hydrogen Separation Membrane



Source: DOE/NETL, *Current and Future Technologies for Gasification-Based Power Generation: Volume 2*, November 2009

Finally, the NETL analysis showed the cumulative benefits of employing all advanced IGCC technologies currently being researched. This case (Case 4), shown in Figure 6, involved replacing the cryogenic air separation technology with an ion transport membrane to produce oxygen for the gasification reactor. Additionally, the Advanced “F” turbine was replaced with the most advanced turbine technology currently being developed by DOE, referred to as an AHT-2 turbine. When combined with a 90 percent capacity factor, this plant configuration leads to a total plant cost of \$1,683/kW and has an efficiency of 40.0 percent, leading to a 20-year levelized cost of electricity of 7.36 cents/kWh.

Figure 6. Case 4: Reference Case Plus Advanced AHT-2 Turbine, 90% Capacity Factor, WGPU and Hydrogen Separation Membrane, Membrane Air Separation



Source: DOE/NETL, *Current and Future Technologies for Gasification-Based Power Generation: Volume 2*, November 2009

4. Technical Plan

The Hydrogen from Coal Program RD&D Plan supports the overall Office of Clean Coal's goals of improved energy security, reduced GHG emissions, high tech job creation, and reduced energy costs through joint public and private RD&D of advanced and novel hydrogen-related technologies for the future low-carbon energy system.

As successes are achieved, this RD&D program will improve existing technology and make available new, innovative technology that can produce affordable hydrogen from coal with significantly reduced or near-zero emissions. These technologies will be discussed in detail in this section, and are further broken down into specific technological areas. Each technology will include goals and milestones as well as technical targets, where appropriate. These goals and milestones are continually validated and/or updated based on the changing market and technical needs and the progress being achieved with individual projects.

FE's Office of Clean Coal and its implementing arm, the National Energy Technology Laboratory's Strategic Center for Coal, have R&D activities on coal gasification, advanced turbine development, fuel cells, and carbon sequestration technologies to improve the efficiency of power production and to reduce the environmental impact of coal use. These efforts are not part of the Hydrogen from Coal Program, but instead are technologies under development in other OCC and NETL programs. Therefore, R&D efforts in these research areas represent associated rather than direct elements of the Hydrogen from Coal Program.

The focus of the Hydrogen from Coal Program RD&D efforts is on those technologies that employ hydrogen membrane separation, sorbent-based concepts, and advanced concepts such as co-production and process intensification. Today's unit operations for producing hydrogen as part of an IGCC power plant are effective but also are expensive and energy-intensive.

Novel technologies could be developed that combine multiple processes into one step (i.e., process intensification technology), be better integrated with highly efficient warm gas cleanup systems, and/or remove impurities such as sulfur and CO₂ into one stream that can be jointly sequestered. The resulting benefits would include higher process efficiency and lower costs.

4.1. Goals and Milestones

The goals of the Hydrogen from Coal Program represent aggressive cost and efficiency savings realized through meeting the Program's technical targets laid out in Section 4.4, and are as follows:

- Prove the feasibility of a 40 percent efficient, near-zero emissions power facility that uses membrane separation technology as well as other advanced technologies to reduce the cost of electricity by at least 35 percent (relative to a base case IGCC with CCS using currently available technologies).
- Develop hydrogen production and processing technologies that will contribute approximately 2.9 percent in improved efficiency and 12 percent reduction in cost of electricity to the 40 percent efficient near-zero emissions power facility.

Technical Targets for the program include the following:

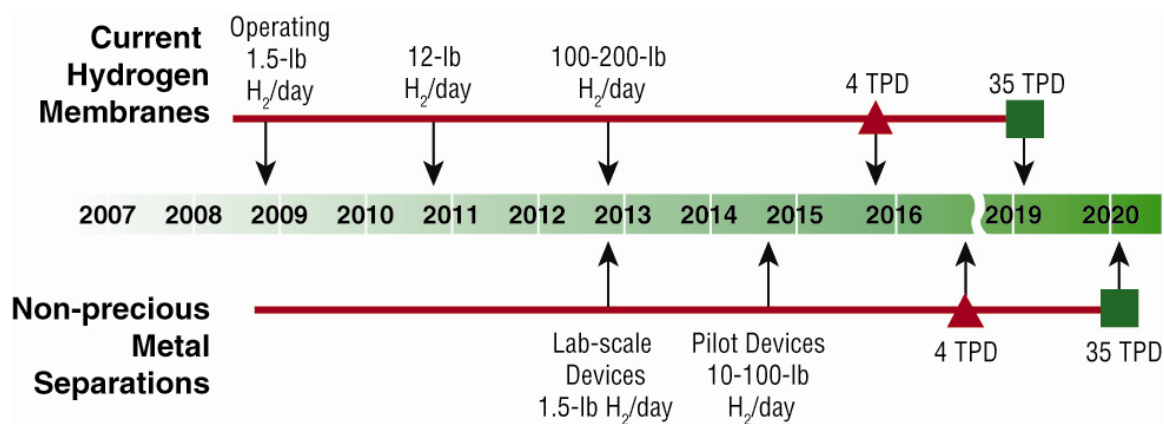
- Develop hydrogen membranes by 2015 that can provide hydrogen fuel that meets gas turbine specifications from syngas under warm gas cleanup conditions at a flux level of 300 SCFH/ft² at

pressures that will reduce compression costs for H₂ and CO₂, and at a membrane of less than \$100 per ft².

- Develop advanced concepts for syngas processing in gasification-based electric power generation systems that will significantly reduce complexity and cost, improve plant and fuel utilization, and/or improve efficiency, to produce H₂ for gas turbine fuel and CO₂ for sequestration.

The program builds on expected RD&D successes in associated programs within FE. After initial success by multiple advanced membrane systems on a laboratory scale, the program has begun to give additional focus to the scale-up of these systems to pilot scale. Figure 7 shows the proposed developmental schedule.

Figure 7. Hydrogen from Coal RD&D Program Milestones



Current Hydrogen Membranes

End of 2008: Operating at 1.5 lb H₂/day

End of 2010: Operating at 12 lb H₂/day

End of 2012: Operating at 100–200 lb H₂/day

End of 2015: Scale-up membrane module to 4 tons H₂/day production for component testing

Beginning of 2019: Scale-up membrane module to 35 tons H₂/day production for integrated testing

Non-precious Metal Separations

End of 2012: Operating lab-scale devices at 1.5 lb H₂/day

End of 2014: Operating pilot-scale devices at 10–100 lb H₂/day

End of 2016: Scale-up non-precious metal membrane module to 4 tons H₂/day for component testing

Beginning of 2020: Scale-up non-precious metal membrane module to 35 tons H₂/day for integrated testing

4.2. Activities

Table 3 lists the RD&D activities under investigation by the Hydrogen from Coal Program.

Table 3. Relevant Current R&D Program Activities

| Category | Technology |
|--------------------------------------|---|
| Advanced Membrane Separation Systems | <ul style="list-style-type: none"> Palladium and palladium alloy membrane reactors Cermet membranes |
| | <ul style="list-style-type: none"> Non-precious metal membranes |
| | <ul style="list-style-type: none"> Microporous membranes (e.g., carbon molecular sieves) |
| Sorbent-based Concepts | <ul style="list-style-type: none"> Chemical looping (e.g., iron-calcium cycle process to produce hydrogen and sequestration-ready CO₂) Hydrogen sorbents |
| Advanced Concepts | <ul style="list-style-type: none"> Process intensification (e.g., WGS membrane reactors) Co-production concepts |

Both FE and NETL have acquired extensive research experience in all aspects of producing hydrogen from coal through their participation in the Advanced Power Systems, Ultra-clean Fuels, and Advanced Research programs. Exploratory research previously sponsored by FE and NETL has pioneered studies on palladium-copper alloy membranes; tested novel membranes with regard to flux, durability, and impurity resistance; evaluated WGS kinetics and advanced reactor systems; and explored new concepts and fundamental studies on novel separation systems.

4.3. Technologies

The technologies within the Hydrogen from Coal Program are provided in the list below and discussed in further detail in the denoted section of the Plan.

4.3.1 Advanced Membrane Separation Systems

4.3.2 Sorbent-based Concepts

4.3.3 Advanced Concepts

4.3.1. Advanced Membrane Separation Systems

Modern gasification and WGS technologies produce synthesis gas (syngas), a mixture of H₂, CO, CO₂, and other chemical compounds. There are several gas separation technologies that could separate constituents of the syngas. The Hydrogen from Coal Program seeks to develop technologies to improve the separation of H₂ and/or conversely, CO₂ from synthesis gas streams, that will reduce capital and operating costs and improve thermal efficiency and environmental performance. Membranes to separate O₂ from air are being developed in the OCC Gasification Technologies Program.

Current hydrogen recovery methods typically employ pressure swing adsorption (PSA), cryogenics (e.g., Selexol), or polymer membrane systems. Each of these technologies has limitations. PSA typically recovers less of the feed-stream hydrogen and is limited to modest temperatures. Cryogenics is generally used only in large-scale facilities with liquid hydrocarbon recovery because of its high capital cost.

Current polymer membrane systems are susceptible to chemical damage from H₂S and aromatics, as well as having limited temperature tolerance.

There are significant opportunities to make advancements in these separations with the development of various types of advanced membranes that can separate hydrogen from CO₂. Much of the work will develop technology modules that are efficiently integrated into the plant systems and optimized with the temperature and pressure requirements of the plant and the specifications of the hydrogen for turbine use.

Advancements in hydrogen membrane separation technologies have the potential to reduce costs, improve efficiency, and simplify hydrogen production systems. Desirable characteristics of separation membranes include high hydrogen flux at low pressure drops; production of H₂ and CO₂ at high pressures; tolerance to contaminants, especially sulfur and CO; low cost; and operation at system temperatures of 250–500°C. Many current hydrogen membrane technologies are at the research phase, but because of their characteristics, they have the potential to provide hydrogen purity above 99.99 percent. Scale-up of these membrane technologies remains a key focus of the Hydrogen from Coal Program, and this activity is ongoing.

Membranes can be classified as organic, inorganic, or hybrid (a mixture of organic and inorganic materials). Within each of these classes, membranes can be characterized based on their properties. The Hydrogen from Coal Program currently is focused on microporous and metallic membranes, which include pure metal and hydrogen-permeable ceramic-metal membranes (i.e., cermets). The program previously included dense ceramic membranes (and also non-hydrogen permeable cermets) as part of its research activities. Dense ceramic membranes separate hydrogen from mixed gas streams by transferring hydrogen ions (i.e., protons) and electrons through the membrane matrix. These membranes have interesting characteristics such as high-temperature operation, mechanical stability, and very high hydrogen selectivity. However, hydrogen flux rates are low at gasifier effluent and gas clean-up technology operating conditions, which would significantly increase the cost of the separation module. Therefore, the program has de-emphasized RD&D activities on dense ceramic membranes.

With the refocus in the activity for increased power production, emphasis will be placed on higher flux and lower purity hydrogen by use of lower cost metal membranes. Membrane separation technology will continue to be the paramount research activity for hydrogen separation within the Program. However, a major refocus will occur based on systems analysis and activity requirements, which will include review of current membrane activities to define their relevance to the modified objectives.

A brief characterization of the current membrane technologies being developed by the Hydrogen from Coal Program is provided below. Other membranes are not precluded, provided that they show potential to meet the technical targets and assist the Hydrogen from Coal Program to meet its goals and milestones.

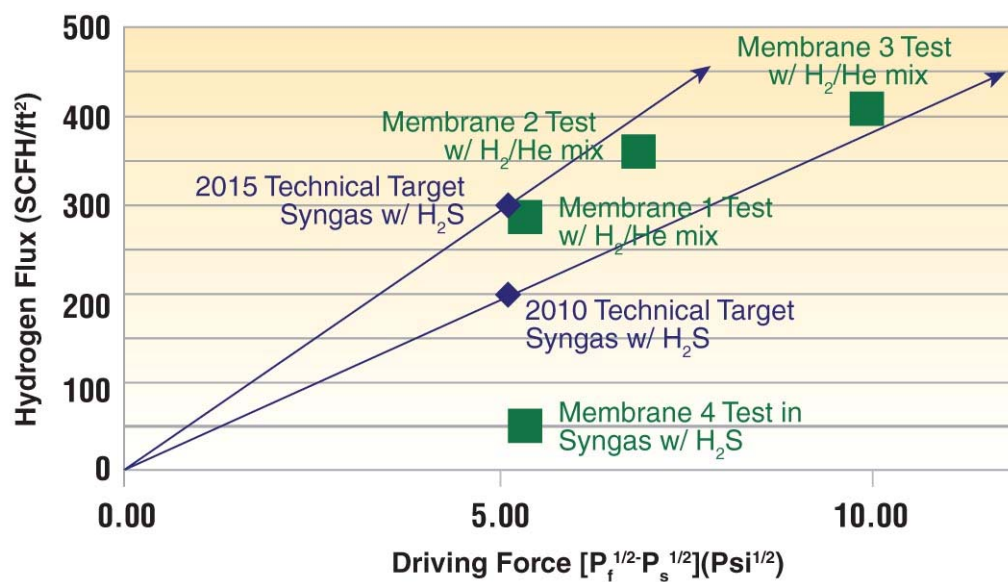
- **Metallic Membranes** – These membranes include pure metal or metal alloys, and hydrogen permeable cermets. The flux for these membranes is proportional to the differences of the square roots of the partial pressures across the membrane. Because of the transfer mechanism involved, 100 percent pure hydrogen can be recovered. A description of the three metallic membrane sub-types is provided below.
 - **Pure metal and metal alloy membranes.** Pure metal and metal alloy membranes transport gaseous hydrogen via an atomic mechanism whereby the metal or metal alloy, usually made with palladium (Pd), dissociates the molecular hydrogen into atoms that pass through the Pd metal film, and the atoms recombine into hydrogen molecules on the other side of the membrane. These metallic membranes typically comprise metal composites, thin Pd, or a Pd-

alloy metal layer supported on an inexpensive, mechanically strong support. The hydrogen diffuses to the metal surface where dissociative chemisorption occurs, followed by absorption into the bulk metal and diffusion through the metal lattice and recombination into molecular hydrogen at the opposite surface, and finally diffusion away from the metal membrane. These micro-thin metallic films are poisoned by gaseous impurities like sulfur compounds and carbon monoxide, and at high temperatures they may undergo phase changes that significantly reduce the hydrogen flux. Alloying with other metals like copper and silver reduces this phase change propensity.

- **Hydrogen permeable cermets.** In the second type of metallic membrane, a dense mixed conducting ceramic matrix phase is combined with a hydrogen-permeable metallic second phase. This metallic phase, which is composed of a hydrogen permeable metal or metal alloy, functions in the same way as the metallic membranes described previously. In this mixed membrane, the mechanism of hydrogen transfer is a combination of proton and electron conductivity in addition to atomic hydrogen transfer. However, atomic hydrogen transfer is orders of magnitude greater than the contribution of proton and electron conductivity, and thus the overriding mechanism in estimating the flux. Therefore, the flux for this membrane is more closely related to that of metallic membranes (i.e., represented by the difference in the square roots of the partial pressures). The membranes can operate at temperatures in the range of 400–600 °C, and can produce 100 percent pure hydrogen because of the transfer mechanism involved. These ceramic/metal composites offer the potential to overcome many of the limitations of metal membranes. This includes inhibition of phase change and increased tolerance to impurities in the synthesis gas.
- **Advanced non-precious metal membranes.** Within the context of the current program – non precious metal membranes will play an important role since the purpose is to find membranes which may not need as stringent hydrogen purity requirement, but would concentrate on higher flux and lower cost domestic materials. Materials will have to be evaluated to define the preferred hydrogen purity and fluxes based on the required conditions of temperature and pressure. It is expected that the types of non precious metal membranes would be similar to the membrane types identified above.
- **Microporous Membranes** – These membranes separate molecules through Knudsen diffusion, molecular sieving, surface flow, or a combination of these transport mechanisms. Flux increases linearly with increasing pressure, and there is usually a flux increase with higher temperatures. Materials such as ceramics, graphite, or metal oxides can be used in making these membranes. These materials can be stable in harsh operating environments. The pores in the membrane may vary between 0.5 nanometers (nm) and 5 nm. These membranes are characterized by higher fluxes and lower hydrogen purities which may have increased relevance with the re-focused emphasis on purities needed for use in hydrogen turbines.

Figure 8 shows the current performance characteristics for Pd or Pd alloy-based metallic or composite membranes under development by FE and NETL. Some of these membranes are approaching the desired flux rates of about 300 SCFH/ft² at 100 psi ΔP hydrogen partial pressure and the desired operating temperature range of 250–550°C. However, these flux measurements have mostly been made in pure gases (H₂ and He), and the addition of H₂S has been shown to reduce hydrogen flux rates in many test membranes. Other characteristics, such as desired durability, have not yet been demonstrated.

Figure 8. Current Status of the Membrane Development Activities Sponsored by FE and NETL



Note: 2010 and 2015 technical targets are extrapolated over all driving force ranges based on Sievert's Law.

Membrane flux is dependent upon the partial pressure of hydrogen, and the relationship between the two differs depending upon the type of membrane. Specifically, microporous membranes exhibit a flux that is directly proportional to the hydrogen partial pressure differential across the membrane. In Pd or Pd alloy-based metallic or composite membranes, the flux is proportional to the difference in the square roots of the partial pressures or the natural log of the partial pressure gradient according to Sievert's Law. In dense ceramic and non-hydrogen permeable cermet, flux is proportional to the natural log of the pressure gradient across the membrane, based on the Nernst potential.

In addition to hydrogen partial pressure, other operating conditions such as temperature and quality of the feed stream can also influence hydrogen flux. Membrane attributes such as durability, cost, tolerance to contaminants, hydrogen recovery, and purity are also important factors in development of robust membranes that can be integrated into coal-based hydrogen production facilities.

Because of the complexities of membrane performance, it is important to set desired technical targets near the expected operating conditions. In the case of hydrogen from coal technologies, hydrogen separation membranes are expected to operate with at least 50 psi hydrogen partial pressure on the permeate side and a hydrogen partial pressure ΔP of 100–300 psi.

To ensure that the many types of membrane technologies and concepts being researched are on a consistent basis, NETL has developed a standardized testing protocol for hydrogen separation membranes. The testing protocol⁴ serves to accomplish a number of objectives with respect to the Hydrogen from Coal Program technical targets. These objectives involve clearly stating expectations to contractors, determining the effectiveness of each membrane on a common basis, and assessing the membrane's compatibility with current gasification operation conditions.

⁴ DOE/NETL, NETL Test Protocol: Testing of Hydrogen Separation Membranes, October 2008

4.3.2. Sorbent-based Systems

Chemical looping (CL) is a process that takes advantage of the ability of some materials to adsorb and desorb oxygen in a cyclic manner, similar to the way that hemoglobin in the blood stream carries oxygen from the lungs to muscle cells. CL is a transformative technology capable of converting carbon-based feedstocks into energy more efficiently than existing combustion or gasification routes, and inherently produces a sequestration-ready CO₂ stream. For gasification applications, the basic concept is to supply oxygen to the gasification process from a metal that is oxidized in air, and then chemically reduced with the fuel. The metal oxidation/reduction process is repeated in a cyclic “loop,” hence the name chemical looping.

Sorbent-based separation systems operate by taking advantage of the physical or chemical properties of certain materials at varying temperatures or pressures. As shown in Figure 9, syngas is fed from the gasifier on to a bed of hydrogen adsorbing material at high temperatures and pressures. Hydrogen preferentially adsorbs onto the sorbent surface, while CO₂ and other syngas components remain in the bulk gas and exit as a permeate. The sorbent is then exposed to lower pressure (i.e., PSA) or temperature (i.e., thermal swing adsorption, or TSA), at which point the sorbent releases the hydrogen on its surface. Two separate sorbent columns are used in this process in order to maintain a continuous system. One column adsorbs hydrogen from syngas while the other is regenerated to remove the majority of trapped hydrogen and a purge gas is used to release the remainder.

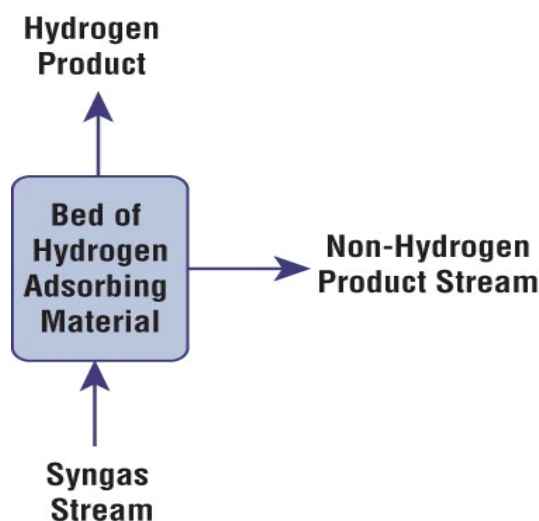
For a TSA-based system, extra bed heating intervals would need to be added to the process, and means would need to be included for introducing heat without diluting the product hydrogen. Heat exchange might be provided by tubes in the bed or transfer of hot solids as in chemical looping processes.

Additionally, the FE Carbon Capture Program is investigating sorbents which preferentially adsorb CO₂. These sorbents may be of particular use in a hydrogen production process, as removing CO₂ from syngas would leave a highly concentrated hydrogen product behind.

4.3.3. Advanced Concepts

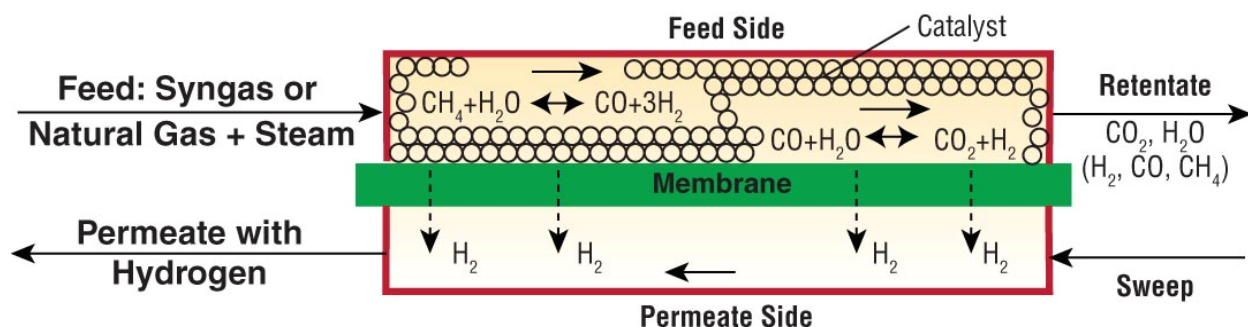
The Hydrogen from Coal Program is investigating advanced concepts through process intensification. Process intensification is the concept of developing novel technologies that, compared to current technology, bring about dramatic improvements that lead to more compact, energy efficient, and lower cost technologies. As related to hydrogen production from coal, these concepts could be a “one-box” process that combines synthesis gas cleanup, the WGS reaction, and hydrogen separation. Others include new process control methods or novel concepts that integrate alternative energy sources into the hydrogen from coal production facility. These advanced concepts will require long-term research efforts before they are ready for larger-scale development, but could significantly improve the production of hydrogen from coal.

Figure 9. Hydrogen Sorbent Separation Process



The WGS membrane reactor (WGSMR) concept is of particular interest as an example of process intensification. The WGSMR concept has been around for some time, dating back to at least the early 1990s. Figure 10 below shows the concept. The membrane and WGS catalyst is combined in such a way as to transport hydrogen through the membrane — away from the feed side of the membrane where the WGS catalyst is located — taking advantage of Le Chatelier's Principle to allow maximum conversion of CO to H₂ in a single reactor.

Figure 10. Advanced WGS Membrane Reactor Concept



The conditions for WGS in a membrane reactor would be very different from those encountered in a conventional shift reactor. In particular, at higher conversion rates, the partial pressure of steam would be low and the gas phase would be predominantly either CO₂ or H₂, depending on which species was not removed through the membrane. The catalysts used in conventional WGS reactors have not been extensively studied at these conditions, and it is not known whether they will be suitable for use in membrane reactors.

In either case, membrane reactors are being considered for this application with the expectation that, among other advantages, using a membrane reactor would not require cooling the gasifier product as much as is required in a conventional shift reactor. WGS is a reversible, exothermic reaction, and consequently the conversion is limited at high temperatures by thermodynamic equilibrium. The use of a highly permeance-selective membrane reactor would avoid this problem, driving the reaction to high conversion rates at elevated temperatures by selectively removing either H₂ or CO₂ (Le Chatelier's Principle). While this conceptually removes the limitation on conversion at high temperature, it is unknown what effect it will have upon the rate of reaction or mass transfer limitations. Conducting the WGS reaction over commercial, high-temperature iron oxide catalysts is known to be inhibited by the CO₂ reaction product. While the kinetics are not inhibited by the H₂ reaction product, it is not known whether the active (Fe₃O₄) state of the catalyst can be maintained in the situation where CO₂ is removed and where an excess of steam is neither needed nor desired. In a membrane reactor, one or the other of these compositional regimes will be encountered.

Another advanced concept being investigated by the Hydrogen from Coal Program is that of co-production, in which part of the fuel gas feed intended for turbine combustion is reacted to form other high-value products (e.g., liquid fuels, chemicals, hydrogen, or substitute natural gas) for export. Varying the use of syngas to produce high-value products offers the potential to maximize gasifier utilization during periods of low daily or seasonal demand for electric power. Additionally, depending on the value of the secondary product, the economics of the plant can be improved. This may result in a lower cost to produce electricity.

4.4. Technical Targets

The technical targets in this RD&D Plan, unless otherwise indicated, represent the status of the specific technologies after completion of R&D, but prior to large-scale demonstration of the technologies. These technologies will be validated in modules at facilities that can accommodate similarly scaled engineering modules, as detailed in the Gantt chart in Figure 7. As a point of reference, the status of the technologies is provided in the technical target tables.

It is important to understand the composition of the synthesis gas exiting the gasifier when developing the targets for contaminant levels for both WGS and hydrogen separation technologies. Table 4 shows the contaminant levels in raw and cleaned synthesis gas from Illinois #6 bituminous coal. Additionally, the FE Gasification Technologies Program goals for synthesis gas cleanup are also shown. It should be noted that raw synthesis gas composition will vary by coal type; therefore, lower sulfur coals could have raw synthesis gas sulfur levels that are much lower than those shown in Table 4, perhaps as low as 700–1,200 ppmv based on some studies.⁵

Table 4. Contaminant Levels in Raw and Cleaned Synthesis Gas using Conventional Cleaning Technologies and FE Gasification Program Goals for Synthesis Gas Cleanup

| Contaminant | Units | Raw Synthesis Gas Composition ^a | Cleaned Synthesis Gas Composition ^a | FE Gasification Program Goals ^b |
|------------------|-------|--|--|--|
| H ₂ S | ppmv | 9,524 | 102 | 0.04 |
| NH ₃ | ppmv | 675 | 0.4 | 1,000 |
| HCl | ppmv | 425 | ~0 | < 1 |
| Hg | ppbv | 3 | 0.3 | < 1 |

^a *Novel Gas Cleaning/Conditioning for Integrated Gasification Combined Cycle: Volume I – Conceptual Commercial Evaluation*, Siemens Power Generation, Inc. and Gas Technology Institute, under DOE Contract DE-AC26-99FT40674, December 2005.

^b Tennant, J., “Gasification: Ultra Clean & Competitive,” DOE/NSF EPSCoR Conference 2005, Morgantown, WV, June 2005.

As Table 4 shows, most major contaminants can be reduced to very low levels through conventional synthesis gas cleaning technologies, and achieve the goals of the Gasification Technologies Program. If that program’s cleanup goals were achieved then conventional WGS, rather than a sour gas shift to produce additional hydrogen, would be preferred. An alternative for advanced systems would be to assume that sulfur can be controlled to about 100 ppmv by use of warm gas cleanup, but without substantial removal of other contaminants such as ammonia, HCl, or mercury below that seen in the gasifier effluent. These contaminants, along with CO₂, would be simultaneously removed by the separation device and thereby significantly reduce the cost to produce hydrogen fuel. The 2015 targets for WGS and membrane separation assume tolerances for the identified contaminants consistent with this methodology. However, under the current cleaned synthesis gas composition, sulfur levels in the form of H₂S are considerably higher than the Gasification Technologies Program goal and would require a sour gas shift that might affect advanced hydrogen membrane separators.

⁵ *Impact of CO₂ Capture on Transport Gasifier IGCC Power Plant*, Bonsu, A., et. al., Southern Company Services – Power Systems Development Facility; Booras, G., Electric Power Research Institute (EPRI), Breault, R., NETL; Salazar, N., Kellogg, Brown and Root, Inc., International Technical Conference on Coal Utilization and Fuel Systems, Clearwater, FL, May 21–25, 2006.

To reiterate, it is also expected that efficiency requirements for advanced concepts (i.e., process intensification) will require “warm gas cleanup,” which will have higher levels of sulfur than conventional cleaning. In addition, these advanced concepts may require that the effluent from the gasifier be processed without major cleaning. Therefore, the advanced concepts may require WGS and membrane separation with sulfur, ammonia, and chloride tolerances that are found in the raw gasifier effluent. This suggests that the WGS and membrane tolerances to contaminants in the synthesis gas require a better quantitative definition and may be different depending on the specific research approach being pursued.

4.4.1. Hydrogen Separation Technical Targets

The performance criteria for successful incorporation of membrane separation reactors into hydrogen from coal configurations are shown in Table 5. Although high flux rates and low cost are the key parameters, there also are other critical criteria that must be satisfied. Ideally, the temperature of operation should be in a range compatible with warm synthesis gas cleaning technologies.

Table 5. Hydrogen Separation Technical Targets

| Performance Criteria | Units | Current Status ^b (Pd-based metallic or composite) | 2010 Target | 2015 Target |
|--------------------------------------|---------------------------------------|---|-------------|--------------------|
| Flux ^a | ft ³ /hour/ft ² | ~200–300 | 200 | 300 |
| Temperature | °C | 300–500 | 300–600 | 250–500 |
| S tolerance | ppmv | tbd | 20 | >100 |
| Cost | \$/ft ² | tbd | 100 | <100 |
| WGS activity | – | N/A | Yes | Yes |
| ΔP Operating capability ^c | psi | tbd | Up to 400 | Up to 800 to 1,000 |
| Carbon monoxide tolerance | – | Some | Yes | Yes |
| Hydrogen purity | % | >99.5 | 99.5 | 99.99 |
| Stability/durability | Years | 0.9 (tested) | 3 | 5 |

^a For 100 psi ΔP (hydrogen partial pressure basis). ΔP = total pressure differential across the membrane reactor.

^b Detailed status of hydrogen membrane separation can be found in Figure 8.

The technical targets for hydrogen membranes relate to hydrogen from coal technology in which ΔP will be around 100 psi and the membrane will require resistance to contaminants (CO and H₂S).

The targets are not independent, but are part of an integrated set of requirements that are necessary for hydrogen separation membranes to be operated in a coal-to-hydrogen production plant using advanced technologies and capable of producing hydrogen with high efficiency and low cost. A typical plant for hydrogen production from coal using advanced separation membranes would use an advanced gasification system, such as an entrained flow, transport or circulating fluidized bed gasifier; a warm or hot gas cleanup system to remove ash, sulfur compounds, and other contaminants such as mercury; WGS catalysts to maximize hydrogen production and reduce carbon monoxide content in the gas; and the advanced hydrogen membrane to separate product hydrogen and capture carbon dioxide for sequestration. The plant might also incorporate membrane separation to separate oxygen from air for gasification. All of these advanced systems are important to achieving the greatest efficiency and lowest cost of production. Hydrogen membrane separation is an enabling technology that allows maximum

flexibility to integrate with other advanced gasification and gas cleanup technologies to achieve high efficiencies, low GHG emissions, and low costs in gasification-based energy systems.

The flux and cost targets, as well as the lifetime target, represent conservative goals that will allow designers to keep overall plant costs down while allowing flexibility in configuration of membrane separation systems in conjunction with other advanced technologies (WGS) to achieve maximum efficiencies and GHG reductions. Very high product purity is required for use of hydrogen in fuel cells. (Note: while the purity of hydrogen product from advanced separation membranes is very high, some hydrogen stays in the gas stream with the CO₂ and multiple membrane stages are needed to recover this hydrogen). The flux targets were established by expert estimation of the degree of performance improvement that is judged to be achievable by membranes research in balance with what is deemed to be acceptable total membrane surface areas and costs in a plant. As an example, the 2015 flux target of 300 SCFH/ft² of pure hydrogen (density of .005 lb/SCF) is approximately 16 kg/day per membrane square foot. For a production plant producing 158 million SCF per day of hydrogen (equivalent to approximately 625 MW or roughly 8,500 barrels per day of liquid fuels), this implies a membrane area for a single stage membrane system of 22,500 ft². More detailed designs estimate that this area will need to increase by a factor of 2 or 3 to allow for multiple separation stages for high hydrogen recovery. The resulting membrane area of ~ 50,000 ft² can be achieved by arrays of separation tubes or other designs. If the membranes are tubular, on the order of 5,000 tubes might be needed. Clearly total hydrogen membrane system costs are inversely proportional to achievable flux levels.

The 2010 Target for membrane temperature (Table 5) allows the hydrogen membrane to be installed and operated in or near a low temperature or high temperature (clean gas) WGS reactor, but the gas must be cleaned of most sulfur compounds first. A higher upper temperature is allowed for the 2010 target because these membranes typically have larger flux at higher temperatures. The 2015 target actually reduces the temperature range slightly because WGS and WGS systems operate in a lower range. However, the 2015 Target allows for higher sulfur levels (see below) and thus more flexibility in configuration, especially with warm gas cleanup systems. Warm gas cleanup systems offer significant improvements in efficiency because less heat exchange is necessary in the gas processing systems.⁶ Warm gas cleanup systems that match the temperature and pressure conditions for the WGS reaction and the advanced hydrogen membranes will minimize the amount of heat lost to inefficiencies in heat exchanges and will improve overall plant efficiency. Warm gas cleanup and WGS reactions typically operate in the 250–500°C range, which was selected as the optimal separation membrane temperature range. Shift reactors must be used to convert water and CO in the gas into additional H₂ and CO₂ in order to maximize the H₂ content for separation and make CO₂ available for sequestration. Raw gas shift reactors using sulfur resistant catalysts can be applied to the gas before desulfurization at temperatures of 250 to 550°C. Alternatively, clean synthesis gas after sulfur removal can be reheated to 315–370°C for WGS reactors that produce additional hydrogen through the catalytic reaction of CO with H₂O to form CO₂ and H₂.

Sulfur tolerance is one of the most difficult elements of the technical targets to achieve. Achievement of membrane tolerance to the 2010 target of 20 ppm level of sulfur species would allow the membrane to be used in a gas stream containing low levels of sulfur, typical of cold gas desulfurization or very effective warm gas cleanup. However, as hydrogen permeates through the membrane, the concentration of sulfur on the non-permeate side is increased due to the decreased total volume. This causes some membrane components to be exposed to higher levels of sulfur, effectively requiring lower levels of

⁶ *Comparison of a New Warm-Gas Desulfurization Process versus Traditional Scrubbers for a Commercial IGCC Power Plant*, presented at Gasification Technologies Conference, Oct 17, 2007 by Jerry Schlather and Brian Turk (RTI/Eastman Chemical).

sulfur in the initial stream. Achievement of the 2015 target of tolerance to more than 100 ppm of sulfur will allow more flexibility in system design, especially if levels in the 1,000 ppm range can be achieved.

The membrane also must be structurally capable of withstanding the expected pressure drop across the system. Current coal gasification systems operate around 40 atmospheres of pressure; therefore, if the hydrogen product from the membrane is at 5–10 atmospheres, the differential pressure across the membrane would be 30–35 atmospheres (440–515 psi). Future coal gasification systems for hydrogen may operate at 80 atmospheres, so that the system pressure differential across the membrane could be as high as 70–75 atmospheres (1,000–1,100 psi). The membrane must also resist or be tolerant to atomic rearrangements, surface roughening, and formation of impurity over-layers that could adversely affect structural integrity in a WGS environment. In addition, it is critical that any membrane system be completely tolerant to carbon monoxide. It is also important to achieve higher hydrogen flux while simultaneously minimizing the pressure drop across the membrane in order to reduce the hydrogen product compression requirement. These target criteria are independent of membrane type.

4.4.2. Sorbent-based Systems Technical Targets

In sorbent-based processes, such as pressure swing adsorption or more advanced concepts such as chemical looping, the process performance depends on important parameters or characteristics for sorbents, which in turn affect energy balances, operating regimes or ranges, rates or throughputs of reactants, replacement rates for sorbents, and costs (capital and operating). In all sorbent-based processes, a sorbent material is exposed to the gas containing the components to be separated. Syngas from coal contains major species of H₂, CO₂, H₂O, and CO. For H₂ production, the CO needs to be “shifted” by reaction with H₂O, producing more H₂ and CO₂. H₂ will be the product stream and needs to be produced at a pressure as close as possible to that needed for end use or transportation. The CO₂ needs to be produced at a pressure suitable for transportation to sequestration sites or other uses. Sorbent capacity is affected by all of the “state parameters” such as temperature and pressure, and will also depend on the partial pressures in the gas to which the sorbent is exposed. The sorbent will need to have a substantial adsorption capacity at the temperature planned for operation. The other critical parameters are the temperature and other conditions at which the products can be driven off the sorbent and the sorbent regenerated for use. If the temperature differential between adsorption and regeneration is too high, the regeneration heating requirements may be impractical.

Chemical looping takes advantage of the ability of some materials to adsorb and desorb oxygen in a cyclic manner, similar to the way that hemoglobin in the blood stream carries oxygen from the lungs to muscle cells. For gasification applications, the basic concept is to supply oxygen to the gasification process from a metal that is oxidized in air, and then chemically reduced with the fuel. Compared to conventional oxygen blown gasification, the process has an advantage in that no dedicated air-separation process is needed. CL can be used to produce hydrogen in gasification applications, where steam is used to oxidize the carrier, producing hydrogen. The metal oxide can again be recycled to a coal reactor where it would be reduced back to a metal.

During the last decade, the CL strategy has been applied to gasification to produce hydrogen from coal and coal derived syngas. The GE fuel-flexible process and the ALSTOM hybrid combustion–gasification process have been studied. These technologies use two different types of particles to convert coal into hydrogen: one type of particle is used to capture CO₂ while the other serves as an oxygen carrier.

More recently, the Ohio State University (OSU) has developed novel chemical looping gasification processes (i.e., the syngas chemical looping process, calcium looping process, and the coal/biomass

direct chemical looping process). OSU is also developing a chemical looping scheme that could find application for treating tail gas from a coal based Fischer-Tropsch (F-T) Coal-to-Liquids process. This chemical looping concept uses iron oxide (Fe_2O_3) to react with the unreacted synthesis gas (H_2 and CO) and light hydrocarbons in the effluent tail gas from an F-T reactor. This reaction that takes place in a fuel reactor that produces CO_2 , H_2O , and reduced iron. The reduced iron is then reacted with steam to produce hydrogen that can be recycled to the F-T reactor to adjust the input hydrogen to carbon monoxide ratio.

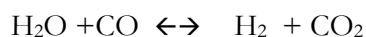
Lehigh University is developing the Thermal Swing Sorption Enhanced Reaction (TSSER) concept. One of the important applications of the TSSER concept is for gasification. The gas mixture from the gasifier would be fed into a TSSER system where the CO and H_2O would be catalytically converted to H_2 and CO_2 by the water gas shift reaction. The CO_2 would simultaneously be adsorbed from the reaction zone by a special chemisorbent material, resulting in a relatively pure product stream of CO_2 -free H_2 gas. Removal of CO_2 from the reaction zone will drive the equilibrium controlled reaction to completion. This will result in extremely high conversion of CO and H_2O to H_2 in the sorber-reactor.

Specific milestones and targets for sorbent-based technologies are being developed in light of the Program's focus on electricity production.

4.4.3. Advanced Concepts Technical Targets

The basis for the 2015 technical targets assumes a single, compact WGS reactor operable over a wide range of temperatures and pressures with minimal undesirable side reactions and tolerance of common impurities found in coal-derived syngas. A catalyst lifetime of greater than 10 years is desirable, and depending on the form of the catalyst within the reactor, it may need to equal the expected operational life of the reactor. The cost goal is a 30 percent reduction over today's fixed-bed systems and a wider range of operating temperatures.

Partial oxidation of coal and other carbon-based solid/liquid feedstocks produces a synthesis gas with a composition ranging from 30–45 percent H_2 , 35–55 percent CO , and 5–20 percent CO_2 (dry basis). This ratio can be adjusted to produce additional hydrogen. The WGS reaction converts CO and H_2O to CO_2 and H_2 :



This reaction also is used to increase the concentration of hydrogen in the syngas, and when coupled with an appropriate separation technology, it can produce high yields of high-purity hydrogen.

The WGS reaction is reversible, with the forward WGS reaction being mildly exothermic. Conversion to H_2 and CO_2 is thermodynamically limited and favored at lower temperatures. Higher temperatures improve the rate of reaction, but decrease the yield of hydrogen. In order to achieve high yields at high rates of reaction, the reaction is typically carried out in multiple adiabatic reactor stages, with lower reactor inlet temperatures in the latter stages. The yield also may be improved by using excess steam or by removing hydrogen to shift the WGS equilibrium to the right, in accordance with Le Chatelier's Principle. Steam also is used to minimize undesirable side reactions that compete with the WGS reaction. WGS catalysts and reactors could be improved by further R&D to increase hydrogen yield at higher operating temperatures, improve catalyst tolerance of syngas impurities, minimize undesirable side reactions, expand pressure and temperature operating ranges, and simplify/combine processing steps to reduce costs.

Some of the literature provides a considerable amount of experimental and modeling detail on WGSMRs, and there are several economic analyses (almost all on IGCC systems). In one study comparing chemical looping and WGSMRs, despite the lowest efficiency loss among the studied systems, the economic performance of the double stage chemical looping process was outperformed by WGSMRs and systems employing physical adsorption due to high costs. Processing modeling may be required to further study these advanced concepts, including co-production.

Specific milestones and targets for advanced concept technologies are being developed in light of the Program's focus on electricity production.

4.5. Technical Barriers

The following technical and economic barriers must be overcome to meet the goals and objectives of the Hydrogen Production Pathway for use in advanced IGCC power concepts.

4.5.1. General Barriers

A. High Cost. The cost of current technologies to produce hydrogen from coal must be reduced. This includes improved efficiency of the process, and reduced capital and operating costs.

B. Lack of Demonstration of Novel Technologies. Many novel separation processes (e.g., advanced membranes) have not been demonstrated at a scale sufficient to determine their potential for lower cost and efficient integration into advanced hydrogen from coal production systems.

C. Complex Process Designs. Complex process systems that have a greater number of process units require a larger plant footprint and are nearly always more difficult to improve in terms of efficiency. "Process intensification," in which multiple process function technologies are integrated into one process step — such as combined gas cleanup, WGS reaction, and hydrogen separation — offer potential advantages in scalability of the design, as well as better efficiency and lower costs. Various candidate process intensification processes and/or units require significant RD&D to establish their techno-economic viability.

4.5.2. Hydrogen Separation Barriers

There are several technology options available that can be used to separate hydrogen from synthesis gas. The following broad set of barriers must be overcome to reduce the cost and increase the efficiency of these separation technologies.

D. Loss of Membrane Structural Integrity and Performance. Depending on conditions, membranes may be subject to atomic rearrangements, surface roughening, pitting, and formation of impurity over-layers that may adversely affect structural integrity and performance. This becomes more important for the supported thin film membranes designed to enhance flux and minimize cost. For example, oxidizing gas mixtures (oxygen, steam, and carbon oxides) have been observed to cause metallic membranes to rearrange their atomic structure at temperatures greater than 450°C. This results in the formation of defects that reduce membrane selectivity for hydrogen. Some ceramic membranes exhibit poor thermo-chemical stability in CO₂ environments, resulting in the conversion of membrane materials into carbonates. In solvent systems, impurities can cause less effective absorption and may lead to excessive loss of solvent, which will increase cost and decrease separation efficiency.

E. Thermal Cycling. Thermal cycling can cause failure in some membranes, reducing durability and operating life.

F. Poisoning of Catalytic Surfaces. Metallic membranes must dissociate molecular hydrogen into hydrogen atoms before it can diffuse through the separation layer. The presence of trace contaminants, particularly sulfur, can poison the surface sites that are catalytically active for this purpose, diminishing the effectiveness of the membrane.

G. Defects During Fabrication. The chemical deposition of thin palladium or palladium-alloy membranes onto support structures is an important technical challenge in the fabrication of defect-free membranes. Large-scale, rapid manufacturing methods for defect-free thin films and membranes and modules in mass production must be developed and demonstrated. Fabrication of microporous membranes requires a reduction in membrane pore size, which is accomplished by deposition techniques. No synthesis and evaluation methods exist for tunable pore-size membranes used in separating H₂ from light gases at high temperature and in chemically challenging environments.

H. Lack of Seal Technology and Materials. High-temperature, high-pressure seals are difficult to make using ceramic substrates.

I. Technologies Do Not Operate at Optimal Process Temperatures. Membrane processes that can be designed to operate at or near system conditions, without the need for cooling and/or re-heating, will be more efficient.

J. Hydrogen Embrittlement of Metals. Below 300 °C, hydrogen can embrittle and induce a phase change in certain types of separation membranes. Embrittlement reduces the durability and effectiveness of the membrane for selectively separating hydrogen. Hydrogen also embrittles the structural steels of the membrane housing and gas handling systems.

K. Development of Lower Cost Non Precious Metal Hydrogen Separation Materials. Materials used in current hydrogen separation membranes are high in cost and not widely available from domestic sources.

4.5.3. Sorbent-based Systems Barriers

L. Low Adsorption Capacity. Current sorbent-based systems have limited adsorption capacity which increases the amount of sorbent required, increasing system capital and operating costs.

M. High Regeneration Energy Requirements. PSA and TSA systems require large variances in pressure and temperature to remove hydrogen. High heating, cooling, or pressurization requirements reduce efficiency and increase cost.

N. Technologies Do Not Operate at Optimal Process Temperatures. Sorbent-based processes that can be designed to operate at or near system conditions with minimized need for heating, cooling, or pressurization will be more efficient.

4.5.4. Advanced Concepts Barriers

O. Impurity Intolerance/Catalyst Durability. The WGS reaction occurs after coal has been gasified to produce synthesis gas. Impurities in the synthesis gas may act as poisons, deactivating the catalyst and damaging the structural integrity of the catalyst bed. Improved catalysts and reactor systems are needed to maintain catalyst activity throughout the reactor, and in some cases, eliminate the post-gasification synthesis gas cleanup step upstream of the WGS reactor.

P. Operating Limits. The synthesis gas produced from gasification exits the gasifier at a high temperature. The WGS reaction then is carried out in two separate stages: a high-temperature shift and a

low-temperature shift. The development of advanced WGS catalysts and reactor systems that are more robust and can operate over a wide range of temperatures can eliminate the need for two separate stages, potentially reducing capital costs.

Q. Undesired Side Reactions. Reactions that produce species other than hydrogen and CO₂ must be minimized in the WGS reactor.

4.6. Technical Task Descriptions

Table 6 summarizes the tasks for the technologies under development.

Table 6. Task Descriptions for Hydrogen Production Technologies

| Task Number | Task Description | Barriers Addressed by Task |
|--------------------|--|-----------------------------------|
| 1 | <p><i>Advanced Hydrogen Separation</i></p> <ul style="list-style-type: none"> Review and analyze separation technology to determine the current status, needs for advanced technology, preferred separation options, and scale-up to prepare modules. Link membrane development work to material surface characterization studies in order to understand effects of impurities and operating conditions on short- and long-term membrane performance. Conduct RD&D to explore technology for preferred advanced separation systems such as PSA, membranes, solvents, reverse selective systems, and other technology alternatives. Identify low-cost materials, such as non-precious metals, for hydrogen separation. Use molecular sieves to stabilize membranes. Develop appropriate membrane seal and fabrication technologies and methods for module preparation and scale-up. | A, B, C, and D through K |
| 2 | <p><i>Sorbent-based Separation Systems</i></p> <ul style="list-style-type: none"> Identify low-cost materials for CO₂ separations. Develop reverse selective hydrogen membranes for cost-effective separation of CO₂ and other gases from mixed gas streams. Develop advanced adsorption, hydrates, or other novel technologies for the cost-effective capture of CO₂ from mixed gas streams. | L, M, N |
| 3 | <p><i>Advanced Concepts</i></p> <ul style="list-style-type: none"> Investigate advanced and novel process concepts that integrate several processes — gas cleanup, WGS reaction, and hydrogen separation — into one step. Investigate novel, “out-of-the-box” technologies that can produce hydrogen from coal directly or indirectly. Develop advanced shift catalysts that are more active and are impurity-tolerant. Conduct the WGS reaction using a high-temperature membrane without added catalyst. Develop integrated single-step shift-membrane separation technology. | O, P, Q |
| 4 | <p><i>Demonstrations</i></p> <ul style="list-style-type: none"> Demonstrate advanced hydrogen separation modules and technologies to confirm laboratory, bench-scale, and pre-engineering module results. | A, B |

5. Implementation Plan

The Hydrogen from Coal Program was initiated in FY 2004 as a component of the overall DOE Hydrogen Program, and supports OCC's goals to develop technologies that would enable near-zero emissions coal facilities. The Program is in an operational mode, having initiated RD&D activities by requesting research proposals and selecting project performers. Continued execution and development of the Hydrogen from Coal Program requires proper management controls to ensure that the Program is progressing toward its goals and objectives.

5.1. Coordination with Other DOE/Federal Programs

The successful development of low-cost, affordable hydrogen production from fossil fuels coupled with sequestration of CO₂ is dependent on technologies being developed in a number of ongoing associated RD&D programs within FE and NETL. These technologies are needed for:

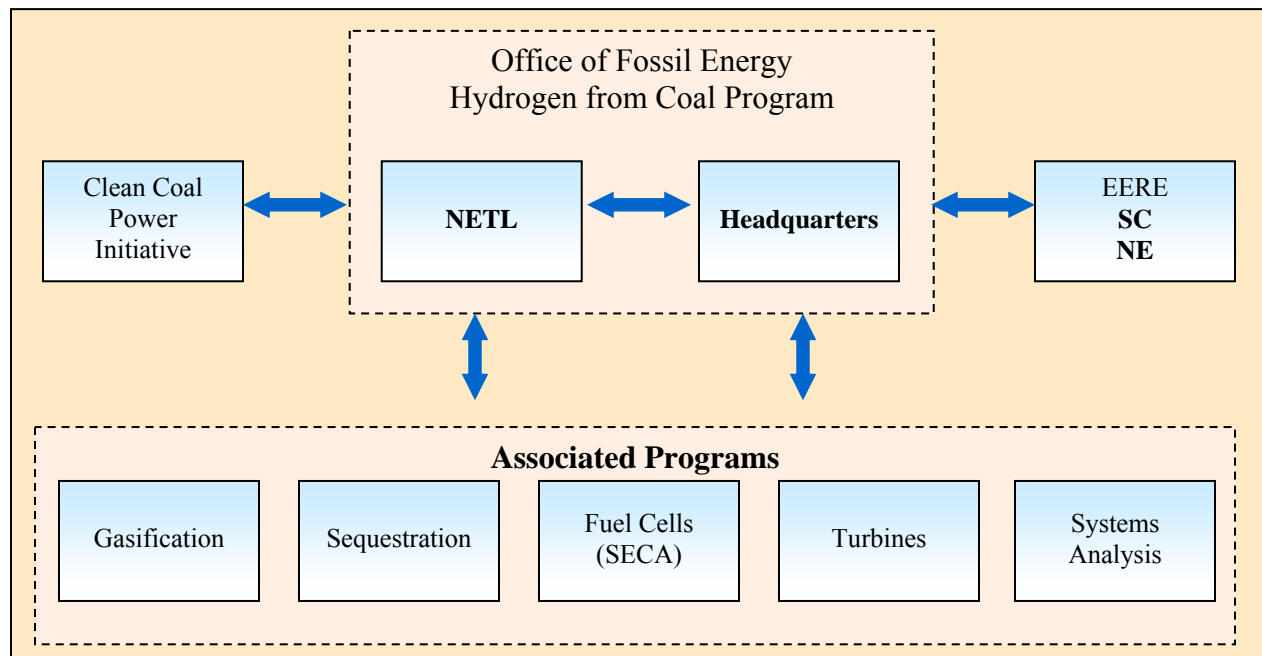
- CO₂ capture and sequestration.
- Advanced coal gasification, including feed handling systems.
- Efficient gasifier design and materials engineering.
- Advanced synthesis gas cleanup technologies.
- Advanced membrane separation technology to produce a lower-cost source of oxygen from air.
- Fuel cell modules that can produce electric power at coal-fired integrated gasification combined-cycle power plants.
- Hydrogen fuel gas turbines.

In response to comments by the National Academy of Sciences, the Hydrogen from Coal Program was organizationally grouped together with the Carbon Sequestration Program to enhance coordination and collaboration with respect to carbon sequestration and hydrogen production from coal. Figure 11 shows the various programs and projects with which the Hydrogen from Coal Program will coordinate in addition to the Sequestration Program. Coordination of efforts and sharing of information and experience will help ensure the successful transition to a hydrogen energy system.

5.1.1. Other Coordination Activities

The Hydrogen from Coal Program interacts with several different programs and federal organizations outside of FE. These include the overall DOE Hydrogen Program, the Hydrogen Interagency Task Force, and the International Partnership for a Hydrogen Economy (IPHE).

Figure 11. Coordination of the Hydrogen from Coal Program with Associated Programs



5.1.1.1. Hydrogen and Fuel Cell Interagency Task Force

The Hydrogen and Fuel Cell Interagency Task Force was established in April 2003 to fulfill a statutory requirement and to serve as a mechanism to facilitate collaboration among federal agencies engaged in hydrogen and fuel cell R&D activities. In November 2006, the Hydrogen and Fuel Cell Technical Advisory Committee (HTAC), an advisory committee to the Secretary of Energy, recommended that agency members on the Interagency Task Force be represented at the Assistant Secretary level to ensure a continued high-level of commitment and decision-making on hydrogen activities. The Assistant Secretary for Fossil Energy represents the Hydrogen from Coal Program on the Interagency Task Force. The Task Force, chaired by the Assistant Secretary of EERE, held its initial meeting in August 2007. The Task Force also includes representatives from the following organizations:

- DOE Offices of Energy Efficiency and Renewable Energy; FE, Nuclear Energy, and Science
- National Institute of Standards and Technology (NIST)
- Department of Defense (DoD)
- Department of Transportation (DOT)
- Department of Education
- Department of Agriculture (USDA)
- Executive Office of the President, Office of Science and Technology Policy (OSTP)
- General Services Administration (GSA)
- United States Postal Service (USPS)
- Environmental Protection Agency
- National Aeronautics and Space Administration
- National Science Foundation (NSF)

5.1.1.2. International Partnership for the Hydrogen Economy (IPHE)

The IPHE was established in 2003 and consists of 16 countries and the European Union (EU). The Hydrogen from Coal Program contributes to the IPHE by attending meetings and offering its expertise on hydrogen from coal production technologies. The partners of the IPHE include nearly 3.5 billion people; account for more than \$35 trillion in Gross Domestic Product (GDP) (approximately 85 percent of the world's GDP), and more than 75 percent of electricity used worldwide; and produce greater than two-thirds of CO₂ emissions, while consuming two-thirds of the world's energy. The IPHE focuses its efforts on:

- Developing common codes and standards for hydrogen fuel utilization.
- Establishing cooperative efforts to advance the RD&D of hydrogen production, storage, transport, and end-use technologies.
- Strengthening exchanges of pre-competitive information necessary to build the kind of common hydrogen infrastructures necessary to allow this transformation to take place.
- Formalizing joint cooperation on hydrogen R&D to enable sharing of information necessary to develop hydrogen-fueling infrastructure.

5.2. Performance Assessment and Peer Reviews

Performance assessment provides essential feedback on the effectiveness of the Program's mission, goals, and strategies. It is built into every aspect of program management and provides managers with a consistent stream of information upon which to base decisions about program directions and priorities. The overall DOE Hydrogen Program has annual merit review meetings of funded projects to report progress and provide program managers the opportunity to evaluate progress toward program goals and milestones. Additionally, NETL hosts periodic peer reviews that are conducted by the American Society of Mechanical Engineers (ASME) to evaluate progress and provide guidance and direction.

The RD&D Plan will be annually reviewed and updated to reflect Department priorities, changes in technical and economic assumptions, and accomplishments of its research activities. These annual reviews of the RD&D Plan will provide program managers the opportunity to update the goals and objectives of the Program by utilizing the most current data generated by the Program and consistent with DOE and NETL's OCC management guidance. On a periodic basis, program managers will provide RD&D direction and the project managers will conduct reviews to evaluate progress toward goals. The project managers will provide their input into the RD&D Plan by review and comment on individual projects, and their assessment of the progress being made to achieve the program goals, milestones, and targets. Formal meetings will be held with the NETL Technology Manager and DOE Program Manager on an annual basis and fact sheets will be provided on individual projects on a periodic basis.

5.3. Accomplishments and Progress

The Hydrogen from Coal Program has successfully transitioned from its initial start-up in FY 2004 to full operations. The Program has been actively soliciting proposals from industry, universities, and other organizations to help achieve its goals. Currently, the program has 23 projects that are conducting research in a wide number of areas (Table 7).

Table 7. Active Hydrogen from Coal Research Projects

| Research Area ^a | Number of Projects |
|--|--------------------|
| Palladium and metallic-based membrane research | 6 |
| Module scale-up | 5 |
| Membrane reactors & process intensification | 1 |
| Microporous membrane research | 1 |
| Sorbent/chemical looping | 3 |
| Non-precious metal separations | 7 |
| TOTAL | 23 |

^a Complementary projects are supported by the Gasification and Sequestration Programs.

5.3.1. Technical Progress

The Hydrogen from Coal Program has been in existence since 2004, with most of its projects initiated in FY2005 and thereafter. Since its inception, the Program has made significant technical progress toward achieving several of its goals, milestones, and technical targets. Several of the activities undertaken by the program have produced advancements and progress in technology development as outlined in the next several paragraphs.

5.3.1.1. Hydrogen Membranes

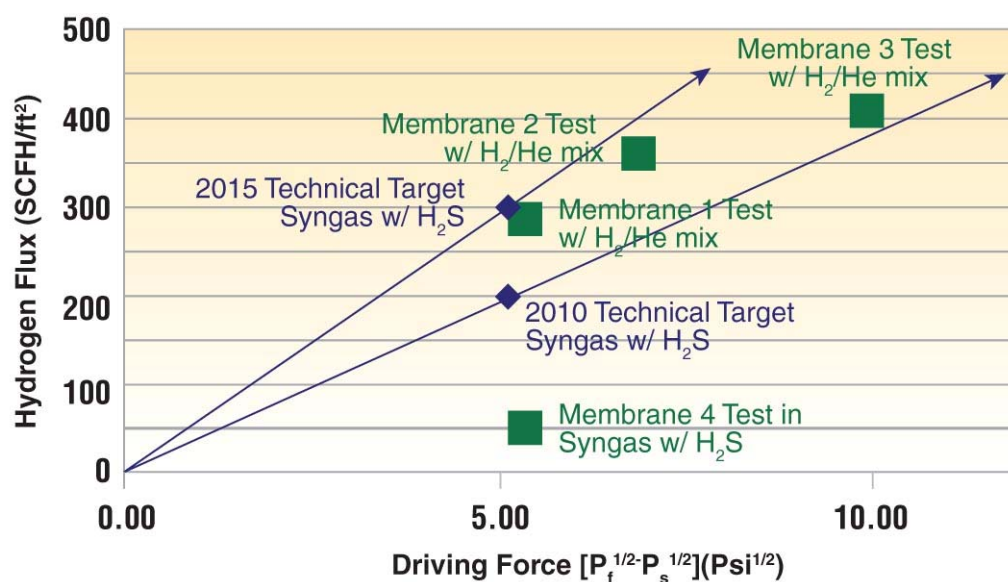
Several of the hydrogen membrane developers have obtained laboratory results that indicate their membranes can achieve the Program's flux Technical Targets using pure gases without sulfur, and some test units show resistance to carbon monoxide and hydrogen sulfide in syngas. NETL has developed and published a Hydrogen Membranes Test Protocol for use by all contractors, and NETL's Office of R&D (ORD) has conducted verification testing.

- Eltron Research, Inc. is developing alloy-based membranes and has developed a separator unit rated to produce 1.5 lbs/day of hydrogen. Eltron's best alloy membrane has demonstrated a H₂ flux rate of 411 SCFH/ft² at specified pressure and gas compositions, which is higher than the Program's Technical Target. Eltron initiated membrane tests under WGS feed stream conditions; tubular membranes were successfully tested for greater than 300 hours with feed gas composition of 50 percent H₂, 29 percent CO₂, 19 percent H₂O, 1 percent CO, and 1 percent He. A lifetime testing reactor has been operated to 600 hours; initial baseline membrane testing in H₂/N₂ feed streams show stable membrane hydrogen flux performance at 200 SCFH/ft². A preferred membrane coating catalyst was tested in streams with 20 ppm H₂S, and stable H₂ flux was observed for 160 hours.
- Worcester Polytechnic Institute (WPI) is developing Pd-based membranes on tubular stainless steel or alloy supports. WPI achieved a H₂ flux of 359 SCFH/ft² in pure gases at 442°C and 100 psi ΔP with a 3–5 μm thick Pd membrane with an Inconel base, exceeding the DOE flux target. WPI has also built an engineering-scale prototype membrane with 8.8 μm thickness, 2" outer diameter, and 6" length. WPI has demonstrated long term membrane testing with total test duration of 63 days at 450°C, 15 psi ΔP, 80 SCFH/ft² H₂ flux, 99.99 percent purity. This flux is equivalent to approximately 340 SCFH/ft² under DOE flux target operating pressures. WPI also is developing new membranes utilizing SS 316L supports.

- Praxair is building a Pd-alloy based prototype multi-tube hydrogen purifier based on U.S. Patent 7,628,842, and will use the unit to demonstrate prototype performance. A Pd-Au membrane (5 percent Au, 9 μ m thickness) was prepared from an extruded substrate and tested at 400°C at a pressure range of 20–200 psi. The H₂ flux in pure gas was 384 SCFH/ft² and the H₂/N₂ selectivity was 495 at 200 psi. Another Pd-Au membrane (9 percent Au, 8 μ m thickness) prepared from an extruded tube, tested at the same conditions, had an infinite selectivity up to 100 psi and a higher H₂ flux, most likely due to a thinner Pd layer.
- United Technologies Research Center (UTRC) is developing two types of membrane separators using metallic supports: one based on a commercial tube design with Pd-based alloy; the other using a novel nano-composite material. UTRC has tested five separators using PdCuTM alloy which showed increased surface stability in bench-scale tests. Sulfur tolerance has been tested at up to 78 ppm H₂S. UTRC's current membrane flux performance is approximately 45 SCFH/ft² at a temperature of 450°C and feed pressure of 200 psi, below the DOE Target. In addition to the Pd-based metallic membranes, the project is also focused on developing an advanced membrane concept which is a hybrid of ceramic and dense metallic membrane technology. Anticipated performance for the nano-oxide membrane projects H₂ flux of 400 SCFH/ft².
- SwRI is developing Pd-foil-based membrane separators. SwRI has tested 70 percent Pd, 20 percent Au, 10 percent Pt foils under the DOE Test Protocol gas composition, with flux levels of approximately 30 SCFH/ft². Testing was conducted done at 400°C, 170 psi with gas composition of 50 percent H₂, 30 percent CO₂, 19 percent H₂O, and 1 percent CO.

Some of the recent contractor results are summarized in Figure 12 showing their relationship to the Program Technical Targets for hydrogen separation membranes.

Figure 12. Membrane Flux Measurements from Research Projects Sponsored by the Hydrogen from Coal Program



Note: 2010 and 2015 Technical Targets extrapolated over all driving force ranges based on Seivert's Law.

In the advanced concepts area of process intensification, a WGS membrane reactor is being developed by several organizations, including Media and Process Technologies. Their goal is to meet performance requirements in terms of H₂/CO selectivity (50 to less than 100), hydrothermal stability (50 psia steam), and chemical stability (resistance to sulfur and hydrocarbons poison). A field test at a commercial

hydrotreating facility was conducted that successfully demonstrated selectivity and chemical stability in a gas stream containing H₂, hydrocarbons, H₂S and ammonia.

NETL's in-house research group also conducts its own exploratory research in the areas of membranes and catalysis in support of the coal-based hydrogen production pathway. Researchers have performed independent verification testing of several membranes. They have also studied the impacts of sulfur on palladium-type membranes and have shown two degradation mechanisms occur and that the concentration of gas species throughout the membrane reactor can have a critical role on membrane degradation.

5.3.1.2. Systems Engineering

Systems engineering analytical activities support the Hydrogen from Coal program by providing: a) current cost estimates for hydrogen production and associated plant/component configurations; and b) R&D guidance regarding the materials, equipment, and system configurations that are likely to offer optimum efficiency and cost. The results of these studies provide assessments of the current and future state of the technologies under development, and help guide program direction.

NETL completed a comprehensive assessment of the production of precious metals currently used in hydrogen membrane construction. The assessment showed:

- Global deposits are primarily located in South Africa and Russia.
- Less than 10 significant mining companies currently exist in the world; production is declining.
- Commercial deployment using precious metals has potential global economic and environmental impacts.

Each of these factors could restrain the ability to deliver hydrogen via membrane separation technologies. Considering these concerns, a competitive Funding Opportunity Announcement (FOA) was released soliciting research projects that would conduct both fundamental and applied research on novel non-precious metal hydrogen separation concepts. The projects were selected in September 2009 and are shown in Table ES-1.

5.4. Communications, Outreach, and Technology Transfer

Information dissemination, communications, and outreach activities are important and integral parts of the Hydrogen from Coal Program. Program officials communicate the Program's mission, strategies, accomplishments, and technology capabilities to a variety of stakeholder audiences including Congress, the public, educational institutions, industry, and other government and non-government organizations. Program staff perform the following communications, outreach, and technology transfer in addition to their other programmatic duties:

- Present technical status and program overviews at public forums.
- Manage the FE and NETL public Web site, and document and references lists.
- Manage official correspondence.
- Coordinate reviews of FE/NETL-related statements by other DOE offices and federal agencies.

The Program also participates in various technical conferences and workshops to exchange information with industry, government, and academia throughout the world.

5.5. Next Steps

The Hydrogen from Coal Program has transitioned from its FY2004 initial start-up mode to an operational/implementation mode. The Program will continue to issue solicitations as appropriate, and will continue with current RD&D activities that support development and deployment of hydrogen from coal technologies to address the overall DOE Hydrogen activity goals of improved energy security and reduced GHG emissions.

NETL has implemented a peer review process that provides for input from technical experts in academia, industry, and other stakeholder organizations on the Strategic Center for Coal's programs. The Hydrogen from Coal Program has undergone one such review and another is scheduled for October 2010. The recommendations from these reviews are addressed from program and technical perspectives to improve the overall quality of the Program and help ensure that goals and targets are met successfully and on schedule. It is intended that this process will continue as the technologies mature.

As previously identified as part of the RD&D Plan review, FE/NETL management has directed the Program to focus on production of hydrogen for use in stationary turbines and possibly solid oxide fuel cells (SOFC) to produce clean electricity from coal. The RD&D plan will continue to be updated periodically based on RD&D progress and subsequent go/no-go decisions and funding appropriations. Systems analysis and evaluation will continue to guide the direction of research and provide input into the Hydrogen from Coal RD&D Plan. The Program will continue collaborating with associated programs in OCC to ensure efficient utilization of resources and successful development and integration of hydrogen from coal technologies into clean coal processes. The Program also will continue to work closely with EERE, SC, and NE on coordinating activities within DOE to meet its goals and objectives.

6. Appendix A – Additional Technology Discussion

6.1. The Relationship between Membrane Flux and Partial Pressure of Hydrogen

With some exceptions, most hydrogen separation membrane research is in the laboratory research phase. Therefore, most of the current information on membranes, particularly the flux, is based on observed data under specifically controlled experiments that may not reflect real-world operating conditions in a hydrogen from coal production facility. However, based on scientific and engineering theory and observation data in the laboratory, estimates of the hydrogen flux at desired operating pressures can be determined.

As previously mentioned, membrane flux is dependent upon the partial pressure of hydrogen, and the relationship between the two differs depending upon the type of membrane. Specifically, microporous membranes exhibit a flux that is directly proportional to the hydrogen partial pressure differential across the membrane. In metal or hydrogen-permeable cermet membranes, the flux is proportional to the difference in the square roots of the partial pressures or the natural log of the partial pressure gradient according to Sievert's Law. In dense ceramic and non-hydrogen permeable cermets, flux is proportional to the natural log of the pressure gradient across the membrane, based on the Nernst potential.

Flux rates need to be converted from observed experimental results to desired operating pressure conditions to evaluate their status relative to technical targets. Table 8 shows these mathematical relationships for the different membrane types.

Table 8. Relationships for Flux as a Function of Hydrogen Partial Pressure Differentials for Different Membrane Types

| Membrane Type | ΔP function | Equation |
|--|---------------------|---|
| Microporous | Linear | $\text{Flux}_{\text{est M}} = \text{Flux}_{\text{obs M}} \cdot M \cdot (\Delta P_{\text{est}} / \Delta P_{\text{obs}})$ |
| Pure metallic (includes pure metal and metal alloys) | Square root | $\text{Flux}_{\text{est P}} = \text{Flux}_{\text{obs P}} \cdot P \cdot [(P_{\text{f est}}^{0.5} - P_{\text{s est}}^{0.5}) / (P_{\text{f obs}}^{0.5} - P_{\text{s obs}}^{0.5})]$ |
| Hydrogen-permeable cermet | Square root | $\text{Flux}_{\text{est P}} = \text{Flux}_{\text{obs P}} \cdot P \cdot [(P_{\text{f est}}^{0.5} - P_{\text{s est}}^{0.5}) / (P_{\text{f obs}}^{0.5} - P_{\text{s obs}}^{0.5})]$ |
| Dense ceramic | Natural logarithm | $\text{Flux}_{\text{est D}} = \text{Flux}_{\text{obs D}} \cdot D \cdot [\ln(P_{\text{f est}}/P_{\text{s est}}) / \ln(P_{\text{f obs}}/P_{\text{s obs}})]$ |
| Dense ceramic with non-hydrogen permeable second phase (electron conducting) | Natural logarithm | $\text{Flux}_{\text{est D}} = \text{Flux}_{\text{obs D}} \cdot D \cdot [\ln(P_{\text{f est}}/P_{\text{s est}}) / \ln(P_{\text{f obs}}/P_{\text{s obs}})]$ |

$\text{Flux}_{\text{est M}}$ is the estimated flux for microporous membranes.

$\text{Flux}_{\text{obs M}}$ is the observed, or tested, flux for microporous membranes.

ΔP_{est} is the ΔP of hydrogen partial pressure to be estimated.

ΔP_{obs} is the observed, or tested, hydrogen partial pressure.

$\text{Flux}_{\text{est P}}$ is the estimated flux for hydrogen permeable metallic, metal alloy, or cermet membranes.

$\text{Flux}_{\text{obs P}}$ is the observed, or tested, flux for hydrogen permeable metallic, metal alloy, or cermet membranes.

$P_{\text{f est}}$ is the estimated feed side hydrogen partial pressure.

$P_{\text{s est}}$ is the estimated sweep (permeate) side hydrogen partial pressure.

$P_{\text{f obs}}$ is the observed, or tested, feed side hydrogen partial pressure.

$P_{\text{s obs}}$ is the observed, or tested, sweep (permeate) side hydrogen partial pressure.

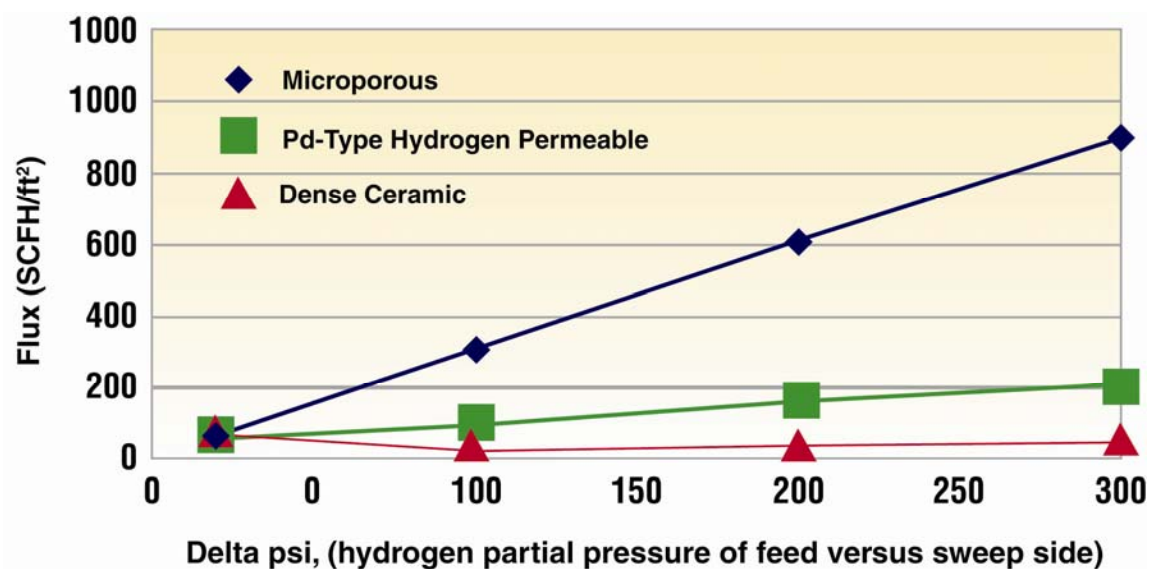
$\text{Flux}_{\text{est D}}$ is the estimated flux for dense ceramic or non-hydrogen permeable cermet membranes.

$\text{Flux}_{\text{obs D}}$ is the observed, or tested, flux for dense ceramic or non-hydrogen permeable cermet membranes.

Figure 13 shows the effect of changes in partial pressure on the flux of hydrogen membranes. This graph is based on a reference assumed flux of 60 SCFH/ft² with a hydrogen partial pressure ΔP of 20 psi and an assumed sweep (permeate) side hydrogen partial pressure of 1 psi for all membrane types. For commercial applications, the sweep, or permeate, side hydrogen partial pressure is assumed to be 50 psi.

One of the key conclusions observed from Figure 13 is that it is important to set desired technical targets near the expected operating conditions. In the case of hydrogen from coal technologies, hydrogen separation membranes are expected to operate with at least 50 psi hydrogen partial pressure on the permeate side and a hydrogen partial pressure ΔP of 100–300 psi is expected. For example, when converting assumed observed test data from a ΔP of 20 psi and a permeate side partial pressure of 1 psi to operating conditions of 100 psi ΔP and 50 psi permeate side, a decline in flux for dense ceramic membranes is seen, a slight increase for Pd-type, but a linear improvement related to ΔP for microporous membranes.

Figure 13. Ideal Effect of Changes in ΔP on Flux of Hydrogen Membranes



6.2. Sorbents

Carbon Dioxide Sorbents

For testing and screening of sorbents, the most basic dataset is an absorption isotherm for single gases for a single temperature at a time over a range of temperatures at various pressures (e.g., amount of CO₂ adsorbed per unit weight of sorbent plotted versus partial pressure). At a minimum, all sorbent candidates should have adsorption isotherms determined for CO₂ and H₂ in the temperature and pressure ranges listed below. Selectivities can be calculated from single gas adsorption isotherms, but these calculations may not accurately represent some interactive effects (e.g., catalysis of the shift reaction). Global kinetics can be calculated from the time dependence of the TGA data, but single purpose kinetics equipment may be needed to provide more accurate information. Thermal properties of the sorbent such as heat capacity can be determined using calorimeters, and these properties may vary with temperature.

In general, sorbents intended for use for separation of CO₂ from syngas need to be tested in the

following ranges:

- Temperature – 150 to 500°C (e.g., ~ 150–200°C for sorption and 250°C for regeneration)
- Pressure – 40 to 60 barg (580 to 870 psig)
- Gas composition – Typical syngas compositions

Once adsorption isotherms and other related data are available over the temperature and pressure ranges of interest, process models can be used to estimate the overall performance of the sorbent in a CO₂ capture process located at a given position in the overall H₂ production process. Process models will need to simulate the energy balance (energy in and out), as well as flows and compositions in and out of the process. An energy balance calculation will need to calculate: (1) energy flows during adsorption which is expected to be exothermic (i.e., the sorbent will be heated up during adsorption and heat may need to be removed via heat exchangers in the bed), and (2) energy flows during additional heating of and/or gas flows through the sorbent needed to cause release of the adsorbed CO₂ and regeneration of the sorbent. Energy flows will be affected by heat capacities and heat transfer rates of the vessels used to house the sorbent as well as sorbent properties. It may be possible to get reasonable estimates by ignoring vessel heating, but heat removed or added by heat exchangers cannot be ignored.

Results of screening tests and process calculations can be used to “weed out” sorbents that are not promising because of low capacity or unfavorable kinetics or selectivity. Sorbents that pass the screening tests can move on to be tested for process-specific applications.

Hydrogen Sorbents

As indicated in the main text, in considering whether to use a hydrogen sorbent in a TSA or PSA process, the economics of the process will depend (among other things) on the ratio of H₂ to CO₂ in the syngas, the compression requirements following separation of the two main streams, and how well the sorbent discriminates between H₂ and CO₂. PSA processes usually produce a higher pressure stream from the gases that pass over the sorbent and a lower pressure stream from the gases that are adsorbed and later desorbed. Since coal contains far more carbon by weight than hydrogen, on a superficial basis it would seem that more energy would be required in recompressing CO₂ than H₂, and therefore it would be preferable to allow the H₂ to be produced at a lower pressure than the CO₂. However, the shift reaction creates more H₂ from CO in the syngas, and one has to look at the overall ratio in the shifted syngas. Typical shifted syngas from coal gasification may contain 40–50 percent H₂ and 40–50 percent CO₂ on a molar basis, but on a weight basis far more CO₂ is produced. It is necessary to examine in detail how the volume, weight and other properties of the gases affect compression requirements.

PSA reactors are operated in a cyclic process. For PSA reactors in which the sorbent adsorbs CO₂ and other non-hydrogen gases, assuming a freshly regenerated sorbent, the major steps are: pressurization, feed, blowdown, purge, and pressure equalization.

- The first step is to pressurize the bed with the input gas. The feed stage involves pumping the mixed gas through the sorbent bed under high pressure, with the bed prepared in advance by covering with hydrogen. This step allows CO₂ and other non-H₂ gases such as CO and water to be adsorbed, and pure hydrogen to pass through.
- When the sorbent bed is nearly saturated with CO₂ and other gases, some of the pressure is released and the remaining hydrogen is allowed to flow out at a lower pressure.

- Then the flow is reversed, allowing the bed to blowdown to a low pressure (typically atmospheric) that releases the adsorbed gases.
- A purge flow is then created with hydrogen or recycled product gas to cause the remaining adsorbed gases to be released due to a reduction in partial pressure of the adsorbed gases.
- The bed is then partially pressurized with the feed gas and then the pressurization started again with product gas to ready the bed for feed again.

In the case of an H₂ sorbent, the sorbent will either react chemically with H₂ or adsorb it by a physical adsorption process. How much H₂ can be adsorbed by the sorbent (sorbent capacity) is characterized by the percentage weight increase of the sorbent when the sorbent is exposed to the mixed gas containing H₂ under fixed conditions of temperature, pressure, gas composition, and flow rate. The sorbent capacity is affected by all of the “state parameters” such as temperature and pressure, and will also depend on the partial pressure of H₂ in the gas to which the sorbent is exposed. The sorbent will need to have a substantial adsorption capacity at the temperature planned for operation. The speed of H₂ removal will be affected by the kinetic rates of reaction. Ideally, the sorbent will adsorb only H₂ and all the CO₂, CO, etc. will remain in the gas phase. In practice, it may be necessary to measure the selectivity to H₂ over other gas components. The other critical parameter is the temperature and other conditions at which the H₂ can be driven off the sorbent and the sorbent regenerated for use. If the temperature differential between adsorption and regeneration is too high, the regeneration heating requirements may be impractical.

6.3. WGS Technologies

One or two staged reactors are typically employed in commercial WGS technology to produce hydrogen by steam reforming of natural gas. Commercial catalysts have been developed to achieve optimum performance in the different stages and are summarized in Table 9. Only fixed-bed reactors are currently used in commercial applications with these catalysts. Multiple reactors with inter-cooling are used to optimize the WGS reaction temperature profile. Steam reforming plants typically employ either a two-stage system using high (Fe/Cr) and low (Cu/Zn) temperature shift catalysts in series, or a single stage with high- or medium-temperature shift catalyst followed by a PSA hydrogen separation system. Partial oxidation plants used to gasify oils, coke, and coal employ multiple reactor stages using either the high-temperature or sour gas (Co/Mo) shift catalyst in all beds. No gas cleanup is required upstream of the WGS reactors with the sour gas shift catalyst. For low-temperature shift, catalyst life is limited due to loss of activity. For high-temperature shift, catalyst life is limited due to increases in pressure drop and loss of activity. Technology options for residual CO cleanup/H₂ purification include methanation (old), PSA (current), and polymer membranes (new). Possible impurities in the product hydrogen are CO, CO₂, CH₄ and higher hydrocarbons, and methanol.

Table 9. Performance of Commercial WGS Catalysts

| Performance Criteria | Units | Low-/Medium-temperature Shift | High-temperature Shift | Sour Gas Shift |
|--------------------------|-------|--------------------------------|------------------------|---------------------|
| Catalyst form | – | Pellets | Pellets | Pellets |
| Active metals | – | Cu/Zn & Cu/Zn/Al | Fe/Cr | Co/Mo |
| Reactor type | – | Multiple fixed beds (last bed) | Multiple fixed beds | Multiple fixed beds |
| Temperature ^a | °C | 200–270/300 | 300–500 | 250–550 |
| Pressure | psia | ~450 | 450–750 | ~1,100 |
| CO in feed | – | Low | Moderate to high | High |
| Residual CO | % | 0.1–0.3 | 3.2–8 | 0.8–1.6 |
| Approach to equilibrium | °C | 8–10 | 8–10 | 8–10 |
| Min steam/CO ratio | Molar | 2.6 | 2.8 | 2.8 |
| Sulfur tolerance | ppmv | <0.1 | <100 | >100 ^b |
| COS conversion | – | No | No | Yes |
| Chloride tolerance | – | Low | Moderate | Moderate |
| Stability/durability | Years | 3–5 | 5–7 | 2–7 |

^a Lower temperature limit is set by water dew point at pressure.

^b Sulfur is required in the feed gas to maintain catalyst activity.

In summary, the advantages of low-/medium-temperature shift processes are:

- WGS equilibrium favors hydrogen production at low temperatures, maximizing hydrogen yield.
- Undesirable side reactions like F-T synthesis are minimized.
- Processes integrate well with conventional gas cleanup technologies that produce hydrogen at near-ambient temperatures and pipeline pressures (400 psi); minimal or no reheat required.
- Temperature range overlaps ranges for advanced gas cleanup processes for sulfur, mercury, etc.
- Processes can be coupled with newer preferential oxidation (PrOx) technologies to produce very low CO in the hydrogen product.
- Steam requirements are low.

The disadvantages are:

- WGS kinetics are more favorable at higher temperatures.
- Low-temperature shift catalysts are easily poisoned.
- Temperature range is below the range of metal and ceramic membranes that could be used for separation.
- Copper (Cu) in catalyst promotes methanol side reaction (methanol emissions from hydrogen plants are regulated by the U.S. Environmental Protection Agency).
- Any condensation of water in the reactor will irreversibly damage the catalyst.

The advantages of high-temperature shift processes are:

- WGS kinetics improve with higher temperatures.
- Processes can operate at very high pressures (~1,000 psi).
- Catalysts exhibit greater tolerance for potential poisons.

- Temperature range is consistent with metal and ceramic membranes.

The disadvantages are:

- WGS equilibrium is less favorable at higher temperatures.
- Undesirable side reactions (F-T synthesis) are favored at higher temperatures.
- Steam requirement increases with temperature, both to improve equilibrium and minimize side reactions.
- Hexavalent chromium (from the catalyst) presents a wastewater treatment and catalyst disposal issue.

7. Appendix B

7.1. Acronyms

Government Agency/Office Acronyms

| | |
|------|---|
| DoD | Department of Defense |
| DOE | Department of Energy |
| DOT | Department of Transportation |
| EERE | Office of Energy Efficiency and Renewable Energy |
| EPA | Environmental Protection Agency |
| FE | Office of Fossil Energy |
| GSA | General Services Administration |
| NASA | National Aeronautics and Space Administration |
| NE | Office of Nuclear Energy |
| NETL | National Energy Technology Laboratory |
| NIST | National Institute of Standards and Technology |
| NSF | National Science Foundation |
| OCC | Office of Clean Coal |
| ORD | NETL's Office of Research & Development |
| OSTP | Executive Office of the President – Office of Science and Technology Policy |
| SC | Office of Science |
| USDA | United States Department of Agriculture |
| USPS | United States Postal Service |

General Acronyms

| | |
|-------------|-----------------------------------|
| ΔP | Delta P (change in pressure) |
| $^{\circ}C$ | degrees Celsius |
| $^{\circ}F$ | degrees Fahrenheit |
| CCPI | Clean Coal Power Initiative |
| CCS | Carbon Capture and Storage |
| CL | Chemical Looping |
| cm^2 | Square centimeter |
| COE | Cost of electricity |
| EPRI | Electric Power Research Institute |
| EU | European Union |
| FOA | Funding opportunity announcement |
| ft^2 | Square feet |
| ft^3 | Cubic feet |
| F-T | Fischer-Tropsch |
| FY | Fiscal year |
| GDP | Gross domestic product |
| GHG | Greenhouse gas |

| | |
|-------|--|
| GTI | Gas Technology Institute |
| HEV | Hybrid electric vehicle |
| HRSG | Heat recovery steam generator |
| IGCC | Integrated Gasification Combined Cycle |
| IPHE | International Partnership for the Hydrogen Economy |
| K | Degrees Kelvin |
| kg | Kilogram |
| kWh | Kilowatt-hour |
| LHV | Lower heating value |
| min | Minute |
| ml | Milliliter |
| MMBtu | Million British thermal units |
| μm | Micrometer |
| mill | One tenth of one cent |
| MW | Megawatts |
| MWh | Megawatt-hour |
| N/A | Not available |
| N/D | Not demonstrated |
| nm | Nanometer |
| OSU | Ohio State University |
| PC | Pulverized coal |
| PM | Particulate matter |
| ppb | Parts per billion |
| ppbv | Parts per billion on a volume basis |
| ppm | Parts per million |
| ppmv | Parts per million on a volume basis |
| ppmw | Parts per million on a weight basis |
| PrOx | Preferential oxidation |
| PSA | Pressure swing adsorption |
| psi | Pounds per square inch |
| psia | Pounds per square inch absolute |
| psig | Pounds per square inch gauge |
| R&D | Research and development |
| RD&D | Research, development, and demonstration |
| SCFH | Standard cubic feet per hour |
| SCR | Selective catalytic reduction |
| SNG | Substitute natural gas |
| SOFC | Solid oxide fuel cell |
| SwRI | Southwest Research Institute |
| TSA | Thermal swing adsorption |
| TSSER | Thermal Swing Sorption Enhanced Reaction |
| U.S. | United States |

| | |
|-------|-------------------------------------|
| UTRC | United Technologies Research Center |
| WGS | Water-gas shift |
| WGSMR | Water-gas shift Membrane Reactor |
| WGPU | Warm gas cleanup |
| WPI | Worcester Polytechnic Institute |

Chemical Symbols/Names

| | |
|--------------------------------|--|
| Ag | Silver |
| Al | Aluminum |
| Ar | Arsenic |
| Au | Gold |
| Ba | Barium |
| Br | Bromine |
| Ca | Calcium |
| CH ₄ | Methane |
| Cl | Chlorine |
| CO | Carbon monoxide |
| CO ₂ | Carbon dioxide |
| COS | Carbonyl sulfide |
| Cr | Chromium |
| Cu | Copper |
| F | Fluorine |
| Fe | Iron |
| Fe ₃ O ₄ | Synthetic Iron Oxide (Magnetite or Iron Oxide Black) |
| H ₂ | Hydrogen |
| Hg | Mercury |
| H ₂ O | Water |
| H ₂ S | Hydrogen sulfide |
| HCl | Hydrogen chloride (hydrochloric acid) |
| HCN | Hydrogen cyanide |
| Mg | Magnesium |
| N ₂ | Nitrogen |
| NH ₃ | Ammonia |
| Ni | Nickel |
| NO _x | Nitrogen oxides |
| O ₂ | Oxygen |
| Pb | Lead |
| Pd | Palladium |
| SO ₂ | Sulfur dioxide |
| V | Vanadium |
| Zr | Zirconium |

7.2. Program Contacts

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