BIG POTENTIAL with Small-Scale Carbon Capture

METRICS and certifications such as "organic," "sustainable," or "sustainability in practice" are key business drivers in the winemaking industry. To achieve sustainable, carbon neutral practices and reduce the industry's carbon footprint, some winemakers have considered renewable energy, such as solar and wind for their operations, along with organic agriculture and bioenergy production from solid wastes. However, for California wineries, the fermentation process alone generates between 400,000 and 450,000 tons of carbon dioxide (CO_2) per year. Methods for significantly reducing CO_2 emissions—a byproduct of microbial fermentation of the sugars in wine grapes—has been an area of great interest to the wine industry.

At Lawrence Livermore, researchers test, prove, and mature CO_2 emissions reduction and management technologies, honing a core capability to address climate challenges and their impacts on the nation's energy security. (See *S&TR*, January/February 2022, pp. 4–11.) When Continuum, a winery in California's Napa Valley, contacted the Laboratory in 2020 to discuss sustainable winemaking efforts, Livermore scientists recognized an opportunity of particular interest. The CO_2 emitted was biogenic—a byproduct of microbial fermentation of the carbohydrates in wine grapes—and thus neutral emissions from a carbon cycle perspective. Therefore, capture and sequestration of this CO_2 would be considered carbon dioxide removal, a way to draw down the amount of CO_2

in the atmosphere. In response, staff scientist Nathan Ellebracht and his team applied advanced manufacturing and industrial chemistry expertise to devise a technology that captures CO_2 from fermentation at the source and then safely and reliably sequesters the carbon from being released back into the atmosphere. This effort has opened a pathway for winemakers and other industries on a similar scale to achieve notable carbon emission reductions.

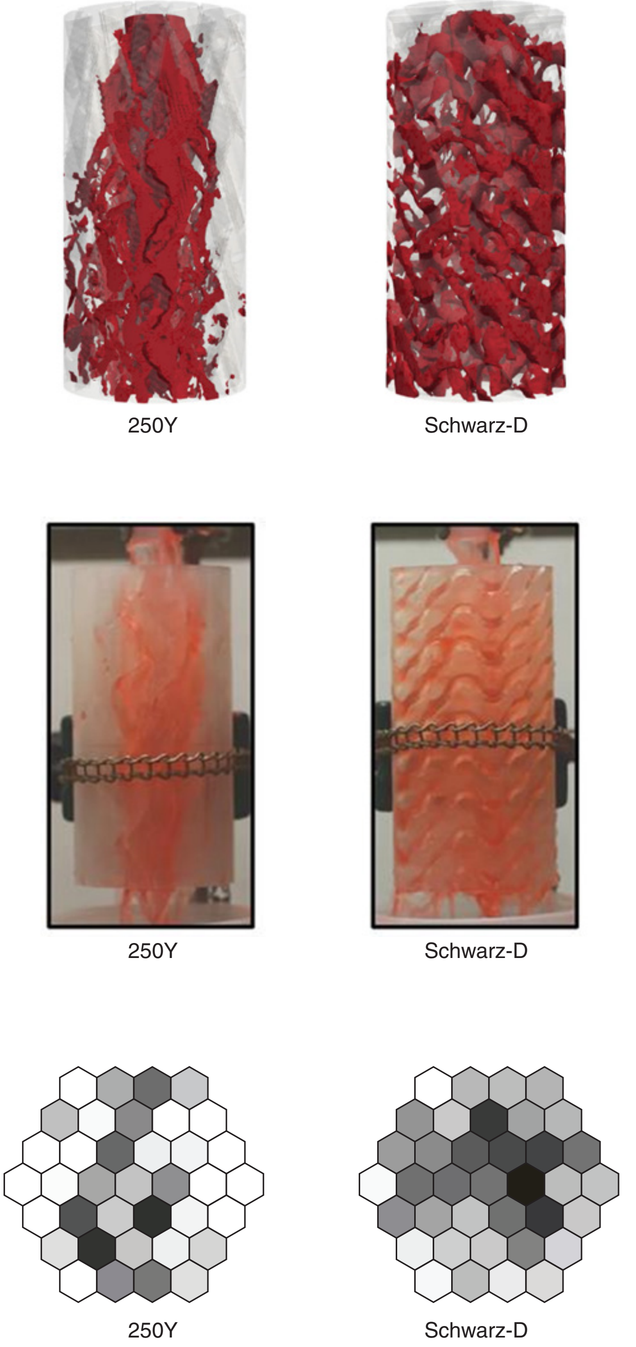
Point Source Carbon Capture

On an industrial scale, point source capture of CO_2 typically involves dissolving the gas into a liquid solvent inside an absorber—a massive cylindrical tower that enables the contact of CO_2 gas and the solvent. For the CO_2 and the liquid solvent to make effective contact in the tower, the liquid travels through a convoluted structure (called "packing") with a high surface area that increases the mass transfer efficiency of CO_2 gas into the solvent. Current packing materials—stacked sheets with a wavy surface similar in appearance to corrugated metal—have not changed much in the last several decades, leading to stalled improvements to the process.

Ellebracht and the Livermore team selected packing materials by simulating ideal flow and maldistribution—a measure of how unevenly flow is distributed across a horizontal cross-section of packing—and then verifying findings experimentally. The team—led initially by Josh Stolaroff and later by Du Nguyen—3D-printed selected geometries with tortuous bends and curves called triply periodic minimal surfaces (TPMS). These geometries were fabricated with the same physical surface area per volume as comparable conventional packing (250 square meters per cubic meter), but the improved geometry significantly increased CO_2 capture via mass transfer, one of the key metrics to determine packing structure effectiveness.

"With normal packing structures in which the liquid is perfectly spread out, we expect to see less than 250 square meters of liquid film because the liquid cannot touch every single centimeter of the packing," says Ellebracht. "With TPMS geometries, the effective area was larger than the geometric area. The liquid and gas were mixing so well, the effect was as if the structure had a much larger surface area." Unlike many absorber towers, which have dedicated sections to redistribute the solvent to improve CO_2 gas capture efficiency, the TPMS geometries also handle redistribution. For some packing configurations, mass transfer increased 50 to 60 percent, reducing the absorber space required and leading to absorber cost savings of more than 30 percent.

Also encouraging to the team was the lack of trade-offs observed for two aspects of fluid mechanics: pressure drop and flooding in the absorber tower. Pressure drop is the force needed to push gas through a column of liquid. Smaller channels in the packing provide a higher surface area but require more force.


250Y Schwarz-D

250Y Schwarz-D

250Y Schwarz-D

Results of simulated flow (top row) and experimentation (second row) for different packing materials such as industry-standard 250Y packing (left column) and Schwarz-D (right column) packing enabled the Livermore team to identify a packing material that maximizes solvent contact with CO_2 effluent gas in the absorber tower. The bottom images demonstrate how the packing materials can redistribute liquid introduced in a small area at the top of 15-centimeter packing sections.

Flooding results when too much liquid and gas flow through the tower and mix so vigorously that they foam over, similar to a covered pot of boiling water. The point of flooding determines the required height and width of the absorber tower. As pressure drop and tower size increase, so do the costs to build and operate the towers, as energy is required to push the gas through the column and overcome pressure drop.

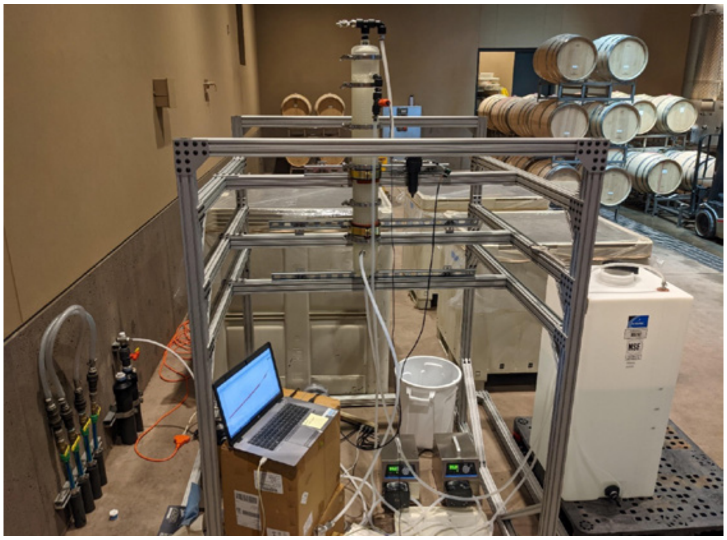
Two-phase flow pressure drop and flooding are challenging to elucidate through modeling, so Ellebracht and his team tested and identified two-phase flow pressure drop through experiments using differential pressure transducers and a custom-built apparatus to measure flooding. Ellebracht says, “We expected the better interaction between gas and liquid to lower the point of flooding as packings with improved surface geometries often experience more rapid flooding and higher pressure drops. Surprisingly, we saw no such trade-offs in our design, which is a good sign for its efficiency and cost-savings potential.”

Mineralizing Carbon Dioxide

Although several liquid solvents can capture CO_2 in larger industrial applications, many do not scale down well for smaller industries. Typical solvents often require large, integrated systems to continuously heat the solvent in a parallel process to strip off and store the CO_2 as a purified gas and recycle the solvent to capture more CO_2. Alkaline caustic solvents such as potassium hydroxide may avoid the use of a heating unit to remove CO_2 as a gas. This strongly basic aqueous solution dissolves CO_2 as carbonate and bicarbonate, similar to the way CO_2 moves in and out of oceans and other natural systems. Harnessing this approach allowed Ellebracht and his team to sequester CO_2 through a process that mimics Earth’s natural carbon cycle: mineralization.

In the mineralization process, the carbonate solution is mixed with another chemical solution that spontaneously converts CO_2 from the carbonate form to a solid form. Lime (calcium oxide) is commonly used to react with carbonates to form limestone. However, Ellebracht and his team wanted to find more effective and efficient options, as the production of lime releases a large amount of CO_2, negating the CO_2 being captured and sequestered.

Working with staff scientist Corey Myers, the team identified magnesium as a promising alternative. Magnesium chloride ($MgCl_2$), a low-value material and byproduct of desalination, was used as the cation source to turn the dissolved CO_2 into a mineral slurry. The team conducted experiments at different temperatures, reagent ratios, and additional conditions to determine how to sequester the most dissolved carbonate from the solution while using as little magnesium as possible. After many trials, mixing the $MgCl_2$ and carbonate at room temperature produced a mineral, nesquehonite, with the optimal one-to-one magnesium-to-carbonate ratio at high yields. By pumping and stirring the $MgCl_2$ solution into the carbonate solution, the contents changed to an opaque, milky solution. When the chemical reaction was complete, the team was left with salty water and a magnesium carbonate that had successfully sequestered the CO_2. Following a simple filtration process, the nesquehonite was isolated.



CO_2 off-gas from tanks of fermenting wine at Continuum, a Napa Valley winery, travels through plastic tubing and into the bottom of Livermore’s absorber tower (center). Liquid solvent from the square container (right foreground) flows through the absorber packing.

Nesquehonite, a magnesium carbonate mineral containing the sequestered CO_2, is produced by mixing the saturated solvent with a magnesium chloride solution. Squeezing excess water from the nesquehonite results in a powdery substance safely containing the captured CO_2.

From Laboratory Setting to Winery Fermentation

In 2021, after demonstrating carbon capture methods at Livermore, the team set out to test them at Continuum. While there, Ellebracht and his team assessed Continuum's fermenters to determine total CO_2 production and release rates. With this information, the team then returned to the Laboratory to build the absorber and packings, test their carbon capture and mineralization process, and prepare to incorporate their setup at the winery during the 2022 fermentation season.

Unlike beer brewing, which uses dry grains and ferments year-round, wine fermentation takes place during a narrow window of a few weeks after each annual harvest. Timing was not anticipated to be a challenge for the Livermore team until a multiday heat wave across California in 2022 accelerated Continuum's picking and fermentation schedule. As a result, Ellebracht and colleagues set up their equipment sooner than initially planned.

Ellebracht and his team connected the absorber tower to off-gas from the fermentation tanks so CO_2 could be captured by the solvent as it flowed through the packing structure. Once the CO_2 was captured, the team deployed the mineralization process they had developed in a laboratory at the winery. "Continuum was extremely generous with its time, space, and equipment," says Ellebracht. Many of the tools used in winemaking also have utility in Livermore's carbon capture and sequestration efforts, including filters that could be repurposed for drying the magnesium carbonate holding the sequestered CO_2. In addition to scientific research, the project involved a fair bit of manual labor. Large-scale facilities typically have machinery that automates the filtering and drying process. For Ellebracht's smaller scale setup, he and the team had to do everything manually. Ellebracht says, "I spent a lot of time shoveling the mineral product into the filter and then using the shovel to press the water out."

Tackling CO_2 emissions at wineries offers opportunities for real environmental improvements with negligible impact on the cost of the product. With approximately 0.11 kilograms of CO_2 emissions produced through fermentation, per wine bottle, and a carbon capture cost between \$100 and \$1,000 per ton of CO_2 emissions, early cost estimates by Ellebracht's team indicate that implementing point source carbon capture technology such as Livermore's would add only \$0.01–\$0.11 in production costs per bottle.

Ellebracht's research and methods for carbon sequestration show great promise for reducing CO_2 emissions within smaller scale settings, but plenty of opportunity exists for growing the technological applications. Following their successful proof-of-concept testing at Continuum Winery, the team seeks to test their packing structures at the National Carbon Capture Center (NCCC) in Alabama. NCCC accesses the flue gas from a nearby power plant, which would allow the Livermore team to test their design with a CO_2 point source at a much larger scale. The unit tested at NCCC will measure about 0.3-meter (m) wide and just over 4.5-m tall, compared to the technology tested at Livermore and Continuum, which was 0.1-m in diameter and 0.6-m tall.

Team members (left to wright) Du Nguyen, Melinda Jue, and Nathan Ellebracht analyze absorber operation data in the lab.

"The NCCC work is the next logical step after the winery project," says Ellebracht. "Testing and proving our technology at this increased scale will be a significant technical validation of our packing technology." With that endorsement, Ellebracht's technology could assist other industrial CO_2 capture applications in agriculture, fertilizer development, power generation, and manufacturing, opening more doors for innovative and effective methods for promoting sustainable operations and combatting climate impacts.

— Sheridan Hyland

Key Words: absorber, carbonate, carbon dioxide removal, nesquehonite, packing, point source carbon capture, Triply Periodic Minimal Surface (TPMS).

For further information contact Nathan Ellebracht (925) 423-5328 (ellebracht1@llnl.gov).