



Original Research Article

Investigating Membranes Used in Gas Separation in Industry

Peyman Ghanbari¹, Moein Nabipour^{1*}¹Department of Chemical Engineering, Marvdasht Branch, Islamic Azad University, Marvdasht, Iran

ARTICLE INFO

Article history

Submitted: 2021-01-15

Revised: 2021-03-26

Accepted: 2021-04-08

Available online: 2021-04-28

Manuscript ID: PCBR-2103-1180

DOI: 10.22034/pcbr.2021.277405.1180

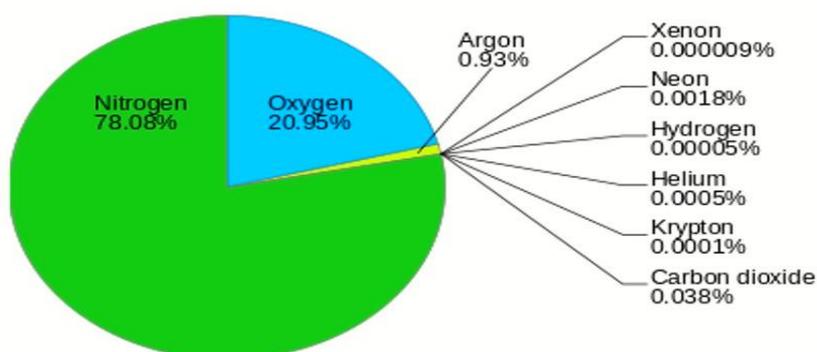
KEYWORDS

Membrane technology,
Separation,
Polymer network,
Nanocomposite,
Gas

ABSTRACT

This paper examines the membranes used in the separation of gases in industry. To date, more than 60% of the application of membrane technology in the separation of gaseous mixtures is related to the separation of nitrogen from air and the recovery of hydrogen from the gas streams of ammonia or synthesis units. These units contain clean gases free of any blocking gases and gases that affect the nature of the polymer. However, the dramatic growth of the use of membrane technology in the field of natural gas treatment, refineries and petrochemical units - which contain compressible compounds and vapors that affect the polymer network - has led to increasing attention to the stability and efficiency of polymer membranes. The flexibility of polymer chains during the manufacturing process of nanocomposite membranes is one of the most important manufacturing parameters. During the process of solvent evaporation from the film placed on the glass plate, due to the stresses caused by the shrinkage and irreversibility of the hard chains of the glass polymers, cracks are formed in the polymer-nanoparticles interface

GRAPHICAL ABSTRACT



* Corresponding author: Moein Nabipour

✉ E-mail: nabipour@miau.ac.ir

© 2020 by SPC (Sami Publishing Company)



Introduction

Oxygen is one of the chemical elements in the periodic table that has the symbol O and its atomic number 8. It is a biological element that is found everywhere, both on Earth and in the universe. The oxygen molecule in the earth is thermodynamically unstable, but it is created by the photosynthesis of anaerobic bacteria and in the next stage by the light action of terrestrial plants. The word oxygen is derived from the two Greek words Oxus meaning acid and Gennan meaning production. Oxygen gas was discovered in 1771 at the same time in a completely separate study by the Swedish scientist Wilhelm Schiele and the English scientist Joseph Priestley. It was named oxygen in 1774 by the famous French scientist Anthony Lavoisier. Oxygen is the smallest member of the 16th group of the periodic table, denoted by the chemical symbol O and atomic number 8. Oxygen has been used extensively as an oxidant, and only fluorine is more electronegative. Liquid oxygen is used as an oxidizer in the propulsion of rockets. It is used in medicine because oxygen is essential for respiration. Sometimes people who climb or fly airplanes carry oxygen tanks. Oxygen is also used in welding and steelmaking as well as methanol. Cijan has a history of use as a sedative, which continues to this day, and there are loads of oxygen in today's parties and banquets. In the 19th century, oxygen was usually combined with nitric oxide, which has a calming effect. Oxygen is the most abundant element in the Earth's crust, and there are estimates of it by 46.7%. Oxygen accounts for 87% of the oceans (in the form of water, H₂O) and 20% of the Earth's atmosphere. Oxygen compounds, especially oxides of metals, silicates, and carbonates, are commonly found in soils and boulders. Frozen water is a common hard object on other planets and comets. Mars ice caps are made of frozen carbon dioxide. Oxygen compounds are found throughout the galaxy, and the spectrum of oxygen light is often found in stars.

Literature review

Due to the importance of gas separation, various researches have been done in this field. A study has defined a model for the separation of other gases ideal in polymer membranes [4]. The aim of this study was to investigate the structure of polymer membrane in gas separation. Also, the ambient pressure parameter of Neszwas studied in this research. This research showed that gas polarization can also affect the performance of gases. In another study [5], the finite difference model was used to study the separation of gases. The purpose of this study was to predict the separation process to improve process efficiency. The finite difference method is a very useful method because it involves the least effort and computational time because it uses algebraic equations instead of differential equations. Also, different configurations such as single-stage and two-stage stages were used in this study. The finite difference method is one of the numerical methods for approximate solving of differential equations. In this method, the derivatives of the functions were approximated by their equivalent differences. The basis of this method for solving equations was to use the function approximation with Taylor method [6].

In a study [7], the temperature stability of polymers, including polymer membranes, was investigated using modeling. The purpose of this study was to investigate the efforts made to produce high performance polymer membranes focusing on the preparation method. Thus, the main limitations and challenges were addressed. Key factors include the type of polymer, the method of preparation of the membrane, the results of thermal analysis and the application of the prepared membranes.

In another study [8], the separation of CO₂ and CH₄ gases in polymer membranes was scrutinized using modeling. The solution method was based on the known SIMPLE algorithm and uses MATLAB to determine the velocity and concentration profiles. Due to the change in

velocity direction in the membrane module, a hybrid separation scheme was used to solve the differential-transformer equation.

Finally, the results of the model were compared with the experimental data obtained as part of this work. The SIMPLE algorithm is an algorithm that is widely used based on the numerical method of solving the Neuner-Stokes's equations. Simple in English stands for semi-implicit method for pressure-related equations. This algorithm is an iterative algorithm [9].

Further, researchers investigated the effect of temperature and pressure on the ability to absorb and separate gases in membrane polymers using electrical energy [10]. The proposed model was able to consider the voltage dependence of the energy parameters of the Arrhenius model, including permeability activation energy and permeability, heat absorption and related predicted factors. The validity of the proposed model was investigated using the CO₂ and N₂ diffusion coefficients in the binary mixture through 6FDA-DAM at different temperatures in the range of 55-55 °C and in the range of 2 to 5 amps. Another method of gas separation is the use of resonance irradiation, which is discussed in a previous study [11]. This model is intended for the transport of gas molecules through dense membranes, which allows the consideration of surface processes on the part of the edible membrane and permeability, as well as external influences on the above processes. The diffusion-solution model is discussed. The effect of resonant radiation on the passage of gas molecules through the membrane has been studied theoretically. The separation of the gas mixture membrane under the effect of resonant radiation in the gas membrane system is analyzed.

In a study, an optimization method was used to separate the gases. The purpose of this research was to optimize the process. In other words, in this research, the separation parameters were determined in such a way that the maximum

separation between different gases was done in a polymer membrane. Also, a mathematical model for the separation of nitrogen and oxygen gases using a polymer membrane was defined [13]. The aim of this study is to determine the role of parameters such as polymer layer thickness and ambient temperature, to perform the best separation in gases. The important point in choosing these two gases is their abundance in the air.

In a study, amorphous perforated glass polymers with high gas permeability, high free volume and the possibility of using them to separate gasoline were investigated. In this study, we have considered the diffusion parameters of gasoline from highly permeable and moderately permeable porphyrin polymers; their free volume is estimated using different methods, the thermodynamic property of adsorption of these materials and the possibility of using They are calculated in several gas separation processes.

In a related inquiry, a high-throughput computational screening method was performed to identify the high-performance limitations of metal-organic framework (MOF) membranes and MOF / polymer composite matrix membranes for O₂/N₂ separation. The results showed that many MOF membranes exceeded the upper limit created for polymer membranes due to their high permeability and / or selectivity. The effects of air mixture purity and structural flexibility of MOF on the gas separation performance of MMMs were also discussed. The results provided molecular level insights into the adsorption and diffusion behaviors of O₂ and N₂ in MOF membranes in addition to providing MOF structure-function relationships, leading to high performance and filler membranes for MMMs.

In another study, to minimize the number of costly and time-consuming experiments, a modified form of the Van Huff-Arrhenius model was developed to investigate the simultaneous effects of temperature and pressure on the separation performance of polymeric and mixed

matrix membranes. In addition, the proposed model could consider the pressure dependence of the energetic parameters of the Arrhenius model, including the energy of permeability activation and diffusion, the heat of adsorption and the corresponding pre-exponential factors. The validity of the proposed model was investigated using the CO₂ and N₂ diffusion coefficient in the binary mixture via 6FDA-DAM at different temperatures in the range of 35-55 °C and in the feed, pressure ranged from 2 to 5atm. In addition, based on the literature, the proposed model predicts the temperature and pressure dependence of the transport properties of glass and rubber polymers as well as mixed matrix membranes (MMM) for various gas molecules including He, H₂, CO₂, O₂, N₂, CH₄ and C₄H₁₀. Forecasts for 300 data points showed that the maximum absolute relative error was 5.1%. Besides, the permeability of gases or vapors through dense polymer membranes in components or module separation design was investigated through a simulation study. The modeling method, for the first time, offered the hardness calculation of transfer fluxes based on different solution diffusion models (dual mode, Flory Huggins, ENSIC) for a set of absolute upstream and downstream absolute pressures. This strategy differs from the classical flux expression in terms of permeability dependence on either upstream or throughput pressure, which has been proposed so far but can cause computational errors. A series of case studies have been reported on simulated glass and rubber membranes. This suggests that the constant permeability hypothesis can lead to significant design errors in some cases. In addition, significant differences were observed compared with the classical variable permeability method and the use of permeability product with pressure difference. A study aimed to review the efforts made to produce high-performance polymer membranes focusing on the preparation steps. Accordingly,

the main limitations and challenges to be addressed were examined. The key factors discussed included the type of polymer, the method of membrane preparation, the results of thermal analysis and the application of the prepared membranes. The main purpose of this study was to draw the basic principles in the selection of polymers, solvents, additives and the appropriate preparation method for the production of polymer membranes with stable heat for gas separation.

An accurate model for polymer hollow fiber membrane modules with non-isothermal separation (Joule-Thomson effect), real gas behavior, and concentration polarization was developed. The model was also variable for temperature-dependent permeability, friction-based pressure loss on both sides of the feed and permeability, and physical properties and transport. The rigid model is used to capture CO₂ before combustion, ie CO₂/H₂ separation, and is compared with a simple model for different polymer membranes by changing the temperature-independent activation energy of the diffusion and pre-exponential factor. Then, two types of selective membranes, H₂- and CO₂, were selected for further analysis. As feed conditions change, the deviation between accurate and simplistic models varied from approximately 2 to 12% for the cutting stage and 20-20% for the infiltration composition. This difference was mostly due to the behavior of the real gas in the low-stage shear, while the Joule-Thomson effect in the high-stage shear (40%) adds to this behavior and results in greater deflection.

However, the effect of concentration polarization is negligible even in step sections. Research has shown the recent trends in fine polymers in a variety of energy-related applications, particularly for gas separation and gasoline storage. New classes of micro-polymers, the so-called thermally reconstituted polymers (TR) and intrinsic microprocessor polymers (PIMs), have

been developed by increasing the strength of the polymer to improve micro-spraying with sufficient free volume. Their strength improves separation performance and separation with extraordinary gas permeability. In addition, their solubility in organic solvents allows them to be potentially used in large-scale industrial applications. Figure 1 shows the molecular structure of this gas. Table 1 also shows the important parameters of this gas. Oxygen forms chemical bonds with almost all other elements, which is the origin of the main definition of oxidation. The only elements that do not undergo oxidation are the original gases. One of the most famous of these oxides is hydrogen oxide or water H₂O. Other well-known oxides are carbon and oxygen. Carbon monoxide and oxygen, also known as carbon dioxide, is another oxygen compound. Alcohols, aldehydes, carboxylic acids are other compounds of oxygen. Other properties

of this gas are: Oxygen is the smallest member of the sixteenth group of the periodic table with the chemical symbol O and atomic number 8. The element oxygen has an atomic weight of 15.9994 gr / mol. Oxygen gas is an odorless, colorless, non-toxic and neutral gas. It is a gas at standard temperature and pressure and an important element of air that is produced through the photosynthesis of plants. It is necessary for animals to breathe. Liquid and solid oxygen are pale blue and both are highly paramagnetic. Liquid oxygen is usually obtained by the partial distillation of liquid air.

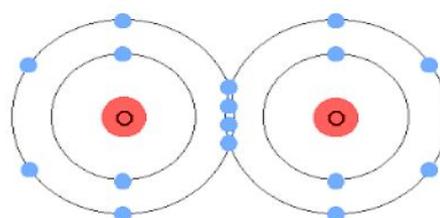


Fig. 1. Molecular Structure of Oxygen

Table 1. Oxygen Gas Parameters

Name, Symbol, Number	8 · O
Group Name for Similar Elements	Non-metals, calcogenes
Group, Course, Block	16· 2· p
Standard Atomic Mass	15.9994 G / mol
Electronic Makeup	1s ² 2s ² 2p ⁴
Electrons to Layers	2, 6
State of	Gas
Density	0 °C 101.325 kPa, (1.429 g/L)
Liquid Density at Boiling Point	1.141 g·cm ⁻³
melting Point	54.36 K· -218.79 °C· -361.82 °F
Boiling Point	90.20 K· -182.95 °C· -297.31 °F
Critical Point	154.59 K · 5.043 MPa
Fusion Heat	(O ₂) 0.444 Kj per mole
Evaporation Heat	(O ₂) 6.82 Kj per mole
Heat Capacity	(O ₂) 29.378 Kj per mole

Based on Table 1 above, a periodic table group is a vertical column in a periodic table that contains several elements. There are 18 groups in a standard periodic table. There are three ways to number groups: the first is to use Indo-Arabic

numerals and the other two are to use Roman numerals. Roman numerals have been used to name groups in the past, but the use of Arabic numerals has been suggested by Iupac to eliminate errors. Place vertical columns below

each other. The elements in each category have the same number of electron layers. In elements of a period, each element has one more proton and one electron than its predecessor element (in terms of group number) and has fewer metallic properties, more electronegativity, and more charge in the nucleus. In this method, the elements are classified according to the orbital of the valence layer that is being filled with electrons. For example, elements of alkaline and alkaline earth groups in which the 1s and 2s orbitals are being filled belong to groups, respectively.

On the whole, the table is classified into 4 blocks s, p, d and f. Atomic mass or relative mass is the mass of an atomic particle, subatomic or a molecule. The unit of atomic mass is one-twelfth of the mass of the isotope carbon-12, corresponding to the absolute mass of $1.6605402 \times 10^{-27}$ kg. Nitrogen or nitrogen is one of the chemical elements in the periodic table that has the symbol N and its atomic number 7.

Nitrogen is usually a gaseous, non-metallic, inert, colorless, tasteless, and odorless gas that makes up 78% of the Earth's atmosphere and is a major element in living tissues. Nitrogen forms important compounds such as ammonia, nitric acid and cyanides. Nitrogen is a non-metallic element with a negative electron charge of 3.0. Nitrogen has five electrons in its shell and is therefore trivalent in most compounds. Pure nitrogen is an inert and colorless gas that occupies 78% of the Earth's atmosphere. Frozen at 63K and liquefied at 77K, it becomes the famous cryogen.

The most important economic use of nitrogen is to make ammonia through the Haber process. Ammonia is commonly used to make fertilizers, fertilizers, and nitric acid. Nitrogen is also used

as inert filler in large tanks to store explosive liquids, in the manufacture of electronic components such as transistors, diodes, and integrated circuits, as well as in the manufacture of stainless metals. Nitrogen is also used as a refrigerant to freeze and transport food, preserve corpses and germ cells, and in biology for the sustainable storage of biological specimens. Nitric acid salt contains important compounds such as potassium nitrate and sodium and ammonium nitrate; the former is used to produce gunpowder and the latter to produce fertilizer. Nitrated compounds such as nitroglycerin and trinitrotoluene are usually explosive. Nitric acid is used as an oxidizing agent in rocket fuel. Hydrazine and its derivatives are also used in rocket fuels. Nitrogen is often used in liquid form in refrigerators. Liquid nitrogen is obtained by distilling air. At atmospheric pressure, nitrogen liquefies at -195.8°C .

Figure 2 shows the molecular structure of nitrogen and Table 2 shows its parameters. The main nitrogen hydride is ammonia (NH_3), although hydrazine (N_2H_4) is also popular. The ammonia compound is simpler than water and forms ammonia ions (NH_4^+) in solution. Liquid ammonia is actually slightly amphiprotic and forms ammonia and amino ions (NH_2^-); Of course, both amides and nitrides are known, but they decompose in water. Ammonia substituents alone or together are called amines. Larger nitrogen hydride chains, rings, and structures are also known, but are in fact unstable.

Biologically-mediated reactions, such as replication, adsorption, and nitrate synthesis, and strongly control nitrogen dynamics in soil.

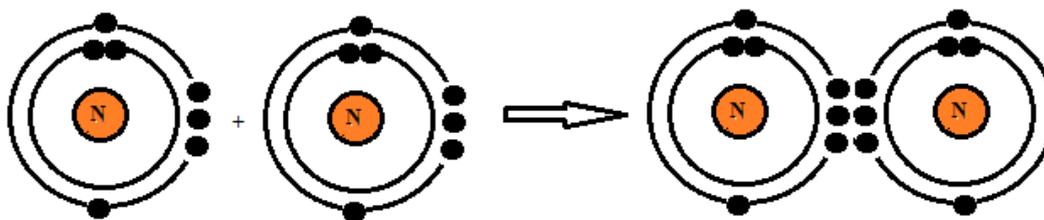


Fig. 2. molecular structure of nitrogen

Table 2. characteristics of nitrogen gas

Name, Symbol, Number	N 7
Group Name for Similar Elements	Non metal
Group, Course, Block	15, 2 p
Standard Atomic Mass	14.0067 gr/mol
Electronic Makeup	$1s^2 2s^2 2p^3$
Electrons to Layers	2, 5
State of	Gas
Density	(0 °C, 101.325 kPa), 1.251 g/L
Liquid Density at Boiling Point	0.808 g·cm ⁻³
melting Point	63.153 K, -210.00 °C, -346.00 °F
Boiling Point	77.36 K, -195.79 °C, -320.3342 °F
Critical Point	63.1526 K (-210°C), 12.53 kPa
Fusion Heat	126.19 K, 3.3978 MPa
Evaporation Heat	(N ₂) 0.72 Kj/mol
Heat Capacity	(N ₂) 5.56 Kj/mol

These compounds usually enrich the N-15 substrate and drain the product. Of course, this rapid process often also involves amounts of ammonium and nitrate, as ammonium is preferentially stored in nitrate barley canopies. Nitrate soil is better absorbed and synthesized by tree roots than ammonium soil. According to Table 2 above, the triple point is the temperature and pressure at which the three phases of a substance are in thermodynamic equilibrium. The critical point, also known as the critical state, is the state at which there is no boundary between the two phases of matter. This occurs at certain values of temperature, pressure and composition. There are several types of critical points, including vapor-liquid critical points and liquid-liquid critical points. The oxidation number of an atom in a chemical species is equal

to the electric charge attributed to the atom of that element, assuming that all bonds are ionic. Oxidation numbers of covalent compounds are determined by some arbitrary rules. Electronegativity or electronegativity of an atom is the relative tendency of that atom to pull an electron pair toward its nucleus. A neutron is the degree to which an atom tends to pull a proton toward its electron. Ionization or ionization is said to be the first ionization energy. If the second electron separates from the atom, the ionization energy is called the second. In the same way, the third, fourth, and ... ionization energies are defined.

The van der Waals rays represent the shortest possible distance between atoms between which there is no chemical bond. This distance is the amount at which the weak gravitational forces

between the atoms are balanced by the repulsive force between the electron shells. Polymeric membrane means shell. The membrane has a selective permeability that acts as a barrier. Another application is the ambiguity of membrane processes. In general, any type of shell or curtain is called thin and permeable or semi-permeable. Plasma membranes in medicine, microbiology, cell physiology, and biochemistry are the thin shells of cells that are a phospholipid bilayer that act as a boundary between various cellular structures.

Membranes are used to separate solutions or mixtures of gases, which can have various applications depending on the properties of the membrane, including strength, support, constituent materials. The membrane also protects the entry and exit of materials while protecting the cell. This membrane is not like a filter that passes materials based on size, but has selective permeability. That is, it allows only the substances needed by the cell to enter and removes waste products and secretions from the cell.

The cell membrane is mainly made up of lipids (fats). There are also a variety of protein and carbohydrate (sugar) molecules in this membrane. Membranes can be made of different materials. As a first classification, membranes can be divided into two groups: biological and synthetic membranes. Biological membranes are essential for life on Earth. Every living cell is surrounded by a membrane, but these membranes are fundamentally different from synthetic membranes in structure and function.

Synthetic membranes can be divided into the following two groups: Polymeric membranes and inorganic membranes. The first large-scale use of membranes was in the use of advanced microfiltration and filtration technology. The use of polymers as a membrane constituent and the production of polymer membranes is very common and today in all known applications for

membranes, polymer membranes have the largest volume of use.

This is due to better process ability and the possibility of optimizing membrane properties in polymer membranes for It has various uses. Types of polymers are used in the manufacture of membranes. Modified natural polymers are one of the most important and widely used materials in this group of cellulose-based products such as cellulose acetate, cellulose nitrate, cellulose sulfate and synthetic polymers like ethylene, polypropylene, fluorinated polymers, elastomers and polyamides.

Optimal properties of a synthetic membrane in terms of material and structure are:

- Optimal selectivity
- High permeability
- Good physical-mechanical strength
- Temperature resistance
- High resistance to chemicals
- Selective performance

Special polymeric materials are used in polymer membrane production technology. The characteristics and specific factors of the polymer chain structure control its physical properties and chemical resistance. As mentioned, these properties play a special role in the final performance of the membrane.

Among the most important features of these specifications can be briefly mentioned as follows:

- Polymer molecular weight and degree of polymerization
- How monomeric units are connected and spatial status of the polymer chain
- Spatial isomeric polymer chain structure
- Polymer chain flexibility

Also, the state of the polymer at the application temperature plays an important role in determining its physical-mechanical properties. The two factors of glass transition temperature and crystallinity percentage are effective in determining the properties of the polymer at any temperature [14-16].

In amorphous polymers, high permeability of glass to high transfer temperatures against gases such as O₂ and N₂ is generally observed. In addition to permeability, selective passage also plays an important role in optimal membrane performance.

Due to this, amorphous glass polymers are used to separate gases such as N₂ from air. Elastomeric membranes are used to separate organic vapors from the air. Glass polymers are also widely used for separation. Although the optimal choice of polymer for the membrane of materials is through high glass transition temperature and melting point, it should be noted that with increasing temperature stability and stiffness of polymer chains, their processing becomes more difficult.

Air Separation

Air separation is the process by which air-forming gases are separated from each other. Respiratory air is mainly composed of two elements, nitrogen (78%) and oxygen (21%).

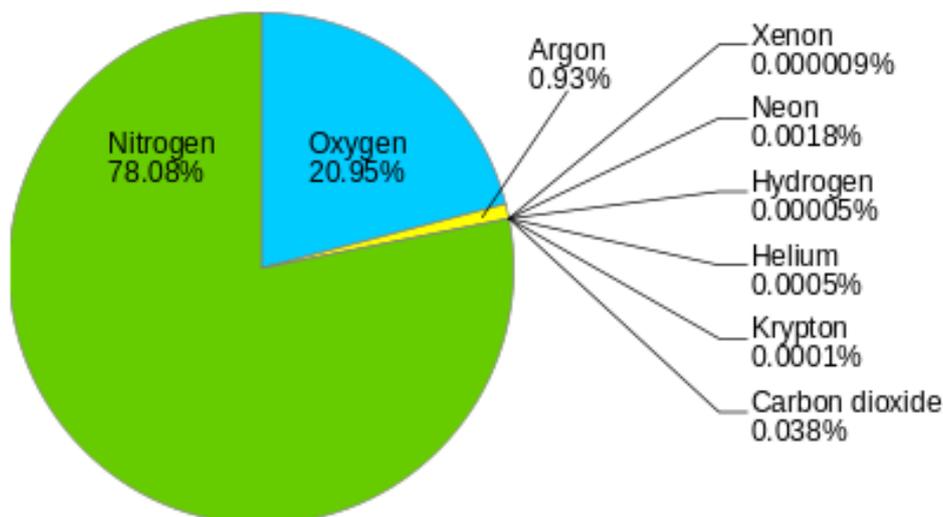


Fig. 3. air components There are major ways to separate different airborne compounds commercially

Membrane method

Membranes have the ability to separate particles based on the size of the molecules. The membrane can be used to produce pure nitrogen and oxygen-rich air up to 40% rich. Due to the

Elements such as neon, argon, xenon, krypton, and helium are also found in small amounts in the air, and compounds such as carbon dioxide, carbon monoxide, methane, and some hydrocarbons, and nitrogen and sulfur oxides, which play a major role in polluting the air. There are also different amounts of water in the form of moisture in the air.

Cooling Distillation

In this method, the air mixture is first cooled to condensate temperature to create liquid air. In the next step, by means of a distillation tower and gradual increase of temperature, the components of air are separated from each other based on the boiling temperature. This method is one of the common methods for mass production of nitrogen and oxygen. There are plates in the distillation tower that separate the members of the mixture based on their boiling point.

low production volume, this method has more laboratory aspects and is less used in mass production.

Use of adsorption

The adsorption method can produce pure nitrogen and oxygen-rich air up to 90% richness. The nominal capacity of this method is about 10 tons per day. The process of adsorbing atoms or molecules in a liquid or gas happens in contact with a solid surface. This adsorption occurs by the forces of adhesion and coherence. Adsorption begins with long-range weak forces such as van der Waals force and ends with strong short-range mandible and metal forces. The covalent force is associated with a chemical reaction and acts not only on the surface but also on the mass of matter and is therefore not part of the adsorption forces.

Separation of nitrogen and oxygen

Isolation of nitrogen in air by membrane processes has the largest share in the use of this technology. In this process, air is separated into streams rich in nitrogen and oxygen, and each stream can be a useful product. Air separation is based on the relative permeability of the components in the air mixture, which occurs due to pressure differences on both sides of the membrane. Membranes used for the first time are based on PMP and ethylcellulose. The selectivity of oxygen to nitrogen in these polymeric materials was 9. Therefore, economically these processes were not very favorable. The new class of polymeric materials currently used for air separation has a selectivity of 6 to 2. The inverse relationship between selectivity and membrane permeability is / is 0% membrane flux. Generally, the permeability of membranes with a selectivity of 6 to 2 is 5 with a selectivity of 2 to 9.

Therefore, it is necessary in the process. For the process of nitrogen production from air to be economical, the selectivity of oxygen to nitrogen must be high. As with other gas separation methods, achieving high purity reduces recovery; therefore, a balance must be struck between high product purity and a high recovery percentage. One way to overcome the behavioral contradiction between seepage is to use

facilitated transfer membranes in nitrogen separation.

Separation of gases separation using polymer membranes

In the early stages of polymer solution formation, the mineral particles are in direct contact with the polymer chains and shrink with the evaporation of the polymer film solvent. For this reason, polymer film is produced at temperatures close to the glass transition temperature. At temperatures close to T_g , the flexibility of the polymer chains increases and the contact surface between the polymer and the nanoparticles increases. Another important factor in the process of making composite mesh membranes is the accumulation of nanoparticles in the polymer lattice. The accumulation of nanoparticles distributed in the polymer network is due to the deposition or movement of nanoparticles towards the surface of the polymer film. Due to differences in physical properties and density between the polymer and nanoparticles, the deposition of nanoparticles during the manufacturing process leads to the formation of heterogeneous phases in the membrane and non-selective gaps are created in the membrane network [17].

One way to reduce the accumulation and deposition of nanoparticles is to increase the concentration of polymer in solution. Also, by distributing the drying conditions of the polymer film, the distribution of nanoparticles is uniform. One of the main criteria for solvent selection is the lack of strong interaction between solvent-polymer and solvent-nanoparticles. Thus, with the addition of polymer to solutions containing solvent-nanoparticles, the force between the particles-polymer prevails and increases the contact surface. If the polymer dissolves well in the solvent (strong polymer-solvent interaction (large polymer molecules), molecular masses are formed. The effect of distributed nanoparticle size on the performance of polymer membranes varies depending on the type of polymer and its

structure. In rubber polymers, due to the high flexibility of the polymer chains, reducing the size of the distributed nanoparticles leads to increasing the contact surface, reducing the permeability and increasing the selectivity of the membrane. The decrease in permeability is due to the decrease in permeability due to the increase in the length and complexity of the penetration path and the decrease in the solubility of gaseous molecules in the polymer network. The behavior of the above polymers can be explained from another aspect. As the size of nanoparticles distributed in the polymer network increases, the tendency of particles to accumulate and form masses larger than nanoparticles increases.

So, the heterogeneity of the network is more difficult to increase and distribute nanoparticles separately and completely uniformly. The permeability of a membrane is defined as the product of the coefficient of permeability and solubility. The degree of permeability of a membrane depends on the structure of its constituent material and the size of the gas molecules.

Membrane selectivity is defined as the ratio of permeability of two components and is equal to the product of the ratio of the coefficients of penetration and adsorption of two gases. The ratio of 1.5 is the ratio of the diffusion coefficients of the two gases and indicates the difference in the sizes of the two gas molecules. The ratio of 1.5 is the ratio of the solubility coefficients of the two gases and shows the relative shrink ability of the two gas molecules. In all polymeric materials, the diffusion coefficient decreases as the molecule size increases because larger molecules interact more with the polymer chains than smaller molecules. Therefore, the selectivity of the diffusion always indicates the passage rate of small molecules relative to large molecules. The second factor that affects the overall selectivity of polymer membranes is the selectivity of solubility or

adsorption. The coefficient of absorption of gases and vapors, which is a measure of the energy required for the adsorption of components by the polymer, increases with increasing its shrinkage capacity. The relationship between the absorption coefficient and the contractility of a gaseous component leads to the concept that the absorption coefficient increases with increasing molecular diameter because with increasing molecular diameter, the contractility also increases.

Theoretical foundations of gas separation using polymer membranes

Membranes used in the field of gas separation, through the dissolution-diffusion mechanism perform the separation action on the gases. In the dissolution mechanism - the penetration of the gas molecule is dissolved in one side of the membrane and through the penetration passes through the width of the membrane and in the other side the membrane is repelled. Therefore, the presence of a selectable dense layer in this type of membrane is necessary.

On the other hand, due to the low rate of gas penetration in the polymer substrate, the high thickness of this selectable layer will increase the resistance to gas passage and consequently the gas flow rate through the membrane will decrease. Therefore, it is necessary to create the membrane structure in such a way that this selectable layer is present with the least possible thickness. The usual method for making polymer membranes for gas separation is the fuzzy separation method. Fuzzy separation is the process by which a polymer is changed from a liquid to a solid in a controlled manner. The solidification process often begins with the transition from a single liquid state to two separate liquids. At a certain stage during the separation process, one of the liquid phases, containing a higher concentration of polymer, solidifies, which will form a solid matrix. By controlling the initial phase of the phase transfer, the morphology of the membrane, which

includes porosity or non-porosity, is controlled. Phase separation during membrane formation in a polymer-solvent system can be accomplished by temperature changes, solvent evaporation, and non-solvent addition during the cooling phase.

Membrane fabrication is divided into three groups through the fuzzy separation process:

- Dry casting / wet fuzzy separation
- Dry casting / dry phase separation
- Dry casting / wet-dry phase separation

The main classification involves the dry casting process. The difference is whether the spun membrane enters the coagulation bath directly or passes through an air gap. This is due to the evaporation of the solvent at the passage of air and the concentration of the polymer at the joint air/solution surface and finally the formation of a shell layer of interest. Membranes used in gas separation are produced by wet-dry phase separation method.

Types of polymer membranes

One of the common classifications of gas membranes is based on the general structure of the membrane. In this case, the membrane is divided into two general categories, porous and non-porous. The transfer mechanisms in these two types of membranes are different. As for porous membranes, the transfer mechanisms in porous membranes are divided into four categories: Knudsen penetration, surface penetration, capillary density and molecular sieve.

Non-Porous Membranes

Infiltration is the main physical model used to describe gas transfer in dense membranes. Polymers used in the manufacture of gas separation membranes are divided into two categories: rubber and glass, based on a glass transition temperature of 51%. In rubber membranes, the mobility of polymer chains is such that the polymer network reaches its specific equilibrium volume. By passing the glass

transition temperature, the mobility of the polymer chains is limited, so that the polymer network will not reach its equilibrium volume. As a result, the volume of the polymer at a temperature lower than the glass transition temperature will be greater than the amount extruded by the rubber region. This excess volume is defined as unsaturated volume. Glass-polymer membranes are hard and are at a temperature lower than the glass-polymer transition temperature. On the other hand, rubber polymer membranes are flexible and soft and operate at temperatures above T_g . In general, polymer membranes exhibit reverse behavior (selectivity / permeability).

In other words, the selectivity of one gaseous component relative to other decreases with increasing permeability of the component, and vice versa. In most cases, rubber polymers show high permeability and low selectivity, while glass polymers have the opposite behavior. Glass polymer membranes are more widely used in industrial separation processes than rubber polymer membranes due to their high selectivity and better thermal and chemical stability.

Conclusion

The separation mechanism in polymer membranes based on the structure and material of the polymer is basically possible in two forms of penetration selectivity and solubility selectivity. The mobility of the polymer chains is negligible and the separation is based on the difference in the size of the gas molecule. So that the permeability of gas molecules with smaller synthetic diameters such as hydrogen is higher. Glass polymer membranes such as polyamides and poly sulfones are examples of these polymers. For example, polyimide membranes are used to separate hydrogen gas from heavy hydrocarbons and nitrogen.

Therefore, the choice of a suitable polymer for separation should be in such a way that it has a higher selectivity than the desired gas molecules.

The second type of polymer membranes are those that separate gas molecules based on their high solubility and gas condensability. In this case, solubility selectivity is the dominant parameter and passes molecules that have a high critical volume, in other words, are condensable.

References

1. M. Jafari, A. Samimi, O. Mayeli, Provide Empirical Solutions and Study Production Problems in Coke Production Cycles in Units of Refinery. *Journal of Applied Researches in Technical and Engineering*, 2 (7) (2018) 247-263.
2. N. Kayedi, A. Samimi, M. Asgari Bajgirani, A. Bozorgian, Enhanced Oxidative Desulfurization of Model Fuel: A Comprehensive Experimental Study. *South African Journal of Chemical Engineering*, 35 (2021) 153-158.
3. S. Delavari, H. Mohammadi Nik, N. Mohammadi, A. Samimi, S. Yaghoub Zolfegharifar, F. Antalovits, L. Niedzwiecki, R. Mesbah, Optimization of Operating Conditions for CO Hydrogenation to Hydrocarbon via Response Surface Method. *Chemical Methodologies*, 5(2) (2021) 178-189.
4. F. Zare Kazemabadi, A. Heydarinasab, A. Akbarzadeh, M. Ardjmand, Preparation, characterization and in vitro evaluation of PEGylated nanoliposomal containing etoposide on lung cancer. *Artificial cells, nanomedicine, and biotechnology* 47 (1) (2019) 3222-3230
5. M. Torkaman, FZ. Kazemabadi, The Use of Ethyl Cellulose Polymer to Control Drug Release of Hydrocortisone Acetate. *Oriental Journal of Chemistry* 33 (4) (2017) 1976-1990
6. F. Zare Kazemabadi, A. Heydarinasab, A. Akbarzadehkhayavi, M. Ardjmand, Development, Optimization and In vitro Evaluation of Etoposide loaded Lipid Polymer Hybrid Nanoparticles for controlled Drug Delivery on Lung Cancer. *Chemical Methodologies* 5 (2) (2021) 135-152.
7. Y. Raziani, S. Raziani, The Effect of Air Pollution on Myocardial Infarction. *Journal of Chemical Reviews* 3 (1) (2021) 83-96.
8. Y. Raziani, S. Raziani, Investigating the Predictors of Overweight and Obesity in Children. *International Journal of Advanced Studies in Humanities and Social Science*, 9(4) (2021) 262-280.
9. KK. Dolisgan, Y. Razisni, A review of child abuses and its management in Iran. *Journal of Critical Reviews* 7 (19) (2020) 9899-9906.
10. G. Mohamadi, A. Kavosi, Y. Raziani, AMP. Nasab, Rhinocerebral mucormycosis and treatment: Report of two cases. *J. Neyshabur Univ. Med. Sci* 2 (2) (2014) 10-13.
11. Scott Matteucci, Roy D. Raharjo, Victor A. Kusuma, Steve Swinnea, and Benny D. Freeman, Gas Permeability, Solubility, and Diffusion Coefficients in 1,2-Polybutadiene Containing Magnesium Oxide, *Macromolecules* 41 (2008), 2144-2156.
12. Rajiv Mahajan and William J. Koros, Factors Controlling Successful Formation of Mixed- Matrix Gas Separation Materials, *Ind. Eng. Chem. Res.* 39 (2000), 2692-2696.

13. Timothy C. Merkel,* Zhenjie He, and Ingo Pinnau, Benny D. Freeman, Pavla Meakin and Anita J. Hill, Effect of Nanoparticles on Gas Sorption and Transport in Poly(1-trimethylsilyl-1-propyne), *Macromolecules* 36(2003), 6844-6855.
14. Scott Matteucci, Victor A. Kusuma, Scott D. Kelman, Benny D. Freeman, Gas transport properties of MgO filled poly(1-trimethylsilyl-1-propyne) Nanocomposites, *Polymer* 49(2008), 1659-1675
15. Toshiki Kono, Yanming Hu, Toshio Masuda, Katsuchisa Tanaka, Rodney D. Priestley, and Benny D. Freeman, Effect of Fumed Silica Nanoparticles on the Gas Permeation Properties of Substituted Polyacetylene Membranes, *Polymer Bulletin* 58 (2007), 995–1003.
16. M. Karami, A. Samimi, M. Ja'fari, The Necessity of Risk Management Evaluations in Petrochemical Industries, *Advanced Journal of Chemistry-Section B, Natural Products and Medical Chemistry* 2 (3) (2020), 151-158
17. S.A. Khoddami, A. Esfandiyari, A. Samimi., Investigating Thermodynamic Mechanism of Gas Hydrate Formation in Natural Gas Transmission Pipelines, *International Academic Journal of Science and Engineering*, 3(1) (2016), 91-99, 2016

HOW TO CITE THIS ARTICLE

Ghanbari p. and Nabipour M., Investigating Membranes Used in Gas Separation in Industry, Prog. Chem. Biochem. Res, 4(3) (2021) 254-267

DOI: 10.22034/pcbr.2021.277405.1180

URL: http://www.pcbiochemres.com/article_129729.html

