Nitrogen gas is a staple in the chemical process industries (CPI). Because it is inert, it is suitable for a wide range of applications in manufacturing, processing, handling, and shipping. Nitrogen is often used as a blanketing and purging gas to protect valuable products from contaminants. It enables flammable materials to be safely stored, and it can protect against combustible dust explosions. Nitrogen gas is also used to remove contaminants from process streams through stripping and sparging.

The widespread use of nitrogen in the CPI has driven nitrogen production and supply methods to become more reliable, efficient, cost-effective, and convenient. Multiple nitrogen technologies and supply modes are available to meet a variety of requirements, including purity, usage pattern, portability, and footprint. Choosing the optimal supply option, however, can be a challenge. Producing nitrogen gas on-site is a proven and cost-effective option for a wide range of flow and purity requirements. These generators use either noncryogenic separation processes, such as membrane permeation and pressure swing adsorption, or cryogenic processes, which rely on very low temperatures to separate nitrogen from compressed air (Figure 1).
Nitrogen gas generation systems

Industrial nitrogen gas is produced by cryogenic fractional distillation of liquefied air, separation of gaseous air by adsorption, or permeation through membranes. Cryogenic distillation of air is the oldest method of nitrogen production and was developed in 1895 (1). The concept of producing and selling industrial gases on-site was introduced in the early 1940s (2). These cryogenic plants were built on or near a customer’s site and the product was delivered via a pipeline. This method allowed customers that required large volumes of gases to significantly reduce product costs while enhancing raw material reliability. The relatively high capital and power costs associated with on-site cryogenic plants, however, limited users of smaller volumes to liquid nitrogen delivered by vacuum-insulated trucks. The nitrogen was stored on-site and then vaporized and piped to the point of use as needed.

The 1980s ushered in alternative methods of on-site generation, including pressure swing adsorption (PSA) and membrane separation. PSA systems operate on the principle of adsorption, whereas membrane systems rely on selective permeation. Early system designs produced nitro-
gen that was suitable mostly for small-volume, low-purity requirements. PSA and membrane systems have since improved and can now meet a range of volume, purity, and usage requirements.

Cryogenic nitrogen generation. Cryogenic air separation systems (Figure 2) compress atmospheric air in the main air compressor and then cool and treat the air to remove water vapor, carbon dioxide, and hydrocarbons. In the vacuum can, a heat exchanger cools and partially liquefies the air, which then passes into the distillation column, where the mixture is separated into nitrogen gas and an oxygen-enriched waste liquid. A small amount of liquid nitrogen may be injected or an expander installed to provide additional cooling. The nitrogen gas then flows into the supply line to downstream applications; the product may be compressed to meet pressure requirements.

Cryogenic nitrogen plants can supply high-purity gas at rates less than 25,000 standard cubic feet per hour (scfh) to more than 2 million scfh. They typically achieve standard purities of 5 ppm oxygen in nitrogen, although higher purities are possible.

PSA nitrogen systems. PSA systems (Figure 3) compress an air stream, which passes through a combination of filters to remove entrained oil and water. The purified air flows to one of two adsorption vessels that are packed with carbon molecular sieve (CMS). The CMS selectively adsorbs oxygen, allowing nitrogen to pass through at the desired purity level. Impurities, such as carbon dioxide and remaining moisture, also get adsorbed by the CMS. While one vessel is producing nitrogen, the second vessel is depressurized to remove adsorbed oxygen and other impurities, which are vented to the atmosphere. Automatic cycling of adsorption and desorption between the two beds enables continuous production of nitrogen.

Adjusting the size of the air compressor and adsorption vessels that contain the CMS enables a large range of flow and purity combinations. PSAs can economically produce nitrogen gas at flowrates from less than 2,000 scfh to greater than 60,000 scfh at purities of 95–99.9995%.

Membrane nitrogen systems. A typical nitrogen membrane system (Figure 4) uses multiple membrane modules that contain thousands of hollow membrane fibers each. Gases have a characteristic permeation rate that is a function of the solubility and diffusivity rate of the gas in the membrane. When compressed air passes through the fibers, oxygen, water vapor, and carbon dioxide are selectively removed, producing a nitrogen-rich product stream. Membrane systems typically produce 95–99.5% nitrogen purity.

Selecting a nitrogen generation system

With the bevy of options available, selecting and specifying the best nitrogen supply technology can seem complicated. You must first determine whether on-site generation or liquid delivery makes sense for your operation. To do this, consider the nitrogen purity required to maintain the safety and product quality of the application. Next, determine the daily nitrogen flow requirements, which will help determine the best system technology and size (Figure 5).

Nitrogen purity. Nitrogen is used in CPI facilities for safety and/or quality (3), but different applications often require different levels of gas purity. Although determining the most suitable nitrogen purity can be a challenge, nitrogen costs can be reduced if a lower purity is acceptable.

PSA and membrane systems can produce broad ranges of purity levels, but the lower the purity, the lower the

![Figure 4. In a membrane system, a compressed air stream flows through a series of nitrogen production membranes that each removes oxygen, water, and carbon dioxide, allowing nitrogen to pass through.](image-url)
unit cost. For example, the quality of some vegetable oils can be maintained by blanketing and/or sparging with a 99.5% nitrogen stream, which can be achieved easily by PSA. There can be a tradeoff between output and purity. For example, PSA nitrogen adsorbers of the same size can make 10,000 scfh of nitrogen at 99.5% purity or 20,000 scfh of nitrogen at 95% purity.

When flammable materials are involved, purity requirements can be determined from the limiting oxygen concentration (LOC). LOC values for many chemicals (Table 1) 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).

NFPA 69 requires operating at 60% of the LOC. For flammable materials with a LOC in the neighborhood of 10%, operating at 94% nitrogen would meet NFPA guidelines. However, operating at a more conservative 25% of LOC, or 97.5% nitrogen, ensures a larger safety buffer. A purity of 94–97.5% could be supplied by a PSA or membrane system.

**Nitrogen demand patterns.** Nitrogen generators operate most economically at full design capacity. Thus, choosing the optimum size during selection is critical to maximize the economic benefit. For this reason, it is important to understand both the utilization rate, or hours of operation per month, as well as the nitrogen flow pattern.

The monthly average nitrogen demand is not sufficient if instantaneous flowrates vary widely. In the case of a new process, for example, predicting the exact nitrogen usage pattern can be difficult. Often, a new process is started with liquid nitrogen for a given period of time to determine the flow pattern. To switch from liquid supply to gas generation, a flow recorder can be installed on the main nitrogen supply line for a period of 2–4 weeks. This provides an accurate picture of the nitrogen flow pattern, making system selection and sizing more apparent.

Nitrogen flow patterns can typically be categorized as steady, periodic, or erratic. A steady flow pattern is an excellent fit for an on-site nitrogen generator system because the usage rate as a function of time is essentially constant. The nitrogen generator size can be readily matched to the measured or estimated usage rate. In addition, the unit will be used continuously at or near its full capacity, which ensures economical nitrogen production.

It can be a challenge to size a gas generator system for a periodic flow pattern. The flow may oscillate between extreme peaks and valleys, sometimes dropping all the way to zero. A generator sized to meet peak demand will operate at partial capacity or be idle for a significant amount of time, which reduces the generator utilization rate and increases nitrogen costs. However, if low utilization valleys exist only for short periods of time, a nitrogen generator combined with a product buffer tank may be a suitable solution.

An erratic flow pattern, in which there is substantial continuous flow with some short irregularities, is the most common scenario. The gas generator system may be sized to handle a range of nitrogen requirements, and liquid nitrogen may be used to meet peak demand. A simulation program is useful for determining the ideal generator size in these instances. Proper design can achieve utilization rates of 90% or better for this demand pattern, providing an optimal economic solution.

**On-site generation vs. delivered nitrogen**

Consider a nitrogen user located in a developed industrial zone near an industrial gas plant that produces liquid nitrogen. The user requires intermittent batches of nitrogen several times per day. Liquid nitrogen delivered by truck makes the most sense to meet this demand pattern, as it is not a good fit for an on-site generator.

<table>
<thead>
<tr>
<th>Table 1. The nitrogen purity requirements for processes that use flammable materials can be determined from the limiting oxygen concentration (LOC).</th>
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</thead>
<tbody>
<tr>
<td><strong>Material</strong></td>
</tr>
<tr>
<td>Propylene Oxide</td>
</tr>
<tr>
<td>Methanol</td>
</tr>
<tr>
<td>Ethanol</td>
</tr>
<tr>
<td>Acetone</td>
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<tr>
<td>Benzene</td>
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<td>Vinyl Chloride</td>
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![Figure 5. Nitrogen users must determine the flowrate and purity required by their processes to select the appropriate and optimal nitrogen production option.](image)
Another nitrogen user requires nitrogen 24 hours per day and is located 50 km from a liquid nitrogen supplier. The facility has an average continuous nitrogen demand of 60 ton/day, with occasional demand peaks throughout the day. This user should consider an on-site nitrogen generation system to meet base load demand and procure liquid nitrogen for peaks beyond the system’s capacity.

Most plants move to on-site generation when their nitrogen requirements increase to a point where generation is more cost-effective than liquid nitrogen delivery. For example, a refinery had been using 12 different liquid nitrogen tanks. After considering flowrate, pressure, purity, and demand patterns, as well as conducting a safety review of the refinery’s system, the plant consolidated four individual tanks into one on-site generator. Combining the separate nitrogen uses took advantage of economies of scale and smoothed out the demand pattern to make it more conducive to on-site gas generation. An analysis of the remaining nitrogen requirements, usage patterns, and locations of the tanks did not justify any other nitrogen supply changes.

In another instance, a foam manufacturer used nitrogen for multiple applications throughout its operation. In addition, it planned to add a new reactor that would require short bursts of several gases, including nitrogen. The plant already had a small on-site generator that used membrane technology, but wanted to optimize nitrogen production and use. Membranes typically do not supply high-purity nitrogen, but 96–97% was sufficient for the applications at the plant. Even before adding the new reactor, the current system was struggling to provide enough nitrogen for the current process.

A flow evaluation and simulation of the flows and pressures in the facility piping revealed that the current system would not be able to provide enough nitrogen for the process and the new reactor. The piping was undersized and, due to pressure drop constraints, could not deliver enough nitrogen without new piping to expand capacity. If the piping of the existing generator had not been undersized, a larger generator would have solved the demand problem. However, in this case, the piping was too small for sufficient flow to reach the process.

Closing thoughts

Virtually any industry can benefit from nitrogen’s unique properties to improve yields, optimize performance, ensure product quality, and increase operational safety. Selecting the appropriate method of nitrogen supply is not always easy. Noncryogenic production of nitrogen by PSA or membrane systems can provide significant advantages in many applications, particularly when high purities of 99.999% are not required. Cryogenic generators, on the other hand, are a better option for applications that require high purities and a large and continuous volume of nitrogen. To determine which method of nitrogen generation is suitable for your application, first consider flow and purity requirements to minimize capital and operating expenses. Consult an industrial gas expert to identify the best and safest solution.

SAFETY MOMENT
Nitrogen Gas

Because nitrogen is nontoxic and largely inert, many consider it to be harmless. However, as with most industrial gases and chemicals, take precautions when handling and using nitrogen. Nitrogen can act as an asphyxiant by displacing the oxygen in air to levels below that required for life. Read the Beacon on p. 30 for a safety lesson on working near tanks purged or inerted with nitrogen, and read the March 2012 CEP article “Use Nitrogen Safely” (5) for more extensive information on safe handling of nitrogen.
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