Phase1 Final Technical Report

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Project Title	**: Scalable Polymerized Metal-Organic Frameworks with CO2-philic Rubbery Polymers for Membrane CO2/N2 Separation**
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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. In 2014, CO_2 emissions from US coal burning power plants was ~ 1562 MM tons/yr, accounting for 76% of the total US power sector emission[1]. Hence, reducing the CO_2 emission footprint from coal plants is widely viewed as a key element in mitigating global warming. Despite significant interest, 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 this approach by developing new membrane materials and scalable membranes based on block copolymers of metal-organic frameworks (BCP-MOFs) and rubbery PEO to achieve superior CO_2/N_2 separation properties and subsequently performing preliminary techno-economic analysis (TEA) by incorporating the membranes into suitable process configurations.

Metal oxide 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 BCP-MOF 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. Preliminary thin film composite (TFC) membranes using these materials were prepared. Further optimization of the gutter layer and coating solution of the mixed matrix materials will improve improve the membrane performance.

The techno-economic analysis was performed based on projected commercial TFC membrane module performance based on the new BCP-MOF 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 BCP-MOF 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. In 2014, CO_2 emissions from US coal-burning power plants was ~ 1562 MM tons/yr, accounting for 76% of the total US power sector emission. Hence, reducing the CO_2 emission footprint from coal plants is widely viewed as a key element in mitigating global warming. Despite significant interest, 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 this approach by developing new membrane materials and scalable membranes based on block copolymers of metal-organic frameworks (BCP-MOFs) and rubbery PEO to achieve superior CO_2/N_2 separation properties and subsequently performing preliminary techno-economic analysis (TEA) 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 thin film composite (TFC) membranes, were successfully synthesized. These nanoparticles were then functionalized with methacrylate groups so that they can 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) can increase the CO_2 permeability from 580 Barrers to 1100 Barrers while retaining CO_2/N_2 selectivity of 43. Introduction of the UIO-66-NH_2 in the blends of XLPEO and crown ether can further improve the 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) exhibits 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. Preliminary thin film composite (TFC) membranes using these materials were prepared. While a gutter layer of Teflon AF2400 on PAN ultrafiltration membrane shows CO_2 permeance of 20,000 – 80,000 GPU, the prepared TFC membranes show CO_2 permeance of 114 GPU and CO_2/N_2 selectivity of 24. Further optimization of the gutter layer and coating solution of the mixed matrix materials are needed to improve the membrane performance.

The techno-economic analysis was performed based on projected commercial TFC membrane module performance based on the new BCP-MOF materials synthesized in Phase1. 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 Membrane Technology and Research, Inc. (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 BCP-MOF membranes for cost-effective CO_2 capture.

2. Detailed discussion of work and accomplishments by task:

Task 1 Design, synthesize and characterize pMOFs

The goal of this task was to screen out the best candidate of polymerizable MOFs (pMOFs) and optimize the synthesis condition to produce pMOFs nanoparticles small enough to make TFC membranes. UiO-66-NH_2 was chosen because of its large pore size and high porosity to provide high gas permeability and excellent stability in the humid and acidic environment.[1,2] It also has amine groups to functionalize with the acrylate groups for polymerization. We have successfully prepared UiO-66-NH_2 nanoparticles as small as 50 nm (Figure 1a). Specifically, 0.80 mmol $ZrCl_4$ and 0.80 mmol NH_2-BDC were dissolved in 81.7 mL DMF, and then 4.83 g HAc and 0.58 g water were added into the solution. The solution was sealed in a glass vial and kept in a 50 °C oven for 12 h. Finally, the UiO-66-NH_2 nanoparticles were purified by centrifugation and washed three times with methanol. Figure 1b shows X-ray diffraction (XRD) patterns of UiO-66-NH_2 nanoparticles synthesized at different reaction time, which agree well with previous reports.[1,3] The results also indicate that the crystalline UiO-66-NH_2 nanoparticles were formed after 0.5 h.

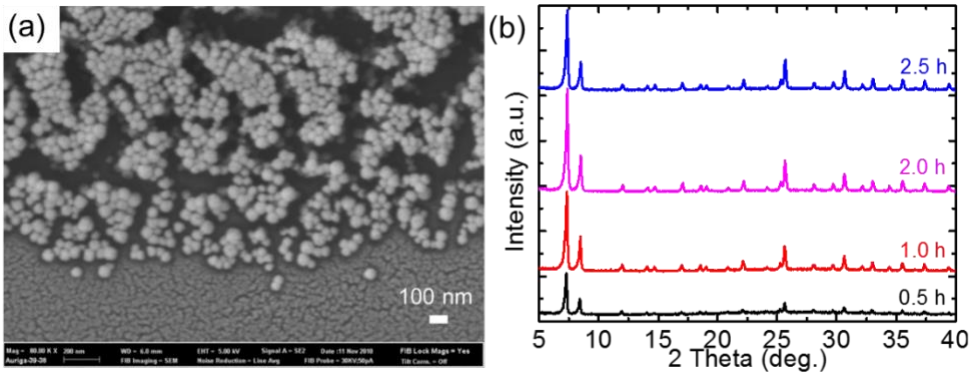

Figure 1. (a) SEM image of UiO-66-NH_2 nanoparticles; (b) XRD patterns of UiO-66-NH_2 nanoparticles synthesized at different reaction times.

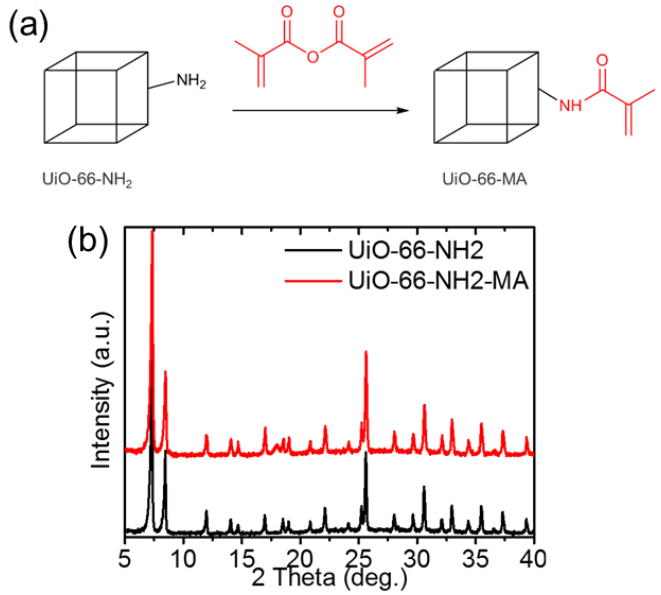

Figure 2. (a) Representative scheme to functionalize UiO-66-NH_2 nanoparticles with MA and (b) XRD patterns of nanoparticles before and after functionalization.

Figure 2a shows the reaction of the UiO-66-NH_2 nanoparticles with methacrylic anhydride (MA) in dichloromethane (DCM) at ≈22 °C for 24 h. Figure 2b shows that the reacted UiO-66-NH_2 shows the XRD patterns similar to the pristine ones, indicating that the crystal structure (including pore size and porosity) is not changed by the functionalization (Figure 2b).

Task 2 Prepare and characterize BCP-MOFs

The goal of this task was to incorporate the as-prepared UiO-66-NH_2 nanoparticles into PEGDA-PEGMEA matrix to make mixed matrix membranes. First, 18-crown-6 with the same ether oxygen content as PEO was added into prepolymer solutions of the PEGDA-PEGMEA (20/80) before photopolymerization. Figure 3a shows that increasing the crown ether content significantly increases CO_2 permeability and has no detrimental effect on the CO_2/N_2 selectivity. For example, adding 50 wt% of crown ether in XLPEO increases CO_2 permeability from 580 Barrers to 1100 Barrers 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.

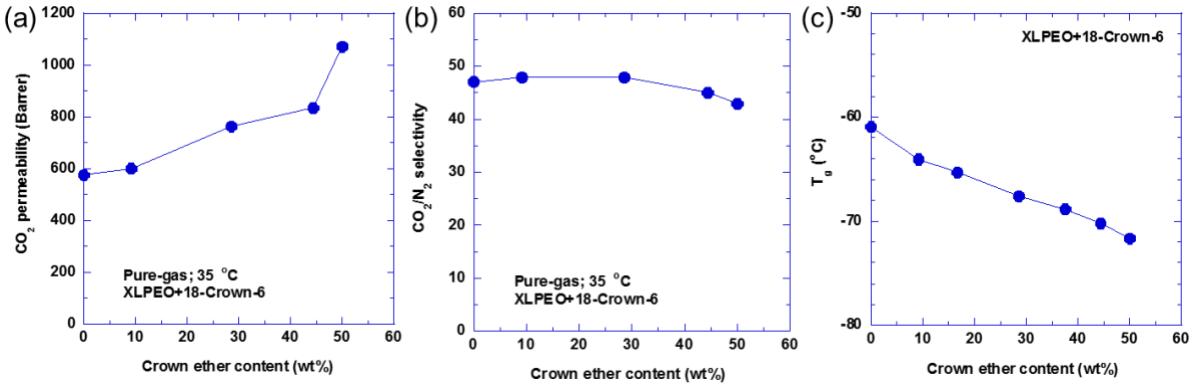

Figure 3. Effect of 18-crown-6 content on (a) CO_2 permeability, (b) CO_2/N_2 selectivity, and (c) T_g in the blends of XLPEO and crown ether. Gas permeability was determined at 35 °C and 30 psig.

Second, the prepared UiO-66-NH_2 nanoparticles were also incorporated into the prepolymer solutions containing PEGDA, PEGMEA, and crown ether before the photopolymerization. As shown in Figure 4, adding 1.0 wt% of MOF can dramatically increase CO_2 permeability from 580 Barrers in XLPEO to 770 Barrers, and from 1100 Barrers in the blend containing 50% XLPEO and 50% crown ether (XLPEO-CE50) to 2200 Barrers. Figure 4c also shows that the increase in CO_2 permeability by adding the MOFs does not decrease CO_2/N_2 selectivity. Figure 5 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 the Robeson's 2008 Upper Bound.[4]

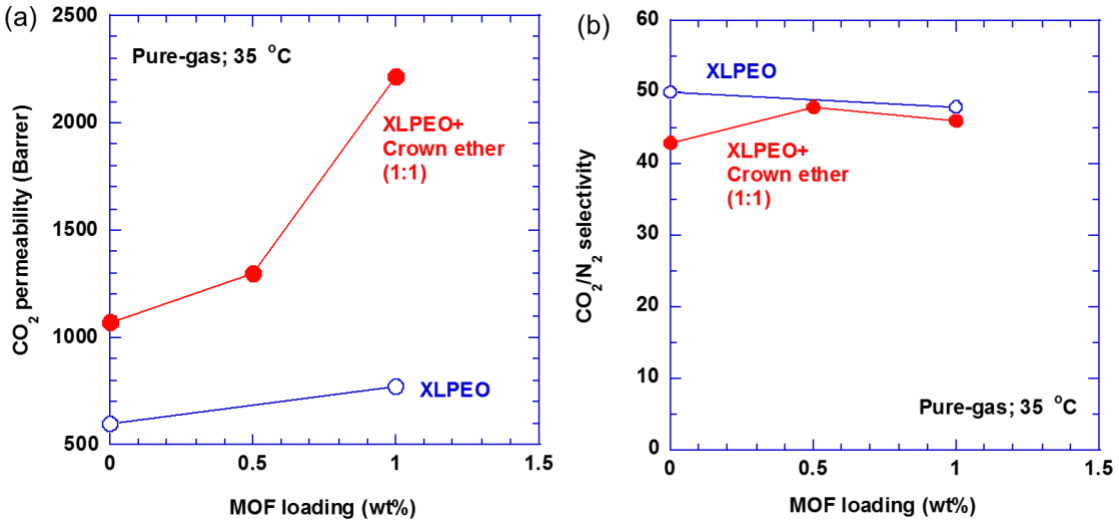

Figure 4. Effect of the MOF loading on (a) CO_2 permeability and (b) CO_2/N_2 selectivity at 35 °C and 30 psig.

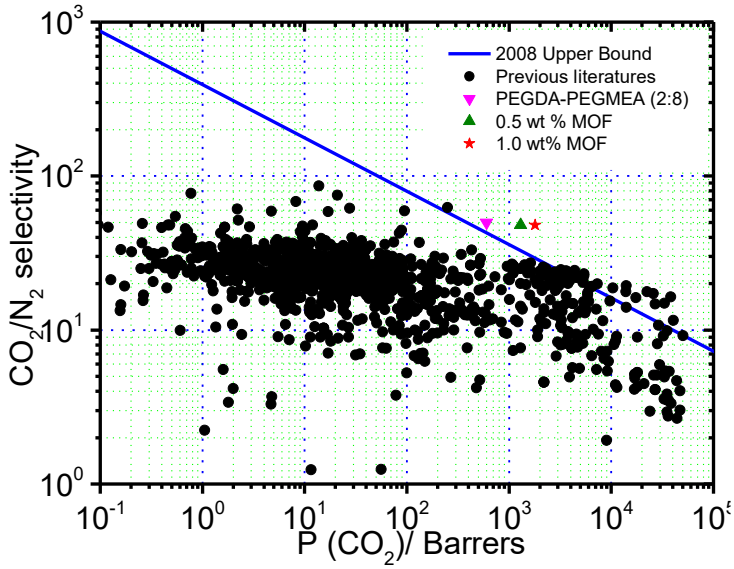

Figure 5. Comparison of our mixed matrix materials (BCP-MOFs) with state-of-the-art membrane materials for CO_2/N_2 separation in the Robeson's 2008 upper bound.

The BCP-MOFs containing 1% MOFs in the XLPEO-CE50 (XLPEO-CE50-MOF1) show the best CO_2/N_2 separation performance and is further evaluated with gas mixtures (20% CO_2/80% N_2) at different temperatures. Table 1 summarizes the results. Mixed-gas separation properties are more or less consistent with the pure-gas properties, and increasing the temperature increases CO_2 permeability and decreases CO_2/N_2 selectivity. There is a tradeoff between permeability and selectivity in operating these membranes. Nevertheless, at 60 °C, the BCP-MOFs show CO_2 permeability of 3000 Barrers and CO_2/N_2 selectivity of 30.

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	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

Flue gas from coal-fired power plants often contains water vapor, SOx, and NOx. Figure 6 presents the long-term stability of the BCP-MOF for mixed-gas CO_2/N_2 separation in the presence of water vapor. The BCP-MOF shows stable dry-gas separation performance. When the water vapor was introduced, CO_2 permeability decreased slightly from 2200 Barrers to 1900 Barrers while the CO_2/N_2 selectivity remained almost the same at 48. These results validate that the BCP-MOFs are good candidates for practical CO_2/N_2 separations.

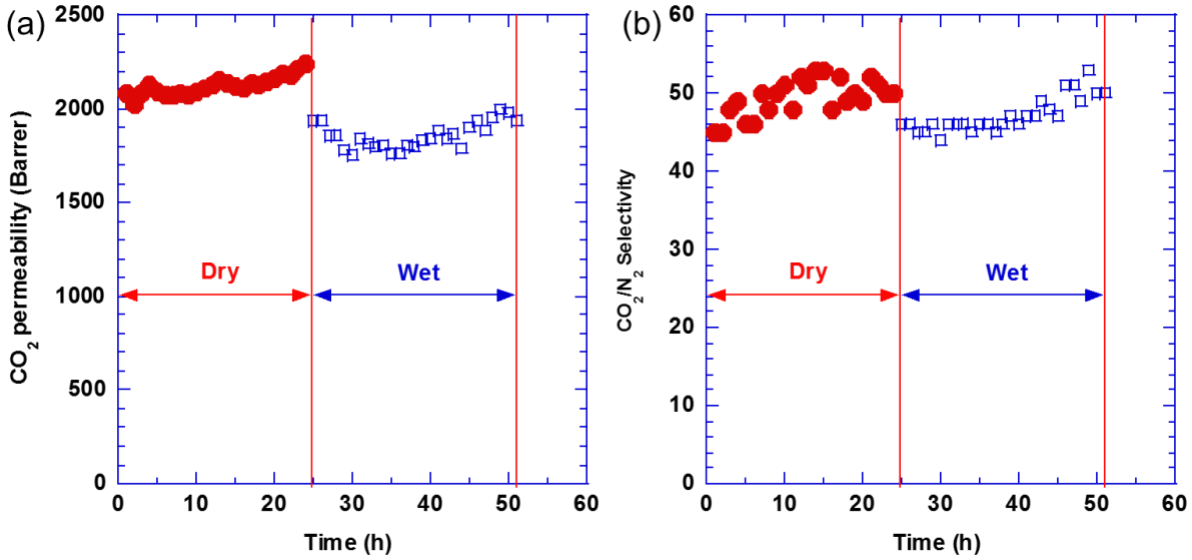

Figure 6. Long-term stability (a) CO_2 permeability and (b) CO_2/N_2 selectivity of the XLPEO-CE50-MOF1 in the presence of water vapor at 35 °C. The dry gas mixture contains 20% CO_2 and 80% N_2, and the wet gas contains 0.3 mol% water vapor.

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 °C. The CO_2/N_2 separation properties do not change after exposure to the mixed gas (cf. Table 2), indicating that the films are stable under such testing conditions.

Table 2. Pure-gas permeability and selectivity at 35 °C 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 °C.

SO_x/NO_x exposure	Pressure (psig)	Permeability (Barrer)		CO_2/N_2 Selectivity
		CO_2	N_2	
No exposure	10	2168	48	45
	20	2211	48	46
	30	2218	48	46
Film 1: After exposure	10	2360	57	41
	20	2401	52	46
	30	2393	52	46
Film 2: After exposure	10	2614	62	42
	20	2573	57	45
	30	2647	57	46

Task 3 Prepare and characterize TFC membranes based on BCP-MOFs

The objective of this task was to prepare thin film composite membranes with the configuration shown in Figure 7a. The selective layer based on the BCP-MOFs 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.

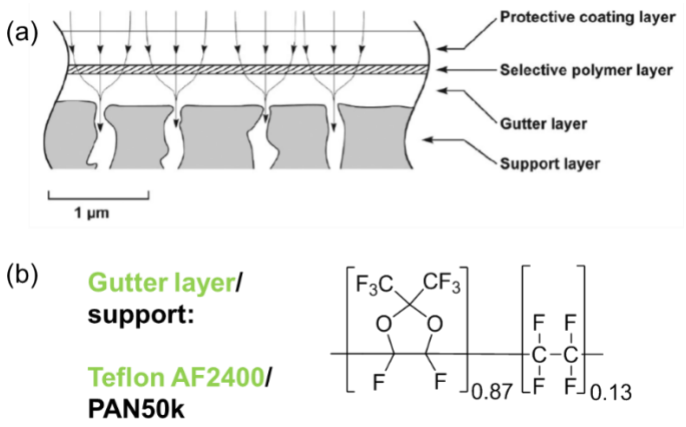

Figure 7. (a) schematic of a thin film composite (TFC) membrane. (b) Gutter layer and porous support.

3.1 Preparation of high-permeance gutter layer

We have identified Teflon™ AF2400 (with a CO_2 permeability of 2200 Barrers and N_2 permeability of 480 Barrers) as the gutter layer, and PAN 50k ultrafiltration (UF) membranes as the porous support, as shown in Figure 7b. Teflon AF2400 exhibits one of the highest gas permeabilities among polymers known and has a good film-forming ability.

Figure 8a exhibits pure-gas permeance of the gutter layer. As the Teflon AF2400 content in the coating solutions increases, gas permeance of the gutter layer on PAN50 decreases while the CO_2/N_2 selectivity remains unchanged. Even at 1.5 wt%, the obtained gutter layer shows a CO_2 permeance of 22,000 GPU, which is much higher than the targeted CO_2 permeance in TFC membranes.

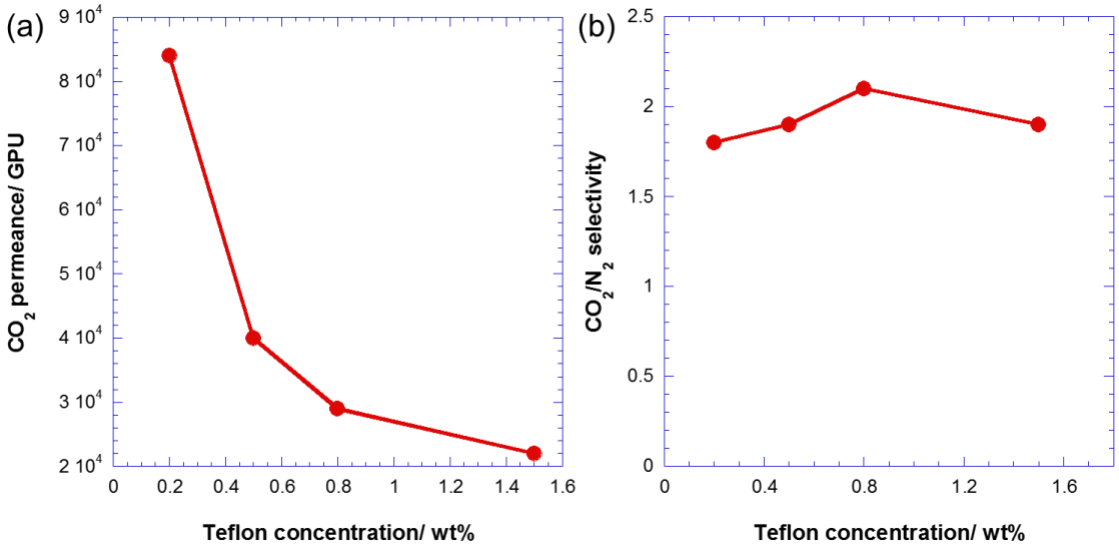

Figure 8. Effect of the Teflon AF2400 content in the coating solutions on (a) CO_2 permeance and (b) CO_2/N_2 selectivity at 35 °C.

Teflon AF2400 is hydrophobic and oleophobic, and therefore, for it to be used for the gutter layer, its surface needs to be modified. We use oxygen plasma treatment at a fixed power (50W), a pressure of 25 mTorr, and an oxygen flow of 30 sccm. Figure 9 shows the water contact angle of the Teflon AF2400 at different plasma treatment times. In general, the contact angle decreases with increasing the plasma treatment time before leveling off, confirming that the surface becomes more hydrophilic. After the 30-s plasma treatment, CO_2 permeance remains at ≈22,000 GPU, and CO_2/N_2 selectivity remains at ≈2.2 at 35 °C, indicating that the thin Teflon layer is still intact gas permeation despite the improve hydrophilicity.

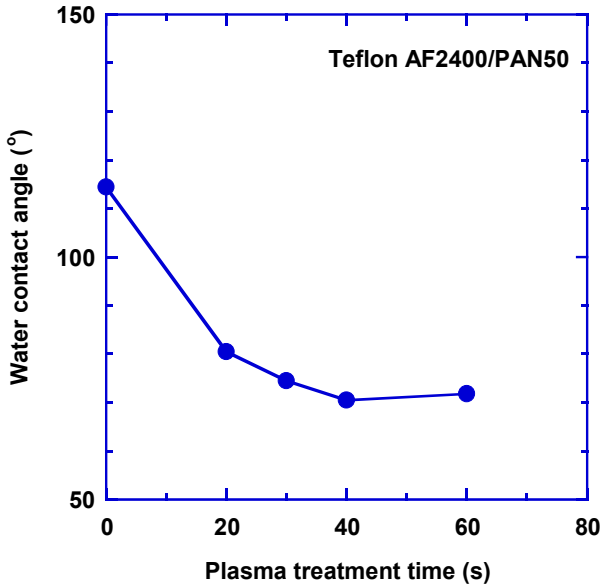

Figure 9. Water contact angle of Teflon gutter changing with plasma treatment time.

3.2 Synthesis of high molecular weight PEO polymer by ATRP reaction

The selective layer can be prepared by coating solutions containing BCP-MOFs, which were prepared using atom transfer radical polymerization (ATRP). Figure 10 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.

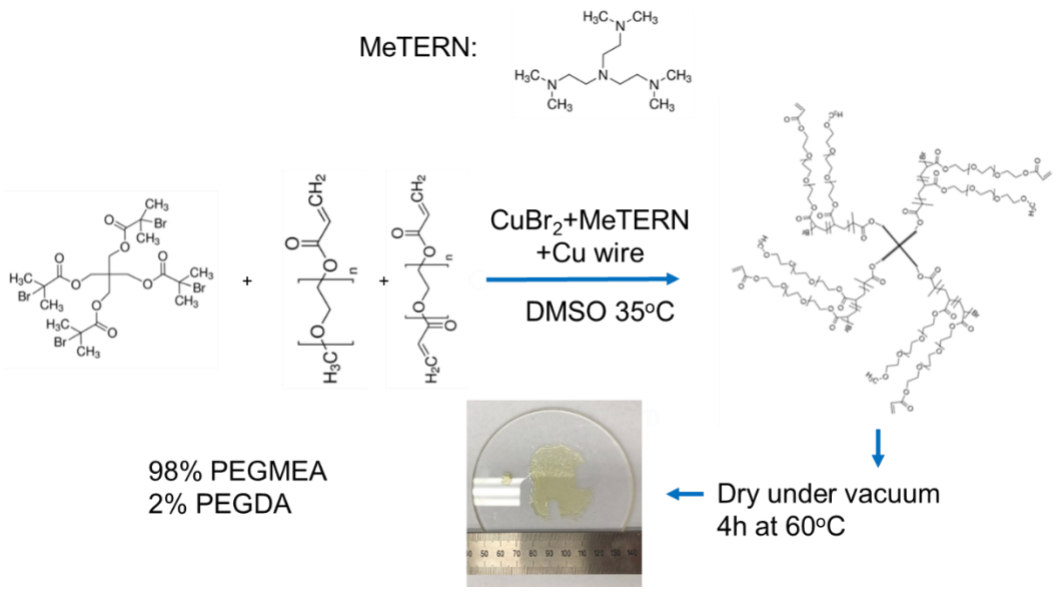

Figure 10. Schematic of ATRP procedure and the photo of an as-prepared film.

3.3 Preparation of the TFC membranes

The TFC membranes were prepared using a dip-coater and a solution containing 13.85% XLPEO. After the coating, the membranes were put in a vacuum oven at 60 °C for 5 h to remove the residual solvent. The membranes exhibit CO_2 permeance of 110 GPU and CO_2/N_2 selectivity of 24. Though the performance is much lower than expected based on the permeability of the selective layer, this work demonstrates the potential. Future work should focus on the improvement of the coatability of the BCP-MOF solutions. Toward this end, the hydrophilicity of the gutter layer needs to be improved, and the solvents used for the BCP-MOF should be optimized to allow the deposition of a thin, defect-free selective layer.

Task 4: 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 3.

Table 3: Flue gas properties used in analysis.[5]

	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 TCF commercial membrane modules were projected based on the advanced materials (BCP-MOF's) developed in the Phase1 project. Table 4 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 4: 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 11 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.

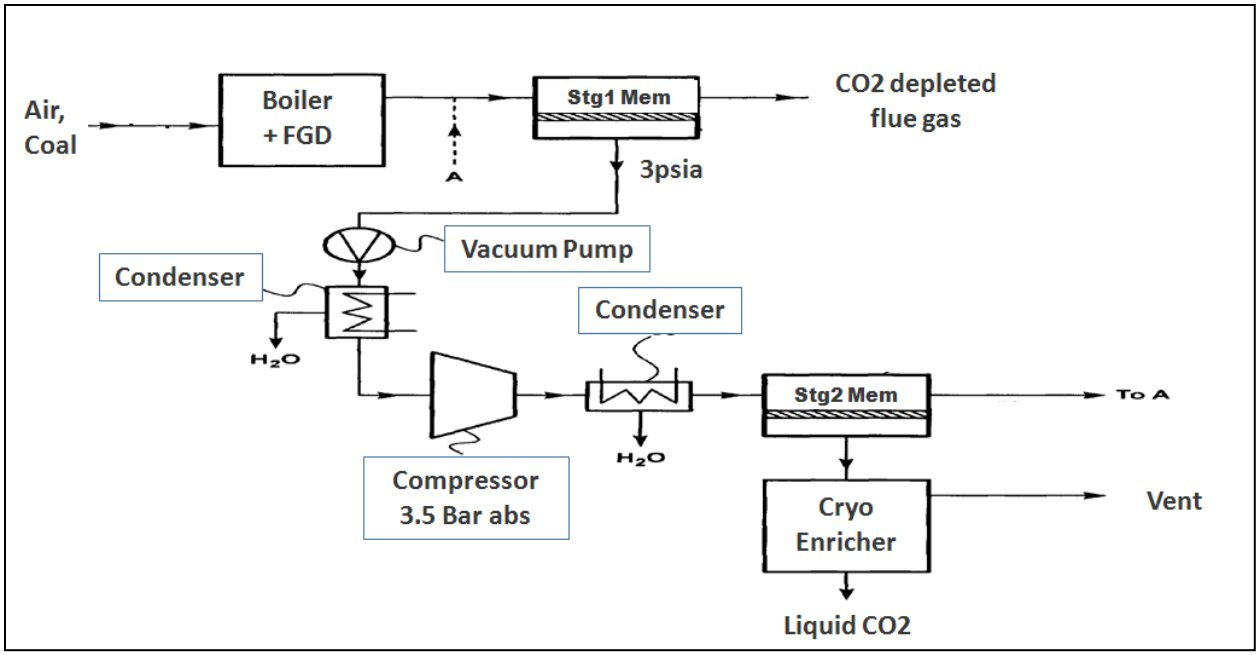

Figure 11: Schematic of the 2-stage process.

Figure 12 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.

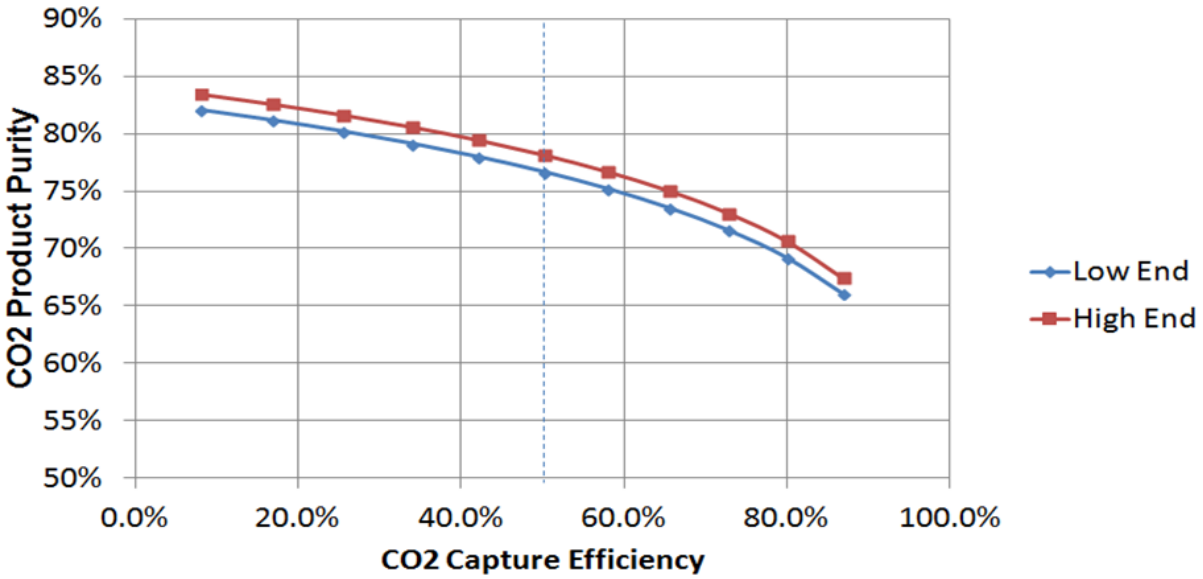

Figure 12: Product purity vs capture efficiency for the 2-stage process

Figure 13 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.

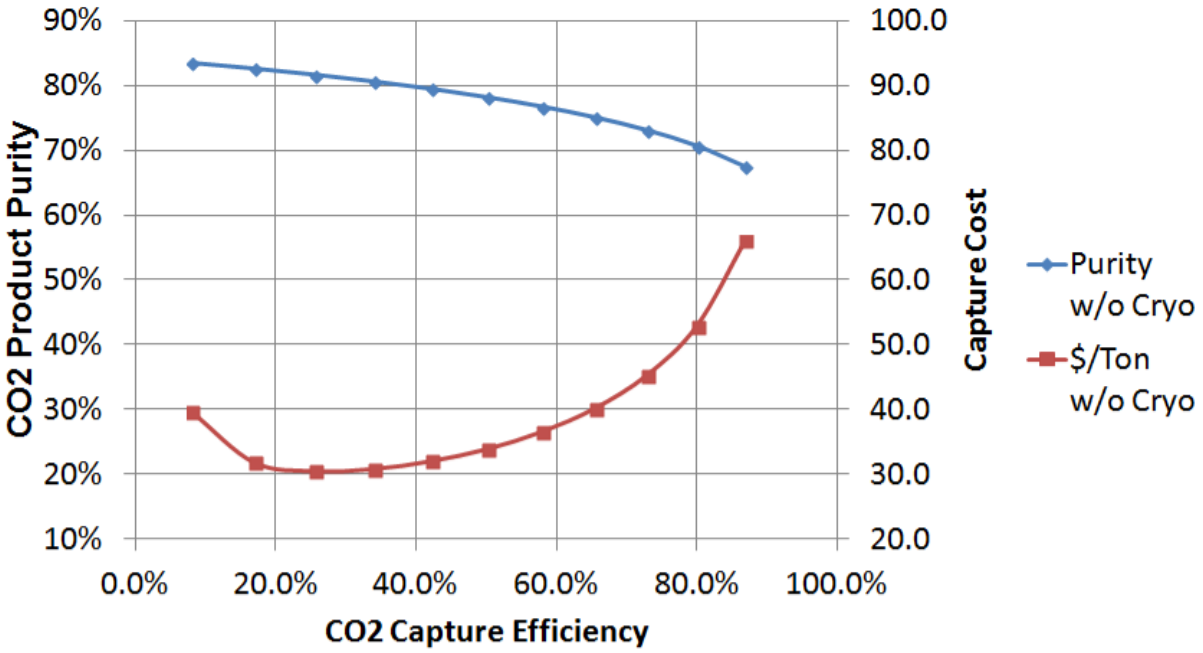

Figure 13: Impact of capture efficiency on product purity and capture cost

Figure 14 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 14 are for the high-end properties, and use of the low-end properties would increase the capture cost by ~$2-3/ton.

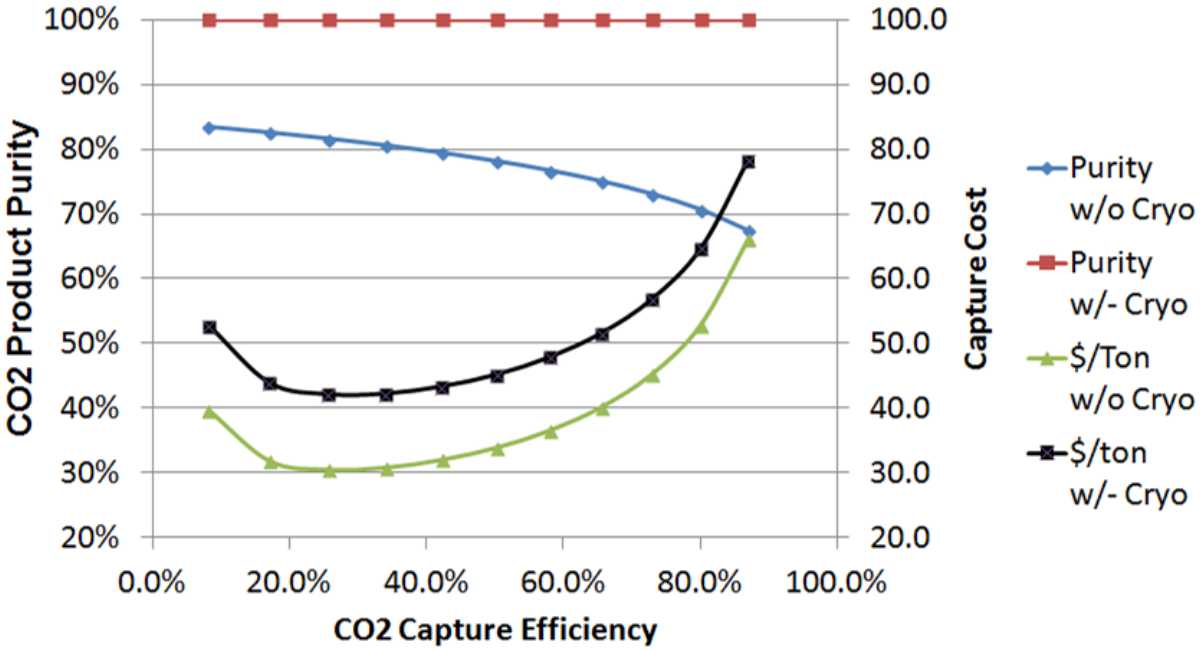

Figure 14: Impact of adding a cryogenic enricher to the 2-stage process

Figure 15 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.

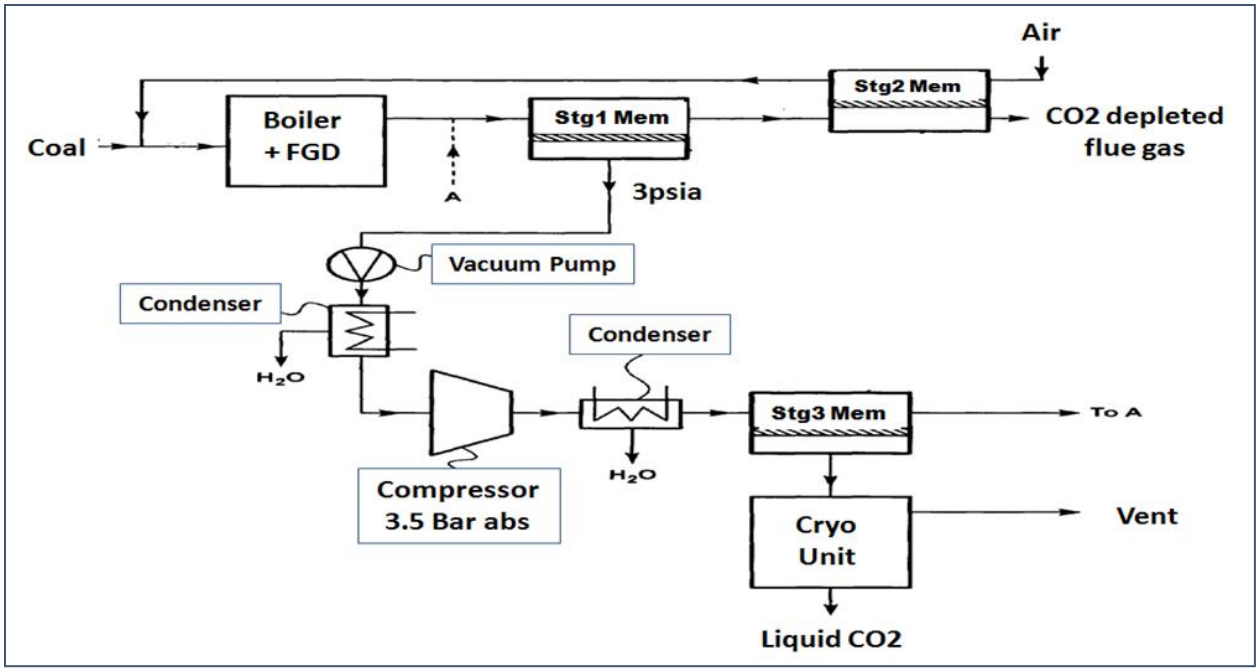

Figure 15: Schematic of MTR's 3-stage process

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 5 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 5: 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 6 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 6: 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

Task 6: 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. However, although an Effective Date of 7/2/18 was stated in the Assistance Agreement, the agreement was only executed by DOE on 9/10/18. Subsequent to signing of the Assistance Agreement with DOE, Helios-NRG executed a sub-award contract with UB on 9/29/18, incorporating all necessary confidentiality agreements and DOE contract terms. Since the project duration was only 9 months, and despite our best efforts, Helios-NRG was unable to make up this lost time. Accordingly, Helios-NRG requested and was granted a 3-month extension of the contract to 7/1/19.

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 $147,585 were submitted and paid by DOE against a budget of $147,585.

Note that actual expenditures for Helios-NRG direct labor, materials, and indirect costs exceeded the invoiced amount by $7,093. 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.

References:

[1] J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud, A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability. *J. Am. Chem. Soc.* **2008,** *130*, 13850-13851.

[2] G. E. Cmarik, M. Kim, S. M. Cohen, K. S. Walton, Tuning the adsorption properties of UiO-66 via ligand functionalization. *Langmuir* **2012,** *28*, 15606-15613.

[3] A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke, P. Behrens, Modulated synthesis of Zr-based metal-organic frameworks: From nano to single crystals. *Chemistry* **2011,** *17*, 6643-6651.
[4] L. M. Robeson, The upper bound revisited. *J. Membr. Sci.* **2008,** *320*, 390-400.
[5] Cost and Performance Baseline for Fossil Energy Plants Volume 1a: Bituminous Coal (PC) and Natural Gas to Electricity Revision 3, July 6, 2015, DOE/NETL
[6] Membrane process to capture co2 from coal-fired power plant flue gas, FINAL REPORT, Award Number DE-NT0005312, Membrane Technology and Research, Inc., December 12, 2012.