Supporting Information

Purification of aggressive supercritical natural gas using carbon molecular sieve hollow fiber membranes

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1. Supplementary figures and tables

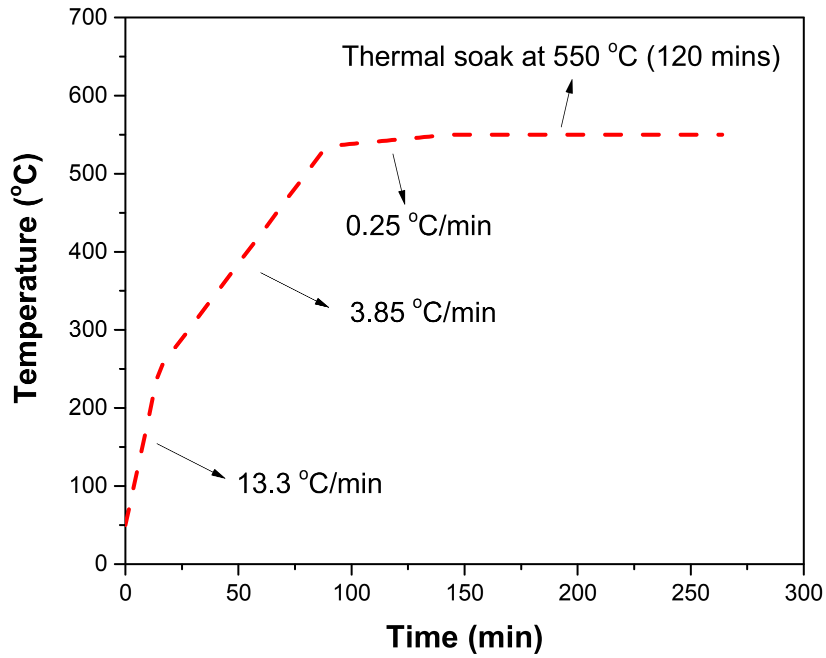

Figure S1. Pyrolysis temperature profile of the CMS hollow fiber membranes.

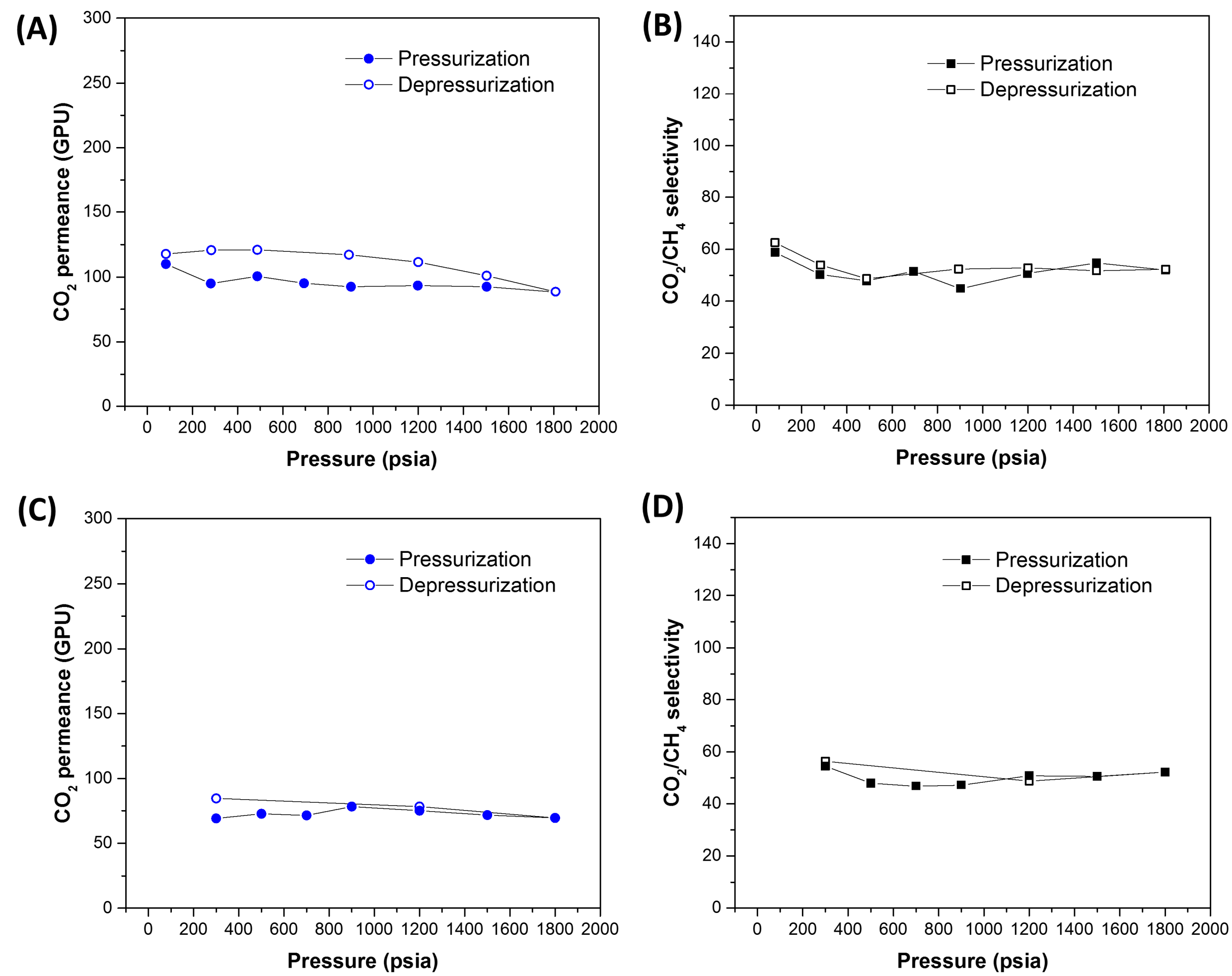

Figure S2. Comparing CMS hollow fiber membrane permeation data during pressurization and depressurization. (A) CO_2 permeances during pressurization and depressurization for feed comprising 50% CO_2/50% CH_4; (B) CO_2/CH_4 separation factors during pressurization and depressurization for feed comprising 50% CO_2/50% CH_4; (C) CO_2 permeances during pressurization and depressurization for feed comprising 10% CO_2/90% CH_4; (D) CO_2/CH_4 separation factors during pressurization and depressurization for feed comprising 10% CO_2/90% CH_4. All measurements were at 35 ^oC.

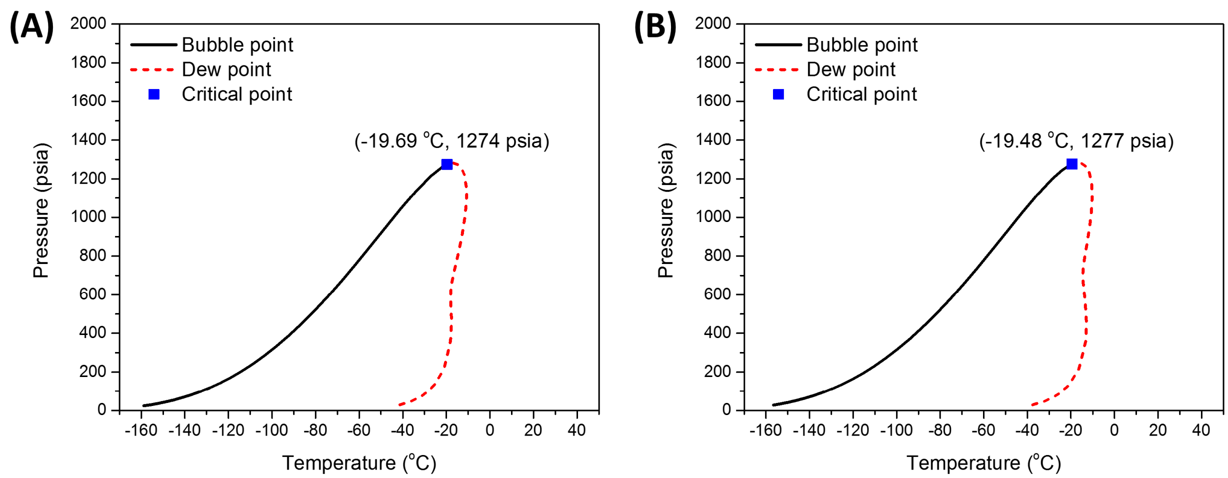

Figure S3. a. Phase envelop of feed C (50% CO_2, 250 ppm toluene, balanced by CH_4). b. phase envelop of feed D (50% CO_2, 250 ppm toluene, 250 ppm n-heptane, balanced by CH_4). The phase envelops were calculated using the Peng-Robinson equation of state by UniSim® Design (Honeywell Process Solutions).

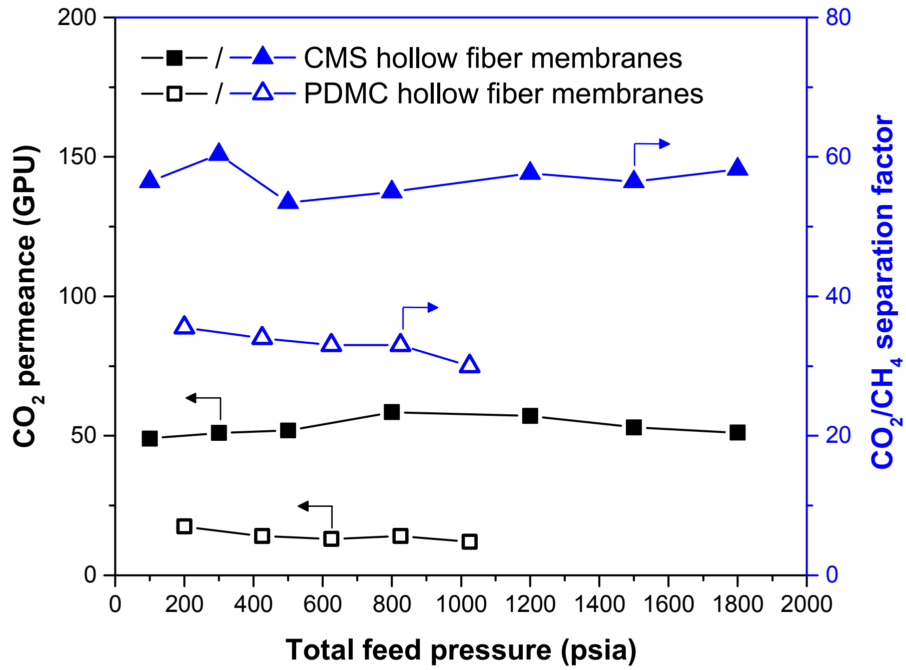

Figure S4. CO_2 permeances (squares) and CO_2/CH_4 separation factors (triangles) of CMS hollow fiber membranes (solid points) and crosslinked PDMC hollow fiber membranes (open points).[1] Permeation were both measured at 35 °C using feeds comprising 50% CO_2 and 500 ppm C_7 hydrocarbons (toluene and/or n-heptane).

Table S1. CO_2 permeances (GPU) of CMS hollow fiber membranes under different feed compositions at 35 ^oC. Feed A: 10%/90% CO_2/CH_4; Feed B: 50%/50% CO_2/CH_4; Feed C: 50% CO_2 with 250 ppm toluene, balanced with CH_4; Feed D: 50% CO_2 with 250 ppm toluene and 250 ppm n-heptane, balanced with CH_4.

Feed pressure/psia	Feed A	Feed B	Feed C	Feed D
~100	N/A	110.0	106.2	49.0
~300	69.1	95.1	70.2	51.0
~500	72.6	100.6	72.7	51.9
~700	71.3	95.3	80.1	N/A
~800	N/A	N/A	N/A	58.4
~900	78.1	92.6	78.4	N/A
~1200	75.0	93.5	80.9	57.1
~1500	71.6	92.7	73.4	53.1
~1800	69.4	88.5	75.8	51.1

Table S2. CO_2/CH_4 separation factors of CMS hollow fiber membranes under different feed compositions at 35 ^oC. Feed A: 10%/90% CO_2/CH_4; Feed B: 50%/50% CO_2/CH_4; Feed C: 50% CO_2 with 250 ppm toluene, balanced with CH_4; Feed D: 50% CO_2 with 250 ppm toluene and 250 ppm n-heptane, balanced with CH_4.

Feed pressure/psia	Feed A	Feed B	Feed C	Feed D
~100	N/A	58.9	65.2	56.5
~300	54.5	50.4	54.6	60.4
~500	48.0	48.0	56.9	53.5
~700	46.9	51.6	55.2	N/A
~800	N/A	N/A	N/A	55.0
~900	47.2	44.9	55.6	N/A
~1200	50.8	50.8	55.8	57.7
~1500	50.6	54.8	54.7	56.4
~1800	52.3	52.1	53.5	58.8

2. Calculation of apparent permeation activation energy

Membrane permeance is pressure difference normalized flux and can be described by dividing permeability by membrane thickness. Since permeability is the product of diffusivity and sorption coefficient, permeance can be written as:

$$\frac{P}{l}\text{ (permeance)} = \frac{D \times S}{l} \tag{S1}$$

in which P is permeability, l is membrane thickness, D is diffusivity, and S is sorption coefficient. The diffusivity and sorption coefficient can be described by the Arrhenius equation and Van't Hoff equation, respectively:[2]

$$D = D_0 \times \exp\ (-\frac{E_D}{RT}) \tag{S2}$$

$$S = S_0 \times \exp\ (-\frac{H_S}{RT}) \tag{S3}$$

in which D_0 is the pre-exponential factor for diffusion, E_D is the apparent diffusion activation energy, S_0 is the pre-exponential factor for sorption, and H_S is apparent heat of sorption. As a result, permeance can be written as:

$$\frac{P}{l}\text{ (permeance)} = \frac{D \times S}{l} = \frac{D_0 \times S_0}{l}\ \exp\ (-\frac{E_D + H_S}{RT}) = \frac{P_0}{l}\ \exp\ (-\frac{E_P}{RT}) \tag{S4}$$

in which P_0 is the pre-exponential factor for permeation, and $E_P = E_D + H_S$ is the apparent activation energy for permeation. By plotting experimentally measured data $\ln(\frac{P}{l})$ vs. $\frac{1}{T}$, the apparent activation energy for permeation E_P can thus be obtained:

$$\ln(\frac{P}{l}) = \ln(\frac{P_0}{l}) - \frac{E_P}{R} \times \frac{1}{T} \tag{S5}$$

References

1. Omole, I. C.; Bhandari, D. A.; Miller, S. J.; Koros, W. J., Toluene impurity effects on CO2 separation using a hollow fiber membrane for natural gas. *J. Membr. Sci.* **2011,** *369* (1), 490-498.

2. Rungta, M.; Xu, L.; Koros, W. J., Structure–performance characterization for carbon molecular sieve membranes using molecular scale gas probes. *Carbon* **2015,** *85*, 429-442.