Recovery of Argon from Ammonia Purge Stream

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Certificate

This is to certify that work in this thesis has been carried out by **Mr. Muhammad Hamza Rashid, Mr. Khizar Hayat Zafar** and **Mrs. Khadijah Ali** and completed under my supervision at School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

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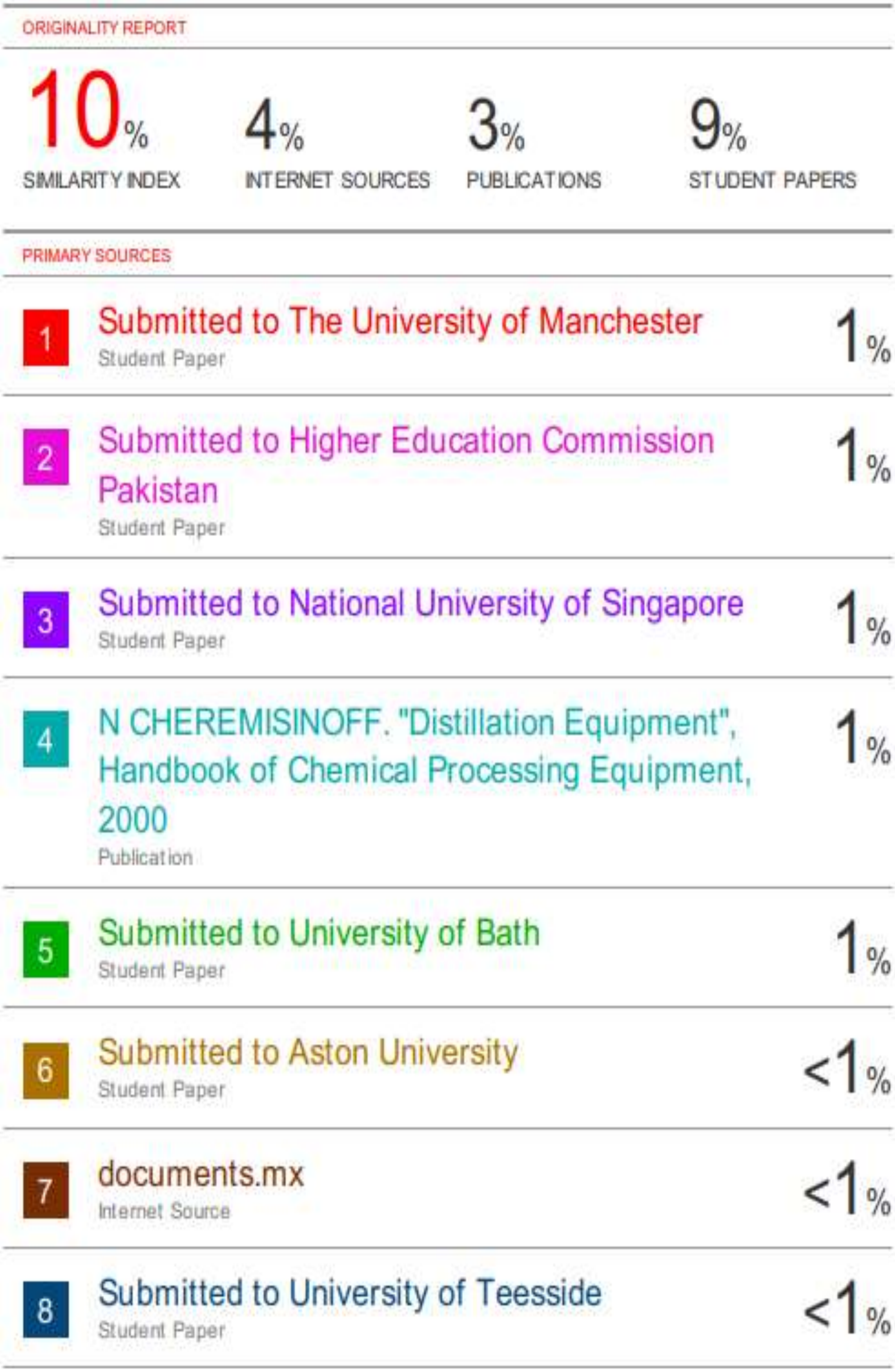

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Dedication

This work is dedicated to our beloved family, friends and all our well-wishers…

Acknowledgements

Firstly, we are thankful to Allah Almighty who is the most Magnificent and Benevolent. Without His consent and help, we would not have been able to complete this project.

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Abstract

In the past 30 years, the chemical industry has been the subject of notable changes due to higher demands and increasing production and operational costs. As a result, it has become imperative for chemical industries to focus on the utilization of products having great economical potential. Chemical processes must be made efficient physically and within the reasonable constraints. Chemical engineers are obliged to find better-operating strategies and products that are valuable yet easy to extract from an existing chemical process. The separation of Argon from the Purge Gas of FFC-1 can generate a revenue of 15 million US dollars per annum which is a significant step towards stability and economic benefit. It will provide positive contribution towards the plants' profitability and in turn, prosperity of the country.

Therefore, this study is focused on the statistical determination of optimum operating parameters for the separation of Argon from the purge gas stream at FFC-1. The separation of Argon from Ammonia purge gas will utilize available resources and convert it into revenue generator.

In this project, two methods namely a cryogenic method and a membrane separation method have been proposed to recover Argon from the Hydrogen depleted purge gas that is, otherwise, being flared in the industry. The process begins with an adsorption column followed by a Palladium (Pd) membrane system to remove Methane and the remainder of Hydrogen, respectively. The cryogenic process consists of a cryogenic distillation column that separates Argon while the latter one features a cascaded polymeric membrane system to recover the same. Both the processes are presented with elaborate detail along with process flow diagrams, material and energy balances, equipment design, simulation, costing and HAZOP analysis. A comparison is given in the end as to determine which method works best.

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Abbreviations

Greek Letters

α	Relative volatility/ Selectivity
γ	Specific heats ratio (Adiabatic index)
ϕ	Pressure ratio
φ	Sphericity of particles
ε	Porosity of adsorbent
ρ	Density

Latin Letters

D_p	Particle diameter
E_p	Polytropic efficiency
A	Area
Q	Volumetric flow rate
v	Velocity
N	Number of plates
R	Reflux ratio
E_o	Over-all column efficiency
P	Pressure
T	Temperature
m	Mass
M	Molar mass
V	Ideal gas volume
R	Ideal gas constant
Z	Compressibility factor
C_o	Inlet concentration
t_b	Break-point time
t^*	50% outlet concentration time
L	Length of bed
n	Polytropic factor
J_A	Membrane flux

Chapter 1: Introduction

1.1 Background

Argon is a noble gas having roughly 1% concentration in the atmosphere which makes it to be the third most abundant gas in the air. It is of great economic value owing to its large number of uses. It is, however, very difficult to separate it from air due to its very small volatility difference with Oxygen. Ammonia purge stream being Oxygen-free as well as considerably enriched in Argon is an ideal source for its extraction.

1.2 Problem Statement

The focus here is to remove Argon as by product from the Ammonia purge stream. The project was assigned by Fauji Fertilizers Company Ltd. An extensive research has been carried out on the said topic after which two separation processes have been proposed. These will ideally provide 99% or higher purity of Argon at the end. Real-time values from FFC Plant-I at Got Machi has been taken into consideration for this project.

1.3 Purpose of Study

Argon is a safe gas and poses no serious threat to the environment. However, this study has been carried out owing to great economic importance of Argon and its uses in the industry. At FFC roughly 350 Nm^3/hr of hydrogen depleted gas is being purged. If Argon is recovered from this purge and sold out separately, it can generate a profit of \$15 million per annum.

1.4 Approach

For the removal and purification of Argon two processes have been proposed and then compared. Firstly, a cryogenic method where Argon is separated from Nitrogen in a cryogenic pressurized distillation process based on their relative volatility. The column has been designed by analytical calculations and the calculations were verified by simulating it in ASPEN® Plus environment. In comparison a membrane process has been developed where the gases are separated in a cascaded hollow-fiber system, composed of special type of polyethylene (Grex) membrane, based on their relative affinity (selectivity) for the material. Similarly, the process has also been simulated in ASPEN® Plus.

1.5 Argon

Argon (Ar) was discovered by Sir William Ramsay in 1894. Argon is a noble gas present in the group VIIIA and period 3 of the periodic table. Its atomic number is 18 and has an atomic mass of 40. Argon has 3 stable isotopes with most abundant being Ar-40.

Argon is a colorless and odorless gas but produces a purple glow when placed in an electric field. It has a boiling point of 87.30 K (-185.85°C) and a melting point: 83.80 K (-189.35°C). This low boiling point can be explained due to the presence of weak dispersion forces due to complete absence of polarity. Since the gas has a completed octet, it is very stable and has no naturally occurring compounds. (Only a handful of its meta-stable compounds have been synthesized. Even those can exist only at temperatures very close to absolute zero. This lack of its reactivity is the reason for its name which literally means “lazy” or “inactive”.

As of today, Argon is already being used for several purposes while research is being carried out to further extend its uses especially in medical, food processing and manufacturing industries.

1.6 Chemical & Physical characteristics

The chemical and physical characteristics of liquid Argon are listed in the table below.

Chemical Formula	Ar
Molecular Mass	39.95
Boiling Point (1 bar)	-185.9°C
Freezing Point (1 bar)	-189.4°C
Critical Temperature	-122.4°C
Critical Pressure	48.0 atm
Liquid density at BP & 1 bar	1394 kg/m^3
Latent Heat of Vaporization	162 kJ/kg

Table 1: Chemical and Physical Characteristics of Argon

1.7 Conventional Methods of Production

There are various separation techniques used to separate out Argon from air or from a mixture of other gases. The most commonly used methods are cryogenic distillation, membrane separation and adsorption. This project will incorporate each one of these methods in detail and carry out a comparative analysis to determine the most feasible method.

1.8 Storage and Safety

Owing to the inert nature of Argon, its storage does not require special construction materials. Argon is commonly used in its gaseous form, but we usually store Argon in liquid state at which it is extremely cold and non-flammable. The liquid storage of Argon provides a cost-effective way of product supply. Large volumes of Argon can be stored in this way reducing vessel and transportation costs. Storage of liquid Argon requires the material to be able to withstand such low temperatures. Standards provided by American Society of Mechanical Engineers (ASME) and Department of Transportation (DOT) are kept in mind while designing the vessels and its piping. The storage system of Argon consists of

- Cryogenic storage tank:
  The cryogenic tank is principally a vacuum bottle. This tank is designed in such a way as to reduce the heat transfer with the surroundings to a minimum.
- One or more vaporizers:
  Vaporizers essentially convert the liquid Argon to gaseous form. It is required at the facility where gaseous Argon has to be utilized.
- Pressure control system:
  This system controls the pressure of gaseous Argon that is released through a vaporizer.
- Piping:
  Piping is naturally required for connecting the storage system equipment with each other.

Argon is a safe gas and does not pose any serious threats to the environment. However, while dealing with cryogenic liquid Argon, safety precautions are to be taken. Possible hazards that are associated with liquid Argon are as follows

- Very cold temperatures that can cause severe burns or frostbite.
- Over pressurization of vessel that can cause explosion
- Displacement of Oxygen in the air in confined work areas that can cause asphyxiation.

Apart from these hazards, there are certain risks that can cause harm to life and assets. Personal protection equipment is highly recommended to be worn by all workers while in field. Engineering controls are also employed to detect Oxygen concentrations. Since Oxygen is easily displaced by Argon, proper ventilation should be provided. Otherwise, it can cause severe respiratory illnesses. It can also result in more severe cases such as suffocation and ultimately death.

1.9 Uses

Argon has many uses mainly because of its inert properties and abundance in nature. A few of its uses are listed below.

- It is widely used in lighting industry with combination of other gases to fill bulbs and tubes for special colored light effects.
- It is used in electronics industry in manufacturing of semiconductors.
- It is commonly used in the welding industry as a protection against oxidation. The inerting properties of Argon is used to shield the weld area from contamination. It also protects against fusion defects, weak welds and porosity.
- It serves as a shield for the production of expensive metals like Platinum and Titanium.
- It has biomedical applications during retinal surgeries.
- It is used for the production and preservation of wine. It basically displaces Oxygen; this phenomenon avoids oxidation of wine and its fouling.
- It is used extensively in plasma cutting process for cutting metals.
- Along with Potassium, Argon is used in radioisotopy dating technique that is primarily used to determine the age of old objects like rocks etc.
- Argon finds its applications in heat treatment processes to provide an Oxygen-free environment.

Chapter 2: Literature Review

2.1 Adsorption

Adsorption occurs when solid substances attract gaseous or liquid molecules on their surface which they are in contact with. Solids that adsorb substances are known as adsorbents while the adsorbed molecules are collectively known as adsorbate. Adsorbents are solids that are porous in nature and the adsorption occurs on their porous walls. Common adsorbents include carbon molecular sieves, activated carbon, silica gel etc. Once the adsorption occurs, we need to regenerate the adsorbent in order to recover the adsorbate and make the adsorbent fit to be used again. Thus, adsorption and regeneration processes form a cycle that can be accomplished in several ways. Most common methods are pressure swing adsorption (PSA), temperature swing adsorption (TSA) and inert/purge stripping.

2.1.1 Pressure Swing Adsorption

PSA technology is used to separate gas species from a mixture of gases based on molecular characteristics and affinity of species for an adsorbent material under pressure. This technique is widely used in separation of carbon dioxide, Methane, Nitrogen etc. It ideally consists of two columns for adsorption and regeneration to take place alternately. A series of valves and controls make it possible to decrease or increase pressure as required. By swinging the pressure from high to low, it is possible to adsorb high quantities of material at high pressure and then release those amounts at low pressure.

2.1.2 Fixed Bed Adsorption

Fixed bed adsorption refers to the process in which the adsorbent is present in the form of a fixed bed in a column. This way, the fluid trickles down the bed and components adsorb in this bed. When the bed gets saturated, the flow is stopped, and the bed is then regenerated to recover the adsorbate. This process is also known as desorption.

2.1.3 Isotherms

Isotherms are graphs plotted at constant temperatures. Adsorption equilibrium data is plotted in the form of isotherms that shows mass adsorbed on the y-axis and the mass in the fluid on x-axis. The shape of curve gives us important details regarding the design of an adsorption process. Usually, as temperature increases the adsorption process slows down.

The most commonly used isotherms are Langmuir and Freundlich. In the Langmuir isotherm it is hypothesized that the number of adsorption sites are fixed and that adsorption is reversible. Freundlich isotherm on the other hand assumes layered absorption and the number of adsorption sites are not constant. It best describes adsorption from liquids and adsorption of hydrocarbons on activated carbon.

2.2 Throttling

Throttling is a process whereby a gaseous stream is cooled down suddenly by expanding it. It works on the principle of Joule-Thomson effect. A throttling valve is required to carry out this process. Throttling is an isenthalpic process and does not support liquefaction of gases until and unless the temperature of gas is first lowered sufficiently. Firstly, these gases are compressed then they are cooled isobarically and then are throttled in order to achieve liquefaction.

2.3 Distillation

Distillation is a technique used for separation of components from a mixture based on their volatility differences. The knowledge of the vapor/liquid equilibrium holds significant importance in distillation. In the process, vapor from the bottom rise up the column whereas the liquid from the top travel down the column. Their contact is enhanced using trays or packaging. As we continued the process, the top phase gets richer in the more volatile components and the bottom phase gets richer in the less volatile components. Distillation is of many types namely binary distillation, fractional/ multi-component distillation, flash distillation etc. Here, we will discuss cryogenic distillation that is being used in this project.

2.3.1 Cryogenic Distillation

The word cryogenic implies that this type of distillation occurs at extremely low temperatures. It is thus used to separate components who have very low boiling points.

A refrigeration system is required to bring down the temperatures to operating conditions. This is done in accordance with the Joule Thomson Effect. Cryogenic distillation is most commonly used to separate air components.

2.3.2 Sections

Distillation has two main sections, and these are explained briefly below.

1. Rectification

   Rectification is a process done to increase the purity of distillate. We can achieve high purity concentration in the distillate when it is distilled again and again. The down flowing liquid takes along the low volatile component from the vapor. This process occurs above the feed plate.

2. Stripping

   Stripping is the same phenomena like rectification but occurs below the feed plate. At the stripping section, the vapor rising above strips the more volatile components from the down-flowing liquid. It works on the principle of concentration difference.

2.3.3 Components

A distillation column consists of many components in order to carry out an effective separation. First of all, a vessel or a column is required in which the whole process takes place. The vessel should be insulated as to minimize the heat transfer to surroundings. Vessel is made up of a material that could withstand the operating conditions. The column internals are packed with trays/plates or other packing that promote heat and mass transfer. These contain valves or bubble caps that actually control the liquid and vapor flow. The feed tray is usually in the middle of column that divides the whole column into rectifying (upper) and stripping (lower) sections.

A reboiler is present at the exit of bottom stream where it provides the necessary vaporization. A condenser is present at the exit of top stream to cool and condense the vapor. A reflux drum is also present which holds the condensed vapor that is then recycled back to the column.

2.3.4 Reflux Ratio

The ratio of reflux flow to the distillate flow is termed as reflux ratio. In simple words, it is a measure of material going up through the top of the column and is recycled back to the column.

2.3.5 Design Principle

As mentioned earlier, distillation is aimed to separate components from a mixture based on their volatility difference. In such a case, vapor characteristics of liquid mixtures and individual species is of great importance. The separation occurs on the basis of Raoult's law. Raoult’s law again gives us an indication of relative volatility which is a measure of the differences in volatility between two components. It directly indicates the ease or difficulty of a particular separation. Mccabe Thiele is a graphical method that uses VLE plot to determine the theoretical number of stages.

The actual number of trays needed can only be determined by knowing the efficiency of plate and packings. Tray efficiencies are severely affected by fouling, corrosion etc.

2.3.6 Vapor-Liquid Equilibrium

The VLE is a relationship which describes the compositions of liquid and vapor at equilibrium conditions at constant pressure. It is a curve that helps us determine the number of trays/height of column required for the desired degree of separation.

2.4 Membrane Separation

Membrane separation is simply the separation that occurs through a semipermeable membrane through which one or more species pass faster than the other. It is easily operated in a modular construction that are more compact and energy efficient. Common membrane modules are tubular, hollow fiber, spiral wound etc.

2.4.1 Membrane Characteristics

- Permeability

  Permeability is a measure of how much a membrane allows a certain gas to pass through it. Mathematically, it is the product of sorption coefficient and permeate diffusion coefficient.

- Selectivity

  Selectivity is an intrinsic property of a membrane that is a measure of the extent to which a membrane allows one component to pass through it than the other.

2.4.2 Membrane Types and Transport Mechanism

Membranes are of several types namely natural (cellulose), metallic, ceramic, polymeric and nonporous membranes. Different transport phenomena occur in each type of membrane. The most common transport phenomena are

- Solution Diffusion
- Knudsen Flow
- Bulk Flow

In this work, a Palladium (Pd) membrane that is a kind of metallic membrane has been used to separate out Hydrogen from rest of the gases. Pd membrane is highly selective towards Hydrogen and can withstand high operating pressures. We have employed Grex membranes, which belong to polyethylene family, to separate out Nitrogen from Argon.

2.5 Heat Exchanger

Heat exchangers are devices used to exchange heat contents of two streams. It is a good way to optimize energy of a process by transferring heat of one fluid to another. There are many kinds of heat exchangers out of which the most popular ones are shell and tube and double pipe heat exchangers; but we will discuss the plate and frame type as we will be using it in our project later on.

Plate and Frame heat exchangers are physically made up of corrugated plates placed firmly on a frame. Such a design promotes high heat transfer due to high turbulence. The two streams in this heat exchanger move counter currently to each other.

2.6 Compressor

Compressors are mechanical devices that are used to increase the pressure of air from low to high by utilizing some external energy. Some important terms considered here are

- Compression ratio: It is the ratio of outlet and inlet pressure. Conversely, it can also be defined as the ratio of inlet volume to outlet volume.
- Compressor capacity: It is the volume of air/ gas that the compressor can process in unit time.
- Swept Volume: The volume displaced or swept by the piston in one complete vibration or by the impeller in one complete rotation.
- Clearance volume: It is essentially the dead region of the compressor i.e. the volume occupied by the impeller or the piston. Mathematically it is the difference between the total volume and the swept.

The two main types of compressors are reciprocating and centrifugal compressors.

2.6.1 Centrifugal Compressors

Centrifugal compressors are the radial flow compressors which provide a continuous, steady flow. They increase pressure of the stream by adding velocity (kinetic energy) to the stream using an impeller.

Chapter 3: Cryogenic Distillation

3.1 Process Description

In fertilizer industry, cryogenic process has been used for separation of valuable gases from the purge stream for a very long time. The purge contains a significant concentration of Nitrogen and Hydrogen along with varying compositions of Methane, Argon and Ammonia. The biggest challenges to Argon recovery are its low concentration and inertness. The recovery is thus carried out in a multistage process.

In the first stage, Ammonia is removed from the stream by using an absorption process with Water as solvent. Next, majority of Hydrogen is removed using a cryogenic process where 93% of the Hydrogen is recovered and recycled back to the synthesis section. These two units are already present and operational in the industry. The Hydrogen depleted purge gas is what will be our main process stream from which we will recover Argon. This stream is significantly enriched in Methane, Argon and Nitrogen. We have employed a multi-bed adsorption process to remove Methane and majority of Nitrogen. The Pressure Swing Adsorption System consists of an adsorbent bed composed activated carbon granules. Here, entirety of the natural gas along with majority of the Nitrogen (about 80%) and moisture (if any) is removed.

The Hydrogen remaining in process stream is removed by passing it through Palladium membrane. 99% pure Hydrogen is obtained as the permeate. The retentate after being cooled and compressed is sent to the cold box for further processing.

Prior to injection into the distillation column, the mixture is cooled to about 85 K using Linde’s liquefaction process. Here, the gas is pre-cooled by contact with the top and bottom product streams of distillation column followed by a throttling process. This way, we reach temperatures up to -180 ^{o}C.

The product gas is next sent to the cryogenic distillation column from where 99.99% pure Argon is obtained as bottom product while the top product is used for the regeneration of the PSA columns. The combined gases are collectively vented. These gases are returned to the secondary reformer or flared as needed.

3.2 Process Flow Diagram

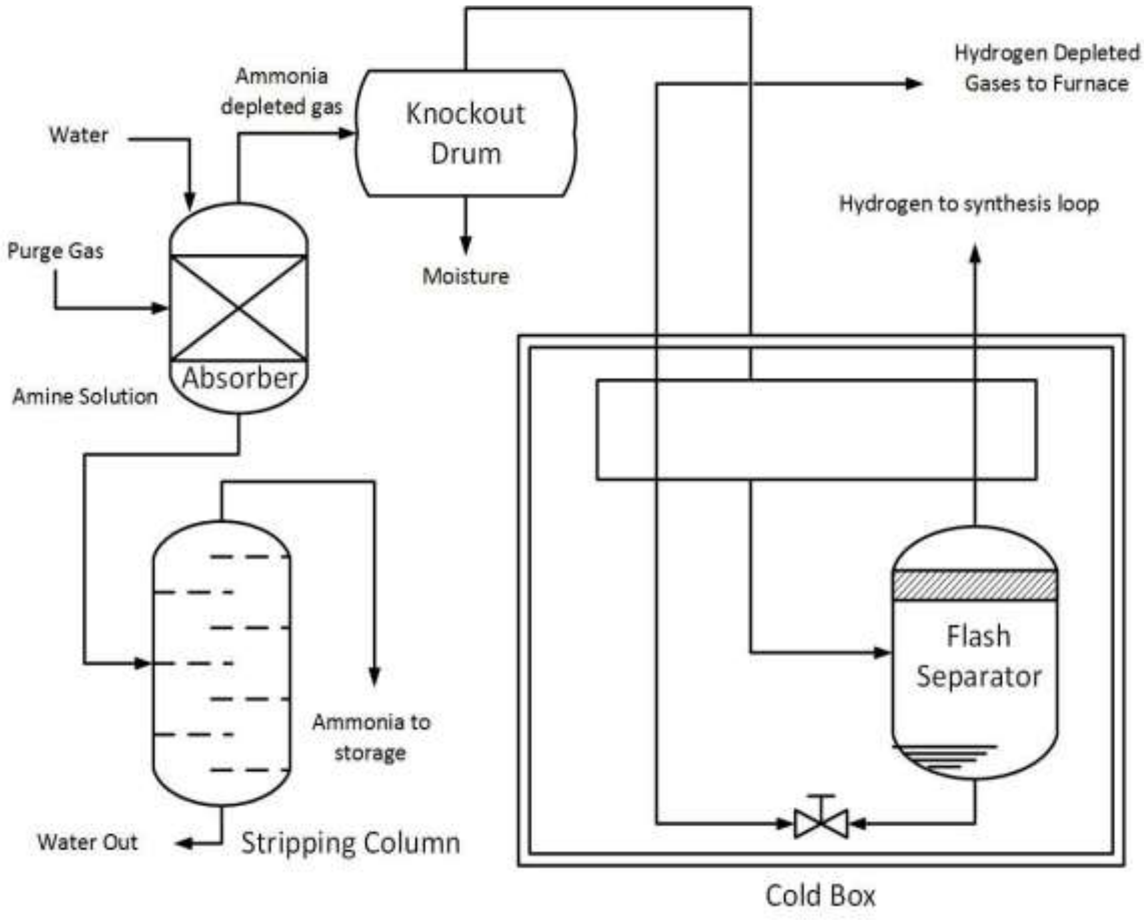


Figure 1: Absorption Unit & Flash Separator

The absorption column and flash separator are already present in the industry. Hydrogen depleted purge will be the feed for our proposed processes.

The diagram below shows all the main as well as auxiliary units needed to carry out the processing. Prior to adsorption, the Hydrogen depleted purge is first compressed (K-1) and then cooled (X-1). Here, permeate stream is recovered while the unabsorbed stream is further compressed and heated to be sent to the Pd membrane section. Separation occurs after which pure Hydrogen is stored separately while the retentate is cooled, compressed and again cooled to be sent to a cold box. Heat exchange occurs in the cold box after which cryogenic distillation is carried out to finally get 99.9% pure Argon.

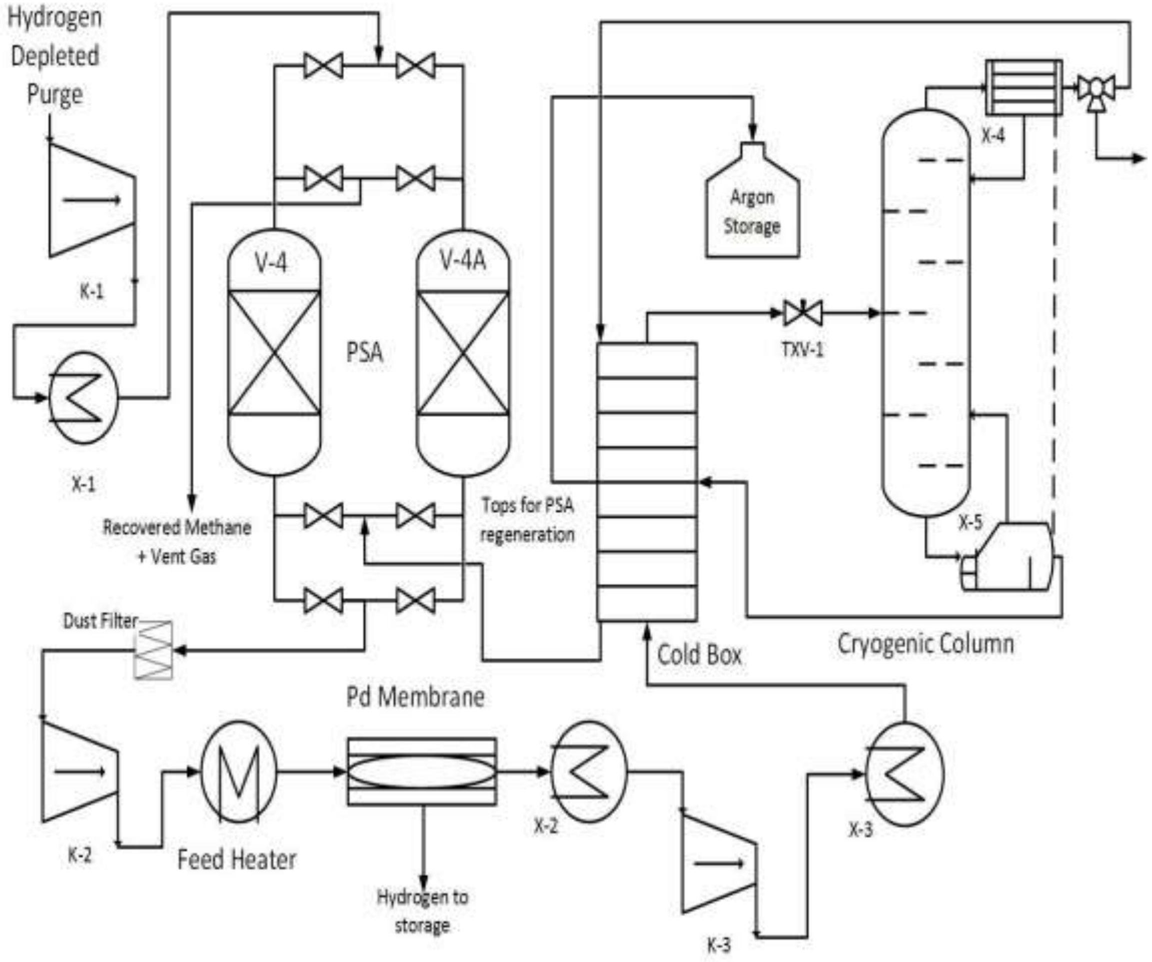


Figure 2: Cryogenic Process PFD

3.3 Material Balance

Material balance is applied on all pieces of equipment where there is flow of material. The basic principle and formula used is

Material in ± Generation = Material out ± Accumulation

Since we have a continuous operation with no chemical reaction, our material balance simply reduces to:

Material In = Material Out

We shall be using this formula to carry out our material balance in the following units:

1. Adsorption Column
2. Palladium Membrane
3. Cryogenic Distillation Column

The Hydrogen depleted gas stream that exits the industry otherwise will be the main process stream from which we will recover Argon. This stream has the following composition:

Component	Composition (Mol %)	Flow Rate (Nm^3/ hr)
H_2	14.87	1034
N_2	52.54	3652
Ar	4.82	335
CH_4	27.52	1913
NH_3	0.24	17
Total	100	6951
		310 kgmol/hr

Table 2: Hydrogen Depleted Gas Composition

System 1: Adsorption Column

In the next step, the Hydrogen depleted gas is sent to a pressure swing adsorption column. Here, entirety of the natural gas along with majority of the Nitrogen (about 80%) and moisture (if any) is removed. The compositions the absorbed and permeated streams are given below:

Component	Composition (Mol %)	Flow Rate (Nm^3/ hr)
H_2	1.04	52
N_2	58.57	2921
Ar	1.68	84
CH_4	38.36	1913
NH_3	0.35	17
Total	100	4987
		222 kgmol/hr

Table 3: Adsorbed Stream Composition

Component	Composition (Mol %)	Flow Rate (Nm^3/ hr)
H_2	50	982
N_2	37.22	731
Ar	12.78	251
Total	100	1964
		88 kgmol/hr

Table 4: Methane Depleted Gas Composition

System 2: Palladium Membrane

Palladium Membrane is employed to remove the entirety of Hydrogen from process stream. The membrane is conditioned to operate at temperature of 400 ^{o}C & inlet pressure of 30 bars. The selectivity of the membrane is roughly 1000 for hydrogen with respect to other two gases.

Component	Composition (Mol %) of permeate	Permeate Flow (Nm^3/ hr)	Composition (Mol %) of retentate	Retentate Flow (Nm^3/ hr)
Hydrogen	99.80	980	0.17	2
Nitrogen	0.13	2	74.30	729
Argon	0.07	1	25.53	250
Total	100	983	100	981

Table 5: Pd Membrane Material Balance

The Hydrogen obtained is about 99.8% pure and can be resold for research purposes or may be utilized in fuel cells.

System 3: Cryogenic Distillation Column

After being cooled to 85K using Linde liquefaction process, the product gas is fed to the cryogenic distillation column operating at 85K and 5 bar. The inlet stream to distillation column has the following composition:

Component	Composition (Mol %)	Flow Rate (Nm^3/ hr)
H_2	0.17	2
N_2	74.30	731
Ar	25.53	250
Total	100	981
		44 kgmol/hr

Table 6: Column Inlet Stream Composition

Out of 44 kmol entering, we obtain 11 kmol in the bottom stream enriched in 100% pure Argon.

Component	Composition (Mol %)	Flow Rate (Nm^3/ hr)
Ar	100	248
Total	100	248
		11 kgmol/hr

Table 7: Bottom Product Composition

The top products are sent to PSA columns for regeneration while the PSA off-gas is recycled to the PSA feed compressor or the secondary reformer.

Component	Composition (Mol %)	Flow Rate (Nm^3/ hr)
H_2	0.31	2.3
N_2	99.29	726.8
Ar	0.40	2.93
Total	100	**732 kgmol/hr**

Table 8: Top Product Composition

Component	Composition (Mol %)	Flow Rate (Nm^3/ hr)
H_2	0.94	53.76
N_2	63.83	3650.44
Ar	1.49	85.21
CH_4	33.43	1911.9
NH_3	-	-
Total	100	5719
		255 kgmol/hr

Table 9: PSA Off-Gas Composition

3.4 Energy Balance

Energy balance has been applied on all those components where energy is being exchanged. These units are:

1. Adsorber Compressor
2. Adsorber Cooler
3. Adsorption Column
4. Membrane Heater
5. Retentate Cooler
6. Retentate Compressor
7. Auxiliary heat exchanger
8. Cooler
9. Cold Box
10. Throttling Valve
11. Distillation Column (Reboiler + Condenser)

System 1: Compressor

In the compressor, gas is compressed from 360 kPa to 1240 kPa in a single stage compressor. The process is assumed to be polytropic. The efficiency of the compressor is taken to be 85%.

Parameter	Inlet	Outlet
Temperature (^oC)	38	178.4
Pressure (kPa)	360	1240
Work done (kW)	0	383.8 kW

Table 10: Energy Balance on Compressor

System 2: Cooler

Here, the gases are brought in contact with Ammonia exiting the storage tank and flowing to the urea reactor. The gases in the process are cooled to 25^{o}C while the pressure of gases remain the same i.e. 1240 kPa. The coolant flow is calculated to be 15913 kg/hr.

Parameter	Ammonia	Gases
Flow rate (kg/hr)	15913	
Cp_{avg} (kJ/kmol.K)		31.94
Inlet Temperature (^oC)	- 4	158
Outlet Temperature (^oC)	14	25
Enthalpy Change (kJ/hr)		1527680

Table 11: Energy Balance on Cooler

System 3: Adsorber

This is a double-bed PSA unit. In an adsorber, the pressure drop is negligible. Chahbani et al, have reported a pressure drop from 2 - 5%. The calculated pressure drop in our case is 40 kPa.

Parameter	Inlet Stream	Vent Gas	Exit Stream	Product
Temperature (^oC)	25	20	23	25
Pressure (kPa)	1240	30	1200	

Table 12: Energy Balance on Adsorber

System 4: Compressor (Membrane)

Here, the PSA product gas is compressed from 1200 kPa to 5000 kPa. These conditions are necessary to be met as to ensure correct pressure difference for effective separation through Palladium membrane. The total work done by this compressor is about 150 kW.

Parameter	Inlet	Outlet
Temperature (^oC)	35	251.7
Pressure (kPa)	1200	5000

Table 13: Energy Balance Compressor

System 5: Heater (Membrane)

Here, the feed is further heated up to 350°C to meet the working conditions of Palladium membrane. Pressure of the stream remains constant.

Parameter	Inlet	Outlet
Temperature (°C)	251.7	350
Pressure (kPa)	5000	5000
Enthalpy Change (kJ/hr)		249751.2

Table 14: Energy Balance on Heat Exchanger

System 6: Retentate Cooler

During separation in Palladium membrane, a pressure drop of 200 kPa is calculated. Ammonia has been used as the coolant to cool the incoming stream to 25°C. The coolant flow is calculated to be 4261.2 kg/hr. This retentate after being cooled to 25°C is sent to a cold box (heat exchanger) to exchange its heat contents with the product streams of distillation column.

Parameter	Inlet	Outlet
Temperature (°C)	350	25
Pressure (kPa)	4800	5000
Enthalpy Change (kJ/hr)	409081.3	

Table 15: Energy Balance Retentate Cooler

System 7: Retentate Compressor

A compressor is installed to compress the incoming gaseous stream to 15000 kPa in order to bring to the operating conditions of distillation column. The power requirement of this compressor is 46.7 kW.

Parameter	Inlet	Outlet
Temperature (^oC)	25	165
Pressure (kPa)	5000	15000

Table 16: Retentate Compressor Energy Balance

System 8: Auxiliary Heat Exchanger

This heat exchanger is installed to remove the heat of compression as such that the Nitrogen stream passing at -50^{o}C exchanges its energy with the hot stream from compressor. The process is optimized, and we get Nitrogen at 18^{o}C.

Parameter	Inlet	Outlet
Temperature (^oC)	165	114
Pressure (kPa)	15000	15000
Enthalpy Change (kJ/hr)		68096.23

Table 17: Aux. Heat Exchanger Energy Balance

System 9: Cooler

A cooler is required to further cool down the stream to room temperature. The coolant used is Ammonia whose flow rate is calculated to be 1301 kg/hr.

Parameter	Inlet	Outlet
Temperature (^oC)	114	25
Pressure (kPa)	15000	15000
Enthalpy Change (kJ/hr)		124923.5

Table 18: Cooler Energy Balance

System 10: Cold Box

Cold box is essentially a heat exchanger where top (N_2) and bottom product (Ar) exchange their energy contents with the inlet stream to distillation column. The energy balance is divided into two parts.

10a: Heat exchange w.r.t Argon

Parameter	Inlet	Outlet
Temperature (^oC)	25	-47.5
Pressure (kPa)	15000	15000
Enthalpy Change (kJ/hr)		116739.9

Table 19a: Ar Heat Exchange Balance

10b: Heat exchange w.r.t Nitrogen

Parameter	Inlet	Outlet
Temperature (^oC)	-47.5	-105
Pressure (kPa)	15000	15000
Enthalpy Change (kJ/hr)		125856.8

Table 19b: N_2 Heat Exchange Balance

Finally, the inlet stream to distillation column is obtained at -105^{o}C. This must be cooled down further to -185^{o}C to meet the cryogenic conditions of distillation for which we throttle the gas.

System 11: Throttling Valve

The gas is suddenly expanded from 15000 kPa to 550 kPa which leads to cooling using Joule-Thomson Effect. This process is isenthalpic.

Parameter	Inlet	Outlet
Temperature (^oC)	-105	-180.5
Pressure (kPa)	15000	550
Enthalpy (kJ/kmol)		0

Table 20: Energy Balance on Throttling Valve

System 12: Cryogenic Distillation Column

The cryogenic distillation column contains bubble-cap trays. There are a total of 30 trays. The reflux ratio is set as 2. For energy optimization, the tops and the bottoms are allowed to exchange heat with each other resulting in partial condensation of the gases and complete vaporization of the liquid Argon. This way, the reboiler can be used as a sink for condenser. Total pressure drop in the distillation column is 30 kPa.

Parameter	Inlet	Outlet
Temperature (^oC)	-186.1	-186.1
Pressure (kPa)	520	500
Heat Duty (kW)		88.3

Table 21a: Energy Balance Reboiler

Parameter	Tops (Condenser)	Bottoms (Reboiler)
Temperature (^oC)	-179	-179
Pressure (kPa)	101	101
Heat Duty (kW)		98.04

Table 21b: Energy Balance Condenser

3.5 Process Modeling and Control

The process was modeled in ASPEN HYSYS with PRSV as fluid package.

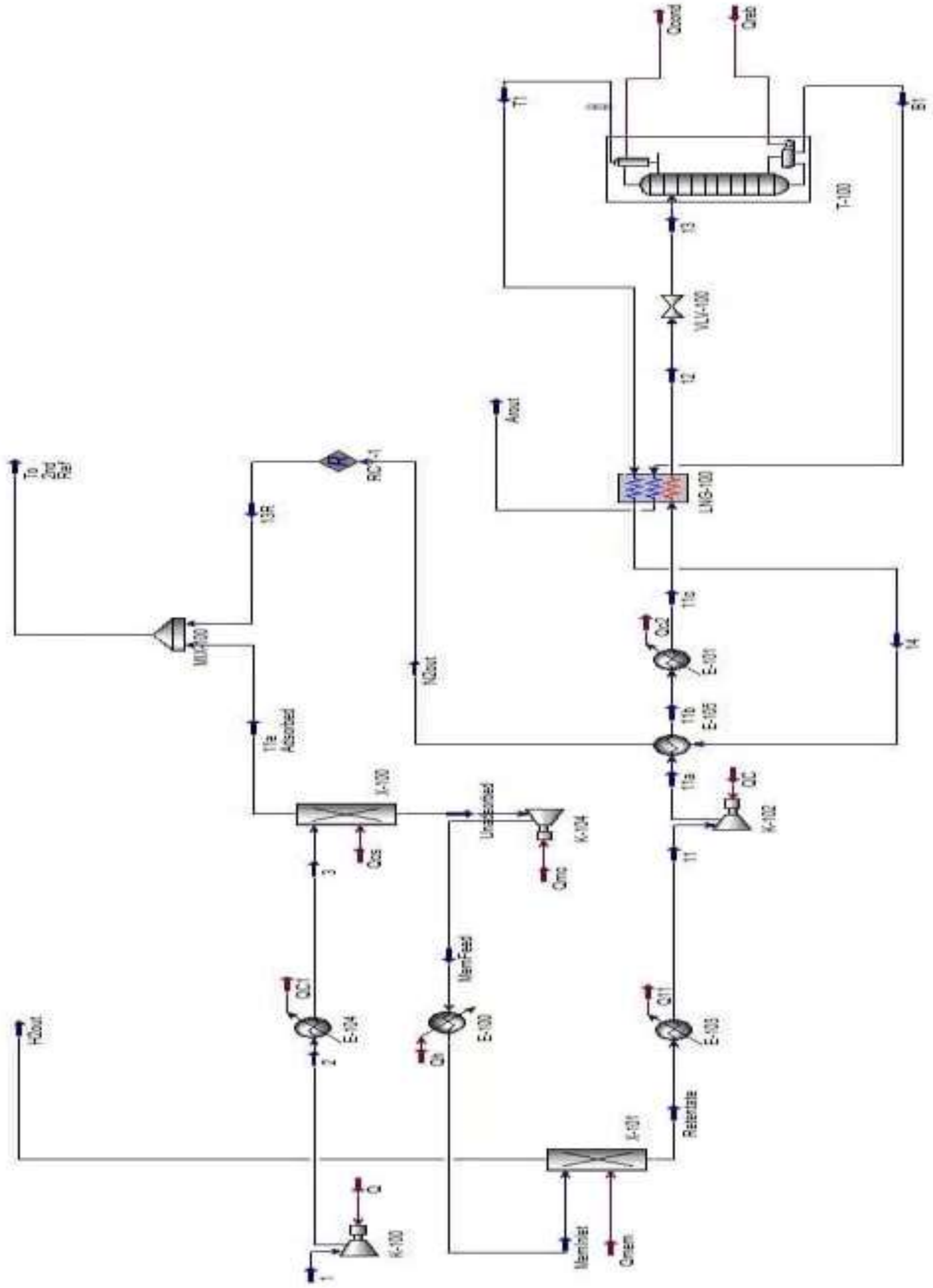


Figure 3: Cryogenic Process Modeling

Process Control

The control of PSA system is displayed here. A multi-nodal microcontroller is used such as the ones supplied by Arduino. It is a simple ON-OFF controller. The supply to the PSA will be regulated by the flow control valve (FV-1) at the inlet of the compressor K-1. The valves used are pneumatic air-to-close valves which only have limited ability to control the flow (such as a ball valve). The controller generates a PWM (pulse width module i.e. a discrete electronic signal) that produced a signal for as long as the motor takes to open/ close the valve.

Schematic of the control is shown below:

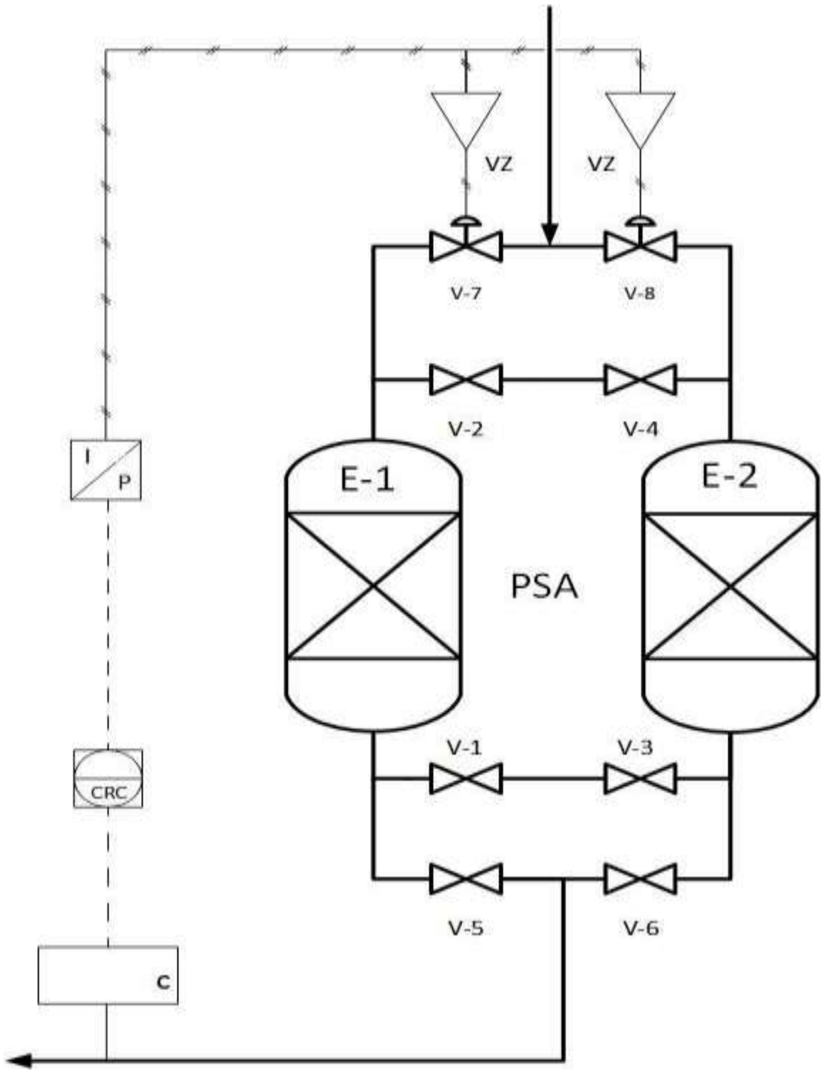


Figure 4: Controls in Adsorption Column

Suppose the flow is initially to the bed E-1 via the valve V-7. Under normal operating conditions, the valve V-8 will be initially closed. After exactly 45 minutes, the control will send a signal to the current to pressure (I-P) converter to open the valve V-8. The valve will remain open for 30 seconds for pressure normalization. After the time has elapsed the controller will again send a signal to the I-P converter to close valve V-7 and V-5 and open valve V-6. The operation will thus similarly continue in alternating cycles.

In case of any abnormality, there is a concentration sensor C at the outlet of the PSA. If the concentration of the Methane in the outlet stream exceeds the required value of 0.5% it sends a signal to the controller which similarly induces the converter to actuate the motor of the valves.

3.6 Equipment Design

3.6.1 Compressor

The compressor is selected to compress a gas from 12.1 bars to 50 bars. The pressure ratio of 4.13 was used. Next, a polytropic efficiency of 85% was assumed as per this pressure ratio. Later, the compressibility factor was calculated by knowing the average reduced pressures and temperatures.

$P_r = P/P_c$ $T_r = T/T_c$

	Critical	Reduced
Temperature	97.5 K	3.189
Pressure	2450 kPa	0.458

Table 22: Compressor P & T values

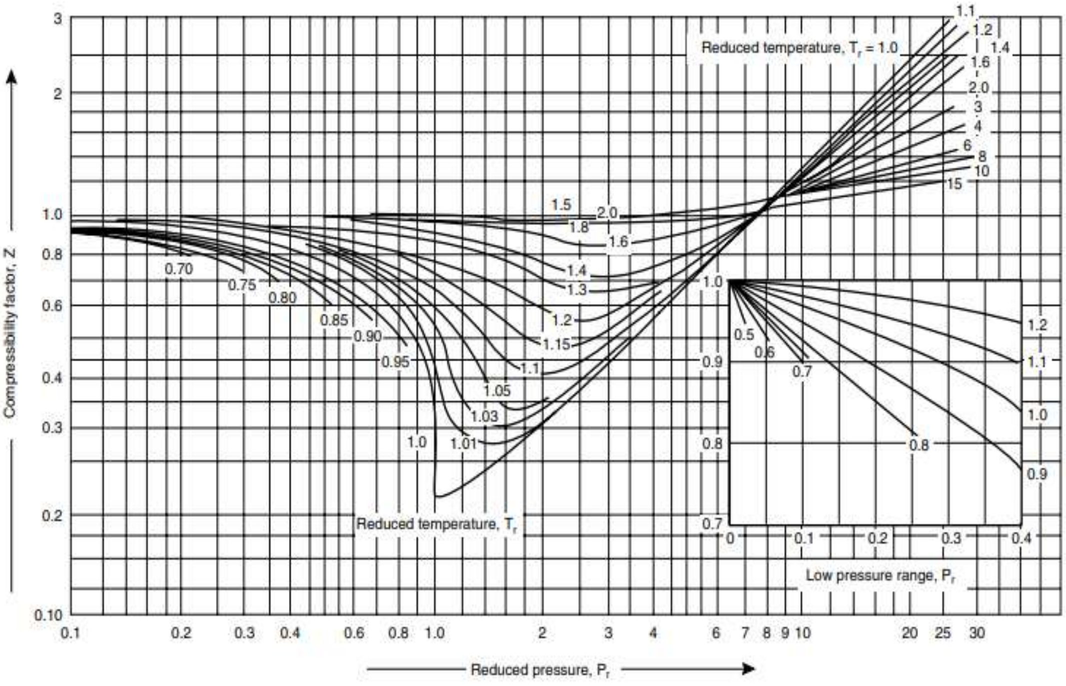


Figure 3.8. Compressibility factors of gases and vapours

Figure 5: Compressibility Chart

From the compressibility factor chart, $Z \approx 1$

In the next step, the polytropic factor n was found as follows:

$n = 1/(1-w)$

For that factor w was found first using the equation below:

$w = (\gamma - 1)/ (\gamma.E_p)$

The adiabatic factor $\gamma = C_p/C_v$ was found from literature.

The table below summarizes the values.

Specific heat ratio ɣ	1.22
Polytropic Efficiency E_p	85%
w	0.33
Polytropic factor n	1.15

Table 23: Compressor Design Summary

Finally, knowing the molar flow rate N, the value of work done was calculated.

$W_{theo} = NZRT_1 (n/n-1)* [(P_2 / P_1)^{(n-1/n)} - 1]$

This was divided by efficiency to find the actual work.

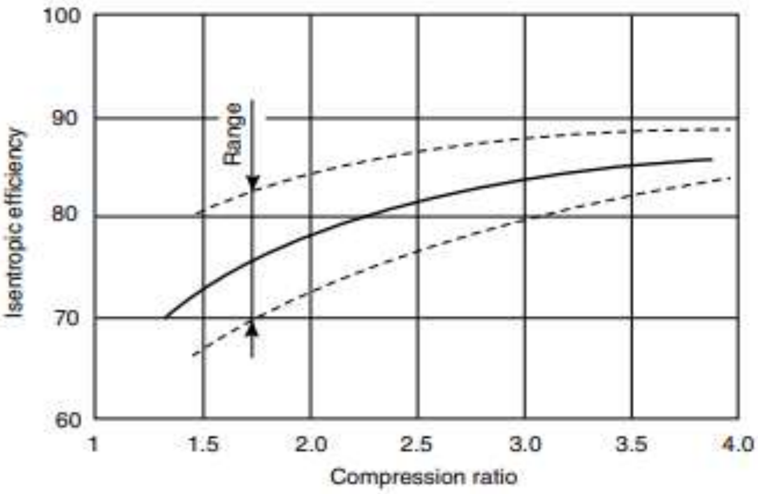


Figure 6: Compression Ratio vs. Efficiency Chart

The table below summarizes the values.

Molar flow rate	310 kmol/hr
Theoretical Work	326 kW
Polytropic Efficiency	85%
Actual Work	384 kW

Table 24: Compression Work Summary

3.6.2 Adsorber

Here a two-bed pressure swing adsorption column was designed. Adsorbent used was BPL type activated carbon. Although zeolites give better results but due to unavailability of their adsorption isotherms as well as their higher price, activated carbon was used. Properties are summed below.

Adsorbent Properties	
Particle Dia (4x10 mesh)	3.5 mm
Particle Density	460 kg/m^3
Void fraction	0.3
Sphericity	0.7

Table 25: Adsorbent Properties

Next, using the isotherms below, the adsorption capacity at the operating pressure and the regeneration pressure of each species was found. The individual working capacities were obtained by taking the difference of the two. By using the ideal adsorption solution theory (IAST), the net working capacity was found by multiplying individual capacities with their weighted averages.

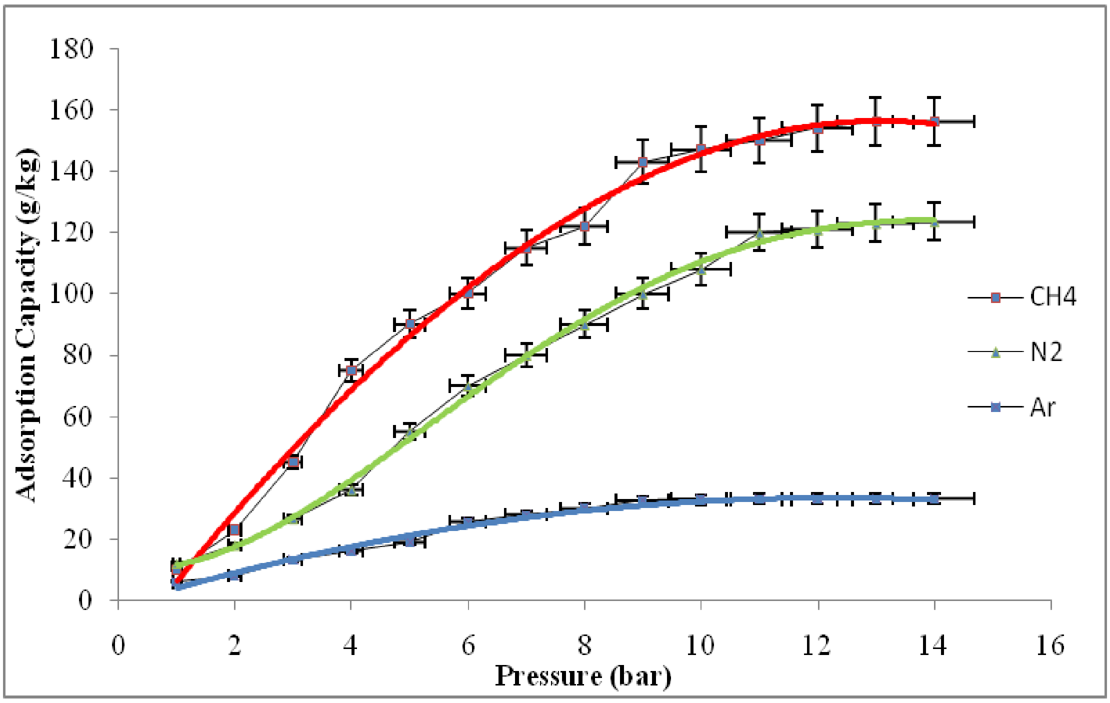


Figure 7: Pressure vs. Adsorption Capacity Graph

Results are summarized below.

Species	@12.4 bar (g/kg)	@3 bar (g/kg)	Working capacity dW (g/kg)
Wo_{CH4}	154	30.8	123.2
Wo_{N2}	121	26.6	94.4
Wo_{Ar}	33	13.2	19.8
Wo_{avg}	136.2	27.2	108.9

Table 26: Working Capacity of Individual Species

Next knowing the amount of gases to be adsorbed and the working capacity mass of adsorbent required was calculated by the formula below:

Adsorbent required: Mass of adsorbate (in grams)/ Working capacity

To be adsorbed
222 kgmol/hr = 4724.16 kg/hr = 4724160 g/hr
Mass of adsorbent
43363.19577 kg => Say 100 tons for 2 beds (incorporating uncertainties)

Table 27: Mass of Adsorbent

In the next step, after assuming a velocity ‘v’ and knowing the volumetric flow rate ‘Q’, the area ‘A’ was calculated by the continuity equation i.e. Q = Av. The length of the bed was assumed such that pressure drop doesn’t exceed the allowed value (40 kPa). Results can be seen below:

Column Specs	
Gas velocity	0.25 m/s
Volumetric flow	7800 Nm^3/hr
Area of column	8.89 m^2
Diameter of bed	3.36 m
Length of bed	12 m

Table 28: Column Specs

Next the cycle time was calculated. For this the inlet concentration was found by using the ideal gas equation. Then the time t* was found. It is the time when $C/C_o = 0.5$ i.e. when the concentration of adsorbate in the outlet stream is half that of inlet. Finally, by assuming a realistic value of length of bed used, the break-point time t_b was calculated (the time when $C/C_o = 0.01$). The formulae used are shown below:

$C_o = m/V = PM/RT$

$t^* = (L\rho_b \, dW)/vC_o$

$t_b = t^* (L_{used}/L)$

Here, M is the molar mass, dW is the working capacity and ρ_b is density of the bed.

The values are summarized below:

Cycle time	
Inlet Concentration C_o	617.52 g/m^3
t*	3895.34 sec
t*	1.08 hr
Bed used L_{used} (assume)	75%
Break-point time t_b	0.81 hr
Cycle time (error margin)	0.75 hr

Table 29: Cycle Time

Finally, the pressure drop was verified using Ergun's equation:

$$\Delta p = \frac{150 \mu L}{D_p^2} \frac{(1-\epsilon)^2}{\epsilon^3} v_s + \frac{1.75 L \rho}{D_p} \frac{(1-\epsilon)}{\epsilon^3} v_s$$

Allowed pressure drop	40 kPa
By Ergun's equation	2.86 kPa/m
Act pressure drop	34.33 kPa

Table 30: Pressure Drop Values

3.6.3 Cryogenic Column

Here, the rough estimate of the column design was thus obtained from Hysys short-cut column. The column was then designed by using Fenske's and Underwood's methods to calculate the minimum number of plates and the minimum reflux ratio respectively.

Knowing the value of the relative volatility at the operating condition and the concentration of the either key in each phase, the minimum number of plates have been calculated by the following formula:

$$N_{\min} = \frac{\ln\left[x_D(1 - x_B)/x_B(1 - x_D)\right]}{\ln \alpha_{AB}} - 1$$

The values are summarized in the table below:

α @ -183 °C	2.72
x_B	0.999
x_D	0.004
N_{min}	11.55 ≈ 12

Table 31: Number of Plate Calculations

Next, using Underwood's correlations, the summation B was first calculated by choosing a value of θ such that the two sides of the equation are equal. The same value of θ is then used to find R_{min}. Here, q is the feed operating line that tells the condition of the feed. The feed in our case is partially vaporized.

$$A = \sum \frac{\alpha_i x_{i,d}}{\alpha_i - \theta} = R_m + 1$$

$$B = \sum \frac{\alpha_i x_{i,f}}{\alpha_i - \theta} = 1 - q$$

The values are summarized in the table below:

α*xf	**B**	**α*xd**	**A**
2.011	1.416	2.673	1.882
0.255	-0.911	0.014	-0.050
1-q	0.506	$R_{min} + 1$	1.832
Θ	1.28		
Q	0.50		

Table 32: Column Design Values

Once the value of R_{min} was found, an operating value of R was selected. At this value, using the Underwood's correlations, the theoretical number of plates was calculated.

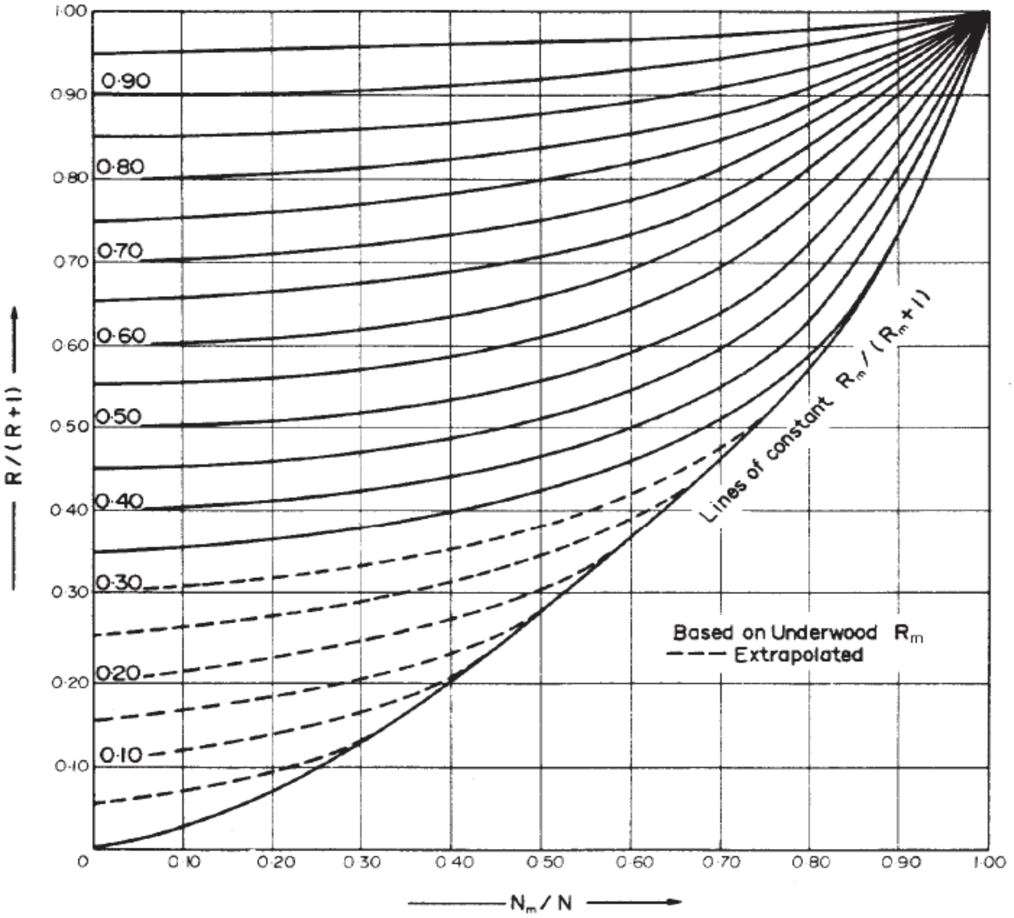


Figure 8: Underwood Graph for Plates Calculation

The values are summarized in the table below:

	Min	Act
R	0.83	2.2
R/ (R+1)	0.45	0.68
N_m/N		0.75
N_{theo}		15.34

Table 33: Reflux Ratio & Min. Number of Plates

Next, by assuming the overall efficiency of the column as stated in the literature, the effective and actual number of plates was calculated. Here, s is the safety coefficient which is taken as 1 in our case.

The efficiency of sieve tray cryogenic columns is between 0.7 – 0.9. The following formula was used.

$$N_{eff} = \frac{N_{th} \cdot s}{E_{OV}}$$

The values are summarized in the table below:

E_{ov}	0.80
S	1
N_{eff}	19.18
N_{act}	20

Table 34: Sieve Tray Efficiency

Finally, the column specs and the pressure drop were calculated. Firstly, a vapor velocity in the operating range is assumed. Next using the continuity equation (see adsorption section), knowing the vapor flow rate, the column cross-sectional area is calculated.

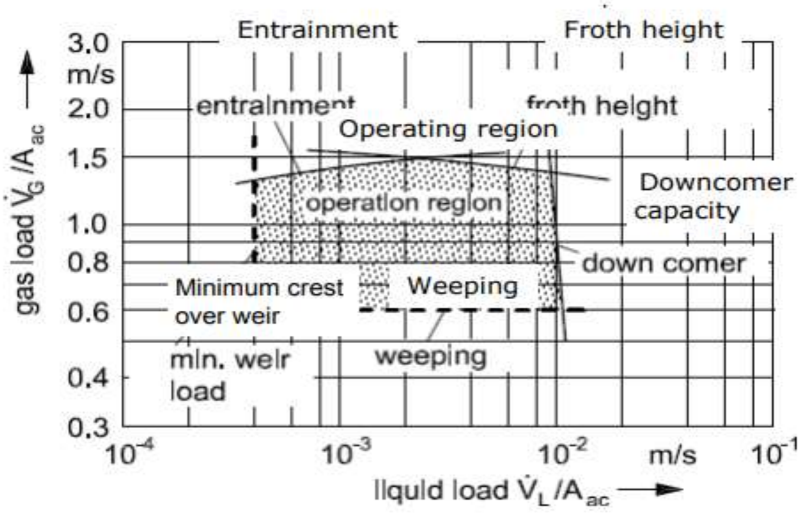


Figure 9: Liquid Load vs. Gas Load Graph

Knowing the plate spacing, the height of the column was calculated using the equation below where Δz is the tray spacing:

$H = N_{eff} \cdot \Delta z + 2\Delta z$

The hydrostatic pressure drop was calculated by the equation below. Here m_L is the liquid rate while the A_Q is the cross-sectional area.

$$\Delta p_{st} = \frac{m_L \cdot g}{A_Q}$$

The values are summarized in the table below:

Vapor velocity	1.2	m/s
Tray spacing (Δz)	0.3	m
Height of column	6.6	m
Max vapour rate	0.28	Nm^3/hr
Cross-sectional area	0.23	m^2
Tray diameter	0.54	m
dP Hydrostatic	18.64	kPa
dP Dry Trays	540	
Total pressure drop	19.19	kPa

Table 35: Distillation Column Specs

Chapter 4: Membrane Separation Process

4.1 Process Description

The first two units in both cryogenic and membrane systems are the same. Adsorption and separation through palladium membrane is carried out in the same manner. The only difference is the use of cascaded membrane system instead of a cryogenic distillation column. The retentate from Pd membrane is fed to the cascaded membrane system from where we get 99.3% pure Argon in the end.

4.2 Process Flow Diagram

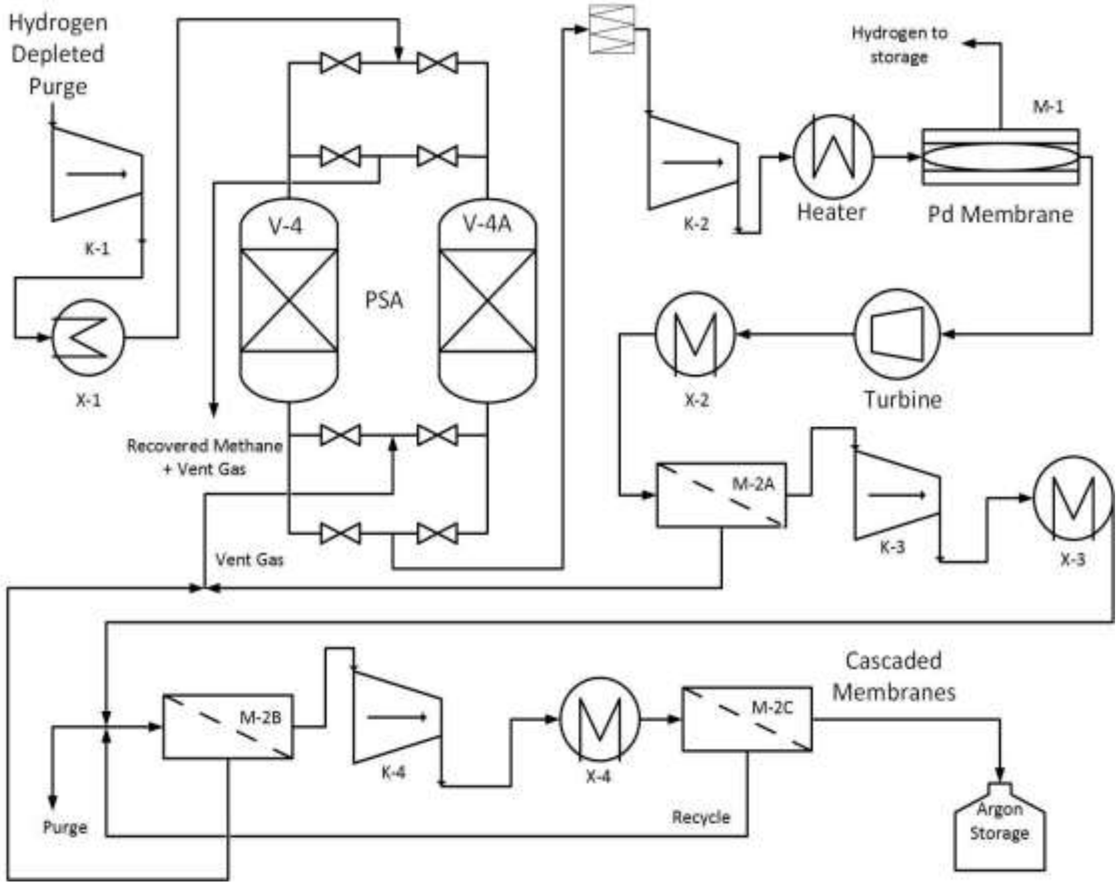


Figure 10: Membrane Separation PFD

The above diagram shows all the components that keep the process functional. The retentate that we obtain from Pd membrane is first expanded in a turbine. The energy extracted is sufficient to run the compressors in the next two stages. Interstage coolers and compressors keep the process stream to its operating temperature and pressure. Here, we are recycling the retentate of M-2C to M-2B as to maintain a continuous operation. Furthermore, the retentates are purged ad used as vent gas. The permeate that we obtain in the end is enriched in Argon that is stored separately.

4.3 Material Balance

The material balance begins with the adsorption column. The formula remains same because no accumulation or generation takes place. Hence,

Material in = Material Out

System 1: Adsorption Column

The first component in the membrane system is the adsorber. The inlet stream to the adsorber has a total flow rate of 6951 Nm^3/hr. Its composition and flow rates in kg/hr as well as Nm^3/hr are given below.

Component	Composition (Mol %)	Vol. Flow Rate (Nm^3/ hr)	Mass Flow Rate (kg/ hr)
H_2	14.87	1034	92
N_2	52.54	3652	4562
Ar	4.82	335	597.8
CH_4	27.52	1913	1365.5
NH_3	0.24	17	12.8
Total	100	**6951**	**6745**

Table 36: Inlet Stream

The inlet stream is subjected to adsorption and we get an adsorbed stream that is rich in Methane and Nitrogen. The total flow rate of this stream is 4987 Nm^3/hr.

Component	Composition (Mol %)	Flow Rate (Nm^3/ hr)
H_2	1.04	52
N_2	58.57	2921
Ar	1.68	84
CH_4	38.36	1913
NH_3	0.35	17
Total	100	**4987**

Table 37: Adsorbed Stream

The permeate that we get contains Hydrogen, Argon and Nitrogen. This stream has a total flow rate of 1964 Nm^3/hr.

Component	Composition (Mol %)	Flow Rate (Nm^3/ hr)
H_2	50	982
N_2	37.22	731
Ar	12.78	251
Total	100	**1964**

Table 38: Permeate Stream

System 2: Palladium Membrane

Palladium Membrane is employed to remove the entirety of Hydrogen from process stream. The assembly used is identical to that in the cryogenic process.

Component	Composition (Mol %) of permeate	Permeate Flow (Nm^3/ hr)	Composition (Mol %) of retentate	Retentate Flow (Nm^3/ hr)
Hydrogen	99.80	980	0.17	2
Nitrogen	0.13	2	74.30	729
Argon	0.07	1	25.53	250
Total	100	**983**	100	**981**

Table 39: Pd Membrane Material Balance

System 3: Cascaded Membranes

Here, instead of a cold box, the retentate of the membrane after being expanded and cooled is fed to the 3 stage cascade system that separates Nitrogen and Argon. The Argon to Nitrogen selectivity of the membrane is roughly 12. Temperature is maintained at 50 ^{o}C while the inlet pressure is 5 bars. The material flow through each individual stage is detailed in section 4.6.2.

Component	Composition (Mol %) of permeate	Permeate Flow (Nm^3/hr)	Composition (Mol %) of retentate	Retentate Flow (Nm^3/hr)	Composition (Mol %) of purge	Purge Flow (Nm^3/hr)
Hydrogen	0.28	1	---	---	---	---
Nitrogen	0.42	2	28.58	213	28.58	3
Argon	99.30	235	71.42	523	71.42	7
Total	100	**238**	100	**736**	100	**10**

Table 40: Polymeric Membrane Material Balance

4.4 Energy Balance

The energy balance is carried out on units after the separation from Pd membrane. All previous units are the same as mentioned in cryogenic method. Energy balance will be carried out on turbine and interstage coolers and compressors.

System 1: Turbine

The turbine extracts energy from the incoming gases and cool them down. Total energy extracted is around 63 kW that can run the compressors of next two membrane stages.

Parameter	Inlet	Outlet
Temperature (^oC)	350	167
Pressure (kPa)	5000	500
Power (kW)		-63.34

Table 41: Energy Balance on Turbine

System 2: Cooler Stage 1

In this cooler, Water has been used as a coolant. Its flow rate is measured to be 1685 kg/hr.

Parameter	Inlet	Outlet
Temperature (^oC)	166.8	50
Pressure (kPa)	500	500
Enthalpy change (kJ/hr)		140904

Table 42: Energy Balance on Membrane Stage 1 Cooler

System 3: Compressor Stage 2

Pressure drop in membranes is about 500 kPa due to which the stream must be recompressed to be sent to the next stage.

Parameter	Inlet	Outlet
Temperature (^oC)	50	337.2
Pressure (kPa)	100	500
Power (kW)		30.89

Table 43: Energy Balance on Membrane Stage 2 Compressor

System 4: Cooler Stage 2

Compression causes heating of the stream. Cooler basically removes this heat and brings the stream back to its operating temperature i.e. 50°C. The coolant used here is Water whose flow rate is around 1329 kg/hr.

Parameter	Inlet	Outlet
Temperature (°C)	337.2	50
Pressure (kPa)	500	500
Enthalpy Change (kJ/hr)		

Table 44: Energy Balance on Membrane Stage 2 Cooler

System 5: Compressor Stage 3

The compressor performs in exactly the same way as the compressor of last stage compressing the gas from atmospheric conditions to 500 kPa.

Parameter	Inlet	Outlet
Temperature (C)	50	426.7
Pressure (kPa)	100	500
Power (kW)		29.4

Table 45: Energy Balance on Membrane Stage 3 Compressor

System 6: Cooler Stage 3

The coolant used here is Water. Its flow rate has been measured to be 1268.7 kg/hr.

Parameter	Inlet	Outlet
Temperature (C)	426.7	50
Pressure (kPa)	500	500
Enthalpy Change (kJ/hr)		106560

Table 46: Energy Balance on Membrane Stage 3 Cooler

4.5 Process Modeling

The process was modeled in ASPEN HYSYS with Peng-Robinson as fluid package.

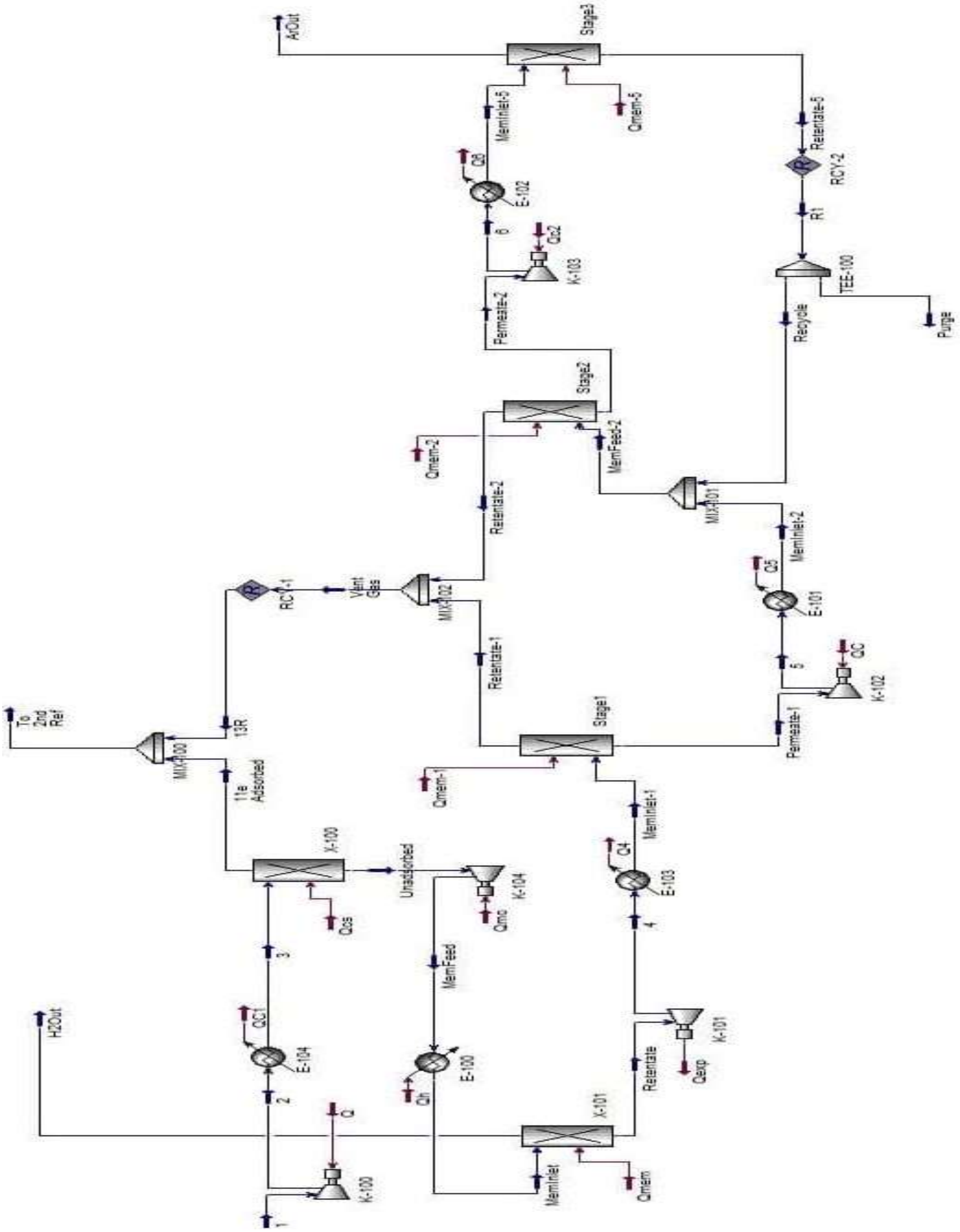


Figure 11: Aspen Modeling Of Membrane Process

At the same time the Pd membrane was modeled in custom modeler for comparison with theoretical results. They were quite similar.

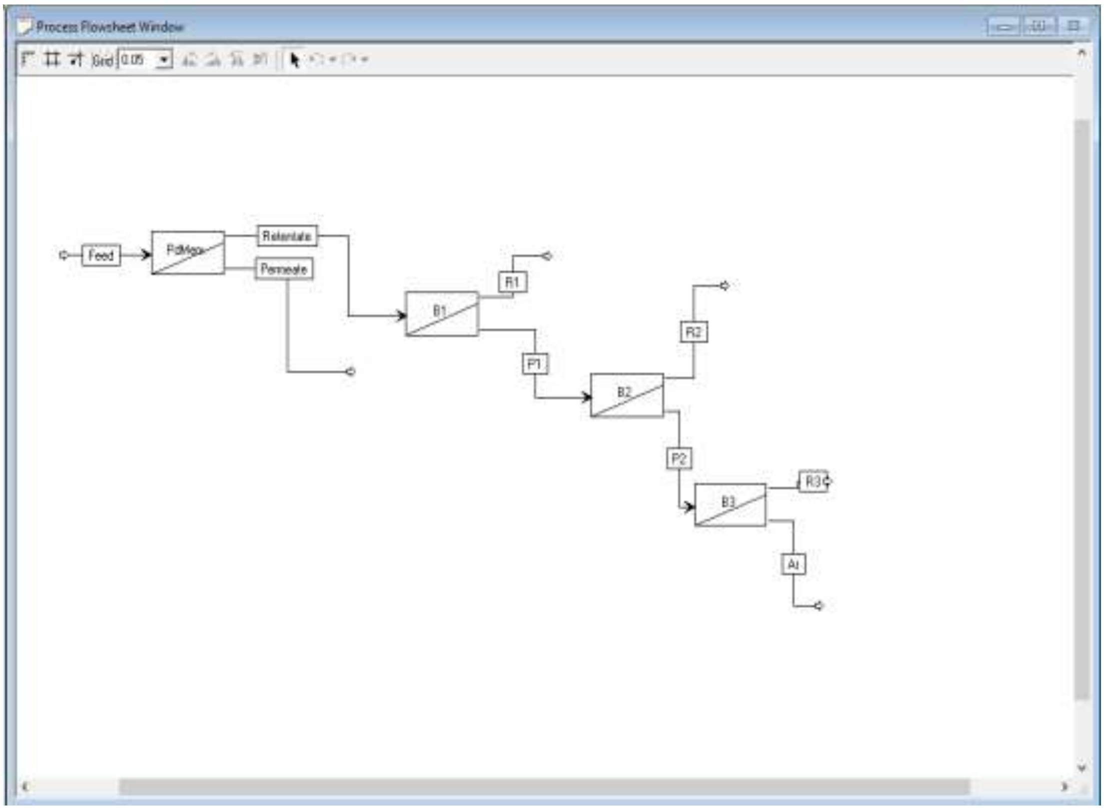
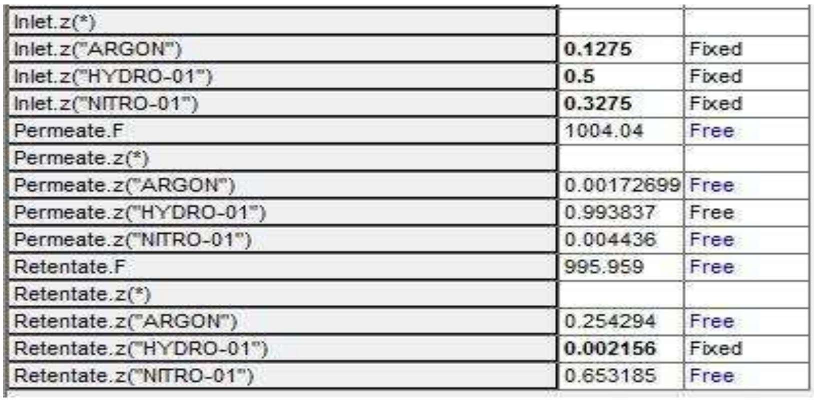


Figure 12: Custom Modeler Simulation Of Cascaded Membranes



Inlet.z(*)		
Inlet.z("ARGON")	**0.1275**	Fixed
Inlet.z("HYDRO-01")	**0.5**	Fixed
Inlet.z("NITRO-01")	**0.3275**	Fixed
Permeate.F	1004.04	Free
Permeate.z(*)		
Permeate.z("ARGON")	0.00172699	Free
Permeate.z("HYDRO-01")	0.993837	Free
Permeate.z("NITRO-01")	0.004436	Free
Retentate.F	995.959	Free
Retentate.z(*)		
Retentate.z("ARGON")	0.254294	Free
Retentate.z("HYDRO-01")	**0.002156**	Fixed
Retentate.z("NITRO-01")	0.653185	Free

Figure 13: Results from Custom Modeler

4.6 Equipment Design

4.6.1 Palladium Membrane

Here, a spiral wound palladium membrane was designed. The membrane contains about 10% Copper, Silver or Yttrium for structural integrity and increased permeability. There are no spacers needed since the feed is gaseous. The permeate pipe is closed at one end making the flow a crossed arrangement.

Knowing the inlet condition; (P_1 = 50 bar, P_2 = 10 bar) the value of pressure ratio R was calculated.

$R = P_2/P_1 = 0.2$

The value of selectivity α was found from the literature for Hydrogen phase and the N_2 and Ar phase (rest). The value of α was found to be 1000.

Next, by using the McCabe’s method, the value of y_i i.e. the concentration of more permeable component (Hydrogen) in the permeate phase was found by the formula below.

The system was optimized by selecting a stage-cut of 0.5. The stage-cut is the ratio of gas exiting as permeate to the feed entering the membrane. Hence, a stage-cut of half means that the feed will be split equally in to Permeate and Retentate streams.

$$(\alpha - 1)y_i^2 + \left(1 - \alpha - \frac{1}{R} - \frac{x(\alpha - 1)}{R}\right)y_i + \frac{\alpha x}{R} = 0$$

The data is summarized below.

Species	**Mol fr inlet**	**Total Flow**	**Mol fr Perm**	**Perm Flow**	**Mol fr Ret**	**Ret Flow**
Total	1	88	44	44		44.000
Hydrogen	**0.5**	44	**0.998**	43.927	0.002	0.073
Rest	0.5	44	0.002	0.073	0.998	43.927
Nitrogen	0.375	32.75	-			32.696
Argon	0.125	11.25	-			11.231
stage-cut		0.5				

Table 47: Flow through Pd Membrane

The next step was to find the area of the membrane required. The value of permeability Q_A was found from the literature. Vy_{out} is the flow rate of Hydrogen in Permeate.

$$A = \frac{(Vy)_{out}}{(J_A)_{ave}} = \frac{(Vy)_{out}}{Q_A(P_1 x - P_2 y_i)_{ave}}$$

The conversion factor for SI units to barrer is:

1 barrer = 1.21 x 10^{-12} kmol*m/m^2*hr*kPa

The permeability was divided by the thickness of the membrane (assumed to be 10-20 micron) and plucked in the formula to obtain the area. Results are summarized below.

Permeability	1.66E-09 kmol*m/m^2*hr*kPa	1376 barrer
Area	17693773.18 m^2/m	176.938 m^2

Table 48: Pd Membrane Area

Knowing the area and thickness, the volume of the flat sheet was obtained. Next assuming a perfect cylinder, the length was assumed. While incorporating the permeate pipe, the interstitial spacing and the Ag/ Cu/ Y coating, the diameter of the module was found.

Results are summarized below.

Volume of the membrane sheet	3.6 x 10^{-3} m^3
Length of the module	1 m
Permeate collector diameter	0.03 m
Module diameter	0.12 m

Table 49: Pd Membrane Design Summary

4.6.2 Cascaded Polymeric Membrane

The design of these cascaded membranes was similar to the Pd Membrane. The membrane consists of 3 hollow fiber modules of variable area to increase the purity from 25% to 99.3%. The modules are presumably bore-side feed and shell side permeate. The fibers are closed at one end making the flow a crossed arrangement.

Knowing the inlet condition; (P_1 = 5 bar, P_2 = 1.01 bar) the value of pressure ratio R was calculated. ($R = P_2/ P_1 = 0.2$)

The value of selectivity α was found to be 11.8 from the literature for Nitrogen and Argon. Hydrogen being highly permeable is assumed to lie largely in the vapour phase.

Stage 1					
Species	**Mol fr inlet 1**	**Inlet 1 (kmol/hr)**	**Mol fr. Permeate 1**	**Permeate 1 (kmol/hr)**	**Retentate 1 (kmol/hr)**
Total		44.000		14.496	29.504
Hydrogen	0.002	0.073	(Neglect)	0.073	0.000
Rest	0.998	43.927		14.496	33
Nitrogen	0.743	32.696	0.252	3.653	32.611
Argon	0.255	11.231	0.748	10.843	0.389
Stage Cut			**0.33**		
Area (km^2)			**2.893**		

Table 50: Stage 1 Calculations

The permeate of stage 1 is fed to stage 2.

Stage 2					
Species	**Mol fr. Perm1 + Rec**	**Perm 1 w/Recycle (kmol/hr)**	**Mol fr. Permeate 2**	**Permeate 2 (kmol/hr)**	**Retentate 2**
Total		18.586			
Hydrogen	0.004	0.073	0.0	0.073	0.000
Rest	0.996	18.513	---	13.144	5.369
Nitrogen	0.309	5.734	0.048	0.636	5.098
Argon	0.688	12.779	0.952	12.508	0.271
Stage Cut			**0.71**		
Area (km^2)			**1.062**		

Table 51: Stage 2 Calculations

The permeate of stage 2 is fed to stage 3.

Stage 3							
Species	**Mol fr. Inlet 2**	**Inlet 3**	**Mol fr. Perm 3**	**Permeate 3**	**Retentate 3**	**Recycle**	**Purge**
Total		13.124		10.485			
Hydrogen	0.006	0.073	0.006	0.073	0.00	0.00	0.000
Rest	0.994	13.051		10.441	2.610	2.236	0.374
Nitrogen	0.029	0.376	0.001	0.029	0.347	0.302	0.045
Argon	0.965	12.675	0.993	10.412	2.263	1.934	0.329
Stage Cut			**0.8**				
Area (km^2)			**0.606**				

Table 52: Stage 3 Calculations

The permeate of stage 3 is our final product. The retentate is recycled back to stage 2 since it contains significant amounts of Argon. The stage cut in each stage was selected to optimize the permeate and retentate distribution.

Table below summarized the final values.

Recovery	**92.7%** of feed
Purge	**14.5%** of Ret 3
Purity	**99.3%**

Table 53: Final Values Summary

The purge is necessary to help system attain equilibrium.

Chapter 5: Costing

Cost Estimates for the Design

Costing was done with reference from Coulson Richardson’s Chemical Engineering Design Volume 6th. Following are the graphs and figures used in cost estimation.

Graph 1

This graph helps in calculation of cost of vessels

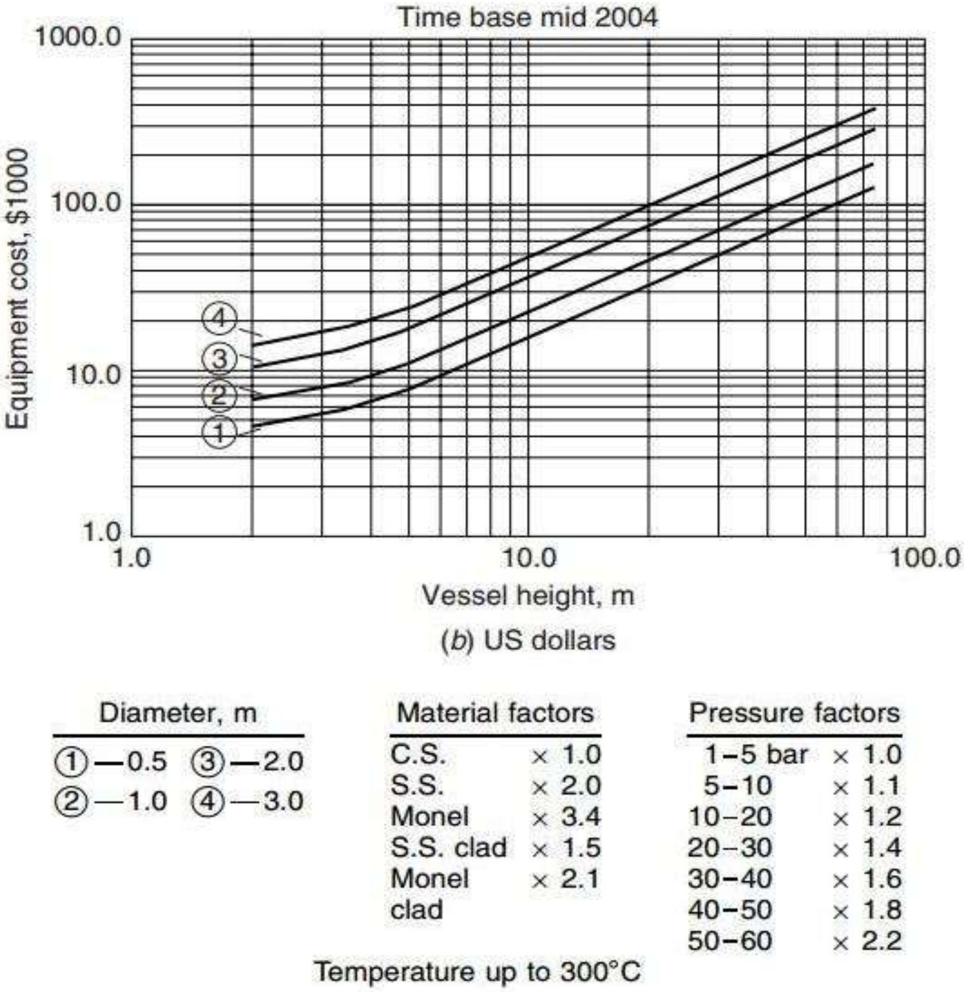


Figure 14: Vessel Costing Graph

Graph 2

Cost of plates is estimated using this graph.

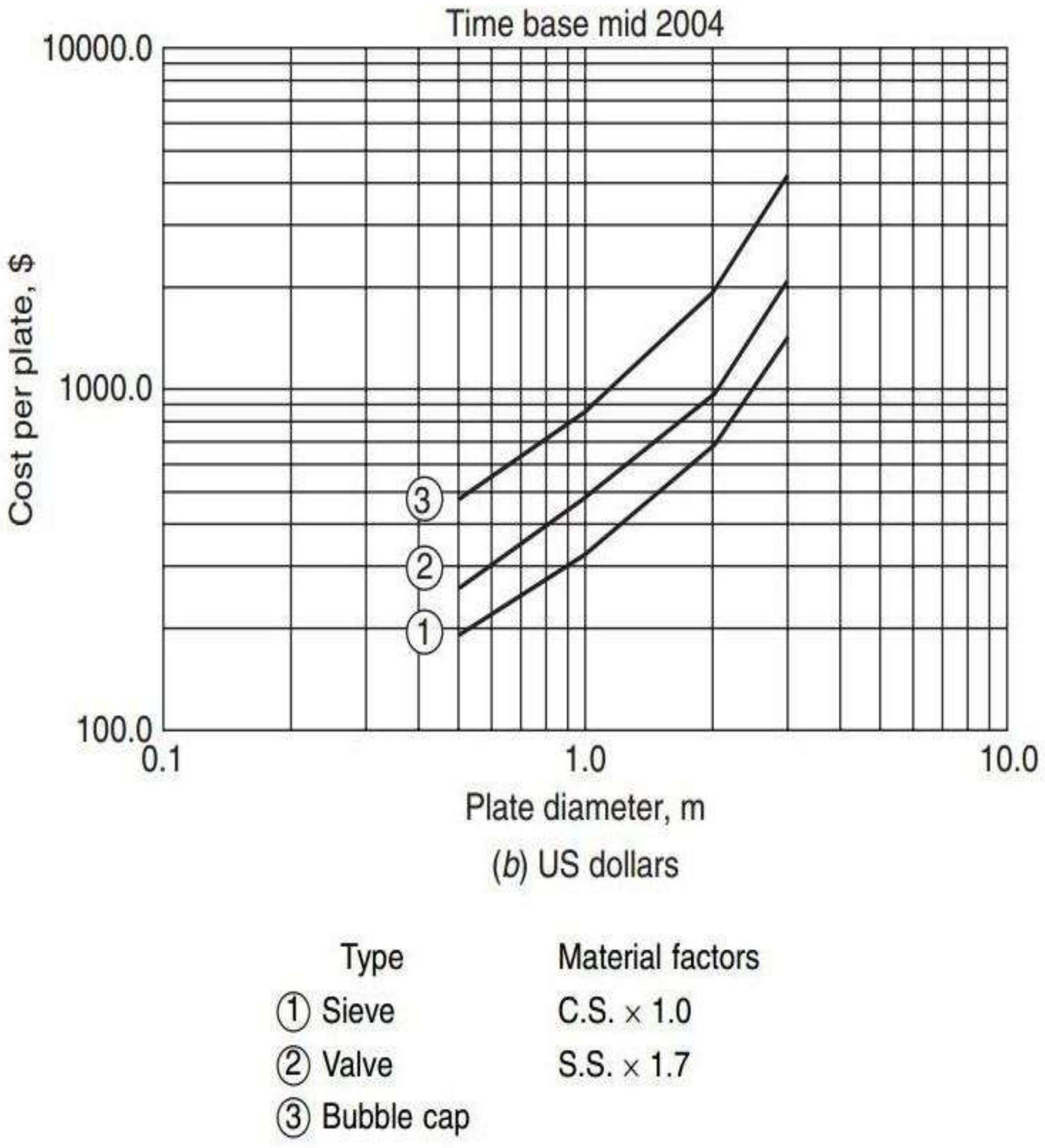


Figure 15: Plate Costing Graph

Graph 3

Cost of Plate and frame type exchanger is estimated using this graph

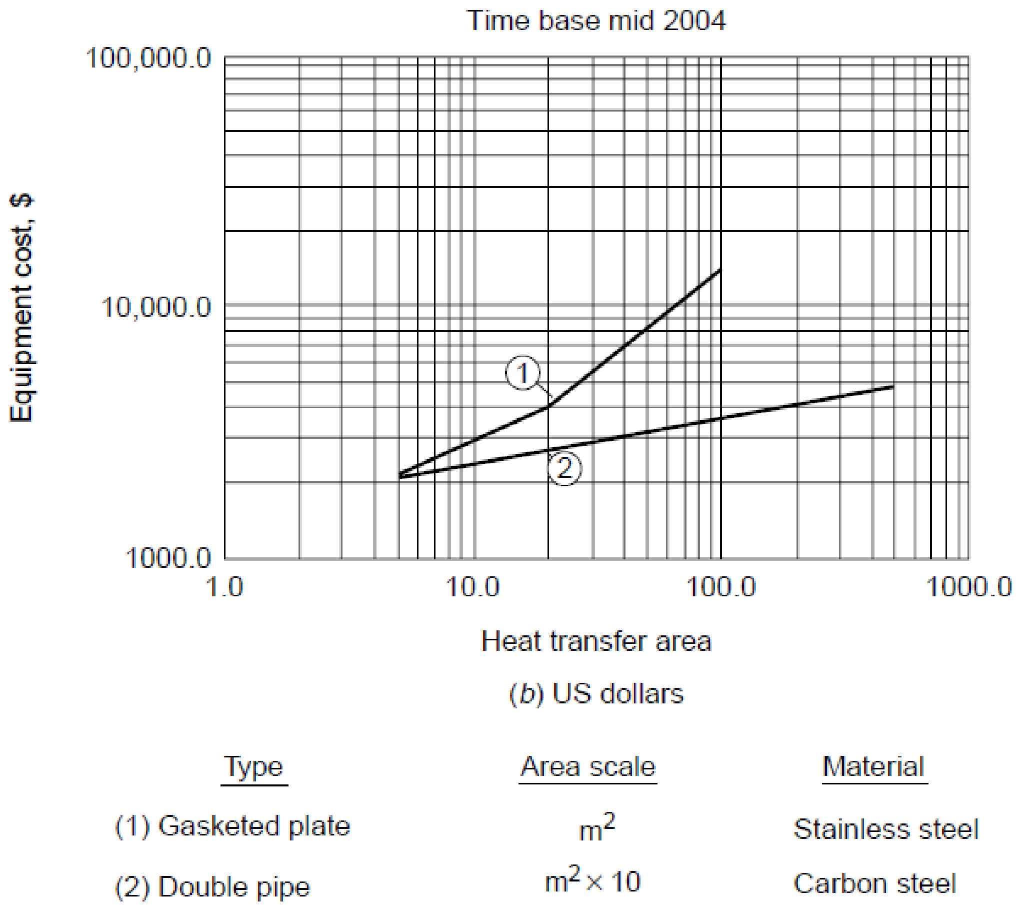
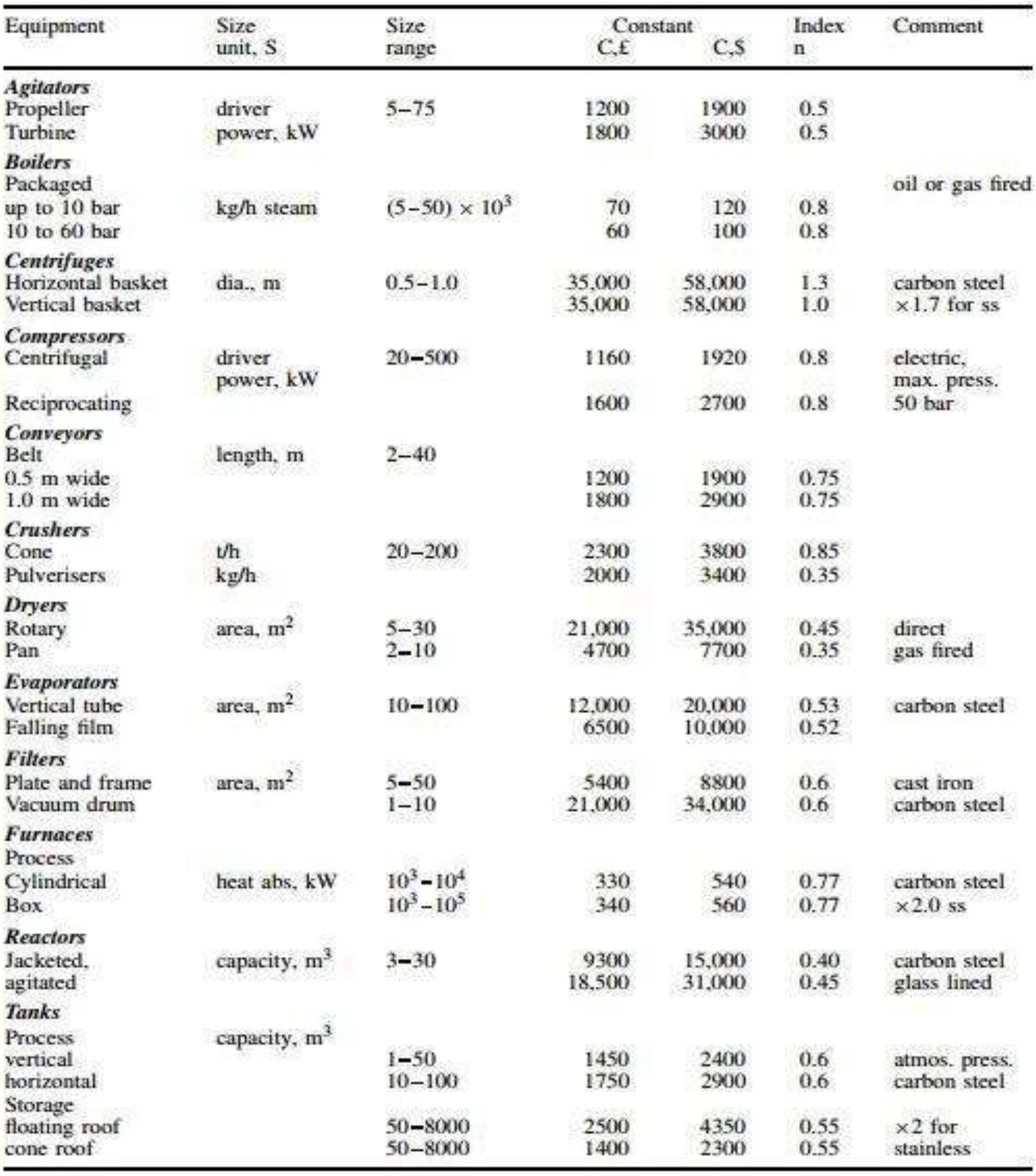


Figure 16: Heat Exchanger Costing Graph

This table helps in cost estimation of other equipment.



Equipment	Size unit, S	Size range	Constant C,£	C,$	Index n	Comment
Agitators						
Propeller	driver	5–75	1200	1900	0.5	
Turbine	power, kW		1800	3000	0.5	
Boilers						
Packaged						oil or gas fired
up to 10 bar	kg/h steam	$(5-50) \times 10^3$	70	120	0.8	
10 to 60 bar			60	100	0.8	
Centrifuges						
Horizontal basket	dia., m	0.5–1.0	35,000	58,000	1.3	carbon steel
Vertical basket			35,000	58,000	1.0	×1.7 for ss
Compressors						
Centrifugal	driver power, kW	20–500	1160	1920	0.8	electric, max. press.
Reciprocating			1600	2700	0.8	50 bar
Conveyors						
Belt	length, m	2–40				
0.5 m wide			1200	1900	0.75	
1.0 m wide			1800	2900	0.75	
Crushers						
Cone	t/h	20–200	2300	3800	0.85	
Pulverisers	kg/h		2000	3400	0.35	
Dryers						
Rotary	area, m^2	5–30	21,000	35,000	0.45	direct
Pan		2–10	4700	7700	0.35	gas fired
Evaporators						
Vertical tube	area, m^2	10–100	12,000	20,000	0.53	carbon steel
Falling film			6500	10,000	0.52	
Filters						
Plate and frame	area, m^2	5–50	5400	8800	0.6	cast iron
Vacuum drum		1–10	21,000	34,000	0.6	carbon steel
Furnaces						
Process						
Cylindrical	heat abs, kW	10^3-10^4	330	540	0.77	carbon steel
Box		10^3-10^5	340	560	0.77	×2.0 ss
Reactors						
Jacketed,	capacity, m^3	3–30	9300	15,000	0.40	carbon steel
agitated			18,500	31,000	0.45	glass lined
Tanks						
Process	capacity, m^3					
vertical		1–50	1450	2400	0.6	atmos. press.
horizontal		10–100	1750	2900	0.6	carbon steel
Storage						
floating roof		50–8000	2500	4350	0.55	×2 for
cone roof		50–8000	1400	2300	0.55	stainless

Figure 17: Other Equipment Costing Table

Hydrogen depleted Gas Cooler (E-104)

Shell and tube heat exchanger of U-tube type.

Heat Transfer Area = 43.4 m^2

Bare Equipment cost = $ 62100 (Using Graph 1)

Pressure factor

= 1.1 Type

factor = 0.85

Cost = Bare equipment cost * Pressure factor *

Type Total Cost = $ 78900

Membrane feed Heater (E-100)

Plate and Frame type Heat exchanger.

Heat Transfer Area = 4.9 m^2

Bare Equipment cost = $ 2000 (Using Graph 4)

Total Cost = $ 2800

Cooler (E-103)

Plate and Frame type Heat exchanger.

Heat Transfer Area = 8 m^2

Bare Equipment cost = $ 2800 (Using Graph 4)

Total Cost = $ 3900

Cold Box (E-103a)

Shell and tube heat exchanger of

kettle type. Heat Transfer Areas =

20.1

Bare Equipment cost = $ 21400 (Using Graph

1) Pressure factor = 1.1

Type factor = 1.3

Cost = Bare equipment cost * Pressure factor * Type factor

Cost = $ 41,700

Cold Box (E-103b)

Shell and tube heat exchanger of kettle type. Heat Transfer Areas = 24.5 m^2

Bare Equipment cost = $ 31,250 (Using Graph 1) Pressure factor = 1.1

Type factor = 1.3

Cost = Bare equipment cost * Pressure factor * Type factor

Cost = $ 60,750

Refrigeration Cycle Cooler (E-105)

Plate and Frame type Heat exchanger.

Heat Transfer Area = 10.2 m^2

Bare Equipment cost = $ 3300 (Using Graph 4)

Total Cost = $ 4500

Inter-Stage Distillation Column Cooler (E-101)

Plate and Frame type Heat exchanger.

Heat Transfer Area = 8 m^2

Bare Equipment cost = $ 2800 (Using Graph 4)

Total Cost = $ 3900

Purge Gas Adsorber (X-100)

Vessel Length = 12 m

Vessel Diameter = 3 m

Pressure Factor = 1.2

Material Factor = 1.0 for Carbon Steel

Purchased cost = Bare cost from figure * Material factor * Pressure factor

Purchased cost = $35,000 * 1.0 * 1.2 * 1.36 * 2

= $115,000

Adsorbent = 50 tons/bed

Adsorbent Price = \$1500/ton

Adsorbent Price = \$1500 * 50 * 2

= \$150,000

Total Adsorber Cost = \$115,000 + \$150,000

=\$265,000

Compressor 1 (K-100)

Size Factor = 383.8 kWh

Base Cost = \$1920

Index number = 0.8

Cost = $C*S^n$

Cost = $1920 * 383.8^{0.8}$ = \$225,000

Compressor 2 (K-102)

Size Factor = 46.8 kWh

Base Cost = \$1920

Index number = 0.8

Cost = $C*S^n$

Cost = $1920 * 46.8^{0.8}$ = \$42,000

Compressor 3 (K-104)

Size Factor = 150 kWh

Base Cost = \$1920

Index number = 0.8

Cost = $C*S^n$

Cost = $1920 * 150^{0.8}$ = \$105,700

Distillation Column (T-100)

Height of column = 7 m

Diameter = 0.5 m

Trays = Bubble Cap Trays

Material Factor = 1.7

Cost of Trays = \$600 * 21 * 1.36 * 1.7

= \$30,000

Column Cost = \$11000 * 2 * 1.1 * 1.36

= \$34,000

Total Cost = \$64,000

Palladium Membrane:

Total Membrane area = 176.6 m^2

Price of Palladium = 30,000 \$/m^2

Cost of Membrane material = \$5,210,000

Cascaded Membrane:

Total Membrane Area = 4560.11 m^2

Material Price = \$50/m^2

Cost of membrane material = \$250,000

The overall costing for the whole Cryogenic Plant and the Membrane plant is as follows, followed by the NCA's

Cryogenic Process		
Costs	Total Price USD	Unit Price USD
Adsorber	250000	1500/ton
E-100	10500	
E-103	17700	
E-104	11200	
E-105	28200	
Pd Membrane	5210000	30000/m^2
K-104	144000	
K-100	305000	
X-1	10000	
Column w/ aux	1220000	
Cold box	141000	
E-101	25600	
K-102	57000	
Base Cost	**7.4 M**	
PCE	**21.5 M**	
PPC	**30.2 M**	

Table 54: Cost of Cryogenic Process

Membrane Process		
Costs	Total Price USD	Unit Price USD
Adsorber	250000	1500/ton
K-102	40600	
K-101	71200	
K-103	40000	
K-100	305000	
K-104	144000	
E-103	9800	
E-104	17700	
E-101	8700	
E-102	8800	
E-100	10400	
Cascade Mem	250000	50/m^2
Pd Membrane	5210000	30000/m^2
Base Cost	**6.4 M**	
PCE	**18.5 M**	
PPC	**25.8 M**	

Table 55: Cost of Membrane Process

Net Cash Flows:

Knowing the operating costs and the capital cost and the revenue, net cash flow (NCF) was calculated for each plant. The payback period for membrane plant was found to be 2 years while that for cryogenic was found to be 2.4 years.

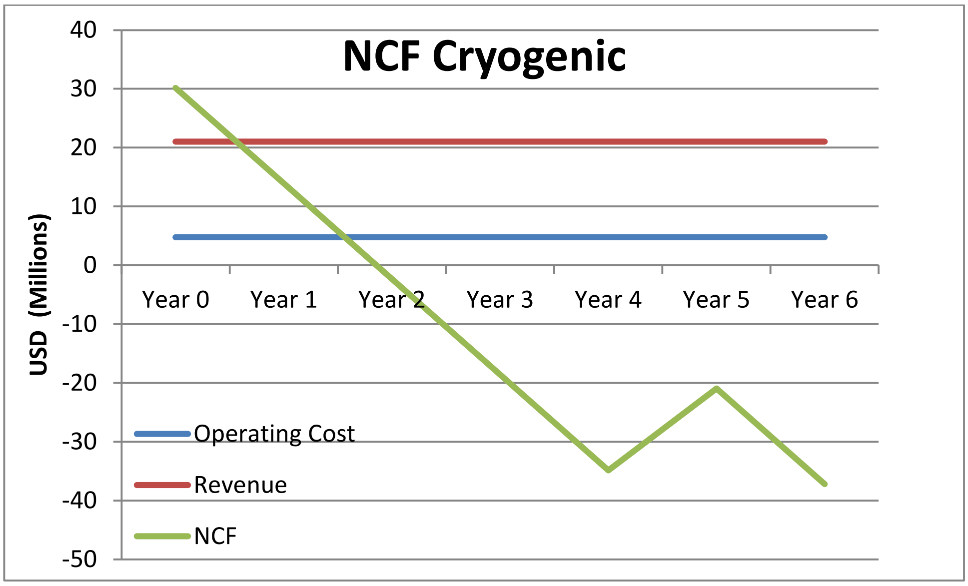


Figure 18: Cryogenic Payback Graph

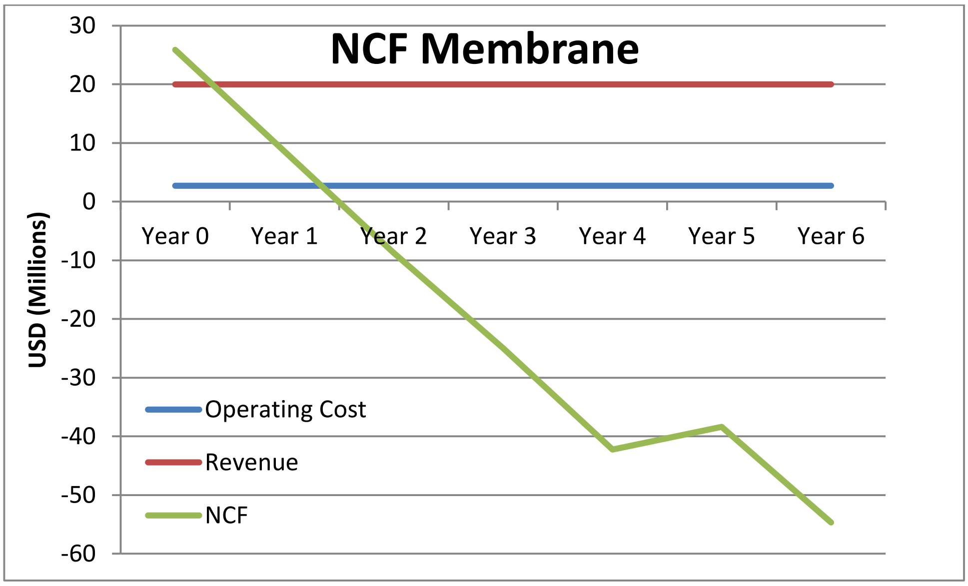


Figure 19: Membrane Payback Graph

Chapter 6: HAZOP Analysis

Hazard and Operability Analysis employs the use of certain guide words to see any probable causes of incidents in any equipment their consequences as well as their controls. A few examples are shown below:

Unit 1: Distillation Column

Guide Word	Deviation	Possible Causes	Consequences	Action Required
NONE	No Flow	1. The pipeline is blocked	The distillation column may not perform the separation	Check for blocked lines
		2. The Throttling valve can fail	Flow of the stream stops and the distillation column may stop operating	Check that the throttling valve is open or not
MORE OF	More Flow	1. The control valve failed and the flow is not controlled	If the flow increases the purity required cannot be achieved.	Check valves which is giving out the distillation feed
	More Pressure	2. The Pressure	Gaseous mixture may	

	More Temperature	increased 3. The Heat exchanger may fail	require other conditions to operate on. Increase in temperature results in zero separation	Open the PSV and vent the extra pressure Increase the coolant flow in the exchanger and give more time to the stream to get cool
AS WELL AS	Hydrogen is in Distillation Feed	The membrane is not working properly	Binary mixture not formed. Separation not possible	Clean the membrane and check for possible error
OTHER	Maintenance	Due to high pressure, leakages can occur.	The Column can get damaged and thus the product can leak in atmosphere	Make possible repairs or change the distillation column

Table 56: HAZOP Analysis of Distillation Column

Unit 2: Pd Membrane

Guide Word	Deviation	Possible Causes	Consequences	Action Required
NONE	No Flow	1. Membrane can be blocked due to dust particles	Desired product purity not achieved.	Quickly back wash the membrane
		2. Low Pressure	Low head means no flow through the membrane or leaks in pipeline	Check pipelines and see for leakages and repair them
		3. The Compressor failed	No flow through membrane. No separation.	Turn on the backup compressor repair the damaged compressor
MORE OF	More Flow	1. The valve opening not controlled	Required purity cannot be achieved	Reduce the stream flow rate by reducing valve opening
	More Pressure	2. The membrane may be blocked due to	Pipeline can burst. Membrane	Clean the membrane. Vent extra pressure

		dust particles	can be damaged	
	More Temperature	3. The cooler may not be functioning	Phase change of membrane occurs. No separation.	Increase the quantity of coolant
LESS OF	Less Flow	1.The turbine may expand the gases too much	Less purity of the final product	Check the turbine and look for possible errors
	Less Temperature	2.The cooling Water supply temperature decreases	Separation may not occur as the palladium membrane require high temperatures	Heat the gases or look for the possible heat exchange losses
AS WELL AS	Membrane fouling	Dust particles can come in the stream	Clogging of membrane. Pipeline can burst	Back washing
OTHER	Maintenance	Membrane can foul, the pipeline can leak	The membrane can get fractured or may be susceptible to damages.	Replace the membrane, or the pipelines

Table 57: HAZOP Analysis of Pd Membrane

Unit 3: Adsorber

Guide Word	Deviation	Possible Causes	Consequences	Action Required
NONE	No Flow	4. The inlet valve not opened	Pipeline can burst and possible explosion can occur	Turn of the pump and bypass the gas stream to the other section of the adsorber.
		5. The Compressor failed	The inlet valve may fail and due to the pressure accumulation compressor failed	Turn on the PSV and vent the gases
MORE OF	More Flow	4. The control valve failed and the flow is not controlled	The required purity might not achieve.	Reduce the valve opening. Check is the compressor working properly
	More Pressure	5. The Pressure increased	The pipeline can burst. Or the adsorber may explode	Open the PSV. Vent

				the extra pressure
LESS OF	Less Flow Less Pressure	3.Possible leakage in pipeline. The compressor may fail 4.The Compressor may not be working. Possible line leakages	Less purity of the final product Less pressure means lesser Adsorption.	Quickly replace pipeline. Check for compressor load. Replace lines. Check compressor
AS WELL AS	Dust Particles may come in the stream	The inlet gas may be full of dust particles	Packing may get damaged or blocked. No adsorption occurs.	Install dust filter before entering the gas in adsorber
OTHER	The Packing life has been completed	Excessive usage or packing life has ended	No adsorption occurs. No product attained	Replace the packing, change the bed

Table 58: HAZOP Analysis of Adsorption Column

Chapter 7: Comparison

While both the processes have their merits and demerits, it can be seen that the product purity is much higher in the cryogenic process and so is the yield. Moreover, cryogenic is an established technique that has been used in the industry for decades. Membrane is a relatively new technique and has a certain degree of uncertainty attached to it, as well. The results are summarized below:

Parameters	**Cryogenic**	**Membrane**
Total Argon obtained	11 kmol/hr	10.4 kmol/hr
Single pass yield	80%	74%
Yield with recycle	90%	85%
Product Purity	99.9*%	99.3%
Capital Cost	$30.2 M	$25.8 M
Operating Cost	$4.8 MPA	$2.6 MPA
Net Revenue	$21 MPA	$19 MPA
Payback Period	2.4 Years	2 Years

Table 59: Comparison of Both Processes

As we can see from the table above, the merits of using cryogenic distillation are very evident. Considering the cost analysis, both capital requirement and operating costs are higher in cryogenic process as compared to the membrane process. The difference in the pay-back period isn't significant. However, the percentage purity and yield obtained from distillation are much better due to which cryogenic process is recommended.

Conclusion

This project featured the process and modeling of two methods to recover Argon from Ammonia purge stream. Using meticulous HYSYS simulations and literature reviews, we conclude that the separation of Argon from the purge gas is more economical and easier using cryogenic separation. Despite the high energy requirement, the revenue generated compensates all the factors yet generates a high value of profit. Moreover, the installation cost is not high which makes it easy for FFC to install the plant without any difficulty. The suggested process does not require huge space yet is very compact. On the contrary, the capital and operating costs of membrane separation is significantly low, but this is being compromised on low purity of Argon in the final stage. Therefore, it is suggested that the installation of this Argon Recovery unit at Plant-1 should take place which can be a milestone for the company itself.

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