

# Air Separation Technologies: Principles, Process Intensification, and Emerging Trends – A Comprehensive Review

Paluri Satya Veera Venkata Durga Phani Kumar<sup>1\*</sup> Solomon Godwin Babu N D<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Vignan's Foundation for Science, Technology and Research (Deemed to be University), Vadlamudi, Guntur-522213, Andhra Pradesh, INDIA

*Abstract — Air separation technologies are fundamental to modern industrial infrastructure, enabling the production of oxygen, nitrogen, and argon for applications in metallurgy, healthcare, electronics, and clean energy systems. Growing demand for high-purity gases and increasing pressure to reduce energy consumption have driven significant advancements in separation methodologies. This review critically examines established technologies, including cryogenic distillation, pressure swing adsorption (PSA), vacuum swing adsorption (VSA), and membrane-based systems, highlighting their governing principles, operational characteristics, and performance limitations. A comparative assessment is presented in terms of purity, energy efficiency, scalability, and economic feasibility. Recent progress in advanced adsorbents, high-selectivity polymeric and mixed-matrix membranes, and hybrid process configurations is discussed to illustrate emerging pathways for process intensification. Integration strategies with renewable energy systems and hydrogen production are also considered in the context of decarbonization. The review identifies key challenges such as energy intensity, material stability, and long-term performance degradation, and outlines research directions aimed at developing sustainable, modular, and energy-efficient air separation systems.*

*Index Terms — Air separation; Adsorption; Zeolites; Carbon molecular sieves; Metal-organic frameworks; Polymeric membranes; Mixed-matrix membranes; Ion transport membranes; Selectivity-permeability trade-off; Process intensification.*

## I. INTRODUCTION

Industrial gases such as oxygen, nitrogen, and argon constitute the backbone of numerous large-scale industrial operations and emerging clean-energy technologies. Oxygen is indispensable in steelmaking,

non-ferrous metallurgy, glass production, wastewater treatment, and medical therapy. Nitrogen is widely used for inerting, blanketing, food preservation, electronics manufacturing, and chemical processing, while argon plays a critical role in welding, semiconductor fabrication, and specialty lighting [1]. The global demand for these gases continues to grow, driven by rapid industrialization, expansion of healthcare infrastructure, and the transition toward low-carbon energy systems.

Atmospheric air, composed primarily of nitrogen (~78%), oxygen (~21%), and argon (~0.93%), represents an abundant and renewable feedstock for industrial gas production. However, the separation of these components into high-purity streams requires energy-intensive and technologically sophisticated processes due to their similar physicochemical properties. The small differences in boiling points and molecular sizes necessitate carefully engineered thermodynamic and kinetic separation strategies.

Cryogenic distillation remains the dominant technology for large-scale air separation, capable of producing ultra-high-purity oxygen and nitrogen along with valuable rare gases. Despite its maturity and reliability, cryogenic processing is capital-intensive and accounts for significant energy consumption in industrial gas production. In response to increasing energy costs and sustainability targets, alternative non-cryogenic approaches such as pressure swing adsorption (PSA), vacuum swing adsorption (VSA), and membrane-based separations have gained considerable attention. These systems offer modularity, rapid start-up, and lower capital

investment, making them attractive for decentralized and medium-scale applications [2].

Recent advances in materials science have further accelerated innovation in air separation technologies. High-performance adsorbents, including lithium-exchanged zeolites and carbon molecular sieves, have improved adsorption selectivity and cyclic stability. Concurrently, developments in polymeric membranes, mixed-matrix membranes, metal–organic frameworks (MOFs), and ion transport membranes have expanded the design space for energy-efficient oxygen and nitrogen production. Nevertheless, challenges such as the permeability–selectivity trade-off, adsorbent degradation under cyclic operation, and scalability limitations remain significant barriers to widespread deployment.

In parallel, global decarbonization initiatives and the emerging hydrogen economy are reshaping the air separation landscape. Oxygen-enriched combustion, blue and green hydrogen production, and integrated gasification processes increasingly rely on efficient air separation units (ASUs). Consequently, there is a pressing need to reassess conventional technologies while exploring hybrid configurations and process intensification strategies that can reduce energy consumption and carbon footprint.

Given the rapid technological evolution and interdisciplinary nature of this field, a comprehensive and critical review of current air separation technologies is warranted. This paper systematically examines the principles, materials, process configurations, performance metrics, and sustainability aspects of cryogenic and non-cryogenic air separation systems. Emerging materials and hybrid process concepts are analyzed from both thermodynamic and techno-economic perspectives, with particular emphasis on energy efficiency and environmental impact. Finally, key research gaps and future directions are identified to guide the development of next-generation air separation technologies.

## II. Fundamentals of Air Separation

### 2.1 Composition and Physicochemical Properties of Air

Atmospheric air is a multicomponent gaseous mixture consisting primarily of nitrogen (78.08 vol%), oxygen (20.95 vol%), argon (0.93 vol%), and trace quantities of carbon dioxide, neon, helium, krypton, and xenon. The feasibility of separating these components depends largely on differences in thermodynamic properties such as boiling point, critical temperature, molecular size, polarizability, and adsorption affinity [3].

Nitrogen and oxygen exhibit relatively close boiling points ( $-196\text{ }^{\circ}\text{C}$  for  $\text{N}_2$  and  $-183\text{ }^{\circ}\text{C}$  for  $\text{O}_2$ ), resulting in a modest relative volatility ( $\sim 1.4$  at cryogenic conditions), which necessitates high-efficiency fractionation in cryogenic systems. Argon, with a boiling point of  $-186\text{ }^{\circ}\text{C}$ , lies between oxygen and nitrogen, making its separation more complex and often requiring an additional side column in cryogenic units. In non-cryogenic systems, separation is governed primarily by differences in adsorption equilibria or diffusion coefficients rather than phase equilibrium. Understanding these thermodynamic and kinetic contrasts forms the basis for selecting appropriate separation strategies [4].

### 2.2 Thermodynamic Basis of Cryogenic Separation

Cryogenic air separation relies on vapor–liquid equilibrium (VLE) principles. The separation efficiency depends on:

- Relative volatility ( $\alpha$ )
- Column pressure
- Reflux ratio
- Number of theoretical stages
- Heat integration efficiency

The double-column configuration (high-pressure and low-pressure columns) is widely adopted to enhance energy efficiency through internal heat exchange. The performance of cryogenic systems is strongly influenced by entropy changes during liquefaction and expansion processes, making heat exchanger effectiveness and compressor efficiency critical design parameters [5].

### 2.3 Adsorption Equilibria and Kinetics

In adsorption-based processes such as PSA and VSA, separation occurs due to preferential adsorption of one component over another on a porous solid surface.

Key governing parameters include:

- Adsorption isotherms (Langmuir, Freundlich, Toth models)
- Heat of adsorption
- Selectivity ( $\alpha_{ads}$ )
- Mass transfer resistance
- Cycle time and pressure ratio

Zeolitic adsorbents typically preferentially adsorb nitrogen over oxygen due to quadrupole interactions, enabling oxygen enrichment. Conversely, carbon molecular sieves exploit kinetic selectivity by allowing faster oxygen diffusion compared to nitrogen. Cyclic operation introduces additional complexities such as thermal effects, bed pressurization dynamics, and adsorbent aging [6].

#### 2.4 Membrane Transport Mechanisms

Membrane-based air separation operates primarily through the solution–diffusion mechanism in polymeric membranes, where permeability (P) is defined as:

$$P=D \times S$$

where:

- D = diffusivity
- S = solubility coefficient

Selectivity arises from differences in diffusivity and solubility between oxygen and nitrogen molecules. However, polymeric membranes face an inherent permeability–selectivity trade-off, often described by the Robeson upper bound. Advanced materials such as mixed-matrix membranes aim to surpass this limitation by incorporating porous fillers into polymer matrices.

#### 2.5 Energy Considerations in Air Separation

Air separation is inherently energy intensive due to compression, cooling, or vacuum generation requirements. Major contributors to specific energy consumption include:

- Air compression work
- Refrigeration duty (cryogenic systems)
- Adsorbent regeneration energy (PSA/VSA)
- Pressure drop losses
- Membrane pressure ratio requirements

Reducing energy intensity remains the central challenge in advancing air separation technologies. Process integration, waste heat recovery, advanced

materials, and optimized cycle design are primary pathways for improvement [7].

### III. MAJOR TECHNOLOGIES

#### 3.1 Cryogenic Air Separation Technology

Cryogenic distillation remains the dominant industrial route for large-scale production of high-purity oxygen, nitrogen, and argon as shown in Figure 1. Commercial air separation units developed by companies such as Linde plc, Air Liquide, and Air Products and Chemicals, Inc. operate on vapor–liquid equilibrium principles at extremely low temperatures. The process involves air filtration and multi-stage compression, removal of moisture and carbon dioxide via molecular sieves, cryogenic cooling through plate-fin heat exchangers, and partial liquefaction using turbo-expanders. Separation is achieved in a double-column configuration consisting of high-pressure and low-pressure distillation columns, with an additional argon side column when high-purity argon recovery is required. Cryogenic systems are capable of achieving ultra-high purities (>99.999%) and are economically favorable for very large capacities; however, they require substantial capital investment and remain energy intensive due to compression and refrigeration demands [8].

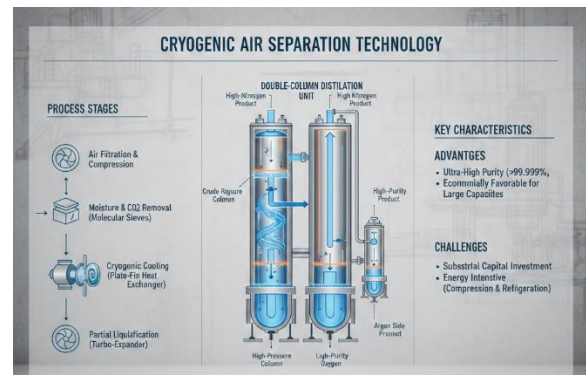


Fig. 1 Overview of Cryogenic Air Separation Technology

#### 3.2 Pressure Swing Adsorption (PSA)

Pressure swing adsorption (PSA) and its variant, vacuum swing adsorption (VSA), separate air components based on preferential adsorption at elevated pressure and desorption at reduced pressure as shown in Figure 2. These systems operate near

ambient temperature and employ porous adsorbents such as lithium-exchanged zeolites, zeolite 13X, and carbon molecular sieves. In oxygen PSA units, nitrogen is selectively adsorbed, enriching oxygen in the product stream, whereas nitrogen PSA systems rely on kinetic selectivity using carbon molecular sieves. Multiple adsorption beds operate in cyclic sequences to ensure continuous output. PSA/VSA technologies offer modular design, lower capital cost, rapid start-up, and suitability for decentralized or medium-scale production. Nevertheless, oxygen purity is generally limited to 90–95% in standard PSA units, and long-term adsorbent stability under cyclic loading remains a technical challenge [9].

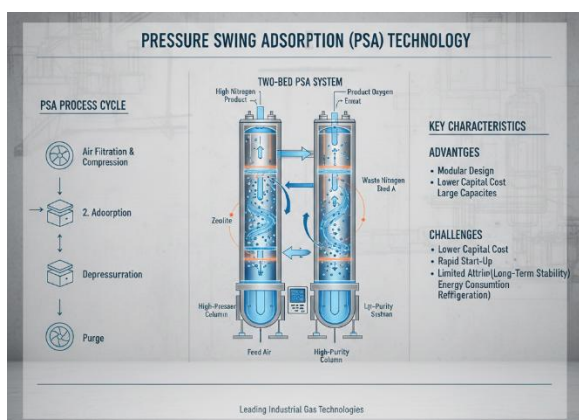


Fig. 2 Overview of Pressure Swing Adsorption Technology

### 3.3 Membrane-Based Air Separation

Membrane-based air separation relies on selective gas permeation through semi-permeable barriers, typically governed by the solution–diffusion mechanism in polymeric materials as shown in Figure 3. Oxygen permeates faster than nitrogen due to differences in diffusivity and solubility, enabling oxygen enrichment or nitrogen production without phase change. Common membrane materials include polyimide, polysulfone, cellulose acetate, and mixed-matrix membranes incorporating porous fillers to enhance performance. Membrane systems are compact, lightweight, energy efficient for moderate separations, and require minimal maintenance, making them attractive for offshore platforms, inerting applications, and portable nitrogen generation. However, single-stage oxygen purity is typically limited to moderate enrichment levels, and membrane performance is

constrained by the permeability–selectivity trade-off, as well as aging, plasticization, and contamination effects [10].

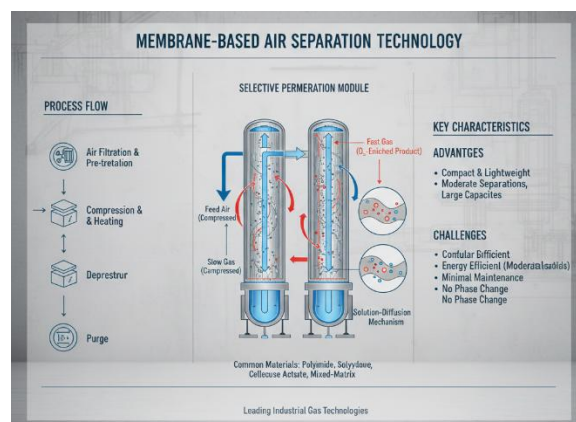


Fig. 3 Overview of Membrane-Based Air Separation Technology

## IV. FUTURE PERSPECTIVES AND RESEARCH GAPS

Despite the technological maturity of cryogenic air separation, significant research gaps remain in reducing specific energy consumption and improving operational flexibility. Cryogenic units are inherently energy intensive due to multistage compression and refrigeration requirements, and further gains depend on advanced heat integration, improved column internals, and high-efficiency turbo-expanders. However, dynamic operability under fluctuating renewable power inputs remains insufficiently explored. The integration of air separation units with hydrogen production, oxy-fuel combustion, and carbon capture systems also requires systematic thermodynamic optimization and real-time control strategies. Additionally, scaling down cryogenic systems for modular deployment without compromising efficiency represents an unresolved engineering challenge [11].

In adsorption-based processes, the primary research gap lies in the development of adsorbents with higher selectivity, faster kinetics, and superior cyclic stability. Although lithium-exchanged zeolites and carbon molecular sieves are commercially established, issues such as thermal degradation, moisture sensitivity, and structural collapse during repeated pressure cycling limit long-term performance. There is

a need for advanced porous materials—such as defect-engineered zeolites, hierarchical structures, and metal–organic frameworks—with improved mechanical strength and resistance to contamination. Furthermore, predictive multiscale modeling that couples adsorption thermodynamics, mass transfer, and heat effects remains underdeveloped, hindering rational cycle optimization and scale-up [12].

For membrane-based systems, overcoming the permeability–selectivity trade-off continues to be a central scientific challenge. While mixed-matrix membranes and facilitated transport membranes show promise, issues related to filler–polymer compatibility, interfacial defects, and long-term aging restrict industrial adoption. Stability under high pressure, resistance to plasticization, and tolerance to impurities require further investigation. Moreover, hybrid process configurations combining membranes with PSA or cryogenic polishing steps have not yet been comprehensively optimized from a techno-economic standpoint. Future research should therefore focus on integrated process design, advanced materials engineering, digital optimization, and sustainability-driven system development to enable next-generation, low-carbon air separation technologies [13].

V. CHALLENGES AND LIMITATIONS

Air separation technologies, despite decades of industrial refinement, face persistent technical and economic constraints. A primary challenge across all process routes is high energy intensity, particularly in cryogenic systems where multistage compression, deep refrigeration, and distillation contribute significantly to operating costs. Fluctuating electricity prices and increasing decarbonization targets further intensify pressure to reduce specific energy consumption. Additionally, large-scale cryogenic units require substantial capital investment and long installation times, limiting flexibility for decentralized or rapidly changing demand scenarios. Operational safety associated with handling cryogenic fluids and high-pressure oxygen streams also necessitates stringent design and maintenance protocols [14].

Adsorption-based systems encounter limitations related to material stability and cyclic durability. Repeated pressurization–depressurization cycles can lead to adsorbent attrition, pore blockage, and

performance degradation over time. Moisture sensitivity and contamination from feed air impurities further compromise selectivity and adsorption capacity. Thermal effects during rapid cycling may induce hot spots within adsorption beds, reducing efficiency and accelerating material aging. Moreover, PSA and VSA systems typically produce oxygen at moderate purity levels compared to cryogenic distillation, restricting their applicability in ultra-high-purity industrial sectors.

Membrane-based air separation faces inherent material and process constraints. The well-known permeability–selectivity trade-off limits the simultaneous achievement of high flux and high separation efficiency in polymeric membranes. Long-term aging, plasticization under elevated pressures, and fouling from particulates or condensable vapors reduce membrane lifespan and reliability. Scaling membrane modules for high-capacity applications while maintaining mechanical integrity and consistent performance remains a challenge. Furthermore, economic viability becomes sensitive to pressure ratio requirements, as increased compression directly impacts energy consumption. Collectively, these limitations highlight the need for materials innovation, process intensification, and advanced system integration to achieve sustainable and cost-effective air separation [15].

VI. COMPARATIVE STUDIES

Table 1 Comparative Analysis of the Technologies

Parameter	Cryogenic Distillation	Pressure Swing Adsorption (PSA/VSA)	Membrane Separation
Separation Principle	Vapor–liquid equilibrium (fractional distillation)	Preferential adsorption under cyclic pressure variation	Selective permeation (solution–diffusion mechanism)
Operating Temperature	Very low (≈ -170 to -196 °C)	Near ambient	Near ambient
Operating Pressure	5–10 bar (typical)	1–10 bar (PSA), vacuum regeneration (VSA)	5–20 bar (feed side)

O <sub>2</sub> Purity	Up to 99.999%	90–95% (standard)	30–45% (single stage)
N <sub>2</sub> Purity	Up to 99.999%	Up to 99.999% (CMS-based)	95–99% (multi-stage)
Argon Recovery	Yes (with side column)	Not practical	Not practical
Production Scale	Large (>1000 TPD O <sub>2</sub> )	Small–Medium	Small–Medium
Specific Energy Consumption	High (≈200–250 kWh/ton O <sub>2</sub> )*	Moderate	Low–Moderate
Capital Expenditure (CAPEX)	Very High	Moderate	Low
Operational Flexibility	Moderate	High	Very High
Start-Up Time	Long (hours–days)	Short (minutes)	Very short
Process Complexity	High	Moderate	Low
Maintenance Requirements	High	Moderate	Low
Main Limitations	High energy and capital cost	Adsorbent degradation, moderate O <sub>2</sub> purity	Permeability–selectivity trade-off, aging

## VII. CONCLUSIONS

Air separation technologies remain indispensable to modern industry, supplying oxygen, nitrogen, and argon for applications spanning metallurgy, healthcare, petrochemicals, electronics, and emerging clean-energy systems. Among the available technologies, cryogenic distillation continues to dominate large-scale production due to its capability to deliver ultra-high-purity gases and co-produce rare components. However, its high capital intensity and energy demand underscore the need for continued improvements in thermodynamic efficiency, heat integration, and operational flexibility.

Non-cryogenic alternatives, including pressure swing adsorption (PSA), vacuum swing adsorption (VSA), and membrane-based systems, provide modular, decentralized solutions with lower capital

requirements and faster start-up times. Adsorption processes are well suited for medium-scale oxygen and nitrogen generation, whereas membrane systems offer compact and energy-efficient options for moderate separations and inert applications. Nevertheless, these technologies are constrained by limitations in achievable purity, material stability, and long-term performance under cyclic or high-pressure conditions.

Future progress in air separation will depend on synergistic advances in materials science, process intensification, and digital optimization. The development of robust high-selectivity adsorbents, advanced membrane architectures, and hybrid process configurations is essential to overcome current performance bottlenecks. Integration with renewable energy systems, hydrogen production, and carbon capture infrastructure will further shape next-generation air separation units. Ultimately, achieving lower energy consumption, improved sustainability, and enhanced operational flexibility will define the trajectory of air separation technologies in the transition toward a low-carbon industrial landscape.

## REFERENCES

- [1] Sekhar, C., Farahani, A. S., Khader, M. A., Kalyvas, C., & Chizari, M. (2026). Simulation and Optimisation of Hydrogen Production from Biogas via Steam–Methane Reforming and Cryogenic Liquefaction Using DWSIM. *Processes*, 14(3), 532.
- [2] Lee, T. H., Lee, B. K., Cho, Y. H., Kim, H. W., Han, S. H., Ha, S. Y., & Park, H. B. (2026). Advanced polymeric membranes for CO<sub>2</sub> separation: Fundamentals, materials, and practical challenges. *Materials Horizons*.
- [3] Ackley, M. W. (2019). Medical oxygen concentrators: a review of progress in air separation technology. *Adsorption*, 25(8), 1437–1474.
- [4] Murali, R. S., Sankarshana, T., & Sridhar, S. (2013). Air separation by polymer-based membrane technology. *Separation & Purification Reviews*, 42(2), 130–186.
- [5] Elehinafe, F. B., Aondoakaa, E. A., Akinyemi, A. F., Agboola, O., & Okedere, O. B. (2024). Separation processes for the treatment of industrial flue gases—effective methods for

- global industrial air pollution control. *Heliyon*, 10(11).
- [6] Prasad, R., Notaro, F., & Thompson, D. R. (1994). Evolution of membranes in commercial air separation. *Journal of Membrane Science*, 94(1), 225-248.
- [7] Thorogood, R. M. (1991). Developments in air separation. *Gas separation & purification*, 5(2), 83-94.
- [8] He, X., Liu, Y., Rehman, A., & Wang, L. (2021). A novel air separation unit with energy storage and generation and its energy efficiency and economy analysis. *Applied Energy*, 281, 115976.
- [9] Young, A. F., Villardi, H. G., Araujo, L. S., Raptopoulos, L. S., & Dutra, M. S. (2021). Detailed design and economic evaluation of a cryogenic air separation unit with recent literature solutions. *Industrial & Engineering Chemistry Research*, 60(41), 14830-14844.
- [10] Castle, W. F. (2002). Air separation and liquefaction: recent developments and prospects for the beginning of the new millennium. *International Journal of Refrigeration*, 25(1), 158-172.
- [11] Zhang, X. B., Chen, J. Y., Yao, L., Huang, Y. H., Zhang, X. J., & Qiu, L. M. (2014). Research and development of large-scale cryogenic air separation in China. *Journal of Zhejiang University SCIENCE A*, 15(5), 309-322.
- [12] Baker, R. W. (2002). Future directions of membrane gas separation technology. *Industrial & engineering chemistry research*, 41(6), 1393-1411.
- [13] Vinson, D. R. (2006). Air separation control technology. *Computers & Chemical Engineering*, 30(10-12), 1436-1446.
- [14] Xu, Z., Zhao, J., Chen, X., Shao, Z., Qian, J., Zhu, L., ... & Qin, H. (2011). Automatic load change system of cryogenic air separation process. *Separation and Purification Technology*, 81(3), 451-465.
- [15] Ebrahimi, A., Meratizaman, M., Reyhani, H. A., Pourali, O., & Amidpour, M. (2015). Energetic, exergetic and economic assessment of oxygen production from two columns cryogenic air separation unit. *Energy*, 90, 1298-1316.