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## APPENDICES

### Appendix A The Experimental Flow Rate of Methane (CH<sub>4</sub>), Carbon Dioxide (CO<sub>2</sub>), and Nitrogen (N<sub>2</sub>) of Dense Membrane and Mixed Matrix Membranes in Performance at 50 psi and 100 psi

**Table A1** Pure Ultem membrane

| Gas             | Pressure (psi) | Flow rate (cm <sup>3</sup> /s) | Permeance (GPU) | Average of Permeance (GPU) | STDEV of Permeance |
|-----------------|----------------|--------------------------------|-----------------|----------------------------|--------------------|
| N <sub>2</sub>  | 50             | 1.81E-05                       | 0.00199         | 0.00199                    | 2.88E-07           |
|                 |                | 1.81E-05                       | 0.00199         |                            |                    |
|                 |                | 1.81E-05                       | 0.00199         |                            |                    |
|                 | 100            | 3.66E-05                       | 0.00201         | 0.00201                    | 3.40E-07           |
|                 |                | 3.66E-05                       | 0.00201         |                            |                    |
|                 |                | 3.66E-05                       | 0.00201         |                            |                    |
| CH <sub>4</sub> | 50             | 6.79E-06                       | 0.00074         | 0.00074                    | 4.05E-08           |
|                 |                | 6.79E-06                       | 0.00074         |                            |                    |
|                 |                | 6.79E-06                       | 0.00075         |                            |                    |
|                 | 100            | 1.36E-05                       | 0.00075         | 0.00075                    | 4.67E-08           |
|                 |                | 1.36E-05                       | 0.00074         |                            |                    |
|                 |                | 1.36E-05                       | 0.00075         |                            |                    |
| N <sub>2</sub>  | 100            | 3.66E-05                       | 0.00201         | 0.00201                    | 1.22E-06           |
|                 |                | 3.66E-05                       | 0.00201         |                            |                    |
|                 |                | 3.66E-05                       | 0.00201         |                            |                    |
| CO <sub>2</sub> | 50             | 1.88E-04                       | 0.02067         | 0.02065                    | 1.80E-05           |
|                 |                | 1.88E-04                       | 0.02064         |                            |                    |
|                 |                | 1.88E-04                       | 0.02064         |                            |                    |
|                 | 100            | 3.76E-04                       | 0.02062         | 0.02063                    | 1.79E-05           |
|                 |                | 3.76E-04                       | 0.02062         |                            |                    |
|                 |                | 3.77E-04                       | 0.02066         |                            |                    |
| N <sub>2</sub>  | 100            | 3.66E-05                       | 0.00201         | 0.00201                    | 8.99E-07           |
|                 |                | 3.66E-05                       | 0.00201         |                            |                    |
|                 |                | 3.66E-05                       | 0.00201         |                            |                    |

**Table A2** 10 wt% MOF-199 MMMs

| Gas             | Pressure (psi) | Flow rate (cm <sup>3</sup> /s) | Permeance (GPU) | Average of Permeance (GPU) | STDEV of Permeance |
|-----------------|----------------|--------------------------------|-----------------|----------------------------|--------------------|
| N <sub>2</sub>  | 50             | 2.41E-05                       | 0.00264         | 0.00264                    | 5.87E-07           |
|                 |                | 2.41E-05                       | 0.00264         |                            |                    |
|                 |                | 2.41E-05                       | 0.00264         |                            |                    |
|                 | 100            | 5.83E-05                       | 0.00320         | 0.00266                    | 4.65E-04           |
|                 |                | 4.36E-05                       | 0.00239         |                            |                    |
|                 |                | 4.36E-05                       | 0.00239         |                            |                    |
| CH <sub>4</sub> | 50             | 1.03E-05                       | 0.00113         | 0.00112                    | 9.23E-08           |
|                 |                | 1.03E-05                       | 0.00112         |                            |                    |
|                 |                | 1.03E-05                       | 0.00112         |                            |                    |
|                 | 100            | 2.05E-05                       | 0.00113         | 0.00113                    | 2.82E-07           |
|                 |                | 2.05E-05                       | 0.00113         |                            |                    |
|                 |                | 2.05E-05                       | 0.00113         |                            |                    |
| N <sub>2</sub>  | 100            | 5.84E-05                       | 0.00320         | 0.00266                    | 4.66E-04           |
|                 |                | 4.36E-05                       | 0.00239         |                            |                    |
|                 |                | 4.36E-05                       | 0.00239         |                            |                    |
| CO <sub>2</sub> | 50             | 3.76E-04                       | 0.04125         | 0.04125                    | 6.20E-05           |
|                 |                | 3.75E-04                       | 0.04119         |                            |                    |
|                 |                | 3.77E-04                       | 0.04131         |                            |                    |
|                 | 100            | 7.46E-04                       | 0.04094         | 0.04082                    | 2.10E-04           |
|                 |                | 7.40E-04                       | 0.04058         |                            |                    |
|                 |                | 7.46E-04                       | 0.04094         |                            |                    |
| N <sub>2</sub>  | 100            | 5.82E-05                       | 0.00319         | 0.00266                    | 4.63E-04           |
|                 |                | 4.36E-05                       | 0.00239         |                            |                    |
|                 |                | 4.36E-05                       | 0.00239         |                            |                    |

**Table A3** 20 wt% MOF-199 MMMs

| Gas             | Pressure (psi) | Flow rate (cm <sup>3</sup> /s) | Permeance (GPU) | Average of Permeance (GPU) | STDEV of Permeance |
|-----------------|----------------|--------------------------------|-----------------|----------------------------|--------------------|
| N <sub>2</sub>  | 50             | 2.53E-05                       | 0.00278         | 0.00271                    | 5.57E-05           |
|                 |                | 2.44E-05                       | 0.00268         |                            |                    |
|                 |                | 2.44E-05                       | 0.00268         |                            |                    |
|                 | 100            | 5.13E-05                       | 0.00282         | 0.00273                    | 1.46E-04           |
|                 |                | 5.13E-05                       | 0.00282         |                            |                    |
|                 |                | 4.67E-05                       | 0.00256         |                            |                    |
| CH <sub>4</sub> | 50             | 1.14E-05                       | 0.00125         | 0.00124                    | 3.75E-06           |
|                 |                | 1.13E-05                       | 0.00124         |                            |                    |
|                 |                | 1.13E-05                       | 0.00124         |                            |                    |
|                 | 100            | 2.27E-05                       | 0.00125         | 0.00125                    | 2.62E-07           |
|                 |                | 2.27E-05                       | 0.00125         |                            |                    |
|                 |                | 2.27E-05                       | 0.00125         |                            |                    |
| N <sub>2</sub>  | 100            | 5.13E-05                       | 0.00281         | 0.00273                    | 1.47E-04           |
|                 |                | 5.13E-05                       | 0.00281         |                            |                    |
|                 |                | 4.67E-05                       | 0.00256         |                            |                    |
| CO <sub>2</sub> | 50             | 4.56E-04                       | 0.05006         | 0.05021                    | 1.92E-04           |
|                 |                | 4.57E-04                       | 0.05015         |                            |                    |
|                 |                | 4.60E-04                       | 0.05042         |                            |                    |
|                 | 100            | 9.09E-04                       | 0.04987         | 0.04994                    | 2.78E-04           |
|                 |                | 9.06E-04                       | 0.04969         |                            |                    |
|                 |                | 9.16E-04                       | 0.05024         |                            |                    |
| N <sub>2</sub>  | 100            | 5.13E-05                       | 0.00282         | 0.00273                    | 1.46E-04           |
|                 |                | 5.13E-05                       | 0.00281         |                            |                    |
|                 |                | 4.67E-05                       | 0.00256         |                            |                    |



**Table A4** 30 wt% MOF-199 MMMs

| Gas             | Pressure (psi) | Flow rate (cm <sup>3</sup> /s) | Permeance (GPU) | Average of Permeance (GPU) | STDEV of Permeance |
|-----------------|----------------|--------------------------------|-----------------|----------------------------|--------------------|
| N <sub>2</sub>  | 50             | 2.79E-05                       | 0.00306         | 0.00306                    | 6.82E-07           |
|                 |                | 2.79E-05                       | 0.00306         |                            |                    |
|                 |                | 2.79E-05                       | 0.00306         |                            |                    |
|                 | 100            | 6.29E-05                       | 0.00345         | 0.00308                    | 3.27E-04           |
|                 |                | 5.33E-05                       | 0.00293         |                            |                    |
|                 |                | 5.20E-05                       | 0.00285         |                            |                    |
| CH <sub>4</sub> | 50             | 1.24E-05                       | 0.00136         | 0.00136                    | 2.72E-07           |
|                 |                | 1.24E-05                       | 0.00137         |                            |                    |
|                 |                | 1.24E-05                       | 0.00136         |                            |                    |
|                 | 100            | 2.49E-05                       | 0.00136         | 0.00137                    | 4.15E-07           |
|                 |                | 2.49E-05                       | 0.00136         |                            |                    |
|                 |                | 2.49E-05                       | 0.00137         |                            |                    |
| N <sub>2</sub>  | 100            | 4.95E-05                       | 0.00271         | 0.00272                    | 2.15E-06           |
|                 |                | 4.95E-05                       | 0.00272         |                            |                    |
|                 |                | 4.96E-05                       | 0.00272         |                            |                    |
| CO <sub>2</sub> | 50             | 5.34E-04                       | 0.05861         | 0.05857                    | 7.22E-05           |
|                 |                | 5.33E-04                       | 0.05849         |                            |                    |
|                 |                | 5.34E-04                       | 0.05861         |                            |                    |
|                 | 100            | 1.06E-03                       | 0.05812         | 0.05771                    | 3.72E-04           |
|                 |                | 1.05E-03                       | 0.05739         |                            |                    |
|                 |                | 1.05E-03                       | 0.05763         |                            |                    |
| N <sub>2</sub>  | 100            | 4.96E-05                       | 0.00272         | 0.00272                    | 1.64E-06           |
|                 |                | 4.95E-05                       | 0.00272         |                            |                    |
|                 |                | 4.95E-05                       | 0.00272         |                            |                    |

**Table A5** 10 wt% ZIF-8 MMMs

| Gas             | Pressure (psi) | Flow rate (cm <sup>3</sup> /s) | Permeance (GPU) | Average of Permeance (GPU) | STDEV of Permeance |
|-----------------|----------------|--------------------------------|-----------------|----------------------------|--------------------|
| N <sub>2</sub>  | 50             | 2.98E-05                       | 0.00327         | 0.00327                    | 3.25E-06           |
|                 |                | 2.98E-05                       | 0.00327         |                            |                    |
|                 |                | 2.98E-05                       | 0.00327         |                            |                    |
|                 | 100            | 6.01E-05                       | 0.00330         | 0.00329                    | 2.74E-06           |
|                 |                | 6.00E-05                       | 0.00329         |                            |                    |
|                 |                | 6.00E-05                       | 0.00329         |                            |                    |
| CH <sub>4</sub> | 50             | 1.15E-05                       | 0.00127         | 0.00126                    | 2.94E-07           |
|                 |                | 1.15E-05                       | 0.00126         |                            |                    |
|                 |                | 1.15E-05                       | 0.00127         |                            |                    |
|                 | 100            | 2.32E-05                       | 0.00127         | 0.00127                    | 8.08E-06           |
|                 |                | 2.29E-05                       | 0.00126         |                            |                    |
|                 |                | 2.32E-05                       | 0.00127         |                            |                    |
| N <sub>2</sub>  | 100            | 6.00E-05                       | 0.00329         | 0.00329                    | 2.41E-06           |
|                 |                | 6.00E-05                       | 0.00329         |                            |                    |
|                 |                | 6.00E-05                       | 0.00329         |                            |                    |
| CO <sub>2</sub> | 50             | 3.35E-04                       | 0.03677         | 0.03674                    | 2.84E-05           |
|                 |                | 3.35E-04                       | 0.03672         |                            |                    |
|                 |                | 3.35E-04                       | 0.03672         |                            |                    |
|                 | 100            | 6.56E-04                       | 0.03600         | 0.03581                    | 1.87E-04           |
|                 |                | 6.53E-04                       | 0.03581         |                            |                    |
|                 |                | 6.49E-04                       | 0.03562         |                            |                    |
| N <sub>2</sub>  | 100            | 6.00E-05                       | 0.00329         | 0.00329                    | 3.97E-06           |
|                 |                | 6.00E-05                       | 0.00329         |                            |                    |
|                 |                | 5.99E-05                       | 0.00328         |                            |                    |

**Table A6** 20 wt% ZIF-8 MMMs

| Gas             | Pressure (psi) | Flow rate (cm <sup>3</sup> /s) | Permeance (GPU) | Average of Permeance (GPU) | STDEV of Permeance |
|-----------------|----------------|--------------------------------|-----------------|----------------------------|--------------------|
| N <sub>2</sub>  | 50             | 3.60E-05                       | 0.00395         | 0.00395                    | 4.73E-06           |
|                 |                | 3.60E-05                       | 0.00395         |                            |                    |
|                 |                | 3.59E-05                       | 0.00394         |                            |                    |
|                 | 100            | 7.27E-05                       | 0.00399         | 0.00398                    | 4.81E-06           |
|                 |                | 7.25E-05                       | 0.00398         |                            |                    |
|                 |                | 7.25E-05                       | 0.00398         |                            |                    |
| CH <sub>4</sub> | 50             | 1.48E-05                       | 0.00163         | 0.00162                    | 4.84E-07           |
|                 |                | 1.48E-05                       | 0.00162         |                            |                    |
|                 |                | 1.48E-05                       | 0.00162         |                            |                    |
|                 | 100            | 2.95E-05                       | 0.00162         | 0.00162                    | 1.52E-06           |
|                 |                | 2.94E-05                       | 0.00162         |                            |                    |
|                 |                | 2.94E-05                       | 0.00161         |                            |                    |
| N <sub>2</sub>  | 100            | 7.24E-05                       | 0.00397         | 0.00398                    | 8.11E-06           |
|                 |                | 7.25E-05                       | 0.00398         |                            |                    |
|                 |                | 7.27E-05                       | 0.00399         |                            |                    |
| CO <sub>2</sub> | 50             | 4.58E-04                       | 0.05024         | 0.05018                    | 5.30E-05           |
|                 |                | 4.57E-04                       | 0.05015         |                            |                    |
|                 |                | 4.57E-04                       | 0.05015         |                            |                    |
|                 | 100            | 8.90E-04                       | 0.04881         | 0.04847                    | 3.43E-04           |
|                 |                | 8.83E-04                       | 0.04846         |                            |                    |
|                 |                | 8.77E-04                       | 0.04812         |                            |                    |
| N <sub>2</sub>  | 100            | 7.27E-05                       | 0.00399         | 0.00398                    | 1.06E-05           |
|                 |                | 7.24E-05                       | 0.00397         |                            |                    |
|                 |                | 7.23E-05                       | 0.00397         |                            |                    |

**Appendix B The Experimental Gas Selectivity of Dense Membrane and Mixed Matrix Membranes in Performance at 50 psi and 100 psi**

**Table B1** Gas selectivity determined from gas permeance of Ultem membrane and MOF-MMMs at pressures of 50 psi and 100 psi

| Membrane        | MOF Loading (wt%) | CO <sub>2</sub> /CH <sub>4</sub> Selectivity |         | CO <sub>2</sub> /N <sub>2</sub> Selectivity |         |
|-----------------|-------------------|--|---------|---|---------|
|                 |                   | 50 psi                                       | 100 psi | 50 psi                                      | 100 psi |
| Pure Ultem      | 0                 | 27.719                                       | 27.696  | 10.396                                      | 10.266  |
| MOF-199<br>MMMs | 10                | 36.394                                       | 36.104  | 15.867                                      | 15.614  |
|                 | 20                | 40.361                                       | 40.025  | 18.501                                      | 18.280  |
|                 | 30                | 42.910                                       | 42.276  | 19.145                                      | 18.758  |
| ZIF-8<br>MMMs   | 10                | 29.042                                       | 28.261  | 11.232                                      | 10.872  |
|                 | 20                | 30.887                                       | 30.008  | 12.707                                      | 12.172  |

**Appendix C The Gas Permeance Predicted by Maxwell Model for MOF-  
MMMs at Pressure of 50 psi**

**Table C1** Comparison of gas permeances for MOF-MMMs at pressure of 50 psi based on Maxwell model and experimental data.

| MOFs    | Gas             | Loading      |               | $P_c$ (GPU) | $P_d$ (GPU) | $P_{eff}$       |            |
|---------|-----------------|--------------|---------------|-------------|-------------|-----------------|------------|
|         |                 | wt. fraction | vol. fraction |             |             | Maxwell's model | Experiment |
| MOF-199 | CO <sub>2</sub> | 10           | 0.168         | 0.02065     | 44          | 0.03314         | 0.04240    |
|         |                 | 20           | 0.312         | 0.02065     | 44          | 0.04869         | 0.05021    |
|         |                 | 30           | 0.437         | 0.02065     | 44          | 0.06862         | 0.05857    |
|         | CH <sub>4</sub> | 10           | 0.168         | 0.00074     | 15          | 0.00119         | 0.00116    |
|         |                 | 20           | 0.312         | 0.00074     | 15          | 0.00175         | 0.05802    |
|         |                 | 30           | 0.437         | 0.00074     | 15          | 0.00246         | 0.06583    |
|         | N <sub>2</sub>  | 10           | 0.168         | 0.00199     | 19          | 0.00320         | 0.00267    |
|         |                 | 20           | 0.312         | 0.00199     | 19          | 0.00470         | 0.00271    |
|         |                 | 30           | 0.437         | 0.00199     | 19          | 0.00662         | 0.07364    |
| ZIF-8   | CO <sub>2</sub> | 10           | 0.168         | 0.02065     | 44          | 0.03314         | 0.08145    |
|         |                 | 20           | 0.312         | 0.02065     | 44          | 0.04869         | 0.05018    |
|         |                 | 30           | 0.437         | 0.02065     | 44          | -               | -          |
|         | CH <sub>4</sub> | 10           | 0.168         | 0.00074     | 15          | 0.00119         | 0.08926    |
|         |                 | 20           | 0.312         | 0.00074     | 15          | 0.00175         | 0.09707    |
|         |                 | 30           | 0.437         | 0.00074     | 15          | -               | -          |
|         | N <sub>2</sub>  | 10           | 0.168         | 0.00199     | 19          | 0.00320         | 0.00327    |
|         |                 | 20           | 0.312         | 0.00199     | 19          | 0.00470         | 0.00395    |
|         |                 | 30           | 0.437         | 0.00199     | 19          | -               | -          |

## CURRICULUM VITAE

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**Presentations:**

1. Ketsuwan, T.; Rirksomboon, T.; Kulprathipanja, S.; and Bowen, T.C. (2014, April 22) Solid-Polymer Mixed Matrix Membranes for CO<sub>2</sub>/CH<sub>4</sub> Separation: Metal Organic Frameworks and Polyetherimide. Paper presented at The 5<sup>th</sup> Research Symposium on Petrochemical and Materials Technology and The 20<sup>th</sup> PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.
2. Ketsuwan, T.; Rirksomboon, T.; Kulprathipanja, S.; and Bowen, T.C. (2014, May 7-8) Enhanced Selectivity of Metal Organic Frameworks-Polyetherimide Mixed Matrix Membranes for CO<sub>2</sub>/CH<sub>4</sub> Separation. Paper presented at ICERE: International Conference on Environment and Renewable Energy, Paris, France.