

Republic of Yemen

Ministry of Higher Education and Scientific  
Research

Emirates International University

Faculty of engineering and IT

Chemical Engineering Department



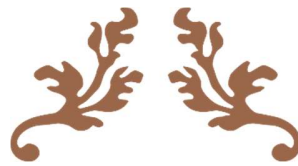
الجمهورية اليمنية

وزارة التعليم العالي والبحث العلمي

الجامعة الإماراتية الدولية

كلية الهندسة وتقنية المعلومات

قسم الهندسة الكيميائية



---

# Feasibility for Industrial Oxygen yemen by using cryogenic

---

**EMIRATES INTERNATIONAL  
UNIVERSITY**

**Project sopervisors:**

**Prof. Hani Damaj**

**Eng.Gamal Saeed**

**Done by:**

**Eng. Afnan Abdullah Naji Al-Zamzami**



## المحتويات

Chapter 1 .....	5
Introduction .....	5
<b>Overview</b> .....	6
<b>Importance of Oxygen:</b> .....	6
<b>Oxygen applications in Medical Sector:</b> .....	6
<b>Challenges shortage of oxygen supply in medical sectors in yamen:</b> .....	6
<b>Aims of the study:</b> .....	6
<b>Project objectives</b> .....	7
<b>Feasibility study</b> .....	7
<b>Technical Analysis:</b> .....	7
<b>Economic Analysis:</b> .....	7
<b>Environmental Analysis:</b> .....	7
<b>Legal Analysis:</b> .....	7
<b>Planning</b> .....	8
<b>Plant Design:</b> .....	8
<b>Equipment Selection:</b> .....	8
<b>Energy Sources:</b> .....	8
<b>Marketing Plan:</b> .....	8
<b>Implementation</b> .....	8
<b>Construction and Installation:</b> .....	8
<b>Trial Operation:</b> .....	8
<b>Performance Evaluation:</b> .....	8
<b>Continuous Monitoring:</b> .....	8
<b>Factors to Consider</b> .....	9
<b>Properties of Cryogenic Fluids:</b> .....	10
Chapter 2 .....	12
Previous Studies .....	12
<b>Technologies:</b> .....	13
<b>Cryogenic Separation</b> .....	13
<b>Pressure Swing Adsorption</b> .....	13
<b>Membrane Technology</b> .....	14
Figure 1: SEOS(TM) Process .....	15

<b>Figure 2: ITM Oxygen Process.....</b>	<b>15</b>
<b>By-Product Oxygen .....</b>	<b>16</b>
<b>Comparison between Cryogenic Air Separation and PSA .....</b>	<b>16</b>
Figure 3: Oxygen Production Cost vs. Purity Desired .....	17
<b>Figure 4.....</b>	<b>18</b>
<b>Study on Water Electrolysis for Oxygen Production - Reduction of Water Circulation and Gas-Liquid Separator .....</b>	<b>19</b>
<b>Important note: .....</b>	<b>19</b>
Chapter 3 .....	20
Methodology .....	20
<b>Methodology .....</b>	<b>21</b>
<b>Integration of oxygen plant with energy system.....</b>	<b>21</b>
<b>Process cycles for cryogenic air separation.....</b>	<b>22</b>
<b>Contribution to total power.....</b>	<b>22</b>
<b>Operability and control.....</b>	<b>24</b>
<b>Future developments.....</b>	<b>24</b>
<b>OXYGEN PRODUCTION USING SOLID ELECTROLYTES .....</b>	<b>25</b>
<b>The oxygen transport process.....</b>	<b>25</b>
<b>Air Products oxygen ITM systems.....</b>	<b>26</b>
<b>Air Products H<sub>2</sub>+CO ITM module .....</b>	<b>27</b>
<b>Norsk Hydro systems.....</b>	<b>27</b>
<b>Praxair systems .....</b>	<b>28</b>
<b>Linde/BOC systems.....</b>	<b>29</b>
<b>Future development of O<sub>2</sub> ion transport systems .....</b>	<b>29</b>
<b>PLANT LOCATION AND SITE SELECTION .....</b>	<b>30</b>
<b>The principal factors to consider are: .....</b>	<b>30</b>
Chapter 4.....	31
The material and energy balances .....	31
<b>Raw Material Requirement.....</b>	<b>32</b>
<b>Plant Production Capacity:.....</b>	<b>33</b>
<b>The material, and energy balances:.....</b>	<b>33</b>
<b>The material balances:.....</b>	<b>33</b>
<b>Material balance for the overall process:.....</b>	<b>34</b>

---

<b>Oxygen Production:</b> .....	34
<b>The average molecular weight of air (M):</b> .....	35
<b>Calculate the inlet air flow rate:</b> .....	35
<b>Balances over individual process units:</b> .....	36
<b>Material balance on the compressor:</b> .....	36
<b>Material balance on the Main Heat Exchanger:</b> .....	36
<b>Material balance on the Cryogenic Distillation Column:</b> .....	37
<b>The energy balances:</b> .....	40

# Chapter 1

## Introduction

---

## Chapter 1: Introduction

### Overview

Oxygen: The Lifeline of Life

Oxygen is an indispensable chemical element for life on Earth. Comprising approximately 21% of the atmosphere, it is fundamental to the respiratory process of living organisms. Oxygen enters the body through the lungs and is transported by the blood to nourish cells with the energy necessary for their vital functions.

### Importance of Oxygen:

Life: Oxygen is the foundation of life on Earth, essential for the respiration of almost all living organisms.

Combustion: Oxygen is involved in combustion reactions that generate heat and light, making it a crucial element in many industries.

Ozone: Oxygen combines with itself to form the ozone layer, which shields the Earth from harmful ultraviolet radiation.

### Oxygen applications in Medical Sector:

Medical Sector: Oxygen is widely used in hospitals to treat various diseases, such as lung and heart diseases, and is also employed in surgical procedures.

Industrial Sector: Oxygen is involved in numerous industries, including steelmaking, glass manufacturing, electronics, and welding.

Environmental Sector: Oxygen is used in water treatment and purification, as well as in other environmental technologies.

### Challenges shortage of oxygen supply in medical sectors in yamen:

- Advanced Technology Requirement: Commercial oxygen production necessitates the use of sophisticated technologies.
- Environmental Regulations: Strict adherence to environmental regulations governing production processes and waste disposal is mandatory.
- Logistics Challenges: Transportation Storage.

### Aims of the study:

- OXYGEN PRODUCTION by using advanced and cheaper Method
- Providing adequate amounts of OXYGEN in Yemen Hospitals
- Adding a new tributary to the national economy
- Infrastructure development IN Medical Sector in Yemen

## Project objectives

1.Establishment of Oxygen Plants in Yemen: This involves setting up factories to produce oxygen for various purposes, including:

Medical Use: Supplying oxygen to hospitals and homes for patients suffering from respiratory problems.

Industrial Applications: Providing oxygen for industries such as steel and glass manufacturing that rely on oxygen in their processes.

Environmental Applications: Producing oxygen from renewable sources to contribute to environmental protection.

2.Economic Objectives:

Cost Reduction: Aiming to decrease the production costs of oxygen

## Feasibility study

### Technical Analysis:

Determine the most suitable technology for oxygen production (air separation, electrolysis, etc.)

Estimate required energy, expected production quantity, and product quality

Assess engineering and infrastructure requirements

### Economic Analysis:

Estimate construction and equipment costs

Estimate operating and maintenance costs

Determine expected selling prices

Calculate return on investment and payback period

### Environmental Analysis:

Evaluate potential environmental impacts of the production process

Develop plans for waste management and mitigation of negative impacts

### Legal Analysis:

Study laws and regulations related to establishing an oxygen production plant

Obtain necessary licenses



## Planning

### Plant Design:

Develop a detailed plant layout showing the arrangement of different equipment and units

Select a suitable location for the plant

### Equipment Selection:

Select equipment and devices necessary for oxygen production based on required quantity and quality

Ensure equipment quality and efficiency

### Energy Sources:

Determine the primary energy source for the plant (electricity, natural gas, etc.)

Conduct a feasibility study for each energy source

### Marketing Plan:

- \* Identify the target market
- \* Develop a marketing plan to market the product

## Implementation

### Construction and Installation:

Construct the plant and install equipment according to the approved design

Conduct necessary tests to ensure the safety and efficiency of the equipment

### Trial Operation:

Operate the plant on a trial basis to ensure all systems work efficiently

Make adjustments to the system if necessary

Full Operation:

Begin commercial production of oxygen

Evaluation and Monitoring

### Performance Evaluation:

- \* Evaluate the plant's technical and financial performance periodically
- \* Compare actual performance to expected performance

### Continuous Monitoring:

- \* Continuously monitor product quality
- \* Monitor energy and raw material consumption
- \* Conduct periodic equipment maintenance

## Factors to Consider

- \* Product quality: Ensure the purity of the produced oxygen according to international standards
- \* Safety: Take all necessary precautions to ensure the safety of workers and the surrounding environment
- \* Efficiency: Achieve the highest possible efficiency in oxygen production to reduce costs
- \* Sustainability: The project should be environmentally and economically sustainable.

**Table () Advantages and disadvantages of cryogenic air separation (ASU).**

Advantages	Disadvantages
High tonnage of oxygen can be produced	Large site space and utility requirements
Commercial (used in refining and large industrial units)	High capital cost due to the large units
Low amount of electricity per unit oxygen	Long start-up and shut down time
Produces very high purity oxygen	
Can generate liquid oxygen for storage on site	

**Table () Advantages and disadvantages of pressure swing adsorption (PSA).**

Advantages	Disadvantages
Quick installation and start-up	Limited scalability
Moderate capital cost	High maintenance (due to the zeolite regeneration)
PSA unit are readily available and can be purchased and delivered quickly	High maintenance equipment
	Extremely noisy operation even when compared with the other process

**Table () Advantages and disadvantages of electrochemical oxygen generation.**

Advantages	Disadvantages
High oxygen purity achievable (> 99.99%)	Multiple electrolytes in research
No moving parts except process fan	High operating and capital costs
Excess hydrogen to sell or burn	Small scale, number up
	require high purity water
	Low pressure

**Table () Advantages and disadvantages of advanced cryogenic air separation.**

Advantages	Disadvantages
Self-heat recuperation technology	O <sub>2</sub> with low purity as no re-boil temperature control (95%)
Only one distillation column in the proposed process	Technical challenges of integration
Energy consumption decrease by about 31%	Paper study - Requires further evaluation

**Table () Advantages and disadvantages of membrane Separation.**

Advantages	Disadvantages
Low capital cost	Uneconomical for high purity requirements
Most economical process at low flow rates	Uneconomical for large outputs
Least costly for repairs and maintenance.	Requires relatively large amount of electricity per unit oxygen

## Properties of Cryogenic Fluids:

Liquid nitrogen is clear, colorless and odorless fluid non-reactive (inert), Because nitrogen is the major constituent of air (78.08 percent by volume or 75.45 percent by weight), it is produced commercially by distillation of liquid air.

Nitrogen with an atomic number of 14 has two stable isotopes with mass numbers of 14 and 15. the relative abundance of these three isotopes is 10,000:38.

40-liter compressed cylinder of 6 Nm<sup>3</sup>

Liquid oxygen has a characteristic blue color ,it is the second most abundant in air (20.95 percent by volume or 23.2 percent by weight).

oxygen with an atomic number of 16 has three stable isotopes with mass numbers of 16,17,and 18.the relative abundance of these three isotopes is 10,000:4:20.

Oxygen (O<sub>2</sub>), an inorganic gas recovered from atmospheric air, is one of the most widely used industrial gases.

Oxygen is not a flammable gas, but it easily supports combustion.

is clear, colorless and odorless fluid

40-liter compressed cylinder of 7 Nm<sup>3</sup>

Liquid argon is clear, colorless fluid with properties similar to those of liquid nitrogen.it is inert and nontoxic. Argon is present in atmospheric air in a concentration of (0.934 percent by volume or 1.25 percent by weight).

Argon with an atomic number of 36 has three stable isotopes with mass numbers of 36,38,and 40.the relative abundance of these three isotopes is 338:63:100,000.

Because the boiling point of argon lies between that of liquid oxygen and that of liquid nitrogen (slightly closer to that of liquid oxygen), a crude grade of argon (90 to 95 percent pure) can be obtained by adding a small auxiliary argon recovery column in an air separation plant.

Saturated liquid property at 1 atm	Units	Liquid Air	Liquid Nitrogen	Liquid Oxygen	Liquid Argon
Normal boiling point	K	78.8	77.36	90.18	87.28
	°R	142	139.3	162.3	157.1
Critical temperature	K	133	126.1	154.6	150.7
	°R	240	277.0	278.3	271.2
Critical pressure	MPa	3.92	3.39	5.08	4.89
	atm	38.7	33.5	50.1	48.3
Triple-point temperature	K	...	63.2	54.4	83.8
	°R	...	113.7	98.0	150.8
Triple-point pressure	kPa	...	12.85	0.152	68.8
	atm	...	0.127	0.0015	0.679
Density	kg/m <sup>3</sup>	874	807.3	1141	1394
	lb <sub>m</sub> /ft <sup>3</sup>	54.6	50.4	71.2	87.0
Latent heat	kJ/kg	205	199.3	213	161.9
	Btu/lb <sub>m</sub>	88.1	85.7	91.6	69.6
Specific heat	kJ/kg. K	1.96	2.05	1.695	1.136
	Btu/lb <sub>m</sub> . °R	0.486	0.490	0.405	0.271
Viscosity	μPa. s	168	158	190	252
	lb <sub>m</sub> /ft. hr	0.407	0.382	0.460	0.610
Thermal conductivity	mW/m. K	141	139.6	151.4	123.2
	Btu/hr. ft. °F	0.0815	0.0807	0.0875	0.0712

# **Chapter 2**

## **Previous Studies**

---

## Chapter 2: Previous Studies

### Technologies:

#### Cryogenic Separation

Cryogenic air separation units (ASU) is an old process used to produce high purity oxygen or nitrogen at high volumes. The process was first developed by Carl Von Linde in 1895 and it remains pretty much the same today. Cryogenics is also the chief method by which liquid oxygen can be produced. The technology is centered on the fact that each of air's constituents has different boiling points. The idea behind the process is to lower the temperature of the air such that nitrogen and oxygen separate based on their boiling points. This occurs at around -300°F.. If higher purity oxygen or liquid oxygen is required, further distillation is required. For liquid oxygen, nitrogen is used as the heat transfer fluid to further cool the oxygen.

Cryogenic separation is most effective when any of the three criteria need to be met: high purity oxygen is required ( $>99.5\%$ ), high volumes of oxygen are required ( $\geq 10^2$  tons of oxygen/day), or high pressure oxygen is required. Cryogenic air separators take more than an hour to start up. Additionally, since cryogenics can produce such a high purity of oxygen, the waste nitrogen stream is of a usable quality. This can add significant financial benefits to a process integrated with a cryogenic ASU.

#### Pressure Swing Adsorption

Pressure swing adsorbers (PSA) are a much newer technology as compared to cryogenic ASU. PSA devices take atmospheric air into a pressurized tank. Inside the tank are zeolites. Zeolites, under pressure, have the ability to deform and create a dipole. Depending on the zeolite chosen, this dipole allows for the collection of nitrogen, but allows oxygen to pass. For oxygen enrichment, the PSA is generally pressurized to a minimum of 1.5 atm. After a certain volume of air has been separated, the zeolite will become saturated with nitrogen. At this point, it needs to be regenerated. This is done by dropping the pressure of the tank back to atmospheric pressure, thus returning the zeolite to its original polarity. This liberates the nitrogen. Vacuum Pressure Swing Adsorbers (VPSA) lower the pressure in the tank to sub atmospheric values, thus improving the regeneration process. In both processes, while one tank is regenerating, another tank is usually charging. This allows for a continuous production of oxygen.

PSA devices are best suited for processes that do not require extremely high purities of oxygen ( $<95\%$ ). While PSAs can achieve as high as 99.9%, the cost associated with going above 99.5% in a PSA device rises tremendously. Furthermore, PSA devices are best suited for small volumes of oxygen production, typically on the order of  $10^1$  tons/day. Since the output of oxygen is largely controlled by the bed size in the PSA systems, costs rise linearly when higher volumes of oxygen are required. PSA devices take a few minutes for start-up.

A mid-sized pressure swing adsorbers running costs are shown below. The data is for an Oxair Model OXT-B14 adsorber.

O <sub>2</sub> output	Compressor Power	Chiller Power	Power Cost	Foot Print
400 Nm <sup>3</sup> or 13.6 tons/day	400 HP or 276 KW	150 HP or 80 KW	0.75 KW/ Nm <sup>3</sup>	190 m <sup>2</sup>

Also, the usability of by-product nitrogen in PSA systems is limited because the nitrogen will have significant levels of oxygen.

## Membrane Technology

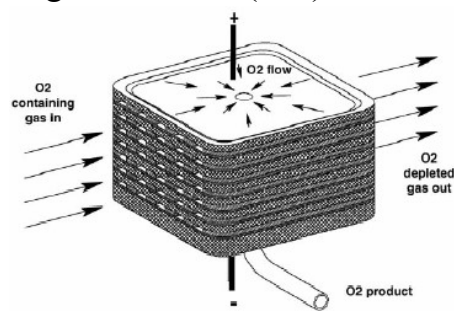
Conventional membrane technology involves passing air over a membrane filter. The filter will allow fast gasses to pass and slow gasses will stay. Oxygen is considered a fast gas and nitrogen and argon are considered slow gasses. Varying levels of purity can be achieved by varying the time that the gas spends undergoing filtration. Previous membrane technology could only produce purity levels of less than 50%. Membrane technology has quick start-up times and operates at near ambient conditions. Capital costs with membrane systems increase linearly with output volume desired. Currently, membrane technologies can satisfy needs of up to 20 tons of oxygen/day.

However, recently there has been a significant technological break through in membrane technology. The ion transport membrane (ITM) was developed by Air Products and Chemicals, in conjunction with the United States Department of Energy and Ceramtec. Reports have shown that this technology can produce greater than 99% purity O<sub>2</sub> at much lower costs than cryogenic separation.

Three separate ITM technologies have been developed: SEOS™ Oxygen Generator, ITM Oxygen, and ITM Syngas.

The SEOS™ system consists of electrochemical cell stacks. These cell stacks are heated to greater than 600°C and a voltage is applied. Under this electric potential, the oxygen in the feed air is ionized, recombined, and collected at an outlet . **Figure 1** illustrates the process.

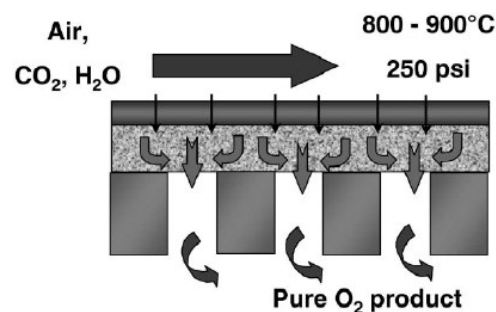
Figure 1: SEOS(TM) Process



ITM Oxygen can generate extremely high purity oxygen streams (in excess of 99.9%) and high volume (equivalent to volumetric flow of cryogenic separation systems). It takes in high pressure, high heat air. This air is passed over a ceramic membrane made of metals that are oxygen depleted. The membrane accepts the oxygen where it is ionized and diffused through the membrane due to a difference in oxygen partial pressures across the membrane. Since the membrane is not attracted to any other compounds, the process only filters oxygen. The oxygen stream is sub-atmospheric. ITM Oxygen represents competition to cryogenic separation units.

**Figure 2** illustrates the process.

Figure 2: ITM Oxygen Process



ITM Syngas is a process still under development. The technology will pass air on one side of a membrane and natural gas and steam on the other. The two by-product streams will be syngas and oxygen depleted air.

Research work is still continuing for ITM technology and is expected to be concluded by 2007. At this time, Air Products aims to be able to produce an economically viable ITM system.



---

## By-Product Oxygen

In some of the processes mentioned above, high volumes of nitrogen will be available to the user for use in another process. Similarly, in processes that produce nitrogen, large volumes of oxygen are readily available. One of the many applications of nitrogen is in the food industry, where oxygen increases fruit respiration, thus leading to a shortened life during which the fruit is edible. Storing fruit in nitrogen enriched environments reduces respiration rates.

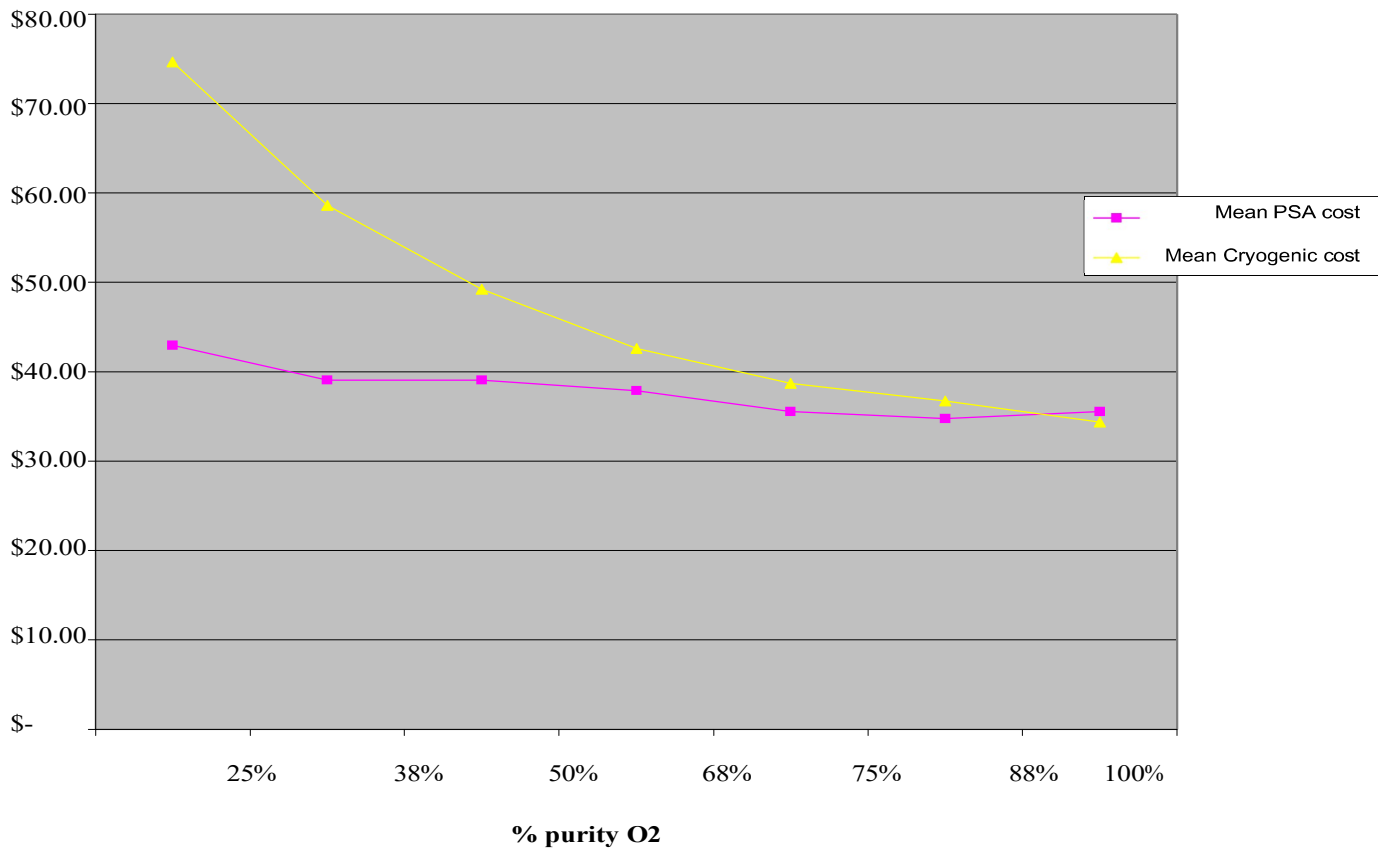
Similarly, hydrogen production results in waste oxygen. All over the world, countries have set measures to increase the amount of energy derived from hydrogen, meaning that the hydrogen economy is certain to grow. Consequently, if a use can be found for the left over oxygen, an overall increase in the hydrogen production process efficiency would lead to potentially large energy savings.

Currently, hydrogen is produced via electrolysis. Electrolysis is the process by which water is broken into hydrogen and oxygen. It is an expensive process. Alkaline electrolysis costs \$500/kW and PEM electrolysis costs \$1000/kW. These costs make process efficiency all the more important. If electrolysis efficiency is 71%, then 5000 kWh of electricity production would result in the generation of 500 Nm<sup>3</sup> of oxygen. Producing this much oxygen via PSA or cryogenics would require 250 kWh of electricity. However, this oxygen is being produced at essentially no additional costs. Therefore, if the oxygen can be used, then the electrolysis efficiency will rise to 76%. One potential application of the by-product oxygen in electrolysis would be in hospitals, where fuel cells would power the facility and the oxygen could be used for patient care.

## Comparison between Cryogenic Air Separation and PSA

**Figure 3**, re-created from literature published by Air-Products and the US Department of Energy, illustrates the mean cost of the cost per ton of oxygen at a desired purity level. Although the data is older, the trends in the cost are the same. As one can see, PSA is a better option in terms of running costs for purity levels slightly less than 100%. However, at high purity levels, i.e. greater than 99%, cryogenics will prove to be less expensive.

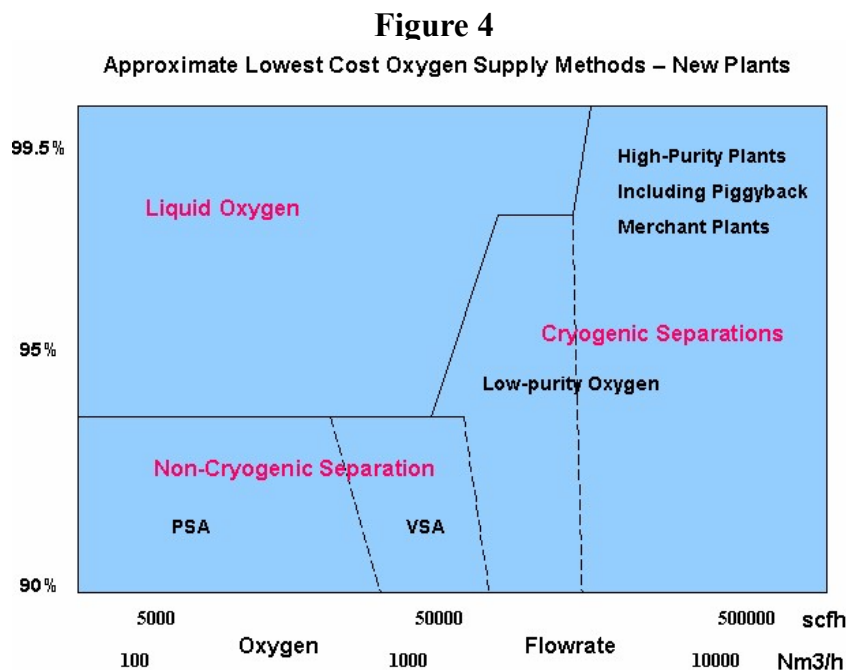
Figure 3: Oxygen Production Cost vs. Purity Desired

**Oxygen Production Cost vs. Purity Desired**

Running cost and purity are not always the only selection criteria. Volume desired is also key parameters in determining the air separation unit best for a particular industry. **Figure 4**, created by Universal Industrial Gases, INC., shows which technology is best suited when all three criteria (volume, purity, cost) are weighed against each other. It should be noted that advancements in zeolites will surely lower the price of PSA systems in the future. There are little expected advancements in cryogenic air separation, and therefore costs can be expected to remain the same.

As **Figure 4** shows, PSA/VPSA is suitable for low volumes and low purity oxygen requirements. Cryogenic separation is best suited for high flow rates and when high purity oxygen is required. Finally, if high purity oxygen at low rates is desired, the plant may want to consider delivery of liquid oxygen.

“Piggyback Merchant Plants” refers to the ability for a plant to produce enough high purity oxygen for itself and for local merchants that would also need the high purity oxygen. This is financially feasible when the plant needs low volumes of high purity oxygen, but merchants in the surrounding community also need high purity oxygen and are willing to buy it from the plant.



Source: From Universal Industrial Gases Inc

---

## **Study on Water Electrolysis for Oxygen Production - Reduction of Water Circulation and Gas-Liquid Separator**

The Japan Aerospace Exploration Agency (JAXA) has been studying and developing Environmental Control and Life Support System (ECLSS) technologies, particularly an air regeneration system to support long-duration manned space missions beyond Earth orbit. One of our goals is to develop a lightweight, compact and energy efficient air regeneration system. The air regeneration system is comprised of a water electrolysis subsystem for oxygen generation, a CO<sub>2</sub> removal subsystem, and a CO<sub>2</sub> reduction subsystem. Previous research had reported on a water electrolyzer unit without water circulation and an independent gas/liquid separator, and made the subsystems more simple and lightweight. This report on the oxygen generation subsystem is updated and scaled up from the previous report. JAXA has developed a new electrolyzer unit level of 100A (3-cell stacks). It also has heatsinks for electrolysis at high current density. The results of this report showed that the characteristics of the new unit are almost the same as those of previous systems, and that heatsinks are also effective in the new unit system.

### **Important note:**

The electrolysis of water is primarily used for the production of hydrogen, and the oxygen obtained in this way is considered a by-product.

Is oxygen usually not manufactured by the electrolysis of water?

Because of the cost. Producing oxygen from atmospheric air is much cheaper than water electrolysis, because breaking down water molecules requires a lot of energy, and this high energy consumption costs more than using any of the different available methods to actually separate oxygen from other gases in the air.

# **Chapter 3**

## **Methodology**

---

## Chapter 3: Methodology

### Methodology

- The air compressor for plants of 4000 to 10000 tonne/day would be an axial/centrifugal combination driven by a steam turbine or electric motor. The compressor manufacturers have the technology, experience and fabrication facilities to extend their current demonstrated capability of 4000 tonne/day oxygen when the demand arises.
- The air purifier is a dual bed system using pelleted adsorbents which is operated on line for periods from 90 min to 6 hrs and then switched to thermal regeneration at typically 150oC with a N<sub>2</sub> stream. The adsorbents are generally arranged with a first layer of an alkali metal doped alumina for bulk water and CO<sub>2</sub> removal followed by a second layer of a 13X zeolite for final clean-up . The preferred bed geometry for very large air flow-rates is an annular vertical arrangement, with radial gas flow. The air flows radially inwards to a central collection tube while the regeneration gas flows outwards.
- Cryogenic heat exchangers are almost exclusively aluminum plate fin units. Blocks are manifolded together to provide units of any required size. These units are used for main heat exchanger, reboiler condenser and sub-coolers.
- The distillation column uses aluminum and copper structured packing in sections separated by carefully designed liquid distributors. Scale-up to column sizes for 10000 tonne/day O<sub>2</sub> plants has been demonstrated for petroleum and petrochemical systems and would not present a process risk for air separation.
- The reboiler/condenser is an aluminum plate-fin heat exchanger assembly located within the distillation column shell. The preferred arrangement is for the liquid O<sub>2</sub> to evaporate as it flows downwards with N<sub>2</sub> condensing also in a downward flowing direction. The operating temperature difference at the O<sub>2</sub> outlet can be 1°C. The O<sub>2</sub> distribution is critical to avoid safety problems caused by accumulation of trace hydrocarbons, N<sub>2</sub>O, CO<sub>2</sub> if dry boiling or a passage blockage occurs. The design and operation of the air purifier adsorbents is critical for safe reboiler operation.

### Integration of oxygen plant with energy system

In a coal fired oxyfuel boiler the feed-water is preheated using steam bled at increasing pressure levels from the steam turbine as the heat source. Using an ASU adiabatic air compressor provides boiler feed-water preheating in the after-cooler giving significant power savings by releasing steam for the turbines and reducing cooling water requirements for the ASU. The compressor erected costs are significantly reduced.

Adiabatic compression of the CO<sub>2</sub> produced will also lead to similar benefits. A fossil fuel oxygen based gasification system with CO<sub>2</sub> capture produces a hydrogen fuel gas which must be diluted with nitrogen from the ASU together with some steam generated by using gasifier low grade heat for controlling NOX levels in the gas turbine exhaust. The resulting fuel gas mixture is typically 6 times the volumetric flow of the usual natural gas fuel. This means that in practice

there will always be sufficient flow in the turbine section to fully load the gas turbine under virtually any air inlet pressure or temperature. The air flow can be regarded as fixed once the volume of fuel gas is fixed. This results in the air compressor section delivering more air than required for low air temperature sea-level locations with progressively less air at high temperature elevated locations. The air balance will vary with gas turbine manufacturer and model. In general excess air may often be available which can be bled in many machine designs from the compressor discharge. This air can be used following pressure reduction and heat recovery for part of the air feed to the ASU. This decoupling of the pressures in the gas turbine and ASU is highly desirable to allow stable ASU operation. Bleed air is usually limited to about 40% of the ASU total requirement so that the ASU can be started up with a separate air compressor. In general all the available nitrogen from the ASU is required for hydrogen dilution.

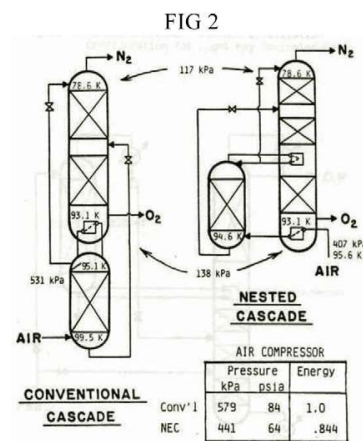
## Process cycles for cryogenic air separation

Analysis of the thermodynamic losses leading to total ASU power consumption requires an exergy analysis. Flow-sheeting programs such as ASPEN PLUS have options for these calculations. The contribution to total power consumption for a simple double column plant producing 99.5% O<sub>2</sub> at 1.1 bar pressure is shown in Table 1. The current use of low pressure drop distillation packing, low temperature difference down-flow re-boilers, longer heat exchangers, larger diameter piping and high efficiency air compression have all reduced power consumption. Further major reductions will result from the use of more efficient distillation involving more levels of heat integration between the high pressure and low pressure distillation columns with accompanying changes to the basic process cycle. The effect of using a nested cascade of two reboiler condensers is shown in FIG 2. Other arrangements are also possible. The use of less than 97% O<sub>2</sub> purity facilitates these integrations. The flow-sheet for a current design of a 95%, 1.6 bar pressure O<sub>2</sub> plant for use in an oxyfuel coal fired boiler having a power consumption of 201 kWhrs/tonne of contained O<sub>2</sub> is shown in FIG 3.

## Contribution to total power

TABLE 1

Item	%
Heat exchangers ♦T	15.8
Expansion turbine	0.9
Pressure drops	5.7
Pressure reducing valves	3.4
Heat leak	0.9
Mixing	0.4
HP (lower) column	3.2
LP (upper) column	16.8
Ideal work of separation	16.9
Product conditions	5.1
Air compressor and motor	30.9
Work input	100.0



The air is compressed to 3.5 bar in K101 while part is compressed to 5.3 bar K102 and used to evaporate the liquid O<sub>2</sub> product stream in E101. The compressors are adiabatic with heat of compression used for condensate and boiler feed-water preheating. There are two high pressures columns. C103 operates at 3.2 bar and produces N<sub>2</sub> which boils low purity O<sub>2</sub> in E104 while C104 operates at 5 bar pressure boiling higher purity O<sub>2</sub> at the base of the LP column C105. Part of the condensed N<sub>2</sub> from E103 provides the top reflux stream to C105 while impure reflux N<sub>2</sub> from E104 provides an intermediate reflux stream. The LP column has 4 feed points, two reflux points and two re-boilers. Each HP column could be surmounted by an identical LP column allowing a 10000 tonne/day O<sub>2</sub> capacity in

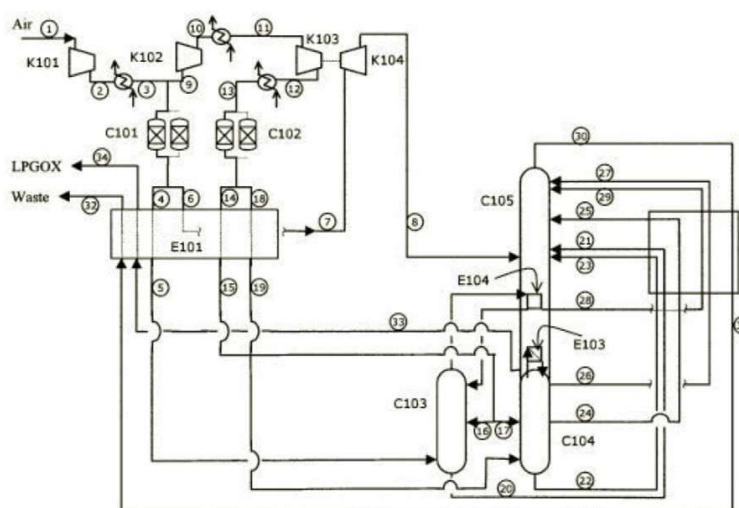


FIG 3

a column diameter of about 7 metres which could be shop fabricated. O<sub>2</sub> for a fossil fuel gasification system with CO<sub>2</sub> capture is required at 45 bar to 100 bar pressure typically at 95% purity and all the N<sub>2</sub> will be required at 20 bar to 25 bar with below 2% O<sub>2</sub> content for dilution of H<sub>2</sub> gas turbine fuel. The most efficient configuration uses an elevated air pressure to facilitate N<sub>2</sub> production at elevated pressure with an efficient distillation system and the option of partial air feed from the gas turbine air compressor. The flow-sheet for a current design is shown in FIG 4. The plant has a single HP column operating at 9.7 bar pressure and two LP columns. One operates at 3 bar producing product liquid O<sub>2</sub> from the sump, which is pumped to delivery pressure and vaporized in the main heat exchanger. The other operates at 5 bar and produces a 70% liquid O<sub>2</sub> product stream from the base which is fed to an intermediate point in the 3 bar column. The N<sub>2</sub> streams from these two columns are compressed and heated against cooling air bleed from the gas turbine compressor then mixed with the H<sub>2</sub> gasifier product. The cooled air is reduced in pressure to 10 bar in a turbine expander and provides up to 40% of the air for the O<sub>2</sub> plant. A separate air compressor delivers 60% of the air which allows the O<sub>2</sub> plant to be started without the gas turbine in operation. About 30% of the air is further compressed to between 60 bar and 100 bar to condense against boiling product liquid O<sub>2</sub> in the main heat exchanger. All the major O<sub>2</sub> plant suppliers have patented process designs which have the same general characteristics as these two illustrations with similar performance.



## Operability and control

New build oxyfuel coal fired power stations will be designed without air firing capability. They require high reliability  $O_2$  production with constant purity and a ramping capability of 5% flow/minute at all operating levels. This is higher than can be achieved by the plant alone, but if a liquid  $O_2$  backup storage and an instant demand vaporizer system is installed this is easy to achieve. Consider a 10000 tonne/day  $O_2$  plant ramping at 5%/min from 60% load to 100% in 8min. The ASU can ramp at 2%/min and it would require an additional 16.7 tonne liquid

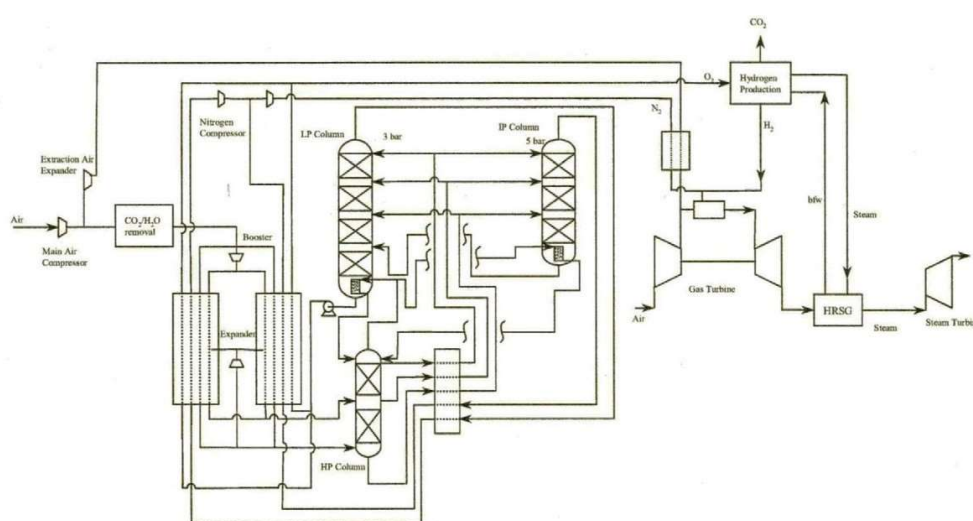


FIG 4

oxygen to be vaporized, a small amount easily produced from the ASU during steady operation. Turndown at 5%/min would be achieved by venting 16.7 tonne of excess oxygen or allowing  $O_2$  purity to rise a little. The dynamic behavior of the  $O_2$  plant with variations in power demand are easily simulated by using one of the options in ASPEN PLUS or other software. Similar considerations apply to the  $O_2$  plant integrated with a fossil fuel gasification system. For both systems the capacity of the liquid  $O_2$  storage tanks should be sufficient to provide capacity to fill the plant with liquid  $O_2$  and produce extra refrigeration to minimize plant startup times from a warm condition

## Future developments

Cryogenic air separation is a mature efficient technology ideally suited for oxyfuel coal fired boilers and capable of efficient integration with fossil fueled gasification systems. The industry currently uses high efficiency aluminum plate-fin heat exchangers, optimized packed column systems, advanced air purification by adsorption, efficient process cycles and advanced control systems all relevant to future technical needs. Modern air compressors having high efficiency with advanced aerodynamic design will be available for the large single train  $O_2$  plants of up to 10000 tonne/day capacity required for power and  $H_2$  systems with  $CO_2$  capture. The main requirement will be for a very large increase in manufacturing capacity to meet demand if  $CO_2$  capture and storage is implemented globally

## OXYGEN PRODUCTION USING SOLID ELECTROLYTES

### The oxygen transport process

Certain electrically conducting mixed metallic oxides can diffuse  $O_2$  ions and electrons through their crystal lattice at temperatures above  $600^\circ C$  when exposed to a difference in activity such as partial pressure or equilibrium  $O_2$  concentration. A concentration cell is set up with an emf  $E$  and  $O_2$  inlet partial pressure  $P$  and outlet pressure (pure  $O_2$ )  $P_{perm}$ .  $R$  is the gas constant and  $F$  is the Faraday constant.  $T$  is the absolute temperature and  $L$  is the active membrane thickness.  $J_{O_2}$  is oxygen flux, and  $\sigma_i$  is ionic conductivity.  $O_2$  diffusion is controlling.

$$E = (RT/4F)\ln(P/P_{perm}) \quad -1$$

$$J_{O_2} = -(RT\sigma_i/16FL)\ln(P/P_{perm}) \quad -2$$

The practical temperature range is above  $750^\circ C$  and typical permeability of a leak-free membrane is  $10^6$  to  $10^7$  barrers. The actual  $O_2$  flux achieved in practice will be reduced by diffusional mass transfer resistances on the feed and permeate side of the membrane and its flow geometry. The recommended operating range for Air Products membranes using air derived feeds are a temperature range from  $800^\circ C$  to  $900^\circ C$ , feed pressure from 6.9 bar to 69 bar with  $O_2$  content from 0.1 to 0.21 mol fraction and permeate pressure from 0.13 bar to 6.9 bar. The maximum achievable  $O_2$  recovery occurs when the  $O_2$  partial pressure in the feed stream falls to the pressure of the  $O_2$  permeate stream and the recommended design recovery should be in the range 50% to 85% of this value. An inert.

purge gas stream such as steam or oxy-fuel recycle flue gas can be used to dilute the  $O_2$  permeate stream. The recommended  $P_{perm}$  is:

$$P_{Xfeed} = 7P_{perm} \quad -3$$

An ITM can be used to either produce a pure  $O_2$  product stream or it can be exposed to a reactive gas mixture on the permeate side such as natural gas,  $H_2$ ,  $CO$ , steam mixtures. The  $O_2$  equilibrium concentration will be extremely low ( $<10^{-16}$  bar at  $>800^\circ C$ ) which would allow operation with atmospheric pressure air on the feed side and high pressure conditions on the permeate side limited only by the mechanical strength of the membrane system. This is due to the diffusion of  $O_2$  being proportional to  $\ln(P/P_{perm})$  compared to pore diffusion where the rate is proportional to  $(P - P_{perm})$ . Operation with  $CH_4:H_2O:O_2$  in the proportions 1:4:0.37 at 20 bar  $800^\circ C$  would result in isothermal conditions for the membrane at equilibrium with a composition  $H_2$  37%,  $CO$  6%,  $CO_2$  8%,  $CH_4$  2%,  $H_2O$  47%. The exothermic oxidation is balanced by the endothermic reforming reaction. Alternatively a lower steam to  $CH_4$  ratio could be used allowing a temperature rise of  $100^\circ C$  maximum. Important features of ITM systems are:

\* Feed and product must be free from particulates or solid products which would block the membrane surfaces. Only clean gas can be used. Reaction conditions must not lead to Boudouard carbon formation.

\* The membrane oxide material must be thermally stable and have stable crystal structures at operating temperature and over the entire oxygen partial pressure operating range.

The preferred ITM materials are perovskites having a cubic structure with a typical overall formula  $AB_{3-x}$  where A is a lanthanide element, B is a transition metal such as titanium, vanadium, chromium, iron, cobalt, copper and zinc with some minor additional components.

O<sub>2</sub> diffusion is maximized when x is in the range 0.05 to 0.5 resulting in vacancies in the O<sub>2</sub> ion positions in the crystal lattice. The basic membrane structure consists of a very thin dense O<sub>2</sub> diffusion layer backed by a porous support layer both usually fabricated from the same perovskite material. The module design must be amenable to standard ceramic forming techniques such as tape casting, shaping, curing, baking and assembly into the final elements. The element must have good hydrodynamic design to minimize mass transfer resistance and its design must ensure dimensional and chemical stability and low stress concentration under thermal and pressure cycling during startup, shutdown and operation. There must be a reliable ceramic to metallic joint to allow gases to enter and leave the elements. The material used must be compatible with high temperature O<sub>2</sub> at the design pressure. Each company engaged in the development of ITM systems has a unique design approach.

### Air Products oxygen ITM systems

The ITM system developed by Air Products for pure O<sub>2</sub> production is shown in FIG 5. The integration of the ITM membrane module with a modified gas turbine for a gasification application involves extracting compressed air

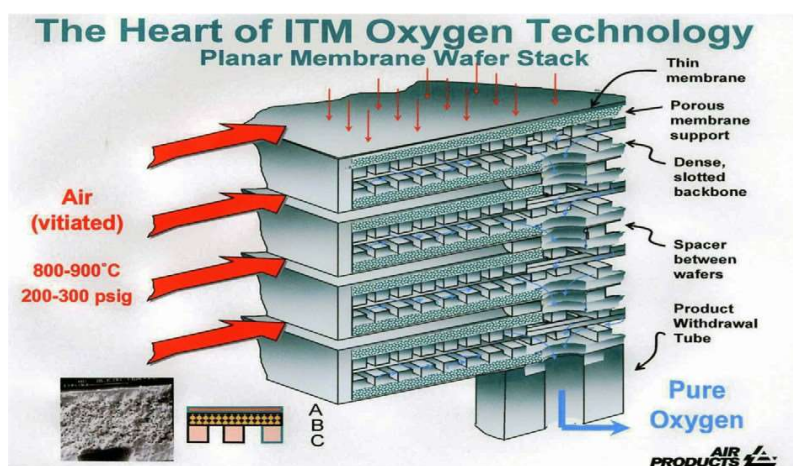


FIG 5

from the turbine compressor discharge at a temperature of about 450°C and heating it up to 800°C to 900°C with a direct combustion of H<sub>2</sub> fuel gas. The hot air is then passed through the membrane module where it flows over the outside of the membrane wafers. O<sub>2</sub> diffuses through the outer dense layer A and the porous layer B to be collected and delivered down the central

collection tube. The backing ribs C provide structural support to resist the external air pressure. The wafers are arranged in modules each capable of producing 0.5 to 1.0 tonne/day of  $O_2$ . The modules are assembled in a pressure vessel and the  $O_2$  is cooled, compressed and delivered to the gasifier. The non-permeate stream contains sufficient  $O_2$  for the second combustion of  $H_2+N_2$  fuel gas in the gas turbine combustor giving the required gas temperature for the gas turbine expander inlet. No additional  $N_2$  for  $H_2$  fuel dilution is required and the deficiency in gas turbine expander flow due to the loss of diffused  $O_2$  can be made up by humidifying the  $H_2$  fuel gas with low level heat from the upstream gasification process. Modules of 0.5 tonne/day capacity have been tested at gas turbine operating conditions. The modules exceeded the mechanical strength and performance requirements defined for commercial operation. The gas turbine air flow must be sufficient to provide both the  $O_2$  required for the gasification process and for the gas turbine combustion. The next stage is operation of the modules integrated with a gas turbine.

### Air Products $H_2+CO$ ITM module

Similar ITM configuration is used for  $H_2+CO$  syn-gas production from natural gas/steam. The wafer module stacks are mounted in a pressure vessel with the high pressure syn-gas and feed gas passing over the wafers on the shell side and low pressure air distributed evenly within each wafer. The thin dense  $O_2$  diffusion layer is on the air side and a layer of active reformer catalyst is impregnated on the outside of the wafers. Full size modules have been tested and have exceeded performance objectives.

### Norsk Hydro systems

The zero emission power plant (AZEP) FIG 6 replaces the combustor of an air cycle gas turbine with a novel oxyfuel system (MCM) using an oxygen transport membrane with natural gas fuel. The MCM consists of a gas turbine air preheater section raising the temperature from  $400^\circ C$  to  $900^\circ C$  followed by the ITM section where  $O_2$  diffuses into the  $O_2$  depleted combustion product and finally a high temperature section where the  $O_2$  depleted air is heated to  $1250^\circ C$  against combustion gas at  $1300^\circ C$  before entering the gas turbine expander. A fan is used to circulate recycled gas on the combustion side of the unit to control the combustion temperature. The net  $CO_2$  and  $H_2O$  combustion products pass through an air bleed heat exchanger and the steam raising section of the plant. The MCM reactor design is a square section multichannel extruded ceramic monolith heat exchange/ITM combination. The material used is a mixed

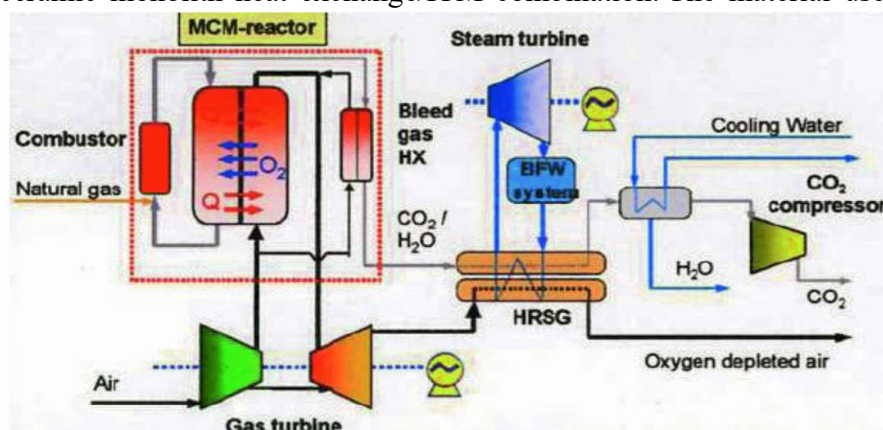


FIG 6

metallic oxide capable of withstanding the 1300°C temperature of the combustion gases. The projected efficiency with near 100% CO<sub>2</sub> capture at pipeline pressure is 50% to 52% (LHV). A 250

MW power system would require an MCM with a volume of 45 m<sup>3</sup>. The development program is focused on scale-up, manufacturing procedures and improvements in module performance.

## Praxair systems

The Praxair O<sub>2</sub> transport membrane (OTM) FIG 7 is fabricated as closed ended tubes 95 sealed into two metallic tube sheets 109 and 94. The tube comprises a heat exchange length adjacent to the sheet lower tube 94 which maintains a temperature at the tube sheet interface at less than 300°C and an upper OTM section. O<sub>2</sub> diffuses into the tubes from the shell side air flow in the upper section. The tubes are arranged in baffled bundles 120 and are free to expand upwards at operating temperature. The minor portion of the air feed enters the lower section at 92, is heated against cooling O<sub>2</sub> and exits at 116 where it is added to the major hot feed air stream entering the upper OTM section at 91. O<sub>2</sub> depleted air leaves at 114. Optionally the OTM tubes can be swept with an inert gas stream to reduce the O<sub>2</sub> partial pressure introduced via inner tubes 112 entering via nozzle 108 and tube sheet 96. Praxair reports good operating experience with the tubes with multiple thermal cycles. These have operated with O<sub>2</sub> partial pressure drive with and without a purge gas stream and also with a fuel gas on the permeate side of the membrane.

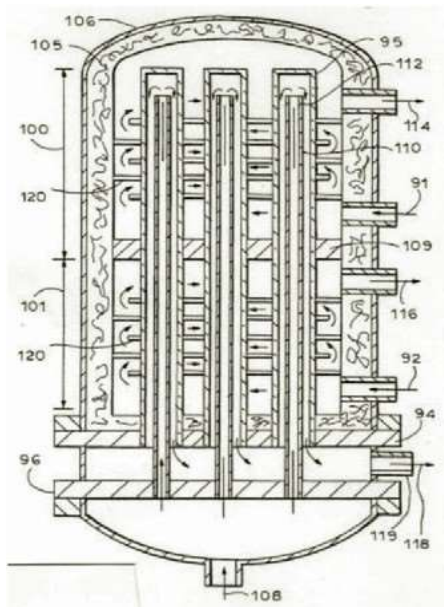


FIG 7

Development work to improve performance and manufacturing methods continue. The OTM system has been applied to an oxy-fuel combustion of a fuel gas stream in which O<sub>2</sub> diffuses and combusts the fuel gas flow across the tubes while the heat released is immediately transferred to adjacent rows of steam raising and superheating tubes to keep the temperature in a controlled range. The combustion product following cooling and water removal is CO<sub>2</sub> which can then be compressed to pipeline pressure. The fuel gas could be natural gas or coal derived synthesis gas. Cryogenic O<sub>2</sub> is used for coal gasification and a first OTM reactor raises the synthesis



gas temperature before expansion to produce power in the syngas expander. The hot syn gas then passes through the second OTM steam raising reactor. The efficiency is 34.5% (LHV). The OTM system has also been proposed for  $H_2+CO$  syn-gas generation and power production when integrated with a gas turbine burning  $H_2$  fuel gas following CO shift and  $CO_2$  removal. The air compressor bleed gas is heated, the OTM unit reacts diffusing oxygen with preheated natural gas and steam to produce the syngas and the depleted air returns to the gas turbine combustor and expander.

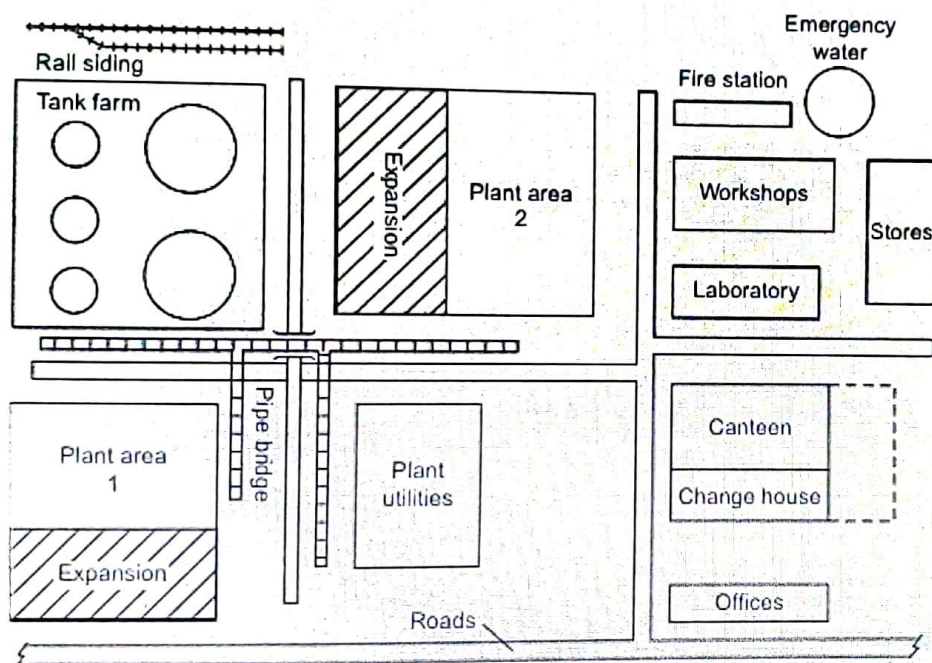
### **Linde/BOC systems**

The ceramic auto-thermal recovery process (CAR) uses mixed oxide perovskite pelleted material as an  $O_2$  adsorbent in a dual bed rapid cycle operation. The  $O_2$  in the feed air ionizes and is adsorbed while the metal ions are raised to a higher valency state providing electrons. The system is regenerated by passing a mixture of steam and natural gas at  $210^\circ C$  counter-currently which results in the release of the  $O_2$  adsorbed while the natural gas is oxidized to  $CO_2$  and water to maintain the beds at high operating temperature. The  $O_2$  steam  $CO_2$  mixture is cooled, water is separated and the oxygen rich gas is used in a pulverized coal oxyfuel boiler for power generation. The net efficiency of the power system is reduced from 42.7% to 34% (LHV) with  $CO_2$  capture and delivery of compressed purified  $CO_2$  at pipeline pressure. The developers claim a 27% reduction in power and a 50% reduction in capital cost compared to a cryogenic ASU. The CAR process is being developed with support from the European Union ENCAP  $CO_2$  SP5 project.

### **Future development of $O_2$ ion transport systems**

High temperature solid electrolyte  $O_2$  separation technology is developing along four parallel and quite different pathways. Air Products is using compact high surface area membrane wafer modules at moderate operating temperatures of  $800^\circ C$  to  $900^\circ C$ . Norsk Hydro is developing composite multi-channel heat exchanger plus membrane modules in extruded ceramics operating at temperatures up to  $1300^\circ C$ . Praxair uses tubes at  $800^\circ C$  to  $900^\circ C$ , while Linde/BOC is using perovskite mixed oxide as  $O_2$  adsorbents. These systems all operate with either oxidizing or reducing condition on the permeate or downstream side and they can be applied for oxyfuel or gasification applications with  $CO_2$  capture. Air Products appears to have the lead in the race to produce a reliable cost effective  $O_2$  production system properly integrated with the proposed processes for power generation or hydrogen production. All companies have significant Future development hurdles for all companies are:

- \* Improve membrane performance in oxidizing and reducing environments,
- \* Long term materials testing programs including temperature and pressure cycling to maximize useful life.
- \* Optimization to give stable hydrodynamics, low stress and vibration, and good system integration.
- \* Optimization of the manufacturing process to give high performance, low rejection rates and low cost.
- \* Reasonable scale demonstration projects under realistic operating conditions.



## PLANT LOCATION AND SITE SELECTION

The location of the plant can have a crucial effect on the profitability of a project, and the scope for future expansion. Many factors must be considered when selecting a suitable site, and only a brief review of the principal factors will be given in this section. Site selection for chemical process Chemical Engineering Design. <https://doi.org/10.1016/B978-0-08-102599-4.00014-X> # 2020 Elsevier Ltd. All rights reserved. 1017 plants is discussed in more detail by Merims (1966) and Mecklenburgh (1985); see also AIChE (2018)

### The principal factors to consider are:

1. Location, with respect to the marketing area.
2. Raw material supply.
3. Transport facilities.
4. Availability of labour
5. Availability of utilities: water, fuel, power.
6. Availability of suitable land.
7. Environmental impact, including effluent disposal.
8. Local community considerations.
9. Climate.
10. Political and strategic considerations

# **Chapter 4**

## **The material and energy balances**



## Chapter 4: The material and energy balances

The pressure of the feed air is increased using a multi-stage compressor. Each compression stage includes a compressor, a water-cooled inter-stage cooler, and a flash separator. The compression of the feed air results in an increase in its temperature. The compressed air is first cooled in the inter-stage cooler and then sent to the flash separator for the removal of condensate.

### Raw Material Requirement

The project would be producing medical grade and industrial oxygen from free saturated air sucked from atmosphere and hence there is no requirement of raw material other than air.

**Standard composition of dry air (detailed Analys).**

Gas	Chemical symbol	% by volume	% by weight	Parts per Million (ppm)
Nitrogen	N <sub>2</sub>	78.084	75.47	780790
Oxygen	O <sub>2</sub>	20.946	23.20	209445
Argon	Ar	0.943	1.28	9339
Carbon dioxide	CO <sub>2</sub>	0.02-0.04	0.062	404
Neon	Ne	0.0018	0.0012	18.21
Helium	He	0.0005	0.00007	5.24
Krypton	Kr	0.0001	0.0003	1.14
Hydrogen	H <sub>2</sub>	0.00005		0.50
Xenon	Xe	0.0000086	0.00004	0.087

**Physical properties of standard dry air.**

English Units			Normal Boiling Point (1 atm)		Gas Phase Properties @ 32°F & @ 1 atm			Liquid Phase Properties @ B.P. & @ 1 atm		Triple Point		Critical Point		
			Temp.	Latent Heat of Vaporization	Specific Gravity	Specific Heat (Cp)	Density	Specific Gravity	Specific Heat (Cp)	Temp.	Pressure	Temp.	Pressure	Density
Substance	Chemical Symbol	Mol. Weight	° F	BTU/lb	Air = 1	BTU/lb ° F	lb/cu. ft	Water = 1	BTU/lb ° F	° F	psia	° F	psia	lb/cu
Air	--	28.98	-317.8	88.2	1	0.241	0.08018	0.873	0.4454	-352.1	--	-221.1	547	21.9

Metric Units			Boiling Point @ 101.325 kPa		Gas Phase Properties @ 0° C & @ 101.325 kPa			Liquid Phase Properties @ B.P., & @ 101.325 kPa		Triple Point		Critical Point		
			Temp.	Latent Heat of Vaporization	Specific Gravity	Specific Heat (Cp)	Density	Specific Gravity	Specific Heat (Cp)	Temp.	Pressure	Temp.	Pressure	Density
Substance	Chemical Symbol	Mol. Weight	° C	kJ/kg	Air = 1	kJ/kg ° C	kg/m3	Water = 1	kJ/kg ° C	° C	kPa abs	° C	kPa abs	kg/m3
Air	--	28.98	-194.3	205.0	1	1.01	1.2929	0.873	1.865	-213.4	--	-140.6	3771	351

### Plant Production Capacity:

The oxygen plant proposed would have a capacity to produce 50 ton per day (15000 ton per year) of gaseous oxygen. The plant is proposed to operate for 24 hours per day at 100% capacity, working in 3 shifts of 8 hours each.

#### Unit conversion data of oxygen.

	Weight		Gas		Liquid	
	pounds (lb)	kilograms (kg)	cubic feet (scf)	cu meters (Nm <sup>3</sup> )	gallons (gal)	liters (l)
1 pound	1.0	0.4536	12.076	0.3174	0.105	0.3977
1 kilogram	2.205	1.0	26.62	0.6998	0.2316	0.8767
1 scf gas	0.08281	0.03756	1.0	0.02628	0.008691	0.0329
1 Nm <sup>3</sup> gas	3.151	1.4291	38.04	1.0	0.3310	1.2528
1 gallon liquid	9.527	4.322	115.1	3.025	1.0	3.785
1 liter liquid	2.517	1.1417	30.38	0.7983	0.2642	1.0
1 short ton	2000	907.2	24160	635	209.9	794.5

Scf (standard cubic foot) gas measured at 1 atmosphere and 70°F.  
 Nm<sup>3</sup> (normal cubic meter) gas measured at 1 atmosphere and 0°C.  
 Liquid measured at 1 atmosphere and boiling temperature.

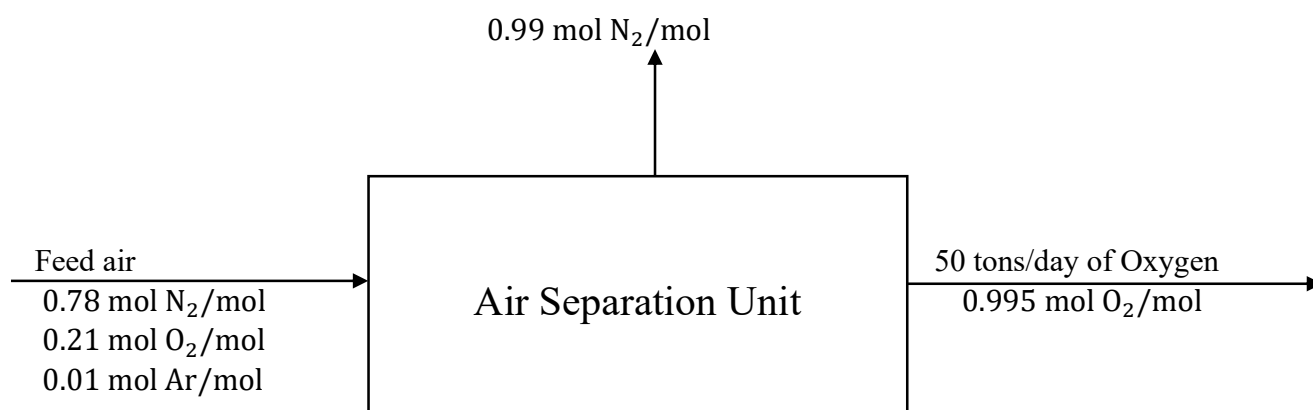
### The material, and energy balances:

The assumptions were used as a foundation of calculating the material and energy balances:

1. The process is a nonreactive process.
2. The operation is a steady state operation.
3. The composition of air, 78% mol N<sub>2</sub>, 21% mol O<sub>2</sub>, 1% mol Ar.
4. The bulk gas phase is considered an ideal gas.
5. A reasonable percentage of the air may be lost through removal.
6. The air leaving the Pre-Purification Unit (PPU) is a dry air.

### The material balances:

Material balances are the basis of process design. A material balance taken over the complete process will determine the quantities of raw materials required and products produced.



### Material balance for the overall process:

First will take the boundary round the complete process to calculate the flows in and out. Raw materials in, products and by-products out.

The capacity of the plant is 50 tons /day of oxygen ( $O_2$ ).

### Oxygen Production:

By assuming that the plant will operate 300 days annually, and the rest shut down for maintenance, then

$$\text{Annual oxygen production} = \frac{50 \text{ tons}}{\text{day}} \left| \frac{300 \text{ day}}{1 \text{ annual}} \right| = 15000 \text{ tons/annual}$$

$$\text{Mass flow rate of oxygen production} = \frac{50 \text{ tons}}{\text{day}} \left| \frac{1000 \text{ kg}}{1 \text{ ton}} \right| \left| \frac{1 \text{ day}}{24 \text{ h}} \right| = 2083.333 \text{ kg/h}$$

$$\text{Molar flow rate of oxygen production} = \frac{50 \text{ tons}}{\text{day}} \left| \frac{1000 \text{ kg}}{1 \text{ ton}} \right| \left| \frac{1 \text{ kmol}}{32 \text{ kg}} \right| \left| \frac{1 \text{ day}}{24 \text{ h}} \right| = 65.104 \text{ kmol/h}$$

At standard temperature and pressure ( $0^\circ\text{C}$  and  $1\text{atm}$ ),  $1 \text{ kmol}$  of gas occupies  $22.415 \text{ m}^3$ .

$$\begin{aligned} \text{Volumetric flow rate of oxygen production} &= \frac{50 \text{ tons}}{\text{day}} \left| \frac{1000 \text{ kg}}{1 \text{ ton}} \right| \left| \frac{1 \text{ kmol}}{32 \text{ kg}} \right| \left| \frac{22.415 \text{ m}^3}{1 \text{ kmol}} \right| \left| \frac{1 \text{ day}}{24 \text{ h}} \right| \\ &= 1459.310 \text{ m}^3/\text{h} \end{aligned}$$

### The average molecular weight of air ( $\bar{M}$ ):

The molecular weight ( $\bar{M}$ ) may be used as conversion factor to convert masses to moles or mass flow rates to molar flow rates and vice versa.

$$\bar{M} = \sum_{\text{all Component}} y_i M_i = y_{N_2} M_{N_2} + y_{O_2} M_{O_2} + y_{Ar} M_{Ar}$$

The average molecular weight of air ( $\bar{M}$ ) =  $(0.78)(28) + (0.21)(32) + (0.01)(40) = 28.96$

### Calculate the inlet air flow rate:

The volume fraction of a substance in an ideal-gas mixture equals the mole fraction of this substance.  
Volume % of oxygen in the air = 21%.

$$\text{Volumetric flow rate of air needed} = \frac{1459.310 \text{ m}^3 \text{ O}_2}{\text{h}} \left| \frac{1 \text{ Air}}{0.21 \text{ O}_2} \right| = 6949.095 \text{ m}^3/\text{h}$$

$$\text{Molar flow rate of air needed} = \frac{65.104 \text{ kmol O}_2}{\text{h}} \left| \frac{1 \text{ Air}}{0.21 \text{ O}_2} \right| = 310.019 \text{ kmol/h}$$

$$\text{Mass flow rate of air needed} = \frac{310.019 \text{ kmol}}{\text{h}} \left| \frac{28.96 \text{ kg}}{\text{kmol}} \right| = 8978.150 \text{ kg/h}$$

$$\text{Mass flow rate of air needed} = \frac{310.019 \text{ kmol}}{\text{h}} \left| \frac{28.96 \text{ kg}}{\text{kmol}} \right| \left| \frac{1 \text{ ton}}{1000 \text{ kg}} \right| \left| \frac{24 \text{ h}}{1 \text{ day}} \right| = 215.476 \text{ ton/day}$$

### Summary of overall process material balance.

Stream	Feed air	Oxygen production
Mass flow rate, kg/h	8978.150	2083.333
Molar flow rate, kmol/h	310.019	65.104
Volumetric flow rate, m <sup>3</sup> /h	6949.095	1459.310

### Balances over individual process units:

Because the cryogenic air separation plant is a nonreactive and continuous processes at steady-state, then the general material balance equation reduces to:

$$\text{Input} = \text{Output}$$

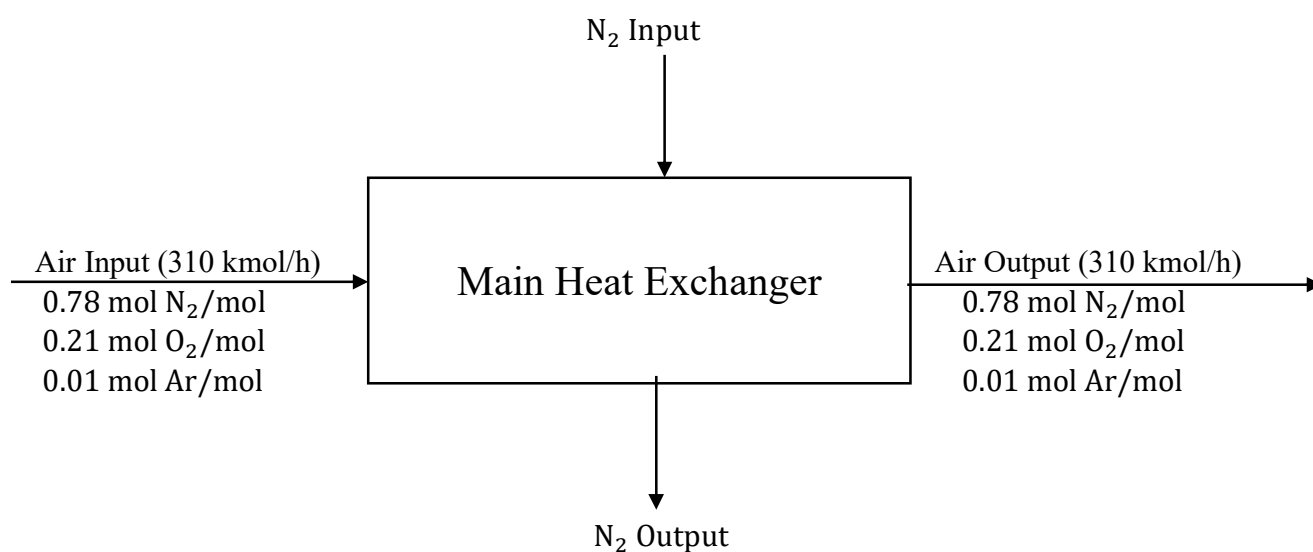
Balances over individual process units set the process stream flows and compositions, and provide the basic equations for sizing equipment.

### Material balance on the compressor:



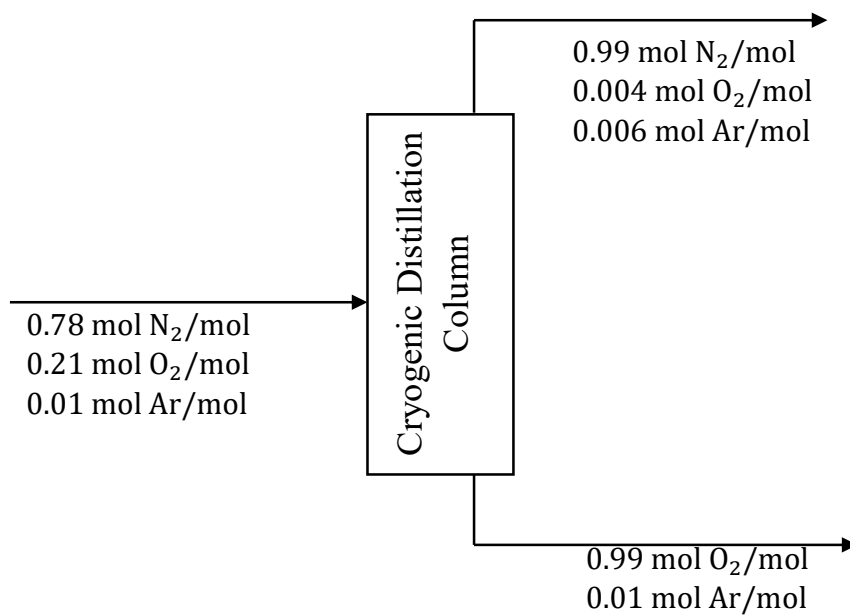
Component	Mol fraction	M.wt (kg/kmol)	Input		Output	
			Mol (kmol)	Mass (kg)	Mol (kmol)	Mass (kg)
N <sub>2</sub>	0.78	28	242	6776	242	6776
O <sub>2</sub>	0.21	32	65	2080	65	2080
Ar	0.01	40	3	120	3	120
<b>Total</b>	<b>1.0</b>		<b>310</b>	<b>8976</b>	<b>310</b>	<b>8976</b>

### Material balance on the Main Heat Exchanger:

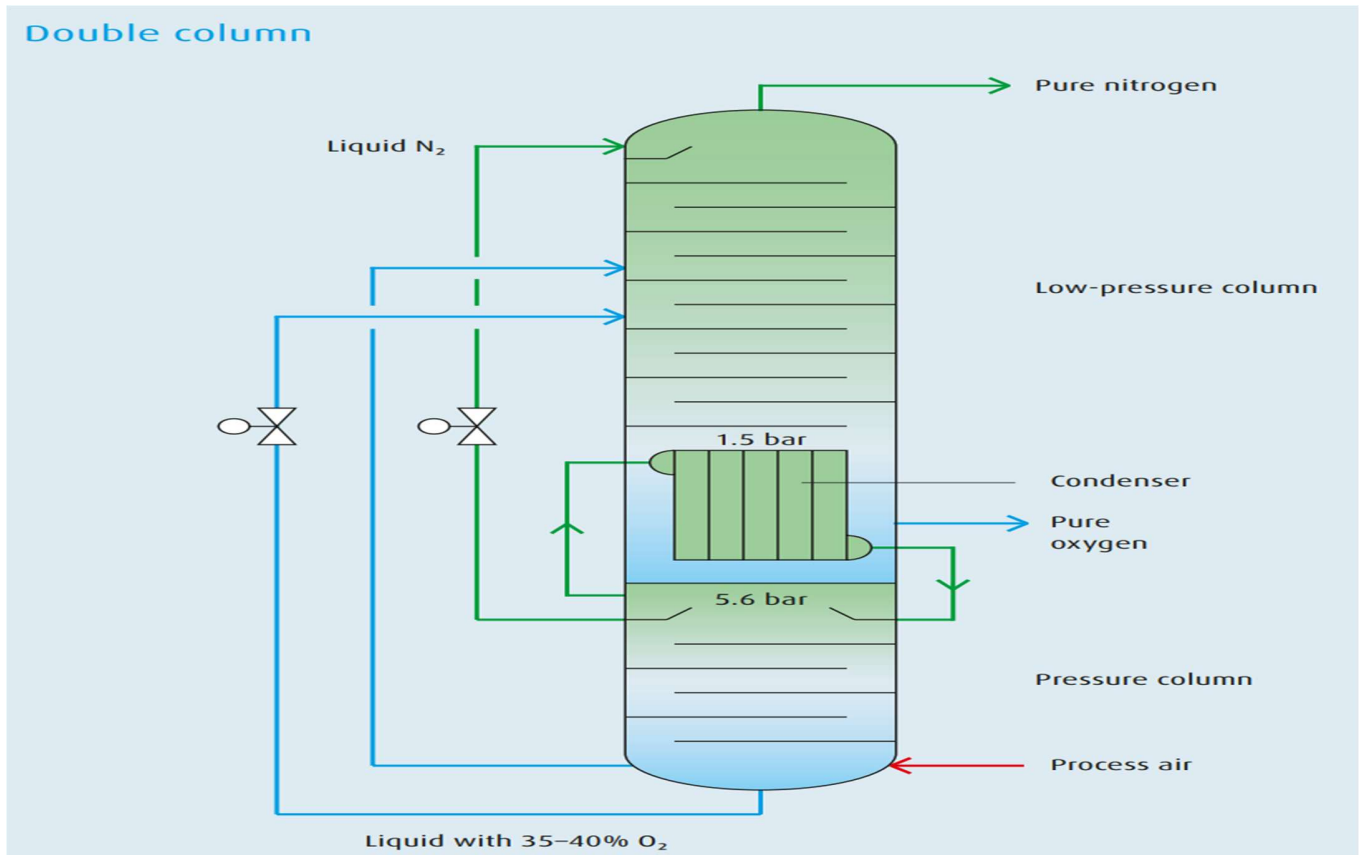


Component	Mol fraction	M.wt (kg/kmol)	Input		Output	
			Mol (kmol)	Mass (kg)	Mol (kmol)	Mass (kg)
N <sub>2</sub>	0.78	28	242	6776	242	6776
O <sub>2</sub>	0.21	32	65	2080	65	2080
Ar	0.01	40	3	120	3	120
<b>Total</b>	<b>1.0</b>		<b>310</b>	<b>8976</b>	<b>310</b>	<b>8976</b>

### Material balance on the Cryogenic Distillation Column:



Component	M.wt (kg/kmol)	Feed		Top		Bottom	
		Mol (kmol)	Mass (kg)	Mol (kmol)	Mass (kg)	Mol (kmol)	Mass (kg)
N <sub>2</sub>	28	242	6776	242	6776	-	-
O <sub>2</sub>	32	65	2080	1	32	64	2048
Ar	40	3	120	2	80	1	40
<b>Total</b>		<b>310</b>	<b>8976</b>	<b>245</b>	<b>6888</b>	<b>65</b>	<b>2088</b>







### Process Flow Diagram for Air Separation Unit.

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Temperature, K	300	446	315	468	315	107	99	99	82	95	78	90	78	300
Pressure, atm	1	3	3	9	9	9	5	5	1	5	1	1	1	1
Vapor fraction	1	1	1	1	1	1	1	0	0	0	0	0	1	1\
Total molar flow rate, kmol/h	310	310	310	310	310	310	310	124	124	186	186	65	245	245
Component molar flow rate, kmol/h														
Nitrogen	242	242	242	242	242	242	242	65	65	182	182	-	242	242
Oxygen	65	65	65	65	65	65	65	57	57	3	3	64	1	1
Argon	3	3	3	3	3	3	3	2	2	1	1	1	2	2

### Equipment key

C-101	Feed Compressor (Stage 1)
C-102	Feed Compressor (Stage 2)
E-101	Interstage Cooler
E-102, E-103	Heat Exchanger
E-104	Reboiler
E-105	Condenser-Reboiler
T-101	Linde Lower Column
T-102	Linde Upper Column

### The energy balances:

Power consumption in an ASU can be divided into three categories:

1. Compression power, to compress gasses from low pressure to high pressure.
2. Separation power, to separate pure components out of a mixture, primarily to separate oxygen from air.
3. Liquefaction power, to liquefy oxygen and nitrogen gas into liquid.

We use the energy difference between the reference condition (298 K and 0.1013 MPa) and the final product condition to calculate the minimum theoretical power.

$$e = h - T_0 \times s$$

e: specific energy, J/mol.

h: specific enthalpy, J/mol.

$T_0$ : reference temperature, K.

s: specific entropy, J/mol. K.

$$\frac{1 \text{ atm}}{1 \text{ atm}} \left| \frac{0.101325 \text{ MPa}}{\text{atm}} \right| = 0.101325 \text{ MPa}$$

$$\frac{9 \text{ atm}}{1} \left| \frac{0.101325 \text{ MPa}}{\text{atm}} \right| = 0.911925 \text{ MPa}$$

We can calculate the theoretical power for air, argon, oxygen, and nitrogen and then the actual is typically about 1.5 times theoretical power.

The below tables thermodynamic properties take from Perry's chemical engineers handbook.(2019)

### Thermodynamic properties of Air.

Temperature K	Pressure MPa	Density mol/dm <sup>3</sup>	Volume dm <sup>3</sup> /mol	Int. energy kJ/mol	Enthalpy kJ/mol	Entropy kJ/(mol·K)	C <sub>v</sub> kJ/(mol·K)	C <sub>p</sub> kJ/(mol·K)	Sound speed m/s	Joule- Thomson K/MPa	Therm. cond. mW/(m·K)	Viscosity μPa·s
100	0.1	0.12283	8.1414	5.6800	6.4941	0.080463	0.021087	0.030116	198.24	17.423	9.4692	7.1068
300	0.1	0.040103	24.936	9.8544	12.348	0.11269	0.020796	0.029149	347.36	2.2510	26.384	18.537
500	0.1	0.024046	41.586	14.072	18.231	0.12770	0.021504	0.029830	446.40	0.50305	39.944	27.090
700	0.1	0.017175	58.223	18.500	24.323	0.13794	0.022817	0.031137	523.89	-0.12430	51.755	34.176
900	0.1	0.013359	74.855	23.201	30.686	0.14593	0.024150	0.032467	589.60	-0.41124	62.543	40.394
1100	0.1	0.010931	91.486	28.145	37.293	0.15255	0.025246	0.033562	648.15	-0.56194	72.680	46.051
1300	0.1	0.009249	108.12	33.282	44.094	0.15823	0.026091	0.034406	701.76	-0.64963	82.381	51.325
1500	0.1	0.008016	124.75	38.568	51.042	0.16320	0.026734	0.035049	751.59	-0.70457	91.781	56.325
1700	0.1	0.007073	141.38	43.966	58.104	0.16762	0.027229	0.035544	798.38	-0.74078	100.97	61.127
1900	0.1	0.006329	158.00	49.453	65.253	0.17160	0.027619	0.035934	842.62	-0.76547	110.01	65.783
100	1	26.593	0.037604	1.2007	1.2383	0.013532	0.027868	0.061355	658.25	-0.14308	104.97	88.326
106.22	1	25.232	0.039632	1.5924	1.6321	0.017351	0.027368	0.065680	582.97	-0.00232	93.879	73.903
108.1	1	1.3836	0.72278	5.5251	6.2479	0.060461	0.024739	0.044597	185.23	15.779	11.965	7.9625
300	1	0.40205	2.4873	9.8022	12.289	0.093372	0.020859	0.029563	348.45	2.1789	26.684	18.672
500	1	0.23974	4.1711	14.046	18.218	0.10851	0.021526	0.029954	448.46	0.47425	40.110	27.179
700	1	0.17119	5.8415	18.485	24.326	0.11877	0.022830	0.031194	525.96	-0.13809	51.868	34.242
900	1	0.13319	7.5079	23.190	30.698	0.12677	0.024159	0.032498	591.54	-0.41899	62.628	40.446
1100	1	0.10902	9.1727	28.138	37.311	0.13340	0.025253	0.033582	649.96	-0.56686	72.748	46.094
1300	1	0.092279	10.837	33.278	44.114	0.13908	0.026096	0.034419	703.44	-0.65304	82.438	51.361
1500	1	0.079999	12.500	38.565	51.065	0.14405	0.026738	0.035057	753.17	-0.70711	91.830	56.357
1700	1	0.070604	14.163	43.964	58.128	0.14847	0.027233	0.035550	799.86	-0.74278	101.01	61.155
1900	1	0.063185	15.827	49.451	65.278	0.15245	0.027622	0.035939	844.02	-0.76711	110.05	65.808

### From the above table by interpolation:

The enthalpy of air at reference condition (298 K and 0.101325 MPa) = 12290 J/mol

The entropy of air at reference condition (298 K and 0.101325 MPa) = 112.4 J/mol.K

The enthalpy of air at reference condition (298 K and 0.911925 MPa) = 12224.1 J/mol

The entropy of air at reference condition (298 K and 0.911925 MPa) = 93.1 J/mol.K

The specific energy at point 1 = 12290 – 298 × 112.4 = –21205.2 J/mol

The specific energy at point 4 = 12224.1 – 298 × 93.1 = –15519.8 J/mol

The energy difference between point 1 & 4 = –15519.8 – (–21205.2) = 5685.4 J/mol

### Thermodynamic properties of Argon.

Temperature K	Pressure MPa	Density mol/dm <sup>3</sup>	Volume dm <sup>3</sup> /mol	Int. energy kJ/mol	Enthalpy kJ/mol	Entropy kJ/(mol·K)	C <sub>v</sub> kJ/(mol·K)	C <sub>p</sub> kJ/(mol·K)	Sound speed m/s	Joule-Thomson K/MPa	Therm. cond. mW/(m·K)	Viscosity μPa·s
100.00	0.10000	0.12304	8.1275	1.2122	2.0249	0.13179	0.012807	0.021852	184.16	25.048	6.4504	8.2341
200.00	0.10000	0.060310	16.581	2.4833	4.1414	0.14649	0.012497	0.020918	263.21	7.4099	12.539	15.998
300.00	0.10000	0.040115	24.928	3.7351	6.2279	0.15495	0.012479	0.020834	322.67	3.6153	17.837	22.741
400.00	0.10000	0.030069	33.257	4.9842	8.3099	0.16094	0.012475	0.020810	372.65	1.9970	22.516	28.704
500.00	0.10000	0.024050	41.580	6.2324	10.390	0.16559	0.012474	0.020801	416.64	1.1105	26.726	34.077
600.00	0.10000	0.020041	49.899	7.4803	12.470	0.16938	0.012473	0.020796	456.40	0.55603	30.573	38.997
700.00	0.10000	0.017177	58.217	8.7279	14.550	0.17258	0.012473	0.020793	492.95	0.17948	34.134	43.556
100.00	1.0000	32.955	0.030345	-4.1375	-4.1072	0.060927	0.019909	0.045870	751.59	-0.32095	110.85	183.08
116.60	1.0000	29.821	0.033533	-3.3421	-3.3086	0.068305	0.018483	0.051339	614.12	-0.10424	87.579	119.65
116.60	1.0000	1.2403	0.80628	1.1435	1.9497	0.11340	0.015159	0.031986	184.63	18.745	8.6079	10.115
200.00	1.0000	0.61937	1.6145	2.3849	3.9995	0.12686	0.012725	0.022195	261.59	7.2269	12.995	16.256
300.00	1.0000	0.40331	2.4795	3.6807	6.1603	0.13563	0.012545	0.021266	323.44	3.5287	18.142	22.901
400.00	1.0000	0.30073	3.3252	4.9476	8.2728	0.14171	0.012507	0.021025	374.06	1.9489	22.749	28.817
500.00	1.0000	0.24013	4.1644	6.2054	10.370	0.14639	0.012493	0.020928	418.25	1.0808	26.915	34.163
600.00	1.0000	0.19997	5.0007	7.4592	12.460	0.15020	0.012487	0.020879	458.06	0.53628	30.733	39.065
700.00	1.0000	0.17137	5.8354	8.7110	14.546	0.15342	0.012483	0.020851	494.61	0.16568	34.272	43.612

**From the above table by interpolation:**

The enthalpy of argon at reference condition (298 K and 0.101325 MPa) = 6186.2 J/mol

The entropy of argon at reference condition (298 K and 0.101325 MPa) = 154.8 J/mol.K

The enthalpy of argon at reference condition (298 K and 0.911925 MPa) = 6117 J/mol

The entropy of argon at reference condition (298 K and 0.911925 MPa) = 135.4 J/mol.K

The specific energy at point 1 =  $6186.2 - 298 \times 154.8 = -39944.2$  J/mol

The specific energy at point 4 =  $6117 - 298 \times 135.4 = -34231.9$  J/mol

The energy difference between point 1 & 4 =  $-34231.9 - (-39944.2) = 5712.3$  J/mol

**Thermodynamic properties of Oxygen.**

Temperature K	Pressure MPa	Density mol/dm <sup>3</sup>	Volume dm <sup>3</sup> /mol	Int. energy kJ/mol	Enthalpy kJ/mol	Entropy kJ/(mol·K)	$C_v$ kJ/(mol·K)	$C_p$ kJ/(mol·K)	Sound speed m/s	Joule- Thomson K/MPa	Therm. cond. mW/(m·K)	Viscosity μPa·s
100.00	0.10000	0.12316	8.1192	2.0355	2.8474	0.17297	0.020885	0.029925	188.37	18.479	9.0852	7.7121
300.00	0.10000	0.040116	24.928	6.2338	8.7265	0.20531	0.021078	0.029435	329.72	2.6530	26.485	20.652
500.00	0.10000	0.024050	41.579	10.604	14.762	0.22069	0.022781	0.031108	421.27	0.75388	41.046	30.486
700.00	0.10000	0.017177	58.216	15.357	21.179	0.23147	0.024672	0.032992	493.31	0.10517	53.966	38.653
900.00	0.10000	0.013360	74.849	20.438	27.923	0.23994	0.026045	0.034363	555.60	-0.18735	63.867	45.806
100.00	1.0000	34.158	0.029276	-3.7444	-3.7151	0.099680	0.028683	0.055399	826.85	-0.27181	137.23	153.89
119.62	1.0000	30.512	0.032774	-2.6131	-2.5803	0.11003	0.027000	0.061476	645.19	-0.085501	107.79	98.249
119.62	1.0000	1.2018	0.83209	2.1662	2.9983	0.15666	0.023665	0.040564	189.41	15.124	12.433	9.3921
300.00	1.0000	0.40337	2.4791	6.1772	8.6563	0.18598	0.021148	0.029887	329.90	2.6066	26.894	20.846
500.00	1.0000	0.24010	4.1649	10.576	14.741	0.20149	0.022802	0.031240	422.68	0.73726	41.288	30.630
700.00	1.0000	0.17135	5.8360	15.340	21.176	0.21230	0.024682	0.033052	494.87	0.098376	54.139	38.766
900.00	1.0000	0.13328	7.5029	20.426	27.929	0.22078	0.026051	0.034395	557.14	-0.19062	66.001	45.899

**From the above table by interpolation:**

The enthalpy of oxygen at reference condition (298 K and 0.101325 MPa) = 8667.7 J/mol

The entropy of oxygen at reference condition (298 K and 0.101325 MPa) = 205 J/mol.K

The enthalpy of oxygen at reference condition (298 K and 0.911925 MPa) = 8593.6 J/mol

The entropy of oxygen at reference condition (298 K and 0.911925 MPa) = 185.7 J/mol.K

The specific energy at point 1 =  $8667.7 - 298 \times 205 = -52422.3$  J/mol

The specific energy at point 4 =  $8593.6 - 298 \times 185.7 = -46754.6$  J/mol

The energy difference between point 1 & 4 =  $-46754.6 - (-52422.3) = 5667.7$  J/mol

**Thermodynamic properties of Nitrogen.**

Temperature K	Pressure MPa	Density mol/dm <sup>3</sup>	Volume dm <sup>3</sup> /mol	Int. energy kJ/mol	Enthalpy kJ/mol	Entropy kJ/(mol·K)	$C_v$ kJ/(mol·K)	$C_p$ kJ/(mol·K)	Sound speed m/s	Joule- Thomson K/MPa	Therm. cond. mW/(m·K)	Viscosity μPa·s
100.00	0.10000	0.12268	8.1514	2.0396	2.8547	0.15950	0.021049	0.030012	201.64	16.082	9.3806	6.9581
600.00	0.10000	0.020037	49.908	12.573	17.564	0.21217	0.021796	0.030118	496.27	0.021483	44.840	29.577
1100.0	0.10000	0.010930	91.489	24.284	33.433	0.23131	0.024932	0.033248	660.05	-0.65654	70.075	44.199
1600.0	0.10000	0.0075152	133.06	37.272	50.579	0.24414	0.026815	0.035130	788.94	-0.81543	92.344	56.398
100.00	1.0000	24.658	0.040554	-2.0907	-2.0501	0.094493	0.027546	0.064564	609.42	-0.054514	100.58	76.255
103.75	1.0000	23.768	0.042073	-1.8441	-1.8020	0.096928	0.027281	0.068113	559.22	0.060996	92.738	67.783
103.75	1.0000	1.4754	0.67778	1.7800	2.4577	0.13799	0.024612	0.046272	182.79	16.471	11.671	7.8351
600.00	1.0000	0.19960	5.0099	12.554	17.564	0.19300	0.021812	0.030198	498.66	0.0061465	44.992	29.626
1100.0	1.0000	0.10899	9.1755	24.277	33.452	0.21216	0.024938	0.033267	662.07	-0.65940	70.155	44.221
1600.0	1.0000	0.074993	13.335	37.270	50.605	0.22499	0.026820	0.035138	790.64	-0.81612	92.399	56.411

**From the above table by interpolation:**

The enthalpy of nitrogen at reference condition (298 K and 0.101325 MPa) = 8679.6 J/mol

The entropy of nitrogen at reference condition (298 K and 0.101325 MPa) = 180.4 J/mol.K

The enthalpy of nitrogen at reference condition (298 K and 0.911925 MPa) = 8369.9 J/mol

The entropy of nitrogen at reference condition (298 K and 0.911925 MPa) = 159.5 J/mol.K

The specific energy at point 1 =  $8679.6 - 298 \times 180.4 = -45079.6$  J/mol

The specific energy at point 4 =  $8369.9 - 298 \times 159.5 = -39161.1$  J/mol

The energy difference between point 1 & 4 =  $-39161.1 - (-45079.6) = 5918.5$  J/mol

#### Summary of the compression power.

Item	Nitrogen	Oxygen	Argon	Air
$T_0$ , K	298	298	298	298
$P_1$ , MPa	0.101325	0.101325	0.101325	0.101325
$h_1$ , J/mol	8679.6	8667.7	6186.2	12290
$s_1$ , J/mol.K	180.4	205	154.8	112.4
$e_1$ , J/mol	-45079.6	-52422.3	-39944.2	-21205.2
$P_2$ , MPa	0.911925	0.911925	0.911925	0.911925
$h_2$ , J/mol	8369.9	8593.6	6117	12224.1
$s_2$ , J/mol.K	159.5	185.7	135.4	93.1
$e_2$ , J/mol	-39161.1	-46754.6	-34231.9	-15519.8
$\Delta E$ , J/mol	5918.5	5667.7	5712.3	5685.4
$\Delta E$ , kWh/Nm <sup>3</sup>				