

Online Gas Analysis in Air Separation Plants

Application

Emerson provides several Rosemount Analytical gas analyzer technologies to meet the process control and purity monitoring needs of air separation plants.

Background

A typical air separation plant divides atmospheric air into the three pure gaseous components of nitrogen (N₂), oxygen (O₂) and argon (Ar). Some plants provide further separation to include other gases such as neon, krypton and xenon. Other gas components of air, such as water vapor, carbon dioxide (CO₂) and hydrocarbons, are contaminants which must be removed to ensure safety, efficient plant operation and product purity/quality.

General Operation of an Air Separation Plant

There are three basic technologies that enable the separation of air into its pure components. These processes include:

- Cryogenic fractionation
- Pressure Swing Absorption (PSA)
- Membrane separation

Reduced cost and easy on-site production in exchange for less purity has made the newer non-cryogenic processes more attractive.

Molecular sieves preferentially absorb gas molecules to separate oxygen from nitrogen in the pressure swing adsorption technology.

Likewise, membrane technology allows for the rapid permeation of oxygen and water away from the remaining nitrogen product stream that flows through membrane fiber bores.

Traditional Cryogenic Fractionation

The primary unit operation of an air separation plant is traditionally based upon the cryogenic fractionation of air into its pure components.

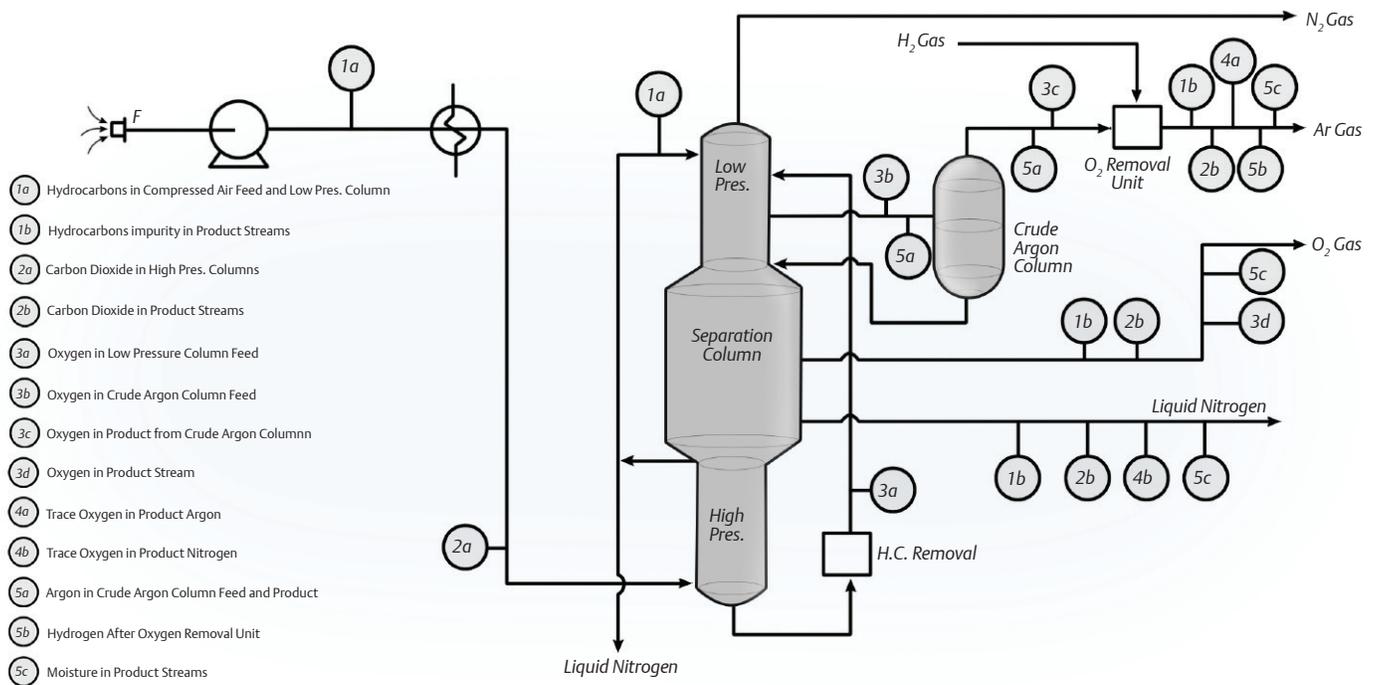
Although product gas type and purity levels affect the variation of plant designs, air separation units operate with a refrigeration cycle system based upon repeated compression, cooling and expansion, and then liquid fractionation. All processes, however, follow these three general stages:

- **Compression:** Normally, the total air feed is compressed to 1500 psig using water sealed, multi-stage compressors to avoid hydrocarbon contamination from lubricating oils. Further compression to about 2000 psig is frequently accomplished by an expansion engine.
- **Refrigeration/Liquefaction:** Cooling is accomplished in stages. Starting with the heat exchange, cooling water removes the heat of compression and is followed by the exchange against various other streams such as waste nitrogen. Final cooling is frequently obtained in an expansion engine which isentropically expands chilled, high-pressure feed and uses the mechanical energy obtained to further compress the feed. The resulting mixture of liquid and vapor air is separated and fed to the fractionator.
- **Separation:** Separation of air into its pure components is accomplished in a two-stage fractionator, usually called the high-pressure and low-pressure columns. Crude feed consisting of about 35 % liquid oxygen is produced as a bottom product from the high-pressure column and then becomes feed to the low-pressure column. Some additional refrigeration is obtained by flashing this stream across an expansion valve. The air fractionator is usually constructed so that the heat released from condensation of vapor in the upper part of the high-pressure column is used to boil the reboiler in the low-pressure column. Pure oxygen (either vapor or liquid) is withdrawn from the lower region of the low-pressure column near the reboiler.

Pure nitrogen gas is taken off the overhead. Liquid nitrogen is usually obtained as a portion of the reflux to the low-pressure column.

The fractionator equipment is located in a well insulated container called a "cold box". As with any fractionation process, it is necessary to control various liquid levels, flow rates and energy inputs to obtain an efficient balance between product purity and throughput.

Figure 1 - Gas Bottling Plant Gas Analyzer Applications



- 1a Hydrocarbons in Compressed Air Feed and Low Pres. Column
- 1b Hydrocarbons impurity in Product Streams
- 2a Carbon Dioxide in High Pres. Columns
- 2b Carbon Dioxide in Product Streams
- 3a Oxygen in Low Pressure Column Feed
- 3b Oxygen in Crude Argon Column Feed
- 3c Oxygen in Product from Crude Argon Column
- 3d Oxygen in Product Stream
- 4a Trace Oxygen in Product Argon
- 4b Trace Oxygen in Product Nitrogen
- 5a Argon in Crude Argon Column Feed and Product
- 5b Hydrogen After Oxygen Removal Unit
- 5c Moisture in Product Streams

Gas Analyzer Applications

Production costs associated with an air separation plant are primarily related to energy costs. These costs can be burdensome to plant goals if process variables are not closely scrutinized. Gas analyzers can be used throughout these processes to monitor efficiency and end product quality.

A summary of applications for traditional cryogenic applications follows below. Non-cryogenic applications will have similar applications for intermediate and final product quality. See figure 1 for source point locations.

1) Trace Hydrocarbon Measurement

Since the starting material for manufacture of pure gases is typically ambient air, there will likely be present some concentration of hydrocarbons in the feed gas. All hydrocarbons have a higher dew point than the three key components of air and therefore will condense long before any of the desired products. In the cryogenic process, these hydrocarbons can accumulate in the reboiler of the low pressure column and reach a concentration level resulting in an explosive mixture. The buildup of hydrocarbons is particularly dangerous because of their explosive nature in combination with liquid oxygen.

a) Hydrocarbons in Compressed Air Feed and Low Pressure Column

Measurements in the range of 0 to 25 and 0 to 50 ppm will meet the monitoring needs of these points.

b) Hydrocarbons Impurity in Product Streams

For assurance of product quality, measurements in the range of 0 to 10 down to 0 to 1 ppm are required.

Trace hydrocarbon measurement is easily achieved using the NGA FID and Model 400A total hydrocarbon analyzers. Sensitivity as low as 10 ppb and full scale ranges as low as 0 to 1 ppm THC make these instruments an ideal solution.

2) Carbon Dioxide Measurement

Carbon dioxide is one of the unwanted impurities found in the ambient air feed gas. By utilizing refrigeration and purification steps, CO₂ is removed prior to introduction to the distillation column. By measuring the concentration after the refrigeration process, the efficiency of the heat exchangers can be monitored and corrected. Trace measurements are also made in product streams to assure product quality.

a) Carbon Dioxide in High Pressure Column Feed

Typically CO₂ is monitored in the 0 to 10 ppm range.

b) Carbon Dioxide in Product Streams

CO₂ is often an unwanted impurity in product due to its oxidizing potential. Typical measurement is in the 0 to 10 ppm range.

Carbon Dioxide impurities can be monitored using the X-STREAM analyzer which uses non-dispersive infrared methodology.

3) Percent Oxygen Measurement

Oxygen is one of the key product components generated in the cryogenic process. The measurement of percent oxygen is important in the low pressure column feed which derives from the bottoms of the high pressure column. This feed liquid is oxygen enriched air and monitoring the oxygen concentration provides information on proper control of the high pressure column.

Following the low pressure column is the crude argon column feed which is typically high in oxygen content. Monitoring the feed and product streams provides information on the operation of the low pressure column and the requirements/efficiency of the crude argon column. The final oxygen measurement requirement is on the oxygen product stream for product purity measurement.

a) Oxygen in Low Pressure Column Feed

This stream typically requires a measurement of 0 to 50% oxygen. If the value is too low, too much liquid is being withdrawn. If the reading is too high, the column is taking too much of the load and greater output may be possible without loss of purity.

b) Oxygen in Crude Argon Column Feed

When argon product is generated, the feed stream comes from the low pressure column and contains in excess of 80 % oxygen. Measuring ranges of 0 to 100 % and 80 to 100 % are desired.

c) Oxygen in Product from Crude Argon Column

The crude argon column basically separates the argon from oxygen. By monitoring the output, column efficiency and oxygen removal load can be determined. Measurement range of 0 to 20 % is typical for this application.

d) Oxygen in Product Stream

The final analysis for oxygen is the purity of the endproduct. This measurement requires a range of 98 to 100 %.

Zero based measurements can be made with the X-STREAM analyzer, while high purity measurements can be made by the MLT analyzer.

4) Trace Oxygen Measurement

The measurement of trace oxygen is important for controlling the product purity of both the argon and nitrogen product streams. Since oxygen is one of the major components of air and it is an unwanted impurity in product argon and nitrogen, the measurement of oxygen is important for process control and product quality. The higher the oxygen impurity present in the product, the less valuable the product becomes.

a) Trace Oxygen in Product Argon

It is desirable to maintain oxygen impurities to less than 5 ppm.

b) Trace Oxygen in Product Nitrogen

Similarly, product nitrogen has an oxygen impurity requirement of less than 5 ppm.

The MLT 2 offers measurements as low as 0 to 100 ppm.

5) Other Measurements

In addition to the major measurements listed above, the following measurements are also part of the air separation process:

a) Argon in Crude Argon Column Feed and Product

These measurements are normally accomplished by thermal conductivity as utilized in the X-STREAM and MLT analyzers. The Feed concentration is typically 0 to 50 % while the product measurement is 85 to 100 %.

b) Hydrogen After Oxygen Removal Unit

Hydrogen is introduced to the crude argon column product in excess of what is stoichiometrically required to remove the oxygen impurity. This excess hydrogen is monitored to control addition and conversion efficiency. The measurement is accomplished with the X-STREAM analyzer with a typical range of 0 to 3 %.

c) Moisture in Product Streams

A summary of the applications discussed above is shown in Table 1.

These analyses can be made in either gas or liquid streams by use of a proper sample handling system, depending upon the type of product.

As mentioned earlier, the specific design of an air separation plant depends upon the type and purity of its products. Consequently, the exact nature of the analysis instrumentation required will depend also upon specific plant design. The possible applications mentioned above are typical and should not be regarded as necessary for all plants.

Gas Phase Samples

Usually, a gaseous phase sample is conditioned in approximately the following sequence:

- Initial filtration
- Pressure reduction and control
- Transport to analyzer location
- Multiple stream switching (if required)
- Sample and bypass flow control
- Calibration gas switching (if needed)
- Analysis

Sample Handling Requirements

As with any process analyzer application, a proper sample conditioning system is required to obtain an accurate and reliable analysis. Air separation plant analyzer applications are no exception. Although the streams to be sampled are almost always clean and free of contaminants, there are several other important factors which, if ignored can result in a faulty analysis.

In air separation plants, where many analyses are in the parts-per-million concentration range, particular attention must be paid to avoiding false analyses which can easily be caused by absorption of the component analyzed on materials used in the sampling system. Another error source can be diffusion of atmospheric constituents into the sampled through small leaks and some plastic materials. The former can be minimized using clean, nonabsorptive materials. Chemically passivated stainless steel is best for low moisture analyses.

Maintaining high by-pass flow rates relative to the tubing size used is an effective means to assure fast equilibration of system and sample. For very low parts-per-million analysis (<25 ppm), it is important to avoid use of plastic tubing for sample lines and other possible diffusion error sources such as elastomer diaphragms in pressure regulators. Where pumping of samples is required and rubber diaphragm pumps are used it is advantageous to back-purge the outside of the diaphragm to keep out the atmospheric contaminants. As with any well-designed system, dead-ended volume should be kept at a minimum to reduce sample transport lag.

Liquid Phase Samples

There are several analysis applications in air separation plants requiring liquid cryogenic stream sampling. These must be vaporized with care to obtain representative compositions and to avoid excessive time lags. The former is not a difficult problem when there is a small difference in volatility between the analyzed component and the main body of liquid. Here it is only necessary to supply the needed latent and appropriate heat to provide a vapor at room temperature.

Representative vaporization can be a serious problem where the component of interest boils at a much higher temperature than the rest of the sample (e.a., hydrocarbons in liquid oxygen). Unless a properly designed vaporizer is used, fractionation will occur in which hydrocarbons accumulate in unvaporized form in parts of the system and vaporize later in larger quantities, causing oscillations in observed hydrocarbon analysis. Two methods which have been successfully used are vaporization by spraying or by dripping liquid

against a heated surface. Sufficient heat is transferred quickly so that the entire sample is very quickly flashed, including any higher boiling materials like hydrocarbons.

A corollary problem lies in making sure that no significant vaporization occurs between the process sample tap and the vaporizer, especially when a liquid bypass is used to speed response time. In such a case it is wise to provide a separating device to assure that only liquid is admitted to the vaporizing section. Such a device is available commercially and is ideally suited for adapting to existing plants because it does not have to be installed within the cold box. Once vaporized, the sample is treated as any vapor sample.

In summary, although samples in air separation plants are generally clean and contaminant-free, special considerations are needed when analyzing for low concentrations, especially in liquid cryogenic streams. These problems, while not difficult to solve, must be dealt with to assure accurate analysis.

Sources:

Hauser, E.A., "The Application of On-Stream Analytical Instrumentation in Air Separation Plants" Beckman Instruments, ©1995

Shelley, Suzanne, "Out of Thin Air," Chemical Engineering, June 1991

Hardenburger, Thomas, "Producing Nitrogen at the Point of Source", Chemical Engineering, October 1992

Table 1 - Gas Bottling Plant Gas Analyzer Applications

No.	Application	Analyzer Model Selection	Range
1a	THC in Compressed Air Feed and Low Pressure Column	NGA FID 400A	0 to 25/50 ppm
1b	THC Impurity in Product Streams	NGA FID 400A	0 to 1/10 ppm
2a	CO ₂ in High Pressure Column Feed	X-STREAM	0 to 10 ppm
2b	CO ₂ in Product Streams	X-STREAM	0 to 10 ppm
3a	O ₂ in Low Pressure Column Feed	X-STREAM	0 to 50 %
3b	O ₂ in Crude Argon Column Feed	X-STREAM	0 to 100 / 80 to 100 %
3c	O ₂ in Product from Crude Argon Column	X-STREAM	0 to 20 %
3d	O ₂ in Product Stream	MLT	98 to 100 %
4a	Trace O ₂ in Product Argon	MLT 2	0 to 100 ppm
4b	Trace O ₂ in Product Nitrogen	MLT 2	0 to 100 ppm
5a	Argon in Crude Argon Column Feed & Product	X-STREAM MLT	0 to 50 % 85 to 100 %
5b	H ₂ After Oxygen Removal Unit	X-STREAM	0 to 3 %
5c	Moisture in Product Streams	X-STREAM	0 to 500 ppm

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