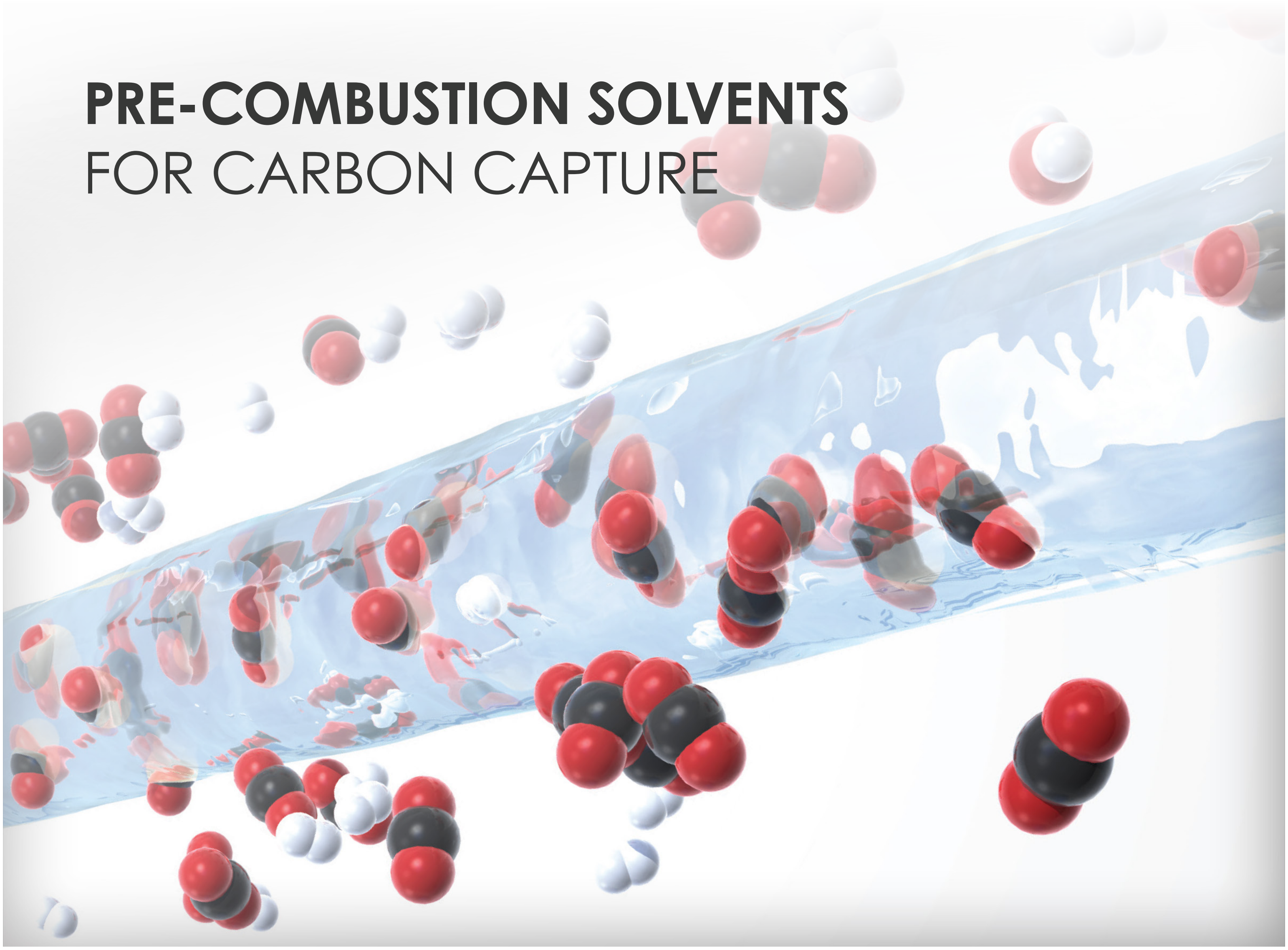
PRE-COMBUSTION SOLVENTS
FOR CARBON CAPTURE



NATIONAL ENERGY TECHNOLOGY LABORATORY

BACKGROUND

Carbon capture and storage from fossil-based power generation is a critical component of realistic strategies for preventing a further rise in atmospheric CO_2 concentrations. One strategy to minimize the cost associated with carbon capture, utilization and sequestration is to exploit industrial streams in which CO_2 is already at high partial pressures, such as the syngas exiting coal gasifiers at integrated gasification combined cycle (IGCC) power plants and the syngas generated at many chemical refineries. In these high-pressure CO_2-containing streams, one well-established approach to removing acid gases (CO_2 and H_2S) from the syngas stream (which also contains H_2O, H_2, CO, CH_4 and N_2) is the use of physical solvents. Selexol® (Union Carbide, Houston, Texas, United States) and Rectisol® (Lurgi AG, Frankfurt am Main, Germany) are the standard, commercially available physical solvents for CO_2 capture. Unfortunately, both are hydrophilic, have high vapor pressure, and can cause significant corrosion at elevated temperatures. To avoid this corrosive damage, the syngas temperature for both processes is typically lowered to sub-ambient conditions (10 °C for Selexol and -10 °C for Rectisol) and then the cost associated with carbon capture, utilization and sequestration to roughly 200 °C for combustion. This process is both inefficient and costly. Instead, hydrophobic solvents with low vapor pressures could be operated at higher temperatures to minimize the energy and cost -associated with cooling the syngas to below ambient conditions. Ideally, a solvent would be chosen that can be regenerated using waste heat.

APPROACH

The National Energy Technologies Laboratory (NETL) is developing low viscosity, hydrophobic solvents with low vapor pressures using a comprehensive approach that includes:

- Molecular design and optimization with assistance of computational chemistry
- Synthesis of novel solvents
- Experimental studies at lab/bench scale
- Process design aided by numerical simulations for industrial scale

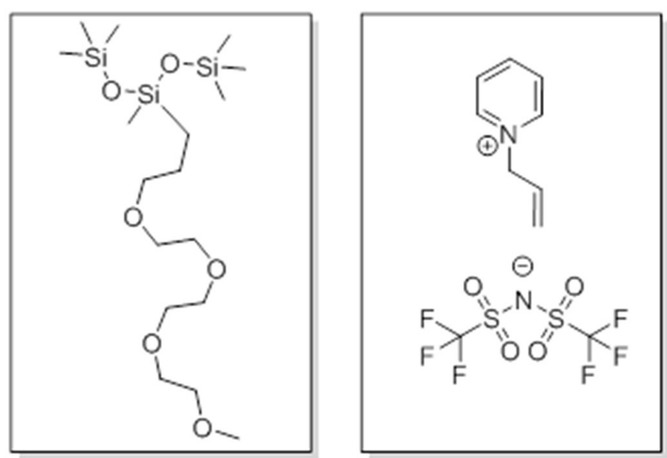
This research leverages cutting-edge facilities, world-class scientists and engineers, and strategic collaborations to foster the discovery, development, and demonstration of efficient and economical approaches to carbon capture. By drawing on many different scientific and engineering disciplines, NETL researchers have created two materials that may have superior performance to the existing commercial capture solvents. First, by chemically combining polyethylene glycol diethyl ether (PEGDME)—the active ingredient in Selexol—with hydrophobic silicone oil and polydimethyl siloxane (PDMS), NETL researchers have synthesized a new class of solvents with the best properties of each parent compound. An example from this PEGDME-PDMS class of synthesized solvents is shown in Figure 1 (left). Also shown in Figure 1 (right) is an example from the second class of synthesized solvents. Allyl pyridinium Tf_2N is an ionic liquid with a low viscosity and extremely high CO_2/H_2 selectivity. NETL researchers have fully characterized these solvents' CO_2 capture performance and CO_2/H_2 selectivity between 25 °C and 100 °C and are also measuring their kinetics, mass transfer, regeneration energy, and stability. Each of these properties may be tuned through additives or minor changes to the solvents' molecular structure to optimize CO_2 separation energetics and ultimately to reduce CO_2 capture cost. NETL is also conducting system and economic studies to determine the precise impact of the new materials on the cost of pre-combustion capture from IGCC power plants. NETL-developed solvents have been tested in a slip stream of synthesis gas at the National Carbon Capture Center in Wilsonville, Alabama. Future work includes testing these solvents using real coal syngas at an existing pilot plant facility at the University of North Dakota's Energy & Environmental Research Center (UND/EERC.)

ACCOMPLISHMENTS

The PEGDME-PDMS hybrid solvents have shown similar or greater CO_2 capacity and CO_2/H_2 selectivity compared to their parent compounds in capture performance testing. The ionic liquid solvent shown in Figure 1 also has shown exceptional performance in both CO_2 uptake and CO_2/H_2 selectivity. Other important parameters such as viscosity, stability, and heat capacity are similar to the commercial materials. The primary advantages of these new solvents are their low vapor pressure, their lack of affinity for water, and their low corrosion on carbon steels, all of which allow these solvents to operate at higher temperatures than the conventional hydrophilic solvents.

A U.S. patent has been awarded for the class of materials shown in Figure 1 (left): U.S. Patent 9643123. In addition, a U.S. patent has been awarded for the ionic liquid shown in Figure 1 (right) (U.S. Patent 9,975,080). We have also filed a U.S. Non-provisional Patent No. 15/989,444 titled "DI-Substituted Siloxane Solvents for Gas Capture," for novel class of PEGDME-PDMS solvents. Industrial partners are currently being sought for transfer, scale-up, and commercialization.

These solvents, and similar solvents being synthesized, are expected to be economically viable replacements for Selexol and Rectisol in pre-combustion capture of CO_2 without requiring the syngas to be cooled below ambient conditions. In addition, these solvents can be regenerated using waste or low-grade heat, which allows net electrical energy savings at a power plant or industrial facility equipped with pre-combustion CO_2 capture.



PEG-Siloxane-1 [aPy][Tf_2N]

Figure 1. (left) Molecular structure of the hybrid PDMS-PEGDME solvent labeled PEG-Siloxane-1; (right) Molecular structure of the allyl pyridinium Tf2N ionic liquid solvent.

Experimental and computational results on these solvents can be found within the following peer reviewed manuscripts:

W. Shi, N.S. Siefert, H.O. Baled, J.A. Steckel, D.P. Hopkinson, "Molecular Simulations of the Thermophysical Properties of Polyethylene Glycol Siloxane (PEGS) Solvent for Pre-combustion CO_2 Capture," J. Phys. Chem. C, 120 (36), pp 20158-20169 (2016).

N.S. Siefert, S. Agarwal, F. Shi, W. Shi, E.A. Roth, D. Hopkinson, V.A. Kusuma, R.L. Thompson, D.R. Luebke, H.B. and Nulwala, "Hydrophobic physical solvents for pre-combustion CO_2 capture: Experiments, Computational simulations, and Techno-economic analysis," International Journal of Greenhouse Gas Control, 49, 364-371 (2016).

W. Shi, N.S. Siefert, and B.D. Morreale, "Molecular Simulations of CO_2, H_2, H_2O, and H_2S Gas Absorption into Hydrophobic Poly(dimethylsiloxane) (PDMS) Solvent: Solubility and Surface Tension," J. Phys. Chem. C, 119 (33), pp 19253–19265 (2015).

BENEFITS

This research will move toward the programmatic goal of capturing 90 percent of the CO_2 produced by an IGCC power plant at a cost of less than \$40/tonne CO_2.

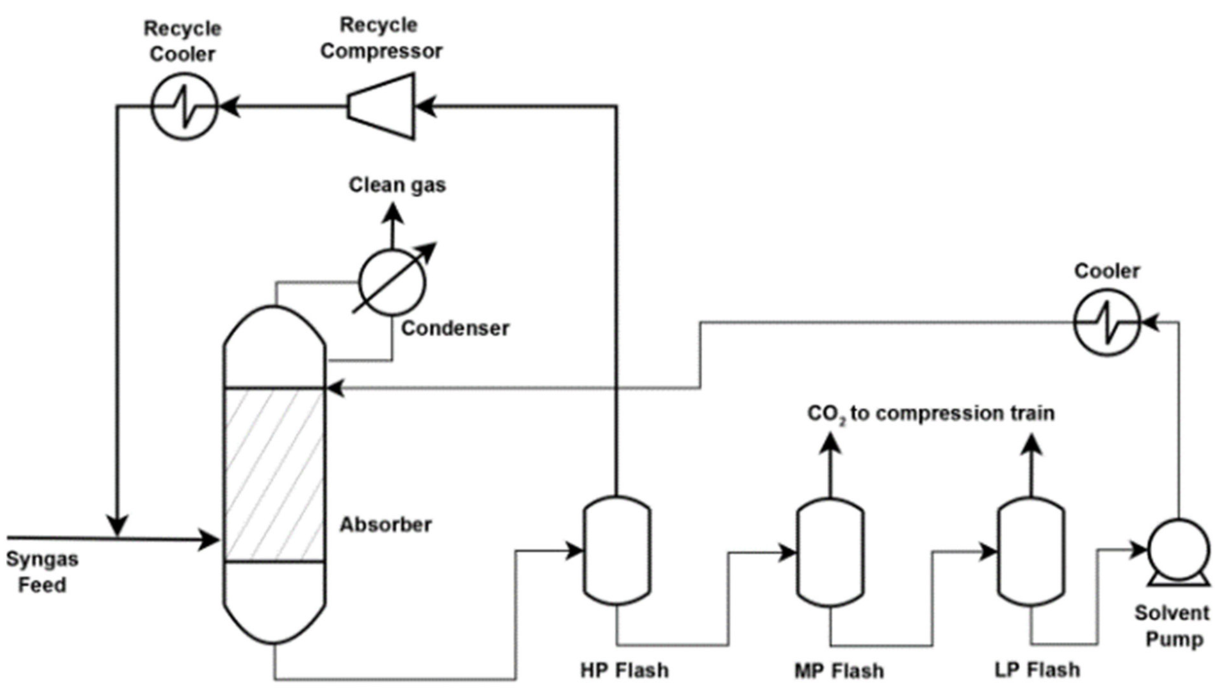


Figure 2. Process flow diagram for NETL's Continuously looping, precombustion CO_2 capture pilot plant facility.

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