MOF-based Cellulose Acetate MMMs For an Advanced C_3H_6/C_3H_8 Separation

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Introduction

Efficiently separating propene and propane is paramount for the chemical industry but notoriously difficult due to their minimal size and volatility differences. Building on our previous findings about the positive effect of ILs, particularly [BMIM][Tf$_2$N], on the C_3H_6 permeability as well as C_3H_6/C_3H_8 ideal selectivity [1], this study aims to further enhance the CA membrane. This objective was achieved by incorporating ZIF-8, ZIF-67, and bimetallic ZIF-8-67 nanoparticles (NPs) in the CA polymeric matrix, where [BMIM][Tf$_2$N] played the role of compatibility enhancer in MMM formation for the challenging propene/propane separation.

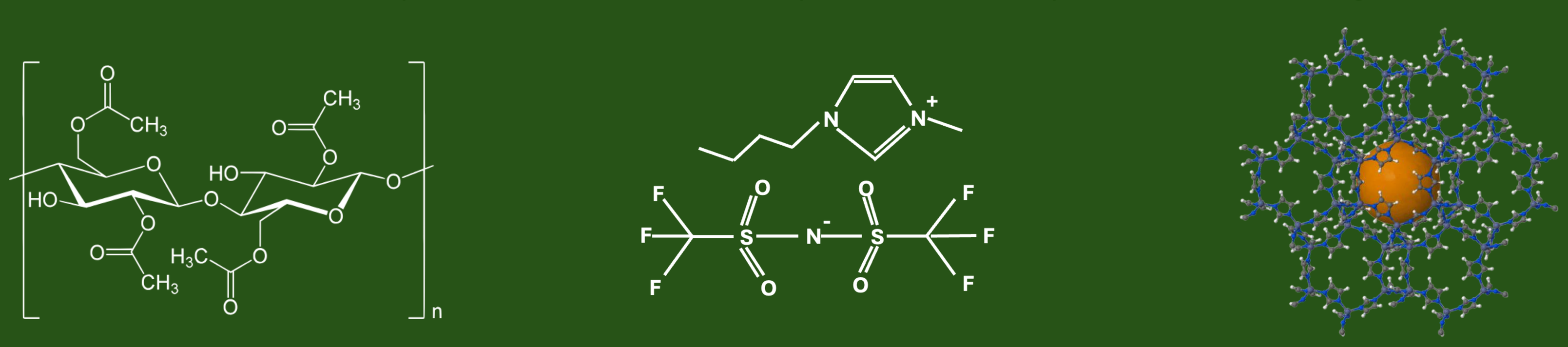
Challenges

- Following an ecofriendly approach to achieve greener membranes for C_3 separation.
- Preparation of defect-free MMMs composed of CA as the polymeric matrix and ZIFs as fillers.
- Preparation of thin film composites (TFCs) to bridge the gap between lab and industrial scales.

Experimental

Membrane Preparation

[BMIM][Tf$_2$N] was added to a 10 wt% the solution of cellulose acetate (CA) in acetone (30 wt% of [BMIM][Tf$_2$N] with respect of the total CA/IL mass). Then a weighed amount of ZIF NPs, synthesized via a green method [2], was dispersed in the IL-CA solution and stirred until obtaining a uniform dispersion (20 wt% ZIF based on the total CA/IL/ZIF mass). Finally, thin film composite (TFC) MMMs were prepared via spin-coating on a polyacrylonitrile (PAN) ultrafiltration membrane support at 5000 rpm and ambient temperature, followed by solvent-evaporation overnight.



Cellulose Acetate — [BMIM]$^+$[Tf$_2$N]$^-$ — ZIF-8-67

Single-Gas Permeability Apparatus (Fixed volume set up)

Pure gas permeation measurements were performed on a fixed volume/pressure increase instrument, constructed by Elektro & Elektronik Service Reuter [3], Figure 1. This technique yields the single gas permeability as the main gas transport parameter, to be determined reliably by Equation 1 [3], and using the time-lag method to obtain the diffusion coefficient, and indirectly the solubility from the P and D. Figure 2 illustrates the general parameters of this concept.

$$P = DS = {}^{Qh}/_{A\Delta P} \qquad \text{Equation 1}$$

where Q is the steady state flux of gas under the pressure difference ΔP through an area A of membrane thickness h.

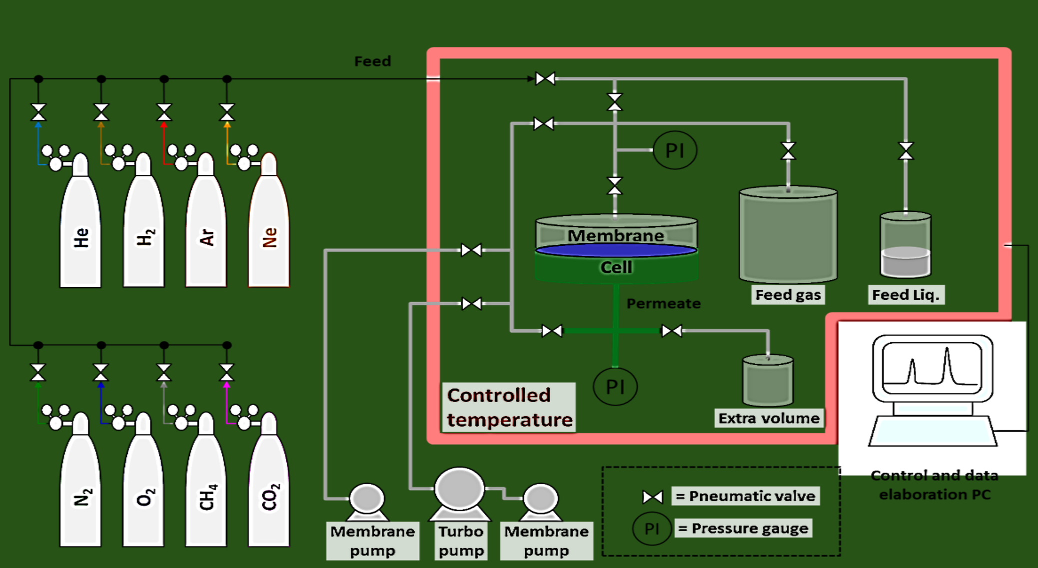


Figure 1. Schematic of the fixed volume/ pressure increase setup

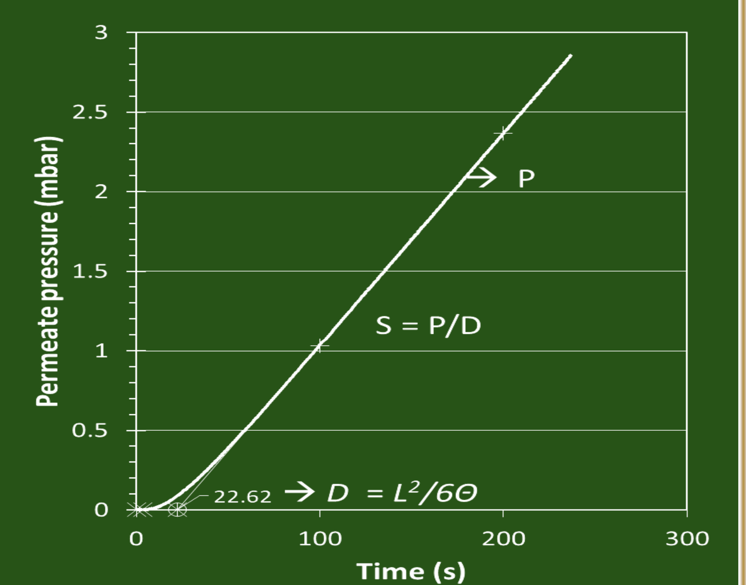


Figure 2. Scheme single gas permeation curve and the obtainable parameters based on the time-lag method and Equation 1

Mixed-Gas Permeability Apparatus (Variable volume set up)

The mixed gas permeation was studied with an innovative permeation setup (Figure 3), based on the continuous online analysis of the permeate composition by a quadrupole residual gas analyzer [3,4]. A dedicated method was developed for the deconvolution of propene signals originating from the ionization of propane to analyze both compounds quantitatively.

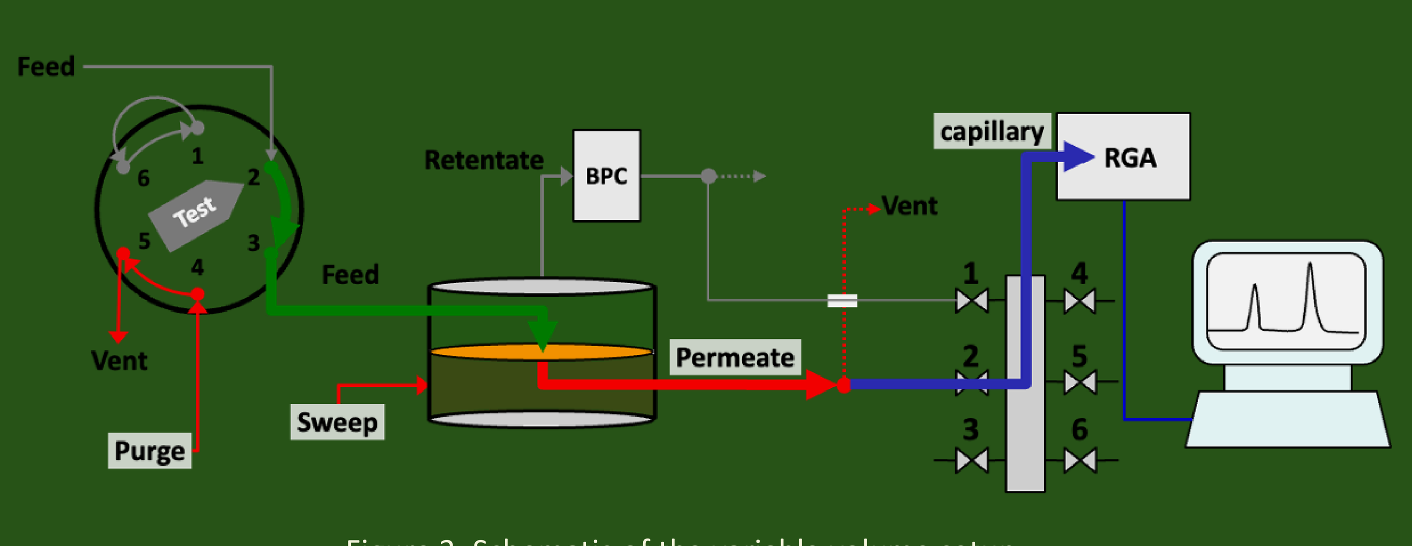


Figure 3. Schematic of the variable volume setup

Results and Discussion

Membrane Characteristics

- ✓ Visually homogeneous appearance of all TFCs.
- ✓ Uniform distribution of ZIF NPs across the polymeric matrix.
- ✓ Very low thickness of MMMs.

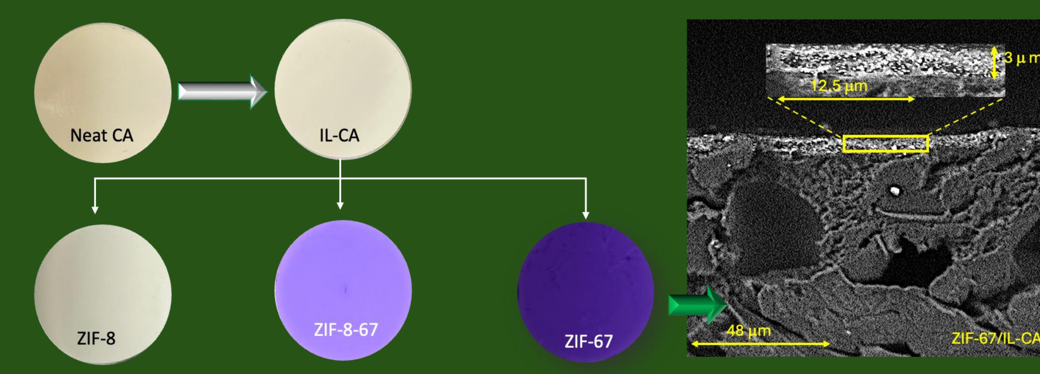


Figure 4. Visual appearance and a representative SEM image of TFCs.

Pure Gas Transport Properties

Figure 5 shows that:

- ✓ Compared to the free-standing film, the neat TFC@5000 rpm showed a slight increase in C_3H_6/C_3H_8 selectivity from 3.5 to 3.9.
- ✓ The IL-CA TFC increased the C_3H_6 permeance of the neat CA TFC from 0.015 to 0.021 GPU, along with a rise in C_3H_6/C_3H_8 ideal selectivity from 4 to 5.
- ✓ The incorporation of ZIFs further increased the propene permeance in the MMM TFCs, noticeably higher for the ZIF-8/MMM (0.17 GPU), along with a rise in the C_3H_6/C_3H_8 ideal selectivity to 2x, 2.5x, and 3x of the neat CA TFC (3.5) when using ZIF-8, ZIF-67, and ZIF-8-67, respectively.
- ✓ Figure 6 demonstrate the dominant size-sieving effect of ZIF-67/ and ZIF-8-67 in C_3 separation while for ZIF-8/MMM both the solubility and diffusivity differences drove the separation.

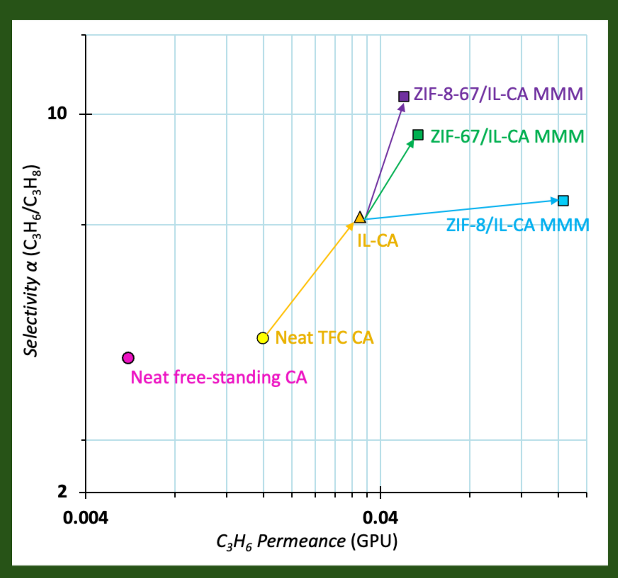


Figure 5- permselectivity plot for C_3H_6/C_3H_8 of TFCs.

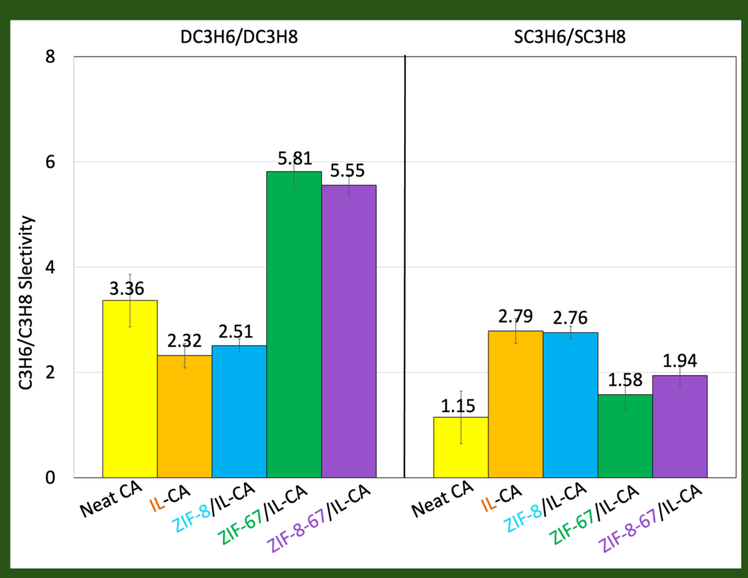


Figure 6- The solubility selectivity and diffusivity selectivity of TFCs for C_3H_6/C_3H_8 .

Mixed-gas Transport Properties

- ✓ The pure propene flow rate in 50/50 vol% C_3 mixture is approximately 8 times higher than that of propane, which confirms a high selectivity for the olefin species (Figure 7).
- ✓ The normalized flow rate, which highlights the differences between the individual gases, shows a much slower transient for propane than for propene, both in the single gases mode (Figure 7A) and in the mixture mode (Figure 7B).
- ✓ The smaller effective diameter of propene, which leads to its higher diffusion coefficient, as well as higher affinity of ZIF-8-67 to absorb propene than propane resulted in obtaining high separation of this pair.

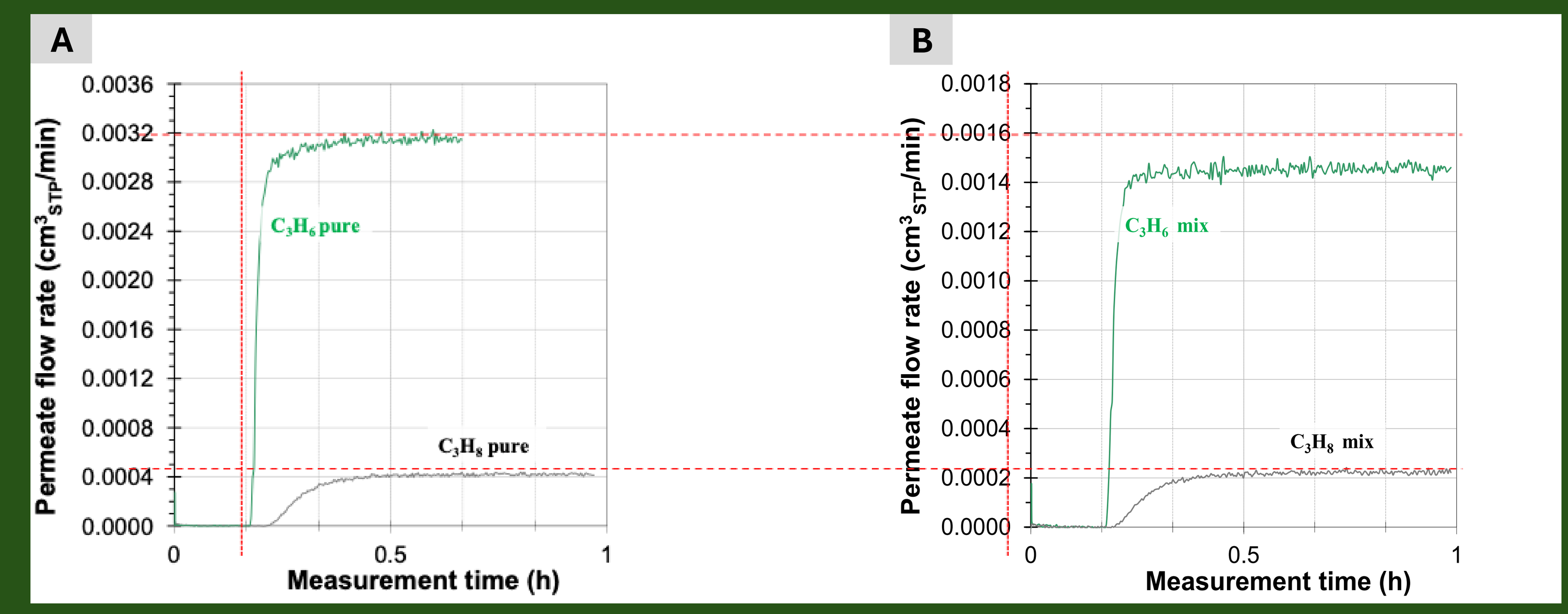


Figure 7- Propene and Propane flow rate for pure gases (A) and as a 50/50 vol% mixture of propene and propane (B).

Achievements

- Tackling the interfacial defects of MOF/CA by introducing an appropriate IL.
- Three-times upgrading of the C_3H_6/C_3H_8 separation by overcoming a usual trade-off behaviour with a promising ZIF-8-67/[BMIM][Tf$_2$N]-CA MMM.

References

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Acknowledgments

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