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Start-Ups To Mine Methane Troves

Small firms are developing technology for converting natural gas to fuel and chemicals

By **Ann M. Thayer**

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METHANOTROPHS

Calysta's Silverman (right) and Sol Resnick, director of the firm's fermentation effort, hope to advance methane-converting bacteria.

Credit: Calysta

Natural gas is quickly rising to the top of the energy charts. In the face of the cheap fuel, wind and solar energy technologies are finding it hard to compete. Private investment in biofuels and biobased chemicals has slowed, and some methods for converting biomass to fuels are pretty much dead. The slower-than-expected pace of development is causing a reassessment among some government backers of new energy technologies, suggests Nicolas Denis, a principal in the sustainability and resource productivity practice at the consulting firm **McKinsey & Co.** At the same time, the discovery of new alternative sources, such as shale gas, is leading governments to rethink where they will place their bets, he says.

In the U.S., confidence in domestic gas supplies brings other options to the fore. One promising approach is the use of natural gas instead of oil, sugar, or biomass as a less expensive feedstock for fuels and chemicals. Selectively converting methane, the main component of natural gas, to something more desirable is notoriously hard, but a handful of small technology firms believe they have ways to overcome the problem.

Existing gas-to-liquids methods usually oxidize methane to syngas, a mixture of carbon monoxide and hydrogen, and then convert the syngas to methanol or other hydrocarbons. The approach works but is challenged by both high capital costs and low conversion efficiencies, the **Department of Energy** said earlier this year.

Calysta Energy, based in Menlo Park, Calif., says it has a lower-capital biological conversion method that operates near room temperature and pressure. The firm sees it being installed at small or remote gas reserves where it doesn't pay to build a traditional gas-to-liquids plant.
"The biology allows us to operate at a much smaller scale economically," says Calysta's chief scientific officer, Josh Silverman. "At stranded gas reserves, the principle would be to have a small—ideally, skid-mounted—conversion unit that can sit on a wellhead and convert the gas to something more valuable than methane."

The firm's technology relies on methanotrophs, naturally occurring bacteria that feed on methane. The bacteria's methane monooxygenase (MMO) enzyme converts methane to methanol. The cell then metabolizes the methanol and incorporates it into cellular material. The cellular material itself, or the output of other enzymatic reactions, can be directed toward desired fuel and chemical products. Because the MMO enzyme as a first step creates a stabilized oxygen radical, it can, for example, convert other alkanes to alcohols, Silverman says.

DOE is pushing methane activation and biosynthesis to produce low-cost liquid transportation fuels up on its agenda. Last month, its Advanced Research Projects Agency-Energy, which looks for transformative technologies, launched the $20 million Reducing Emissions Using Methanotrophic Organisms for Transportation Energy program. Calysta was on the **ARPA-E** list of potential partners along with 26 universities, six national labs, and 10 technology companies. Calysta also has a Small Business Innovation Research grant from the National Science Foundation.

Calysta was spun off of the synthetic biology company **DNA2.0** two years ago to apply DNA2.0's gene and enzyme engineering technology to methanotrophs. It's headed by Alan Shaw, the former chief executive officer of **Codexis**, a biocatalysis firm that Shaw built into a developer of biomass-based fuels and chemicals.

Shaw now champions natural gas with the same fervor he once had for cellulose. "There's a bit of a mea culpa here," he admits. "Only recently it dawned on me that we were really pushing water up a hill" by trying to convert biomass-derived sugars into hydrocarbons.

"It just doesn't make sense for lots of reasons," Shaw continues, listing among them supply, logistics, cost, and processing issues around using biomass. "The whole sector is troubled. A lot of the attempted innovation that has failed was all very high profile, and it was fueled by government incentives that were misplaced.

"The market is still real—we still need lower-cost hydrocarbons—the biology is real, but the feedstock is broken," he says. Shaw now believes that natural gas, which he says is one-fifth to one-tenth the cost of oil or sugar on a per-carbon-atom basis, is the fix. "The trick here is directing the biology to a feedstock that makes sense," he says.

Through fermentation, Calysta envisions using its bacteria to produce lipids and fatty acids for subsequent conversion into diesel. The company estimates that a methane-based biological process can produce liquid fuel at less than half the cost of other biological methods, allowing direct competition with petroleum-based fuels.

To make chemicals, Calysta intends to select and extract enzymes for use in direct oxidations or on the front end of a synthesis. Here it aims to license its technology and work with partners to repurpose their current synthesis pathways to start from methane instead of sugar. And to make that switch easier, "we are designing our systems to fit within the existing infrastructure as much as possible," Silverman says.

To compete in the market, the bioconversion of methane to liquid fuels faces three primary challenges, according to DOE: low carbon yield, low energy efficiency, and slow kinetics. Calysta has been working to optimize its technology by improving the bacteria's growth rates and tolerance to fermentation conditions, Silverman says. "Currently we are in the lab at the 3- to 5-L fermenter range." He expects to get to pilot scale within the next couple of years.

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HIGH MILEAGE

Methane can be a more efficient source of fuels than biomass

FEEDSTOCK	MOLECULAR WEIGHT	CARBON CONTENT	PROCESS	THEORETICAL DIESEL YIELD, G/G[a]
Sugar/biomass	~180	40%	Fermentation	31%
			Pyrolysis	47%
Methane	16	75%	Fermentation	59%

a Grams product/grams feedstock. **SOURCE:** Calysta Energy

For many of the products Calysta wants to make, the company calculates that its process will still be cost-competitive even if natural gas prices are three to four times what they are now, Silverman says, and he expects they will stay low for the foreseeable future. Compared with oil and sugar prices, "that gives us a lot of headroom," he says.

Calysta isn't alone in trying to turn methane into useful products. San Francisco-based **Siluria Technologies** is tackling the oxidative coupling of methane to produce the building-block chemical ethylene using specially designed catalysts. Methane is cheaper than current ethylene cracker feedstocks, such as naphtha or even ethane.

Unlike major petrochemical firms that tried to develop oxidative coupling technology in the 1980s, Siluria has been able to create a process that makes economic sense, says CEO Edward J. Dineen. A 32-year petrochemical industry veteran, he joined Siluria in March from the biobased fuels and chemicals firm **LS9**.

Siluria's technology originates from biotemplating work by Massachusetts Institute of Technology professor Angela M. Belcher. The company grows inorganic catalysts on a virus that provides surface morphologies optimized for oxidative coupling.

The five-year-old company has attracted more than $60 million in financing and has run its process at its own pilot-scale facility for about a year. There, Dineen says, the process runs at better conditions, such as lower temperatures, than did previous efforts in the field and is hitting the commercial targets that Siluria needs to move forward.

Siluria is now planning a demonstration unit that will produce thousands of pounds of ethylene per day. The company has hired a contractor to pick a site for the plant, likely on the U.S. Gulf Coast and near the energy and petrochemical companies that might be interested in the technology.
Dineen sees advantages of the technology over other chemical processes. As a route to ethylene, he says, it will be less capital-intensive and consume up to two-thirds less energy than naphtha steam-cracking and likely will have advantages even over ethane cracking. It will be less capital-intensive and more energy efficient than methanol-to-olefins, a route to ethylene by way of syngas, and also will compete with Fischer-Tropsch processes that make fuels and chemicals, Dineen says.

Russell Heinen, director of technology and analytics for the consulting firm IHS Chemical, spoke highly of Siluria's approach at a conference his firm sponsored last month. He noted in particular how combining molecular biology and nanotechnology has advanced the field of oxidative coupling and said the technology "holds great promise for improving catalysis" in other chemical disciplines as well.

Several other firms are pursuing the conversion of methane to fuels and chemicals. England-based **Oxford Catalysts** is looking to use Fischer-Tropsch chemistry cost-effectively at small scale. The more-than-10-year-old company has developed microchannel gas-to-liquids reactors that could run on remote or unconventional gas sources. In 2012, the firm said it successfully installed and operated a commercial-scale unit producing 25 barrels of fuel per day at an unidentified client's location.

Meanwhile, Illinois-based **Coskata** and New Jersey-based **Primus Green Energy** have increased their emphasis on natural gas. Both have nonbiological technologies that make syngas out of natural gas as well as biomass. Coskata ferments the resulting syngas, whereas Primus chemically converts it to chemicals and fuels. Last month, Primus began supporting research at Princeton University on synthetic fuels, including the assessment of the economics and sustainability of various gas-to-liquids technologies.

The companies' shift toward natural gas is in recognition of the fuel's new economics. McKinsey's Denis points out that many companies using gasification to process biomass have shut down or moved to other feedstocks.

But investments in the biological transformation of biomass are "on the verge of being proven commercially viable," and he's especially interested when it can turn waste materials into something useful. Overall, Denis sees value in pursuing multiple approaches that will take advantage of different feedstocks and will play differently in the marketplace.

"Diversification is good," Denis says. "It is a formidable asset that the industry has created by having the option to use both gas and biological waste."
*With additional reporting by **Alex Tullo***

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