Abstract
Air separation process is an emerging technology which is widely used in many fields. The air separation methods, processing parameters, techniques and external factors such as pressure and temperature can be varied based on the end use application. Inert gas generation, oxygen enrichment, natural gas dehydration, sour gas treatment, air humidification, purging gas, acid gas treatment etc., are the main application area of the air separation. Now a days, binary gas separation widely used in huge variety of application. It also plays a role in reduction of air pollutants in many industries. Recently membrane takes a huge part in air separation as efficient and simple method. The usage of membrane will reduce the cost and energy. This paper reviews the available methods, principle, properties and applications of different air separation process and also it reviews about the different forms of available materials for air separation.

Keywords: Air separation, methods, principles, membrane, applications

Introduction
Recently, air separation has an application in many fields due to its requirements in the present scenario. Air separation is the process of segregating primary components from the atmospheric air. Air separation in other words reveals the information of selective separation of air components from its volume and oxygen plays an important role in chemical industry, medical field, combustion process [1], isolation of pollutants and recovery of reactants [2]. It also plays a role in reduction of greenhouse gas emission, elimination of pollution factor, lower industrial waste and also controls global climatic change [2]. For the past few decades, the development of innovation in air separation carried out with various methods. Large scale production of air separation carried out by traditional methods such as cryogenic distillation and adsorption [3]. Recently, there is a huge development in membrane for gaseous separation [4]. Membrane for gas separation has vital application in many areas due to their inherent characteristics like simple, continuous in operation, reduced startup time and low cost with high economical to operate [5]. In order to overcome the disadvantages in the conventional operation, membrane technology has been exposed to the area of gas separation. Negligible amount of mechanical complexity in membrane is another added value for their development in air separation. Various forms of polymeric/fibrous membranes and its construction initiates lots of developments for gas separation [6]. Most of the researchers aiming to increase the rate of separation and purity of the separated component in the air components. This review highlights the methods, properties, principles involved in air separation and also states the development in the membrane technologies to exhibit improved mechanical properties and performance characteristics.

Principles and methods of air separation
The conventional and widely using technique for air separation is cryogenic distillation and it consumes high energy for separating specific gas from air with the purity of 99% [7]. Oxygen or nitrogen can be separated by fractional distillation or high volume of separation column [8]. Large amount of energy is consumed for separation by freezing atmospheric air up to -200°C and the principle is shown in Figure 1 [40]. Alternative method for air separation is adsorption way of isolating single selective gas components from atmospheric air [9]. In this process, there are two divisions of separation such as pressure swing adsorption (PSA) (Figure 2) and vacuum pressure swing adsorption (VPSA) (Figure 3) [10]. Pressure swing adsorption is an economical technology which is used to isolate oxygen or nitrogen with 90-95% of purity by applying pressure. Special adsorptive solid materials like zeolite are used to achieve the adsorption of targeted gas species under high pressure. High pressure will enhance the attraction of gas molecules in solid surface. Different gases can able to get attracted by different solids surfaces. Depending upon the
selectivity of the required gas component, different adsorptive materials are used such as activated carbon, carbon nanotubes, carbon molecular sieves etc., [29]. Vacuum pressure swing adsorption works with lower pressurized feed air to separate gas component, hence the permeate gas molecules is generated at sub-atmospheric pressure level. In pressurized mode, the operation carried out at higher driving force than the vacuum mode. In contrast to pressure swing adsorption (PSA), the driving force in vacuum mode is limited and it influences the permeation rate of gas molecules. This limitation leads to attain reduction of permeation rate in vacuum mode hence higher membrane area is required for vacuum mode. Performance of membrane based on selection of membrane material, membrane module design, system design and engineering [4]. Membrane technology comprises different characteristics of simple, efficient, economic methodology, low cost, energy consumption compared to others [11]. In commercial point of view, new membrane preparation methods like hollow spinning fiber makes reduction in thickness of membrane layer which significantly improves the permeation rate and larger surface area in membrane module [12]. Higher gas permeation will reduce the selection of gas molecules and its purity is a disadvantage of the membrane technology. To equalize this, larger surface area of membrane is required [13]. Developments in membrane technology lead to defect free membrane, higher permeation rate and purity of gas molecules [14].

Figure 1 Principle diagram of cryogenic distillation

Figure 2 Principle diagram of pressure swing adsorption
Basic terminologies in air separation

Permeability

Permeability is defined as the ability of membrane to transport selected gas molecules in a given area [7]. Permeability decides the quantity of the penetrant molecules which is passed through the membrane. The permeate flux rate is the rate of transport of gas molecules in a given thickness of material [21]. In order to achieve separation in economical mode, high flux with low cost membranes is required [15]. The standard SI units for permeate flux is given by m$^3$/m$^2$/s and non SI unit is Barrer [17]. In polymeric membrane, the transport of gas molecules takes place due to random molecular motion of individual gas molecules [25]. Mostly polymeric membrane shows good selectivity due to the presence of low free volume. Free volume decides the permeation phenomenon for gas separation [16].

Selectivity

It is defined as the membrane ability to separate particular gas molecule from the air. It is a key parameter to decide the purity of the penetrant molecule [16]. There is a problem to achieve both permeability and selectivity by polymeric membrane. Higher range of permeability will reduce the range of selectivity. The selectivity of polymeric membrane decreases due to membrane instability, compaction and fouling nature [15].

Mechanism of gas separation

Transport mechanism through the polymeric membrane (non-porous) is commonly elaborated by solution diffusion mechanism as shown in Figure 4. Three types of mechanisms involved in that such as sorption of gas molecules takes place at the surface of the membrane from the feed gas. After sorption, diffusion process takes place to make the gas molecules to penetrate through the membrane depending on the pores present in the internal structure of membrane. Finally desorption process takes place on the other side opposite to the feed area [16]. This mechanism based on the interactive force between the permeating gas molecules and material for membrane. In polymeric membrane, the solution diffusion mechanism occurs based on the mobility factors like size and shape of the molecules and solubility parameters [20].

Principle of gas separation

Simple transport mechanism is the line diagram as shown in figure 5, which explains the principle behind the gas separation. This line diagram consists of three stages such as feed, permeate and retentate. Different types of membranes are used depends on the application like flat sheet, spiral wound and hollow fiber module [15]. Among these, hollow fiber shows higher advantages compared to other form of membrane due to their highest packing...
density [16]. Recently, electro spun web also developed for air separation by using polymers like polysulfone, cellulose acetate, polyimide etc., [19]

![Figure 4](image_url) Solution-diffusion mechanism

**Feed**

The feed is the passage where the atmospheric air passed in to the simplified transport of air separation unit. The flow rate is an important criterion for separation. Feeding gas molecules with pressure factor is important parameter for easy gas mobility, permeability and selectivity [1].

**Permeate**

Permeate represents the separated gas components by membrane from the atmospheric air/feed air. Permeate is the passage for flow of separated gas molecules from membrane. Permeate can be influenced by the thickness of the membrane [22]. It is also achieved by certain pressure which is created by external factors. The product of total pressure and mole fraction of gas molecule is termed as partial pressure gradients [1].

**Retentate**

Retentate is the term or passage for gas molecules which does not passed through the membrane and it is otherwise called as reject phase. When we concentrate on separating oxygen from air, the retentate must be nitrogen due to their volume occupied in atmospheric air. Pressure range or mole fraction of retentate gas molecules is higher compared to permeate gas percentage. On the basis of these three parameters, principles of gas transport takes place in an efficient manner.

![Figure 5](image_url) Principle of air separation in membrane

**Types of membranes for air separation**

*Pure polymeric membrane*

Different types of polymers are used for membrane production. Poly (1-trimethylsilyl-propyne) polymer used for gas separation which shows temperature independent characteristics for separation [23]. Rubbery polymers like poly dimethyl siloxane and silicon rubber are used and glassy polymers like polyimide, polysulfone, cellulose acetate, polycarbonates are also used. Polymeric membrane generally contains limitations to attain permeability and selectivity. Wide range of sizes and topologies present in pores and channels of the membrane [16]. The polymeric membrane should also comprise the following features such as defect free membrane, mechanical stability under pressurized conditions, reduced physical ageing and plasticization [34]. Polymeric nanofibres are developed for many applications like filtration, drug delivery system, separation, tissue engineering due to its inherent characteristics such as very large surface are to volume ratio [59]. Polymeric membrane has poor temperature stability, mechanical
stability and inability to withstand pressure when it is used in high pressure area and also aggressive chemical environment [16]. Fouling, physical instability, chemical and thermal instability are the major disadvantages in the pure polymeric membrane [52]. Selectivity/permeability combination cannot be achieved by this membrane [23]. Poly(1-trimethylsilyl-1-propyne) (PTMSP) shows ten times higher oxygen permeation than Polydimethylsiloxane (PDMS) [24]. Different polymers with permeability ranges are given in Table 1 [19].

### Table 1 Different polymers with permeability ranges

<table>
<thead>
<tr>
<th>SL. NO</th>
<th>Polymers</th>
<th>Oxygen Permeability (barrer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polyvinylchloride (PVC)</td>
<td>0.025</td>
</tr>
<tr>
<td>2</td>
<td>Polyaramid (PA)</td>
<td>3.1</td>
</tr>
<tr>
<td>3</td>
<td>Ethyl cellulose (EC)</td>
<td>11.2</td>
</tr>
<tr>
<td>4</td>
<td>Cellulose acetate (CA)</td>
<td>0.59</td>
</tr>
<tr>
<td>5</td>
<td>Polycarbonate (PC)</td>
<td>1.4</td>
</tr>
<tr>
<td>6</td>
<td>Polydimethylsiloxane (PDMS)</td>
<td>638</td>
</tr>
<tr>
<td>7</td>
<td>Polyphenylene oxide (PPO)</td>
<td>16.8</td>
</tr>
<tr>
<td>8</td>
<td>Poly(1-trimethylsilyl-1-propyne)</td>
<td>7600</td>
</tr>
</tbody>
</table>

Dense ceramic membrane

Dense ceramic membranes can be prepared by using ion transport materials like Pervoskites (ABO₃) and fluorite (AO₂). Pervoskites are crystalline ceramic with general formula of (ABO₃) with a cubic structure [26]. The Pervoskites are referred to as mixed ionic electronic conductor (MIEC) due to its excellent gas ion conduction (especially oxygen) from air. MIEC material does not require external electrical circuit for gas ion conduction. Low operational energy requirement for gas separation, good oxygen permeability, less complex engineering design and mechanical strength are the advantages of MIEC materials [27]. Among all MIEC material (BSCF) Ba₅Sr₅5CO₂₈Fe₂O₈-8 is considered as having highest oxygen fluxes [28]. In the area of membrane technology, thickness of membrane also plays a significant role in the permeate flux and in the case of fluorite, electric unit is essential for gas separation. Electric current which is flowing in the device is directly related to O₂ permeation rate [29]. Fluorite cannot separate oxygen from air due to their lack of electronic conductivity. The gas transport in dense ceramic membrane was done by the transport of gas molecules from gas phase to membrane surface by diffusion. After this, dissociation of gas molecules takes place by catalytic activity of the ceramic material [26]. In order to maintain electrical neutrality the transport of electrons takes place in opposite direction. Finally, association (surface reaction) on permeate side takes place which makes the O₂ molecules desorbed from the membrane surface. Oxygen ion and electronic conductivity were taken for constructing membrane for gas separation. It shows higher O₂ permeation rate up to 3.0 ml min⁻¹ cm⁻² [39].

Mixed matrix membrane

Mixed matrix membrane is developed to improve the properties of air separation process [30]. Micro or Nano level inorganic materials are added in to the polymeric matrix for better permeation and separation. It will also enhance the physical, thermal and mechanical properties for aggressive environment [14]. The polymer and inorganic Nano composites are interlinked by covalent bonds, Vander walls force or by materials like zeolite, CNT, CMS, M-organic frameworks, covalent organic framework etc., are used as fillers in mixed matrix membrane [33]. These materials offer high attractive transport properties of gas molecules. Hence the material enhance the selectivity for the given gas mixture. Zeolite materials are widely used in both rubbery and glassy polymer. CMS are used due to its high surface area to volume ratio and also it will facilitate high gas separation. Adding CNT in weight percent properties of 0, 2, 10 in PDMS will improve permeation rate of O₂ in the range of 32, 36 and 40 respectively [14]. The compatibility between filler and polymer is improved by introducing interacting functional group like silane. This will increase the filler- polymer interaction [31]. Zeolitic imidazolate framework (ZIFs) are synthesized and added to PVAm coating solution to form film like membrane to achieve higher selectivity [35]. ITQ -29 zeolite crystals are added to the polysulfone membrane to obtain limited aggregation of the particles in the mixed matrix membrane and to obtain good H₂/CH₄ gas permeation [36]. High cost of fabrication is the major disadvantage in the construction of the mixed matrix membrane [14]. The selection of suitable organic filler, polymer, brittleness, large scale of manufacturing process are the important future challenges in mixed matrix membrane fabrication [30]. Composite membranes are
developed in the area of gas separation in which a highly porous membrane act as supportive layer and thin permselective layer is placed over the support layer for effective separation [57].

**Polymeric membrane with nano particles**

Pure polymeric membrane limitations can be minimized by adding nano particles to prepare membrane and to improve both the combination of selectivity and permeability. The mechanical stability of the membrane also be improved by the addition of nanoparticles. SiO$_2$ doped PVC polymeric membranes are widely used for air separation and it gives higher selectivity than the pure polymer membrane [32]. Synthesis of silica can be done by various routes such as chemical and eco-friendly method. Amorphous silica can be extracted from rice husk [60] [66]. Precipitation of silica from rice husk is an effective method to utilize the agricultural wastes in efficient manner [61]. Electro spun membranes are used extensively in filtration and separation [67]. This membrane has several undefined pores hence it can offer good permeability [33]. The addition of silica with varying weight proportions to the polymer solution to prepare PVC silica nano composite membrane. The permeability range of O$_2$, CO$_2$, Nitrogen and methane gases in pure PVC membrane is 0.023, 0.105, 0.0066 and 0.005 barrer which is increased to 0.048, 0.1908, 0.0105 and 0.007 barrer in PVC silica nano composites. The silica nano particles (maximum of 30 weight percentage) will improve the number of polar OH groups in the membrane which leads to enhance the solubility parameters in the membrane [32]. The poor adhesion between polymers – particle interface in nanocomposite membrane will always exhibits defects in their interface [18]. The permeability is increased due to the reduced kinetic diameter of a gas molecule. The penetrant mobility through the polymer is higher due to lesser kinetic diameter ($\sigma_K$) and it's comparison is given below [16].

$$\text{PCO}_2 > \text{PO}_2 > \text{PN}_2 > \text{PCH}_4$$

$$\sigma_{\text{KCO}_2} < \sigma_{\text{KCO}_2} < \sigma_{\text{KN}_2} < \sigma_{\text{KCH}_4}$$

Supported ionic liquid membrane (SILM) configuration is used to measure permeability, solubility and diffusivity of gases in RTIL (Room Temperature Ionic Liquid) [37].

**Parameters of gas separation**

**Temperature**

Higher temperature will increase the permeation rate, on the other hand it will reduce the selectivity of the given couple of gases. Positive value of the activation energy decides the permeation through the polymeric membrane [49]. In high temperature, N$_2$ permeability is higher compared to O$_2$ permeability. The gas molecule movement through the membrane is basically related to an activation energy which states about the diffusivity, solubility and permeation coefficient related to temperature [64]. The followings are the Arrhenius relationship which states about the diffusivity, solubility and permeation co-efficient related to temperature [65].

$$D = D_0 e^{\frac{E_d}{RT}}$$

$$S = S_0 e^{\frac{\Delta H_s}{RT}}$$

$$P = P_0 e^{\frac{E_p}{RT}}$$

The polymers selected for membrane preparation should not undergoes thermally induced morphological changes like rearrangement and restructure. Some polymers can attain higher crystallinity due to temperature application which will affect the permeate flux. Higher temperature will leads to increases segmented mobility which influence the movement of gas molecule. This allows different dimensions of penetrants through the membrane but it shows a loss of selectivity. The chemical nature of penetrant and polymer- penetrant interaction will take part in solubility and selectivity [16].

**Pressure**

Another major factor which affects the permeation flux rate is pressure variation. The pressure application along with gas mixture will vary the perm selectivity of targeted gas species. Nitrogen purity of 95-99% can be obtained by membrane due to compressed air application [50]. Organic vapour through rubbery polymer shows linear increase in permeability when high pressure is applied, CO$_2$ shows lesser permeability with increased pressure through glassy polymer. This condition is applicable to the highly soluble gases. Some polymers and gas components are having
pressure independent nature of air separation. For example: \( \text{N}_2 \) and \( \text{H}_2 \) are pressure independent gaseous components [49]. Glassy and rubbery polymers exhibit different permeation behavior with respect to different pressure values.

**Membrane structural requirements for air separation**

**Porosity**

Porosity is the amount of total void space present in the material. The pore volumes are usually calculated by using specific volume [46]. Based on the porous nature of membrane, selectivity and permeability of gas molecules are increased [16]. Porosity is artificially employed by adding pore formers such as PEG (polyethylene glycol) in the molecular range of 600-1000. PEG act as pore former which is dispersed along the polymer solution. Higher number of pores will reduce the selectivity and lesser number of pores will improve the selectivity and decrease the permeability. Due to the porous nature, electrospun membranes are employed for air separation. 0 wt. % to 8 wt. % of PEG added to polymer solution to incorporate the pores in the membrane by casting solution method. PEG will also improve the hydrophilic property of the membrane. Addition of PEG 600 will increase the number and size of macro voids. The pore radius range lies between 12.6-12.8nm [47]. The porosity also decides the mechanical strength, flux rate and solubility of gas molecules. Upper bond correlation can be used to analyse the changes of permeability process from solution- diffusion to Knudsen diffusion [38].

**Thickness**

The thickness of the membrane also reduces the permeability of gas molecules. Electrospinning process contains challenges related to uniform fiber diameter distribution throughout the process. The polymer concentration shows the variation in fibre parameter such as thickness, diameter, length, viscosity and spinnability [59]. The mechanical stability of membrane is achieved by the thickness and molecular weight. It shows the influence on the entanglement of fibres and viscosity range of polymer solution. Higher molecular weight automatically increases the viscosity which significantly improves the thickness of the membrane which increases the separation factor and reduces the permeate flux. Membrane with higher thickness will give greater distance for the gas molecules to travel which reduce the gas diffusion and solubility through the membrane [48].

**Crystallinity**

Glassy and rubbery polymers are used for gas separation and the transport properties of gas molecules depend on the free volume and segmental mobility in the polymeric chain [63]. The measurement of gas permeation properties in dry state can be evaluated through constant volume variable pressure method. The amount of free volume, gas-membrane phases and membrane environmental conditions changes the permeability and perm selectivity of the gases [58]. The segmental mobility is affected by crystallinity range of the polymer. Flexibility in the backbone of the polymer chain will increase the diffusion and transport properties. Rigidity of polymer backbone will reduce the solubility and diffusivity. The crystallinity nature of membrane is obtained due to the presence of homogeneous structure. Semi crystalline polymeric membrane always exhibit good permeability and selectivity. poly[bis-(phenoxyp)phosphazene] is a semi crystalline polymer having property of hydrophobic nature shows appreciable air separation due to the presence of amorphous structure. It has excellent resistance to degradation agents [62].

**Evaluation of the quality of air**

The purity of oxygen enriched air from the separation unit is evaluated by various methods. The copper wire or metal has been used to assess amount of oxygen present in air [43]. The gas (oxygen) from the permeate vent was taken to the evaluation experimental setup to obtain the exact analyses about the percentage of gas. The enriched air contains major components of oxygen, nitrogen and argon. Gas chromatography method is evolved to determine the various percentages of gas species like \( \text{N}_2 \), \( \text{Ar} \), \( \text{O}_2 \) [41]. Thermal conductivity detector is installed in the gas chromatography for oxygen analysis. An analytical column which was packed or filled with molecular sieves like carbon nanotubes and zeolite. Oxygen and nitrogen are having dissimilarity in molecular size and oxygen having ability to pass in to the pores of absorbent than nitrogen. Oxygen and argon are not easily separable due to its molecular size similarity. To determine the percentage of oxygen, carrier gas is used (helium) with a flow rate of 40ml/min. Depending on the percentage of oxygen, nitrogen and argon in the air volume, respective peak of the gas mixture is loaded on the chart [42].
By this equation, the theoretical percentage of argon was obtained and the percentage of $O_2$ is extracted by subtracting the theoretical percent of argon to % determined by $O_2$/Ar peak. This process is more accurate method to obtain $O_2$ percentage. Modified atmosphere packaging (MAP) is a technique to improve the self-life of fresh vegetables. To design MAP, the correct determination of the concentration of $N_2$, $O_2$, $CO_2$, and Ar is required. Gas chromatography method is used to access the $N_2$ and $O_2$ to design MAP [44]. Stainless steel and packed column are used to separate these four gases. The two columns are linked in parallel manner to analyse these four gases simultaneously. Evaluation of oxygen by using copper turnings is another one method to obtain $O_2$ percentage. The permeate gas ($O_2$) components are fed in to the evaluation setup and the oxygen reacted with red hot copper turnings to give copper oxide [43]. This reaction gives information about the reaction between copper and oxygen, and then unreacted gas will reveals the information about other gaseous component percentage in the gas mixture [45].

**Application**

The separation process is having high potential application in many industrial areas. Six major areas covered by both filtration and separation membrane such as microfiltration, ultrafiltration, reverse osmosis, electro dialysis, gas separation and prevaporation [51]. Carbon dioxide and methane are the two major components which is responsible for the global warming. Methane gas having high potential to produce global warming compared to $CO_2$. The binary gas separation is the only way to reduce the contamination from the industry. Several membrane technologies are involved in this field to reduce the emission of $SO_2$, carbon monoxide, $CO_2$ and methane [52]. In large scale of air separation unit, there is a chance of high energy consumption and operational inconvenience. New algorithm was developed to optimize the problem associated in energy consumption. The developed system consumes lower energy (7.55 MW) compared to the original process [53]. In medical application, membranes are preferentially prepared by the biodegradable polymers in order to reduce the waste generation, improve the degradation time and control the environmental pollution factor. Biopolymers are mostly preferred due to its capable of undergoing enzymatic and hydrolytic degradation [54]. Polymeric cellulose acetate membrane is the commercially available membrane for removal of $CO_2$ and $H_2S$. The performance of the cellulose acetate membrane towards gas separation is based on the degree of acetylation present in the polymer. The flexibility of polymer chain, chain packing and mobility parameters are decided by the size difference between the hydroxyl and acetyl groups. This influences the gas permeation rate of the membrane [55]. The removal of $CO_2$ from flue gas can be achieved by using hollow fiber membrane module. It has high permeable nature compared to gas permselectivity [56].

**Conclusion**

The developments in the area of air separation are focused by the researchers to reach the maximum permittivity with higher selectivity. The growth of the utilization of polymer and its derivatives in the area of membrane construction is continuously growing and still lots of research are under development. Polymer with additives and other forms of polymeric materials will leads to the development of composite membrane for various applications. Construction of composite structural membrane with different forms of materials will give higher permittivity of the selected gas and membrane stability with higher life time.

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