SPECIAL SECTION: HYDROGEN DEPLOYMENT

- 26 Advancements in Hydrogen Deployment
- 28 Research and Development to Enable Hydrogen at Scale
- **33** Hydrogen's Expanding Role in the Energy System
- 42 Large-Scale Hydrogen System Safety Issues
- 47 Renewable Hydrogen for Sustainable Ammonia Production

Advancements in Hydrogen Deployment

The quest to harness the energy of clean, renewable hydrogen is now becoming a global initiative, as many countries look to address the impacts of climate change. Hydrogen is a valuable industrial commodity with tremendous potential to help stabilize the electric grid, reduce dependency on petroleum, and reduce the carbon footprint across the transportation, power generation, and industrial sectors.

Relevant stakeholders are just now starting to tap hydrogen's true potential on a worldwide scale. Global partnerships, central to the success of any technology, are popping up around hydrogen advancements and developments. The World Hydrogen Council, which was launched in 2017 (and now has 60 member companies), brings together many of the industry's CEOs to accelerate the development and use of hydrogen through pooled investment.

The U.S. uses hydrogen at a rate of 10 million metric tons per year, primarily in the petroleum refining and ammonia manufacturing industries. Most of it is produced by natural gas reforming, but hydrogen can also be generated by splitting water molecules using electrical, thermal, or solar energy. As the transportation sector now includes more than 7,000 registered light-duty fuel cell electric vehicles and 40 commercial hydrogen refueling stations in California, there is no doubt that the need for hydrogen will continue to increase. New markets for hydrogen as a fuel are emerging across several sectors, including heavy-duty trucks, maritime, rail, air, and backup power. Additionally, the industrial sector increasingly uses hydrogen in metals refining and synthetic fuel production.

Recognizing the enormous potential for hydrogen in transportation, power generation, and industrial applications, the U.S. Dept. of Energy's Office of Energy Efficiency and Renewable Energy (DOE-EERE) has launched the Hydrogen at Scale (H2@Scale) initiative. H2@Scale addresses the research and development required to safely support the expanding role of hydrogen across all energy sectors. This issue of *CEP* highlights the H2@Scale

initiative, including critical analyses performed by the DOE's national laboratories to assess the impact of the growth of hydrogen on our economy and the safety aspects required to sustain a large-scale hydrogen distribution and utilization network in the U.S. This special section also reviews and discusses the value proposition and technology advancement of H2@Scale happening globally around ammonia produced from renewable hydrogen.

Sunita Satyapal, director of the DOE Fuel Cell Technologies Office (FCTO), offers an overview of the DOE's H2@Scale effort and provides insight into the research and development (R&D) portfolio that the DOE is investing in to advance the H2@Scale initiative. She gives a perspective on the potential R&D gaps that require future investment to fulfill this initiative. Authors Mark Ruth, Brian Pivovar, and Josh Eichman from the DOE's National Renewable Energy Laboratory (NREL) discuss hydrogen production, including detailed analysis of the potential impact of transforming the energy, transportation, and manufacturing space with hydrogen. Chris LeFleur of Sandia National Laboratory discusses the safety requirements to enable the vision of H2@Scale to safely produce, deliver, store, and utilize hydrogen at such an expanded scale. Trevor Brown of the Ammonia Energy Association discusses the state of ammonia production from renewable hydrogen, which is one of the primary focuses of H2@Scale.

With these insights in mind, we work toward creating innovative large-scale efforts to alter our energy production and use with the growth of the hydrogen sector.

Bond Calloway, Associate Laboratory Director Scott McWhorter, Director Energy Science & Technology Will James, Senior Fellow Program Manager Savannah River National Laboratory



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The Center for Hydrogen Safety (CHS) is a not-for-profit, non-bias, corporate membership organization within AIChE that promotes the safe operation, handling, and use of hydrogen and hydrogen systems across all installations and applications. CHS will:

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Research and Development to Enable Hydrogen at Scale

Sunita Satyapal U.S. Dept. of Energy (DOE) The Dept. of Energy's H2@Scale initiative promotes the development, growth, and implementation of technologies based on hydrogen's versatility.

ydrogen technologies are rapidly entering the market in a variety of applications worldwide. Today, thousands of hydrogen fuel cell systems are in service — including in forklifts used in warehouses, commercial vehicles on the roads, and stationary or backup power systems — providing clean and reliable power. Hydrogen is also increasingly being used to store energy generated by intermittent renewable sources such as solar or wind, and used as a feedstock for industrial processes. These applications are receiving increased attention as key components of the U.S. Dept. of Energy's (DOE) H2@Scale initiative (www.energy.gov/eere/fuelcells/h2scale).

The DOE's national laboratories coined the term H2@Scale to describe the large-scale production, delivery, storage, and utilization of hydrogen across sectors and applications. Through the DOE's national labs, which house unprecedented capabilities and expertise — including more than 50 Nobel Prize winners — a team of leading researchers along with the DOE's Fuel Cell Technologies Office (FCTO) developed the H2@Scale concept to articulate hydrogen's potential in helping to achieve energy security, resiliency, and environmental and economic benefits for the nation. Achieving economies of scale can reduce costs, foster the development of a hydrogen infrastructure (including the required supply chain, and codes and standards), and accelerate acceptance by users and the public. The key to achieving such scale is diversifying and increasing the use of hydrogen across multiple sectors and applications. In principle, this should not be difficult, because hydrogen







can be used as a fuel or commodity chemical feedstock, an energy carrier, or an energy storage medium. It is one of the most versatile chemicals and is essential in the synthesis of numerous industrial products, such as ammonia, plastics, and pharmaceuticals. (Editor's note: See pp. 47–53 for more on hydrogen's role in ammonia production.)

Opportunities enabled by hydrogen

Figure 1 depicts the H2@Scale concept and illustrates a scenario in which hydrogen could achieve parity with today's electric grid (red circle) and natural gas infrastructure (or natural gas "grid") (brown circle). Producing hydrogen could enable users to connect or disconnect from either the electric grid or the gas grid in unique ways. Hydrogen can be produced by electrolyzing water when there is excess solar or wind energy, or using baseload power (such as nuclear), which cannot be easily turned down to accommodate the variability of intermittent renewables. The hydrogen could then be stored and subsequently used for various purposes, including in turbines or fuel cells to provide power back to the grid. Because such systems are scalable and relatively easily dispatched, options such as microgrids and grid-independent systems provide additional resilience for dealing with weather or other power disruptions.

However, rather than the limiting case of moving electrons as in grid electricity-to-battery storage, producing hydrogen from electricity opens up completely new markets.

Hydrogen can be reacted with carbon dioxide to produce synthetic fuels, or used directly in fuel cells for power or electric vehicles. Hydrogen is a feedstock in conventional industrial processes, such as ammonia and methanol production, and in oil refining. Perhaps most noteworthy are the potential new opportunities for innovative industrial processes, such as using hydrogen directly as a reducing agent in steel production. Other emerging opportunities include the direct injection of hydrogen into the gas grid, and its use for heating in either industrial or even residential applications. Such uses point to the value of hydrogen as a means for one-way energy storage, which can supplement conventional energy storage systems that are designed exclusively to provide power back to the grid.

Examples of hydrogen-based one-way energy storage are emerging rapidly worldwide. A steel plant in Austria operates with hydrogen obtained by wind-powered electrolysis. The world's largest (6 MW) wind-to-hydrogen electrolysis demonstration project, in Germany, has been injecting nearly 10% hydrogen into the natural gas pipeline for the last three years. In an unprecedented move, the city of Leeds in the U.K. is considering completely retrofitting the town's district heating system to operate on hydrogen gas instead of natural gas. The DOE and its stakeholders track these global developments through the International Partnership for Hydrogen and Fuel Cells in the Economy (IPHE; www.iphe.net) and other collaborations. IPHE was formed in 2003 to foster intergovernmental collaboration and accelerate the deployment of hydrogen and fuel cell technologies worldwide. Now, with 19 countries and the European Commission as partners, IPHE members collectively represent over two-thirds of the world's population and GDP and invest nearly \$1 billion per year in hydrogen infrastructure and research and development.

While the IPHE is a partnership of governments and government agencies, the Hydrogen Council is a global industry partnership. Formed in 2017, it now has commitments from more than 50 CEOs of major companies for investments totaling more than \$10 billion to advance hydrogen development and deployment. The Hydrogen Council estimates a potential for \$2.5 trillion in revenues and 30 million jobs by 2050, along with a reduction of 6.5 gigatons of carbon dioxide (1). In this scenario, it envisions hydrogen contributing to 18% of total energy consumption worldwide. The challenge is transforming today's hydrogen market to the H2@Scale vision of the future.

Hydrogen today

Currently, the U.S. produces over 10 million metric tons (m.t.), of hydrogen per year from natural gas, mostly for oil refining and for making ammonia, which is used in fertilizer production. Although not widely known, the U.S. already has more than 1,600 miles of hydrogen pipeline, as well as several underground geological caverns, including the world's largest in Texas, which stores thousands of tons of hydrogen. The newest development is the increase in hydrogen fueling stations for fuel cell vehicles. California has around 40 retail stations today where consumers can fuel their vehicles with hydrogen as easily as fueling gasoline-powered vehicles. Japan has over 100 hydrogen stations, Germany has over 50, and other countries are also ramping up.

Early developments such as hydrogen-fueled forklifts have helped catalyze the market and infrastructure. The Hydrogen and Fuel Cells program within DOE initiated the deployment of several hundred industry cost-shared hydrogen-powered forklifts. This successfully stimulated the deployment of an additional 25,000 forklifts without DOE funding. To date, forklifts at manufacturing facilities and warehouses around the country have refueled with hydrogen over 20 million times. In fact, with the recent increase in hydrogen demand for such applications, supply is starting to become a challenge. More hydrogen will be needed as other emerging uses, such as medium- and heavy-duty fuel cell vehicles, expand.

Renewable energy

In addition to expanding hydrogen production to meet the demands of the transportation sector, low-cost solar and wind power are also providing an opportunity to expand hydrogen use. As costs have fallen, the amount of solar and wind generated has increased (Figure 2). But because such sources are intermittent, supply and demand profiles do not always align. Any excess must be stored for dispatching when the sun is not shining or the wind is not blowing. Hydrogen is one means of energy storage.

In addition, as the use of renewables increases, power generation over the course of a day is often described as the duck curve (Figure 3). The black curve represents total electricity demand from the grid - power consumption is typically low around midnight, increases in the morning hours, drops for a few hours when many people are at work or school, and then increases again in the evening when most people return to their residences. Solar power production (orange curve) peaks during the day. The net load on the grid (green curve) is the difference between total electricity demand and solar production. This imbalance between demand and renewable energy production resembles the silhouette of a duck, hence the name duck curve (and the term duck's belly to refer to the net demand in the middle of the day). A means to store the excess energy generated would alleviate the need to curtail renewable power production and prevent the loss of that excess power.

Figure 4 presents examples of duck curves in the California energy market. The various bellies of the duck are predictions based on solar production capacity buildout by year. However, actual capacity outpaced predic-



▲ Figure 2. As the cost of solar PV and wind power have decreased, deployments have increased.

tions, and as the asterisk shows, by May 2017 the actual net demand (green line) was more than 20 GW less than what had been predicted for 2020. In addition, in locations with a significant amount of solar electricity generation, the amount of power that has to be produced from sources other than solar or wind increases rapidly around sunset (as indicated by the arrow from the belly of the duck to its neck).

In just one day in 2016, for instance, an increase of roughly 13 GW of electricity was required over a 3-hr ramp period. Because electrolyzers and fuel cells can ramp up and down to use (or produce) more or less power rapidly with excellent dynamic response, they can help compensate for power fluctuations associated with such increases in the penetration of renewables.

Hydrogen tomorrow

As refineries handle crude oils with higher sulfur content, more hydrogen will be needed for desulfurization to produce fuels that comply with vehicle tailpipe emission standards. The global desire to achieve zero-emissions vehicles makes transportation one of the largest potential markets for hydrogen growth. For instance, only 7,000 hydrogen-fueled passenger cars are on the road today, but the U.S.'s current hydrogen production of 10 million m.t./yr provides sufficient fuel for nearly 50 million passenger cars, which could eliminate a large amount of the consumer-generated pollution. The average American household spends nearly one-fifth of its total family budget on transportation — making it the most expensive spending category after housing (2). Thus, incorporating hydrogen into a broad portfolio of fuels would expand the options available to the consumer.

Perhaps the most notable development is the rapid increase in the number of hydrogen fueling stations under construction or planned. This is catalyzing private-sector investment in infrastructure, including hydrogen liquefaction plants and distribution systems. California plans to



▲ Figure 3. The so-called duck curve illustrates the deviation between electricity demand and net load due to solar power in the middle of the day, in the case of high solar penetration.



build 200 stations in the next few years, increasing to 1,000 by 2030, according to the 2018 plan by the California Fuel Cell Partnership. Japan, Korea, Germany, China, and other countries are collectively planning for thousands of stations and millions of fuel cell vehicles in the next one to two decades.

Maritime and rail applications are also of interest. The world's first hydrogen fuel cell passenger train began operating in Germany in 2018. As such markets develop, economies of scale will help to reduce costs and increase the attractiveness of investing in a hydrogen infrastructure. While electrolysis is the main focus of much attention today, the H2@Scale vision does not preclude any resource or generation method. Fossil fuels or biomass conversion approaches that do not rely on electrolysis are options, depending on regional availability and cost. Thus, across virtually all applications and sectors, hydrogen can serve in the unique role of an enabler and not just a direct competitor to other energy pathways.

Remaining challenges and R&D needs

As with most innovative and high potential initiatives, a key challenge in realizing the H2@Scale vision is cost. The current costs of electrolyzers are still more than \$1,000/kW and efficiencies are roughly 60%. However, these costs are projected to decline to about \$400/kW in the next few years (3). At electricity prices of roughly \$0.05/kWh, the cost of hydrogen is estimated to be roughly \$5/kg, even with today's technology (assuming economies of scale). This does not include delivery, compression (for use in fuel cell cars that operate with 700-bar hydrogen storage tanks) or dispensing; these steps can add more than \$12/kg to the cost of hydrogen (4). In fact, at today's retail hydrogen stations, consumers can pay as much as \$16/kg for the hydrogen. (Note that since one kilogram of hydrogen has about the same energy content as one gallon of Power Consumption, MW gasoline — simply a coincidence of nature — the unit gasoline gallon equivalent, or gallon gasoline equivalent [gge], is used interchangeably with kilogram.)

Although fuel cell cars can achieve two to three times greater fuel economies than conventional gasoline-powered cars, the DOE long-term target for economically competitive hydrogen is \$4/gge. This takes into consideration the total cost of ownership, the higher cost of fuel cell vehicles, and the projected low cost of petroleum. In the near term, even \$7/gge would enable fuel cell vehicles to be competitive. Each application (such as steel or ammonia production, trucks, stationary fuel cells, etc.) will have its own cost threshold at which the technology will be competitive with incumbent or other advanced technologies.

To meet consumer expectations for affordability, durability, and reliability, the DOE focuses on early-stage R&D to catalyze innovations and breakthroughs across hydrogen production, delivery, storage, and conversion technologies. Examples include advanced water splitting (e.g., by electrolysis, direct photoelectrochemical production, or solar/high-temperature thermochemical production) and biological approaches for hydrogen production, as well as low-cost delivery components (compressors, nozzles, hoses, dispensers), low-cost hydrogen storage (e.g., materials that can store hydrogen at pressures much lower than today's 700-bar carbon fiber tanks), and catalysts, membranes, and other components for fuel cell technologies. In parallel, DOE established the H2@Scale consortium, through which national laboratories and industry can work together on projects co-funded by the government to accelerate the early-stage research, development, and demonstration of new technologies.

Chemical engineering, along with other disciplines such as materials science, chemistry, physics, and other engineering fields, are critical to achieving the H2@Scale vision. Research will be needed for low-cost, durable materials, synthesis, characterization, and optimization, as well as process designs, component development, and systems integration. Finally, all of these efforts will require consideration of safety across installations and the entire hydrogen value chain. Safe practices in the production, storage, distribution, and use of hydrogen are an integral part of future plans.

To emphasize the importance of safety, the DOE's Pacific Northwest National Laboratory (PNNL) and the Ameri-



▲ Figure 4. In California, the duck curve has changed over time as the use of renewable energy has increased.

can Institute of Chemical Engineers (AIChE) partnered in 2018 to launch the Center for Hydrogen Safety (CHS; www.aiche.org/CHS). This global nonprofit organization builds on AIChE's experience in industrial chemical process safety and its access to 60,000 members in 110 countries to promote hydrogen safety and best practices worldwide. Like other fuels, hydrogen can be used safely with appropriate handling, including the use of appropriate detection, engineering, and risk-mitigation measures. Training for first responders, code officials, and technicians or other personnel handling hydrogen and infrastructure components needs to be expanded. The global portal H2Tools.org, funded by the DOE FCTO, was incorporated into the new CHS, along with access to PNNL's Hydrogen Safety Panel, which consists of technical experts with over 400 years of collective hydrogen safety experience.

As the production, delivery, and use of hydrogen become more widespread, lessons learned and best practices will be disseminated through various partnerships and stakeholder groups, such as the CHS, the IPHE, the Hydrogen Council, and others. Continued collaboration, focus, and momentum are essential to reducing costs and improving the performance, reliability, and durability of various components and systems to enable success of the H2@Scale vision.

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Hydrogen's Expanding Role in the Energy System

Mark Ruth Bryan Pivovar Josh Eichman National Renewable Energy Laboratory (NREL) Realizing the vision of H2@Scale will require research and investment in efficient hydrogen production methods and upgraded infrastructure.
Advances in hydrogen production will allow new applications, such as steelmaking, biofuels production, and fuel cell electric vehicles, to thrive.

2@Scale is a U.S. Dept. of Energy (DOE) initiative that brings together stakeholders to advance affordable hydrogen production, transport, storage, and utilization in multiple energy sectors. H2@Scale will improve the resiliency and reliability of the energy supply chain, increase the competitiveness of U.S. manufacturing, create jobs, and reduce emissions, thereby improving environmental sustainability.

Hydrogen has a unique ability to transfer energy across time and economic sectors. The electric grid was designed so that the generated load varies with changes in demand. However, wind and solar power technologies can only generate electricity when each resource is available, making it more difficult to balance the grid. Because hydrogen production can be a large-scale controllable load, it can help address that challenge. Hydrogen can serve as a clean feedstock for diverse applications within the transportation, process industries, and energy sectors.

This article describes hydrogen production, application, and infrastructure opportunities. The first part of the article discusses hydrogen production and describes current costs and potential cost reductions that could be enabled by research and development (R&D). The second section discusses key applications that take advantage of hydrogen's chemical properties and its potential as an energy carrier. The final section of the article describes the current hydrogen infrastructure and how it must grow to meet the H2@Scale vision.

Hydrogen production opportunities

Hydrogen can be produced in several ways. In the U.S., approximately 10 million metric tons (MMT) of hydrogen is produced annually by steam methane reforming (SMR) of natural gas (1). That technology also dominates global hydrogen production, because it is the lowest-cost option where natural gas resources are plentiful.

Two alternative production options couple hydrogen production with support from the electric grid. The first is low-temperature electrolysis (LTE), which uses electricity to split water into hydrogen and oxygen. The second is hightemperature electrolysis (HTE), which uses both electricity and heat to split water. HTE is a more efficient process than LTE, but requires more expensive materials and can pose thermal management challenges.

Another production option that is being developed is reforming of carbon-rich energy sources, such as coal, biomass, and bioderived liquids. Other hydrogen production technologies that are in the early stages of development include photoelectrochemical water splitting, photolytic biological production, and high-temperature thermochemical processing.

Producing hydrogen via electrolysis can decouple energy production from energy consumption because electrolyzers are flexible loads — their loads can be ramped in response to grid needs (2). LTE has already been shown in lab environments to be capable of responding to fluctuations in grid signals in less than a second (3). These response times meet

the requirements to supply regulatory and other grid ancillary services — controls that provide short-term balancing of supply and demand on the grid, thus managing voltage and frequency. Therefore, LTE has the potential to receive revenue for providing those services. That revenue would offset the cost of hydrogen production (4).

As an example of the mutually beneficial integration of hydrogen production and the grid, Figure 1 shows how the cost to produce hydrogen can be reduced by simultaneous participation in multiple markets (5). The red bar shows traditional operation, where an electrolyzer is operated using electricity sourced from the grid at its designed capacity for 90% of the year. If onsite renewables are available, the electrolyzer optimally uses a combination of grid and renewable power to achieve the lowest cost.

In Figure 1, each green step represents the impact of participation in different markets that are currently available in California. These markets include flexible operation and renewable and low-carbon credit programs — such as the low-carbon fuel standard (LCFS), utility demand response (DR) programs, and wholesale ancillary service markets (met by a spinning reserve program). In addition, the purple bars show how future changes in those markets — and the introduction of new markets — can further reduce the cost of hydrogen production and delivery via LTE.

Unsurprisingly, market drivers change as market conditions change. Changing electricity market conditions can significantly affect the cost of hydrogen production. Over the past decade, the costs of wind and solar photovoltaic (PV) electricity generation have dropped. Reductions in the costs of renewable electricity, increases in state and municipal renewable energy targets, and deregulated electricity markets have caused considerable volatility in electricity prices, and at times prices have dropped to negative values.

Figure 2 shows the net electricity generation in the California Independent System Operator's regions on

March 11, 2017, and the real-time average hourly prices during that same day (6). The average hourly electricity price was negative for 8 hours. Negative pricing occurs when generation exceeds load and cannot be reduced because renewable electricity generation is incentivized (through a production tax credit or other means) and thermal generators (natural gas, coal, and nuclear) are at their minimum operating levels. In many cases, the thermal generators cannot be turned off because they will be needed overnight and cannot be shut down or started up quickly.

Volatile and low electricity prices can impact generators negatively; however, they can be beneficial for electrolyzers and other flexible loads that can take advantage of the availability of low-priced electricity. R&D to reduce the capital cost of LTE is needed to take advantage of these opportunities. R&D efforts could involve increasing power density in the electrolyzer stack, reducing catalyst loading, developing lower-cost catalysts, reducing membrane costs, and improving automated manufacturing techniques.

Low electricity prices impact hydrogen production costs

To demonstrate potential impacts of sporadic low electricity prices on hydrogen production costs, we can look at an illustrative example using the DOE's Hydrogen Analysis (H2A) financial tool. Figure 3 demonstrates how the future costs of centralized electrolytic hydrogen production are affected by different market and technology conditions. The bar on the left shows a characteristic breakdown of capital (blue), operation and maintenance (red), and feedstock, *i.e.*, electricity (green) cost components at a high cost of electricity of 6.6 cents per kilowatt-hr (¢/kWh). The center bar represents cases where the LTE utilizes low-cost electricity that is intermittently available, rather than higher-cost electricity that is consistently available. In the middle bar, the cost of electricity is 4, 2, or 1 ¢/kWh. The annual capacity



◄ Figure 1. The cost to produce hydrogen can be reduced with a few key developments. The red bar shows traditional low-temperature electrolysis (LTE) operation. Each green step shows how much that cost can be reduced by participation in different markets (currently available in California). Purple bars show potential future cost reductions. DR = demand response, LCFS = low-carbon fuel standard, RINs = renewable identification numbers. Source: (5).



◄ Figure 2. For eight hours on March 11, 2017, the average hourly electricity price was negative in the territories regulated by the California Independent System Operator. The price peaked around 5 pm as the solar generation decreased and demand increased. Source: (6).

factor of 40% is also lower for the three cases in the center bar, because low-cost electricity is likely to be available only intermittently. However, the assumed lifetime and maintenance schedule are the same at both capacity factors.

The center bar has a lower hydrogen production cost overall, but the capital costs contribute more to the total hydrogen production cost. As the price of electricity drops, the efficiency of the electrolyzer is a smaller fraction of the levelized cost. As electricity rates (*e.g.*, time-of-use and real-time utility rates) become more dynamic, and as R&D to reduce hydrogen production costs continue, the tradeoffs between energy and capital costs will become more impactful.

The capital and fixed O&M costs may not increase as much as they do in the figure because the calculations used to generate the figure assume that the electrolyzer's lifetime



▲ Figure 3. Typical cost breakdown of future electrolytic hydrogen production under different market and technology conditions.

and annual O&M costs are the same at all capacity factors. If reduced use extends life or reduces annual O&M cost, those factors would be lower in the center and right bars.

In Figure 3, the left and center bars assume the LTE capital cost is \$400/kW, which is an estimate of the cost of current technology with a manufacturing capability and supply chain at full capacity (7). The right bar demonstrates the benefit of reducing capital cost to \$100/kW through R&D improvements. The reduction in capital cost is accompanied by a reduction in the efficiency due to use of low-cost materials, manufacturing processes, etc. that negatively impact performance. The feedstock cost increases slightly due to the lower efficiency. However, more importantly, the capital and maintenance costs are significantly reduced. This shows that both electricity cost and electrolyzer capital cost have a role to play in reducing the total cost of producing hydrogen.

Electrolyzers and nuclear energy

Because electrolyzers can ramp up and down quickly with changes in demand, they can also improve the profitability of nuclear power plants. Some nuclear power plants struggle to remain economically viable in competitive power markets, where wholesale electricity prices are low, driven by such factors as:

• minimal load growth, due to increased end-use efficiency

• low natural gas prices coupled with low-cost natural gas generation

• increased penetration of renewable energy resources.

Selling an additional product, such as hydrogen, could improve the net revenue of a nuclear power plant.

The generation of hydrogen using nuclear energy could also utilize HTE technologies such as solid-oxide electrolysis cells. In HTE, which uses both electricity and heat to split water, the energy requirement can be as much as 30% lower than that of LTE because it has lower kinetic losses at higher temperatures (8). Integrating an HTE process within a nuclear power plant can take advantage of the heat generated in these plants. Because nuclear power plants produce heat and then use a steam turbine to generate electricity at around 32% efficiency, that heat is less expensive than electricity on an equivalent energy basis.

HTE systems are not as developed as LTE systems — R&D is underway to reduce cell degradation that negatively impacts performance and lifetime. The objective is to make operational lifetimes and equipment replacement periods long enough to achieve economic viability.

Nuclear power plants are more valuable to the grid than just the energy they produce. Because they are always operating, they provide energy at times when the load is the highest (*i.e.*, they provide valuable generation capacity). That capacity is compensated in some locations through capacity payments. Capacity payments are made to electricity generators that guarantee they will produce electricity when required. They are usually called upon during peak demand times. Hybrid energy systems like the one illustrated in Figure 4 may represent a valuable opportunity in such situations.

The hybrid system in Figure 4 would produce hydrogen during hours when electricity prices are low and electricity when its prices are high (9). By doing so, it could be more economically viable than a plant with a single product, because it can produce the higher-value product at any given time while still receiving capacity payments for providing generation at times of peak loads. HTE systems are being further developed so that they can respond quickly to grid signals and meet operational flexibility requirements.

Hydrogen application opportunities

Currently, the U.S. produces about 10 MMT/yr of hydrogen for use in petroleum refining and ammonia production via steam methane reforming, and an additional 6 MMT/yr is produced as a byproduct of the refining process and



▲ Figure 4. A nuclear power plant could be used to generate hydrogen by high-temperature electrolysis (HTE) during periods when less power is needed for the grid (or when electricity prices are low). Likewise, wind power could also be used to produce hydrogen in response to grid demand. Source: (9). consumed internally by the refinery (10). The efficiency of steam methane reforming is 70% on a higher heating value (HHV) basis. Therefore, 2 quad/yr (1 quad = 10^{15} Btu) of natural gas are required to produce that hydrogen — about 2% of the annual domestic energy use of 98 quad/yr (11).

Molecular hydrogen's (H_2) chemical properties are the key driver for those applications. In refining, hydrogen is used for cracking and desulfurization (12). It is an important feedstock to the Haber-Bosch process, and the ammonia generated by the process is either used directly as a fertilizer or converted to other fertilizers, such as urea, that are easier to handle.

Steelmaking

Additional applications that take advantage of hydrogen's properties are emerging. Steelmaking is one such application. Currently, the most common steelmaking process starts with a coal-fired blast furnace that provides thermal energy and removes oxygen from iron ore, which is rich in one or more iron oxides such as magnetite (Fe_3O_4), hematite (Fe_2O_3), and goethite [FeO(OH)]. Pig iron, the blast furnace's product, is subsequently carbonized in a basic oxygen furnace. Instead of a blast furnace, some steel mills reduce iron in a direct reduced iron (DRI) process fueled by syngas (a mixture of carbon monoxide and hydrogen produced from natural gas).

In 2017, DRI processes produced 71.4 metric tons (m.t.) of refined iron (13); this was about 4% of the total global steel production of 1,700 m.t. (14). DRI is widely used (along with scrap metal) to supply electric arc furnaces, which are the dominant method of steelmaking in the U.S. today (15).

Several organizations have been developing DRI processes that use hydrogen exclusively to remove oxygen from iron ore. Figure 5 depicts one option, the MIDREX H₂ process (16). In that process, hydrogen can be injected directly as the reducing agent, and, if desired, it can be combusted as the heat source. A range of 0.08–0.12 kg of hydrogen is required to produce 1 kg of DRI product, depending on the DRI technology, whether hydrogen is used to provide the heat, and whether carbon monoxide is added to provide a carbon source and make the reaction more exothermic (17).

Flash ironmaking technology (FIT) is another steelmaking technology that uses hydrogen instead of natural gas (18). Further development and demonstration of these technologies are underway.

Biofuel production

Biofuels are another application that capitalizes on molecular hydrogen's chemical properties. Ethanol, which is produced by fermenting starch in corn grain, is currently the most common biofuel in the U.S. Although ethanol production does not require hydrogen, some second-generation biofuels do.

Second-generation biofuels convert lignocellulosic biomass (the dry matter in wood, stems, stalks, leaves, and other non-seed portions of plants) either via fermentation to ethanol or via gasification or pyrolysis to hydrocarbons that can be used directly as gasoline or diesel blendstocks. Blendstocks are likely to be more easily integrated into the fuel system, because they are less reactive than ethanol and they do not increase the oxygen content of the fuel they are added to as much as ethanol does. In addition, blendstocks retain more of the carbon in the feedstock, because less carbon dioxide is produced when they are synthesized from biomass than during the fermentation process to produce ethanol.

Many processes are being developed to produce blendstocks. One such process starts with a dilute acid pretreatment of the lignocellosic biomass, followed by enzymatic saccharification of the cellulose, purification, and catalytic deoxygenation and oligomerization of the biomass hydrolysates to produce diesel- and naphtha-range fuel blendstocks. The estimated hydrogen demand for that process is 0.5 kg of hydrogen per gallon of gasoline equivalent (GGE) of the fuel blendstock (19). That hydrogen could be produced via gasification of a portion of the biomass or produced elsewhere and delivered to the biomass conversion plant. Producing the hydrogen elsewhere increases the yield of the fuel blendstock by over 50% (19).

Increasing renewable fuel standards and limitations on fuel properties are likely to drive markets for these types of blendstocks. R&D is underway to make them more cost-competitive.



▲ **Figure 5.** In the MIDREX H₂ process, hydrogen is injected directly and serves as the reducing agent to produce direct reduced iron (DRI). Hydrogen can also be combusted as the heat source. Source: Adapted from (16).

Upgrading carbon dioxide

Hydrogen could also be employed to produce a wide range of organic chemicals and fuels through reactions with carbon dioxide. Electrochemical techniques are being developed to convert carbon dioxide and hydrogen to syngas. Catalytic upgrading of syngas produced in this fashion could produce several valuable products, including methanol (20).

An alternative is the production of methane or other organic chemicals from hydrogen and carbon dioxide in a bioreactor. Electrochaea has patented a strain of *Methanogenic archaea* that produces methane, and the company reports that other products are possible (21). Ideally, this type of process would use a concentrated carbon dioxide stream and thus be located near a source, such as an ethanol plant.

Market opportunities are likely to be driven either by a desire to use carbon dioxide or by the ability to tailor specific products that may be difficult to produce directly from natural gas. However, more R&D will be needed to produce those products economically.

Fuel cell electric vehicles (FCEVs)

Transportation is an emerging application that uses hydrogen as an energy carrier. For example, forklifts in warehouses must be able to run continuously throughout the day and must not produce emissions. Under these constraints, hydrogen fuel cells have an advantage over batteries, because forklifts can be filled with hydrogen faster than batteries can be typically be swapped in and out. As of 2018, over 20,000 fuel cell forklifts were in operation *(22)*.

Another emerging sector for fuel cells is in cars and trucks. Fuel cell electric vehicles (FCEVs) do not generate emissions and have fast refueling times of 3–5 minutes. Over 6,700 FCEVs have been bought or leased in the U.S. to date, primarily in California.

Drayage trucks, which transport cargo between ports and warehouses, represent another market for fuel cell vehicles. Areas near ports are often highly congested, and idling trucks can generate significant amounts of air pollution. Additionally, drayage trucks often run many hours at a time and require fast refueling rates. Fuel cells have the potential to solve some of these challenges because they do not produce emissions and they can be refueled quickly. Toyota is developing fuel cell Class 8 trucks for such service. Toyota's trucks have been shown to accelerate faster than comparable diesel trucks, which could help to reduce congestion as well (23).

Electrical energy storage

Hydrogen fuel cells can also provide portable and offgrid power. This could be especially beneficial in remote locations where resilience to long-term outages is critical,



Figure 6. Major hydrogen production sites are connected to large refineries by hydrogen and natural gas pipelines.

such as cellphone towers, surveillance equipment, off-grid pipeline operations, and railway signals and crossings. In many of these applications, hydrogen fuel cells can provide backup power at lower maintenance costs than diesel generators. Because hydrogen fuel cells operate nearly silently, powering lighting towers where low levels of noise are required is another opportunity.

In the future, hydrogen could provide long-duration (multi-day) energy storage for the electric grid. As wind and solar energy generation increase, the number of hours with very low or negative electricity prices is likely to increase, especially during the spring and fall, when electricity load is low because air conditioning and electrical heating loads are lower. Batteries are likely to be the lowest-cost option for frequent-use diurnal and short-term energy storage, but hydrogen is likely to be more competitive for longer durations (24).

Natural gas supplementation

Hydrogen can also supplement the natural gas system in certain cases, depending on economics. In Europe, where natural gas prices are relatively high, several power-to-gas projects are underway. Power-to-gas projects generate hydrogen from water using electricity and that hydrogen can be blended into the natural gas system at low concentrations. Alternatively, hydrogen can be reacted with carbon dioxide to produce methane. Those projects are driven by a desire to:

• diversify energy sources and create markets that support increased penetrations of wind and solar photovoltaic generation

• support nuclear power generation in locations where generation exceeds load (at times) due to high levels of nuclear generation and/or increasing penetrations of wind and solar photovoltaic generation; in these cases, excess wind, solar, and nuclear power is converted to hydrogen.



Blending up to 20% hydrogen (on a volume basis) is likely to be feasible for natural gas applications, although not all natural gas pipeline systems are constructed of materials that can withstand that concentration of hydrogen for long periods (25). Increasing the hydrogen concentration in natural gas reduces carbon dioxide emissions from gas that is combusted to provide heat or generate electricity.

Thus, additional testing of appliances that use natural gas and the natural gas infrastructure is needed to identify the R&D opportunities that enable higher concentrations of hydrogen.

Hydrogen infrastructure opportunities

Because hydrogen production and demand locations are likely to be largely separated, the hydrogen infrastructure must be improved before any of these applications can become more widespread. The U.S. currently has more than 1,600 miles of hydrogen pipelines (26). These are primarily located such that they connect merchant hydrogen producers with large users — primarily refineries (Figure 6). In addition, three geologic hydrogen storage locations in Texas help buffer the system.

While hydrogen is typically delivered via pipeline to larger users, hydrogen is liquefied and transported via truck to smaller-scale users. In some cases, it is transported as a compressed gas. Because hydrogen has a lower volumetric energy density than other liquid fuels, transportation by truck is not cost-effective.

To achieve the H2@Scale vision, a much more comprehensive hydrogen transport and storage network will be needed. Long-distance transport to move hydrogen from where it is produced to support the grid (*e.g.*, the Midwest and Southwest) to large demand centers (*e.g.*, where the

Additional Resources

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Closing thoughts

While hydrogen currently plays a large role in the global energy system, that role has the potential to grow. The Hydrogen Council estimates that the global hydrogen market could increase from 8 exajoules (EJ) to 78 EJ by 2050 if

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tion into the electricity and natural gas networks. Prior to his position at NREL, he participated in the Dept. of Energy's EERE Postdoctoral Fellowship program. Eichman received his BS from Clemson Univ. in mechanical engineering and his MS and PhD from the Univ. of California, Irvine, in mechanical engineering, where his research focused on electric grid planning and operations.

hydrogen were used in transportation, energy storage, biofuels production, and the other applications as described here. Global energy consumption is about 370 EJ and projected to grow to 640 EJ by 2050, so the role of hydrogen could grow from 2% to 12% in the next 30 years (27).

R&D is also ongoing to address challenges in mak-

ing, moving, storing, and using hydrogen. Those efforts are reducing the cost of hydrogen production and uncovering opportunities to move and store hydrogen economically. This will enable hydrogen to be used in a wider variety of applications, which will then enable further growth in infrastructure and reduce the cost of additional opportunities.

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Large-Scale Hydrogen System Safety Issues

CHRIS LAFLEUR, P.E. Sandia National Laboratories As hydrogen's applications grow and develop across many sectors, industrial systems must identify the necessary precautions to be able to safely handle the material.

 \checkmark ome of the biggest challenges to hydrogen as an energy solution are the safety issues and the perceptions of the risks associated with hydrogen systems. Liquefied and gaseous forms of hydrogen have been used since the industrial revolution in various processes, such as ammonia production, chemical processing, and petroleum refining. As technologies evolve to make hydrogen a sustainable energy carrier, hydrogen will emerge in larger scale applications, as envisioned in the U.S. Dept. of Energy's (DOE) H2@Scale framework (1). Hydrogen's versatility and strength as an energy carrier allow it to be used directly to power fuel cells or indirectly to store excess energy from renewable sources. Large amounts of energy can be stored in tanks as high-pressure gas, or even larger amounts can be stored as a liquid at low pressure and cryogenic temperature. However, hydrogen is flammable, and any system handling it must be designed to address the relevant safety hazards unique to its material properties.

Research into new methods of hydrogen production, storage, and transportation is ongoing. The codes and standards that govern the safe use of hydrogen must keep pace with evolving technology. For example, standards that cover storage tank designs must account for higher storage pressures, fire codes must consider fire safety issues presented by new applications, and vehicle safety standards and emergency response protocols must address crashworthiness of fuel cell vehicles. This article discusses some of the safety issues that arise as large-scale hydrogen applications become more prevalent.

Hydrogen's basic properties

Table 1 compares hydrogen's properties to those of other fuels. Natural gas is a mixture of several gases, but it is composed primarily of methane, so values for methane are typically used for comparison of physical characteristics.

Lower and upper flammability limits (LFL and UFL). Upon initial inspection, the much larger range (4% to 74%) of flammable concentrations for hydrogen versus other fuels might seem to be a concern. However, the lower flammability limits of the other fuels (1% to 5%) are close to that of hydrogen, with gasoline vapor and propane having LFLs lower than hydrogen's.

Hydrogen is not treated differently than other flammable gases in indoor or enclosed applications, where hazards are of greater concern, albeit easier to monitor with conventional sensors. Regardless of flammable material type, sensors are typically programmed to alert and alarm at 25% and 50% of the LFL, respectively. This corresponds to 1% and 2% by volume for hydrogen. However, sensors are placed differently due to the variation in buoyancy properties.

Natural gas (methane) and hydrogen are lighter than air, so sensors for those gases are placed in upper areas of enclosed spaces or in ventilation ducts. Propane and gasoline vapors are heavier than air, so sensors for those are placed in pits or at the lowest levels on the floor.

Minimum ignition energy (MIE). This property measures the amount of energy that can ignite a mixture of the flammable material with air or oxygen and is a function of the mixture concentration. Hydrogen has a much lower MIE than the other fuels, and it can ignite by common static discharges. However, the value in Table 1 of 0.02 mJ is the energy needed to ignite a stoichiometric mixture (29%) of hydrogen and air. At lower concentrations, near the alarm and alert levels for enclosed spaces, hydrogen's MIE is closer to the MIE values for methane and gasoline vapor (Figure 1).

Buoyancy. Hydrogen is more buoyant than all other flammable gases. In outdoor applications, this property allows any hydrogen released to the atmosphere to rise away from ignition sources. It also causes hydrogen-air mixtures to dissipate, minimizing the potential for an explosive atmosphere to form. The buoyancy, however, can make detection difficult in outdoor spaces. Small leaks and releases could go undetected and evolve into larger releases before actions can be taken to stop the leaks.

Hydrogen's unique properties and behaviors are well documented in the literature and are also an area of active research. As hydrogen applications proliferate, more research will be needed to characterize hydrogen risks. The behaviors of liquefied hydrogen and cold vapor releases, such as occur when a liquefied-hydrogen storage tank releases boil-off gas through a vent, are currently being studied. Cold hydrogen vapor is denser than air only at less than approximately 2K above the temperature that hydrogen is liquid (20K). At those temperatures, the gases that make up air (primarily nitrogen and oxygen) condense into their liquid form. These multiphase phenomena are very complex and a detailed understanding of the physics is needed to precisely characterize the behavior.

Production

As hydrogen demand increases, the supply will need to increase similarly to enable its use as a viable energy source. A production capacity increase will either require an increase in the natural gas supply (to produce hydrogen via steam methane reforming) or increase the demand for renewable energy collection setups. Existing solar fields and wind farms could be adapted to produce hydrogen via electrolysis and store excess energy created during the day for use at night. This requires the deployment of electrolyzers, hydrogen storage tanks, and associated compressors at these sites.

Nuclear power plants also have the potential to benefit from increased hydrogen production. Because nuclear power plants function best at a steady state, excess energy is often being produced above the electricity demand. This excess energy can be used to generate hydrogen. Pipelines or other transportation modes will be needed to move the hydrogen from the production sites to users. To support this increase in energy supply, storage capacity at the sites will also need to increase.

Distribution safety

Large-scale hydrogen systems will need access to a sustainable supply of hydrogen. Transporting the hydrogen between the production plants and the sites that use it requires multiple modes of transportation. Pipelines are one mode of transport — currently 1,600 miles of pipeline are dedicated to hydrogen transportation in the U.S. (2). However, most of these pipelines are concentrated in the Gulf Coast areas of Texas and Louisiana, so additional pipelines will be needed. Expanding the existing pipeline system poses permitting, right-of-way, and construction issues that need more time and resources. For example, underground pipelines require burial permits and signage to warn ground-level activities against digging in that area. Above-ground pipelines must pass over or under roads, waterways, or other obstructions as well as being protected from impacts. Gaining access to right-of way for placement of the pipeline may require permission from multiple juris-

Table 1. Basic material properties are critical to understanding the safety-related risks and requirements of fuels.				
Property	Hydrogen	Methane	Propane	Gasoline Vapor
Upper Flamability Limit in Air, %	74	15	10.1	7.6
Lower Flamability Limit in Air, %	4.1	5.3	2.1	1.4
Most Easily Ignited Mixture in Air, %	29	9	14	2
Adiabatic Flame Temperature, °F	4,010	3,562	3,573	3,591
Buoyancy (Ratio of Fuel Density to Density of Air)	0.07	0.55	1.52	4
Minimum Ignition Energy (MIE), mJ	0.02	0.29	0.48	0.2
Autoignition Temperature, °F	1,085	1,003	914	450

dictions as the pipeline passes across city, county, or state lines. Natural gas pipelines may also be used to transport hydrogen, but applications that need a high-purity hydrogen may require scrubbing of the hydrogen after its journey through the pipeline.

In addition, pipelines present safety hazards, such as leaks and ruptures. Hydrogen leaked underground can travel through the soil some distance from the pipeline, and depending on soil permeability, there is a potential for the leaked hydrogen to reach an ignition source. However, unlike hydrocarbon fuels, hydrogen is not toxic or detrimental to the environment. Leaks from above-ground pipelines may rise harmlessly into the atmosphere, or ignite spontaneously due to a variety of physical phenomena. The specific mechanism that causes spontaneous ignition and sudden releases of high-pressure hydrogen is not well understood, but could be a result of static electric discharge, highvelocity particle impact, or transient shocks from a burstdisc rupture *(3)*.

A significant volume of hydrogen may need to be transported via tanker truck over roads, which involves safety risks related to traffic incidents, weather incidents, and truck mechanical failures. Railroads may also be utilized to transport large volumes of hydrogen. Currently, large amounts of flammable hydrocarbon-based fuels are transported across the U.S. Introducing hydrogen to this network can reduce the amount of other fuels that need to be transported and their associated risks. As hydrogen is still not yet transported on a large scale, its safety risks and overall impact need further investigation.





Storage safety

Hydrogen's high energy content and high compressibility ratio allow it to store a large amount of energy. Gaseous hydrogen is routinely compressed and stored at high pressures that present pressure safety hazards. The industry standard for storage in light-duty fuel cell vehicles is 10,000 psi (700 bar), while fuel cell buses also store hydrogen at 5,000 psi (350 bar).

The reliability of these high-pressure tanks is an important factor in safely storing high-pressure hydrogen. Pressure relief devices are required on all single-walled tanks to relieve extraordinary pressures above the maximum allowable storage pressure and to prevent catastrophic failures.

Storage vessels must also have vents that direct any released hydrogen to heights above people, ignition hazards, and building air intakes. The sudden release of high-pressure hydrogen can trigger spontaneous ignition at the exit of the vent stack. The mechanisms behind this phenomenon are not yet fully understood and are the subject of ongoing research. The potential for spontaneous ignition should be accounted for in the design, location, and height of the stack exit.

Fuel cell electric vehicles

Hydrogen fuel cell vehicles represent an important market for hydrogen. As of early 2019, over 7,000 passenger vehicles are on the road and 40 refueling stations are open to the public in California. Growth in hydrogen-fueled passenger vehicles is planned for the Northeast, and hydrogen fuel cells are expected to be deployed to fuel longhaul truck transport.

The hydrogen tanks for vehicle use are typically Type 3 and Type 4 storage vessels. These vessels make use of carbon fiber and epoxy wrapping to provide strength without unnecessary weight. The pressure vessels include a thermal pressure relief device (TPRD), which, in the event of a fire, releases the hydrogen to prevent the vessel from over-pressurizing.

Global Technical Regulation (GTR) No. 13 specifies requirements for the integrity of compressed- and liquidhydrogen motor vehicle fuel systems. The test procedures and methods specified in GTR No. 13 include pressure cycling tests (pneumatic and hydraulic testing with temperature variations), a burst test, a permeation test, and a bonfire test (localized and engulfing). The pressure cycling test evaluates a container's ability to withstand 22,000 cycles of pressurization and depressurization without bursting. The burst test evaluates a container's initial strength and resistance to degradation over time. The bonfire test evaluates the ability of the container's TPRD to open in a fire scenario. This test starts with a localized fire at 600°C impinging on a portion of the tank distant from the TPRD for 10 min, followed by an engulfing fire at 800°C for an additional 10 min. The TPRD must uninterruptedly release until the tank reaches a pressure of 1 MPa before the end of the test. If the TPRD does not release during the test, the tank is considered to have failed. The tank cannot burst or leak during the test.

In the U.S., fuel cell electric vehicles are required to undergo the same crash tests as gasoline vehicles. Details of these crash tests are found in the Federal Motor Vehicle Safety Standards, which specify tests for impacts with barriers, rear-end collisions, and side impact crashes. In the event of a crash, sensors in the vehicle detect the forces of impact and activate a valve within the storage vessels to ensure that the hydrogen does not escape if the fuel line to the cell is damaged. These safety features help ensure that the hydrogen stays within the system as designed and prevent a catastrophic failure of the pressure vessel. To date, published crash test data has not shown any vehicle to release hydrogen, and no severe real-world accidents involving hydrogen have been reported.

Liquid hydrogen

The storage of liquefied hydrogen (LH2) has some unique safety issues as well. A phase diagram (Figure 2) shows that hydrogen is a liquid only at extremely cold temperatures (20 K), regardless of pressure (4). Because of this, LH2 is typically stored below 150 psi (10 bar). The lower storage pressure allows the use of storage tanks with thinner, lighter walls and lower pressure ratings. This provides an incentive for large-scale systems to use liquefied hydrogen storage tanks for the onsite hydrogen supply.

The LH2 storage tanks are double-walled with the interstitial space evacuated to a vacuum that provides insulation to maintain the extremely cold temperature. If the LH2 is not used at the rate for which the tank was sized, boil-off hydrogen will need to be vented once the internal tank reaches the maximum allowed pressure. As the boil-off gas is generated,



▲ Figure 2. The phase diagram shows that liquid hydrogen exists only between the triple point at 21.2 K and the critical point at 32 K. the cold LH2 slowly warms as it sits unused in the storage tank. The boil-off gas increases the pressure in the vapor space of the tank. The vent stacks on LH2 storage tanks need to be designed specifically for cold hydrogen, because the nitrogen and oxygen in the air will condense and solidify when exposed to cold hydrogen vapor.

Piping carrying LH2, such as lines transferring hydrogen from the storage tank to a vaporizer, need vacuum jacketing and should be located over a concrete pad. This mitigates issues of high oxygen concentration caused by the condensation of the oxygen in the ambient air. As the LH2 travels through the piping, the piping cools below the condensation temperature of oxygen and nitrogen in the air. Liquid and solid oxygen and nitrogen can condense on the outside of the piping. These liquids can then drip off the piping onto the ground, and then revaporize, causing localized areas of high oxygen concentrations that could be hazardous. Concrete pads are less hazardous and reactive than petroleum-based surfaces such as asphalt. Also, large LH2 storage tanks that may be part of large-scale hydrogen systems need to be located away from critical exposures such as facilities like schools or residential areas, where large numbers of people may be present.

Extremely large-scale storage systems store gaseous hydrogen below ground in geologic formations such as empty salt domes, depleted oil and gas reservoirs, aquifers, or hard rock caverns. Geologic storage options have the potential to store vast amounts of hydrogen and provide a buffer for seasonal demand for energy. Oil, natural gas, and compressed air are currently stored underground successfully. Underground hydrogen storage has been studied since the 1970s, and four hydrogen geologic storage locations, three within the U.S, are currently in operation (5). Town

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gas, which is up to 60% hydrogen, was used extensively for lighting and heating prior to the development of natural gas, and was successfully stored underground.

The use of existing natural gas geologic storage facilities for hydrogen will be hampered by the requirement to evaluate and retrofit steel structures and components that may be vulnerable to hydrogen embrittlement. Safety issues associated with underground storage are limited to the development of leak pathways. In salt domes, the surrounding rock formations are highly impermeable and unlikely to leak (6); any leaks would be through imperfectly sealed wells. Other geologic storage options, such as depleted gas reservoirs, may not have the same impermeability. Any hydrogen that leaks out of an aquifer or rock formation and finds a pathway to the surface may be released into an area where ignition sources are present. Any gas that does not find a pathway to the surface and instead becomes trapped in an enclosure could create a flammable atmosphere.

Closing thoughts

The U.S. has a long history of using hydrogen in processing and manufacturing. Many industries have developed an infrastructure to produce, store, transport, and utilize hydrogen safely. To enable the growth of hydrogen for large-scale systems, this infrastructure will need to be expanded.

Hydrogen is no more or less hazardous than other flammable materials commonly used by the general public, including gasoline, propane, and natural gas. All flammable and hazardous materials must be handled responsibly, with systems designed to address the risks specific to each application. However, the growing hydrogen energy industry needs to learn from previous incidents in all relevant industries and apply the lessons learned to the emerging hydrogen applications.

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Renewable Hydrogen for Sustainable Ammonia Production

TREVOR BROWN Ammonia Energy Association

More than half of all produced hydrogen is consumed in ammonia plants. Ammonia's potential as a carbon-free fuel, hydrogen carrier, and energy store represents an opportunity for renewable hydrogen technologies to be deployed at an even greater scale.

he Haber-Bosch process reacts atmospheric nitrogen with hydrogen to produce ammonia (NH_3), which is 17.8% hydrogen by weight. Ammonia is the precursor to most modern nitrogen-based fertilizers. More than half of all the hydrogen produced around the world today is consumed in ammonia plants — in fact, ammonia production represents 55% of total global hydrogen use (1).

Hydrogen is typically produced on-site at ammonia plants from a fossil fuel feedstock. The most common feedstock is natural gas, which feeds a steam methane reforming (SMR) unit. Coal can also be used to produce ammonia via a partial oxidation (POX) process. Different regions favor different feedstocks. For example, some ammonia producers use naphtha, petroleum coke, or even heavy fuel oil as their hydrogen source.

Ammonia is the second-most synthesized chemical on the planet (behind sulfuric acid), with a global production in 2018 of around 170 million metric tons (m.t.) (2). Thirty million m.t. per year of hydrogen is produced in the SMR and POX units of ammonia plants around the world. But this hydrogen is captive: All of the 30 million m.t. of hydrogen produced each year in SMR and POX units is consumed in the production of ammonia, and none is available for sale as a hydrogen product. It is easy, therefore, to overlook the ammonia industry when considering the hydrogen industry. However, in the context of scaling up hydrogen, it is crucial to understand the role that ammonia will play.

Today's ammonia producers have more operational know-how regarding hydrogen production than all other hydrogen-producing industry segments combined. In competitive commodity markets, that knowledge is the difference between profit and loss.

However, ammonia producers are beginning to demand a different kind of hydrogen — decarbonized, renewable, sustainable hydrogen — and they will require huge quantities of it. In the long term, there will be many large markets for renewable hydrogen; but in the near term, renewable fertilizers represent a feasible, early market opportunity that is orders of magnitude greater in scale than other existing markets.

From fossil to renewable inputs

Industrial nitrogen fixation is arguably one of the greatest accomplishments in human history. From the 19th century electric-arc Birkeland-Eyde process and oven-baked Cyanamid process, to the 20th century high-pressure, hightemperature Haber-Bosch process, radical improvements in production techniques and energy efficiency helped to make nitrogen fertilizers affordable and ubiquitous. Cheap and accessible ammonia-based fertilizers have allowed farmers around the world to feed billions more people than previously possible. Vaclav Smil famously described Haber-Bosch as the "detonator of the population explosion," without which, in simple terms, "almost two-fifths of the world's population would not be here" (3).

The Haber-Bosch process made those older, more energy-intensive processes obsolete a century ago, but the drive for efficiency did not stop. For a hundred years, incremental innovations in engineering, catalysis, scale, and optimization succeeded in maximizing energy efficiency. Today, the specific energy consumption of the Haber-Bosch process is about only one-quarter of what it was in 1930, and it is approaching the theoretical minimum (4). Bestavailable technologies offer specific energy consumptions less than 28 GJ/m.t. (using natural gas feedstocks), nearing the technical limit of 20.9 GJ/m.t. (5). However, efforts to further improve the energy efficiency of the Haber-Bosch process have been delivering diminishing returns for several decades.

Now, a second metric is becoming important: carbon efficiency. Carbon might not be valued today, but there is a significant possibility that it will be in the future — by markets, by consumers, by investors, by regulators, or, perhaps most likely, by an international patchwork that includes all of those.

"Green ammonia" is the term given to ammonia that is produced entirely from sustainable, carbon-free or carbonneutral inputs, like renewable electricity or biomass. This article describes a pathway for navigating the technoeconomic transition from fossil-based ammonia, where energy efficiency is prized above all, to green ammonia, where carbon efficiency drives technology choices.

Energy efficiency

The International Fertilizer Association (IFA) publishes an Energy Efficiency and CO_2 Emissions Benchmark every three years. Data is self-reported by IFA members who volunteer to participate; participants in the 2018 Benchmark included 78 plants in 26 countries operated by 30 companies, representing roughly a quarter of global ammonia production (6).

The Benchmark includes old and new plants, with capacities ranging from small-scale (*e.g.*, 200,000 m.t./yr) to world-scale (*e.g.*, 1,000,000 m.t./yr). However, it is reasonable to assume that these self-reporting producers represent the best-in-class (because, for example, companies who do not join industry associations are not included). Few, if any, coal-fed ammonia plants are represented in the Benchmark. While the Benchmark does not present data for the entire industry, it does provide average net energy efficiency data for its sample of operating plants, and a time-series analysis of the Benchmark data reveals efficiency trends in the industry (Figure 1) (6-8).

Between the first Benchmark in 2003 and the latest one in 2018, the average reported specific energy consumption dropped by about 5%, from 37.5 to 35.8 GJ/m.t. of ammonia (black line in Figure 1).

The range of energy efficiencies captured in that 2018 average is very wide, from a high of 56.6 GJ/m.t. to a low of 25.3 GJ/m.t. While the data is anonymous, the high figure



Figure 1. Energy efficiency in ammonia production is expected to increase in the coming decades, despite diminishing returns on investment, as demonstrated by the IFA benchmark data from 2003 to present (black line). However, even with future improvements, it will not be possible to meet Paris Agreement mandates (orange line) with the typical Haber-Bosch production process that relies on fossil feedstocks. Sources: Adapted from IFA's Energy Efficiency and CO₂ Emissions Benchmark data (from 2003-2018), and Refs. 7 and 8.

was reported by an old plant that uses a heavy hydrocarbon feedstock (coal, naphtha, heavy fuel oil, or petroleum coke); the low figure, on the other hand, represents a plant that bypasses normal measurements of efficiency by using byproduct hydrogen feedstock without the need for any fossil fuel reformation. The most efficient plants (top quartile) operate in the range of 28–33 GJ/m.t., which is near the optimum efficiency level of 28–29 GJ/m.t. for a new, worldscale, natural-gas-fed ammonia plant.

Looking to the future, the executive summary of the 2018 Benchmark suggests that it would be possible to further improve the overall energy efficiency by up to 25%, by replacing old, inefficient plants with new, efficient ones and by replacing heavy hydrocarbon feedstocks, like coal or heavy fuel oil, with natural gas (6). (The Benchmark does not imply that such an improvement is likely, only that it is technically possible.) These changes would require huge investments over several decades, and the resulting fleet of ammonia plants would be, on average, about as efficient as a new plant built today, with a specific energy consumption of 27 GJ/m.t. ammonia (a 25% improvement over the 2018 Benchmark of 35.8 GJ/m.t.). For the sake of visualizing a future-facing time-series, Figure 1 charts this speculative data for 2050.

What this means for technology development, however, is that there is no longer any significant potential for energy efficiency improvements in the Haber-Bosch process itself, because Haber-Bosch is already highly optimized for energy efficiency and its technical limits are insurmountable (refer to the blue line on Figure 1).

Fertilizer producers will need to contribute their fair share of emission reductions, mandated by the Paris Agreement (orange line on Figure 1). (In Figure 1, we assume that energy efficiency is a proxy for carbon dioxide emissions.) But if ammonia plants continue to rely on fossil feedstocks, they will need far greater improvements in the energy efficiency of the Haber-Bosch process. To meet the Paris Agreement targets by 2050, natural-gas-fed ammonia plants would need to perform with a specific energy consumption of only 7 GJ/m.t. of ammonia. This is not possible with the traditional Haber-Bosch technology.

Increasing energy efficiency in order to continue using fossil feedstocks cannot be the future for ammonia production technology.

We can draw some important conclusions from Figure 1:

• A 25% increase in ammonia-production energy efficiency is possible by 2050. This scenario would not be achieved through new technological innovation but, rather, by replacing old and inefficient ammonia plants with natural-gas-fed plants that use modern, energy-efficient technologies.

• Even if this 25% increase in energy efficiency were

realized (and there is no suggestion that this is likely), it would be inadequate to meet the emission reduction targets mandated by the Paris Agreement.

• Energy efficiency is not a perfect proxy for carbon dioxide emissions, but it is a close enough match to demonstrate that future regulatory requirements cannot be met through efficiency improvements in traditional fossil-based Haber-Bosch production. The mandated emission reductions require a shift away from fossil feedstocks and fuels.

• Although it has driven innovation in this industry for decades, energy efficiency will no longer be the dominant metric that drives investments in new ammonia production technologies — carbon efficiency is likely to be the driving metric.

Carbon efficiency

Today's installed ammonia plants are responsible for more than 1% of total global greenhouse gas emissions (9), and regulators around the world are setting targets for reducing those emissions. Technology diversification provides ammonia producers an immediate opportunity to mitigate the risk of punitive regulations. Other reasons to pursue green ammonia include: capturing premium market prices, investing in local business models, avoiding oil and gas market volatility, reducing import reliance, and building resiliency.

The barrier stopping the fertilizer industry from producing green ammonia today is not technological. In the 1920s, the Haber-Bosch process used hydroelectric power to electrolyze water and distill air, making carbon-free hydrogen and nitrogen for use in green ammonia synthesis. In the second half of the 20th century, however, natural gas became the dominant input to Haber-Bosch. Today, only one commercial electrolysis ammonia plant remains in operation because, everywhere else on the planet, it is cheaper to make hydrogen from fossil fuels than from electric power.

Conventional ammonia production is so energy efficient today because the Haber-Bosch process evolved in conjunction with the SMR process, which turns natural gas into hydrogen. These two technologies developed into one co-optimized, highly integrated process. Green ammonia technologies are not yet as mature but, as this article demonstrates, we are now in a period of intense, coordinated research and development.

As Haber-Bosch and electrolysis technologies become increasingly co-optimized, energy efficiency will improve. And as these technologies are deployed at an increasing scale, manufacturing volumes will drive down the marginal cost of green ammonia plants. Additionally, the cost of renewable power inputs will continue to decrease. These three cost-reduction pathways are complementary and mutually reinforcing, and they will help reduce capital and

operational costs and improve process efficiency in the coming decade.

To illustrate the carbon intensity of ammonia production, Figure 2 presents the IFA Benchmark data in Figure 1 from a different perspective: energy efficiency vs. carbon emissions through time and across feedstocks. Various carbon-free technologies will be available in the near future, as estimated by the European Chemical Industry Council (CEFIC) Energy Roadmap 2050 (10) (green line in Figure 2).

The key takeaways from Figure 2 are:

• To reduce carbon emissions sufficiently, ammonia producers will need to phase out the use of fossil feedstocks and fuels and adopt carbon-neutral or carbon-free technologies.

• Future technologies may be less energy-efficient than today's technologies, but they will be more carbon-efficient, and they will be sustainable.

• To support the economics of innovation, the fertilizer industry should value carbon efficiency as well as energy efficiency (pricing both the x and y axes). If only energy efficiency is valued, there will be limited economic rationale for developing and operating low-carbon ammonia plants. In that case, the cost of innovation will be driven by regulations imposed on the fertilizer industry.

Technology development

In 2018, all four of the main ammonia synthesis technology licensors — KBR, ThyssenKrupp, Haldor Topsøe, and Casale — began marketing engineering plans that combine their ammonia synthesis loop with hydrogen produced by electrolyzers. In addition, start-ups and research groups around the world developed green ammonia technologies.

Mature technologies for water electrolysis and ammo-

nia synthesis can be combined, enabling the production of hydrogen from renewable power and the full electrification of the ammonia plant. As of 2018, green ammonia plants combining these technologies are commercially available from industry-leading technology and engineering firms.

Today, all-electric ammonia plants have a specific energy consumption estimated to be 10 MWh/m.t. ammonia, roughly 36 GJ/m.t., and equivalent to the ammonia industry's current average net energy efficiency. By 2030, following technology improvements to optimize the combination of electrolysis and Haber-Bosch, all-electric ammonia plants are expected to have a specific energy consumption approaching 7 MWh/m.t. ammonia (roughly 26 GJ/m.t.) — more efficient than the best natural gas technology available today.

Even with the most efficient technology, ammonia synthesis is energy-intensive because ammonia molecules contain a great deal of chemical energy. The energy density of ammonia is 4.25 kWh/L, or 5.16 kWh/kg. For comparison, gasoline has an energy density of 8.76 kWh/L, and hydrogen contains 0.8 kWh/L (11). Although green ammonia is only half as energy dense as gasoline, it contains no carbon and is more energy dense than hydrogen.

Like the other forms of chemical energy that we use every day (*e.g.*, fossil fuels), ammonia can be combusted in engines, turbines, furnaces, or fuel cells to produce power. In addition, ammonia can be cracked on demand to produce hydrogen. The fact that ammonia can work as either a hydrogen carrier or as a direct fuel makes it viable across a variety of low-carbon energy applications.

Major energy firms consider green ammonia to be a viable technology for long-term and large-scale renew-



Figure 2. IFA benchmark data show that the energy efficiency of ammonia production is increasing and the emissions are decreasing (solid black line). To illustrate the carbon intensity of different fossil feedstocks, IFA benchmark data for a range of best-available technologies is shown (dashed black line). Estimated data for lowcarbon technologies, from the European Chemical Industry Council (CEFIC) (green line), demonstrates the potential value of a portfolio of alternative technologies. Sources: Adapted from IFA's Energy Efficiency and CO. Emissions Benchmark data (from 2003-2018), and Refs. 7, 8, and 10.

able energy storage. Electric power in excess of traditional demand would be used to produce ammonia, which would be stored until it is required as a fuel for power generation or exported to other regions or markets. The long-term storage market is distinctly different from the short-term storage market, which is dominated by battery technologies. For example, the largest battery in the world, the recent Tesla installation at Hornsdale in South Australia, has a capacity of 129 MWh. A standard industrial ammonia tank, on the other hand, has a capacity of 60,000 m.t. — more than 300 GWh — and can store 2,000 times more energy than the world's biggest battery.

In addition, because of its density and ease of transport, ammonia is a cost-effective and safe technology for moving hydrogen in bulk. As a result, companies like Siemens, Engie, Equinor, and Saudi Aramco are now investing in green ammonia.

The current ammonia industry structure developed over decades into a complex integration of upstream fossil fuel producers and downstream fertilizer producers. The future industry structure may repeat this evolution, but with renewable energy firms — power producers, wind turbine manufacturers, and electricity distributors and resellers — becoming more invested in large-scale green ammonia projects. The energy market is orders of magnitude larger than the fertilizer market and energy firms have significant commercial motivation to invest in green ammonia. This has tremendous implications for scaling up hydrogen production.

The opportunity is illustrated in Figure 3, which charts a hypothetical scenario in which a single large-scale energy project using ammonia would dwarf the entire existing global ammonia fertilizer market (12). Using ammonia as a chemical energy storage medium to export 500 GW of renewable power — as has been suggested by Siemens to export Australian solar power to markets in Japan and Germany (13) — would effectively double the total global installed ammonia capacity by 2050.

We can draw some important conclusions from Figure 3:

• The energy market is orders of magnitude larger than the fertilizer market.

• Companies facing the energy market have greater commercial motivation to invest in green ammonia technologies than companies restricted to the fertilizer market. Fertilizer producers risk being left behind in efforts to commercialize green ammonia technologies.

• The energy opportunity for ammonia producers, distributors, traders, and technology licensors is vast, but the market structure is completely different than the existing market. Commercial know-how could therefore become as valuable as new technologies.

There are other technology pathways to green ammo-

nia. For example, Haber-Bosch plants can source hydrogen from non-fossil, carbon-neutral feedstocks, like municipal solid waste, biomass, or recycled plastic, as Showa Denko does in Kawasaki, Japan. Or they can use pure byproduct hydrogen from another industrial process, like Nutrien does at its plant in Joffre, Alberta, which uses hydrogen from a nearby ethane cracker.

Carbon capture and sequestration (CCS) is another decarbonization pathway often linked with ammonia production. This is not a particularly viable option from the perspective of green ammonia, yet it could offer a large-scale bridge solution between the current fossil-based production and future renewable methods.

Several alternative processes for ammonia synthesis are under development. These include electrochemical technologies, as well as new thermochemical processes, including plasma and solar processes, advanced nuclear concepts, and even biological processes that use gene-editing to adapt ammonia-producing bacteria for industrial applications. Some of these technologies may be available at industrial scale in the decades to come; however, this article focuses solely on the technologies that are already at or approaching commercial readiness, an area of innovation dominated by the combination of Haber-Bosch with renewable or lowcarbon hydrogen production.



▲ Figure 3. The energy market is orders of magnitude larger than the fertilizer market. Steady growth in the fertilizer market is illustrated by applying a 2% compound annual growth rate to the current production rates in China (red line). However, if ammonia were used as a chemical energy storage medium to export 500 GW of renewable power from Australia, ammonia production would grow exponentially. By 2050, global installed ammonia capacity would be more than double the capacity in 2019. Sources: Adapted from U.S. Geological Survey "Mineral Commodity Summaries: Nitrogen (Fixed)-Ammonia" reports from 1947 through 2014 and Ref. 12.

Project development

Dozens of green ammonia pilot plants and technology demonstrations are under development worldwide. Some of these are already operational, and a few are summarized here. These projects suggest that the economics of green ammonia will be demonstrated at sites where cheap renewable electricity is competitive with local fossil fuel prices.

Port Lincoln, Australia. ThyssenKrupp is developing a hydrogen power plant in South Australia, due to begin construction this year. The pilot plant will comprise a 30-MW electrolyzer to produce hydrogen from wind and solar (as a form of energy storage), and two technologies for converting the hydrogen back into electricity: a 10-MW gas turbine and 5-MW fuel cell (power generation). The system will also include a small but significant ammonia plant (for fertilizer production), with a capacity of 50 m.t./day, making it among the first commercial facilities to produce distributed ammonia from intermittent renewable resources (*14*). As well as being one of the leading licensors of ammonia synthesis technology, ThyssenKrupp is already a global market leader in electrolysis plants that serve the chlorine industry.

Koriyama, Japan. A green ammonia pilot plant began operations in Fukushima in April 2018 (Figure 4), testing the performance of new Haber-Bosch catalysts in a low-pressure system (15). Unlike SMR units, electrolyzers produce hydrogen at low pressure; identifying and optimizing catalysts to match the operating conditions of electrolyzers reduces the need for hydrogen compression, which adversely impacts the economics of electric ammonia production, especially at small scales. This project is part of the Green Ammonia Consortium, a new industry association that launched in April 2019. Consortium members, including Mitsubishi Heavy Industries, IHI Corp., Ube Industries, Mitsui Chemicals, and Marubeni Corp., among others, are focused on the use of ammonia as an economical way to import carbon-free energy to fuel Japan's hydrogen economy.

Delfzijl, Netherlands. The Dutch government's hydrogen economy roadmap, published in late 2017, called for 4 GW of offshore wind to be developed, enabling the operation of a 1-GW electrolyzer unit to produce 60,000 m.t. of hydrogen, which will be used to feed a Haber-Bosch plant that will produce 300,000 m.t./yr of green ammonia. These green ammonia plants are expected to begin operations in phases, from 2022 to 2024 (*16*).

Ben Guerir, Morocco. In August 2018, the Moroccan phosphate producer OCP announced its intention to develop green ammonia as a sustainable raw material in its fertilizer supply chain. In its supply chain, ammonia is combined with phosphates to produce important fertilizers like di- and mono-ammonium phosphate (DAP and MAP). So far, OCP's plan includes investing in pilot plants in both Germany, which is already under construction (at the Fraunhofer Institute), and Morocco, which has not yet begun construction. In Morocco, the power for the electrolyzers will come from concentrated solar plants.

Oxford, U.K. Siemens began operations at its Green Ammonia Demonstrator in June 2018 (Figure 5). This small pilot plant can produce 30 kg of ammonia per day and is providing insights into the business case for ammonia as a market-flexible energy storage vector. Siemens is not looking to enter the fertilizer market, but is instead looking for new energy technologies in the carbon-free economy.

As a manufacturer of electrolyzer units, wind turbines, electricity management systems, and gas turbines, Siemens is using the site to showcase a range of previously unrelated technologies. As well as the all-electric ammonia synthesis system, the proof-of-concept site also includes combustion assets: an internal combustion engine adapted to generate



Figure 4. As part of the Green Ammonia Consortium, JGC Corp. built a pilot plant capable of synthesizing ammonia with hydrogen produced through the electrolysis of water. The plant, which runs on renewable energy, is located in Koriyama, Japan. Photo by Trevor Brown.



▲ Figure 5. The Siemens Green Ammonia Demonstrator can produce 30 kg of ammonia per day. Image courtesy of the U.K. Science and Technology Facilities Council.



electricity using ammonia as a fuel, which demonstrates the full round trip of renewable power to ammonia and back to electricity (17).

In August 2018, Siemens Gamesa, a subsidiary of Siemens and the world's largest wind turbine manufacturer, announced an agreement to jointly explore eco-friendly ammonia production as a way to store surplus electricity from wind turbines. The goal: a pilot plant at GreenLab Skive in Denmark (18). In the same way that conventional ammonia is a downstream product for today's fossil fuel producers, green ammonia will be a value-added product for tomorrow's electricity producers.

Freeport, TX, U.S. When Freeport Ammonia began operations in 2018, it became the newest world-scale ammonia plant in the U.S. The Yara-BASF joint venture is also the largest producer of low-carbon ammonia on the planet fed with byproduct hydrogen instead of natural gas. Similar engineering was completed during revamps at Yara's Sluiskil (19) and Pilbara (20) ammonia plants, in the Netherlands and Australia, where dedicated hydrogen pipelines can now supply the Haber-Bosch units directly.

The decarbonization of existing ammonia plants is not just feasible but already underway. The companies behind these demonstration plants are not scrappy startups hoping to disrupt the sleepy fertilizer industry. They are global energy and engineering firms and major fertilizer producers shifting toward sustainability.

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