

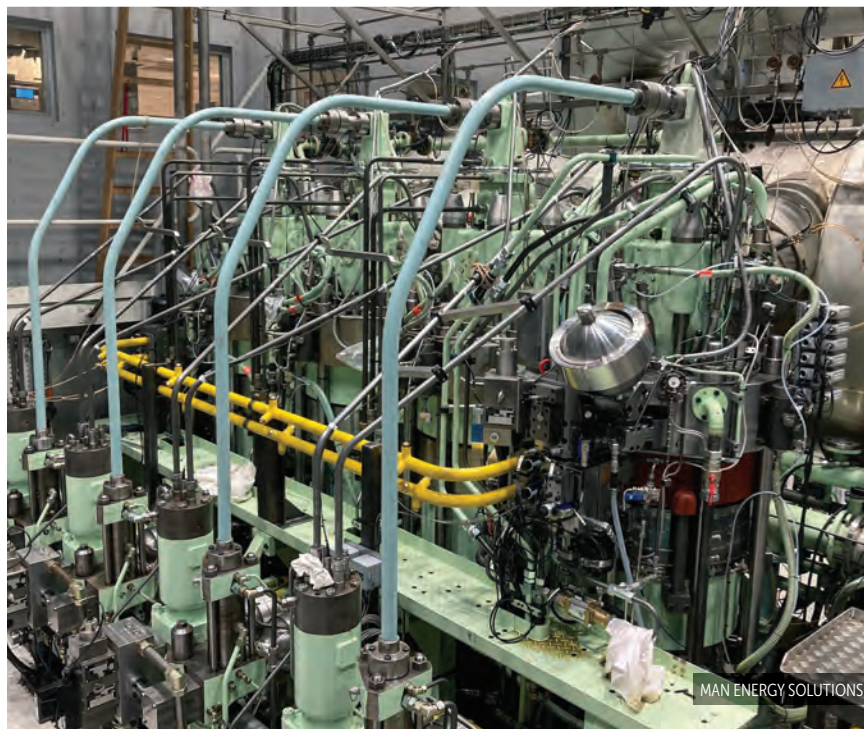
Green ammonia can be a clean energy source

The world's second-most-produced chemical is poised to grow beyond its use in fertilizers to become an efficient medium to carry green hydrogen across the oceans.

As most of the world strives to attain net-zero carbon dioxide emissions by mid century, no fuel is cleaner than hydrogen produced with renewable energy. But hydrogen has a low energy content—just one-tenth that of natural gas at ambient temperature and pressure and one-sixth in liquid form. Ammonia packs more energy per molecule, and it's getting attention for its potential to carry hydrogen—and hence carbon-free energy. Liquid ammonia stores much more hydrogen than liquid hydrogen: 121 kg per m³, compared with 71 kg per m³. And liquefying ammonia is far easier and consumes much less energy.

Ammonia, however, must first solve its own carbon problem. Synthesis by the conventional process is a major contributor to climate change, accounting for 620 million tons of CO₂ each year, about 1.3% of annual global anthropogenic emissions of the greenhouse gas, according to the International Energy Agency (IEA). Nearly all of the approximately 200 million tons of ammonia produced annually by that process is so-called gray ammonia. It originates with hydrogen that is steam-reformed from natural gas or coal and leaves CO₂ as the byproduct. The atmosphere provides ammonia's nitrogen content.

Substantial reductions in CO₂ emissions would be achieved if the greenhouse gas were to be captured and stored—the so-called blue-ammonia method. Green ammonia—manufactured entirely without hydrocarbons—obtains its hydrogen from splitting water in electrolyzers pow-



A PROTOTYPE ammonia-powered ship engine built by MAN Energy Solutions. The company is now building a commercial engine for a Japanese shipbuilder.

ered by renewable electricity. Adding 10 electrolyzers of 30 MW each per month and one large carbon capture and storage plant every four months between now and 2050 would reduce emissions from ammonia production by only 70%, according to the IEA. Near-zero emissions from ammonia production would require even more rapid deployment of blue and green technologies, the agency says.

Hydrolysis is a mature technology and is widely available. But green hydrogen, the component of ammonia made with hydrolysis, is more costly than the hydrogen produced with blue or gray methods. Depending on the cost of electricity where it's produced, green hydrogen ranges from \$4.50/kg to \$12/kg, according to an August 2023 report from BloombergNEF. Gray hydrogen ranges from \$0.98/kg to \$2.93/kg, and blue, from \$1.80/kg to \$4.70/kg. The US Department of Energy has set a goal for green hydrogen to fall to \$1/kg by 2031, the point at which it would become competitive with blue or gray.

"Green hydrogen deployed at manufacturing scale would enable all sorts of technological advancements for green chemicals, ammonia among them. Ammo-

nia is an obvious fit," says Nicholas Thornburg, senior reaction engineer at the National Renewable Energy Laboratory. But green ammonia is not mature enough for industrial-scale manufacturing, he says.

Sameer Parvathikar, director of renewable energy and energy storage at RTI International, says the cost competitiveness of green ammonia is highly dependent on location. His modeling has indicated that green ammonia produced at a small scale in three Minnesota counties already competes with gray, even without subsidies. Using green ammonia as an energy source could provide a buffer between intermittent wind and solar energy sources and the more constant demand for electricity, he says, noting that ammonia is far easier to store than hydrogen. With funding from DOE's Advanced Research Projects Agency-Energy, RTI and its partner organizations are building a portable green-ammonia synthesis plant adjacent to wind and solar farms.

A carrier of energy

Today, about 70% of ammonia is used in the manufacture of fertilizer; the rest goes to various industrial applications.

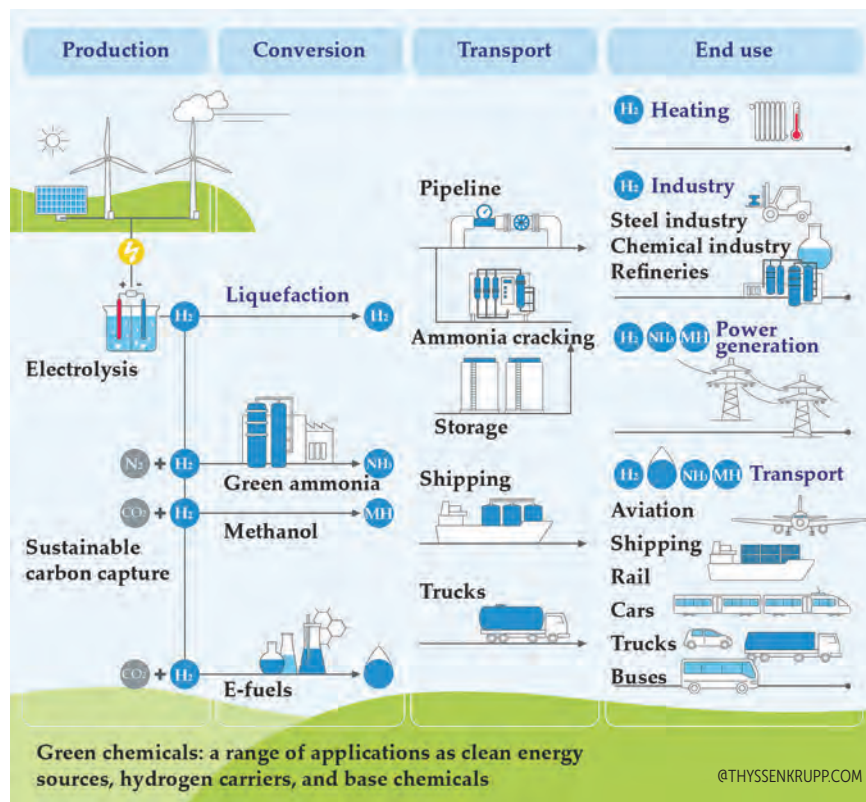
Ammonia can produce energy through direct combustion. Alternatively, once its hydrogen is separated from the nitrogen—by a process known as cracking—it could power many types of fuel cells, including the polymer-electrolyte membrane found in most vehicle applications. Steelmaking, refineries, and chemical plants can also be decarbonized with hydrogen cracked from ammonia. Most fuel-cell types cannot accept ammonia directly; solid-oxide fuel cells can, but they are impractical for mobile and other intermittent applications because of their high operating temperatures of 400–600 °C, notes Thornburg.

Australia, Brazil, India, and South Africa are among the nations that aspire to become suppliers of green hydrogen. On the demand side, energy-poor Japan and South Korea are striving to decarbonize their economies. Hydrogen, though, is not easily transportable by ship. Cooling it to a liquid is highly energy intensive, and much of the liquid will boil off during transit. Ammonia, on the other hand, has long been moved across oceans.

Green-ammonia exports are expected to surge from virtually none today to 121 million tons per year by 2050, says a report from Rystad Energy, a Norway-based market forecasting firm. If announced projects are completed, African nations will generate the most exports, with 41 million tons, followed by Australia with 36 million tons, the report says. Existing liquefied petroleum gas (LPG) terminals in ports could readily be converted to handle ammonia, but there are far too few of them to handle the anticipated demand. Australia currently has seven ammonia terminals and a storage capacity of 173 000 tons. That would accommodate just two to three days of proposed clean-ammonia exports, according to Rystad.

Around 200 very large carriers would be needed to meet the projected 2050 green-ammonia demand, requiring an investment of \$20 billion. Rystad cites growing interest in retrofitting some of the globe's 1500 LPG carriers to transport ammonia.

"Ammonia has a very established supply chain, and hydrogen's supply chain isn't global, only regional," says Thornburg. "So ammonia has some head starts as a favorable solution. It could also be a bridge solution, used for a couple decades as a hydrogen economy



AMMONIA made with power from renewable-energy sources is likely to transport the hydrogen needed for a clean-energy future. Other candidates to serve as hydrogen carriers, including methanol and other reversible hydrocarbons, are low carbon but not CO₂-emissions-free.

grows, and then phased out if there are more compelling solutions."

Europe, keen to shed its dependence on Russian natural gas, is looking to ammonia to meet some of its energy needs. In 2022 Germany unveiled a €900 million (\$970 million) tender for green hydrogen to be imported from outside the European Union. That prompted oil giant BP to announce plans to build a green-ammonia terminal at the port of Wilhelmshaven, Germany. Up to 130 000 tons per year could be imported and cracked to hydrogen there. The derived hydrogen would be fed into a distribution-pipeline network to which Germany has committed €20 billion to build. Meanwhile, the Japanese electricity producer JERA in 2022 initiated a tender for an annual supply of 500 000 tons of green ammonia, with deliveries set to begin in 2027. JERA initially plans to crack the ammonia and blend the hydrogen into the natural gas fuel at a single power station, lowering its CO₂ output.

In the US the DOE last October selected seven regional hydrogen hubs to

share \$7 billion in hopes of stimulating a domestic energy market for green hydrogen. Green-ammonia production is included in the plans of at least one of them, the Heartland hub to be located in the Dakotas and Minnesota.

An IEA report issued in 2021 concluded that producing and transporting ammonia over long distances would be cheaper than shipping liquefied hydrogen: \$14–\$27/GJ for ammonia and \$22–\$35/GJ for hydrogen. A 2021 study by Sudipta Chatterjee, Rajesh Kumar Parsapur, and Kuo-Wei Huang, however, found that for fuel cells, the need for cracking could limit ammonia's economics. Cracking consumes about 46 kJ per mole of ammonia, says Thornburg. "It's not an insanely high energy barrier," he says. It's far less than the 804 kJ per mole required to strip hydrogen from natural gas.

National Renewable Energy Laboratory scientists are nonetheless exploring less-energy-intensive cracking technologies such as photochemistry and autothermal reforming, which couple the endothermic ammonia-dissociation re-

action with the heat from the exothermic oxidative ammonia-reforming reaction.

Shipping Potential

A prime candidate market for green ammonia is maritime shipping, which experts say will be one of the most difficult industries to decarbonize. The 33 000 merchant vessels that ply the high seas belch out around 1 billion tons of CO₂ each year, about 3% of the global total, according to the International Maritime Organization, the United Nations agency that oversees shipping. That's equivalent to the emissions from all passenger vehicles in the US. Nearly all ships today burn heavy fuel oil in their hulking two-cycle engines, says Nikolaos Kourtidis, principal promotion manager and business developer for dual-fuel engines at Denmark's MAN Energy Solutions. MAN engines power around 23 000 merchant ships.

Shipowners today are starting to order dual-fuel vessels, which are capable of burning LPG and other hydrocarbons such as biogas and methanol in addition to fuel oil; about half of MAN's 2760 total marine-engine orders are dual fuel, Kourtidis says. While dual-fuel engines can be retrofitted to burn ammonia, they are not optimized for it, he says. MAN is supplying a purpose-built ammonia-fueled engine for a shipbuilder in Japan. Its maiden voyage will be in late 2025 or early 2026, aboard the world's first ammonia-powered ship, he says.

Other collaborations have said that they will be first with an ammonia-powered ship. Those include ventures headed by Norway-based companies NCE Maritime Cleantech and Yara International, a major ammonia producer.

Shipowners are expected to initially switch to methanol and, to a lesser extent, LPG to lower their emissions. MAN expects ammonia to become a significant player beginning around 2035 and to become the most widely used fuel by 2050. Methanol is expected to rise in tandem with ammonia to around 26% of the total fuel mix, just ahead of fuel oil, which will fall to a 20% share by mid century, according to MAN's outlook.

Special considerations

Ammonia could also be blended into fuel oil to lighten a ship's carbon footprint. Because it ignites at a higher temperature

and higher pressure than fuel oil, burning a fuel mix with more than 50% ammonia will require engine components that can handle those conditions. Kourtidis says MAN's ammonia-engine design has combustion chambers with a geometry designed specifically for ammonia.

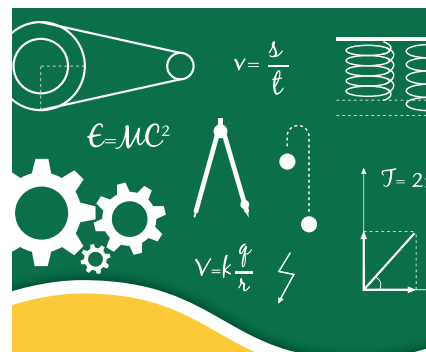
Because of its higher ignition temperature, ammonia requires a pilot fuel—about 5% of the total volume—to initiate combustion. That could be methane or another hydrocarbon. It could also be hydrogen supplied by cracking some of the ammonia on board the ship, notes John Steelman, deputy director of the transportation-decarbonization program at the Clean Air Task Force, a Boston-based nonprofit.

An ammonia-fueled vessel would require three times as much onboard fuel storage as fuel oil. That's more than a small consideration for a seagoing ship that burns 100–200 tons of fuel oil each day, notes Kourtidis. Ammonia's toxicity—high exposures in the blood can cause convulsions—also mandates more safety measures than those needed for fossil fuels, adding further to capital requirements.

Ammonia combustion emits oxides of nitrogen, which are far more potent greenhouse gases than CO₂. Nitrous oxide, for example, has 265 times as much greenhouse effect per unit mass as CO₂ and lasts for more than 100 years in the atmosphere. Ships are already equipped with selective-catalytic-reduction devices that can remove around 80% of those emissions. R&D is underway to further reduce maritime pollution of oxides of nitrogen, says Steelman.

Regulating or imposing a price on carbon emissions will encourage the adoption of low-carbon fuels and ammonia to power ships. That is happening in the European Union, where beginning next year, vessels that move between its ports will be required to reduce their greenhouse gas emissions by an initial 2% and reaching 80% by 2050. The International Maritime Organization has called for a minimum 20% reduction in total maritime greenhouse gas emissions by 2030, and at least 70% by 2040. With the anticipated increase in the volume of trade during that period, individual ships will need to cut emissions by more than 90%, according to the Global Maritime Forum, an industry trade group.

David Kramer



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