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Separation of Isoprene from Biologically-Derived Gas Streams

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Abstract

Renewable organic precursors, including olefinic compounds such as isoprene, have attracted interest from the polymer and pharmaceutical industries. Biologically-derived processes can generate these target compounds; however, their gaseous product streams are complex mixtures of condensable organic vapors (COVs), water vapor, carbon dioxide (CO_2), and/or nitrogen (N_2). Because COVs, CO_2 and water vapor are known to alter polymer membranes, mixed gas separations data at ambient and elevated temperatures are limited. This study focused on two classes of polymer membranes, glassy [polyetherimide (Ultem®)] and a rubbery [polydimethylsiloxane (PDMS)] with results indicating that isoprene separation is possible in humidified gas environment (2-4 vol% water). Gas permeabilities of these membranes did not noticeably change in the presence of humidity; however, the selectivity of these membranes was significantly lower compared to their performance under dry conditions. The role of water vapor in gas transport was derived from the energy of activation of permeation (E_p) for PDMS and Ultem® from 30-80°C in humidified mixed gas streams. For both polymers, E_p data shows a slight decrease in selectivity with the other gases (hydrogen, N_2, CO_2, and methane) at elevated temperatures in the presence of water vapor. Thus, these COVs separations are feasible with polymer membranes in the presence of humidified gas streams, even in the case of glassy and rubbery membranes in series.

Keywords: polyetherimide, polydimethylsiloxane, polymer membrane separations, isoprene, gas permeation analysis, water vapor

Introduction

Organic compounds derived from biological processes are important alternatives to those obtained from fossil fuels.[1–9] Several biologically-derived organic compounds produce condensable organic vapors (COVs), such as isoprene (2-methyl-1,3-butadiene), a potential renewable carbon sources. Current olefin production is accomplished through large-scale production from fossil fuels, with subsequent olefin separations carried out through energy intensive cryogenic distillation and multi-staged distillation processes.[10–14] Alternatively, membrane separations of biologically-derived olefins, such as isoprene, can create a product absent the complex gas mixtures formed in petrochemical processes. However, the COVs produced in biological processes are much more dilute, making them suitable for polymer membrane separations. The membrane-based separation of bio-derived olefins may be implemented with economical and sustainable sources of olefins.[15]

Several microbial pathways provide renewable sources of isoprene. Some known microbial processes use genetically engineered strains of *E. Coli* bacteria[16] (*Saccharomyces cerevisiae* yeast or *Synechocystis* cyanobacteria).[17] In this pathway, the production of isoprene is achieved in a fed-batch reactor using glucose as a carbon source for bacteria and yeast, producing isoprene and carbon dioxide (CO_2). Another microbial pathway utilizes cyanobacteria with CO_2 as the carbon source and isoprene and oxygen (O_2) as products.[18] Whited et al.[8]

reported *E. coli* production titers for isoprene at 60g/L (after 55hrs) using glucose as a carbon source, while Melis and Lindberg[6,19] reported *Synechocystis* titers of 40 mg/L/hr with CO_2 as the carbon source. In *Saccharomyces cerevisiae* isoprene production, an engineered strain accumulates up to 37 mg/L/hr of isoprene under aerobic conditions with glycerol-sucrose as a carbon source.[20] These biological processes demonstrate the increasing relevance of bio-derived olefin resources.

Regardless of the bio-generation method, separations are required to achieve a high purity isoprene. Well-developed economical modular configurations, such as spiral-wound (SW) or hollow fibers (HFs), are suitable for separation of products originating from biological feedstocks.[21,22] However, bio-derived isoprene separation may be complicated by the presence of humidity, CO_2, and condensable organic vapors (COVs) at ambient temperatures and pressures. Since isoprene is a volatile liquid at sub-ambient temperatures (boiling point [bp] = 34°C), minor gas compressions at or below room temperature can condense these vapors in the polymer membrane and in the separation assembly.[23] As a result, the apparatus must be heated to maintain the feed components in the vapor phase.

For bio-derived isoprene processes, separation requires more than a single membrane stage due to the concentrations and classes of gaseous contaminants. A conceivable separation process can include a combination of glassy and rubbery polymer membrane modules at elevated temperatures (34°C and higher). At these temperatures, a two-stage separation can provide an isoprene separation while capturing or removing other condensable vapors and gases. A recent Air Liquide US patent application describes such a separation process for biomethane generation.[24] Their route employs multiple polymer membranes (glassy and rubbery) to purify methane (CH_4) from CO_2 and hydrogen sulfide (H_2S). Similarly, it is anticipated that the separation of bio-produced isoprene also will require multiple membrane modules to achieve a high-purity product.

The functional differences between glassy and rubbery polymeric membranes in isoprene separation can be evaluated by gas transport. Gas transport is best described by the solution diffusion model where permeability (P) is the product of diffusion (D) and solubility (S).[25–27] Glassy polymers separate the gases by molecular size, where the smaller kinetic diameter gases pass through the polymer while the larger ones are retained to a greater degree. Examples of diffusion-controlled transport (D) polymers are polyetherimides (PEI), polyamide-imides (PAI), and polyimides (PI). Some of the first membrane modules developed for large scale gas separations of air employed a PI as the selective layer (Medal™, from Air Liquide and DuPont).[28] A typical large-scale hollow fiber (HF) or spiral-wound (SW) membrane module consists of plastic or stainless-steel housings with connections to the feed gas, permeate gas (vent) and retentate gas. Selected penetrants tend to be gases that are unwanted minor components, where maintaining pressure is less important to process economics. The retentate is usually the major constituent that has downstream uses, which allows for maintaining pressure, thus obviating recompression costs. HF and SW modules are commonly employed due to their large membrane surface areas in each module.

Membrane module that consists of rubbery polymers tend to partition gases and vapors based on solubility (S). For example, polydimethylsiloxane (PDMS) is a solubility-selective polymer that is commercially available as either HF or SW membrane modules that have medium to high flow capacities for gases and vapors. In a rubbery membrane, gases with a stronger solubility interaction with the membrane will pass at higher permeation rates. Conversely, gases with weaker solubility interactions will have lower permeation rates.[29]

A solubility-selective module can be employed in several different configurations such that vacuum assists in COV removal. Figure 1 (left) outlines several configurations, which can be considered for either vacuum or pressure driven membrane systems from flat sheets to hollow fiber modules. In this work, possible systems configurations using both sieving and solubility driven membrane modules are investigated for the isolation of isoprene from biological sources. Similar modular systems applied to biologically derived feed streams were recently demonstrated by Air Liquide.[24]

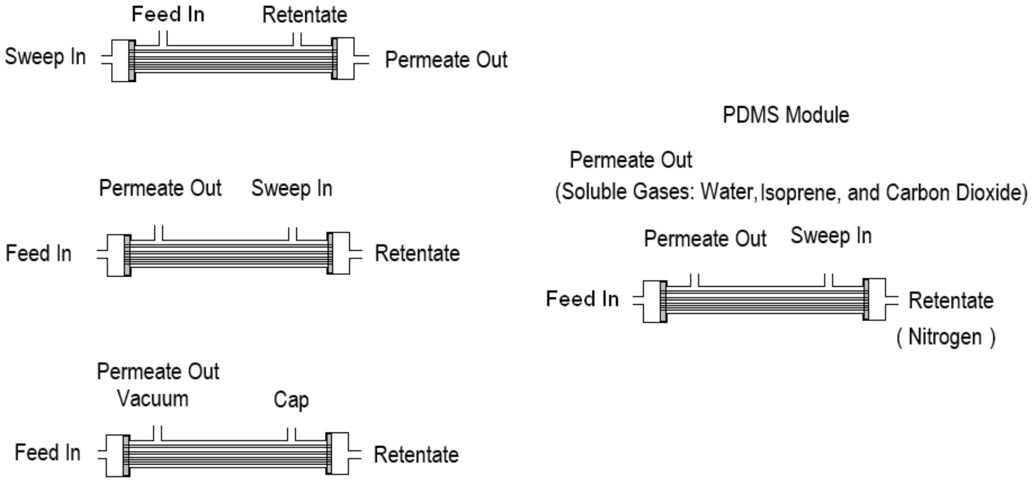

Figure 1. Utilization Options (left) for PDMS Module Assembly (right)

Experimental

Materials and General Procedures. Thin films investigated in the work reported here were: Polydimethylsiloxane (PDMS, sheets from Aldrich, PermSelect, HF Silicone Membranes) and Ultem® 1000 (polyetherimide, 0.2-0.35 μm sheets from GE plastics). Ultem® and PDMS films were used directly from the manufacturer.

Isoprene Feed Stream Composition. A gas mix was acquired from Scott Specialty Gases, Inc., and water vapor was introduced to create the surrogate feed stream. This gas stream was comprised of 19.5% carbon dioxide, 80% nitrogen and 5000 ppm of isoprene. For these experiments, the isoprene gas cylinder was heated 50-70°C to supply isoprene as a gas/vapor.

Humidified Mixed Gas Permeability Testing. Gas permeability data were obtained using a membrane cell area was 13.8 cm^2 using a circular 47 mm flat sheet modified filtration cell obtained from Millipore, Inc. Membrane thicknesses were determined by direct caliper measurement and ranged from 80 to 400 μm. Permeabilities were measured in Barrers (10^{-10})((cm^3 x cm)/(cm^2 x sec x cmHg)). Gas experiments have been carried out using a method previously described in the literature.[30–35]

In the mixed gas procedure, permeation is determined analytically by gas chromatography. The feed gas was a mixture of gases (3% by volume) for H_2, CH_4 and CO_2 with helium making up the balance gas and was obtained from Scott Specialty Gases, Inc. Addition of water to the mixed gas feed stream was performed by passing the feed gas from the supply through a water filled chamber and then through an empty demisting chamber prior to entry into the membrane cell. This technique provided a water vapor concentration of 2-4% by volume. The water vapor concentration was verified using an IR detector (LI-COR, model LI-840). The feed gas pressure was 206.8 KPa and temperatures were varied from 30˚C to 80˚C. Figure 2 provides a schematic diagram of the gas humidification apparatus, and the permeability in the humidified mixed gas tests was determined by gas chromatography (SRI GC Mixed Gas Analyzer Model 860; GC is equipped with helium-ion detector and thermal conductivity detector). Helium is the sweep gas. Variable temperature data was treated with an Arrhenius type analysis to determine activation energies of permeation (E_p).[36]

The isoprene mixed-gas studies (no water vapor) used a separate technique to acquire the gas permeability data at 40ºC. The data was acquired the permeate gas by Tedlar® bags into a higher resolution GC/MS (Agilent Model 7890 GC/5973C MS). The data attained using this method (Tedlar bags®) was more accurate than direct data acquisition from the system and integrated with the GC detector.

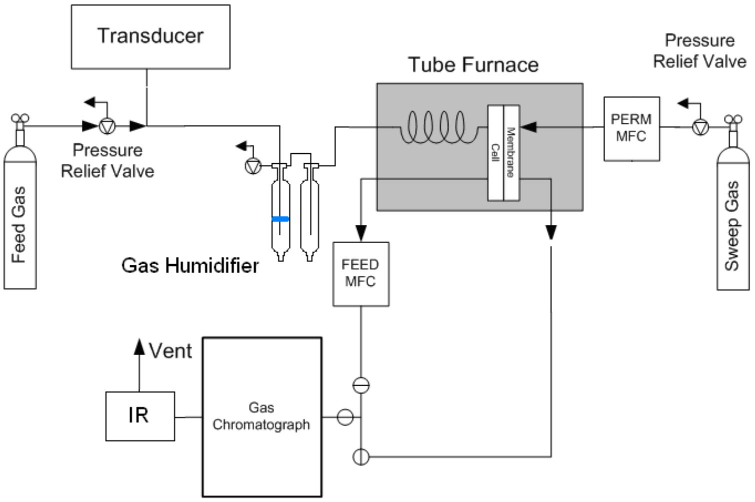

Figure 2. Humidified Mixed Gas Testing Apparatus.

Results and Discussion

Isoprene is naturally produced by several tree species, such as poplars and eucalyptus, and is also produced by microbial processes.[2] Isoprene is a colorless, volatile liquid that is used as a building block of natural rubber and its co-block polymers (styrene-isoprene thermoplastic elastomer); lesser amounts of isoprene are used in specialty chemicals, such as pharmaceuticals and epoxy hardeners.[10] As a renewable chemical, isoprene production by biological conversion is early in development,[37] but it has attracted increasing interest as an alternative olefin resource.

This work focuses on separation of gas mixtures that closely resemble those relevant to biological isoprene production, containing CO_2, water vapor, and nitrogen (N_2) in addition to isoprene. Furthermore, this isoprene separation requires better descriptions on the noted problems in this mixed gas feed stream, including: 1) determining polymer swelling gases and necessary temperatures to maintain a gas separation; 2) examining the differences in gas permeabilities in glassy and rubbery polymers and compare them to the boiling point, kinetic gas diameter, and Van der Waals volume; and 3) differentiating water vapor and CO_2 activation energies by obtaining Arrhenius plots of rubbery and glassy polymers. As a result, an effective separation of the gases will produce high-purity isoprene from the system.

During the microbial production of isoprene from anaerobic fermentations, the vapors of water and isoprene will contain CO_2 and N_2 influencing membrane performance. CO_2 is an acid gas that can influence the permeation rate of polymer membranes through swelling and/or plasticization.[38,39] Isoprene also impacts the efficiency of the separation and can swell or plasticize membrane materials. Compressibility of a gas is often used to describe and explain swelling and plasticization effects, which can be quantified by gas characteristics such as boiling point, Van der Waals volume, and kinetic gas diameters.[40]

Aside from CO_2 and isoprene, water vapor also has the potential to induce membrane swelling. Water vapor has a small Lennard-Jones kinetic gas diameter (2.65Å)[41] and high condensability, as exhibited through its critical temperature (647.2 K), leading to higher permeability through many polymer systems than the other gases.[42] Condensation of vapors in the system during the separations process introduces inconsistency in permeability measurements if the temperature reaches the dew point of water.[43] Water vapor and CO_2 can affect the transport performance of glassy or rubbery polymers through swelling and/or condensation in interstitial spaces. In this work, the added complexity of measurement in the presence of water vapor and CO_2 is addressed by using a higher operating temperature, thus maintaining the gas/vapor mixture in the gas phase and minimizing the residence time of these condensable gases in the polymer membrane.

Water vapor, CO_2, and isoprene can each have differing effect on these polymer membranes. In their interactions with the polymer membrane, these gases can alter the molecular structure of the polymer chain by swelling or plasticization. The critical temperatures of water vapor and isoprene permits condensation within the polymer at 30°C. As a result, these gases lower gas selectivity ratio by altering the gas permeabilities of the other gases in the mixture. Operating at normal ambient temperatures (~30°C or lower temperatures), the gas selectivity ratio will favor gases with higher molecular interactions in the polymer (e.g., water and isoprene), resulting in a gas-liquid separation (pervaporation). Thus, temperature is a vital portion to this separation for isoprene gas separations.

Consistent and reproducible permeability measurements for isoprene vapor requires heating the testing equipment to 40ºC and the gas cylinder to 50-70°C. Table 1 shows data obtained for soluble and diffusive gases in PDMS flat sheet testing at 30 ºC, with the highlighted row indication the measurement for isoprene conducted at 40°C. Paraffins such as propane (C_3H_8) through octane (C_8H_{16}) have kinetic gas diameters between 4.3-6 Å. From the data in Table 1, kinetic gas size does not change in PDMS; however, gas permeability is more dependent on the liquid-vapor states of these compounds.[44] For reference, pentane (bp = 36 ºC), hexane (bp = 69 ºC), and octane (bp = 126 ºC) are liquids at the test temperature in Table 1, which may explain the divergence of permeability data for these compounds from the shorter paraffins.[45]

Table 1. Data Obtained for Soluble Gases and Diffusive Gases Data for PDMS Flat Sheet Testing at 30°C.

Formula	**Gas**	**Van der Waals Volume[a] (cm^3/mol)**	**Boiling Point[b] (K)**	**Kinetic Gas diameter[c] (Å)**	**Permeability[d] (Barrers)**
NH_3	Ammonia	37	240	2.6	5900
He	Helium	24	4	2.6	350
H_2O	Water	30	373	2.65	36000
H_2	Hydrogen	27	20	2.89	650
CO_2	Carbon Dioxide	43	217	3.3	3200
Ar	Argon	32	83	3.4	600
O_2	Oxygen	32	54	3.46	600

N_2	Nitrogen	39	77	3.64	280
CH_4	Methane	42	110	3.8	950
C_2H_4	Ethylene	57	170	3.9	1350
C_2H_6	Ethane	63	145	4.4	2500
C_3H_8	Propane	84	231	4.3	4100
C_4H_{10}	n-butane	122	274	4.3	9000
C_4H_8	1-Butene	108	267	4.5	not available
C_3H_6	Propylene	83	226	4.5	6000[e]
C_4H_{10}	Isobutane	114	260	5.0	~10000[f]
C_5H_{10}	Isoprene	129	307	~4.5–6	5100[e]
C_5H_{12}	n-Pentane	146	309	~4.3–6	20000
C_6H_{14}	n-Hexane	173	342	~4.3–6	9400
C_8H_{16}	n-Octane	237	399	~4.3–6	8600

Data obtained from the following sources:
[a] Van Der Waal volumes (cm^3/mole), CRC Handbook of Chemistry and Physics.
[b] Boiling points at standard pressure (Kelvin), CRC Handbook of Chemistry and Physics.
[c] Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry, and Use*; R.E. Krieger ed., 1984. (Å: 10^{-10} m) and Matteucci, S., Yampolskii, Y., Freeman, B.D., Pinnau, I., 2006. In *Materials Science of Membranes for gas and vapor separation*. 1–48.
[d] Robb, W.L., *Thin Silicone Membranes-Their Permeation Properties and Some Applications*, 1968, Annals of the N.Y. Acad. of Sciences, Wiley Online Library doi:10.1111/j.1749-6632.1968.tb20277.x (Barrer: (cm^3 *cm / cm^2 *sec*cmHg)*10^{-10}).
[e] From this work, isoprene and propylene measurements conducted at 40°C.
[f] *50th Anniversary Edition, Parker O-Ring Handbook - ORD 5700*, Parker Hannifin Corp., Cleveland, OH, **2018**.

As seen in Table 1, isoprene and pentane have similar boiling points, Van der Waals volumes and Lennard-Jones gas diameters. These data indicate that isoprene and pentane may be examined analogously, where molecular interactions and transport behavior are closely related in glassy and rubbery polymers. As isoprene data are not available in literature, we use pentane as a model compound to isoprene to analyze gas permeability. Figures 3, 4 and 5 illustrate the relationship between penetrant size and solubility to their gas permeability for PDMS and a glassy polymer (e.g., polyimide, Ultem®, etc.). These data are consolidated from various sources.[25,29,33,44]

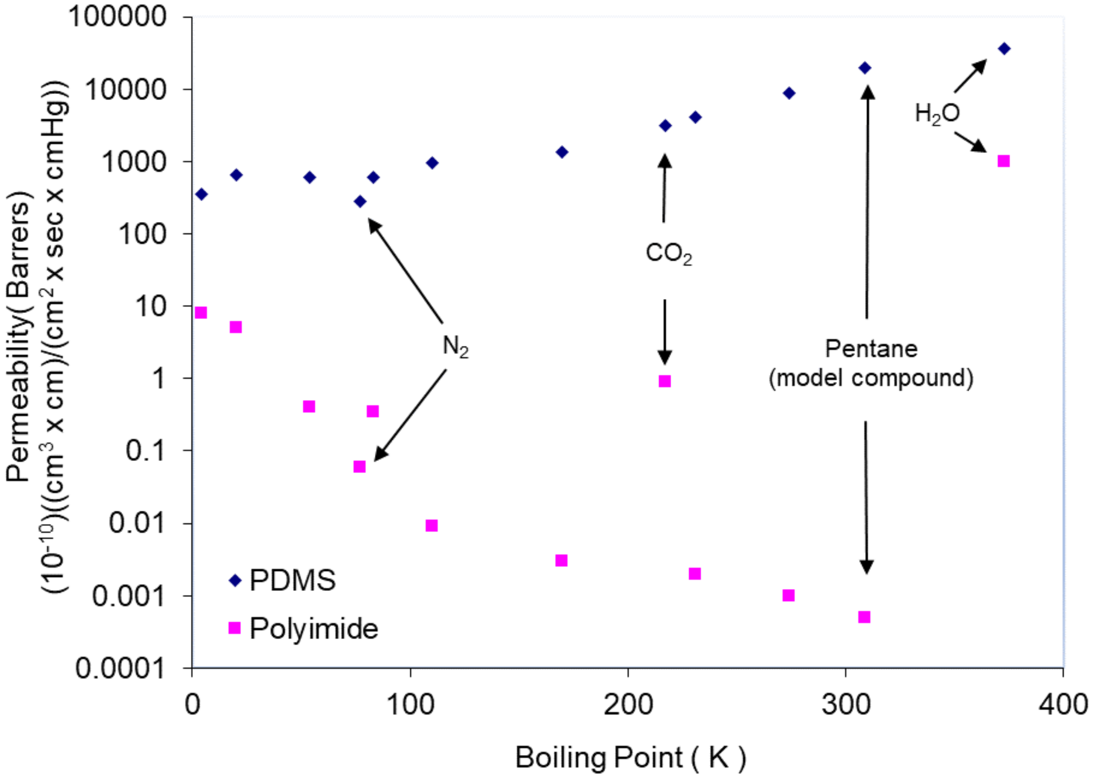

Figure 3. Differences in Permeability and Boiling Point as Indicator of Condensability in PDMS and Polyimide Polymer Membranes

In Figure 3, the boiling point of each penetrant shows a strong correlation to gas permeability in PDMS. This trend is also seen in a glassy polymer (polyimide) with the exceptions of water and CO_2. For the polyimide, water vapor and CO_2 data points have significant upward deviations from the boiling point versus permeability correlation, which is a function of the mechanism responsible for controlling transport in this class of polymer. Compounds with higher boiling points tend to have lower permeation rates in a glassy size-selective polymer due to their increasing molecular size. Conversely, permeation in solubility-driven membranes is less affected by the size of the penetrant and instead influenced by condensability and solubility in polymers such as PDMS.

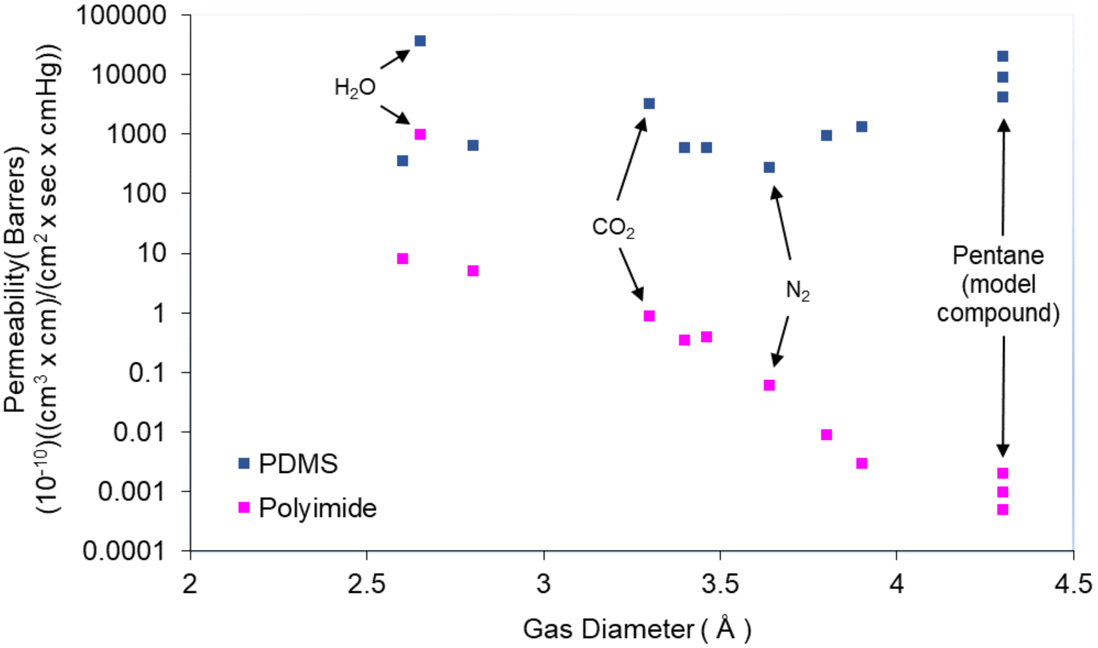

Figure 4. Differences in Permeability and Kinetic Gas Diameters in PDMS and Polyimide Polymer Membranes

In Figure 4, correlation of the kinetic gas diameters to permeability shows that increasing gas diameter results in diverging permeability for the two membranes for nearly all gases. The sole outlier is water vapor, which reveals a higher permeability in PDMS and polyimide than the other gases with a comparable gas diameter. Permeability vs. gas diameter for the PDMS membrane shows a slight rise in permeability with increasing molecular size, except for CO_2 and H_2O which show higher permeabilities. Permeability vs. gas diameter for the polyimide membrane shows a nearly linear decrease in permeability with increasing gas diameter, with the exception of H_2O, which shows high permeability. Permeability vs. gas diameter for both water and CO_2 suggest they have unique permeation characteristics, as they demonstrate high permeability in both PDMS and polyimide membranes. Given that transport mechanisms are always dependent on temperature and pressure, it is likely that permeability experiments conducted at constant temperature (40°C) may induce condensation of water vapor and C4-C5 as pressure increases. Thus, transport may shift from gas transport to gas-liquid transport (or pervaporation) through the membrane. As a result, the condensable gas may have considerably higher transport and increased selectivity due to the membrane's gas-liquid interface. This hypothesis is borne out in permeability data for the organic gases (C1-C5), which are strongly influenced by solubility characteristics in the rubbery polymer (PDMS) but show low permeabilities in the glassy polymer (polyimide).

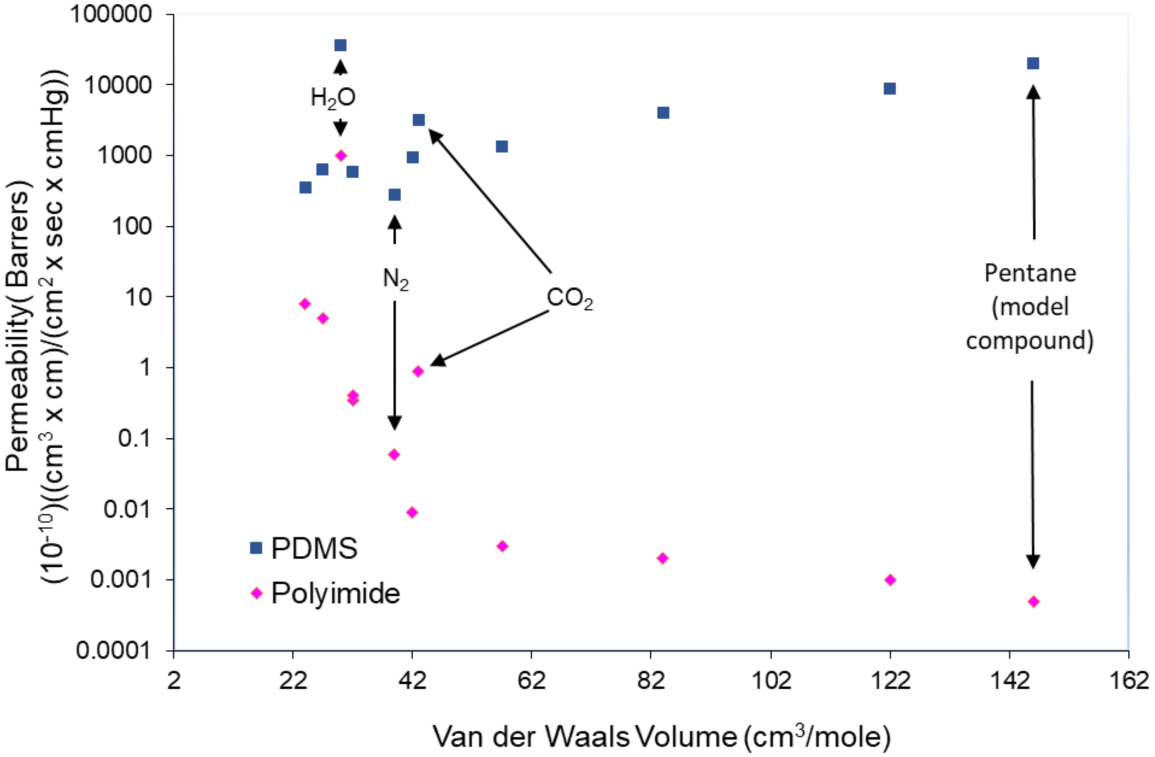

Figure 5. Differences in Permeability and Van der Waals Volumes in PDMS and Polyimide Polymer Membranes

Figure 5 displays similar trends as seen in Figure 4 with the Van der Waals volumes of gases, where membrane separations can be accomplished using either the solubility or molecular

Figure 5 shows gas permeability as a function of Van der Waals volume, with a comparable trend to gas permeability vs. gas diameter as shown in Figure 4. Membrane separations can be accomplished using either the solubility or molecular sieving behaviors of the rubbery and glassy polymers, respectively, depending on the desired separation. With molecular volumes of the organic compounds serving as a guide, permeabilities provide a clearer trend in relation to the solubility properties observed in rubbery polymers and size sieving commonly observed in glassy polymers.

Water vapor is the main outlier when gas permeability is viewed as a function of boiling point (Figure 3), gas diameter (Figure 4), and Van der Waals volume (Figure 5). As water vapor is a favored penetrant for either polymer class, it can be separated from the gaseous mixture through the first stage, regardless of the polymer membrane used. Both water vapor and CO_2 are considered to have high throughput through polymer membranes, and while CO_2 has higher permeability through rubbery materials, both can be separated from a gas stream leaving behind N_2 and the hydrocarbons. Therefore, separation of water vapor, N_2, CO_2 and organic gases can be accomplished using a staged approach, with both glassy and rubbery polymers, to collect a high purity organic gas such as isoprene.

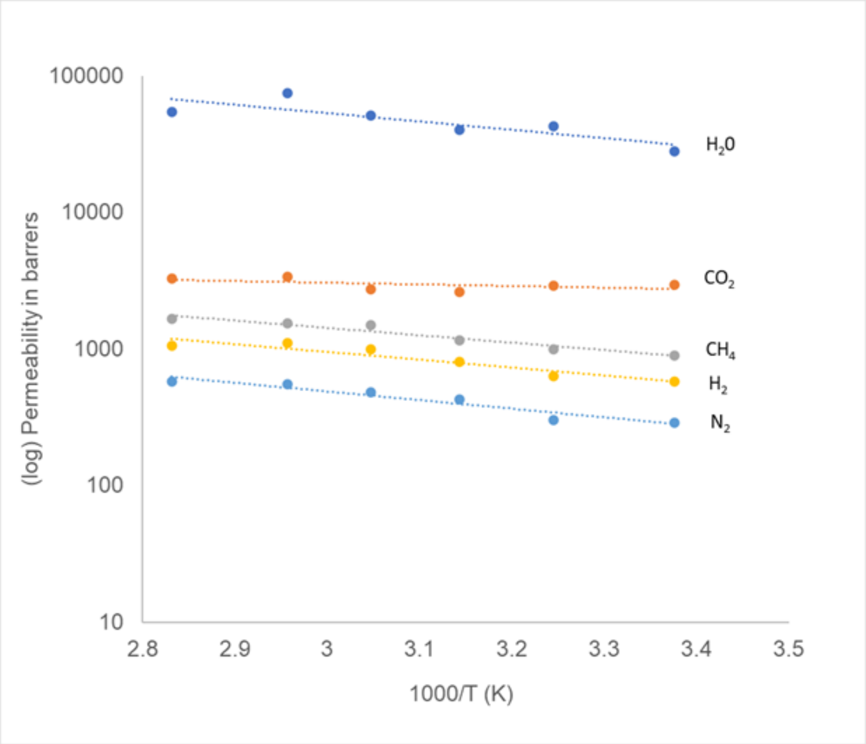

Figure 6. Activation Energy (E_p) Data Collected on PDMS from 30-80°C - Mixed Gas Feed Streams containing 2-4 vol% Water Vapor Composition.

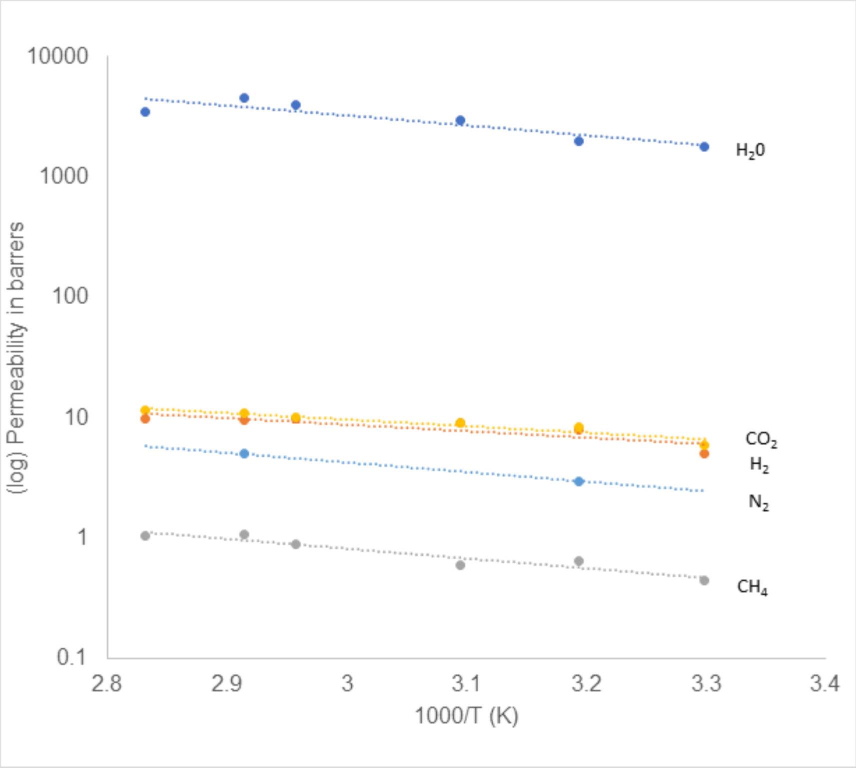

Figure 7. Activation Energy (E_p) Data Collected on Ultem® from 30-80°C - Mixed Gas Feed Streams containing 2-4 vol% Water Vapor Composition.

Table 2. Activation Energy (E_p) for Ultem® and PDMS under Humidified in Mixed Gas Streams.

Gas	**Energy of Activation [kJ/(mol · K)]***	
	Ultem®	**PDMS**
H_2O	16	12
H_2	11	11
CO_2	10	2
N_2	16	12
CH_4	10	10
*2-4 vol% Water Vapor Composition		

To differentiate the isoprene data from the water vapor and CO_2, Arrhenius plots were generated to investigate mixed-gas feed streams containing water vapor and CO_2 (See Figures 6 and 7) The slopes of these Arrhenius plots correspond to the activation energy (Ep, see Table 2) for mixed gas transport of water vapor, H_2, CO_2, N_2, and CH_4 through PDMS (250 µm thick) and Ultem® (75 µm thick) flat sheet films.[36] These results suggest that water vapor and CO_2 are the selected penetrants from this gas stream for both polymer membranes. However, the slopes of Ep plots are not especially pronounced for either polymer from 30-80°C, indicating that the gas permeability mechanisms are not dramatically influenced over this temperature range. This result suggests that the gas permeation of water vapor and CO_2 will remain similar under these given temperature ranges. In addition, Figures 6 and 7 demonstrate that water vapor has orders of magnitude greater permeability over the other gases for both membranes. Differences between the two membranes are more pronounced for CH_4 and H_2. CH_4 has higher permeability in PDMS than Ultem® due to its strong solubility, while H_2 has a higher permeability in Ultem® due to greater molecular sieving seen in this polymer. Data for N_2 indicates that it will tend to stay in the retentate for both membranes.

Table 3. Mixed-Gas Permeation of Isoprene, Carbon Dioxide and Nitrogen at 40°C

Polymer Membrane	N_2 (Barrer)	CO_2 (Barrer)	Isoprene (Barrer)	CO_2/Isoprene Selectivity Ratio	Isoprene/CO_2 Selectivity Ratio	Isoprene/N_2 Selectivity Ratio
Ultem® (78µm)	1.5±0.5[a]	120±20[a]	17±1	~7	not selective	~11
PDMS (250 µm)	350±20[a]	2200±900[a]	5100±20	not selective	~2.3	~15

Mixed-Gas Concentrations: 80 vol% of N_2, 19.5 vol% of CO_2, and 0.5 vol% of isoprene
Barrer: $(cm^3 * cm / cm^2 * sec * cmHg) * 10^{-10}$
[a] The permeability results are different from literature due to isoprene.

Overall, the gas permeability data in Tables 1 and 3 supports the concept that isoprene is condensable and has a high solubility interaction with PDMS and Ultem®. In Table 3, the permeability CO_2 and N_2 data of both polymers are higher than normal at 40°C and have some error, which suggests that isoprene is changing the transport mechanism by plasticization;

however, the isoprene permeability data is more precise. An observation that can be made is that CO_2 and isoprene selectivity ratios are different between PDMS and Ultem®. The mixed-gas permeation data in Table 3 reveals that PDMS has a gas selectivity ratio favoring isoprene, whereas Ultem® has a good gas selectivity ratio favoring CO_2. However, both polymers have good isoprene/N_2 gas selectivity ratios and N_2 will remain in the retentate. Because CO_2 and isoprene selectivity ratios differ between PDMS and Ultem®, Ultem® is the preferred candidate for CO_2 separation from isoprene, and isoprene is the selected penetrant in PDMS. Selectivity ratios for isoprene over other compressible gases such as CO_2 make a solubility-based membrane module (e.g., PDMS) a viable candidate for isoprene recovery and isolation. Another finding from this work is that both polymers were influenced by isoprene (plasticization), where the mixed gas permeabilities for CO_2 and N_2 were much higher than from reported literature data. Nevertheless, Ultem® retains a decent selectivity ratio between CO_2 over isoprene for this gas mixture.

Due the water's kinetic gas diameter and critical temperature, water vapor has the greatest effect on polymers. Water vapor (and isoprene) can interact with polymer membrane and tend to alter the molecular structure of the polymer chain through swelling or plasticization. At ambient temperatures (~30°C), the gas selectivity ratio will favor the gases that will have higher molecular interactions with polymer. Thus, use of an elevated separation temperature maintains water vapor and isoprene as a gas to minimize the effects of the overall transport of the other gases and maintain the mentioned isoprene selectivities.

A potential isoprene separation scenario is considered to remove water vapor and to be carbon neutral (see Figure 8). In this scenario, a multi-step process is needed to separate the isoprene from the other gases/vapors. A strategy for the recovery of isoprene through membrane separation modules will require a separate diffusive/size-sieving membrane module and a solubility-selective module at an elevated temperature. In this diagram, the diffusive membrane module removes the waste gases (water vapor and CO_2), while a solubility-driven membrane module isolates isoprene from N_2. The final steps feature a series of water-cooled condensers that are held at 20-25ºC to recover the liquid isoprene. In this scenario, CO_2 can be recycled back into the system as a cover gas and/or carbon source in the biological process.

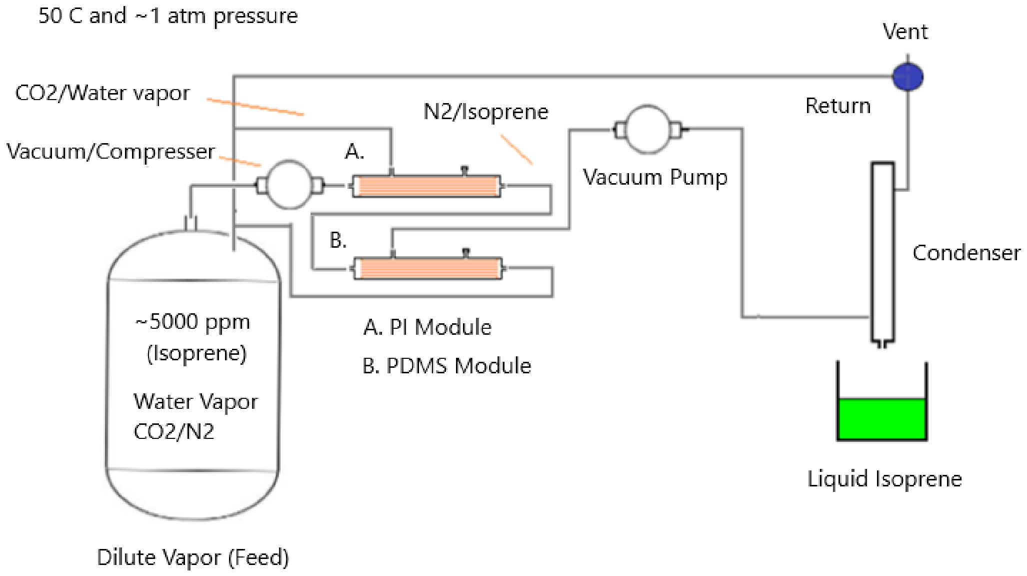

Figure 8. Proposed Two-Stage Separation – Water Vapor Separation, Isoprene Separation and Capture.

Current processes for isoprene bio-conversion use a condenser coil to capture the condensable gases, but still require the condensed water/isoprene mixture to be separated by distillation to remove water from isoprene. The primary challenge is the small quantity of isoprene generated compared to carbon dioxide and water vapor present in the gas feed stream. Other isolation processes (e.g., distillation) are more suitable for larger product quantities. In addition, the other isolation methods do not address carbon dioxide and further separations are necessary to isolate isoprene from water. In addition, water vapor can dominate sorptive processes and reduce the overall recovery of isoprene. Ultimately, a carbon neutral process will require that the carbon dioxide is recovered back to the bio-conversion system.

Conclusions

Condensation of isoprene and water vapors poses a challenge for separation processes operated at room temperature. Moreover, water vapor and CO_2 may alter the membrane properties and performance over long time periods. Therefore, it is necessary to consider the condensability of gases from the perspective of operating pressure and temperature, and the operational windows of individual membrane modules. Since both water and isoprene can be liquids at standard temperature and pressure, effective analysis requires the entire analysis system to be heated above ambient temperature (preferably $\geq$40°C) to prevent condensation. In the proposed separation (Figure 8), a two-stage membrane system is capable of isolating isoprene from a gas mixture containing water vapor, CO_2, and N_2. This two-stage separation could potentially provide high purity isoprene (90%+) and achieve carbon neutrality.

In this study, we proposed that the isolation of isoprene from a biological gas mixture is possible using a two-stage membrane approach consisting of both glassy and rubbery polymer modules to achieve high purity isoprene. However, careful consideration is required for biological systems, as minor changes may produce byproducts that may interact chemically with membrane substrates and potentially impact on membrane module(s).

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Idaho National Laboratory, Idaho Falls, Idaho.

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