GREEN CHEMISTRY

Industrial ammonia production emits more CO_2 than any other chemical-making reaction. Chemists want to change that

Scientists around the world are working to reduce how much greenhouse gas the ammonia-making process emits

by ***Leigh Krietsch Boerner, special to C&EN***

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Credit: Siemens

The Siemens green ammonia test plant uses wind power to convert hydrogen and nitrogen to ammonia.

The **Haber-Bosch process**, which converts hydrogen and nitrogen to ammonia, could be one of the most important industrial chemical reactions ever developed. The process made ammonia fertilizer widely available, helping cause a world population boom as yields from agriculture increased rapidly in a short time.

Globally, ammonia production plants made 157.3 million metric tons (t) of the compound in 2010, according to the Institute for Industrial Productivity's Industrial Efficiency Technology Database. Between 75 and 90% of this ammonia goes toward making fertilizer, and about 50% of the world's food production relies on ammonia fertilizer.

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The rest of the ammonia helps make pharmaceuticals, plastics, textiles, explosives, and other chemicals. Almost every synthetic product we use containing nitrogen atoms comes to us through the Haber-Bosch process in some way, says Karthish Manthiram, a chemical engineer from the

Massachusetts Institute of Technology. “All those nitrogen atoms came from ammonia, which means that there is this enormous carbon dioxide footprint embedded in all the different products that we use.”

That massive carbon footprint exists because although the Haber-Bosch process represents a huge technological advancement, it’s always been an energy-hungry one. The reaction, which runs at temperatures around 500 °C and at pressures up to about 20 MPa, sucks up about 1% of the world’s total energy production. It belched up to about 451 million t of CO_2 in 2010, according to the Institute for Industrial Productivity. That total accounts for roughly 1% of global annual CO_2 emissions, more than any other industrial chemical-making reaction (**see page 23**).

The carbon footprint of ammonia synthesis goes well beyond its energy demands. Hydrogen used for the reaction comes from natural gas, coal, or oil through processes that release CO_2. According to a 2013 joint report from the International Energy Agency, the International Council of Chemical Associations, and the Society for Chemical Engineering and Biotechnology, CO_2 emissions from hydrogen production account for more than half of those from the entire ammonia production process. In total, from hydrocarbon feedstocks to NH_3 synthesis, every NH_3 molecule generated releases one molecule of CO_2 as a coproduct.

And our hunger for ammonia fertilizer is increasing. According to the Food and Agriculture Organization of the United Nations, nitrogen fertilizer demand is projected to increase from 110 million t in 2015 to almost 119 million t by 2020.

Chemists and engineers across the world are trying to make ammonia synthesis sustainable. Some are working to power the reaction with renewable energy sources and to generate hydrogen without fossil fuels. Others want to find a more efficient reaction than Haber-Bosch to synthesize ammonia. The researchers admit that progress has been slow but worth it.

“Ammonia as it’s produced today for fertilizers is effectively a fossil-fuel product,” says Douglas MacFarlane, an electrochemist from Monash University. “Most of our food comes from fertilizers. Therefore, our food is effectively a fossil-fuel product. And that’s not sustainable.”

Ammonia by the numbers

157.3 million:

Metric tons of NH_3 produced worldwide in 2010

451 million:

Metric tons of CO_2 emitted by NH_3 synthesis worldwide in 2010.

~1%:

Percentage of global CO_2 emissions that come from NH_3 synthesis.

Sources: Institute for Industrial Productivity.

At green ammonia plants around the world, including in Japan, England, Australia, and the US, researchers have been experimenting with using renewable energy and feedstocks to make the valuable chemical on small scales. These companies mostly use the conventional Haber-Bosch process, but instead of relying on fossil fuels to generate hydrogen and power the reactions, they’re using water electrolysis and alternative energy sources.

Since last year, the Japanese company JGC has been trying these approaches at a trial plant at the Fukushima Renewable Energy Institute. Through a national program called the SIP Energy Carriers, the company has teamed up with the National Institute of Advanced Industrial Science and Technology (AIST) to get the green ammonia demonstration plant up and running. It can run on solar power, produces hydrogen through water electrolysis, and operates a Haber-Bosch-type reaction using a new ruthenium catalyst that JGC developed with AIST.

“The major advantage of our process is that hydrogen is produced at a much lower pressure than the conventional process,” says Mototaka Kai, project manager at the plant. The hydrogen pressure is around 5 MPa, Mototaka says, which is around one-third to one-quarter that of a traditional Haber-Bosch plant. This lower pressure has two advantages. The reaction is safer because it’s operating at a lower pressure. Plus, the plant requires less energy to pressurize the system. Currently, the plant produces 20–50 kg of ammonia per day.

Siemens in the UK is working with researchers at the University of Oxford, the UK's Science and Technology Facilities Council, and Cardiff University to run a demonstration plant using the typical Haber-Bosch process, powering it with wind. Ian Wilkinson, program manager in corporate technology at Siemens, names two reasons the firm chose to use only mature technology available today to run its plant. First, Siemens wants to show that it can produce ammonia renewably, in a way that it can quickly scale up. The company also views the plant as a test system for ongoing technology development, including Haber-Bosch catalyst development and ammonia combustion tests.

The plan has worked so far. The small plant, set up in shipping containers, takes electricity from a wind turbine, runs it through a hydrogen electrolysis unit, and then uses the resulting hydrogen to synthesize ammonia. If the company runs the plant continuously, it gets 30 kg of ammonia a day, Wilkinson says. "It's a small-scale, proof-of-principle system," he says, noting that the only thing in the plant that the firm didn't buy off the shelf is the synthesis loop in which the actual Haber-Bosch reaction takes place. "We had to build our own. You can't buy them this small," he says.

Ammonia synthesis at a wind farm could help solve one of the biggest problems with renewable energy sources—they produce energy intermittently. The sun doesn't always shine and the wind doesn't always blow, so how do you generate electricity consistently? Burning ammonia produced renewably may be one answer, Wilkinson says. Both Siemens and JGC are interested in green ammonia production not just to make fertilizer but also to synthesize a carbon-free fuel. Similar to gasoline, ammonia can be shipped and stored, and it is easier to deal with than gaseous hydrogen, another possible carbon-free fuel.

"Ammonia is what I like to call a nexus molecule," Manthiram says. "It's useful as a fertilizer. It's useful for food. It's useful for energy storage." Electricity generated through renewable sources can combine nitrogen from the air and hydrogen from water to make a transportable fuel, he says. And companies already ship ammonia across oceans for current uses, MacFarlane says. "That technology is well understood in large quantities of ammonia."

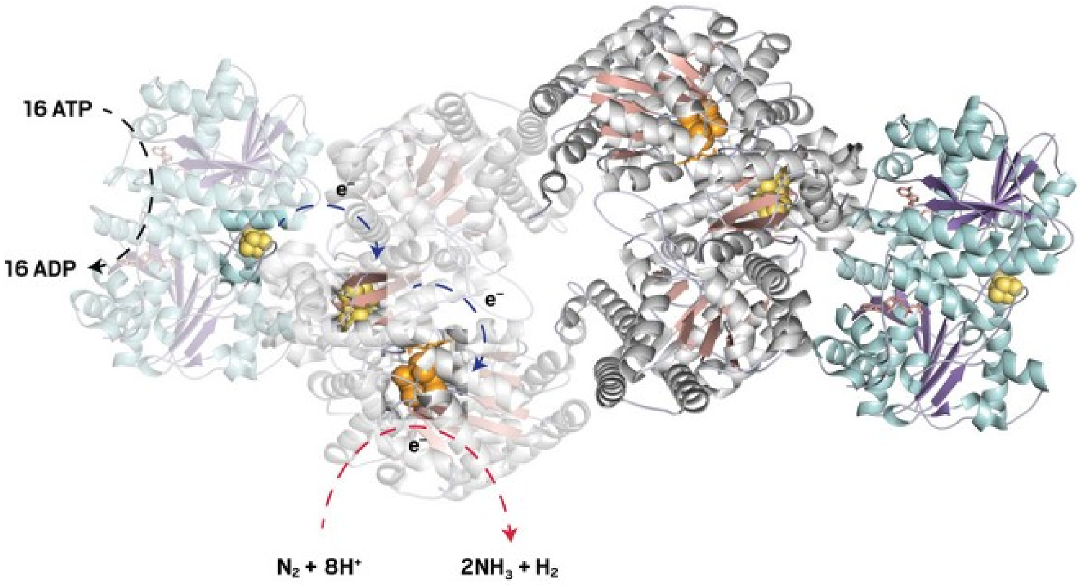
Related: Tackling sustainable fertilizer production with an alternative electrolyte

But no matter how these companies plan to use the ammonia produced by their green plants, they're still mostly using Haber-Bosch to synthesize the molecule. The reaction involves combining hydrogen and nitrogen gas over an iron catalyst, at high temperatures and pressures. And it isn't efficient, MacFarlane says. Each metric ton of ammonia packs about 5 MW h of energy. "The best, most efficient Haber-Bosch plants work at around 10 MW h per metric ton of ammonia," MacFarlane says. "So we're approximately only 50% efficient. It's wasting a lot of energy for what you get."

Switching to renewable feedstocks and energy sources is a good solution in the short term, Manthiram says, because companies can effectively combine current renewable energy technologies with Haber-Bosch. But to improve the sustainability of ammonia synthesis over the long term, scientists have to change the game entirely.

"Many people are looking at alternatives to Haber-Bosch," says Shelley Minteer, a bioelectrochemist at the University of Utah. "How can we do something at low temperatures and atmospheric pressure or near atmospheric pressure?"

Research in the field has taken off since about 2015, perhaps because of expanded funding availability as federal agencies have started to focus on the topic, says Lauren Greenlee, a chemical engineer at the University of Arkansas. Researchers are trying a wide range of approaches:



Credit: Rong Cai

Nitrogenase is the only enzyme known to reduce N_2 to NH_3 at ambient temperature and pressure. The enzyme breaks down the energy-rich adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and uses that energy to power the transfer of electrons from an iron-sulfur cluster (cyan/yellow) through a phosphorus cluster (pink/yellow) to the iron-molybdenum catalytic cofactor (orange), where N_2 gets reduced.

electrochemistry, electrocatalysis, **photocatalysis**, and photoelectrocatalysis. And they're even **taking inspiration from biochemistry**. "That diversity as a field that's growing so quickly is actually fantastic because then you're able to learn from each other what works and what doesn't," Minteer says.

Electrochemical reduction of nitrogen to ammonia over a catalyst has captured the imagination of many scientists. The chemists apply a voltage across an electrochemical cell to drive both water oxidation and nitrogen reduction simultaneously. The catalyst at the anode oxidizes water to form hydrogen ions, which migrate to the cathode, where a different catalyst reduces nitrogen to ammonia. Scientists have developed numerous electrochemical ammonia-synthesis catalysts, including noble-metal nanostructures, metal oxides, metal nitrides, metal sulfides, nitrogen- and boron-doped carbon, and lithium metal.

"What's enticing about [electrochemistry] is that you can get your hydrogen atoms directly from water molecules without having to go through molecular hydrogen," Greenlee says. "If, in theory, your electrochemical process is being driven by renewable energy, you eliminate the need for fossil fuels both from an energy input standpoint for electricity, but also from a hydrogen production standpoint." This method also avoids the need to do electrolysis as a separate step and has the potential to operate at low pressure and possibly low temperature, she says. There are "a lot of pieces of it that are really positive, if we can get it to work."

Electrochemistry also presents a good way to solve a trade-off between reaction rates and yields that chemists must face when running the Haber-Bosch reaction, Manthiram says. The reaction has good yields at very low temperatures, he says, but the rate is sluggish. To speed it up, chemists raise the temperature. But at those high temperatures, the reaction's thermodynamics change, and the yield goes down. So chemists raise the pressure to bring the yields back up. What's special about an electrochemical system is that chemists can increase voltage instead of pressure, Manthiram says. "What normally takes hundreds of bar pressure to achieve can be done with fractions of a volt."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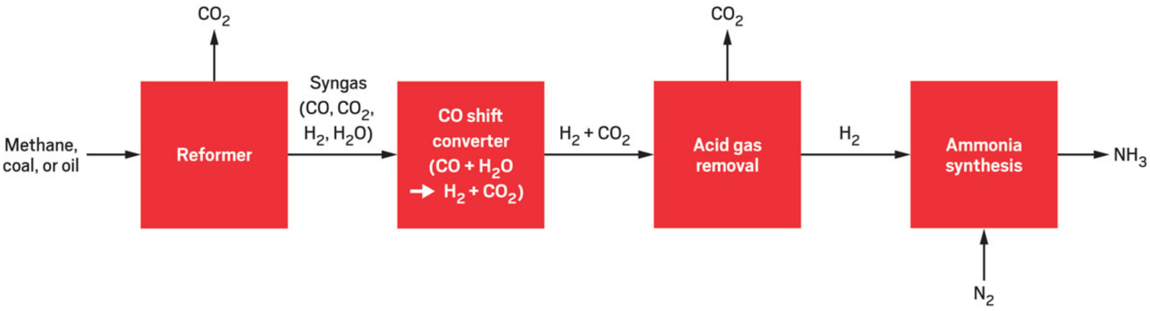
Current process

Today, ammonia synthesis starts with generating hydrogen gas from fossil-fuel feedstocks. A reformer turns the feedstocks into a mixture of gases called synthesis gas (syngas), which includes hydrogen. A CO shift converter combines water and the carbon monoxide from syngas to form CO_2 and more hydrogen, and then acid gas removal isolates the hydrogen for ammonia synthesis. This process releases CO_2 at various steps along the way.



One of the other possible advantages of the electrochemical approach is that the reaction system can be small. A device under development in MacFarlane's lab is about the size of a cell phone. The idea is that it could synthesize ammonia for fertilizer on the scale of a farm or greenhouse, so the material could be used right where it's made, eliminating the need for transport, MacFarlane says.

Meanwhile, other researchers are looking to nature to understand how to efficiently reduce nitrogen to ammonia. Some bacteria use large protein complexes called nitrogenases to grab nitrogen out of the air and make ammonia. Minteer and her team have been studying this system to connect these bacterial enzymes to electrodes to create new electrocatalysts. But they still have a long way to go, Minteer says. Their systems do more proton reduction than ammonia production. The goal is to get to the point where they're making 99% ammonia and 1% hydrogen. Right now, their systems make about 40% ammonia and 60% hydrogen, she says.

Credit: Douglas MacFarlane

This device, developed by Douglas MacFarlane and coworkers at Monash University, can convert hydrogen and nitrogen to ammonia inside a cell phone–sized package.

Scientists throughout the field face this problem with catalyst yield and selectivity. As a result, the ammonia coming out of these non-Haber-Bosch systems is a trickle, not a torrent. It's easier, chemically, to make hydrogen gas than ammonia. "Most catalysts that would be active for nitrogen reduction are also really active for hydrogen evolution," Greenlee says.

"The catalyst needs to be able to break the nitrogen triple bond, which is a very strong and inert bond," Manthiram says. Once the bond breaks, the catalyst needs to form the three nitrogen-hydrogen bonds, all at ambient conditions without high temperatures to accelerate the kinetics. That's a tall order and something that hasn't yet been accomplished, he says.

But maybe chemists have accomplished it and just didn't notice, Minteer says. Scientists have been intensely studying hydrogen-evolution catalysts for about the past 20 years. "We've learned a lot about how to make good hydrogen-evolution catalysts." It's possible, she thinks, that some of the catalysts that failed at hydrogen evolution were actually good at making ammonia. "We need to essentially learn about all those catalysts that people made that didn't work, that don't produce hydrogen, and see if they are useful for producing ammonia," she says.

Greenlee points out that the solutions have to go beyond catalyst design. Scientists need to figure out how to control, reduce, or eliminate the hydrogen-evolution reaction. "It's going to be some combination of catalyst design and controlling the surface environment of the catalyst or the interface to be able to control or suppress hydrogen," she says.

Besides this selectivity issue, scientists also have to worry about.

how long these catalysts last, MacFarlane says, and it's something that many groups are not thinking about yet. For a new ammonia production system to be practical, such as in an electrochemical device like the one his group is working on, catalysts will need to remain active and viable for years, even if the system could be taken apart and refurbished, he says. "Catalyst lifetime is a challenge that's yet to be clearly identified and understood." Most people are not publishing data on lifetimes, but the longest he's seen is about a day, he says.

Related: Nabbing nitrogen from the air to make fertilizer on the farm

The road to Haber-Bosch-free ammonia is long, Minteer says. Whether it's an electrocatalysis, photocatalysis, or biocatalysis system, any promising lab-scale reaction will still take at least a decade or two to make commercial scale, she says.

Searching for alternatives to Haber-Bosch is also risky, Manthiram says, because what scientists are pursuing now may not pan out. But with ammonia production touching so many things that we use every day, including our food and pharmaceuticals, scientists need to find a way to make these lab-scale systems work on larger scales, he says. "It's hard to imagine a world where we're just going to be OK with the way that we make ammonia today."

Errors from the air: The trials and tribulations of developing ammonia catalysts

When Shelley Minteer at the University of Utah first got started studying how bacterial enzymes called nitrogenases produce ammonia, she noticed something funny. Some days, the complexes wouldn't produce ammonia. On other days, they'd produce a lot. The culprit? The cleaning lady.

"We would see spikes in production the days she cleaned the floor," Minteer says.

Nitrogen and ammonia are all around us. Nitrogen makes up 78% of the air we breathe, and nitrogen-containing molecules like ammonia are in numerous plastics, textiles—and cleaning supplies. These molecules can stick to tubing, gloves, and glassware. "It's very difficult, if not impossible, to get all of the contaminants of ammonia out of all the samples," Minteer says. Contaminants also include other nitrogen-containing compounds, such as nitrites and nitrates, which can easily react to make ammonia.

The field of new ammonia-producing catalysts is still young, says Lauren Greenlee, a chemical engineer at the University of Arkansas. "The catalysts just are not very efficient." Scientists make small amounts of a catalyst and then test it in small-scale setups. "The problem is that the amounts of ammonia that are actually produced by many electrocatalysts are not much larger than what you might measure in the background."

So how do you know if the ammonia you're measuring actually came from your catalyst instead of from contaminants in the lab? Without proper controls, you don't, Minteer says. If part of that ammonia is coming from the background, scientists might think that their catalyst is working well when it may not be.

Currently, journals don't require data on specific control experiments to publish data from an ammonia-producing catalyst. Whether the journals should require those controls is a matter of debate in the community. "I've talked to some people who have argued that we should wait and not do controls," Greenlee says. Maybe, these members of the field argue, the catalyst community will move forward, and catalysts will get more efficient so that the difference between what the catalyst is producing and the amount of ambient ammonia will become larger.

While that may happen, that wait-and-see approach has issues, Greenlee says. If a group reports a high-performing catalyst, other researchers may start working with it, thinking that it’s an improvement. “But what if that’s not the right direction to go because the group didn’t measure their background correctly?” Greenlee asks.

Greenlee thinks that researchers should run controls and take background measurements for every catalyst on every day they run experiments. Such controls would include running experiments with isotopically labeled molecules as a final evaluation of successful catalysts so scientists know where the nitrogen in ammonia came from. Papers should also report the results from these control experiments. “Even if a lab is doing appropriate controls, it’s very hard to tell as a reviewer” because they’re not adequately reported in the paper, she says.

“There are surely errors made in the history of science,” says Karthish Manthiram, a chemical engineer at the Massachusetts Institute of Technology. “As long as everyone admits to their errors, we all move forward together.”

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