CO_2 CAPTURE FROM FLUE GAS USING SOLID MOLECULAR BASKET SORBENTS

Primary Project Goals

Pennsylvania State University (PSU) is developing a new generation of solid and regenerable polymeric molecular basket sorbent (MBS) for more cost-efficient capture and separation of carbon dioxide (CO_2) from flue gas of coal-fired power plants.

Technical Goals

- A regenerable working sorption capacity higher than 70 mg-CO_2/g-S.
- A significantly lower cost for the sorbent preparation compared to the early generations of MBS.

Technical Content

The current state-of-the-art post-combustion capture technology—aqueous amine scrubbing—is a highly energy-intensive process estimated to increase the cost of electricity (COE) by about 75–85%, according to U.S. Department of Energy (DOE) reports. The goal of DOE's Existing Plants, Emissions, and Capture (EPEC) Research and Development (R&D) Program is to achieve 90% CO_2 capture with an increase in COE less than 35%. Therefore, it is important to develop inexpensive, effective, and robust materials and technologies that can reduce CO_2 emission and are suitable for installation in power plants to maintain the cost-effectiveness of U.S. coal-fired power plants. Recently, a new sorbent concept called MBS has been developed for CO_2 capture from flue gas. The idea of MBS development, as shown in Figure 1, is to load CO_2-philic polymers on to high surface area mesoporous materials. This process increases the number of approachable sites on/in the sorbent and enhances the sorption/desorption rate by increasing the gas-sorbent contacting interface and by improving the mass transfer in the sorption/desorption process. The expected result of this project will be a concentrated CO_2 stream that can be directed to CO_2 sequestration or CO_2 utilization.

The researchers are using the following approaches to accomplish the technical project goals:

- Using cheaper nanoporous materials to replace SBA-15 and MCM-41 to reduce the cost for the sorbent.
  - Silica-gel, fumed silica, carbon.
- Using cross-linkers to improve the thermal stability and regenerability of MBS via chemical bonding.

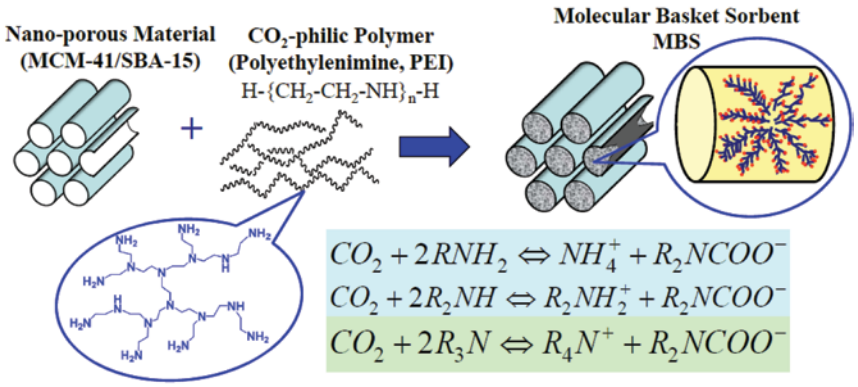

Figure 1: Molecular Basket Sorbent (MBS) Concept

Technology Maturity:
Bench-scale

Project Focus:
Solid Molecular Baskets

Participant:
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Project Number:
FE0000458

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Performance Period:
9/1/09 – 8/31/11

Table 1: Process Parameters for Sorbents

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Solid amine	Solid amine
	Heat of adsorption (kJ/mole CO_2)	~69	—
	CO_2 loading/working capacity, wt%	140/80	120/70
	Surface area, m^2/g	20–80	~60
	Particle density, g/cm^3	N/A	—
	Packing density, g/cm^3	0.4–0.8	~0.8
	Particle size (mm)	~0.05	~0.05
	Heat capacity (kJ/K/kg)	~1.6	—
	Thermal stability, °C	~100	120
	Hydrothermal stability, °C	<90	120
Process Configuration	Attrition rate (fluidized bed), %/year	N/A	N/A
	Cycle time (fixed bed), minutes	60	40
	Pressure drop (fixed bed), psia	<10	<5
Operating conditions	Adsorption temperature, °C	75	75
	Adsorption pressure, atm	1 (CO_2, 0.15%)	1
	CO_2 capture efficiency, %	>90	>95
	Regeneration method	PSA+TSA	PSA/TSA
	Regeneration temperature, °C	100	100
	Regeneration pressure, atm	0.01	—
Heat Integration	Required regeneration steam temperature, °C	N/A	—
Miscellaneous	Sorbent make-up rate, kg/kg CO_2	N/A	—
Product Quality	CO_2 purity, %	~90%	>95%
	N_2 concentration, %	N/A	—
	Other contaminants, %	N/A	—
Process Performance	Electricity requirement, kJ/kg CO_2	N/A	—
	Heat requirement, kJ/kg CO_2	N/A	—
	Total energy (electricity equivalent), kJ/kg CO_2	N/A	—

Technology Advantages

- High capacity: 3.2 mol-CO_2/kg (or 14%) at CO_2 conc. of 15%.
- High selectivity: CO_2/N_2>1,000.
- No (or less of a) corrosion problem.
- Suitable operation conditions.
- High sorption/desorption rate.
- Positive effect of moisture.
- Regenerable at mild conditions.

R&D Challenges

- High cost of nanoporous materials (SBA-15 and MCM-41).
- Low packing density.
- Thermal and regenerable stability needs to be improved.

Results To Date/Accomplishments

- Four types of nanoporous supports, including silica-gel, Cab-O-Sil, carbon black, and mesoporous foam silica either purchased or synthesized in the lab, have been tested for polyethylenimine loading.
- More than 50 sorbent samples have been prepared and examined for CO_2 capture using thermogravimetric analysis, fixed-bed flow system, and temperature-programmed desorption methods.
- Several sorbents have showed comparable sorption capacity to SBA-15-based molecular basket sorbent, reaching about 140 mg-CO_2/g-sorbent, while the cost for the sorbent is much lower, being ~$40/kg. It exceeds the project goals of higher than 70 mg-CO_2/g-sorbent with less than $240/kg cost.
- A new approach, polymer cross-linking, has been proposed and tested to further improve the thermal and regenerable stability of molecular basket sorbents. More than 15 samples have been tested with thermal degradation at heating over 100 °C, CO_2 sorption at 75 °C, and desorption at 100 °C cycling.
- Primary computational calculations show that the addition of cross-linker can promote the stability of the cross-linked polymer and improve the sorption strength between CO_2 and amine sites; thus, both the thermal stability and regenerability may be enhanced.

Next Steps

- More experimental and computational work will be conducted to identify a proper way to prepare and obtain a highly thermal stable molecular basket sorbent, and it will be applied to the low-cost sorbents developed in this project.
- The best regeneration conditions and method (TAS and/or PSA) will be determined.
- Based on the developed MBS, scale-up of CO_2 sorption process using MBS will be carried out (about 200 ml sorber in the lab).
- Based on the selected materials and sorption performance, a primary analysis on the techno-economy of MBS technology will be conducted.

Available Reports/Technical Papers/Presentations

Peer-Reviewed Journal Papers:

DX Wang, C Sentorun-Shalaby, XL Ma, CS Song, High-capacity and low-cost carbon-based molecular basket sorbent for CO_2 capture from flue gas. *Energy Fuels* **2011**, 25, 456–458.

Presentations:

XX Wang, SQ Zhao, XL Ma, CS Song, CO_2 capture from gas streams with low CO_2 concentrations using solid molecular basket sorbent. 241st ACS National Meeting, Anaheim. CA, USA, March 27–31, **2011**.

XX Wang, SQ Zhao, XL Ma, CS Song, Carbon dioxide sorption over molecular basket sorbents: a detailed TPD study. 22th North American Catalysis Society meeting, Detroit, MI, June 2–10, **2011**.

XL Ma, ZH Zhang, J Zhu, XX Wang, CS Song, CO_2 capture from the atmosphere using nano-porous-material-supported polyethylenimine sorbents. 241st ACS National Meeting, Anaheim. CA, USA, March 27–31, **2011**.

XL Ma, XX Wang, CS Song, Advances and challenges in development of amine-functionalized and amine-immobilized solid sorbents for CO_2 capture. The International Chemical Congress of Pacific Basin Societies, Honolulu, HI, USA, December 15–20, **2010**.

XX Wang, DX Wang, EP Fillerup, E Peduzzi, ZH Zhang, XL Ma and Chunshan Song. CO_2 Capture from Flue Gas Using Solid Molecular Basket Sorbents. Oral Presentation. 2010 NETL CO_2 Capture Technology Meeting. Pittsburgh, September 13–17, **2010**. http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Xiaoxing Wang-FE0000458.pdf

EP Fillerup, XX Wang, XL Ma, and CS Song. Utilization of Polymer Cross-linkers to Improve the Thermal Stability of Molecular-Basket Sorbents. Oral Presentation. American Chemistry Society 240th National Meeting, Boston, MA, August 22–26, **2010**.

XL Ma, XX Wang, CS Song, "Molecular Basket" Sorbents for CO_2 Capture from Flue Gas. 26th International Pittsburgh Coal Conference, Pittsburgh, PA, September 21–24, **2009**.

Manuscript in Preparation:

XX Wang, SQ Zhao, XL Ma, ZH Zhang, DX Wang, CS Song, SBA-15-supported polyethylenimine sorbents for CO_2 capture from flue gas. **2011**, in preparation.

XX Wang, SQ Zhao, XL Ma, CS Song, CO_2 sorption over polyethylenimine loaded SBA-15 sorbents: a TPD study. **2011**, in preparation.

XX Wang, XL Ma, V Schwartz, JC Clark, SH Overbury, SQ Zhao, XC Xu, CS Song, Superior solid sorbent for CO_2 capture and separation from gas steams with low CO_2 concentration at ambient conditions. **2011**, in preparation.