Microporous Polymeric Sorbent Technology for Post-Combustion CO_2 Capture

primary project goal

The National Energy Technology Laboratory's Research and Innovation Center (NETL-RIC) is developing new, microporous polymeric (m-poly) sorbent technology with a demonstrated carbon dioxide (CO_2) uptake capacity of 10 wt% and a selectivity of greater than 500 under a "simulated gas" environment for natural gas flue gas (NGFG). The most promising m-poly sorbents are to be integrated into a prototype modular system for long-term field testing (such as at the National Carbon Capture Center [NCCC]) under actual post-combustion flue gas.

technical goals

- Identify a sorbent material with a potential of achieving a CO_2 uptake property of 7 wt% and a CO_2/Nitrogen (N_2) selectivity of 500. Evaluate materials under NGFG environments.
- Demonstrate the sorbent material in fiber form with a potential of achieving a CO_2 uptake property of 7 wt% and a CO_2 selectivity of 500. Evaluate the fiber materials under neat environments.
- Test a sorbent prototype under simulated or actual NGFG.
- Perform a techno-economic analysis (TEA) with experimental data to calculate the cost of achieving 95% capture efficiency (conducted by Strategic Systems Analysis and Engineering [SSAE] team).

technical content

The selective removal of CO_2 from dilute, mixed gas streams at the scales associated with centralized power generation represents a significant challenge. Adding to this challenge is the need to rapidly develop and deploy a separation technology that delivers a viable option in the next few years with the delivered technology also having minimal impact on the delivered cost of electricity (COE) to the customer. Sorbent materials have been studied intensively in recent years for CO_2 capture. Inorganic sorbents, such as aminated silica and metal organic frameworks (MOFs), showed significant CO_2 capture performance. However, chemical stability, amine leaching, high regeneration temperature, slow sorption kinetics, and poor cyclability have been major drawbacks for these sorbents. On the other hand, polymeric sorbents, such as porous polymeric networks (PPNs) and benzimidazole linked polymers (BILPs), have been developed with high chemical stability and fast adsorption/desorption cycles. In general, porous polymers suffer from use of costly monomers/reactants, harsh synthesis conditions, and lower CO_2 capture capacity compared to their inorganic counterparts.

The removal of CO_2 from natural gas combined cycle (NGCC), as compared to coal-derived flue gas (pulverized coal), can be considered even more challenging. Carbon dioxide is present at lower levels (~4 vol% versus >12 vol%), representing less partial pressure driving force available for separation. Oxygen (O_2) is significantly higher (~12 vol% versus 3 vol%), necessitating that the sorbent

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post-Combustion Power Generation PSC

key technology:
Sorbents

project focus:
Shapeable Microporous Polymeric Sorbent

participant:
National Energy Technology Laboratory–Research and Innovation Center

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2020 Carbon Capture FWP

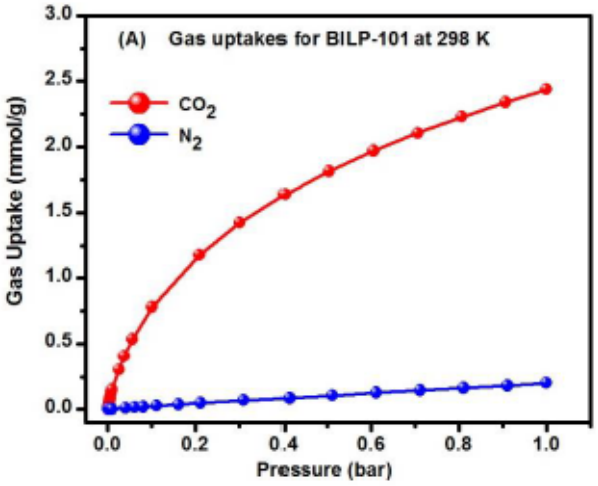
NETL technical portfolio lead:
David Hopkinson
david.hopkinson@netl.doe.gov

NETL principal investigators:
Ali Sekizkardes
ali.sekizkardes@netl.doe.gov
James Hoffman
james.hoffman@netl.doe.gov

partners:
National Carbon Capture Center (NCCC)

possesses oxidative stability, a valid concern for amine-based materials. Moisture is lower for NGCC flue gas (~8 vol%) versus pulverized coal flue gas (~14 vol%), but can still include the difficulty of competitive adsorption of H_2O being favored over CO_2. There is a need for high CO_2 capacity sorbents that are chemically stable, inexpensive, and have a simple synthesis procedure.

Over the past several years, NETL has provided the foundational knowledge and technology progress that can overcome the challenges associated with the maturation of polymer-based sorbent technology. For example, NETL has developed BILPs demonstrating the highest CO_2 uptake and CO_2/N_2 selectivity of all other PBIs reported to date (Figure 1). Low-temperature CO_2 regeneration, fast kinetics, and high chemical stability all combine to make this sorbent a promising candidate for carbon capture (Figure 1). The team recently developed a soluble m-poly functionalized with carboxylic acid groups. Functionalized polymers were impregnated with alkyl amines that formed a stable sorbent. These polymers showed high CO_2 uptake and CO_2/N_2 selectivity, which is more than four times higher compared to similar sorbents. Sorbents tested under humid conditions showed chemical stability and the CO_2 uptake performance remained intact after several cycles. Moreover, these sorbents were able to be regenerated at 85°C.



Sorbent	ΔN_1	R	α_{12}^{ads}	S
BILP-101 (POP)	0.80	84.8	70.3	556
SNU-Cl-va[33](POP)	0.41	87.3	38.0	262
Zeolite-13X[34] (Zeolite)	1.35	54.2	86.2	128
ZIF-78[35] (MOF)	0.58	96.3	34.5	396
ZIF-82[35] (MOF)	0.38	92.5	22.7	101
MOF-4b[36] (MOF)	0.06	83.8	154	104
HKUST-1[37](MOF)	0.55	89.0	20.4	46.2
Ni-MOF-74[38](MOF)	3.20	73.7	41.1	83.5
NoritR1 extra[39] (Activated Carbon)	0.28	73.7	10.7	5.09

ΔN_1= CO_2 working capacity (mol/kg), R= Regenerability, α_{12}^{ads}= IAST selectivity, S=Sorbent selection parameter (Eq. S3). [11]

Figure 1: CO_2 and N_2 adsorption isotherm of the BILP sorbent and the list of top-performing sorbents for flue gas (CO_2/N_2:10/90) separation using vacuum swing adsorption at 298K, P_{ads}=1 bar, and P_{des}=0.1 bar.

In the first phase, several proposed polymeric sorbents were developed. Specifically, the sorbent series PIM-1-AO-DETA (Figure 2) showed high CO_2 uptake capacity (Figure 3) and CO_2/N_2 selectivity, exceeding the 7 wt% CO_2 uptake milestones of the first year. Carbon dioxide uptake capacity of sorbents remains intact in humid conditions after several regeneration cycles (Figure 4). As-synthesized sorbents were characterized and scaled up to be processed into fibers in the second year.

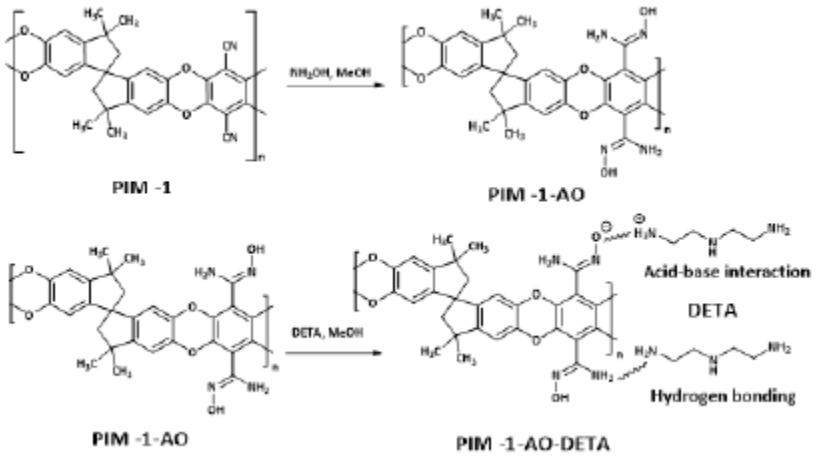


Figure 2: Reaction scheme and preparation of PIM-1-AO-DETA sorbent.

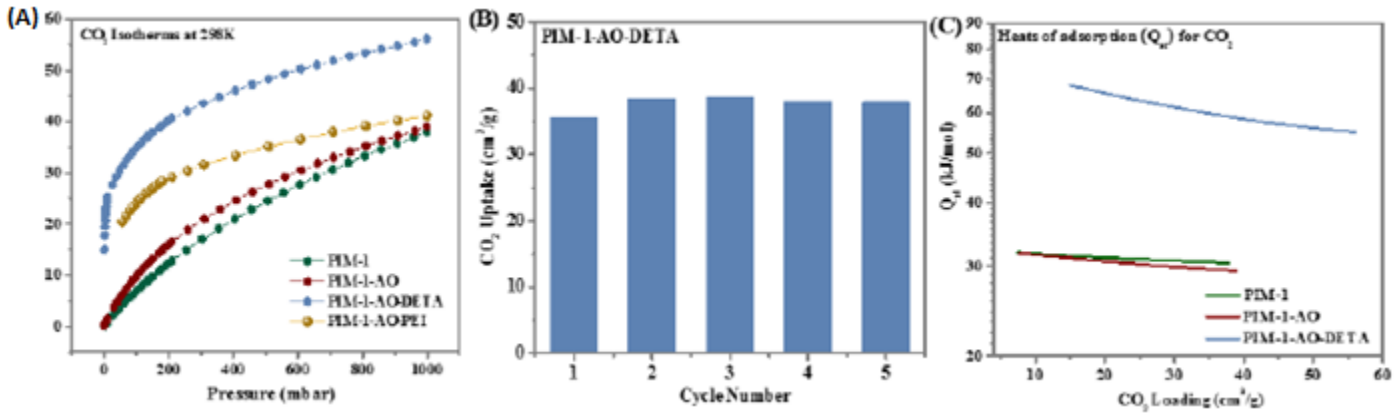


Figure 3: (A) CO_2 uptake isotherm of the discovered sorbent (PIM-1-AO-DETA) in comparison with neat PIM-1, functionalized (PIM-1-AO), and PEI impregnated PIM-1 (PIM-1-PEI). (B) CO_2 cyclability of PIM-1-AO-DETA (regenerated only at 80°C). (C) Heat of adsorption for CO_2 for the sorbents.

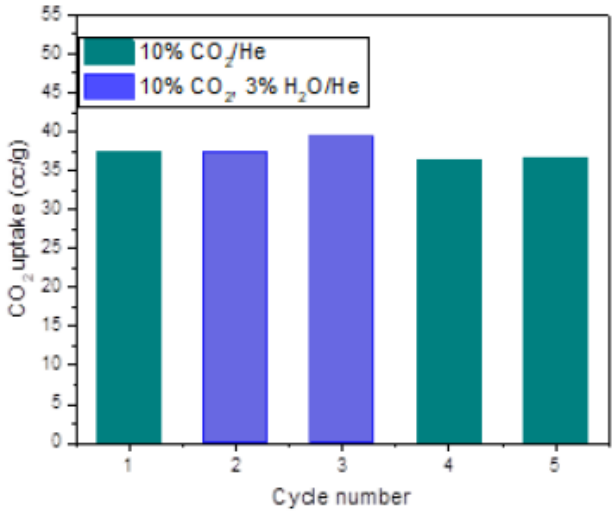


Figure 4: Preliminary CO_2 uptake performance of NETL's high-performance m-poly-1 tested in packed-bed reactor with gas breakthrough analysis under dry and humid conditions.

Continued work is being directed toward the development of new m-poly sorbents. The major advantage of m-poly over other porous materials, such as MOFs and zeolites, is very high chemical stability because of the strong covalent bond linking the polymer backbone. Unlike previous work with BILPs, these sorbents are being structured from contorted one-dimensional monomers, which provide sorbent solubility in common solvents. In the case of other sorbents, such as BILPs, MOFs, silica, and zeolites, they need to be processed with other additives, which usually causes a large decrease in their CO_2 uptake capacity. On the other hand, the proposed m-poly sorbents can be processed into desired sorbent shapes such as pellets, beads, fibers, etc., depending on the reactor design configuration envisioned for the capture process.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	—	—
Bulk Density	kg/m^3	1.1	—
Average Particle Diameter	mm	1	—
Particle Void Fraction	m^3/m^3	—	—
Packing Density	m^2/m^3	—	—
Solid Heat Capacity @ STP	kJ/kg-K	—	—
Crush Strength	kg_f	—	—
Manufacturing Cost for Sorbent	$/kg	—	—
Adsorption			
Pressure	bar	0.1	—
Temperature	°C	25	—
Equilibrium Loading	g mol CO_2/kg	2.1	—
Heat of Adsorption	kJ/mol CO_2	47	—
Desorption			
Pressure	bar	1	—
Temperature	°C	75	—
Equilibrium CO_2 Loading	g mol CO_2/kg	0.1	—
Heat of Desorption	kJ/mol CO_2	—	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— —	—
Adsorber Pressure Drop	bar	—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption 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 sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. 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 coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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) unit (wet basis) should be assumed as:

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Chemical structure of the sorbent consist of porous polymer with amidoxime and alkylamines functionalities.

Sorbent Contaminant Resistance – Sorbent is stable through humidity, sulfur oxide (SO_x), and nitrogen oxide (NO_x).

Sorbent Attrition and Thermal/Hydrothermal Stability – 200°C.

technology advantages

- M-poly sorbent technology has small footprint, simplicity of device and process, ease of operation, modularity, and low parasitic energy requirements through low-temperature desorption (<85°C) to remove all adsorbed gases.
- The m-poly sorbent has high surface area, permanent microporosity, functionable structure, uniform pore size distribution, and high chemical and thermal stability, helping to address the challenges facing carbon capture from centralized point sources.
- Carbon dioxide uptake capacity of sorbents remains intact in humid conditions after several regeneration cycles.
- In contrast to other sorbents, soluble m-poly can be dissolved in common solvents and processed into the desired shape without any other material.

R&D challenges

- There is a lack of polymer functionalization study and a lack of a detailed processability study to transfer technology to market.

available reports/technical papers

Ali K. Sekizkardes, Sonia Hammache, James S. Hoffman, Polymers of Intrinsic Microporosity Chemical Sorbents Utilizing Primary Amine Appendance Through Acid–Base and Hydrogen-Bonding Interactions, David Hopkinson, ACS Appl. Mater. Interfaces 2019, 11, 34, 30987–30991, *https://doi.org/10.1021/acsami.9b09856*.

D. Hopkinson, A.K. Sekizkardes, Polymer for carbon dioxide capture and separation, U.S. Department of Energy, USA Patent no 10,323,125. 2019, pp. 22 *https://www.osti.gov/servlets/purl/1568476*.

A. Miles, W.C. Wilfong, D. Hopkinson, A.K. Sekizkardes, Alkylamine Incorporation in Amidoxime Functionalized Polymers of Intrinsic Microporosity for Gas Capture and Separation, Energy Technol. (Weinheim, Ger.), 8 (2020) 2000419. *https://doi.org/10.1002/ente.202000419*.

A.K. Sekizkardes, V.A. Kusuma, J.T. Culp, P. Muldoon, J. Hoffman, D. Hopkinson, Single polymer sorbent fibers for high performance and rapid direct air capture, ChemRxiv, (2022) 1-4. *https://doi.org/10.26434/chemrxiv-2022-jgpqv*.