Modification of Cellulose Acetate Membranes by Incorporation of Triptycene Molecules for Gas Separations

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Abstract

Title: Modification of Cellulose Acetate Membranes by Incorporation of Triptycene Molecules for Gas Separations*

Author: Maria Salome Tavera Villamizar**

Key words: Cellulose acetate, triptycene, membranes, polymer, gas separations, characterization.

Description:

Cellulose acetate is a widely used polymeric material due to its physical and chemical resistance, and low cost. However, for gas separations in presence of CO_2, its selectivity and is not ideal due to the plasticization of the polymer. To address this issue, cellulose acetate membranes were modified by incorporating triptycene molecules in the polymer matrix. Triptycene-1,4-hydroquinone was synthesized and four cellulose acetate membranes with varying triptycene content were fabricated using the solution casting method and they were characterized using SEM, FTIR, DSC, and XRD. The Fractional Free Volume (FFV) for each membrane was calculated to compare the effect of incorporating triptycene molecules in the free intrinsic volume of the polymer. permeation tests were run using single gases: H_2, CH_4, and CO_2 at 1 bar, 5 bar, and 10 bar to evaluate the separation performance of the modified membranes. It was found that the triptycene molecules were molecularly mixed with the cellulose acetate by interaction of the hydroxyl groups. The membranes with stoichiometric excess of hydroxyl groups (1.5 -OH ratio) showed crystallization. The presence of triptycene reduced the thermal stability of the membranes, and the modified membranes showed a decrease in the FFV and permeability. However, the selectivity of the membrane with 0.5 -OH ratio increased compared to the neat cellulose acetate membrane, showing an improvement in the permeability-selectivity trade-off.

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*Bachelor Thesis

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Resumen

Título: Modificación de Membranas de Acetato de Celulosa por Icorporación de Moléculas de Tripticeno para Separación de Gases*

Autor: Maria Salome Tavera Villamizar**

Palabras clave: Acetato de celulosa, triptyceno, membranas, polímeros, separación de gases, caracterización.

Descripción:

El acetato de celulosa es un material polimérico ampliamente utilizado debido a su resistencia física y química, y su bajo costo. Sin embargo, para separaciones de gases en presencia de CO2, su selectividad no es ideal debido a la plastificación del polímero. Para abordar este problema, se modificaron membranas de acetato de celulosa incorporando moléculas de tripticeno en la matriz polimérica. Se sintetizó tripticeno-1,4-hidroquinona y se fabricaron cuatro membranas de acetato de celulosa con diferentes contenidos de tripticeno utilizando el método de colada de solución, las cuales se caracterizaron mediante SEM, FTIR, DSC y XRD. Se calculó el Volumen Libre Fraccional (FFV) de cada membrana para comparar el efecto de la incorporación de moléculas de tripticeno en el volumen intrínseco libre del polímero. Se realizaron pruebas de permeación utilizando gases individuales: H2, CH4 y CO2 a 1 bar, 5 bar y 10 bar para evaluar el rendimiento de separación de las membranas modificadas. Se encontró que las moléculas de tripticeno se mezclaron molecularmente con el acetato de celulosa mediante la interacción de los grupos hidroxilo. Las membranas con exceso estequiométrico de grupos hidroxilo (relación de 1,5 -OH) mostraron cristalización. La presencia de tripticeno redujo la estabilidad térmica de las membranas, y las membranas modificadas mostraron una disminución en el FFV y la permeabilidad. Sin embargo, la selectividad de la membrana con una relación de 0,5 -OH aumentó en comparación con la membrana de acetato de celulosa sin modificar, lo que muestra una mejora en el equilibrio permeabilidad-selectividad.

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Introduction

Membranes are currently competitive among gas separation technologies in the industry. Advantages offered by this technology such as easy manufacture, and energy efficiency place it ahead of traditional thermal separation technologies like distillation and absorption (Box et al., 2021). Thermal separation processes represent 50% of the total energy consumed by separation processes in the American industry, by implementing membrane-based separations the energy consumption would decrease 90% (Sholl & Lively, 2016), therefore, the need to develop a more energy-efficient technology for gas separations. The broadest application for gas separation membranes is the removal of CO_2 from raw natural gas (Scholes et al., 2012). Natural gas contains considerable amounts of acid gases like CO_2 that require removal to below 2 mol % to meet pipeline specifications in the US (Achoundong et al., 2013). Cellulose acetate membranes are currently the most utilized industrial material for the removal of CO_2 from natural gas due to their availability and wide industrial acceptance. Cellulose acetate is characterized by its good flexibility, durability, biodegradability, chemical resistance, non-toxicity, and low cost. However, it suffers a loss of selectivity due to plasticization caused by CO_2. This phenomenon reduces the rigidity of the polymer and its mechanical strength, also affecting its transport properties and separation performance, due to an increment in the permeability which leads to a significant selectivity loss after the membrane is exposed to CO_2.

To achieve a better separation, it is necessary to develop cellulose acetate polymer derivatives that demonstrate a more stable performance with highly selective separations without affecting the permeability of the membrane. In recent research, new materials have appeared on the market with outstanding performance. These special materials are polymers with triptycene units in their backbone. Triptycenes are 3D structures formed by three aromatic rings arranged in

a paddlewheel-like configuration (Box et al., 2021). They present internal free volume due to their configurational free volume which maintains the polymer stable over the operation. Additionally, the internal free volume of these molecules is comparable to the size of a single CO_2 molecule, making triptycene-based polymers highly selective due to their size sieving capacity. According to the previously discussed properties, the proposal of this work is addressing the plasticization issue present in the cellulose acetate membranes by introducing triptycene units in the polymer's backbone that improves chain mobility and stability, thus provides size sieving capacity to the polymer and as a consequence enhances the membrane's CO_2 selectivity and gas separation performance making this polymer membranes more competitive towards the traditional thermal separations processes.

Objectives

General objective

To develop a cellulose acetate derivative polymer that shows enhanced mechanical and transport properties and thus, better performance in the CO_2 separation process.

Specific objectives

- To incorporate triptycene molecules in the cellulose acetate backbone.
- To identify the changes in the chemical structure of the polymer.
- To determine the triptycene molecules' effect in the polymer's mechanical and transport properties.
- To calculate the permeability of the modified cellulose acetate membranes.
- To determine the effect of the triptycene molecules on the polymer separation performance of CO_2.

State of the art

Gas separations using polymer membranes are based on the solution-diffusion model, in which gas molecules dissolve into the high-pressure face of the membrane, which is the upstream, diffuse across the membrane, down a concentration gradient, and desorb on the low-pressure face, known as the downstream. This model allows the separation of different permeants because they dissolve a different amount of material through the membrane at a different rate. Mass transport in polymer membranes is characterized by two parameters: permeability and selectivity. The permeability coefficient (P) measures the gas throughput and it is the product of the solubility (S) and the diffusion coefficient (D) as showed in the following expression:

$$P = D * S \quad \text{(Eq. 1)}$$

The solubility represents the thermodynamic factor, and the diffusivity represents the kinetic contribution to the permeability (Wiegand, 2017). On the other side, selectivity ($\alpha_{A/B}$) represents the separation capability of the material in study, and it is given by the ratio of the permeabilities of two different components as showed below:

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

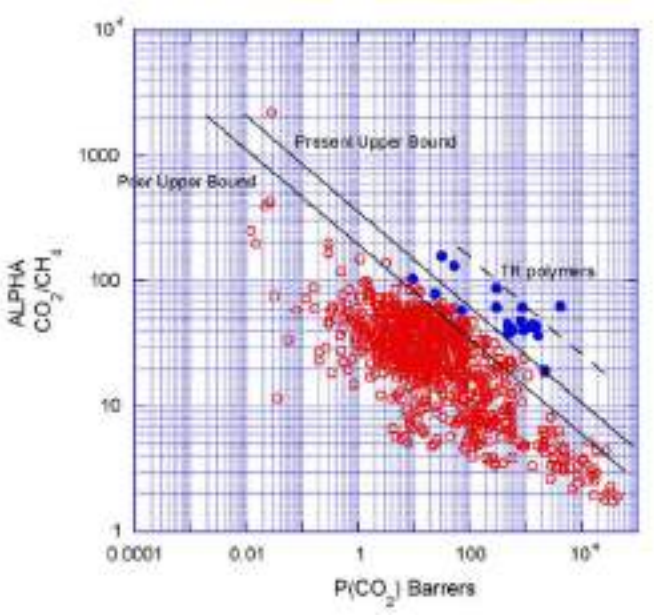
For gas separation membranes, it is necessary to develop materials with high permeability, so that the required surface area for the mass transfer is reduced, and high selectivity, to ensure high separation efficiency and thus, elevated purity products. (Wiegand, 2017). Polymers that are based in the solution-diffusion mechanism present a trade-off between the permeability and the selectivity, explained by (Robeson, 2008) with the "upper bound," which is a series of plots that show experimental permeability and selectivity data of different polymers used in gas separations with membranes. These plots show the permeability/selectivity trade-off date of different polymers

used to fabricate membranes that work with different gas mixtures, the position of the permeability/selectivity data for a specific material relative to the upper bounds is used to evaluate the potential of a polymer for gas separations.

One of the most studied gas pairs is CO_2/CH_4, which is the case of study for this research because it is methane (CH_4) the most abundant component in natural gas. The following upper bound plot shows the polymers' CO_2/CH_4 permeability/selectivity data of different polymer materials reported in the literature that constructed the upper bound review in (Robeson, 2008).

Figure 1

Upper bound correlation for CO2/CH4 separation.



Taken from "The Upper Bound Revisited." (p.320) by Robeson, Lloyd M. 2008. *Journal of Membrane Science,* no. 1–2.

Over the last few decades, research has been focused on developing better polymeric materials with maximized permeability/selectivity trade off, representing a huge effort by many academic and industrial research groups. (Wiegand, 2017)

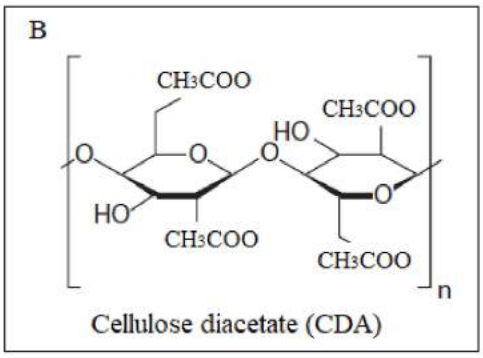
Cellulose is a natural polymer that is predominantly extracted from wood and cotton. Its repeating glucoside units consist of three hydroxyl groups, which are accountable for the strong intermolecular hydrogen bonding. Cellulose acetate (CA) is produced by treating cellulose with acetic acid and acetic anhydride, resulting in a chemical reaction that substitutes some of the hydroxyl groups with acetate groups. This substitution improves the material's properties, making it more resistant to water and heat, and increasing its solubility in organic solvents. In the 1970s, cellulose acetate was first utilized for gas separation, with a particular focus on eliminating CO_2 from natural gas. By the 1980s, the first cellulose acetate membranes process for CO_2 removal from natural gas was established commercially, and it has been the dominant player in the CO_2 membrane separation market since then.(Raza et al., 2021).

The vast use of cellulose acetate is due to its availability, price, and mechanical and chemical stability.(Genduso & Pinnau, 2020). The commercial cellulose acetate is the cellulose diacetate, which has a degree of substitution (DS) of the hydroxyl groups of 2.45, that is, the repeating unit of the polymer has 2.45 acetyl groups as substituents of the hydroxyl groups.

Cellulose acetate membranes can lose selectivity when they are exposed to CO_2 due to the plasticization. When CO_2 comes into contact with the cellulose acetate membrane, it can dissolve into the membrane and cause a change in the polymer's physical properties. This can cause the polymer chains to become more flexible and less packed, resulting in an increase in the permeability of the membrane. This loss of rigidity can lead to a decrease in the membrane's selectivity.

Figure 2

Cellulose diacetate repeating unit.



Taken from "Performance Analysis of Blended Membranes of Cellulose Acetate with Variable Degree of Acetylation for CO2/CH4 Separation." (p.3) By Raza, 2021, *Membranes 11, no. 4*.

Modification of the membranes is a common technique that has been studied as the main strategy to address this problem. This technique modifies the polymer's matrix by introducing molecules or functional groups that can contribute to an improvement in transport properties by, for example, getting properly sized free-volume pores, narrow free volume, or adequate pore size distribution.

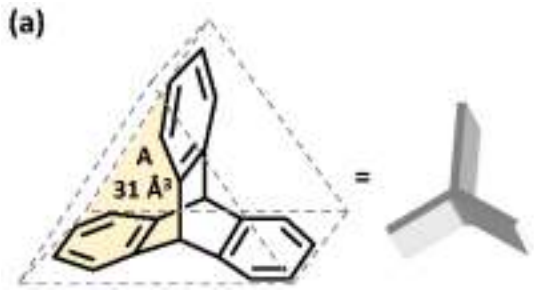
In the past few years, the use of triptycene as an element to construct polymers with tunable free volume has been studied to address material-related issues like the plasticization and loss of selectivity. Triptycene is a 3-dimensional molecule, formed by 3 aromatic rings. It is synthesized through the reaction of anthracene with benzyne (Wiegand, 2017). The structural advantages and uncomplicated synthesis of this molecule offer opportunities for developing better polymeric membranes.

Triptycene molecules are favorable to gas transport when incorporated into the polymer backbones. The bulky, rigid nature introduces internal free volume due to the configuration of the aromatic rings.

The internal free volume is integrated in the molecular configuration of triptycene; therefore, it is insusceptible to collapse. The molecule's elements have well-defined sizes, similar to penetrant gas molecules such as CO_2. This characteristic is favorable for developing tunable free volume polymers and thus elaborate membranes with molecular sieving capacity by incorporating these organic molecules into the polymers' backbones. adding the triptycene molecule in the polymer backbone modifies its chemical structure and an essential characteristic for polymers: fractional free volume.

Figure 3

Triptycene molecule with an internal free volume element of 31 Å.



Taken from "Triptycene as an Architectural Motif in the Macromolecular Design of Polyimides for Gas Separation Membranes." by Wiegand, Jennifer R. University of Notre Dame, 2017.

Fractional free volume is a generally used parameter that describes the empty space in a polymer membrane as a consequence of inefficient packing of the chains. It represents a structural property of the polymer that affects the gas separation performance. The FFV (fractional free

volume) is determined empirically in function of the free volume (V_f), the specific volume (V), and the volume occupied by the polymer chains (V_{oc}), where the occupied volume is determined as a function of the Van de Waals volume (V_W).

$$FFV = \frac{V_f}{V} = \frac{V - V_{oc}}{V} \quad \text{(Eq. 3)}$$

$$V_{oc} = 1.3 * V_W \quad \text{(Eq. 4)}$$

V_W is called the Van der Waals volume, and it is calculated using Bondi's group contribution method, that determines the V_W of two bonded atoms by adding the V_W of each functional group and subtracting the overlap volume on the bonds, in order to connect the groups. This method follows the next Equation:

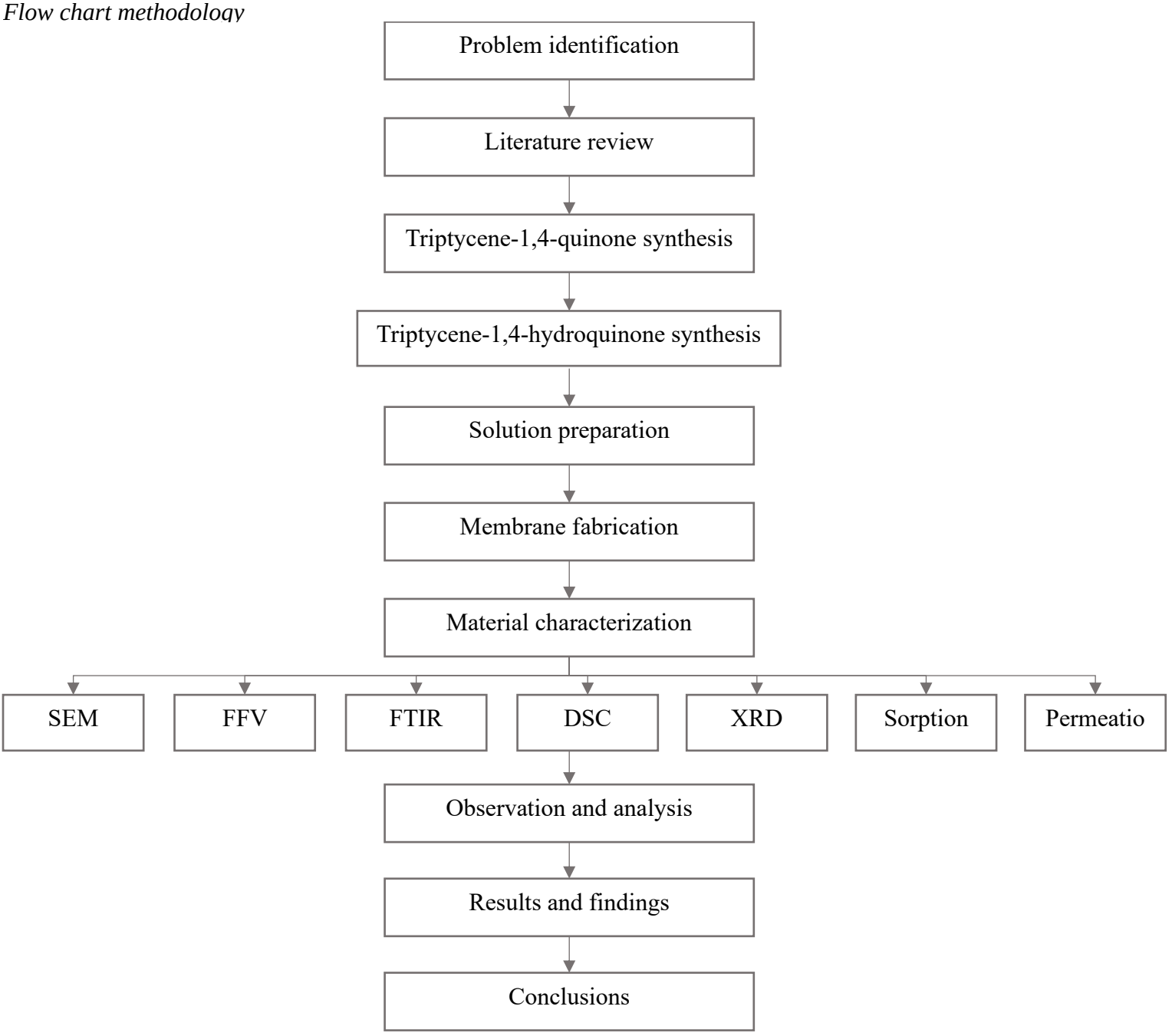
$$V_{w,tot} = \sum_{i=1}^{n} V_{w,i} - \sum_{j=1}^{m} V_{overlap,j} \quad \text{(Eq. 5)}$$

Where n is the number of the functional groups and m is the number of connections between these groups, $V_{w,i}$ corresponds to the van der Waals volume of the groups, and $V_{overlap,j}$ is the overlap volume for each connection between the groups. The just mentioned volumes are reported in "revisiting group contribution theory for estimating fractional free volume of microporous polymer membranes". Tables 1-3 and table 4 by Smith (2021).

By tunning the fractional free volume with the incorporation of the triptycene molecule to achieve the size sieving and hence, a higher selectivity, addressing the plasticization issue and improving the cellulose acetate membranes separation performance, a more efficient and competitive material is developed for separating CO_2 from natural gas in the industry.

Figure 4

Flow chart methodology



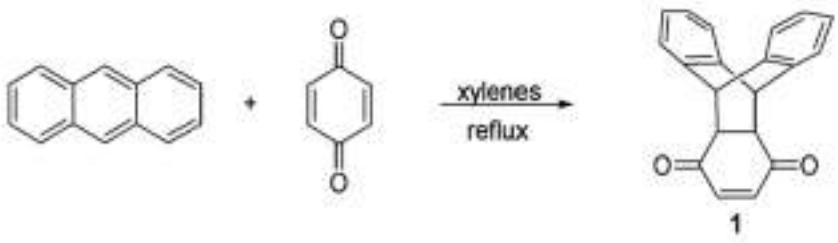
1. Triptycene- 1, 4-quinone Synthesis

The triptycene-1,4-quinone was synthesized via Diels-Alder cycloaddition reaction between anthracene and *p*-benzoquinone.

Anthracene (28.58 g) and *p*-benzoquinone (28.82 g), and xylenes (200mL) were added into a round-bottom flask. This was continuously stirred with a stir bar and refluxed at 140 ℃ in a nitrogen atmosphere for six hours. Then, the mixture was cooled to room temperature and filtered. The product was washed three times with 500 mL of hot water and then dried at 60 ℃ in a vacuum oven overnight.

Figure 5

Synthesis of the triptycene 1,4-quinone



Taken from "Synthesis and Characterization of Triptycene-Based Polyimides with Tunable High Fractional Free Volume for Gas Separation Membranes." (p. 13311) by Wiegand, Jennifer R. et. Al, 2014, *J. Mater. Chem. A* 2, no. 33

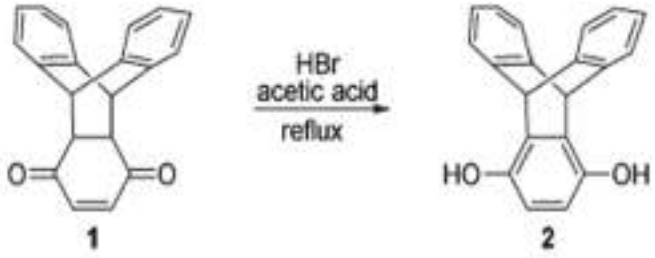
2. Triptycene-1,4-hydroquinone Synthesis

To synthesize triptycene-1,4-hydroquinone, the quinone product from the first reaction was reduced with glacial acetic acid and hydrobromic acid. The quinone product (18.69 g) and the glacial acetic acid (236.84 mL) were added into a round-bottom flask. To carry out the reaction, the mixture was continuously stirred and refluxed at 118 ℃ in a nitrogen atmosphere. Once the

system is brought to reflux, hydrobromic acid was added and the mixture is refluxed for 30 minutes. The resulting mixture was then cooled at room temperature and filtered. Finally, the product was dried at 60 °C in a vacuum oven overnight.

Figure 6

Synthesis of the triptycene 1,4-hydroquinone



Taken from "Synthesis and Characterization of Triptycene-Based Polyimides with Tunable High Fractional Free Volume for Gas Separation Membranes." (p. 13311) by Wiegand, Jennifer R. et. Al, 2014, *J. Mater. Chem. A* 2, no. 33

3. Solution Preparation

Materials

- Cellulose diacetate (CDA, degree of substitution=2.45). Purchased from Sigma Aldrich.
- Acetone, 99.9%. Purchased from Sigma Aldrich.
- Triptycene-1,4-hydroquinone. Synthesized in the laboratory.

In order to study the effect of incorporating triptycene units in the cellulose acetate backbone, 4 solutions were prepared with varying triptycene content.

One solution with only cellulose acetate and three solutions of cellulose acetate and triptycene-1,4-hydroquinone using acetone as the solvent were prepared with different triptycene concentrations to cast different membranes with varying triptycene content.

- Neat cellulose acetate in acetone.
- 0.5 OH ratio (triptycene/cellulose acetate), to have a cellulose acetate excess.
- 1.0 OH ratio (triptycene/cellulose acetate), to have a stoichiometry equilibrium.
- 1.5 OH ratio (triptycene/cellulose acetate), to have a triptycene excess.

Table 1 shows the experimental design for the previously described solutions.

Table 1

Experimental design for solution preparation.

Hydroxyl ratio (CA/Triptycene)	**Triptycene wt%**	**CA (g)**	**Acetone (mL)**
0	0	0.306	9.29
0.5	12.93	0.306	10.67
1.0	22.89	0.306	12.05
1.5	30.81	0.306	13.43

4. Membrane Fabrication

Solution casting technique was used for membrane fabrication with the prepared solutions. These solutions were prepared with 4 wt.% of polymers (CA + triptycene) in acetone, with the aim of achieving a membrane thickness (l) of 30 µm.

The solutions were poured onto a flat, 10 cm glass plate, covered with a filter paper and a weighty lid, and left for 24 hours to allow for the evaporation of the acetone. The resulting membranes were removed from the glass plate and subjected to overnight drying in a vacuum oven

at 60 ℃ to eliminate any remaining solvent. The resulting membrane were employed for carrying out characterization and gas permeation testing.

5. Scanning electron microscopy (SEM)

In order to see the membranes' morphology at microscopic levels and study the differences in the physical properties in function of the triptycene content, the cross-sections of the membranes were characterized using SEM.

6. Fractional Free Volume Calculation (FFV)

This property was calculated for each one of the membranes to determine how the FFV changed by introducing triptycene units in the polymer's backbones. To do so, the van der Waals volume was determined for the repeating unit of cellulose acetate and for the triptycene molecule, using the Bondi's group contribution method and the (Eq. *5*) and the volumes reported in (Wu et al., 2021) as described before. The following picture shows the Van der Waals volume for the triptycene molecule.

Figure 7

Van der Waals volume of the triptycene molecule

Taken from "Revisiting Group Contribution Theory for Estimating Fractional Free Volume of Microporous Polymer Membranes." By Wu, Albert X. 2021, *Journal of Membrane Science* 636

Once the V_W of each unit was determined, it was possible to determine the occupied volume (V_{oc}).

Subsequently, the density of the membranes was measured using a balance, to be able to calculate the specific volume (V) as the inverse of the density.

The density was measured using a Mettler Toledo balance equipped with a density kit. After weighting the samples in air and water at 21 ℃, the density was calculated as follows:

$$\rho = \frac{m_{air}}{m_{air} - m_{water}} (\rho_{water} - \rho_{air}) + \rho_{air} \quad \text{(Eq. 6)}$$

Where ρ_{water} is the water density and ρ_{air} is the density of air.

Once the Van der Waals volume (V_W), the occupied volume (V_{oc}) and the specific volume (V), the fractional free volume was calculated for each membrane using (Eq. 3).

7. Fourier-transform Infrared Spectroscopy (FTIR)

A Nicolet iS50R Fourier-transform infrared spectroscope in the iS50 attenuated total reflectance (ATR) mode using 64 scans was used to analyze the functional groups and chemical bonds present in four different membranes that were fabricated. Specifically, the research examined the interaction between the functional groups of the cellulose acetate and those of triptycene and observed how this interaction changed with varying concentrations of triptycene.

8. Differential Analysis Calorimetry (DSC)

Differential analysis calorimetry instruments (DSC 2500) were utilized to analyze the thermal properties of the membranes, such as the glass transition temperature. In a typical procedure, the sample was first heated from 40 ℃ to 250 ℃ with a heating rate of 10 ℃/min. aluminum pans with a pierced lid were used with a sample size ranging from 1,2 mg to 3.4 mg. The melting curves

for each membrane were compared to study how their thermal properties changed with different triptycene concentrations.

9. X-ray Diffraction (XRD)

A crystalline analysis was made for the membranes to study the effect of the presence of the triptycene on the crystallinity of the polymer. The XRD analyses were conducted on a Rigaku Ultima IV diffractometer, the scans were taken in the 2θ range with a step size of 0.02 ° from 5° to 70°.

10. Sorption Test

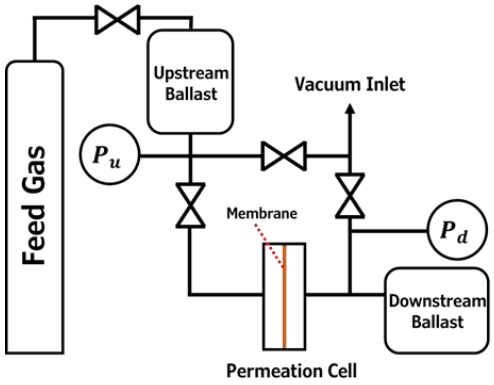
To assess the affinity of the porous material for methanol, a sorption test was conducted using this solvent. the test involved cutting a piece of each membrane, measuring its thickness and mass when dry, and soaking it in a vial containing 10 mL of methanol for 24 hours. Following this, the mass and thickness of the samples were measured again to compare their properties and determine the percentage of dilation for each sample.

11. Permeation Test

To evaluate the permeability of the membranes, a permeation test was carried out. It involved exposing each one of the membranes to a single gas that acted as a permeant. The sample of membrane was exposed to a gas and the rate at which the permeant passed through the material was measure. The method used to the permeation test was the constant-volume method, which involved placing the sample of the membrane over a reservoir containing the permeant and measuring the pressure changes in the reservoir over time, as depicted below:

Figure 8

Permeation apparatus model



The permeation test was carried out at 35 °C. The gases used for the test were H_2, CH_4, and CO_2 at feed pressures of 1 bar, 5 bar, and 10 bar.

The gas permeability was calculated with the pressure data obtained by the following equation:

$$P_i = \frac{Q_i\, l}{A\, \Delta P} \qquad \text{(Eq. 7)}$$

Where P_i is the gas permeability in Barrer; i is the gas; Q_i is the volumetric flow rate of the permeated gas; l is the thickness of the membrane; A is the effective area of the membrane; and ΔP is the pressure difference across the membrane. (Raza et al., 2021)

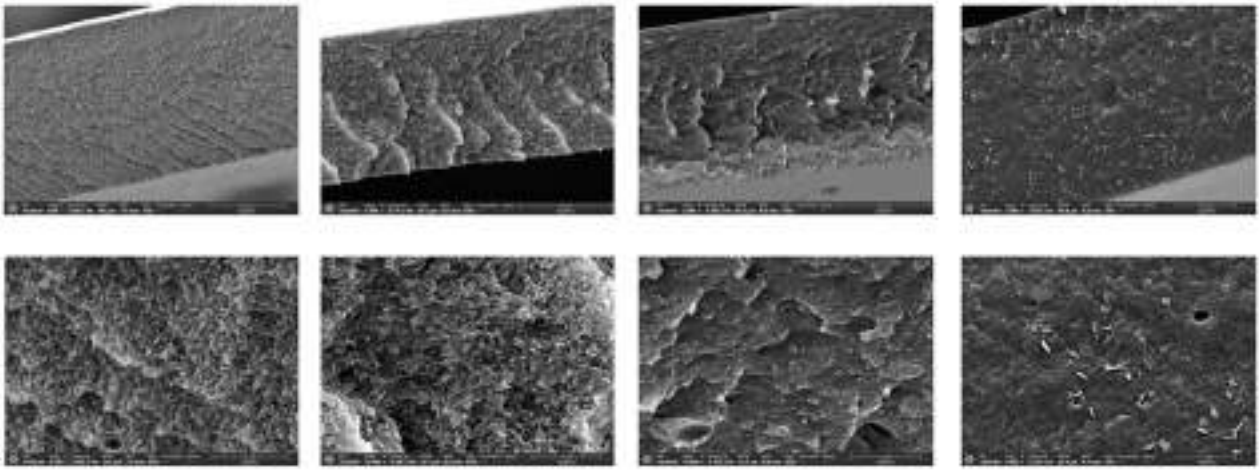
Once the permeability of the membranes for each gas was obtained, the selectivity of CO_2/CH_4 was calculated using (Eq. 2) previously discussed.

Results

Scanning electron microscopy (SEM)

Figure 9

SEM characterization of the membranes with varying triptycene content



a) Neat cellulose acetate b) 0.5 OH ratio Tr-Hq/CA c) 1.0 OH ratio Tr-Hq/CA d) 1.5 OH ratio Tr-Hq/CA

SEM characterization of membranes cross-sections reveals defects at a stoichiometric excess of triptycene hydroxyl groups, relative to cellulose acetate hydroxyl groups. These images allow to identify the formation of possible crystals in the membrane with 1.5 -OH ratio, due to the aggregation of the excess of the hydroxyl groups from the triptycene. Regarding the membranes with 0.5 and 1.0, the topography of the cross sections shows no defects, which confirms a molecularly mixed structure of the polymer.

Fractional Free Volume (FFV) and XRD analysis

Figure 10

Fractional Free Volume of the membranes in function of the triptycene content

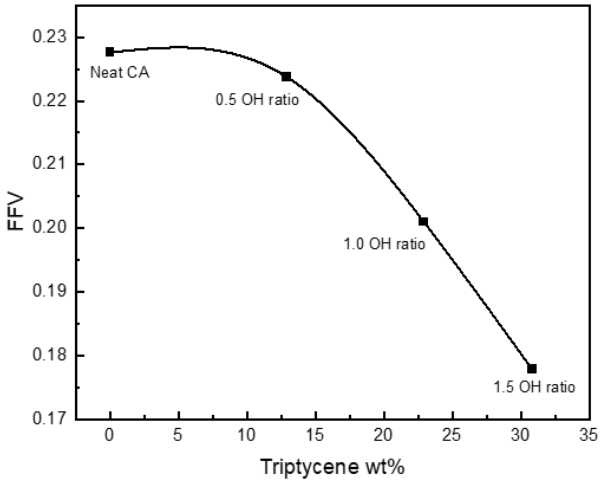
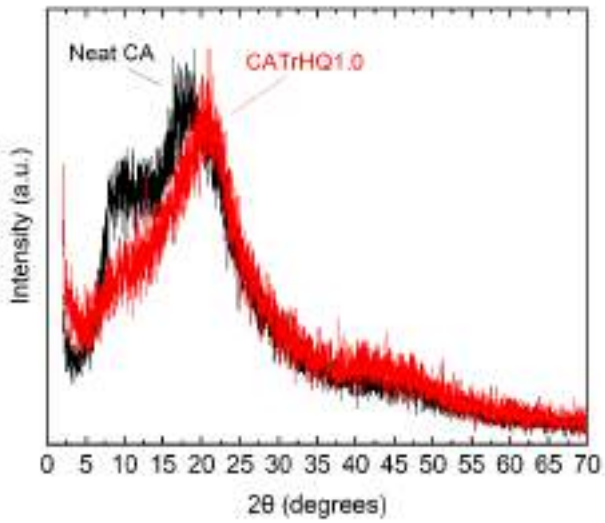


Figure 10 shows how FFV increases in the presence of triptycene in the polymer. A higher triptycene content leads to an increase in the FFV of the polymer, causing a possible decrease in permeability and an increase in selectivity.

Figure 11

XRD pattern for neat CA membrane and 1.0 -OH ratio Tr/CA membrane



In the XRD pattern, it is noticed that the peak of the membrane with triptycene content shows a shift to the right. This means that the atomic planes are more closely spaced than those in the neat cellulose acetate membrane. This shift can be caused by an increased crystallite size.

The presence of triptycene appears to densify the polymer structure, likely due to H- bonding interactions.

Fourier-transform infrared spectroscopy (FTIR)

Figure 12

FTIR spectrum of the membranes with varying triptycene content

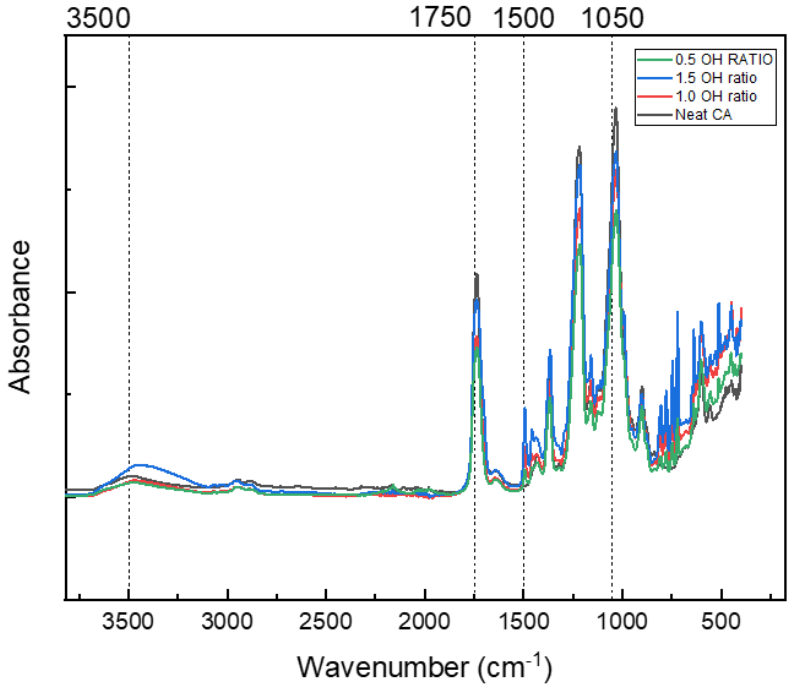


Figure 12 shows the FTIR spectrum for all fabricated membranes. The peak at a wavenumber of 1500 cm^{-1} corresponds to the aromatic C=C stretching of the triptycene phenylene groups. Moreover, the peak at 1750 cm^{-1} shows the C=O stretching of the acetyl group, from the cellulose acetate. Additionally, the peak at 1050 cm^{-1} indicates the presence of C-O-C of the cellulose acetate backbon. Finally, at a wavenumber of 3500 cm^{-1} there is a small peak that indicates the presence of hydroxyl groups.

Figure 13

FTIR spectrum for all fabricated membranes

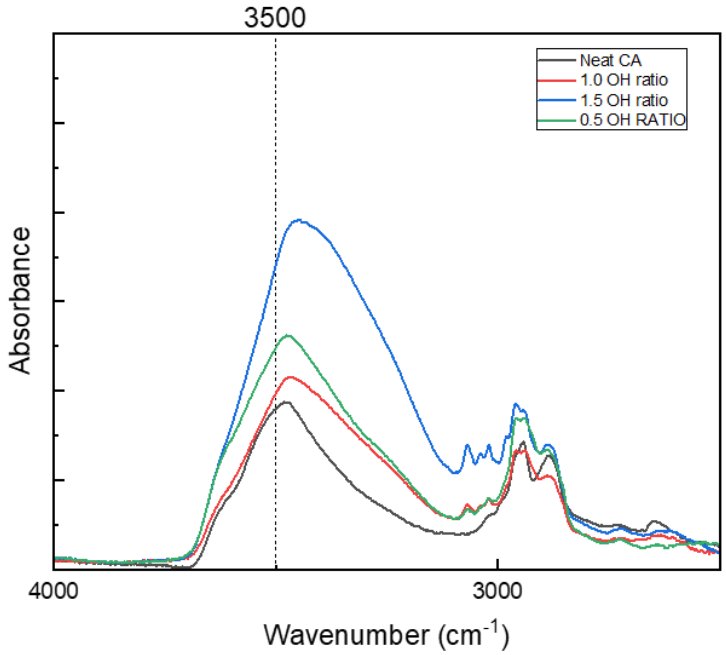


Figure 13 shows a closer look to the peak at 3500 cm^{-1} corresponding to hydroxyl groups present in the membranes. There is a slight shift in the peaks from the membranes that were modified with triptycene, indicating an interaction between the hydroxyl groups of the cellulose and the triptycene. This shift also indicates changes in the environment of the hydroxyl groups such as changes in the chemical composition of the molecule. Moreover, at a wavenumber of 3100 cm^{-1} an appearance of aromantic C-H stretches only in the spectrum of the modified membranes.

Figure 14

FTIR spectrum of the fabricated membranes

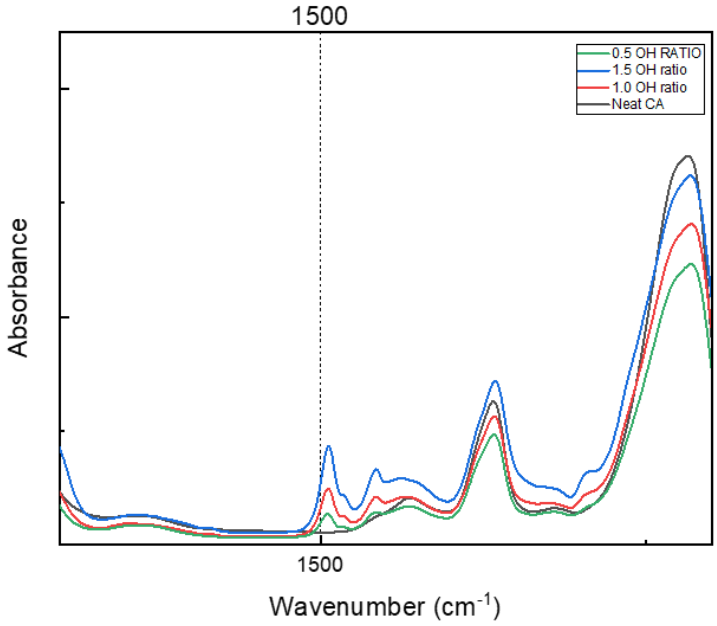


Figure 14 offers a closer look to the peak at 1500 cm^{-1} which corresponds to the aromatic C=C stretching only present in the modified membranes.

Differential analysis calorimetry (DSC)

Figure 15

First melt for the fabricated membranes on DSC characterization

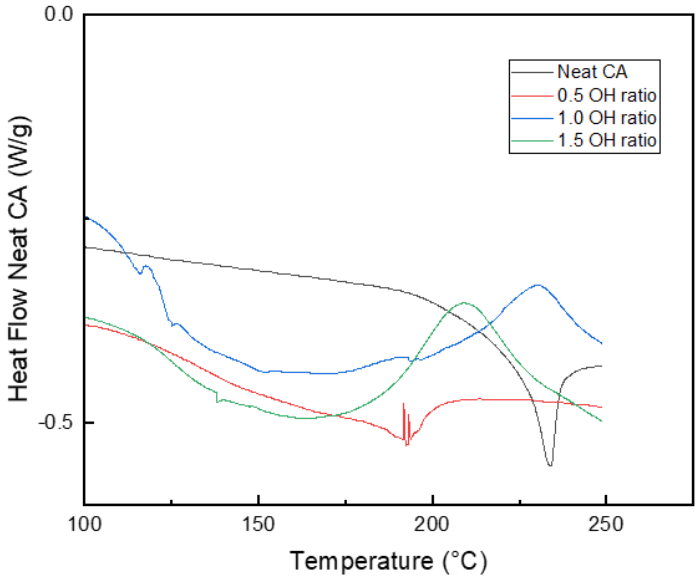
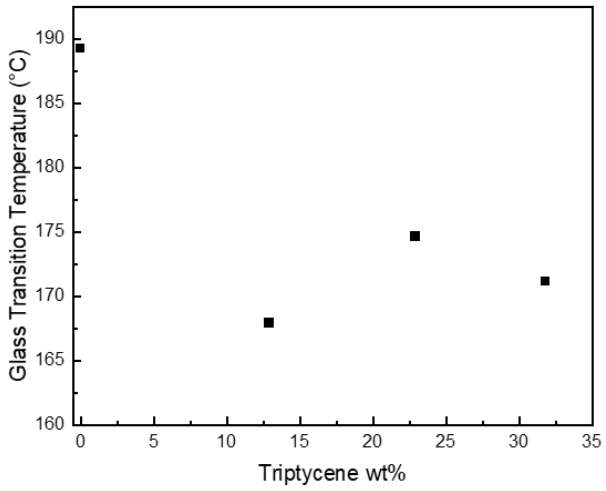


Figure 15 shows the first melt in the thermal analysis run with DSC. A crystalline endotherm is evident for the neat cellulose acetate and 0.5 -OH ratio membranes, indicating that there was a phase transition from solid to liquid at the temperature where the endotherm peak is. While an exotherm is observed for the 1.0 -OH ratio and 1.5 -OH ratio membranes, which can be due to a chemical reaction.

Figure 16

Glass transition temperatures for varying triptycene content membranes

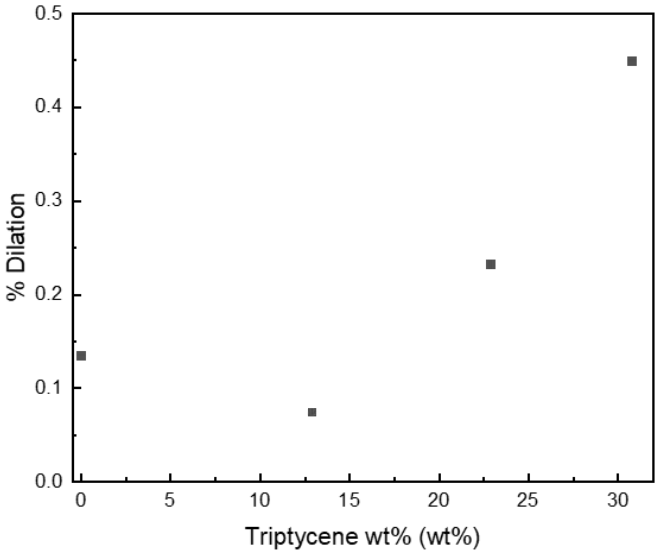


Glass transition temperatures were determined by running DSC analysis. In Figure 16 it is observed how the triptycene in the polymer lowers the glass transition temperature, since it allows chain mobility. This decrease in the glass transition temperature (Tg), indicates that the membrane has become less rigid. It can also indicate a reduced thermal stability.

Sorption

Figure 17

Dilation percentage of the fabricated membranes in function of the triptycene content



The change in thickness of the membranes after being immersed in methanol is referred to as dilation. Based on Figure 17, it is evident that an increase in the concentration of the triptycene in the polymer leads to a higher degree of dilation, meaning a more significant change in the thickness of the membrane. This is primarily due to increased interaction between the hydroxyl groups of the methanol and the triptycene, particularly when there is a stoichiometric excess of this functional group, like in the case on the 1.5-OH ratio, which displays the highest percentage of dilation.

Permeation

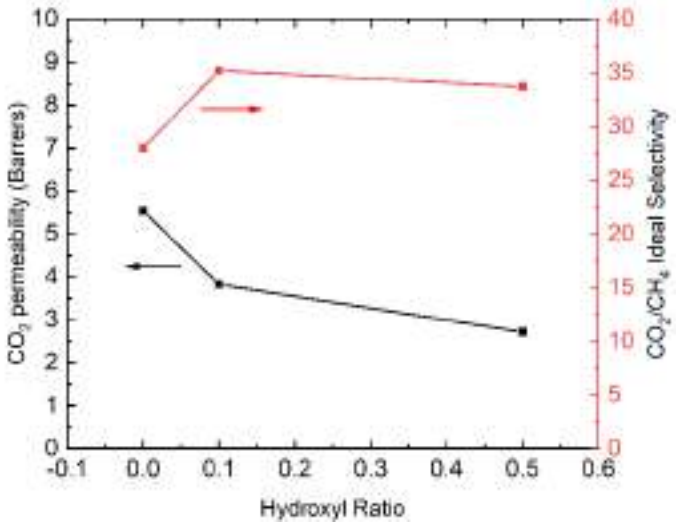
Table 2

CO_2 permeabilities and CO_2/CH_4 selectivities at 1 bar

Polymer	Permeability (Barrers)	Selectivity
Neat cellulose acetate	5.53592	28.02593
0.5 -OH ratio	3.82381	35.23559
1.0 -OH ratio	2.72031	33.71282

Figure 18

CO_2 permeabilities and CO_2/CH_4 selectivities at 1 bar



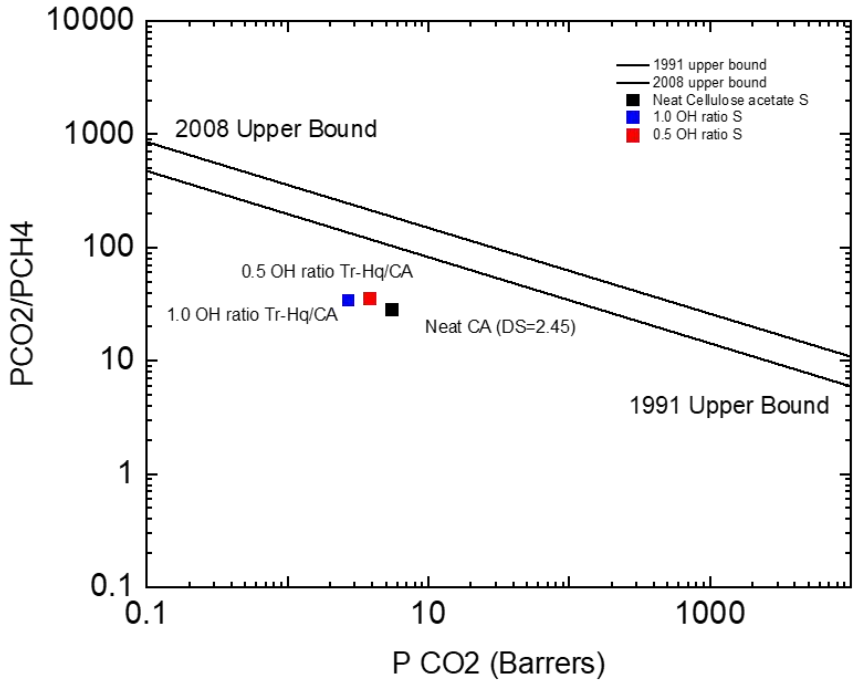
According to

Figure ***18***, a decrease in permeabilities is observed with higher hydroxyl ratios, as an effect of the reduced fractional free volume. An increase in selectivities is observed for the membrane

with 0.5 -OH ratio. However, further increases in selectivity are not observed with higher hydroxyl ratios, as in the case of the 1.0 -OH ratio membrane.

Figure 19

Fabricated membranes positioned in the Upper bound plot.



The upper bound plot was used to compare the neat cellulose acetate membrane with the 0.5 -OH ratio and 1.0 -OH ratio membranes based on data obtained from the permeation test regarding their permeability and selectivity. The aim was to evaluate their performance in separating CO_2 from methane (CH_4). The 0.5 -OH ratio membrane showed an improvement in the trade-off between permeability and selectivity, which is attributed to an increase in its selectivity. Its gas separation performance was found to be closer to the upper bound plots, indicating that it performed better than the neat cellulose acetate membrane.

Conclusions

Cellulose acetate membranes were fabricated by mixing cellulose diacetate and varying triptycene-1,4-hydroquinone concentration, based on the hydroxyl ratio of triptycene to cellulose acetate. The membranes were characterized by SEM, FTIR, XRD, and DSC. The change in structure and transportation properties were evaluated by calculating the FFV and running permeation tests respectively. The formation of a homogenous blend and defect-free membranes were confirmed from the SEM results. The incorporation of the triptycene in the polymer backbone resulted in densification of the membranes and a decrease in the FFV. The XRD analysis also confirmed the densification and reduction of the spacing in the polymer matrix, as well as the increase in the crystallite size of the modified membranes. FTIR results verified the interactions between the hydroxyl groups of the cellulose and the triptycene, confirming that these two were molecularly mixed. Moreover, the appearance of peaks that indicate the presence of aromatic groups introduced in the membranes by the triptycene. Thermal analysis run with DSC instruments found a reduction in the chemical stability with the incorporation of the triptycene and a decrease in the glass transition temperature of the membranes. The gas permeation study for CO_2 and CH_4 was carried out using a single gas at 1 bar, 5 bar and 10 bar, at a temperature of 35 ℃. Reliable and comparable results were reported at 1 bar. A reduction in the permeability with an improvement in the selectivity and plasticization were achieved for the 0.5 -OH ratio membrane. The separation performance for the fabricated membranes were compared based on Robeson's upper bound plot. The 0.5 -OH ratio membrane was found to have acquired a better position in Robeson's upper bound plot, compared to the neat cellulose acetate membrane. It was concluded that the modification of membranes with triptycene has potential for the separation of CO_2 and CH_4, however, more

research needs to be done to optimize the increment in selectivity without affecting permeability, in order to achieve a better permeability/selectivity trade-off, and thus, a better position in Robeson's upper bound plot.

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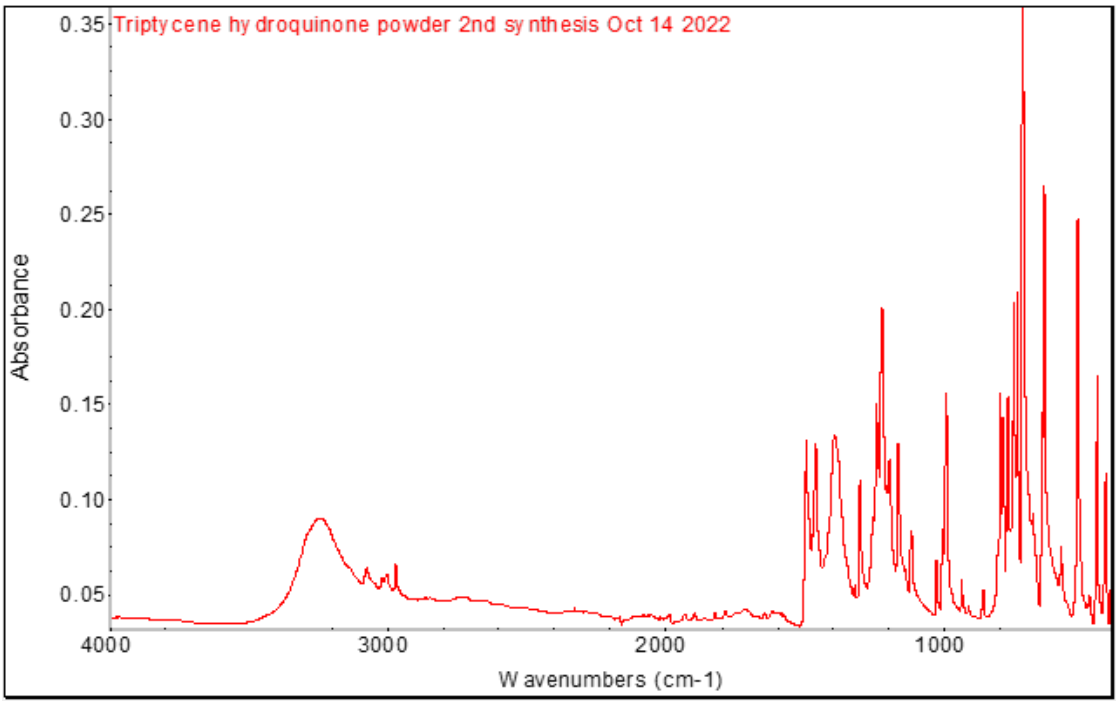
Appendix A: FTIR analysis on triptycene-1,4-hydroquinone



Appendix B: DSC curves on fabricated membranes

Figure B 1

DSC curve of neat cellulose acetate membrane.

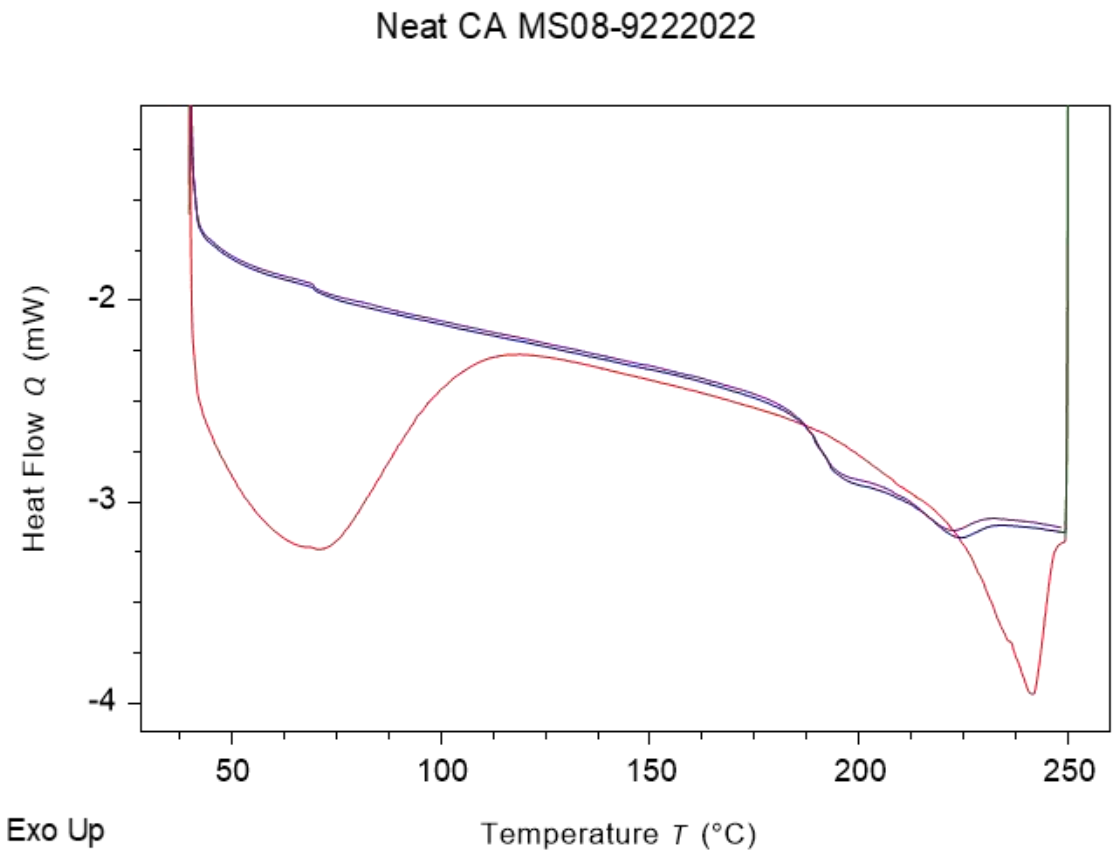


Figure B 2

DSC curve of 0.5 -OH ratio membrane

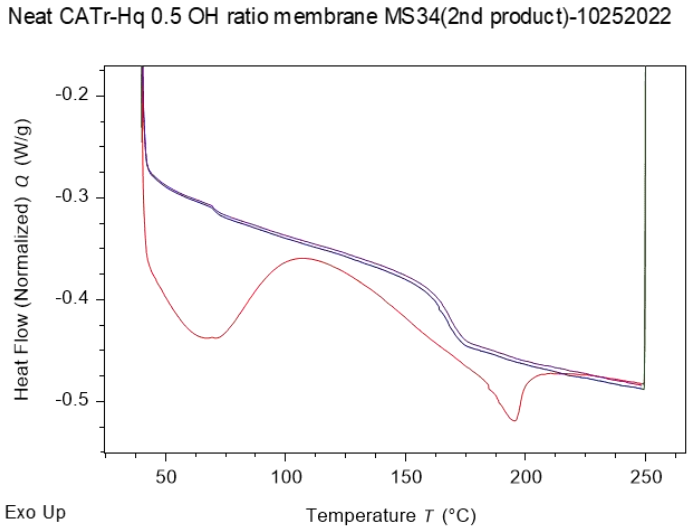


Figure B 3

DSC curve of 1.0 -OH ratio membrane

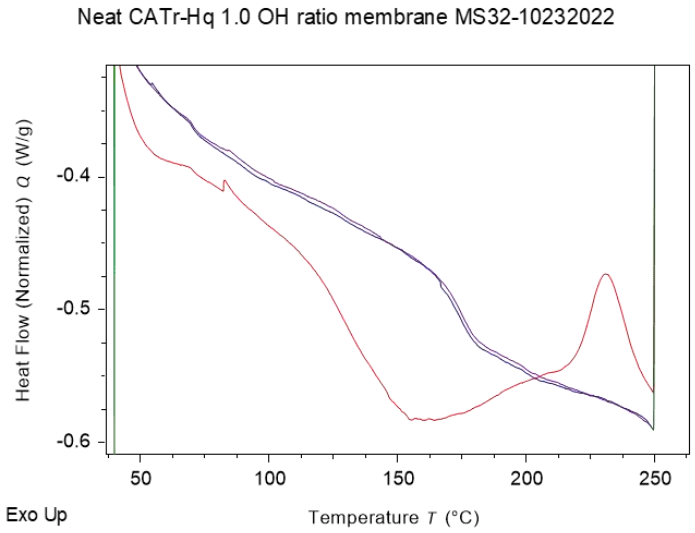


Figure B 4

DSC curve of 1.5 -OH ratio membrane