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INTRODUCTION

Scope

This design guideline covers the basic elements of air separation units in sufficient detail to allow an engineer to design an air separation units with the suitable size of wall thickness, reflux ratio, actual stages, heat duties of a reboiler and a condenser, and permissible pressures.

For air separation, as with any process equipment, successful sizing and selection is always a combination of empirical observation/experience and analytical modeling. The air separation process requires a very tight integration of heat exchangers and separation columns to obtain a good efficiency and all the energy for refrigeration is provided by the compression of the air at the inlet of the unit. There are several methods to separate the air such as Cryogenic Distillation, Membrane, Pressure Swing Adsorption (PSA) and Vacuum Pressure Swing Adsorption (VPSA)

The design of air separation may be influenced by factors, including process requirements, economics and safety. In the design section, there are tables that assist in making these factored calculations from the vary reference sources. Include in this guideline is a calculation spreadsheet for the engineering design. .All the important parameters use in the guideline are explained in the definition section which help the reader more understand the meaning of the parameters or the term used.

The theory section explains the material balance in cryogenic distillation, how to calculate the air separation requirements, and the equipment which is influenced in air separation system. The application of the air separation theory with the example will make the engineer understand the air separation process and be ready to perform the actual design of the air separation.

General Design Consideration

An air separation plant separates atmospheric air into its primary components, typically nitrogen and oxygen, and sometimes also argon and other rare inert gases (see table 1).

Air separation plants are constructed in different forms depending on what products are produced, production capacity, and purity. Then the most appropriate process which has the lowest energy consumption and purchase price is selected. Cryogenic air separation unit (ASU) is a process of high energy consumption. There are various technologies that are used for the separation process, the most common is via cryogenic distillation.

The cryogenic separation process requires a very tight integration of heat exchangers and separation columns to obtain a good efficiency and all the energy for refrigeration is provided by the compression of the air at the inlet of the unit. In addition to the cryogenic distillation method there are other methods such as Membrane, Pressure Swing Adsorption (PSA) and Vacuum Pressure Swing Adsorption (VPSA), which are typically used to separate a single component from ordinary air.

Table 1: Gas Component

Component	Concentration	Boiling point (ºC)
Nitrogen oxide	0.35 ppm	-88
Xenon	0.1 ppm	-108
Krypton	1 ppm	-153
Oxygen	20.9%	-183
Argon	0.93%	-186
Nitrogen	78.1%	-196
Neon	18 ppm	-246
Hydrogen	0.5 ppm	-253
Helium	5 ppm	-169

Membrane Separation

Membrane separation isolates nitrogen from atmospheric air by selective permeation across a membrane wall. The membrane used in this method consists of a bundle of selectively permeable hollow fibers. These fibers allow the “fast” gases (oxygen, carbon dioxide and water vapor) to permeate the membrane wall much faster than the “slow” gas (nitrogen).

The membrane separates the original gas mixture into two streams. One stream, called the permeate, contains oxygen, carbon dioxide and water vapor. The other stream, called the product, consists of high-pressure nitrogen. The permeate is vented to the atmosphere and the product, nitrogen, exits the downstream end of the membrane for delivery to the end-user or to a booster if further compression is required.

The purity of the product can be adjusted by changing the operation conditions. If the nitrogen flow rate is decreased, nitrogen purity increases and conversely, by increasing nitrogen flow, nitrogen purity is decreased. A flow/purity control valve at the discharge end of the nitrogen stream, downstream of the flow meter and nitrogen analyzer, allows finite control of flow and therefore purity.

The advantages:

1. Most economical process at low flow rates (up to 40,000 SCFH)
2. Simplest process in terms of calculators and engineering design
3. Least costly for repairs and maintenance.
4. Lowest tax and insurance
5. Requires the least amount of equipment for start-up

The disadvantage: Nitrogen purity is not good enough for certain process where there must be 1 part per billion purity.

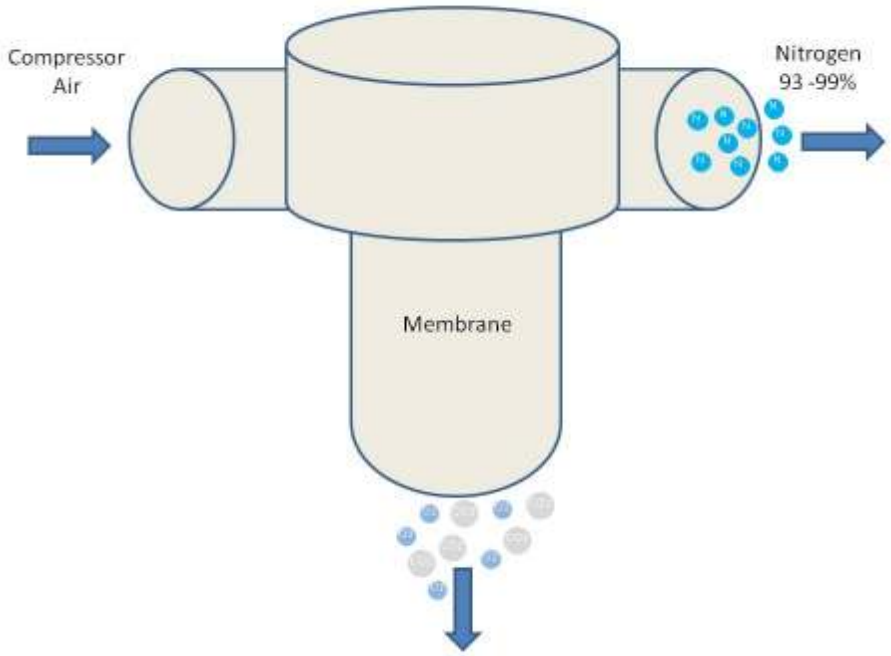

Figure 1: Membrane separation

Pressure Swing Adsorption (PSA)

Pressure swing adsorption (PSA) is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material. It operates at near-ambient temperatures and so differs from cryogenic distillation techniques of gas separation.

Special adsorptive materials (e.g., zeolites) are used as a molecular sieve, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbent material.

Pressure swing adsorption processes rely on the fact that under high pressure, gases tend to be attracted to solid surfaces, or "adsorbed". The higher the pressure, the more gas is adsorbed; when the pressure is reduced, the gas is released, or desorbed. PSA processes can be used to separate gases in a mixture because different gases tend to be attracted to different solid surfaces more or less strongly.

If a gas mixture such as air, for example, is passed under pressure through a vessel containing an adsorbent bed of zeolite that attracts nitrogen more strongly than it does oxygen, part or all of the nitrogen will stay in the bed, and the gas coming out of the vessel will be enriched in oxygen. When the bed reaches the end of its capacity to adsorb nitrogen, it can be regenerated by reducing the pressure, thereby releasing the adsorbed nitrogen. It is then ready for another cycle of producing oxygen enriched air.

This is exactly the process used in portable oxygen concentrators used by emphysema patients and others who require oxygen enriched air to breathe.

Using two adsorbent vessels allows near-continuous production of the target gas. It also permits so-called pressure equalization, where the gas leaving the vessel being depressured is used to partially pressurize the second vessel. This results in significant energy savings, and is common industrial practice.

Aside from their ability to discriminate between different gases, adsorbents for PSA systems are usually very porous materials chosen because of their large surface areas. Typical adsorbents are activated carbon, silica gel, alumina and zeolite. Though the gas

adsorbed on these surfaces may consist of a layer only one or at most a few molecules thick, surface areas of several hundred square meters per gram enable the adsorption of a significant portion of the adsorbent's weight in gas. In addition to their selectivity for different gases, zeolites and some types of activated carbon called carbon molecular sieves may utilize their molecular sieve characteristics to exclude some gas molecules from their structure based on the size of the molecules, thereby restricting the ability of the larger molecules to be adsorbed.

One of the primary applications of PSA is in the removal of carbon dioxide (CO_2) as the final step in the large-scale commercial synthesis of hydrogen (H_2) for use in oil refineries and in the production of ammonia (NH_3). Refineries often use PSA technology in the removal of hydrogen sulfide (H_2S) from hydrogen feed and recycle streams of hydrotreating and hydrocracking units.

Another application of PSA is the separation of carbon dioxide from biogas to increase the methane (CH_4) content. Through PSA the biogas can be upgraded to a quality similar to natural gas. Nitrogen generator units employ the PSA technique to produce high purity nitrogen gas (99.5% or greater) from a supply of compressed air.

PSA is an economic choice for small-scale production of reasonable purity oxygen or nitrogen from air. PSA technology has a major use in the medical industry to produce oxygen, particularly in remote or inaccessible parts of the world where bulk cryogenic or compressed cylinder storage is not possible. PSA is also used in hypoxic air fire prevention systems to produce air with a low oxygen content. PSA is also used in an on purpose propylene plant via propane dehydrogenation. It consists of a selective media for the preferred adsorption of methane and ethane over hydrogen.

The advantages

1. PSA units can be placed on-site which makes the N_2 readily available as needed
2. It the amount of N_2 needed is less than 20,000 SCFH, the using PSA unit is more economical than a cryogenic process.
3. During shutdown, less money is lost than would be in a cryogenic process
4. PSA unit are readily available and can be purchased and delivered quickly

The disadvantages

1. If the flow rate is increased to 40,000 SCFH, then it becomes significantly cheaper to buy N_2 from a cryogenic source.
2. There is possible down time with respect to the compressor that is being used
3. Extremely noisy even when compared with the other process.

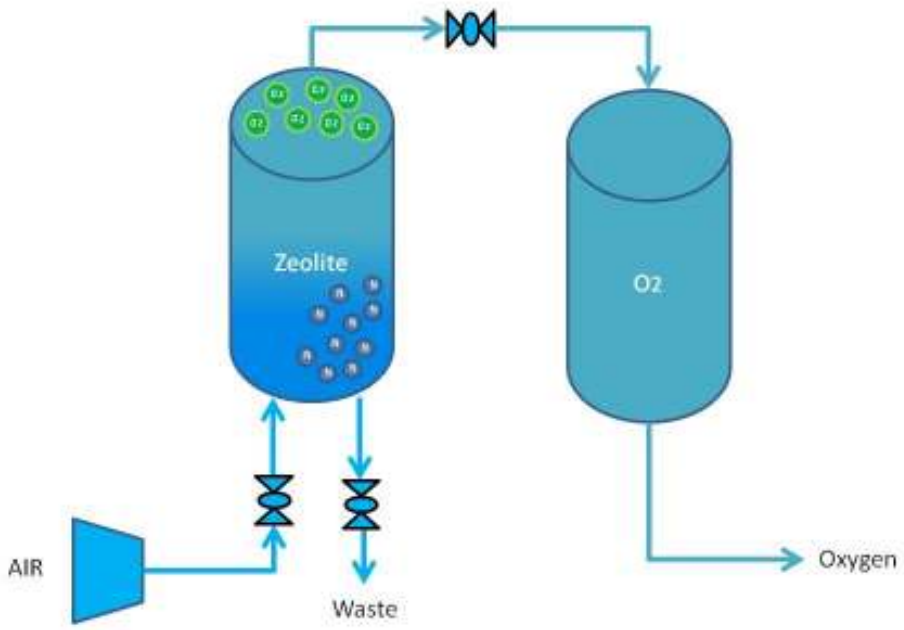

Figure 2: Pressure Swing Adsorption (PSA)

Vacuum Pressure Swing Adsorption (VPSA)

The Vacuum Pressures Swing Adsorption (VPSA) process is a variation on the Pressures Swing Adsorption (PSA) process, which is more applicable for certain applications. VPSA uses a feed blower instead of an air compressor to supply air to the system and the purified gas is collected using a vacuum blower to desorb the adsorber vessels. The use of different technology in VPSA results in a significant decrease in the power consumption of the system. Although power savings are clear with this system, they are typically cost effective only for plants requiring very large oxygen producing capacities.

Each VPSA system includes a rotary-lobe feed air blower, vacuum blower (two bed systems only), one or two adsorbent vessels, an oxygen surge tank, switching valves and computer controls.

In the single-bed system, the blower draws in air, compresses it and sends it to the adsorbent vessel to remove impurities, leaving 90 to 94 percent pure oxygen as the product. The adsorbent is then regenerated as the blower removes gas by reducing the pressure inside the vessel. The waste gas (nitrogen, water and carbon dioxide) is then discharged into the air. Since oxygen is not produced during regeneration, the system includes a low-pressure surge tank to allow for continuous oxygen supply.

The two-bed system uses a similar adsorption process cycle that relies on swings in pressure -- from above one atmosphere to below atmospheric pressure (vacuum) -- to cycle each bed sequentially from adsorption to desorption.

One bed is always adsorbing impurities to separate oxygen from air, while the other bed regenerates. Thus, the beds alternately produce oxygen into a surge tank which ensures that product is available continuously at a consistent pressure and purity.

Comparison of VPSA with PSA and cryogenic separation

1. Though VPSA systems are more costly to build, they are comparatively more energy efficient than PSA systems for the same product flow, pressure and purity conditions.

2. Oxygen VPSA units are economical than oxygen PSA units only when the desired production rate is greater than about 20 tons per day, up to 60 tons per day or more.
3. They are more preferred in those cases when providing high purity oxygen is not required. · Cryogenic plants are preferred production rate is 60 tons or above per day.
4. However, two oxygen VPSA plants can also perform in the same manner when they allow for better matching of large step-changes in demand.
5. PSA specific power is approximately 1/3rd less than that for oxygen PSA plants, but almost same to the specific power of cryogenic air separation units.

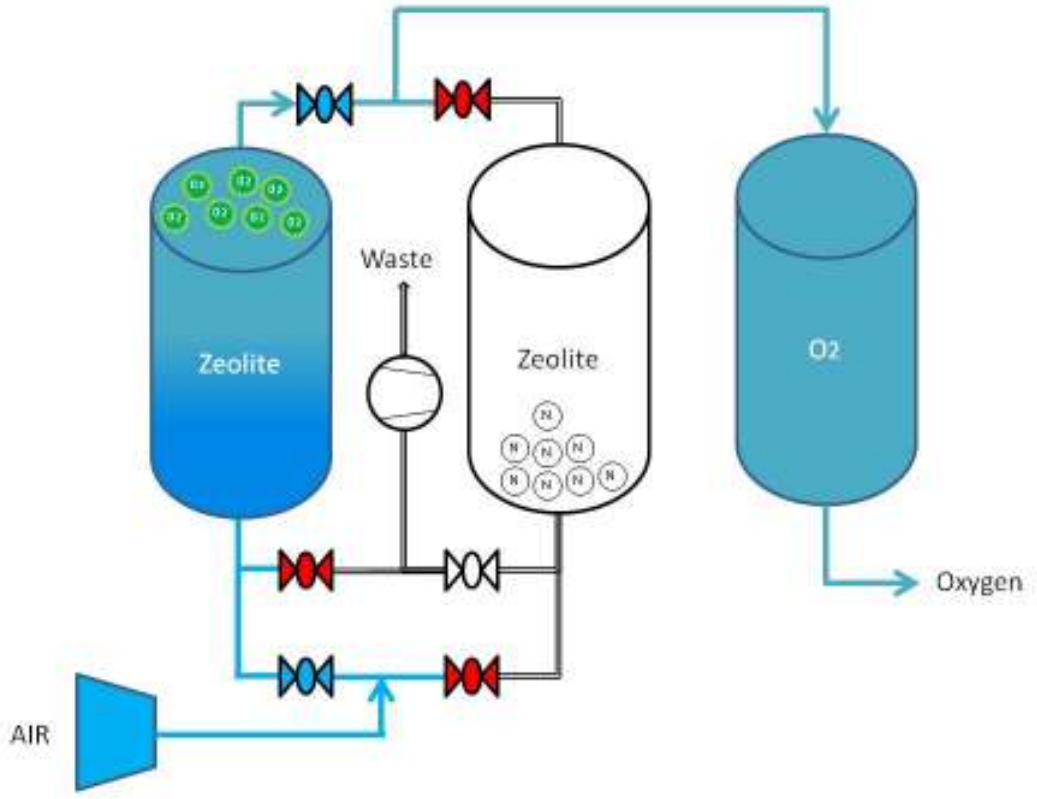

Figure 3: Vacuum Pressure Swing Adsorption (VPSA). (ranacaregroup.com)

Cryogenic distillation

Production of high purity oxygen, nitrogen, and argon as used for Semiconductor device fabrication requires cryogenic distillation. Similarly, the only viable sources of the rare gases neon, krypton, and xenon is the distillation of air using at least two distillation columns. Cryogenic ASU's are built to provide nitrogen and/or oxygen and often co-produce argon where liquid products (Liquid nitrogen "LIN", Liquid oxygen "LOX", and Liquid argon "LAR") and gases product (Gaseous oxygen “GOX” and Gaseous nitrogen “GAN”) can only be produced if sufficient refrigeration is provided for in the design.

Below are the main process functions from figure 4 below

1. **Air compressor with filter**. Dust free air is compressed tp a pressure sufficient to get it through the equipment.
2. **Air purifying**. Mole sieves are used to remove water vapor, carbon dioxide and certain other contaminants.
3. **Cooling down the air.** In a heat exchanger the air is cooled down close to the dew point by the cold separated gases, which come from the distillation column. If a suitably large enough heat exchanger is used the cold gases can be warmed to a temperature just under that of the incoming air, so that the cold losses become acceptable.
4. **Cold production**. Production of liquid products requires cold and cold losses occur through the equipment insulation and in the heat exchanger. this cold is produced in a recycle because the gas which does not condense is warmed up and is fed back to the compressor again.
5. **Cooling with cooling water**. Compressors and other machines need large amounts of cooling water. A large part of the heat removal is in fact cold production.
6. **Air separation.** The liquid is separated into oxygen, argon, and nitrogen in the distillation columns. The cold gases are fed through the heat exchanger and are warmed-up while the liquids are fed into tank.
7. **Coldbox.** The cold equipments demand much insulation order to get an acceptable cold loss. So columns, heat exchangers and parts of the cold production equipment are built in a large tower like box, the so-called coldbox.

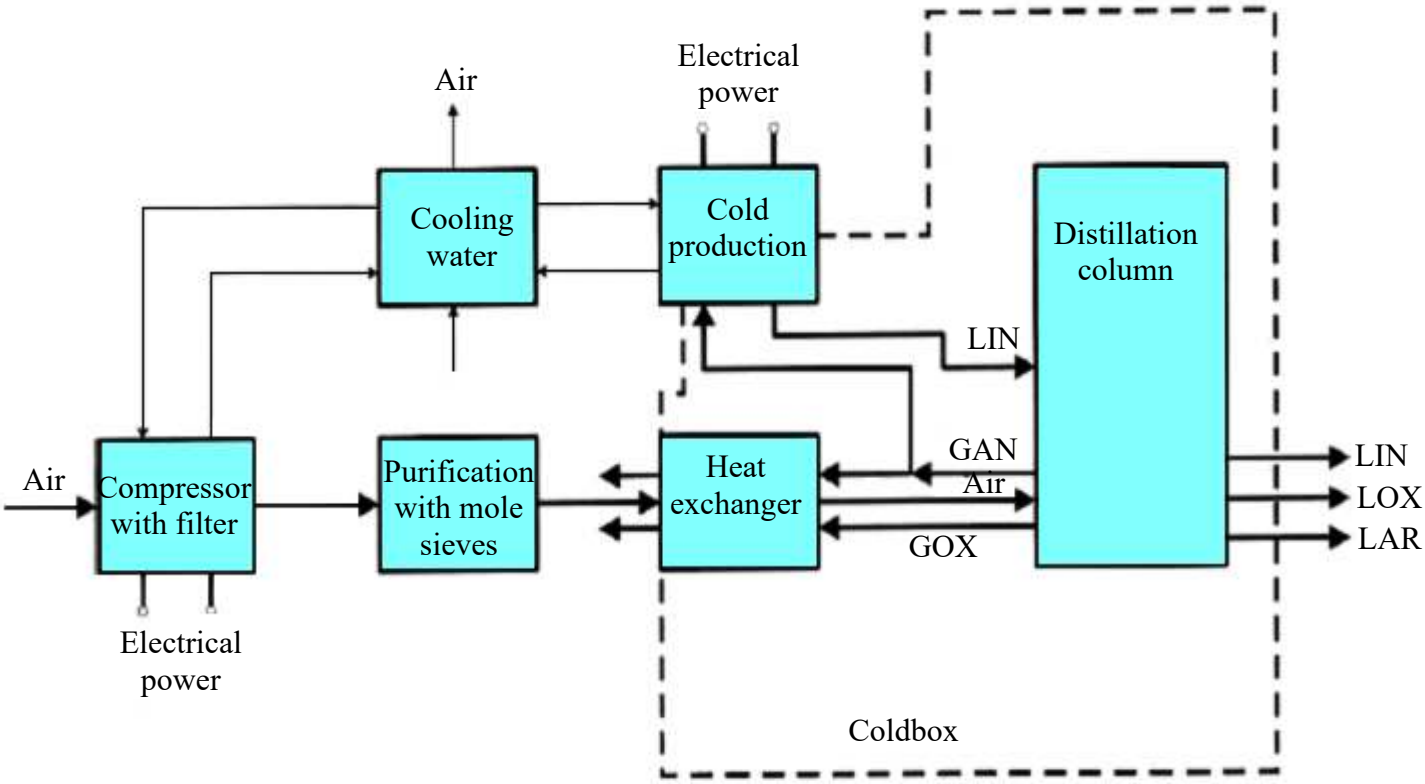

Figure 4: Original air separation process

To achieve the low distillation temperatures an Air Separation Unit (ASU) requires a refrigeration cycle that operates by means of the Joule–Thomson effect, and the cold equipment has to be kept within an insulated enclosure (commonly called a "cold box"). The cooling of the gases requires a large amount of energy to make this refrigeration cycle work and is delivered by an air compressor. The process consists of the following main steps.

Before compression the air is pre-filtered of dust. Air is compressed where the final delivery pressure is determined by recoveries and the fluid state (gas or liquid) of the products. Typical pressures range between 5 and 10 bar gauge. The air stream may also be compressed to different pressures to enhance the efficiency of the ASU. During compression water is condensed out in inter-stage coolers.

The process air is generally passed through a molecular sieve bed, which removes any remaining water vapor, as well as carbon dioxide, which would freeze and plug the cryogenic equipment. Molecular sieves are often designed to remove any gaseous hydrocarbons from the air, since these can be a problem in the subsequent air distillation that could lead to explosions. The molecular sieves bed must be regenerated. This is done by installing multiple units operating in alternating mode and using the dry co-produced waste gas to desorbs the water.

Process air is passed through an integrated heat exchanger (usually a plate fin heat exchanger) and cooled against product (and waste) cryogenic streams. Part of the air liquefies to form a liquid that is enriched in oxygen. The remaining gas is richer in nitrogen and is distilled to almost pure nitrogen (typically < 1ppm) in a high pressure (HP) distillation column. The condenser of this column requires refrigeration which is obtained from expanding the more oxygen rich stream further across a valve or through an Expander, (a reverse compressor).

Alternatively the condenser may be cooled by interchanging heat with a reboiler in a low pressure (LP) distillation column (operating at 1.2-1.3 bar abs.) when the ASU is producing pure oxygen. To minimize the compression cost the combined condenser/reboiler of the HP/LP columns must operate with a temperature difference of only 1-2 degrees Kelvin, requiring plate fin brazed aluminum heat exchangers. Typical oxygen purities range in from 97.5% to 99.5% and influence the maximum recovery of

oxygen. The refrigeration required for producing liquid products is obtained using the JT effect in an expander which feeds compressed air directly to the low pressure column. Hence, a certain part of the air is not to be separated and must leave the low pressure column as a waste stream from its upper section.

Because the boiling point of argon (87.3 K at standard conditions) lies between that of oxygen (90.2 K) and nitrogen (77.4 K), argon builds up in the lower section of the low pressure column. When argon is produced, a vapor side draw is taken from the low pressure column where the argon concentration is highest. It is sent to another column rectifying the argon to the desired purity from which liquid is returned to the same location in the LP column.

Use of modern structured packings which have very low pressure drops enable argon purities of less than 1 ppm. Though argon is present in less to 1% of the incoming, the air argon column requires a significant amount of energy due to the high reflux ratio required (about 30) in the argon column. Cooling of the argon column can be supplied from cold expanded rich liquid or by liquid nitrogen.

Finally the products produced in gas form are warmed against the incoming air to ambient temperatures. This requires a carefully crafted heat integration that must allow for robustness against disturbances (due to switch over of the molecular sieve beds[8]). It may also require additional external refrigeration during start-up.

The air gases are sometimes supplied by pipeline to large industrial users adjacent to or nearby to the production plant. Unless a viable pipeline system exists, long distance transportation of products is usually done as a liquid product for large quantities or as dewar flasks or gas cylinders for small quantities.

The unique feature of air separation is the great interdependency of the different flows. This is because it is cryogenic process, in which the external media such as cooling water and steam cannot be used. The different products or internal flows are used for boiling and condensing in the column, as reflux, for cooling the incoming air and for subcooling the liquid products.

For example, cold nitrogen gas is used in the recycle for cold production for liquid faction. A changed gas flow gives the different pressure, and a change of pressure can

have a considerable effect on the other flows as their boiling points change with the pressure also changed temperature.

The advantage:

1. Cryogenic can produce large quantities of high purity of nitrogen.
2. Some process like the humid air expansion process have a yield of about 40 – 60% pr pass which allows to produce large quantities of nitrogen efficiently.
3. Cryogenic process do not have economics scale such as expansion or reduction of product quantity requirements generally does not necessitate new equipment.

The disadvantages

1. Cryogenic process in general have very large capital cost, due mostly to the cost of compressors and turbines.
2. The high pressure requirements and the recovery of refrigeration energy explains the need for this equipment.
3. Cryogenic separation requires numerous of heat exchangers, insulators, and a distillation column. All of which add to the high costs of the process.

Table 2: Compare the process of air separation method

Process	Advantages	Disadvantages
Cryogenic	Low amount of electricity per unit nitrogen Produces very high purity nitrogen Can generate liquid nitrogen for storage on site	Large site space and utility requirements High capital cost Limited scaleability in production Long start-up and shutdown
PSA	Low to moderate capital cost Cost-effective nitrogen production of relatively high purities Quick installation and start-up	High maintenance equipment Noisy operation Limited scalability
Membrane	Low capital cost Production output is very flexible Quick installation and start-up Easy to vary purity and flow rate.	Uneconomical for high purity requirements Uneconomical for large outputs Requires relatively large amount of electricity per unit nitrogen.

DEFINITIONS

Adsorbed - undergo or cause to undergo a process in which a substance, usually a gas, accumulates on the surface of a solid forming a thin film,

Air separation – process to separates atmospheric air into its primary components, typically nitrogen and oxygen, and sometimes also argon and other rare inert gases

Bottoms – The stream of liquid product collected from the reboiler at the bottom of a distillation tower.

Condensation - The change of a gas or vapor to a liquid, either by cooling or by being subjected to increased pressure.

Control valve - valves used to control conditions such as flow, pressure, temperature, and liquid level by fully or partially opening or closing in response to signals received from controllers that compare a "setpoint" to a "process variable" whose value is provided by sensors that monitor changes in such conditions

Cold box - The cryogenic equipment and piping and its structural enclosure.

Cold Standby - The condition where equipment is held at cryogenic conditions for immediate service on demand.

Cryogenic - pertaining to the production or use of very low temperatures. The branches of physics and engineering that involve the study of very low temperatures, how to produce them, and how materials behave at those temperatures.

Dew point – The temperature at constant pressure (or the pressure at constant temperature) at which the first liquid droplet forms when a gas (vapor) is cooled (or compressed).

Distillate – The vapor from the top of a distillation column is usually condensed by a total or partial condenser. Part of the condensed fluid is recycled into the column (reflux)

while the remaining fluid collected for further separation or as final product is known as distillate or overhead product

Downcomer - a vertical channel that connects a tray with the next tray below which carries froth and creates residence time which helps the vapor disengage from the froth.

Heat exchangers - equipment to transfer heat between different gas or liquid flows, without the different flows coming into direct contact with each other.

Hydrocracking - A process by which the hydrocarbon molecules of petroleum are broken into simpler molecules, as of gasoline or kerosene, by the addition of hydrogen under high pressure and in the presence of a catalyst.

Hydrotreating - Oil refinery catalytic process in which hydrogen is contacted with petroleum intermediate or product streams to remove impurities, such as oxygen, sulfur, nitrogen, or unsaturated hydrocarbons.

Inert gases - Also called noble gas. Any of the six gases helium, neon, argon, krypton, xenon, and radon. Because the outermost electron shell of atoms of these gases is full, they do not react chemically with other substances except under certain special conditions.

Light key – The lighter (more volatile) of the two key components. Light key is collected at the distillate. All non-key components lighter than the light key are known as the light components.

Main Reboiler - An integrated heat exchanger used to heat-couple the two primary distillation columns of an air separation unit (ASU), simultaneously condensing a high pressure fluid while vaporizing a low pressure liquid, thereby producing reflux for one column and boil-up for the other.

Material balance - A calculation to inventory material inputs versus outputs in a process system.

Membrane process - separation isolates nitrogen from atmospheric air by selective permeation across a membrane wall.

Molecular sieve - a material with very small holes of precise and uniform size. These holes are small enough to block large molecules and allow small molecules to pass. Many molecular sieves are used as desiccants. Examples: Activated charcoal and silica gels are molecular sieves

Pressure swing adsorption (PSA) - a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material.

Reboiler –Is a heat exchanger typically used to provide heat to the bottom of industrial distillation columns. They boil the liquid from the bottom of a distillation column to generate vapors which are returned to the column to drive the distillation separation.

Reflux ratio – The ratio of the reflux stream to the distillate. The operating reflux ratio could affect the number of theoretical stages and the duties of reboiler and condenser.

Relative volatility –Defined as the ratio of the concentration of one component in the vapor over the concentration of that component in the liquid divided by the ratio of the concentration of a second component in the vapor over the concentration of that second component in the liquid. For an ideal system, relative volatility is the ratio of vapor pressures i.e. $\alpha = P2/P1$

Rich liquid - The bottom product which contains about 35 – 40% oxygen

Subcooling - The difference between the temperature of a pure condensable fluid below saturation and the temperature at the liquid saturated state, at the same pressure. the process by which a saturated liquid refrigerant is cooled below the saturation temperature, forcing it to change its phase completely.

The Vacuum Pressures Swing Adsorption (VPSA) process - a variation on the PSA process, which is more applicable for certain applications. VPSA uses a feed blower instead of an air compressor to supply air to the system and the purified gas is collected using a vacuum blower to desorb the adsorber vessels

Vaporization - phase transition of a substance from the liquid phase to the gas phase. The conversion of a solid or liquid into a vapor without chemical change

Volatile - Volatile means tending to become violent or something that is rapidly evaporating. Tending to become violent or something that is rapidly evaporatin

Zeolites - mineral of aluminum silicate use as mole sieve which manufactured from a man made

NOMENCLATURES

B	Bottom flow rate, kmol/hr
c	Metal corrosion, cm
D	Distillate flow rate, kmol/hr
D_B	Internal diameter bottom, cm
D_{in}	Internal diameter, cm
D_T	Internal diameter top, cm
E	Weld integrity.
E_{OC}	Overall column efficiency, %
F	Feed flow rate, kmol/hr
m	Mass, kg
MP	Measured power, kW
Mr	Molecular weight, kg/kmol
N	Number of theoretical stages,
N_{act}	Actual stages
N_m	Minimum stages
p	Partial pressure of the component in the vapor phase, kg/cm^2
P	Process pressure, kg/cm^2
P_B	Pressure bottom, kg/cm^2
Po	The vapor pressure of the pure component at the temperature T_o of the Mixture, kg/cm^2
P_T	Pressure top, kg/cm^2
[P]	Permissible pressure in the selected wall thickness, kg/cm^2
q	q line
Q_{con}	condenser heat requirement, kJ/hr

Q_{Re}	Reboiler heat requirement, kJ/hr
R	Calculate reflux ratio
R	Gas constant = 0.08314 m^3 bar/K
R_m	Minimum reflux ratio
S	Maximum allowable stress, kg/cm^2
t	Cylinder wall thickness, cm
T	Temperature, K
V	Volume, m^3
V_o	Volume, Nm^3
x	The mole fraction of the component in the liquid phase.
x_B	Mole fraction bottom light key
X_B	Mole fraction bottom light key
x_D	Mole fraction overhead light key
x_F	Mole fraction feed light key

Greek Leters

α	Realtive volatility,
δ	seizure against the wall, kg/cm^2
δc	Authorized Pressure and seizure on the top wall, kg/cm^2
Δvh_{con}	Heat evaporation of condenser, kJ/kmol
ΔvhH	Heat evaporation of heavy key, kJ/kmol
ΔvhL	Heat evaporation of light key,kJ/kmol)
Δvh_{re}	Heat evaporation of reboiler, kJ/kmol
η	Plate efficiency, %

Superscript

B	Bottom flow rate, kmol/hr
D	Distillate flow rate, kmol/hr
F	Feed flow rate, kmol/hr
N	Number of theoretical stages,
R	Calculate reflux ratio
T	Temperature, K
V	Volume, m^3