

Producing Nitrogen via Pressure Swing Adsorption

SVETLANA IVANOVA
ROBERT LEWIS
 AIR PRODUCTS

Pressure swing adsorption (PSA) can be a cost-effective method of onsite nitrogen generation for a wide range of purity and flow requirements.

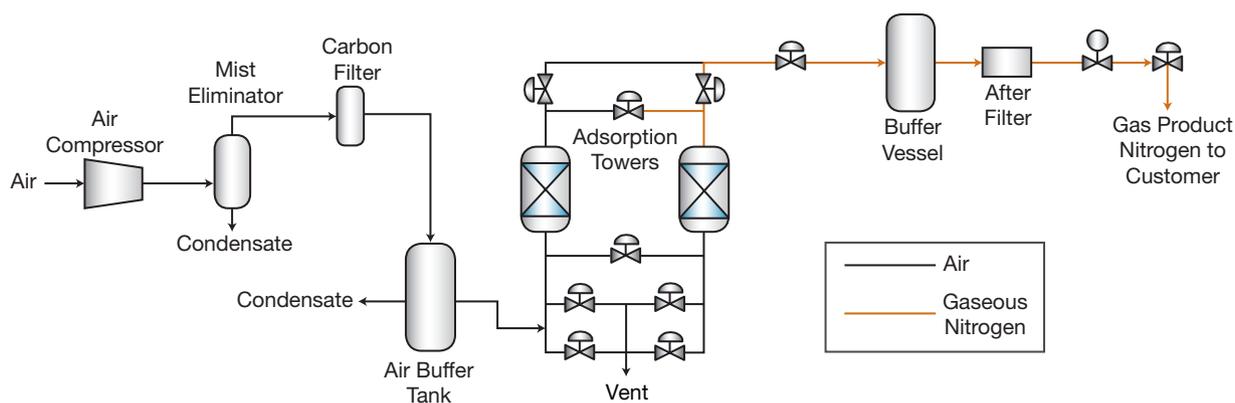
Nitrogen gas is a staple of the chemical industry. Because it is an inert gas, nitrogen is suitable for a wide range of applications covering various aspects of chemical manufacturing, processing, handling, and shipping. Due to its low reactivity, nitrogen is an excellent blanketing and purging gas that can be used to protect valuable products from harmful contaminants. It also enables the safe storage and use of flammable compounds, and can help prevent combustible dust explosions. Nitrogen gas can be used to remove contaminants from process streams through methods such as stripping and sparging.

Because of the widespread and growing use of nitrogen in the chemical process industries (CPI), industrial gas companies have been continually improving methods of nitrogen production and supply to make them more efficient, cost-

effective, and convenient for chemical processors. Multiple nitrogen technologies and supply modes now exist to meet a range of specifications, including purity, usage pattern, portability, footprint, and power consumption. Choosing among supply options can be a challenge. Onsite nitrogen generators, such as pressure swing adsorption (PSA) or membrane systems, can be more cost-effective than traditional cryogenic distillation or stored liquid nitrogen, particularly if an extremely high purity (*e.g.*, 99.9999%) is not required.

Generating nitrogen gas

Industrial nitrogen gas can be produced by either cryogenic fractional distillation of liquefied air, or separation of gaseous air using adsorption or permeation. German engineer Carl von Linde developed cryogenic distillation of



▲ **Figure 1.** PSA systems can provide a reliable, low-cost nitrogen supply to meet a wide variety of process requirements.

air, the oldest method of nitrogen production, in 1895 (1). Cryogenic distillation is still used today in large commercial air separation plants, and accounts for nearly 65–70% of the total nitrogen production (2).

Leonard Pool (the founder of Air Products) introduced the concept of generating industrial gases onsite in the early 1940s. Onsite cryogenic plants were built on or near the user's site, and the product was delivered by pipeline. This method provided a low-cost, reliable supply for large-volume users of industrial gases. However, due to the relatively high capital and power costs associated with onsite cryogenic plants, smaller-volume users were typically limited to liquid nitrogen supply delivered by vacuum-insulated trucks. The stored liquid nitrogen was vaporized and piped as needed.

In the 1980s, alternative methods of onsite gaseous nitrogen generation, such as PSA and membrane separation, came into practice. Initially, these techniques were suitable only for small-volume, low-purity applications. Today, however, PSA and membrane systems are an efficient supply mode for a variety of volumes, purity requirements, and usage patterns.

PSA systems operate on the principle of adsorption, whereas membrane systems separate based on selective permeation.

Pressure swing adsorption. In the PSA process (Figure 1), compressed air first passes through a combination of filters to remove entrained oil and water. The purified air is then directed to one of two adsorption vessels that are packed with carbon molecular sieves (CMS). The remaining impurities, such as carbon dioxide and residual moisture, are adsorbed by the CMS at the entrance of the adsorbent bed. At high pressures, the CMS selectively adsorbs oxygen, allowing nitrogen to pass through at the desired purity level. While one vessel is producing nitrogen, the second vessel

The two most important factors to consider when choosing among nitrogen supply options are the required nitrogen purity and the required nitrogen flowrate.

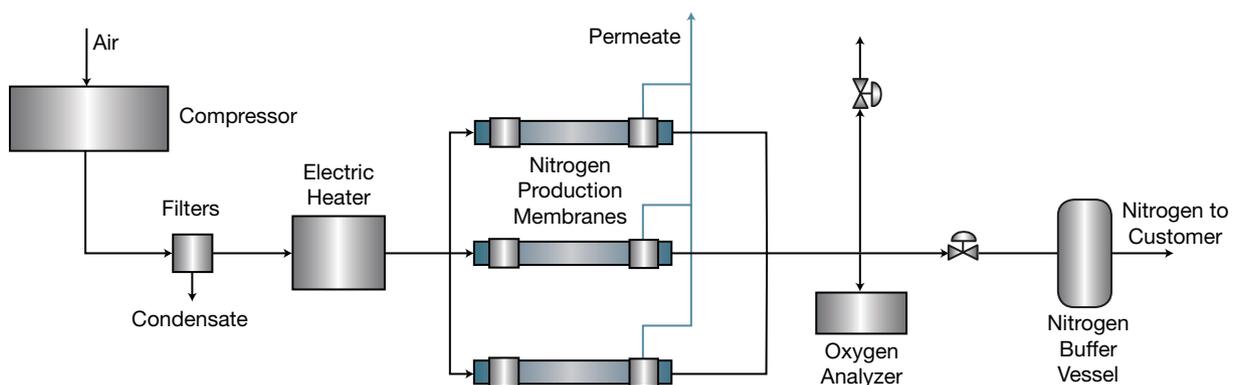
is depressurized to remove the adsorbed oxygen, which is then vented to the atmosphere. The automatic cycling of adsorption and desorption between the two beds enables the continuous production of nitrogen.

A large range of flow and purity combinations can be met by adjusting the size of the air compressor and adsorption vessels containing the CMS. PSAs can economically produce nitrogen gas at flowrates from less than 5,000 scfh to greater than 60,000 scfh, and at purities ranging from 95% to 99.9995%.

Membrane separation. Membrane systems operate on the principle of selective gas permeation. A typical membrane process (Figure 2) uses several membrane modules, each containing thousands of hollow fibers. Every molecule passing through the fibers has a characteristic permeation rate that is a function of its ability to dissolve in, diffuse through, and dissolve out of the hollow-fiber membrane. The permeation rate is the product of the solubility and diffusivity rates of the gas in the membrane. When compressed air passes through the fibers, oxygen, water vapor, and carbon dioxide are selectively removed, creating a nitrogen-rich product stream.

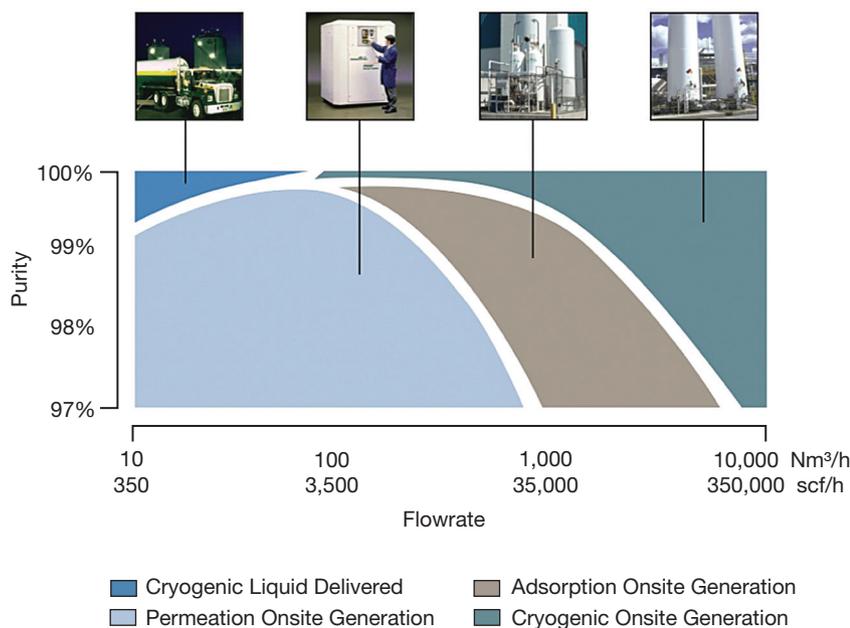
Membrane systems typically produce nitrogen with a purity of 95–99.5%, and, in some cases, greater than 99.9% nitrogen purity. Product purity depends on the feed purity, available differential partial pressure, and desired recovery level.

Article continues on next page

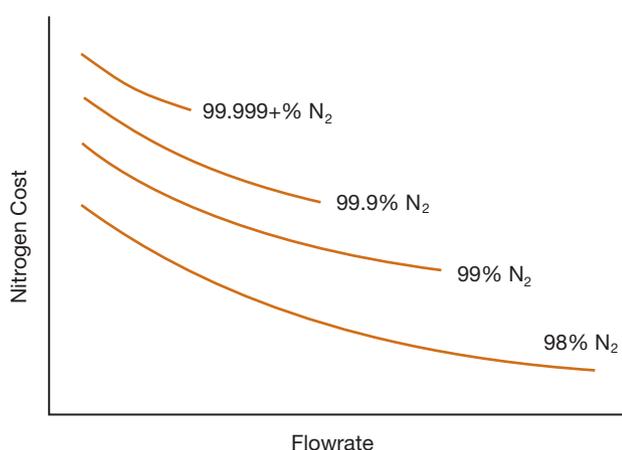


▲ Figure 2. Membrane systems use selective gas permeation to generate nearly pure nitrogen.

Reactions and Separations



▲ **Figure 3.** Choosing between nitrogen supply options depends on flowrate and purity requirements.



▲ **Figure 4.** Nitrogen purity and flowrate requirements can affect nitrogen cost. Higher purity comes at a price, but higher volume generally reduces the unit cost of nitrogen. For maximum savings, use a nitrogen purity no higher than the application requires.

When to select PSA

With multiple nitrogen supply options and technologies available, selecting the right system for a specific application can seem complicated. However, the two most important factors to consider when choosing among PSA onsite generation, permeation membrane systems, cryogenic distillation, and liquid delivery are the required nitrogen purity and the required nitrogen flowrate. The nitrogen purity necessary to meet the application's safety and product quality require-

ments must be determined, as well as the plant's day-to-day nitrogen flow requirements. These two factors will help determine the best system for nitrogen supply (Figure 3).

Nitrogen purity. Nitrogen provides safety and quality for chemical manufacturing processes (3). Because nitrogen is an inert gas, it is used to protect sensitive materials and prevent fires and explosions. It can be a challenge to determine the most suitable nitrogen purity. However, nitrogen costs can be reduced if a low purity is acceptable.

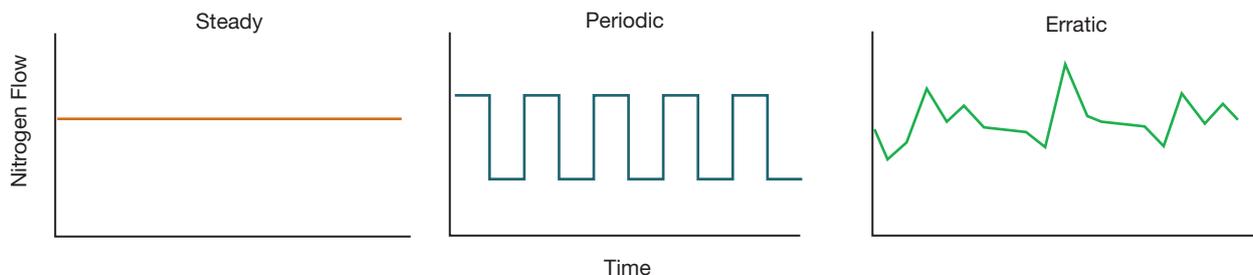
PSA can produce nitrogen at a range of purities. The lower the purity, the lower the unit cost of the nitrogen (Figure 4). For example, the quality of some vegetable oils can be maintained by blanketing and/or sparging with 99.5% nitrogen purity. This can be achieved easily by PSA.

The nitrogen purity required to blanket a flammable material can be determined based on the material's limiting oxygen concentration (LOC) or lower flammability limit (LFL). LOC values for many chemicals can be found in chemical engineering and chemistry handbooks, as well as in the National Fire Protection Association's NFPA 69: Standard on Explosion Prevention Systems (4). Table 1 lists the LOC for a few common chemicals. A substance's LFL can be found on the safety data sheet (SDS) provided by the manufacturer.

NFPA 69 requires hazardous processes to operate well below the LOC and LFL, typically at around 60% of these values. For example, a flammable material with an LOC of 10% would require an atmosphere of 94% nitrogen to meet NFPA guidelines. However, a more-conservative 25% of the LOC, or 97.5% nitrogen, adds a larger safety buffer. A purity of 94–97.5% can be supplied by a PSA system.

Table 1. LOC for some common materials at ambient temperature and pressure. A table of LOC for many more materials can be found in NFPA 69 (4).

Material	LOC, vol.% O ₂
Propylene Oxide	5.8
Methanol	8.0
Ethanol	8.5
Acetone	9.5
Benzene	10.1
Vinyl Chloride	13.4



▲ **Figure 5.** Plotting nitrogen flowrate versus time reveals the application's flow pattern.

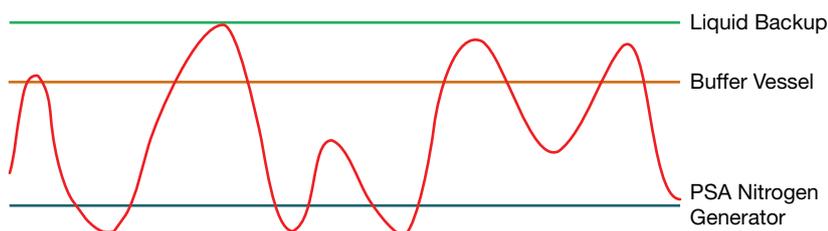
Nitrogen demand patterns. PSA nitrogen generators operate most economically at their full design capacity. Size optimization is critical for maximizing the economic benefit of a PSA system. For this reason, it is important to understand both the utilization rate (*i.e.*, hours of operation per month) as well as the nitrogen flow pattern. Identifying the flow pattern is crucial if instantaneous flowrates vary widely.

It can be difficult to predict the exact nitrogen usage pattern for a new process. Often, a new process is started up using liquid nitrogen and operated with a flow recorder installed on the main nitrogen supply line for an extended period of time (*e.g.*, 2–4 weeks). This will provide an accurate picture of the nitrogen flow pattern.

Nitrogen flow patterns at chemical plants typically fit into one of three categories: steady, periodic, or erratic (Figure 5).

A PSA nitrogen system is an excellent fit for a steady flow pattern, where the usage rate as a function of time is essentially constant. The PSA unit size can easily be matched to the measured or estimated usage rate. Furthermore, the unit will operate continuously at or near its full capacity, which makes nitrogen production the most economical.

A PSA system is not a good fit for a process with a periodic flow pattern, where the flow is characterized by peaks and valleys. An onsite generator feeding this flow demand, particularly if it is sized for a peak flow, will operate at partial capacity or idle for a significant amount of time. This results in operational inefficiency and high operating costs.



▲ **Figure 6.** The use of a PSA generator with liquid nitrogen backup for peak shaving can provide the optimal nitrogen supply system for erratic usage patterns.

However, if the duration of the valleys is short, a PSA combined with a large product buffer tank may be sufficient.

An erratic flow pattern represents the most common scenario in chemical plants. This flow pattern has a substantial continuous flow with some short irregularities. A PSA system can be sized to handle most of the nitrogen requirements, supplemented with liquid nitrogen during peak-demand periods (Figure 6). A properly designed system can achieve a utilization rate of 90% or better for this demand pattern.

Using nitrogen safely

Nitrogen is often mistakenly considered harmless because it is nontoxic and largely inert. However, nitrogen can act as an asphyxiant by displacing oxygen in air to levels below those required for survival. Therefore, use caution when handling nitrogen. Reference 5 provides more information about the safe handling of nitrogen.

Typical applications

Because nitrogen generated by PSA generally contains small amounts of oxygen, some types of chemical processes lend themselves better than others to this type of supply.

Manufacturing pressure-sensitive adhesives. The manufacture of pressure-sensitive adhesives involves flammable solvents and powders that present some safety hazards. In this process, finely ground rubber and fillers are added to flammable organic solvents in agitated tanks. Because vapors from the solvents are typically flammable in air, and the powders can generate significant sparks from the buildup of static electricity, reactions involving these materials can be dangerous in the presence of air (*i.e.*, 20.9% oxygen). For these reasons, an adhesives manufacturer was compelled to take steps to reduce the risk of explosions and fires.

First, the company installed static electricity eliminators. However, as these devices do not provide complete protection, occasional sparking was still a risk. Consequently, the manufac-

Reactions and Separations

turer installed a nitrogen purge system to reduce the oxygen content in the tanks to a nonflammable level of no more than 2.5%. A PSA system that produced nitrogen containing 2% oxygen was combined with an inerting system to achieve a safe operating atmosphere.

Storing and handling free-radical polymerization monomers. In some situations, it is desirable to have small amounts of oxygen present in an inert nitrogen atmosphere. For these applications, if the nitrogen is delivered as a liquid and then vaporized, some amount of air must be blended with the high-purity nitrogen to achieve the desired oxygen concentration. However, PSA nitrogen generators are a more economical and convenient alternative, as they provide nitrogen with a small oxygen content.

One manufacturer's process involved the storage and handling of monomers prior to free-radical polymerization. Monomer vapors are highly flammable and require an inert atmosphere in the storage headspace to prevent a safety hazard.

The monomers contained hydroquinone as an inhibitor to prevent premature polymerization during storage. To keep the hydroquinone active and to ensure the safe handling of the materials, a small volume of oxygen was required in the inert nitrogen gas. Two options could provide an inerting atmosphere with 2–4% oxygen: use liquid nitrogen, continuously blending it with oxygen, or install a PSA unit to provide a nitrogen product with the necessary oxygen level. The manufacturer selected a PSA system, which produced the required atmosphere and eliminated the additional blending steps.

Handling vinyl chloride monomer. Vinyl chloride monomer (VCM) is an important industrial chemical because of its use in a variety of products, including low-cost polymers. Almost all of the vinyl chloride produced goes into the manufacture of polyvinyl chloride (PVC), which is used in automotive parts, packaging, pipes, construction materials, furniture, and numerous other products (6).

VCM is extremely flammable as both a vapor and a liquid. When VCM is stored in closed containers, a flammable atmosphere can develop. Flammable mixtures of VCM can be readily ignited, even by static discharge (7).

The LFL for VCM is 3.8% (7). To prevent flammability, 25% of the LFL, which corresponds to 0.95% VCM or 99.05% nitrogen by volume, may be considered a sufficient atmosphere. However, because VCM can undergo polymerization or decomposition under certain conditions and in the presence of moisture and oxygen, a higher-purity nitrogen atmosphere was recommended.

Because of the application's purity and pattern requirements, a VCM manufacturer installed an inerting system with nitrogen supplied by a PSA unit, which provides 99.5% nitrogen.

Closing thoughts

Nitrogen is valued both as a gas for its inert properties and as a liquid for cooling and freezing. It supports a multitude of commercial and technical applications. Virtually any industry can benefit from nitrogen's unique properties to improve yields, optimize performance, protect product quality, and make operations safer.

Adsorption and other technologies for air separation continue to advance as more efficient, highly packaged, and compact gas generators are developed. Increased power efficiency in PSA nitrogen generators is being driven both by process improvements and enhanced adsorption materials. Nitrogen users will benefit from these advances as they evaluate supply options for new facilities and manage increased demand at existing plants.

CEP

LITERATURE CITED

1. **Linde, C.**, "Process of Producing Low Temperatures, the Liquefaction of Gases, and the Separation of the Constituents of Gaseous Mixtures," U.S. Patent 727,650 (1903).
2. **SRI Consulting**, "Air Separation Gases," IHS Chemical, www.ihs.com/products/chemical (Nov. 2011).
3. **Yanisko, P., et al.**, "Nitrogen: A Security Blanket for the Chemical Industry," *Chem. Eng. Progress*, **107** (11), pp. 50–55 (Nov. 2011).
4. **National Fire Protection Association**, "NFPA 69: Standard on Explosion Prevention Systems," Publication No. 69, NFPA, Quincy, MA (2008).
5. **Yanisko, P., and D. Croll**, "Use Nitrogen Safely," *Chem. Eng. Progress*, **108** (3), pp. 44–48 (Mar. 2012).
6. **Centers for Disease Control and Prevention**, "Vinyl Chloride: 5. Production, Import/Export, Use, and Disposal," www.atsdr.cdc.gov/toxprofiles/tp20-c5.pdf, CDC, Agency for Toxic Substances and Disease Registry, Atlanta, GA (Jul. 2006).
7. **The Dow Chemical Co.**, "Vinyl Chloride Monomer Material Safety Data Sheet," www.dow.com/webapps/msds/ShowPDF.aspx?id=090003e8800ec04d, Midland, MI (2011).

SVETLANA IVANOVA is a marketing and applications manager in the Merchant Gases Div. at Air Products (7201 Hamilton Blvd., Allentown, PA 18195-1501; Phone: (610) 481-1474, Fax: (610) 706-5665; Email: ivanovsm@airproducts.com), where she is responsible for developing and providing industrial gas-related technologies and solutions for the chemical, pharmaceutical, and biotech industries. She has diverse experience in technology, business development, and marketing, and her technical expertise includes developing new materials and processes for a variety of applications, including specialty surfactants, gas adsorption, and water treatment and analysis. Ivanova holds an MS from Moscow Chemical Technological Univ. and a PhD from Moscow Institute of General and Inorganic Chemistry of the Russian Academy of Sciences. She has been with Air Products for seven years.

ROBERT LEWIS is a marketing manager in the Merchant Gases Div. at Air Products (7201 Hamilton Blvd., Allentown, PA 18195-1501; Phone: (610) 481-4929; Fax: (610) 706-7394; Email: lewisrl@airproducts.com), where he is responsible for marketing activities related to onsite gas generation. He holds a BS in business and an MBA from the Univ. of Maryland, and has been with Air Products for 21 years.

For more information,
please contact us at:

Corporate Headquarters

Air Products and Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195-1501
T 800-654-4567 or 610-706-4730
F 800-272-4449
gigmrktg@airproducts.com

Asia

Air Products Asia, Inc.
1001, 10/F, Sunning Plaza
10 Hysan Avenue, Causeway Bay
Hong Kong
T +852-2527-1922
F +852-2527-1827

China

Air Products and Chemicals (China)
Investment Co. Ltd.
5/F, Building 72
887 Zu Chongzhi Road
Zhangjiang Hi-Tech Park
Shanghai, 201203
P.R. China
T +86-21-38962000
F +86-21-50807525

Europe

Air Products PLC
2 Millennium Gate
Westmere Drive
Crewe CW1 6AP
United Kingdom
T +44-800-389-02020
F +44-1932-258652
apbulkuk@airproducts.com



tell me more
airproducts.com