Penelitian Terkini tentang Pengembangan Pemisahan dan Penangkapan Karbon dengan Membran Berbahan Dasar Polimer: Tinjauan Kebaruan

Current Research on The Development of Carbon Separation and Capture with Polymeric Membrane: A State of The Art Review

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ABSTRAK: Kajian dan penelitian mengenai pemisahan dan penangkapan karbon dioksida (CO₂) semakin meningkat. Peningkatan jumlah karbon dioksida dilingkungan membuat pencemaran lingkungan yang sangat berarti. Teknologi membran menjadi salah satu alternatif proses pemisahan karbon yang semakin diminati, dikarenakan teknologi membran memberikan keuntungan yang sangat baik dalam hal kebutuhan energi yang digunakan, investasi modal yang ditanam, serta kemudahan dalam mengoperasikan peralatan dibandingkan dengan proses yang lain. Banyak bahan penyusun membran yang dapat digunakan untuk menjadi bahan dasar pembuatan membran, diantaranya adalah bahan polimer. Tinjauan ini membahas mengenai macam-macam bahan polimer yang dapat digunakan sebagai bahan dasar penyusun membran gas yang ditinjau dari sisi plastisisasi, komponen penyusun, fleksibilitas, dan kekuatan mekanik. Tinjauan ini juga memberikan pemahaman alternatif untuk menaikkan properti dari membran yang berbahan dasar polimer.

Kata Kunci: Membran, Penangkapan Karbon, Polimer

ABSTRACT: Studies and research on carbon dioxide (CO₂) separation and capture are increasing. The increase in the amount of carbon dioxide in the environment has caused significant environmental pollution. Membrane technology is one of the alternative carbon separation processes that are increasingly in demand, because membrane technology provides excellent advantages in terms of energy requirements used, capital investment invested, and ease of operating equipment compared to other processes. Many membrane constituent materials can be used to be the basic material for making membranes, including polymeric materials. This review discusses the various polymeric materials that can be used as basic materials for gas membranes in terms of plasticization, constituent components, flexibility, and mechanical strength. It also provides an understanding of alternatives to improve the properties of polymer-based membranes.

Keywords: Membrane, Carbon Capture, Polymeric

1. Introduction

The industrial world produces hazardous gas waste, including carbon dioxide and carbon monoxide pollution (Xie et al., 2022). High levels of carbon dioxide can harm the human body and lead to a condition called acidosis, where excess levels of carbon dioxide prevent the release of oxygen into the body's cells, causing a lack of oxygen (Han & Ho, 2018; Peng et al., 2022; shahCosta et al., 2021). This excess carbon dioxide is generated from factory processes, burning of solid waste, forest fires, vehicle exhaust, and other sources, with the manufacturing industry being the largest contributor (Rahmah et al., 2022). Each year, about

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30 billion metric tons of CO2 waste are generated, contributing to over 77% of all gas emissions (Abdullah et al., 2020; Han & Ho, 2018).

To reduce CO2 concentrations in the atmosphere, various technologies for capturing carbon dioxide have been developed and applied, including membrane technology, which is currently very advanced (Kawakami et al., 1982; B., Li et al., 2013). Membrane technology has several advantages, including lower energy requirements, low investment costs, ease of operation, and less equipment needed compared to other processes (Buddin & Ahmad, 2021). The selectivity of the separation process is largely determined by the membrane material, including its structure, pore size, flexibility, and mechanical strength.

Polymeric materials have been studied by many researchers for the application of CO2 filtration membranes, due to their advantages such as good mechanical properties, low operational costs compared to inorganic membranes, and high selectivity with low permeability levels. However, polymeric membranes still have some drawbacks in the permeability-selectivity exchange process (Buddin & Ahmad, 2021). Inorganic membranes have good thermal stability but are more expensive to produce.

This review discusses the mechanism of gas transfer through polymeric membranes and the latest developments in the basic materials for forming these membranes, including polymers rich in ether oxygen, cellulose groups, polyamide, polynorbornene, and membranes with ionic liquids.

2. Mechanism of CO2 Gas Filtration in Polymer Membranes

![Fig 1. Scheme of Membrane Separation](image)

Gas separation using a membrane involves the application of a driving force, such as pressure, and utilizes the difference in permeation rate of each component present in the gas to be separated, adhering to the principle of selectivity. Polymer membranes can be classified into porous and non-porous membranes based on their structure (Ramezani et al., 2022). The transfer of gas during separation occurs through diffusion, which is the movement of a substance from a high concentration to a low concentration in a solvent. The mechanism of transport in the membrane can be broadly categorized into three types of diffusion: non-selective convection diffusion, Knudsen diffusion, and molecular sieving (Mulder, 1996).

The process of diffusion increases the entropy of the system, driven by the chemical potential of the components being transferred. The concept of gas separation with a membrane can be depicted in Fig. 1. The feed gas contains a higher concentration of solute components. After passing through a semi-permeable membrane during the filtration process, the permeable component is referred to as permeate and the component that cannot pass through the membrane is called retentate (Dai et al., 2023; Han & Ho, 2018).

2.1 Solution-diffusion mechanism

The solution-diffusion model is the most popular transport mechanism for membrane separation processes. Almost all membranes that use polymer-based materials employ this transport process. Average types of dialysis, reverse osmosis, gas separation, and pervaporation use this model. The principle of separation using the solution-diffusion model starts from the permeate dissolving in the membrane material and then diffusing along the existing concentration gradient. The separation occurs due to a difference in the amount of material that dissolves in the membrane and the rate at which it diffuses through the membrane. The separation process using the solution-diffusion method involves three steps: first, the gas is scattered into high pressure, also known as a high chemical potential process, at the polymer upstream surface; second, the gas diffuses through the polymer; and third, the low-pressure chemicals desorb from the low chemical potential to flow downstream of the polymer. The first and last steps are very fast in comparison to the second step, which makes polymer diffusion become the rate-limiting step in bulk transport across the membrane (Zoppi & Gonçalves, 2002).

Parameters that determine the permeability properties of a membrane can be found in its matrix properties, such as density, flexibility or glass-like properties, and the presence of free volume in the membrane. Another factor that can affect permeability is the physico-chemical interactions between gas molecules and polymer chains in some of the polymers used. Therefore, permeability can be calculated using equation (1):

\[ P = D \times S \]  

The parameters D and S determine the permeability properties of the membrane. P represents the permeability coefficient, D represents the diffusion coefficient, and S represents the solubility of gas in the membrane. Polymer-based membranes experience a gas diffusion process that is driven by differences in thermodynamic activity at the upstream and downstream surfaces of the membrane. The adsorption process can be categorized based on the type of polymer used. In the case of crystal-type polymers, the first gas adsorption takes place in the polymer crystal, which has the lowest value. For amorphous polymers, small gas molecules have a highly permeable properties due to the irregular conformation of the polymer chains, which results in a constant D coefficient value and little swelling. If larger
molecules can induce swelling in the polymer matrix, the speed of the diffusion process may change and the resulting D coefficient may depend on the permeate concentration. The elastomeric type of polymer has long, high chain mobility, and the swelling process takes place faster than the diffusion process. The value of the D coefficient depends only on the produced permeate. Polymers with a rigid structure swell the membrane slowly, which can result in the diffusion process being induced by the relaxation of the micro-molecules. In this case, the coefficient D is time-dependent.

2.2 Principle of the gas separation process
The working principle of a gas membrane separation starts from gas molecules crossing the membrane through an adsorption process of the membrane surface on the feed side, after which it goes through a diffusion process, then it finally goes through a desorption process on the permeate side of the membrane. The driving force of membrane separation can be the difference of concentration, pressure, or temperature gradient between the feed and permeate sides of the membrane. The performance of a membrane is derived from the Fick’s law equation which can be illustrated in equation (2):

\[ J_A = \frac{P_A}{l} \Delta P \]  

(2)

Where the \( J_A \) is the gas flux, while \( P_A \) is the resulting permeability and \( \Delta P \) is the partial pressure difference across the polymer-based membrane, while \( l \) is the thickness of the membrane.

3. Polymer membranes in gas separation
The first scientist who study gas diffusion in polymer membranes is Thomas Graham in 1866. He explained that there were two categories of polymers in solid membranes that could achieve high selectivity. The two types of polymers are spongy polymers and glassy polymers (Al-Ghouti et al., 2005).

As it is known that the separation process depends on different properties, not only based on the polymer glass transition temperature, permeability and separation factor, but it can also base on operating conditions such as temperature and pressure, membrane configurations such as flat sheets, and hollow fibres, when viewed from the membrane structure such as its relationship with free volume and system design (Han & Ho, 2021a).

Polymers with glass properties have a rigid chain structure with low free volume properties, which can result in low permeability but high selectivity. Low free volume properties can result in low permeability but high selectivity with high operating pressures up to 9-10 bar and the phenomenon that occurs is the phenomenon of plasticization. As for polymers that have a rubbery structure, the resulting chains are more flexible with low diffusion selectivity but high permeability (Kagramanov & Farnosova, 2017).

3.1 Polyamide and Ether oxygen-rich polymers
Membranes rich in ether oxygen are very good for the basic ingredients of gas membrane synthesis, because ethylene oxide groups have a high affinity for CO\(_2\) through quadrupole-quadrupole interactions (Drohmann & Beckman, 2002). The mechanism of CO\(_2\) filtration using an ethylene oxide-based membrane is the first distribution of charge into the membrane, this distribution is considered uneven in the molecule which can eventually carry a partial positive charge and finally the oxygen atom carries the negative charge of the partial. CO\(_2\) molecules and membrane material in the form of oxygen atoms are parallel and close together in the negatively charged area of the polymer, therefore allowing it to have a strong net attraction. This can make the solubility of CO\(_2\) become higher. CO\(_2\) binding with oxygen-rich ether polymer oligomers is classified into 3 oligomers namely nonane; diethyl glycol dimethyl ether; and 1 methoxy-2-(methoxy-methoxy)ethane. In a study conducted by Liu et al.,(2019) which separate CO\(_2\) and N\(_2\) using polymers with ether oxide content showed better properties than other contents. Liu et al., (2019) also simulated the calculated bond energy between oligomers and CO\(_2\) in several ether oxygen contents, showing that the bonding energy between CO\(_2\) and nonane oligomers is -9.1 kJ/mol; CO\(_2\) with diglyme oligomers is -16.8 kJ/mol and the bond between CO\(_2\) with TOO oligomers is -20.70 kJ/mol.

| Table 1. Value of membrane filtration with selected ether oxygen-rich polymers (Han & Ho, 2018) |
|-----------------------------------------------|----------|-------|--------|
| Category                                      | Material | T (°C) | P (CO\(_2\)) (Barrer) | \( \alpha \) (CO\(_2\)/N\(_2\)) |
| Polymers derived from heterocyclic acetics     | Poly (1,3-dioxolane) | 70     | 1400   | 64     |
| Copolymerization & crosslinking               | PEO-POSS-NH\(_2\) | 35     | 1567   | 69     |

The crystallinity of polymer rich in ether oxygen has a high crystallinity value, to suppress this, several modifications are made, including the process of copolymers with large and rigid segments, mixing with polymers that have a lower molecular weight to reduce the chain of the polymer itself, and initiation of secondary polymer chains by crosslinking or branching. Of these, the ethylene oxide segment copolymer method is the most efficient method. To suppress the crystallinity of poly(ethylene oxide) (PEO), the segment copolymer method of ethylene oxide is used. The hard and rigid segment shape can interfere with the membrane synthesis process because it can suppress the fractional free volume (FFV). When the polymer segment is soft, it can increase the affinity of CO\(_2\) which can improve filtration performance with the membrane (Rahmah et al., 2022).

Research conducted by Zhao & Ho, (2013) has been conducted, in the study discussed the decrease in crystallinity of ether oxygen-rich polymers using variations of heterocyclic acetal groups. This heterocyclic acetal is
reacted using alkoxy acrylate to open the chain ring of the acetate after which the chain is grafted with a chain containing ether into the vinyl substrate. After the process is running, the next step is photopolymerization by polymerizing the monomer and producing vinyl polymers with ether oxygen-rich side chains.

The identification of ether oxygen-rich polymer materials that have a good level of selectivity towards CO\textsubscript{2} separation is by looking at the glass transition temperature of the polymer itself, a low glass transition temperature below -60°C shows good affinity and can improve the performance of CO\textsubscript{2} separation. The disadvantage of this class of ether oxygen-rich polymers lies in the decreased permeability value due to the high ether oxygen content causing a low fractional free volume (Han & Ho, 2020).

### 3.2 Cellulose and Nanocomposite Groups

Polymer membrane base material has recently become the center of attention of the research audience, because by using this polymer material the gas capture process with filtration system becomes very active, good and economical on an industrial scale (Ansali et al., 2017). Membrane division in terms of glass transition temperature (T\textsubscript{g}) can be divided into more flexible glass and rubber membranes. Glass membrane material is considered to have shortcomings when applied to gas filtration, because it has excess free volume which results in low permeability values. If the rubber type polymer membrane material has the advantage of a good thermodynamic equilibrium value that can have a higher level of mobility and can more easily diffuse across the membrane, but still has the disadvantage of low permeability values (Du et al., 2019).

Khamwichit et al., (2021) tried to conduct research on CO\textsubscript{2} separation in biogas units using a membrane based on bio-cellulose from coconut juice. The results show that membranes with thicker bio-cellulose-based materials can increase selectivity, in low pressure operations, therefore the permeability obtained can decrease. As it happens that the membrane with Cellulose base material has the advantage of being selective to low concentrations but cannot work at high pressures.

Therefore, recently many researchers have tried to combine with better materials with basic materials in the form of nanocomposites, one of which is research conducted by X. Li et al., (2015) stating that the Microfibrillated Cellulose (MFC) membrane type is a type of nanocellulose obtained from the homogenization process at high pressure with delamination of cellulose fibers. Microfibrillated Cellulose (MFC) is a bio-based nano material that has strong mechanical properties and is good at binding gases. X. Li et al., (2015) also reported that by using this MFC material, it has a high selectivity level of up to 500 but still has a low permeability below 25 Barrer.

### 3.3 Polynorbornenes

Another type of polymeric CO\textsubscript{2} membrane constituent is polynorbornenea, which is highly glassy, allowing for very low permeability values. Some researchers tried to vary the alkoxy silyl pendant groups into monomers of norbornene, where the results showed that the monomers that had been characterized produced polymers with high free volume and better affinity for CO\textsubscript{2}. Table 2 is a summary of the performance results of polynorbornenes-based membranes categorized into 3 types with CO\textsubscript{2} pressure used in operation is 1 atm (Han & Ho, 2020).

<table>
<thead>
<tr>
<th>Category</th>
<th>Material</th>
<th>T (°C)</th>
<th>P (CO\textsubscript{2}) (Barrer)</th>
<th>α (CO\textsubscript{2}/N\textsubscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polynorbornenes</td>
<td>PNB-Si(OEt)\textsubscript{(0,5)}</td>
<td>35</td>
<td>868.8</td>
<td>21.6</td>
</tr>
<tr>
<td>Polynorbornenes with alkoxy silyl pendant group</td>
<td>Si(OEtOMe)\textsubscript{(0,5)}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Janus tri-cyclo-norbornenes with alkoxy silyl groups</td>
<td>TCN-Si(OBU)\textsubscript{3}</td>
<td>35</td>
<td>1100</td>
<td>16.2</td>
</tr>
<tr>
<td>Crosslinked Polynorbornenes</td>
<td>Polyvinyl-norbornene</td>
<td>35</td>
<td>104.3</td>
<td>21.7</td>
</tr>
</tbody>
</table>

Dujardin et al., (2019) conducted research using mono-tri polyamide substituted with PNB-Si(Me), using ethoxy groups (-OEt), which has the highest selectivity (\(\alpha\)) value of 21.6 among other types of PNB-Si(Me), but has a decreased permeability value. In addition to norbornene-derived polymers, triclononene which has 3 melt rings is also used for membrane synthesis, shown in Table 2, that permeability increases up to 1100 Barrer but there is a decrease in selectivity, while there is another variation that is using crosslinked polynorbornenes material, this material is obtained from the polymerization process of 5-vinyl-2-norbornene with alkene in monomer and the result is a strong crosslinked polymer network with a more rigid ring structure. This type has a good filtration ability that can be proven by high selectivity, but because this polymer is more glassy, the free volume value of the polymer decreases which results in decreased membrane permeability as well (Karpov et al., 2020).

### 3.4 Ionic Liquid

Ionic liquids (ILs) are class of salts that have solvent-like properties at certain temperatures (Han & Ho, 2021b), these ILs have been known to have low vapor pressure and good thermal stability, which is expected to improve the permeability properties of CO\textsubscript{2} membranes in addition to having high selectivity. But it is possible that membranes made using ionic liquids have shortcomings in the membrane formation process because the incorporation of ILs in the membrane can weaken some of the properties of the membrane, which can interfere with the process of making thin-film membranes. There are several methods in dealing with these problems including the manufacturing process with the cross-linked ion-gel technique; coupled with poly ionene and polyionomers. The value of some analysis can be seen in Table 3.
The process of using ILs in the membrane is done by mixing with polymers that have rubber polymer properties, where these polymers are selected that have strong cross-linking this mixture produces an ion-gel mixture. The pEO polymer type has the best ability to form, resistant to low concentrations and much in demand, where polymers have several advantages as Polyamide, Ether oxygen rich polymers, cellulose, and nanocomposites, Polynorbornenes have several advantages, namely easy to form, resistant to low concentrations and disadvantages. Of the several membrane materials used, membranes with polymeric base materials are still very much in demand, where polymers have several advantages, namely easy to form, resistant to low concentrations and toxins of the several polymers that have been discussed such as Polyamide, Ether oxygen-rich polymers, cellulose, nanocomposites, Polynorbornenes have several advantages and disadvantages. The weakness that may occur in each polymer is a decrease in membrane performance value, namely in the permeability value caused by a decrease in the free volume value of the polymer due to the polymer used is a glass polymer type. Therefore, this review provides an alternative to improve membrane performance by varying the membrane to be made with the addition of ionic liquid which can improve the thermal properties of the membrane which in turn will improve the performance of the membrane permeability.

4. Conclusion
Recent developments regarding polymeric membranes as CO₂ gas capture media have been reviewed in this study. The use of membranes in gas separation is still an alternative that is widely offered because it has several features. Therefore, the increasing interest and development of membrane materials used is increasingly trending among researchers, because some membranes still have shortcomings in terms of performance. Of the several membrane materials used, membranes with polymeric base materials are still very much in demand, where polymers have several advantages, namely easy to form, resistant to low concentrations and toxins of the several polymers that have been discussed such as Polyamide, Ether oxygen-rich polymers, cellulose, nanocomposites, Polynorbornenes have several advantages and disadvantages. The weakness that may occur in each polymer is a decrease in membrane performance value, namely in the permeability value caused by a decrease in the free volume value of the polymer due to the polymer used is a glass polymer type. Therefore, this review provides an alternative to improve membrane performance by varying the membrane to be made with the addition of ionic liquid which can improve the thermal properties of the membrane which in turn will improve the performance of the membrane permeability.

References


