Intricacies of CO_2 removal from mixed gases and biogas using polysulfone/ZIF-8 mixed matrix membranes – Part 1: Experimental

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Supplementary Information

S1. Gas Permeation Setup

The setup used for gas permeation studies is shown in Figure S1. The setup consists of a membrane test cell of diameter 2.5 cm in which the membrane is kept supported on a porous disc. The disc is made of stainless steel and offers negligible resistance to gas transport. The test cell allows the feed gas to enter on the one side of the membrane and the permeate is collected from the opposite side. The flow rate of the gases was controlled using Brooks Delta mass flow controllers [Range: 1-100 ml/min (feed gases) & 1-50ml/min (sweep gas); accuracy: 90%]. The retentate outlet is present on the same side as feed inlet and is connected to a back-pressure regulator to maintain the desired feed pressure. Helium was used as a sweep gas on the permeate side to maintain the partial pressure of the gas to be near zero. The system is also equipped with a vacuum pump to evacuate the system before each run. The permeate gases were analysed using a 5700 Nucon gas chromatograph equipped with Porapac-Q column and Thermal conductivity detector (TCD). Pure gases (CO_2 and CH_4). their mixtures (CH_4:CO_2 = 50:50, 60:40, 70:30 and 90:10) and biogas, at a total feed pressure in the range 2-6 bar were used in the experiments. The permeability P_A of the membrane was calculated using the following equation:

$$P_A = \frac{Q_A.\delta}{A.\Delta p_A} \quad (1)$$

where, Q_A is the flow rate of gas (cm^3/s), δ the thickness of membrane (cm), A the available membrane area for permeation (cm^2) and Δp_A the partial pressure difference across the membrane (cm Hg). Permeabilities were expressed in GPU.

The selectivity $(\alpha_{A/B})$ of the membrane for gas A over gas B is calculated as follows:

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$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (2)$$

where P_A and P_B are the respective permeabilities of gas A and gas B. More detailed calculations are given in supporting information.

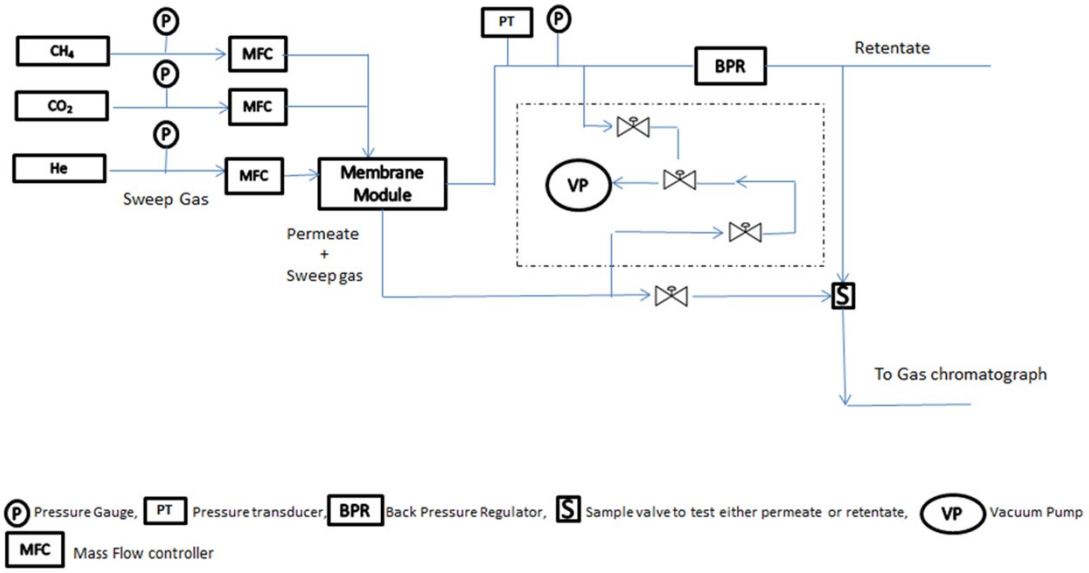

Figure S1 Schematic of lab scale setup used for gas permeation experiments

S2. ZIF-8 Characterization

The weight loss of for ZIF-8 is shown in Figure S2. The sorption isotherm for ZIF-8 is shown in Figure S3.

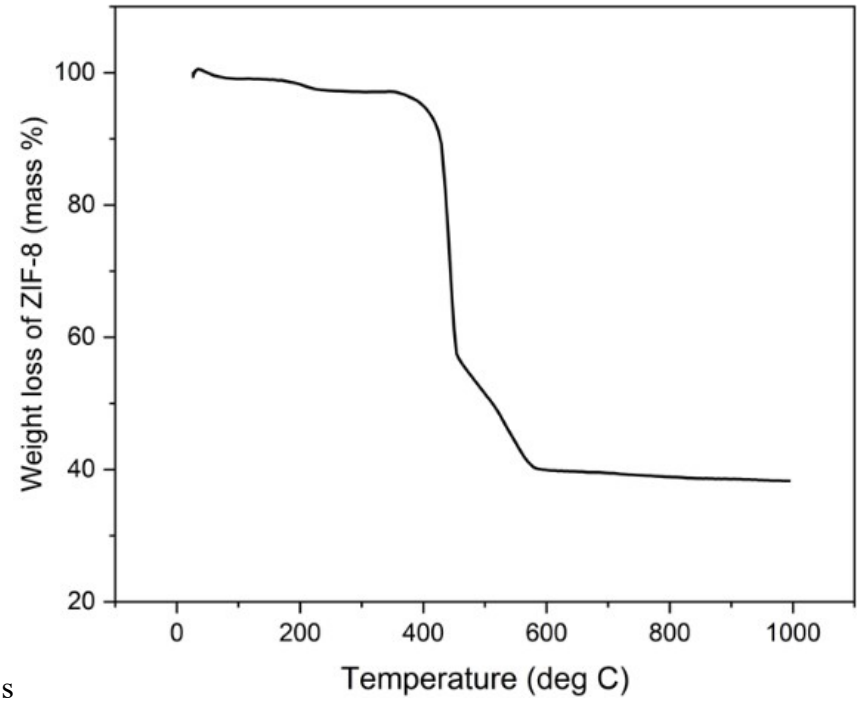

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Figure S2 Thermal degradation of ZIF-8 nanoparticles in presence of Nitrogen.

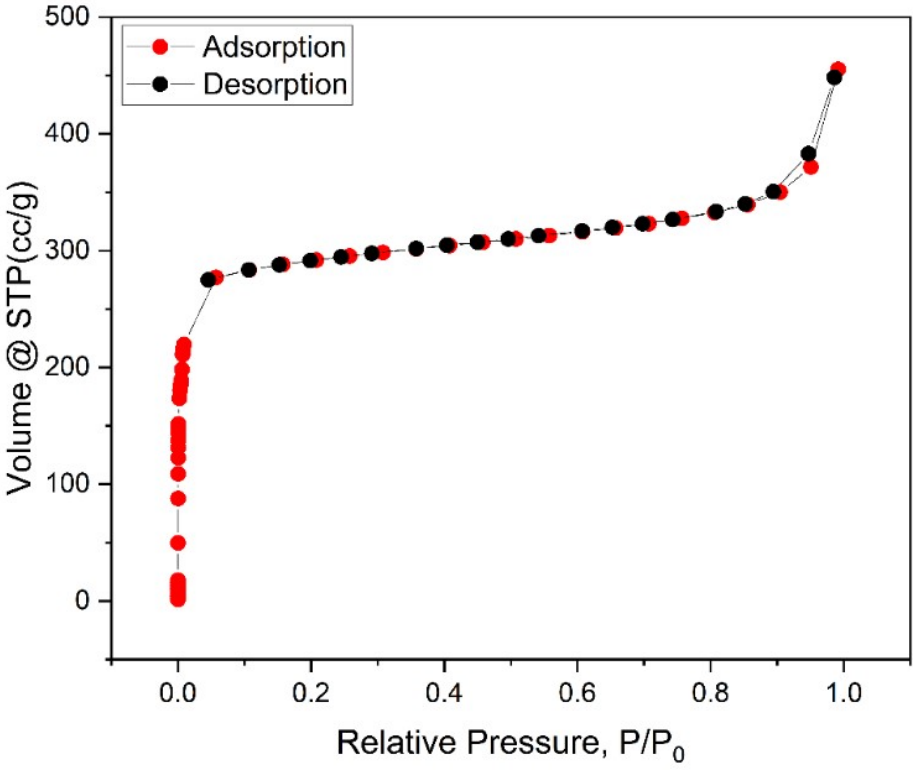

Figure S3 The N_2 *adsorption isotherm on ZIF-8 nanoparticles at 77 K. Red line: adsorption; black line- desorption*

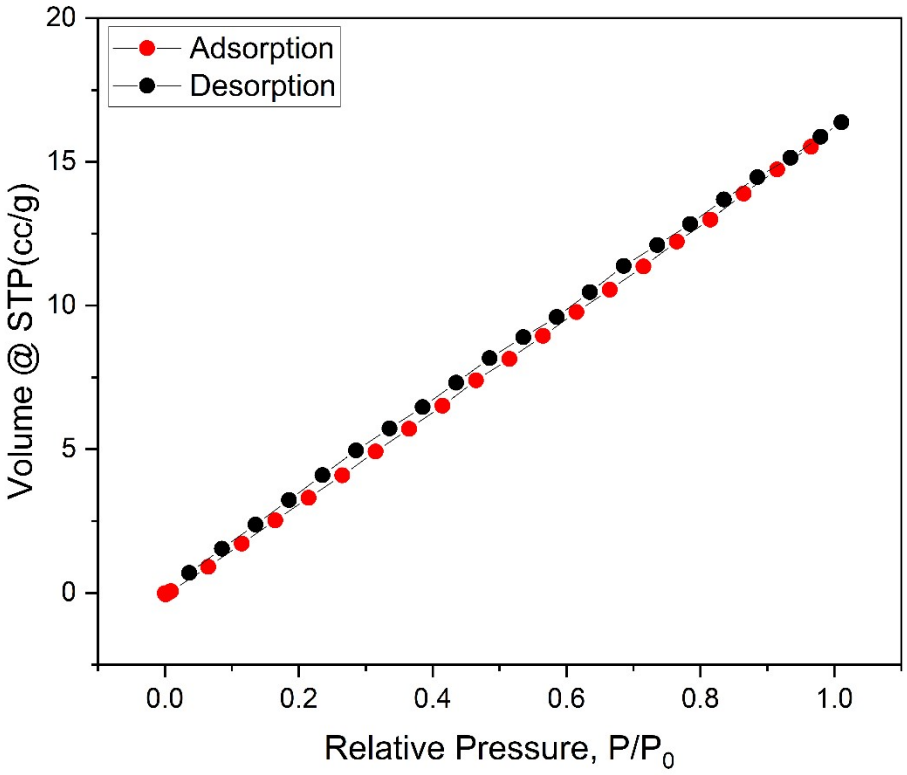

Figure S4 The CO_2 *adsorption isotherm on ZIF-8 nanoparticles at 298 K. Red line: adsorption; black line- desorption*

S3. Mixed Matrix Membrane Characterization

The Figure S5 shows the micrograph for DZ5 membrane focusing on agglomeration

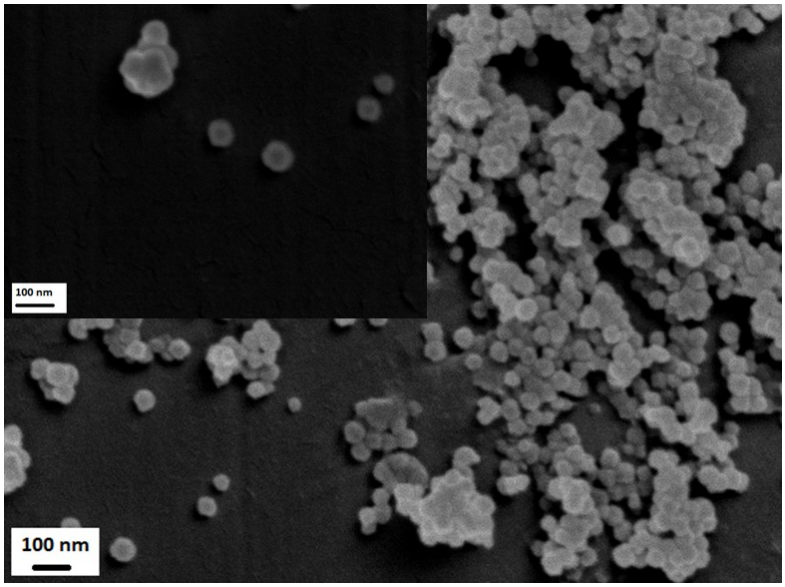

Figure S5 SEM micrograph for DZ5 MMM showing particle agglomeration at higher loading with the inset showing polymer particle interface

S4. Standard deviations in permeability and selectivity data

Three membranes were tested in permeation experiments for reproducibility. Table S1, Table S2 and Table S3 show standard deviation in permeability and selectivity for pure PSF, DZ1 and DZ5 membranes respectively.

Table S1 Standard deviation for permeance and selectivity through pure polysulfone membranes.

	Pure gas			CH_4:CO_2- 50:50			CH_4:CO_2- 60:40			CH_4:CO_2- 70:30			CH_4:CO_2- 90:10			Biogas		
Pressure	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$
2	0.020	0.001	0.159	0.023	0.012	0.463	0.017	0.005	0.288	0.081	0.008	0.711	0.153	0.000	0.438	0.030	0.003	0.189
3	0.063	0.006	0.612	0.059	0.014	0.500	0.062	0.005	0.467	0.015	0.000	0.049	0.016	0.006	0.524	0.030	0.002	0.145
4	0.019	0.002	0.118	0.085	0.007	0.644	0.109	0.002	0.177	0.046	0.011	0.805	0.064	0.006	0.921	0.025	0.003	0.183
5	0.024	0.000	0.098	0.003	0.003	0.189	0.149	0.002	0.593	0.025	0.003	0.174	0.075	0.003	0.018	0.030	0.001	0.146
6	0.013	0.000	0.007	0.019	0.004	0.167	0.015	0.002	0.209	0.119	0.002	0.605	0.023	0.004	0.304	0.040	0.003	0.285

Table S2 Standard deviation for permeance and selectivity through DZ1 membranes.

	Pure gas			CH_4:CO_2- 50:50			CH_4:CO_2- 60:40			CH_4:CO_2- 70:30			CH_4:CO_2- 90:10			Biogas		
Pressure	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$
2	0.025	0.001	0.003	0.025	0.003	0.123	0.020	0.003	0.134	0.025	0.004	0.219	0.027	0.003	0.154	0.030	0.004	0.066
3	0.029	0.005	0.532	0.351	0.003	0.685	0.020	0.003	0.136	0.025	0.004	0.231	0.027	0.003	0.148	0.025	0.003	0.038
4	0.077	0.004	0.623	0.268	0.003	0.501	0.020	0.003	0.140	0.025	0.004	0.230	0.027	0.003	0.166	0.030	0.004	0.047
5	0.128	0.009	1.293	0.164	0.003	0.224	0.020	0.003	0.144	0.025	0.004	0.217	0.027	0.003	0.157	0.020	0.004	0.093
6	0.207	0.003	1.037	0.342	0.003	0.732	0.020	0.003	0.121	0.025	0.004	0.205	0.027	0.003	0.160	0.035	0.002	0.029

Table S3 Standard deviation for permeance and selectivity through DZ5 membranes.

	Pure gas			CH_4:CO_2- 50:50			CH_4:CO_2- 60:40			CH_4:CO_2- 70:30			CH_4:CO_2- 90:10			Biogas		
Pressure	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$	$E(P_{CO2})$	$E(P_{CH4})$	$E(P_{CO2}/P_{CH4})$
2	0.052	0.005	0.309	0.667	0.000	1.760	0.869	0.000	2.513	0.622	0.008	1.052	0.608	0.013	0.543	0.031	0.039	1.726
3	0.065	0.001	0.098	0.385	0.017	2.377	0.097	0.004	0.035	0.476	0.005	0.947	0.654	0.011	0.936	0.159	0.049	1.929
4	0.189	0.005	1.055	0.203	0.004	0.850	0.515	0.000	1.569	0.369	0.007	0.588	0.183	0.006	0.067	0.573	0.042	0.385
5	0.122	0.000	0.424	0.379	0.009	2.005	0.224	0.001	0.599	0.205	0.011	0.286	0.341	0.008	0.400	0.411	0.045	0.964
6	0.120	0.008	0.353	0.190	0.004	0.323	0.390	0.008	0.592	0.111	0.011	0.582	0.098	0.007	0.344	0.186	0.052	1.929