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Biopolymeric membranes and their role in CO_2 separation: A review

R. Basrur, L. Ledwani*

Faculty of Science, Manipal University, Jaipur, India

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A new avenue in combatting carbon dioxide emissions is "Membrane Engineering Technology". Membranes are used to separate mixtures by allowing some substances to pass through and not others. Thus, selective permeability is a big factor in the manufacturing of membranes. There are several chemicals used to make the varied layers that are utilized to obtain the exact permeability required. The purpose of this review paper is to discuss the need and usage of such polymeric membranes, with specific attention to the usage of biopolymers in membranes. The focus is primarily on membranes designed to allow the passage of CO_2 while the other components of air do not pass through. Polymeric membranes are used for the separation of CO_2 produced during various chemical reactions before it is released into the air. The separation of carbon dioxide with the help of membranes made up of biopolymers will be a new approach to green chemistry. The biopolymers utilize animal or plant-based polymers like cellulose, starch and polylactic acid which is beneficial to the environment in more ways than one. The world relies heavily on the combustion of fossil fuels for its energy needs. The increasing amount of carbon dioxide emitted by industries is concerning because of its contribution to climate change. The increased usage of membranes would therefore aid in containing the emissions and reusing the CO_2 for more beneficial purposes.

Keywords: CO_2 separation, Biopolymer membranes, Membrane separation, Biopolymer

INTRODUCTION

Over the last century, the rise in carbon dioxide in the atmosphere has increased drastically. The relationship between CO_2 emissions and global warming was a point of critical debate among many scholars [1]. Carbon dioxide is responsible for over 60% of the greenhouse effect, causing a rise in global temperatures [2].

It is predicted that by the year 2100 the temperature of oceans will increase by 3-4°C [3]. Therefore, researchers have been looking at methods to reduce the rate at which the global temperature rises. In lieu of this, biopolymeric membranes are being developed and used to reduce the emissions of carbon dioxide in combustion and other manufacturing reactions. This paper will focus on the process of the membrane-employed separation as well as review some of the bio-polymeric membranes that are being utilised. It will also enumerate the advantages and disadvantages of the process.

The greenhouse effect has multiple causes. The Intergovernmental Panel on climate change (IPCC) has reported that agriculture accounted for about 23% of net global greenhouse gas emissions produced by the human population during the period 2007-2016 represents, which in turn consisted of CO_2 (13%), CH_4 (44%), and N_2O (43%). It is reported that approximately 21%–37% greenhouse gas emission was by 2050 [4,5]. The main role to CO_2 emission because of the global energy consumption by fossil fuels is connected to the electricity grid 44.4%, followed by transportation 24%, industry 19.4% and residential 7% and can be seen in Fig. 1 [6]. Bio-membrane technology is used in the industrial sector addressing 19.4% of CO_2 emissions.

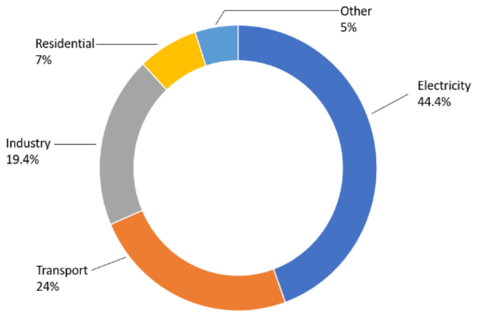

Fig. 1. CO_2 emissions by each sector

Of all the greenhouse gases, carbon dioxide is the biggest threat. Carbon dioxide absorbs the infra-red radiation (i.e., heat) reflected from the earth by virtue of its carbon- oxygen bonds vibrating more strongly; and so, the heat is trapped within the Earth's atmosphere. Carbon dioxide is a stable molecule and removing it from the atmosphere by reaction is not viable. Methane traps heat more effectively than carbon dioxide by its carbon-hydrogen bond vibrations but its concentration in the atmosphere has not increased as significantly as that of carbon dioxide and its shorter lifetime in the atmosphere is less important of a crisis.

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* To whom all correspondence should be sent:
E-mail: lalitaledwani@gmail.com**;**
lalita.ledwani@jaipur.manipal.edu

To abate this crisis, many researchers have proposed various technological solutions for lowering the CO_2 emissions. Some include decreasing the global energy usage, substituting carbon fuels with other sources, and CO_2 capture by membrane engineering technology. This separation technology is believed as a possible avenue because of the numerous advantages compared to other conventional techniques like adsorption and cryogenic distillation. The advantages such as higher separation efficiency, higher stability, low operating cost and investment, low energy requirement, and ease of operation have created a new focus on this technology.

The separation of gases through a polymeric membrane is a pressure-based process. A mixture of gases is fed into a diffusion mechanism where a specific gas is allowed to pass through the membrane. For an effective separation of CO_2 there are two requirements: high CO_2 permeability and CO_2 selectivity with respect to the other gases present in the mixture [7].

The introduction of various membranes in the same industrial cycle can lead to other important advantages in terms of product quality, installation compactness, environmental impact and energy consumption [8].

The selectivity of the membrane is important. Such as the selectivity between CO_2 and CH_4 or CO_2 and N_2, the stability of the materials used to manufacture the membranes can have their own impact on the separation process.

The membranes used for these procedures are inorganic and organic. The inorganic membranes are most commonly used in combustion processes due to their high thermal resistance. Unfortunately, compared to organic membranes, inorganic membranes show the disadvantage of increased production costs [8].

The usage of biopolymers for these membranes further reduces the carbon footprint as the polymers will not be synthetic (i.e., made from fossil fuels), they will also be biodegradable. Cellulose [9] and thermoplastic starch are produced in plants and can be utilised in the manufacture of the membranes. Chitosan is a polymer that can be found in the shell of crustaceans. Polylactic acid (PLA), polyhydroxyalkanoates (PHA), and polyvinyl alcohol (PVA) are synthetically manufactured but are biodegradable, which reduce its carbon footprint, and non-toxic and are better suited for the manufacture of the membranes because of the modification that can be made to their properties.

There are different time periods during which separation can occur. This is integral to the efficiency of the process. CO_2 can be separated at pre-combustion, post-combustion and oxy-combustion. In the pre-combustion, the efficiency of CO_2 capture is close to 90-95%. The fuel is converted into hydrogen and carbon monoxide, which is then transformed to CO_2 by a water-gas shift reaction and is separated from hydrogen. In post-combustion capture, CO_2 is ventilated to liquid state. This facilitates the separation of CO_2 from the gas escape while the gas mixture is in contact with a liquid solvent. This solvent is usually an aqueous amine that absorbs about 85% of the CO_2 The oxy-combustion shows 100% of CO_2 capture but it requires a lot of energy input for combustion in oxygen with recycling of exhaust gases (CO_2 and H_2O) and purification of the CO_2 flow [10].

POLYMERIC MEMBRANES AND THE SEPARATION PROCESS

As iterated above, the process and its efficacy are reliant on 3 factors: the stage of combustion, the selectivity and the physical structure of the membrane itself. This section of the paper will explain and provide insight on the impact of these factors and its respective influence on the selection of the membrane being used in the actual process.

Combustion

In the range of methods employed for CO_2 capture, membranes are used in post-combustion capture, pre-combustion capture and oxy-combustion. Pre-combustion separation is when fossil fuels are converted into a synthesis gas which mainly consists of hydrogen and carbon monoxide. CO can undergo additional conversion with steam to form more hydrogen and CO_2 through the water-gas shift reaction. The CO_2 and hydrogen can be separated with the help of membranes. CO_2 is separated using physical adsorption through the membrane and is sent to the compression unit. The most optimal separation process takes place as a function of partial pressure of CO_2 in the gas to be separated. In pre-combustion, the separation of the carbon dioxide depends on the pressure of the process selected for natural gas. The rise in pressure is not a free operation and must assure the increase in capture due to the high pressure and additional energy needed to achieve it [11].

Oxy-fuel combustion or oxy-combustion is a process of combustion where nitrogen is separated from the air that is used for combustion. This is so that combustion takes place in oxygen and recycled flue gas. Flue gas consists mostly of carbon dioxide and water vapour. Most industrial plants are designed to involve flue gas recirculation to the combustion to control the temperature of the flame. The modifications that are needed in the powerplants to apply oxy-fuel combustion is larger than that of post-combustion. This is due to the fact that the combustion process is modified by the recycling of flue gas in place of the nitrogen present in the oxidiser [12].

Post- combustion separation is when the carbon dioxide is separated after the combustion process has taken place. The gases produced by combustion are allowed to interact with the membrane and the CO_2 is separated.

Selectivity and permeability

A membrane is a selective barrier that allows only specific species to pass through it. In this instance the polymeric membranes are designed to separate CO_2 from a feed mixture of gases. It is effective as they have high efficiency and low operation costs compared to orthodox separation methods as mentioned earlier.

The most critical criteria for a membrane are permeability and selectivity. For membranes to be effective there has to be a trade-off between selectivity and permeability. The permeability will reduce with an increase in selectivity. However, this can be overcome by adopting a selective CO_2 carrier and a selective metal-organic framework (MOFs) because the porosity and selectivity properties can be manoeuvred in MOFs using a combination of metallic ions and organic linkers during the manufacture [13].

Metal-organic frameworks (MOFs) are solid crystalline porous materials that have been broadly studied in the last few decades due to their unique yet useful properties that they tend to display, like gas adsorption and separation, which are significant in this topic, while they also show properties of magnetism, conductivity, catalysis, and water harvesting [14].

The comprehension of the interaction between gases and adsorbent properties of the MOFs are very important in the implementation of materials in the separation process. One such MOF is derived from L-histidine amino acid and has a formula of Cu(II) 2(S,S)-hismox·5H2O, it has a structure of a hemilabile chiral 3D MOF with a qtz-e-type topology. It exhibits a constant reversible breathing behaviour due to the hemi ability of the carboxylate groups from the L-histidine. The breathing motion is used to create an efficient separation of gases of significance, CO_2/NO_2 and CO_2/CH_4. The MOF is stacked in columns and dispersed in a matrix membrane [14].

The membrane-based separation selectivity is based on the membranes itself. The shapes of the polymers used to make the thin layers of the membranes allow the passage of gases. The rate of separation differs based on the size of the gas molecules and the diffusion coefficients in the membrane material [15].

Physical structure

Structures of polymeric membranes are very irregular and random. The membrane morphology depends on the material fabricated and its production processes [16]. The matrix of a membrane is the space or free volume available between the polymer chains which is where the molecules will interact in their process to move to the other side of the membrane.

The movement that occurs across a polymeric membrane is different. The gas through a dense membrane is described with the help of a solution-diffusion (SD) model. This mechanism has 3 key steps; 1-the desired gas molecules dissolve into the polymer matrix and move about the chains. 2- the molecules are moved down the concentration gradient to the other side. 3- the dissolved gases are desorbed out of the other side of the membrane. The S-D system takes place because of the thermodynamic differences between the two sides of the membrane. The permeability properties are defined by the matrix properties of the polymeric membranes. This can be seen in Fig 2. These encompass the density, rubbery or glassy texture of the membrane, and the amount of free volume present. Another factor in the gas permeability is the physical interaction between the gas molecules and the polymer chains in the membrane. Permeability is calculated by multiplying the solubility coefficient and the diffusion coefficient P=S×D [7].

The solubility differs with the chemical similarity of the gas molecules and the polymer chains of the membrane. Whereas the diffusivity varies on the free volume and the size of the gases in the polymer membrane matrix [7].

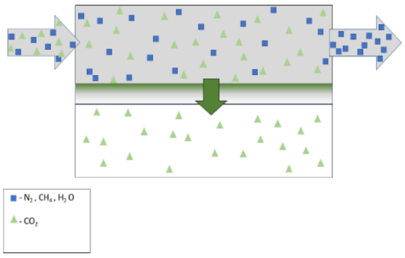

Fig. 2. Separation mechanism.

BIOPOLYMERS USED AND MANUFACTURE OF THE MEMBRANES

The world of biopolymers is vast and neverending. It is the perfect alternative to synthetic polymers, even in membrane preparation. They can be sourced from animals, plants, bacterial fermentation or even synthetically produced. At the moment, several biopolymeric membranes are being used in different separations. Chitosan, starch, polyvinyl alcohol, polylactic acid, and polyisoprene can be used in the separation of CO_2 from a concoction of gases with the help of SD model as the main principle, which is the separation that is obtained by a difference in solubility and the capacity for diffusion across the dense membrane of chemical products in a mixture [15-17]. This paper will review four of them and shine light on their properties and influence in the process of the membrane separation.

Chitosan

Natural form. Chitosan is a polymer that has a large portion of its residues in deacetylated form. It can be found in nature in a pure state but is usually found in a combined manner with polysaccharides, proteins, and the possibility of minerals. Chitosan is obtained by the deacetylation of chitin. It is a copolymer of glucosamine and N-acetyl-glucosamine, a deacetylated monomer and acetylated monomer respectively. They are linked through a β-4 glycosidic bond. It is usually manufactured by deacetylation of a-chitin by 40-50% aqueous alkali solution at a temperature of 100-160°C for a number of hours. The achieved degree of chitosan can reach to about 0.95. The alkaline treatment can be done again to attain complete deacetylation. Chitin (Fig. 3) and chitosan are produced from waste by-products of the crustacean products in the food industry [18].

Processing of Chitosan. The processing of chitosan involves the crushing of crustacean shells. The proteins are then separated and washed with NaOH. Followed by a washing with HCl to ensure mineralisation does not take place. Washing and dewatering is the next step, after which decolouration takes place, at this step chitin is obtained. Deacetylation with NaOH, washing and dewatering give us the final product of chitosan (Fig. 4) [18].

Properties. Chitosan (Fig. 5) is a linear amino polysaccharide with a high nitrogen content, in a rigid D-glucosamine structure. This causes the following properties: high hydrophilicity due to the crystallinity. Chitosan is a weak base due to the deprotonated amino group acting as a powerful nucleophile. The structure enables the formation of hydrogen bonds intermolecularly, which in turn expresses a high viscosity in the polymer. The reactive functional groups present cause cross-linking and chemical activation of the polymer chain. Chitosan is soluble only in dilute acidic solutions. It also has the capacity to form salts with organic and inorganic acids. It is a cationic biopolymer with high charge density. It has entrapment and adsorption properties which benefits its application in filtration and separation. As it is a biopolymer it is biodegradable [19]. Owing to the hydrophilicity and chemical resistance chitosan is used in dense membranes for pervaporation and gas separation [17]. A chitosan membrane alone is too rigid a polymer due to its glass transition temperature being around 130°C, but when the membrane is swollen in water the Tg (glass transition temperature) decreases, and the membrane is turned from a glassy condition to a rubbery one. This helps to increase the gas permeability; the gas permeation tests were carried out at room temperature where the CO_2 permeability was around 163 and the CO_2/N_2 separation ratio at 42 which is ideal [19].

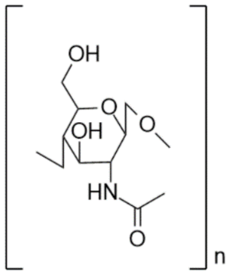

Fig. 3. Structure of chitin

Starch

Natural Form and Structure. Starch is a natural polymer which holds numerous unique properties and drawbacks. Starch-based polymers have the potential for applications in environmental fields due to the biodegradable and naturally occurring properties. Therefore, it receives extra attention and more in-depth research. Starch is predominantly made up of two homopolymers of D-glucose: amylose, typically a linear D(1,4) glucan and branched amylopectin, having a similar structure as amylose but with many 1,6 linked branch points. There are multiple hydroxyl groups, two secondary hydroxyl groups at C_2 and C_3 of each glucose residue, in addition to a primary hydroxyl group at C_6 when it is not linked (Fig. 6) [20, 21].

Properties. Starch membranes by themselves are too brittle so glycerol and sorbitol are used as plasticisers, which reduces the intermolecular interactions between the chains and improves the bad mechanical properties of starch [18].

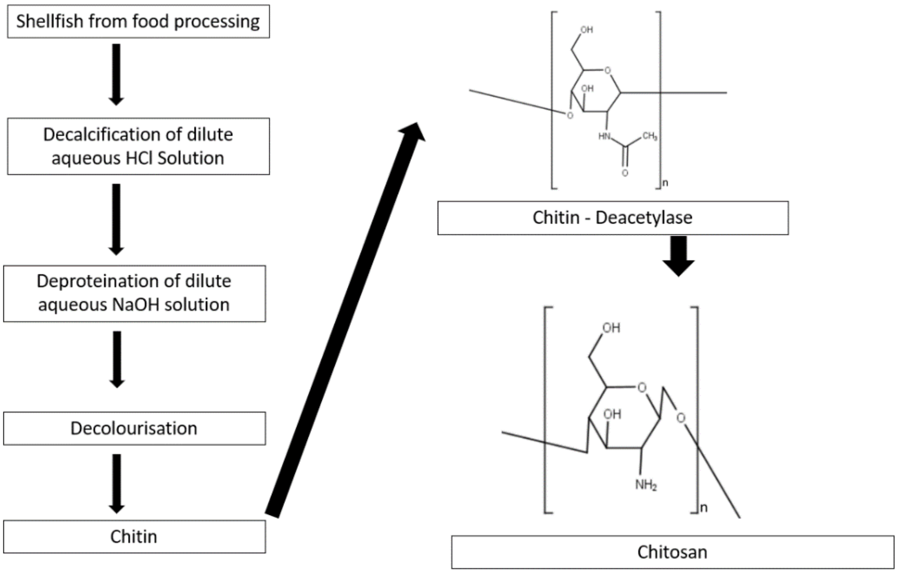

Fig. 4. Processes that give chitin and chitosan.

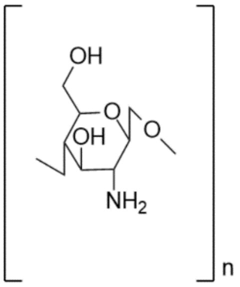

Fig. 5. Structure of chitosan.

A small amount of starch can be used without the loss of its plasticity properties. Starch is then transformed into a thermoplastic polymer by the application of forces and heat with the plasticisers [21].

A starch and chitosan polymer-based membrane has an antibacterial property. This was tested with *E. coli*; the growth of the bacteria was entirely inhabited on the membrane surface. This demonstrates the possible application of starch-chitosan membranes in the medical and food industry.

The addition of carboxymethyl cellulose and nano clay to starch improves the water resistance which is helpful as starch is hydrophilic. Thin films of thermoplastic starch and poly(butylene trans-1,4-cyclohexanedicarboxylate) blends were manufactured and the gas permeability for CO$_2$ and O$_2$ were tested under wet and dry conditions. There were no considerable differences registered between the different tests conducted (dry and wet) with a permeability in terms of gas transmission rate of ~20 cm^3 cm m^{-2} d^{-1} bar^{-1} for CO$_2$ and ~6 cm^3 cm m^{-2} d^{-1} bar^{-1} for O$_2$ [6].

Dialdehyde starch and chitosan have a good biocompatibility which is why they were selected to build self-healing films. The dynamic Schiff base linkage between the monomers gives the film/membrane a self-healing property. In the separation process the carbon dioxide reacts with the amino acids and water in the membrane to form a bicarbonate ion. The ion is then transferred through the membrane and converted back to carbon dioxide. In the experiment conducted the water content of the membrane was an important factor in the case of the carbon dioxide separation [22].

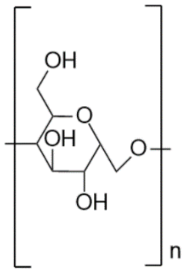

Fig. 6. Structure of starch [19]

Polylactic acid (PLA)

Properties. It has the properties of high-water resistance, solubility in various non-polar organic solvents, high melting point (between the range of 170-180°C) and a Tg of 50 to 65°C, depending on the degree of crystallinity of the structure [6]

The thermal resistance and mechanical properties can cause issues during the production of PLA products. By compounding PLA and blending it with other polymers, it improves the properties so that it can be utilised for in many sectors of the market.

Processing of PLA. Lactic acid is the single and only polymer in PLA (Fig. 7). 2-hydroxy propionic acid is produced through the processes of fermentation or chemical synthesis. The L+ and D- stereoisomers are optically active and can be produced by the fermentation of carbohydrates carried out by bacteria. The bacterial fermentation is carried out in homofermentation and heterofermentation. The industrial production of lactic acid is usually carried out by the fermentation over synthesis because the latter process is dependent on the by-product of another reaction which tends to reduce the yield of lactic acid. The homofermentative method is favored because the reaction pathway results in a greater yield of lactic acid and lower levels of waste by-products. Pure lactic acid is used to produce PLA. PLA is produced by three techniques: direct condensation polymerisation, direct polycondensation in an azeotropic solution, and polymerisation through the formation of lactide formation. Direct condensation is centred around the esterification of the lactic acid monomers by the aid of solvents while the by-product, water, is separated using progressive vacuum and high temperatures. Gaining high molecular weight polyesters with ideal properties through this method is not easy. The production of high molecular weight PLA can be attained by direct polycondensation in azeotropic solutions and catalysts. PLA separation from the solvent is aided by the azeotropic solution by forming molecular sieves, it also decreases the pressure needed for distillation. The molecular weight of the polylactic acid obtained is 6.6×10^4 [23].

PLA pellets were dissolved in 1,4-dioxane to form solutions by stirring at 40°C. this is followed by the degassing of the solutions under a vacuum at 0.1MPa to remove air bubbles. The solutions are then cast onto glass plates and are then placed in a coagulating container. A metal tube is used to connect the container to a steam generator to supply hot water droplets continuously. The drops fall onto the surface of the membranes to induce phase inversion. The glass plates are kept inside for 2 hours to form porous membranes by coagulation, next the glass plates are removed and positioned in distilled water to remove traces of the dioxane. Later the membranes are dried in an oven for 72 hours at a temperature of 30°C ± 2. This step is taken to dry up any leftover water [24]. The permeability of the membrane does not depend on the dilution of the solution used to prepare the membranes, while the resistance of the membrane increases as the concentration of the PLA used is more [25].

Poly-hydroxybutyrate (PHB) compounded with an oligomer of lactic acid (OLA). OLA is a green plasticizer used to enhance the ductility of the membrane which increases the suitability for gas separation. Membranes of PLA formed using phase inversion were used in the separation of CO_2. The CO_2 permeability was around 70 Barrer. Overcoming the upper bound for CO_2/CH_4 selectivity at 285. This brought special interest for the purpose of biogas separation. The selectivity of H_2/CO_2 was also tested and found to be 26.5. until recently PLA was predominantly used in the medical field but with new studies and new methods of manufacture, PLA with higher molecular weights is made for multiple uses, one of which being gas separation [6, 26].

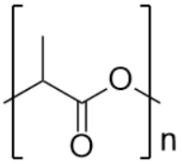

Fig. 7. Structure of PLA

Poly (vinyl alcohol)

Although poly (vinyl alcohol) (PVA) is a synthetic polymer, it is biodegradable. It is not a biopolymer, but it is still an important polymer in the membrane industry and therefore this paper includes a brief review of it.

PVA is obtained by the polymerisation of a single monomer - vinyl alcohol (Fig. 8). It is known for the properties it possesses such as transparency, toughness, barrier properties, non-toxicity, and biodegradability [27]. The solubility of PVA creates some problems when membranes made from it are used in separating processes. To overcome this, it is compounded with several chemicals to increase its hydrophobia. Glycerol, ethylene, glycol, citrate, urea, formamide, and ethanolamine are all added to decrease the solubility and crystallinity, which in turn will improve the performance of the membranes. PVA membranes can be used in pervaporation, for the separation of different organic mixtures, or for the dehydration of organic solvents for instance acetic-acid, alcohol, and ethyl-acetate.

A membrane made from PVA selective layer and a PSF porous support was synthesized. A light enzyme, Zn-cyclen, was added to the composite of the membrane to improve the CO_2 permeability. The results obtained displayed a CO_2/N_2 separation factor equal to 107 with 255.5 GPU as its CO_2 permeation, this is much higher than that of a pure PVA membrane. These membranes were then fortified with carbon nanotubes (CNT). This helped in reaching an ideal CO_2/N_2 selectivity and an optimal CO_2 permeation. This is due to the capability of the CNTs to stimulate swelling in the membrane [28].

A membrane made from PVA, and polyvinyl amine (PVAm) was created on a polysulfone support. The CO_2/N_2 separation factor was found to be up to 174 and the permeance of CO_2 to be up to $0.58m^3$. The experiment conducted found that the CO_2 was transported by binding to the fixed amino groups in the PVAm while the PVA added mechanical strength to the membrane. The entwined polymer chains created a supporting network, where the mechanical properties of the PVA goes hand-in-hand with the transportation factor of the PVAm resulting in high selectivity and permeance. Stability is also seen as a major problem that is solved by the blend of PVA and PVAm, which is stable at 2 atm and 35°C [29, 30].

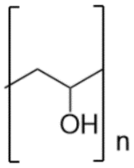

Fig. 8. Structure of PVA

CONCLUSION

The need for carbon-based energy resources is not reducing which sequentially causes a large amount of carbon dioxide to be released into the atmosphere. The increase in carbon dioxide is escalating the rise in planetary temperatures and climate change. To help address this, the study of membranes has progressed bounds in the last few years. The membranes are used to separate out the carbon dioxide and store it in tanks so that it does not get into the atmosphere.

This review has concentrated on the usage of biopolymers to manufacture these membranes. Biopolymers are readily available and biodegradable. They have good physical, and chemical properties to be used as effective and efficient membranes. If biopolymers are able to replace synthetic polymers, it allows for eco-friendlier operations. By the usage of biopolymers, the cost of production and installment of the membranes decrease drastically. This makes it easier for power plants and manufacturing plants to set it up.

While biopolymeric membranes are effective there are shortcomings which should be fixed in the future. The lifetime of biopolymer membranes needs to extend. The durability and strength tend to reduce with usage over time. The process of manufacture is not easy to build in bulk, if these processes can be refined and distributed, it will assist in the establishment of these membranes as a permanent and common fixture in the plethora of industries that use carbon-based fuels.

In this review, the discussion of various biopolymers that are used in the manufacture of membranes utilised for the separation of CO_2 from feed gases. The need for the usage of biopolymers is progressively increasing and new polymers and materials with new properties are being discovered and created. However, with what is available to us now, bio-polymers seem to hold a large share of the hope that we can have towards reducing our carbon footprint and mitigating the dire consequences of former practices on the planet and our survival.

REFERENCES

1. Y. Cai, C, Y. Sam, T. Chang, *Journal of Cleaner Production*, (2018), doi:10.1016/j.jclepro. 2018.02.035.
2. Sh. P. Raghuvanshi, A. Chandra, A. Kumar, *Energy Conversion and Management* **47,** 427 (2006), doi:10.1016/j.enconman.2005.05.007
3. S. Alfonso, M. Gesto, B. Sadoul, Temperature Increase and Its Effects on Fish Stress Physiology in The Context of Global Warming, doi:10.1111/jfb.14599.
4. G. D. Sharma, M. I. Shah, U. Shahzad, M. Jain, R. Chopra, *Journal of Environmental Management*, **297** 113316 (2021), https://doi.org/10.1016/j.jenvman. 2021.113316.
5. W. F. Lamb, T. Wiedmann, J. Pongratz, R. Andrew, M. Crippa, J. G. J. Olivier, D. Wiedenhofer, G. Mattioli, A. A. Khourdajie, J. House, S. Pachauri, M. Figueroa, Y. Saheb, R. Slade, K. Hubacek, L. Sun, S. K. Ribeiro, S. Khennas, S. D. L. R. D. Can, L. Chapungu, S. J. Davis, I. Bashmakov, H. Dai, S. Dhakal, X. Tan, Y. Geng, B. Gu, J. Minx, *Environ. Res. Lett.*, **16** 073005 (2021), https://doi.org/10.1088/1748-9326/abee4e.
6. F. Russo, *Fuel Processing Technology*, 106643 (2020) https://doi.org/10.1016/j.fuproc.
7. Basile, E. P. Fawas, Current Trends and Future Developments on (Bio-) Membranes, Elsevier, 2018, 978-0-12-813645-4.
8. F. Macedonio, E. Drioli, *Engineering*, **3** 290 (2017), https://dx.doi.org/10.1016/J.ENG.2017.03.026.
9. Zh. Dai, V. Ottensen, J. Deng, R. M. L. Helberg, L. Deng, *Fibers*, **7**, 40 (2019), doi:10.3390/fib7050040
10. M. Wang, A Lawal, P Stephenson, J Sidders, C Ramshaw, *Chemical Engineering Research and Design* **89,** 1609 (2011), doi:10.1016/j.cherd. 2010.11.005.
11. M. Kanniche, R. Gros-Bonnivard, Ph. Jaud, J. Valle-Marcos, J.-M. Amann, Ch. Bouallou, *Applied Thermal Engineering*, **30,** 53 (2010), doi:10.1016/j.applthermaleng.2009.05.005.
12. M. B. Toftegaard, J. Brix, P. A. Jensen, P. Glarborg, A. D. Jensen, *Science*, **36,** 581 (2010), doi:10.1016/j.pecs.2010.02.001.
13. J. Kim, J. Choi, Y. S. Kang, J. Won, *J. Appl. Polym. Sci.*, **133**, 42853 (2016), DOI:10.1002/APP.42853.
14. M. Mon, R. Bruno, E. Tiburcio, A. G. Atienza, A. S. Escribano, E. V. R. Fernandez, A. Fuoco, E. Esposito,

M. Monteleone, J. C. Jansen, J. Cano, J. F. Soria**,** D. Armentano, E. Pardo**,** *Chem. Mater.*, **31**, 5856 (2019).

15. R. Castro-Munoz, J. Gonzalez-Valdez, *Molecules*, **24**, 3584 (2019), doi:10.3390/molecules24193584.
16. K.-J. Hwang, T.-T. Lin, *Journal of Membrane Science*, **199,** 41 (2002).
17. F. Galiano, K. Briceno, T. Marino, A. Moliono, K. V. Christensen, A. Figoli, *Journal of Membrane Science* **564,** 562 (2018), https://doi.org/10.1016/j.memsci.2018.07.059.
18. V. Zargar, M. Asghari, A. Dashti, *ChemBioEng Rev*, **2** (3), 204 (2015), DOI:10.1002/cben.201400025.
19. L. A. El-Azzami, E. A. Grulke, *Journal of Membrane Science*, **323,** 225 (2008), doi:10.1016/j.memsci.2008.05.019.
20. D. R. Lu, C. M. Xiao, S. J. Xu, *Express Polymer Letters*, **3** (6) 366 (2009), DOI:10.3144/expresspolymlett.2009.46.
21. Kh. M. Dang, R. Yoksan, *Carbohydrate Polymers* **115**, 575 (2015), https://dx.doi.org/10.1016/j.carbpol.2014.09.005.
22. J. Ren, H. Xuan, L. Ge, *Appl. Surface Sci.*, **469**, 213 (2018), https://doi.org/10.1016/ japsusc.2018.11.001.
23. M. Jamshidian, E. Arab Tehrany, M. Imran, M. Jacquot, S. Desobry, *Comprehensive Reviews in Food Science and Food Safety*, **9,** 552 (2010), doi:10.1111/j.1541-4337.2010.00126.x.
24. A. Ch. Chinyerena, H. Wang, Q. Zhang, Y. Zhuang, K. H. Munna, Ch, Ying, H. Yang, W. Xu, *Polymer*, **141**, 62 (2018), https://doi.org/10.1016/j.polymer.2018.03.011.
25. T. Tanaka, D. R. Lloyd, *Journal of Membrane Science* **238,** 65 (2004), doi:10.1016/j.memsci.2004.03.020.
26. A. Iulianeli, F. Russo, F. Galiano, G. Desiderio, A. Basile, A. Figoli, *Science and Technology*, **9** 360 (2019).
27. H. Xu, L. Zhu, Y. Nan, Y. Xie, D. Cheng, *Ind. Eng. Chem. Res.*, 58, 21403 (2019), dx.doi.org/10.1021/ie502531w.
28. F. Liu, B. Qin, L. He, R. Song, *Carbohydrate Polymers*, **78,** 146 (2009), doi:10.1016/j.carbpol.2009. 03.021.
29. M. Saeed, L. Deng, *International Journal of Greenhouse Gas Control*, **53,** 254 (2016), https://dx.doi.org/10.1016/j.ijggc.2016.08.017.
30. L. Deng, T.-J. Kim, M.-B. Hagg, *Journal of Membrane Science*, **340,** 154 (2009).