Phase1 Final Technical Report

DOE Award: DE-SC-0020730

Project Title	**: CO_2-philic Block Copolymers with Intrinsic Microporosity for Post-combustion CO_2 Capture**
Recipient	**:** Helios-NRG, LLC
Team Members	**:** University at Buffalo, The State University of New York
PI	**:** Ravi Prasad
Co-PI	: Haiqing Lin
Period Covered	**:** 6/29/2020 - 7/28/2021
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Public Summary
Non-Confidential

The United States, the world's largest energy user and second largest CO_2 emitter, is heavily dependent on fossil energy. Coal has a particularly high CO_2 footprint; CO_2 emissions from US coal-burning power plants accounted for 60% of the total US power sector emissions in 2019. Hence, reducing the CO_2 emission footprint from coal plants is widely viewed as a key element in mitigating global warming. Despite significant interest, the implementation of CO_2 capture technologies have been hamstrung by high capture costs, which significantly increases the cost of electricity.

In this project, supported by a STTR grant from the US DOE, Helios-NRG in collaboration with the State University of New York at Buffalo (UB) aimed to develop a novel, step-change membrane that can significantly reduce the cost of CO_2 capture from coal-fueled power plants. The Phase 1 project was aimed at demonstrating the technical feasibility of developing a novel, step-change membrane that can significantly reduce the cost of CO_2 capture from coal-fueled power plants. Our approach was to develop new membrane materials and scalable membranes based on block copolymers (BCPIMs) of rubbery poly(ethylene oxide) (PEO) and polymerizable metal-organic frameworks (polyMOFs) to achieve superior CO_2/N_2 separation properties. ***We have successfully developed BCPolyMOFs with the CO_2/N_2 separation properties meeting the target (CO_2 permeability of 2,000 Barrer and CO_2/N_2 selectivity of 40), and proof concept of thin-film composite (TFC) membranes were fabricated.*** A preliminary techno-economic analysis (TEA) was performed by incorporating the membranes into suitable process configurations.

PolyMOFs nanoparticles with sizes of 40-60 nm, which are small enough to prepare thin film composite (TFC) membranes, were successfully synthesized and subsequently functionalized with methacrylate groups. Introduction of the functionalized nanoparticles into blends of XLPEO and crown ether improved gas permeability. Mixed matrix BCPolyMOF materials were prepared which exhibited CO_2 permeability of 2200 Barrers and CO_2/N_2 selectivity of 48 at 35 ºC, which exceeded the Phase1 target. The mixed matrix materials showed good stability in the presence of water vapor, SOx, and NOx. To make thin film composite (TFC) membranes, microporous membranes were selected for the substrate and a very high permeability polymer was selected for the gutter layer. While a gutter layer of PDMS on PES UF membrane showed a CO_2 permeance of ~10,000 GPU, the prepared TFC membranes showed CO_2 permeance of 630-2500 GPU and CO_2/N_2 selectivity of 43-30. TFC membranes were systematically tested with pure- and mixed-gas at various temperatures, pressures, and compositions. Increasing the temperature increases gas permeance and decreases the selectivity, and the separation properties are independent of the feed gas compositions and pressures, demonstrating their potential for flue gas treatment. Further optimization of the gutter layer and coating solution of the mixed matrix materials are needed to improve the membrane performance further.

The techno-economic analysis was performed using projected commercial TFC membrane module performance based on the new BCPolyMOF materials synthesized in Phase1. Two membrane process configurations were investigated - a two-stage process and an advanced 3-stage process developed by Membrane Technology and Research, Inc. (MTR). The results indicate that, with membranes alone, CO_2 purities of 78-90% can be achieved. The capture cost is projected to be $20-22/ton for the 3-stage process and $32-35/ton for the 2-stage process. Adding a cryogenic back end increases the product purity to ~100% for both cases at an added cost of ~$8-10/ton. The results confirm the potential of the advanced BCPolyMOF membranes for cost-effective CO_2 capture.

Plans to advance the technology in Phase II were developed and potential partners identified.

1. Executive Summary:

The United States, the world's largest energy user and second largest CO_2 emitter, is heavily dependent on fossil energy. Coal has a particularly high CO_2 footprint; CO_2 emissions from US coal-burning power plants accounted for 60% of the total US power sector emissions in 2019. Hence, reducing the CO_2 emission footprint from coal plants is widely viewed as a key element in mitigating global warming. Despite significant interest, the implementation of CO_2 capture technologies has been hamstrung by high capture costs, which significantly increases the cost of electricity.

Helios-NRG in collaboration with University at Buffalo, the State University of New York (UB) aims to develop a novel, step-change membrane that can significantly reduce the cost of CO_2 capture from coal-fueled power plants. The Phase 1 project was aimed at demonstrating the technical feasibility of developing a novel, step-change membrane that can significantly reduce the cost of CO_2 capture from coal-fueled power plants. Our approach was to develop new membrane materials and scalable membranes based on block copolymers (BCPIMs) of rubbery PEO and polyMOFs to achieve superior CO_2/N_2 separation properties. ***We have successfully developed BCPolyMOFs with the CO_2/N_2 separation properties meeting the target (CO_2 permeability of 2,000 Barrer and CO_2/N_2 selectivity of 40), and proof concept of thin-film composite (TFC) membranes were fabricated.*** A preliminary techno-economic analysis (TEA) was performed by incorporating the membranes into suitable process configurations.

In the first step, UiO-66-NH_2 nanoparticles with sizes of 40-60 nm, which are small enough to prepare TFC membranes, were successfully synthesized. These nanoparticles were then functionalized with methacrylate groups so that they could be polymerized with poly(ethylene glycol) diacrylate (PEGDA) and poly(ethylene glycol) methyl ether acrylate (PEGMEA). Adding 50 wt% of 18-crown-6 molecules in PEGDA-*co*-PEGMEA (or XLPEO) increased the CO_2 permeability from 580 Barrer to 1100 Barrer while retaining a CO_2/N_2 selectivity of 43. Introduction of the UIO-66-NH_2 in the blends of XLPEO and crown ether further improved gas permeability. For example, mixed matrix materials containing 1.0 wt% of UiO-66-NH_2 nanoparticles in a blend of XLPEO and crown ether with a weight ratio of 1:1 exhibited CO_2 permeability of 2200 Barrer and CO_2/N_2 selectivity of 48 at 35 °C, which exceeded the Phase1 target. Increasing the temperature increased the permeability and decreased CO_2/N_2 selectivity. The BCPolyMOFs showed good stability in the presence of water vapor, SOx, and NOx. To make TFC membranes, microporous membranes were selected for the substrate, and a very high permeability polymer was selected for the gutter layer. Preliminary TFC membranes using these materials were prepared. While a gutter layer of PDMS on PES UF membrane showed a CO_2 permeance of ~5,000 GPU, the prepared TFC membranes showed CO_2 permeance of 630-2500 GPU and CO_2/N_2 selectivity of 43-30. TFC membranes were systematically tested with pure- and mixed-gas at various temperatures, pressures, and compositions. Increasing the temperature increases gas permeance and decreases the selectivity, and the separation properties are independent of the feed gas compositions and pressures, demonstrating their potential for flue gas treatment. Further optimization of the gutter layer and coating solution of the mixed matrix materials are needed to improve the membrane performance further.

The techno-economic analysis was performed based on projected commercial TFC membrane module performance based on the new BCPolyMOFs materials synthesized in Phase 1. Two membrane process configurations were investigated: a two-stage process that is easy to retrofit in existing plants and an advanced 3-stage process developed by MTR that is best suited for new plants. The results indicate that, with membranes alone, CO_2 purities of 78-90% can be achieved. The capture cost is projected to be $20-22/ton for the 3-stage process and $32-35/ton for the 2-stage process. Adding a cryogenic back end increases the product purity to ~100% for both cases at an added cost of ~$8-10/ton. The results confirm the potential of the advanced BCPolyMOF membranes for cost-effective CO_2 capture.

2. Detailed discussion of work and accomplishments by task:

2.1 Design and Synthesis of High-Performance BCPIMs

2.1.1 Design Rationale

In striking contrast to the conventional MMMs comprising size-sieving MOFs in glassy polymers, we propose to develop scalable membranes based on block copolymers of intrinsic microporosity (BCPIMs) to achieve superior CO_2/N_2 separation properties. The BCPIMs are micro-phase separated. The continuous phase is based on state-of-the-art amorphous PEO with superior CO_2/N_2 separation property. The discontinuous phase of PolyIMs has extremely high gas permeability, dramatically increasing gas permeability without reducing CO_2/N_2 selectivity. More importantly, the configuration of polymers only minimizes the formation of voids between polymers and MOFs in traditional MMMs and allows facile integration into the current membrane manufacturing trains.

To demonstrate the feasibility, we propose to prepare two series of copolymers, block copolymers (BCPolyMOFs) derived from polymerizable MOFs (polyMOFs) and interpenetrating networks (IPNs) containing PIMs.

Approach I: Design of PolyMOFs and BCPolyMOFs. Fig. 6a shows a strategy to prepare PolyMOFs and the associated BCPolyMOFs. First, the MOFs with amine groups on the organic ligand react with methacrylamide groups to graft methacrylate groups. Second, the polyMOFs with methacrylate groups can be copolymerized with PEGMEA and/or PEGDA via photo- and thermal-polymerization or ATRP. PEGDA also serves as a cross-linker for the curing process. The resulting copolymers have a general chemical structure shown in Fig. 1a. The cross-linking scheme is under mild conditions such as room temperature, and thus, the MOFs structure will not be damaged. The MOFs with large pore sizes and high porosity are preferred to provide high gas permeability, and yet they have amine groups to functionalize with the acrylate groups for polymerization.

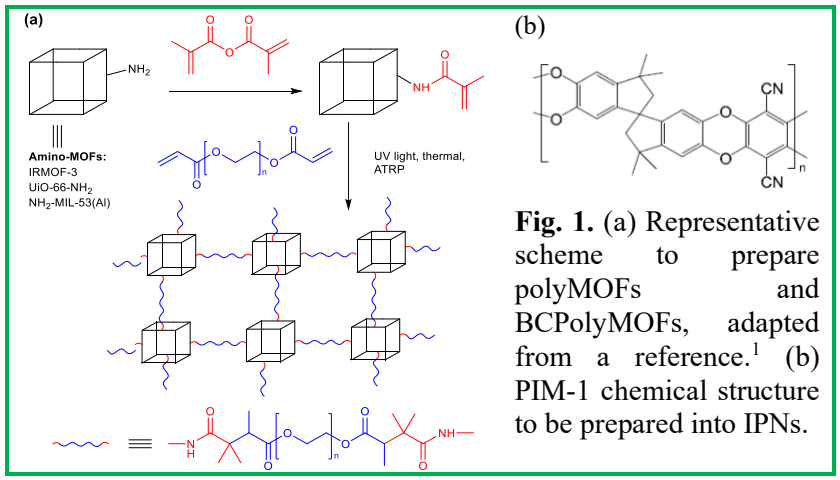

Fig. 1. (a) Representative scheme to prepare polyMOFs and BCPolyMOFs, adapted from a reference.[1] (b) PIM-1 chemical structure to be prepared into IPNs.

Approach II: IPNs Containing PIMs. IPNs can be easily prepared by dissolving the PIMs (such as PIM-1 with chemical structure shown in Fig. 1b) and the macromonomers of PEGMEA before the polymerization. PIMs can be prepared using widely reported methods in the literature. These polymers can provide a quick indication of the effect of the PIM phase on the CO_2/N_2 separation properties.

2.1.2 Proof of Concept of High-Performance BCPIMs

Approach I: BCPolyMOFs. We identified UiO-66-NH_2 as a good candidate for polyMOFs because of its large pore size and high porosity to provide high gas permeability and excellent stability in the humid and acidic environment. It also has amine groups to

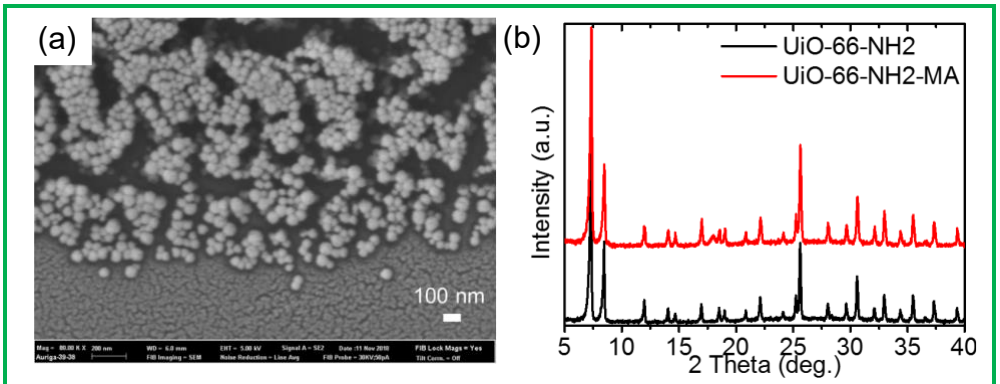

Fig. 2: (a) SEM image of UiO-66-NH_2 nanoparticles; (b) XRD patterns of nanoparticles before and after the functionalization.

functionalize with the acrylate groups for polymerization. We have successfully prepared UiO-66-NH_2 nanoparticles as small as 50 nm (Fig. 2a). Fig. 2b shows that the reacted UiO-66-NH_2 exhibits the X-ray diffraction (XRD) patterns similar to the pristine ones, indicating that the crystal structure (including pore size and porosity) is not changed by the functionalization.

To prepare BCPolyMOFs, we first optimized the polymer matrix to improve the CO_2 permeability. 18-Crown-6 with the same ether oxygen content as PEO was added into prepolymer solutions of the PEGDA and PEGMEA (20/80) before the photopolymerization. Increasing the crown ether content significantly increased the CO_2 permeability without a significant effect on the CO_2/N_2 selectivity.[2] For example, adding 50 wt% of crown ether in XLPEO increases CO_2 permeability from 580 to 1100 Barrer while retaining CO_2/N_2 selectivity of 43. Such an increase can be ascribed to the decrease in the glass transition temperature (T_g), indicating the increased flexibility of polymer chains and thus gas diffusivity.

Second, the prepared UiO-66-NH_2 nanoparticles were also incorporated into the prepolymer solutions containing PEGDA, PEGMEA, and crown ether before the photopolymerization. Adding 1.0 wt% of MOF dramatically increased CO_2 permeability from 580 Barrer in XLPEO to 770 Barrer and from 1100 Barrer in the blend containing 50% XLPEO and 50% crown ether (XLPEO-CE50) to 2200 Barrer, as shown in Fig. 3a. The increase in CO_2 permeability by adding the MOFs does not decrease CO_2/N_2 selectivity (Fig. 3b).

The BCPolyMOFs containing 1% MOFs in the XLPEO-CE50 (XLPEO-CE50-MOF1) showed the best CO_2/N_2 separation performance and were further evaluated with a gas mixture (20% CO_2/80% N_2) at different temperatures (Table 1). Mixed-gas separation properties are more or less consistent with the pure-gas properties. Increasing the temperature increases CO_2 permeability and decreases CO_2/N_2 selectivity. Although there is a tradeoff between permeability and selectivity in operating these membranes, the BCPolyMOFs show CO_2 permeability of 2200 Barrer and CO_2/N_2 selectivity of 50 at 35 °C, which meets the target for the proposed project.

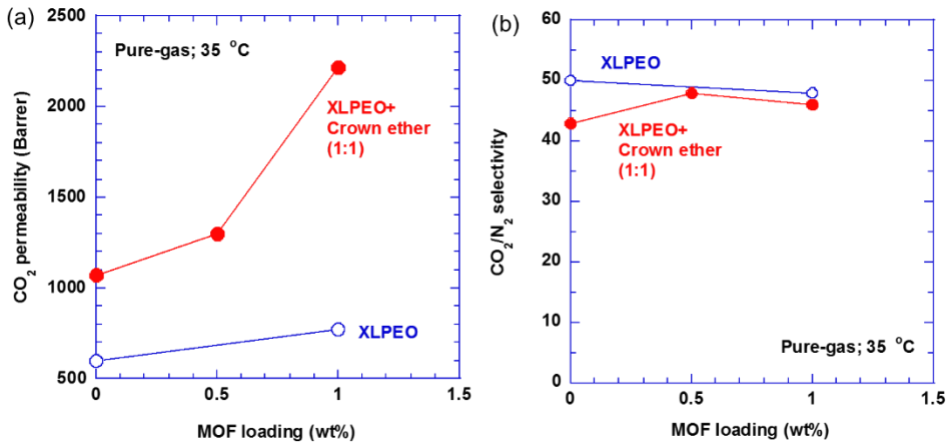

Fig. 3: Effect of the MOF loading on (a) CO_2 permeability; (b) CO_2/N_2 selectivity at 35°C and 30 psig.

Table 1: Pure- and mixed-gas CO_2/N_2 separation properties in XLPEO-CE50-MOF1 at various temperatures. The mixed gas contains 20% CO_2 and 80% N_2 at 150 psig.

T (°C)	Pure- or Mixed-gas	Feed pressure (psig)	Permeability (Barrer)		CO_2/N_2 Selectivity
			CO_2	N_2	
35	Pure	30	2200	48	46
35	Mixed	150	2200	44	50
50	Mixed	150	2900	100	29

60	Mixed	150	3000	100	30

Fig. 4 benchmarks these new materials with the state-of-the-art membrane materials developed for CO_2/N_2 separation. The mixed matrix materials have surpassed Robeson's 2008 Upper Bound, demonstrating the potential of our approach.

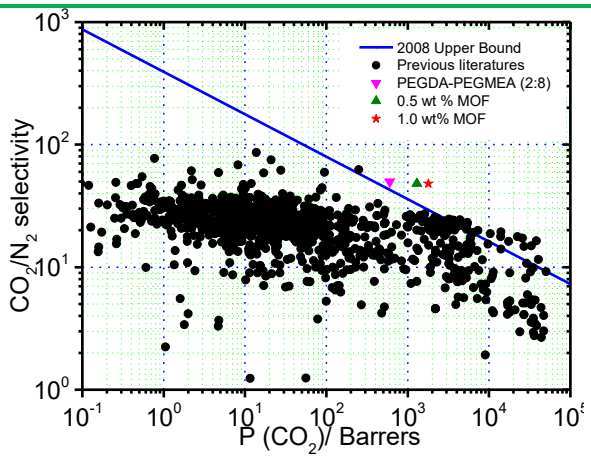

Fig. 4: Comparison of our mixed matrix materials (BCPolyMOFs) with state-of-the-art membrane materials for CO_2/N_2 separation in Robeson's 2008 upper bound.

Flue gas from coal-fired power plants often contains water vapor, SOx, and NOx. Fig. 5 presents the 50-h stability test of the BCPolyMOF for mixed-gas CO_2/N_2 separation in the presence of water vapor. The BCPolyMOFs showed stable dry-gas separation performance. When the water vapor was introduced, CO_2 permeability decreased slightly from 2200 Barrer to 1900 Barrer while the CO_2/N_2 selectivity remained almost the same at 48. These results validate that the BCPolyMOFs are good candidates for practical CO_2/N_2 separations.

The XLPEO-CE50-MOF1 films were also exposed to 75 ppm SO_x and 75 ppm NO_x in N_2 for 100 hours at 35 ℃. The CO_2/N_2 separation properties do not change after exposure to the mixed gas (Table 2), indicating that the films are stable under such testing conditions.

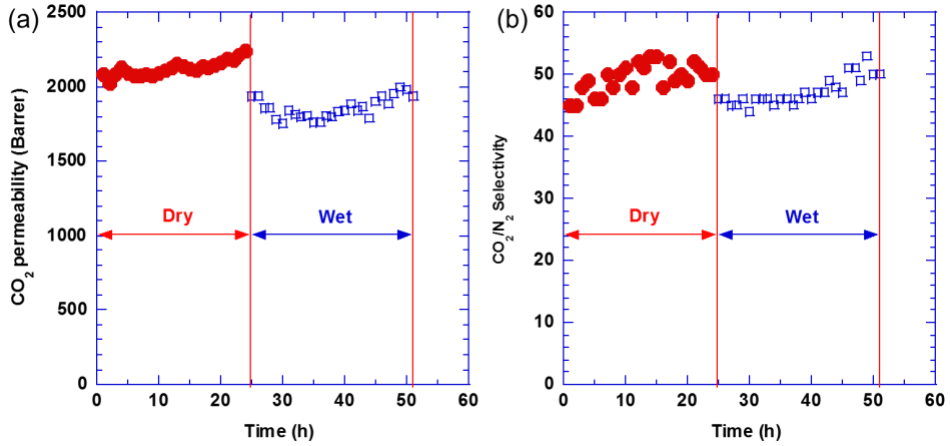

Fig. 5: A 50-h stability test of (a) CO_2 permeability and (b) CO_2/N_2 selectivity of the XLPEO-CE50-MOF1 in the presence of water vapor at 35 ℃. The dry gas mixture contains 20% CO_2 and 80% N_2, and the wet gas contains 0.3 mol% water vapor.

Table 2: Pure-gas permeability and selectivity at 35°C and 30 psig for the XLPEO-CE50-MOF1 films with and without exposure to 75 ppm SO_x and 75 ppm NO_x in N_2 for 100 hours at 35 ℃.

Samples	SO_x/NO_x exposure	Permeability (Barrer)		CO_2/N_2 Selectivity
		CO_2	N_2	
1	No exposure	2218	48	46

	After exposure	2393	52	46
2	No exposure	1800	36	50
	After exposure	1870	38	49

Approach II: IPNs containing PIMs. We have prepared IPNs by dissolving the monomers (PEGMEA and PEGDA) and PIM-1 in chloroform before the Photopolymerization. Fig. 6 shows the effect of the PIM-1 content in the copolymers of PEO/PIM-1 blends on pure-gas CO_2/N_2 separation properties at 35 °C. Increasing the PIM-1 content initially decreases CO_2 permeance, presumably because the polyether chains penetrate into the PIM-1 phase and decrease the free volume. At the PIM-1 content of higher than 50%, the CO_2 permeance starts to increase. Nevertheless, these blends do not seem to follow the Maxwell model or Lewis-Nielsen model. Given the very positive results achieved in Approach 1, we decide not to continue this path. Instead, we will focus on the BCPolyMOFs route.

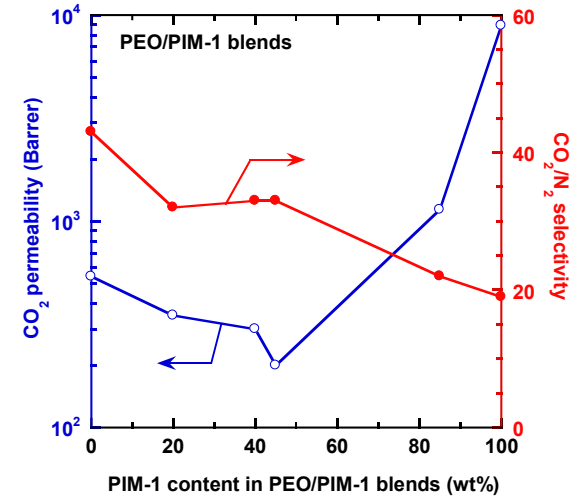

Fig. 6. Pure-gas CO_2/N_2 separation properties of PEO/PIM-1 blends at 35 °C.

2.2 Prepare and Characterize TFC Membranes Based on BCPIMs

The objective of this task was to prepare thin-film composite membranes with the configuration shown in Fig. 7. The selective layer based on the BCPolyMOFs will provide the CO_2/N_2 separation properties; the gutter layer provides a smooth surface for the selective layer to deposit and extremely high gas permeance; and the porous support provides mechanical properties needed for handling and separation operation.

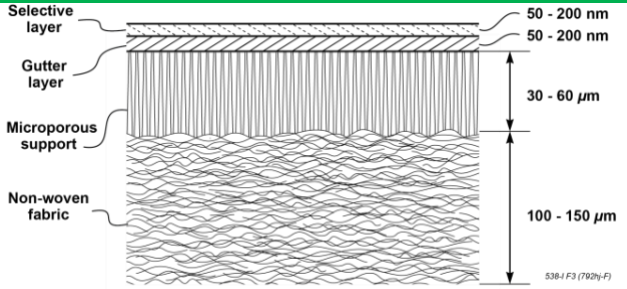

Fig. 7. Schematic of TFC membranes comprising a selective layer, gutter layer, and porous support.[3]

2.2.1 Synthesis of high molecular weight PEO polymer by ATRP reaction

The selective layer can be prepared by coating solutions containing BCPolyMOFs, which were prepared using atom transfer radical polymerization (ATRP). Figure 8 shows the schematic of the ATRP reaction, including the monomers, initiator, catalyst, and ligands. Specifically, a mixed solution with PEGMEA and PEGDA in 10 ml anhydrous DMSO were add in 250 ml three-neck flask. Copper(II) bromide and pentaerythritol tertrakis(2-bromo-isobutyrate) were added into the pre-mixed solution. The reactant mixture was mechanically stirred at ≈ 22 °C for 2 h to make sure initiator and copper bromide dissolved in solution. Then Me6TERN and copper wire were added. Followed by degassing with three freeze-pump-thaw cycles, the polymerization was allowed to proceed at 30 °C under argon flow for 35 mins.

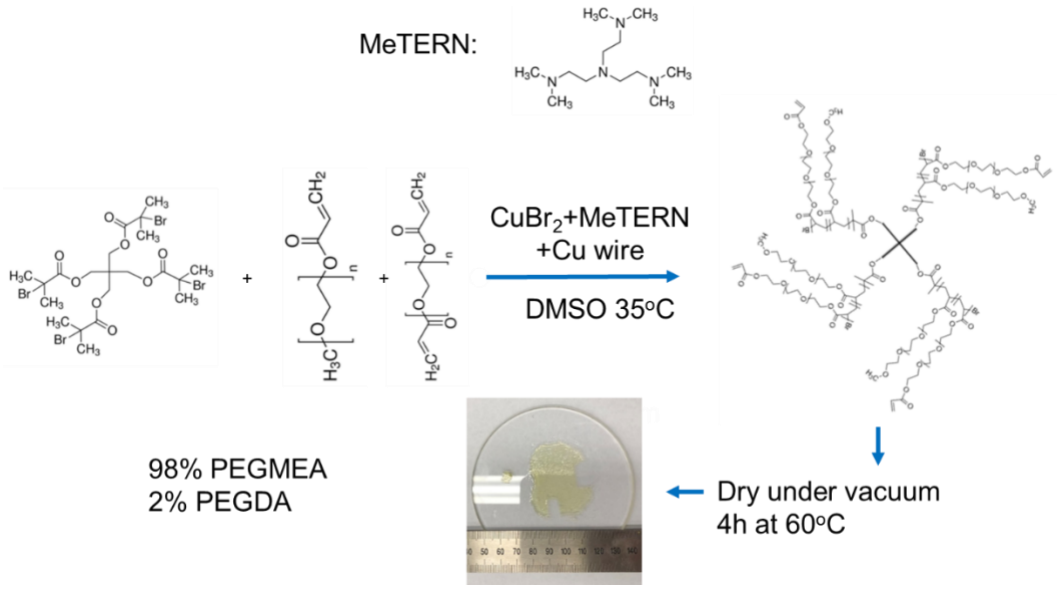

Fig. 8. Proof of concept of synthesis of high molecular weight PEO and the photo of an as-prepared film.

2.2.2 Preparation of the TFC membranes

To demonstrate the promise of these new materials for practical applications, we prepared TFC membranes with the configuration shown in Fig. 7. The selective layer based on the BCPIMs will provide the CO_2/N_2 separation properties; the gutter layer provides a smooth surface for the selective layer to deposit and extremely high gas permeance and to channel the permeating gas to the open pores of the substrate; and the porous support provides mechanical properties needed for handling.

We have identified polysulfone (PSF) ultrafiltration (UF) membranes as the porous support and polydimethylsiloxane (PDMS) with a CO_2 permeability of 3000 Barrer and N_2 permeability of 300 Barrer as the gutter layer. PEGMEA was polymerized using ATRP, which was then coated onto the gutter layer using a dip-coater. Table 3 summarizes the pure-gas CO_2/N_2 separation properties of a few examples. The PEO layer increases the CO_2/N_2 selectivity compared with the PDMS layer. The performance of CO_2 permeance ranging from 630 to 2500 GPU and CO_2/N_2 selectivity ranging from 43 to 30 is comparable with the leading membranes, demonstrating their potential.

Table 3: CO_2/N_2 separation properties in TFC membranes comprising PEO on the PDMS gutter layer at 35 °C.

Samples	Selective layer	Permeance (GPU)		CO_2/N_2 Selectivity
		CO_2	N_2	
1	None	5400	500	11
2	PEO	2500	85	30
3		1100	29	38
4		1070	36	30
5		630	15	43
6	98% PEO + 2% MOF	1140	45	25

To improved the hydrophilicity of the gutter layer, we have used polydopamine (PDA) to modify the PDMS gutter layer surface. Table 4 shows the effect of PDA modification on PDMS gutter layer gas permeance and water contact angle. After the PDA modification, the PDA-PDMS gutter layer shows water contact angle 60° and CO_2 permeance of 6500 GPU. We also prepared the TFC membrane with a PDA-PDMS gutter layer, and the results are summarized in Table 5.

With the same coating solution, the membrane based on PDA/PDMS shows higher CO_2 permeance and higher CO_2/N_2 selectivity than that based on PDMS.

Table 4: Effect of PDA modification on the hydrophilicity and CO_2/N_2 separation properties of the PDMS gutter layer.

Samples	Water contact angle (°)	Permeance		CO_2/N_2 Selectivity
		CO_2	N_2	
PDMS/PSF	100	10000	1100	9
PDA-PDMS/PSF	61	6500	900	7.2

Table 5: CO_2/N_2 separation properties of TFC membranes with different gutter layers at 35°C.

Gutter layer	Coating solution concentration (wt%)	Permeance (GPU)		CO_2/N_2 Selectivity
		CO_2	N_2	
PDMS	0.5	1044	27	39
PDA-PDMS	0.5	1260	28	45
PDA-PDMS	0.3	2300	70	33

We have determined TFC membranes with CO_2/N_2 mixtures with various compositions at 25, 35, and 60 °C, and the results are summarized in Table 6. To demonstrate the concept here, the membranes were prepared using the polymer prepared from PEGMEA via ATRP without the polyMOFs. Increasing the temperature increases the gas permeance and decreases the CO_2/N_2 selectivity. We have also varied the feed pressure from 15 psig to 30 psig and feed CO_2 content from 10% to 30% (typical operating conditions for flue gas treatment), and the mixed-gas CO_2/N_2 separation properties remain similar.

Table 6. Mixed-gas separation properties at 30 psig in a TFC membrane with a mixture of 15% CO_2 and 85% N_2.

T (°C)	Mixed-gas permeance (GPU)		Mixed-gas CO_2/N_2 selectivity
	CO_2	N_2	
25	645	13	50
35	796	22	36
60	1030	51	20

Fig. 9 shows the long-term stability with CO_2/N_2 mixture in the presence of water vapor. The membrane was initially exposed to 15% CO_2 and 85% N_2 at 30 psig and 35°C for 15 h before 1.5 mol% water vapor was introduced to the feed. The presence of water vapor decreases CO_2 permeance from 950 to 850 GPU and N_2 permeance from 36 to 32 GPU while retaining the CO_2/N_2 selectivity of ≈27, presumably because of the increased selective layer thickness by water absorption. The membrane shows stable separation performance with water vapor in 98 h. When tested again with a dry binary mixture, the CO_2/N_2 separation properties are restored to the original values, indicating the membrane stability.

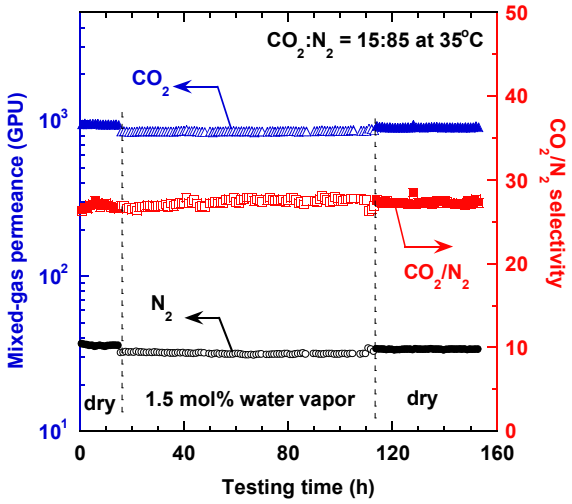

Fig. 9. Long-term stability with a CO_2:N_2 of 15:85 and 1.5 mol% water vapor at 2 atm and 35°C.

2.3: Process Development and Economics

Preliminary techno-economic analysis was performed to assess the potential of the BCP-MOF membranes for CO_2 capture from a 550 MW power plant burning sub-bituminous coal with the post FGD flue gas properties used were obtained from DOE's baseline studies and shown in Table 7.

Table 7: Flue gas properties used in analysis.

	Raw Flue
Flow (MM SCFD)	1511
T	50
P (bar)	1.1
CO2	11.6%
H2O	10.2%
N2	73.8%
O2	4.3%

Properties of TFC commercial membrane modules were projected based on the advanced materials (BCP-MOF's) developed in the Phase1 project. Table 8 summarizes the low- and high-end properties used in the present analysis. Given the use of rubbery polymers, the O_2/N_2 selectivity of the membrane was assumed to be 2 in all cases.

Table 8: Range of commercial membrane module properties used in the analysis.

Low End			High End		
Gas	GPU	Alfa	Gas	GPU	Alfa
CO2	3500	1.00	CO2	4500	1.00
N2	100	35.00	N2	113	40.00

The following assumptions were used in the analysis:

- Pressure drops within the module were neglected
- A skidded membrane cost of \$50/m^2 was assumed
- Power cost was assumed to be \$0.05/kWh
- Capital costs for compression equipment were based on those reported in the EPRI-Worley Parsons study of the MTR membrane process[6]

Figure 10 shows a schematic of the 2-stage cascade process used in the analysis. Post-FGD flue gas from the coal power plant, at close to ambient pressure, enters a stage 1 membrane operated under partial vacuum. The CO_2 depleted retentate from the membrane is vented. The permeate, enriched in CO_2, first enters a vacuum pump and subsequently a condenser where liquid water is removed. This gas is then compressed to 3.5 bar and cooled in the condenser, where additional water is removed, prior to entering the second membrane stage, which produces a CO_2 enriched permeate and a CO_2 depleted retentate. The CO_2 depleted retentate from stage 2 is recycled to a point upstream of the Stage1 membrane. The CO_2 enriched permeate can be optionally processed in an externally refrigerated cryogenic enricher which produces a liquid CO_2 product (close to 100% purity) and a vent stream comprised primarily of the non-condensibles such as N_2 and O_2.

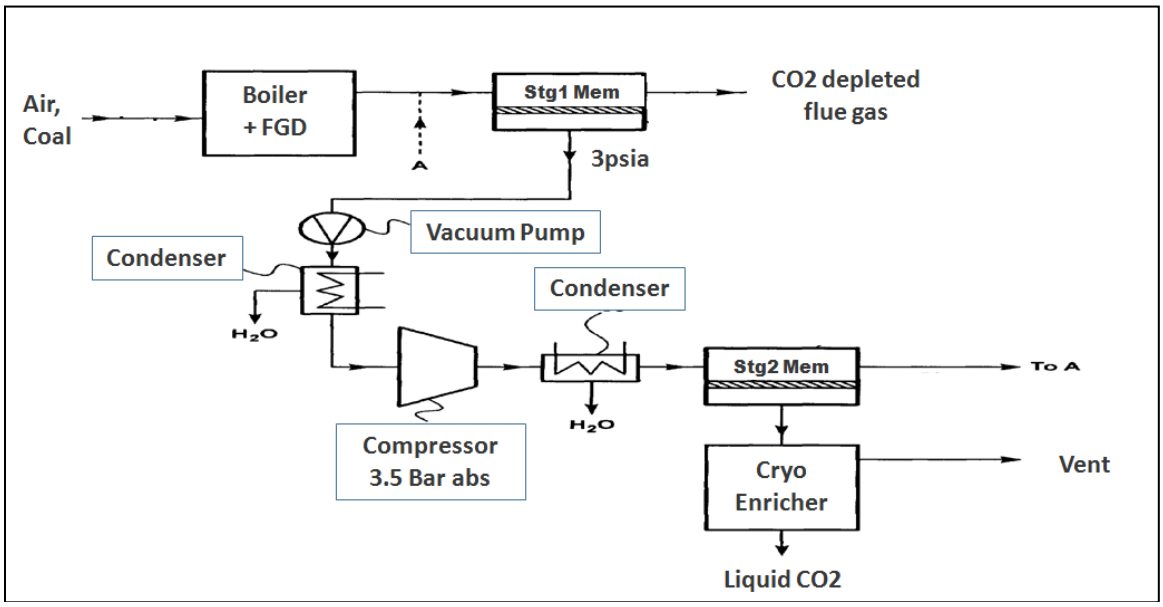

Figure 10: Schematic of the 2-stage process.

Figure 11 shows the CO_2 purity from the membrane process (before cryo) as a function of capture efficiency. The CO_2 purity is in the range of 65-82% with the purity declining with increased capture efficiency. At the same product purity level, the high-end properties increase the capture efficiency level by ~10% over the low-end properties.

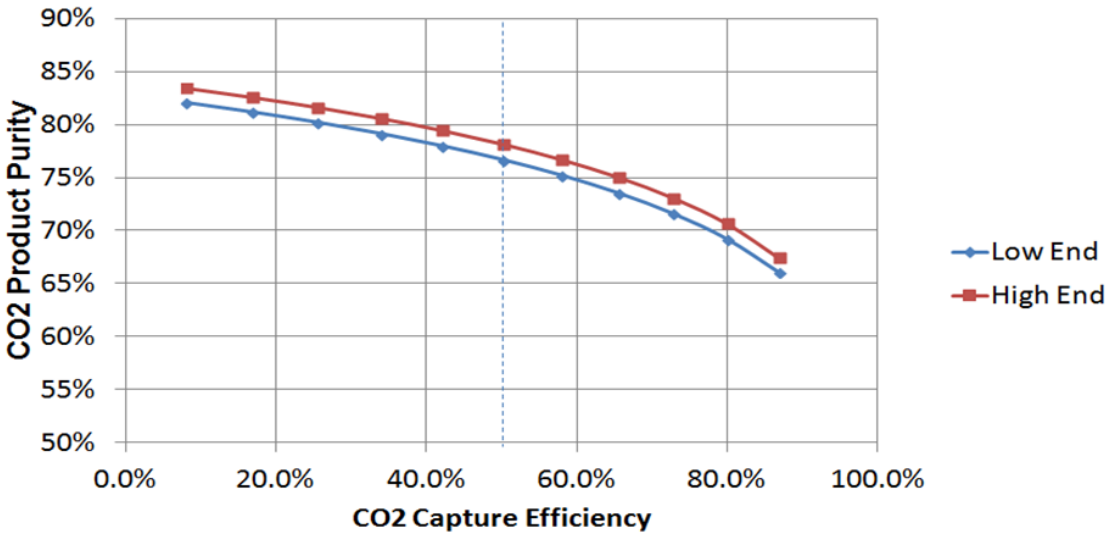

Figure 11: Product purity vs capture efficiency for the 2-stage process

Figure 12 shows the CO_2 product purity and CO_2 capture cost for the high-end properties for the 2-stage process as a function of capture efficiency for the membrane only case. While the product purity decreases monotonically with increased capture efficiency, the capture cost is minimum at ~30% capture. The capture cost does not change much between 20-45% capture efficiency but rises rapidly beyond ~60% capture. The use of low-end properties increases the capture cost by ~$2-3 /ton, but the trends are similar.

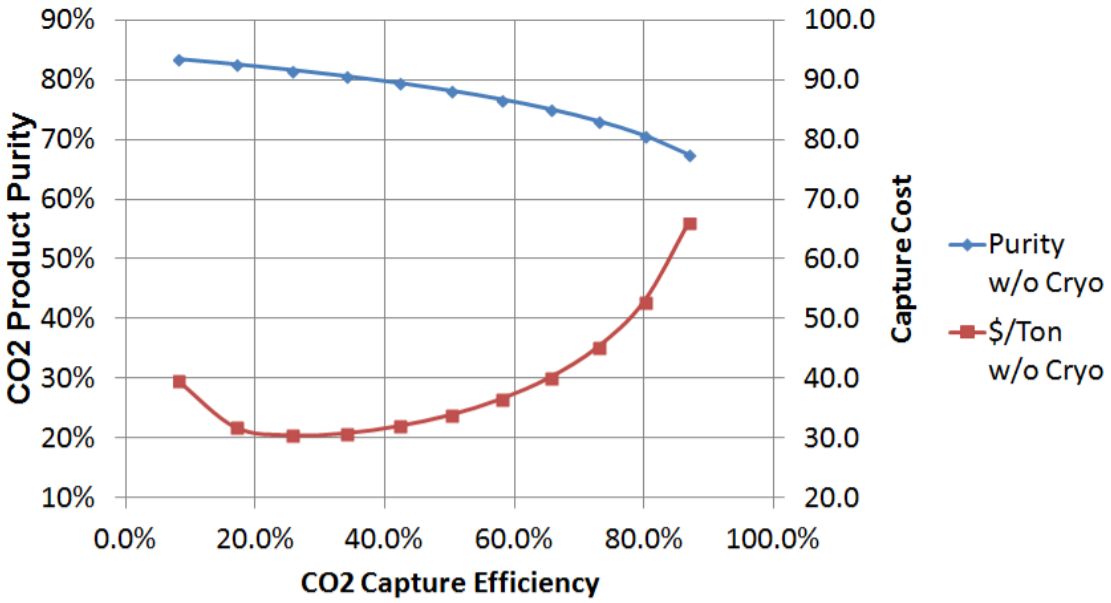

Figure 12: Impact of capture efficiency on product purity and capture cost

Figure 13 shows that adding a cryogenic enricher increases the product purity to ~100% but increases the capture cost by ~$10-12 /ton. Again the results in Figure 12 are for the high-end properties, and use of the low-end properties would increase the capture cost by ~$2-3/ton.

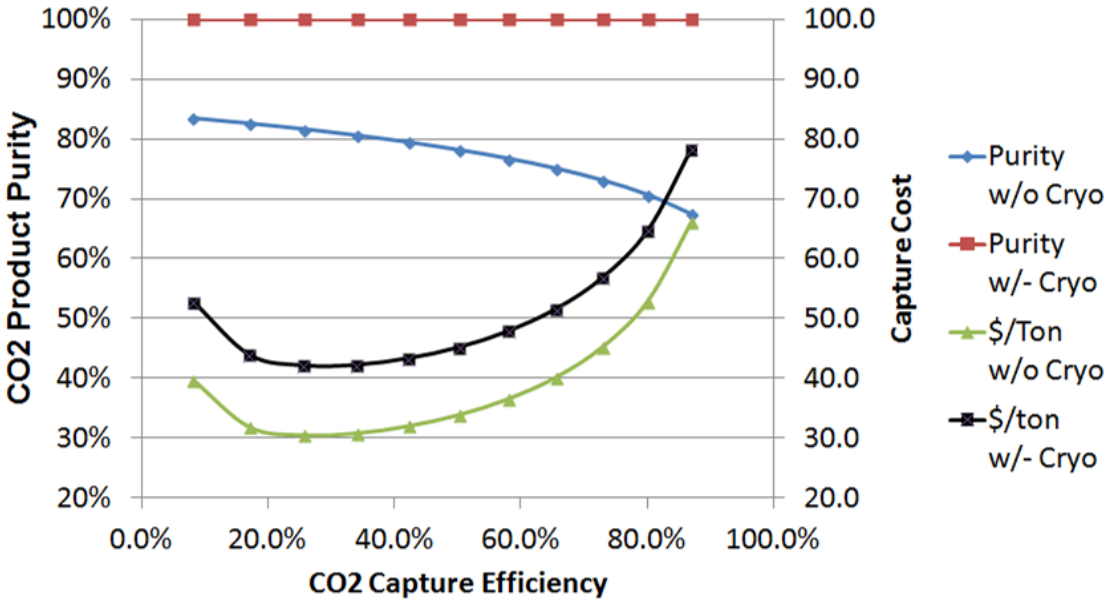

Figure 13: Impact of adding a cryogenic enricher to the 2-stage process

Figure 14 shows MTR's novel air refluxed 3-stage process. As before, post-FGD flue gas from the coal power plant, at close to ambient pressure, enters a Stage 1 membrane operated under partial vacuum. The CO_2 depleted retentate from the membrane is passed through a 2nd stage which is refluxed on the permeate side with the feed air to the boiler. Since ambient air has negligible CO_2, this stage permits very high CO_2 capture efficiency without resorting to permeate side vacuum. The permeate side stream leaving Stage 2 is enriched in CO_2 and is fed as the oxidant to the boiler thus increasing the CO_2 concentration in the flue gas stream, which permits increased driving force in Stage 1 for CO_2 separation as well as reduced area. The Stage 2 retentate is CO_2 depleted flue gas that is vented. As before, the Stage 1 permeate, enriched in CO_2, first enters a vacuum pump and subsequently a condenser where liquid water is removed. This gas is then compressed to 3.5 bar and cooled in a condenser, where additional water is removed, prior to entering the second membrane stage which produces a CO_2 enriched permeate and a CO_2 depleted retentate. The CO_2 depleted retentate from stage 2 is recycled to a point upstream of the Stage1 membrane. The CO_2 enriched permeate can be optionally processed in an externally refrigerated cryogenic enricher which produces a liquid CO_2 product (close to 100% purity) and a vent stream comprised primarily of the non-condensibles such as N_2 and O_2. The clever use of the boiler feed air as a sweep stream to increase capture efficiency as well as boost the CO_2 concentration in the flue gas results in a significant reduction in CO_2 capture cost.

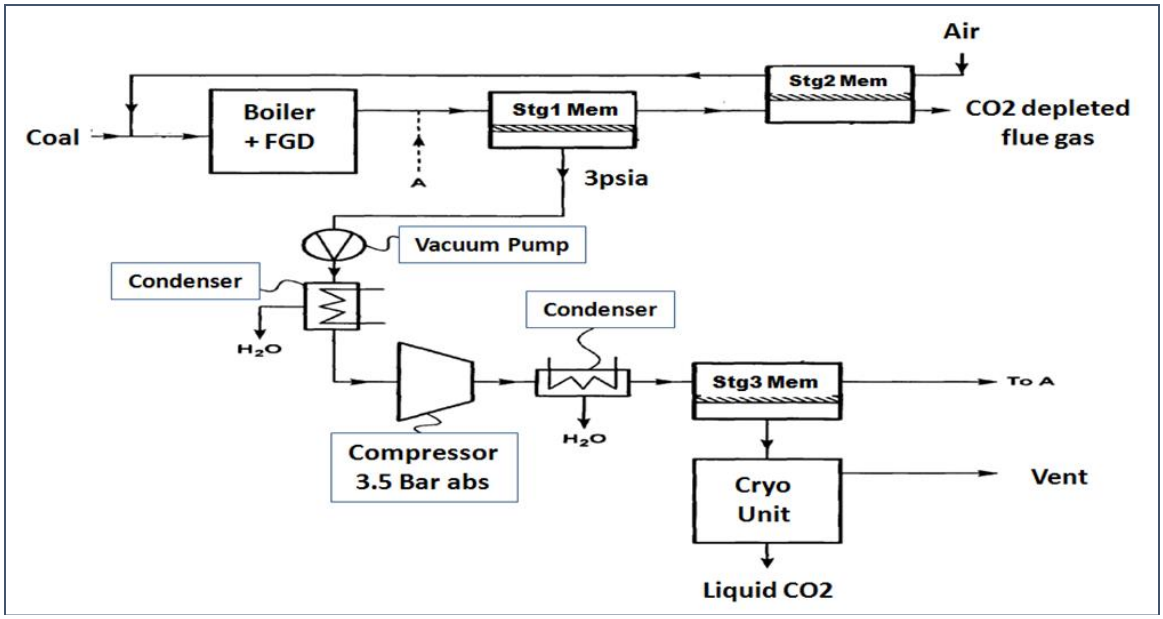

Figure 14: Schematic of MTR's 3-stage process

A very large number of representations of the 3-stage process are possible representing different pressures, vacuum levels, area distributions, capture efficiency, and the design of the cryogenic enricher. While determining the optimum is well beyond the scope of a Phase1 project, the cases shown below represent reasonable examples. These cases have an overall capture efficiency of ~91.5% and a CO_2 purity of 85-90% in the permeate from the 3rd stage. Table 9 shows the total area and area distribution for the low- and high-end properties. 11MM ft^2 of membrane area is required for the high-end properties with that for the low-end properties being about 20% higher. While this is a large number, reverse osmosis (RO) membrane plants of comparable scale have been built for desalination. Most of the areas are in the first two stages, and Stage 3 is relatively small.

Table 9: Area required and area distribution for the 3-stage process

	Low Prop		High Prop	
	Area	Power (KW)	Area	Power (KW)
Total Area (MM ft2)	13.6		11.0	
Stg 1 Membrane	52.6%		54.6%	
Stg 2 Membrane	43.6%		41.7%	
Stg 3 Membrane (est)	3.8%		3.7%	
Compression Equipment		59,380		58,586

Table 10 shows the total capital cost, total power consumed, and the CO_2 capture cost for these cases with and without a cryogenic enricher. The CO_2 capture cost is $20-21/ton for the membrane alone process and $28.5-29.5/ton with the cryogenic enricher added. These results show that the BCP-MOF membranes have the potential for a significant reduction in CO_2 capture cost if the material properties are realized in commercial TCF membrane modules.

Table 10: TEA results for 3-stage process

	Low Prop		High Prop	
	W/o Cryo	W/- Cryo	W/o Cryo	W/- Cryo
Overall Capture eff	91.5%	91.5%	91.5%	91.5%
Prod CO2 Conc.	85.5%	100.0%	87.0%	100.0%
Total Capital cost (MM $)	191.0	224.0	177.0	210.0
Power Used (MW)	59.5	109.0	58.5	108.0
CO2 Capture Cost ($/ton)	21.2	29.5	20.1	28.5

2.4: Project Management

The goal of this task was to assure that all programmatic activities were completed on time and within budget while achieving successful completion of the overall project. The effective project start date was initiated on 6/29/2020 as stated in the Assistance Agreement. Subsequent to signing of the Assistance Agreement with DOE, Helios-NRG executed a sub'-award contract with UB on 7/15/2020 incorporating all necessary confidentiality agreements and DOE contract terms. Due to the COVID-19 pandemic, work and progress on the project was highly affected due to the mandated NYS and local guidelines. This resulted in ~50% reduction in operational capacity at both Helios and UB. Accordingly, Helios-NRG requested and was granted a 3-month extension of the contract to 7/28/2021.

In the course of executing the project, progress review meetings were held on a bi-weekly basis with Dr. Haiqing Lin of UB and his team. Progress and financial reports were submitted to DOE in accordance with the Federal Assistance Reporting Checklist. Invoices for the final project cost totaling $256,420 were submitted and paid by DOE against a budget of $256,420.

Note that actual expenditures for Helios-NRG direct labor, materials, and indirect costs exceeded the invoiced amount by $9,460. Helios-NRG absorbed this cost overrun. UB team also incurred an additional $15,000 for the labor, materials, and indirect costs, which were kindly provided by the office of the Research and Economic Development of UB.

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