Overview of integrated PVA-membrane with Zn-cyclen for CO$_2$ separation

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Abstract. Carbon dioxide (CO$_2$) is a greenhouse gas that produces from the combustion of fossil fuel. The consumption of fossil fuel in industrial activity has increased the concentration of CO$_2$ emitted in the atmosphere. When the concentration of CO$_2$ increases, the more heat are released. Thus, creating the global warming issue and climate change to the world. This climate change and global warming issue have attract the attention of worldwide. There are lot of carbon capture techniques proposed to overcome these problems. However, most of it are costly, and need a long dissociation and CO$_2$ separation process. Therefore, innovative technique and process optimization are needed in order to improve the process efficiency of this technology. The most common techniques used in this technology are cryogenic, biological technique, and membrane technique. Membrane technique with a biological approach has promising high CO$_2$ separation performance. This mimic enzyme based membrane has several advantages such as low cost, simple production procedure and high CO$_2$ separation performance. From the review, the use of PVA membrane integrated with mimic enzyme could be work together towards the improvement of carbon capture technology. This review provides the information and potential of an alternative approach of carbon capture technology to reduce the amount of CO$_2$ emitted from the fossil fuel industry.

1. Introduction
Carbon dioxide (CO$_2$) is one of greenhouse gas. It is a gas that releases thermal radiation and leads to greenhouse effect. At normal concentration CO$_2$ is odorless, but at high concentrations, it has a sharp and acidic odor [1]. The rapid increase in CO$_2$ emission is due to the Industrial Revolution because of the rises consumption of the fossil fuels in the industry. Sharma and Bhattacharya [2] and Yong et al. [3] also said that the industrial activities such as thermoelectric power plants, cement plants, and steel plants are the reason of significant growth in CO$_2$ emissions. Due to the nature of CO$_2$ which is inert and unreactive molecule. Therefore, it becomes thermodynamically stable, which makes it difficult to capture and separate. When CO$_2$ concentration in the atmosphere is increasing, the more heat is release thus creating a global warming issue. European Commission was reported that the quantity of CO$_2$ emitted into atmosphere shall be approximately 34 billion tonnes in 2011 and predicted to increase over the next few decades [3][4]. This global warming issue has attracted the attention of the worldwide. By the 2100, the International Panel of Climate Change (IPCC) had also predicted that the atmospheric content of CO$_2$ could be up to 570 ppm, the sea level rises up to 3.8 m, and global mean temperature rises about 21 °C with crucial impact on the environment [5].

However, the IPCC has believed that by the usage of carbon capture and storage technology, the CO$_2$ emission into the atmosphere can be decreased into 80-90 % [6]. Therefore, the carbon capture and storage technology are introduced as one of the solutions for this global warming issue.
2. Carbon Dioxide Separation Technique
There are many approaches that have been taken in order to reduce the emission of CO$_2$ into the atmosphere. One of the ways to help in overcoming this issue is known as Carbon Capture Technology and Storage (CCS). In this CCS, CO$_2$ will undergo absorption and CO$_2$ separation will take place. There are several CO$_2$ separation techniques involved in CCS. However, biological separation technique and membrane separation technique are the most popular techniques used in CCS. Table 1 shows a summary of the inherent advantages and disadvantages of each of these techniques.

**Table 1. Summary of Carbon Dioxide Separation Technique.**

| Separation technique | Principle of methods | Separation agent | Findings | Advantages | Disadvantages | Ref. |
|----------------------|----------------------|------------------|----------|------------|---------------|------|
| **Biological approach** | The introduction of carbonic anhydrase enzyme (CA) in the solvent for enhancing CO$_2$ absorption rate | CA enzyme in N-methyldiethanolamine solvent (MDEA) | Efficiently improved CO$_2$ absorption | The application of green technologies and no harmful chemicals involved | Low CA stabilities at high temperature | [3] |
| | CA enzyme in potassium carbonate solvent (K$_2$CO$_3$) | | | | | [7] |
| **Membrane separation** | Selectivity of certain components toward membrane | Fixed carrier thin film composite membrane combine with tertiary amino | Good CO$_2$ separation performance | Highly product purity, rapid mass transfer rate | Need additional treatment for high temperature practices | [8] |
| | Hybrid membrane of PEG containing polymeric submicron-sphere | | | | | [9] |
| | Integration of dual layer flat sheet of mixed matrix membrane with zeolite | | | | | [10] |
| **Physical and chemical absorption separation** | Reaction between CO$_2$ and chemical solvent or aqueous solution | Absorption capacity of CO$_2$ by amino acid compared to monoethanolamine (MEA) | Amino acid possess better CO$_2$ absorption capacity compared to MEA | High capture efficiency and required low cost of solvent | High energy consumption, and high solvent regeneration | [11] [12] [13] |
| **Solid adsorption separation** | Involves the reaction of CO$_2$ adsorption with solid material | The combination of starch and gelatin in CO$_2$ adsorption process | Gives high CO$_2$ adsorption | Low energy consumption and occurs in a dry process | Low CO$_2$ selectivity, lower removal efficiency, and difficult in the reusability of absorbent | [14] |
| **Cryogenic technology** | Involves CO$_2$ separation through distillation column | Gives high CO$_2$ purity and recovery | No chemicals involved, and easy for transportation as CO$_2$ product is in liquid form | Not practically applicable because of severe interference of gas mixture with cooling process | | [12] |

2.1. Biological Separation Technique
This biological separation technique does not involve harmful chemical. Therefore, it is known as a green application approach. For biological separation, it involves the use of carbonic anhydrase (CA) as a catalyst to enhance the absorption rate of CO$_2$ and convert the CO$_2$ into HCO$_3^-$ at higher turnover rates (up to $1 \times 10^6$ s$^{-1}$) [15]. The CO$_2$ will undergo hydration step to produce carbonic acid (H$_2$CO$_3$) and then it will be converted into bicarbonate ion (HCO$_3^-$) and further converted into solid calcium carbonate precipitate (CaCO$_3$) by the help of CA. The CO$_2$ hydration mechanism via CA is shown in Figure 1.

![Figure 1. CO$_2$ hydration mechanism of CA [15].](image)

Many researches have studied on the combination of CA with potential solvent like N-methyldiethanolamine (MDEA). Huttenhuis et al. [7] found that the use of CA in MDEA has effectively increased the efficiency of CO$_2$ absorption. The CO$_2$ selectivity of CA is tabulated in Table 2.

| Facilitator                          | CO$_2$/N$_2$ Selectivity | Ref. |
|--------------------------------------|--------------------------|------|
| Carbonic anhydrase                   | 35.6                     | [16] |
| Carbonic anhydrase                   | 224                      | [17] |
| Carbonic anhydrase Poly (N-vinylimidazole)/zeolite Zn-$\beta$ hybrid membrane | 820 | [15] |
| Carbonic anhydrase PVDF hollow fiber membrane reactor | | |

From the result tabulated in Table 2, it can be analysed that the CO$_2$ selectivity of CA with facilitated potassium bicarbonate and sodium metaarsenite has higher selectivity compared to others. The higher selectivity shows a better CO$_2$ separation performance among the others. The advantage of this biological technique is its environmental friendly with no usage of harmful chemicals. This technique also possesses some limitations such as the shorter lifetime of around 6 months and the enzyme activity undergone permanent loss due to pH and temperature change [18]. In addition, the enzymes are very expensive and not applicable for large-scale applications [15]. Thus, the use of immobilized CA based membrane has a potential to overcome this obstacle and can also increase enzyme stability and avoid thermal denaturation in the reactor [3].
2.2. *Membrane Separation Techniques*

There are several choices in order to use membrane as CO\textsubscript{2} recovery from flue gas. CO\textsubscript{2} would pass through the membrane and be absorbed in the solvent or catalyst as shown in Figure 2.

![Figure 2](image)

**Figure 2.** Schematic illustration on the CO\textsubscript{2} separation through membrane [19].

Polymeric membranes have become one of particular interest for CO\textsubscript{2} separation because of their low cost, high performance separation, easy synthesis and mechanical stability [20]. The usage of polymeric membrane for CO\textsubscript{2} separation has significantly reduced the energy demand to less than 0.8 of recovery ratio and permeate composition as compared with amine absorption-based process [21]. Recently, Saeed and Deng [18] were developed the facilitated transport membranes containing a low molecular weight mimic enzyme (Zn-cyclen) using polyvinyl alcohol (PVA) as the polymer membrane material cast on PSf membrane. The presence of mimic enzyme is to mimic the active site of CA. The CO\textsubscript{2} selectivity of membrane with PSf based is tabulated in Table 3. The PVA cast on the PSf membrane shows the highest CO\textsubscript{2} selectivity compared to others.

| Membrane                        | CO\textsubscript{2}/N\textsubscript{2} Selectivity |
|---------------------------------|---------------------------------------------------|
| PSf                             | 24.8                                              |
| MCM41/PSf                       | 25.3                                              |
| PVAm/PVA cast on PSf            | 94                                                |
| Amine-MCM41/PSf                 | 29                                                |
| MCM48/PSf                       | 23.6                                              |

3. **Characteristics of PVA membrane for CO\textsubscript{2} Separation**

Polyvinyl alcohol (PVA) is a polymer that formed from repetition of ethanol monomer. Alcohol group makes PVA hydrophilic. Therefore, it is used as the hydrophilic polymer membrane material in the selective layer to retain water so that excellent separation can be achieved [18]. Moreover, its good thermal properties and chemical stability are important for CO\textsubscript{2} capture in post combustion to handle process parameters and resist to the solvent without chemical reactions. With the use of PVA membrane, only low concentration of mimic enzyme is added, in order to get an excellent CO\textsubscript{2} separation [18]. It has been proved by the study from Saeed and Deng [18], which is with the low concentration of mimic enzyme (0.008 mmol/g PVA) the membrane showed a CO\textsubscript{2} permeance of 0.69 [m\textsuperscript{3} (STP)/(m\textsuperscript{2} bar hr)] and a CO\textsubscript{2}/N\textsubscript{2} selectivity of 107. The membrane has high capacity to swell if the transport is facilitated by PVA.

4. **Integration of PVA membrane with Zn-cyclen for CO\textsubscript{2} Separation**

The combination of membrane method with other methods of carbon capture have been studied by researchers and it shows a great potential in improving the CO\textsubscript{2} absorption into the membrane. Rahaman et al. [23] claimed that the integration of CA with 1-butyl-3-methyl-imidazolium
bis(trifluoromethanesulfonyl)imide (ionic liquid) on PVDF membrane gives higher permeability and selectivity which is 733.73 and 35.6 respectively as compared with the absence of CA. This is due to the characteristic of ionic liquid which has higher CO\textsubscript{2} solubility and CA is function to enhance the CO\textsubscript{2} absorption. Ionic liquids are salts that typically containing an organic cations (charge +1) and either an inorganic or organic anions (charge -1). The combination of cations and anions has gave advantage for carbon capture process. However, this studies have some limitations such as it is only applicable for small scale of application and very costly. Therefore, M. Saeed et al. [18] has conducted studies on the combination of mimic enzyme with membrane to replace the CA enzyme. In this finding, it shows that the combination of mimic enzyme with membrane has possess higher permeability and selectivity compared with the usage of CA with membrane. From Table 4, the CO\textsubscript{2}/N\textsubscript{2} selectivity of PVA/mimic enzyme is higher as compared with PVDF/CA which is 107 and 35.6 respectively. Therefore, it is showing that CO\textsubscript{2} absorption and separation can still be achieved as compared to CA. It can be used in large scale application as it is low cost and only need small amount of mimic enzyme in order to achieve an excellent CO\textsubscript{2} separation. Hence, this mimic enzyme based membrane has other advantages such as simple production procedure and high CO\textsubscript{2} separation performance.

| Membrane          | CO\textsubscript{2}/N\textsubscript{2} Selectivity | Ref. |
|-------------------|-----------------------------------------------|------|
| PVDF/CA           | 35.6                                          | [23] |
| PVA               | 58                                            | [18] |
| PVAm/PPO          | 60                                            | [24] |
| PVA/mimic enzyme  | 107                                           | [18] |

A zinc based mimic enzyme is efficient for a large range of pH and has high stability in terms of temperature which is over 200 °C [18]. When comparing with CA, mimic enzyme has showing fast reaction rates in terms of weight. Even at low molecular weight of the mimic enzyme, a higher number of active sites per unit mass of compound can also be obtained and hence providing cost-effective technique for CO\textsubscript{2} [18]. The mimic enzyme is created from the mixture reaction of cyclen and zinc salt to form Zn-cyclen. The molecular structure of cyclen and Zn-cyclen are shown in Figure 3 and 4 respectively.

![Figure 3. Molecular structure of cyclen [18].](image)

![Figure 4. Molecular structure of Zn-cyclen [18].](image)

### 4.1. Mechanism Reaction of Zn-cyclen in CO\textsubscript{2} Separation

A CO\textsubscript{2} molecule is attached to the Zn\textsuperscript{2+} active site of Zn-cyclen to form a meta-stable complex. A Lewis base (OH\textsuperscript{-}) is then attacked the complex to form bicarbonates (HCO\textsubscript{3}\textsuperscript{-}). Then, CO\textsubscript{2} is converted to HCO\textsubscript{3}\textsuperscript{-} and the active sites in the Zn-cyclen are left unreacted. The mechanism is additionally explained in equations (1) – (5) [25]. Since the conversion reaction cycle of CO\textsubscript{2} into HCO\textsubscript{3}\textsuperscript{-} involved H\textsubscript{2}O, therefore, PVA is used in the selective layer of polymer membrane to retain water as it properties is hydrophilic. Therefore, the membrane can operate in high water swollen in order to achieve the best separation performance. From equation (3), when it is in a protonated state, the Zn-cyclen (C\textsubscript{8}H\textsubscript{20}N\textsubscript{4}ZnOH) catalyzes the hydration reaction. Therefore, the membrane should have an excessive amount of OH\textsuperscript{-} ions.
2H₂O ⇌ H₂O⁺ + OH⁻  

CO₂ + OH⁻ ⇌ HCO₃⁻  

C₆H₁₀N₂ZnOH⁻ + CO₂ + H₂O ⇌ C₆H₁₀N₂ZnHCO₃⁻ + H₂O ⇌ C₆H₁₀N₂ZnH₂O + HCO₃⁻  

C₆H₁₀N₂ZnH₂O ⇌ H⁺C₆H₁₀ZnOH⁻  

H⁺C₆H₁₀ZnOH⁻ + H₂O ⇌ C₆H₁₀N₂ZnOH⁻ + H₂O⁺  

4.2. Carbon Sequestration of CO₂ using Zn-cyclen (Mimic Enzyme)

Zn-cyclen catalysed CO₂ by convert it into bicarbonate ion in aqueous solution [26]. This step known as hydration reaction of CO₂. The carbon sequestrate on CO₂ to form CaCO₃ are shown in equation (6) and (7). The conversion are involves HCO₃⁻ ion with divalent cation such as Ca²⁺ and converted into CaCO₃.

H₂CO₃ ⇌ H⁺ + CO₃²⁻  

Ca²⁺ + CO₃²⁻ ⇌ CaCO₃  

HCO₃⁻ ion can be converted into stable carbonate solid. This step is called as bio-sequestration process and CO₂ can be stored in solid form for long term storage to delay and avoid global warming [27]. Wanjari et al. [28] also proposed the study on the effect of time and CaCO₃ mass of carbon sequestration by using immobilized bio-composite materials. It was reported that it produced 33.05 mg and 24.84 mg CaCO₃/mg enzyme at reaction time of 20 s and 39 s respectively in the presence of immobilized CA. On the other hand, Prabu et al. [28] reported that the presence of free and immobilize CA produced of 33.06 mg and 19.22 mg CaCO₃/mg enzyme at reaction time of 20 s and 55 s respectively. Fei et al. [29] studied the effect of CaCO₃ mass produced by carbonation reaction in the presence of CA. The mass of CaCO₃ with free CA and immobilized CA were 241 mg CaCO₃/mg and 227 mg CaCO₃/mg respectively. The time reaction of immobilized CA will be higher if the mass of CaCO₃ is lower. This is due to the mass transfer limitation of a substrate with immobilized CA [28][29].

4.3. Factors that Influence the CO₂ Capture Performance

There are many factors that influencing the membrane performance in a gas permeation process including a change in feed flowrate [30]. The permeation characteristics are greatly affected by the feed flowrate due to the gaseous component diffusion on the concentration and solubility of the component. The partial pressure gradient across the membrane is the driving force in gas separation. The component transport through the membrane can only happen if partial pressure at the feed side of the membrane is higher than that at the permeate side [31]. In general, as the temperature increases, solubility decreases but diffusivity increases. At higher temperatures, the membrane yield poor separation while processing high selectivity at ambient temperature. The effect of every factor towards the performance of CO₂ separation is tabulated in Table 5.

| Factor       | Result                                                                 | Ref.   |
|--------------|-------------------------------------------------------------------------|--------|
| Feed flowrate| Higher feed flowrate of CO₂ (optimum at 500mL/min), the higher the amount of CO₂ absorption on the graphene nanosheets membrane. | [32]   |
| Temperature  | The higher the temperature (optimum at 60 °C), the higher the amount of CO₂ absorption on the polymeric composite membrane. | [33]   |
5. Summary
As a conclusion, in this present study, the Zn-cyclen known as mimic enzyme is chosen to replace the CA for carbon capture and sequestration. The Zn-cyclen is integrated with membrane method to achieve high CO₂ selectivity and permeability. This technology is environmental friendly compared to other carbon capture technologies. Thus, Zn-cycle has the same function with CA at which catalyzing hydration reaction of CO₂ into aqueous solution. Furthermore, PVA is chosen as a polymer membrane material in the selective layer to retain water due to its hydrophilic behaviour. The membrane is designed to work in a condition that is highly swollen with water to accomplish the best separation.

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