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Biohydrogen: prospects for industrial utilization and energy resiliency in rural communities

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Biohydrogen (bioH₂) production in rural regions of the United States leveraged from existing biomass waste streams serves two extant needs: rural energy resiliency and decarbonization of heavy industry, including the production of ammonia and other H₂-dependent nitrogenous products. We consider bioH₂ production using two different strategies: (1) dark fermentation (DF) and (2) anaerobic digestion followed by steam methane reforming of the biogas (AD-SMR). Production of bioH₂ from biomass waste streams is a potentially 'greener' pathway in comparison to natural gas-steam methane reforming (NG-SMR), especially as fugitive emissions from these wastes are avoided. It also provides a decarbonizing potential not found in water-splitting technologies. Based on literature on DF and AD of crop residues, woody biomass residues from forestry wastes, and wastewaters containing fats, oils, and grease (FOG), we outline scenarios for bioH₂ production and displacement of fossil fuel derived methane. Finally, we compare the costs and carbon intensity (CI) of bioH₂ production with those of other H₂ production pathways.

KEYWORDS

biorefinery, biohydrogen, biogas, dark fermentation, anaerobic digestion, energy resiliency

1 Introduction

H₂ production through renewables could play a major role in combating the effects of climate change via applications in industrial, transportation and utility/microgrid-scale electricity, provided the cost of production can be reduced. The Hydrogen Earthshot initiative (EERE, 2021) targets production of clean hydrogen at a cost of \$1 per kg in 1 decade ("111"). Around 70 million metric tons (MMT) of H₂ are produced annually, 10 MMT/year in the U.S., with 95% produced by steam methane reforming of natural gas (NG-SMR) at high temperatures and pressures, i.e., 'grey H₂'. The remainder is produced by gasification of coal and oil (Ferraren-De Cagalitan and Abundo, 2021). Process emissions and the use of natural gas as a precursor has led to interest in cleaner

technologies and feedstocks for H₂ production. While ‘green H₂’ (produced using renewable energy, usually via electrolysis of water) has lower emissions than NG-SMR and gasification, those from biohydrogen (bioH₂) can be even lower.

Ideally, bioH₂ production leverages an integrated biorefinery where biomass collection, transport, separations of components, followed by valorization of intermediates through process streams, and complete utilization of the feedstock is achieved. BioH₂ refineries can produce H₂ from waste biomass either directly through dark fermentation (DF) or through anaerobic digestion followed by biogas SMR, among others. An ideal bioH₂ refinery would, therefore, utilize process waste biomass residues that are locally available and produce H₂ for use either as a source of fuel for electricity, or a feedstock for the manufacture of chemicals – allowing for industrial decarbonization.

For context in production cost and GHG emission, grey H₂ has the lowest cost ~\$1/kg H₂, but also generates high greenhouse gas (GHG) emissions (Majumdar et al., 2021). It was estimated that median CO₂ emissions from NG-SMR facilities in the US was ~9 kg CO₂/kg H₂ (or ~75 g CO₂/MJ) (Sun et al., 2019). Cho, et. al (Cho et al., 2022). found that H₂ production using NG-SMR led to direct GHG emissions of 9.35 kg CO₂e/kg H₂ (and 11.2 kg CO₂e/kg H₂ when upstream emissions of H₂ production were included). This analysis further found that replacing fossil-derived CH₄ with landfill gas and AD-derived biomethane (using animal manure) as feedstocks reduced the GHG potential by 68% and 54%, respectively. Other studies have found similar improvements to the life cycle carbon emissions of H₂ production using vegetable oils (Marquevich et al., 2002) and biomass gasification (Susmozas et al., 2013), among others.

Several biological pathways exist to produce H₂ as described here. Using water molecules (H₂O) as the starting feedstock, biophotolysis (BP) uses sunlight to dissociate H₂O into oxygen (O₂) and hydrogen (H₂) by photosynthetic organisms (Kamran, 2021). H₂ can also be generated through photo-fermentation (PF) and dark fermentation (DF) using organic compounds as the starting feedstock. For photo-fermentation, specialized photosynthetic organisms (e.g., purple non-sulfur bacteria) use light energy to convert volatile fatty acids such as acetate, butyrate, lactate among others to H₂ and CO₂ without oxygen (Yin and Wang, 2022), whereas for dark fermentation, H₂ is typically produced from carbohydrates (e.g., glucose, or more commonly known as “sugars”) anaerobically without light input (Kamran, 2021). Two-stage processes integrating PF and DF have also been explored. Amongst these processes, BP suffers low light conversion efficiency (Oh et al., 2013) and high oxygen sensitivity of hydrogenase that are specialized enzymes catalyzing the biosynthesis of H₂ from protons (H⁺) and electrons (e⁻) (Ghirardi, 2015). While PF can achieve higher H₂ yield than DF, growth rates of the photo-fermenting bacteria without oxygen are much lower and the H₂ productivity of these bacteria is about two orders of magnitude lower than that of DF (Zhang and Zhang, 2018). In addition, high cost in feedstock pretreatment and enzymatic hydrolysis of lignocellulosic biomass that may be

required for photo-fermentative H₂ production renders it economically unfavorable. Taking these together, H₂ production from DF remains compelling and favorable among biological processes. In-depth description of these processes is beyond the scope of this paper, but we point to relevant articles that discuss these (Manish and Banerjee, 2008). The term bioH₂ herein refers to H₂ produced using microbial pathways and those using biomass-based feedstocks.

BioH₂ via DF using thermophilic bacteria offers sustainable H₂ generation pathways with lower GHG emissions. Utilizing waste biomass sources (such as crop residues, municipal solid wastes, seafood industry wastes, etc.) for H₂ production using DF can improve process economics due to reduced feedstock costs. An advantage of fermentative biological H₂ production is reduced electricity demand—a current study estimated over 50% reduction in electricity requirement by DF-integrated with microbial electrolysis cell (MEC) compared with clean H₂ produced by water electrolysis (Liu et al., 2022a). One of the challenges, however, is incomplete feedstock utilization by the microbial systems due to biomass recalcitrance and low accessibility to the sugars embedded in the biomass. Recent research has shown increased H₂ production using *Clostridium thermocellum* engineered to co-utilize both cellulose and hemicellulose in waste plant biomass (i.e., lignocellulose) through consolidated bioprocessing (CBP) (Xiong et al., 2018; Chou et al., 2024).

Waste streams high in fats, oils, and grease (FOG), such as fish and seafood processing wastewaters, have the highest biogas potential, but also tend to adsorb to sludge and inhibit microbial activity (Holohan et al., 2022), particularly that of methanogens (Nges et al., 2012). Anaerobic co-digestion of various wet wastes with lignocellulosic feedstocks such as sugarcane bagasse, rice husks, corn stover, etc., which are rich in cellulose and hemicelluloses, is known to increase biogas and H₂ production (Carver et al., 2011; Li et al., 2013; Bohutskyi et al., 2018; Adarme et al., 2019; Fernando Herrera Adarme et al., 2022). Anaerobic co-digestion of FOG with high fiber feedstocks can improve biomethane potential (BMP), dilute toxins, improve nutrient balance, and allow for increasing the load of biodegradable organic matter (Shah et al., 2015). Blending carbohydrate-rich crop residues could be reasonably expected to enhance bioH₂ production from seafood industry wastes and wastewaters through added minerals and nutrients as well as diluting inhibitory compounds.

Sparging to lower the partial pressure of H₂ in the reactor can also enhance H₂ production (Kim et al., 2023). Biogas CH₄ is separated from CO₂ and trace gases such as H₂S, NH₃, CO, etc. using processes such as temperature and pressure swing adsorption, pressurized water scrubbing, membrane separations, etc (Chen et al., 2015). Due to their lower installation and operational costs, membranes represent a cost-effective solution for recovery of biomethane in high purity. Biogas can be upgraded through multiple reforming processes (Kumar et al., 2022), resulting in H₂ production with lower GHG emissions compared to NG-SMR. Siloxanes, sulfur species, and other gases should be removed to

increase reaction specificity and reduce energy consumption (Zhao et al., 2020). Biogas reforming can also overcome the theoretical Thauer limit of DF processes (4 mol H₂ per mol glucose).

2 Technoeconomics and emissions associated with H₂ production

The net energy ratio (NER) for three different bioH₂ production technologies was calculated, and it was found that gasification of forest residues via the Gas Technology Institute (GTI) gasifier resulted in the highest NER (of 9.3) with GHG emissions ranging between 1.2 to 8.1 kgCO₂e/kgH₂ (Kabir and Kumar, 2011). Manish and Banerjee (2008) compare the efficiency and emissions from several biohydrogen production processes with those of NG-SMR. DF was compared with PF, a two-stage process combining DF and PF, and bio-catalyzed electrolysis, and it was found that efficiencies of the fermentative approaches improved in comparison to NG-SMR when removal and utilization of by-products from the former was considered. Carbon capture and storage (CCS) is another aspect of H₂ production that can reduce emissions. It can potentially add to the costs or offsets cost through decarbonizing tax credits (e.g., IRA 45Q). Modeling scenarios project that up to 80% of CO₂ emissions in NG-SMR can be inexpensively abated, whereas the remainder of the 20% are expensive to avoid (Pruvost et al., 2022). Table 1 shows a compilation of some of the reported findings on emissions from various H₂ production pathways. In general, the source of electricity plays a key role in carbon intensity. As exemplified by DF, CI is substantially lower when renewable electricity is utilized compared to grid electricity. When renewable electricity is utilized for bioH₂ production followed by CCS, there is a removal of CO₂ per kilogram H₂ generated (Table 1), providing a decarbonization potential not associated with H₂ production from water-splitting technologies. In essence, not only can biological H₂ displace energy demands currently filled by fossil-derived energies, concentrated streams of CO₂ co-released during the oxidation of organic compounds for the production of bioH₂ from DF can be removed (Lou et al., 2023) through point-source carbon capture rather than direct air capture (DAC), with the latter generally understood to be more energy intensive.

Based on recent technoeconomic analysis for H₂ production via dark fermentation through consolidated bioprocessing (CBP) configuration (van Zyl et al., 2007), top drivers for the production cost are capital expenses (CAPEX) in the bioreactor and cost associated with the feedstock (Randolph et al., 2017). As the cost of the bioreactor directly correlates with bioreactor footprint, economic DF must operate at high loadings of lignocellulosic biomass at high H₂ yield for a given amount of feedstock while minimizing bioreactor footprint. Efficient feedstock deconstruction, utilization, and conversion to H₂ in this condition is therefore a priority for ongoing research and development through which novel chassis organisms and bioprocess designs are pursued.

3 BioH₂ in rural energy resiliency

BioH₂ can impact energy resiliency where access to reliable energy is a concern. Disaster recovery and energy resilience are not equitably distributed—rural areas witness disproportionate impacts and have been shown to be less energy-resilient than urban regions (Mitsova et al., 2018). Grid susceptibility is likely to worsen due to the projected increased frequency of tropical storms as a result of climate change in combination with aging grid infrastructure (Casey et al., 2020). Existing power systems that are reliable under ‘normal conditions’ are not necessarily resilient under high-impact events (Panteli and Mancarella, 2015; Hussain et al., 2019). Emergency diesel generators (EDGs) are the main source for backup power during extended power outages (Phillips et al., 2016) and can be unreliable (Marqusee and Jenket, 2020), contribute to greenhouse gas emissions (Jakhrani et al., 2012), require expensive transported fuel, and have negative human health impacts due to exhaust exposure (Gilmore et al., 2006; Gilmore et al., 2010). Microgrids (groups of interconnected loads and distributed energy resources that act as singular entities and have the ability to operate in either grid-connected or island modes) are increasingly suggested as alternatives to EDGs for reliable backup power during disasters (Callaway et al., 2014). The benefit of microgrids during power disruptions is that they can avail local energy assets to improve costs and reliability, particularly for rural areas (NREL, 2023). Solar photovoltaics (PV) and wind energy have been typical microgrid candidates, however, the stochastic nature of these requires the inclusion of backup power sources, historically fossil fuel-based (Singh et al., 2016). Utilizing biomass resources such as those generated from agricultural operations or the vision of utilizing renewable carbons sourced from biogenic waste streams (Langholtz, 2024) for backup power can reduce the carbon footprint of microgrids and improve their life cycle emissions (Aberilla et al., 2019), while improving energy resiliency.

BioH₂ production can be leveraged for energy resiliency as microgrids, either by combustion for power or through the deployment of H₂ fuel cells, the latter having the advantage of instantaneous deployment. Rural microgrids have been evaluated as hybrid systems based on solar photovoltaic (PV) or other renewable energy technologies in combination with biomass-based energy. Many of these analyses have been conducted for other nations and typically involve thermochemical biomass conversion (combustion or gasification) (Mazzola et al., 2016; Kaur et al., 2020; Ribó-Pérez et al., 2021; Singh and Basak, 2022). Similarly, H₂ fuel cells have been evaluated as potential electrification devices in rural and remote areas (Cotrell and Pratt, 2003; Munuswamy et al., 2011). Taking this further, there is the potential for bioH₂ to play key roles in rural electrification and energy resiliency (especially in the aftermath of emergencies) in the form of microgrids or fuel cells, especially when incorporating biomass waste residues generated in these communities.

TABLE 1 Comparison of H₂ production pathways.

H ₂ Technology	CI (kgCO ₂ e/kgH ₂)	Proj. Cost (\$/kgH ₂)	Refs.
NG-SMR	9–11	~1	(Sun et al., 2019; Roussanaly et al., 2020; Majumdar et al., 2021)
NG-SMR-CCS (Blue H ₂)	1.1	1.5–2.9	(Roussanaly et al., 2020; Majumdar et al., 2021; Shiva Kumar and Lim, 2022)
Electrolysis using Renewable Energy (Green H ₂)	1–1.8	3.6–5.8	(Yadav and Banerjee, 2020; Shiva Kumar and Lim, 2022)
DF using grid electricity Grid electricity + CCS Using renewable electricity Renewable electricity + CCS	13.5 2.7 2.4 -8.5	3.40–7.91	(Randolph et al., 2017; Liu et al., 2022a)
AD-SMR	3.36	1.39	(Braga et al., 2013; Hajizadeh et al., 2022)

4 BioH₂ in chemical manufacturing

Of the three waves of clean H₂ adoption proposed in the 2023 DOE National Clean Hydrogen Strategy and Roadmap (DOE, 2023), NH₃ production was identified as the second-largest captive market following refining, and was suggested to provide a stable market for clean H₂. Current consumption of H₂ produced from NG-SMR is primarily due to chemical manufacturing of NH₃. Due to its high energy density and ease of shipping internationally, NH₃ is considered an energy carrier and has applications as a direct fuel source in the electricity, transportation, and heating sectors (Nayak-Luke et al., 2018; Joseph Sekhar et al., 2024). Approximately 80% of industrial NH₃ production is used for fertilizer, indicating bioH₂ for NH₃ production could play a major role in decarbonizing agriculture (Yüzbaşıoğlu et al., 2022). Each ton of NH₃ produced via NG-SMR and tertiary reactions generates 2.6 tons of GHG emissions over its life cycle (Liu et al., 2020) (or 114.4 g CO₂e/MJ (Busch et al., 2023)); NH₃ production can be attributed to 2% of worldwide fossil fuel consumption, resulting in 420 million tons of CO₂ emissions each year (Liu et al., 2020). In a life cycle assessment study (Singh et al., 2018) comparing several pathways for NH₃ production, it was found that NG-SMR and coal gasification led to the greatest carbon intensity (CI) of 3.85 kg CO₂e/kg NH₃, whereas biomass gasification led to the lowest CI of 0.38 kg CO₂e/kg NH₃. Local production of bioH₂ as a feedstock for this NH₃ production

capacity can aid in emissions reductions and, therefore, decarbonize a hard-to-abate sector. ‘Green NH₃’, produced from bioH₂, can reduce the GHG burdens and CI associated with the fossil fuel based SMR process.

5 Impact on energy equity for rural, disadvantaged communities

Applications of bioenergy (including biofuels) in a rural perspective have previously been explored (Hiloidhari et al., 2020), leveraging particularly the agroforestry industries in these regions (Dubois and Kristensen, 2018). A Hungarian study found that rural ethanol-producing biorefineries can stimulate employment and drive rural development (Heijman et al., 2019). Stöhr et al. developed a rural-centric outline to establish a bioH₂ value chain comprised of 7 steps that differentiate rural needs from urban. This study incorporated distinctions between urban and rural environments by focusing on a central supply chain (hub concept) versus a distributed/decentralized supply chain, with pros and cons for each type. They also suggest that community engagement between population, industry, and stakeholders is critical when it comes to acceptance and sustainability of hydrogen production technologies in rural regions (Stöhr et al., 2024). As conventional H₂ production is energy intensive, bioH₂ also provides more opportunities for energy-poor areas as it only requires organic waste and water for production (Goria et al., 2022). An interesting recent development is technology to convert diesel engines to run on H₂ or diesel/H₂ blends (Liu et al., 2022b). In addition to multiple efforts in developing rural H₂ from electrolysis with renewable energy, efforts are underway to transition rural communities to bioH₂, including transitioning from diesel to dual fuel to H₂ powered generators (ABB in Australia) (ABB, 2023) and exploring bioH₂ from biogas (European Biogas Association) (EBA, 2024).

6 Discussion

Biohydrogen represents a clean, renewable, low-carbon energy source for industrial and flexible-scale use. The potential of producing bioH₂ from waste biomass material provides production options that do not rely on sunlight or wind and can be bolted on or adapted to existing waste digestors. Rural communities particularly stand to benefit from this approach as they tend to be spatially more distributed (compared to urban areas), have existing waste and agricultural feedstocks available, and are subject to elevated energy cost and limited supply chain due to transportation costs and logistics of bringing in outside fuels and power. As part of a biorefinery, bioH₂ production can deliver localized energy security to communities, especially during disruptive weather or natural disasters, while enabling other fuels, chemicals, and bioproducts to be produced locally. Depending on

the local energy needs and resources, bioH₂ could be augmented with H₂ from electrolysis when excess renewable electricity is available from wind or solar. Advances in converting diesel engines to run on H₂ or H₂/diesel blends makes bioH₂ even more attractive as a locally produced, renewable fuel, especially during energy disruptions in rural areas reliant on generators.

There is a substantial knowledge gap on operational data and performance pertaining to not only commercial-scale but also pilot-scale bioH₂ systems, a fact underscored by uncertainties associated with scaleup (Zhang et al., 2024). To our knowledge, there are few commercial-scale projects that have been announced globally. A project based in the United Kingdom integrates AD with DF to produce bioH₂ and NH₃ from feedstock such as chicken litter (EcoScience, A, 2024). An operation based in Czechia supplies modular units ranging between 40 to 120 Nm³/h H₂ to produce bioH₂ via AD-SMR (Mega, 2024). The nascent stage of current implementation of bioH₂ is evidence for greater R&D efforts in this area—the realization of a bioH₂ economy will require persistent R&D with concerted effort in genome editing to produce robust microbial consortia which can metabolize seasonally-varying organic waste streams (e.g., changes in feedstock quality due to prevailing weather, or introduction of new feedstock blends depending on availability, etc.). Addressing the production cost of hydrogen and efforts to bring it within parity of costs associated with NG-SMR will require innovative solutions, particularly strategies which can integrate bioH₂ production methods, such as DF and PF, and with other co-products which can improve energy recovery compared to a single-stage H₂ production process (Brar et al., 2022). Technoeconomic assessments of niche applications of bioH₂ as a source of energy (as discussed in Section 4) are needed in scenarios where the lack of access to reliable energy can lead to loss of life; such studies can incentivize bioH₂ even if it is not currently cost-competitive against the current grid mix. Along with the applications of H₂ as a fuel source, it would be prudent to explore additional applications, including H₂ utilization in biomass/crude oil upgrading, production of synthetic fuels and chemicals, reduction of iron in steelmaking, and finally, NH₃ production, which was briefly discussed in Section 5 (Elgowainy et al., 2020). We suggest that concerted efforts in laboratory and pilot-scale R&D,

technoeconomic, life-cycle, and regio-specific sociological are necessary to realize the true potential of a bioH₂ economy.

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Conflict of interest

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