Novel Flow Sheet for Low Energy CO_2 Capture Enabled by Biocatalyst Delivery System

primary project goals

Akermin developed an advanced biocatalyst enabled solvent system for lower cost carbon dioxide (CO_2) capture. The project focused on the development of encapsulated carbonic anhydrase (CA) biocatalyst technology. The project combines an improved biocatalyst delivery system (BDS), a new solvent, and process improvements tested in a modified bench-scale system incorporating these new advancements.

technical goals

- Demonstrate a second-generation biocatalyst that has lower production costs, is more readily scaled up, and enables on-stream catalyst replacement.
- Optimize production of the BDS.
- Demonstrate consistent long-term performance in lab-scale closed loop reactor.
- Design and modify bench-scale test unit to incorporate the next-generation BDS and to accommodate the novel process improvements.
- Optimize the process flow sheet to utilize low grade steam for solution regeneration and to achieve parasitic power less than 220-kWh/t CO_2.
- Evaluate performance of advanced AKM24 solvent.
- Complete field testing with the bench-scale test unit at the National Carbon Capture Center (NCCC) using coal-derived flue gas.
- Demonstrate on-stream biocatalyst maintenance.
- Perform techno-economic assessment and engineering study to demonstrate viability of the new technology, targeting at least 30 percent reduction in cost of CO_2 capture.

technical content

Akermin is developing a low-energy, enzyme-catalyzed solvent system for CO_2 capture and testing in a bench-scale unit to continue advancing the technology that was previously developed under project DE-FE0004228. The novel system combines the next-generation BDS and a non-volatile salt solution (AKM24 "solvent"). Updates to an existing 500 standard liters per minute (SLPM) bench-scale test unit incorporated the process and solvent advancements. The process scheme is shown in Figure 1.

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Carbonic Anhydrase Catalyzed Advanced Carbonate and Non-Volatile Salt Solution ("Solvents")

participant:

Akermin, Inc.

project number:

FE0012862

predecessor projects:

FE0004228

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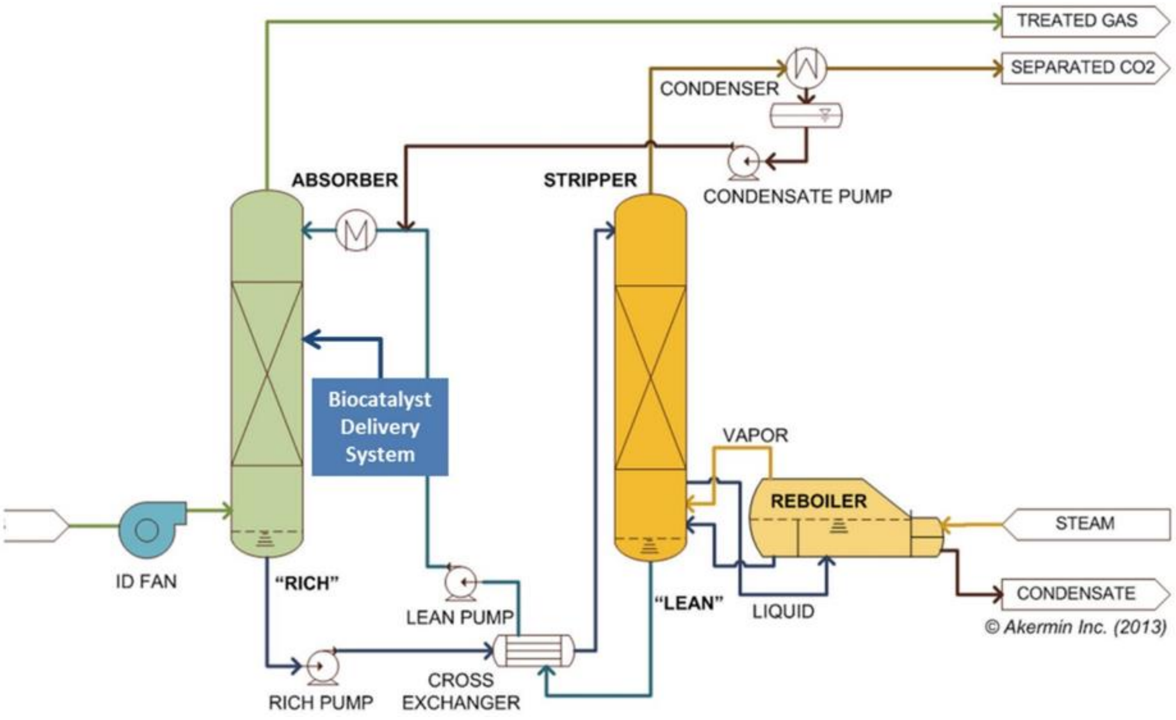

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Figure 1: Akermin's CO_2 capture process

The technology uses a next-generation BDS, in which, the CA enzyme is immobilized within proprietary polymeric microparticles. CA accelerates hydration of CO_2 to bicarbonate to enhance the performance of the solvent for CO_2 capture. The microparticles have high surface area to enable higher mass transfer rates and provide a protective environment for the enzymes against inactivation by temperature, solvent and shear forces. The catalyst can be delivered by two potential concepts: (1) by recirculation in the absorber only, which requires particle separation, or (2) by continuous circulation in the absorber and stripper, which would not require particle separation, but would require lower temperature stripping to avoid denaturation of the enzyme-based biocatalyst. By incorporating the non-volatile salt solution that has significantly lower regeneration energy combined with using lower temperature steam from the power plant, the result is significant reductions in parasitic power requirements and also lower capital costs for the power plant and integrated CO_2 capture system. Since AKM24 operates with higher CO_2 loading capacity, lower circulation rates can be realized. The modified bench-unit was operated with actual coal-derived flue gas at the NCCC to evaluate performance and validate process modeling performance estimates.

The solvent and process parameters are provided in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	not disclosed	not disclosed
Normal Boiling Point	°C	107	107
Normal Freezing Point	°C	-8	-8
Vapor Pressure @ 15 °C	bar	non-volatile	non-volatile
Manufacturing Cost for Solvent	$/kg	not disclosed	not disclosed
Working Solution			
Concentration	kg/kg	not disclosed	not disclosed
Specific Gravity (15 °C/15 °C)	—	1.18	1.18
Specific Heat Capacity @ STP	kJ/kg-K	3.33	3.33
Viscosity @ STP	cP	3.98	33.98
Absorption			
Pressure	bar	1.07	1.07
Temperature	°C	50	50
Equilibrium CO_2 Loading	mol/mol	0.80	0.80
Heat of Absorption	kJ/mol CO_2	52	52
Solution Viscosity	cP	2.01	2.01
Desorption			
Pressure	bar	1.07	1.07
Temperature	°C	107	107
Equilibrium CO_2 Loading	mol/mol	0.40	0.40
Heat of Desorption	kJ/mol CO_2	70	70

Proposed Module Design			*(for equipment developers)*	
Flue Gas Flowrate	kg/hr		40	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90	>99	1.05
Absorber Pressure Drop	bar		<0.02	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		—	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are processdependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Chemical/Physical Solvent Mechanism – The reaction of CO_2 with water (H_2O) in the presence of CA and base (B) is as follows:

$$H_2O + CO_2 \longleftrightarrow HCO_3^{-} + H \qquad \textit{(slow without catalyst)}$$

$$H^{+} + B \longleftrightarrow BH^{+} \qquad \textit{(fast)}$$

$$H_2O + CO_2 + B \longleftrightarrow BH^{+} + HCO_3^{-} \qquad \textit{(overall reaction)}$$

The presence of CA increases the rate of conversion of CO_2 to bicarbonate (improving the slow step above), but does not affect the equilibrium properties of the solvent. The rate of hydration of CO_2 (i.e., the reaction with H_2O) in the absence of the enzyme is exceedingly slow; however, the enzyme provides dramatic acceleration of the reaction (kcat ≈1/microsecond) and is limited only by diffusion.

Solvent Contaminant Resistance – Studies with K_2CO_3 and CA in solution indicate that the enzyme is not inhibited by sulfate, sulfite, nitrite, nitrate, or chloride ions in solution at levels expected for coal flue gas. Divalent metal ions (e.g., mercury [Hg^{2+}], lead [Pb^{2+}]) inhibit the activity of soluble CA, because the active site in the enzyme itself contains a divalent metal ion (mainly zinc). However, the low solubility of their hydroxide and carbonate salts in carbonate solutions and the stabilizing role of the immobilization system alleviate some of the decrease in CA activity.

Solvent Foaming Tendency – The presence of soluble enzyme can contribute to foaming, especially in the stripper, whereas the tendency to foam is mitigated by using immobilized enzyme. Previous work has used small quantities of anti-foam.

Flue Gas Pretreatment Requirements – Standard sulfur oxides (SO_x), nitrogen oxides (NO_x), and mercury control systems that meet local air emission requirements will be sufficient.

Solvent Make-Up Requirements – The capture of acid gases, such as sulfur dioxide (SO_2) and nitrogen dioxide (NO_2), will reduce carrying capacity over time. Initial tests indicated the loss of capacity to be on the order of 2 percent per year or less. K_2CO_3 is non-volatile and has excellent oxidative stability (an inorganic salt solution). Akermin's new solvent (AKM24) is based on a non-volatile salt solution; therefore, it is expected to have similar benefits.

Waste Streams Generated – In the first-generation technology, the deactivated packing would need to be replaced (recycled) to maintain CA activity on an ongoing basis. Notably, the second-generation BDS provides for on-stream biocatalyst maintenance as a microparticle, which reduces the volume and cost of solid waste management.

Process Design Concept – Figure 1 presents the basic process flow sheet.

technology advantages

- Advanced solvent in the presence of Akermin's BDS has high CO_2 absorption rates and higher capacity relative to first generation. It also has significantly lower regeneration energy compared to amine-based solvents.
- Solvent is non-volatile, oxidative stable, and environmentally benign.
- Advanced solvent uses lower-grade steam with lower regeneration temperatures than amine solvents; resulting in lower auxiliary power requirements, more power generated, lower unit capital costs, and lower CO_2 capture costs.

R&D challenges

- Scaling up and manufacturing of the immobilized biocatalyst batches that consistently achieve the critical performance metrics (cost, efficiency, ease of integration with BDS, etc.).
- Determining the optimal catalyst recirculation option.
- Demonstrating an effective BDS in the lab- and bench-scale test units to achieve stable and consistent long-term performance.

status

Akermin has produced and tested multiple biocatalyst batches on the kilogram scale. They have demonstrated an average 90 percent CO_2 capture over extended testing in the lab-scale closed loop reactor. An enzyme kinetic model was built in Aspen and validated with test data. The 500 SLPM bench unit located at the NCCC was modified and commissioned in June 2016, and testing was initiated. The project ended in July 2016, prior to the planned September 30, 2016, end date, due to unexpected circumstances.

available reports/technical papers/presentations

Zaks, A., "Novel Flow Sheet for Low Energy CO_2 Capture Enabled by Biocatalyst Delivery System," presented at the Budget Period 1 Review Meeting, Pittsburgh, PA, July 2015. *https://netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0012862-BP1-Review-Meeting-07-15-2015.pdf.*

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Zaks, A., "Low Energy CO_2 Capture Enabled by Biocatalyst Delivery System," 12th Greenhouse Gas Control Technologies (GHGT-12) Conference Presentation, October 2014. *http://www.netl.doe.gov/File Library/Research/Coal/carbon capture/post-combustion/FE0012862-GHGT-12-Presentation-10-07-14.pdf*.

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Zaks, Alex, and Reardon, J., Final Report, "Advanced Low Energy Enzyme Catalyzed Solvent for CO_2 Capture," 2013. *http://www.osti.gov/scitech/servlets/purl/1121752*.

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http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/J-Reardon-Akermin-Enzyme-Catalyzed-Solvent-for-CO2.pdf

Reardon, J., et al., “Enzyme-Catalyzed Process for Low-Cost CO_2 Separation and Capture,” presented at the 2012 MEGA Conference, Baltimore, MD, August, 2012.
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Zaks, A., “Advanced Enzyme-Catalyzed CO_2 Capture in Low-Energy Solvents,” presented at the 2012 NETL Annual CO_2 Capture Technology Meeting, July, 2012, Pittsburgh, PA.
http://www.netl.doe.gov/File%20Library/research/coal/cross-cutting%20research/advanced%20materials/advanced-low-energy-enzyme-catalyzed-solvent-july2012.pdf.

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http://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/23Aug11-Zaks-Akermin-Enzyme-Catalyzed-Solvent.pdf.

Gifford, P., “Advanced Low Energy Enzyme Catalyzed Solvent for CO_2 Capture,” Presented at the 2010 NETL Annual CO_2 Capture Technology Meeting, September, 2010, Pittsburgh, PA.
http://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/Paul-Gifford---Akermin-Inc.pdf.