Computational Tools Accelerate Development of Innovative Membranes to Cut Cost of Carbon Capture

By Cassie Shaner

As the U.S. energy landscape evolves, the nation's abundant coal resources continue to provide valuable energy that helps meet growing demand at an affordable cost. Coal accounted for more than 27% of U.S. power produced in 2018, supplying more than 1.1 trillion kilowatt hours of electricity. Yet, as energy demand continues to rise around the world, cost-effective carbon capture technologies are needed to boost the viability of the nation's coal-fired power fleet and ensure responsible stewardship of the environment.

Carbon capture technologies reduce harmful greenhouse gas emissions by capturing carbon dioxide (CO_2) from coal-fired power plants; however, existing options are often costly for industry and consumers. Polymer-based membranes used to separate CO_2 from post-combustion flue gas offer simplicity for conventional pulverized-coal plants, with reduced up-front and long-term costs. However, capturing significant amounts of CO_2 using current technology remains cost-prohibitive, with costs estimated at about $60 or more per metric ton of CO_2 captured.

NETL is working to cut that cost by exploring the use of mixed matrix membranes (MMMs), which combine sturdy polymers with inorganic crystalline particles that enhance selectivity and permeability. An ongoing project is using powerful computational tools to screen more than 1 million potential MMMs, evaluate their properties and estimate the associated cost of carbon capture (CCC) — ultimately indicating that costs could be reduced to less than $50 per metric ton of CO_2 removed using MMMs.

Bridging atomic-level models to real-world challenges is what first attracted Jan Steckel, Ph.D., to NETL about 16 years ago. She appreciated that NETL, as an applied lab, offered an opportunity to use her education in theoretical chemistry to solve timely problems. Now, Steckel is collaborating with the University of Pittsburgh's Chris Wilmer, Ph.D., and NETL colleagues Olukayode Ajayi, Ph.D., and Samir Budhathoki, Ph.D., to accelerate development of innovative carbon-capture membranes that boost performance and affordability using the Lab's advanced computational tools. Their work was highlighted on the cover of the April 2019 print edition of the prestigious journal *Energy and Environmental Science*, featuring artwork by Steckel's 13-year-old daughter.

The cover art for the April 2019 edition of the high-impact Energy & Environmental Science journal was created by Anastasia Piacentini, daughter of NETL's Jan Steckel. Each petal features the chemical structure of a metal-organic framework.

"We just keep trying to make materials that are better," Steckel said. "We're trying to discover crystalline materials that can make mixed matrix membranes that are more permeable and selective than existing polymers."

DEFINING MMM RELATIONSHIPS

An ideal carbon-capture membrane is both highly selective and highly permeable, meaning that it captures CO_2 while allowing other gases to pass through. Though membranes fabricated from pure polymers are cheap and possess good mechanical properties, their ability to be both highly selective and highly permeable is limited.

Metal-organic frameworks (MOFs) are crystalline materials made from metal or metal oxide subunits joined with organic linking molecules. MOF particles incorporated with polymers in MMMs can either enhance or worsen membrane performance, depending on the structure of the MOF. A polymer must be paired with a complementary MOF to create a membrane that achieves optimal results, but millions of possible MOF structures exist. To add an additional challenge, it is not feasible to measure the gas permeation properties of an MOF in the lab. NETL's computational effort addresses these challenges by enabling researchers to predict the properties of a large number of MOFs as well as determine which MOF-polymer pairings will create the best MMMs.

NETL's world-class supercomputing tools offer the capability to screen a vast number of MOFs for use in MMMs, understand the relationship between MOF and MMM properties and connect atomistic calculations with process simulations to predict carbon-capture costs. Steckel's team used databases of real and hypothetical MOFs and experimental properties for nine pure polymers to predict properties for more than 1 million MMMs.

The computations allowed researchers to draw useful conclusions about the performance of MMMs, separate from cost considerations. For instance, many MOFs can be used to create MMMs that improve upon the performance of pure polymers for carbon capture. MOFs offer the most significant gains when paired with highly permeable polymers. To achieve an MMM with the highest possible CO_2 permeability, a polymer with the highest possible

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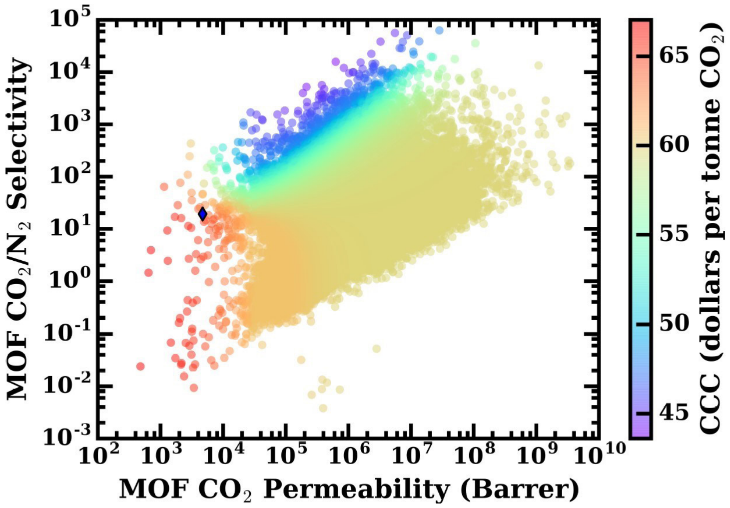

This chart depicts selectivity as a function of CO_2 permeability for the hypothetical MOF database. Color denotes the predicted CCC for a MMM generated with the MOF and PIM-1 polymer. The performance of a membrane composed of PIM-1 alone ($64 per metric ton of CO_2 removed) is indicated by a blue diamond.

permeability must be paired with an MOF that is at least 10 times more permeable than the pure polymer. For an MMM with the highest permeability and selectivity, a highly permeable polymer must be paired with an MOF that is at least 100 times more permeable and 1,000 times more selective.

CALCULATING COSTS

The techno-economic analysis portion of the project estimated the CCC for about 1 million MMMs, indicating that 1,153 MMMs could achieve a CCC of less than $50 per metric ton of CO_2 removed. In comparison, the CCC for the highly permeable PIM-1 polymer alone is estimated at $64 per metric ton. The promising estimates highlight the potential for MMMs to meet a DOE goal to cut the CCC to less than $40 per metric ton for pulverized coal power plants.

Design and operating conditions — such as temperatures, pressures, flow rates, etc. — were optimized for 12 distinct selectivity and permeance points. Those conditions could be adjusted to further cut costs — much like turning a knob, according to Steckel. She said flexibility and creativity can improve upon the process.

The techno-economic evaluation relied on several assumptions, including a fixed three-stage carbon-capture configuration. That means three membranes would be used for carbon capture, each with the same permeability and selectivity. Steckel noted that this configuration was selected because it has been demonstrated to be effective for post-combustion carbon capture, but it could be changed in future studies to reduce the cost further — by altering the number of membranes or using different membranes at different points in the process, for instance.

Beyond the CCC, the techno-economic analyses reiterated the importance of choosing an MOF that complements the polymer. The bottom line? "We believe that it is possible to create membranes that would bring the cost of carbon capture down dramatically," Steckel said.

FUTURE WORK

The collaborative NETL-led team is now working to narrow and refine its analyses based on the project's initial discoveries. Steckel explained that the simplest computational methods were used initially to model a vast number of possible MMMs. Now that researchers have a better idea of how to pair MOFs and polymers to create MMMs with promise, they can start with fewer MOFs — perhaps 6,000 or less — and run more complex calculations to better predict performance and cost for MMMs.

Rather than simply talking about how molecules interact, Steckel is using her background in theoretical chemistry to generate practical results that will steer investments to incorporate MOFs into polymer-based membranes for carbon capture. Several of the thick-film MMM materials created at NETL have been tested using actual flue gas at the National Carbon Capture Center in Wilsonville, Alabama, where they showed stable performance compatible to testing results from NETL's lab-based measurements. NETL is working with flat-sheet and hollow-fiber support materials to create thin-film composite materials featuring MMMs as the selective layer.

The development of MMMs with exceptional permeability and selectivity offers possibilities to cut capital costs, downsize equipment and curb emissions at coal-fired power plants. Once deployed at commercial scale, these innovative membranes will help to boost the long-term viability of the nation's abundant fossil fuel resources and ensure access to clean, reliable and affordable energy for all Americans.