



# HYDROGEN *from* COAL PROGRAM

RESEARCH, DEVELOPMENT, AND  
DEMONSTRATION PLAN  
FOR THE PERIOD 2004 THROUGH 2015

EXTERNAL DRAFT FOR REVIEW  
JUNE 10, 2004



SECURING  
OUR  
ENERGY FUTURE



## Table of Contents

	Page
Executive Summary .....	iv
1. Introduction .....	1
2. Overall DOE Hydrogen Program and Vision .....	4
3. Hydrogen from Coal Program – Mission and Goals .....	4
4. Technical Discussion .....	5
4.1 Current Technology .....	5
4.2 Comparison of Current and Future Technology .....	8
5. Technical Plan .....	12
5.1 Central Production Pathway .....	17
5.1.1 Goal and Milestones – Central Production Pathway .....	17
5.1.2 Activities – Central Production Pathway .....	18
5.1.3 Technologies – Central Production Pathway .....	19
5.1.3.1 Advanced water-gas shift reaction systems .....	19
5.1.3.2 Advanced membrane separation systems .....	21
5.1.3.3 Advanced CO <sub>2</sub> separations systems .....	26
5.1.3.4 Polishing filters (ultra-clean hydrogen purification systems) .....	27
5.1.3.5 Advanced concepts .....	27
5.1.4 Technical Targets – Central Production Pathway .....	28
5.1.4.1 Water-Gas Shift Reaction Technical Targets .....	29
5.1.4.2 Hydrogen Separation Technical Targets .....	30
5.1.5 Technical Barriers – Central Production Pathway .....	31
5.1.5.1 Barriers .....	31

5.1.5.2 Water-Gas Shift Reaction Barriers .....	31
5.1.5.3 Hydrogen Separation Barriers .....	31
5.1.6 Technical Task Descriptions – Central Production Pathway .....	33
5.2 Alternate Hydrogen Production Pathway .....	34
5.2.1 Goal and Milestones – Alternate Hydrogen Production Pathway .....	34
5.2.2 Activities – Alternate Hydrogen Production Pathway .....	34
5.2.3 Technologies – Alternate Hydrogen Production Pathway .....	35
5.2.3.1 Liquid Fuels Production/Delivery/Conversion .....	35
5.2.3.2 Fuels Reforming in Distributed Production Facilities .....	35
5.2.4 Technical Targets – Alternate Hydrogen Production Pathway .....	36
5.2.4.1 Fuel Production and Conversion via Reforming Technical Targets .....	36
5.2.5 Technical Barriers – Alternate Hydrogen Production Pathway .....	37
5.2.5.1 General Barriers .....	37
5.2.5.2 Liquid Fuels Production, Delivery and Conversion via Reforming Barriers .....	37
5.2.6 Technical Task Descriptions – Alternate Hydrogen Production Pathway .....	38
5.3 Delivery .....	38
5.3.1 Goal – Delivery .....	39
5.3.2 Activities – Delivery .....	39
5.3.3 Technologies – Delivery .....	39
5.3.3.1 Hydrogen/Natural Gas Delivery Mixtures .....	39
5.3.4 Technical Targets – Delivery .....	40
5.3.4.1 Hydrogen/Natural Gas Mixture Technical Targets .....	40
5.3.5 Technical Barriers – Delivery .....	40
5.3.5.1 Technical Barriers – Hydrogen/Natural Gas Mixtures .....	40
5.3.6 Technical Task Descriptions – Delivery .....	40

5.4 Storage.....	41
5.4.1 Goal and Milestones – Storage .....	41
5.4.2 Activities – Storage .....	41
5.4.3 Technologies – Storage .....	42
5.4.4 Technical Targets – Storage.....	43
5.4.5 Technical Barriers – Storage .....	43
5.4.6 Technical Task Descriptions – Storage .....	44
5.5 Utilization .....	45
5.5.1 Goal and Milestones – Utilization .....	45
5.5.2 Activities – Utilization .....	46
5.5.3 Technologies – Utilization .....	46
5.5.3.1 Advanced Engine Types .....	46
5.5.4 Technical Targets – Utilization .....	46
5.5.5 Technical Barriers – Utilization .....	47
5.5.6 Technical Task Descriptions – Utilization .....	47
<b>6. Implementation Plan .....</b>	<b>48</b>
6.1 Coordination With Other DOE/Federal Programs (Associated Programs): Jointly Funded Projects.....	48
6.2 Next Steps .....	49
<b>7. Appendix .....</b>	<b>50</b>
7.1 Acronyms .....	50
7.2 Contacts .....	52



## Executive Summary

In last year's State of the Union address, President Bush announced a \$1.2 billion Hydrogen Fuel Initiative to reverse America's growing dependence on foreign oil and reduce greenhouse gas emissions. The President urged the development of commercially viable hydrogen fuels and technologies for cars, trucks, homes, and businesses. In support of this year's budget request, Secretary of Energy Spencer Abraham stated "[The U.S. Department of Energy (DOE) will work with its stakeholders] to develop both the vehicle and the infrastructure in parallel – and by so doing, advance a commercialization decision by 15 years, from 2030 to 2015."

DOE requested that the National Academies of Science (NAS) review the proposed coordinated Hydrogen Program. The NAS concluded that "A transition to hydrogen as a major fuel in the next 50 years could fundamentally transform the U.S. energy system, creating opportunities to increase energy security through the use of a variety of domestic energy resources for hydrogen production while reducing environmental impacts, including atmospheric CO<sub>2</sub> emissions and criteria pollutants."

The DOE Hydrogen Posture Plan describes the planned activities, milestones and targets for successfully integrating and implementing technology research, development and demonstration needed to cost-effectively produce, store, and distribute hydrogen for use in fuel cell vehicles and electricity generation. The Posture Plan was developed by the Offices of Energy Efficiency and Renewable Energy (EERE), Fossil Energy, Science, and Nuclear Energy. The Office of Energy Efficiency and Renewable Energy (EERE) is the lead office for the President's Hydrogen Fuel Initiative.

The use of coal – America's largest domestic fossil energy resource offers the potential for producing abundant, economically attractive hydrogen to provide both increased energy security and reduction of carbon dioxide. The Hydrogen from Coal RD&D Plan encompasses DOE's Office of Fossil Energy technical activities to meet the goals of the Hydrogen Posture Plan.

## The Hydrogen from Coal RD&D Plan

The Office of Fossil Energy's (FE) Hydrogen from Coal Program was initiated in fiscal year 2004 (FY 2004) to support the President's Hydrogen Fuel Initiative, DOE's goals in the Hydrogen Posture Plan, and the FutureGen project. The mission of the Hydrogen from Coal Program is to develop advanced technologies through joint public and private research, development, and demonstration (RD&D). These technologies will facilitate the transition to the hydrogen economy and the use of our nation's abundant coal resources to produce, store, deliver, and utilize affordable hydrogen in an environmentally responsive manner.

**Goals:** The goals of the Hydrogen from Coal Program for the four elements of the hydrogen energy system (production, delivery, storage, and utilization) are:

### FutureGen

DOE's FutureGen initiative will serve as a platform to demonstrate hydrogen production and CO<sub>2</sub> sequestration at commercial scale. FutureGen is a government/industry cost-shared project to build a 275-megawatt IGCC test facility for evaluating cutting-edge technologies. Program objectives are to produce hydrogen at \$4/ million Btu (\$0.54/kg), sequester up to 100% of the CO<sub>2</sub> by-product, and produce electricity with zero emissions with less than 10% increase in cost compared to non-sequestration systems.

- Production
  - Central Production Pathway
    - By 2015, demonstrate a 60 percent efficient, near-zero emissions, coal-fueled hydrogen and power co-production facility which reduces the cost of hydrogen by 25 percent compared to current coal-based technology.
  - Alternate Hydrogen Production Pathway
    - By 2011, an alternative hydrogen production pathway and reforming system to produce decentralized hydrogen is optimized and available.
- Delivery – In collaboration with DOE's Office of Energy Efficiency and Renewable Energy (EERE) and the FE Office of Natural Gas and Petroleum Technology, define and identify by 2010 materials requirements and system modifications necessary for using natural gas pipelines to deliver hydrogen/natural gas mixtures.
- Storage – By 2010, define and identify, in collaboration with EERE and the FE Office of Natural Gas and Petroleum Technology, viable hydrogen storage technologies for transportation and stationary applications.
- Utilization – By 2010, develop hydrogen and/or hydrogen/natural gas mixture fuel protocol and engine modifications for advanced engine systems needed to achieve optimum performance and lowest emissions.

### *Technology Elements*

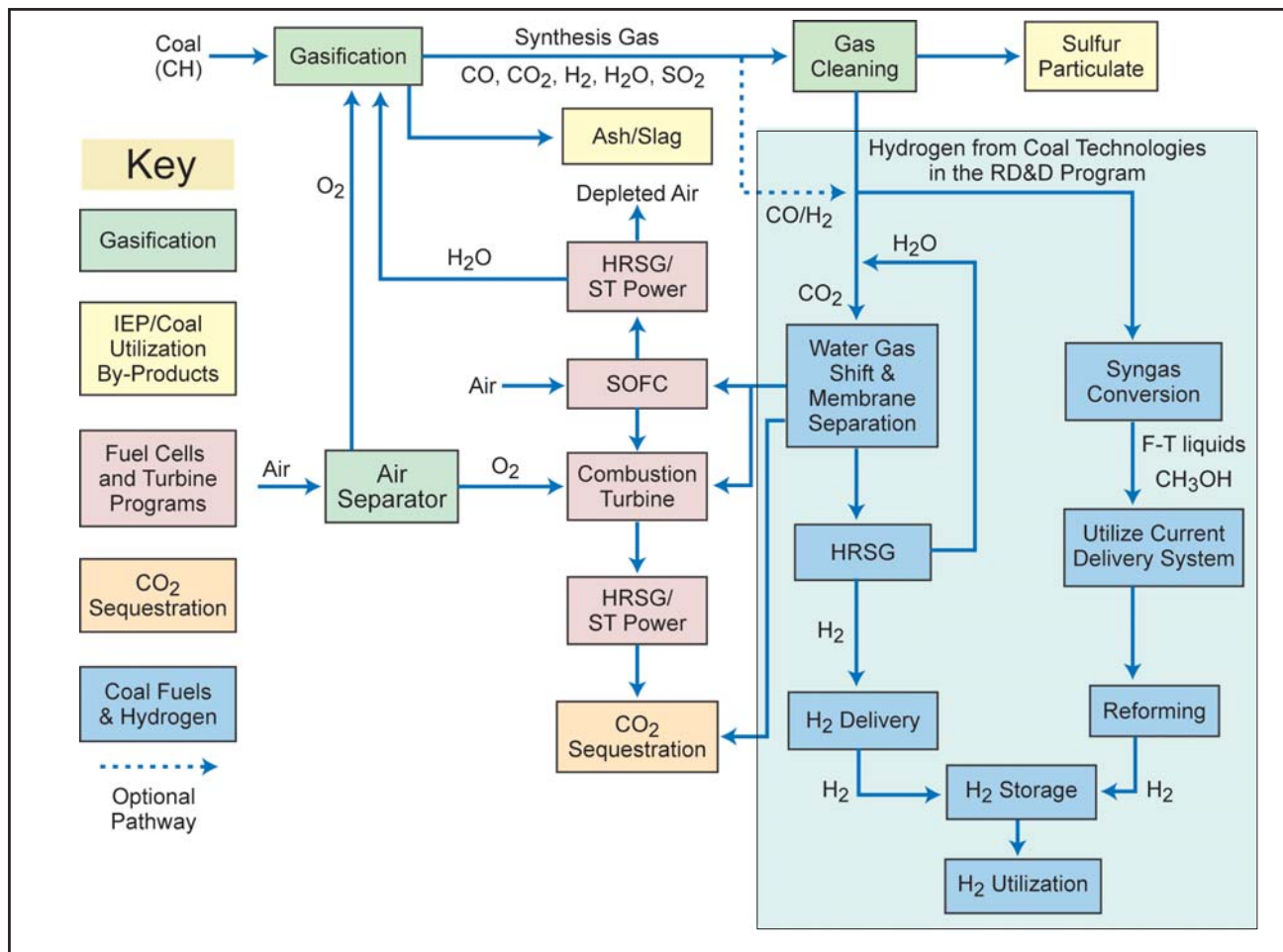
The Hydrogen from Coal Program will improve current technology and make available new, innovative technology that can produce and deliver affordable hydrogen from coal with significantly reduced or near-zero emissions. The technologies that comprise the program, and those that enable the achievement of the program's goals, include activities that are a part of the Hydrogen Fuel Initiative and those that are associated technologies being developed in other coal-related and sequestration-related programs. The specific activities in this RD&D Program are shown in the large shaded box in Figure ES-1. There are two hydrogen production pathways for the program – the central production pathway (gaseous hydrogen) and the alternate hydrogen production pathway (hydrogen-rich liquid fuel), both of which are shown in the large blue shaded box. The program relies on successful RD&D achievements being made in associated programs within the Office of Fossil Energy.

The two pathways to produce hydrogen from coal are:

- 1) Central production pathway – Hydrogen is produced at a large, central facility by converting coal into hydrogen. These plants may or may not co-produce electricity or other products, and will be designed to allow capture and ultimately sequestration of carbon dioxide (CO<sub>2</sub>).
- 2) Alternate production pathway – Hydrogen-rich, zero-sulfur liquids are produced from coal at a central location. These liquids potentially can be transported through the existing petroleum pipeline distribution network to sub-central or distributed locations where they can then be reformed into hydrogen near the end-user.

In addition to these two production pathways, the program is performing research on hydrogen delivery, storage, and utilization.

Figure ES-1. Office of Fossil Energy Hydrogen Program Components



### Overview of Technology in the RD&D Plan

The areas of research and technical elements that the program will pursue include:

- Central Production
  - Perform research on advanced water-gas shift reaction, membrane separations, and adsorption/solvent separation systems; polishing filters; and advanced concepts including process intensification, the concept of developing novel technologies that combine multiple processes into one step, use new control methods, or integrate alternative energy technologies with hydrogen from coal technologies, and chemical looping.
- Alternate Hydrogen Production Pathway
  - Develop hydrogen-rich, liquid fuels production, delivery, and conversion via reforming.
- Delivery
  - Evaluate optimal hydrogen-natural gas mixtures and effects on metallurgy, and hydrogen-natural gas mixture separation devices.

- Storage
  - Investigate the hydrogen storage capabilities of unique storage systems such as metal-organic frameworks.
- Utilization
  - Modify and optimize advanced engine types to operate on hydrogen or hydrogen-natural gas mixtures and demonstrate the performance of these engines in vehicles or stationary applications.

Research efforts also will be coordinated with other programs, such as EERE's Hydrogen, Fuel Cells, and Infrastructure Technologies Program, as necessary, to leverage technical skills and funding, minimize duplication, optimize resource (funds/manpower) utilization and achieve maximum synergism while ensuring that the nation's energy security and environmental goals are addressed.

## Benefits

- Achieve energy security and a sustainable hydrogen economy by the economic production of hydrogen from coal. The United States is becoming increasingly dependent on imported oil for transportation fuels. Increased demand from developing countries for the finite world oil reserves is expected to raise crude oil prices and cause world oil production to peak possibly over the next 20-30 years. U.S. coal reserves nearly equal the total proved world conventional oil reserves – a 250-year supply of U.S. coal at today's domestic production rates. Hydrogen represents a clean alternative fuel.
- Reduce environmental concerns associated with energy use in automotive and stationary power applications through the clean production of hydrogen from coal in tandem with carbon sequestration. Gasification technologies have shown the potential to produce clean synthesis gas from coal with virtually zero pollutant emissions. Carbon sequestration technologies are providing the means to cost-effectively use concentrated CO<sub>2</sub> streams, for example, in enhanced oil recovery. Fuel cells are poised to provide efficient, emission-free power from hydrogen in both automotive and stationary power applications. The potential emissions benefits for hydrogen from coal with sequestration and use in fuel cell vehicles compared to hybrid electric vehicles and internal combustion vehicles are shown in Figure ES-2.
- Ensure the availability of a major primary energy resource that can be used for the production of hydrogen in volumes sufficient to fuel the fuel cell-powered vehicles expected to enter the transportation market sector in the future.

## Technical Activity Gantt Chart Summary

The specific sub-element activities and their associated timelines are shown in the Gantt charts in Figures ES-3 and ES-4. Figure ES-3 contains the activities and technologies associated with hydrogen production from central plants and the alternate pathway of hydrogen-rich liquids. Figure ES-4 contains delivery, storage and utilization technologies for hydrogen from coal.



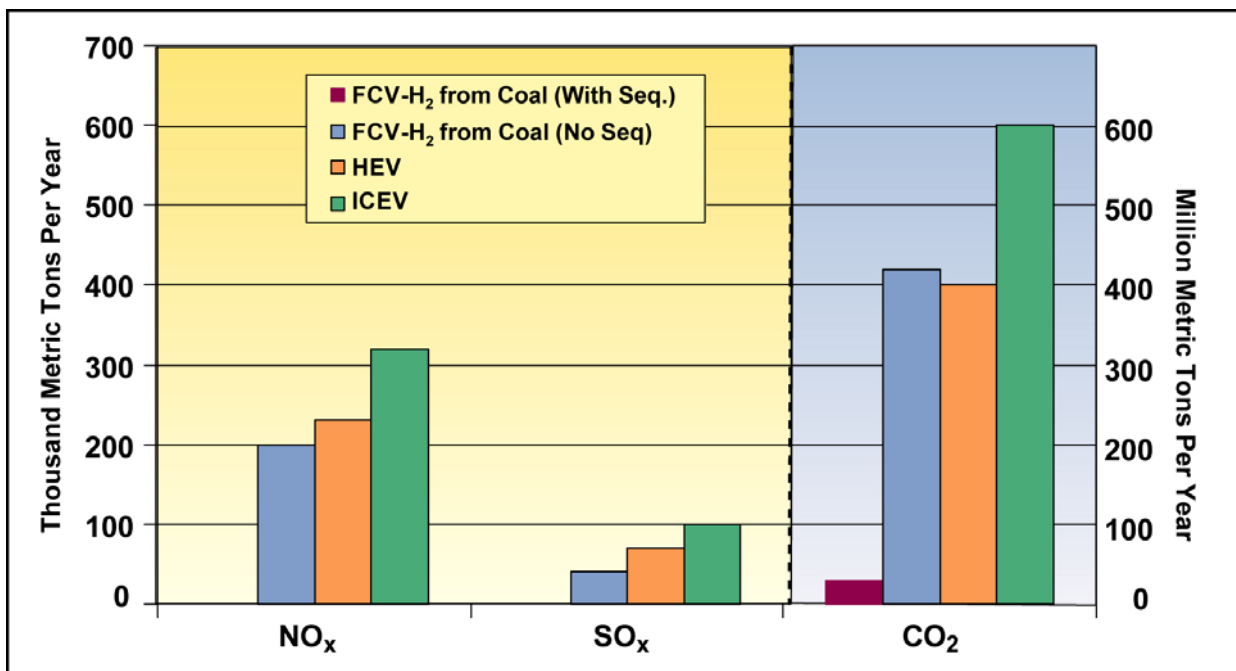
This Multi-Year Research, Development, and Demonstration Plan (MYP) addresses the strategies and goals of the program and defines the research areas where the program will use its expertise to support the President’s Hydrogen Fuel Initiative and the FutureGen project.

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

- Section 1. Introduction
- Section 2. Overall DOE Hydrogen Program and Vision
- Section 3. Hydrogen from Coal Program Mission and Goals
- Section 4. Technical Discussion
- Section 5. Technical Plan
- Section 6. Implementation Plan

Detailed activities and technical targets are provided in the Technical Plan in Section 5. Implementation of the above activities will be coordinated closely with the related activities supported by FE, EERE, and other organizations both inside and outside the government.

**Figure ES-2. Resource Extraction through Vehicle End Use - System Emissions Hydrogen from Coal and Use in Fuel Cell Vehicles Compared to Gasoline Use in Hybrid Electric and Internal Combustion Engine Vehicles**



Environmental benefits of fuel vehicles (FCV) versus hybrid electric vehicles (HEV) and internal combustion engine vehicles (ICEV) based on 100 million cars. Statistics include production of fuel, delivery to fueling stations, and the end use in the vehicles.

Figure ES-3. Hydrogen from Coal Research, Development, and Demonstration Program

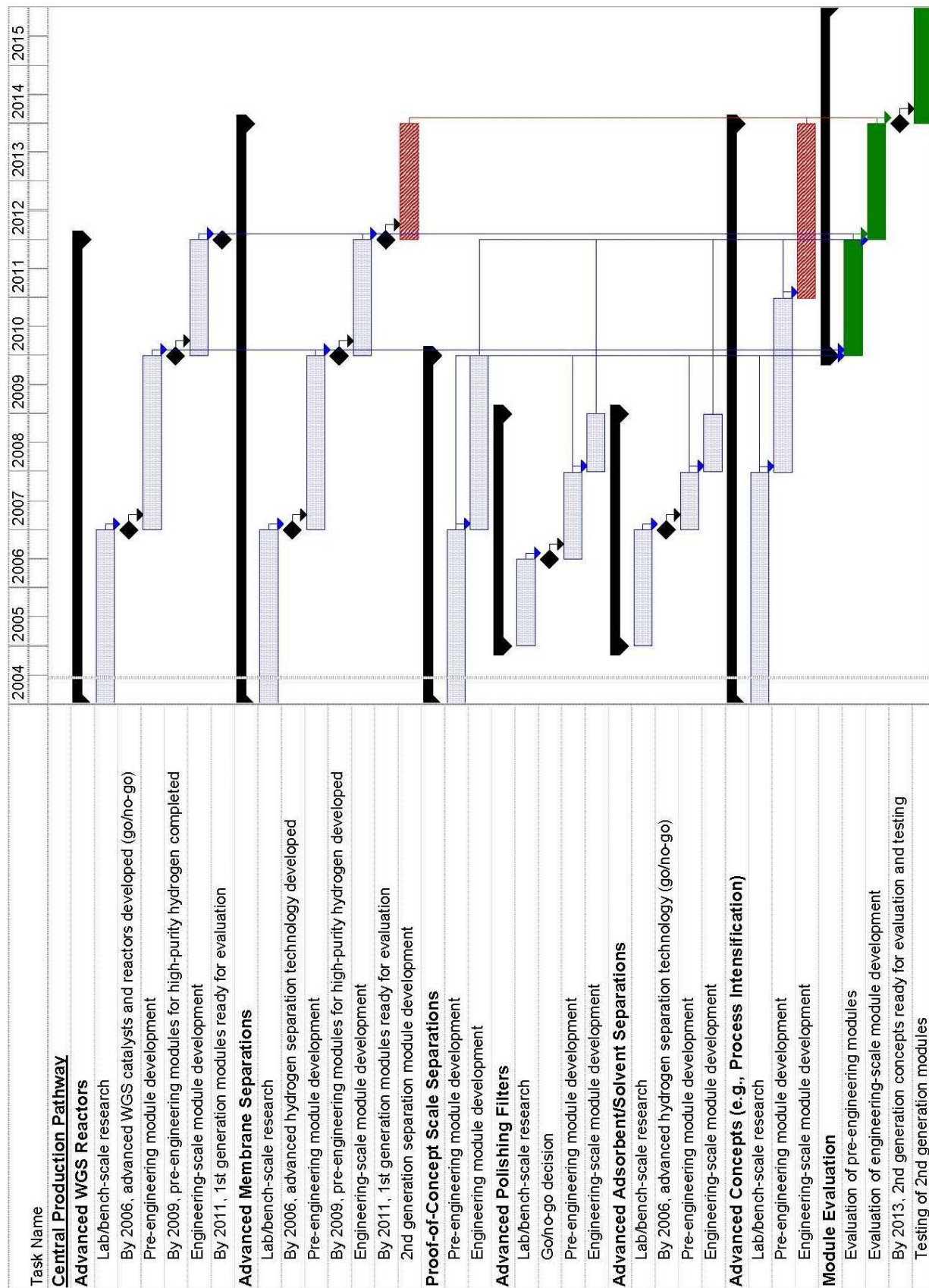
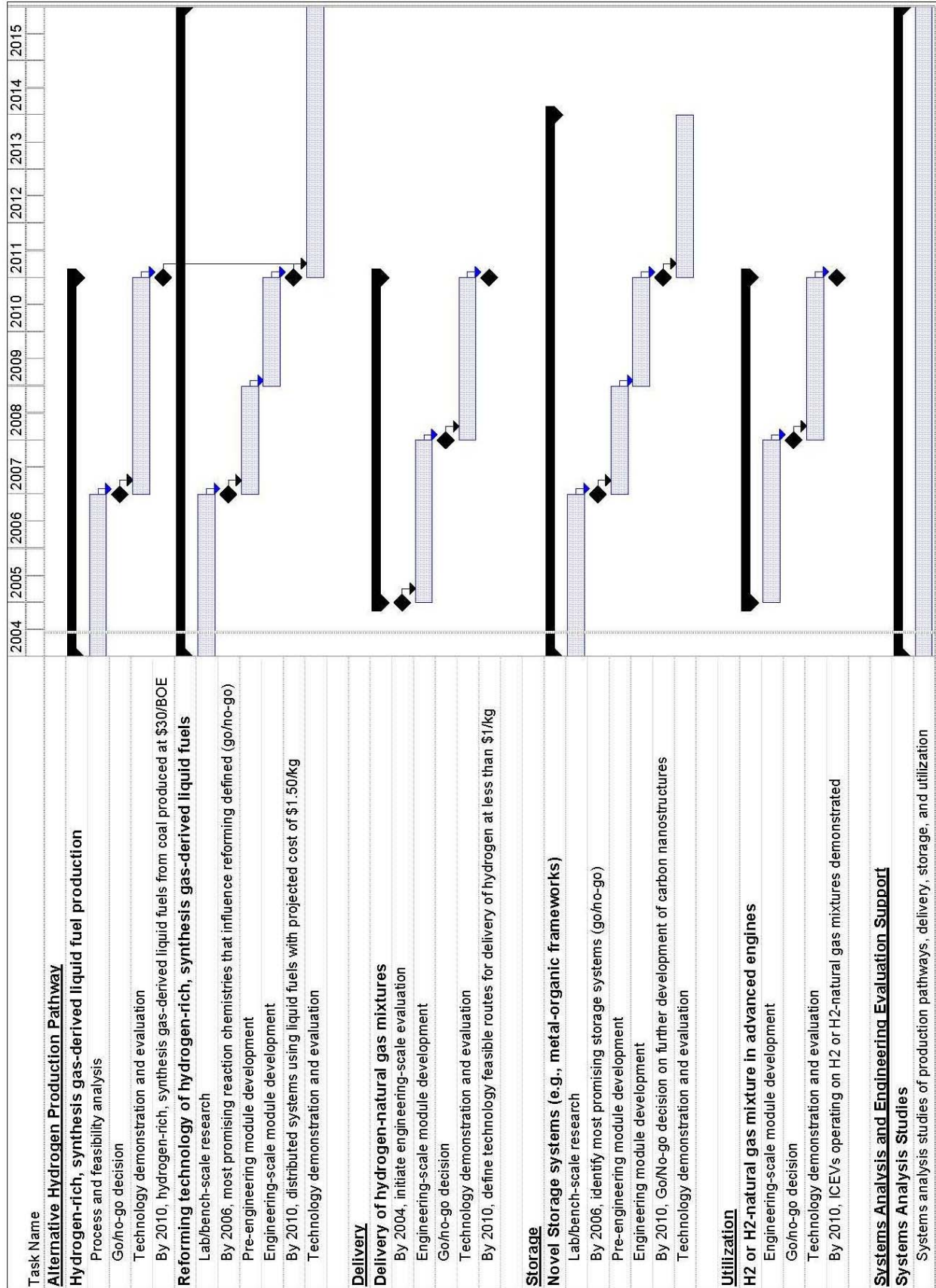


Figure ES-4. Hydrogen from Coal Research, Development, and Demonstration Program





## 1. Introduction

The Administration’s National Energy Policy (NEP) was released in May 2001. The NEP made over 100 recommendations to achieve the goals of:

- Modernizing energy conservation,
- Modernizing our energy infrastructure,
- Increasing our energy supplies,
- Accelerating protection of the environment, and
- Increasing our nation’s energy security.

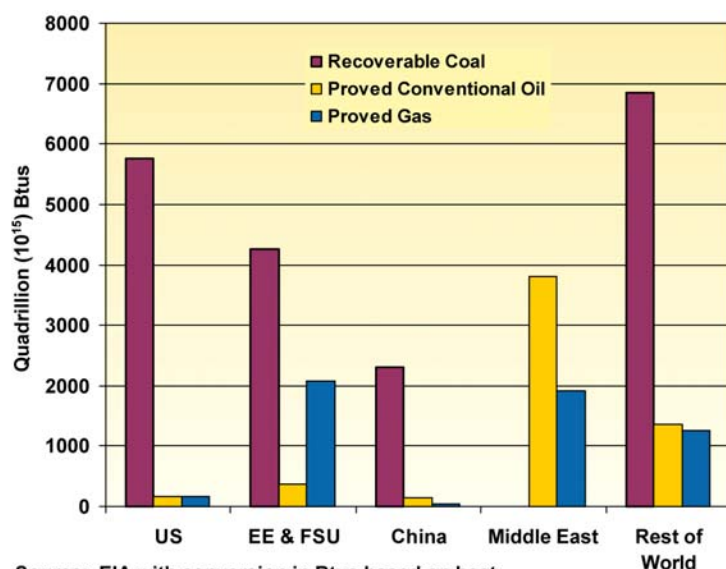
In response to recommendations in the NEP with regard to hydrogen and fuel cell technologies, the Department of Energy (DOE) organized meetings in November 2001 and April 2002, which resulted in the *National Vision of America’s Transition to a Hydrogen Economy – to 2030 and Beyond* and the *National Hydrogen Energy Roadmap*. These documents summarize the potential for hydrogen in America’s future and the challenges that must be overcome to realize the vision of a hydrogen economy.

Providing further support for the development of hydrogen technologies, the President announced the Hydrogen Fuel Initiative in his State of the Union address in January 2003, proposing \$1.2 billion in research funding to develop pathways for the production, delivery, and storage of hydrogen. DOE’s Office of Energy Efficiency and Renewable Energy, with support from the Offices of Fossil Energy, Science, and Nuclear Energy, Science and Technology, prepared the Hydrogen Posture Plan to outline DOE activities, milestones and deliverables to facilitate the United States’ transition to a hydrogen economy.

**Hydrogen from Coal  
Program Mission**

The mission of the Hydrogen from Coal Program is to develop advanced and novel technologies that will ensure the use of our nation’s abundant coal resources to produce, store, deliver, and utilize affordable hydrogen in an environmentally clean manner through public/private RD&D. This activity will facilitate the transition to the hydrogen economy.

**Figure 1. Fossil Fuel Reserves**



Source: EIA with conversion in Btus based on heat

*U.S. coal reserves nearly equal total proved world conventional oil reserves*

Additionally, Secretary of Energy Spencer Abraham announced the FutureGen project in February 2003. FutureGen is a prototype plant that will integrate hydrogen and power production from coal, and utilize carbon sequestration, serving as a testing facility for future technologies.

In support of these various initiatives and projects, the DOE Office of Fossil Energy has established the Hydrogen from Coal program. This program will develop advanced, novel, and innovative technologies to produce, deliver, store, and utilize hydrogen produced from coal, our nation’s most abundant domestic fossil fuel resource (see Figure 1). This Multi-Year Research, Development, and Demonstration Plan



(MYP) develops the strategies and goals of the program and defines the research areas where the program will focus its expertise to develop the technologies needed to support the President’s Hydrogen Fuel Initiative, the Hydrogen Posture Plan, and the FutureGen project.

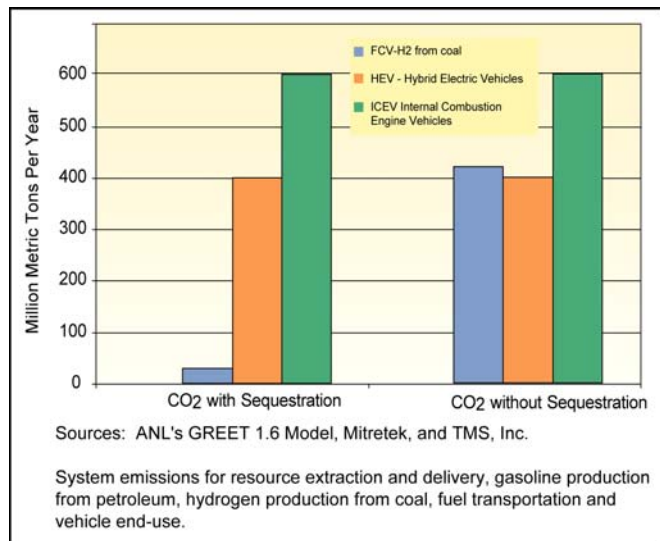
As a pre-eminent primary source of energy, coal is an abundant domestic resource, with the United States boasting hundreds of years of supply at current demand levels. The production of hydrogen from coal for use in fuel cell vehicles in the transportation sector will reduce U.S. reliance on foreign imports of petroleum. It is estimated that, when used in 100 million fuel cell vehicles, hydrogen produced from coal could reduce petroleum demand by 3 million barrels per day.

A benefits analysis that evaluated the system of resource extraction and transportation, followed by conversion (e.g., petroleum refinery to make gasoline, or coal to hydrogen plant) and finally end use in vehicles estimated that hydrogen produced from coal can offer environmental benefits compared to gasoline powered vehicles, as shown in Figures 2 and 3.

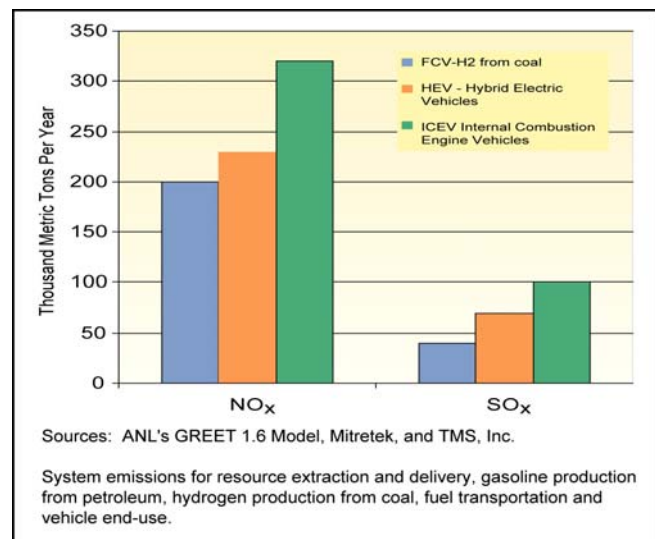
Figure 2 shows that, with carbon sequestration in the production of hydrogen from coal, net system emissions of carbon dioxide will be nearly eliminated compared to the internal combustion engine vehicle and hybrid electric vehicles systems. Without carbon sequestration, emissions of carbon dioxide will be lower than internal combustion engine systems. Figure 3 shows the analysis results in which emissions of criteria pollutants will be reduced.

The Hydrogen from Coal MYP provides an RD&D roadmap that the program will pursue to develop the technologies necessary for coal to meet the goals of the President’s Hydrogen Fuel Initiative and the FutureGen project. It discusses current and future technologies for the production of hydrogen from coal, and identifies associated programs that will contribute to the development of facilities for the co-production of hydrogen and power with near-zero emissions. The MYP will serve as a resource document for the program and will be updated as goals, milestones, and targets are achieved, and as assumptions on markets and technologies change.

**Figure 2. CO<sub>2</sub> Emissions from FCV, HEV, and ICEV Transportation Systems (100 million vehicles)**



**Figure 3. Criteria Emissions from FCV, HEV, and ICEV Transportation Systems**



## **FutureGen – The World’s First Zero-Emission, Coal-Based Electricity and Hydrogen Power Plant**

On February 27, 2003, the President announced that the United States would sponsor the world’s first coal-based, integrated zero-emission electricity and hydrogen power plant. Secretary of Energy Spencer Abraham unveiled FutureGen as a prototype fossil fuel power plant of the future — a \$1 billion government/industry partnership that would simultaneously test and verify the large-scale sequestration of CO<sub>2</sub> from a process that produces significant quantities of electricity and hydrogen by use of coal gasification processes. As a Presidential Initiative, FutureGen aims to draw upon the best scientific research to address the issue of global climate change.

FutureGen is highly relevant to the DOE mission and is designed to achieve the goals of several overarching Presidential initiatives and priorities. FutureGen will establish the technical and economic feasibility of zero-emission power plants by producing electricity and hydrogen from coal, while capturing and sequestering CO<sub>2</sub> emissions. FutureGen’s ability to produce hydrogen using current technology and to evaluate advanced hydrogen production technology will support the President’s Hydrogen Fuel Initiative.

The FutureGen plant will be a nominal 275-MW (net equivalent output) prototype that produces electricity and hydrogen, and sequesters one million metric tons of carbon dioxide per year. FutureGen will support efforts to assure that U.S. fossil energy resources can meet increasing demands for affordable energy without compromising the quality of life for future generations of Americans. The FutureGen project will employ coal gasification technology integrated with combined-cycle electricity generation and hydrogen production, while capturing and sequestering the carbon dioxide. When operational, this zero-emission prototype will be the cleanest fossil fuel-fired power plant in the world. The project will be designed and constructed as a living laboratory with the flexibility to conduct full-scale and scaleable slipstream tests of advanced technologies as they emerge from the DOE Office of Fossil Energy core research program. The R&D activities performed under the Hydrogen from Coal Initiative will provide advanced modules for evaluation in the FutureGen facility. Hydrogen will enable the use of pollution-free, commercially viable fuel cells to power cars, trucks, homes, and businesses. Within this context, FutureGen can be regarded as a means for establishing coal as a clean, reliable, and secure source of hydrogen. Hydrogen is being viewed as the fuel of the future for the transportation sector. The project will require 10 years to complete. The results will be shared among all participants, industry, the environmental community, and the public. Further, DOE intends to invite participation from international organizations. This will maximize the global applicability and acceptance of the FutureGen concept and technology, thereby building an international consensus on the role of coal and carbon sequestration in addressing global climate change and energy security issues.

## 2. Overall DOE Hydrogen Program and Vision

The Department of Energy is responsible for implementing the President's Hydrogen Fuel Initiative. The Hydrogen Posture Plan outlines the activities, milestones, and deliverables that DOE plans to pursue to facilitate our nation's transition to a hydrogen economy. Because hydrogen can be produced from a wide variety of resources – fossil fuels, renewables, and nuclear – several offices within DOE will play a key role in the Initiative. The Offices of Energy Efficiency and Renewable Energy (EERE); Nuclear Energy, Science, and Technology (NE); Science (SC); and Fossil Energy (FE) will each utilize their unique technological expertise and experience with their respective resources to successfully develop technologies to produce, deliver, store, and utilize hydrogen from a diverse group of feedstocks for a broad range of technologies and markets. EERE will coordinate DOE's overall Hydrogen Program.

The vision statement for the overall DOE Hydrogen Program, encompassing efforts in all DOE program offices, was developed during the National Hydrogen Vision Meeting in November 2001. The vision of what a future hydrogen economy could be was developed during this meeting. It states: "Hydrogen is America's clean energy choice. Hydrogen is flexible, affordable, safe, domestically produced, used in all sectors of the economy, and in all regions of the country."

## 3. Hydrogen from Coal Program – Mission and Goals

The mission of the Hydrogen from Coal Program is to develop advanced and novel technologies, through joint public and private RD&D, that will facilitate the use of our nation's abundant coal resources to produce, store, deliver, and utilize affordable hydrogen in an environmentally clean manner. This activity will facilitate the transition to the hydrogen economy as outlined in the Hydrogen Posture Plan.

The goals for the four elements of the Hydrogen from Coal Program (production, delivery, storage, and utilization) are provided below, with a brief discussion of the production pathway goals.

In the Central Hydrogen Pathway approach, hydrogen is produced at a large-scale central facility where coal is converted into hydrogen or into hydrogen and electric power as co-products. This approach allows for ready capture of the carbon dioxide generated during the production of the hydrogen, which then could be sequestered. This configurational concept is similar to that of FutureGen. The hydrogen produced at these central plants then must be distributed to the end users.

- Production
  - Central Hydrogen Pathway
    - By 2015, demonstrate a 60 percent efficient,<sup>1</sup> near-zero emissions, coal-fueled hydrogen and power co-production facility that reduces the cost of hydrogen by 25 percent compared to current coal-based technology.

An alternative to producing hydrogen gas at a central location and having to deliver this hydrogen to the end users is to produce zero-sulfur liquid fuels from coal in a large-scale central facility that also could co-produce electric power. The liquid product (i.e., a hydrogen carrier) would be transported through the existing petroleum fuels network to sub-central stations close to the end users. At these sub-central plants, the liquid

<sup>1</sup>Overall efficiency depends on product mix (i.e., electricity and hydrogen). The 60 percent efficient facility is based on the product mix in Case 3 in Section 4.2 of this MYP.

fuels would be reformed into hydrogen. This hydrogen would be delivered to the end-user local filling stations by tube trailer where it would be used in FCVs or hydrogen ICEs. This pathway is envisioned as an interim pathway until a widespread hydrogen delivery infrastructure is available.

- Alternate Hydrogen Production Pathway
  - By 2011, optimize and make available an alternative hydrogen production pathway and reforming system to produce decentralized hydrogen.
- Delivery – By 2010, define and identify, in collaboration with EERE and the FE Office of Natural Gas and Petroleum Technology, materials requirements and system modifications necessary for using natural gas pipelines to deliver hydrogen/natural gas mixtures.
- Storage – By 2010, define and identify, in collaboration with EERE and the FE Office of Natural Gas and Petroleum Technology, viable hydrogen storage technologies for transportation and stationary applications.
- Utilization – By 2010, develop hydrogen and/or hydrogen/natural gas fuel protocol and engine modifications for advanced engine systems needed to achieve optimum performance and lowest emissions.

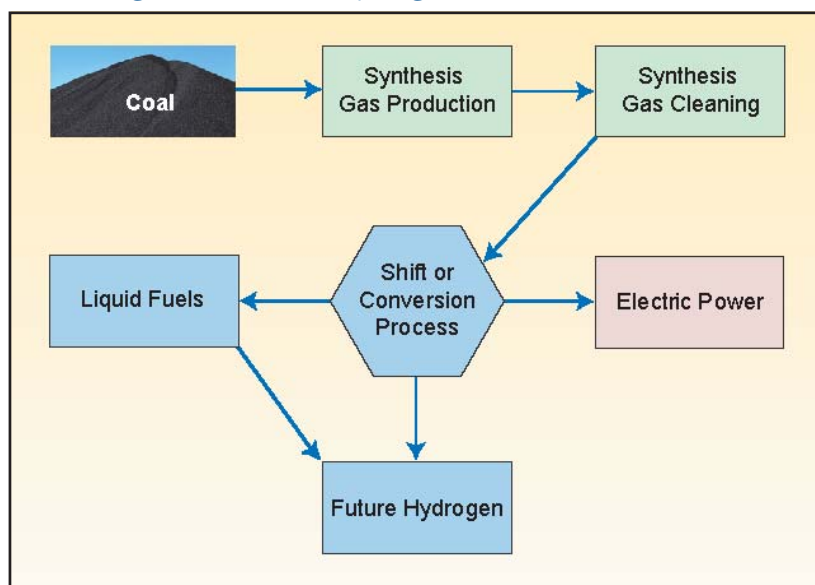
## 4. Technical Discussion

### 4.1 Current Technology

Today, hydrogen is produced from coal by gasification followed by processing of the resulting synthesis gas, and is used primarily to produce hydrogen for the production of ammonia for fertilizer. Coal-derived synthesis gas also is being converted to methanol for use as an intermediate product in the chemical industry. Methanol also can be used as a hydrogen carrier for subsequent reforming applications or use in fuel cells, such as those being considered for small portable devices including laptop computers. Advanced liquid-phase methanol production from coal technology has been successfully demonstrated at the Eastman Chemical Complex in Kingsport, Tennessee, a DOE Clean Coal Technology Demonstration Program project.

In its simplest form, the process used to produce hydrogen from coal is shown schematically in Figure 4. The coal first is gasified with oxygen and steam to produce a synthesis gas consisting mainly of carbon monoxide and hydrogen, with some carbon dioxide, sulfur, particulates, and trace elements. Oxygen is added in less than stoichiometric quantities

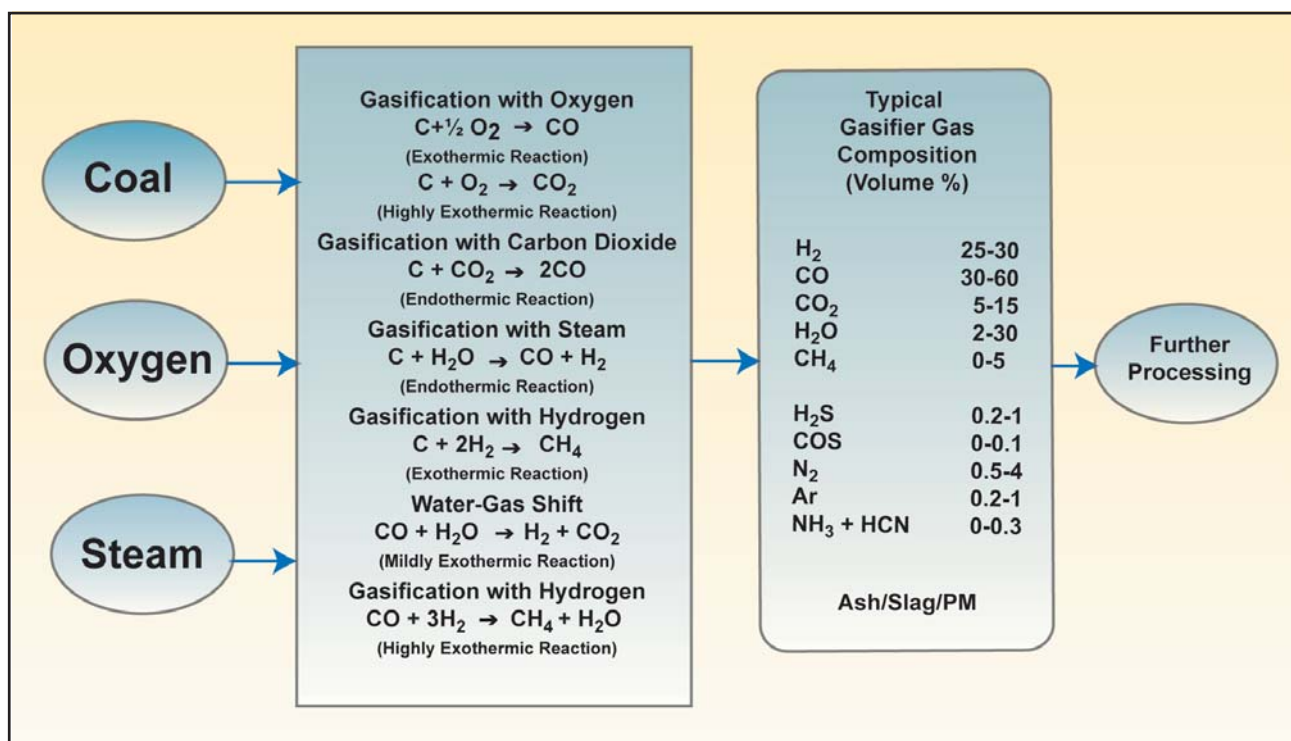
Figure 4. Current Hydrogen from Coal Production





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  $H_2$ ,  $CO$ , and  $CO_2$ . The fixed carbon that remains after devolatilization is gasified through reactions with  $O_2$ , steam, and  $CO_2$  to form additional amounts of  $H_2$  and  $CO$ . These gasification reactions are shown in Figure 5.

Figure 5. Major Gasification Reactions



The minor and trace components of coal also are transformed in the gasification reactor. Under the substoichiometric reducing conditions of gasification, most of the fuel's sulfur converts to hydrogen sulfide ( $H_2S$ ), but some (3-10 percent) also converts to carbonyl sulfide ( $COS$ ). Nitrogen bound with the fuel generally converts to gaseous nitrogen ( $N_2$ ), with some ammonia ( $NH_3$ ) 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.<sup>2</sup> 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 filtration and water scrubbers. This particulate typically is recycled to the gasifier to ensure high carbon conversion. Some gasifiers also yield devolatilization or pyrolysis products (e.g., coal tars, oils, phenols) that can and must be controlled.

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)

<sup>2</sup>When applicable, char must be separated from slag or bottom ash before it can be marketed.

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 slightly below 1,900 °F. 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, NH<sub>3</sub>, HCl, H<sub>2</sub>S and particulates that operates at low temperatures with synthesis gas leaving the process at about 72 °F. H<sub>2</sub>S, 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.

This 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 through the catalytically assisted equilibrium reaction of CO with H<sub>2</sub>O to form CO<sub>2</sub> and H<sub>2</sub>. 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 water-gas shift reaction alters the H<sub>2</sub>/CO ratio in the final mixture. Overall, about 70 percent of the feed fuel's heating value is associated with the CO and H<sub>2</sub> components of the gas, but can be higher depending upon the gasifier type. Hydrogen must be separated from the shifted gas containing CO<sub>2</sub>, CO, and other trace contaminants, and polished to remove remaining sulfur, CO, and other contaminants to meet the requirements for various end-uses (e.g., fuel cell vehicles).

Instead of maximizing conversion of synthesis gas to hydrogen production, an alternate pathway prior to the introduction of a hydrogen infrastructure could be to convert the synthesis gas into hydrogen-rich liquids (e.g., Fischer-Tropsch liquids or methanol) for use as liquid transportation fuels or reformable fuels to produce hydrogen for fuel cell applications.

## 4.2 Comparison of Current and Future Technology

At the present time, no coal-based facilities employing modern entrained gasification have been constructed that produce both hydrogen and electric power; however, similar facilities based on heavy oil partial oxidation are in operation. Conceptual plants fed with coal have been simulated using computer models to estimate the technical performance and economics of a co-production plant producing hydrogen and power, based on current technology. Computer simulations also have 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 are close to commercialization while others are farther back in the R&D pipeline. Table 1 summarizes the information developed from three of these computer simulations, all of which include carbon sequestration technologies. A more detailed evaluation of additional co-production cases can be found in the Mitretek report, Hydrogen from Coal.<sup>3</sup>

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

	<b>CASE 1</b>	<b>CASE 2</b>	<b>CASE 3<sup>4</sup></b>
Technology Readiness Goal	Current	2015	2015
Carbon Sequestration	Yes (87%)	Yes (100%)	Yes (100%)
Hydrogen (MMscfd)	119	158	153
Coal (tons/day) (AR)	3,000	3,000	6,000
Efficiency (%HHV)	59	75.5	59
Excess Power (MW)	26.9	25	417
Power Value (mills/kWh)	53.6	53.6	53.6
Capital (\$million)	417	425	950
RSP of Hydrogen (\$/MMBtu/\$/kg)	8.18/1.10	5.89/0.79	3.98/0.54

Notes:

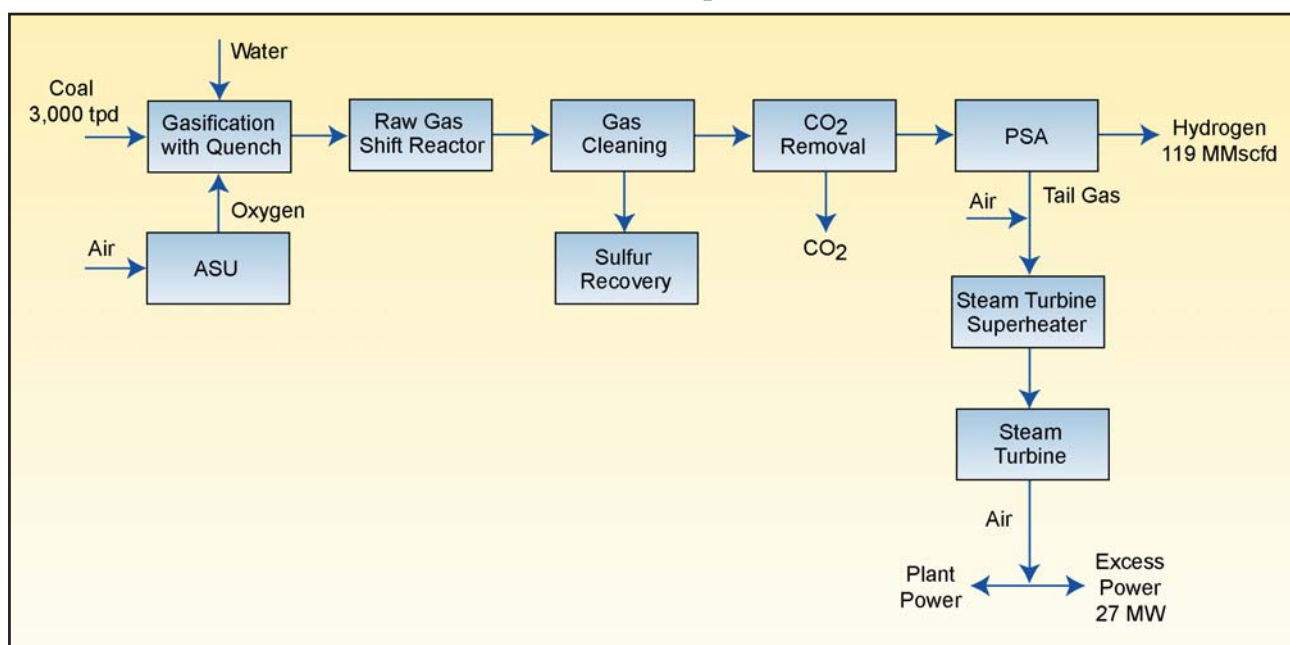
- Coal cost is \$29/ton (and is assumed to de-escalate at 1.5% below general inflation), and the assumed plant capacity factor is 85%.
- For carbon sequestration, the co-produced power is assumed to have a value of \$53.6/MWh, based on an additional cost of power production from natural gas combined-cycle (NGCC) plants with sequestration of 18 mills/kWh and natural gas priced at \$3.15/MMBtu (reference EPRI report 1000316).
- For sequestration, it is assumed that \$10 per ton of carbon is added for sequestration after the concentrated carbon dioxide stream has been isolated, and the carbon dioxide stream is compressed to 200 bars (2,900 psi).
- Financial assumptions used for these simulations: 25-year plant life; 67/33% debt/equity financing; 15% return on equity; 8% interest for a 16-year term; 3% inflation with coal de-escalation of 1.5% per annum below general inflation; 16-year double declining balance depreciation; 40% combined Federal and State tax rate; 3-year construction with 50% output in start-up year; carbon sequestration cost of \$10/ton.

<sup>3</sup>*Hydrogen from Coal*, Mitretek Technical Paper MTR 2003-31, July 2002

<sup>4</sup>Case 3 is a co-production case with twice the coal feedstock as Cases 1 and 2, with equal quantities of coal feed used to produce hydrogen and electricity. Efficiency for this case is reduced compared to Case 2, because of the lower efficiency associated with the large quantity of electric power production in Case 3.

Case 1, shown schematically in Figure 6, is a process to produce hydrogen using conventional technology coupled with carbon capture and sequestration. The process assumes that a Texaco quench gasification system with conventional acid removal and a pressure swing adsorption (PSA) system for hydrogen recovery are used. All of the carbon dioxide is removed prior to the PSA unit, compressed to 200 bars (2,900 psi), and sequestered for an additional cost of \$10 per ton of carbon. In this configuration, 87 percent of the carbon in the feed is sequestered. The capital cost of the plant is estimated at \$417 million with a required selling price (RSP) of the hydrogen at \$8.18/MMBtu (\$1.10/kg). The amount of hydrogen produced is 119 MMscfd, and there is 27 megawatts (MW) of excess power.

**Figure 6. Schematic of Current Technology to Produce Hydrogen from Coal with Carbon Sequestration (Case 1)**



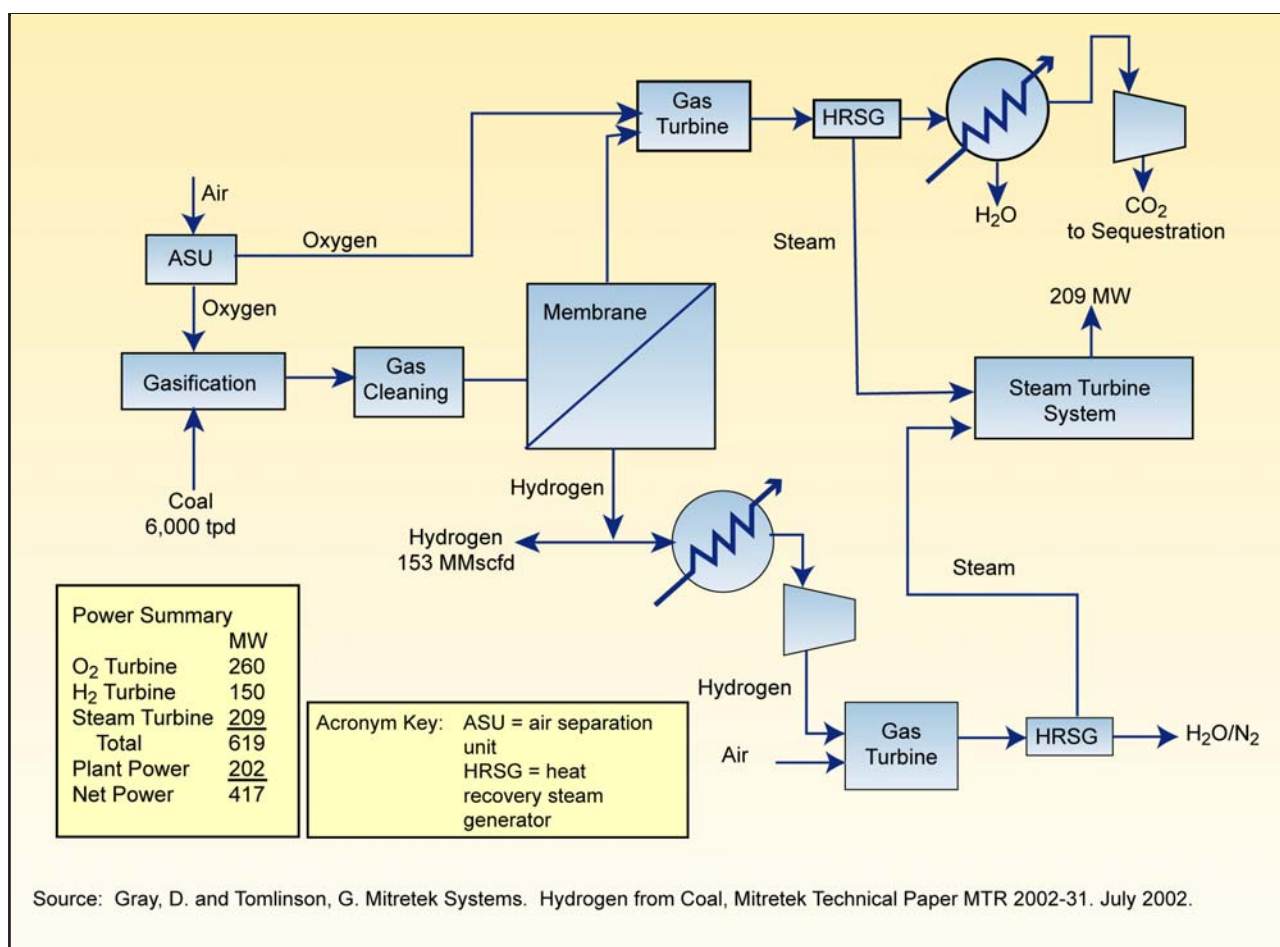




Case 3, shown in Figure 8, is an example of an advanced co-production concept plant that is expected to be developed by 2015. The concept of this co-production plant is similar to the FutureGen prototype fossil fuel power plant of the future, and produces 153 million scfd of hydrogen and 417 MW of excess power. This case will employ advanced gasification, combustion and turbine systems, membrane separation, and carbon capture and sequestration in a co-production plant producing hydrogen and electric power using technologies similar to Case 2. In Case 3, a separate gasification train is utilized specifically to produce clean electric power. These highly efficient hydrogen and electricity co-production plants could provide significant additional reductions in the cost of hydrogen, reducing the cost to \$4/MMBtu (\$0.54/kg) assuming power is sold at \$53.6/MW-hr.

The use of solid oxide fuel cells to generate electricity from hydrogen also can be introduced in these plants. In this configuration, hydrogen production costs can be reduced to about \$3/MMBtu (\$0.40/kg), depending on the price of electric power.

**Figure 8. Schematic of Advanced Co-Production Concept with Carbon Sequestration (Case 3)**



In summary, successful DOE-sponsored R&D efforts in the Hydrogen from Coal Program and associated programs are necessary to achieve the goal of a 25 percent reduction in hydrogen cost as shown in Case 2 and the additional cost reductions depicted in Case 3.

## 5. Technical Plan

The Hydrogen from Coal Multi-Year RD&D Plan supports the President's Hydrogen Fuel Initiative and the FutureGen project through joint public and private research, development, and demonstration of advanced and novel hydrogen-related technologies in the four hydrogen system elements. The number preceding each element below references the section under which that element of the technical plan is discussed.

- 5.1 Production – Central Production Pathway
- 5.2 Production – Alternate Hydrogen Production Pathway
- 5.3 Delivery
- 5.4 Storage
- 5.5 Utilization

If successful, this R&D program will improve existing technology and make available new, innovative technology that can produce and deliver 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.

The technologies that comprise the plan include activities in the Hydrogen Fuel Initiative and those associated technologies that are being developed in other coal-related and sequestration-related programs. The specific activities in this RD&D Program are shown in the large shaded box in Figure 9. There are two hydrogen production pathways included in this Plan, the central production pathway (gaseous hydrogen) and the alternate hydrogen production pathway (hydrogen-rich liquid fuel) – both of which are shown in the large blue shaded box. The program builds on expected RD&D successes in associated programs within the Office of Fossil Energy. Figure 10 shows the interrelationship between each of these elements. The Gantt charts in Figures 11 and 12 show the schedule proposed for each of the technologies being developed by the program.

Figure 9. Office of Fossil Energy Program Components

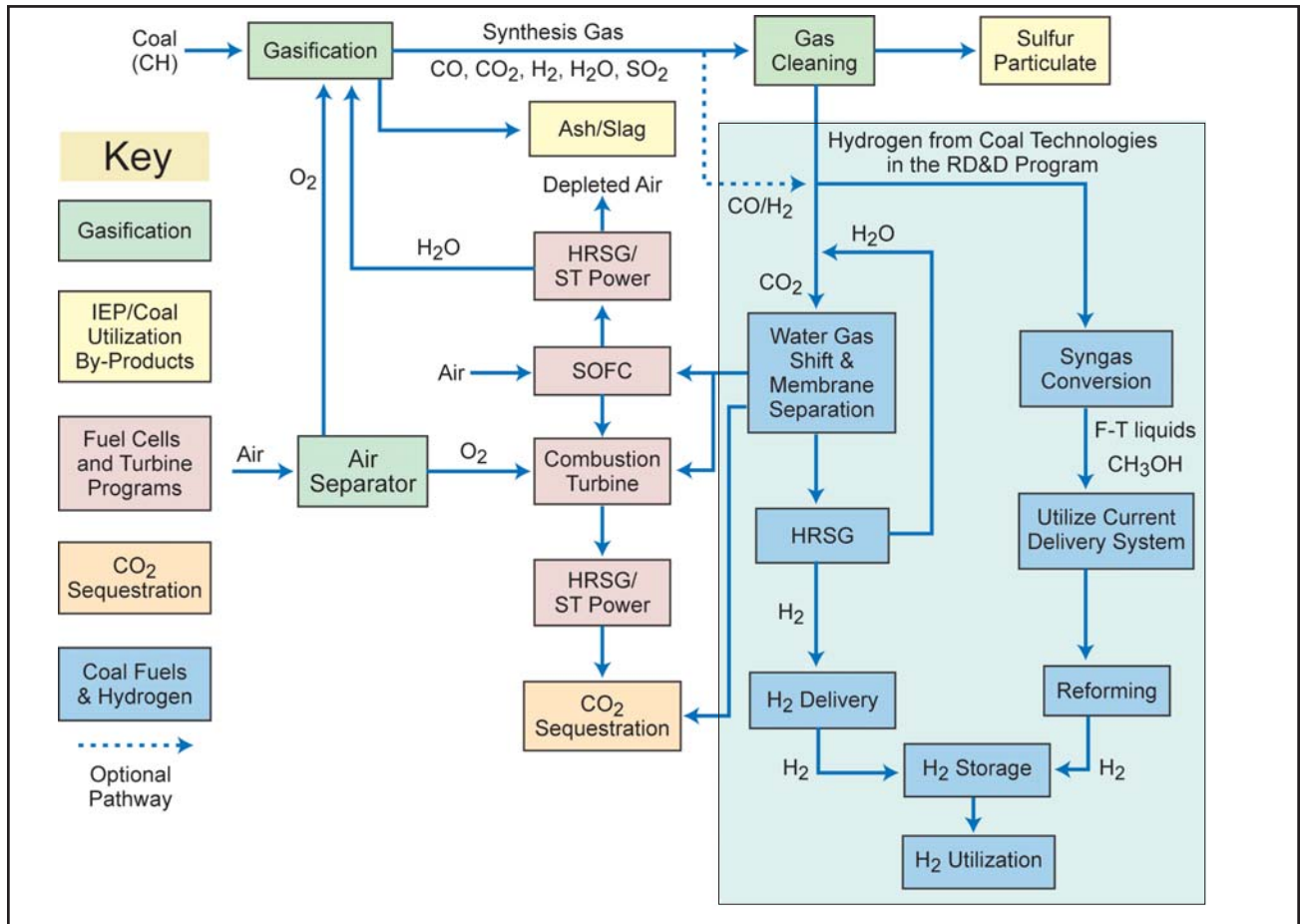




Figure 10. The Hydrogen from Coal Program and Support of Other Programs and Initiatives

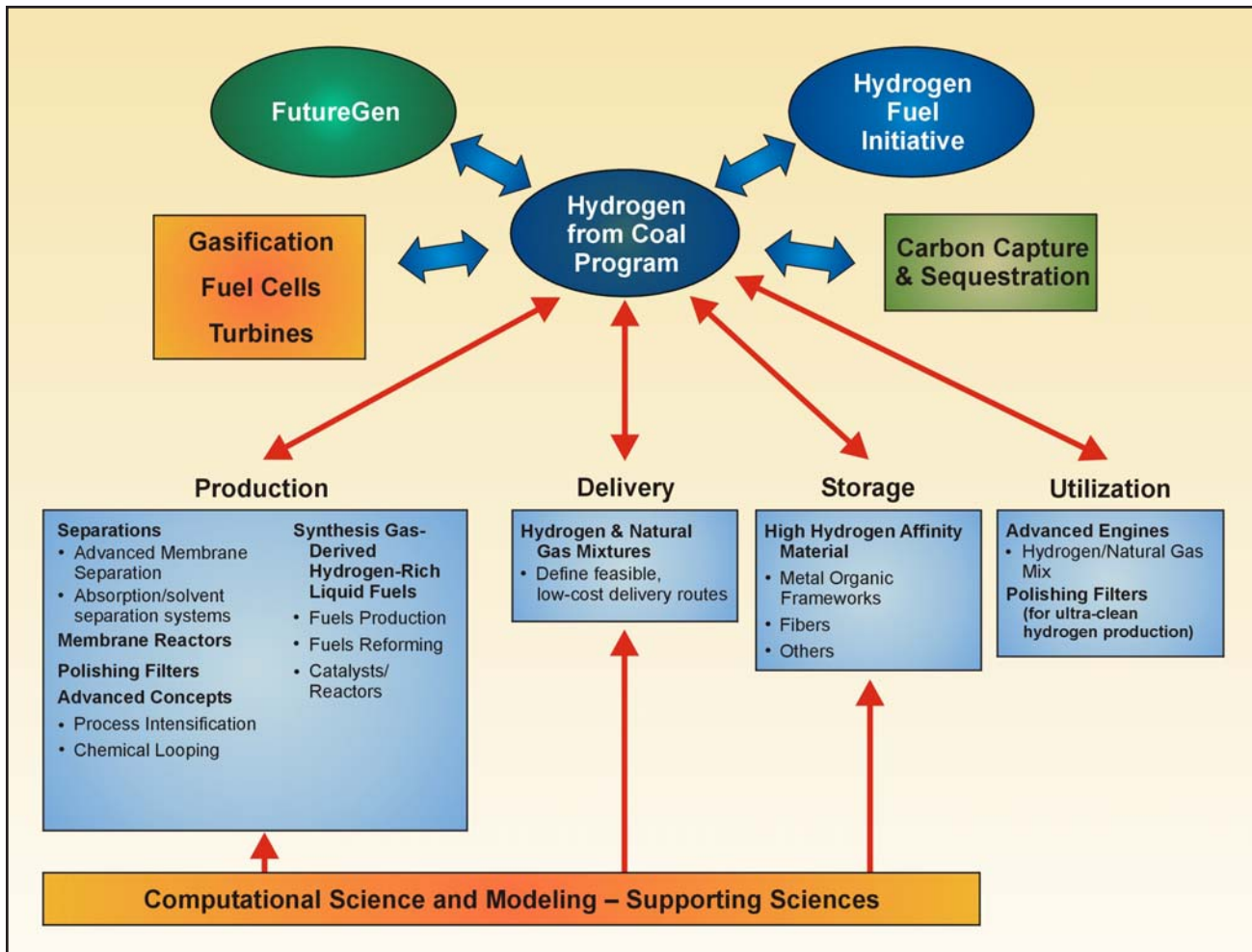


Figure 11. Hydrogen from Coal Research, Development, and Demonstration Program

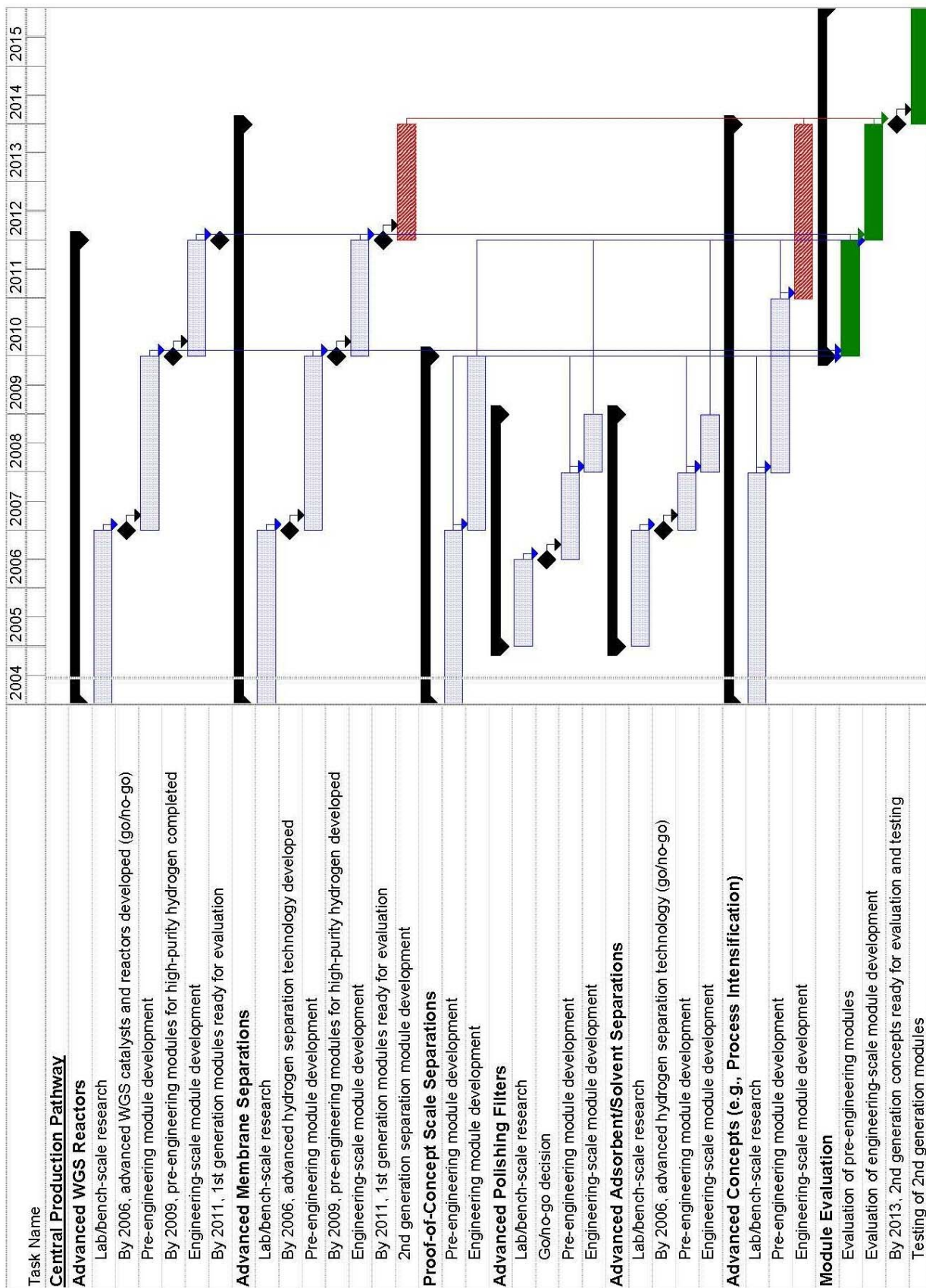
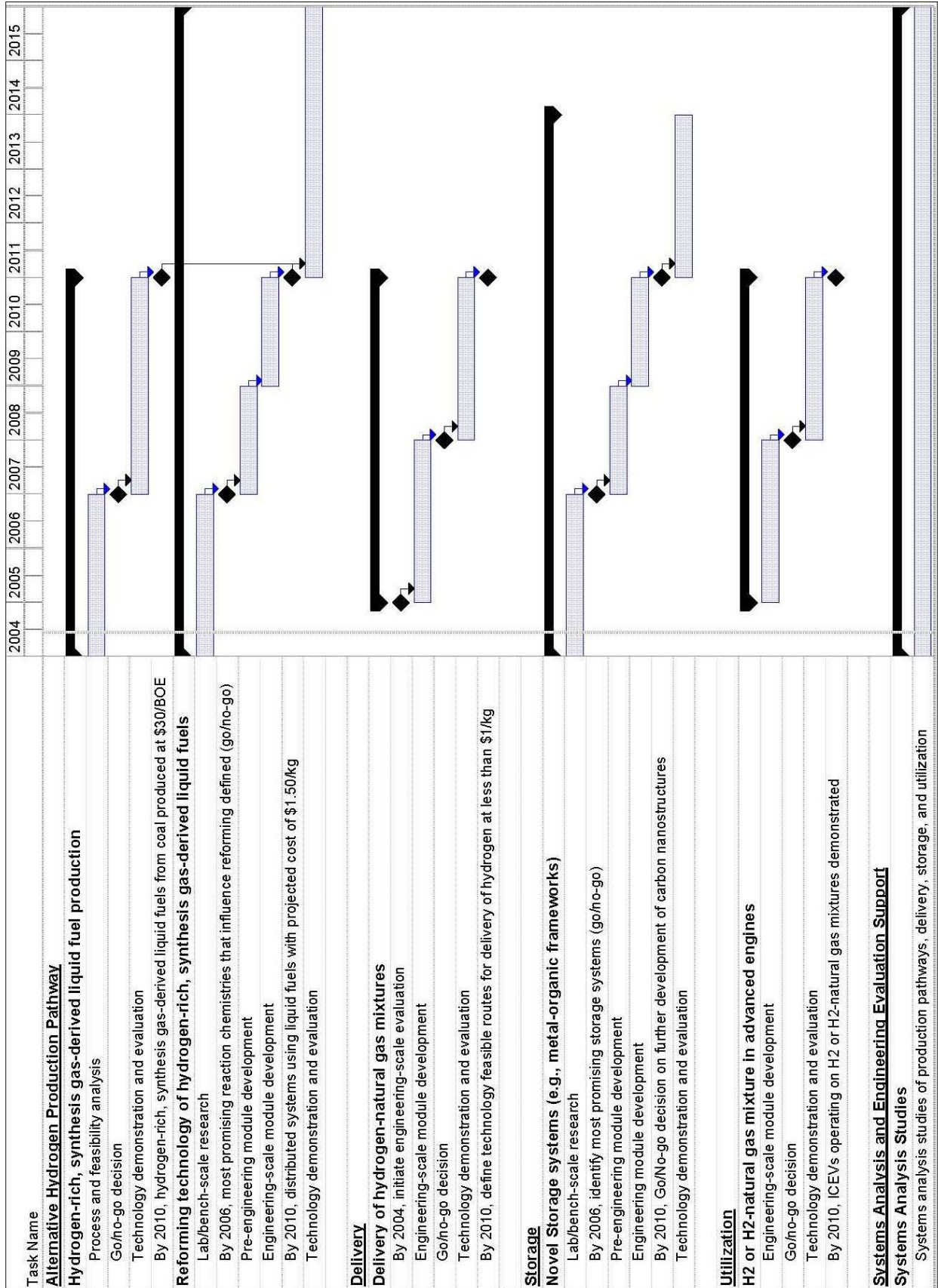


Figure 12. Hydrogen from Coal Research, Development, and Demonstration Program





## 5.1 Central Production Pathway

A hydrogen from coal process, in a carbon-constrained world, requires developing technologies that can reduce the cost of producing high-purity hydrogen from coal while generating sequestration-ready carbon dioxide streams. The initial step to produce hydrogen from coal involves coal gasification to produce synthesis gas. This gas, requiring subsequent cleaning, is mainly a mixture of hydrogen and carbon monoxide, with some carbon dioxide, sulfur, particulate matter, and trace components. The resulting clean synthesis gas is shifted to produce more hydrogen in the water-gas shift reactors. Hydrogen, CO<sub>2</sub>, and trace components are separated for final use, or captured for sequestration in the case of CO<sub>2</sub>.

FE's Office of Coal & Power Systems (OC&PS) presently has in progress R&D activities on coal gasification and carbon sequestration technologies to improve the efficiency of power production and to reduce the environmental impact of coal use. These gasification, sequestration, gas turbine, and fuel cell development efforts are not part of the direct Hydrogen from Coal Program, but instead are technologies under development in other OC&PS 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 R&D effort in the Hydrogen from Coal Program is on those technologies that shift and separate hydrogen from coal-derived synthesis gas, including process intensification efforts that reduce processing steps, combine functions, and significantly improve efficiency. Today's unit operations are effective but also are expensive and energy-intensive. For example, the initial cleaning step requires the synthesis gas to be cooled from over 1,800 °F as it leaves the gasifier, to ambient temperature for gas cleanup. The synthesis gas must be re-heated to 650–700 °F for the first of two water-gas shift reactors for production of additional hydrogen. Hydrogen must be separated and purified from the mixed gas stream.

Technology that can combine one or more of these steps without the inefficiency of cooling and reheating will make the process more efficient. Novel technologies could be developed that can not only combine the processes into one step (process intensification technology), but also remove pollutants, such as sulfur, and carbon dioxide into one stream that can be jointly sequestered.

### 5.1.1 Goal and Milestones – Central Production Pathway

**Goal:** By 2015, demonstrate a 60 percent efficient, near-zero emissions, coal-fueled hydrogen and power co-production facility which reduces the cost of hydrogen by 25 percent compared to current coal-based technology.

**Milestones:**

- By 2006, develop advanced water-gas shift catalysts and reactors
- By 2006, identify advanced hydrogen separation technology including membranes tolerant to trace contaminants
- By 2009, complete engineering design of modules for producing high-purity hydrogen, based on integrated process studies
- By 2011, demonstrate hydrogen modules for coal gasification combined-cycle co-production plant
- By 2015, demonstrate hydrogen modules integrated into near-zero emission plant concept producing hydrogen and electric power with sequestration at a 25 percent lower cost (to produce hydrogen)

### 5.1.2 Activities – Central Production Pathway

Although the Hydrogen from Coal Program is being initiated in FY 2004, there are ongoing technology development efforts in other OC&PS programs, Advanced Research Programs, and NETL that support the MYP, either as direct or associated activities. Some of the current R&D program activities that support this MYP are shown in the following table.

**Table 2. Some Relevant Current R&D Program Activities**

Category	Technology
<i>Metallic Membranes</i>	<ul style="list-style-type: none"> <li>• Palladium membrane reactors</li> <li>• Palladium-copper alloys for membrane reactors</li> <li>• Manufacturing techniques for palladium alloy membranes</li> </ul>
<i>Dense Phase Membranes</i>	<ul style="list-style-type: none"> <li>• Development of proton conducting and mixed conducting membranes and materials</li> <li>• Membranes based on SrCeO<sub>3</sub> on porous substrates</li> <li>• Mixed conducting perovskite/oxide membranes</li> </ul>
<i>Microporous Membranes</i>	<ul style="list-style-type: none"> <li>• Development of zeolite membranes</li> <li>• SiC selective membranes</li> <li>• Metal-composite membranes</li> <li>• Fabrication methods</li> </ul>
<i>Reverse Selective Membranes</i>	<ul style="list-style-type: none"> <li>• Nanocomposite membranes for reverse selective separation</li> </ul>
<i>Process Intensification</i>	<ul style="list-style-type: none"> <li>• Integrate water-gas shift and hydrogen separation – chemical vapor deposition (CVD) silica membranes (microporous)</li> <li>• High temperature shift catalyst integrated with a palladium-copper alloy membrane</li> </ul>
<i>Non-Membrane Based Technologies</i>	<ul style="list-style-type: none"> <li>• Iron-calcium cycle process to produce hydrogen and sequestration-ready CO<sub>2</sub></li> <li>• CO<sub>2</sub> sorbent process to produce hydrogen and simultaneously capture CO<sub>2</sub></li> <li>• CO<sub>2</sub> hydrate process for gas separations</li> <li>• Advanced Solvent Systems</li> </ul>

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 water-gas shift kinetics and advanced reactor systems; and explored new concepts and fundamental studies on novel separation systems such as CO<sub>2</sub>-permeable membranes and CO<sub>2</sub> hydrate formation processes.

These programs have funded research with both near- and long-term potential. For example, NETL provides support for slipstream tests of hydrogen membrane separation technology that will be tested at an IGCC site, as well as support for design and fabrication of a prototype, full-scale membrane module (NETL is looking for opportunities to field-test this technology). Finally, advanced microporous inorganic membrane technology that has been developed with FE support is very promising and is ready for proof-of-concept engineering and demonstrations.



### 5.1.3 Technologies – Central Production Pathway

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

5.1.3.1 Advanced water-gas shift reaction systems

5.1.3.2 Advanced membrane separation systems (for hydrogen separation)

- Microporous membranes
- Palladium metallic
- Dense ceramic

5.1.3.3 Advanced CO<sub>2</sub> separation systems

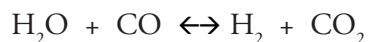
5.1.3.4 Polishing filters (ultra-clean hydrogen purification systems)

5.1.3.5 Advanced concepts

- Intensified processes for gas cleanup, water-gas shift, and hydrogen separation systems
- Chemical looping

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

Partial oxidation of coal and other carbon-based solid/liquid feedstocks produces a synthesis gas with a composition ranging from 30-45 percent H<sub>2</sub>, 35-55 percent CO, and 5-20 percent CO<sub>2</sub> (dry basis). 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 water-gas shift (WGS) reaction. The WGS reaction converts CO and H<sub>2</sub>O to CO<sub>2</sub> and H<sub>2</sub>:



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

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 to shift the WGS equilibrium to the right. Steam also is used to minimize undesirable side reactions that compete with the WGS reaction.

Commercial WGS technology, most often used in the production of hydrogen by steam reforming of natural gas, typically employs one or two staged reactors. Commercial catalysts have been optimized to maximize performance in the different stages and are summarized in Table 3.

Only fixed-bed reactors are currently used in commercial applications with these catalysts. Multiple reactors with intercooling 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 pressure swing adsorption (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/H<sub>2</sub> purification include methanation (old), PSA (current), and polymer membranes (new). Possible impurities in the product hydrogen are CO, CO<sub>2</sub>, CH<sub>4</sub>, and higher hydrocarbons, as well as methanol.

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 Fischer-Tropsch 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., particularly the SCOHS sulfur removal process.
- Processes can be coupled with newer preferential oxidation (PrOx) technologies to produce very low CO in the hydrogen product.
- Steam requirements are low.

**Table 3. 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	Fe/Cr	Co/Mo
Reactor Type	–	multiple fixed beds (last bed)	multiple fixed beds	multiple fixed beds
Temperature <sup>a</sup>	°C	200-250/350	300-450	300-550
Pressure	psia	~450	450-750	~1100
CO in Feed	–	low	moderate to high	high
Residual CO	%	0.1-0.2	–	–
Approach to Equilibrium	°C	8-10	8-10	–
Min Steam/CO Ratio	molar	2.6	2.8	2.8
Sulfur Tolerance	–	low	moderate	high
Chloride Tolerance	–	low	moderate	moderate
Water Tolerance	–	low	moderate	high
Stability/Durability	yrs	3-5	5-7	2-7

<sup>a</sup>Lower temperature limit is set by water dew point at pressure.

The disadvantages are:

- WGS kinetics are more favorable at higher temperatures.
- Low-temperature shift catalysts are easily poisoned.
- Temperature range is outside the range of metal and ceramic membranes that could be used for separation.
- Cu in catalyst promotes methanol side reaction (methanol emissions from hydrogen plants are regulated by the U.S. EPA).
- 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 (Fischer-Tropsch 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.

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.

### *5.1.3.2 Advanced membrane separation systems*

Modern gasification and WGS technology produce synthesis gas, a mixture of hydrogen, CO, CO<sub>2</sub>, and other chemical compounds. There are several gas separation technologies that could separate constituents of the synthesis gas (syngas), mainly H<sub>2</sub> and CO<sub>2</sub>, and that could supply oxygen (O<sub>2</sub>) from air for gasification reactions. 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. Membranes to separate O<sub>2</sub> from air are being developed in the OC&PS gasification program.

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 significant opportunities to make advancements in these separations with the development of various types of advanced membranes that can separate hydrogen from CO<sub>2</sub>, advanced solvent systems, and other advanced systems such as reverse selective membranes and low-temperature hydrate processes that can separate CO<sub>2</sub> from hydrogen. 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 product for delivery.

Reductions in cost, improved efficiency, and simplified systems are potentially possible with advancements in hydrogen membrane separation technologies. 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 250–500 °C. Many current hydrogen membrane technologies are at the basic research phase, but because of their characteristics, they have the potential to provide hydrogen purity above 99.99 percent. Other membranes, such as microporous membranes (e.g., those under development by ORNL), are much farther advanced and have nearer-term potential to reduce the cost of hydrogen production. These membranes can produce hydrogen with purity up to the high 90 percent, which is suitable for solid oxide fuel cell (SOFC) use. Attaining hydrogen purity above 99 percent would require these membranes to be used in several stages in series.

By way of background, 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 following discussion will detail three membrane types that currently are being developed by FE and NETL. This is not an exhaustive list, and is not meant to preclude other potential membrane types that could be included in the Hydrogen from Coal RD&D Program. Several basic membrane characterizations are:

- **Microporous Membranes** – These membranes are microporous filters that separate molecules through a molecular diffusion transport mechanism determined by the pore diameter and particle size. Flux increases linearly with increasing pressure, and there is usually a strong dependence of flux increase with higher temperatures. Materials such as ceramics, graphite, or metal oxides can be used in making these membranes. These materials provide significant thermal and chemical stability in harsh operating environments. The pores in the membrane may vary between 1 nanometer (nm) and 20 microns. The promising microporous membrane being developed at ORNL is an example of this membrane type that can produce hydrogen with purity up to the high 90 percent, which is suitable for solid oxide fuel cells. If these membranes are used in series, they can produce 99.99 percent pure hydrogen, but this purification process may be less efficient than other processes.
- **Palladium-type (Pd) Metallic Membranes** – These Pd-type metallic membranes transport gaseous hydrogen via an atomic mechanism whereby the metal, usually Pd, dissociates the molecular hydrogen into atoms that pass through the Pd metal film, where the atoms recombine into hydrogen molecules. 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 undergo phase changes that significantly reduce the hydrogen flux. Alloying with other metals like

copper and silver reduces this phase change propensity. The flux for these membranes is proportional to the difference of the square roots of the partial pressures across the membrane. Because of the transfer mechanism for Pd-type metallic membranes, 100 percent pure hydrogen can be recovered.

- **Dense Ceramic Membranes.** Dense phase ceramic membranes offer interesting possibilities in terms of high temperature separation, mechanical stability, very high selectivity and adequate flux. Generally, hydrogen flux increases with operating temperature. Dense phase membranes can be configured in many forms, and it is best to sub-categorize them as follows:
  - **Purely mixed conducting:** This type of dense membrane is a ceramic membrane (usually a perovskite/oxide composition) that provides the highest flux rates at high temperatures (around 800–900 °C). It is an ionic transfer membrane where the mechanism is the transfer of hydrogen ions (protons) and electrons through the ceramic matrix. Once through the membrane, the protons and electrons recombine to form hydrogen molecules. The flux depends on the proton and electron conductivities because, to produce molecular hydrogen, every two protons transferred must react with two electrons. The flux is proportional to the natural log of the partial pressure gradient. The problem with this type of membrane has been low electron conductivities and hence very low fluxes. Flux can be improved by doping to increase electron transfer. This ionic transfer membrane approach has been very successful in oxygen transfer systems for air separation. However, the operating temperature must be significantly reduced to meet the needs of some gasifier effluents and clean-up requirements.
  - **Cermet membranes:** These types of membrane are a composite dense phase ceramic with a metallic phase, hence the term cermet. Two general approaches to cermet membrane configuration are identified.
    - In the first type, a **dense mixed conducting ceramic matrix phase is combined with an electron conducting metallic second phase.** The purpose of the metal in this type (often nickel) is to increase the electron conduction and thereby increase the overall hydrogen flux. The transfer mechanism is predominantly the conductivity of protons and electrons through the ceramic/metal membrane, where they recombine to form molecular hydrogen on the other side of the membrane. Like the purely mixed conducting type, the flux is a function of the natural log of the partial pressure gradient.
    - In the second type, a **dense mixed conducting ceramic matrix phase is combined with a hydrogen-permeable metallic second phase.** This metallic phase (like Pd or Pd/Ag) functions in the same way as the Pd-type membrane 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 the overriding mechanism in estimating the flux (orders of magnitude greater than the contribution of proton and electron conductivity). Therefore, the flux for this membrane is more closely related to that of Pd-type 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. This ceramic/metal composite overcomes many of the limitations of Pd-type metal membranes. This includes inhibition of phase change and increased tolerance to impurities in the synthesis gas.



Table 4 shows the wide range of performance for various membranes under development that are sponsored by FE and NETL. As discussed under technical targets in section 5.1.4.2, some of these performance metrics are approaching the desired flux rates of about 300 ft<sup>3</sup>/hr/ft<sup>2</sup> at 100 psi delta P hydrogen partial pressure and the desired operating range of 300– 600 °C. However, other characteristics, such as the ability to withstand harsh chemical environments and desired durability, have not been demonstrated.

**Table 4. Examples of Current Status of Membrane Development Sponsored by FE and NETL**

Type	Microporous	Dense Phase Ceramic	Hydrogen Permeable Cermet*
Flux <sup>(a)</sup>	100	2	36
Temp, °C	300-600	900	600
S tolerant	Yes	nd	nd
Cost, \$/ft <sup>2</sup>	150-200	na	na
Potential timing <sup>(b)</sup>	5 years	10+ years	10+ years
ΔP Estimated <sup>(c)</sup>	100	100	100
ΔP function	linear	logarithmic	sq. root

<sup>(a)</sup> ft<sup>3</sup>/hour/ft<sup>2</sup> for 100 psi ΔP (hydrogen partial pressure basis)

<sup>(b)</sup> Potential timing for development

<sup>(c)</sup> ΔP Estimated – all flux rates have been corrected to an estimated 100 psi ΔP (hydrogen partial pressure basis) across the membrane at 50 psia on the permeate or sweep side

nd = not demonstrated; na = not available

\* Hydrogen permeable (Pd-type) cermet membrane

### The Relationship between Membrane Flux and Partial Pressure of Hydrogen

Most hydrogen separation membrane research, with the exception of those under development at ORNL, 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 does not reflect real-world operating conditions in a hydrogen-from-coal production facility. However, based on the observed data in the laboratory and scientific and engineering theory, 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 is different 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-type 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 Sieverts' Law. In mixed conducting ceramics and electron conducting cermet membranes, 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 5 shows these mathematical relationships for the different membrane types.

**Table 5. Relationships for Flux as a Function of Hydrogen Partial Pressure Differentials for Different Membrane Types**

Membrane Type	$\Delta P$ function	Equation*
Microporous	linear	$\text{Flux}_{\text{est}} M = \text{Flux}_{\text{obs}} M * (\Delta P_{\text{est}} / \Delta P_{\text{obs}})$
Pd-type (includes pure Pd and Pd alloys with structural support)	square root	$\text{Flux}_{\text{est}} P = \text{Flux}_{\text{obs}} P * \left[ \frac{(P_{f_{\text{est}}}^{0.5} - P_{s_{\text{est}}}^{0.5})}{(P_{f_{\text{obs}}}^{0.5} - P_{s_{\text{obs}}}^{0.5})} \right]$
Dense mixed conducting ceramic (perovskite/oxide is an example)	natural logarithm	$\text{Flux}_{\text{est}} D = \text{Flux}_{\text{obs}} D * \left[ \frac{\ln(P_{f_{\text{est}}}/P_{s_{\text{est}}})}{\ln(P_{f_{\text{obs}}}/P_{s_{\text{obs}}})} \right]$
Cermet - Dense ceramic with an electron conducting metallic second phase	natural logarithm	$\text{Flux}_{\text{est}} D = \text{Flux}_{\text{obs}} D * \left[ \frac{\ln(P_{f_{\text{est}}}/P_{s_{\text{est}}})}{\ln(P_{f_{\text{obs}}}/P_{s_{\text{obs}}})} \right]$
Cermet – Dense ceramic with a Pd-type hydrogen permeable second phase (typically Pd or Pd/Ag)	square root	$\text{Flux}_{\text{est}} P = \text{Flux}_{\text{obs}} P * \left[ \frac{(P_{f_{\text{est}}}^{0.5} - P_{s_{\text{est}}}^{0.5})}{(P_{f_{\text{obs}}}^{0.5} - P_{s_{\text{obs}}}^{0.5})} \right]$

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

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

$\Delta P_{\text{est}}$  is the  $\Delta P$  of hydrogen partial pressure to be estimated

$\Delta P_{\text{obs}}$  is the observed, or tested, hydrogen partial pressure

$\text{Flux}_{\text{est}} P$  is the estimated flux for hydrogen permeable membranes

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

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

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

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

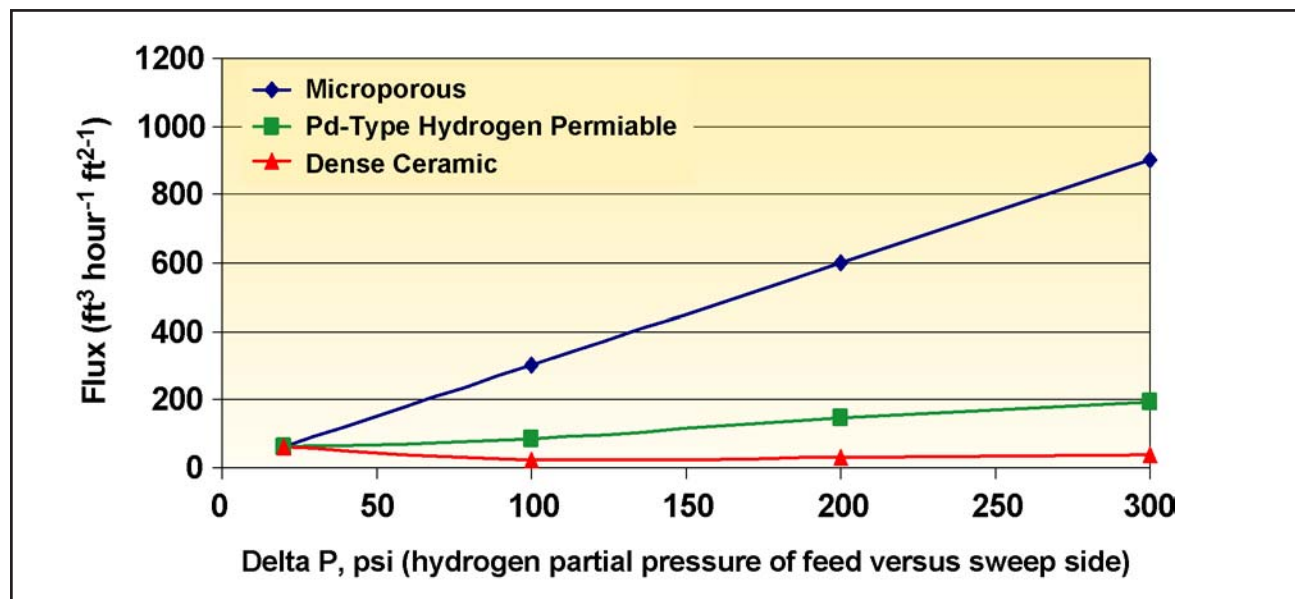
$P_{s_{\text{obs}}}$  is the observed, or tested, sweep (permeate) side hydrogen partial pressure

$\text{Flux}_{\text{est}} D$  is the estimated flux for dense ceramic membranes

$\text{Flux}_{\text{obs}} D$  is the observed, or tested, flux for dense ceramic 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  $60 \text{ ft}^3 \text{ hour}^{-1} \text{ ft}^{-2}$  with a hydrogen partial pressure  $\Delta P$  of 20 psi and an assumed sweep (permeate) side hydrogen partial pressure of 1 psi for all membrane types. In the desired case, 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  $\Delta P$  of 100 to 300 psi is expected. For example, when converting assumed observed test data from a  $\Delta P$  of 20 and a permeate side partial pressure of 1 psi to operating conditions of 100 psi  $\Delta P$  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  $\Delta P$  for microporous membranes.

Figure 13. Effect of Changes in  $\Delta P$  and Sweep Side Pressure on Flux of Hydrogen Membranes

In addition to hydrogen partial pressure, other operating conditions can also influence hydrogen flux. Temperature and quality of the feed stream are also important factors that could influence the flux. Membrane qualities 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.

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

Another method to separate H<sub>2</sub> from 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 psi, which results in liquid CO<sub>2</sub> that is transported to a utilization site (e.g., enhanced oil recovery) or to a sequestration site (e.g., abandoned oil well).

Advanced CO<sub>2</sub> separation technologies have as their objective the removal of CO<sub>2</sub> and other trace impurities from the hydrogen-CO<sub>2</sub> mixtures efficiently and at a low cost. These technologies include membranes, CO<sub>2</sub> hydrates, and improved adsorbent/solvent systems. In the membrane area, the nanostructured, polymeric membranes, which are imbedded with nanoparticles to modify the gas transport properties of the base polymer, show potential to achieve the desired selective CO<sub>2</sub> separation. Polymeric membranes also can be incorporated with amine groups to facilitate the H<sub>2</sub>S and CO<sub>2</sub> removal.<sup>5</sup> These membranes are known as reverse selective membranes.

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. Commercial processes are available, but

<sup>5</sup>Winston Ho, "Development of Novel Water-Gas-Shift Membrane Reactor," Paper presented at the Hydrogen, Fuel Cells, and Infrastructure Technology Program Review Meeting, May 19-22, 2003.

they are expensive and energy-intensive, operate at cold gas temperatures, and have low CO<sub>2</sub> sorption capacity. New CO<sub>2</sub> sorbents have the potential to remove CO<sub>2</sub> at warm gas temperatures (250–350 °C), which is ideal for IGCC systems. Additionally, these new sorbents could remove CO<sub>2</sub> at WGS temperature conditions without additional cooling. However, no sorbents that are regenerable and operate at warm gas temperatures are available.

CO<sub>2</sub> hydrates remove CO<sub>2</sub> by forming a crystalline lattice around the gas molecule, subsequently trapping the molecule. The solid hydrate is formed by reducing the temperature of the synthesis gas stream to 34 °F at pressures ranging from 500–600 psi. Water nucleates and surrounds the CO<sub>2</sub> molecule, trapping it within the crystalline lattice of the hydrate. The solid hydrate, contained within a slurry, is removed and heat is added to release the CO<sub>2</sub> molecule. The process shows promise but must be further researched and demonstrated to continuously control production of hydrates, and to gain an understanding of system integration issues.

There also is potential to improve current commercial solvent and adsorbent technologies with the specific aim of adapting them for coal-based H<sub>2</sub> production applications with improved system efficiency. These technologies could lower the cost and improve efficiency of hydrogen separation until more advanced technologies, such as membranes, are available.

#### *5.1.3.4 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. PEM fuel cells, which are used in fuel cell vehicles, require the most stringent standard of less than 10 ppm of CO, and very low levels of sulfur that may be limited to 10–50 parts per billion (ppb) levels or lower. A polishing filter device using an absorbent will be required to meet the particular application requirement. For coal-based hydrogen, technology R&D has to identify and define the preferred absorption material or materials and conditions to successfully remove the last trace impurities to meet the standards, with more focus on the sulfur removal process.

#### *5.1.3.5 Advanced concepts*

The Hydrogen from Coal Program is investigating advanced concepts through process intensification. Process intensification is the concept of developing novel technologies which, 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. One of the more developed advanced concepts being investigated is the integration of the WGS reaction with hydrogen separation.

Advanced water-gas shift reactors need to be developed using sulfur-tolerant catalysts to produce more hydrogen from synthesis gas at lower cost. Membrane reactors have been identified as a potentially beneficial technology for use in new water-gas shift applications. By combining the reaction with selective removal of one of the reaction products, a single reactor can operate simultaneously at high temperature and high

conversion, and possibly without the requirement of excess steam. Conceptually, such a reactor could use a membrane that is highly permselective for either  $H_2$  or  $CO_2$ .

The conditions for water-gas shift 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  $CO_2$  or  $H_2$ , whichever was not removed through the membrane. The catalysts used in conventional water-gas shift 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 required in a conventional shift reactor. Water-gas shift is a reversible, exothermic reaction, and consequently the conversion is limited at high temperatures by thermodynamic equilibrium. The use of a highly permselective membrane reactor would avoid this problem, driving the reaction to high conversion rates at elevated temperatures by selectively removing either  $H_2$  or  $CO_2$ . While this conceptually removes the limitation on conversion at high temperature, it is unknown what effect it will have upon the rate of reaction. Water-gas shift over commercial, high-temperature iron oxide catalysts is known to be inhibited by the product,  $CO_2$ . While the kinetics are not inhibited by the other product,  $H_2$ , it is not known whether the active ( $Fe_3O_4$ ) state of the catalyst can be maintained in the situation where  $CO_2$  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.

Chemical looping is another advanced concept for producing and separating streams of hydrogen and carbon dioxide from mixed gases and trace constituents. In chemical looping processes, combustion of a fossil fuel occurs in two steps: in the first step, air is used to oxidize a metallic oxygen carrier; in the second step, the metallic oxide carrier is used to oxidize a fuel (with the carrier reduced to a lower oxidized state). In this process, the carrier is circulated in two separate reactors: a combustion step where the oxygen carrier reacts with the fuel, and an oxygen regeneration step in which the carrier is oxidized with air. This process is an alternative to expensive cryogenic oxygen production, and may have advantages to membrane separation of oxygen since the two-step looping process can occur at low pressures.

#### 5.1.4 Technical Targets – Central Production Pathway

The technical targets in this MYP, unless otherwise indicated, represent the status of the technology after completion of research and development, but prior to demonstration of the technology in modules at engineering scale in a FutureGen facility, for example. These technologies will be validated in modules in FutureGen, or similarly scaled engineering modules as detailed in the Gantt charts in Figures 11 and 12. In addition, as a point of reference, the status of the technology is provided in the following tables.



### 5.1.4.1 Water-Gas Shift Reaction Technical Targets

Table 6 summarizes the performance criteria and targets for the WGS reaction. The 2015 technical target includes a single, compact WGS reactor operable over a wide range of temperatures and pressures with minimal undesirable side products and a complete 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 with a wider range of operating temperatures.

**Table 6. Water-Gas Shift Reaction Technical Targets**

Performance Criteria	Units	Current Status	2005 Target	2010 Target	2015 Target
Reactor Type	-	Multiple fixed beds	To be determined		
Catalyst Form	-	Pellets	To be determined		
Active Metal	-	Cu/Zn or Fe/Cr or Co/Mo	To be determined		
Temperature	°C	200-550	300-450	300-500	200-600
Pressure	psia	450-1150	450	750	>1,000
Approach to Equilibrium	°C	8-10	10	6	<4
Min Steam/CO Ratio	Molar	2.6	3.0	2.5	<2
Sulfur Tolerance	-	Varies	Low	Moderate	High
Chloride Tolerance	-	Varies	Low	Moderate	High
Water Tolerance	-	Varies	Low	Moderate	High
Stability/Durability	Years	3-7	3	7	>10
Reactor Cost Reduction	%	-	-	>15 %	>30%

### 5.1.4.2. Hydrogen Separation Technical Targets

The key performance criteria for successful incorporation of membrane separation reactors into hydrogen from coal configurations are shown in Table 7. 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 7. Hydrogen Separation Technical Targets\***

Performance Criteria	Current Status <sup>(a)</sup> (Microporous)	2007 Target	2010 Target	2015 Target
Flux <sup>(b)</sup>	100	100	200	300
Temp, °C	300-600	400-700	300-600	250-500
S tolerance	Yes	Yes	Yes	Yes
Cost, \$/ft <sup>2</sup>	150-200	150	100	<100
WGS Activity	No	Yes	Yes	Yes
ΔP Operating Capability <sup>(c)</sup>	100 (tested)	100	Up to 400	Up to 800 to 1,000
Carbon monoxide tolerance	Yes	Yes	Yes	Yes
Hydrogen Purity <sup>(d)</sup>	90-98%	95%	99.5%	99.99%
Stability/Durability (years)	-	3	7	>10

<sup>a</sup> Current status is shown for only one separation membrane – microporous. Additional current status information is provided for dense phase ceramic and thin film palladium membranes in Table 4 of this report.

<sup>b</sup> ft<sup>3</sup>/hour/ft<sup>2</sup>/100 psi ΔP (hydrogen partial pressure basis)

<sup>c</sup> ΔP = 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 carbon dioxide 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 palladium 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.*

Because the WGS reaction is exothermic and a large amount of shift is expected to occur within the membrane reactor, the membrane reactor should also operate in a temperature range compatible for the WGS to occur. An acceptable range would be 400–500 °C. It has been demonstrated that WGS activity is an essential function of the membrane reactor for coal-to-hydrogen applications. Tolerance to sulfur compounds (H<sub>2</sub>S and COS) in the range expected in the effluent from warm gas cleaning also is desirable. This is expected to be in the range of less than 10 ppm. Failure to achieve sulfur tolerance would require an additional sulfur polishing step in the coal-to-hydrogen plant configuration.

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 about 450–525 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 800–1,000 psi. In addition, it is critical that any membrane system be completely tolerant to carbon monoxide. These target criteria are independent of membrane type. One of the goals of these systems is to increase flux while reducing the pressure drop across the membrane in order to reduce the hydrogen product compression requirement.

### 5.1.5 Technical Barriers – Central Production Pathway

The following technical and economic barriers must be overcome to meet the goals and objectives of the Hydrogen from Coal Production Program element:

#### 5.1.5.1 Barriers

**A. High Cost.** The cost of current technologies to produce hydrogen from coal must be further reduced to accelerate the timing of the transition to a hydrogen economy by providing a low-cost source of hydrogen derived from domestic resources. This includes improved efficiency of the process, reduced capital costs including the cost of materials used in advanced technologies, and reduced 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, water-gas shift 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 have not been fully identified, and require significant RD&D to establish the technology viability.

#### 5.1.5.2 Water-Gas Shift Reaction Barriers

**D. Impurity Intolerance/Catalyst Durability.** The water-gas shift 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 run, and in some cases, eliminate the post-gasification, synthesis gas cleanup step upstream of the water-gas shift reactor.

**E. Operating Limits.** The synthesis gas produced from gasification exits the gasifier at a high temperature. The water-gas shift reaction then is carried out in two separate stages, a high-temperature shift and a low-temperature shift. The development of advanced water-gas shift catalyst and reactor systems that are more robust and can operate at a wide range of temperatures can eliminate the need for two separate stages, potentially reducing capital costs.

**F. Undesired Side Reactions.** Side reactions that are undesirable in the WGS reactor must be minimized.

#### 5.1.5.3 Hydrogen Separation Barriers

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

**G. Hydrogen Embrittlement of Metals.** Below 300 °C, hydrogen can embrittle certain types of membranes used in separation technologies, inducing a phase change. Embrittlement reduces the durability and effectiveness of the membrane for selectively separating hydrogen.

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

**I. Impurity Intolerance.** The presence of trace contaminants as well as CO, water, and CO<sub>2</sub> in the exit gas from the gasifier can reduce the hydrogen flux across different types of membranes. It is not understood whether these effects are caused by competitive adsorption or compositional changes on the membrane surface. Additionally, some membranes exhibit poor thermochemical stability in carbon dioxide 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.

**J. Undesired Atomic Rearrangement.** 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.

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

**L. Defects During Fabrication.** Fabrication of microporous membranes requires a reduction in membrane deposition cycles. It is ideal to prepare a high-flux, continuous zeolite membrane with one synthesis layer that is free of defects. No synthesis and evaluation methods exist for tunable pore-size membranes used in separating H<sub>2</sub> from light gases at high temperature and in chemically challenging environments. 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 manufacturing methods for defect-free thin films and membranes and modules in mass production must be developed and demonstrated.

**M. Low Selectivity.** Hydrogen selectivity of some zeolite-supported membranes decreases with increasing temperature (inadequate above 150 °C). However, temperatures typically need to be greater than 300 °C to produce the hydrogen flux rates needed for commercial applications.

**N. Technologies Do Not Operate at Optimal Process Temperatures.** 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. For example, dense ceramic hydrogen separation membranes currently operate only at high temperatures (~900 °C), which would require re-heating synthesis gas after the WGS reactor. Ideally, the temperature of operation should be in a range similar to outlet conditions from the second WGS reactor at 300–500 °C to eliminate the need for this re-heating. However, the lower operating temperature potentially will lower the flux rate, which poses a technical challenge.

**O. Low Flux and Conductivity Rates.** Proton and electron conductivities across ITM membranes have to be improved, as does mixed conductivity.

**P. Excessive Heat.** Some novel separation processes, such as CO<sub>2</sub> removal through the formation of hydrates, are highly exothermic, requiring the integration of heat transfer systems in these processes.

**Q. Impurities in Hydrogen from Coal.** PEM fuel cells require a highly pure hydrogen product. Technologies are needed that can reduce the carbon monoxide in hydrogen product streams to 10 ppm, and sulfur-containing compounds to parts per billion (ppb) levels.

### 5.1.6 Technical Task Descriptions – Central Production Pathway

Table 8 summarizes the tasks for the central production pathway technologies.

**Table 8. Task Descriptions for Central Production Pathway Technologies**

<b>Task Number</b>	<b>Task Description</b>	<b>Barriers Addressed by Task</b>
1	<p><i>Advanced Shift Technologies</i></p> <ul style="list-style-type: none"> <li>➤ Develop advanced shift catalysts that are more active and are impurity-tolerant.</li> <li>➤ Conduct the WGS reaction using a high-temperature membrane without added catalyst.</li> <li>➤ Develop integrated single-step shift-membrane separation technology.</li> </ul>	A, C, D, E, F
2	<p><i>Advanced Hydrogen Separation</i></p> <ul style="list-style-type: none"> <li>➤ Review and analyze separation technology to determine the current status, needs for advanced technology, preferred separation options, and scale-up to prepare modules.</li> <li>➤ Conduct RD&amp;D to explore technology for preferred advanced separation systems such as PSA, membranes, solvents, reverse selective systems, and other technology alternatives.</li> <li>➤ Identify low-cost materials for hydrogen separation.</li> <li>➤ Use molecular sieves to stabilize membranes.</li> <li>➤ Develop appropriate membrane seal and fabrication technologies and methods for module preparation and scale-up.</li> </ul>	A, C, and Barriers G through Q
3	<p><i>Polishing Filters Development</i></p> <ul style="list-style-type: none"> <li>➤ Develop polishing filter technologies that enable hydrogen product streams to meet fuel quality requirements for PEM fuel cells efficiently and at low cost.</li> </ul>	A, Q
4	<p><i>Advanced CO<sub>2</sub> Separations</i></p> <ul style="list-style-type: none"> <li>➤ Identify low-cost materials for CO<sub>2</sub> separation.</li> <li>➤ Develop reverse selective membranes for cost-effective CO<sub>2</sub> separation from mixed gas streams.</li> <li>➤ Develop advanced adsorption, hydrates, or other novel technologies for the cost-effective capture of CO<sub>2</sub> from mixed gas streams.</li> </ul>	M, N through Q
5	<p><i>Advanced Concepts</i></p> <ul style="list-style-type: none"> <li>➤ Investigate advanced and novel process concepts that integrate several processes – gas cleanup, WGS reaction, and hydrogen separation – into one step.</li> <li>➤ Investigate novel, “out-of-the-box” technologies that can produce hydrogen from coal directly or indirectly.</li> </ul>	A, C
6	<p><i>Demonstrations</i></p> <ul style="list-style-type: none"> <li>➤ Demonstrate and test advanced technologies to confirm laboratory, bench-scale, and pre-engineering module results.</li> </ul>	A, B



## 5.2 Alternate Hydrogen Production Pathway

An alternate hydrogen production pathway can be achieved through the use of coal-derived synthesis gas-based liquid fuels, either hydrocarbons or possibly methanol. These liquids are characterized by high weight content of hydrogen and can be transported, in the case of the hydrocarbon fuels, in the existing fuel delivery system. The evaluation and identification of this alternate pathway for hydrogen production, delivery, and reforming to produce the hydrogen at a distributed site will be an important part of this MYP. This pathway is discussed in more detail in section 5.2.3.

Computational studies and analyses of candidate liquid hydrogen carriers are required in order to identify the most promising reaction catalysts and chemical processing routes. This Hydrogen from Coal MYP therefore includes several pathways to deliver hydrogen, as previously discussed. The cost, efficiency, and benefits associated with these pathways has to be evaluated on a system basis for comparison to other possible hydrogen system pathways. These activities will be coordinated with the EERE hydrogen delivery and distribution activities.

### 5.2.1 Goal and Milestones – Alternate Hydrogen Production Pathway

**Goal:** 2011 – Optimize and make available an alternative economic and environmentally responsive hydrogen production pathway and reforming system to produce decentralized hydrogen.

**Milestones:**

- By 2005, identify and evaluate the most promising approaches and options for economic production of hydrogen from coal-derived synthesis gas, with the subsequent reforming of this fuel to produce hydrogen near the end-use.
- By 2008, complete bench-scale tests of liquid fuel production and reforming technologies that, when integrated with the entire fuel production and delivery cycle, will cost the consumer no more than the equivalent of \$2.00 per gallon of gasoline (about \$2.00/kg of hydrogen).
- By 2011, complete proof-of-concept tests and evaluations of the most promising hydrogen-rich, synthesis gas-derived liquid fuel candidates for reforming applications.

### 5.2.2 Activities – Alternate Hydrogen Production Pathway

Although the Hydrogen from Coal Program is being initiated in FY 2004, there is ongoing technology development in programs, such as the Ultra-Clean Fuels Program, which could apply to this alternate hydrogen production sub-element pathway in this MYP. Table 9 lists some of these activities.

**Table 9. Some Relevant R&D Program Activities**

Category	Technology
Liquid Fuels Production	<ul style="list-style-type: none"> <li>• Convert Cl compounds into F-T fuels or methanol</li> <li>• Develop active, stable, iron-based catalysts for use in slurry phase F-T synthesis</li> <li>• Demonstrate coal-to-liquid fuel production processes</li> </ul>
Fuels Reforming	<ul style="list-style-type: none"> <li>• Conduct fundamental studies to reform liquid fuels into hydrogen</li> </ul>

The DOE Office of Fossil Energy (FE) has been a leader in researching, developing, and demonstrating the production of synthesis gas. FE's research and development program has included the Liquid Phase Methanol (LPMEOH) demonstration project, another DOE Clean Coal Technology Demonstration Program project. Air Products and Chemicals, Inc. (APCI) was the lead on the \$213-million project, which demonstrated on a commercial scale the production of methanol and dimethyl ether from coal-derived synthesis gas. The project produced nearly 104 million gallons of methanol, subsequently used by Eastman Chemical in the production of methyl acetate.

Until recently, the DOE has been funding the LaPorte Alternative Fuels Development unit (AFDU) located at LaPorte, Texas and operated by APCI. This unit demonstrated the production of zero-sulfur Fischer-Tropsch (FT) liquid fuels from simulated coal-derived synthesis gas, and also the production of dimethyl ether (DME), higher alcohols, and liquid phase water gas shift. The current cost to produce liquid fuels from coal is projected to be about \$40 per barrel. Systems analysis studies of advanced conceptual plants that co-produce FT fuels and electric power have projected that liquid fuels can be produced in these advanced facilities for about \$30 per barrel. Although significant improvements in the cost of liquid fuels have been made in the past, additional improvements can enable this hydrogen production pathway to become an economic alternative.

More recently, as part of the President's Clean Coal Power Initiative (CCPI), Waste Management and Processors, Inc. and its partners were selected to perform a six-year project to convert coal waste into electric power and clean, synthesis gas-derived liquid fuels. It is anticipated that the project will convert over 4,700 tons per day of anthracite coal waste into electric power and over 5,000 barrels per day of liquid fuels as an interim step until widespread hydrogen delivery infrastructure becomes available.

### **5.2.3 Technologies – Alternate Hydrogen Production Pathway**

The following R&D elements are contained in the Hydrogen from Coal Delivery Program. These elements are listed by the section in which they are discussed.

5.2.3.1 Liquid fuels production/delivery/conversion

5.2.3.2 Fuels reforming in distributed production facilities

#### ***5.2.3.1 Liquid Fuels Production/Delivery/Conversion***

Hydrogen-rich liquid fuels that are produced from synthesis gas, including coal-derived synthesis gas, have the potential to use the existing petroleum product delivery and storage infrastructure with little to no modification. These liquid fuels can be delivered, using the existing petroleum infrastructure, either to individual filling stations where the liquids can be reformed on-site, or to sub-central hydrogen production locations to produce pure hydrogen. In the latter case, final delivery of the hydrogen to individual filling stations can be made using hydrogen tube trailers. In the longer term, with advancements in carbon sequestration technologies, there is the possibility of capturing and sequestering carbon from the much larger sub-central liquid fuels reforming facilities so that environmental concerns are alleviated. The two pathways for the production of hydrogen-rich liquids included in this RD&D Plan are the synthesis gas-to-methanol process and the Fischer-Tropsch process to convert synthesis gas to liquid fuels.

#### ***5.2.3.2 Fuels Reforming in Distributed Production Facilities***

Separation of hydrogen from synthesis gas-derived liquid fuels through fuels reforming in sub-central and

distributed hydrogen production sites has many benefits, including the ability to use the existing liquid fuels infrastructure to deliver these liquids to distributed generation sites. Distributed and sub-central generation of hydrogen through steam methane reforming currently is the most promising technology to produce hydrogen from natural gas and hydrogen-rich liquids. There is potential to use advanced technology for the reforming of liquid fuels to produce hydrogen, which would take advantage of process intensification with a corresponding reduction in product cost.

#### 5.2.4 Technical Targets – Alternate Hydrogen Production Pathway

The technical targets in this MYP, unless otherwise indicated, represent the status of the technology after completion of research and development, but prior to demonstration of the technology in modules at engineering scale in a FutureGen facility, for example. These technologies will be validated in modules in FutureGen, or similarly scaled engineering modules as detailed in the Gantt charts in Figures 11 and 12.

##### 5.2.4.1 Fuel Production and Conversion via Reforming Technical Targets

In Table 10, it is assumed that the zero-sulfur hydrogen-rich liquid fuels produced from coal-derived synthesis gas at a central plant are transported via the existing petroleum pipeline system to a sub-central facility where the liquids are reformed into hydrogen, and at which carbon could be feasibly captured. The size of this sub-central plant is in the range of 10–20 million standard cubic feet of hydrogen per day (25,000–50,000 kg/day of hydrogen). The hydrogen produced at this facility can be delivered to individual refueling stations via tube trailers.

The current cost of producing hydrogen from liquids reforming is estimated to be \$1.93/kg if the liquid feed cost is \$40/bbl and derived from the Fischer-Tropsch (FT) process. The estimated cost of delivery of this hydrogen by tube trailer is \$0.64/kg, for a total delivered hydrogen cost of \$2.57/kg. Deployment of advanced technology for the production of coal-derived FT fuels is expected to lower the cost from \$40 to \$30 per barrel. The cost of hydrogen produced by fuels reforming then will decrease to \$1.54/kg. If tube trailer pressure can be doubled to 10,000 psi, the cost of delivery could be reduced to \$0.32/kg for a total delivered cost of \$1.86/kg. Advanced reforming is expected to reduce the capital cost of the current reformer configuration by 25 percent, resulting in a delivered cost of hydrogen of \$1.76/kg, close to the DOE target of \$1.50/kg.

**Table 10. Fuel Production and Conversion via Reforming Technical Targets**

	<b>Current Status</b> <sup>(a)</sup>	<b>2010 Target</b>	<b>2015 Target</b>
Hydrogen-Rich Synthesis Gas-Derived Liquid Fuel Production Cost (\$/bbl) <sup>(b)</sup>	40	30	30
Reforming Cost to Produce Hydrogen from Synthesis Gas-Derived Liquid Fuels (\$/kg of H <sub>2</sub> ) <sup>(c)</sup>	1.93	1.54	1.44
Hydrogen Tube Trailer Delivery (\$/kg of H <sub>2</sub> )	0.64	0.32	0.32
Total Cost of Delivered Hydrogen (\$/kg of H <sub>2</sub> )	2.57	1.86	1.76

<sup>(a)</sup> Current status of technology assuming nth plant production.

<sup>(b)</sup> Synthetic liquid fuel production from coal derived synthesis gas.

<sup>(c)</sup> Total production cost that includes capital, O&M, and feedstock cost to produce hydrogen at 5,000 psi.

## 5.2.5 Technical Barriers – Alternate Hydrogen Production Pathway

### 5.2.5.1 General Barriers

**A. Lack of Demonstration of Novel Technologies.** Integrated operation of the coal-to-syngas into the hydrogen-rich liquids process has to be demonstrated at a commercial scale unit. Use of hydrogen-rich liquids derived from synthesis gas needs to be demonstrated in reforming/fuel cell systems to confirm their suitability as hydrogen carriers, and to identify and confirm the optimal liquid to be used through computational chemistry analysis.

### 5.2.5.2 Liquid Fuels Production, Delivery, and Conversion via Reforming Barriers

**B. Low Efficiency.** To be an effective hydrogen carrier, synthesis gas-derived liquids must be produced, delivered, and converted back to hydrogen in an efficient manner that overrides the number of energy-using steps required to provide the hydrogen. The current system is inefficient, and improvements must be made through improved catalysts, reactors, and production of optimal liquids.

**C. Catalyst and Reactor Systems Not Optimized.** These systems require improvements in reactor design and advanced catalysts to improve the liquid fuel production process, including the use of coal-derived CO-rich synthesis gas.

**D. The Optimal Hydrogen-Rich, Synthesis Gas-Derived Liquid Fuel for On-Board Reforming Has Not Been Identified.** Work must be done to identify the most optimal hydrogen-rich, synthesis gas-derived liquid fuel that can be used for hydrogen generation at distributed hydrogen production sites or in on-board reforming.

**E. High Capital Costs.** Current small-scale distributed reformer technologies are too expensive to supply hydrogen at a cost comparable to that of gasoline. An alternative plant could be a sub-central reformer. Multiple-unit operations and insufficient heat integration contribute to large, costly production and purification subsystems. Improved reforming and shift catalysts are needed to reduce side reactions and improve performance, bearing in mind the availability of the catalyst materials. Shift, separation, and purification costs need to be reduced by developing new technology such as single-step shift with integrated membrane technology.

**F. High Operating Costs.** Operating and maintenance costs are too high for distributed hydrogen generation plants that use hydrogen-rich, synthesis gas-derived liquids as feedstocks. Improved processes that require less operator control and maintenance are needed.

**G. Lack of Carbon Dioxide Capture.** Small-scale, distributed generation and on-board reforming of fossil fuel-derived liquid fuels will emit greenhouse gases. Capture of carbon dioxide from on-board reforming is highly unlikely. Additionally, cost-effective capture of CO<sub>2</sub> from distributed generation facilities is more difficult than at central locations. Research is needed to discover potential options to sequester CO<sub>2</sub> from distributed generation systems.

**H. Excessive Size, Weight, and Volume of On-Board Reformers.** The size, weight and volume of on-board reformers for fuel cell vehicles must be reduced to meet vehicle specifications.

### 5.2.6 Technical Task Descriptions – Alternate Hydrogen Production Pathway

Table 11 shows the technical tasks for the alternative hydrogen production pathway – hydrogen-rich, synthesis gas-derived liquid fuel production, reforming technology, computational analysis, and demonstrations.

**Table 11. Tasks for Alternate Hydrogen Production Technologies**

<b>Task Number</b>	<b>Task Description</b>	<b>Barriers Addressed by Task</b>
1	<p><i>Computational analysis</i></p> <ul style="list-style-type: none"> <li>➤ Develop computational and analytical tools to simulate hydrogen-rich, synthesis gas-derived liquid fuels production to determine the optimum processes for producing hydrogen-rich liquid fuels.</li> <li>➤ Develop the computational and analytical tools to simulate the separation of hydrogen from hydrogen-rich, synthesis gas-derived liquid fuels in small-scale, distributed generation facilities and for on-board reformers</li> </ul>	C, D, H
2	<p><i>Hydrogen-rich, synthesis gas-derived liquid fuels production</i></p> <ul style="list-style-type: none"> <li>➤ Develop novel reactor and catalyst systems to produce the most optimal, hydrogen-rich, synthesis gas-derived liquid fuels for reforming applications</li> </ul>	B, C
3	<p><i>Reforming technology</i></p> <ul style="list-style-type: none"> <li>➤ Optimize sub-central generation and on-board reformers for hydrogen-rich, synthesis gas-derived liquid fuels</li> </ul>	D, E, F, G, H
4	<p><i>Demonstrations</i></p> <ul style="list-style-type: none"> <li>➤ Demonstrate reforming of the most optimal, hydrogen-rich, synthesis gas-derived liquid fuels in distributed generation and on-board reforming applications</li> </ul>	A

### 5.3 Delivery

Currently, a hydrogen delivery infrastructure exists for only the small merchant hydrogen market, whereas a large capital-intensive network of pipelines and other infrastructure exists for both the delivery and storage of natural gas and liquid petroleum fuels. The small size of hydrogen molecules allows hydrogen to easily leak from systems where other gases do not – a barrier that must be overcome before its use becomes widespread. Also since hydrogen has physical properties that are known to cause embrittlement of high-strength steel in natural gas pipelines, RD&D is needed to identify modifications to the natural gas pipeline system, or an affordable alternative hydrogen delivery system.

The Office of Fossil Energy will expand its expertise in the delivery of natural gas by studying and perfecting the transport of natural gas and hydrogen mixtures. These mixtures will provide effective and economical delivery of natural gas and hydrogen, which could be separated after transport for use of the separated hydrogen, or for direct use of these mixtures in combustion engine or turbine applications.

Systems analysis studies must be conducted on the delivery element within the context of the entire hydrogen system, including production, delivery, and storage, with the goal of meeting the FreedomCAR



target of delivering hydrogen to end-users at \$1.50/kg, the equivalent of \$1.50/gallon of gasoline. This analysis will evaluate the trade-off between massive capital investments in central location hydrogen plants (associated pipelines) and delivery in a dedicated hydrogen infrastructure, against the use of a liquid and natural gas infrastructure to deliver hydrogen-rich fuels, which then can be reformed or used at distributed locations, ultimately with carbon sequestration.

EERE's Multi-Year RD&D Plan details the other pathways by which hydrogen may be delivered and provides further information about those technologies. FE will collaborate with EERE to ensure coordination of all DOE hydrogen delivery RD&D activities.

### 5.3.1 Goal – Delivery

*Goal:* Identify and evaluate the use of the natural gas pipeline system to deliver several combinations of natural gas and hydrogen, either for separation at the end of distribution, or for end-use applications where the mixture would be utilized.

This work will be done in conjunction with the FE Office of Natural Gas & Petroleum Technology and EERE.

### 5.3.2 Activities – Delivery

This is a new activity that will be initiated with this MYP.

### 5.3.3 Technologies – Delivery

The following technology to deliver a hydrogen and natural gas mixture is the only technology included in the Hydrogen from Coal Delivery Program.

#### 5.3.3.1 Hydrogen/Natural Gas Delivery Mixtures

Hydrogen is known to cause embrittlement of high-strength alloys used in natural gas pipeline systems, and therefore its widespread use in existing natural gas pipelines is limited unless novel methods of handling can be developed. These technologies, if developed, can eliminate embrittlement in the pipeline, for example, through a hydrogen-resistant lining or coating of the pipeline, or other means. These and other alternatives are included in the activities in EERE's Multi-Year RD&D Plan.

In the Hydrogen from Coal Multi-Year RD&D Plan, an alternative to delivery of pure gaseous hydrogen is delivery of mixtures of hydrogen and natural gas within the natural gas pipeline system. Research must be performed to evaluate the optimal concentrations at which hydrogen can be mixed with natural gas and used in various pipeline systems without causing embrittlement. Once delivered, hydrogen can be separated and polished to meet PEM fuel cell tolerances. Separation and polishing technologies must be developed to enable this pathway.

In addition to separation and polishing of the hydrogen/natural gas mixture, this low-carbon gaseous mixture can be used, as is, in engines and turbines that have been “tuned” to optimally process this lower-Btu, cleaner-burning mix, while emitting fewer harmful emissions.

These two end-use alternatives for transporting a hydrogen and natural gas mixture need to be more fully researched, with the impact on metallurgy demonstrated and optimal quantities of hydrogen in the mixture identified. Research must be completed on development of novel processes that can separate and polish hydrogen from the mixture when delivered to distributed sites. This research must be followed by bench-scale testing and then by proof-of-concept testing in pilot plants.

### 5.3.4 Technical Targets – Delivery

#### 5.3.4.1 Hydrogen/Natural Gas Mixture Technical Targets

**Technical Target:** Demonstrate the successful delivery of low-cost, optimal hydrogen/natural gas mixtures to distributed sites, followed by production to PEM-quality hydrogen.

### 5.3.5 Technical Barriers – Delivery

#### 5.3.5.1 Technical Barriers – Hydrogen/Natural Gas Mixtures

**A. Lack of Hydrogen Infrastructure Options Analysis.** A good understanding does not exist about options and trade-offs of hydrogen and hydrogen-carrier fuels, particularly coal-derived, from central and distributed facilities.

**B. Lack of Data Demonstrating the Effectiveness of Current Infrastructure to Deliver Hydrogen/Natural Gas Mixtures.** The use of existing natural gas pipelines to transport hydrogen and natural gas mixtures without causing pipeline embrittlement or leakage has to be explored, along with technologies to separate hydrogen from these mixtures.

**C. High Capital Cost of Pipeline Infrastructure.** A limited number of hydrogen pipelines currently exist; these are used primarily to transport hydrogen short distances to petrochemical facilities. Additionally, the construction of new pipelines requires a large amount of capital investment.

### 5.3.6 Technical Task Descriptions – Delivery

Table 12 lists the tasks for delivery technologies to be developed by the Hydrogen from Coal Program in coordination with EERE as appropriate.

**Table 12. Tasks for Delivery Technologies**

Task Number	Task Description	Barriers Addressed by Task
1	<p><i>Hydrogen-natural gas delivery mixtures</i></p> <ul style="list-style-type: none"> <li>➤ Analyze, investigate, and develop existing natural gas pipelines for transporting hydrogen-natural gas mixtures</li> <li>➤ Develop appropriate enabling technologies, such as separation technologies, for hydrogen-natural gas delivery mixtures</li> </ul>	A, B, C
2	<p><i>Demonstrations</i></p> <ul style="list-style-type: none"> <li>➤ Demonstrate the safe delivery of hydrogen-natural gas mixtures through natural gas pipelines, utilizing any enabling technologies, as appropriate</li> </ul>	A, B, C

## 5.4 Storage

NETL has unique capabilities in the area of R&D for hydrogen storage. The hydrogen storage program element within the Hydrogen from Coal MY RD&D Plan focuses on developing novel storage systems such as metal-organic frameworks. In addition, FE will use its expertise to identify and explore, in collaboration with EERE, new and novel approaches for on-board storage of hydrogen that meet the challenging goals and milestones shown below.

### 5.4.1 Goal and Milestones – Storage

**Goal:** By 2010, define and identify, in collaboration with EERE and the FE Office of Natural Gas and Petroleum Technology, viable hydrogen storage technologies for transportation and stationary applications.

**Milestones:**

- By 2005, develop and verify on-board hydrogen storage systems achieving 1.5 kWh/kg (4.5 weight percent), 1.2 kWh/L, and \$6/kWh.
- By 2010, develop and verify on-board hydrogen storage systems achieving 2 kWh/kg (6.0 weight percent), 1.5 kWh/L, and \$4/kWh.
- By 2015, develop and verify on-board hydrogen storage systems achieving 3 kWh/kg (9.0 weight percent), 2.7 kWh/L, and \$2/kWh.

### 5.4.2 Activities – Storage

Projects dealing with hydrogen storage or the development of materials with hydrogen storage applications that are funded by DOE and NETL are listed in the table below.

**Table 13. Some Relevant R&D Program Activities**

Category	Technology
Carbon Nanotubes	<ul style="list-style-type: none"> <li>• Hydrogen storage on carbon nanotubes – activation by oxidation</li> <li>• Carbon growth on supported catalysts – kinetics and mechanism</li> <li>• Synthesis of bulk amounts of double-walled carbon nanotubes</li> <li>• Pyrolytic mass production of carbon nanotubes using advanced catalysts</li> <li>• Carbon nanostructures from coal-derived liquid feedstocks</li> </ul>

Fossil Energy's storage research efforts have been focused on the potential for high surface area carbon nanotubes to meet the Department's goals for total weight percent storage. Thus far the research has not progressed to a point at which a definitive answer can be provided as to whether carbon materials can ever meet the Department's storage criteria. NETL, through its in-house research, has significantly helped to elucidate the challenges associated with storing significant amounts of hydrogen on these materials and provided a path for some limited additional research in this area in the short term.

The following excerpt from a paper by Bradley Bockrath, *et al.* (NETL) provides a glimpse of the nature future research may pursue on carbon materials.

*“Many techniques have been developed to activate conventional carbons over the years. Perhaps a similar array of methods can be employed to tailor the adsorption properties of nanotubes as well. This work has a theoretical as well as experimental dimension. ... [Researchers] at the University of Pittsburgh have been simulating the physisorption of hydrogen and other gases on nanotubes for several years. [They] are now modeling these experimental results. The more refined models take into account complex arrays of nanotubes and the introduction of functional groups. The Monte Carlo simulation for an array of tubes of similar dimensions as the purified sample that was used at NETL agrees with the experimental results quite well. The next step is to identify the physical and chemical features of a nanotube array that would lead to the result obtained with the carbon dioxide activated materials. This coordinated approach leads to the design of better experiments both in the laboratory and on the computer.”*

In addition to work that NETL has performed on improving the storage capacity of nanotube materials, their initial exploratory work on metal organics is showing promise as potential storage materials for hydrogen.

### 5.4.3 Technologies – Storage

Carbon atoms can bond to themselves to form extremely strong, two-dimensional sheets. When arranged in a honeycomb pattern, these sheets form a very stable, strong, yet flexible material known as graphite. These two-dimensional sheets can be folded and shaped into three-dimensional structures such as ball-shaped fullerenes or nanotubes. Carbon nanotubes are extremely strong, but also possess interesting electrical properties that can make a nanotube behave as a semiconductor or a metal, depending upon how the nanotube is rolled. To date, research has shown that hydrogen storage capabilities for carbon nanotubes are limited and do not achieve the requirements necessary for on-board storage systems. Some additional theoretical and experimental work will be directed over the short-term toward providing sufficient information to base a decision for continuing research on carbon-based materials.

There are other hydrogen storage technologies, such as compressed and liquefied gas storage and chemical and metal hydrides. The Hydrogen, Fuel Cells, and Infrastructure Technologies Program within EERE is investigating many of these technologies. The Hydrogen from Coal Program will coordinate activities with EERE, and will investigate other materials; one possibility is metal organic frameworks for novel hydrogen storage. Crystalline metal-organic frameworks represent one advanced material that has potential for hydrogen storage. These materials have cubic cavities of uniform size and internal structure. Furthermore, the preparation of metal-organic frameworks is simple, inexpensive, and of high yield. Initial experiments on these materials have shown potential to meet DOE's targets for hydrogen storage; however, more research on these and other novel storage materials is required to better understand and develop this technology.

#### 5.4.4 Technical Targets – Storage

The technical targets in this section were developed by EERE and also are included in the Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year RD&D Plan. These technology targets represent the status of the technology after completion of research and development, but prior to technology validation.

Table 14 information is from EERE's Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year RD&D Plan, Table 3.3.2 Technical Targets: DOE's Hydrogen Storage System Targets (p. 3-45)

**Table 14. Hydrogen Storage Technical Targets**

Performance Criteria	Units	2005	2010	2015
Usable, specific-energy from H <sub>2</sub> (net useful energy/max system mass) <sup>a</sup>	kWh/kg (kg H <sub>2</sub> /kg)	1.5 (0.045)	2 (0.06)	3 (0.09)
Usable energy density from H <sub>2</sub> (net useful energy/max system volume)	kWh/L (kg H <sub>2</sub> /L)	1.2 (0.036)	1.5 (0.045)	2.7 (0.081)
Storage system cost <sup>b</sup>	\$/kWh net (\$/kg H <sub>2</sub> )	6 (200)	4 (133)	2 (67)

<sup>a</sup> Generally the full mass (including hydrogen) is used; for systems that gain weight, the highest mass during discharge is used.

<sup>b</sup> 2003 US\$; total cost includes any component replacement if needed over 15 years or 150,000-mile life.

#### 5.4.5 Technical Barriers – Storage

**A. High Cost.** The cost of on-board hydrogen storage systems is too high, particularly compared to conventional storage systems for petroleum fuels. Low-cost materials and components for hydrogen storage systems are needed, as well as low-cost, high-volume manufacturing methods.

**B. Excessive Weight and Volume.** The weight and volume of hydrogen storage systems that can be carried onboard a vehicle is presently much too low, resulting in inadequate vehicle range compared to conventional petroleum-fueled vehicles. Materials and components are needed that are compact, lightweight, and would permit greater storage capacity of hydrogen per unit weight of storage media, enabling greater than a 300-mile range in all light-duty vehicle platforms.

**C. Low Efficiency.** Energy efficiency is a challenge for all hydrogen storage approaches. For reversible solid-state materials, the energy required to move hydrogen in and out is an issue. Lifecycle energy efficiency is a challenge for chemical hydride storage in which the by-product is regenerated off-board. In addition, the energy associated with compression and liquefaction must be considered for compressed and liquid hydrogen technologies.

**D. Lack of Durability.** Durability of hydrogen storage systems is inadequate to meet automobile manufacturer's requirements. Materials and components are needed that allow hydrogen storage systems with a lifetime of 1,500 cycles.

**E. Excessive Refueling Time.** Refueling times are too long. Hydrogen storage systems need to be developed with refueling times of three to five minutes, over the lifetime of the system.



**F. Lack of Codes and Standards.** Applicable codes and standards for hydrogen storage systems and interface technologies, which will facilitate implementation/commercialization and ensure safety and public acceptance, have not been established. Standardized hardware and operating procedures, and applicable codes and standards are required.

**G. Lack of Life Cycle and Efficiency Analyses.** There are no analyses of the full life cycle cost and efficiency for hydrogen storage systems.

#### 5.4.6 Technical Task Descriptions – Storage

Table 15 lists the tasks for development of hydrogen storage technologies.

**Table 15. Tasks for Hydrogen Storage Technologies**

<b>Task Number</b>	<b>Task Description</b>	<b>Barriers Addressed by Task</b>
1	<p><i>Hydrogen Storage Materials R&amp;D</i></p> <ul style="list-style-type: none"> <li>➤ Develop promising storage materials to meet targets</li> <li>➤ Verify most promising storage materials to meet targets</li> </ul>	A through G
2	<p><i>Advanced Concepts R&amp;D</i></p> <ul style="list-style-type: none"> <li>➤ Develop and characterize advanced storage concepts that meet 2015 targets</li> </ul>	A through G

## 5.5 Utilization

Hydrogen could be used directly as a fuel for advanced engine and vehicle types that could be designed to use gaseous fuels, either hydrogen alone or as a hydrogen-natural gas mixture. The benefit of this pathway is that it represents a nearer-term, low-emission strategy that could result in an acceleration of hydrogen demand into the economy. Although the DOE is focusing its research on fuel cell-powered vehicles in its FreedomCAR program, fuel cell costs must be significantly reduced before they achieve widespread market penetration. Blending hydrogen with natural gas and its use in advanced engine types, such as early development, non-commercial homogeneously charged compression ignition (HCCI) engines, could enable a new, low emission demand for hydrogen. Conceptually, as the hydrogen infrastructure expands in the mid-term, these same engine systems, with further retrofits and advanced engine systems now being developed, could be used in the mid-term with 100 percent hydrogen.

Natural gas has become the fuel of choice for many transit vehicle operators. However, when compared to conventional diesel fuel emissions of primary pollutants and greenhouse gases, natural gas may not provide the levels of advantage that were initially anticipated; in some fleets that have been studied, the emissions actually can be greater. One study of natural gas-fueled heavy-duty vehicles indicated that methane emissions led to higher carbon dioxide-equivalent emissions than the diesel-fueled vehicles. There is room for improvement, potentially through displacement of some of the natural gas with hydrogen.

Combustion of mixtures of hydrogen with methane should lead to lower emissions than use of natural gas alone, while providing enhancements to the combustion process that permit recovery of the power and energy consumption penalties associated with natural gas. Two broad areas of research need to be addressed: 1) optimizing the ratio of hydrogen to methane in the fuel mixture, based on emissions and engine performance, and coordinated with research being performed on delivery and storage of hydrogen/methane mixtures; and 2) computational and laboratory research on the use of hydrogen/methane mixtures in advanced engines that offer step-out advantages in emissions and performance.

In summary, this activity may enable hydrogen from coal to be delivered along with natural gas and be used in internal combustion engines, thus assisting the nation in its transition from liquid fuels to hydrogen.

### 5.5.1 Goal and Milestones – Utilization

**Goal:** By 2010, develop hydrogen and/or hydrogen/natural gas fuel protocol and engine modifications for advanced engine systems needed to achieve optimum performance and lowest emissions.

**Milestones:**

- By 2006: Modify and optimize advanced engine types to operate on hydrogen and/or hydrogen-natural gas mixtures.
- By 2009: Demonstrate advanced engine types that operate on hydrogen and/or hydrogen-natural gas mixtures in vehicles and stationary applications.

## 5.5.2 Activities – Utilization

The Hydrogen from Coal Program has recently initiated this RD&D element; therefore major accomplishments have not yet been achieved. It is anticipated that activity will be implemented in this program element in FY 2004.

## 5.5.3 Technologies – Utilization

### 5.5.3.1 Advanced Engine Types

Fuel cells are the optimal choice for utilization of hydrogen in transportation and stationary applications. However, because fuel cell technology has to overcome significant barriers before major commercialization, the modification and optimization of current technologies, such as advanced engine types (e.g., homogeneously charged compression ignition (HCCI) engines) may act as interim technologies until fuel cells are advanced to the point of commercial viability.

Hydrogen used in advanced engines can achieve near-zero emissions. The only minor pollutant emission is NO<sub>x</sub>, due to the nature of the combustion process. However, the amount of NO<sub>x</sub> emitted is quite low, and the prospect of zero emissions of CO<sub>2</sub> and the use of hydrogen produced from domestic resources offer considerable advantages. Research is needed to develop and optimize advanced engines for hydrogen use to minimize emissions of NO<sub>x</sub> while maximizing the distance traveled by vehicles between refueling trips.

## 5.5.4 Technical Targets – Utilization

The technical targets in Table 16 represent the status of the technology after completion of research and development, and include demonstration of the technology in heavy-duty advanced engines. The timing of the RD&D is provided in the Gantt charts in Figures 11 and 12.

**Table 16. Hydrogen Utilization Technical Targets**

Performance Criteria (Based on 35% H <sub>2</sub> , 65% Methane Mixture)	Units	Current Status (100% Methane) <sup>(a)</sup>	2010 Target (50% reduction)	2015 Target (75% reduction)
Emissions				
Total Hydrocarbons	g/mile	20.04	10	5
Non-CH <sub>4</sub> Hydrocarbons	g/mile	2.19	1.1	0.55
NO <sub>x</sub>	g/mile	9.06	4.5	4.25
CO	g/mile	0.34	0.17	0.09
CO <sub>2</sub>	g/mile	1,690	1,100	1,100
PM	g/mile	0.02	0.01	0.005
Efficiency/Fuel Economy		Reference	No more than natural gas	No more than natural gas
Cost		Reference	No more than natural gas	No more than natural gas

<sup>(a)</sup> McCormick, Graboski, Alleman, Herring and Nelson, "In-Use Emissions from Natural Gas Fueled Heavy-Duty Vehicles," Society of Automotive Engineers Technical Paper No. 1999-01-1507, presented at the 1999 Spring Fuels and Lubricants Meeting, Dearborn, MI.

### 5.5.5 Technical Barriers – Utilization

**A. High Cost.** The cost of modifying engines to operate on hydrogen or hydrogen-natural gas mixtures must be evaluated. If performance and cost are competitive with current technologies, engines that operate on hydrogen or hydrogen-natural gas mixtures may be a plausible interim option until fuel cell technology is fully developed.

**B. Lack of Optimized Design and Operation.** The low heating value of a hydrogen and natural gas mixture will require adjustments in the operation and design of engines.

### 5.5.6 Technical Task Descriptions – Utilization

Table 17 describes the tasks for development of hydrogen utilization technologies.

**Table 17. Tasks for Hydrogen Utilization Technologies**

<b>Task Number</b>	<b>Task Description</b>	<b>Barriers Addressed by Task</b>
1	<p><i>Advanced engines research</i></p> <ul style="list-style-type: none"> <li>➤ Modify and optimize advanced engine systems to operate on hydrogen or hydrogen-natural gas mixtures</li> <li>➤ Demonstrate optimized engines in vehicles or stationary power systems</li> <li>➤ Evaluate and compare the emissions and economics of advanced engines operating on hydrogen or hydrogen-natural gas mixtures to conventional technologies</li> </ul>	A, B

## 6. Implementation Plan

Execution and continued development of the Hydrogen from Coal Program requires proper management controls to ensure that the program is progressing toward its goals and objectives. Annual merit review meetings of funded projects should be held to report progress and provide program managers the opportunity to evaluate progress toward program goals and milestones. The MYP will be periodically reviewed and updated to reflect changes in technical and economic assumptions. Periodic reviews will provide program managers the opportunity to update the goals and objectives of the MYP by utilizing the most current data generated by the program activities.

### 6.1 Coordination With Other DOE/Federal Programs (Associated Programs): Jointly Funded Projects

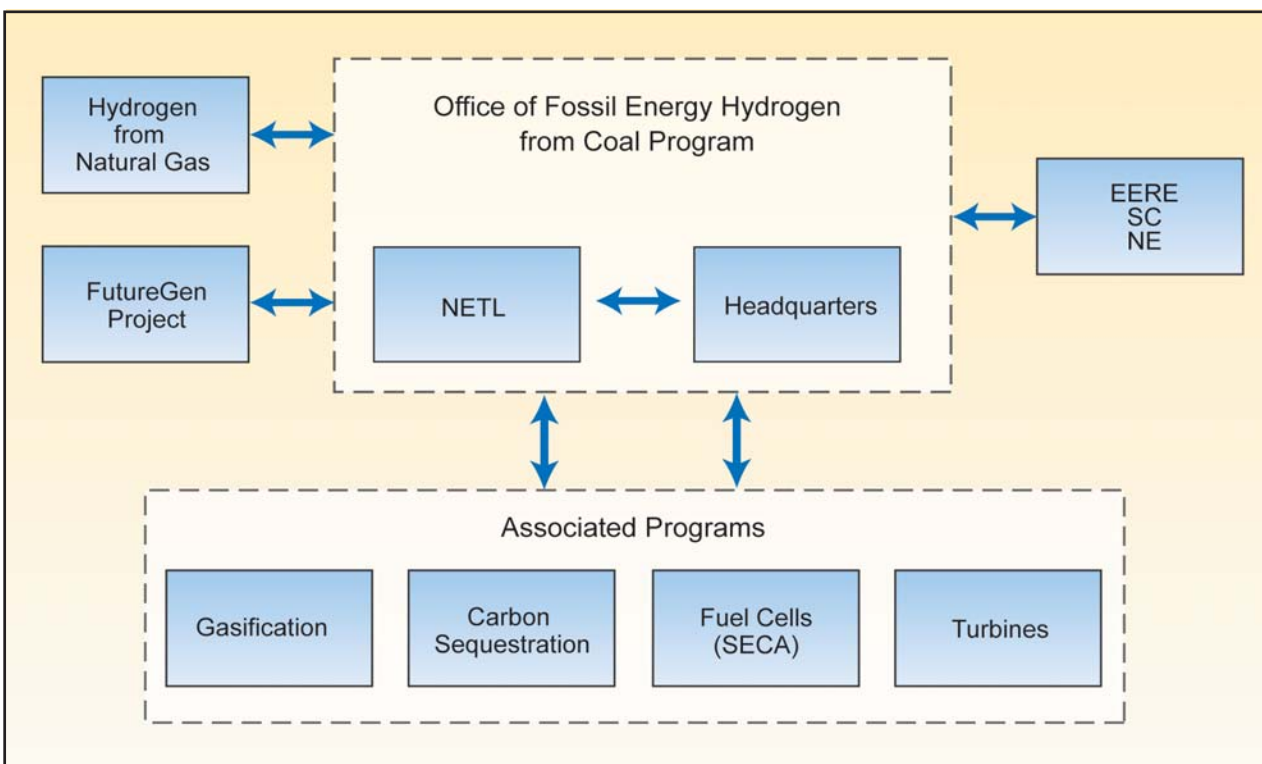
The successful development of low-cost, affordable hydrogen production from fossil fuels, with sequestration of carbon dioxide, is dependent on technologies being developed in a number of ongoing associated RD&D programs within the Office of Fossil Energy. These technologies are needed for:

- Carbon dioxide 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



Figure 14 shows the various programs and projects with which the Hydrogen from Coal Program will need to coordinate.

**Figure 14. Coordination of the Hydrogen from Coal Program with Associated Programs, the FutureGen Project, and EERE's Hydrogen Program**



The FE hydrogen program also will need to coordinate its activities with the hydrogen programs in the Office of Energy Efficiency and Renewable Energy (EERE), the Office of Nuclear Energy (NE), and the Office of Science (SC) within DOE. Coordination of efforts and sharing of information and experience will help ensure the successful transition to a hydrogen energy system.

## 6.2 Next Steps

This RD&D Plan will be updated periodically based on RD&D progress and funding appropriations. Prior to FY 2004, the Hydrogen from Coal Program did not exist, although some related technologies were included in other programs, such as the coal gasification, advanced research for coal power systems, and carbon sequestration programs. The RD&D projects that will be included in the Hydrogen from Coal Program will be selected from proposals submitted through competitive solicitations – some of which may be co-sponsored with other government offices that share goals consistent with this RD&D Plan. There also will be, where appropriate, cost-sharing of existing projects currently within the gasification and sequestration program areas. In the future, as hydrogen from coal technologies mature, additional input from and technical and merit reviews by academia, industry, and other stakeholders will enable updates to the technical targets and sub-program elements in this Plan. Furthermore, go/no-go decisions will be made on technologies to ensure that projects included in the program are making sufficient technological progress to warrant their continuation.

## 7. Appendix

### 7.1 Acronyms

#### Department of Energy Acronyms/Offices

DOE	Department of Energy
EERE	Office of Energy Efficiency and Renewable Energy
FE	Office of Fossil Energy
NE	Office of Nuclear Energy
NETL	National Energy Technology Laboratory
OC&PS	Office of Coal and Power Systems
ORNL	Oak Ridge National Laboratory
SC	Office of Science

#### General Acronyms

$\Delta P$	Delta P (change in pressure)
AFDU	Alternative Fuels Development Unit
APCI	Air Products and Chemicals, Inc.
AR	As received
bbbl	Barrel
CCPI	Clean Coal Power Initiative
CVD	Chemical vapor deposition
FT	Fischer-Tropsch
FCV	Fuel Cell Vehicle
HCCI	Homogeneously charged compression ignition
HHV	Higher Heating Value
ICEV	Internal Combustion Engine Vehicle
kg	Kilogram
l	Liter
LPMEOH	Liquid Phase Methanol (plant)
MMBtu	Million Btu
MMscfd	Million standard cubic feet per day
MW	Megawatts

MYP	Multi-Year Plan
NEP	National Energy Policy
NGCC	Natural Gas Combined Cycle (power plant)
nm	Nanometer
ppb	Parts per billion
PSA	Pressure Swing Adsorption
R&D	Research and Development
RD&D	Research, Development, and Demonstration
RSP	Required Selling Price
SOFC	Solid Oxide Fuel Cell
WGS	Water-Gas Shift

**Chemical Symbols/Names**

Ag	Silver
CO	Carbon Monoxide
Co	Cobalt
CO <sub>2</sub>	Carbon Dioxide
COS	Carbonyl Sulfide
Cr	Chromium
Cu	Copper
DME	Dimethyl ether
Fe	Iron
Fe <sub>3</sub> O <sub>4</sub>	Synthetic Iron Oxide (Magnetite or Iron Oxide Black)
H <sub>2</sub>	Hydrogen
H <sub>2</sub> S	Hydrogen Sulfide
HCl	Hydrogen Chloride (Hydrochloric Acid)
HCN	Hydrogen Cyanide
Mo	Molybdenum
N <sub>2</sub>	Nitrogen
NH <sub>3</sub>	Ammonia
O <sub>2</sub>	Oxygen
Pd	Palladium

## 7.2 Contacts

### **C. Lowell Miller, Ph.D**

Office of Fossil Energy (FE-24)  
U.S. Department of Energy  
Washington, DC 20585  
301-903-9451  
lowell.miller@hq.doe.gov

### **Edward Schmetz**

Office of Fossil Energy (FE-24)  
U.S. Department of Energy  
19901 Germantown Road  
Germantown, MD 20874  
301-903-3931  
edward.schmetz@hq.doe.gov

### **John Winslow**

National Energy Technology Laboratory  
P.O. Box 10940  
U.S. Department of Energy  
Pittsburg, PA 15236  
412-386-6072  
john.winslow@netl.doe.gov