

# Nitrogen fixation research could shed light on biological mystery

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Fertilizer is applied to an agricultural field. Credit: SoilScience.info (CC BY 2.0)

Inspired by a natural process found in certain bacteria, a team of Caltech researchers is inching closer to a new method for producing fertilizer that could some day hold benefits for farmers—particularly in the developing world—while also shedding light on a biological mystery.

Fertilizers are chemical sources of nutrients that are otherwise lacking in

soil. Most commonly, fertilizers supply the element nitrogen, which is essential for all living things, as it is a fundamental building block of DNA, RNA, and proteins. Nitrogen gas is very abundant on Earth, making up 78 percent of our atmosphere. However, most organisms cannot use nitrogen in its gaseous form.

To make nitrogen usable, it must be "fixed"—turned into a form that can enter the food chain as a nutrient. There are two primary ways that can happen, one natural and one synthetic.

Nitrogen fixation occurs naturally due to the action of microbes that live in nodules on plant roots. These organisms convert nitrogen into ammonia through specialized enzymes called nitrogenases. The ammonia these nitrogen-fixing organisms create fertilizes plants that can then be consumed by animals, including humans. In a 2008 paper appearing in the journal *Nature Geoscience*, a team of researchers estimated that naturally fixed nitrogen provides food for roughly half of the people living on the planet.

The other half of the world's food supply is sustained through artificial [nitrogen fixation](#) and the primary method for doing this is the Haber-Bosch process, an industrial-scale reaction developed in Germany over 100 years ago. In the process, hydrogen and nitrogen gases are combined in large reaction vessels, under intense pressure and heat in the presence of a solid-state iron catalyst, to form ammonia.

"The gases are pressurized up to many hundreds of atmospheres and heated up to several hundred degrees Celsius," says Caltech's Ben Matson, a [graduate student](#) in the lab of Jonas C. Peters, Bren Professor of Chemistry and director of the Resnick Sustainability Institute. "With the iron catalyst used in the industrial process, these extreme conditions are required to produce ammonia at suitable rates."

In a recent paper appearing in *ACS Central Science*, Matson, Peters, and their colleagues describe a new way of fixing nitrogen that's inspired by how microbes do it.

Nitrogenases consist of seven iron atoms surrounded by a protein skeleton. The structure of one of these nitrogenase enzymes was first solved by Caltech's Douglas Rees, the Roscoe Gilkey Dickinson Professor of Chemistry. The researchers in Peters' lab have developed something similar to a bacterial nitrogenase, albeit much simpler—a molecular scaffolding that surrounds a single iron atom.

The molecular scaffolding was first developed in 2013 and, although the initial design showed promise in fixing nitrogen, it was unstable and inefficient. The researchers have improved its efficiency and stability by tweaking the chemical bath in which the fixation reaction occurs, and by chilling it to approximately the temperature of dry ice (-78 degrees Celsius). Under these conditions, the reaction converts 72 percent of starting material into ammonia, a big improvement over the initial method, which only converted 40 percent of the starting material into ammonia and required more energy input to do so.

Matson, Peters, and colleagues say their work holds the potential for two major benefits:

### **Ease of production:**

Because the technology being developed does not require high temperatures or pressures, there is no need for the large-scale industrial infrastructure required for the Haber-Bosch process. This means it might some day be possible to fix nitrogen in smaller facilities located closer to where crops are grown.

"Our work could help to inspire new technologies for fertilizer

production," says Trevor del Castillo, a Caltech graduate student and co-author of the paper. "While this type of a technology is unlikely to displace the Haber-Bosch process in the foreseeable future, it could be highly impactful in places that don't have a very stable energy grid, but have access to abundant renewable energy, such as the developing world. There's definitely room for new technology development here, some sort of 'on demand' solar-, hydroelectric-, or wind-powered process."

## **Understanding natural nitrogen fixation:**

The nitrogenase enzyme is complicated and finicky, not working if the ambient conditions are not right, which makes it difficult to study. The new catalyst, on the other hand, is relatively simple. The team believes that their catalyst is performing fixation in a conceptually similar way as the enzyme, and that its relative simplicity will make it possible to study fixation reactions in the lab using modern spectroscopic techniques.

"One fascinating thing is that we really don't know, on a molecular level, how the nitrogenase enzyme in these bacteria actually turns nitrogen into ammonia. It's a large unanswered question," says graduate student Matthew Chalkley, also a co-author on the paper.

Peters says their research into this catalyst has already given them a deeper understanding of what is happening during a nitrogen-fixing reaction.

"An advantage of our synthetic iron nitrogenase system is that we can study it in great detail," he says. "Indeed, in addition to significantly improving the efficiency of this [new catalyst](#) for nitrogen fixation, we have made great progress in understanding, at the atomic level, the critical bond-breaking and making-steps that lead to ammonia synthesis from [nitrogen](#)."

If processes of this type can be further refined and their efficiency increased, Peters adds, they may have applications outside of fertilizer production as well.

"If this can be achieved, distributed solar-powered ammonia synthesis can become a reality. And not just as a fertilizer source, but also as an alternative, sustainable, and storable chemical fuel," he says.

**More information:** Matthew J. Chalkley et al. Catalytic N-to-NH Conversion by Fe at Lower Driving Force: A Proposed Role for Metallocene-Mediated PCET, *ACS Central Science* (2017). [DOI: 10.1021/acscentsci.7b00014](https://doi.org/10.1021/acscentsci.7b00014)

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