

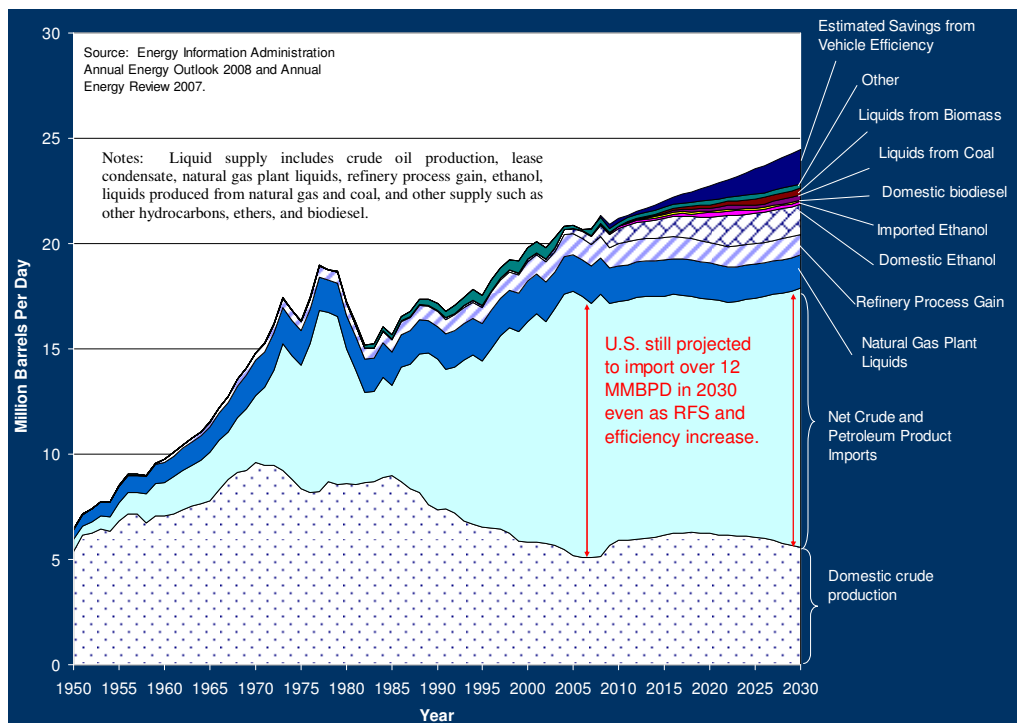
# OVERVIEW OF THE U.S. DOE HYDROGEN FROM COAL PROGRAM

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## 1. Introduction

Two of the major concerns confronting the energy sector today and for the future are energy security and the environmental impact of energy use, including the potential for reduction and stabilization of greenhouse gas emissions and atmospheric concentrations. As shown in Figure 1, imports of liquid fuels will continue to remain a large part of the United States' total liquid fuels supply [1,2] even as actions to increase the amount of renewable fuels and vehicle fuel economy as a result of the Energy Independence and Security Act of 2007 are implemented.

**Figure 1: U.S. Liquid Fuels Supply (1950-2030)**



Hydrogen has the potential to play a significant role in America's energy future because it can be produced from a variety of domestic feedstocks and its use produces little or no emissions. Realizing this potential, the U.S. government launched the Hydrogen Fuel Initiative in 2003.

In support of this initiative, the Hydrogen from Coal Program was launched in fiscal year 2004 (FY2004) to perform the necessary research, development, and demonstration (RD&D) activities to develop technology to cleanly produce, deliver, store, and utilize hydrogen produced from our abundant domestic coal resources. In addition to managing its respective

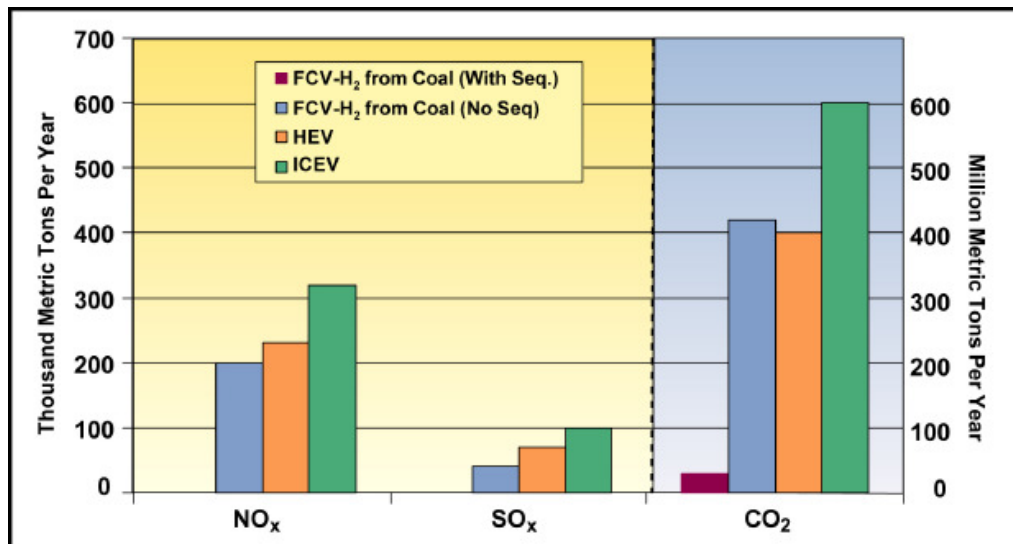
RD&D portfolio, the Program also cooperates on joint efforts with other DOE and FE offices to coordinate and integrate planning efforts on key activities such as the Hydrogen Posture Plan.

## 2. Benefits of Hydrogen Production from Coal

As a pre-eminent primary source of energy, coal is an abundant domestic resource, with the United States possessing hundreds of years of supply at current demand levels. The production of hydrogen from coal for use in fuel cell vehicles (FCVs) in the transportation sector has the potential to reduce U.S. reliance on foreign imports of petroleum. It is estimated that, if used hydrogen from coal was used in 100 million FCVs it could reduce petroleum demand in the transportation sector by three million barrels per day.

An analysis of the NO<sub>x</sub>, SO<sub>x</sub>, CO<sub>2</sub> emissions from hydrogen from coal plants was performed that evaluated and compared the environmental benefits of hydrogen produced from coal when used in FCVs with gasoline-powered internal combustion engine vehicles (ICEVs) and hybrid electric vehicles (HEVs) [3]. The analysis was done on a systems basis that calculated the energy and emissions for resource extraction and transportation, conversion of the resource to fuel and fuel delivery (i.e., refining of petroleum to gasoline or processing of coal to produce hydrogen), and finally use in a vehicle. Figure 2 shows that, with carbon sequestration in the production of hydrogen from coal, net system emissions of CO<sub>2</sub> will be nearly eliminated compared to the internal combustion engine vehicle and hybrid electric vehicle systems with carbon sequestration. The analysis results also show that emissions of nitrogen oxides (NO<sub>x</sub>) and sulfur oxides (SO<sub>x</sub>) will be reduced.

**Figure 2: Well-to-Wheels Emissions of Hydrogen from Coal and Use in Fuel Cell Vehicles Compared to Gasoline Use in Hybrid Electric and Internal Combustion Engine Vehicles (100 million vehicles)**

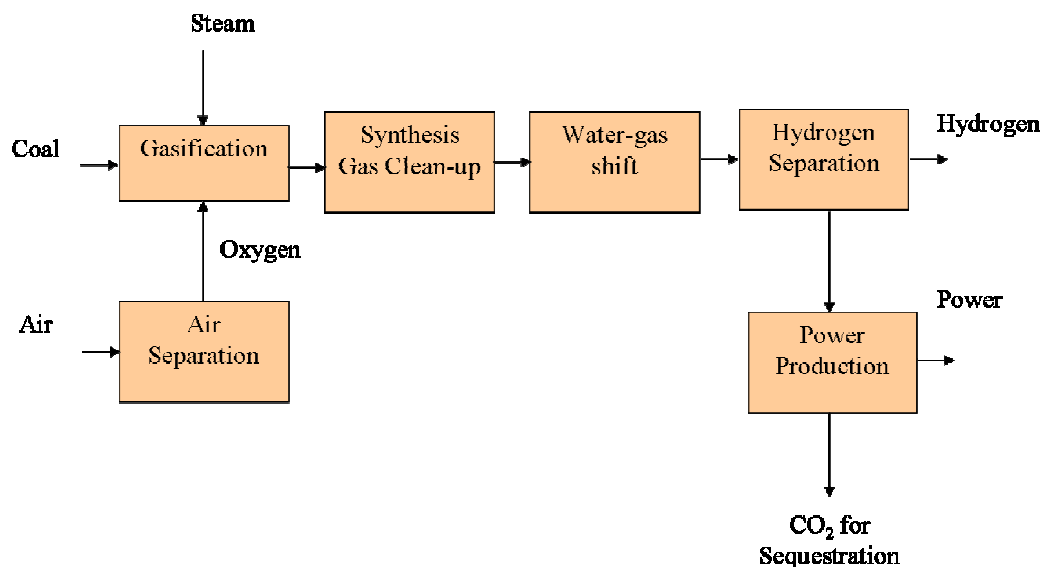


### 3. Hydrogen from Coal Production Process

A simplified flow diagram of the hydrogen from coal process is shown in Figure 3. The process begins by first gasifying coal to produce synthesis gas, a mixture of hydrogen, carbon monoxide, carbon dioxide and other gaseous compounds. The synthesis gas is cleaned of impurities and undergoes the water-gas shift reaction which converts water (steam) and carbon monoxide to hydrogen and carbon dioxide. Purified hydrogen is separated from this stream and the remaining tail gas can be combusted to produce power and the resulting CO<sub>2</sub> stream subsequently sequestered.

At the present time, no coal-fed facilities based on modern entrained gasification have been constructed that co-produce both hydrogen and electric power. Conceptual commercial plants have been simulated using computer models to estimate the technical performance and economics of a co-production plant based on current technology. Computer simulations have also been developed for conceptual plants that produce hydrogen and some excess power, based on advanced technologies that are presently not available for commercial deployment. The status of these advanced technologies varies. Some technologies are already close to commercialization and others are further back in the RD&D pipeline. Table 1 summarizes the information developed from three of these computer simulations discussed in the Mitretek Systems (now Noblis) Technical Report, *Hydrogen from Coal – July 2002* [4]. This study is currently being updated to reflect recent trends in materials of construction prices and engineering, procurement, and construction availability. Additionally, the updated study will evaluate the impact of technologies under development by the program.

**Figure 3. Schematic of the Hydrogen from Coal Production Process**



**Table 1: Summary of Hydrogen from Coal Cases**

	CASE 1	CASE 2	CASE 3
Carbon Sequestration	YES (87%)	Yes (100%)	Yes (100%)
Hydrogen (MMscfd)	119	158	153
Coal (Tons/day) (AR)	3000	3000	6000
Efficiency (%HHV)	59	75.5	59
Excess Power (MW)	26.9	25	417
Power Value (mils/kWh)	53.6	53.6	53.6
Capital (\$million)	417	425	950
RSP of Hydrogen (\$2002)	\$/MMBtu (\$/kg)	8.18 (1.10)	5.89 (0.80)

Notes: 1) Coal cost is \$29/ton (and is assumed to de-escalate at 1.5 percent below general inflation), and the assumed plant capacity factor is 85 percent. 2) For carbon sequestration, the co-produced power is assumed to have a value of \$53.6/MWh (megawatt-hour), based on an additional cost of power production from Natural Gas Combined-Cycle (NGCC) plants with sequestration of 18 mils/kWh (reference EPRI report 1000316). 3) For sequestration, it is assumed that \$10 per ton of carbon is added for sequestration after the concentrated CO<sub>2</sub> stream has been isolated, and the CO<sub>2</sub> stream is compressed to 200 bars (2,900 pounds per square inch (psi)). 4) Financial assumptions used for these simulations: 25-year plant life; 67/33 percent debt/equity financing; 15 percent return on equity; 8 percent interest for a 16-year term; 3 percent inflation with coal de-escalation of 1.5 percent per annum below general inflation; 16-year double declining balance depreciation; 40 percent combined federal and state tax rate; 3-year construction with 50 percent output in start-up year; carbon sequestration cost of \$10/ton.

#### 4. Hydrogen from Coal Program

The challenges to a sustainable supply of energy and the benefits of hydrogen as an alternate fuel serve as drivers for the Hydrogen from Coal Program. The Hydrogen from Coal Program has an established history, based on prior activities, of performing research on novel technologies to produce hydrogen from coal. The Program has RD&D activities focused on the production and delivery of hydrogen in large, central, single product and coproduct facilities, production of hydrogen-rich liquid fuels, and production of substitute natural gas (SNG) from coal. Central production of hydrogen relies upon gasification of the coal with steam and oxygen to produce synthesis gas, a mixture of hydrogen, carbon monoxide, and trace amounts of other components. The synthesis gas can be further processed to remove impurities and produce additional hydrogen. As noted, central production also offers the potential of coproduction of hydrogen and electric power with capture and sequestration of CO<sub>2</sub>.

An alternative production pathway investigates the production of hydrogen-rich liquid fuels and SNG that have the advantage of using the existing petroleum product and natural gas delivery and storage infrastructures with little to no modification. Liquid fuels and SNG can be delivered either to individual filling stations where they can be reformed on-site, or to sub-central hydrogen production locations to produce pure hydrogen.

The program is also investigating the use novel materials, such as metal-organic frameworks, as a potential option for storing hydrogen on-board vehicles, and novel engine systems that may potentially utilize hydrogen or hydrogen-natural gas mixtures in vehicular or stationary applications. Activities in hydrogen storage and utilization will be completed by the Program in FY2009.

More details about the Program can be found in FE's *Hydrogen from Coal Research, Development, and Demonstration Plan, External Draft for Review – September 2008* [3].

#### 4.1 Budget

Past budget appropriations and the current budget request for the Hydrogen from Coal Program are shown in Table 2. The Program initiated activities under the Hydrogen Fuel Initiative in FY2004 and funds are typically leveraged in cost-sharing activities with project partners, allowing greater project scope and participation.

**Table 2: Past and Recent Budget Data for the Hydrogen from Coal Program**

Program	FY04	FY05	FY06	FY07	FY08*	FY09**
Hydrogen from Coal	5.0	17.1	28.7	22.1	24.8	10.0

\* Includes funding for hydrogen activities and coal-biomass research as directed by Congress.

\*\* FY09 budget request.

#### 4.2 Central Station Production of Hydrogen

##### Advanced water-gas shift reaction systems

Partial oxidation (i.e., gasification) of coal and other carbon-based solid/liquid feedstocks produces a synthesis gas with a composition ranging from 30 to 45 percent H<sub>2</sub>, 35 to 55 percent carbon monoxide (CO), 5 to 20 percent CO<sub>2</sub> (dry basis), and trace amounts of other components. If the H<sub>2</sub> to CO ratio of the syngas from the gasifier is not appropriate for the synthesis of fuels or chemicals, the ratio can be adjusted using the WGS reaction. This reaction increases the concentration of hydrogen in the synthesis gas by converting CO and H<sub>2</sub>O to CO<sub>2</sub> and H<sub>2</sub>. When coupled with an appropriate separation technology, high yields of high-purity hydrogen are produced.

The WGS reaction is reversible, with the forward WGS reaction being mildly exothermic. Conversion to H<sub>2</sub> and CO<sub>2</sub> is thermodynamically limited and favored at lower temperatures. Higher temperatures improve the rate of reaction, but lower 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 from the reactor to shift the WGS equilibrium to produce more hydrogen. Steam also is used to minimize undesirable side reactions that compete with the WGS reaction.

## Hydrogen separation

Current hydrogen recovery methods typically employ pressure swing adsorption (PSA), cryogenics, or membrane systems. Each of these technologies has limitations: PSA typically recovers less of the feedstream 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; and current membrane systems are susceptible to chemical damage from H<sub>2</sub>S and aromatics as well as having limited temperature tolerance.

There are several gas separation technologies under development by the Program that could separate constituents of the synthesis gas (syngas). These technologies are advanced membrane separation systems, advanced CO<sub>2</sub> separation systems, polishing filters, adsorption/solvent systems, and advanced concepts such as process intensification or chemical looping. The Hydrogen from Coal Program seeks to develop technologies to improve the separation of H<sub>2</sub> and/or CO<sub>2</sub> from synthesis gas streams that will reduce capital and operating costs and improve thermal efficiency and environmental performance.

### Advanced membrane separation systems

Reductions in cost, improved efficiency, and simplified systems are potentially possible with advancements in hydrogen membrane separation technologies. Membranes can be classified as organic, inorganic, or hybrid (a mixture of organic and inorganic materials). Within each of these classes, membranes can also be characterized based on their properties. Although there are many types of membranes, the Hydrogen from Coal Program has focused its efforts on microporous membranes, pure metallic membranes, and hydrogen-permeable ceramic-metallic (i.e., cermet) membranes. Desirable characteristics of separation membranes are high hydrogen flux at low pressure drops; tolerance to contaminants, especially sulfur; low cost; and operation at system temperatures of 250 to 500°C. The pressure drop across the membrane is a critical aspect of membrane technologies. Because hydrogen produced at central plants will ultimately be needed at high pressures to both deliver and store adequate volumes, it is critical that this pressure drop be minimized, otherwise expensive re-compression may be needed which could negate any competitive advantage of membranes compared to other technologies.

### Advanced CO<sub>2</sub> separations systems

Another method to separate H<sub>2</sub> mixed with CO<sub>2</sub> is to remove the CO<sub>2</sub> from the process stream. CO<sub>2</sub> currently is separated from syngas through commercially available CO<sub>2</sub> absorption systems. These are continuous scrubbing systems that typically are available as three basic types: chemical, physical, and hybrid. All the processes operate in essentially the same manner by scrubbing the mixed gas in absorption towers to collect the CO<sub>2</sub>, and then regenerating the solvent and releasing the CO<sub>2</sub>. After separation, the CO<sub>2</sub> stream is dried and compressed to approximately 1,600 pounds per square inch (psi), which results in liquid CO<sub>2</sub> that is transported to a utilization site (e.g., enhanced oil recovery) or to a future sequestration site.

Advanced CO<sub>2</sub> separation technologies have as their objective the efficient, low-cost removal of CO<sub>2</sub> and other trace impurities from the H<sub>2</sub>-CO<sub>2</sub> mixtures. Reverse selective

membranes, such as nanostructured, polymeric membranes, show potential to achieve the desired selectivity for CO<sub>2</sub> separation. CO<sub>2</sub> sorbents and hydrates are other options that selectively remove CO<sub>2</sub> from mixed gas streams. Sorbents work by adsorbing CO<sub>2</sub> gas molecules onto the surface of a solid. CO<sub>2</sub> hydrates remove CO<sub>2</sub> by forming a crystalline lattice of water molecules around the gas molecule, subsequently trapping the molecule.

#### Polishing filters (ultra-clean hydrogen purification systems)

Hydrogen produced from coal can be used for various applications, including transportation, gas turbine and solid oxide fuel cell (SOFC) power generation, and crude oil refining. The hydrogen purity requirement is dependent on the applications in which it is used. Proton exchange membrane (PEM) fuel cells, which are the preferred technology for use in FCVs, currently require the stringent standard of less than 1 ppm of CO, and very low levels of sulfur that may be limited to 10 to 50 parts per billion (ppb) levels or lower. A polishing filter device using an absorbent may be required to meet the particular application requirement. For coal-based hydrogen production, RD&D efforts have to identify and define the preferred absorption material or materials and conditions to successfully remove the trace impurities to meet the standards, with more focus on the sulfur removal process.

#### Advanced adsorption/solvent systems

Advanced adsorption (i.e., advanced PSA) and other solvent systems have the potential to improve current hydrogen separation technologies. These technologies can help lower the cost of current hydrogen separation from large centralized coal plants until membrane technologies become commercially available. These technologies may include novel catalysts, adsorbers, or solvents that make current technologies more efficient, improve environmental performance, increase operating capacity, reduce operating and maintenance costs, or improve processing.

#### Advanced concepts

The Hydrogen from Coal Program is investigating advanced concepts for producing and separating hydrogen such as process intensification. Process intensification is the concept of developing novel technologies which, when compared to current technology, identifies 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. Other advanced concepts 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. One of the more developed advanced concepts being investigated is the integration of the WGS reaction with hydrogen separation. Chemical looping is another advanced concept for producing and separating streams of hydrogen and CO<sub>2</sub> from mixed gases and trace constituents.

### 4.3 Alternate Hydrogen Production Pathway

The Hydrogen from Coal Program is also pursuing an alternative pathway to produce hydrogen from coal by producing liquid fuels or SNG as an intermediate step. The Office of Fossil Energy has been a leader in researching, developing, and demonstrating the production of synthesis gas and subsequent conversion to liquid fuels and chemicals. FE's research and development program has included the \$213 million Liquid Phase Methanol (LPMEOH) demonstration project, led by Air Products and Chemicals, Inc. (APCI), which demonstrated on a commercial scale the production of methanol and dimethyl ether from coal-derived synthesis gas.

Liquids and SNG are characterized by high weight content of hydrogen and can be transported in either the existing liquid fuel or natural gas delivery system. They can subsequently be reformed closer to the end-user in sub-central or distributed locations. Some of the processing steps used to produce hydrogen in the central production pathway are similar for the alternative pathway. For example, coal needs to be gasified to produce synthesis gas for both pathways. However, for liquid fuels and SNG, the synthesis gas is then converted into liquid fuels via the synthesis gas to methanol or the Fischer-Tropsch (F-T) synthesis process or into SNG through methanation. Because these plants are centrally located, they can capture any of the CO<sub>2</sub> that is produced during these synthesis processes. The liquid fuels and SNG can be delivered to sub-central or distributed sites by the existing liquid fuel or natural gas delivery systems. Once at the sub-central or distributed plant, technologies such as steam methane reforming and autothermal reforming can produce hydrogen from the liquid fuel or SNG. There is potential to use advanced technology for the reforming of liquid fuels and SNG to produce hydrogen, which would take advantage of process intensification with a corresponding reduction in product cost. For sub-central plants, final delivery of the hydrogen to individual filling stations can be made using hydrogen tube trailers.

Two key benefits of this pathway are use of domestic coal as a hydrogen feedstock and use of existing delivery infrastructure, thus eliminating the need for construction of a new, capital-intensive hydrogen infrastructure. However, the trade-offs between capital investment in infrastructure and the addition of further processing needs to be evaluated. The cost, efficiency, and benefits associated with these pathways have to be evaluated on a system basis for comparison to other possible hydrogen system pathways.

Systems analysis studies of advanced conceptual plants that co-produce liquid fuels and electric power have projected that liquid fuels can be produced in these advanced facilities for about \$40 to \$50 per barrel. Site-specific studies have also shown that SNG can be produced from coal for about \$6/MMBtu to \$8/MMBtu based on various plant designs and configurations. Although significant improvements in the cost of liquid fuels and SNG production have been made in the past, additional improvements in production and reforming can enable this hydrogen production pathway to become an economic alternative.



## 5. Accomplishments and Progress

The Hydrogen from Coal Program has successfully transitioned from its initial start-up in FY2004 to full operations. The Program has been actively soliciting proposals from industry, universities, national laboratories and other organizations to help the program achieve its goals in support of the HFI. As of September 2008, the program has 34 projects that are conducting research in a wide number of areas (Table 3).

**Table 3: Hydrogen from Coal Research Projects**

Research Area*	Number of Projects
Membrane research	10
Membrane reactors & process intensification	5
CO <sub>2</sub> removal	2
Polygeneration	3
Liquid H <sub>2</sub> carriers	4
SNG production and reforming	2
Storage	3
Utilization	5
<b>TOTAL</b>	<b>34</b>

*\*Complementary projects are supported by the Gasification and Sequestration Programs.*

The Hydrogen from Coal Program is making progress towards achieving some of its goals, milestones, and technical targets. For example, in the area of hydrogen separations, early laboratory-scale research has demonstrated significant progress towards the Program's long-range targets. Additionally, some of these projects are beginning to advance to larger scales of development to obtain engineering data. Table 4 shows the progress towards the hydrogen separation technical targets by the Program's research activities.

NETL's Office of Research and Development (ORD) has also established a high-pressure hydrogen test facility that is currently testing membranes developed by the Program's research contractors' to verify their results. The facility has performed molecular chemistry and laboratory testing of sulfur-resistant palladium alloys for water-gas shift (WGS) membrane reactors. Testing has shown:

- that sulfur resistance has been observed for palladium-copper alloys in the presence of H<sub>2</sub>S;
- corrosion and/or catalytic poisoning play a significant role in the permeability decreases observed in the presence of H<sub>2</sub>S;
- H<sub>2</sub> permeability of palladium-copper alloys is strongly dependent on crystalline structure; and
- Enhanced CO conversion has been demonstrated in catalyst-free palladium-based membrane reactors at elevated temperatures in simulated coal-derived synthesis gas.

**Table 4: Progress Towards Separation Technical Targets**

Performance Criteria	Current Status (a)	2010 Target	2015 Target
Flux (b)	>300	200	300
Temperature, °C	300–400	300–600	250–500
S Tolerance	Yes (preliminary)	Yes	Yes
Cost, \$/ft <sup>2</sup>	<200	100	<100
WGS Activity	Yes	Yes	Yes
ΔP Operating Capability (c)	1,000	Up to 400	Up to 800 to 1,000
Carbon Monoxide Tolerance	Yes	Yes	Yes
Hydrogen Purity (d)	>99.999%	99.5%	99.99%
Stability/Durability (years)	<1	3	5

<sup>a</sup> Current status is based on best available membrane technology to date (2006) that meets the targets under laboratory conditions.

<sup>b</sup>  $\text{ft}^3/\text{hour}/\text{ft}^2/100 \text{ psi } \Delta P$  (hydrogen partial pressure basis)

<sup>c</sup>  $\Delta P$  = total pressure differential across the membrane reactor (psi)

<sup>d</sup> Polishing filters may be needed downstream of the separation system in order to remove final traces of CO, sulfur, and other impurities to meet PEM fuel cell requirements. These targets exclude the effect of polishing filters.

\* *Technical targets are for membrane types described previously; research that is currently supported by FE and NETL Research on other membranes is not precluded if the potential flux, cost, and tolerance to impurities are promising. Research is also encouraged on advanced solvent and adsorption technologies to separate hydrogen. Reverse selective systems that separate CO<sub>2</sub> also are promising. The technical targets for hydrogen membranes relate to hydrogen from coal technology in which delta P will be around 100 psi and the membrane will require resistance to contaminants (CO and H<sub>2</sub>S). Technical targets for hydrogen membranes that are included in the EERE HFCIT RD&D Plan are for systems that operate at lower delta P and have less contaminants.*

## 6. Future Efforts

Future efforts will emphasize continued production and purification of hydrogen from coal, particularly membrane separations. These activities will focus on scale-up of technologies to further advance and validate laboratory results. Additionally, the program will continue to re-evaluate its program goals in consideration of budget projections and modifications to key activities.

## 7. References

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