

Summary Report of the Carbon-Negative Hydrogen Workshop

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Technical Report

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NOTICE

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List of Acronyms

CCUS	carbon capture, utilization, and storage
CO	carbon monoxide
CO ₂	carbon dioxide
DAC	direct air capture
DOE	U.S. Department of Energy
FECM	Office of Fossil Energy and Carbon Management
H ₂	hydrogen
HER	hydrogen evolution reaction
LCA	life cycle assessment
LLNL	Lawrence Livermore National Laboratory
NETL	National Energy Technology Laboratory
NREL	National Renewable Energy Laboratory
OER	oxygen evolution reaction
PEM	proton exchange membrane
R&D	research and development
TEA	techno-economic analysis
TRL	technology readiness level

Executive Summary

This report summarizes the outcomes of the Carbon-Negative Hydrogen Workshop held at the National Renewable Energy Laboratory in Golden, Colorado on June 22–23, 2023. The workshop was co-sponsored by Lawrence Livermore National Laboratory and the National Energy Technology Laboratory and focused on developing a shared understanding of the importance of and opportunities for generation and use of carbon-negative hydrogen in industrial decarbonization. For the purposes of this workshop, carbon-negative hydrogen was defined as hydrogen (H₂) produced in a manner that leads to net carbon dioxide removal from the atmosphere thus giving rise to a life cycle cradle-to-grave carbon intensity that is below zero.

This invitation-only workshop brought together 57 thought leaders from industry, the U.S. Department of Energy (DOE) national laboratory system, and academia for one-and-a-half days to examine the value proposition of carbon-negative hydrogen from a technical and economic perspective. The workshop included insights related to community impacts and other societal aspects of this new technology space.

Major insights from the workshop included:

1. Carbon-negative hydrogen nomenclature and fit within the broader clean H₂ and carbon dioxide removal landscape needs to be more clearly defined and established.
2. While the value proposition of carbon-negative hydrogen is conceptually understood it requires better quantification and benchmarking.
3. A diverse slate of technologies leveraging a wide variety of feedstocks exists across technology readiness levels; these technologies span several DOE offices. Accordingly, there is significant opportunity for innovation, but a coordinated research and development strategy is necessary.

Recommendations from this workshop include establishing a multipronged coordinated research and development strategy at the federal level that encompasses foundational science and applied engineering in alignment with the needs of each technology area and in close cooperation with industry. This strategy should include and be guided by analysis to solidify the business case, value proposition, and sustainability goals. In addition, the strategy should be coordinated across multiple DOE offices to address the entire value chain from feedstock to product, as well as with DOE's Regional Clean Hydrogen Hubs program.

More information on the workshop content including copies of all presentations can be found at the following website: nrel.gov/bioenergy/carbon-negative-hydrogen-workshop-presentations.html.

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1 Introduction

1.1 Background

As the world's largest economies grapple with rising carbon emissions and commence strategies for decarbonization, it is becoming clear that there are no one-size-fits-all solutions. Renewable energy projects utilizing wind, solar, and hydropower continue to make significant strides in decarbonizing the energy and light-duty transportation sectors, yet there are limits to the reach of electricity and what can reasonably be electrified.

Other sectors such as aviation, industrial manufacturing, and chemicals manufacturing for example, often require specialized and/or more extreme operating conditions that have, so far, been shown to be largely incompatible with conventional electrification strategies.

Furthermore, strategies that are exclusively carbon-neutral will be inherently unable to address the high carbon dioxide (CO₂) levels currently impacting the climate. Drawing down legacy carbon emissions as well as counteracting future emissions will be critical to ongoing global carbon management efforts as indicated in the latest analyses from the Intergovernmental Panel on Climate Change.

In the future, clean hydrogen (H₂) has the potential to sit at a critical intersection between carbon management and industrial decarbonization. As an essential industrial chemical feedstock, hydrogen represents an important connector linking many industry segments including fuels and chemicals, transportation, and essential materials (Figure 1).

Carbon-negative hydrogen can be seen as an enabling technology for industrial decarbonization. Recent studies have demonstrated that a fully decarbonized economy will require CO₂ removal, or negative emissions technologies, due to difficulties in decarbonizing certain processes (Baker et al. 2020). In this sense, utilization of carbon-negative hydrogen could serve as a key enabler for the transition to net-zero or even net-negative carbon supply chains for industry.

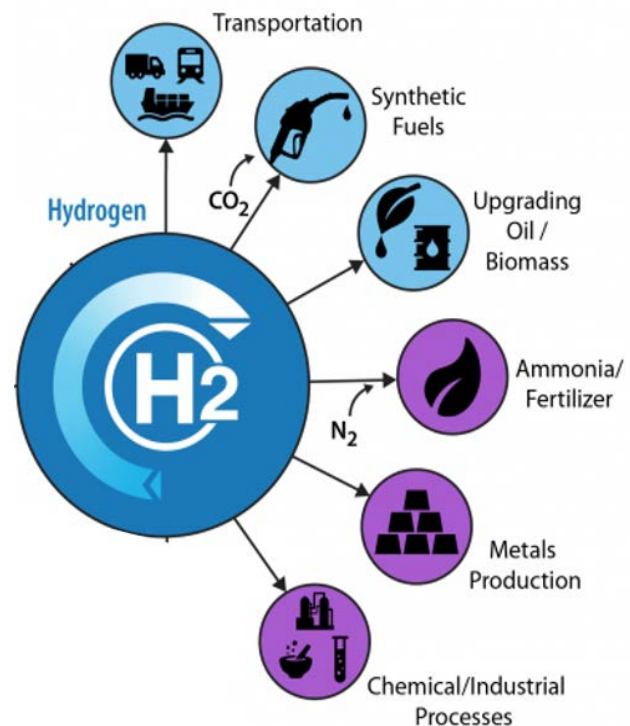


Figure 1. Hydrogen is a coupling agent between diverse, domestic resources with multiple industrial and transportation sectors

Source: Figure adapted from DOE's H₂@Scale initiative (HFTO 2024)

What Is Carbon-Negative Hydrogen?

Defining carbon-negative hydrogen first requires an understanding of broadly the two types of carbon present across our planet, those of biogenic and non-biogenic origin. Biogenic carbon includes all products of natural photosynthetic processes that convert atmospheric CO₂ into products, including plant biomass and the carbon inside all living organisms. Conversely, non-biogenic sources of carbon like fossil fuels (e.g., coal, natural gas, and petroleum) represent a form of carbon that was previously sequestered and locked away that is intentionally brought above ground by human activities and ultimately contributes to an increase the total amount of carbon within the atmospheric carbon cycle.

Herein, carbon-negative hydrogen is defined as H₂ produced in a manner that leads to net CO₂ removal from the atmosphere thus giving rise to a life cycle cradle-to-grave carbon intensity that is below zero. By definition, this necessitates the use of biogenic carbon sources, which through conversion, act to effectively draw down atmospheric CO₂ levels during H₂ production. One often cited example is biomass gasification paired with carbon capture and storage. In this case, the carbon, hydrogen, and oxygen atoms contained in the biomass molecules formed during photosynthesis are converted into light gases of carbon monoxide (CO), CO₂, and H₂. When this transformation is performed in an environmentally conscious manner, and if the produced CO₂ is stored in a durable form (>100-year lifetime), the resulting H₂ can be delivered with a net negative carbon footprint as CO₂ has effectively been removed from the atmosphere. In addition to biomass gasification, many other pathways and feedstocks are potentially available to produce carbon-negative hydrogen. Some emerging technologies, such as seawater electrolysis, offer a means to store CO₂—in the form of mineral carbonates—and produce H₂ in a single step. Ultimately, the use of carbon-negative hydrogen in chemicals, materials, and fuels manufacturing gives rise to the exciting prospect that some of the greatest contributors of global carbon emissions, such as ammonia synthesis, ethylene synthesis, steel production, and jet fuel production could technically be turned into carbon sinks (Schaidle et al. 2022).

1.2 Goals

The goal of the Carbon-Negative Hydrogen Workshop was to develop a shared understanding of the importance of and opportunities for generation and use of carbon-negative hydrogen in industrial decarbonization. Recognizing that this topic has been overlooked in the current literature, the organizers established a targeted workshop devoted to exploring the topic in more detail with key stakeholders.

The workshop was by invitation only with approximately equal representation from industry, U.S. Department of Energy (DOE) national laboratories, and academia. A total of 57 attendees were present for the day-and-half meeting, which was held at the National Renewable Energy Laboratory's (NREL's) campus in Golden, Colorado.

1.3 Objectives and Outcomes

The major objectives of the workshop were to:

1. Identify major technical challenges and knowledge gaps.
2. Define research needs.

3. Identify barriers to commercialization including systems and supply-chain barriers and draw attention to community impacts.

The primary outcomes from this workshop are this report and an impending journal article that serves to highlight the importance of and raise awareness for the role of carbon-negative hydrogen technologies as a pathway to a net-zero carbon economy. The information embodied in these resources will identify gaps and research and development (R&D) focus areas and serve as the basis for a technology roadmap that will be useful for industry, academia, and federal and state policy makers.

2 Workshop Structure, Agenda, and Content

The workshop was sponsored by DOE's NREL, Lawrence Livermore National Laboratory (LLNL), and National Energy Technology Laboratory (NETL). The scope of the workshop was intended to cover a broad spectrum of topics with specific attention to the following subject areas:

- Technologies and pathways to carbon-negative hydrogen
- Techno-economic analysis (TEA) and life cycle assessment (LCA) of pathways to carbon-negative hydrogen
- Existing projects at various stages of development, from startups through commercialization.

The agenda is shown in Appendix A and was organized around a keynote address and three plenary talks to set the background:

1. **Keynote Address:** “Overview of the Office of Fossil Energy and Carbon Management (FECM) Hydrogen Program R&D,” Jai-woh Kim, DOE FECM
2. **Plenary 1:** “Pathways for Negative-Emissions Hydrogen: Opportunities and R&D Needs,” Gary Grim, NREL
3. **Plenary 2:** “Systems Analysis on Biomass Gasification to Carbon-Negative Hydrogen,” Nathan Weiland, NETL
4. **Plenary 3:** “Insights from DOE Roads to Removal Analysis: Impacts of Carbon-Negative Hydrogen from Biomass,” Sarah Baker, LLNL.

These presentations were followed by a series of nine “lightning talks” that highlighted innovative pathways, emerging technologies, and selected commercialization activities in carbon-negative hydrogen. The titles and presenters of these talks are listed in Appendix B. Copies of the slides for all plenary addresses and lightning talks can be found at the workshop website.¹

The lightning talks were followed by a panel discussion titled, “Considerations Beyond Technology: Feedstocks, Policy, Carbon Accounting, and Beyond.” The panel was moderated by Josh Schaidle and consisted of six panelists from federal and state government, industry, and non-governmental organizations:

- DOE Office of Fossil Energy and Carbon Management
- DOE Bioenergy Technologies Office
- DOE Hydrogen and Fuel Cell Technologies Office
- California Air Resources Board
- Chevron

¹ See <https://www.nrel.gov/bioenergy/carbon-negative-hydrogen-workshop-presentations.html> for more information.

- Rocky Mountain Institute.

Panelists and their affiliations are shown in Appendix B. The remainder of the workshop was devoted to breakout sessions and split into three discussion groups:

- Thermochemical Pathways: Discussion leader Jonathan Lekse, NETL
- Electrochemical Pathways: Discussion leader Adam Holewinski, University of Colorado
- Biological and Hybrid Pathways: Discussion leader Katherine Chou, NREL.

Topics for discussion included technical challenges, R&D needs, and barriers to commercialization.

3 Pathway-Specific Insights and Recommendations

Outcomes of the breakout sessions were organized around three key technology pathways to carbon-negative hydrogen:

- Thermochemical pathways
- Electrochemical pathways
- Biological and hybrid pathways.

These pathways are graphically represented in Figure 2.

	Feedstocks	Conversion Technology	Products	Additional Conversion	Final Product
Thermochemical	Biomass Algae	HTL	Carbon-Negative H ₂		Carbon-Negative H ₂
			CO	Water Gas Shift → Carbon Capture and Sequestration	
	Light Gases	Reforming → Carbon Capture and Sequestration			
	Biocrude	Reforming → Carbon Capture and Sequestration			
		Gasification			
		Carbon-Negative H ₂			
	Biomass	Gasification	CO	Water Gas Shift → Carbon Capture and Sequestration	
Biomass Biogas	Pyrolysis	Carbon-Negative H ₂			
		CO	Water Gas Shift → Carbon Capture and Sequestration		
Light Gases	Reforming → Carbon Capture and Sequestration				
Bi-Oils	Reforming → Carbon Capture and Sequestration				
Gasification → Carbon Capture and Sequestration					
Biogas Wastewater	Reforming <small>- Steam Reforming - Partial Oxidation - Dry Reforming - Aqueous Phase Reforming</small>	Carbon-Negative H ₂			
CO	Water Gas Shift				
Biomass	Hydrolysis	Sugars	Reforming		
Biogas	Plasma	Carbon-Negative H ₂			
Electrochemical	Biomass Wastewater CO ₂ Seawater	Electrolysis	Carbon-Negative H ₂		
			Hydrocarbons	Reforming → Carbon Capture and Sequestration	
			Oxygenates	Reforming → Carbon Capture and Sequestration	
			Carbonates		
CO	Water Gas Shift → Carbon Capture and Sequestration				
Biological & Hybrid	Biomass	Fermentation	Carbon-Negative H ₂		
			Oxygenates	Reforming → Carbon Capture and Sequestration Electrolysis	
			Acids	Reforming → Carbon Capture and Sequestration Electrolysis	
			CH ₄	Reforming → Carbon Capture and Sequestration	
	Algae	Photobiological	Carbon-Negative H ₂		
Algal Oils	Reforming → Carbon Capture and Sequestration				

Figure 2. Pathways to carbon-negative hydrogen

(HTL = hydrothermal liquefaction; CH₄ = methane)

Participants in the breakout sessions were asked to address technical challenges and commercial barriers and were asked to provide recommendations to address these challenges and barriers. The summary of the findings from these sessions is below.

3.1 Thermochemical Pathways to Carbon-Negative Hydrogen

3.1.1 General Background

The thermochemical pathway refers to technologies that use high temperatures to convert a carbonaceous feedstock into gas products that include H₂ as a major component.

Thermochemical conversion typically covers two distinct technologies—gasification and pyrolysis. While these technologies have similarities, they each have their own distinct advantages and challenges.

3.1.1.1 Gasification

Gasification is a thermochemical process that uses heat and pressure—often in the presence of inert or reactive gases—to convert solid carbonaceous feedstocks to gases (collectively called synthesis gas or syngas).

Syngas primarily consists of H₂ and CO, but can also contain CO₂, water, other impurities, and nitrogen (if air is the primary oxidant rather than oxygen). The water-gas shift reaction can be used on syngas to convert CO to H₂ and CO₂.

In addition to the carbonaceous feedstock, water and oxygen are often added to drive the process forward. The ratios of oxygen and water to fuel can be adjusted to control the composition of the product gas, which can further be controlled by factors such as the gasifier's operating temperature and pressure, as well as the addition of catalysts.

When a gasifier is operated using a significant amount of biomass (e.g., municipal solid waste, low-moisture agricultural, or forest thinning residues) along with a carbon capture system, carbon-negative hydrogen can be obtained.

3.1.1.2 Pyrolysis

Pyrolysis is the thermal decomposition of typically solid carbonaceous feedstocks, which characteristically takes place at high temperature in the absence of oxygen. Through pyrolysis, the solid phase will thermally decompose into gases (including H₂, CO, methane, and higher-order hydrocarbons), liquid oils and tars, and carbon-heavy solids called “char.” Further heating converts these heavy compounds into lighter compounds through a process called “volatile cracking,” or the very reactive lighter compounds may “condense” back to heavy compounds.

Pyrolysis is effectively an incomplete gasification process, as it occurs at lower temperature and lacks sufficient oxidants (water and oxygen in this case) to promote volatile cracking, and additional gas-phase reactions.

The most relevant pyrolysis technology for H₂ production is the cracking of natural gas into H₂ and a solid carbon product. If instead of natural gas, biomass or biogas are converted to H₂ through pyrolysis, then that H₂ has the potential to be carbon-neutral or even carbon-negative with the addition of carbon capture.

In addition, biomass pyrolysis has the added benefit of producing carbon-neutral bio-oil and/or bio-char—which can also be used for carbon sequestration.

3.1.2 R&D Needs and Funding Gaps

R&D Needs: The biggest R&D needs for thermochemically produced carbon-negative hydrogen are likely not unique to the thermochemical pathway. However, feedstock preparation is the one area where there are some unique challenges faced by thermochemical methods. Feedstock consistency, preparation, and introduction into a reactor are one of the largest challenges facing the thermochemical pathway.

Funding Gaps: Thermochemical methods for carbon-negative hydrogen tend to be some of the higher technology readiness level (TRL) options available considering the available pathways (Figure 2). At these TRL levels, significant progress necessitates larger scale projects that require larger amounts of funding. Acquisition of funding is hampered by high costs associated with pilot/demo projects and proving the viability of thermochemical systems for carbon-negative hydrogen will likely require systems that are more expensive than even carbon-neutral systems. A major gap exists between funding requirements and funding sources for thermochemical processes producing carbon-negative hydrogen.

3.1.3 Recommendations To Address Challenges and Barriers

There are several research activities that could assist in the deployment of thermochemical carbon-negative hydrogen production technologies. Some of the largest opportunities reside in feedstock characterization and preparation, as well as feeding system design. Tools and databases need to be developed to provide the information required for the modeling of the transport mechanisms and chemistry in the reactor as well as the balance of plant.

Of particular interest is the generation of a database of kinetic data for different feedstocks. While the basic gasification reactions are well understood from a thermochemical and mechanistic perspective, each type of biomass has a unique composition of elements and functional groups that complicates kinetic performance in a gasification environment. Creating a database with all these parameters would allow for modeling that would enable the prediction of performance of gasifier systems operating on different feedstocks.

Additionally, if a feedstock composition needed to be adjusted based on availability, the impact to variables such as product gas composition could be determined. Ideally this information would be publicly available and easily accessible.

There is also the need for real-time monitoring of feedstocks and control systems that can use this data to tune the operation of the plant to account for feedstock variability.

Carbon capture, transport, storage, and utilization are also technologies that would facilitate the deployment of thermochemical carbon-negative hydrogen production systems. If the waste CO₂—or waste solid carbon in the case of pyrolysis—could be converted into a valuable product, the commercial viability of these systems would be greatly improved.

In addition to the recommended research activities, there are several opportunities that exist for thermochemical H₂ production. Due to the relative maturity of this technology, there are opportunities to learn from experience.

Though the scales of past systems may be different (larger) than likely future opportunities, there are still many takeaways that can aid in future system development. There are also several gasification projects that are currently deployed, or that are planned for deployment soon, that address some of the technical challenges discussed previously. These projects provide valuable opportunities to see what works and what may need to be changed for future systems, thus we recommend this information be collected and disseminated in an anonymized way so as to help accelerate technology development.

3.2 Electrochemical Pathways to Carbon-Negative Hydrogen

3.2.1 General Background

Electrochemical pathways to carbon-negative hydrogen generally encompass any modification to conventional electrolytic H₂ production that simultaneously utilizes or sequesters carbon. Examples of technologies in this category include:

- “Alternative anode” reactions that oxidize biomass-derived molecules instead of performing oxygen evolution. These may produce value-added partial oxidation products or involve total oxidation to CO₂, coupled to carbon capture, utilization, and storage (CCUS).
- Cathodic processes that directly reduce CO₂ and separate/collect any H₂ that is coproduced at the same electrode.
- Alkali-generating membrane electrolysis is used to adjust the pH of seawater.
- Novel reaction cascades and membrane configurations allowing electrochemically induced precipitation of minerals, for example, to produce cement.
- Combinations or hybrid configurations between these examples.

3.2.1.1 Modified Electrolysis

Electrolytic production of H₂ ordinarily involves splitting water with the application of voltage across two electrodes in an electrochemical cell. Reduction occurs at the cathode and drives the hydrogen evolution reaction (HER). Oxidation occurs at the anode and drives the oxygen evolution reaction (OER). There is not a proportionate demand for H₂ and oxygen, and thus the OER is essentially a sacrificial process. It requires a high cell voltage and is the rate limiting reaction in the cell. Alternative anode reactions are thus sought to lower cell voltage, add value through the coproduct, and/or achieve targets such as negative emissions.

A wide range of oxidative electrochemical processes are possible using biomass-derived molecules. Common examples include the partial oxidation of glycerol or furanic compounds toward commodity chemicals that would be used in replacements for petrochemical materials such as plastics. These processes can be considered carbon negative if the final product represents a durable form of storage that will not be re-emitted. Total oxidation of biomass compounds is thus also in principle carbon negative since the CO₂ product can be captured passively as carbonates in alkaline electrolytes or fed to various other CCUS technologies in a secondary unit. Organic oxidations can often also lower the carbon footprint by having lower voltage requirements than OER.

Direct reduction of CO₂ to durable products is also possible alongside cathodic HER, although these reactions will consume some of the electricity that is nominally intended for H₂ production. If the operating potential is kept near the equilibrium potential for formation of H₂ and all products are easily separable, electrolysis processes could also be considered routes to carbon-negative hydrogen.

3.2.1.2 Membrane Separation, pH Adjustment, and Mineralization

Reduction processes involving water generally either consume protons or create hydroxyl ions, depending on the ambient pH. Oxidations naturally do the opposite, generating protons or consuming hydroxyl ions. Electrochemical cells configured with ion-selective membranes can thus be used to drive pH gradients and even produce net acidity or alkalinity if one reaction involves species other than water—as a prototypical example, chlor-alkali electrolysis oxidizes aqueous sodium chloride (NaCl) to form chlorine (Cl₂) opposite to a cathode performing HER. The HER generates hydroxide (OH⁻) and a cation-selective membrane allows sodium (Na⁺) to cross the cell, forming sodium hydroxide (NaOH).

Performed at large scale, an appropriate alkalinity-producing scheme could be used to raise the pH of seawater, counteracting acidification induced by rising CO₂ levels and allowing the water to continue acting as a sink. Alkalinity can further drive the precipitation of carbonate minerals and raise sequestration capacity. In some cases, local acidity may alternatively be used to extract minerals (e.g., liberating calcium from calcium carbonate [CaCO₃] and assuming coupled CO₂ capture). Local alkalinity can then precipitate calcium hydroxide (Ca(OH)₂) as a carbon-free precursor to cement.

3.2.1.3 Technology Readiness

Electrolytic H₂ production by alkaline electrolysis is deployed with TRL 9, although costs are not competitive to meet H₂ demand. Proton exchange membrane (PEM) electrolysis, capable of higher current densities and pressures, is also demonstrated and generally considered TRL 8–9. Coupling this electrolysis to additional reactions is generally only in lab-demonstration or prototyping phases and ranges from TRL 1 to 4. The chlor-alkali process (TRL 9) gives some indication that coupled electrolysis can be developed, but bio-based feedstocks and mineral producing reactions have comparatively more complexities and technical barriers.

3.2.2 R&D Needs and Funding Gaps

Continued and intensified fundamental and applied research is necessary to resolve challenges in feedstock preparation, catalyst performance/stability, and device durability. Specific recommended R&D thrusts include:

- TEA and LCA to identify necessary electrochemical device performance benchmarks and to clarify which outputs constitute “durable storage”
- Studies characterizing and developing mitigation strategies for reactant or impurity-induced membrane fouling and catalyst deactivation
- Systems integration research characterizing and improving tolerance and operability of carbon-negative chemistries with intermittent electricity and developing methods for heat management and utilization with these chemistries.

Toward these R&D needs, identifiable funding gaps include:

- Opportunities for large device and demonstration-scale electrochemistry to understand scale-up challenges for unconventional reactions underpinning carbon-negative hydrogen strategies
- Broad TEA and LCA funding to guide targets for scale-up studies and assess their impacts.

3.2.3 Recommendations To Address Challenges and Barriers

Given the wide array of options and low TRLs, it is recommended to increase efforts in TEA and LCA to understand the true cost and impact of implementing carbon-negative electrochemical H₂ processes. These will need to define priorities not only via necessary performance benchmarks, but also clarify which outputs constitute “durable storage” through the eventual fate of given products.

Continued and intensified fundamental and applied research are also necessary to resolve challenges in feedstock preparation, catalyst performance/stability, and device durability. It is recommended to leverage insights that continue to come from deployment of conventional electrolysis, for example in common issues such as:

- Corrosion
- Membrane degradation
- Bubble handling
- Heat management/utilization
- Load following.

3.3 Biological and Hybrid Pathways to Carbon-Negative Hydrogen

3.3.1 General Background

This technical pathway refers to biological and integrated biological with non-biological (e.g., bioelectrochemical, thermochemical, and hybrid) approaches to convert organic wastes as feedstocks to H₂. Broadly, technologies in discussion include:

1. Microbial, fermentative conversion, and anaerobic digestion of organic wastes for H₂ production
2. Oxidation of organic matter by microbial fuel cells or microbial electrolysis cells to produce H₂
3. Integrated biological/biochemical approaches with thermochemical or electrochemical approaches to produce chemicals including H₂.

Feedstocks associated with these technologies include solid, biogenic wastes such as plant biomass (i.e., lignocellulose), wet wastes such as sludges, aqueous wastes such as wastewater, and various other organic waste sources. Common between these feedstocks is that they are rich

in organic content that may be in the form of polysaccharides (e.g., sugars and carbohydrates) and volatile fatty acids amongst others, and rich in chemical or biological oxygen demand.

In general, the biological and hybrid pathways involve oxidation of hydrocarbons or carbon-rich chemicals to more oxidized intermediates or CO₂, which generates electrons or reducing equivalents that are used to generate H₂. Microorganisms or other forms of biocatalysts play a substantial role as the “workhorse” to drive the conversion process.

As above, carbon-negative hydrogen refers to a conversion process in which the coproduced CO₂ is captured, utilized, and sequestered away from the atmosphere as H₂ is produced. The carbon-negative potential is inherent in biohydrogen. In this case, full oxidation of the hydrocarbons embodied in feedstocks to CO₂ provides the reducing equivalent (i.e., electrons) for H₂ generation. However, due to variations in feedstock composition and forms, different conversion processes utilize a specialized microbe or microbial consortium as well as process design to achieve the conversion.

One critical advantage of biological conversion in comparison to other clean H₂ technologies (e.g., non-biological water electrolysis) is the high likelihood of reduced energy/electricity consumption as the biotechnologies harness the power of living organisms to subsidize energy/electricity required for the conversion.

TRL level for biological and hybrid conversion processes spans widely from 1 to around 7, as traditional anaerobic digestion and dark fermentation are relatively mature pathways. However, much of the applied R&D to improve the conversion process for economic biohydrogen production falls between TRL 2 and 4.

3.3.2 R&D Needs and Funding Gaps

R&D needs specific to this pathway include:

- Development of technologies compatible with existing biological conversion process(es) to sequester and/or utilize the coproduced CO₂. For instance, such technology can be integrated into fermentation and/or microbial electrolysis cell to remove or sequester the coproduced CO₂ *in situ* as H₂ is generated rather than separating the H₂ and CO₂ gaseous mixture at the back end post their production.
- Basic R&D and exploration of novel microbial and bioelectrochemical conversion systems designed for improved carbon efficiency without compromising the H₂ yield.
- Development and integration of non-biological approaches (e.g., nanotechnology and advanced materials) to trap CO₂ as it is produced during H₂ generation.

Funding gaps include:

- Investment in techno-economic analysis to set targets for the cost of *in situ* carbon removal or sequestration technologies using the cost of the incumbent technology that separates the gaseous H₂ and CO₂ mixture at the back end (i.e., pressure swing adsorption) as the baseline.

- Investigation of the compatibility of currently successful and novel CO₂ trapping or sequester technologies with carbon neutral H₂ production technologies such as dark fermentation and bio-electrochemical systems.

3.3.3 Recommendations To Address Challenges and Barriers

To advance toward successful commercialization, key enablers include R&D investments, partnerships between stakeholders and R&D communities, socialization of an emerging technology, setting policies and regulations to support the implementation of a new technology, and more.

In terms of R&D investments, a focus on developing new technologies to sequester and utilize the coproduced CO₂ and its integration with existing technologies is needed. Basic R&D in microbial conversion systems, feedstock characterization, synthetic biology, and (bio)process design is essential to fill knowledge gaps in the conversion process, reduce risk, and accelerate commercialization.

3.4 Technical Challenges and Commercial Barriers

Each of the breakout groups were asked to identify technical challenges and commercial barriers associated with their pathways, and to recommend how best to address these barriers. Since most of these challenges and barriers are common to all three pathways, we combined the output from the three sessions into a single section encompassing all of the input received on this subject. The following challenges and barriers were identified.

Feedstocks: When it comes to feedstocks, a renewable and biogenic carbon source coupled with a durable carbon capture system (>100-year lifetime) will be required to produce carbon-negative hydrogen. For all three pathways (thermochemical, electrochemical, and biochemical and hybrid), characterization of the feedstock is key to reliable system operation. The inherent variability of the biomass feedstock needs to be understood and managed as it will affect the handling, pretreatment, and feeding of the biomass to the primary conversion reactor. In addition, sourcing and availability of a consistent and low-cost feedstock is required before commercialization can be viable. With several emerging technologies in a variety of industries and application areas seeking to use biomass as a feedstock, current availability and costs cannot be relied upon to predict future expenses. There are plans underway to increase biomass availability by sustainably using land that is not currently ideal for commercial farming; however, these plans are still in the early stage and their level of success is not easily nor reliably predictable. Specifically for biological pathways, feedstock deconstruction remains a challenge, especially with the use of microbes. Process and microbial sensitivities to feedstock variabilities from seasonal batches and different sources may further compromise the conversion efficiency of biological processes, thus hindering successful commercialization.

Cost: Cost is an obvious hurdle that is present as all three pathways will generally involve higher cost than the incumbent technologies; H₂ from steam reforming of fossil methane still provides the lowest cost product in the absence of carbon credits. Thermochemical processes involve high capital expenditure and economies of scale are difficult to achieve for biomass-based gasification operations due to the distributed nature of the resource. For electrochemical processes, electrode materials, catalysts, membranes, power electronics, and other balance-of-plant components are

all significant high-cost components in these systems. Electrochemistry at scale generally requires higher capital cost than equivalent thermally driven chemical processes. Rare earth elements used as catalysts in some conversion processes may be subject to large and sudden price swings depending on demand and geopolitical factors. Renewable electricity also remains a non-negligible cost, so advances in technology to achieve cost savings through process intensification are of value. Finally, the cost of the biomass feedstock itself is critical; feedstock cost often comprises 50% or more of the total cost of production of the final product.

System Integration: Additional technical challenges come during integration of the primary reactor with the rest of the equipment in a facility or balance of plant. Once the reactor is selected, there are still associated technologies that are required for the process train. For thermochemical processes like gasification, these include feedstock handling, pre-processing and feeding, syngas cleanup, heat integration, oxygen production, and CO₂ capture and utilization. While there may be commercial options for these processes, new problems are almost always encountered when these technologies are connected in an integrated process and operated in a continuous mode. One common problem is that the quality of the stream exiting one unit operation does not always meet the required specifications for the downstream unit operation that receives this stream. In principle, one can set specifications for the quality requirements at each step of the process, but in practice these requirements are difficult to meet because of variability in the feedstock and changes in process operations. Another problem in system integration is the incompatibility of processing scale between unit operations; there are often bottlenecks at one stage that force other stages to perform at lower, less than optimal throughput.

Reliability and Operability: A key technical challenge is the reliability and operability of the systems themselves; some of these come from feedstock variability. For example, one of the largest operability issues is feeding material, at scale and continuously into the reactor system, especially in cases where biomass must be fed across a pressure boundary into a reactor operating at pressures above ambient. Lock hoppers can be used with a solid feedstock, but in practice there have been problems with rapid wear, gas leakage, poor reliability and short service life of equipment. Other methods of feedstock introduction include creating a slurry from the solid with (most commonly) water. Research is being conducted to investigate a dry solids pump for high-pressure systems, but there are currently no known commercial examples of this technology.

In addition to the upstream challenges prior to the conversion step, downstream upgrading and purification processes required to produce H₂ at required purity levels (e.g., 99.999% for some fuel cells) are sources of operability and reliability issues. Gas cleanup operations are expensive and generate secondary effluent streams that are difficult and expensive to dispose of.

Separations: Separations are a ubiquitous part of any chemical process; these systems and unit operations add cost and complexity to all three pathways studied in the workshop. This will include both operational costs and costs due to logistics for feed stream preparation. For example, various components in seawater—organic matter or trace elements—will require evaluation and appropriate engineering solutions to avoid membrane fouling or catalyst deactivation in electrochemical cells. On the product side, poor selectivity from the conversion step will contribute to needs and cost for post-reaction separation.

Complexity: Process cost and reliability is intimately connected to process complexity. This complexity is magnified in some cases by the desire to produce low-carbon products by the use of renewable energy (wind/solar). As one example, reactors that are targeted to run on “excess” electricity will need coupling to storage for load balancing or will need the ability to load-follow and dynamically vary production with availability of power on the electric grid. Transient operation can lead to very large capacitive current transients in cells, and these can cause extra ohmic losses and degradation of components and performance. Similar situations exist for thermochemical and biological processes where integration with renewable energy will add complexity and be challenging for reliability.

Deployment: The viability of carbon-negative hydrogen technologies will first and foremost be tied to continued development of deployment systems for H₂ itself. Issues such as cost and operational complexity are common threads in developing these systems, and other necessary infrastructure such as H₂ distribution networks and the supply chain for certain components will inherently couple the markets. There are currently very few dedicated pipelines that carry H₂ in the United States, and most of these are located in the Gulf Coast. Co-location of production facilities with processes that consume carbon-negative hydrogen will thus provide opportunities to simplify deployment logistics and improve the technology value chain by reducing transportation cost and also will minimize resulting community impacts associated with transport of H₂ from production to utilization. The recent DOE Regional Clean Hydrogen Hubs program may offer solutions to some of these issues associated with deployment.

Logistics: As a shared challenge with all pathways producing H₂, infrastructure supporting the safety of H₂ storage, materials, transportation, and monitoring of potential leakage is not established. Planning and assessment of the allocation of land and/or biomass for biofuels including biohydrogen are needed. It is also important to implement workforce development in preparation of next-generation, low-carbon, or carbon-negative technologies. For example, electrochemical manufacturing is currently a much smaller industry than traditional chemicals and will require workforce development through adjusted emphases in curricula, particularly for skilled trades and engineering fields that work most directly with the processes. It is also anticipated that a favorable public policy environment will be necessary to surmount the barriers to deployment and achieve a critical mass for a self-sustaining industry.

Carbon Footprint: Recognizing the importance of maintaining a strong sustainability profile for each process pathway, carbon life cycle and techno-economic analyses across the entire technology value chain are essential and represent critical components for successful commercialization of carbon-negative hydrogen.

3.4.1 Commercialization Barriers

Beyond the technical challenges identified, there are also commercialization challenges. Mismatches arise from the availability of equipment, skilled manpower, resources, locations, logistics for feedstock, and other inputs. There are also many uncertainties that can pose significant investment risk, such as the future of regulations, carbon credits, the cost of feedstocks moving into the future, and the future H₂ market. There is also a desire for mechanisms to de-risk scale-up and ensure production to attract investors. In the end, developing a technology that provides cost-parity with conventional H₂ from methane steam reforming will be essential, although it is recognized that this is an extremely challenging goal.

4 Conclusions and Overarching Learnings

As was evident from our “lightning talks,” plenary lectures, and breakout sessions, a diverse slate of technologies leveraging various feedstocks exist—spanning a broad range of TRL—for achieving carbon-negative hydrogen. There is significant opportunity for innovation, especially given this paradigm as opposed to siloed clean H₂ production and CO₂ removal technology development.

A conclusion from the workshop is that the “carbon-negative hydrogen” nomenclature and fit within the broader clean H₂ and CO₂ removal landscape needs to be clearly defined and established. While we used the terminology “carbon-negative hydrogen” for this report, this terminology does not readily show up in recent hydrogen-related strategies and roadmaps and has only recently come to the forefront through publications related to CO₂ removal (Baker et al. 2020).

A significant learning from the workshop is that—while the life cycle accounting frameworks for H₂ are set up to handle carbon-negativity—there is no additional value from a regulatory standpoint under the Inflation Reduction Act of 2022 and the 45V Hydrogen Production Tax Credit to actively promote an industry that will achieve carbon-negative hydrogen. In this regard the work of GTI Energy and its partners on the Open Hydrogen Initiative is noteworthy, where efforts are underway to redefine how the world measures and benchmarks the carbon intensity of H₂ production at the asset level.

The value proposition of carbon-negative hydrogen is conceptually understood in terms of having a single process that produces two revenue-generating streams. However, it needs further quantification and benchmarking. Specifically, the community would benefit from evaluating the trade-offs between having one process that generates both H₂ and carbon/CO₂ in a form that is durable and storable versus separate processes for clean H₂ production and CO₂ removal. These trade-offs include economic, environmental, supply chain, societal, and business case metrics, as well as regulatory implications. From the federal perspective, due to the high potential for industrial decarbonization that would be enabled by carbon-negative hydrogen, there is a compelling need for a financial rewards and incentive structure for carbon-negative hydrogen like what is now in place for CO₂ with respect to the Inflation Reduction Act 45V tax credit for H₂ projects.

5 Recommendations

Carbon-negative hydrogen introduces a new objective function that has not yet been optimized, opening considerable R&D whitespace and analysis opportunities. Specific R&D needs in the three pathways featured in this workshop have been itemized previously and we recognize a clear imperative for seeding technology development in these white spaces.

From the workshop outcomes we recognize several overarching holistic recommendations for future R&D funding that span all three pathways.

- 1. Analysis to Demonstrate the Value Proposition:** The concepts of low-carbon hydrogen and direct air capture (DAC) and storage of CO₂ are at the forefront of the clean energy transition. A flurry of recent activity in these two areas are highlighted by the development and investments in regional DAC and DOE Hydrogen Hubs as part of the Bipartisan Infrastructure Law. Carbon-negative hydrogen pathways sit at the intersection of both topics whereby these select pathways (see Figure 2) can concentrate biogenic CO₂ *in situ* for storage or utilization while producing clean H₂ *at the same time*. When compared to discrete two-step processes (e.g., PEM H₂ production with separate direct air capture), these carbon-negative hydrogen pathways have the potential for higher capture efficiencies, higher energy efficiencies, and lower costs, yet may introduce new challenges, such as logistics (e.g., transportation of feedstock, H₂, and CO₂ to/from a single site). Consequently, up-front techno-economic, life cycle, and market analyses will be a crucial first step to evaluate and differentiate the various carbon-negative hydrogen strategies and highlight the unique value proposition and synergies in combining biogenic CO₂ capture/concentration and H₂ production into a single integrated process.
- 2. R&D Investment in Proof-of-Concept and Demonstration Projects:** Specific recommendations here include imbedding carbon-negative hydrogen as a funding opportunity topical area within DOE's Small Business Innovation Research and Small Business Technology Transfer programs to provide early entry points and to foster industry engagement. In addition, standing up programs and solicitations in DOE's Office of Science and Advanced Research Projects Agency-Energy to explore innovation will be essential as will promulgating applied R&D solicitations from DOE's Bioenergy Technologies Office, Industrial Efficiency and Decarbonization Office, Hydrogen and Fuel Cell Technologies Office, and Office of Fossil Energy and Carbon Management for development of more mature technologies. Finally, demonstration at pilot scale or larger of end-to-end deployment will enable identification of mismatches in process parameters and unit operations within an integrated system. Providing a funding mechanism to move from innovation to proof-of-concept to demonstration with Notices of Funding Opportunity that incorporate a phased approach (design, test, and implement) is one way to accomplish this goal.
- 3. Research Consortium on Carbon-Negative Hydrogen:** We recommend the investigation of the feasibility of the formation of a DOE-supported research consortium on carbon-negative hydrogen to enable close collaboration and coordination across the ecosystem. Existing research consortia, such as Chemical Catalysis for Bioenergy (ChemCatBio), Agile BioFoundry, Bio-Optimized Technologies to keep Thermoplastics out of Landfills and the Environment (BOTTLE), HydroGEN, Hydrogen from Next-

generation Electrolyzers of Water (H₂NEW), BioHydrogen (BioH₂), and others, provide evidence that this model is effective in helping to create partnerships and facilitated engagement across academia, industry, national laboratories, and various stakeholders to overcome commercialization barriers.

4. **R&D on Systems Integration:** We recommend additional R&D investment in systems integration, as this aspect is often overlooked but can present deal-breakers to adopting carbon-negative hydrogen technologies at scale. As noted earlier, carbon-negative hydrogen sits at the intersection of low-carbon hydrogen generation and CO₂ removal and at the intersection of multiple DOE offices, thus certain process steps are being developed independently. Systems integration R&D is needed to evaluate end-to-end performance with real-world feedstocks, identify full process bottlenecks, collect high-integrity data on material and heat balances, generate models (e.g., process-level, computational fluid dynamics, and kinetics) to verify and guide modes of operation, and perform accelerated durability testing.
5. **Materials R&D for H₂ Production:** Acknowledging ongoing DOE investment, we recommend that continued investments be made in basic and applied R&D for materials that are useful for H₂ production and H₂/CO₂ separations from mixed process streams. Applications in electrochemical and bio/hybrid hydrogen production pathways often produce complex mixtures that require unique separations technologies. One specific example is materials development for membranes. Cost-effective separation of H₂ using membrane technologies that do not involve the use of expensive materials such as noble metals (e.g., palladium membranes) will be an enabling technology that could be transformative to scaling and commercializing these pathways.
6. **Energy Justice:** In all of the areas mentioned above it is important to consider the impact of the technology being developed on energy and environmental justice aspects and to understand the societal impacts and social perceptions of any new processes or industries that may result. *This is not a stand-alone recommendation*, but rather a reminder that energy justice concepts should be included in any new R&D initiatives to ensure fair and equitable benefit to society as the technology is deployed.

References

Baker, Sarah E., Joshua K. Stolaroff, George Peridas, Simon H. Pang, Hannah M. Goldstein, Felicia R. Lucci, Wenqin Li, et. al. 2020. *Getting to Neutral: Options for Negative Carbon Emissions in California*. Livermore, CA: Lawrence Livermore National Laboratory. LLNL-TR-796100. https://gs.llnl.gov/sites/gf/files/2021-08/getting_to_neutral.pdf.

Schaidle, Joshua A., R. Gary Grim, Huyen N. Dinh, and Robert M. Baldwin. 2022. “The Power of Being Negative: Producing H₂ and Sequestering Carbon from Biomass and Waste Resources.” *The Bridge* 52 (4): 34–37.

HFTO (U.S. DOE Hydrogen and Fuel Cell Technologies Office). 2024. “H₂@Scale.” Accessed February 2024. <https://www.energy.gov/eere/fuelcells/h2scale>.

Appendix A: Workshop Agenda

Day 1, June 22, 2023

- 7 a.m. Breakfast
- 8:10 a.m. Welcome—Workshop Purpose and Overview: Josh Schaidle, NREL
- 8:20 a.m. Keynote: Overview of the Office of Fossil Energy and Carbon Management (FECM) Hydrogen Program R&D: Jai-woh Kim, DOE FECM

Session 1: Background Studies on Carbon-Negative Hydrogen

- 8:50 a.m. Pathways for Negative-Emissions Hydrogen—Opportunities and R&D Needs: Gary Grim, NREL
- 9:15 a.m. Systems Analysis on Biomass Gasification to Carbon-Negative Hydrogen: Nathan Weiland, NETL
- 9:40 a.m. Insights from DOE Roads to Removal Analysis—Impacts of Carbon-Negative Hydrogen from Biomass Carbon Removal and Storage (BiCRS): Sarah Baker, Lawrence Livermore National Laboratory

Session 2: Innovative Pathways and Emerging Technologies—Lightning Talks

- 10:15 a.m. 10-Minute Presentations (selection of pathways)
- 12 p.m. Luncheon Presentation—Integrating Energy Justice in Early-Stage Research: Kate Anderson, NREL

Session 3: Panel Discussion—Considerations Beyond Technology: Feedstocks, Policy, Carbon Accounting, and Beyond

- 1 p.m. Panel Discussion with Q&A for Technology Pathways
- 2 p.m. Break—Attendees divided into three groups around these following technology pathways:
 - Group A: Electrochemical Pathways
 - Group B: Thermochemical Pathways
 - Group C: Biological and Hybrid Pathways
- 2:30 p.m. Breakout #1: Technical Challenges (Groups A, B, and C)

Day 2, June 23, 2023

- 7 a.m. Breakfast
- 8:00 a.m. Instructions and room finding
- 8:15 a.m. Breakout #2: R&D Needs (Groups A, B, and C)
- 10:15 a.m. Breakout #3: Barriers to Commercialization (Groups A, B, and C)
- 11:30 a.m. Report Out on Group A

12 p.m. Lunch: Report Out on Groups B and C
1 p.m. Closing Remarks: Josh Schaidle, NREL
1:30 p.m. Tours of NREL

Appendix B: Lightning Talks and Panel Discussion Participants

Lightning Talk Presenters

- Robert Do, SGH2 Energy
- Joshua Stolaroff, Mote Hydrogen
- Colin Anson, Virent
- Ted Sargent, Northwestern University
- Anthony Spizuoco, Monolith Materials
- Jason Ren, Princeton University
- Katherine Chou, National Renewable Energy Laboratory
- Greg Rau, Planetary Hydrogen
- Zach el Zahab and Rosa Dominguez-Faus, Gas Technology Institute/Open Hydrogen Initiative

Panel Discussion Participants

Moderator

- Josh Schaidle, National Renewable Energy Laboratory

Panelists

- Jai-Woh Kim, DOE Office of Fossil Energy and Carbon Management
- Marc Melaina, DOE Hydrogen and Fuel Cell Technologies Office
- Alex Jansen, DOE Bioenergy Technologies Office
- Kaycee Chang, California Air Resources Board
- Rudy Kahsar, Rocky Mountain Institute
- Allan Toweill, Chevron

For more information, visit: www.nrel.gov/bioenergy/carbon-management-utilization-research.html

