HYDROGEN PRODUCTION ROADMAP

Technology Pathways to the Future

January 2009

FreedomCAR & Fuel Partnership

Hydrogen Production Technical Team

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This roadmap was created by the Hydrogen Production Technical Team (HPTT) of the FreedomCAR and Fuel Partnership. This is a partnership of industry's U.S. Council for Automotive Research (USCAR), energy companies and the U.S. Department of Energy (DOE) to advance technologies that enable reduced oil consumption and increased energy efficiency in passenger vehicles. The Partnership focuses on the pre-competitive, high-risk research needed to develop the component and infrastructure technologies necessary to enable a full range of affordable cars and light trucks, and the fueling infrastructure for them in order to reduce the dependence of the nation's personal transportation system on imported oil and minimize harmful vehicle emissions, without sacrificing freedom of mobility and freedom of vehicle choice.

In FreedomCAR, "CAR" stands for cooperative automotive research. The word "Freedom" frames the partnership's principles, which are freedom: from dependence on imported oil; pollutant emissions; for Americans to choose the kind of vehicle they want to drive, and to drive where they want, when they want; and to obtain fuel affordably and conveniently.

A major thrust of the Partnership is to examine and advance collaborative research and development (R&D) of technologies to enable high volume production of affordable hydrogen fuel cell vehicles and the national hydrogen infrastructure to support them. The Partnership also examines and advances R&D for other advanced automotive technologies through the continuation of key enabling research on advanced internal combustion engines and emission control systems; lightweight materials; power electronics and motor development; high-power/energy battery development; and alternative fuels. Each of these advanced technologies also has the potential to dramatically reduce oil consumption and environmental impacts in conventional, hybrid, and/or hydrogen fuel cell vehicles.

The FreedomCAR and Fuel Partnership operates through technical teams of scientists and engineers with technology-specific expertise from USCAR member companies, energy partner member companies, national laboratories, and DOE technology development managers. Each team is responsible for developing R&D plans and roadmaps, identifying data gaps and R&D needs, reviewing research results, and evaluating the technical progress of the FreedomCAR and Fuel Partnership toward meeting the established research goals in their respective technical areas.

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Developed by the

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Contents

3.2. Barriers

List of Exhibits

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Disclaimer

Roadmap Introduction

This Hydrogen Production roadmap was constructed by the Hydrogen Production Technical Team (HPTT) of the FreedomCAR and Fuel Partnership to identify the key challenges and priority research and development (R&D) needs associated with various hydrogen fuel production technologies. The partnership is a collaborative effort by industry's U.S. Council for Automotive Research (USCAR), energy companies, and the U.S. Department of Energy (DOE) to advance some of the most promising hydrogen fuel production technologies.

The aim of the roadmap is to identify research pathways leading to hydrogen production technologies that produce near-zero net greenhouse gas (GHG) emissions[1] and use renewable energy sources, nuclear energy, and coal (with carbon capture and storage). To help ensure an adequate supply of clean energy to meet global needs, energy efficiency is an important target for these production technologies. This roadmap focuses on the initial development of the technologies, identifies obstacles to be avoided or minimized, and describes activities by various DOE offices to address the key challenges.[2]

Roadmap Introduction

Hydrogen Production
- DOE R&D Leadership
- Types of Technologies
- Production Scales and Locales

Seven Major Technology Pathways
- Timeline, Feedstocks, and Energy Sources

Key Roadmap Elements
- DOE Cost Goals
- Common Technology Barriers
- Community Barriers
- Critical Technology Needs

Path Forward
Appendices

The goal of the roadmap is to facilitate development of commercial hydrogen production via various technology pathways in the near and long term. DOE's current hydrogen cost targets are $3.00 per gallon of gasoline equivalent[3] (gge) at fueling stations and $2.00 per gge at a central facility (also known as the "plant" gate).

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[1] Assumptions and analyses used in calculating GHG emissions are shown in Report 9002, available online at http://www.hydrogen.energy.gov/program_records.html. Accessed 8 May 2009.

[2] Appendix D shows current projects; for updates, see http://www.hydrogen.energy.gov/annual_review.html and http://www.hydrogen.energy.gov/annual_progress.html. Accessed 8 May 2009.

[3] The energy content of a gallon of gasoline and a kilogram of hydrogen are approximately equal on a lower heating value basis; a kilogram of hydrogen is approximately equal to a gallon of gasoline equivalent (gge) on an energy content basis.

HYDROGEN PRODUCTION

DOE R&D LEADERSHIP

The mission of the DOE Hydrogen Program is to work with industry, government, and academia to research, develop, and validate hydrogen production, storage, and fuel cell technologies to overcome the barriers to commercialization of these technologies. The program is organized into distinct sub-programs that address the specific research and supporting activities needed to overcome the barriers to hydrogen and fuel cell commercialization including: hydrogen production; hydrogen storage; conversion/fuel cells; applications/technology validation; safety, codes, and standards; education; basic research; and systems analysis and integration.

Within the DOE Hydrogen Program, work on hydrogen production technologies integrates basic and applied research, technology development and demonstration, and other supporting activities. To adequately address the diverse range of technologies and feedstocks, the program is closely coordinated with activities within the DOE Offices of Energy Efficiency and Renewable Energy (EERE), Nuclear Energy (NE), Fossil Energy (FE), and Science (SC). The Department of Transportation (DOT) also participates in activities involving codes and standards development, infrastructure safety, and hydrogen vehicle safety. The key DOE offices involved in hydrogen production R&D are shown in Exhibit I.1.

Exhibit I.1 DOE Partners in Hydrogen Production R&D

Role	Office
Direct and Integrate Hydrogen Production R&D Activities	Hydrogen Fuel Cells & Infrastructure Technologies Program (HFCIT), EERE
Hydrogen from Natural Gas	EERE and FE
Hydrogen from Coal	FE
Hydrogen from Nuclear Power	NE
Hydrogen from Renewable Resources	Biomass Program, Wind Program, HFCIT, Geothermal Technologies Program, and Solar Energy Program
Basic Research	SC

TYPES OF TECHNOLOGIES

Thermal Processes Some thermal processes use the energy contained in resources, such as natural gas, coal, or biomass, to release the hydrogen that is part of their molecular structure. In other processes, heat is used in combination with closed chemical cycles to produce hydrogen from feedstocks, such as water. These latter processes are known as "thermochemical" processes. Thermal processes include reforming of natural gas, gasification of coal, gasification of biomass, reforming of renewable liquid fuels, and high-temperature water splitting.

Electrolytic Processes Electrolytic processes use electricity to split water into hydrogen and oxygen. Hydrogen produced via electrolysis can result in zero GHG emissions, depending on the source of the electricity used. The source of the required electricity—including its cost and efficiency, as well as emissions resulting from electricity generation—must be considered when evaluating the benefits of hydrogen production via electrolysis. The two electrolysis pathways of greatest interest for wide-scale hydrogen production are electrolysis using low- or zero-carbon sources of electricity (such as wind or solar) and high-temperature nuclear electrolysis.

Photolytic Processes Photolytic processes use light energy to split water into hydrogen and oxygen. These processes offer long-term potential for sustainable hydrogen production with low environmental impact. Two main categories are photobiological, in which the metabolism of certain algae or cyanobacteria are harnessed to do the splitting, and photoelectrochemical, in which a special class of semiconductors absorb sunlight and use the light energy to completely separate water molecules into hydrogen and oxygen.

PRODUCTION SCALES AND LOCALES

Hydrogen can be produced in small, medium, and larger scale facilities. Small-scale (distributed) facilities would produce from 100 to 1,500 kilograms (kg) of hydrogen per day at fueling stations. Medium-scale (also known as semi-central or city-gate) facilities would produce from 1,500 to 50,000 kg per day on the outskirts of cities. The largest (central) facilities would produce more than 50,000 kg of hydrogen per day. Co-production facilities, which would combine the production of hydrogen, fuel, heat, and electric power, are also being explored.

Distributed Production Distributed production of hydrogen may be the most feasible approach for introducing hydrogen as an energy carrier in the near term. This approach requires less capital investment for the smaller capacity of hydrogen needed initially, and it does not require a substantial hydrogen transport and delivery infrastructure.

Two types of distributed hydrogen production technologies that show promise for near-term development are (1) reforming of natural gas or liquid fuels, including bio-derived liquids, such as ethanol and bio-oil, and (2) small-scale water electrolysis. Small-scale natural gas reformers are the closest to meeting DOE’s hydrogen production cost targets.

Research will focus on applying the latest small-scale natural gas reforming systems to reform renewable liquid feedstocks at a competitive hydrogen cost. The second research focus is on small-scale electrolyzers for splitting water. To be competitive, the cost of electricity used for this production process needs to be very low. Use of a renewable energy source for the electricity presents the opportunity for electrolytic hydrogen production without carbon emissions.

Semi-Central/City-Gate Production Hydrogen may be produced in semi-central facilities, which offer intermediate production capacity, typically on the outskirts of urban areas. These facilities provide some economies of scale and are relatively close to refueling sites, thus reducing the cost and infrastructure for hydrogen delivery. Several technologies are well suited to this scale of production, including wind- or solar-driven electrolysis, reforming of renewable bio-derived liquids, natural gas reforming, and photoelectrochemical and biological hydrogen production.

Central Production Large hydrogen production facilities will be needed in the long term to meet major increases in hydrogen fuel demand. DOE is pursuing central production of hydrogen to take advantage of economies of scale and improved management of GHG emissions through strategies like carbon capture and storage. Central production of hydrogen will require development of a robust hydrogen distribution and delivery infrastructure. Central production also provides the capability to produce hydrogen from a variety of resources: fossil, nuclear, and renewable.

Seven Major Technology Pathways

This *Hydrogen Production Roadmap* addresses seven promising hydrogen production pathways. These pathways are summarized in Exhibit I.2 and discussed in detail in separate chapters of the document.

Exhibit I.2 Major Hydrogen Production Technology Pathways[4]

Distributed Natural Gas Reforming	Natural gas reforming is employed on a large scale to produce much of the commercial and industrial hydrogen used today. This roadmap identifies the technical barriers in scaling this technology down to the distributed generation scale. Distributed natural gas reforming is the most mature technology and closest to achieving the projected DOE hydrogen cost targets. To fully commercialize small-scale hydrogen production by natural gas reforming, additional development will be needed in areas that have not been addressed by DOE, including system integration, optimization, and technology validation.
Bio-Derived Liquids Reforming	Reforming of ethanol and other bio-derived liquids is similar to natural gas reforming but presents several unique issues, such as catalyst and water requirements. This technology is suitable for application in distributed and semi-central production. Technology readiness is expected by 2017.
Coal and Biomass Gasification	Gasification technologies can use coal, biomass, or a mixture of the two as their feed streams. Co-gasification of coal and biomass helps to address both the carbon issues associated with coal and the cost and supply issues associated with biomass. Coal gasification is suitable for central production, and biomass gasification is suitable for both central and semi-central production. Technology readiness is expected by 2017.
Water Electrolysis	Water electrolysis uses existing water and electricity infrastructures to generate hydrogen on demand. In addition to near-term distributed generation, larger central production via wind power is being studied. Technology readiness is expected by 2017.
Thermo-chemical Production	High-temperature, thermochemical water splitting is an immature technology that holds the potential to produce only hydrogen and oxygen. EERE is developing thermochemical cycles with the thermal energy supplied by solar power, while NE is developing nuclear-driven thermochemical cycles using waste heat from the reactors. The technology is suitable for central production, and technology readiness is expected by 2017.
Photoelectro-chemical Hydrogen Production	Photoelectrochemical direct water splitting is similar to photovoltaics in that it uses semi-conductor material to collect the sun's energy. Instead of producing electrons, however, it produces hydrogen and oxygen. The technology requires long-term development and is suitable for semi-central and central hydrogen production. Technology readiness is expected beyond 2018.
Biological Hydrogen Production	Biological hydrogen production uses microorganisms to produce hydrogen. Four main pathways constitute biological hydrogen production: photolytic (direct water splitting), photosynthetic (solar aided organic decomposition), fermentative (organic decomposition), and microbial-aided water electrolysis (microorganisms provide some of the power for water electrolysis).[5] The first viable biological pathway may combine some or all four of these technologies. The technology is suitable for semi-central and central hydrogen production. Technology readiness is expected beyond 2018.

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[4] Technology development target dates are dependent on funding.

[5] While fermentative and microbial-aided electrolysis are not strictly biological pathways, they fit best in this technology grouping.

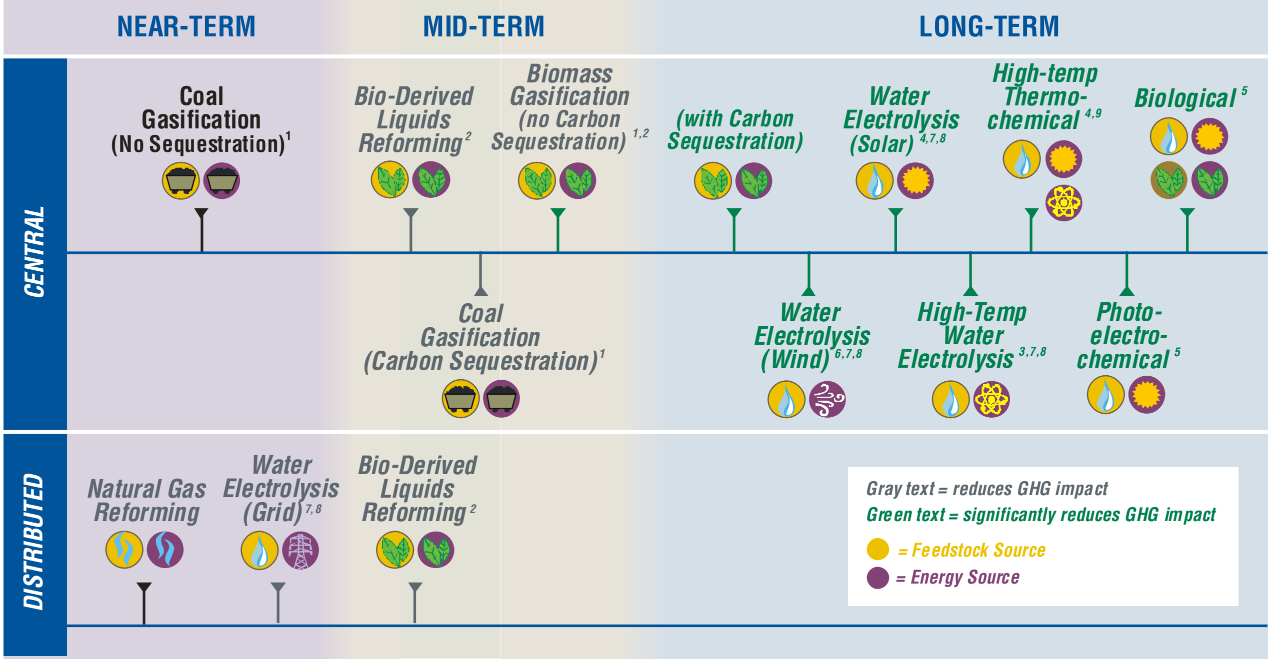
TIMELINE, FEEDSTOCKS, AND ENERGY SOURCES

All hydrogen production technologies discussed in this roadmap require further development prior to commercial use. While some sustainable technologies may be furthest from commercial readiness, all of these production pathways should improve hydrogen availability and affordability through reliance on domestic energy resources.

In the 21st century, our nation will deploy a range of hydrogen production technologies as allowed by progress in the R&D, infrastructure readiness, and demand. Some technologies will be cost-competitive for the transition period, while others are considered longer-term technologies.

Exhibit I.3 provides a broad overview of the general timeframes in which these technologies are expected to move into commercial production. The feedstocks, energy sources, and production scale for each technology option influence the time to market. For this reason, some technology options are subdivided on this timeline. The icons on the timeline reflect the feedstocks from which the technologies isolate the hydrogen (gold circles) and the energy sources used to power the process (maroon circles).

Exhibit I.3 Technology Pathway Development Timelines, Feedstocks, and Energy Sources for Hydrogen Production



Enabling technologies under development by

1 The Office of Fossil Energy
2 The Biomass Program
3 The Nuclear Hydrogen Initiative
4 The Solar Energy Technologies Program
5 The Office of Basic Energy Sciences
6 The Wind Program
7 The Geothermal Technologies Program
8 The Hydrogen Utility Group
9 The International Partnership for a Hydrogen Economy

KEY ROADMAP ELEMENTS

Each chapter in this roadmap describes the technology pathway, the DOE cost targets, the barriers to address, and critical technology needs to achieving success.

DOE COST GOALS

The overarching technical challenge to hydrogen production is reducing cost. As of 2006, hydrogen cost is projected to be \$3 per gge[6] (untaxed) dispensed to a car at a fueling station, based on distributed production using natural gas. The DOE cost targets shown in Exhibit I.4 are based upon the Energy Information Administration's (EIA's) forecast of gasoline cost in 2015 and the fuel economy of hydrogen fuel cell vehicles (FCVs) relative to that of advanced vehicle technology, as projected for 2015 in the *NRC Hydrogen Economy Report*. The methodology used ensures that consumer operating cost (\$/mile) for a hydrogen fuel cell vehicle will be equal to or less than that for a competitive gasoline-fueled internal combustion engine (ICE) vehicle in 2015. All costs are reported in 2005 dollars and assume 2005 costs for the feedstocks (as reported by the DOE EIA) and for manufacturing. DOE will periodically reassess these targets based on updated gasoline cost projections and vehicle fuel economy assumptions.

Exhibit I.4 Derivation of DOE Cost Goals

Mechanics:

$$\text{H2 Cost } (\$/\text{gge}) \leq (\text{EIA Gasoline Price in 2015}) \left(\frac{\text{Fuel Economy H2 FCV}}{\text{Fuel Economy Competitive Vehicle}} \right)$$

Input	Cost (per gallon untaxed, 2005 \$)	Source
Gasoline price projection for 2015	\$1.26	*EIA Annual Energy Outlook, 2005*
Ratio of FCV fuel economy to evolved gasoline ICE	\$2.40	*NRC H_2 Economy Report*
Ratio of FCV fuel economy to gasoline hybrid	\$1.66	*NRC H_2 Economy Report*

Result: Hydrogen Cost Goal Range = \$2.00 to \$3.00/gge

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[6] This cost range results in equivalent fuel cost per mile for a hydrogen fuel cell vehicle compared to gasoline internal combustion engine and gasoline hybrid vehicles. The full explanation and basis can be found in DOE Record 5013 (see www.hydrogen.energy.gov/program_records.html). All costs, unless otherwise noted, are in 2005 dollars. The 2006 price of \$3.00/gge is confirmed by the 2006 Independent Assessment of the Status of Distributed Natural Gas Reforming (www.hydrogen.energy.gov/peer_review_production.html).

DOE’s cost goals for hydrogen production are quantified in Exhibit I.5 as the cost of dispensed hydrogen.

Exhibit I.5 DOE Hydrogen Production Cost Reduction Goals ($/gge dispensed)[7]

Overall:
Reduce the cost of hydrogen to $2.00-$3.00/gge dispensed at the pump.
This goal is independent of the technology pathway.

By 2010	$2.50/gge	Distributed production of hydrogen from natural gas[8]
By 2012	$3.80/gge	Distributed production of hydrogen from biomass-derived renewable liquids[9]
	$3.70/gge	Distributed production of hydrogen from distributed water electrolysis[10]
	$4.80/gge	Central production of hydrogen from wind water electrolysis[11]
	<$3.30/gge	Central production of hydrogen from biomass gasification[12]
By 2015	$2.00/gge	Distributed hydrogen production from natural gas[8]
By 2017	<$3.00/gge	Distributed production of hydrogen from biomass-derived renewable liquids[9]
	<$3.00/gge	Distributed production of hydrogen from water electrolysis[10]
	<$3.00/gge	Central production of hydrogen from wind water electrolysis[11]
	$2.10/gge	Central production of hydrogen from biomass gasification[12]
	<$4.50/gge	Central production of hydrogen from nuclear thermochemical or electrolysis

All of the cost and technology advances described in this roadmap must take place within the constraints of the regulatory environment, limited physical space, and other resource limitations.

COMMON TECHNOLOGY BARRIERS

Numerous technical barriers remain to be conquered. Many are unique to one technology pathway, but quite a few are cross-cutting. Each chapter explores the barriers specific to a technology pathway and identifies the most critical technology needs. Those barriers that are common to multiple production technologies are described here.

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[7] Future funding levels may accelerate or decelerate commercialization targets.
[8] Assumed natural gas cost of $5.24/MMBTU (LHV)
[9] Assumed ethanol cost of $1.07/gallon with no tax credit
[10] Assumed electricity cost of $0.039/kWh
[11] Assumed selling electricity as a by-product
[12] Assumed biomass cost of $41/dry metric ton

Hydrogen Quality

Hydrogen purity is a major issue for hydrogen destined for use in fuel cells aboard vehicles. The problem arises because the platinum catalysts used in most vehicle fuel cells can be easily "poisoned" by any impurities in the hydrogen, ultimately rendering them ineffective. Hydrogen production technologies must therefore either produce high-purity hydrogen outright or incorporate additional purification processes.

Requirements for the quality of hydrogen to be used in fuel cell vehicles are becoming increasingly stringent.[13] These stricter requirements represent a major hurdle for technology and production costs, and they add a further cost burden in the form of support and equipment for quality assurance. In addition, no standard test methods are readily available to detect some of the contaminant species at the prescribed level. Solutions for this issue continue to be a research priority.

Control and Safety

All hydrogen production technologies will be required to meet the strictest safety requirements. The permitting process relies on proven technology reliability and safety. Production units for placement at refueling stations, in particular, must be designed to operate with minimal manual assistance. This capability will use back-up and fail-safe modes, remote monitoring, and infrequent maintenance schedules.

Capital and Operating Costs

To offer a competitive energy alternative, hydrogen must be economically attractive to American consumers. Capital costs for many hydrogen production technologies today remain well above the targets. These costs should drop as developers apply the principles of design for manufacturing, identify better materials, and move into larger-scale manufacturing. Operating costs will similarly decline as equipment developers identify improved materials, consolidate processing steps, and otherwise enhance equipment performance and integration.

Codes, Standards, and Regulations

The establishment and adoption of codes and standards is performed on a national level through code and standard development organizations and federal agencies. On the state level, state legislatures and various agencies determine which codes and standards will be adopted. Local Authorities Having Jurisdiction (AHJ), of which there are approximately 144,000 in the United States, can further increase the regulatory requirements through adoption of more stringent codes and standards than those adopted into state regulatory law. In addition, for permit approvals, local communities can provide input on whether a new technology should be installed and operated in or around their neighborhoods.

COMMUNITY BARRIERS

Technology advances require accompanying outreach efforts to encourage public acceptance of fuel cell vehicles and fueling stations. Community barriers that are shared by all production pathways include regulations, codes and standards, and education to assure wide public acceptance of hydrogen fuel.

Codes, Standards, and Regulations

Inspection, testing, certification, and permitting necessary to move new hydrogen production technologies into commercial use will require amending existing and creating new regulations,

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[13] A draft version of current hydrogen quality specifications is available through SAE TIR J2719.

codes, and standards. This process will require extensive outreach to familiarize regulatory agencies with the technologies.

Regulations, codes, and standards have been in place for many years to address the public safety issues associated with large-scale, centralized hydrogen production through natural gas reforming. Nevertheless, compact reformers at fueling stations represent a new application and product design. Regulations, codes, and standards must be created or amended to cover all fabrication, inspection, testing, certification, and permitting prior to commercial adoption.

Exhibit I.6 lists *some* of the currently applicable codes and standards for design, fabrication, testing, certification, permitting, and installation of natural gas compact reformers for distributed hydrogen production.[14] The regulations for hydrogen production (reforming) from bio-derived liquids, electrolysis, other technologies, and hydrogen storage will likely be derived from current natural gas reforming regulations. Additional issues relate to on-site feedstock storage, gas emissions, and waste (solid/liquid) storage and disposal. Some areas not effectively covered by current regulations, codes, and standards include the following:

- **Operations and Maintenance Plans** are dependent upon the standards set by individual companies. A minimum standard is needed.
- **Certification Testing**: Certification procedures and related costs vary widely among third-party certifiers. These disparities can lead to certification of less-than-optimal reformer designs that may not be ready for commercial use. Uniform testing with industry-recognized pass/fail criteria is needed.
- **Renewable Liquids On-site Storage** (when used): Issues may arise regarding the storage of renewable feedstocks on site. Some feedstocks will be relatively benign (e.g., carbohydrates) and will likely require minimal regulation, while others may fit under the regulations now being developed for E85, E100, and bio-diesel. Standards for still other types of feedstocks may need to be developed.
- **Permitting:** The permitting process varies from state to state and from municipality to municipality. State and perhaps even national standardization of the process should be encouraged.
  - **Renewable liquid feedstock on-site storage** permitting will need to be addressed. Since ethanol is well received and the number of forecourt stations offering it is growing rapidly, this permitting process may be fairly simple.
  - **Emissions** Although some regulated gas emissions will still be generated by some near- and mid- term production technologies (notably reforming and gasification), emissions from hydrogen production are generally lower than for gasoline. For example, the nitrogen-containing fertilizer used to grow many feedstocks generates a relatively small amount of NOx emissions, and the opening of storage tanks for refueling may release some volatile organic compounds (VOCs). Industrial experience in dealing with these types of emissions in other facilities can be applied to address them in hydrogen production.

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[14] This section is not comprehensive as many related codes and standards are in the process of being amended.

Exhibit I.6 Codes, Guidelines, and Regulations Potentially Applicable to Hydrogen Production, Based on Natural Gas or Renewable Feedstocks[15,16]

Function	Applicable Codes/Guidelines
Reformer Design and Manufacture	
Mechanical Safety	UL795, ANSI Z-21.83, NFPA 70
Prevention of Unexpected Start-Ups, Safety Guards, Interlocks, Burner Control, Acoustic Emissions	UL-795
Vibration Isolation	UL 795, ANSI Z21.83
Liquid Pumps, Compressors	ANSI Z21.83
General Electrical Safety	NFPA 70, NFPA 52, UL-508, NEMA, IEEE
Electrical Equipment; Medium Voltage, Explosion Atmosphere Protection, Hazardous Location Electrical Equipment	NFPA 70
Pressure Vessel	ASME Boiler and Pressure Vessels Section VIII, Div1
Pressure Piping	ANSI B31.3, ANSI Z21.83, UPC, NFPA, ASME, UL, NFPA 70, 52, 54, ASTM, UL
Certifications	UL, METLAB
Reformer Installation and Operation	
Setback distances, equipment assemblies, installation	NFPA 30A, 52, 50a
Signage, setbacks, materials, designs ASME Boiler and Pressure Vessels	B31.3, NFPA 50, 496, API Standard 620, CGA Pamphlet S-1
Wiring and Lighting in classified areas, grounding	1999 National Electrical Code, NFPA 70, ASME, ASTM
Heating, ventilation and cooling systems	2000 Uniform Mechanical Code
Construction and electrical safety	NFPA 30, 70, UL
Purged Enclosure	NFPA 496, 497a
Classification of Vapors, Dust for Electrical Equipment in Hazardous Classified Location	NFPA 497 M
Emissions	
Environmental impacts, emissions, criteria pollutants, hazardous waste, etc.	CEQA, NEPA etc.

- **Waste storage and disposal** Depending upon the particular feedstock and reforming technology, hydrogen production processes may generate solid or liquid wastes. For example, crude glycerol is an inexpensive feedstock containing salts that must be removed prior to reforming. The salt removal process may create wastes that require disposal. Similarly, aqueous-phase reforming may produce some liquid organic and/or inorganic wastes that require disposal. If the wastes are non-toxic, conventional disposal methods (garbage, sewer, etc.) may be used (assuming proper permits), to minimize or

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[15] Ohi, J., "Hydrogen Codes and Standards," *U.S. DOE Annual Progress Report 2007,* 1045-1049.

[16] Ohi, J., "The Department of Energy's Hydrogen Safety, Codes and Standards Program: Status Report on the National Templates," SAE 2006 World Congress.

negate any on-site storage issues. However, if conventional disposal methods are not an option, then the waste material will need to be stored and disposed of using more costly industrial waste methods. These costs will need to be included in the models and analyses. Permits may be required for on-site waste storage and disposal, depending on the type of reforming used and the wastes produced. For steam reforming, the contaminant removal step is likely to generate a small waste stream—comparable to that of sulfur in natural gas reforming. Aqueous phase reforming may create a larger waste stream; however, this technology remains in a relatively early stage of development, so the significance of this issue is difficult to determine. Industry has a great deal of experience in addressing waste storage and disposal, and that experience can be applied to these issues for hydrogen production.

- **Insurance Risk Mitigation**: Lack of an extensive historical database documenting field reliability, performance, durability, and safety issues hinders risk assessment by insurers. This could limit broad establishment of insurance coverage for hydrogen fueling stations and/or lead to high rates. A national insurance pool may be needed for partial coverage of deductibles and to limit liability.

Community Education and Outreach

Increased public understanding is needed to facilitate acceptance and adoption of fuel cell vehicles and smooth permitting of hydrogen stations. As a new application, the production of hydrogen for commercial sale will involve national and state regulators, standard and code-writing bodies, local officials, permitting authorities, emergency responders, and local communities. All of these stakeholders must be educated about the technology and applicable regulations, codes, and standards.

As a first step, DOE and other municipalities are supporting demonstration projects that give a limited number of communities an opportunity to gain first-hand experience with fuel cell vehicles and associated fueling stations. Providing accurate and timely information on an ongoing basis is also of paramount importance. Selected information about hydrogen and fuel cells is available on the DOE website.

CRITICAL TECHNOLOGY NEEDS

Collectively, the critical R&D activities for each technology pathway described in this roadmap make up the hydrogen production R&D program. The technologies are in different stages of development, and each offers unique opportunities, benefits, and challenges. Economics favor certain technologies over others in the near term, but as the technologies mature and market drivers shift, a broad range of technologies are expected to become economically viable and take advantage of the range of energy and feedstock resources available in each region.

Each of the technology-specific chapters identifies the critical technology needs for the specific production technology under discussion. Determination of critical technology need is based on consideration of the core barriers as well as the outlook for achieving technical targets. DOE has established clear technical targets for each hydrogen production technology and applicable feedstock. These targets and associated timelines reflect the expected capacity of a production unit, the current stage of technology development, the costs and characteristics of the feedstock, and other factors.

PATH FORWARD

For hydrogen to become a major energy carrier, consumers will need to see that hydrogen and the vehicle power systems in which it is used are cost-competitive with other options on the market. For light-duty vehicles, the cost per mile to the consumer must be roughly the same as for conventional fuels in ICE or hybrid vehicles.

Currently, the estimated cost range at which hydrogen is competitive with gasoline ICE or hybrid is $2.00 to $3.00 per gge (untaxed, "2005 cost basis") at the dispenser. DOE periodically revises this estimate to reflect projected fuel costs and the evolving energy efficiencies of vehicle power systems on a cost-per-mile basis. The DOE goal for all seven technologies under development is to produce hydrogen that can be dispensed to vehicles at a cost competitive with other options. Current priorities for R&D and supporting activities in the seven major hydrogen production technology pathways are summarized in Exhibit I.7.

Exhibit I.7 Pathways Forward

Production Technologies	R&D Priorities
Distributed Natural Gas Reforming	Pre-competitive technical and cost challenges have been sufficiently addressed so that industry may complete technical development without additional DOE resources
Bio-Derived Liquids Reforming	Catalyst development and capital cost reduction
Coal and Biomass Gasification	Capital cost reduction, carbon capture and storage, and greater use of renewable biomass feedstock
Water Electrolysis	Capital cost reduction, efficiency, and materials development
Thermochemical Hydrogen	Chemical cycle selection and materials development
Photoelectrochemical	Increased understanding of the fundamental processes and breakthroughs in materials
Biological	Biological candidate identification and engineering
Regulations, Codes, Standards, and Education	**Priorities**
Operations and Maintenance Plans	Establish minimum standards or guidelines for hydrogen station operation and maintenance
Certification Testing	Minimize disparity in certification procedures among third-party certifiers and establish a minimum set of uniform criteria and procedures to be performed
Permitting	Facilitate more uniform implementation of regulations, codes, and standards for fire and safety, establish standardized education modules with targeted information for state legislators, municipal officials, permitting authorities, and first responders; establish a comprehensive handbook on permitting requirements and train state and local fire marshals to serve as the main points of contact for the local permitting process; and provide a national fund for module development and training
Insurance Risk Mitigation	Create a broad international database to document field performance, reliability, durability, and safety issues for easy access by insurance risk analysts and investigate need for a national insurance pool for partial coverage of deductibles and liability limitations
Community Education & Outreach	Develop and implement standardized education awareness and outreach programs

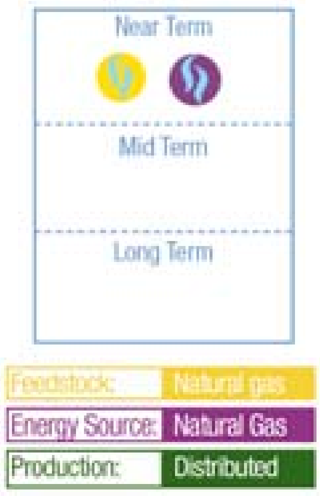
APPENDICES

At the end of this document, four appendices provide supplemental material. **Appendix A** defines the acronyms and abbreviations used throughout the document, which are defined only upon their first occurrence. **Appendix B** provides a series of tables that briefly summarize the key barriers and R&D needs for each production technology. **Appendix C** contains a single table that summarizes the key features, cost targets, and other attributes of each production technology and specific variations of some of those technologies. Finally, **Appendix D** lists all current DOE-funded projects that are expected to contribute to progress in bringing these technologies closer to commercial readiness.

1.0 Distributed Natural Gas Reforming

The distributed natural gas reforming (DNGR) pathway calls for producing hydrogen in distributed facilities via steam reforming of natural gas. Natural gas reforming is currently used on a large scale (semi-central, central) to produce much of the commercial and industrial hydrogen used today.

Distributed Natural Gas Reforming



1.1. INTRODUCTION

Analysis of distributed natural gas reforming indicates that federal R&D partnerships have addressed the major technical and cost challenges to the extent that private industry should be able to tackle the remaining technical and cost barriers and complete the commercial development of this production technology without additional DOE resources. This technology may be applicable to LNG with minimal additional development. Barriers discussed herein remain for industry to resolve in commercialization.

DNGR offers the most economical and technically viable near-term approach to hydrogen (H_2) production. Early availability is key to promoting acceptance of hydrogen fuels and creating the market demand that will drive future R&D of more sustainable hydrogen production technologies. As this technology would ultimately increase demand for natural gas, it is viewed as a stepping stone to the future rather than a long-term solution. Mid- and longer-term hydrogen production technologies will use low or zero-carbon domestic feedstocks and production energy sources.

Environmental Benefits

Although greenhouse gas emissions from distributed natural gas reforming are already lower than for gasoline use, R&D should reduce them further by increasing the efficiency of feedstock conversion to hydrogen.

Natural gas reforming consists of two sequential processes: steam reforming followed by water-gas-shift. Simplified reactions of these processes are:[17]

Methane steam reforming:	$CH_4 + H_2O \rightarrow CO + 3H_2$
Water-gas-shift:	$CO + H_2O \rightarrow CO_2 + H_2$

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[17] Holladay, J.D., Y. Wang, and E. Jones, “Review of Developments in Portable Hydrogen Production Using Microreactor Technology,” *Chemical Reviews* 104 (2004), 4767-4789.

The main deactivation mechanism for hydrocarbon reforming is coke (carbon) formation. The following are simplified reactions for coke formation:[17]

$$C_mH_n = xC + C_{m-x}H_{n-2x} + xH_2$$

$$2CO = C + CO_2$$

$$CO + H_2 = C + H_2O$$

The most common way to eliminate coking is to increase the amount of water in the feed stream. Therefore, most methane steam reforming techniques use three to six times more water than is required.

COST TARGETS

R&D on the DNGR pathway focuses on achieving the DOE cost targets shown in Exhibit 1.1 for dispensing hydrogen at the pump.

Exhibit 1.1 Distributed Natural Gas Reforming: DOE Cost Targets

Target Year	Production Scale	Cost/gge (production)*	Cost/gge (dispensed)*
2010	Distributed	$2.05	$2.50
2015	Distributed	$1.70	$2.00

* On a 2005 capital cost basis, assuming $5.24/MMBtu lower heating value (LHV) and in 2005 dollars. 2007 cost projection in 2005 dollars, natural gas at $5.24/MMBtu, using H2A was >$3/gge.[18]

1.2. KEY BARRIERS

DOE's research activities were strategically directed at overcoming specific barriers identified in the Hydrogen, Fuel Cells & Infrastructure Technologies Program's (HFCIT's) *Multi-Year Research, Development, and Demonstration Plan (MYPP)*[19] as well as other barriers identified by the FreedomCAR and Fuel Partnership's HPTT. These barriers are listed in Exhibit 1.2 and described more fully below.

REFORMER CAPITAL COSTS

The capital costs associated with small-scale technologies for DNGR are currently too high to achieve the production cost targets. These high capital costs are a result of low energy efficiencies and many process steps entailed in converting natural gas to hydrogen. The balance-of-plant (BOP) components are too expensive and not sufficiently durable. Finally, the high purity of hydrogen required for fuel cells puts upward pressure on the capital costs.

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[18] Lomax, F. "Low-Cost Hydrogen Distributed Production System Development," 2007 DOE Hydrogen Program Review. http://www.hydrogen.energy.gov/pdfs/progress07/ii_a_2_lomax.pdf. Accessed 2 May 2009.

[19] Department of Energy, *Hydrogen Program Multi-Year RD&D Plan*, available at: http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/ Accessed 2 May 2009.

REFORMER MANUFACTURING

Distributed reformer units are currently designed and built one at a time, so the capital cost for each is high and the units are typically not optimized for size. This limited manufacturing approach increases the cost of equipment manufacturing and installation. Moreover, the low durability and relatively short service life of BOP keep capital costs above economically feasible levels.

Exhibit 1.2 Distributed Natural Gas Reforming – Summary of Barriers

Reformer Capital Costs	Current, small-scale, distributed natural gas and renewable liquid feedstock reforming technologies have capital costs that are too high to achieve the targeted hydrogen production cost.
Reformer Manufacturing	Distributed reforming units are currently designed and built one at a time. These custom units tend to be too large and too expensive.
Station Footprint	To be economically feasible in urban settings, the physical footprint of stations needs to be reduced.
Operation and Maintenance (O&M)	O&M costs for distributed hydrogen production from reforming natural gas and renewable feedstocks are too high. Current systems require too much maintenance and in-person monitoring. Finally, there is currently no simple, low-cost way to ensure that the hydrogen meets the high quality standards necessary for proper fuel cell operation (as discussed in the Introduction).
Feedstock Issues	Variations in the chemical composition of natural gas will require prospective DNGR sites to have reformers and catalysts capable of processing that range to produce hydrogen of acceptable quality on a consistent basis.
Control and Safety	DNGR sites will need reliable hydrogen control to assure public safety and address environmental issues without escalating costs. Specifically, controls are needed to avoid hydrogen leakage and minimize emissions.

STATION FOOTPRINT

The specific location of a DNGR station determines the constraints on the station footprint. Refueling stations providing an average 1,500 gge per day of hydrogen will tend to occupy a relatively large footprint due to the size and amount of process equipment involved. Reformer and BOP size reduction may be needed to decrease this footprint and enable wider adoption of distributed generation technologies.

As an example, a station that produces an average 1,500 gge per day and is capable of simultaneously dispensing fuel to six vehicles with an average fill-up time of three minutes would result in a footprint target of 14,000 square feet—a size comparable to that of typical urban gasoline stations.[20] This example assumes a targeted 2 gge per minute dispensing capability[21] and storage capacity of up to 35% of maximum daily production[22]. The total area of the production plant, compressor, storage, dispensers, and portion of apron/common area (total footprint is split with convenience store) is estimated to be half of the station footprint.[23] The target footprint breakdown for the major process equipment is as follows:

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[20] Information from the Service Station Dealers of America and Allied Trades suggests that economic models for new urban service stations are larger than 14,000 square feet. Telecon with Michael Ingle, February 2009.

[21] Based on DOE *MYPP* target for 2015

[22] H2A Forecourt Assumption

[23] HPTT and Hydrogen Delivery Technical Team joint meeting 2008 discussions

- Forecourt hydrogen production plant: 900 ft^2
- Storage system (primary and secondary): 1,300 ft^2
- Hydrogen compressor system: 500 ft^2
- Dispensers and portion of apron/common area: 4,300 ft^2

Projected system size thus appears too large for the available space in many existing urban service stations.

OPERATION AND MAINTENANCE COSTS

Multiple barriers will need to be addressed to minimize the operation and maintenance (O&M) costs for producing hydrogen via distributed reforming of natural gas. Cost performance must be benchmarked versus conventional fueling stations. Moreover, all system components must be considered in O&M cost projections, including feed pre-conditioning (e.g., sulfur removal), reforming, controls, process utilities, quality assurance and control (QA/QC) (e.g., sensors), compression, storage, dispensing, and safety.

Durability Both the frequency and cost of repairs for the fuel processor system and BOP must be considered. Down time also impacts co-located businesses (e.g., convenience stores), which may account for a significant portion of site profits.

Scheduled Maintenance Cost prohibits full-time, on-site maintenance staff, so routine maintenance will need to be minimized and system troubleshooting will need to be automated or monitored remotely.

Demand Management Hourly and daily variations in demand must be handled in a way that is transparent to the customer and the on-site fueling station staff. Design and operational decisions to address demand variability will impact O&M as well as capital costs (e.g., turn-down, periodic shut-down and restart).

Desulfurization A variety of sulfur-containing odorants are used in natural gas to facilitate easy detection in case of a leak. This sulfur must be removed prior to reforming to protect reformer catalysts from deactivation; sulfur in the dispensed hydrogen can also lead to serious fuel cell damage. Sulfur removal devices may require routine maintenance (e.g., replacement of adsorbents). Both the maintenance and disposal operations must be appropriately designed for safety.

Other O&M costs must also be lowered wherever possible by minimizing the number of system components, the amount of material required, and energy losses. The technology also suffers from the high costs of separation and purification technologies, BOP components, and limited system reliability and lifespan.

FEEDSTOCK ISSUES

The chemical composition of natural gas is not constant and may vary considerably depending on the source of the gas and pretreatment prior to delivery. Typically, natural gas is comprised primarily of methane. However, the concentration of methane can range from approximately 80% by volume to a theoretical value of 100%. Such wide variation in composition could affect performance and the stability of the catalytic reformer.

Chemically, methane (CH_4) is the simplest hydrocarbon, containing four symmetrical C-H bonds. Methane has high bond strength (approximately 104 kcal/mole) and is one of the least reactive organic components in natural gas. An effective reformer catalyst must be capable of promoting the selective conversion of relatively inert methane (and the other hydrocarbons) while minimizing side reactions and products of the generally more reactive and larger hydrocarbons.

In addition to odorant additives and known catalyst poisons such as sulfur compounds, natural gas can include a variety of other chemical compounds—sometimes in relatively high concentration. Depending on the source of the gas, inorganic impurities such as nitrogen, oxygen, carbon dioxide, and water may be present. Inert materials such as nitrogen may have been added to adjust the energy content of the gas. In general, most of these inorganic compounds would be fairly unreactive; however, their presence needs to be considered when selecting a reformer design and catalyst[24].

Actual hydrocarbon concentrations can be influenced by a number of factors. Raw gas can contain a variety of higher hydrocarbons, some of which may be as large as C_{12}. Processing will remove many of these as “gas-liquids,” and the resulting gas will be highly methane enriched. However, high gas prices and the ability to charge customers on an energy basis make it practical to leave the higher Btu hydrocarbons in the natural gas. Based on the chemical economics, gas from a constant source may or may not be processed. Increased use of liquefied natural gas (LNG) can also have a significant effect on the natural gas composition. The liquefaction process results in the removal of all hydrocarbons greater than C_3. Depending on the gas source, liquefaction can result in a high-Btu gas due to the presence of high concentrations of C_2 hydrocarbons (and some C_3 materials).

Clearly, the composition and delivery pressure of natural gas can be highly variable depending on the processing and/or blending. Recent concerns with gas interchangeability/gas quality have prompted efforts to standardize delivered natural gas based on a range of the Wobbe Index (higher heating value/square root of the specific gravity); however, this approach does not necessarily define any specific gas composition. Gas composition may vary over time, and these fluctuations could be significant. To avoid potentially complex and costly on-board conditioning, the reformer unit (and catalyst) must be capable of accommodating a wide range of natural gas compositions and fluctuations in the feedstock composition.

In addition, a scenario of viable hydrogen production from natural gas poses sizeable challenges in terms of the impact on natural gas demand, supply, and transmission. Although an established natural gas infrastructure in the United States supports the viability of hydrogen production from DNGR, the existing infrastructure would be inadequate to meet significantly increased demands for natural gas. A 2006 report published by Energy and Environmental Analysis, Inc. used income and demographics to identify 27 cities as sites likely to participate in the initial phases of hydrogen use in vehicles. These 27 transition cities could add 1.2 billion cubic feet per day (cfd) of natural gas demand by 2025 from steam methane reforming (SMR) refueling stations. This is about 2.1% of daily average 2004 national gas loads and 1.6% of projected 2025

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[24] Natural gas supply in some areas of the country is augmented during peak heating seasons. This is accomplished by the addition of an LPG/air mix. As air is used to maintain the combustion characteristics of the enriched natural gas, oxygen may be introduced at rates as high as ~ 5% by volume in the infrastructure. This often causes serious challenges in fuel pre-treatment for reforming processes, as oxygen and some LPG components interact with sulfur removal technologies and can cause coking.

national daily average gas loads. The changes to pipeline capacities needed to accommodate the additional 1.2 billion cfd capacity in hydrogen-related load will depend on the LNG terminal, pipeline, and storage assets built over the next 20 years to meet the overall growth in natural gas demand.

CONTROL AND SAFETY

Control and safety issues associated with natural gas reforming include integration of system components, optimization of start-up and shut-down processes, improving turn-down capability, and enabling rapid on-off cycling. The control system costs remain high and need to be further reduced through system simplification and/or reduced sensor count. The sensors should be more cost-effective and reliable compared to currently available technology. The permitting process critically relies on the proven reliability and safety of these units in the forecourt environment, which will be a key qualification target. These units must be designed to operate in an environment of minimal manual assistance, which will require attributes such as a back-up, fail-safe mode; remote monitoring; and sparse maintenance schedules. The system design should ensure that any effluents (like SO_2 and other gas and liquid exhausts) meet all requirements for local and national permitting processes.

1.3. CRITICAL TECHNOLOGY NEEDS

The critical technology needs for DNGR address the various barriers previously discussed. Certain technology needs may address multiple barriers at once. For more detail on the relationships between barriers and needs, please see Appendix B. The table in Exhibit 1.3 lists the critical technology needs for producing hydrogen through distributed natural gas reforming. Discussion of these efforts follows the table.

Exhibit 1.3 DNGR Critical Technology Needs

Reduce Capital Costs	➔ Improve catalysts ➔ Improve separations and purification technologies ➔ Integrate system components; develop one-step reforming/shift ➔ Optimize system turn-down capability to manage variable demand ➔ DFMA/high-volume equipment manufacturing and BOP optimization
Reduce O&M Costs	➔ Automate process control ➔ Improve equipment reliability ➔ Minimize material and energy losses ➔ Capital utilization

REDUCE REFORMER CAPITAL COSTS

Equipment capital costs are a significant factor in the cost of producing hydrogen with the DNGR technology and reducing them is a high research priority. Major efforts center on overcoming the technical barriers associated with process intensification, since combining process steps will lower capital costs by reducing the part count for process equipment (e.g., combining the shift reaction and hydrogen separation processes into a single step). Additional efforts will be needed to implement a design for manufacturing that facilitates mass production of equipment and development of lower-cost, easier to manufacture, and more durable materials.

Improve Catalysts To lower catalyst cost, DOE is sponsoring development of catalysts that use non-precious metals. Lower operating temperatures will reduce the material costs for reactor systems and will also reduce the energy required for heating the feed mixture to high reaction temperatures. Catalysts under development provide high steam reforming activity and are non-selective for various undesired side reactions, such as methanation, dehydration, dehydrogenation, coking, and reverse water-gas-shift reaction. The resultant high yields will help increase the energy efficiency of production.

Improve Separations Process intensification is a key strategy for reducing the capital cost of distributed hydrogen production from steam methane reforming. For example, development of improved membranes for separating hydrogen from other gases during the reforming/shift reactions could contribute to the success of process intensification for SMR.

Improve Feedstock Pre-Treatment Typically, reforming catalysts require odorant-free natural gas and de-ionized water. Feedstock pretreatment systems that achieve these conditions can represent a significant share of the capital, operating, and maintenance costs. Several approaches can reduce the costs associated with these systems.

Sulfur can be removed from pipeline natural gas by employing such processes as direct physical adsorption, selective oxidation, and hydro-desulfurization. Since the types of odorants in pipeline natural gas are location specific, a one-size-fits-all design for sulfur removal is not feasible. Each process has unique advantages and disadvantages. Adsorption and hydro-desulfurization pose a disposal problem for the spent adsorbents and the sulfur, while selective oxidation negatively affects system efficiency. Sulfur-tolerant catalysts are therefore ideal. However, these catalysts are likely to be more costly, and all options must be considered to balance cost and functionality.

The effects on catalyst performance from inorganic contaminants present in the water remain unclear. Inorganic compounds tend to cause scaling/fouling problems in a system's internal piping and heat exchangers. At the very least, chlorine must be removed from municipal water because it is detrimental to the catalysts and all metals with which it comes into contact in the reforming system. Current water standards for the distributed reformers are similar to those for the water used in fuel-cells. Clearly, some level of purity is required, yet the reformer's feed water does not necessarily have to be as low in conductivity as fuel-cell-grade water (<5 microS·cm^{-1}). If the standard for required purity could be relaxed without affecting the performance of reforming systems, the cost and complexity of feed water treatment systems could be greatly reduced.

Optimize System to Manage Variable Demand Demand for hydrogen refueling will vary significantly over the course of a day. This demand variability may be handled through a combination of on-site hydrogen storage and load-responsive capability in the reformer. The extent to which each of these two strategies is used to handle demand variability will have a significant impact on capital costs and the station footprint. Sizing the reformer to handle peak demand will increase capital costs for the reformer, whereas increasing storage will increase the system footprint to accommodate storage tanks. Optimizing this balance must also consider the relative impacts on maintenance costs and safety. Prospective station owners need a model or tool that can be readily calibrated with local data and projections to suggest a feasible balance between storage and load-responsive capability for a specific station.

DFMA/High-Volume Equipment Manufacturing and BOP Optimization Design for manufacture and assembly (DFMA) will be a key component of cost reduction efforts for distributed reformer units, both for near-term, semi-custom installations and for longer-term, higher-volume manufacturing. In the near-term, in light of limited production volumes, DFMA should focus on developing reformer designs that incorporate commonly available (commodity) materials and use common tooling and standard sizing for procured components (e.g., tubing, heat exchanger, and reactor components). Design for modularity will be especially important for semi-custom installations. Modular design will allow incorporation of improvements in specific subsystems without redesigning the entire process. Flexible, modular design will also allow scalable systems, increasing the application domain and overall production volumes.

In the long-term, on-site reformers will be manufactured in large quantities (hundreds of systems per year), and the goals for DFMA will shift toward incorporating optimal, high-volume production methods. Research efforts in DFMA for higher-volume manufacturing should focus on three critical aspects of the design and manufacturing process: 1) optimal design of subsystems to reduce size/part-count and enhance maintainability; 2) substitution of less costly materials and reduction of the total amount of material (e.g., catalyst) used; and 3) integration of whole system design (including compression, storage, and dispensing) to reduce the costs of installation and operation.

Optimization of subsystem design will consider several aspects of manufacturing and operation including:

- Design for serviceability, allowing for operable connections between subsystems and consideration of the service schedules for different components
- Tuning of reaction conditions and flow rate design to optimize overall plant equipment needs for the targeted application.

The use of less costly materials could provide significant savings, especially the substitution of iron-based alloys for the super nickel alloys currently used in steam service, condensers, and heat exchangers. However, R&D is needed to produce new tooling, dies, and optimized manufacturing techniques. Manufacturing and construction techniques that minimize the amount of material used will provide significant savings.[25,26]

BOP components also constitute a significant part of the capital cost. Improved, low-cost sensors, pumps, blowers, and monitoring equipment need to be developed. The BOP costs can be further reduced by developing common, interchangeable components, automated joining processes, and low-cost stamping and extrusion methods that will permit high-volume, assembly-line production of critical components that are currently machined and welded.

REDUCE OPERATING AND MAINTENANCE COSTS

Costs for O&M also have a significant impact on the overall cost for producing hydrogen. Improvements in process design that increase energy efficiency and/or allow for greater variability and higher levels of contaminants in feedstocks will reduce O&M costs. O&M costs will also be reduced by improving process controls for cycle optimization, including the development of better and less expensive sensors and the development of better turn-down capability.

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[25] Lomax, F., Chief Technology Officer, H2Gen Innovations, Inc., Alexandria VA. Personal communication, 9 August 2007.

[26] MIT Lecture 19 DFM. IPPD 4/25/00. web.mit.edu/2.742/www/syllabus/4_20_eng.pdf Accessed 3 August 2007.

Automated Process Control On-site, planned maintenance must be minimized both in terms of cost and frequency. The need for on-site labor must be eliminated and replaced with automated process control and remote monitoring, including automatic fault detection. Low-cost sensors will need to be developed.

Increase Equipment Reliability The reliability of BOP equipment with moving parts (such as pumps, compressors, and blowers) is often a limiting factor in the reliability of the overall system. Increasing the reliability of these components along with minimizing equipment complexity is critical for improving system reliability. For reformer systems, sustained catalyst activity is also essential to reliable and efficient operation. Impurities in feedstocks (e.g., natural gas and water) must be controlled to protect reactor components. Monitoring techniques for inert components in the feed stream (nitrogen, water, etc) will need to be implemented.

Minimize Material and Energy Losses Any leak of natural gas or hydrogen must be virtually eliminated to ensure safety, minimize loss of process efficiency, and minimize GHG emissions. Heat loss and heat rejection must also be minimized through well-designed insulation and heat integration. Currently, EE's Hydrogen Delivery and Safety, Codes, and Standards program elements are working to address hydrogen leakage.

Capital Utilization Peaks and valleys in hydrogen demand for transportation must be leveled to maximize the utilization of capital. Reformer size must be balanced with an appropriate hydrogen storage system. Utilization may also be increased by finding alternate uses for the hydrogen or generating revenue from co-produced products. A distributed natural gas reformer has the potential to co-produce a variety of products in addition to hydrogen, such as heat, electricity, and steam. Local use or sale of these products can either increase site revenue or help to load-level reformer operation.

Water Purity Natural gas steam reforming requires water to generate the steam. It is unclear how the presence of inorganic compounds in water may affect catalyst performance. Heavy metals tend to cause scaling/fouling problems to a system's internal piping and heat exchangers. At the very least, chlorine must be removed from municipal water because it is detrimental to the catalysts and all metals with which it comes into contact in the reforming system. Clearly, some level of purity is required for the reformer's feed water. However, the feed water need not be as low in resistivity as fuel-cell-grade cooling water (less than 5 microS·cm^{-1}). If the standard for required purity can be relaxed without adversely affecting the performance of the reforming systems, the cost and complexity of feed water treatment systems could be greatly reduced.

2.0 Bio-Derived Liquids Reforming

The bio-derived liquids reforming pathway calls for producing hydrogen in distributed facilities via gas-phase or aqueous-phase reforming. Hydrogen can be produced by reforming bio-liquids such as sugars, ethanol, or bio-oils. Reforming of ethanol and other bio-derived liquids is similar to natural gas reforming, but has several unique challenges, such as improved catalyst activity and durability. Some bio-derived liquids may also be cost effectively reformed at larger semi-central plants.

Bio-Derived Liquid Reforming

2.1. INTRODUCTION

Distributed hydrogen production technologies such as bio-derived liquid reforming may afford the most viable renewable hydrogen pathways due to their relatively low capital costs compared to other renewable hydrogen technologies. Processing facilities will be able to take advantage of the latest and most efficient technologies as well as many of the lessons learned by the petroleum industry. Reformers can be scaled for distributed or semi-central hydrogen production, depending on the feedstock. For example, ethanol can be supplied to a semi-central reformer from several smaller plants.

Biomass is an abundant renewable resource (over 1 billion dry tons could be available in the United States annually), enabling decreased dependency on foreign oil and increased energy and economic security.[27] This technology is considered a mid-term option, and DOE-funded development should be completed by 2017.

Environmental Benefits

Renewable liquid feedstocks tend to have significantly lower greenhouse gas emissions in comparison to petroleum on a well-to-wheels basis. Efforts are being made to further reduce these emissions.

A wide range of biomass materials can be reformed to hydrogen. Similar to natural gas reforming, the process often requires two steps: conversion to carbon monoxide, then shifting the carbon monoxide to carbon dioxide and hydrogen, although coking is a

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[27] *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply,* prepared by Oak Ridge National Laboratory for the U.S. Department of Energy, April 2005.

problem. To avoid coking, four to ten times the stoichiometric amount of water is required. The reactions can be generalized as follows[17]:

Steam reforming: $C_mH_n + mH_2O = mCO + (m + (½)n)H_2$
Water-gas-shift: $CO + H_2O = CO_2 + H_2$
Coking reactions: $C_mH_n = xC + C_m\text{-}xH_n\text{-}2x + xH_2$

$2CO = C + CO_2$
$CO + H_2 = C + H_2O$

DOE COST TARGETS

R&D on the bio-derived liquids reforming pathway is focused on achieving the DOE cost targets for hydrogen production shown in Exhibit 2.1.

Exhibit 2.1 Bio-Derived Liquids Reforming Cost Targets [4]

Target Year	Production Scale	Cost/gge (production)	Cost/gge (dispensed)
2014	Distributed	\$3.25[9]	\$3.80
2019	Distributed	<\$2.65[9]	<\$3.00*

* Current projected cost/gge: gas phase reforming: \$3-3.15[28] with ethanol at \$1.07/gallon no tax credit; aqueous phase reforming: \$6.50[29] using 2005 capital costs and glucose feed at \$0.064/lb.

2.2. KEY BARRIERS

Driving DOE's research activities are specific barriers identified in the MYPP[19] as well as others identified by the FreedomCAR and Fuel Partnership's HPTT. These are summarized in Exhibit 2.2 and described more fully below.

REFORMER CAPITAL COSTS

Currently, the capital cost of small-scale distributed reformers for biomass-derived liquid feedstock is too high to achieve target hydrogen production costs. High capital costs are caused by low energy efficiencies and multiple-unit operations that entail many process steps in converting bio-derived liquids to hydrogen. Additionally, manufacturing and installation costs are too high, while components have insufficient reliability, durability and life span. Reforming and water-gas shift unit operations also generate considerable costs. Finally, the high purity of hydrogen required for fuel cells puts upward pressure on the capital costs.

REFORMER MANUFACTURING

Distributed reformer units are currently designed and built one at a time. The capital cost contribution to total hydrogen production cost is higher for smaller hydrogen production

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[28] James B., "Analysis of Ethanol Reforming System Configurations," *2008 DOE Hydrogen Program Review*. http://www1.eere.energy.gov/hydrogenandfuelcells/annual_review.html

[29] Rozmiarek B., "Hydrogen Generation from Biomass Derived Carbohydrates via Aqueous Phase Reforming Process", *2008 DOE Hydrogen Program Review*. http://www1.eere.energy.gov/hydrogenandfuelcells/annual_review.html

facilities designed for distributed applications. This limited manufacturing approach results in expensive system components with poor life span and durability, as well as increased BOP component cost. Finally, current systems are too large and too expensive, in part due to the need for site-specific fabrication of subsystems.

Exhibit 2.2 Bio-Derived Liquids Reforming – Summary of Barriers

Reformer Capital Costs	Current small-scale distributed renewable liquid feedstock reforming technologies have capital costs that are too high to achieve the DOE-defined, targeted hydrogen production cost.
Reformer Manufacturing	Distributed reforming units are currently designed and built one at a time. Current manufacturing processes are not sufficiently cost effective and do not have sufficiently high throughput. Systems produced are large and non-portable.
Station Footprint	To be economically feasible in urban settings, the physical footprint of stations needs to be reduced.
Feedstock Issues	Liquid feedstock supplies may vary by region and season, requiring prospective bio-derived liquids reforming sites to develop diverse feedstock handling procedures and reformers that can consistently process the available range of liquid feedstocks into hydrogen of acceptable quality.
Operation and Maintenance	O&M costs for hydrogen production from bio-derived liquids are too high. Current systems require extensive maintenance and in-person monitoring that cannot be accommodated at distributed production sites. There is currently no simple, low-cost way to ensure that the hydrogen meets the high standards necessary for proper fuel cell operation (as discussed in the Introduction).
Control and Safety	Bio-derived liquids reformers will need reliable hydrogen control to assure public safety and address environmental issues without escalating costs. Specifically, controls are needed to avoid hydrogen leakage and minimize emissions.

STATION FOOTPRINT

The specific location of a distributed or semi-central liquids reforming station determines the constraints on the station footprint. Refueling stations providing an average 1,500 gge per day of hydrogen will tend to occupy a relatively large footprint due to the size and amount of process equipment involved. Reformer and BOP size reduction may be needed to decrease this footprint and enable wider adoption of distributed generation technologies. The station footprint challenges for bio-derived liquids reforming are the same as those for DNGR (please see Section 1.2 for more detail).

OPERATION AND MAINTENANCE

All system components (feed pre-conditioning such as contaminant removal, reforming, controls, utilities, sensors, compression, storage, dispensing, and safety) must be considered in O&M cost projections which currently are too high. Hydrogen quality monitoring is also a potential barrier, as described in the Introduction. Although similar to DNGR, reforming of bio-derived liquids is more complex and will require a more complicated overall system. For distributed production, however, the O&M issues related to scheduled maintenance and demand management are nearly identical to those for DNGR systems (please see Section 1.2).

Catalysts Bio-derived liquids reforming can be accomplished using gas-phase or liquid- (aqueous) phase reactions. Gas-phase reforming of liquids is very similar to natural gas reforming and has many of the same barriers. The main differences are that vaporization must occur, the catalysts may need to be adjusted, and the steam-to-carbon ratio typically needs to be higher. The primary focus of bio-derived liquid gas phase reforming is ethanol processing. In some ways, ethanol is more difficult to process than natural gas. Specifically, coke tends to form and deactivate the catalyst even at higher steam-to-carbon ratios. Aqueous-phase reforming (APR) is not as well developed as its gas-phase reforming counterpart. Currently, catalysts for APR are not sufficiently developed.

Durability For current systems, repairs are necessary too frequently, and the cost of repairs too high. Down-time may adversely affect co-located businesses (e.g., car washes). The durability and service life of the reactor and the catalyst are also less than satisfactory.

Contaminant Removal The feedstock may contain trace levels of contaminants that will need to be removed prior to reforming. Both the safety of the maintenance operation as well as the disposal method must be appropriately designed.

FEEDSTOCK ISSUES

Feedstock availability may be limited in some areas, or the lower-cost feedstock may change throughout the year. The primary issues are (1) the effects of impurities from multiple feedstocks, and (2) the effects of impurities from variations in single feedstocks or those introduced during feedstock transport.

While carbohydrate-based feedstocks such as glucose could eventually be available, several barriers exist that must be addressed. Specifically, variations in the feedstocks, transportation logistics, and storage issues may increase. Additionally, inert gas from these feedstocks may also increase in the hydrogen product.

CONTROL AND SAFETY

Control and safety barriers associated with reforming include poor performance of start-up and shut-down processes, insufficient turn-down capability, general feedstock issues, a lack of rapid on-off cycling, and feedstock storage tank refilling difficulties. Many of the control systems issues for renewable liquids reforming are the same as those for natural gas reforming. Reforming control and safety costs are high due to complex system configuration and too many necessary sensors. The sensors are not cost-effective or reliable enough today. A lack of back-up fail safe mode and remote monitoring as well as demanding maintenance schedules necessitate manual assistance for operation, increasing costs. The permitting process critically relies on the proven reliability and safety of these units in the forecourt environment and these criteria will be key qualification targets. Local and national permitting for effluent (gases and liquid exhaust) requirements will have to be met by any system design. If underground storage tanks are used, they will need to comply with Leaking Underground Storage Tank regulations. In addition, many bio-derived liquid feedstocks have a high vapor pressure compared to gasoline. This pressure may be particularly important during filling of the storage tanks, when VOCs could be released to the atmosphere. Since the VOCs tend to be flammable, this may create issues with permitting (high gas emissions) and safety.

2.3. CRITICAL TECHNOLOGY NEEDS

Exhibit 2.3 lists the critical technology needs for bio-derived liquid reforming hydrogen production, and these needs are discussed in the following text. Some of the R&D activities address more than one barrier. For a more detailed alignment of R&D needs with the barriers discussed above, please see Appendix B.

Exhibit 2.3 Bio-Derived Liquids Reforming Critical Technology Needs

Reduce Capital Costs	➔ Capital costs reduced to \$0.40/gge ➔ Improved catalysts • Steam reforming • Aqueous phase reforming ➔ Low-cost separations and purification technologies ➔ One-step reforming/shift ➔ Manufacturing and Installation • System optimization and load following capability to reduce footprint • DFMA/high-volume equipment manufacturing • Reduce BOP cost
Reduce O&M Costs	➔ Low cost • Feedstock characterization • Supply analysis • Feedstock candidates • H_2 quality assurance ➔ Improved feedstock pre-treatment ➔ Minimize labor cost ➔ Increase equipment reliability ➔ Minimize material and energy losses in reforming ➔ Increase co-product revenue

REDUCE CAPITAL COSTS

Capital equipment represents a significant cost component in the production of hydrogen from bio-derived liquids reforming, and reduction of these costs should be a high-priority research focus. The MYPP sets the “Production Unit Capital Cost Contribution” in 2014 to \$0.45 (to achieve the \$3.80 gge target) and in 2019 to \$0.40 (to achieve the <\$3.00 gge target). However, some of the efforts to reduce capital costs may restrict feedstock flexibility options. A technoeconomic cost analysis for specific cases is required to determine the cost advantages on a case by case basis.

Improve Catalysts

Steam Reforming   A multitude of catalyst systems have been investigated for the steam reforming of ethanol, bio-oil, sugar alcohols, and other bio-liquids.[30,31] A common problem with the catalysts reviewed is deactivation due to coking, which occurs when side reaction products (e.g., acetaldehyde, ethylene) deposit on the catalyst. To a certain degree, process parameters such as the steam-to-carbon (water-to-ethanol) ratio can be

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[30] Vaidya P.D. and A.E. Rodrigues, “Insight into Steam Reforming of Ethanol to Produce Hydrogen for Fuel Cells” *Chem. Eng. J.* 2006, 117, 39-49.

[31] Davda R.R., J.W. Shabaker, G.W. Huber, R.D. Cortright, and J.A. Dumesic, “A Review of Catalytic Issues and Process Conditions for Renewable Hydrogen and Alkanes by Aqueous-Phase Reforming of Oxygenated Hydrocarbons over Supported Metal Catalysts,” *Appl. Cat B.* 2005, 56, 171-186.

modified—in this case increased—to limit carbon deposits, but at the cost of increased process energy requirements.[32,33] The water-to-ethanol feed ratio and operating temperature also influence the selectivity to hydrogen. Water-to-ethanol molar ratios of three or greater and temperatures above 500°C have been shown to favor the production of hydrogen over methane or other reaction intermediates. However, higher water-to-ethanol ratios will require increased energy inputs.

Low-temperature (<500°C) reforming technologies are also under investigation. The advantages of low-temperature technologies are reduced energy intensity, compatibility with membrane separation, favorable conditions for water-gas shift reaction, and minimization of the undesirable decomposition reactions typically encountered when carbohydrates are heated to high temperatures.[34,35]

Progress will require better understanding of the coking mechanisms, developing kinetic models, and performing parametric studies. A better understanding of coking mechanisms may enable the identification of operating conditions that will minimize coking, the identification of materials that will inhibit coking, and the development of long life, durable reactors. Kinetic modeling is needed to facilitate improved reactor design and development of control algorithms. Parametric studies are required to understand how the reactor will operate under various conditions and how the reactor operates under off-specification conditions. In addition, parametric studies are needed to optimize the start up and shut down procedures. As part of these studies, strategies should be identified and developed to regenerate catalysts with reduced activity. Coking, kinetic, and parametric studies should be done on a variety of feedstocks and should include development of strategies to switch between feedstocks without shutting down. Kinetic and parametric studies will enable the system design and may be used in system and process control models for distributed and central hydrogen production facilities.

Aqueous Phase Reforming Aqueous-phase reforming is a promising technology that can process water-soluble carbohydrates such as glucose, ethylene glycol, sorbitol, glycerol, methanol.[36, 37] Studies have shown that the following factors promote selectivity to hydrogen rather than alkanes**.**

- Catalysts made of platinum, palladium, and nickel-tin (nickel catalysts favor alkane production)
- More basic catalyst support materials (e.g., alumina)
- Neutral and basic aqueous solutions

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[32] Comas J., F. Marino, M. Laborde, and N. Amadeo, "Bio-Ethanol Steam Reforming on Ni/Al_2O_3 Catalysts," *Chem. Eng. J.* 2004**,** 98, 61-68.

[33] Yang Y., J. Ma, and F. Wu, "Production of Hydrogen by Steam Reforming of Ethanol over a Ni/ZnO Catalyst," *Int. J. Hydrogen Energy.* 2006, 31, 877-882.

[34] DOE Hydrogen Program, *FY 2005 Progress Report*, IV.A.6 Production of Hydrogen by Biomass Reforming, 98-105.

[35] DOE Hydrogen Program, *FY 2005 Progress Report*, IV.A.5 Hydrogen Generation from Biomass-Derived Carbohydrates via the Aqueous-Phase Reforming (APR) Process, 96-97.

[36] Cortright R.D., R.R. Davda, and J.A. Dumesic, "Hydrogen from Catalytic Reforming of Biomass-Derived Hydrocarbons in Liquid Water," *Nature*, 2002, 418, 964-967.

[37] Huber G.W., J.W. Shabaker, and J.A. Dumesic, "Raney Ni-Sn Catalyst for H_2 Production from Biomass-Derived Hydrocarbons," *Science*. 2003, 300, 2075-2077.

- Feedstock type (in descending order of hydrogen selectivity): polyols (selectivity decreases with increasing carbon number), glucose (selectivity decreases as weight % increases from 1 to 10).

Catalyst coking is not a significant problem for aqueous-phase reforming compared to low-temperature steam reforming and may be the result of differences in feedstock reaction pathways. While hydrogen yields are highest from the aqueous-phase reforming of sorbitol, glycerol, and ethylene glycol; glucose reforming, which has lower hydrogen yields, may be more practical due to lower feedstock cost. Improvements in catalyst performance, reactor design, and reaction conditions may help increase hydrogen selectivity. Low-temperature gas-phase reforming of ethanol is also being investigated, but a tradeoff exists between catalyst activity and resistance to deactivation (due to coking). Low- temperature gas-phase reforming research is ongoing. Similar to steam reforming, kinetic and parametric studies, including catalyst regeneration, should be conducted using the aqueous-phase technology to size the reactor, develop the system, and implement a control strategy.

Develop Low-Cost Separations and Purification Technologies

Lower cost separation and purification technologies, such as membranes, need to be developed. Membrane-specific technical targets are being addressed through research in improved membrane materials, module design, and manufacturing techniques. Improvements in membrane materials will result in membranes with greater flux and hydrogen selectivity; greater resistance to impurities such as H_2S, N, Cl, and Na; and greater durability under more extreme conditions of temperature and pressure. Research in module design is focused on developing membrane configurations that increase surface area per unit volume, enable simpler manufacturing and assembly methods, and provide leak-free seals. New manufacturing techniques will provide more cost-effective and durable substrates, less energy and material-intensive manufacture, and more uniform and higher-quality finished membranes.

Pursue Process Intensification

Capital cost is the second largest cost contributor to hydrogen generation costs at small, on-site plants designed for forecourt refueling stations, accounting for approximately 20% of the hydrogen cost. Process intensification is a strategy that could potentially substantially reduce product hydrogen costs by introducing advanced technology that can reduce the number of unit operations and capital cost, improve process efficiency, and lower equipment manufacturing and maintenance costs. An example of process intensification is a one-step reformer/shift reactor for gas phase ethanol reforming. Membrane advances may offer another opportunity for process intensification, as in the use of a membrane reactor that combines reforming and separations into a single step.

Improve Manufacturing and Installation

System optimization and load following capability to reduce footprint Demand for hydrogen refueling will vary significantly over the course of a day. This variable demand may be handled through a combination of on-site hydrogen storage and load-following capability in the reformer. The use of storage versus load-following to handle variability will have a significant impact on capital cost and station footprint. Sizing the reformer to handle peak demand will result in higher capital costs for the reformer; while using increased storage to handle peak demand may increase the footprint and material costs required for storage. This optimization must also consider the relative impact on maintenance costs and safety.

DFMA/High Volume Equipment Manufacturing Most of the critical technology needs in DFMA for bio-derived liquids are the same as those discussed in the DNGR Section.

Reduce BOP Cost BOP components are a significant part of the capital cost. Improved, low-cost sensors, pumps, blowers, and monitoring equipment need to be developed.

REDUCE OPERATION AND MAINTENANCE COSTS

Costs for O&M have a significant impact on the overall cost for producing hydrogen. Improvements in process design that increase energy efficiency and/or allow for greater variability and higher levels of contaminants in feedstocks will reduce operating and maintenance costs. Development of reactors that are fuel flexible is important to enable the operators to use the lowest cost feedstocks available. Changing the feedstock should be simple and seamless. O&M costs will be further reduced by improved process controls for cycle optimization, including the development of better and less expensive sensors and development of better turn-down capability. It should be noted that efforts to make reactors fuel flexible may not be compatible with some of the efforts to reduce O&M. The advantages and disadvantages of such efforts will be dependent on the technologies and approaches and therefore must be evaluated on a case by case basis.

Address Feedstock Issues

Feedstock Characterization Efforts to clearly identify the range of feedstock(s) and the baseline characteristics of each major feedstock would enable closer consideration and analysis of issues such as storage, contaminants, waste generation/disposal, and system design. Since various feedstocks have different carbon contents in them, understanding the constituents is necessary to determine the amount of water needed to maintain the desired steam-to-carbon ratio. In addition the volatility, or lack thereof, will need to be addressed. For example, bio-oil has a low volatility, but this may be overcome by cracking it in a pre-reformer. Feedstock characterization is essential to support development of a flexible fuel system.

Supply Analysis For a feedstock to be a suitable candidate for distributed reforming, it should be inexpensive, relatively non-toxic, easily reformed, require a relatively small amount of storage or be capable of pipeline transport, and available in sufficient quantity to support year-round station operation. A supply analysis may be required to identify the candidates that best meet these requirements. Some individual feedstocks may not meet all requirements, yet may be useful in minimizing annual costs when included with more abundant feedstocks. Many feedstocks may be viable for use at a single station if the station can process them. A supply analysis can identify the likely feedstock candidates and scenarios that stations may face. Different areas of the country are expected to use different feedstocks or mixtures of feedstocks, and these may change over time.

Feedstock Candidates Ethanol is the most heavily researched renewable liquid because it is easy to store, handle, and transport due to its low toxicity and volatility.[38,39] The

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[38] Benito, M.,J.L. Sanz, R. Isabel, R. Padilla, R. Arjona, and L. Daza, "Bio-Ethanol Steam Reforming: Insights on the Mechanism for Hydrogen Production," *J. Power Sources* 2005, 151, 11-17.

[39] Haryanto A., S. Fernando, N. Murali, and S. Adhikari, "Current Status of Hydrogen Production Techniques by Steam Reforming of Ethanol: A Review," *Energy & Fuels*. 2005, 19, 2098-2106.

ethanol production and transportation infrastructure already exists and is undergoing expansion to meet the increasing demand created by the Energy Policy Act of 2005, the Energy Independence and Security Act of 2007, and other legislation.[40,41,42] Ethanol therefore appears to be the most viable mid-term approach to bio-liquid reforming. Other renewable liquid options include sorbitol, glucose, glycerol, bio-oil, methanol, propylene glycol, and less refined sugar streams (cellulose, hemicellulose). Exhibit 2.4 lists the potential bio-liquid feedstocks, reforming technology and feedstock development time frame, feedstock cost, theoretical hydrogen yield, and the advantages and disadvantages of individual bio-liquid feedstocks.

As Exhibit 2.4 shows, ethanol has the highest theoretical hydrogen yield per pound of feedstock. Based on current hydrogen yields from ethanol steam reforming and the potential biomass resources available domestically (1 billion dry tons annually), ethanol reforming could supply nearly 64 billion gge of hydrogen annually on an energy content basis.[43,44] This level of supply represents approximately 45% of our nation's 2005 gasoline consumption.[45]

Hydrogen Quality Assurance One of the advantages of PEM fuel cells is that they do not care about the source of the hydrogen. However, they do care about the purity of it. Effects from the impurities introduced by variable feedstocks must be addressed to deliver hydrogen that will maintain the durability and efficiency of the fuel cells.

Develop Feedstock Pre-Treatments

Typically, reforming catalysts require contaminant-free and de-ionized water. Feedstock pretreatment systems that achieve required feedstock and water purity can represent a significant portion of the capital, operating, and maintenance costs. Feedstocks will need to be analyzed to determine what main contaminants are present and strategies will need to be developed to remove them. For example, crude glycerol contains salts which may need to be removed prior to reforming. For some feedstocks (i.e., ethanol) there will likely be no contaminants remaining after production; however, it may pick up some particles, unwanted chemicals, etc., in transportation. In addition, if the ethanol is de-natured, the effect on the reformer of the added chemicals needs to be investigated. Bioderived liquids reforming requires more water than natural gas reforming. The water purity needs are similar to those of natural gas reforming, as detailed in the section covering DNGR.

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[40] *Energy Policy Act of 2005, H.R.6, 28* June 2005. http://thomas.loc.gov.

[41] "Legislative Actions: State," Renewable Fuels Association, updated March 2006. Accessed 3 August 2006. http://www.ethanolrfa.org/policy/actions/state/. Accessed 21 January 2009.

[42] Renewable Fuels Association, "Ethanol Industry Outlook 2006," February 2006. http://www.theanolfra.org.

[43] The calculation assumes the following: 1) an average hydrogen yield of 5.4 mole H_2 per mole ethanol; 2) an average ethanol yield of 90 gallons of ethanol per dry ton biomass; 3) biomass feedstock availability of 1 billion dry tons annually; and 4) a gallon gasoline equivalent of 1kg H_2 (ignores increased efficiency of fuel cells compared to gasoline internal combustion engines).

[44] "Theoretical Ethanol Yield Calculator," U.S. Department of Energy, Office of Biomass Program, updated 20 Jan 2006.

[45] 2005 gasoline consumption was approximately 8,933,000 barrels per day. U.S. Department of Energy, Energy Information Administration, *Annual Energy Review 2005*, Table 5.13c, Estimated Petroleum Consumption: Transportation Sector, Selected Years, 1949-2005.

Exhibit 2.4 Potential Bio-Liquid Reforming Pathways

Bio-Liquid	Time Frame[ab]	Bio-Liquid Cost (Plant – Gate)	Theoretical H_2 Yield	Feedstock Advantages/Disadvantages
Denatured Ethanol	Mid-term	$1.07/gallon[c]	0.78 kg H_2/gallon ethanol 0.26kg H_2/kg ethanol	Low toxicity Low sulfur content Use of dilute ethanol would reduce reforming feedstock costs Ethanol production/delivery infrastructure is already established
Glucose	Mid-term	$0.07/lb[c]	0.13 kg H_2/kg glucose	Low volatility Non-toxic, non-flammable
Glycerol	Mid-term	$0.15/lb (80% glycerol, ~20% water from biodiesel production)[e,]	0.15 kg H_2/kg pure glycerol	Utilizes low-value glycerol by-product from biodiesel production Low volatility Non-toxic, non-flammable
Crude Glycerol (CG)	Mid-term	<$0.15/lb[f]	0.24 kg H_2/ kg CG	Low volatility
Bio-Oil	Mid-term	$0.03-0.04/ lb bio-oil[g]	0.14g H_2/100g bio oil	High reactivity; potential of forming carbonaceous deposits or converting to aromatics that are more difficult to reform to H_2
Sorbitol	Long-term	$0.10/lb[h]	0.13kg H_2/kg sorbitol	Low volatility Non-toxic, non-flammable
Ethylene Glycol (EG) &Propylene Glycol (PG)	Long-term	EG: $0.44-0.46/lb[,I] PG: $0.71-1.02/lb[,i]	0.15 kg H_2/kg EG 0.22kg H_2/kg PG	Low volatility Non-toxic (PG), non-flammable (both)
Cellulose/ Hemicellulose	Long-term	$0.07/lb[j]	~0.13kg H_2/kg cellulose-hemicellulose	Low volatility Non-toxic, non-flammable
Methanol	Long-term	$0.78-0.91/gallon[,j]	0.64 kg H2/gallon methanol; 0.22kg H2/kg methanol	More easily reformed to hydrogen than ethanol High toxicity Higher corrosivity, volatility than ethanol

[a] Near term (2012), mid term (2012-2017), long term (2017+)
[b] Based on the market readiness of both the reforming technology and the bio-liquid production and distribution infrastructure
[c] This is the DOE EERE Biomass Program target for cellulosic ethanol in 2012.
[d] This glucose price from the 2004 H2A Central Sorbitol Production analysis assumes an nth plant bio-refinery with glucose as one product.
[e] Methanol, fatty acids, and most of the water have been removed.
[f] Assumes the cost of crude glycerol is lower than semi-purified glycerol. Crude glycerol is defined as 55% glycerol and 45% methyl esters of fatty acids.
[g] This represents the DOE Biomass Program 2010 and 2020 pyrolysis oil production cost goals of $5.10/MM Btu and $4.30/MM Btu, respectively. Bio-oil energy content is assumed to be 7.500 Btu/lb.
[h] This is from the 2004 H2A Central Sorbitol Production analysis (2000$) using $0.07/lb glucose.
[I] This is the cost of the fossil-derived product. The bio-based product will have to be cost-competitive.
[j] Consistent with the target cost of cellulosic sugar for ethanol production in 2012 in the DOE EERE Biomass Program

Reduce Labor Cost

On-site, planned maintenance must be minimized both in terms of cost and frequency. The need for on-site support must be removed and replaced with automated process control and remote monitoring.

Enhance Equipment Reliability

The reliability of BOP equipment (pumps, compressors, blowers, sensors, etc.) is often the limiting factor in overall system reliability. Increasing the reliability and service life of these components is critical, as is minimizing equipment complexity. For reformer systems, catalyst activity is also critical for reliable and efficient operation. Impurities in feedstocks (bio-derived liquids, water, etc.) must be removed to protect components in the reactor.

Reduce Material and Energy Losses in Reforming

Loss of efficiency through leaks of feedstock or hydrogen must be virtually eliminated. Heat loss and heat rejection must also be minimized through well-designed insulation and heat integration.

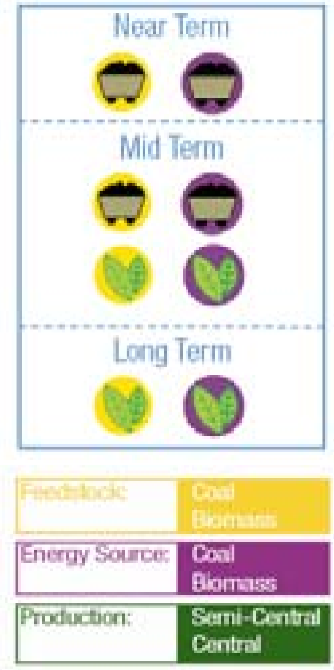
Explore Co-Product Revenue

A central bio-derived liquids reforming facility has the potential to co-produce a variety of products along with hydrogen, such as heat, electricity, and steam. Local use or sale of these products can either increase site revenue or help to load level reformer operation. In the case of aqueous-phase reforming, the reformer may be operated to produce organic liquids or other organic chemicals, which may form an additional source of revenue but may also incur additional disposal cost.

3.0 Coal and Biomass Gasification

Gasification is a mature set of technologies that has the potential to supply the United States with a significant amount of low-cost hydrogen. Currently, these technologies are being applied to areas other than hydrogen generation, such as electrical power production, chemical production, and synthetic fuel production.

Coal and Biomass Gasification



3.1. INTRODUCTION

The coal and biomass gasification pathway calls for producing hydrogen in semi-central and central facilities via thermochemical processing of coal, biomass, and a mix of the two. Gasification technologies using coal as a feedstock are commercially available today. Gasification typically creates a synthesis gas that can be used in chemical applications. DOE's current R&D priorities include capital cost reduction, carbon capture and storage (CCS), and enabling greater use of renewable biomass feedstock.

Coal gasification is a potentially inexpensive way to convert coal into hydrogen as well as electricity and other valuable materials.[46] Some commercial coal gasifiers are in use today. However, for coal to be viable in a carbon-constrained world, efficient carbon capture and storage technologies need to be developed and implemented. While biomass potentially minimizes the carbon impact due to its renewable nature, cost and feedstock issues associated with using biomass feedstock must be addressed. Co-gasification of coal and biomass leverages the abundance and low cost of coal with the renewable nature of biomass. Gasification is considered to be a near- to long-term technology for central and semi-central hydrogen production with initial development completed by 2017.

Environmental Benefits

Co-gasification of coal and biomass leverages the abundance and low cost of coal with the renewable nature of biomass. DOE is working on developing efficient carbon capture and storage technologies for coal and on reducing cost and supply issues for biomass. For more information on DOE's carbon capture and storage activities see www.fe.doe.gov/programs/sequestration/index.html

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[46] http://www.fossil.energy.gov/programs/powersystems/gasification/index.html. Accessed 21 January 2008.

DOE COST TARGETS

R&D on the coal and biomass gasification pathway focuses on achieving the DOE-defined, at-the-pump cost targets for hydrogen production shown in Exhibit 3.1.

Exhibit 3.1 Coal and Biomass Gasification: DOE Cost Targets Cost/gge (plant gate)

Year	Coal (no carbon capture and storage)	Coal (with carbon capture and storage)	Biomass
Current Projected[a]	$1.35	$1.60	<$2.00
2017 Target[b]	<$1.10	<$1.10	<$1.10
Production Scale	**Central**	**Central**	**Semi-Central**

a. On 2005 basis. Coal at $26.70/ton and biomass at $38/bone dry metric ton.
b. On 2005 cost basis. Coal at $26.70/ton and biomass at $41/bone dry metric ton.

COAL AND BIOMASS FEEDSTOCKS

Coal is America's largest domestic fossil energy resource, with hundreds of years of proven reserves and energy content that exceeds the world's known recoverable oil.[47] Additionally, over a quarter of the world's known coal reserves are found within the United States.[47] Coal is a resource that the United States has in abundance and that could be exploited for hydrogen production at the central production size range (>50,000 kg/day). However, a number of barriers need to be overcome prior to coal becoming a clean source of hydrogen. Improved carbon capture and storage are among the top technology needs.

Another major resource that America can tap for energy is biomass, with an estimated billion dry tons potentially available annually[48]. In general, the two types of biomass feedstocks available for use in hydrogen production are (1) primary biomass, such as energy crops like poplar, willow, and switchgrass, and (2) biomass residues, from sources such as animal waste, wood or processed agricultural biomass, and municipal solid waste.[49]

3.2. BARRIERS

Driving DOE's research activities are specific barriers identified in the MYPP[19] and the DOE FE's Hydrogen from Coal RD&D Plan,[50] as well as others identified by the FreedomCAR and Fuel Partnership's HPTT. These are summarized in Exhibit 3.2 and described more fully on the following pages.

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[47] http://www.doe.gov/energysources/coal.htm. Accessed 21 January 21 2008.

[48] http://www1.eere.energy.gov/biomass/pdfs/final_billionton_vision_report2.pdf. Accessed 21 January 2008.

[49] *The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs*. National Academy of Sciences, 2004.

[50] Office of Fossil Energy Hydrogen from Coal Research, Development, and Demonstration Plan – Extern Draft, September 2008, http://www.fe.doe.gov/programs/fuels/publications/programplans/H2fromCoalRDDPlan08.pdf.

Exhibit 3.2 Coal and Biomass Gasification – Summary of Barriers

GHG Emissions (primarily coal)	GHG emissions, specifically carbon dioxide, result from the use of coal. Technologies to capture and store these emissions effectively do not exist.
Feedstock Issues (primarily biomass)	Sources and supplies of the same type/quality of feedstock are not reliable. Feedstock preparation, storage and handling systems, and transportation are all costly and underdeveloped.
Capital Costs	Current reforming systems are capital intensive due to non-standardized plant designs and inefficient, multi-step processes. Hydrogen quality requirements for PEM fuel cells also result in significant capital costs. Minimal data is available on the numerous combinations of coal and biomass types and concentrations that can be co-fed into high-pressure gasifiers.
Operation and Maintenance	The operating and maintenance costs need to be reduced. Balance-of-plant equipment needs to be made more efficient and durable than that which is currently available. Feedstock on-site storage, handling, and preparation need to be improved. Hydrogen monitoring increases the O&M costs as described in the Roadmap Introduction.
Control and Safety	Improved sensors and controls that enable feed flexible operation would reduce costs.

EMISSIONS (PRIMARILY COAL)

Coal gasification generates significant amounts of GHG emissions, specifically carbon dioxide. Other gas, liquid, and solid emissions are regulated and are currently being addressed by industry and do not pose a significant technical barrier, but will have added costs associated with them.

Greenhouse Gas Emissions Gasification technologies produce significant amounts of GHG emissions. Coal is primarily carbon. During the gasification process, the carbon is partially oxidized in the presence of oxygen and steam to produce synthesis gas, a mixture of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), and trace amounts of other compounds. Additional hydrogen is then produced in a second process called water-gas-shift (WGS), which reacts the CO with water (H_2O) to produce CO_2 and H_2. Reducing GHG emissions is one of the primary goals in developing hydrogen technologies. Without sufficient separation and capture of CO_2, the advantages of hydrogen are negated.

One of the advantages of renewable feedstocks is that they generate significantly lower lifecycle GHG emissions than petroleum and other hydrocarbon fuels. Some GHG emissions are associated with biomass feedstock production and collection activities, and the DOE Biomass Program is addressing these issues. Emissions may also be associated with the production of electricity to power auxiliary equipment at gasification facilities. GHG emissions associated with gasification increase due to a number of factors, such as the following:

- Inefficiency of converting the feedstock to hydrogen
- Inefficiency during the handling/preparing of feedstocks
- Emissions during the gasification process
- Poor, underdeveloped hydrogen separation processes.

FEEDSTOCK ISSUES (PRIMARILY BIOMASS)

Biomass feedstock issues include cost, quality, availability, on-site storage, handling, and conversion to useful form. To meet a 50,000 kg/day hydrogen production rate, the gasification plant is designed to process 200 dry metric tons of biomass per day.[19] The DOE Biomass Program reports 2007 biomass feedstock costs to be $60.10 per dry ton delivered, with most of the cost associated with delivery ($13.10/dry ton minimum grower payment, $47/dry ton delivery cost).[51] Biomass costs are projected to rise to more than $59 per dry ton delivered by 2017 due to increased demand.[51] Transportation costs, associated in part with increased demand, also constitute a substantial barrier. In addition to cost, biomass feedstock quality and availability may be limited in some areas, or the quality of the feedstock may change throughout the year. Effects of impurities on the system from multiple feedstocks as well as the effects of impurities from variations in single feedstocks will affect the gasifier system design. Once the biomass feedstock is on site, issues of storage, handling, and preparation will affect production cost. Many gasifiers require the feedstock to be dried and ground prior to use.

CAPITAL COSTS

Since coal and biomass gasification is a capital-intensive process, capital cost function is a key barrier. Capital costs are increased by non-standardized plant designs and inefficient, multi-step reforming processes. The BOP costs associated with maintaining high reliability and safety standards are too exorbitant. Additionally, system durability and lifespan is insufficient, while certifications, codes, and standards requirements are too onerous, increasing capital costs. Hydrogen quality requirements for use in fuel cell vehicles are becoming increasingly stringent, and satisfying these stipulations is a challenge for incumbent technology. These issues are discussed in the roadmap introduction.

Some gasifier technologies use large amounts of oxygen. Air can be directly fed to the gasifier to provide the oxygen; however, the nitrogen in the air dilutes the product stream and increases the cost of hydrogen separation and purification. Alternatively, pure or nearly pure oxygen can be fed to the gasifier, but air separation units tend to be large, inefficient, high maintenance, and expensive. More efficient, safe, low-cost, and durable oxygen separations units are needed.

The syngas produced from the gasifier is composed mostly of carbon monoxide, carbon dioxide, hydrogen and trace amounts of impurities such as particulates, alkali, ammonia, chlorine, sulfur, toxic metals (e.g., mercury, arsenic) and in the case of biomass, tar/pyrolysis oil. Prior to feeding the syngas to the WGS reactors, cleanup is required to remove the majority of these trace contaminants. Stipulations on the quality of hydrogen for use in fuel cell vehicles are becoming increasingly stringent (reductions of some contaminants to the parts per billion (ppb) level), and satisfying these stipulations is a challenge for incumbent technology.

OPERATION AND MAINTENANCE

The O&M costs are too high. More efficient and durable system and BOP equipment is required. On-site feedstock storage, handling, and preparation are barriers to be

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[51] http://www1.eere.energy.gov/biomass/pdfs/biomass_program_mypp.pdf. Accessed 28 January 2008.

addressed. Hydrogen quality monitoring also increases the O&M costs, as described in the roadmap introduction.

O&M barriers in a number of areas will need to be addressed to achieve hydrogen cost targets. All system components must be considered in O&M, including feed pre-conditioning (grinding, drying, etc.), gasification, controls, utilities, QA/QC (sensors), compressors and other BOP, storage, dispensing, and safety. Other areas in which O&M barriers persist include equipment durability and reliability, oxygen plant optimization, scheduled maintenance, feedstock issues, material loss minimization, energy loss reduction, waste disposal, and hydrogen quality.

Durability Both the frequency and cost of repairs must be considered. Catalysts for some water gas shift reactors and some gasification technologies require enhanced catalyst durability and lifetime as well as increased tolerance to impurities and operating temperatures.

Equipment Reliability The reliability of equipment (such as pumps, compressors, blowers, sensors, and other BOP) is often a limiting factor in overall system reliability. Incumbent equipment is often too complex and does not meet reliability needs for O&M cost targets.

Oxygen Plant Optimization Gasification technology uses oxygen and steam to partially oxidize the coal to carbon monoxide and hydrogen. Air can be injected into the gasifier, but the large amount of nitrogen dilutes the exit gas stream containing hydrogen and increases the cost of the hydrogen separation process. Therefore, oxygen is removed from the air prior to injection into the gasifier, but this is also costly and requires a significant amount of energy.

Scheduled Maintenance Frequent scheduled maintenance and on-site maintenance staff are costly. Robust systems that require little routine maintenance will require automated or remotely handled system troubleshooting.

Feedstock Issues Biomass feedstock supplies, consistency, distribution, cost, preparation, handling, and on-site storage issues need to be addressed.

Minimized Material and Energy Losses On-site feedstock storage, handling, and preparation must be efficient in terms of energy while also minimizing feedstock waste. Gas leaks result in loss of process efficiency, decreased safety, and excessive GHG emissions. Heat loss and heat rejection are also barriers to system efficiency.

Waste Disposal For O&M, permitting, storage, and disposal issues may need to be addressed for gas emissions and for liquid and solid wastes. These issues will depend on the feedstock and the technology employed. Conversion rates currently result in too much waste generation, and alternative markets for the wastes are unavailable.

Hydrogen Quality Continuous hydrogen quality monitoring may be required for central hydrogen production. This topic is discussed in the roadmap introduction.

CONTROL AND SAFETY

Control and safety issues associated with gasification technologies need to be further addressed. These issues are particularly important in the biomass and co-gasification scenarios, in which the type, quality, and/or mix of biomass feedstock may vary. More generally, high control costs persist due to a lack of system simplification, system standardization, and reduced sensor count. Currently available sensors are not cost-effective or sufficiently reliable. Certifications, safety codes and standards should be standardized and met. These units must be designed to operate in an environment of minimal manual assistance, which will entail attributes such as back-up fail-safe mode, remote monitoring, and sparse maintenance schedules. The system design faces barriers in meeting all requirements of local and national permitting processes for effluents such as SO_2 and other gas and liquid exhausts.

3.3. CRITICAL TECHNOLOGY NEEDS

Exhibit 3.3 lists critical technology needs for coal and biomass gasification for hydrogen production, and a discussion of these efforts follows. Note that a single R&D activity may address more than one barrier or multiple R&D activities may be needed to address a single barrier. For more detail on the alignment of R&D needs with technology barriers, please see Appendix B.

Exhibit 3.3 Coal and Biomass Gasification Critical Technology Needs

Reduce Capital Costs	➔ Reactor capital costs ➔ Low-cost separation and purification technologies ➔ Improved catalysts ➔ Low-cost coal and biomass feed preparation and handling ➔ Carbon capture and storage ➔ Balance-of-plant
Reduce O&M Costs	➔ System durability and robustness ➔ Emission controls ➔ Feedstock storage, preparation, and handling ➔ Hydrogen quality monitoring

REDUCE CAPITAL COSTS

Individual unit operations that have the potential for capital cost reductions include the WGS reactors, hydrogen separation/purification, oxygen separation, syngas cleanup, and hydrogen compression/storage. To substantially decrease the plant capital cost, elimination of some unit operations may be required. For example, tar reformers in biomass gasification could be combined with WGS reactors or WGS reactors can be combines with hydrogen separation and purification technologies. On a larger scale, the gasifier itself could be integrated with existing commercial processes such as electricity in a co-production concept. Similarly, a biomass gasifier may be integrated with an ethanol production plant,[52] with a paper mill to gasify the solid organic wastes, or with a municipal waste facility.

Additional activities that can contribute to reducing capital costs include increasing system durability/lifespan; developing low-cost feedstock preparation and handling equipment; developing carbon capture and storage technology; and developing common certifications, codes, and standards.

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[52] See the Range Fuels plant project to produce ethanol via gasification of biomass. Accessed 13 January 2009. http://www.energy.gov/print/4827.htm and http://www.energy.gov/media/Range_Fuels_One_pager.pdf.

Reactor Capital Costs Capital costs for gasification plants can be reduced by designing more efficient and less expensive units or through process intensification, whereby multiple units are combined. Additionally, the co-gasification of different coal and biomass types is not well-understood and needs further investigation regarding feeding systems and characterization of the synthesis gas and potential downstream impacts. A stronger fundamental understanding of the mechanisms in both the gasifier and the reforming reactions may help in designing more efficient reactors and conditions that would maximize production while decreasing costs.

Separation and Purification PEM fuel cells require highly pure hydrogen which places a significant requirement on hydrogen separation and purification technologies. More robust hydrogen separation and purification technologies may lead to reduced capital and costs and improved efficiency.

Improved Catalysts The WGS and tar reformers need improved catalysts that are tolerant to impurities such as sulfur. Membrane reactors may be able to combine the WGS and separations, also decreasing the capital costs.

Balance-of-Plant More durable, efficient, and robust BOP components (pumps, blowers, air separation units, water purification, desulfurization, emission controls, sensors, and other components) are needed.

Feed Preparation and Handling Improved feed preparation and handling equipment is needed to decrease the capital costs. The equipment should be able to process multiple types of feedstocks, particularly for biomass applications.

Carbon Capture and Sequestration Analyses indicate that sufficient CO_2 storage resources exist in close proximity to where coal is found and used.[53] Improving the efficiency of CO_2 capture and storage and developing new methods will reduce the associated costs. Improved and lower-cost approaches to carbon capture and storage need to be identified and developed.

REDUCE OPERATION AND MAINTENANCE COSTS

O&M costs must be addressed through several R&D needs. System component integration and low-cost separation/purification and monitoring technologies will help drive down these costs. Improved oxygen separations would reduce the energy costs and improve the efficiency of the process. Energy losses must also be minimized through well-designed insulation and heat integration. Finally, waste management should explore alternative markets for the wastes to transform them into commercial products.

System Durability, Robustness, and Lifespan Coal and biomass gasification units require regularly scheduled maintenance, which requires that they be taken off-line. Increasing the system durability and robustness would decrease the downtime, resulting in lower O&M costs. In addition, system component integration and low-cost separation/purification and monitoring technologies will help drive down O&M costs.

Emission Controls Improved unit operations that are more efficient and less expensive to operate are required to handle the pollutant emissions found in coal and, to a lesser extent, biomass. Less expensive, more robust sensors and control systems are needed to

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[53] www.fossil.energy.gov/programs/sequestration/index.html. Accessed 22 January 22 2008.

increase efficiency in meeting emission control requirements. BOP energy efficiency improvements will lower overall GHG emissions by reducing the use of grid electricity and reducing feedstock use for energy production. In addition, plant footprint reduction, design for manufacturing, and systems integration efforts have the potential to reduce life-cycle GHG emissions by reducing the energy and materials used to manufacture plant equipment.

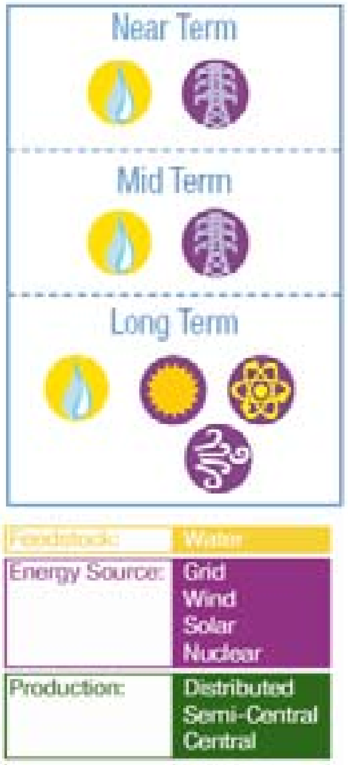
Feedstock Storage, Preparation and Handling More robust, efficient, flexible, and less expensive feedstock storage, preparation, and handling systems are needed. The best way to reduce these costs may be to increase the feedstock supply and decrease the transportation costs. Transportation costs can be reduced more effectively for distributed, medium-sized (semi-central) plants rather than larger central facilities. One way to decrease the biomass feedstock issues is to co-gasify it with coal. Co-gasification decreases the carbon impact of the coal, since the biomass is considered renewable, and it promotes biomass use by decreasing the feedstock issues (coal is more cost-effective, available, and easier to handle). Efficient, feedstock-flexible gasifiers are needed to address location-specific feedstock supply and quality issues. Gasifiers that can operate efficiently with a wet stream need to be developed. Development may also be required for in-plant feedstock handling systems that can economically and efficiently convert a wide range of feedstocks into a consistent form so that existing, low-cost feeders can function reliably.

Hydrogen Quality Monitoring Hydrogen quality monitoring requires developments of standard test methods that can detect some contaminant species at very low levels.

4.0 Water Electrolysis

The near-term pathway for hydrogen production through water electrolysis calls for using the existing infrastructure for water and electricity. GHG impacts of this technology will be greatly reduced when the electricity to power the electrolysis is supplied by near-zero emissions sources.

Water Electrolysis



4.1. INTRODUCTION

Water electrolysis capability is being pursued for distributed, semi-central, and central production. Production systems will generate hydrogen with alkaline electrolyzers, proton exchange membrane electrolyzers, or solid-oxide electrolysis cells (SOEC). DOE's current R&D priorities focus on capital cost reduction, efficiency improvements, and materials development.

Initially, water electrolysis is expected to be deployed on site at distributed/forecourt hydrogen refilling stations, where it could stimulate market acceptance. Distributed commercial hydrogen production via water electrolysis is considered a near- to mid-term technology and is expected to outgrow the need for DOE funding by 2017.

In the longer term, centralized production has the potential to expand substantially the commercial supply of hydrogen by water electrolysis. Larger, semi-central and central production via wind and nuclear power is being investigated by both NE and EERE within DOE.

Environmental Benefits

Hydrogen production by water electrolysis has the potential for positive environmental impacts. Carbon emissions from grid electricity will decrease as carbon capture and storage technologies are developed and implemented for power plants and as electricity is increasingly generated with renewable and nuclear power. Capture and storage of CO_2 emissions is not feasible for use on the 225 million vehicles traveling over 8 billion miles per day in the United States. However, grid-powered electrolysis centralizes the emissions, improving the feasibility of a technology solution to address the issue. Other emissions, such as NOx, VOC, and especially carbon monoxide, would be significantly reduced through use of hydrogen as a transportation fuel.

DOE COST TARGETS

R&D on the water electrolysis pathway focuses on achieving the established at-the-pump cost targets for hydrogen production, as shown in Exhibit 4.1.

Exhibit 4.1 Water Electrolysis: DOE Cost Targets
Cost/gge (Produced)

Year	Alkaline Electrolyzer		Proton Exchange Membrane Electrolyzer		Solid Oxide Electrolysis Cell
Current Projected	$5.20		$4.80		NA
2017 Target	<$2.70*	<$2.00	<$2.70*	<$2.00	<$2.00
Production Scale	Distributed	Semi-Central/ Central	Distributed	Semi-Central/ Central	Central

* For distributed production, add $0.30 for on-site compression, storage, and dispensing in 2017.[19]
2005 capital cost basis and electricity at 3.9¢/kWh.

PRODUCTION SCALE

Distributed hydrogen production has near- to mid-term potential because many existing forecourt stations may be able to incorporate an electrolysis unit. Low-temperature, modular units have the potential to be reasonably small (~100 kg/day) and able to use the existing water and electricity infrastructures, although this deployment scenario may require changes to current codes and standards.[49] The compact, modular, nature of the technology will enable hydrogen production to grow as demand increases simply by adding electrolysis units. This modularity decreases initial installation costs. In addition, this forecourt production can stimulate market acceptance and foster demand while central production and pipeline distribution infrastructures develop.

The electricity costs and GHG emissions associated with this technology will vary widely from one region to another. Analyses suggest that using the current grid mix will increase GHG emissions compared to gasoline vehicles on a well-to-wheels basis, even if the hydrogen is used in the highly efficient fuel cell cars under development. Over time, however, electricity generation is projected to make increasing use of renewable resources and cleaner technologies.

Central hydrogen production will require larger facilities that co-generate electricity with the hydrogen and can take advantage of economies of scale. Water can often be obtained in high volumes at low cost, and the electricity will be generated on site from low carbon sources. Large electrolysis modules can be built, and cascaded modules can then be brought on line as needed.

Electrolytic hydrogen production may be particularly useful for load-leveling of the electricity generated from wind turbines, reducing fluctuations in capacity or augmenting capacity during periods of peak electricity demand. Thus, it may be feasible to negotiate favorable electrical rates by operating the electrolyzers during “off-peak” periods (>90% of the time).

Finally, the DOE’s NE program is examining the option of using waste heat from nuclear power plants to provide thermal energy for high-temperature electrolysis. High-temperature electrolyzers require about two-thirds of the electrical energy needed by low-temperature electrolyzers to produce the same amount of hydrogen; the additional energy is provided by heat added to the system.[54] For the first time in 25 years, there is serious discussion of building new nuclear power plants.[55] As of September 2007, companies have announced that they intend to submit applications to the U.S. Nuclear Regulatory Commission (NRC) to build 25 new power plants.[56]

4.2. KEY BARRIERS

Driving DOE's research activities are specific barriers identified in the MYPP[19] as well as others identified by the FreedomCAR and Fuel Partnership's HPTT. These are summarized in Exhibit 4.2 and described more fully below.

Exhibit 4.2 Water Electrolysis – Summary of Barriers

System Efficiency And Electricity Cost	Electricity is the dominant cost in water electrolysis hydrogen production. System inefficiencies results in significant power cost requirements.
Renewable and Nuclear Electricity Generation Integration	Supply variability in renewable sources of power as well as inefficient conversion technologies pose barriers to integrating water electrolysis with renewable energy. Power conversion and other system component barriers exist inhibiting high-efficiency, low-cost, integrated hydrogen production from nuclear sources.
Capital Costs/Footprint	Capital costs for current electrolyzer technologies are a barrier to attaining the targeted hydrogen production cost. High capital costs are caused by expensive materials, relatively small systems, relatively low efficiencies, customized power electronics, and labor-intensive fabrication.
Manufacturing	Current electrolysis units are assembled using low-volume manufacturing techniques. Mass production is capital intensive, while substantial returns on investments are not assured. Current designs are insufficiently reliable and require intensive labor and parts.
Operation and Maintenance	O&M costs for water electrolysis systems are currently too high. Frequent routine maintenance and on-site staff are prohibitively expensive.
Grid Electricity Emissions	The current grid electricity mix in most areas adds significantly to the electrolysis systems' life–cycle carbon footprint. Low-cost, carbon-free electricity generation is not yet widely available.
Control and Safety	Costs associated with control and safety are too high. Current certifications, codes, and standards are inconsistent, complicating oversight. Nuclear generation presents special control and safety issues.

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[54] Holladay J. D., J. Hu, D.L. King, and Y. Wang, "An Overview of Hydrogen Production Technologies," *Cat. Today*. 139 (2009), 244-260.

[55] http://www.ne.doe.gov/np2010/neNP2010a.html# Accessed 11 October 2007.

[56] http://www.nei.org/resourcesandstats/documentlibrary/newplants/graphicsandcharts/newnuclearplantstatus/ Accessed 11 October 2007.

SYSTEM EFFICIENCY AND ELECTRICITY COST

For electrolyzers in all applications, electricity is a significant portion of the hydrogen production cost. Major inefficiencies exist in current electrolysis stack, compressor, and drying subsystems. In addition, the power electronics that convert the AC power to suitable DC power generate some power losses.

Current low-temperature electrolysis systems range from 50 to 62% efficient (based on the lower heating value (LHV) of hydrogen and all systems and auxiliaries except compression). Based on analysis to achieve the cost targets, the stack efficiency needs to be increased to 74% (LHV), and the system should be made 71% (LHV) efficient, including all auxiliaries except compression.[57] The primary losses are currently in the oxygen-generating electrode. Improved catalysts and membranes may enable some efficiency improvements. In addition, operating at high temperatures, made possible with use of SOEC technology, will increase the electrical efficiency of the systems. These higher-temperature systems will need greater durability, requiring the development of corrosion-resistant materials and improved seals.

Increasing compressor efficiency would also increase total system efficiency. Improvements in the compressors are being developed by the Hydrogen Delivery Technology Team. Producing the hydrogen at higher pressures may decrease the need for compressors and make it feasible to eliminate the compressors completely. Traditionally, water electrolysis is performed at low pressures (100 psig or less), so development of high-pressure systems will require significant changes in the stack design, modifications to the membranes and seals, and development of appropriate safety codes and standards.

Finally, once the hydrogen is produced, residual water needs to be removed prior to compression. Depending on the method used to dry the gas, 10% or more of the generated hydrogen may be lost or a significant amount of electricity may be consumed. Improved processes must be identified and deployed to decrease these losses.

RENEWABLE AND NUCLEAR ELECTRICITY GENERATION INTEGRATION

The chief concern in powering water electrolysis with renewable energy is the variability of the renewable energy source. Wind and solar systems require grid back-up or sufficient storage to weather the times of low resource availability. (Based on high storage costs, the most likely scenario is grid back-up). Integration with nuclear generation presents barriers associated with system component designs as well as certifications, codes, and standards.

Additionally, both renewable generation and water electrolysis use power electronics, which convert the AC grid or other power source to a DC source with the desired voltage. Today, power electronics are generally custom-built devices that may account for up to 30% of system cost. For example, a wind turbine produces AC electricity at a frequency dependent on wind speed. This “wild” AC current is converted to grid frequency (60Hz) by power electronics at the turbine. The electrolysis system then converts this AC current to DC power.

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[57] Efficiencies were calculated using the lower heating value. Electrolyzer systems (including all auxiliaries other than compression) were targeted to operate at 46.9 kWhr/kg or 71% efficiency using the lower heating value. *Hydrogen, Fuel Cells, & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan*, April 2007, http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/.

CAPITAL COSTS

Capital costs for current electrolyzer technologies are a barrier to attaining the targeted hydrogen production cost. High capital costs are caused by expensive materials, relatively small systems, relatively low efficiencies, customized power electronics, and labor-intensive fabrication.

The high costs of noble metals and the lack of durability drive up membrane costs. Current production rates are below targeted levels, and systems are incapable of efficiently operating at the high current densities that would allow decreased stack size. Cell and stack architecture is often too complex and does not have a long enough life span. Generally, production volume is insufficient to meet projected future demand. Custom built-power electronics also contribute to increased capital costs. Higher-temperature systems need low-cost thermal management (e.g., vaporizers, recuperators).

FOOTPRINT

Station footprint is dependent on the location and needs of each locality. In general, the footprint will have the same limitations as described in the Station Footprint section of the DNGR chapter.

MANUFACTURING

Electrolysis units are currently produced in low volume. Mass production is capital intensive, and manufacturers must therefore have assurance that the product demand will be high enough to enable adequate return on investment. The industry believes that manufacturing techniques can progress sequentially from hand processes to low-volume, semi-automated, automated, and finally high-volume automated processes, similar to automotive construction, at unit demands of 10; 100; 1,000; and 10,000 units per year, respectively.[58] A step change in cost is anticipated for each change in manufacturing technique. Currently, low-volume production gives suppliers greater leverage with manufacturers to increase overall cost. For example, SOECs require stainless steel manifolds and interconnects. The optimal thickness of the steel is not a standard size, and to get the desired thickness would require a steel run of approximately 70,000 pounds. At low-volume production, manufacturers would be forced to pay extra for the steel or use plates that are of less than optimal thickness.

The cost of water electrolysis systems is driven up by the high costs of BOP and the poor lifespan and durability of system components. Site-specific fabrication drives up manufacturing costs of crucial system components and of BOP components, and often results in systems that are larger than necessary.

OPERATION AND MAINTENANCE

O&M costs for distributed hydrogen production from water electrolysis are too high. Diverse barriers need to be addressed to achieve the stated targets. For distributed production, some of the O&M issues related to durability, scheduled maintenance, and demand management are nearly identical to those for DNGR systems (see Section 1.2). Central hydrogen production entails O&M costs, and even though the specific needs and constraints may vary from the distributed case, the themes will be similar. All system

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[58] From discussions with the DOE Water Electrolysis Group Industry Experts, 28 February 2008.

components must be considered in O&M, including power conditioning/management, feed pre-conditioning (e.g., water purification), controls, utilities, QA/QC (e.g., sensors), compression, storage, dispensing, and safety.

Efficiency The major cost during operation is electricity, so the efficiency of the electrolysis system (stack, BOP, power conditioning/management, etc.) is crucial. However, there are trade-offs between efficiency and capital cost. The stacks could be operated at extremely high efficiencies, but to achieve the desired production rates, larger stacks (increased capital cost) would be required. Techno-economic analysis can be used to help determine the projected optimal balance between efficiency and capital costs.

Durability High-temperature stacks require improved materials that are inexpensive, efficient, and highly resistant to corrosion. In addition, high-temperature seals must be able to operate at moderate pressures and withstand thermal cycling.

Transients and Duty Cycles For central wind and distributed production cases, water electrolysis units will not be operated at constant levels due to variations in power (wind) or fluctuating demand (distributed). Efficient operation over a wide range of conditions and quick and safe response to transient changes represent major challenges to water electrolysis systems.

Water Purification Water electrolysis requires a pure water stream. This purity is typically achieved through reverse osmosis, deionization filters, or other pretreatment. The technologies involved are mature and used in a variety of fields. Cost and durability of the units must be considered along with ease of operation.

GRID ELECTRICITY EMISSIONS

The most likely initial introduction of water electrolysis will be in distributed hydrogen generation stations using the existing electric grid. As noted previously, the current grid mix in most locations generates greenhouse and other gas emissions. Until low-cost, low-emissions electricity generation becomes widely available, renewable energy credits could be purchased to offset the emissions; however, such purchases will increase the hydrogen cost.

CONTROL AND SAFETY

Control and safety barriers associated with water electrolysis include the efficiency of start-up and shut-down processes, turn-down capability, and the capability for rapid on-off cycling. Control and safety system costs remain high due to complex system designs and multiple high-cost, necessary sensors. Currently available sensors are too expensive and insufficiently reliable. For distributed production, the permitting process critically relies on the proven reliability and safety of these units, which are a key qualification target. These units must be designed to operate in an environment of no manual assistance, which will require attributes such as back-up/fail-safe mode, remote monitoring, and sparse maintenance schedules. Centralized production will require development of new control and safety procedures. This is particularly true for central generation using nuclear power. Key questions need to be answered, such as how close the hydrogen generation facilities should be to the nuclear generator and how close should the compressed hydrogen pipeline be to the nuclear reactors.

4.3. CRITICAL TECHNOLOGY NEEDS

Exhibit 4.3 lists critical technology needs for water electrolysis hydrogen production. Discussion of these efforts follows. Note that a single R&D activity may address more than one barrier or multiple R&D activities may be needed to address a single barrier. For more detail on the alignment of R&D needs with technology barriers, please see Appendix B.

Exhibit 4.3 Water Electrolysis Critical Technology Needs

Reduce Capital Costs	➔ Materials ➔ Improved catalysts ➔ Architecture ➔ H2 quality control/hydrogen drying ➔ System optimization to manage variable demands ➔ DFMA/high-volume equipment manufacturing and BOP
Reduce Operation and Maintenance Costs	➔ Automated process control ➔ Reliability ➔ Minimized material and energy losses ➔ Hydrogen drying ➔ Water conditioning ➔ Capital utilization

Meeting the foregoing challenges and achieving the commercialization cost targets for hydrogen production from water electrolysis will require diverse R&D efforts as well as the development of policies and standards. Many nuclear facilities currently have hydrogen safety protocols that may be adapted for production. In addition, standardizing certifications, codes, and standards will minimize control and safety concerns. Technology improvements must be developed in the context of a stringent regulatory environment, limited physical space, and resource limitations. Accompanying outreach efforts will be needed to encourage public acceptance of fuel cell vehicles and hydrogen fueling stations.

The cost of producing hydrogen from water electrolysis is largely determined by the electricity and capital equipment costs. Thus, improved system efficiency and reduction of capital cost are the primary technology needs. For distributed installations, HFCIT's *MYPP* sets the "Electrolysis Unit Capital Cost Contribution" in 2010 to \$0.70 per gge (to achieve the \$3.70 gge DOE cost target for hydrogen at the pump) and \$0.30 per gge in 2015 (to achieve the <\$3.00 gge DOE cost target for hydrogen at the pump). For central hydrogen electrolysis units, the capital costs are \$0.80 per gge to achieve \$3.10 gge (plant gate) in 2012, and \$0.20 per gge to achieve <\$2.00 gge (plant gate) in 2017.[7, 19]

REDUCE CAPITAL COSTS

Currently, significant research efforts are directed toward developing new and improved materials, increasing stack and system efficiency, reducing part count, improving electrodes, and integrating renewable power. Advances have been achieved in all of these areas, and additional efforts are needed to facilitate mass production of equipment and development of materials that are lower cost, easier to manufacture, and more durable.

Materials The materials cost discussion is divided into improvements needed in low-temperature systems and in high-temperature systems.

Low-temperature water electrolysis units need improved materials in several areas: membranes, membrane electrode assembly (MEA) bi-polar plates, frames/support structures, and seals. Membranes tend to be expensive and/or require expensive processing techniques; development work is needed for membranes that are inexpensive, easy to manufacture, and easy to process. The ionic conductivity of the membranes needs to improve to decrease the over-potential. This would result in higher efficiency or higher electric current capability, depending on how the stack is operated. Operation at higher temperatures may increase the efficiency of the systems. Finally, the membranes need to be more durable. Less expensive, more durable materials that are easier to process would help to lower costs.

Alkaline electrolyzer cells need materials with improved CO_2 tolerance. In alkaline systems, CO_2 reacts with the electrolyte potassium hydroxide (KOH) to form carbonates, which have a number of undesirable effects on the cell. Carbon dioxide scrubbers and/or gas diffusion layers need to be improved to inhibit CO_2 from gaining access to the electrolyte. New, inexpensive materials are needed to decrease the cost of the frames and electrode support structures. This is particularly important to enable systems to operate at elevated pressures.

Current electrolysis units typically produce hydrogen at 100-150 psig. Development of systems capable of operating at higher pressures would decrease the capital and operational costs for compressors. Finally, improved seals are needed to enable high-pressure, long-life operation. Low-cost, durable seals need to be developed to connect the SOECs to their BOP. For both low- and high-temperature technologies, detailed models are needed to aid in stack and system scaling. Finally, advances in fuel cell development should be monitored and applied, as appropriate, focusing on work by DOE's EE low-temperature and Solid State Energy Conversion Alliance (SECA) high-temperature programs.

High-temperature SOEC systems have materials needs similar to their lower-temperature counterparts; however, there are enough differences to warrant a separate discussion. High-temperature systems now operate at 800° to 850°C and use a solid oxide electrolyte rather than the organic separator found in low-temperature (<150°C) systems. The cost of the system could be decreased if inexpensive, durable electrolytes could be developed to offer higher ionic conductivity at operating temperatures of 550° to 750°C. These electrolytes need to be able to operate for long periods of time and withstand occasional thermal cycles without de-lamination from electrodes and interconnects. Interconnects need development to improve their corrosion resistance and increase their useful life. Current SOEC stacks have issues with manifold scaling and corrosion due to the high-temperature steam used in the systems. Materials with improved corrosion resistance are needed to enable long-life operation. Finally, high-temperature steam tends to pull chrome from the steel tubes and interconnects that are often used in these systems. The chrome can deposit onto the electrodes, poisoning them. Coatings, filters, and/or improved catalysts need to be developed to prevent the chromium from migrating from the steel tubes.

Improved Catalysts Although the catalysts vary, the needs are the same for high- and low-temperature systems. Electrodes need improved catalyst durability and activity at lower cost. For the SOEC and alkaline systems that currently use low-cost electrodes (typically nickel or lanthanides), catalyst activity and durability could be improved with novel deposition techniques, nano-catalysts, or improved supports. For PEM electrolysis cells, non-precious metal catalysts with high activity and durability would decrease overall capital costs.[59] SOEC systems have the added need to depress reverse water-gas-shift side reactions.

Architecture Current water electrolysis units have relatively low production rates (typically 100kg/day or less). These units need to be scaled up, particularly to achieve the massive production rates required in central production (>50,000 kg/day). Novel architectures may be required to maintain low cost. These architectures will need the following characteristics:

- Low-cost support structures
- Oxidation/corrosion resistance
- Durable seals
- Low-pressure drop flow fields
- High-pressure operation
- Able to operate at appropriate temperatures for long life
- Chemical compatibility with the systems
- Even gas flow distribution
- Appropriate electric current distribution
- Reduced part count
- Amenable to low-cost, high-volume manufacturing

Of particular interest is increasing the operating pressure. Increasing the stack operating pressure to 300-1,000 psi may help decrease compressor and hydrogen drying costs with minimal impact on stack costs.

For SOEC-based technologies, the following characteristics are also needed:

- Good coefficient of thermal expansion (CTE) match for higher temperature operation
- Chromium migration mitigation
- Uniform stack temperature distribution

H_2 Quality Control/Hydrogen Drying Requirements on the quality of hydrogen for use in fuel cell vehicles are becoming increasingly stringent, and incumbent technologies need to satisfy these requirements. (A draft version of current hydrogen quality specifications is available through SAE TIR J2719). Strict quality requirements also introduce the need for low-cost support and equipment to conduct quality control. Standard test methods need to be developed and made readily available to detect some of the contaminant species at the prescribed level. This continues to be a research priority. For water electrolysis technologies, the primary contaminant is water. The most popular drier technologies include adsorption techniques or membrane driers. The adsorption technologies can be disposable (increased operation costs and a disposal cost) or regenerable (increased operation costs). Typically, a water transport membrane (for

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[59] For PEM systems, it is unlikely that a non-noble metal catalyst will be identified, but ways to decrease metal loading may be discovered. From discussions with the DOE Water Electrolysis Group industry experts, 28 February 2008.

example Nafion™) is used to keep drying gas separate from the wet hydrogen stream. Hydrogen drying decreases efficiency either by requiring generation of a dry nitrogen stream or using a hydrogen stream, which entails loss of some of the hydrogen produced. Novel, more efficient drier technologies are needed to decrease these costs.

System Optimization to Manage Variable Demands For distributed hydrogen production, demand for hydrogen refueling will vary significantly over the course of a day. This variable demand may be handled through a combination of on-site hydrogen storage and load-responsive capability in the water electrolysis system. The use of storage versus load-response capability to handle variability will significantly impact capital cost, electrolyzer system utilization, service station footprint, and cost at the pump. In some cases, reduced electricity rates may be negotiated by operating primarily during off-peak times. This may make it more economical to have larger storage tanks compared to other distributed hydrogen technologies. Optimizing the balance between storage and production rate capacity must also consider the relative impacts on maintenance costs and safety.

In some central wind scenarios, the hydrogen production rate will vary significantly. The water electrolysis system will need to be able to operate over a wide range of conditions with high efficiency. In addition, suitable power electronics will need to be developed to enable efficient power conversion.

DFMA/High-Volume Equipment Manufacturing and BOP DFMA will be a key component of cost reduction efforts for water electrolysis units, both for near-term, semi-custom installations, and for longer-term, higher-volume manufacturing. In the near term, in light of limited production volumes, DFMA should be focused on developing water electrolysis designs that incorporate commonly available (commodity) materials and use common tooling and available standard sizing of procured components, (such as tubing, driers, and power electronic components). Design for modularity will be especially important for semi-custom installations. Modular design will allow improvements in specific subsystems to be incorporated without redesigning the entire process. Flexible, modular design will also allow scalable systems, thereby increasing the application domain and overall production volumes. Other critical technology needs in DFMA for water electrolysis are the same as those discussed in the DNGR Section.

REDUCE OPERATION AND MAINTENANCE COSTS

O&M costs produce a significant impact on the overall cost of producing hydrogen. Electricity costs can be decreased by increasing system efficiency and negotiating lower rates with the electric utility (e.g., by agreeing to operate the electrolyzer system primarily during off-peak hours). O&M costs may also be reduced through improved process design and technologies that increase energy efficiency, including improved process controls for cycle optimization, better and less expensive sensors, and better turn-down capability.

Automated Process Control Planned maintenance must be minimized both in terms of cost and frequency. For distributed hydrogen production, on-site labor support must be replaced with automated process control and remote monitoring. For central hydrogen production, automated process control with limited monitoring will reduce the on-site labor support, but is not as crucial as in the distributed case.

Reliability Equipment reliability (especially pumps, compressors, and blowers) is often a limiting factor in reliability of the overall system. Increasing the reliability of these components, along with minimizing equipment complexity, is critical for improving system reliability. For water electrolysis systems, sustained catalyst activity is important for reliable and efficient operation. Impurities in water must be controlled to protect water electrolysis components.

Minimized Material and Energy Losses Hydrogen leakage must be virtually eliminated to minimize loss of process efficiency as well as for safety. Heat loss and heat rejection must also be minimized through well-designed insulation and heat integration.

Hydrogen Drying The hydrogen produced by water electrolysis contains a considerable amount of water. Typically, adsorbents or membrane driers are used, and each technology has its advantages and disadvantages. More efficient methods are needed to dry the hydrogen with little or no hydrogen loss.

Water Conditioning High-purity water is required for long-life water electrolysis operation. Municipal water needs to have contaminants removed, typically by reverse osmosis or similar purification systems, to achieve a resistivity of less than 2kΩ-cm for alkaline electrolyzers or 1-5MΩ-cm (ASTM Specification 2) for PEM and SOEC electrolyzers. Efficient conditioning systems need to be developed. Unused water from the water electrolysis could then be recycled to decrease water conditioning costs.

Capital Utilization Electrolyzer systems require less maintenance if operated at constant load. Peaks and valleys in hydrogen demand for vehicles must be leveled to maximize the utilization of capital and decrease maintenance costs. Water electrolysis unit size must be balanced with an appropriate hydrogen storage system. Increased utilization may also be accomplished by finding alternate uses for the hydrogen or generating revenue from co-produced products. This is particularly important for the central production cases, where electricity can be sold as co-product.

Reduce BOP Cost BOP components are a significant part of the capital cost. Improved, low-cost sensors, pumps, water purification systems, and monitoring equipment need to be developed.

5.0 Thermochemical Hydrogen

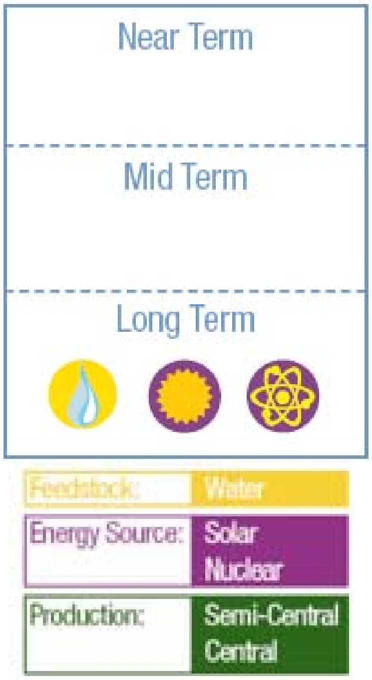
The thermochemical hydrogen (TCH) pathway calls for producing hydrogen in semi-central and central facilities via high-temperature thermochemical water splitting. TCH offers a potential technology for clean, sustainable hydrogen production.

5.1. INTRODUCTION

The TCH pathway uses only water; heat from the sun, nuclear energy, or other source; and chemicals that are recycled. Only hydrogen and oxygen are produced, and all that is consumed is water and solar thermal or other energy. Similar thermochemical cycles are being developed under the Nuclear Hydrogen Initiative (NHI) using nuclear energy as the heat source. This roadmap focuses on solar-powered TCH pathways (STCH) and summarizes NHI's strategy. The high-temperature energy source for nuclear hydrogen production is being developed under the Next Generation Nuclear Plant project within the NE.[60] DOE's current R&D priorities for this hydrogen production pathway are chemical cycle selection and materials development.

TCH is an immature technology requiring long-term development. Most of the chemical cycles for this application were identified from the 1960s through the early 1980s, after which nearly all research in this area stopped.[61] Making TCH technically viable will require long-term research into basic chemistry and materials. The technologies can be divided into those that only use thermal energy for the cycle and hybrid cycles which incorporate an electrolyzer to complete the cycle at a relatively lower cost.

Thermochemical Production



Environmental Benefits

Thermochemical hydrogen production offers a potential route to clean, sustainable hydrogen production. It uses only water, heat, and chemicals that are recycled. When the heat comes from the sun, only hydrogen and oxygen are produced and only water and solar thermal energy are consumed.

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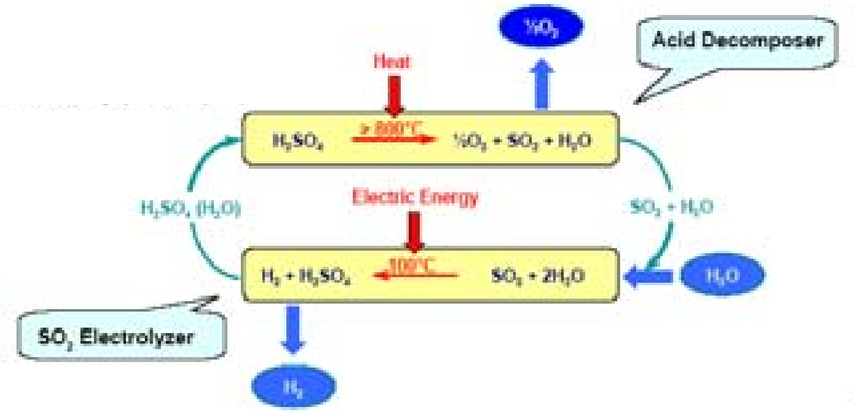
[60] http://www.ne.doe.gov/pdfFiles/factSheets/NextGenerationNuclearEnergy.pdf Accessed 21 January 2009.

[61] Lewis M., M. Serban, J. Basco, and J. Figueroa, "Low Temperature Thermochemical Cycle Development," Argonne National Laboratory presentation to NEA/OECD, 2-3 October 2003.

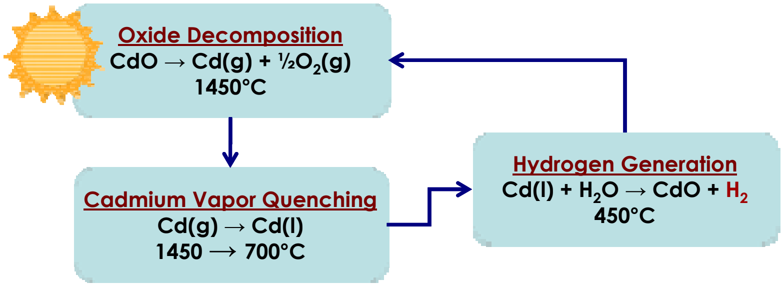
An example of a thermal cycle would be the cadmium-hydrogen cycle (as shown in Exhibit 5.1).

Exhibit 5.1 Cadmium Oxide Thermochemical Cycle for Hydrogen Production



A promising example of the hybrid thermochemical cycles is the Hybrid Sulfur process (as shown in Exhibit 5.2). This process is being developed by the NE.

Exhibit 5.2 Hybrid Sulfur (HyS) Thermochemical Cycle for Hydrogen Production



Hydrogen production using STCH technologies faces obstacles associated with daily and seasonal fluctuations in solar power; the need for low-cost, compact, efficient solar collectors; materials development; catalyst development; interfacing the STCH reactor with the solar receivers; hydrogen separation and purification; compression; and storage. More than 300 water splitting cycles are described in the literature, and R&D is needed to identify the most promising.[54] Primary considerations in selecting locations for STCH hydrogen production facilities will be solar availability and regulatory constraints associated with environmental considerations; other considerations will include local water supplies and infrastructure.

Solar power fluctuates throughout the day and is unavailable at night and during periods of low sunlight. Accordingly, reactors must endure daily cycling from low to high temperatures. Efforts are underway to decrease reactor cycling by storing the thermal energy in salts or other materials to enable continuous production. For most of the cycles, the solar power is used to convert the chemicals into an activated state. Hydrogen is generated by reacting the activated material with steam. For some cycles, it may be possible to store the activated chemical in conditions appropriate for the particular cycle (i.e., high temperatures, dry conditions) for later use. One way to mitigate solar power variations is to produce excess activated chemicals and store them for off-sun use. Thermal storage materials may be needed to enable these cycles to maintain the necessary high temperatures.

DOE COST TARGETS

Making TCH technically viable will require long-term, high-risk research. The technology may not meet DOE's cost targets (see Exhibit 5.3) in the next 10 years; however, the opportunity to potentially harvest such tremendously clean energy makes this risk acceptable at this time. When the technology has become further developed, a go/no-go decision can be made.

Exhibit 5.3 Thermochemical Hydrogen Production: DOE Cost Targets

Year	Production Scale	Cost/gge (produced)
2014 Target	Semi-Central/Central	$3.90-5.50
2019 Target	Semi-Central/Central	<$3.00

5.2. KEY BARRIERS

Driving DOE's research activities are specific barriers identified in the *MYPP*[19] as well as others identified by the FreedomCAR and Fuel Partnership's HPTT. These are summarized in Exhibit 5.4 and described on the following pages.

HELIOSTAT DEVELOPMENT AND COST

A heliostat is a reflective device that tracks the sun to keep the mirrors focused onto a target receiver. Current heliostat costs need to be reduced by 50% to achieve the targeted cost of $\$80/m^2$ installed.

The heliostat is a key unit in the development of STCH production. Currently the units are too expensive and development is needed to reduce their cost. High costs are in part due to a lack of standardization in their designs, as well as inefficient manufacturing and poor durability. DFMA will not be applicable until the units are closer to commercialization.

THERMOCHEMICAL CYCLE SELECTION

The literature has over 300 thermochemical cycle candidates and new cycles continue to emerge. The most promising cycles need to be identified for further development. The criteria for selection include the following: thermal efficiency, operation temperature (lower temperatures are desired), within the temperature gradient considered, the ΔG of individual reactions must approach zero, the number of steps should be minimal, each individual step must have both fast reaction rates and rates which are similar to the other steps in the process, the reaction products cannot result in chemical-by-products, separation of the reaction products must be minimal in terms of cost and energy consumption, intermediate products must be easily handled, low raw material cost, cycle

Exhibit 5.4 Thermochemical – Summary of Barriers

Heliostat Development and Cost	Current heliostat costs need to be reduced by 50% to achieve the targeted cost of \$80/m^2 installed, while O&M costs are similarly too high. In addition, current heliostats lack the durability and efficiency required to operate at acceptable costs.
Thermochemical Cycle Selection	The two dozen+ thermochemical cycles identified as promising are too many to advance into detailed technoeconomic analysis.
Materials and Catalyst Development	Many thermochemical cycles require reaction temperatures in excess of 1,000°C. Materials for the receiver reactor, seals, catalysts, supports, etc. are insufficiently developed to handle the required temperatures. Critical parameters of these materials are chemical stability and thermal compatibility. Similarly, thermal or chemical storage materials or processes will need to be identified or developed.
Reactor Development and Capital Costs	Current reactors are inefficient, costly, and require excessive BOP components to meet the cost targets.
Solar Receiver and Reactor Interface Development	The receiver is the focal point of the heliostat and directs the thermal power to the reactor and/or thermal storage. Technology does not currently exist to provide the necessary interface for the heliostat as well as the chemical cycle, the reactor, the mode of thermal storage, and other considerations that may develop as the cycles move toward commercialization.
Chemical and Thermal Storage (Capital Utilization)	Thermal and chemical energy is difficult and expensive to store efficiently. Any storage system utilized must be chemically compatible with the overall process. Materials barriers associated with the high temperature of operation persist.
Feedstock Issues	The primary feedstock for STCH is water, yet areas with significant solar resources tend to be arid. Water resources and rights, H_2O purification, and high-cost of BOP components are key barriers.
Operation and Maintenance (O&M)	O&M costs are too high to achieve the desired hydrogen cost. Current system designs will require intense, on-site maintenance that is prohibitively expensive.
Control and Safety	Ineffective operation and control strategies are barriers to minimizing cost and emissions, maximizing efficiency, and enhancing safety. Specific safety issues must be addressed for the use of hazardous materials and chemicals associated with some thermochemical cycles. Thermal and/or chemical storage also face safety barriers.
Diurnal Operation	Solar power fluctuations will strongly influence the design, performance, and economic viability of this technology. Systems should be developed to produce hydrogen during off- or low-sun conditions.

life, and non-hazardous materials and intermediates are preferred.[54] The process efficiency needs to exceed 35% in order achieve the DOE *MYPP* targets[19]. The DOE EE program has reduced the initial list of 300 cycles to approximately 25 based on the above listed requirements. A second screening process will be done to develop preliminary process analysis including preliminary receiver design development and efficiency analysis, culminating in a preliminary technoeconomic analysis using H2A. From the results of the preliminary technoeconomic evaluation, 3-12 candidates will be identified for further screening and development.

MATERIALS AND CATALYST DEVELOPMENT

Many thermochemical cycles require reaction temperatures in excess of 1,000°C. Materials for the reactor, seals, catalysts, and supports are insufficiently developed to handle the required temperatures. The critical parameters of these materials are chemical stability and thermal compatibility. Cost-effective, solar-driven hydrogen production requires that cycles incorporate either thermal or chemical storage to enable time-shifted hydrogen production; however, the appropriate materials or processes have yet to be identified or developed.

Materials for some high-temperature thermochemical processes may need to endure extreme heat (>1,500°C) as well as corrosive and reactive environments. Such conditions pose major challenges for the development of durable, inexpensive materials for receiver, reactor, and thermal storage. Moreover, these materials would have to be capable of enduring extreme thermal shock and be easy to manufacture. Some of the chemical cycles may require catalysts and/or supports. These catalysts and supports will also need to endure aggressive environments. The materials will need to endure daily cycles and severe thermal temperature cycling (in some cases >1,500°C). Ceramics that can endure high temperatures have issues with the cycling and issues with seals. Metals, such as Hastelloy steel, have better cycle life and fewer seal issues, but have a lower usable temperature. These materials issues are the same for solar- and nuclear-driven cycles.

CHEMICAL REACTOR DEVELOPMENT AND CAPITAL COSTS

As the cycles become better understood, chemical reactor designs will need to be developed. These reactors will need to be efficient, inexpensive, and entail minimal BOP to meet the cost targets.

The high cost of current materials is due to the requirements for high durability and chemical and thermal stability. While a number of reactor types have been proposed for the TCH cycles, certain cycles will require specialized reactors, including the rotating disk reactor, fluid wall reactor, and centrifugal reactor. In some cases, more conventional designs may be applicable.

High-temperature operation necessitates extreme thermal management to achieve high efficiencies. Thermal losses result from inefficient process flow and a lack of integration among unit operations.

Other barriers to reactor development and capital costs include hydrogen separation and purification. Ideally, the product stream will be composed of only hydrogen and water. However, there may be small amounts of other contaminants similar to those in hydrogen produced via water electrolysis.

SOLAR RECEIVER AND REACTOR INTERFACE DEVELOPMENT

STCH reactors can be broadly classified as directly heated by the sun or indirectly heated (e.g., a thermal transfer medium absorbs the thermal energy and transfers the energy to the reactor). The solar receiver is the focal point of the heliostat and directs the thermal power to the reactor and/or thermal storage. Efficient heat transfer at the interface with the heliostat remains a barrier as the cycles move toward commercialization.

The interface with the chemical reactor is an important consideration in the selection of a solar receiver. For directly heated reactors (e.g., rotating disk, fluid wall, and centrifugal), the receiver and reactor are integrated, enabling solar flux to heat the reactor. In the ideal case, the solar thermal input rate would match the heat of reaction at constant temperature. However, the chemistry and dynamics of each system establishes the equilibrium temperature required.

The solid particle and volumetric receivers are heated indirectly by the sun. For these reactors, the heat is absorbed by solid particles (e.g., sand) or molten salts, which then heat the reactors. Heat addition is, therefore, not isothermal. In addition, the amount of energy transferred to the thermochemical reaction from the intermediate heat transfer media depends on the range of temperature absorbed by the chemical reaction. The non-isothermal nature of these receivers may be suitable for cycles with steps requiring different temperatures. In addition to interfacing with the receiver, the reactor must also interface with thermal storage, if used.

CHEMICAL AND THERMAL STORAGE (CAPITAL UTILIZATION)

High capital utilization will be necessary to maintain low capital costs. The key factor to limiting capital utilization is the intermittency of solar power. This intermittency may be managed by thermal or chemical storage, which will need to be thermally efficient, inexpensive, and chemically compatible with the process.

Capturing and storing thermal energy during peak solar times will extend the operational time of the STCH reactor. However, thermal storage will also require some of the solar power, adding complexity and cost to the receiver reactor interface. In addition, insulated storage sites and increased BOP components would be required, adding to the capital and O&M costs.

Among thermal storage media in current use, molten nitrate salts which cycle up to 650°C provide the highest temperature. Molten carbonate salts can go to higher temperatures, but are extremely corrosive—creating materials issues. The 650°C top temperature range of the molten nitrate salts may be sufficient for some of the lower-temperature cycles, such as the copper chloride cycle; however, some cycles require higher temperatures (>1500°C). Molten metals may also be an option, but severe corrosion and safety issues are associated with these candidates (e.g., sodium). Thermal storage materials and/or containment materials for the reactor, pumps, sensors, piping, seals, etc. thus pose a barrier to storage at higher temperatures.

FEEDSTOCK ISSUES

The primary feedstock required for TCH hydrogen production is water, and an adequate supply is essential for large-volume hydrogen production. This supply is a particular concern in arid regions, which tend to have significant solar resources. Water purity is another concern as impurities may cause deposits that foul the reactor system, decrease its operating life, and increase O&M costs.

OPERATION AND MAINTENANCE

O&M costs are a major barrier to achieving the desired hydrogen cost. All system components must be considered in O&M, including feed pre-conditioning, heliostats, solar receivers, reactor, hydrogen purification, controls, utilities, QA/QC (e.g., sensors), compression, storage, and safety. Although 24/7 operation would be ideal, this may not be possible due to the variability of the power source. Storing the activated materials and/or use of thermal storage may not be feasible or cost-effective.

Durability Both the frequency and cost of repairs could be barriers to development of the heliostat, mirrors, reactor, receiver, thermal management/storage, hydrogen purification, compression, on-site storage, and BOP.

Scheduled Maintenance Heliostat maintenance may pose a significant cost unless more robust devices are created. In addition, cleaning of the mirrors will potentially be an involved and cost-intensive process.

Storage (O&M Side of Capital Utilization) Solar power varies by the hour and day, potentially affecting the amount of hydrogen produced. Meeting hydrogen demand will necessitate sufficient on-site storage capacity to minimize the effects of thermal cycling, shut-down, and restarting caused by insufficient solar power to drive the chemical cycles. However, storage will increase the O&M, add to the capital costs, increase the complexity of system design and controls, and may introduce safety implications. Design and operational decisions to address demand variability will impact O&M as well as capital costs (e.g., turn-down, periodic shut-down, and restart).

Hydrogen Quality Monitoring Hydrogen purity needs to be monitored to assure that it meets accepted standards. If there are cycle-centric contaminants, purification costs must be considered.

CONTROL AND SAFETY

Control and safety issues associated with STCH include optimization of start-up and shut-down processes, improved turn-down capability, activated material and thermal storage integration and control (if used), and the capability for rapid on-off cycling. Control system costs may remain high due to system complexity and/or substantial sensor count to assure reliability. These units must operate in an environment of minimal manual assistance, which will require attributes such as back-up fail-safe mode, remote monitoring, and sparse maintenance schedules. Some of the cycles use gaseous chemicals, posing a potential safety issue from leaks or chemicals being released to the environment—should a rupture of the reactor or system occur. Finally, if the activated material is stored, it will be in a highly reactive state, which will also raise safety implications.

DIURNAL OPERATION

Solar power availability and fluctuations will strongly influence the design, performance, and economic viability of this technology. In the absence of strategies to successfully manage resource variability, capital and O&M costs may affect the cost-competitiveness of this technology.

5.3. CRITICAL TECHNOLOGY NEEDS

Exhibit 5.5 lists critical technology needs for TCH production. A discussion of these efforts follows. Note that a single R&D activity may address more than one barrier or multiple R&D activities may be needed to address a single barrier. For more detail on the alignment of R&D needs with technology barriers, please see Appendix B.

Exhibit 5.5 STCH Critical Technology Needs

Improve Materials	➔ Develop receiver materials ➔ Engineer chemical cycle materials ➔ Develop reactor materials ➔ Develop thermal storage materials
Reduce Capital Costs	➔ Reduce heliostat cost ➔ Reduce receiver and reactor cost ➔ Reduce thermal and chemical storage cost ➔ Optimize system to manage variable demand and solar power ➔ Implement DFMA/high-volume equipment manufacturing ➔ Reduce BOP cost
Reduce Operation and Maintenance Costs	➔ Automate process control ➔ Increase system reliability ➔ Minimize material and energy losses ➔ Maximize capital utilization

Addressing all of the barriers to commercialization cost targets for TCH production will require simultaneous R&D efforts in several areas, along with efforts to develop policy, standards, and delivery infrastructure technology. Although these efforts are taking place concurrently, the impact of each effort on the entire hydrogen production system must be kept in mind and integrated into systems optimization efforts.

Identifying and developing the most promising cycle chemistries is a high research priority. Other critical technology needs include: designing efficient reactors and receivers suitable for the chemistries identified, materials development, heliostat capital cost reduction, and thermal management. Eventually, additional efforts will be needed to develop and implement DFMA that will facilitate mass production of equipment and development of lower-cost, easier-to-manufacture, and more durable materials.

Costs for O&M will also have a significant impact on the overall cost of producing hydrogen. The O&M requirements will need to be included in process design development to minimize these costs. O&M costs can also be reduced by improving process controls for cycle optimization, which should include development of better and less expensive sensors and development of supplemental technologies to enable off-sun operation. Further, all of these technology improvements must take place within the constraints of the regulatory environment, limited physical space, and resource limitations.

IMPROVE MATERIALS

Receiver materials Common solar receivers under consideration for STCH include parabolic troughs, parabolic dishes, molten salt power towers, and volumetric receivers. Different receivers may be applicable to different STCH cycles, depending on the operating temperatures and other conditions. Current receivers are expensive, and new materials and designs should be developed that are more efficient and affordable, require less maintenance, and enable low-cost fabrication methods. Improved materials may enable increased efficiency and lower maintenance costs.

Chemical cycle materials Considerable effort in material development is needed to enable both chemical and thermal cycling. Methods may need to be developed to appropriately deposit the active materials onto supports. New support materials may need to be designed and engineered to be chemically and physically compatible and to endure the thermal cycles. In some cases, catalysts may be used. The catalysts and their supports will need to be engineered to be chemically and mechanically compatible, provide a long service life, and tolerate chemical and thermal cycling.

Reactor materials Reactor materials that can thermally cycle to extreme temperatures and are chemically resistant to highly reactive environments will need to be identified or developed. In addition, these materials should be cost-effective, easy to manufacture, easy to machine, adaptable to high-volume production, and capable of integration with the heliostat. For high-temperature applications, considerable effort may be required to develop seals for some chemical systems. In addition, the reactor must interface with the receiver and with thermal or chemical storage systems. The materials must be chosen or developed for these interfaces.

Thermal storage materials Although the sun may shine for many hours a day, useful solar energy (peak sun-hours[62]) is available on average for 3-8 hours per day, depending on location and time of year.[63] One option for increasing the daily reactor operating time is to store some of the thermal energy for use during off-sun times. Molten salts have been used to store thermal energy by cycling between 290°C and 560°C.[64] Storage systems that can achieve even higher temperatures need to be developed.

REDUCE CAPITAL COSTS

Hydrogen Heliostat Cost To achieve the 2017 project cost target of \$3/gge H_2, heliostat costs need to be reduced by more than half to \$80/m^2 (installed). These cost targets are consistent with those set by the EERE Solar Program, but the program is in the process of updating them. The Solar Program will be responsible for developing the improved heliostats.[19]

Receiver and Reactor Cost Low-cost receivers and reactors need to be developed. Several designs for both receivers and reactors (mentioned previously) have been proposed. As the chemical cycles become better defined, these designs can be finalized. Energy analysis would be useful in optimizing process flow to integrate the unit operations and minimize thermal losses. In general, the designs will need to be easy to manufacture and should incorporate low-cost materials. The receiver will need to be designed to interface with the reactor and thermal storage. The system cost of the reactor could be minimized through efforts to develop more compact units that can be produced using currently available, low-cost, high-throughput manufacturing methods. Developing standard designs will eliminate the need for site-specific fabrication of systems and sub-systems. The BOP costs could be minimized by developing common, interchangeable components, automated joining processes, and low-cost stamping and extrusion methods that would permit high-volume, assembly-line production of critical components that are currently machined and welded.

Thermal and Chemical Storage Cost The design for chemical and thermal storage needs to enable efficient energy capture and storage to extend the daily operating time of

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[62] One peak sun hour is approximately the amount of solar energy striking a one-square-meter area perpendicular to the sun's location over a summertime 1-hour period straddling solar noon. It is standardized at 1 kilowatt hitting that 1-square meter surface. For more information, see http://photovoltaics.sandia.gov/docs/FAQ.html#AnchorSolar

[63] For more information on peak sun hours see http://rredc.nrel.gov/solar/pubs/redbook/.

[64] www.sandia.gov/Renewable_Energy/solarthermal/NSTTF/salt.htm

TCH production. Ideally, the storage materials would be the activated materials, but this may not always be possible. The materials and the process need to be developed. Cost should be considered during materials selection and development to create a system that is economically feasible to build. Ideally, the system should use low-cost raw materials that are relatively easy to process. Management to decrease losses will be important, yet may add components and complexity to the system. BOP components should be included in design optimization.

For example, some cycles, such as the Zn/ZnO cycle, have intermediates that can be stored under controlled conditions, enabling 24/7 hydrogen production. For the Zn/ZnO cycle, the high-temperature process for reducing ZnO to Zn would have to be engineered to produce more activated Zn than is consumed during on-sun operation. The excess Zn would then be stored in a dry, warm unit and reacted with water to produce ZnO and H_2 during off-sun periods.

System Optimization to Manage Variable Demands and Solar Power The variable solar power supply may be handled through a combination of on-site hydrogen storage, storage of activated materials, and thermal storage. Thermal storage and storage of activated materials will require investments in storage facilities and BOP components that are chemically and thermally compatible with the chemicals in use. These additions will add to the maintenance costs as well as the capital costs. Using hydrogen storage alone will require that the STCH system produce enough hydrogen during the 3 to 8 hours of solar power availability to last the rest of the day, and for "rainy" days as well. Hydrogen storage will necessitate increased heliostat size and cost; increased capital cost for the reactor, receiver, and BOP; and increased hydrogen storage costs. The use of geologic storage for hydrogen may significantly reduce these storage costs, but may not be available in all locations. Optimizing the balance among these options must also consider relative impacts on maintenance costs and safety.

DFMA/High-Volume Equipment Manufacturing DFMA will be a key component of cost reduction efforts for the heliostat, receiver, reactor, and thermal storage. DFMA will also help to reduce installation costs. Initially, while technology production volumes are limited, DFMA should focus on developing designs that incorporate commonly available (commodity) materials and use common tooling and standard sizing for procured components (such as tubing, heat exchanger, and reactor components). Design for modularity will be especially important for semi-custom installations. Modular design will allow for improvements in specific subsystems to be incorporated without necessitating a redesign of the entire process. Flexible, modular design will also allow scalable systems, thereby increasing the application domain and overall production volumes. Other critical technology needs in DFMA for thermochemical production are the same as those discussed in DNGR Section.

Reduce BOP Cost BOP components represent a significant portion of capital costs. Improved, low-cost sensors, pumps, and water purifying, and monitoring equipment need to be developed.

REDUCE OPERATION AND MAINTENANCE COSTS

All components will need optimization to increase total system efficiency and reliability while decreasing O&M costs.

Automated Process Control Robust systems that require little routine maintenance need to be developed. On-site, planned maintenance must be minimized both in terms of cost and frequency. The need for on-site labor support must be minimized or replaced with automated process control and remote monitoring. Specifically, cleaning of the mirrors will need to be automated or other low-cost technologies (such as self-cleaning mirrors) will need to be developed.

Equipment Reliability The reliability of the overall system is often limited by the reliability of BOP equipment (such as the heliostat, pumps, hydrogen driers, and sensors). Increasing the reliability of these components while also minimizing equipment complexity is critical for improving system reliability. For example, water impurities must be tightly controlled to protect reactor components.

Material and Energy Losses Hydrogen leakage must be virtually eliminated to maximize process efficiency. Efficiency losses in the drier equipment may reach 10% (assuming similarity to drier issues in electrolysis). Hydrogen leakage is being addressed by DOE's Hydrogen Delivery and Safety, Codes, and Standards program elements. Heat loss and heat rejection must also be minimized through well-designed insulation, heat integration, and thermal storage (if used).

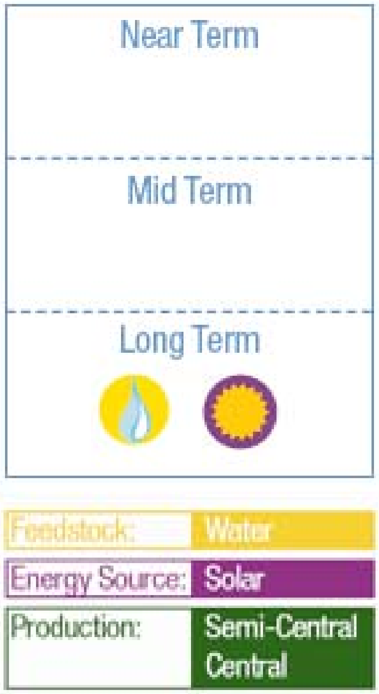
In addition to hydrogen losses, the chemical constituents of the cycles may potentially escape the reactor. This possibility must be avoided to decrease the O&M costs for the reactor as well as the hydrogen separation and purification costs.

Capital Utilization Solar power variability may result in poor utilization of capital equipment, unless low-cost thermal storage is available. Sufficient on-site storage capacity will be needed to meet the hydrogen demand and adequately minimize the effects of thermal cycling, shut-down, and restarting. STCH system size must be balanced with an appropriate hydrogen storage system to account for solar power variability. The STCH system has the potential to co-produce a variety of products in addition to hydrogen, such as heat, electricity, and steam. Local use or sale of these products can increase site revenue.

6.0 Photoelectrochemical

The photoelectrolysis or photoelectrochemical (PEC) pathway calls for producing hydrogen via photoelectrochemical water-splitting using semi-conductor material to collect the sun's energy. It is a long-term technology that will most likely be suitable for semi-central and central hydrogen production. The current R&D priority is on materials development.

Photoelectrochemical Production



6.1. INTRODUCTION

PEC hydrogen production uses the process of photoelectrolysis to convert solar energy directly to chemical energy in the form of hydrogen. Photoelectrochemical direct water splitting is similar to photovoltaics in that it uses semiconductor material to collect solar energy; however, instead of producing electrons, hydrogen and oxygen are produced. By solely using water and sunlight, PEC offers the potential for clean, sustainable hydrogen production. This roadmap focuses primarily on the initial development of the technology, but also reports obstacles that will need to be avoided or minimized to reduce time to deployment.

PEC is in the early stages of development and will require increased understanding of the fundamental processes and breakthroughs in materials to achieve the long-term goals. Since the technology operates at low temperatures, the O&M may be simpler than for higher-temperature technologies. In addition, the feedstock is simply water with a controlled pH, likely making the feed preparation much easier than in some other low-temperature technologies.

Environmental Benefits

By solely using water and the power of sunlight, photo-electrochemical technology offers the potential for clean, sustainable hydrogen production.

PHOTOELECTROLYSIS

Photoelectrolysis uses sunlight to directly split water into hydrogen and oxygen. The semiconductor materials used in the process are similar to those used in photovoltaics. In *photovoltaics*, two doped semiconductor materials, a p-type and an n-type, are brought together to form a p-n junction.[65] At that junction, a permanent electric field is formed

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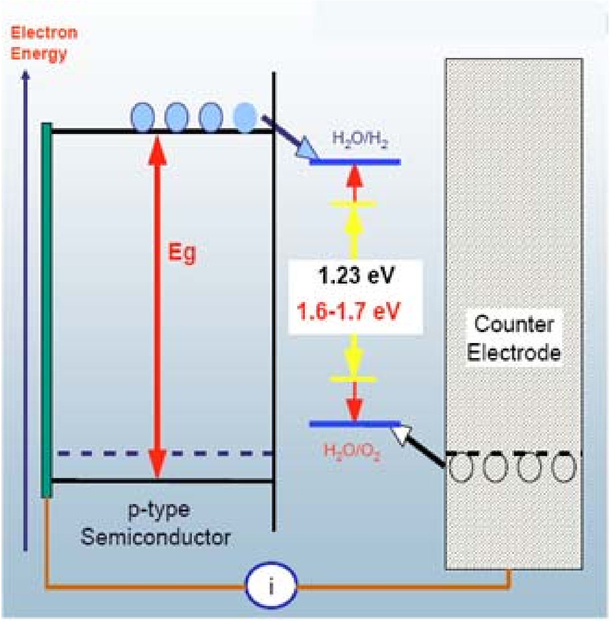
[65] Norbeck J.M., J.W. Heffel, T.D. Durbin, B. Tabbara, J.M. Bowden, and M.C. Montani, *Hydrogen Fuel for Surface Transportation,* Society of Automotive Engineers, Inc., 1996.

when the charges in the p- and n- type of materials rearrange. When a photon with energy greater than the semiconductor material's band gap hits the junction, an electron is released, and a hole is formed. A band gap is the energy difference between the top of the valence band and the bottom of the conduction band (i.e., the amount of energy required to free an outer shell electron from its orbit around a nucleus into a free state). Since an electric field is present, the hole and electron are forced to move in opposite directions, creating an electric current if an external load is connected. This type of situation occurs in *photoelectrolysis* when either a photocathode (p-type material with excess holes) or a photoanode (n-type of material with excess electrons) is immersed in an aqueous electrolyte, but instead of generating an electric current, water is split to form hydrogen and oxygen (see Exhibit 6.1).[66,67]

Exhibit 6.1 Photoelectrolysis Process



The process can be summarized for a *photoanode-based system* as follows. 1) A photon with greater energy than the band gap strikes the anode, exciting an electron out of its ground state, thereby creating an electron-hole pair. 2) The holes decompose water at the anode's front surface to form hydrogen ions and gaseous oxygen, while the electrons flow through the back of the anode, which is electrically connected to the cathode. 3) The hydrogen ions pass through the electrolyte and react with the electrons at the cathode to form hydrogen gas. 4) The oxygen and hydrogen gases are separated, perhaps by the use of a semi-permeable membrane, for processing and storage.

Various materials have been investigated for use in photoelectrodes, such as thin-film WO_3, Fe_2O_3, and TiO_2, as well as n-GaAs, n-GaN, CdS, and ZnS for the photoanode; and Cu(In,Ga)Se_2/Pt, p-InP/Pt, and p-SiC/Pt for the photocathodes.[68,69,70,71] For the materials to perform well, they must have the correct band gap, and the band edges must straddle the water's redox potential (see Exhibit 6.2). The materials for the photoelectrodes and the semiconductor substrate determine the performance of the system. Hydrogen production efficiency is generally limited by imperfections in the crystalline structure, the bulk and surface properties of the

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[66] Aroutiounian V.M., V.M. Arakelyan, and G.E. Shahnazaryan, "Metal Oxide Photoelectrodes for Hydrogen Generation Using Solar Radiation-Driven Water Splitting," *Solar Energy*, 78 (2005) 581-592.

[67] Turner J., T. Deutsch, J. Head, and P. Vallett, "Photoelectrochemical Water Systems for H2 Production," 2007 DOE Hydrogen Program Annual Merit Review. PD-10. http://www.hydrogen.energy.gov/pdfs/review07/pd_10_turner.pdf. Accessed 12 February 2007.

[68] Licht, S., "Solar Water Splitting to Generate Hydrogen Fuel: Photothermal Electrochemical Analysis," *J. Phys. Chem. B*, 107 (2003) 4253-4260.

[69] Akikusa, J. and S.U.M. Khan, "Photoelectrolysis of Water to Hydrogen in p-SiC/Pt and p-SiC/n-TiO_2 Cells," *Int. J. Hydrog. Energy*, 27 (2002) 863-870.

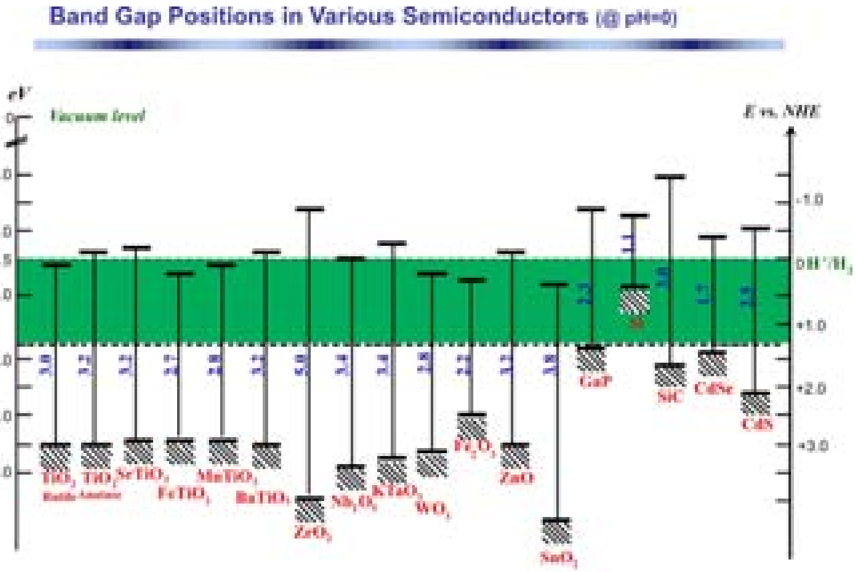
[70] Arriaga, L.G. and A.M. Fernandez, "Determination of Flat Band Potential and Photocurrent Response in (Cd, Zn)S used in Photoelectrolysis Process," *Int. J. Hydrog. Energy* 27 (2002) 27-31.

[71] Mor, G.K., O.K. Varghese, M. Paulose, K. Shankar, and C.A. Grimes, "A Review on Highly Ordered, Vertically Oriented, TiO_2 Nanotube Arrays: Fabrication, Materials Properties, and Solar Energy Applications," *Solar Energy Materials and Solar Cells*, 90 (2006) 2011-2075.

photoelectrodes, material corrosion from the aqueous electrolytes, and the strength of the water decomposition reactions. To maximize the efficiency of this process, the energetics of the electrochemical reaction must be harmonized with the solar radiation spectrum. A mismatch of the solar radiation and materials can produce photo-generated holes that can cause surface oxidations, which lead to either a blocking layer on the semiconductor surface or corrosion of the electrode via dissolution.

Exhibit 6.2 Band Structure of Several Photocatalysts As Measured via UPS

Dotted lines show water's redox potential that must be straddled by the band gap.



To maximize the solar spectrum available, tandem cell configurations have been proposed. In single photoelectrode PEC devices, only the high-energy photons (1.6 – 2.0 eV) are captured, since they translate into the highest efficiency devices with the highest hydrogen production rates. The tandem configuration adds a layer to capture the lower-energy photons (0.8-1.2 eV), which are not captured in single photoelectrode configurations. The photoelectrodes are stacked with the higher-energy electrode on top of the lower-energy electrode. Each electrode produces an electric current when the photons are absorbed. For efficiency, the tandem electrodes must be "tuned" so that the currents produced are the same, or "matched." Depending on the materials used, a good "tuned" system can achieve better than 10% solar-to-hydrogen (STH) efficiency.

Current materials for PEC hydrogen production can be broadly divided into three groups, each with its own characteristics and research challenges: Group 1 are stable materials with low visible light absorption efficiency (e.g., oxides), Group 2 materials are highly efficient light absorbers with short lifetimes, and Group 3 includes hybrid and multi-junction systems that combine multiple materials in multi-photon devices. The Group 1 materials are characterized by high band gaps and low, integrated, incident-photon-to-electron conversion (IPEC) over the solar spectrum; the Group 2 materials have very high IPEC (better than 90% throughout the visible spectra), but have low corrosion resistance; and the Group 3 systems can have extremely high efficiency and long service life, depending on the material set, but can be complicated and expensive to build. Each group of materials has advantages and disadvantages, and DOE is funding research in each area. To date, a range of materials and material systems have met individual 2010 targets for chemical efficiency or durability, but no single material/system has simultaneously met efficiency, durability, and hydrogen cost targets. This is the primary R&D challenge for PEC hydrogen production.[19] The barriers and needs of this technology are outlined in the following sections.

DOE COST TARGETS

Cost targets are not specified for PEC hydrogen production because the technology is at an early stage of development. PEC research supports the goal of long-term commercial hydrogen production using renewable sources at costs ultimately competitive with other renewable production methods. The objective of current research is to verify by 2020 the feasibility of making PEC competitive in the long term.

6.2. KEY BARRIERS

Driving DOE's research activities are specific barriers identified in the *MYPP*[19] as well as others identified by the FreedomCAR and Fuel Partnership's HPTT. These barriers are summarized in Exhibit 6.3 and further described on the following pages.

Exhibit 6.3 Photoelectrochemical Hydrogen Production – Summary of Barriers

Materials Barriers	**Efficiency** Materials that provide a STH efficiency of >16% and meet the durability requirements have not yet been identified or developed.
	Durability Semiconductor materials have not yet been developed that are capable of operating at high efficiency in an aqueous environment while generating hydrogen gas. Corrosion from oxidation and reduction, both under illumination and in the dark, presents a substantial barrier to semiconductor materials to reach the technology readiness durability target of ≥15,000 hours.
	PEC Device and System Auxiliary Materials The functional requirements for auxiliary materials to facilitate PEC device and system development remain to be determined.
Device and System Barriers	**Configuration and Designs** Multi-layer, multi-junction devices or colloidal systems may address a number of the barriers, including high efficiency and corrosion protection, but could be difficult to produce at commercial scale, depending on the structure. Depending on configuration, produced hydrogen and oxygen may need to be separated. Current manufacturing techniques may not be able to create the materials and devices cost effectively.
	System Design, Evaluation, and Capital Costs Integration of the PEC device with reactor materials, controls, sensors, BOP, compressors, and storage could raise capital and operation costs. A range of important operational constraints and parameters, including diurnal operation limitations and the effects of water purity on performance and service life, may constitute barriers to complete system optimization.
Diurnal Operation Barriers	**Diurnal Operation Limitations** Photolytic processes are discontinuous because they depend on sunlight, which is unavailable at night and available only at low intensities on cloudy days. A reliable and cost effective system solution has not been developed to accommodate this limitation.

MATERIALS EFFICIENCY

Current photoelectrodes proposed for PEC that are stable in aqueous solutions have a <4% efficiency for using photons to split water to produce hydrogen. The target plant STH efficiency is greater than 16%. Three material-system characteristics are necessary for efficient conversion: (i) the band gap should fall in the range sufficient to achieve the energetics for electrolysis, yet allow maximum absorption of the solar spectrum (1.6-2.0 eV for single photoelectrode cells and 1.6-2.0 eV/0.8-1.2 eV for top/bottom cells in stacked tandem configurations); (ii) the material must have a high quantum yield (better than 80%) across its absorption band to reach the efficiency necessary for a viable device;

and (iii) the conduction and valence band edges should straddle the redox potentials of the H_2 and O_2 half reactions, respectively. Efficiency is directly related to the semiconductor band gap E_g (i.e., the energy difference between the bottom of the conduction band and the top of the valence band) as well as the band edge alignments, since the material or device must have the correct energy to split water. The band edges must straddle water's redox potential with sufficient margin to account for inherent energy losses.

MATERIALS DURABILITY

The semiconductors and other materials used must be stable in aqueous environments. The high-efficiency materials currently available corrode quickly during operation, and the most durable materials are inefficient for hydrogen production. Semiconductor materials that are capable of operating at high efficiency in an aqueous environment while generating hydrogen gas have yet to be developed. The material must resist corrosion from oxidation and reduction both under illumination and in the dark. In addition, in hybrid multi-layered systems, the materials may be deposited in thin-films, yet hydrogen gas nucleation can cause these layers to delaminate. The technology readiness target for durability is at least 15,000 hours.

PEC DEVICE AND SYSTEM AUXILIARY MATERIALS

Materials barriers constitute challenges to PEC system development beyond the semiconductors and catalysts. Auxiliary materials may include protective coatings, photoelectrode substrates, hydrogen and oxygen barrier films, hydrogen-impervious materials, and photovoltaic layer materials. The functional requirements for these materials have yet to be defined, but will depend on the electrodes and catalysts ultimately employed. The materials will need to be cost effective and have appropriate optical, chemical, and physical characteristics.

DEVICE CONFIGURATION AND DESIGNS

Multi-layer, multi-junction devices can address a number of the above issues, including high efficiency and corrosion protection, but could be difficult to produce at commercial scales, depending on the structure. Based on the configuration, produced hydrogen and oxygen may need to be separated. Issues related to thin metal corrosion and inter-layer adhesion must be addressed. A need for new materials for substrates, adhesive layers, and protective coatings could be a barrier to further development. Once developed, these new materials face obstacles due to the lack of cost-effective, high-volume manufacturing techniques.

SYSTEM DESIGN, EVALUATION, AND CAPITAL COSTS

The PEC device must be integrated with reactor materials, controls, sensors, and BOP components (such as compressors and storage) without unduly elevating costs. The complete system must address a range of important operational constraints and parameters, including diurnal operation limitations, and hydrogen separation and purification. The major impurity in the hydrogen product will most likely be water, necessitating low-cost hydrogen driers that have yet to be identified and included in the system. Without design for manufacturing techniques to enable effective production and to minimize BOP, capital costs will remain high.

PEC systems require adequate quality feed water and appropriate safeguards to protect the device. These safeguards will need to be robust, inexpensive, well-matched with the PEC system, and, to some extent, tailored to the specific contaminants in the feed water and the extent of automation in the water treatment system.

DIURNAL OPERATION LIMITATIONS

Photolytic processes are discontinuous because they depend on sunlight, which is unavailable at night and available only at low intensities on cloudy days. This limited resource availability poses system challenges in terms of producing sufficient hydrogen for customer needs, the ability to operate at less than maximum solar power, and the ability to startup/shutdown quickly and easily.

OPERATION AND MAINTENANCE

Potential O&M costs for PEC hydrogen production could make the technology too costly to compete in the marketplace. Barriers to minimizing these costs will need to be addressed in a number of areas. For example, effects from diurnal cycling will need to be accommodated, and self-cleaning designs using self-healing, multi-functional materials could decrease O&M costs. All system components must be considered in O&M, including feed pre-conditioning (e.g., water conditioning), hydrogen separation/purification, controls, utilities, and QA/QC (e.g., sensors).

Durability and Reliability Both the frequency and cost of repairs must be considered.

Scheduled Maintenance Robust systems that require little routine maintenance do not yet exist for these systems. Minimal on-site maintenance staff is preferred to minimize cost. System troubleshooting will need to be automated or monitored remotely.

Production Management Hourly and daily production levels will fluctuate with changes in the sun's intensity. Design and operational decisions to address production variability will impact O&M as well as capital costs (e.g., turn-down, periodic shut-down, restart, and storage).

Contaminant Removal Water quality may vary from one area to another. In any case, the water will need to be conditioned to the appropriate levels of purity.

Hydrogen Separation and Purification Hydrogen produced from the PEC system will most likely have similar contaminants to hydrogen produced via electrolysis. It is important to minimize losses (parasitic and hydrogen) and consumables to minimize O&M costs. The roadmap Introduction provides more discussion of these requirements.

Reduce BOP O&M BOP components are a significant part of the system. In many applications, BOP failure caused by inefficient or ineffective sensors, pumps, water purification systems, and monitoring equipment is the main limitation on service life and the main source of O&M costs.

CONTROL AND SAFETY

Control and safety issues associated with PEC hydrogen include optimization of start-up and shut-down processes, turn-down capability (for cloudy days), and rapid on-off cycling. Control system costs cannot be excessive so the sensors should be cost-effective and reliable. The permitting process critically relies on the proven reliability and safety of these units. Systems must be designed to operate with minimal manual assistance, which will require such attributes as back-up fail-safe mode, remote monitoring, and sparse maintenance schedules. System design will have to meet all requirements by local and national permitting processes for effluents (e.g., liquid exhausts).

6.3. CRITICAL TECHNOLOGY NEEDS

Exhibit 6.4 lists the critical technology needs for PEC hydrogen production. Discussion of these efforts follows the exhibit. Note that a single R&D activity may address more than one barrier, and multiple R&D activities may be needed to address a single barrier. For more detail on the alignment of R&D needs with technology barriers, please see Appendix B.

Exhibit 6.4 Photoelectrochemical Critical Technology Needs

Increase Efficiency	→ Increase photocatalyst efficiency to achieve STH of 16% → Minimize parasitic power consumption from BOP
Address Materials Needs	→ Obtain materials properties information → Develop catalyst materials → Increase materials durability
Reduce Capital Costs	→ Reduce raw materials and component costs → Develop low-cost hydrogen separation and purification technologies → Reduce manufacturing costs → Optimize system for turn-down operation → Implement DFMA/high-volume equipment manufacturing
Reduce Operation & Maintenance Costs	→ Engineer for automated process control → Increase equipment reliability, durability, and life → Minimize material and energy losses

INCREASE EFFICIENCY

Solar energy is variable, depending on the time of day and atmospheric conditions (e.g., clouds, rain, dust), so hydrogen production must be maximized for most daylight conditions. Since the near commercialization target for STH efficiency is 16%, the component efficiencies must be greater than 16%. These high efficiencies must be attained by durable devices able to achieve the lifetime operation targets. One way to achieve these targets may be to develop hybrid designs that are capable of converting more of the light to hydrogen than is possible using a single material. In addition, parasitic power losses must be minimized by increasing the efficiency of BOP, sensors, controls, compressors, etc. or by BOP component elimination.

ADDRESS MATERIALS NEEDS

Create Photoelectrochemical Hydrogen Materials Database The central focus of current PEC R&D is materials discovery and characterization. A centralized database of potential material characteristics would enable researchers to avoid duplicating earlier studies and find likely directions for further research. Such a database would aid hybrid and multi-junction system development by facilitating identification of materials with synergistic characteristics. Computational prediction of theoretical materials aids in directing the research. Combinatorial techniques are used to screen for likely candidates and narrow the selection of candidates within a material set for further development using conventional synthesis and characterization techniques. The database will include PEC active materials and auxiliary materials (coatings, substrates, etc).

Develop Photoelectrochemical Hydrogen Catalyst Materials Effective, durable photocatalysts and electron transfer catalysts are needed to capture solar power and efficiently use it to split water. High- volume synthesis techniques will need to be developed for the materials. Cost-efficient, durable catalysts with appropriate E_g and band edge positions must be developed. To achieve the highest efficiency possible in a tandem configuration, "current matching" of the photoelectrodes must be accomplished.

Electron transfer catalysts and other surface enhancements may be used to increase the efficiency of the system. These enhancements can minimize the required surface over-potentials and facilitate the reaction kinetics, thereby decreasing losses in the system. Research is ongoing to better understand the mechanisms involved and to discover or develop appropriate candidates for these systems.

Increase Photoelectrochemical Hydrogen Materials Durability Highly active, durable materials are a critical need for PEC. Currently studied durable materials exhibit low activities. The materials must also be stable in aqueous environments; they will be on-sun and must withstand the formation of gas bubbles at the catalysts' surfaces. PEC devices may be built using thin layers that can delaminate during bubbling. The thin film adhesion will need to be improved. In all configurations, surface treatments and enhancements can be employed to prolong device service life. The service target for these materials is at least 15,000 hours. Materials that need to be developed include catalysts, supports, substrates, coatings, and housings.

REDUCE CAPITAL COSTS

Reduce Photoelectrochemical Hydrogen Materials and Component Costs The raw materials used for these systems need to be available in large, cost-effective quantities. It may be necessary to develop new manufacturing techniques to provide the materials at low cost.

Due to the diurnal characteristic of PEC hydrogen production, excess hydrogen will likely need to be stored for use when production is offline. Therefore, PEC systems will need to be sized adequately to produce sufficient hydrogen during operation to satisfy demand for immediate consumption *plus* storage. The most significant capital cost reduction typically occurs with the elimination of components, therefore multi-functional materials and minimization of BOP may aid in cost minimization.

Develop low cost hydrogen drier technologies General hydrogen quality stipulations are described in the roadmap Introduction. For PEC, it is anticipated that the primary contaminant will be water, with perhaps some alkali—similar to that in hydrogen from an alkaline electrolyzer. The most popular current drier technologies include adsorption techniques or membrane driers. The adsorption techniques can be disposable (increasing operation costs and incurring a disposal cost) or regenerable (increasing operation costs). In membrane systems, the wet gas flow typically will be separated from a dry gas flowing in the opposite direction by a water transport membrane (e.g., Nafion™). The dry gas is a parasitic cost due to generation of a dry nitrogen stream or due to a hydrogen stream that loses some of the hydrogen produced. Novel, more efficient drier technologies may decrease these costs.

Photoelectrochemical Hydrogen Manufacturing Costs Manufacturing techniques are needed to produce PEC materials and systems with consistent, uniform characteristics and minimum defects. The manufacturing process must include in-line measurement of quality control parameters to minimize rejection of finished products.

System Optimization to Manage Variable Production Hydrogen production rates will vary over the course of a day. This variability may be handled through on-site hydrogen storage. The cycling may increase the O&M costs. Designs that enable remote monitoring will be needed to decrease the costs associated with variable production.

Implement DFMA/High-Volume Equipment Manufacturing DFMA will be a key component of cost minimization efforts for PEC systems. Ultimately, PEC will be manufactured in large quantities (hundreds of systems per year) and the goals for DFMA will change accordingly to accommodate optimal, high-volume production methods. Other critical technology needs in DFMA for Photoelectrochemical are the same as those discussed the DNGR Section. Additionally, the materials developed are initially fabricated in lab quantities. High-volume synthesis pathways will need to be identified and developed to manufacture promising materials and substrates cost effectively while maintaining the desired characteristics for further deployment of the systems.

LOWER OPERATION AND MAINTENANCE COSTS

Design for Photoelectrochemical Hydrogen Automated Process Control Planned maintenance must be minimized in terms of cost and frequency. The need for on-site labor support must be kept to a minimum or replaced with automated process control and remote monitoring that ensures robust, reliable process control.

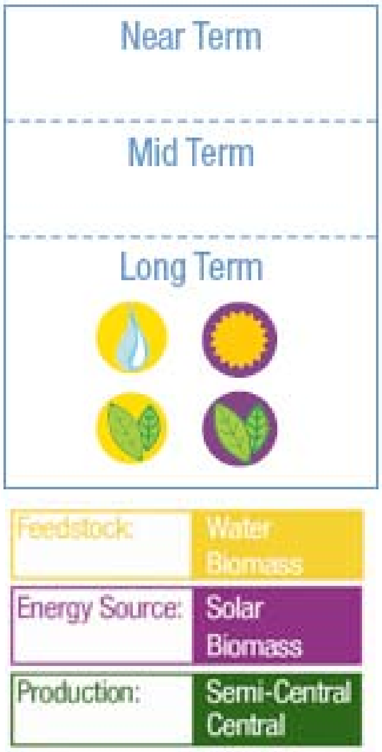
Photoelectrochemical Hydrogen Equipment Reliability, Durability, and Life Reliability of equipment with moving parts (such as pumps, compressors and blowers) is often a limiting factor in the overall reliability of a system. Increased reliability of these components and minimized equipment complexity are critical for improving system reliability. For PEC systems, sustained catalyst activity is also important for reliable and efficient operation. Impurities in the water feedstock must be controlled to protect system components.

Minimize Material and Energy Losses Hydrogen leakage must be virtually eliminated to minimize loss of process efficiency. The major losses may be in the drier equipment, which in electrolysis (a technology with similar hydrogen drying requirements) can be as high as 10%.

7.0 Biological

The biological pathway calls for producing hydrogen using microorganisms. This is a long-term technology that will most likely be suitable for semi-central and central hydrogen production facilities.

Biological Hydrogen Production



7.1. INTRODUCTION

DOE's current R&D priority for biological hydrogen production is on the initial development of the technology. This roadmap focuses primarily on initial development needs, but it also reports obstacles that will need to be avoided or minimized to reduce time to deployment.

BIOLOGICAL PROCESS TECHNOLOGIES

The four main pathways for biological hydrogen production are photolytic (direct water splitting), photosynthetic bacterial (solar-aided organic decomposition), dark fermentative (organic decomposition), and microbial-aided electrolysis (electric power-aided organic decomposition). While the last one is not strictly a biological process, it shares some key aspects. Photolytic production uses microorganisms such as green microalgae or cyanobacteria and sunlight to split water. In photosynthetic hydrogen production, sunlight is the driver for photosynthetic bacteria to break organics down, releasing hydrogen. In dark fermentative technology, bacteria decompose organics into hydrogen and by-products without the aid of sunlight. Microbial electrolysis uses microbes and an electric current to decompose biomass producing hydrogen.

Environmental Benefits

Research in biological hydrogen has progressed substantially in recent years with increased focus on sustainability. In the long term, these biological production technologies may provide economical hydrogen production.

Perhaps the nearest-term opportunity is a system in which several or all of these technologies would be combined to generate hydrogen, and the waste products from some sub-systems would serve as feedstock for other sub-systems. In such a system, barriers for individual technologies would not have to be completely overcome, as long as the system itself could produce hydrogen at a reasonable cost.

In recent years, the number of microorganisms identified for potential use in these technologies has increased substantially. Only a small fraction of naturally occurring microorganisms have so far been discovered and functionally characterized, so research is ongoing to discover those with the necessary characteristics. Known organisms are also being modified to improve their characteristics. Several recent review articles provide in-depth descriptions of the reaction pathways and types of enzymes being used in studies of biological hydrogen production.

Photolytic hydrogen production uses light to split water into hydrogen and oxygen. This can be accomplished in two ways, depending on the microorganism. Green algal and cyanobacterial photosynthesis capabilities can be used to generate oxygen and hydrogen ions.[72] A hydrogenase enzyme then converts the hydrogen ions to hydrogen gas. The second pathway, present only in cyanobacteria, is similar; it uses direct photolysis to split the water, but employs a nitrogenase (nitrogen fixing) enzyme to produce hydrogen.

Photosynthetic bacterial hydrogen production capitalizes on the nitrogenase functionality of purple non-sulfur bacteria to evolve hydrogen. The process occurs in deficient nitrogen conditions using primarily near-infrared light energy and, preferably, organic acids, although other reduced compounds can be used.

Dark fermentation uses anaerobic bacteria on carbohydrate-rich substrates grown, as the name indicates, in the dark.[73] For fermentative processes, the biomass used needs to be biodegradable, available in high quantities, inexpensive, and possess high carbohydrate content.[74] Pure, simple sugars (like glucose and lactose) are preferred because they are so easily biodegradable, but microorganisms are now being developed that can use other, less costly, feedstocks.

Microbial electrolysis cells (MEC) are a variation of microbial fuel cells. A low voltage is produced at the anode by the immobilized bacteria during the decomposition of acetic acid and/or other organics. Oxygen from the water is consumed at the anode to make CO_2. Hydrogen is produced at the fully submerged cathode with the input of a small amount of additional energy. Much of the power required to generate hydrogen is provided by the bacteria, requiring little external electric power relative to electrolysis.

Exhibit 7.1 Microbial Electrolysis Cell Reactions for the Decomposition of Acetic Acid to Hydrogen and Carbon Dioxide.

$$\begin{array}{ll} \text{Anode:} & C_2H_4O_2 + 2\,H_2O \rightarrow 2\,CO_2 + 8\,e^- + 8\,H^+ \\ \text{Cathode:} & 8\,H^+ + 8\,e^- \rightarrow 4\,H_2 \end{array}$$

Integrating the different technologies makes it possible to create an economically and technically viable system without overcoming all of the individual technology barriers. In the scenario presented here (Exhibit 7.2), (blue) green algae and photosynthetic bacteria are co-cultured in a photoreactor to produce hydrogen using water, small organic molecules, and a wider spectrum of sunlight than any of the individual microorganism types alone. The dark fermentative bacteria in a subsequent, dark reactor consume the cell biomass waste from the photoreactor, along with optionally added lignocellulosic

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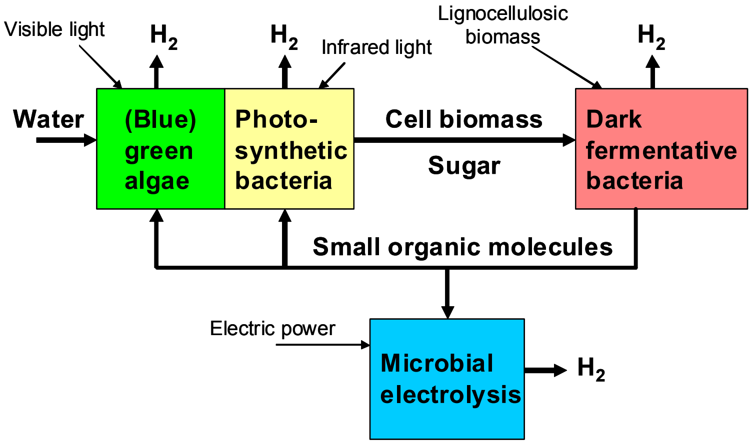
[72] Kovacs K.L., G. Maroti, G. Rakhely, ”A Novel Approach to Biohydrogen Production,” *Int. J. Hydrog. Energy*, 31 (2006) 1460-1468.

[73] Kapdan I.K. and F. Kargi, “Bio-Hydrogen Production from Waste Materials,” *Enzyme and Microbial Technology*, 38 (2006) 569-582.

[74] Levin D.B., H. Zhu, M. Beland, N. Cicek, and B.E. Holbein, “Potential for Hydrogen and Methane Production from Biomass Residues in Canada,” *Bioresource Techn.*, 98 (2007) 654-660.

biomass, to produce hydrogen and small organic molecules. The organic waste products from the dark fermentative reactor then provide feedstock for the MEC reactor and the photoreactor. An integrated biological system increases the feasible hydrogen production capability vs. stand-alone, single technology systems because hydrogen is produced at each step. This design also addresses the issues of diurnal operation (the dark fermentative and MEC reactors can operate independent of light availability) and provides internally generated feedstock for the system reactors.

Exhibit 7.2 A Combined Biological System



The DOE goal for biological hydrogen production is to use rational design, strain development, and optimization to advance these varied production pathways and achieve the hydrogen production cost targets as necessary to become competitive with other renewable production methods. This roadmap identifies knowledge and technological gaps and outlines strategies for addressing them to develop low-cost, highly efficient, biological hydrogen production technologies.

DOE COST TARGETS

Cost targets are not specified for biological hydrogen production because the technology is in the early stages of development. DOE's research supports the goal of long-term commercial hydrogen production using renewable sources at costs ultimately competitive with other renewable production methods. The current objective of the research is to verify by 2020 the feasibility of using biological systems to produce cost-competitive hydrogen in the long term.

7.2. KEY BARRIERS

Driving DOE's research activities are specific barriers identified in the *MYPP*[19] as well as others identified by the FreedomCAR and Fuel Partnership's HPTT. Barriers facing cost-effective biological hydrogen production are divided into the major technologies as well as barriers that are applicable across all pathways. They are summarized in Exhibit 7.3 and described more fully on the following pages.

LIBRARY OF MICROORGANISMS

Despite the substantial research involving microorganisms, only a small fraction of the world's vast supply of microorganisms have been identified and functionally characterized. Research is ongoing to identify microorganisms with the characteristics needed for biological hydrogen production and to identify and/or engineer organisms with the required characteristics. A greatly expanded library of organisms would facilitate discovery of promising microbes for hydrogen production.

Exhibit 7.3 Biological Hydrogen Production – Summary of Barriers

Lack of Adequate Library of Naturally Occurring Microorganisms for Characterization	
Microorganism Characterization	Only a small percentage of the multitude of naturally occurring microorganisms has been identified and characterized.
Photolytic Hydrogen Production from Water Barriers	
Light Utilization	The conversion of incident light to electrons is currently inefficient and must be increased in the organisms.
Rate of Hydrogen Production	The hydrogen production rate is insufficient for commercially competitive technologies.
Continuity of Photoproduction	Oxygen co-produced with hydrogen in water splitting inhibits the microbes' hydrogen production activity.
Systems Engineering	Once candidate organisms have been characterized, meeting microbes' needs will be a barrier to systems designed to maximize hydrogen production while managing the oxygen co-product at a low cost.
Diurnal and Seasonal Operation Limitation	Photolytic processes are discontinuous because they depend on sunlight, which is unavailable at night and available only at low intensities on cloudy days.
Photosynthetic Bacterial Hydrogen Production Barriers	
Light Utilization	Similar issues apply as for photolytic systems
Efficiency of Hydrogen Production	Generation of competing products through currently developed pathways reduces the hydrogen production rate of the microbes.
Hydrogen Re-oxidation	The pathway for hydrogen re-oxidation needs to be reduced or eliminated.
Carbon/Nitrogen Ratio	The carbon/nitrogen (C/N) ratio dramatically affects nitrogenase activity and must be properly maintained or the enzyme must be re-engineered to reduce nitrogen inhibition.
Systems Engineering	Similar to the systems engineering issues for photolytic hydrogen production
Diurnal and Seasonal Operation Limitation	Similar to the diurnal operations issues for photolytic hydrogen production
Dark Fermentative Hydrogen Production Barriers	
Hydrogen Molar Yield	Current hydrogen yield is around 2 moles H_2 per mole glucose with current pathways limiting the maximum yield to 4. The theoretical maximum yield is 12 moles H_2.
Waste Acid Accumulation	Waste by-products (e.g., acetic and butyric acid) compete with hydrogen production in fermentation and may inhibit further hydrogen production in subsequent steps to fermentation in a combined system. Metabolic pathways that eliminate the production of acids have yet to be found.
Feedstock Cost	Glucose feedstock is a major cost driver for hydrogen production using this technology. Pathways and microbes for using lower-cost feeds are unknown.
Systems Engineering	The same issues apply as above, plus system methanogen contamination and accumulation of acids will be barriers.

Microbial Electrolysis Cell Hydrogen Production Barriers	
Biological System Performance	Improved microbes that enable a faster hydrogen production rate have yet to be discovered or engineered.
Materials	This technology uses materials similar to electrolyzers in conjunction with microbes for the anode, but novel, durable cathodes and non-precious metal catalysts are needed for the cathode to enhance hydrogen evolution. Lower-cost materials and/or multifunctional materials have yet to be identified and evaluated for long-term performance.
Reactor Design	Laboratory-scale reactors are not sufficient for commercially viable hydrogen production. Issues relating to the scale-up of the reactor will be barriers to maximizing hydrogen production while minimizing cost and maintenance.
Feedstock Cost	This technology has been shown to operate on acetic acid and several other volatile acids (commonly produced as fermentation end products), glucose, and cellulose, and other sources of organic matter (e.g., municipal and industrial wastewater) are feasible. Low-cost, abundant feedstock will help to improve the economics of hydrogen production.
Systems Engineering	The same issues apply as above. Hydrogen gas produced by the system will need to be evaluated for purity. In addition, the feasibility of using part of the hydrogen gas produced (in a conventional fuel cell) should be explored to provide the additional electrical energy needed for the process to make it completely sustainable.

Photosynthetic Bacterial Hydrogen Production Barriers	
Photosynthesis/ Respiration Capacity Ratio	Optimum photosynthesis/respiration (P/R) ratio of <1 needs to be maintained. This is currently accomplished by nutrient deprivation, which decreases the production rates.
Co-Culture Balance	Proper mixtures of microbes must be established, and techniques to maintain the optimal balance have not been developed.
Biomass Utilization	The combined system will use the by-products and cell biomass from components of the system as feed for other system processes. These feed concentrations must be tightly controlled to maximize the performance and life of the system.
System Design	A system complete with BOP, controls, compression, and storage has not yet been designed to produce hydrogen at the target costs.
Operation and Maintenance	Effects from diurnal cycling as well as cleaning maintenance and start-up/shut-down requirements tend to increase operations and maintenance costs.
Control and Safety	The effect of cycling may increase the requirements on the control and sensor systems. Passive controls would be ideal as they could lower the O&M costs, but they can only be used if strict safety requirements are met. Depending on configuration, produced hydrogen and oxygen require separation.

PHOTOLYTIC HYDROGEN PRODUCTION FROM WATER

Light Utilization The conversion efficiency of incident light to electrons is insufficient in current organisms. Light is harnessed in the microorganisms by the relatively large arrays of light-capturing antenna pigment molecules. Under bright sunlight, pigment antennae absorb much more light than can be utilized by the photosynthetic electron transport apparatus of the organism, resulting in the need for significant heat dissipation and loss of up to 80% of the absorbed sunlight. Currently identified and engineered photosynthetic organisms are inefficient at light conversion. The technology readiness efficiency target is 25% utilization efficiency of absorbed incident solar light energy.

Rate of Hydrogen Production Significant improvement in the rate of production is required to make this technology commercially viable.[75] The low rates have been attributed to (1) the non-dissipation of a proton gradient across the photosynthetic membrane, which is established during electron transport from water to the hydrogenase (H_2-producing enzyme) under anaerobic conditions and (2) the existence of competing metabolic flux pathways for reductant (i.e., the microorganisms making other products in addition to hydrogen).

Continuity of Photoproduction Oxygen, co-produced with hydrogen in water splitting, inhibits the hydrogen photoproduction processes (the hydrogen enzyme activity) for the algae and cyanobacteria characterized to date. When the organism senses oxygen, the microbe stops producing hydrogen and initiates other metabolic processes. The hydrogen-producing enzymes in the naturally occurring organisms have a half life of 1 second in air, which remains far too short. The oxygen tolerance is affected by (1) the O_2-sensitive enzymes, (2) the lack of separation in the O_2 and the H_2 production cycles, and (3) the ratio of photosynthesis to respiration, causing O_2 to accumulate in the medium and reduce the quantum yield of photosynthesis. This inhibition must be removed to achieve the technology readiness target of at least 12-hour operation and at least 6-hour half life in air.

Systems Engineering Once the candidate microorganisms have been characterized, a system will need to be designed. Analysis, research, and materials development may be needed for a cost-effective photoreactor system to collect product, separate hydrogen from oxygen and any other components, and provide continuous operation, nutrient re-circulation or management, culture maintenance, minimized land area requirements, and cost-effective capital costs.

Diurnal and Seasonal Operation Limitation Photolytic processes are discontinuous because they depend on sunlight. The systems will need to be designed (e.g., sized) to accommodate this barrier.

PHOTOSYNTHETIC BACTERIAL HYDROGEN PRODUCTION

Light Utilization This barrier has the same issues as listed for photolytic production. The technology readiness target for incident light utilization is 5.5% light to hydrogen from organic acids.

Efficiency of Hydrogen Production Photosynthetic bacteria can metabolize a variety of organic substrates that are waste by-products of various fermentative processes. However, the metabolism of acetic and lactic acids for H_2 also generates by-products. Synthesis of these by-products by certain genes competes with H_2 production for the same source of electron donors. Available types of nitrogenase do not produce sufficient hydrogen.

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[75] Levin D.B., L. Pitt, and M. Love, "Biohydrogen Production: Prospects and Limitations to Practical Application," *Int. J. Hydrog. Energy*, 29 (2004) 173-185.

Hydrogen Re-oxidation Most photosynthetic bacteria contain an enzyme that consumes produced hydrogen to support cell growth. The enzyme(s), known as uptake hydrogenase enzymes, inhibit net hydrogen accumulation.

Carbon/Nitrogen Ratio Nitrogenase activity is strongly influenced by the carbon to nitrogen (C/N) ratio. This ratio must be properly maintained for maximum hydrogen production. In systems integrating multiple technologies, where the product from a dark fermentator is used as the feed to the photosynthetic reactor, this media will negatively affect the C/N ratio. Bacteria have not been identified or engineered that are capable of suitable operation using a wider C/N ratio than currently available.

Systems Engineering This barrier includes many of the issues listed in photolytic production. The main difference is that photosynthetic bacteria do not evolve oxygen with the hydrogen. However, they release CO_2, which must be removed.

Diurnal and Seasonal Operation Limitations These barriers are similar to the diurnal and seasonal operation issues for photolytic hydrogen production.

DARK FERMENTATIVE HYDROGEN PRODUCTION

Hydrogen Molar Yield The maximum hydrogen content based on glucose's chemical components is 12 moles of H_2 per mole glucose. However, known biological pathways can theoretically produce up to 4 moles H_2/mole glucose and, in practice, 2 moles H_2/mole glucose are generated. The limiting factors are believed to be H_2-end by-product accumulation, including waste-acids and solvents. Current pathways and metabolic engineering do not yield microorganisms that are able to directly take advantage of the 12 mole maximum yield potential. The ultimate goal of this technology pathway is to generate 10 moles H_2/mole glucose.

Waste Acid Accumulation Fermentation produces organic acids, such as acetic and butyric acids. The production of these acids poses several challenges, such as lowering the molar yield of H_2 by diverting the metabolic pathway toward solvent production and requiring wastewater treatment.

Feedstock Cost For renewable hydrogen to be competitive with other transportation fuels, the glucose (sugar) feedstock cost must be reduced from $0.135/lb to $0.05/lb and provide a yield approaching 10 moles H_2/mole glucose. Currently available cellulolytic microbes and other organisms require too pure feedstocks as they are unable to directly ferment cellulose (along with the mixed sugars in hemicellulose) and have insufficient yields. This lack of flexibility drives up feedstock costs. In systems combined with photolytic and photosynthetic bacteria, dark fermentative microbes are needed to efficiently use the cell biomass constituents of the algae and photosynthetic bacteria.

Systems Engineering Systems engineering barriers are similar to those enumerated for photolytic and photosynthetic production, except that light capture and oxygen gas separation are not of concern. For the fermentative system, prevention of methanogen contamination is also required. Methanogens are single–cell, anaerobic microorganisms that produce methane. They are often found in the same environments as bacteria used in dark fermentation and consume hydrogen produced by the dark fermentation species.

MICROBIAL ELECTROLYSIS CELL HYDROGEN PRODUCTION

Biologic System Performance Electrochemically active microbes were relatively recently discovered.[76] The mechanisms for electron transfer from the microbe to the environment are not well understood. The lack of enhanced microbes negatively affects system durability and increases the need for external power, while the hydrogen production rate remains insufficient. In addition, hydrogen-consuming microbes, such as microbes that produce methane from hydrogen and organics, currently grow in similar environments and must be controlled.

Materials Materials similar to those used in conventional PEM low-temperature water electrolysis are used in MECs. Currently, expensive platinum is the catalyst of choice on the cathode.[77] Lower-cost alternatives with the same performance have yet to be identified. Electrode materials range from carbon cloths and papers to graphite rods, plates, and granules. These materials are not suitable for practical-scale units due to their lack of durability and strength (carbon paper) or their high costs (graphite rods). In addition, high surface areas are needed for high reaction rates.

Reactor Design MEC reactors need to be scaled up from the current laboratory-scale devices in use. The electrodes need to have high surface areas and will be connected to external power supplies similar to electrolysis devices. The scaled up reactors will need to offer performance similar to or surpassing that of the current lab-scale reactors while minimizing BOP, maintenance, and cost. The lab-scale reactors have shown high yields (2-4 moles H_2/mole acetic acid, which is 50-99% of theoretical), but the production rates need to be increased substantially.

Feedstock Cost The primary feedstock for this technology is acetic acid, although other organics have been demonstrated, such as glucose and even municipal waste. Low-cost feedstock supplies are needed. In theory, the acetic acid could be obtained from the waste product of the dark fermentative hydrogen production. This would solve the feedstock problem for microbial electrolysis and the waste problem for the fermentative process.

Systems Engineering The same issues apply as above. Hydrogen gas produced by the system will need to be evaluated for purity. In addition, the feasibility of using part of the hydrogen gas produced (in a conventional fuel cell) should be explored to provide the additional electrical energy needed to make the process completely sustainable.

COMBINED BIOLOGICAL SYSTEM

Photosynthesis/Respiration Capacity Ratio Green algae and cyanobacteria become anaerobic when their photosynthesis/respiration (P/R) capacity ratio is 1 or less. Under such anaerobic conditions, photosynthetic water oxidation produces H_2 instead of starch, and the oxygen evolved by photosynthesis is consumed by respiration to produce CO_2. Currently, this process is achieved by nutrient deprivation, with the drawback that the resulting P/R ≤ 1 ratio is achieved by partially decreasing the quantum yield of photosynthesis. Alternative mechanisms to bring the P/R ratio to 1 have yet to be developed, but may affect the quantum yield of photosynthesis. Two further barriers will need to be investigated under these conditions: (1) rate limitations due to the non-

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[76] Call, D. and B.E. Logan, "Hydrogen Production in a Single-Chamber Microbial Electrolysis Cell Lacking a Membrane," *Envir. Sci. and Tech.* 42. (2008) 3401-3406.

[77] Cheng, S. and B.E. Logan, "Hydrogen Production in a Single-Chamber Microbial Electrolysis Cell Lacking a Membrane," *Proceed. NAS.* 104, 47 (2007) 18871-18873.

dissipation of the proton gradient, and (2) the ability of the culture to take up a variety of exogenous carbon sources under the resulting anaerobic conditions.

Co-Culture Balance To extend the absorption spectrum of the H_2-photoproducing cultures to the infrared (700-1000 nm), the possibility of co-cultivating oxygenic photosynthetic organisms with anoxygenic photosynthetic bacteria should be investigated. However, photosynthetic bacteria also absorb light in the visible region (400-600 nm), thus potentially competing with green algae for these latter wavelengths. Developing and maintaining the appropriate biomass ratio of the two organisms, as suspensions in the same cultures or separating them in the same photoreactor via immobilization of one or both cultures, will be a barrier to development of such systems. The competition for the acetic acid organic carbon substrate between two organisms in the same medium will also be an issue.

Biomass Utilization In a combined system, cell biomass from either green algae/cyanobacteria or photosynthetic bacteria can serve as the substrate for dark fermentation. The green algal and cyanobacterial cell walls are made mostly of glycoproteins (sugar containing proteins), which are rich in sugars like arabinose, mannose, galactose, and glucose. Purple photosynthetic bacterial cell walls contain peptidoglycans (carbohydrate polymers cross-linked by protein, and other polymers made of carbohydrate protein and lipid). These forms of cell biomass are not ideally suitable for dark fermentation, so pretreatment may be necessary. Methods for cell concentration and processing will depend on the type of organism used and how the biological system is combined.

SYSTEM DESIGN

Once a combined biological arrangement is developed, a complete system (including controls, hydrogen separation, purification, compression, storage, and other BOP equipment) must be designed. Optimizing hydrogen production and durability may increase capital cost, down time, and necessary maintenance. Diurnal operation limitations, feed impurity effects on performance and lifetime, and recovery from “off-spec” operation will be barriers to address through system evaluation.

OPERATION AND MAINTENANCE

O&M costs for biological hydrogen production must be comparable with those for other production techniques. Barriers in a number of areas will need to be addressed to achieve this target. Effects from diurnal cycling and seasonal fluctuations will need to be accounted for in O&M costs. All system components must be considered in O&M, including feed pre-conditioning, co-culture balance, inter-stage feed monitoring and conditioning, waste processing, hydrogen separation/purification, controls, utilities, QA/QC (e.g., sensors), compression, storage, dispensing, and safety. Since biological hydrogen production is in an early development stage, opportunity exists to develop the materials and microorganisms for a system that will minimize O&M.

Monitoring and Control Reactors, feed, purge, and inter-reactor transfer streams, will need to be monitored and controlled to attain satisfactory production. Automated instrumentation and manual sampling and analyses will be required to 1) verify identity, condition, and density of cells, and 2) maintain acceptable conditions, including temperature, pH, and medium composition in reactors. Contamination, back mutation, co-culture instabilities, disease, nutrient or other deficiency, or other conditions may be barriers to reactor or system productivity. Large reactor volumes are impediments to good control due to the slow speed with which they respond to change; thus, monitoring of streams will be especially important. Control systems must ensure that nutrients are balanced and circulate amongst reactors at rates that support satisfactory production. Any material that cannot be metabolized within a reactor must be removed before accumulating to deleterious levels. This includes product, waste materials, or other elements that are introduced with make-up water, lignocellulosic biomass, and acid/base addition. These must be monitored and controlled by transfer to other reactors or purged from the combined system. System purge streams must be carefully monitored to ensure that nutrients that leave with wastes are accounted for and replaced.

Scheduled Maintenance Robust systems that require little routine maintenance need to be developed, as on-site maintenance staff would be prohibitively expensive. System troubleshooting will need to be automated or monitored remotely. Hydrogen compression and storage requirements will need to be included in the maintenance schedule.

Production Management Hourly and daily production rates due to changes in the sun's intensity will occur. Design and operational decisions to address production variability will impact O&M as well as capital costs (e.g., turn-down, periodic shut-down, restart, and storage).

Hydrogen Separation and Purification Biologically produced hydrogen will most likely contain contaminants such as water, volatile organics, and other gases – the most important may be oxygen. The co-production of oxygen presents a significant safety and engineering challenge. The hydrogen will need to be purified to meet the strict standards required for fuel cell use. These standards are detailed in the roadmap Introduction. It is important to minimize losses (parasitic and hydrogen) and consumables to minimize O&M costs.

CONTROL AND SAFETY

Control and safety issues associated with biological hydrogen production include optimization of start-up and shut-down processes, improving turn-down capability (for cloudy days), and enabling rapid on-off cycling. The control system costs may be high and need to be minimized through system simplification and/or reduced sensor count. Passive controls would be ideal as they could lower the O&M costs, but they will be used only if strict safety requirements can be met. The sensors should be more cost effective and reliable compared to currently available technology by the time these technologies are ready for deployment. The permitting process critically relies on proven reliability and safety of these units. The units must be designed to operate in an environment of minimal manual assistance, which will require attributes such as back-up fail-safe mode, remote monitoring and infrequent maintenance schedules. The system design should meet all requirements of local and national permitting processes for effluents like liquid exhausts.

7.3. CRITICAL TECHNOLOGY NEEDS

Exhibit 7.4 lists critical technology needs for biological hydrogen production. Discussion of these efforts follows the exhibit. Note that a single R&D activity may address more than one barrier, and multiple R&D activities may be needed to address a single barrier.

For more detail on the alignment of R&D needs with technology barriers, please see Appendix B.

Exhibit 7.4 Biological Critical Technology Needs

Optimize Microorganism Functionality Integration	→ Integrate the optimal functionality of the microorganisms into single organism.
Address Materials Needs	→ Develop list of characteristics for the reactor materials. → Identify or develop appropriate materials.
Reduce Capital Costs	→ Utilize low-cost microorganisms → Reduce materials and component costs → Reduce manufacturing and installation costs • Optimize system to manage variable production • Implement DFMA/high-volume equipment manufacturing
Reduce Operation and Maintenance Costs	→ Engineer automated process control → Increase equipment reliability, durability, and life

Optimize Microorganism Functionality Integration

Various research groups are developing strategies to overcome barriers for each technology. The results of these research efforts will be needed to develop a single, optimal microorganism for hydrogen production. Using photolytic hydrogen production as an example, one group is developing algae with increased light utilization, while another is improving tolerance to oxygen. These developments will need to be integrated into a single organism for the photolytic technology to meet its targets.

Address Materials Needs

Biological hydrogen production requires materials with special characteristics for the bioreactors. These materials will need to be identified or developed if not currently available. For example, low-cost, transparent, durable, hydrogen-impermeable materials will be needed for photolytic and photosynthetic hydrogen production. Materials may be needed for the immobilization of cultures to prevent migration from the bioreactors to undesired areas and to increase hydrogen production rates. Hydrogen collection and gas separation technologies appropriate for biological hydrogen may require membranes integrated into the system. These membranes would need to have the hydrogen separation qualities necessary to achieve hydrogen purity targets while being chemically compatible with the microorganisms.

Reduce Capital Costs

Utilize Low-Cost Microorganisms

Processes will need to be developed to grow in mass quantities the engineered microorganisms selected. These microorganisms will need to be inexpensive, easy to produce, and simple to keep alive in bulk quantities.

Reduce materials and component costs

Capital costs must be minimal to enable low-cost hydrogen production. Low-cost bulk materials, high-volume manufacturing, and DFMA techniques will need to be used to achieve the low capital costs required. The most significant capital cost reduction typically occurs with the elimination of components, therefore multi-functional materials and minimization of BOP may aid in cost reduction. The diurnal and seasonal nature of photolytic and photosynthetic technologies needs to be considered in the system design. For the combined system, it will be necessary to correctly size the photosynthetic reactor such that it can produce enough organics for continuous feed to the fermentative reactor even during times of low or no sun. The feed will need to be stored during the daytime and then accessed as needed. Otherwise, the entire combined reactor system would only be able to operate during times of sufficient light. This would decrease the utility of the system and increase costs.

Reduce manufacturing and installation costs

Optimize system to manage variable production Hydrogen production may vary significantly over the course of a day. In a multi-technology combined system, for example, photolytic and photosynthetic hydrogen production as well as fermentative and microbial electrolysis production will occur during daylight hours. However, during low light times, hydrogen production will be accomplished solely by the fermentative and microbial electrolysis technologies. This variable supply may be handled through on-site hydrogen storage. Designs that enable remote monitoring will need to be used to decrease the O&M costs due to this variable production.

Implement DFMA/High-Volume Equipment Manufacturing DFMA will be another key component of cost reduction efforts for hydrogen production units. If successfully developed, biological hydrogen systems will be manufactured in large quantities (hundreds of systems per year) and the goals for DFMA will need to accommodate optimal, high-volume production methods. Other critical technology needs in DFMA for Biological production are the same as those discussed in the DNGR Section.

REDUCE OPERATION AND MAINTENANCE COSTS

Reduce Waste Acid Accumulation The organic acids production pathway needs to be eliminated or minimized to increase hydrogen production in dark fermentation systems. In addition, integration of the dark fermentation technology with photosynthetic hydrogen production could increase the hydrogen yield and eliminate the need for wastewater treatment to remove the acids.

Feedstock Cost Reducing the feedstock costs while increasing the feedstock availability will require intensive bio-prospecting for cellulolytic microbes that directly ferment cellulose along with the mixed sugars in hemicellulose and for organisms that offer higher yields. The efforts by DOE's Biomass Program should be leveraged to meet the cost target. In systems combined with photolytic and photosynthetic bacteria, dark fermentative microbes are needed to efficiently use the cell biomass constituents of the algae and photosynthetic bacteria.

Engineer automated process control On-site, planned maintenance must be strictly minimized both in terms of cost and frequency. The need for on-site labor support must be curtailed and replaced with automated process control and remote monitoring.

Increase equipment reliability, durability, and life Reliability of equipment with moving parts (such as pumps, compressors and blowers) is often a limiting factor in the reliability of an overall system. Increased reliability of these components along with minimized equipment complexity will be critical for improving system reliability. Biological hydrogen systems must provide for continuous maintenance of reactor temperature, pH, microbe compositions, feed concentrations, and any other material required to maintain the health of the microorganisms. Impurities in feedstocks must be controlled to protect reactor components. Innovative ways to purify the hydrogen may need to be developed to safely remove the oxygen.

Appendices

APPENDIX A: ACRONYMS AND ABBREVIATIONS

kΩ-cm	kilo-ohm centimeter
AHJ	authorities having jurisdiction
aka	also known as
APR	aqueous-phase reforming
BOP	balance of plant
Btu	British thermal unit
CCS	carbon capture and storage
cfd	cubic feet per day
CG	crude glycerol
CH_4	methane
Cl	chlorine
CO	carbon monoxide
CO_2	carbon dioxide
CTE	coefficient of thermal expansion
DFMA	design for manufacture and assembly
DNGR	distributed natural gas reforming
EERE	Energy Efficiency and Renewable Energy (DOE Office)
E_g	energy difference between the bottom of the conduction band and the top of the valence band in photoelectrode materials
EIA	Energy Information Administration
eV	electron volts
FCV	fuel cell vehicle
FE	Office of Fossil Energy
FY	fiscal year
gge	gasoline gallon equivalent
GHG	greenhouse gas
H_2	hydrogen
H2A	Hydrogen Analysis
H_2O	water
H_2S	hydrogen sulfide
HFCIT	Hydrogen, Fuel Cells & Infrastructure Technologies Program
ICE	internal combustion engine
IPEC	incident-photon-to-electron conversion
kcal/mole	kilocalorie/mole (a mole being one elemental unit of a chemical or Avogadro's number of molecules)
kg	kilogram
KOH	potassium hydroxide
LHV	lower heating value
LNG	liquefied natural gas
LUST	leaking underground storage tank
$\text{microS}\cdot\text{cm}^{-1}$	microSiemens/centimeter (a measure of electrical conductivity associated with water hardness)
MEC	microbial electrolysis cells
MMBtu	million Btu
MYPP	Multi-Year Program Plan
N	nitrogen
Na	sodium
NE	Office of Nuclear Energy
NHI	Nuclear Hydrogen Initiative

NOx	nitrogen oxides
NRC	Nuclear Regulatory Commission
O&M	operation and maintenance
OS	Office of Science
PEM	proton exchange membrane
psig	pressure per square inch gauge
QA/QC	quality assurance and control
R&D	research and development
SECA	Solid-State Energy Conversion Alliance
SMR	steam methane reforming
SOEC	solid oxide electrolysis cell
SOx	sulfur oxides
STH	solar-to-hydrogen
STCH	solar-driven thermochemical hydrogen production
TCH	thermochemical hydrogen production
USDA	U.S. Department of Agriculture
VOCs	volatile organic compounds
WGS	water-gas shift

APPENDIX B: BARRIERS AND R&D NEEDS

Attaining the full potential of hydrogen production requires simultaneous R&D efforts and a holistic approach that takes into account a variety of challenges, including risk, performance and quality requirements, and resource availability, as well as cost. It will require review of current regulations, codes, and standards, plus outreach efforts to encourage public acceptance of fuel cell vehicles and the associated fueling stations.

DISTRIBUTED NATURAL GAS REFORMING

Key barriers to addressing the technical challenges and lowering the cost of producing hydrogen by DNGR are summarized in Exhibit B.1.

Exhibit B.1 Distributed Natural Gas Reforming Barriers and Technology Needs

Reformer Capital Costs	Reformer Manufacturing	Station Footprint
• Develop multiple unit operations • Improve catalysts • Improve feedstock pre-treatment • Develop one step reforming/shift • Develop low cost separation/purification technologies • Increase system durability/lifespan • Optimize turn-down capability, start/stop cycling to manage variable demands • Improved energy efficiency by reducing temperature and reducing noble metal content • Develop certifications, codes and standards • DFMA/high-volume equipment manufacturing and BOP optimization	• Develop modular design • Develop low cost separation/purification technologies • Increase system durability/lifespan • DFMA/high-volume equipment Manufacturing and BOP optimization	• Reduce size of BOP water purification and utilities • Reduce system size
Operation & Maintenance Costs	**Feedstock Issues**	**Control and Safety**
• Integrate system components • Develop de-sulfurization technologies • Minimize material and energy losses • Develop separation/purification technologies • Increase system reliability, durability, and lifespan • Automate process control for low-labor operation • Maximize capital utilization by designing for turn-down capability • Develop low cost BOP • Design for remote monitoring	• Develop de-sulfurization technologies • Monitor presence of inert gas in the product • Understand feedstock supply – Grid PSI/Location pressure or benign odorants • Develop pressure regulation • Analyze natural gas supply to ensure adequacy	• Integrate system components • Optimize turn-down capability • Develop certifications, codes and standards • Develop inexpensive BOP – sensors • Automate process control for low-labor operation • Develop effluent control systems

BIO-DERIVED LIQUID REFORMING

Key barriers and R&D needs to address technical challenges and lower the cost of producing hydrogen from bio-derived liquid reforming are listed in Exhibit B.2.

Exhibit B.2 Bio-Derived Liquid Reforming Barriers and R&D Needs

Reformer Capital Costs	Reformer Manufacturing	Footprint Component
• Capital costs reduced from >\$0.75/gge H_2 to \$0.40/gge H_2 by 2019 • Improved catalysts • Integrate system components/one step reforming/shift • Reduce manufacturing and installation costs: optimize system, load following, DFMA, and reduce BOP • Develop low cost separation/purification technologies • Improve reliability, durability, and lifespan • Optimize turn-down capability • Develop feedstock flexibility • Decrease operational temperature • Improve thermal integration • Reduce catalyst content • Develop certifications, codes and standards	• Decrease reformer cost • Develop modular design • Develop low cost separation/purification technologies • Improve reactor reliability, durability and lifespan • Reduce manufacturing and installation costs: optimize system, load following, DFMA, and reduce BOP. • Develop Feedstock flexibility reactors	• Decrease system footprint • BOP Water Purification, Utilities, Nitrogen • Feedstock storage • Water storage
Operation & Maintenance Cost	**Feedstock Issues**	**Control and Safety**
• Minimize labor costs • Increase equipment reliability and durability • Maximize capital utilization: fast start-up/shut-down, optimize turn-down capability • Minimize material and energy losses • Increase co-product revenue • Integrate system components • Develop separation/purification technologies • Improve catalyst durability/lifespan, reduce coking • Develop BOP, water purification, feedstock purification, utilities • Develop feedstock flexible reactor • Reduce reactor size • Identify contaminants and develop removal technologies • Improve system efficiency • Minimize VOC release during feedstock tank filling	• Develop contaminant mitigation technologies • Decrease inert gas in the product • Improve feedstock type(s), supply, and distribution* • Develop feedstock flexible reactor • Reduce feedstock cost* * These needs are being addressed by the Office of Biomass Programs (http://www1.eere.energy.gov/biomass/program_areas.html)	• Integrate system components • Optimize turn-down capability • Design for feedstock flexibility • Develop certifications, codes and standards • Develop inexpensive, reliable sensors • Develop effective feedstock storage tank refilling

Coal and Biomass Gasification

Key barriers and R&D needs to address the technical challenges and lower the cost of producing hydrogen from coal and biomass gasification are listed in Exhibit B.3.

Exhibit B.3 Coal and Biomass Gasification Barriers and R&D Needs

Capital Costs	Operation & Maintenance	Feedstock Issues
• Reduce reactor capital costs • Integrate system component • Develop separation/purification technologies • Improve WGS catalysts • Increase system durability/lifespan • Develop low-cost feedstock preparation and handling techniques • Carbon Capture and Storage • Certifications, codes, and standards • Decreased cost of BOP: water purification, utilities, nitrogen, sensors, air separation units • Develop standardized plant design • Improve plant efficiency	• Increase system durability and reliability • Integrate system components • Develop contaminant handling technologies and decrease waste disposal • Develop low-cost separation/purification and hydrogen monitoring technologies • Improve efficiency • Develop low-cost feedstock storage, preparation, and handling • Improve BOP reliability and efficiency: water purification, utilities, nitrogen, sensors • Develop feedstock system improvements • Reduce required maintenance • Reduce material energy load • Optimize oxygen plant • Decrease emissions other than CO_2	• Develop biomass/coal co-fed gasifiers • Develop feedstock-flexible gasifiers • Develop wet-feed gasifiers • Characterize biomass supply/ quality • Decrease biomass cost • Develop low-cost, on-site feedstock storage and handling technologies • Decrease feedstock transportation costs • Decrease feedstock preparation costs

Emissions	Control and Safety
• Develop carbon capture • Improve process efficiency • Mitigate other gas emissions • Mitigate liquids emissions • Mitigate solids emissions	• Develop certification, codes, and standards • Develop inexpensive sensors • Decrease control system costs

WATER ELECTROLYSIS

Key barriers and R&D needs to address technical challenges and lower the cost of producing hydrogen from water electrolysis are shown in Exhibit B.4.

Exhibit B.4 Water Electrolysis Barriers and R&D Needs

System Efficiency and Electricity Cost	Power Electronics/ Renewable Electricity Generation Integration	Capital Costs/Footprint
• Improve membranes • Improve catalysts, electrodes • Optimize architecture • Improve hydrogen driers • System optimization to manage variable demands and power supplies • Improve high-temperature operation • Improve compressor efficiency • Improve power electronics • Develop moderate to high pressure operation	• Standardize power electronics to take advantage of economies of scale • Integrate renewable source power electronics with electrolyzer system power electronics • Decrease cost • Improve efficiency	• Low-cost membranes • Low-cost catalysts • Improved architecture • Improve hydrogen driers and quality control • Decrease manufacturing and installation costs • Increase system efficiency • Increase production rates • Increase system size • Develop low-cost thermal management and seals • Optimize system to manage variable demand • DFMA/volume manufacturing and BOP • Integrate system component • Increase system durability/lifespan • Develop certifications, codes, and standards • Meet distributed system footprint target of 7,000 ft^2

Manufacturing	Operation & Maintenance Costs
• Develop low-cost separation/purification technologies • Increase system durability/lifespan • Decrease cost of BOP (water purification, utilities, sensors, etc.) • DFMA modular design for distributed production technologies • DFMA scaled-up designs for central production	• Design for low-labor operation, automated process control • Increase system reliability, durability, and life span • Minimize material and energy losses • Reduce O&M costs for BOP water conditioning, utilities, and sensors • Improve hydrogen driers • Integrate system components • Increase capital utilization by optimizing turn-down capability • Improve system efficiency

Grid Electricity Emissions	Control & Safety
• Improve system efficiency • Decrease grid emissions	• Integrate system components • Optimize turn-down capability • Standardize certifications, codes, and standards • Develop inexpensive sensors

THERMOCHEMICAL HYDROGEN

Key barriers and R&D needs to address technical challenges and lower the cost of TCH production are listed in Exhibit B.5

Exhibit B.5 Thermochemical Barriers and R&D Needs

Heliostat Development and Cost	Thermochemical Cycle Selection	Materials and Catalyst Development
• Increase efficiency • Lower maintenance requirements • Increase durability/life • Standardize design(s) • Apply DFMA • Develop low-cost manufacturing and installation methods	• Down select to 3-12 cycles for screening • Screen 3-12 cycles and select up to two for further development	• Develop receiver • Improve chemical cycle catalysts and supports • Develop durable, long lasting reactor materials and seals • Develop high temperature thermal storage materials and processes
Reactor Development and Capital Costs	**Solar Receiver and Reactor Interface Development**	**Chemical & Thermal Storage (Capital Utilization)**
• Reduce reactor capital costs • Develop high-efficiency, standard reactor designs • Integrate system and components • Develop low-cost separation/ purification technologies • Increase system durability/lifespan • Optimize turn-down capability • Develop certifications, codes and standards • Decrease BOP cost - water purification, utilities, sensors etc. • DFMA to reduce capital and manufacturing costs • Optimize process flow	• Develop efficient heat transfer • Improve interface with thermal storage • Increase durability/lifespan • Decrease costs • Engineer for low maintenance	• Engineer for high-temperature operation • Develop efficient high heat capacity materials • Develop durable, long lasting storage material • Develop materials with low corrosivity/reactivity • Engineer for low maintenance • Decrease primary system cost • Decrease BOP cost - water purification, utilities, sensors, etc.
Feedstock Issues	**Operation & Maintenance**	**Control and Safety**
• Develop low cost water purification • Develop low cost BOP	• Engineer for automated process control • Minimize maintenance • Maximize capital utilization • Develop low-cost separation/ purification technologies • Increase system reliability, durability and lifespan • Engineer for low-labor operation • Develop low cost BOP water purification, utilities, sensors, etc • Engineer for remote monitoring	• Engineer for automated process control • Integrate system components • Optimize start-up, shut-down, and turn-down capability • Standardize certifications, codes, and standards • Develop inexpensive sensors • Develop safe thermal and/or chemical storage systems
	Diurnal Operation	
	• Minimize thermal cycling • Enable Rapid start-up/shut-down	

PHOTOELECTROCHEMICAL

Key barriers and R&D needs identified for photoelectrochemical hydrogen production are shown in Exhibit B.6.

Exhibit B.6 Photoelectrochemical Barriers and R&D Needs

Materials Efficiency	Material Durability	PEC Device and System Auxiliary Materials	Bulk Materials Synthesis	Device Configurations and Designs
• Develop materials with a band gap of 1.6-2.0 eV • Develop materials with band edge to straddle water's redox potential • Develop electron transfer catalysts or other surface/ interface modifications • Improve solar to hydrogen efficiency >16%	• Increase stability in aqueous solutions • Increase thin film adhesion to substrates • Increase hydrogen gas nucleation /generation tolerance	• Increase stability in aqueous solutions • Increase chemical compatibility with photo-catalysts • Develop protective coatings • Develop hydrogen impermeable layers • Develop photoelectrode substrates	• Develop high-volume manufacturing • Develop low-cost raw materials	• Increase efficiency • Design for low cost • Design for durability • Create hybrid designs, as appropriate • Engineer to be stable in aqueous solutions

System Design, Evaluation, and Capital Costs	Diurnal Operations	Operation and Maintenance	Control and Safety
• Decrease materials and component costs • Develop low-cost hydrogen separation and purification technologies • Reduce manufacturing and installation costs • Apply DFMA and decrease BOP • Integrate system components • Engineer for system durability/ lifespan • Develop effective water purification	• Engineer for cycling • Design for rapid start-up/shut-down • Optimize system for rapid start-up/shut-down and high turn-down operation • Optimize for rapid start-up/shut-down and turn-down operation	• Engineer for automated process control • Design for high system durability and reliability • Minimize material and energy losses • Integrate system components • Utilize low-cost water purification technologies • Develop low-cost hydrogen separation/ purification technologies	• Integrate system components • Develop controls for start-up and shut-down cycle and turn-down operation • Design for low-labor operation • Standardize certifications, codes and standards • Develop inexpensive sensors

Biological Hydrogen Production Barriers and R&D Needs

Key barriers and R&D needs for biological hydrogen production are listed in Exhibit B.7.

Exhibit B.7 Biological Hydrogen Production Barriers and R&D Needs

Characterize Microorganisms	• Lack of an adequate library of naturally occurring microorganisms • Increase number of organisms characterized • Identify microorganisms with promising characteristics (as outlined below) for further study	
Develop Photolytic Hydrogen Production from Water	**Increase Light Utilization**	• Decrease heat dissipation required • Increase light utilization efficiency to >25%
	Increase Production Rate	• Eliminate competing metabolic pathways • Decrease proton gradient non-dissipation
	Improve Production Continuity	• Identify/engineer more O_2 tolerant microbe • Separate O_2 and H_2 production cycles • Improve photosynthesis to respiration ratio
	Perform Systems Engineering	• Integrate desirable traits into single organism with >10% light-to-hydrogen efficiency • Develop effective reactor materials/components • Hydrogen separation/purification • Start-up/shut-down cycle life • Remote monitoring • Turn-down capacity • Balance-of-plant • Cost-effective sensors • System durability
	Overcome Diurnal and Seasonal Operational Limitations	• Develop flexible operational cycle • Start-up/shut-down cycle life • Turn-down capacity • System durability
Develop Photosynthetic Bacterial Hydrogen Production	**Increase Light Utilization**	• Decrease heat dissipation required • Increase incident light to hydrogen efficiency to >5.5% • Increase spectrum utilization
	Increase Production Efficiency	• Decrease/eliminate by-products
	Reduce Hydrogen Re-oxidation	• Eliminate hydrogenase uptake enzymes
	Overcome Carbon/Nitrogen Ratio Limitations	• Increase nitrogenase tolerance to nitrogen
	Perform Systems Engineering	• Integrate desirable traits into single organism with >5.5% incident light-to-hydrogen efficiency • Hydrogen separation/purification • Start-up/shut-down cycle life • Remote monitoring • Turn-down capacity • Design CO_2 removal system • Inexpensive sensors and balance of plan • System durability
	Overcome Diurnal and Seasonal Operation Limitations	• Start-up/shut-down cycle life • Turn-down capacity • System durability
Develop Dark Fermentative Hydrogen	**Increase Hydrogen Molar Yield**	• Identify new pathways to access 12 moles H2 available • Eliminate by-products (waste acid) • Increase production rate

Production	**Decrease Feedstock Cost**	• Reduce glucose cost • Discover/ engineer cellulolytic microbes • Increase feedstock utilization • Develop low-cost, low-maintenance feedstock preparation, storage and handling technology • Increase feedstock flexibility
	Decrease Waste Acid Accumulation	• Identify new pathways to eliminate acid production • Develop systems to remove waste acid
	Perform Systems Engineering	• Integrate desirable traits into single organism • Develop low-cost hydrogen separation/ • purification technologies • Optimize start-up/shut-down cycle life • Develop remote monitoring • Engineer for suitable turn-down capacity • Integrate CO_2 removal technologies • Develop cost-effective sensors and BOP • Engineer for maximum system durability • Prevent methanogen contamination
Develop Microbial Electrolysis Cell Hydrogen Production	**Improve Biologic System Performance**	• Understand biological mechanisms • Increase production rate • Improve durability • Increase feedstock flexibility
	Improve Reactor Materials	• Modify PEM electrolyzer materials for MECs • Improve catalysts • Improve inexpensive electrode materials • Increase durability • Increase surface areas
	Decrease Feedstock Cost	• Develop low-cost, low-maintenance feedstock preparation, storage, and handling technology • Increase feedstock flexibility • Develop contaminant removal technology • Increase feedstock utilization • Increase feedstock flexibility
	Perform Reactor Design/Systems Engineering	• Improve efficiency • Increase production rate • Increase active surface area • Scale-up from lab units • Increase feedstock utilization • Integrate cost-effective sensors and balance-of-plant • Design for low-cost material/system fabrication • Engineer for low maintenance • Identify low-cost electricity sources
	Systems Integration	• Optimize start-up/shut-down cycle & turn-down capacity • Engineer for remote monitoring • Integrate with CO_2 removal technologies • Engineer for high system durability
Develop Combined System	**Develop Manageable Photosynthesis/Respiration Ratio**	• Design system for photosynthesis/respiration ratio <1
	Develop Co-Culture Balance Technologies	• Increase light spectrum utilization using multiple microorganisms • Maintain appropriate microorganism ratio • Develop balanced light absorption limitation design • Balance feedstock needs
	Increase Biomass Utilization	• Integrate biomass preprocessing technology • Develop methods for cell concentration

Develop System Design	• Utilize low-cost microorganisms • Reduce materials and component costs • Reduce manufacturing and installation costs • Integrate system components • Develop low-cost hydrogen separation and purification system • Design for system durability/reliability • Optimize start-up and shut-down cycle life/turn-down operation • Utilize low-cost feedstock storage, processing, and quality control • Design inter-stage feed monitoring/ control • Design to maximize light utilization/diurnal operation • Develop reactor conditions control strategy • Implement DFMA/high volume manufacturing • Utilize low cost balance-of-plant, sensors, water purification, utilities
Design for Optimized Operation and Maintenance	• Engineer automated process control • Increase equipment reliability, durability, and life • Develop reactor self-cleaning strategies • Design for low-labor operation/maintenance • Utilize low-cost feedstock, storage, processing, handling, and quality control technologies • Design for optimal co-culture balance • Design for Inter-stage feed monitoring/control/ reactor monitoring • Optimize start-up and shut-down cycle life/turn-down operation
Optimize Control and Safety	• Integrate system components • Optimize start-up and shut-down cycle life/turn-down operation • Design for minimal manual assistance • Standardize certifications, codes, and standards

APPENDIX C: SUMMARY OF PRODUCTION TECHNOLOGIES

Technology	Feed Stock	Scale[a]	Efficiency	Current Projected Cost[b] (prod. only)	2017 Cost[c] (prod. only, $/gge)	Maturity	Inter-actions with Others in DOE
Distributed Natural Gas Steam Reforming	Natural Gas	All	65-80%[d,18,78]	D: <$2.50[18] S,C:<$1.00[49]	D <1.70 S,C <$1.00	Commercial	None
Bio-Derived Liquids Reforming	Biomass						
Gas Phase Reforming	Bio-liquids (ethanol)	S,D	67%[d,28]	D: $3.00-3.15[28]	<$2.65	Mid-term	OBP
Aqueous Phase Reforming	Biomass	S,D	35-55%[d,29]	D: $6.50[29]	<$2.65	Mid-term	OBP
Gasification	Coal, biomass						
Coal (no sequestration)	Coal	C	58%[d,47]	$1.35[c, 47]	<$1.10	Commercial	FE
Coal (w/sequestration)	Coal	C	51%[d,47]	$1.60[c, 47]	<$1.10	Mid-term	FE
Biomass	Biomass	S	35-45%[d,49]	<$2.00	<$1.10	Mid-term	OBP
Co-gasification (w/seq)	Coal, biomass	C,S	NA	NA	<$1.10	Mid-term	FE, OBP
Water Electrolysis	Electricity (solar, wind, nuclear, geothermal) H_2O, heat						
Alkaline Electrolyzer	H_2O, electricity	S,D	50-60%[d,79,80]	D: $5.20[81]	D: <$2.70 C: <$2.00	Commercial	NE
Proton Exchange Membrane Electrolyzer	H_2O, electricity	S,D	55-70%[d, 79,80]	D: $4.80	D: <$2.70 C: <$2.00	Near term	None
Solid Oxide Electrolysis Cell	H_2O, heat,	C	30-60%[e, 49]	NA	C: <$2.00	Long term	NE

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[78] McHugh, K. “Hydrogen Production Methods”, (2005). MRP-WP-001. Prepared for MPR Associates February 2005. Available on the internet at: http://www.mpra.com/.

[79] Sørensen, B. Hydrogen and Fuel Cells Emerging Technologies and Applications. 2005, Elsevier Academic Press. New York. 450p

[80] Turner, J., Scerdrup, G., Mann, M.K., Maness, P.C., Kroposki, B., Ghirardi, M., Evans, R.J., Blake, D., “Renewable Hydrogen Production” (2008), *Int. J. Energy Res.* 32, pp 370-407.

[81] Porter, S., “Hydrogen Generation from Electrolysis: 100 kgH_2/day Trade Study” 2008 DOE Hydrogen Program Review. http://www1.eere.energy.gov/hydrogenandfuelcells/annual_review.html

Technology	Feed Stock	Scale[a]	Efficiency	Current Projected Cost[b] (prod. only)	2017 Cost[c] (prod. only, $/gge)	Maturity	Inter-actions with Others in DOE
	electricity						
Thermochemical Hydrogen Production	Solar, nuclear, H_2O, heat	C, S	NA	2025 projected: $3.2 - $5.3[82]	C: <$3.00	Long term	Solar, NE
Photoelectrochemical	H_2O, solar	C, S	12%[f,80]	NA	NA	Long term	SC
Biological	Biomass, solar, electricity						
Photolysis[83]	H_2O, solar	S	0.5%[f,83]	In process	NA	Long term	SC
Dark Fermentation	Biomass	S	60-80%[g,80]	In process	NA	Long term	SC, OBP
Photosynthetic Bacterial Hydrogen	Biomass, solar	S	0.1%[h, 19]	In process	NA	Long term	SC, OBP
Microbial Electrolysis Cell	Biomass, electricity	S	78%[i,7672]	In process	NA	Long term	SC, OBP

a) Scale: C = central hydrogen production, S = semi-central hydrogen production, D = distributed hydrogen production.

b) Current cost as submitted by project PI's or found in the *MYPP*. The costs were determined using H2A and are in 2005 dollars. They do not include the cost for compression and storage.

c) Based on H2A projections to 2017 reported in 2005 dollars and using H2A cost assumptions. They do not include compression and storage costs.

d) Thermal efficiency defined as the lower heating value of the hydrogen out, divided by the lower heating value of the feedstock plus any other energy used. Electrical energy utilized does not include the efficiency losses during electrical power generation.

e) Thermal efficiency defined as the lower heating value of the hydrogen out, divided by the lower heating value of the feedstock plus any other energy used. Electrical energy utilized does not include the efficiency losses during electrical power generation. The efficiency for SOEC depends on the temperature and heat source. For heat from nuclear reactors the efficiency can reach up to 60%. If the heat must be generated, then the efficiency is significantly less.

f) Solar to hydrogen via water splitting. Does not include hydrogen purification.

g) Percent of 4 mole H_2 per mole glucose theoretical maximum.

h) Solar to hydrogen via organic materials. Does not include hydrogen purification.

i) Overall energy efficiency including applied voltage and energy in the substrate. Does not include energy for purification.

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[82] Presentation to the HPTT Team at UNLV, Las Vegas Nevada, by the STCH team. January 22, 2009.

[83] Kosourov, S.N. and M. Seibert (2008) "Hydrogen Photoproduction by Nutrient-Deprived Chlamydomonas reinhardtii Cells Immobilized within Thin Alginate Films under Aerobic and Anaerobic Conditions," Submitted for publication.

APPENDIX D: CURRENT DOE PROJECTS ADDRESSING BARRIERS AND GUIDELINES FOR HYDROGEN PRODUCTION

Exhibit D.1 DOE Distributed Natural Gas Research Objectives Matrix

DOE Project	Principal Technology Developer	Barriers Addressed									
		Technology	Reformer Capital Costs	Reformer Manufacturing	Purification	Station Footprint	O & M	Feedstock Issues	Greenhouse Gas Emissions[84]	Control and Safety	Regulatory Issues
Distributed Reforming from Natural Gas: (2005-2008)	H2Gen HGM 2000 and HGM 10,000	SMR/ Advanced S Removing Catalysts	X	X		X	X	X	X	X	
	GE Global Research	Short Contact Partial Oxidation Reactor	X	X		X	X	X	X	X	
	Linde/MRT/ Ergenics	Fluidized Bed Membrane Reactor and Integrated Metal Hydride Compression	X	X		X	X		X	X	
Distributed Reforming from Natural Gas: (2002-2005)	Air Products and Chemicals Inc.	SMR Turn-Key Fueling Station	X	X	X	X	X		X	X	
	GE Global Research	Authothermal Cyclic Reformer	X	X		X					
	Praxair	SMR DFMA Analysis	X	X		X	X		X	X	
	Innovatek	Small scale reformer with Pd membrane	X		X						
	GTI	SMR/ Advanced Dispensing Algorithms	X	X		X	X		X	X	

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[84] On a Well to Wheels basis, DNG, when used as a feedstock for Hydrogen Fuel Cell Vehicles, emits less greenhouse gas emissions than high-efficiency internal combustion engine vehicles. (ANL GREET Data)

DOE Project	Principal Technology Developer	Barriers Addressed									
		Technology	Reformer Capital Costs	Reformer Manufacturing	Purification	Station Footprint	O & M	Feedstock Issues	Greenhouse Gas Emissions[84]	Control and Safety	Regulatory Issues
Separations and Purification - EERE	U of Arizona	Zeolite Membrane Reactor for Water-Gas-Shift			X				X		
	Media and Process Technologies	Carbon Molecular Sieve Membrane Reactor	X	X	X				X		
	NETL	WGS Membrane Reactor	X		X						
	Air Products and Chemicals, Inc.	Ceramic Membrane Reactor System	X		X						
	Pall Corporation	High-Performance, Durable, Pd-Alloy Membrane	X	X	X				X		
	Praxair	Integrated Ceramic Membrane System	X	X	X				X		
	ORNL	Low-Temperature Ion Transport Membrane			X				X		
Separations and Purification – FE[85]	Eltron R&D	Scale-Up Ceramic Membrane			X				X		
	United Technologies Corporation	Pd-Cu Alloy Membranes			X				X		
	Southwest Research Institute	Thin Dense Self-Supported Pd-Cu Alloy Membrane			X				X		

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[85] *DISCLAIMER*: Fossil Energy (FE) develops these technologies only for coal as a feedstock for producing H_2; these projects are included in this matrix because FE projects may be applicable to hydrogen production from distributed natural gas reforming.

DOE Project	Principal Technology Developer	Barriers Addressed									
		Technology	Reformer Capital Costs	Reformer Manufacturing	Purification	Station Footprint	O & M	Feedstock Issues	Greenhouse Gas Emissions[84]	Control and Safety	Regulatory Issues
	Western Research Institute	WGS Vanadium Alloy Hydrogen Transport Device			X				X		
	Aspen Group Inc.	WGS Membrane Reactor			X				X		
	REB Research and Consulting	High Flux Metallic Membranes			X				X		
	U. of Kentucky CFFLS	Production and Storage of H_2 with C_1 Chemistry			X				X		
Small Business Innovative Research	InnoSense LLC	High Volume Production of Hydrogen Sensor using Intrinsically Safe Optical Sensor Platform								X	X
	Lynntech, Inc.	Interior Surface Modified Novel Zeolite Adsorbents for Preferential CO_2 Adsorption at High Relative Humidity			X				X		
	Genesis Fueltech, Inc.	Membrane Structures for Hydrogen Separation			X				X		
	PoroGen Corporation	Composite Hollow Fiber Membrane for Natural Gas Treatment			X				X		

Exhibit D.2 DOE Bioderived Liquids Reforming Research Objectives Matrix

DOE Project (End Date)	Principal Technology Developer	Barriers Addressed						
		Technology	**Reformer Capital Costs**	**Reformer Manufacturing**	**Station Footprint**	**Operation and Maintenance**	**Feedstock Issues**	**Control and Safety**
End Sept. 30 2009	Pacific Northwest National Laboratory	Gas phase and aqueous phase reforming	X		X	X	X	
May 2005 – April 30 2010	Ohio State Univ.	Investigation of Reaction Networks and Active Sites in Bio-ethanol Steam reforming over Co-Based Catalysts	X			X		
End Sept. 30 2009	NREL	Distributed Bio-Oil Reforming	X			X	X	X
Sept. 2009	Virent	Aqueous Phase Reforming	X	X	X	X	X	X
End Sept. 30 2009	ANL	High Pressure Ethanol Reforming	X					
End Sept. 30 2009	ANL	Renewable Liquids Reforming using Dense Ceramic Membranes	X			X		
End Sept. 30 2008	Directed Technologies Inc.	Cost Anaylsis of Dist. Bio-derived Liquids Reforming	X	XX				

Exhibit D.3 DOE Coal and Biomass Gasification Research Objectives Matrix

DOE Project (End Date)	Principal Technology Developer	Barriers Addressed					
		Technology	**Capital Costs**	**O&M**	**Feedstock Issues**	**Emissions**	**Control and Safety**
Jan. 2011	GTI	One Step Biomass Gas Reforming-Shift Sep. Membrane Reactor	X	X	X	X	X
Feb. 2009	UTRC	Novel Slurry Based Biomass Reforming Process	X	X	X		
End Sept. 30 2009	NREL	Biomass Gasification	X	X	X		X
Separations and Purification – FE[86]	Eltron R&D	Scale-Up Ceramic Membrane					
	United Technologies Corporation	Pd-Cu Alloy Membranes					
	Southwest Research Institute	Thin Dense Self-Supported Pd-Cu Alloy Membrane					
	Western Research Institute	WGS Vanadium Alloy Hydrogen Transport Device					
	Aspen Group Inc.	WGS Membrane Reactor					
	REB Research and Consulting	High Flux Metallic Membranes					
	U. of Kentucky CFFLS	Production and Storage of H_2 with C_1 Chemistry					

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[86] *DISCLAIMER*: Fossil Energy (FE) develops these technologies only for coal as a feedstock for producing H_2;

Exhibit D.4 DOE Water Electrolysis Research Objectives Matrix

DOE Project (End Date)	Principal Technology Developer	Barriers Addressed									
		Technology	System Efficiency	Power Electronics	Capital Costs	Manufac-turing	Station Footprint	O&M	Grid Electricity Emissions	Renewable Energy Integration	Control and Safety
End Sept. 30 2009	NREL	Renewable Electrolysis Int. Sys Dev	X	X	X				X	X	
April 2011	Giner	PEM Electrolyzer Incorp. Low Cost Membrane	X	X	X	X	X	X	X		X
Dec. 2008	GE Global	Adv. Alkaline Electrolysis	X		X	X			X		
July 2009	MSRI	Solid-Oxide Hybrid for Co-Generation of H2 and Electricity	X		X						
June 2009	ASU	Water Splitting Catalysts using a Novel Molecular Evolution Approach	X		X						
Nov. 2010	Avalence	High-Capacity, High Pressure Electrolysis System with Renewable Power Sources	X	X	X	X	X	X	X	X	X
	ANL (Part of NHI)	Materials Issues and Experiments for HTE and SO_3 Electrolysis	X					X			

DOE Project (End Date)	Principal Technology Developer	Barriers Addressed									
		Technology	System Efficiency	Power Electronics	Capital Costs	Manufac-turing	Station Footprint	O&M	Grid Electricity Emissions	Renewable Energy Integration	Control and Safety
	INL (Part of NHI)	Lab. Scale THE	X	X	X			X	X		
	ANL	SOEC Modeling, Electrode Characterization Studies and Process Flowsheet Analysis	X		X			X	X		
2008	Cerametec	Reversible SOFC	X		X						
2007	Teledyne	High Pressure Alkaline Electrolysis	X		X						X
2009	Proton Energy	High Pressure Electrolysis	X		X						
2007	SRI	Modular High T Electrolysis	X		X						
2005	INL	High T Electrolysis	X		X						
2003	LLNL	Reversible SOFC	X		X						
2003	TMI	Reversible SOFC	X		X						

Exhibit D.5 DOE Thermochemical Hydrogen Production Research Objectives Matrix

DOE Project (End Date)	**Principal Technology Developer**	**Barriers Addressed**											
		Tech	**Helio-stats**	**Cycle Selection**	**Materials**	**Reactor Develop/ Cost**	**Receiver/ Reactor**	**Chemical/ thermal storage**	**Feed-stock issues**	**O&M**	**Diurnal Op**	**Control & Safety**	**Process Control**
May 2009	Unic. Colorado-Boulder	Solar-Thermal H2 Prod. Using Metal-Oxide Based TC		X	X		X						
	UNLV	Develop. Of Solar Powered TCH		X	X	X	X	X			X		
	SAIC	Solar HT Photo-catalytic Assist Water Splitting		X	X	X	X						
Sept. 2010	SRNL (Part of NHI)	Process Cost for Solar Hybrid Sulfur Cycle		X	X	X							
2008	SNL (Part of NHI)	Sulfur-Iodine TCH		X	X	X							
Sept. 2007	ANL (Part of NHI)	High Temp. TCH Process		X		X							
Sept. 2010	INL	NHI Catalyst & Membrane Studies for TCH at INL		X	X	X							
	ANL (Part of NHI)	Materials Issues and Experiments for HTE and SO_3 Electrolysis		X	X								
	ORNL (Part of NHI)	Membrane Applications for Nuclear Hydrogen Production Processes			X	X							

DOE Project (End Date)	Principal Technology Developer	Barriers Addressed											
		Tech	Helio-stats	Cycle Selection	Materials	Reactor Develop/ Cost	Receiver/ Reactor	Chemical/ thermal storage	Feed-stock issues	O&M	Diurnal Op	Control & Safety	Process Control
	INL (Part of NHI)	Nuclear Reactor/ Hydrogen Process Interface Including the HyPEP Model		X	X	X							

Exhibit D.6 DOE Photoelectrochemical Hydrogen Production Research Objectives Matrix

DOE Project (End Date)	Principal Technology Developer	Barriers Addressed										
		Tech	Materials/ Eff.	Material Durability	PEC Device and System Aux mat.	Bulk Material Synthesis	Device Config Designs	Capital Costs	Diurnal Op.	O&M	Control and Safety	Reg Issues
End Sept. 30 2009	NREL	Photo-electro-chemical Systems for H2 Prod	X	X								
Sept. 2009	Midwest Optical	Critical Research for Cost-Effective PEC	X	X	X	X X	X					
Sept. 2009 (Directed by Congress)	Univ. Nevada Reno	University of Nevada, Reno PEC	X	X								
Sept. 2009	UNLV	PEC H2 Production: UNLV SHGR Program	X	X		X	X					
May 2010	UC- Santa Barbara	PEC Production using New Combinatorial Chemistry Derived Materials	X	X	X	X						
Aug. 2011	MV Systems	PEC	X	X	X	X	X					
2005	SRI	Photo-catalysts	X									
	Univ. of Hawaii	PEC H2	X	X	X							
2007	GE	PEC H2	X	X	X	X						

Exhibit D.7a DOE Biological Hydrogen Production Research Objectives Matrix – Photolytic

DOE Project (End Date)	Principal Technology Developer	Barriers Addressed						
		Tech	Char. Organ	Light Util.	H2 prod.	Continuity of Prod	System Engineering	Diurnal/ seasonal Operation
April 2010	J. Craig Venter	H2 from H2O in a Novel Recombinant O2 Tolerant Cyanobacteria System	X		X	X		
Sept. 2009	NREL	Biological Systems for H2 Production				X		
Dec. 2010	UC Berkley	Maximizing Light Util. and H2 Prod. in Microalgal Cultures						

X

Exhibit D.7b DOE Biological Hydrogen Production Research Objectives Matrix – Photosynthetic

DOE Project (End Date)	Principal Technology Developer	Barriers Addressed							
		Tech	Char. Organ.	Light Util.	H2 prod.	H2 re-oxidation	Carbon/ N2 ratio	System Eng.	Diurnal/ seasonal Operation
Sept. 2009	Montana State Univ	Biological Materials and Biologically Inspired Materials for H2 Catalysis			X	X		X	
July 2009	Florida Inter. Univ	Photobiological H2 Research	X		X	X			

Exhibit D.7c DOE Biological Hydrogen Production Research Objectives Matrix – Fermentative

DOE Project (End Date)	Principal Technology Developer	Barriers Addressed					
		Technology	Char. Organ.	H2 Molar yield	Acid Accum.	Feedstock	Systems Eng.
Sept. 2009	NREL	Fermentation Approaches to H2 Production	X	X	X	X	

Exhibit D.7d DOE Biological Hydrogen Production Research Objectives Matrix – Microbial Electrolysis Cell

DOE Project (End Date)	Principal Technology Developer	Barriers Addressed					
		Technology	Micro-biology	Materials	Reactor Design	Feedstock	Systems Eng.
	Penn State	MEC Development	X	X	X	X	X

Exhibit D.8 DOE Biological Hydrogen Production Research Objectives Matrix – Combined Biological System

DOE Project (End Date)	Principal Technology Developer	Barriers Addressed						
		Photo/ Respiration Cap. Ratio	Co-Culture Balance	Concentration/ processing of cell biomass	System design/ eval./ cost	O&M	Control and Safety	Reg. Issues.
No research is being conducted in this are yet. The biological hydrogen production technologies are not ready to be integrated together.