Chapter 1

Introduction

Cryogenic air separation process is one of the most popular air separation process used to produce purified components of air, in particular oxygen, nitrogen and argon. Large quantities of industrial gases such as oxygen, nitrogen, argon, and other rare gases are required by various industries to run their production processes. Cryogenic air separation is the preferred technology for producing very high purity oxygen, nitrogen and argon. It is the most cost effective technology for high production rate plants. Oxygen plays an important role in coal/biomass gasification by increasing the efficiency of the gasifier and downstream processes. The syngas produced by gasification with oxygen as gasifying agent can be used in applications like Integrated Gasification Combined Cycle (IGCC), Chemical productions and Fischer-Tropsch process. Ambient air is available as basic raw material with its content of nitrogen (79 %), oxygen (21 %) and small quantities of argon and other rare gases for cryogenic air separation. Cryogenic air separation technology is based on the fact that the different constitute gases of air all have different boiling points and by manipulating immediate environment in terms of temperature and pressure the air can be separated into its components. There are various thermodynamic processes needed in cryogenic air separation, of which fundamental ones are: air compression, air purification, heat exchanging, distillation and product compression. The block diagram of the cryogenic air separation plant with thermodynamic processes is shown schematically in Fig.1.1.

Air compression

Atmospheric air is pre-filtered (to remove dust), and compressed using a centrifugal compressor to a pressure required, depending upon the intended product mix and desired product pressures. Since the compressor heats up the air, it is cooled in inter stage coolers and water-cooled after cooler to condense any water vapors. This can also achieve the removal of some ambient moisture. The compressed air is often cooled to a somewhat lower temperature in a mechanical refrigeration system. In some cases, cooling may be accomplished with a direct contact after cooler system (DCAC) instead of mechanical refrigeration. DCAC systems utilize cool, dry waste
gas to chill a circulating cooling water stream in a chill tower, and then use the chilled water stream to cool the compressed air in a second tower.

**Air purification**

Air is then processed through a pre-purification unit. During this process, compressed air is generally passed through a pre-purification unit which removes any remaining water vapors, as well as carbon dioxide to avoid freeze of water vapors and carbon dioxide in the cryogenic equipments. The pre-purification unit is often designed to remove any gaseous hydrocarbons from the air, since these can be a problem in the subsequent air distillation. There are two basic approaches to remove the water vapors and carbon dioxide which are as molecular sieve and reversing heat exchangers.

**Heat exchanging for cooling**

After purification, air passes through a plate-fin heat exchanger where it is cooled to a temperature at which it is partially liquid. This cooling is done in brazed aluminum heat exchangers which allow the exchange of heat between the incoming feed air and cold products and waste gas streams exiting the separation process. The exiting gas streams are warmed to close-to-ambient air temperature and incoming feed air liquefied. Recovering refrigeration from the gaseous product streams and waste stream minimizes the amount of refrigeration that must be produced by the plant.

**Distillation**

Partially liquefied air is sent to the double column distillation system integrated with crude argon column, where it is separated into O₂, N₂ and crude argon fractions. The distillation is the heart of the cryogenic air separation process. The air stream which is part liquid and part gas enters the base of the high-pressure fractionating or distillation column. As the air moves up the column, it loses additional heat. The oxygen continues to liquefy, leading to the formation of oxygen-rich mixture in the bottom of the column, and other gases like nitrogen and argon flow to the top as a vapor. Product O₂ is taken from the bottom of the low pressure column (LP column). If liquid oxygen is desired, part of total product O₂ may be taken as liquid product, the remaining is passed through main heat exchanger, where it converts into gaseous O₂ product after recovery of its cold. Liquid nitrogen is drawn from the top of the high pressure column (HP column). Gaseous N₂ is drawn from the top of the LP column and is also sent to the main heat exchanger through sub-cooler. The crude argon is drawn from the top of the crude argon column and processed in purification unit to achieve the required purity level.
**Product compression**

The gases are sometimes pressurized to meet user requirement and supplied by pipeline to large industrial users adjacent to or nearby to the production plant or stored as liquid. Unless a viable pipeline system exists, long distance transportation of products is usually done as a liquid product for large quantities.

![Block diagram of cryogenic air separation plant](image)

**Fig. 1.1:** Block diagram of cryogenic air separation plant [Sap 01]

### 1.1 Introduction to composition of air

The state and quality of atmospheric air is always changing with location and altitude. The atmospheric air contains mainly permanent atmospheric gases and variable atmospheric gases/substances. Natural biological processes within the earth’s atmosphere system maintain the amounts of permanent gases to near constant proportion from earth surface up to about 80 kilometers above the earth. Unlike the permanent gases, the concentration of numerous other substances found in the earth’s atmosphere is variable. The permanent atmospheric gases listed in **Table 1.1** remain unchanged in the concentration in...
the dry atmosphere. The variable atmospheric gases/substances listed in Table 1.2 are representative of the average concentrations of the variable substances found in our atmosphere.

**Table 1.1:** Standard dry air composition [Sap 02]

<table>
<thead>
<tr>
<th>Gas</th>
<th>Chemical symbol</th>
<th>% by volume</th>
<th>Parts per million (ppm)</th>
<th>Boiling point (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>78.08</td>
<td>---</td>
<td>77.36</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O₂</td>
<td>20.95</td>
<td>---</td>
<td>90.18</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>0.93</td>
<td>---</td>
<td>87.28</td>
</tr>
<tr>
<td>Neon</td>
<td>Ne</td>
<td>0.0018</td>
<td>18.21</td>
<td>27.09</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>0.0005</td>
<td>5.24</td>
<td>4.21</td>
</tr>
<tr>
<td>Krypton</td>
<td>Kr</td>
<td>0.000114</td>
<td>1.14</td>
<td>119.83</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H₂</td>
<td>0.00005</td>
<td>0.50</td>
<td>20.3</td>
</tr>
<tr>
<td>Xenon</td>
<td>Xe</td>
<td>0.0000086</td>
<td>0.086</td>
<td>165.0</td>
</tr>
</tbody>
</table>

**Table 1.2:** Variable substances in air near the earth's surface [Sap 02]

<table>
<thead>
<tr>
<th>Gas</th>
<th>% by volume</th>
<th>Parts per million (ppm)</th>
<th>Boiling point (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water vapor</td>
<td>0 to 4</td>
<td>---</td>
<td>373</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.035</td>
<td>350</td>
<td>---</td>
</tr>
<tr>
<td>Methane ( CH₄)</td>
<td>0.00017</td>
<td>1.7</td>
<td>214.3</td>
</tr>
<tr>
<td>Nitrous oxide (N₂O)</td>
<td>0.00003</td>
<td>0.3</td>
<td>183.7</td>
</tr>
<tr>
<td>Ozone (O₃)</td>
<td>0.000004</td>
<td>0.04</td>
<td>---</td>
</tr>
<tr>
<td>Particulate matter</td>
<td>0.000001</td>
<td>0.01</td>
<td>---</td>
</tr>
<tr>
<td>Chlorofluoro carbons (CFCs)</td>
<td>0.0000001</td>
<td>0.0001</td>
<td>---</td>
</tr>
</tbody>
</table>
1.2 Applications of nitrogen, oxygen and argon

Cryogenic air separation plants produces industrial gases like oxygen, nitrogen and argon in gaseous or in liquid form in a wide variety of purities. Such gases produced have a variety of uses in various applications. The global market share of products of air separation unit and other gases is shown in Fig. 1.2.

![Fig. 1.2: Global Industrial gas market share](image)

A few applications of these gases have been discussed in the following sections.

Nitrogen

1. Metals

Nitrogen is used to treat the metal in the manufacture of steel and other metals and as a shield gas in the heat treatment of iron, steel and other metals. It is also used as a process gas, together with other gases for reduction of carbonization and nitriding. “Flash” or “fins” on cast metal can be removed by cooling with liquid nitrogen, making them brittle.

2. Manufacturing and Construction

Shrink fitting is an interesting alternative to traditional expansion fitting. Instead of heating the outer metal part, the inner part is cooled by liquid nitrogen so that the metal shrinks and can be inserted. When the metal returns to its normal temperature, it expands to its original size, giving very tight fit. Liquid nitrogen is used to cool concrete, which leads to better cured properties. When construction operations must be done in soft, water-soaked ground such as tunnel construction underneath waterways, the ground can be frozen effectively with liquid nitrogen. Pipes are driven
into the ground; liquid nitrogen is pumped through the pipes under the earth’s surface. When the nitrogen exits from the soil, it vaporizes, removing heat from the soil and freeze it.

3. Chemicals, Pharmaceuticals and Petroleum

Refineries, petrochemical plants and marine tankers use nitrogen to purge equipment, tanks and pipelines of dangerous vapors and gases (for example, after completing a pipeline transfer operation or ending a production run) and to maintain an inert and protective atmosphere in tanks storing flammable liquids. Cold nitrogen gas is used to cool reactors filled with catalyst during maintenance work. The cooling time can be reduced substantially. Cooling reactors (and the materials inside) to low temperature allows better control of side-reactions in complex reactions in the pharmaceutical industry. Liquid nitrogen is often used to provide the necessary refrigeration as it can produce rapid temperature reduction and easily maintain the required cold reaction temperatures. Reactor cooling and temperature control systems usually employ a circulating low-temperature heat transfer fluid to transfer refrigeration produced by vaporizing liquid nitrogen to the shell of the reactor vessel. The liquid nitrogen is vaporized in specially-designed heat exchangers that transfer refrigeration to the circulating heat transfer fluid. Nitrogen is used an inert gas to push liquids through lines, to clear lines and to propel "pigs" through pipelines to sweep out one material before using the line to transport another material.

4. Health care

Nitrogen is used as a shield gas in the packing of some medicines to prevent degradation by oxidation or moisture adsorption. Nitrogen is used to freeze blood, as well as viruses for vaccination. It is also used to freeze livestock semen, which can then be stored for years. The quick freezing resulting from the intense cold minimizes cell wall damage. Liquid nitrogen is also used in some MRI (Magnetic Resonance Imaging) devices to pre-cool the low temperature magnets prior to using much more expensive liquid helium for final cooling. Liquid nitrogen is used in cryo-surgery to destroy diseased tissues.

Oxygen

1. Metals

The largest user of oxygen is the steel industry. Modern steel making relies heavily on the use of oxygen to enrich air and increase combustion temperature in blast furnaces and open hearth furnaces as well as to replace coke with other combustible
materials. During the steel making process, unwanted carbon combines with oxygen to form carbon oxides, which leave as gases. Oxygen is fed into the steel bath through a special lance. Oxygen is used to allow greater use of scrap metal in electric arc furnaces.

2. Glass and Ceramics
Conversion of combustion systems from air-fuel to oxy-fuel results in better control of heating patterns, higher furnace efficiencies (lower fuel consumption) and reduction in particulate and NOx emissions.

3. Health Care
In medicine, oxygen is used during surgery, intensive care treatment, inhalation therapy etc. High standards of purity and handling must be maintained. Oxygen is typically supplied to hospitals though bulk liquid deliveries, then distributed to usage points. It assists with respiratory problems, saving lives and increasing patient comfort. Small portable air separation units are gaining wide use in homes. Compact non-cryogenic units, typically producing 93% purity medical grade oxygen, are being utilized in small and/or remote hospitals where demand is high enough to make cylinder deliveries a logistical problem but where liquid deliveries are unavailable or very costly.

4. Pulp and Paper
Oxygen is increasingly important as a bleaching chemical. In the manufacture of high-quality bleached pulp, the lignin in the pulp must be removed in a bleaching process. Chlorine has been used for this purpose but new processes using oxygen reduce water pollution. Oxygen plus caustic soda can replace hypochlorite and chlorine dioxide in the bleaching process, resulting in lower costs. In a chemical pulp mill, oxygen added to the combustion air increases the production capacity of the soda recovery boiler and the lime-reburning kiln. The use of oxygen in black liquor oxidation reduces the discharge of sulfur pollutants into the atmosphere.

5. Gasification
As air gasification produces poor quality syngas, therefore oxygen is used as gasifying agent for biomass/coal gasification. Oxygen plays an important role in biomass/coal gasification by increasing the efficiency of the gasifier and downstream processes. O₂ purities of up to 97% are favored as this requires the much easier separation of N₂ from O₂. Production of 99.5% O₂ requires the more difficult O₂/Ar separation with up to double the number of separation stages in a distillation column.
**Argon**

1. **Multi-Industry uses**

Pure argon is used as a shield gas in TIG welding and in MIG welding of aluminum. Argon or various argon mixtures are used as shield gases in many gas metal arc welding methods. The most common mixture is argon and carbon dioxide, which permits a high welding rate in the MIG welding of ordinary structural steel and minimizes post-weld dressing of the welded joint. The function of the shield gas is to protect the electrode and the weld pool against the oxidizing effect of the air. Plasma-arc cutting and plasma-arc welding employ plasma gas (argon and hydrogen) to provide a very high temperature when used with a special torch.

1.3 **Outline of the thesis**

The thesis is divided into seven chapters and appendices.

**Chapter 1**

Introduction to cryogenic air separation technology is presented in this chapter. The main processes taking place in cryogenic air separation plant are discussed with a schematic diagram. The few applications of industrial gases like nitrogen, oxygen and argon produced by cryogenic air separation plant are briefly discussed.

**Chapter 2**

Here the summary of the literature survey which gives description regarding history of cryogenic air separation by distillation, development in the process cycle, power consumption in cryogenic air separation, biomass gasification, use of oxygen in gasification and exergy analysis.

**Chapter 3**

In this chapter the objectives of the present research work and method of analysis are discussed. The modeling of cryogenic air separation unit and biomass gasification with the help of Aspen plus is also discussed. It also covers the development of process model for cryogenic air separation unit and biomass gasification unit in Aspen plus software. The procedure of process design calculations of cryogenic air separation unit on the basis of mass balance and energy balance is presented.

**Chapter 4**

Chapter 4 is dealing with syngas production by using updraft gasifier. In this case various feed stocks are considered with different gasifying agents like air, oxygen and steam. The syngas analysis techniques are also discussed in brief.
Chapter 5
In this chapter concept of exergy and its components like physical and chemical exergy are discussed. The exergy calculations of various thermodynamic processes like compression, expansion, heat exchange, separation and chemical processes like combustion are presented. The rational exergy efficiency of various unit operations like compressor, expander, heat exchanger and distillation columns is discussed.

Chapter 6
In this chapter, simulation of various configurations of cryogenic air separation plant and its unit operations are performed. The sensitivity analysis of various parameters is also presented. The exergy analyses of various unit operations are presented for understanding thermodynamic perfection of the processes. The summary of the results of simulations is also discussed.

Chapter 7
This includes the conclusions drawn based on simulation results. It also provides scope for future work in this field.

Appendices
In the appendices the process design calculations, the detail results of simulation of different configurations of cryogenic air separation plant and the results of exergy analysis are included.