Economic Recovery of Hydrogen from Purge Gas

By

Awwab Ahmed	**00000147477**
Syed Muhammad Waqas Ali	**00000126642**
Muhammad Awab Elahi	**00000134787**

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST)

2019

Economic Recovery of Hydrogen from Purge Gas

Awwab Ahmed	**00000147477**
Syed Muhammad Waqas Ali	**00000123456**
Muhammad Awab Elahi	**00000123456**

This thesis is submitted as a partial fulfillment of the requirements for the degree of

BE in Chemical Engineering

Supervised by: Lec. Ayesha Raza
Co-supervised by: Dr. Erum Pervaiz

School of Chemical and Materials Engineering (SCME)
National University of Sciences and Technology (NUST)
H-12 Islamabad, Pakistan
May, 2019

CERTIFICATE

This is to certify that work in this thesis has been carried out by Awwab Ahmed, Syed Muhammad Waqas Ali and Muhammad Awab Elahi and completed under our supervision in School of Chemical and Materials Engineering (SCME), National University of Sciences and Technology (NUST), H-12, Islamabad, Pakistan.

Supervisor: Lec. Ayesha Raza

Lecturer

Department of Chemical Engineering

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST), Islamabad

Co Supervisor: Dr. Erum Pervaiz

Assistant Professor

Department of Chemical Engineering

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST), Islamabad

Submitted through

HoD: Dr. Bilal Khan Niazi

Department of Chemical Engineering

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST), Islamabad

Dean and Principal: Dr. Arshad Hussain

Department of Chemical Engineering

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST), Islamabad

Dedication

This work is dedicated to SCME, our beloved parents and respected teachers.

Acknowledgements

All thanks to Allah Almighty for His countless blessings and rewards, Who gave us the strength and ability to complete this thesis.

We would like to thank our supervisor Lec. Ayesha Raza and our Co. Supervisor Dr. Erum Pervaiz for their support and guidance during our project. They have been very generous and supportive and helped a lot to complete this thesis. We are thankful to other faculty of SCME as well for their assistance.

We would also like to thank our industrial supervisor for his guidance and help throughout the project and Fauji Fertilizer Company (FFC) for giving us such useful project and providing us all the data and details needed for completion of project.

We are also thankful to our parents, without their support and encouragement, it would not have been possible to complete the project successfully.

Authors

Abstract

Synthesis of Urea fertilizer requires production of Ammonia first. In the Ammonia synthesis, conversion is low, about 20-30%. So, after product separation, the stream is recycled. But, this closed loop synthesis causes accumulation of inerts. Hence, for optimum conversion, it is required to purge a certain amount of this recycled gas. It is economically feasible to recover valuable gases rather than burning them. Therefore, important components including Hydrogen gas are recovered. After recovery, it is sent back into the synthesis loop which decreases the amount of Natural Gas required as raw material and enhances the production efficiency. The most economical process for Hydrogen recovery is proposed in this project. As per the industrial directive, two processes are studied in depth; **Linde's Technology** (Cryogenic Separation) and **Prism Technology** (Membrane Separation). A detailed study has been carried out on each process's Material & Energy Balance, Equipment Design, Simulation, Instrumentation & Process Control and ultimately the Economic Analysis, which is the main objective of the project. Finally, an optimized and economically feasible option for the industry for installation has been proposed.

Table of Contents

List of Figures

List of Tables

Chapter 1: Introduction

1.1 Background:

Pakistan is an agricultural land where the need of cheap and abundant fertilizer is very important. The most widely used fertilizer is urea which is produced by the reaction of ammonia with carbon dioxide. Hence production of ammonia is more critical in fertilizer plants.

One of the highly produced inorganic chemical in the world is ammonia. There are countless large-scale ammonia production plants worldwide, which produced a total of 144 million tons of nitrogen. The world production of China was 31.9 %, followed by Russia with 8.7 %, India with 7.5 %, and the United States with 7.1 %. For fertilizing agricultural crops, 80 per cent or more of the ammonia produced is used. Ammonia is also used for the production of the dyes, pharmaceutical and plastics, fibers, explosives, acid nitrics (via the Ostwald process). [17]

Ammonia synthesis begin with the pretreatment of natural gas which includes sulfur and carbon dioxide removal to increase the heating value of gas and also to remove sulfur related compounds which will cause immense pollution during burning. After that natural gas reforming is carried out to produce hydrogen because a large amount of hydrogen is required to produce ammonia.

Steam reforming reaction: $CH_4 + H_2O \rightarrow CO + 3H_2$

The next step is to convert carbon monoxide into carbon dioxide and more hydrogen with a catalytic shift convert:

$$CO + H_2O \rightarrow CO_2 + H_2$$

In order to produce the required ammonia, hydrogen is reacted to form anhydrous liquid ammonia along with nitrogen (derived from the process air) in the presence of a catalyst. The ammonia loop (also known as the Haber-Bosch process) is known as that step. The step is.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

The conversion of this reaction is very low, and the continuous recycling is necessary to increase the production of ammonia. With perpetual recycling, the inert components in the stream are accumulated in reactors and cause disruptions in the process. Those inert components include unreacted hydrogen and ammonia along with methane, nitrogen, argon and methane which come from the reforming section. Therefore, it is economical in the long run that these valuable components like ammonia and hydrogen are recovered from the purge stream. Purge gas has typically 60 – 65 % hydrogen gas by volume and ammonia recovery unit is installed before the hydrogen recovery unit. [18]

1.2 Problem Statement:

Plant-II of FFC Goth Machhi is using cryogenic separation for the recovery of hydrogen from the purge stream and they want to install another hydrogen recovery unit for their older plant that is Plant-I. They have asked us to carry out a detailed comparison between the two major processes of Hydrogen recovery i.e. Cryogenic separation and membrane separation and propose them the most suitable, economical and efficient process so that they can install that for their facility.

1.3 Purpose of the study:

Purpose of the study is to propose the most economical and efficient method for the recovery of hydrogen from the purge gas. Hydrogen recovery is very critical in ammonia synthesis process because it increases the production of ammonia by 4 to 5%, which is a very significant number and this describes the importance of the efficient, environmental friendly and economical process of hydrogen recovery.

The above mentioned purpose was met by analyzing and assessing the available techniques in minute details. The techniques were compared on the basis of following parameters.

- Percentage recovery
- Percentage purity
- Operating conditions
- Fixed capital cost
- Operational cost
- Ease of operation

1.4 Brief history of Hydrogen:

The hydrogen is a highly combustible diatomic gas with molecular formulation H_2 which is colorless, odorless, tasteless, non-toxic, and non-metallic. Its density is the lowest of all gases. It is a commercially important element. Hydrogen is the universe' most abundant chemical, making up about 75 percent of the total baryonic mass. Melting point of Hydrogen is - 259.16°C while boiling point is - 252.879°C. [19]

1.4.1 Uses of Hydrogen:

I. The largest use of hydrogen is in Haber's process to produce ammonia (NH_3), where nitrogen from air is combined with hydrogen to produce Ammonia.

II. Liquid hydrogen finds its use in the study of superconductors and hydrogen blended with liquid oxygen, serves as an excellent fuel used in rockets etc.

III. Hydrogenation of oils uses large quantities of hydrogen to convert them into fats, Margarine production is one such example.

IV. Hydrogen is also coming as an option for clean burning fuel in the near future. Hydrogen powered fuel cells are increasingly being used nowadays.

V. One common use of hydrogen is as coolant due to its properties like lower density, lower viscosity and also because it surpasses other gases by having highest specific heat and thermal conductivity value.

VI. Hydrogen gas is extensively used in various crude oil refining processes. For example, Hydrodesulphurization, Hydrocracking, de-aromatization etc. [19]

Chapter 2: Literature Review

2.1 Hydrogen Separation:

Hydrogen is a very light gas and its size is also really small which makes it difficult separate from other gases. It can be done through various well known established processes which are explained below.

I. Cryogenic Distillation
II. Membrane Separation
III. Pressure Swing Adsorption

2.1.1 Cryogenic Distillation:

The word cryogenic means "very low temperatures". This distillation process is used to separate gas components at extremely low temperatures. This technique is used widely to separate different constituents of air from one another e.g. N_2, O_2 etc.

The principle of this separation process is the fact that different gases have different boiling points when they are in liquid state and hence they can be separated by distillation. Therefore, this process is a combination of two words, Cryogenic and distillation.

In the case of hydrogen recovery from purge gas, the cryogenic distillation requires pretreatment to remove ammonia and water from the purge stream before entering the cold box. Because otherwise these components will be frozen at such low temperatures and the heat exchangers and other piping can be damaged.

The cryogenic separation process need a tight coordination of heat exchangers and partition segments to acquire a decent proficiency and all the vitality for refrigeration is given by the pressure of the air at the gulf of the unit.

To accomplish the low refining temperatures, the air separation unit needs the refrigeration cycle that works by method for the Joule–Thomson effect, and the cool hardware must be kept inside a protected cold box. The cooling of the gases requires a lot of vitality to work the refrigeration cycle and is done by the air compressor.

The heart of the cryogenic distillation is the cold box inside which the temperatures are reduced up to -188 °C. Hence, heavy duty heat exchangers and cooling environment is required. The nitrogenous environment is maintained inside it to keep the temperatures low.

This procedure depends on the distinction in boiling points of fluid gases in the stream. The fundamental rule embraced in our refrigeration circuit is utilized here. NH_3 line 1 PGR and IGP depends on this procedure. The Energy sparing is 0.11 Gcal/MT NH_3 with purge gas recuperation for 1864TPD NH_3 plant and correspondingly 0.06Gcal/MT urea. Yearly benefit from PGR after restitution period is around Rs 15 crore (USD 2238806).

1. Hydrogen becomes liquid at **-253°C, 1** atm pressure.

2. Nitrogen becomes liquid at **-196°C, 1** atm pressure.

3. Methane becomes liquid at **-161°C, 1** atm pressure.

4. Ammonia becomes liquid at **-33°C, 1** atm pressure.

The pre-purified purge gas from the NH_3 recuperation plant is saturated with water. As an initial step, the purge gas is dried and liberated from hints of NH_3 in an adsorbing station. The hydrogen is isolated in a coldbox. The decrease in temperature essential for a steady procedure is accomplished with a throttle valve utilizing the Joule-Thomson effect. The purge gas is chilled off in the coldbox heat exchanger utilizing the cooling intensity of a portion of the cryogenic hydrogen isolated in the coldbox. A The pre-purified purge gas from the NH_3 recuperation plant is saturated with water. As an initial step, the purge gas is dried and liberated from hints of NH_3 in an adsorbing station.

The hydrogen is isolated in a coldbox. The decrease in temperature essential for a steady procedure is accomplished with a throttle valve utilizing the Joule-Thomson effect. The purge gas is chilled off in the coldbox heat exchanger utilizing the cooling intensity of a portion of the cryogenic hydrogen isolated in the coldbox. Accordingly, the gas somewhat becomes liquid. The gas phase is isolated in the hydrogen separator, heated up, and the hydrogen is sent to the syngas compressor. accordingly, the gas somewhat becomes liquid. The gas phase is isolated in the hydrogen separator, heated up, and the hydrogen is sent to the syngas compressor. [2]

2.1.2 Membrane Separation:

Membrane separation processes work without heating and therefore utilize less vitality than customary thermal partition procedures, e.g. refining, sublimation or crystallization. The division procedure is absolutely physical and both portions (penetrate and retentate) can be utilized. It is difficult to isolate the constituents of azeotropic fluids or solutes by refining or recrystallization however such partitions can be accomplished utilizing membrane technology.

2.1.2.1 Membranes for Gases:

For separation of gases, membranes can compete with other separation processes economically, environmental friendly, from safety and technical point of view. Various improvements in membranes have been made since its first-time usage. Membranes can be integrated with the existing industrial processes.

Different types of membranes are used for separation of different molecules. In our case, we are separating gas mixture so membranes for gas separation are used.

There are different categories of membranes and one particular membrane for our case is chosen on the basis of various factors.

Generally, there are two major types of membranes:

- Porous Membranes
- Dense Membranes

Porous membranes have pores of various sizes through which particles pass. If the molecules have diameter smaller than the pore size then they will pass but if they have larger diameter than the pore size of membranes, they will remain behind. These membranes are used for separation of particles with large atomic diameter. In these membranes separation occurs on the basis of Knudsen diffusion, surface diffusion, capillary condensation and molecular sieving.

Dense membranes have no pores and used for separation of particles with very small particle diameter. These membranes work on the principle of Solution Diffusion theory. According to this theory, molecules are firstly absorbed to the surface of membrane, then they diffuse through the membranes, transported from one side to other and finally desorbed on the other side.

Molecules are separated on the basis of solubility of different molecules for particular membrane.

Another classification of membranes is on the basis of glass transition temperature.

- Glassy membranes
- Rubbery membranes

If material of membrane is below its glass transition temperature, such membrane is called glassy membrane while if the material of membrane is below its glass transition temperature, such membrane is called rubbery membrane. For smaller molecules as in our case, glassy membranes are used.

After above selection, material of membrane is selected. Membranes can be made from:

- Metals
- Ceramic
- Polymers

For gases, mostly polymeric membranes are used. For hydrogen separation, three different polymeric membranes are available.

- Polysulfone
- Polyimide
- Ethyl acetate

Membranes are selected on the basis of permeability, selectivity, mechanical strength and cost. Our main focus was selectivity and also considering other factors, we have chosen Polysulfone membrane.

Membranes performance depend upon

1. Stage cut
2. Performance ratio

Stage cut: It is the ratio of permeate flow rate and feed flow rate.

$$\theta = \frac{Permeate\ flow}{Feed\ flow} \tag{2.1}$$

Higher is the value of stage cut, higher will be the recovery. It value should be 0.5 - 0.6.

Performance ratio: It is the ratio of feed pressure and permeate pressure.

$$\varphi = \frac{Feed\ Pressure}{Permeate\ Pressure} \tag{2.2}$$

2.1.2.2 PRISM Membranes

At 110– 130 barg, the synthesis loop purge-gas enters the film (membrane) separator. The gas arrangement incorporates hydrogen and high percentage of methane and argon that collect in the synthesis circle. Hydrogen particles rapidly saturate through the skin of the membrane and move out of the permeate port at a lower weight (25– 70 barg). This redesigned hydrogen stream come back to the synthesis loop to enhance the feed supply of synthesis gas. Bigger particles don't penetrate through the membrane boundary. They structure the 'non-pervade' gas stream leaving the non-saturate port at 100– 120 barg. The progression of non-permeate gas, which contains argon, nitrogen, methane, and some hydrogen, is appropriate for some fuel gas heat applications. Sometimes, the argon is very significant, so it tends to be additionally refined in different procedures. [4]

NH_3 is created by bringing a synthesis gas stream into a catalytic reactor. The synthesis gas is included hydrogen, NH_3 conversion does not totally synthesize in the primary pass, so the procedure requires the parts to be looped through cycle. This procedure makes the latent side-products collect and purge. The subsequent purge gas contains high percentages of the synthesis gas parts. It additionally incorporates NH_3, which isn't evacuated by the liquefaction step. If not recovered, this can be an exorbitant misuse of smelling salts. Crystal Membrane Systems treat the cleanse stream by recuperating NH_3 as the item and restoring the hydrogen to the blend circle. The framework more often than excludes a water scrubber to recuperate NH_3 lost in the cleanse. Crystal Membranes recuperate 90% of the hydrogen in the purge gas to build NH_3 generation. The framework is effectively acclimated to meet fluctuating generation of the NH_3 plant.

Gas atoms saturate over the slender skin of the hollow fiber divider driven by a fractional pressure distinction. The pervasion rate is explicit to the gas– polymer pair. The transport component is a blend of solubility into and diffusion. through the layer. Partition ability is dictated by the relative penetration rates of the individual gas segments. The more prominent the distinction in penetrability, the more noteworthy the successful partition by diffusion. [4]

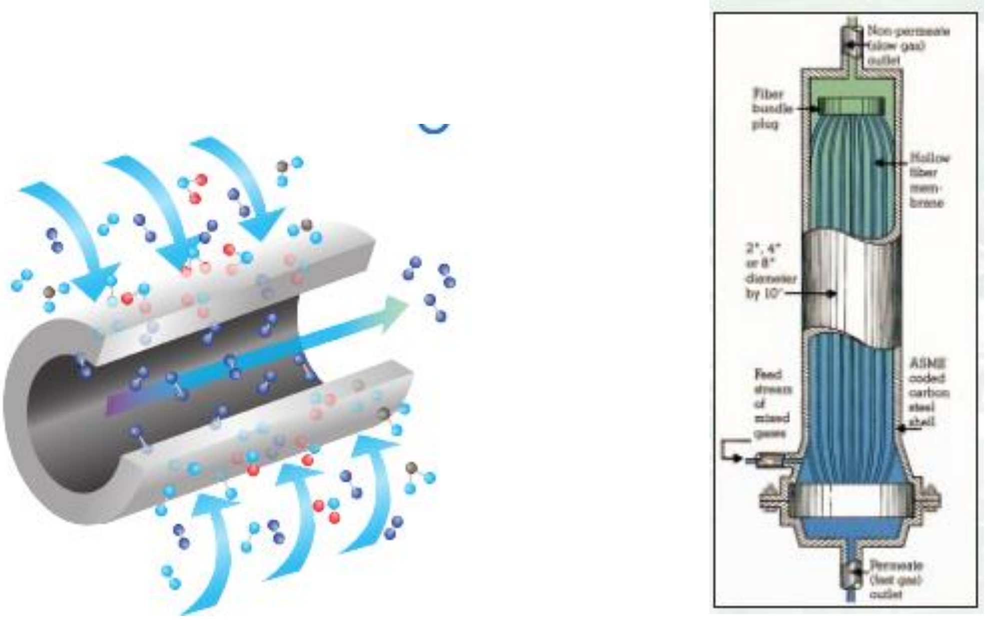


Figure 1- Hydrogen recovery from ammonia purge gas

2.1.3 Pressure Swing Adsorption:

PSA is a kind of gas separation technology which is used to separate gas or gases from a blend of gases under the pressure as indicated by the gas’s sub-atomic qualities and its affinity for the adsorbent. It works at close encompassing temperature ranges and varies essentially from the cryogenic gas separation systems. Particular adsorptive materials are utilized as a trap, specially adsorbing the objective gas type at high pressures. Then the pressure is lowered in the system to desorb the adsorbed material.

Pressure swing adsorption process relies upon the path that under the influence of high pressure, gases gets adsorbed on surfaces of solid substances. Higher the pressure will be, more will be the gas which is adsorbed. And by decreasing the pressure, the adsorbed gas is released. PSA systems can be used to disengage gases in a mix in light of the fact that unmistakable gases tend to be pulled into different solid surfaces basically unequivocally. If a gas mix, for instance, air is applied on with pressure through a vessel which contains a bed of zeolite as an adsorbent that pulls-in Nitrogen more firmly as compared to Oxygen, a little portion or most of Nitrogen will stay in the zeolite bed, while the gas leaving the tank will be progressed in oxygen. Exactly when the bed reaches its maximum capacity to adsorb the nitrogen gas, it is recouped by decreasing the pressure, consequently desorbing the adsorbed nitrogen. It is then arranged for another cycle of making oxygen-improved air.

POLYBED™ Pressure Swing Adsorption units for hydrogen decontamination depend on the capacity of adsorbents to assimilate more impurities at high gas-stage incomplete weight than at low partial pressure. Polluting influences are adsorbed in a adsorber at high partial pressure and after that desorbed at low partial pressure. The impurity partial pressure is brought down by swinging the pressure of absorber from the feed pressure to the tail gas pressure and by utilizing a high-virtue purge gas. The main force for the detachment is the distinction in contamination incomplete weight between the feed and tail gas. A minimum pressure proportion of around 4:1 is required. The feed pressure is as a rule in the scope of 14 to 35 atm. Ideal tail-gas pressure is as low as could reasonably be expected. Since vacuum is ordinarily stayed away from, tail-gas weights under 1 atm is regularly utilized when high hydrogen recuperation is wanted. The PSA tail-gas is as often as possible compacted from this low strain to fuel-gas pressure. Hydrogen is basically not adsorbed in the PSA procedure and is accessible at near feed pressure: the run of the mill pressure drop between the feed and product battery limits is under 10 psi. The two key points of interest of the PSA procedure are its capacity to evacuate contaminations to any dimension and to create a high-immaculateness high-pressure hydrogen product. The immaculateness of the hydrogen item from a PSA unit is ordinarily more than 99 vol-% and as often as possible 99.999 vol-%. Expulsion of CO and CO2 to a volume dimension of 0.1 to 10 ppm is normal and promptly accomplished. [2]

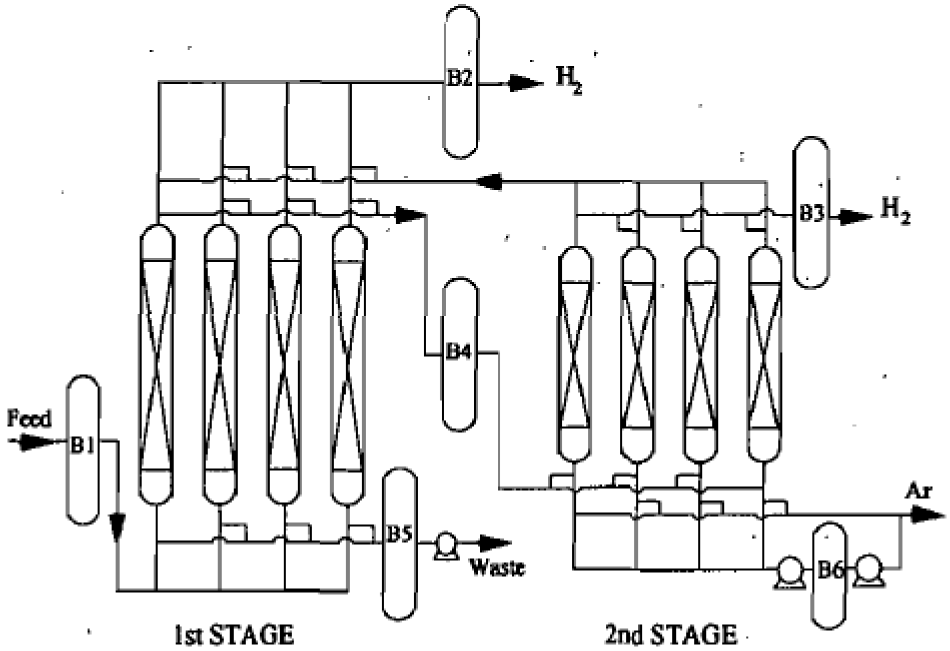


Figure 2-Pressure Swing Adsorption

2.1.3.1 Vacuum Swing Adsorption:

Utilizing unique solids, adsorbents, VSA isolates certain gasses from a vaporous blend under insignificant pressure as indicated by the species' atomic attributes and partialityfor the adsorbents. These adsorbents (e.g., zeolites) frame a sub-atomic strainer and specially adsorb the objective gas species at close encompassing pressure. The procedure then moves to a vacuum to recover the adsorbent.

VSA contrasts from the cryogenic distillation system and also pressure swing adsorption (PSA) methods since it works at close encompassing temperature and pressure ranges. VSA may really be best portrayed as a subset of the bigger class of PSA. It varies basically from Pressure Swing Adsorption in that PSA regularly vents to barometrical pressure, and uses a pressurized gas encourage into the division procedure. VSA normally draws the gas through the partition procedure with a vacuum. For Oxygen & Nitrogen VSA frameworks, the vacuum is commonly produced by a blower. VPSA frameworks apply pressurized gas to the partition procedure furthermore apply a vacuum to the purge gas. Usually, higher recuperation prompts a small compressor, a small blower, or other compacted gas. Higher profitability prompts smaller sieve beds. The consumer will no doubt consider which have an all the more straightforwardly quantifiable distinction in the general framework, similar to the measure of item gas isolated by the framework weight and size, the framework beginning and upkeep costs, the framework power utilization or other operational expenses, and dependability.

2.1.4 Purge Gas Recovery Advantages

1. Total flow rate of purge gas is 15000 Nm^3/hr out of which hydrogen is 9000 Nm^3/hr. 2.175 Tons/hr of natural gas feed is saved because of this.

2. Feed can also continue to increase the production of ammonia and urea if bottlenecks are not present.

3. Reduction in the firing of primary reforms that corresponds to feed reduction and methane slip increase.

4. Additionally the reduction in the production of HP Steam in RG Boiler will save less than 7 T/hr of SM Steam in the reforming.

2.1.5 Purge Gas Recovery Disadvantages

1. In secondary reformer, process air is to be made up which is equivalent to hydrogen (for feed 15000 Nm^3/hr) is approximately 3.8 KNm^3/hr.

2. Nonetheless, due to the reduction in feed, the depletion in the process air is approximately 3.5 KNm^3/hr

3. Hence, in secondary reformer, the increase in process air is around 0.3 KNm^3/hr

4. Carbon Dioxide Recovery (CDR) is an expensive matter and the loss of CO2 is around 2.66 KNm3/hr, which means full loading. GV energy is, however, reduced as well.

Overall however there is net energy saving in the PGR project and is considered feasible [4]

2.1.6 Processes Comparison [4]

Table 1 Comparison between three methods of hydrogen separation

Factors	PSA	Membrane	Cryogenic
Min Feed H_2, %	50	15	15
Feed pressure, psig	150-1000	200-2000	200-1200
H_2 purity, %	99.9+	98 max.	97 max.
H_2 recovery, %	Up to 90	Up to 97	Up to 98
$CO + CO_2$ removal	Yes	No	No
H_2 product pressure	Approx. feed	Much less than feed	Approx. feed

Factors	PSA	Membrane	Cryogenic
Feed pretreatment	No	Yes	Yes
Flexibility	Very High	High	Average
Reliability	High	High	Average
By product Recovery	No	Possible	Yes
Ease of Expansion	Average	High	Low

2.2 Equipment:

2.2.1 Heat Exchangers:

It is a device which is used to transfer heat between one or more than one fluids, which are either in direct contact or separated by a wall so that the liquids do not mix with each other.

Selection of the appropriate heat exchanger is of prime importance in cryogenic distillation system. There are different types of heat exchangers used for different industrial processes. Some most commonly used are described below.

2.2.1.1 Shell and tube heat exchangers:

These are the most commonly used as well as the most popular heat exchangers in many industries. The reason lies in the fact they are capable of being operated in a wide range of pressures and temperatures.

There are several tubes mounted in a cylindrical shell in a shell and tube exchanger. The typical Unit found in a petrochemical plant is illustrated in the figure below. The heat can be exchanged for two fluids, and one fluid flows across the pipes while the second fluid passes through them. The fluids can be single or two phases and flow in parallel or in counter current.

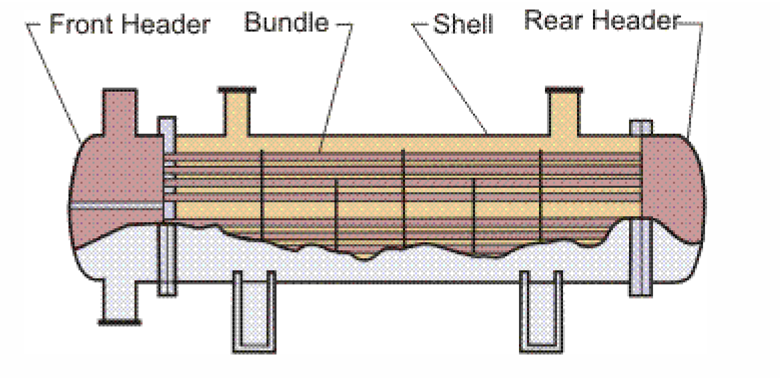


Figure 3-Shell and tube heat exchangers

- **Front header:** This is the point from the fluid is entered in the tube side of the heat exchanger. It is also called as stationary header.
- **Rear header:** This is the point from where the fluid either leaves the heat exchanger or can be retuned back to tube side for another pass.
- **Tube bundle:** Tube bundle is the set of tubes, baffles and tubesheets and rods to keep the tubes fixed in one place.
- **Shell:** It is the outer body of the exchanger enclosing all the internal components.

The fluids used in the exchanger can be both liquid and gas. When operating a shell and tube heat exchanger, large heat transfer area must be used, because in this way, the waste heat can also be used up in the system.

The tubes inside the shell can be arranges in different geometries in order to broaden the use under various circumstances. Following three combinations are mostly used.

- **Fixed tube sheet exchangers**: in this type the tubes bundle is welded to the shell. These are not very recommended to use because of difficulty in cleaning of tubes.
- **U-tube Exchangers:**
  Any front header types and the rear header is normally M-Type can be used in the U-tube exchange. The U tubes allow unlimited thermal expansion and can be removed for cleaning and small bundles can be achieved with shell clearance.
- **Floating Head Exchanger:** The tube sheet on the back of the header is not sold to the shell in this type of exchanger, but can be moved or floated. The pipe board at the front end is larger in diameter than the shell and is sealed in a similar way as the one used in the design of the fixed tube board. The pipe sheet at the end of the shell's back header is slightly smaller in diameter than the shell, so that the shell can be pulled. Using a floating head allows for thermal expansion and can remove the tube bundle for purification.

2.2.1.1.1 Factors affecting the performance of shell and tube heat exchangers:

- Fouling in tubes decreases the performance of exchanger
- Baffle types and spacing
- Log mean temperature difference
- Tubes arrangements and type of material
- Pitch of tubes

- Shell diameter
- Tube length

2.2.1.1.2 Industrial applications:

- In the generation of power
- Marine Applications
- HVAC
- Paper and pulp industries
- Mining and metals
- Refrigeration systems
- Pharmaceutical industries
- Air Processing and Compressor Cooling

2.2.1.1.3 Advantages:

- Lower cost compared to plate-type coolers
- Less pressure drop on tube sides
- Tube leaks are effortlessly found and stopped since pressure test is simple
- The recipient can also be tubular coolers in the cooling frame.
- The use of sacrificial anodes guarantees the whole erosion cooling framework
- Tube cooler could be used to grate oil because of the difference in weight.

2.2.1.1.4 Disadvantages:

- Cleaning and maintenance is difficult, as a cooler tube needs enough space to expel the nest on one side.
- In comparison with plate type cooler, heat exchange is less effective
- Expansion of the tube cooler capacity is not possible.

- More space is required as compared to plate type heat exchangers [20]

2.2.1.2 Plate and fin heat exchangers:

A type of heat exchanger design that transfers heat between fluids through plates and finned chambers. It is frequently classified as a compact heat exchanger, in order toemphasize its relatively high-volume heat transfer area.

Well placed between plates are the splinters of corrugated metal. Brazing unites the structure. The purpose of the fine is twofold to hold the plates together, thereby containing pressure and to form a secondary (fin) surface for heat transfer. Bars containing every fluid in the area between adjacent plates are at the borders of the plates.

The height of the bulb and the bars can vary. We are able to use a low-height corrugation for a liquid stream, which corresponds to a high heat transfer coefficient with a smaller surface area while we can use a high height for a low pressurized stream, which combines a low coefficient with a higher surface area, and also a larger area for lower pressure drops. An industrial unit has around 1000 m2 per cubic meter of surface area.

2.2.1.2.1 Corrugations (Fins)

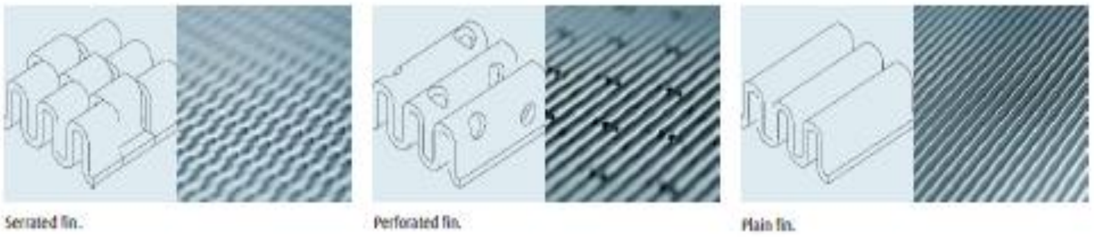
Heat transfer improvement devices are also used to make corrugations .

Plain fins are normally used for low pressure fall streams.

Perforated fins shows a slight increase in performance over simple corrugation, but this is reduced because of perforation by loss of area. The main purpose is to allow fluid to move across fine canals, usually in boiling task

Serrated fins are cut every 3.2 mm and the second fin is displaced halfway between the previous fins at one point. This increases the heat transfer dramatically.

Herringbone fins are made to give a zigzag trail by moving the fins sideways every 9.5 mm. Performance between plain and serrated types is intermediate. In contrast to the tightened factor, Reynolds continue to show advantages at higher speeds and pressure at high friction numbers.



Serrated fin.

Perforated fin.

Plain fin.

Figure 4-Types of fin

The plate-Fin heat exchanger design offers a high degree of flexibility because it can operate with any gas, liquid and two-phase liquids combination. Heat transfer between different streams is also accommodated for each stream with a range of fines and types as different entry and exit points.

2.2.1.2.2 Industrial applications:

- Brazed aluminum plate and fin heat exchangers are used in cryogenic applications because they can easily handle such low temperatures.
- Liquefaction of natural gas
- Ammonia production
- Offshore processing
- Cryogenic air separation
- Nuclear engineering
- Production of syngas

2.2.1.2.3 Advantages:

- Simple and compact size
- Maintenance and cleaning is easy

- By introducing plates, capacity can be increased.
- No requirements of additional space for dismantling in it
- High value of overall heat transfer coefficient

2.2.1.2.4 Disadvantages:

- Pressure drop is higher
- Initial cost is very high
- Clogging can occur because of narrow pathways
- Not suitable for high temperature fluids
- Potential for leakages [21]

2.2.2 Compressors:

The main equipment used in membrane separation is the compressor. So, the choice of a particular compressor for a particular process is very important.

There are many types of compressors like reciprocating compressors, centrifugal compressors, rolling piston compressors, diaphragm compressors, rotary screw compressors and rotary vane compressors etc. But following two are most widely used in industries.

2.2.2.1 Reciprocating compressors:

It is a type of positive displacement compressor in which the pistons are used to drive the crankshaft to generate high pressure gases. For high compressions, reciprocal compressors are used. The compression machines at high pressure have been used for many years.

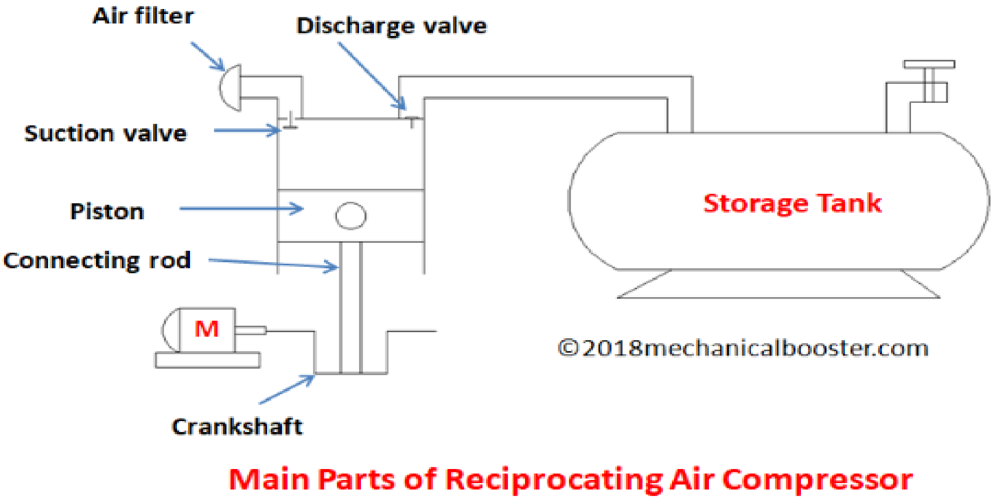


Figure 5-Main parts of Reciprocating compressors

2.2.2.1.1 Working Principle:

The air is sucked in the cylinder from the atmosphere by the reciprocal compressor while the piston moves to the BDC, and when it moves to the TDC, the air compression starts and continues to increase with increasing pressure. If the pressure rises up to the design limit, the unit is pushed open and the compressed air is supplied to the storage tank.

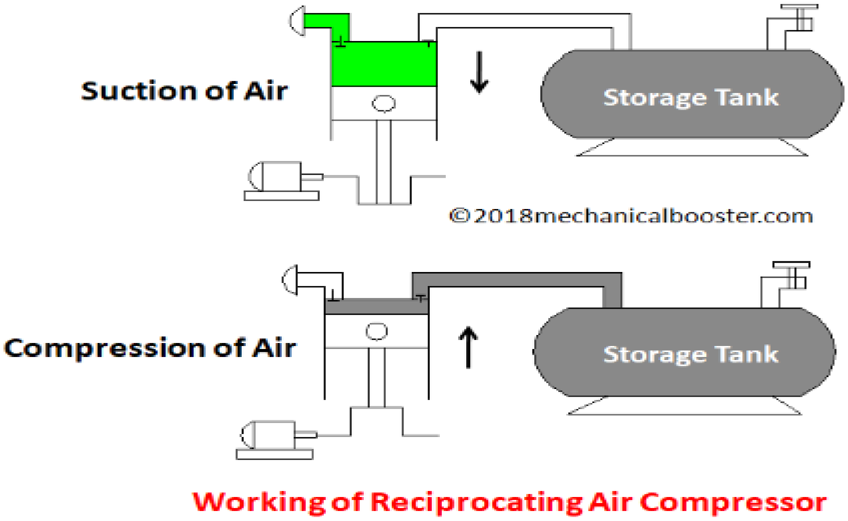


Figure 6-Working of reciprocating compressors

If higher pressures are required then either double stage or triple stage reciprocating compressors are used in which compression is achieved in multiple stages with inter stage cooling so that the increase in temperature, due to compression, can be lowered before next stage compression.

2.2.2.1.2 Industrial applications:

- Processing of natural gas and its delivery
- Almost all chemical plants including gases
- Oil refineries
- Refrigeration systems
- HVAC

2.2.2.1.3 Advantages:

- Initial cost of installation is lower
- Low maintenance cost
- Capable of providing continuous flow
- Can produce both high pressure and high power
- Extremely efficient

2.2.2.1.4 Disadvantages:

- Pulsating flow
- Separate heavy foundation
- Vulnerable to dirt and liquid
- Torsional implications
- Low reliability [22]

2.2.2.2 Centrifugal Compressors:

A centrifuge compressor is a type of radially designed dynamic or turbocharged compressor. In contrast to constant-flux displacement compressors, dynamic compressors are at a constant pressure. External conditions, such as changes in input temperatures, affect performance.

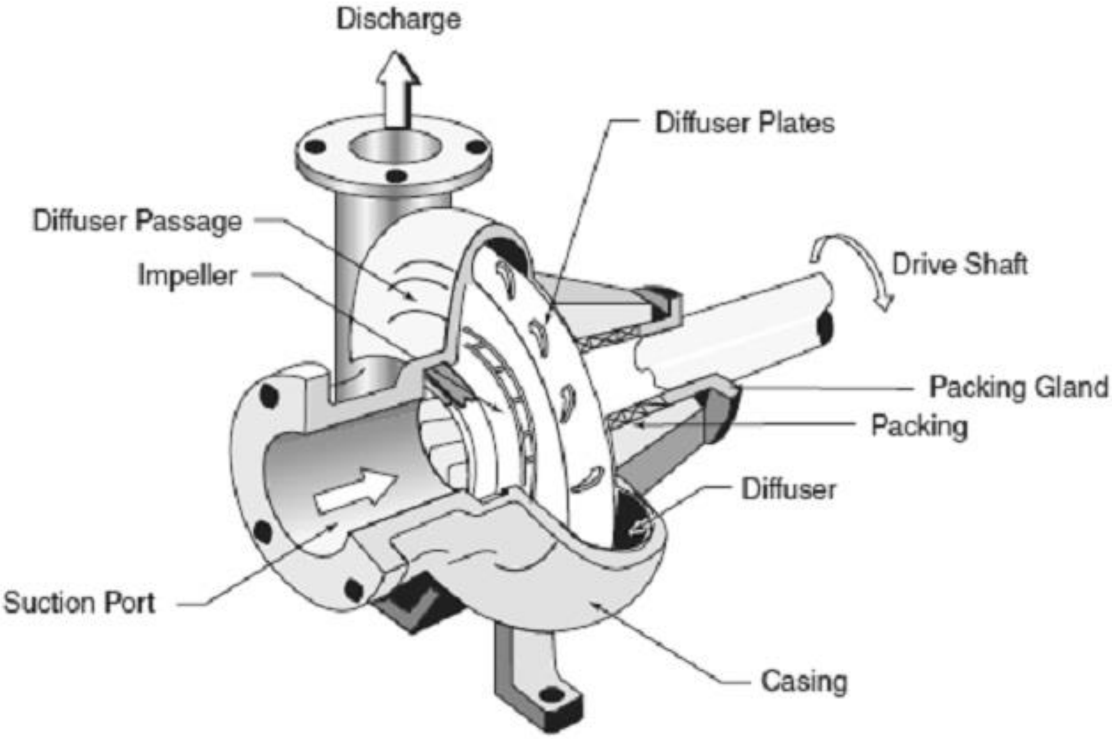


Figure 7- Centrifugal Compressor

2.2.2.2.1 Working:

Air is drawn into the center with radial blades of a rotating spiral, and centrifugal force is directed towards the centre. This radial air movement leads to an increase in pressure and a kinetic energy generation. The kinetic energy is also converted to a pressure by passing through a diffuser and volute before an air is carried into the center of the impeller.

Each stage is part of the compressor unit's overall pressure increase. A series of steps can be arranged to achieve a higher pressure depending on the pressure required for the application. In the oil and gas and process industry this type of multi-stage application is usually used.

2.2.2.2.2 Industrial applications:

- In turbochargers and superchargers of diesel and automotive engines.
- In gas turbines
- Refrigeration systems
- HVAC
- Chemical plants

2.2.2.2.3 Advantages:

- Less wear and tear
- Doesn't require special foundation
- Energy efficient
- Light weight
- Easy to design and manufacture

2.2.2.2.4 Disadvantages:

- For the given air flow, frontal area is large
- Very high pressures cannot be achieved
- Surging and choking problems
- Sensitive to the change in gas composition [23]

2.2.2.2.5 Multi-Stage Centrifugal Pumps:

Multi-stage Centrifugal pumps have essentially the same principal as all multi-stage machinery such as heat exchangers and crystallizers or distillation columns. The multiple stages amplify the effect of one and build on it to create a much more powerful compounded effect than a single stage. For instance, it is very expensive and tedious to design a pump that can account for a pressure drop of 150 psig, but a Multi-Stage pump can do the job for a lower price. For a Multi-Stage Centrifugal Pump, there is more than one impeller either mounted on one or on different shafts. If impellers are connected in series, a greater pressure will be registered at the outlet but a greater flowrate will result when the impellers are connected in parallel. Multi-Stage Centrifugal Pumps are very common for the propulsion of Boiler Feed Water (BFW).

Note: As per industrial directive, we were asked by our industrial supervisor to carry out detailed analysis on the two of the established technologies for Hydrogen Recovery, that is, Linde's Cryogenic separation and Prism Membrane separation. Our following analysis centers around these two processes.

Chapter 3: Process Description

3.1 Pretreatment:

The purge gas coming to Hydrogen Recovery Unit contains H_2, N_2, Ar, CH_4, NH_3 and H_2O. Pretreatment for both processes is same and includes removal of NH_3 and H_2O as they can freeze and clog lines at cryogenic temperatures or, in the case of membrane, foul it and reduce its H_2 separation efficiency. Purge Gas at 52 °C is cooled down to 40 °C by cooling water in Shell and Tube heat exchanger to partly liquify NH_3 and H_2O and are separated in two phase separator, knockout vessel. Then the process stream is passed through an Adsorber containing a zeolite bed to completely remove NH_3 and H_2O.

3.2 Cryogenic Process:

This pretreated gas enters the cold box and passes through two aluminum brazed plate fin heat exchangers in series being cooled down to -188 °C. This causes most components in the stream to largely liquify except H_2 which primarily remains in the gas phase. The two phases are separated in a separating vessel and now the streams are passed back through the exchangers to cool down new incoming gases. Product H_2 is sent to syngas compressor while the bottoms of the separator after extracting heat is used as fuel gas.

3.3 Membrane Process:

The pretreated gas is compressed to 110 bar and then cooled to 40 °C, optimum conditions for membrane separation. The membranes are dense poly-sulfone membranes in hollow fiber modules from which H_2 permeates out due to its high permeability while other components are held back and passed as retentate to be used as fuel gas. The H_2 permeate product is collected, compressed and cooled to desired conditions and then sent to be mixed in syn-loop.

Purge Gas Composition:

Table 2 Purge gas Composition

Component	Composition (%)	Moles (kmol)
H_2	66.68	650.7
N_2	22.22	216
Ar	1.78	17.4
CH_4	9.05	88.3
NH_3	0.0774	0.755
H_2O	0.1798	1.75
Total	100	976

Following are the simplified PFDs of Cryogenic and Membrane process respectively.

LINDE'S CRYOGENIC PROCESS PFD

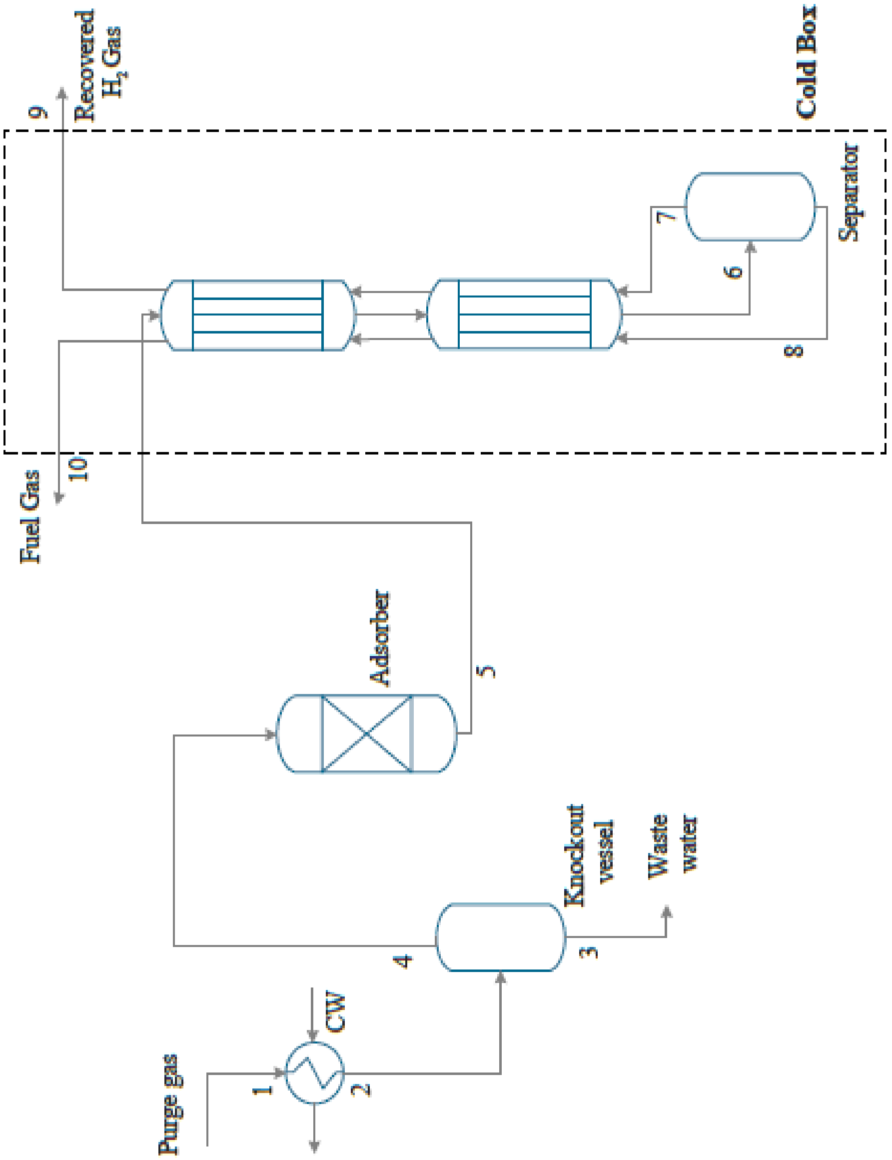


Figure 8 Process Flow Diagram of Cryogenic Distillation

PRISM MEMBRANE PROCESS PFD

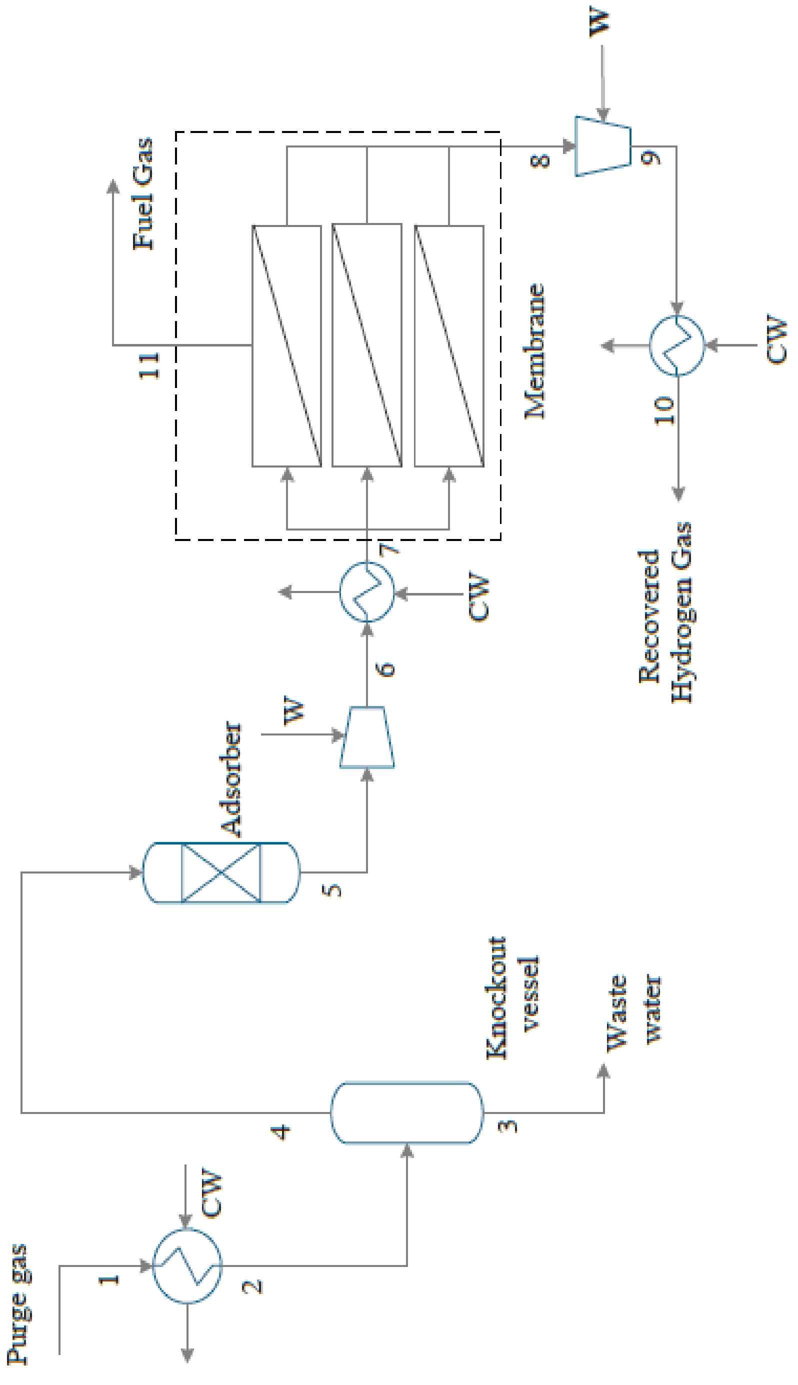


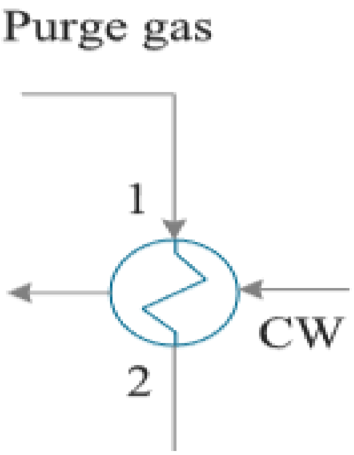
Figure 9 Process Flow Diagram of Membrane Separation

Chapter 4: Material Balance

Steady state process without reaction so Mass In = Mass Out

4.1 Cryogenic Separation

4.1.1 Cooler 1:



Inlet Stream (Stream 1)

Inlet Conditions:

Mass flow of purge gas = 9502 kg/hr

Inlet T = 52 °C Inlet Pressure = 85 bar

Table 3 Inlet stream composition and mass flow rates

Component	Composition (wt %)	Mass (kg)
H_2	13.7	1301.4
N_2	63.6	6048
Ar	7.4	696
CH_4	14.9	1412.8
NH_3	0.1	12.835
H_2O	0.3	31.5
Total	100	9502.5

Outlet Stream (stream 2)

Outlet Conditions:

Mass Flow at cooler outlet = 9502 kg/hr

Outlet Temperature = 40 °C

Table 4-Material balance for stream 2

Component	Composition (wt %)		Mass (kg)	
	Liquid	Vapors	Liquid	Vapors
H_2	-	28.4	-	1301.4
N_2	-	52.9	-	6048
Ar	-	6.1	-	696
CH_4	-	12.4	-	1412.8
NH_3	4	0.1	0.635	12.2
H_2O	96	0.14	14.508	17

Applying component balance on Ammonia and Water

Ammonia:

Ammonia in inlet = Ammonia in outlet

Ammonia in inlet= liquid ammonia + vapor ammonia

12.835 kg = 0.635 kg + 12.2 kg

12.835 kg = 12.835 kg

Water:

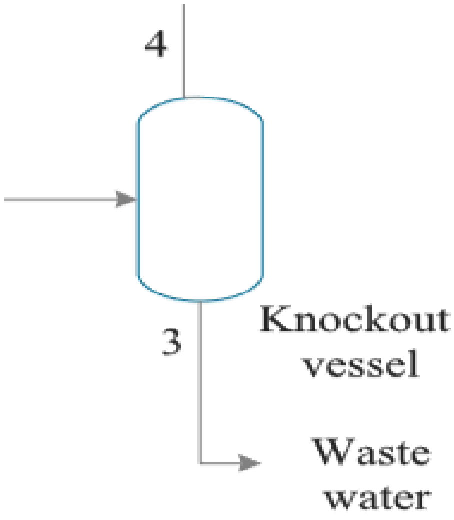
Water in inlet = Water in outlet

Water in inlet= liquid water + water vapors

31.5 kg = 14.5 kg + 17 kg

31.5 kg = 31.5 kg

4.1.2 Two phase separator



Inlet Stream:

Mass flow rate at inlet = 9502 kg/hr

Inlet Temperature = 40 °C

Qualities NH_3 = 0.04; H_2O = 0.46 (from literature)

Table 5 Material Balance for stream 2

Component	Composition (wt %)		Mass (kg)	
	Liquid	Vapors	Liquid	Vapors
H_2	-	28.4	-	1301.4
N_2	-	52.9	-	6048
Ar	-	6.1	-	696
CH_4	-	12.4	-	1412.8
NH_3	4	0.1	0.635	12.2
H_2O	96	0.14	14.508	17

Stream 3

Mass flow rate = 15.08 kg/hr

Table 6-Material balance for stream 3

Component	Composition (wt %)	Mass (kg)
H_2	-	-
N_2	-	-
Ar	-	-
CH_4	-	-
NH_3	4	0.5712
H_2O	96	14.508

Stream 4

Mass flow rate = 9486.12 kg/hr

Table 7 Material Balance for stream 4

Component	Composition (wt %)	Mass(kg)
H_2	13.7	1301.4
N_2	63.7	6048
Ar	7.3	696
CH_4	14.9	1412.5
NH_3	0.13	12.2
H_2O	0.17	17

Applying component balance on Ammonia and Water

Ammonia:

Ammonia in inlet = Ammonia in outlet

Ammonia in inlet= ammonia in stream 3 + ammonia in stream 4

12.835 kg = 0.635 kg + 12.2 kg

12.835 kg = 12.835 kg

Water:

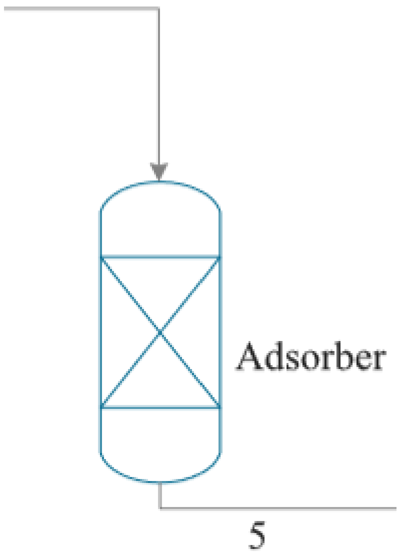
Water in inlet = Water in outlet

Water in inlet= water in stream 3 + water in stream 4

31.5 kg = 14.5 kg + 17 kg

31.5 kg = 31.5 kg

4.1.3 Adsorber



Inlet Stream

Mass flow rate = 9486.12 kg/hr

Table 8 Material Balance for inlet stream to adsorber

Component	Composition (wt %)	Mass(kg)
H_2	13.7	1301.4
N_2	63.7	6048
Ar	7.3	696
CH_4	14.9	1412.5
NH_3	0.13	12.2
H_2O	0.17	16.92

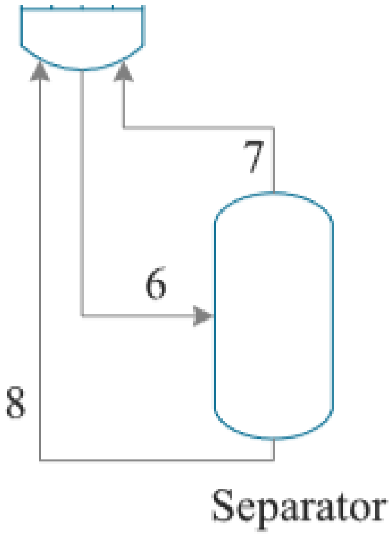
Stream 5

Mass flow rate = 9458.2.12 kg/hr

Table 9 Material Balance for stream 5

Component	Composition (wt %)	Mass(kg)
H_2	13.8	1301.4
N_2	64	6048
Ar	7.3	696
CH_4	14.9	1412.8

4.1.4 Two Phase separator



Stream 6
Mass flow rate = 9458.2.12 kg/hr

Qualities: H_2 = 0.94; N_2 = 0.25; Ar = 0.14; CH_4 = 0.035 (from literature)

Table 10 Material Balance for stream 6

Component	Composition (wt %)		Mass(kg)	
	Liquid	Vapors	Liquid	Vapors
H_2	1.1	42.3	71.3	1230.3
N_2	69	52.6	4490.6	1533.3
Ar	9.1	3.4	594	100
CH_4	20.8	1.7	1360	50

Stream 7 (vapors)
Mass flow rate = 2913.6 kg/hr

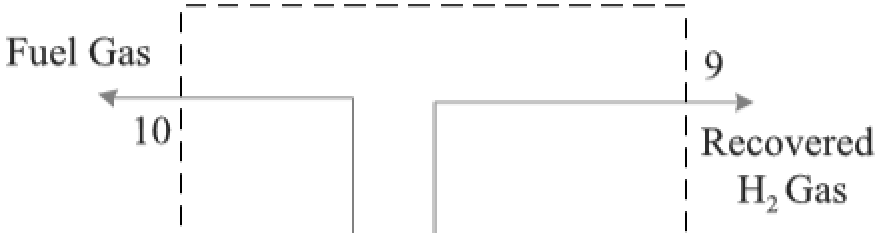
Table 11 Material Balance for stream 7

Component	Composition (wt %)	Mass(kg)
H_2	42.3	1230.3
N_2	52.6	1533.3
Ar	3.4	100
CH_4	1.7	50

Stream 8 (liquid)
Mass flow rate = 6515.9 kg/hr

Table 12 Material Balance for stream 8

Component	Composition (wt %)	Mass (kg)
H_2	12	71.3
N_2	54	4490.6
Ar	5	594
CH_4	28	1360



Stream 9
Mass flow rate = 2913.6 kg/hr

Table 13 Material Balance for stream 9

Component	Composition (wt %)	Mass(kg)
H_2	42.3	1230.3
N_2	52.6	1533.3
Ar	3.4	100
CH_4	1.7	50

Stream 10

Mass flow rate = 6515.9 kg/hr

Table 14 Material Balance for stream 10

Component	Composition (wt %)	Mass (kg)
H_2	12	71.3
N_2	54	4490.6
Ar	5	594
CH_4	28	1360

4.2 Membrane Separation

After same pretreatment, the balance continues from stream 5 out of the adsorber.

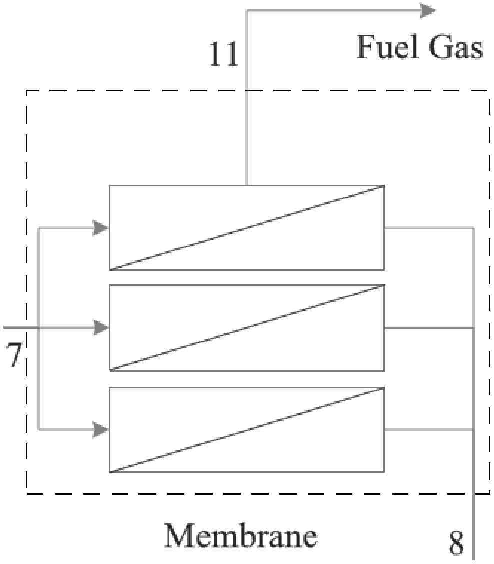
Stream 5

Mass flow rate = 9458.2.12 kg/hr

Table 15 Material Balance for stream 5

Component	Composition (wt %)	Mass(kg)
H_2	13.8	1301.4
N_2	64	6048
Ar	7.3	696
CH_4	14.9	1412.8

4.2.1 Membrane



Stream 7
Mass flow rate = 9458.2.12 kg/hr

Table 16 Material balance for stream entering membrane

Component	Composition (wt %)	Moles (kmol)
H_2	13.7	1301.4
N_2	64	6048
Ar	7.3	696
CH_4	15	1412.8

Stream 8
Mass flow rate = 2013.2 kg/hr

Table 17 Material balance for Permeate

Component	Composition (wt %)	Mass(kg)
H_2	55	1106
N_2	30.3	610.4
Ar	5.7	117.6
CH_4	9	179.2

Stream 11

Mass flow rate = 7451.8 kg/hr

Table 18 Material Balance for retentate

Component	Composition (wt %)	Mass (kg)
H_2	2.6	194.2
N_2	73	5437.6
Ar	7.9	588
CH_4	16.5	1232

Chapter 5: Energy Balance

Steady state process without reaction so Energy In = Energy Out

Formula:

$$H = mC_p\Delta T \qquad (5.1)$$

$$H = mC_p\,(T - T_{ref})$$

Reference temperature = **0 °C**

Using this formula enthalpies were calculated. Table is Given below

Average specific heats were used which were provided by the FFC in the literature, we requested.

5.1 Cryogenic Separation

Table 19 Energy Balance for Cryogenic separation

Stream No.	**Temperature (°C)**	**Flow Rate (kg/h)**	**Enthalpy (kJ/h)**
1	52	9502.5	1.5×10^6
2	40	9502.5	1.20×10^6
3	40	15.08	2.5×10^3
4	40	9486.12	1.20×10^6
5	40	9458.12	1.20×10^6
6	-187	9458.12	7.03×10^6
7	-187	2913.6	4.18×10^6
8	-187	6515.6	2.84×10^6
9	40	2913.3	8.12×10^5
10	40	6515.6	3.84×10^5

For Streams involving both vapor and liquid phase enthalpy for both phases was added as follow:

Stream 2

H_{vap}=1.20 x 10^6 kJ + H_{liq}=2.55 x 10^3 kJ

$H_2=H_{vap}+H_{liq}$

H_2=1.20 x 10^6 kJ

Qualities: (from literature)

H_2O x=0.54

NH_3 x=0.96

5.1.1 Water Cooler

$\Delta H = H_2 - H_1 = 3.60 \times 10^5$ kJ

$$Q = \Delta H \tag{5.2}$$

Cooling Water $\dot{m}$ = 1.70 x 10^4 kg (ΔT = 5°C)

5.1.2 Separating Vessel

$H_2 = H_3 + H_4$

=2554 kJ + 1197316.03 kJ

= 1199870.97 kJ

5.1.3 Adsorber

Adsorbed in zeolite bed

H_2O=0.94 kmol, NH_3=0.722 kmol

$H_4 = H_5 + H_{adsorbed}$= 1.2x10^6 kJ

Stream 6

H_{vap}=4.18 x 10^6 kJ+ H_{liq}=2.84 x 10^6 kJ

$H_6=H_{vap}+H_{liq}$

H_6=7.03 x 10^6 kJ

5.1.4 Cold Box Plate Fin Exchanger

$$\Delta H = H_6 - H_5 = 5.8 \times 10^6 \text{ kJ}$$

$H_9 = 8.12 \times 10^5$ kJ $H_{10} = 3.84 \times 10^5$ kJ

$H_7 = 4.18 \times 10^6$ kJ $H_8 = 2.84 \times 10^6$ kJ

$\Delta H_a = H_9 - H_7 = -3.37 \times 10^6$ kJ $\Delta H_b = H_{10} - H_8 = -2.45 \times 10^6$ kJ

$$\Delta H_a + \Delta H_b = -5.8 \times 10^6 \text{ kJ}$$

5.2 Membrane Separation

Table 20 Energy Balance for Membrane Separation

Stream No.	Temperature (°C)	Flow Rate (kg/h)	Enthalpy (kJ/h)
1	52	9502.5	1.5×10^6
2	40	9502.5	1.20×10^6
3	40	15.08	2.5×10^3
4	40	9486.12	1.20×10^6
5	40	9458.12	1.20×10^6
6	188	9458.12	5.82 x 106
7	40	2913.6	1.21×10^6
8	40	2013.2	5.28×10^5
9	480	2013.2	1.83×10^7
10	40	2013.2	5.31×10^5
11	40	7451.8	6.90×10^5

5.2.1 Pre-Compressor

$\Delta H = H_6 - H_5 = 4625352.665$ kJ

$$W = \frac{\Delta H}{\varepsilon} = \frac{4625352.665}{0.84 \times 3600} = 1.6 \text{ MW} \tag{5.3}$$

5.2.2 Pre-Cooler

$\Delta H = H_7 - H_6 = 4602862.488$kJ

$Q = \Delta H$

Cooling Water $\dot{m} = 110116$ kg ($\Delta T = 10°C$)

5.2.3 Membrane

$H_7 = H_8 + H_{11}$

$= 528907.5$ kJ $+ 690873.6$ kJ

$= 1219781.1$ kJ

5.2.4 Post-Compressor

$\Delta H = H_9 - H_8 = 17774037.2$ kJ

$$W = \frac{\Delta H}{\varepsilon} = \frac{17774037.2}{0.8 \times 3600} = 6.1 \text{ MW}$$

5.2.5 Post-Cooler

$\Delta H = H_{10} - H_9 = 17771686.44$ kJ

$Q = \Delta H$

Cooling Water $\dot{m} = 425{,}160$ kg ($\Delta T = 10°C$)

Chapter 6: Equipment Design

6.1 Two Phase Separator; Vertical Vessel [1]

6.1.1 Pretreatment Vessel

Settling theory results in the following relationship. For liquid drops in gas phase

$$d^2 = 5.054\frac{TZQ_g}{P}\left[\left(\left|\frac{\rho_g}{\rho_l-\rho_g}\right|\right)\frac{C_D}{d_m}\right]^{1/2} \qquad (6.1)$$

Where,

- d = vessel internal diameter, in.
- d_m = drop diameter, µm
- T = operating temperature, °R
- Q_g = gas flow rate, MMscf/D
- P = operating pressure, psia
- Z = gas compressibility
- ρ_l = liquid density, lbm/ft^3
- ρ_g = gas density, lbm/ft^3
- C_D = drag coefficient.

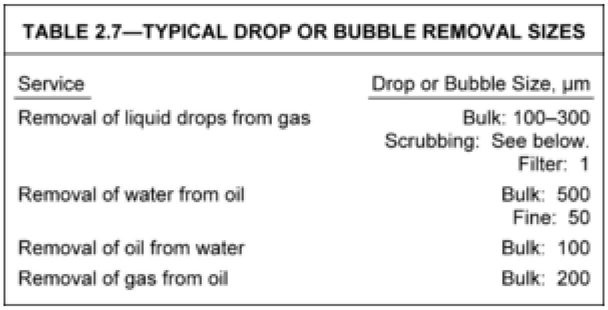


TABLE 2.7—TYPICAL DROP OR BUBBLE REMOVAL SIZES

Service	Drop or Bubble Size, µm
Removal of liquid drops from gas	Bulk: 100–300 Scrubbing: See below. Filter: 1
Removal of water from oil	Bulk: 500 Fine: 50
Removal of oil from water	Bulk: 100
Removal of gas from oil	Bulk: 200

$$C_D Re^2 = \frac{4}{3}\frac{d_v^3|\rho_c-\rho_d|\rho_c g}{\mu_c^2} \qquad (6.2)$$

Where,

Re = Reynolds number, $(V_T.d_v.\rho_c)/\mu_c$

C_D = drag coefficient of drop/bubble;

ρ_c continuous phase density, g/cm^3

ρ_d = dispersed phase density, g/cm^3

g = gravitational constant, 981 cm/sec^2

μ_c = continuous phase viscosity, g/(cm/sec) = poise,

Using L/d = 3 and above equations,

d = 0.46 m

L = 1.3 m

$$\boldsymbol{V = \pi r^2 l} \tag{6.3}$$

V = 0.4m^3

Wall thickness

$$e = \frac{P_i D_i}{2Jf - 0.2P_i} \tag{6.4}$$

Ellipsoidal Head thickness

$$e = \frac{P_i D_i}{2Jf - P_i} \tag{6.5}$$

Design Pressure = 9.22 N/mm^2

Design Temperature = 82 ^{o}C

Joint efficiency = 1.0

Corrosion allowance = 3 mm

f = Stress Factor from following table;

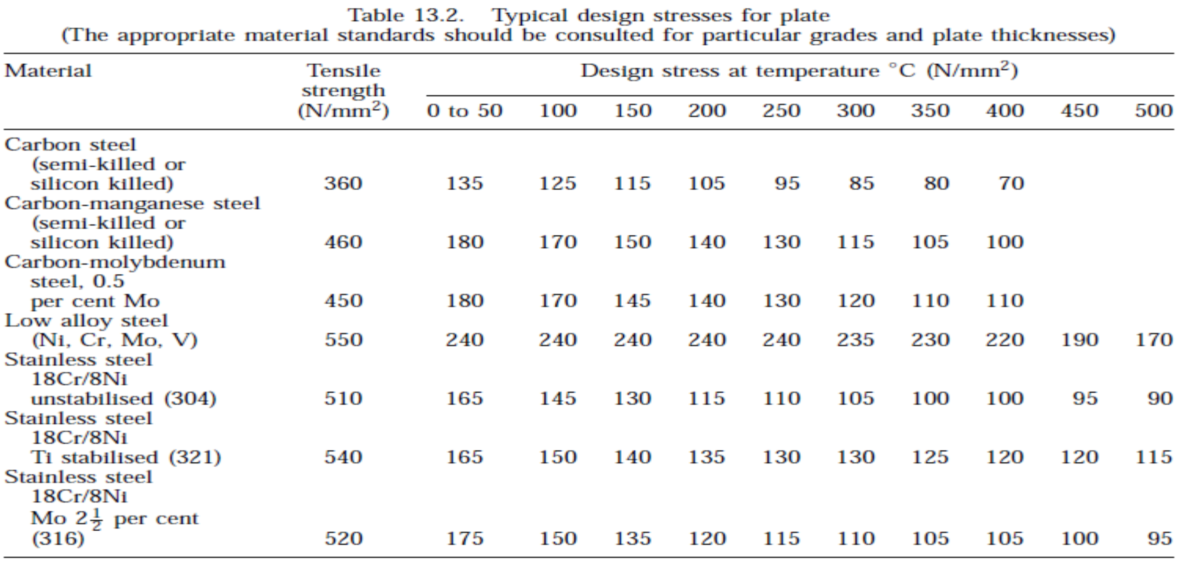


Table 13.2. Typical design stresses for plate
(The appropriate material standards should be consulted for particular grades and plate thicknesses)

Material	Tensile strength (N/mm^2)	Design stress at temperature °C (N/mm^2)									
		0 to 50	100	150	200	250	300	350	400	450	500
Carbon steel (semi-killed or silicon killed)	360	135	125	115	105	95	85	80	70		
Carbon-manganese steel (semi-killed or silicon killed)	460	180	170	150	140	130	115	105	100		
Carbon-molybdenum steel, 0.5 per cent Mo	450	180	170	145	140	130	120	110	110		
Low alloy steel (Ni, Cr, Mo, V)	550	240	240	240	240	240	235	230	220	190	170
Stainless steel 18Cr/8Ni unstabilised (304)	510	165	145	130	115	110	105	100	100	95	90
Stainless steel 18Cr/8Ni Ti stabilised (321)	540	165	150	140	135	130	130	125	120	120	115
Stainless steel 18Cr/8Ni Mo $2\frac{1}{2}$ per cent (316)	520	175	150	135	120	115	110	105	105	100	95

Wall thickness = e = 70 mm

Ellipsoidal head thickness = e = 30 mm

6.1.2 Cold Box Vessel

Using same procedure as above:

Settling theory results in the following relationship. For liquid drops in gas phase

$$d^2 = 5.054\frac{TZQ_g}{P}\left[\left(\left|\frac{\rho_g}{\rho_l-\rho_g}\right|\right)\frac{C_D}{d_m}\right]^{1/2}$$

Where,

- d = vessel internal diameter, in.
- d_m = drop diameter, µm
- T = operating temperature, °R
- Q_g = gas flow rate, MMscf/D
- P = operating pressure, psia
- Z = gas compressibility
- ρ_l = liquid density, lbm/ft^3
- ρ_g = gas density, lbm/ft^3
- C_D = drag coefficient.

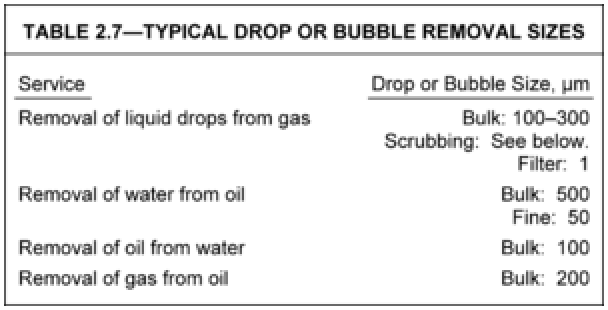


TABLE 2.7—TYPICAL DROP OR BUBBLE REMOVAL SIZES

Service	Drop or Bubble Size, µm
Removal of liquid drops from gas	Bulk: 100–300 Scrubbing: See below. Filter: 1
Removal of water from oil	Bulk: 500 Fine: 50
Removal of oil from water	Bulk: 100
Removal of gas from oil	Bulk: 200

$$C_D Re^2 = \frac{4}{3}\frac{d_v^3|\rho_c - \rho_d|\rho_c g}{\mu_c^2}$$

where,

Re = Reynolds number, $(V_T.d_v.\rho_c)/\mu_c$

C_D = drag coefficient of drop/bubble;

ρ_c continuous phase density, g/cm^3

ρ_d = dispersed phase density, g/cm^3

g = gravitational constant, 981 cm/sec^2

μ_c = continuous phase viscosity, g/(cm/sec) = poise,

Using L/d = 3 and above equations,

d = 0.8 m

L = 2.185 m

$$V = \pi r^2 l$$

V = 1.0 m^3

Wall thickness

$$e = \frac{P_i D_i}{2Jf - 0.2P_i}$$

Ellipsoidal Head thickness

$$e = \frac{P_i D_i}{2Jf - P_i}$$

Design Pressure = 9.22 N/mm^2

Design Temperature = 50/-196 °C

Joint efficiency = 1.0

Corrosion allowance = 0 mm

f = Stress Factor from following table;

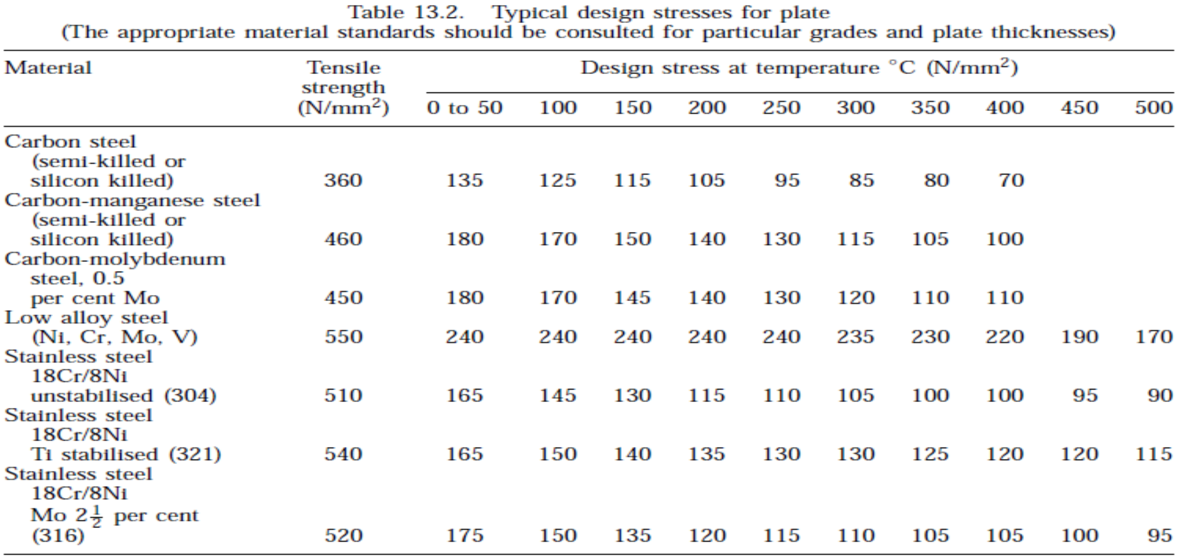


Table 13.2. Typical design stresses for plate
(The appropriate material standards should be consulted for particular grades and plate thicknesses)

Material	Tensile strength (N/mm^2)	Design stress at temperature °C (N/mm^2)									
		0 to 50	100	150	200	250	300	350	400	450	500
Carbon steel (semi-killed or silicon killed)	360	135	125	115	105	95	85	80	70		
Carbon-manganese steel (semi-killed or silicon killed)	460	180	170	150	140	130	115	105	100		
Carbon-molybdenum steel, 0.5 per cent Mo	450	180	170	145	140	130	120	110	110		
Low alloy steel (Ni, Cr, Mo, V)	550	240	240	240	240	240	235	230	220	190	170
Stainless steel 18Cr/8Ni unstabilised (304)	510	165	145	130	115	110	105	100	100	95	90
Stainless steel 18Cr/8Ni Ti stabilised (321)	540	165	150	140	135	130	130	125	120	120	115
Stainless steel 18Cr/8Ni Mo $2\frac{1}{2}$ per cent (316)	520	175	150	135	120	115	110	105	105	100	95

Wall thickness = e = 50 mm

Ellipsoidal head thickness = e = 30 mm

6.2 Plate and Fin Heat Exchanger (Cold Box) []

The actual design of a plate fin heat exchanger is done through extensive CFD and modelling. However, since we knew the specs of the plate fin heat exchanger manufactured by Linde, we use the dimensions of those plates only and verify design to accommodate for our requirements.

6.2.1 Formulas:

$$A_p = \emptyset W_p L_p \tag{6.6}$$

$$A = N_p A_p \tag{6.7}$$

$$Q = UA\Delta T_M \tag{6.8}$$

$$\Delta T_{LM} = \frac{\Delta T_1 - \Delta T_2}{ln(\frac{\Delta T_1}{\Delta T_2})} \tag{6.9}$$

$$P = \frac{dT_{hot}}{dT_{max}} \tag{6.10}$$

$$R = \frac{dT_{cold}}{dT_{hot}} \tag{6.11}$$

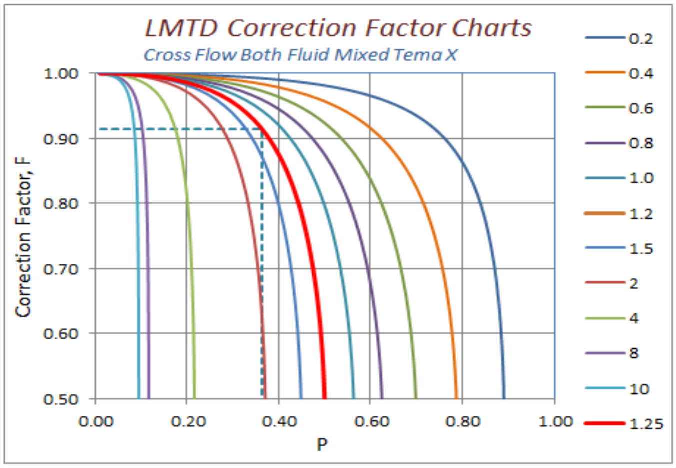
$$UA_{required} = \frac{Q}{(CMTD)} \tag{6.12}$$

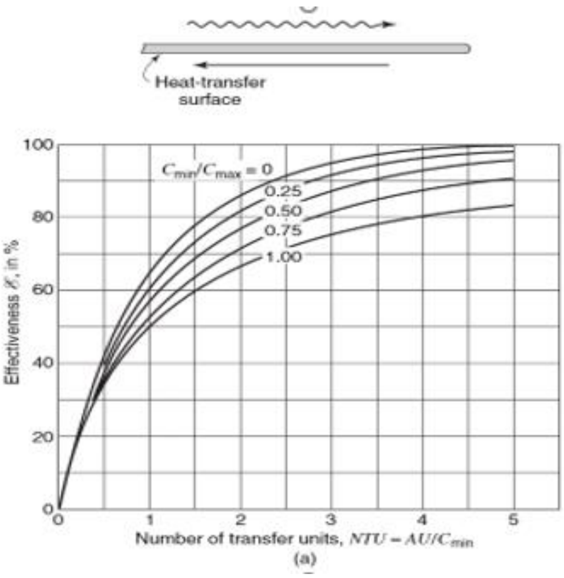
$$CMTD = (CF)(LMTD) \tag{6.13}$$

$$HCRR = \frac{HCR_{min}}{HCR_{max}} \tag{6.14}$$

$$NTU = \frac{UA}{HCR_{min}} \tag{6.15}$$

$$E = \frac{Q}{Q_{max}} \tag{6.16}$$





6.2.2 Calculations:

L= 0.7m

W=0.69 m

Area of a single plate = 0.585 m^2

No. of plates = 16

Total area of plates = 16 * 0.585 = 9.36 m^2

Q = 5.8 * 10^6 kJ

LMTD = 5.87 ^oC

CMTD = 5.6 ^oC

NTU = 1.7

6.3 Shell and Tube Heat Exchanger

6.3.1 Water Cooler (Pretreatment)

Exchanger type: Shell and tube Heat Exchanger

Shell Passes = 1

Tube Passes = Np = 2

Shell Side Fluid: Cooling water

Tube Side Fluid: Purge Gas

Purge gas inlet temperature = T1 = 52 °C

Purge gas outlet temperature = T2 = 40 °C

Cooling water inlet temperature = t1 = 30 °C

Cooling water outlet temperature = t2 = 35 °C

Cp of purge gas = 1.011 kcal/kg °C

Cp of cooling water = 0.999 kcal/kg °C

Flow rate (shell) = 9544 kg/hr

Flow rate (tube) = 1.70×10^4 kg/hr

$$Q_{shell} = m\ C_p\ \Delta T \qquad (6.17)$$

$Q = 3.94 \times 10^5$ kJ/hr

$$Q=UA\Delta T_m \qquad (6.18)$$

$$\Delta T_m = F_t * LMTD \qquad (6.19)$$

$$\Delta T_{LM} = \frac{(T_1 - t_2) - (T_2 - t_1)}{ln\frac{(T_1 - t_2)}{(T_2 - t_1)}} \qquad (6.20)$$

Shell Inlet/outlet temperature =30/35

Tube Inlet/outlet temperature = 52/40

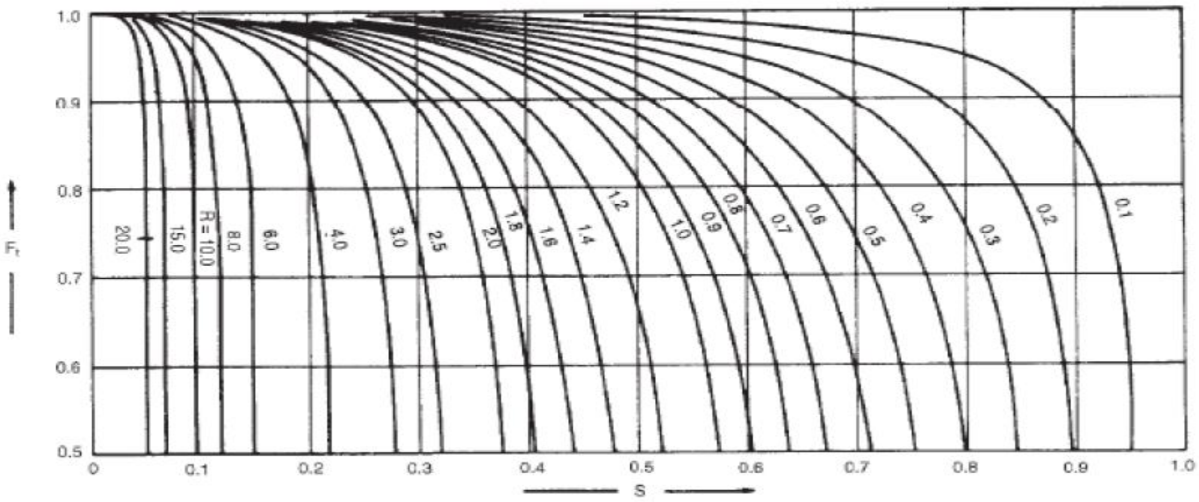
LMTD = 13.2

$$R = \frac{T_1 - T_1}{t_2 - t_1} \qquad (6.21)$$

$$S = \frac{t_2 - t_1}{T_1 - t_1} \tag{6.22}$$

From Figure for 1 shell pass and 2 tube passes using values of S and R, we get

$F_t = 0.713$

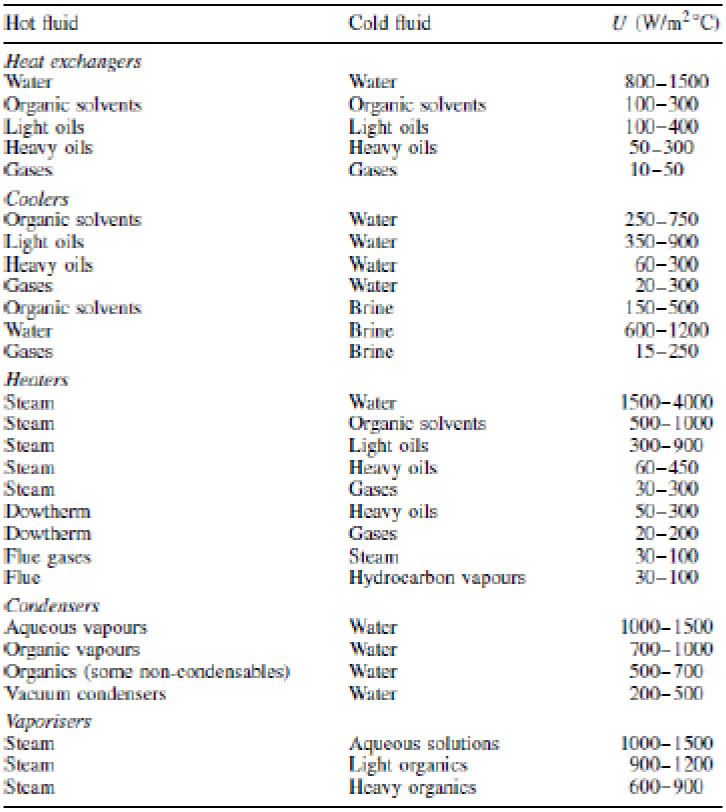


$\Delta t = F_t * LMTD$

$\Delta t = 9.37°C$

Overall heat transfer coefficient for this system is assumed.

$U = 300\ W/m^2\ {}^\circ C$



Hot fluid	Cold fluid	U (W/m^2°C)
Heat exchangers		
Water	Water	800–1500
Organic solvents	Organic solvents	100–300
Light oils	Light oils	100–400
Heavy oils	Heavy oils	50–300
Gases	Gases	10–50
Coolers		
Organic solvents	Water	250–750
Light oils	Water	350–900
Heavy oils	Water	60–300
Gases	Water	20–300
Organic solvents	Brine	150–500
Water	Brine	600–1200
Gases	Brine	15–250
Heaters		
Steam	Water	1500–4000
Steam	Organic solvents	500–1000
Steam	Light oils	300–900
Steam	Heavy oils	60–450
Steam	Gases	30–300
Dowtherm	Heavy oils	50–300
Dowtherm	Gases	20–200
Flue gases	Steam	30–100
Flue	Hydrocarbon vapours	30–100
Condensers		
Aqueous vapours	Water	1000–1500
Organic vapours	Water	700–1000
Organics (some non-condensables)	Water	500–700
Vacuum condensers	Water	200–500
Vaporisers		
Steam	Aqueous solutions	1000–1500
Steam	Light organics	900–1200
Steam	Heavy organics	600–900

Assumptions:

Choose 25mm outer diameter, 22.5mm inner diameter and 4124 mm long tubes

Inner diameter of tube = d_i = 0.025 m

Outer Diameter of tube = d_o = 0.0225 m

Length of tube = L = 4.124 m

Area of one tube = π * L * d = π * 3.66 * 0.02 = 0.23 m^2

Number of tubes = N_t = *Heat transfer area/Area of one tube* = 18.77 / 0.23 = 82 tubes

Use triangular pitch,

Pitch = p_t = 1.25 * d_o = 1.25 * 0.02 = 0.025 m

Bundle diameter is calculated as follow:

$$D_b = d_o\left(\frac{N_t}{K_1}\right)^{\frac{1}{n}} \qquad (6.23)$$

K_1 and n_1 are constants. For 1 shell pass their values are,

K_1 = 0.319, n_1 = 2.142

By putting values in the above formula, bundle diameter is found.

D_b= 267.7 mm = 0.2677 m

Clearance for shell diameter = 0.088 m (from graph)

Shell Diameter = Bundle Diameter + Clearance

Shell Diameter = D_o = 0.2677 + 0.088 = 0.3557 m

Baffle spacing = l_B = 0.5 * D_o = 0.5 * 0.3557 = 0.1778 m

Number of baffles = 14

$length\ of\ tube/Baffle\ Spacing$ = 3.66 / 0.1778 = 20

6.3.2 Tube Side Co-efficient:

Mean temperature = 85.75 °C

Density of solution = ρ = 888.2 kg/m^3

Viscosity of solution = μ = 0.0002723 kg/m.sec

Heat capacity of solution = C_p = 4468 J/kg °C

Thermal conductivity of solution = K = 0.6182 W/m. °C

Tubes per pass = total tubes / 2 = 82/2 = 41

Total flow area = Tube Cross-sectional area * Tubes per pass

Total flow area = 0.000201 * 41

Total flow area = 0.008 m^2

Linear velocity = u_t = (mass velocity / density) = 279 / 888.2 = 0.315 m/sec

From graph between Re_t and J_H factor, it is found that

J_H = 0.0039

By putting all values in above equation, we get h_i = 3094.15 W/m^2 ^{o}C

6.3.3 Shell Side Co-efficient:

Mean temperature = 135.25 ^{o}C

Density of solution = ρ = 912.5 kg/m^3

Viscosity of solution = μ = 0.000158kg/m.sec

Heat capacity of solution = C_p = 4511 J/kg ^{o}C

Thermal conductivity of solution

Equivalent diameter = d_e = 1.10 ($pt2-0.917\ do2$) = 14.2 mm = 0.0142 m

Linear velocity = u_t = (mass velocity / density) = 160.34 / 912.5 = 0.175 m/sec

Reynolds Number in tubes = $Re_s = \frac{\rho d_e u_t}{\mu} = \frac{912.5*0.0142*0.175}{0.000153}$ (6.24)

$$=14411.63$$

From graph between Re_t and J_H factor, it is found that

J_H = 0.0038

$$\frac{h_i}{d_i k} = J_H R_e P_r^{0.33} (\frac{\mu}{\mu_w})^{0.14} \qquad (6.25)$$

By putting all values in above equation, we get h_s = 2676.701 W/m^2 ^{o}C

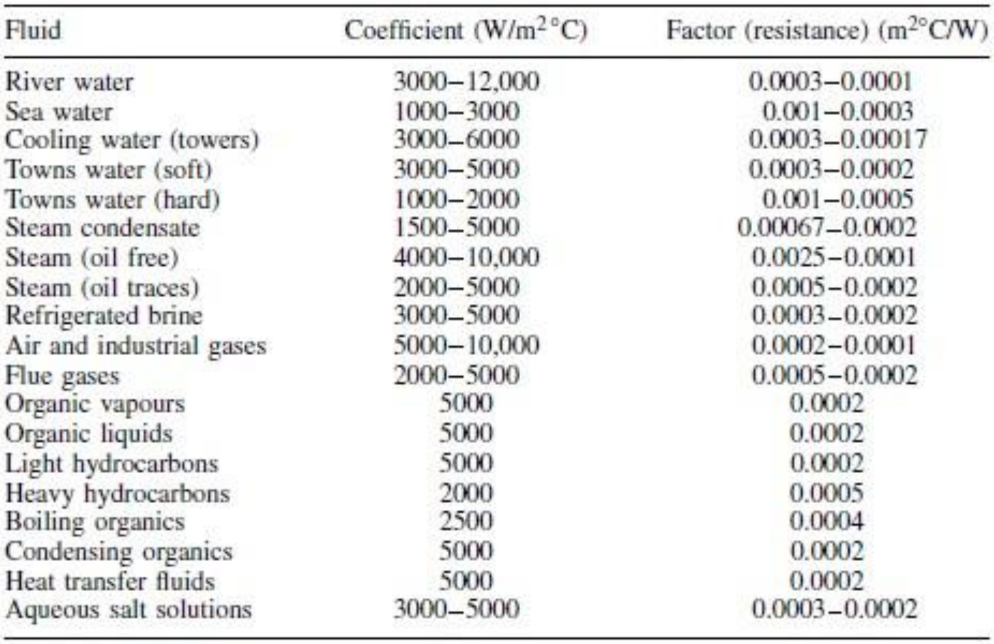
$$U_c = \frac{h_{io} * h_o}{h_{io} + h_o} \qquad (6.26)$$

Fouling Factor for shell side = h_{od} = 5000 W/m^2 ^{o}C

Fouling Factor for tube side = h_{id} = 5000 W/m^2 ^{o}C

K_w = 50 W/m^2 ^{o}C

Table 6. 2: Fouling Factor



Fluid	Coefficient (W/m^2°C)	Factor (resistance) (m^2°C/W)
River water	3000–12,000	0.0003–0.0001
Sea water	1000–3000	0.001–0.0003
Cooling water (towers)	3000–6000	0.0003–0.00017
Towns water (soft)	3000–5000	0.0003–0.0002
Towns water (hard)	1000–2000	0.001–0.0005
Steam condensate	1500–5000	0.00067–0.0002
Steam (oil free)	4000–10,000	0.0025–0.0001
Steam (oil traces)	2000–5000	0.0005–0.0002
Refrigerated brine	3000–5000	0.0003–0.0002
Air and industrial gases	5000–10,000	0.0002–0.0001
Flue gases	2000–5000	0.0005–0.0002
Organic vapours	5000	0.0002
Organic liquids	5000	0.0002
Light hydrocarbons	5000	0.0002
Heavy hydrocarbons	2000	0.0005
Boiling organics	2500	0.0004
Condensing organics	5000	0.0002
Heat transfer fluids	5000	0.0002
Aqueous salt solutions	3000–5000	0.0003–0.0002

Put all the values in above equation to get overall heat transfer coefficient.

$\boldsymbol{U = 286\ W/m^{2o}C}$

The value of overall coefficient is almost equal to the assumed value so all assumptions regarding design are true.

6.3.4 Pressure drop:

$$\Delta P_s = \frac{G_s^2 D_s (N+1)}{2 d \rho D_s \emptyset_s}$$

$$= \frac{f G_g^2 D_g (N+1)}{5.22 * \ 10^{10} D_s s \emptyset_s} \qquad (6.27)$$

Pressure Drop (shell side) = 4.41 psi

$$\Delta P_t = \frac{f G_t^2 L_n}{5.22 * 10^{10} Ds \emptyset_t} \quad (6.28)$$

$$\Delta P_t = \frac{4nV^2 * 62.5}{s2g' * 144} \quad (6.29)$$

$$\Delta P_T = \Delta P_t + \Delta P_r \quad (6.30)$$

Pressure Drop (tube side) = 2.84 psi

6.3.5 Exchanger Design Summary

Flow rate (shell) = 9544 kg/hr

Flow rate (tube) = 1.70 x 10^4 kg/hr

Q = 3.94 x 10^5 kJ/hr

Shell Inlet/outlet temperature =30/35

Tube Inlet/outlet temperature = 52/40

LMTD = 13.2

Shell dia = 386 mm

Tube length = 4124 mm

No. of tubes = 90

Tube dia = 25 mm

Pitch = 32 mm

No. of Baffles = 14

Pressure Drop (tube side) = 2.84 psi

Pressure Drop (shell side) = 4.41 psi

Corrosion Allowance shell/tube = 3/1 mm

U = 137 W/m^2K

Heating Area = 28.9 m^2

6.4 Membrane

$$A = \frac{(Vy)_{out}}{(J_A)_{av}}$$

$$= \frac{(Vy)_{out}}{Q_A(P_1x - P_2y_i)_{av}} \quad (6.31)$$

Figure 10 Membrane fiber

1 barrer = $3.35\text{x}10^{-16}\frac{mol.m}{m^2.s.Pa}$

V_{out} y = Flow H_2 Out

= 553 kmol/hr

=153.6 mol/s

$P_1 = 110 \text{ x } 10^5$ Pa

$P_2 = 26 \text{ x } 10^5$ Pa

Area = $\frac{153.6}{14 \text{ x } 3.35 \text{ x } 10^{-16}(110 \text{ x } 10^5 \text{ x } 0.668 - 26 \text{ x } 10^5 \text{ x } 0.938)}$

= $6.67 \text{ x } 10^9$ m^2/m

Since membrane thickness is 10^{-6} m, therefore

Area = $6.67 \text{ x } 10^9$ m^2/m x 10^{-6} m

= $6.67 \text{ x } 10^3$ m^2

Module dimension = 8-inch dia x 10 feet length

Effective area per fiber = $2\pi rl$ = $2.89 \text{ x } 10^{-3}$ m^2

Required fibers = 2308304

Module volume = 3.5 ft^3

1 hollow fiber volume = $9.88 \text{ x } 10^{-6}$ ft^3

No. of fibers per module = 303643

Modules Required = $\frac{2308304}{303643} = 8$ modules in parallel

6.5 Adsorber

The kinetics and isotherms were not found for the adsorption process so a detailed designed is not carried out for the adsorber column. However, a similar column to that already installed in FFC is taken as reference with the following specifications.

Normal operation Operating temperature: 40°C

Normal operation Operating pressure: 84.8 kg/cm^2

Regeneration Operating temperature: 230°C

Regeneration Operating pressure: 78.4 kg/cm^2

Type of Adsorbent: UOP Zeolite 5A TRIS

Bulk Density:660 kg/m^3

Mass of Adsorbent: 1200kg

Height of Bed: 2.653m

Inner diameter: 0.934m

Cross sectional Area: 0.685 m^2

Pressure Drop across bed: 0.14

Onstream Time: 2 hours

Joint efficiency: 1

Corrosion allowance: 1mm

Volume: 3.2m^3

Chapter 7: Costing

$$\text{Cost in year A} = \text{Cost in year B} * \frac{\text{Cost index in year A}}{\text{Cost index in year A}} \quad (7.1)$$

Process Engineering Index in2004 = 400

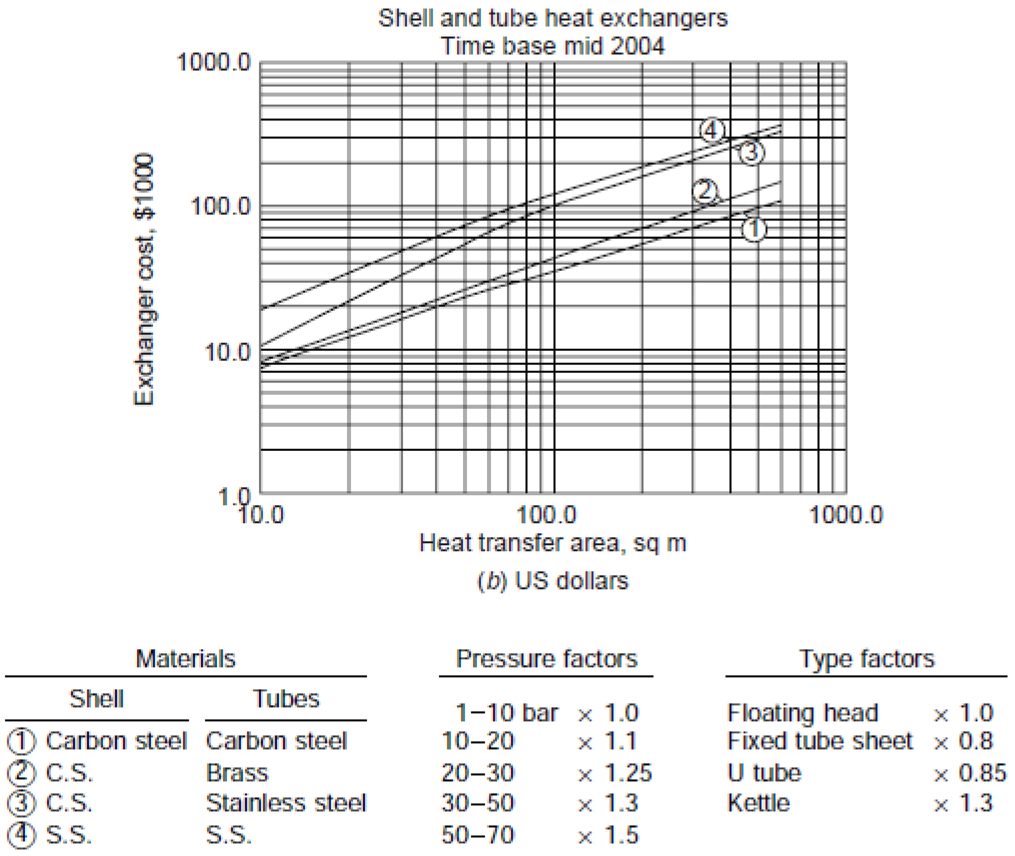
Process Engineering Index in 2018 = 575

7.1 Factorial Method for Cost Estimation [14]

Capital cost estimates for chemical process plants are often based on an estimate of the purchase cost of the major equipment items required for the process, the other costs being estimated as factors of the equipment cost. The accuracy of this type of estimate will depend on what stage the design has reached at the time the estimate is made, and on the reliability of the data available on equipment costs. In the later stages of the project design, when detailed equipment specifications are available and firm quotations have been obtained, an accurate estimation of the capital cost of the project can be made.

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

.



Materials

	Shell	Tubes
①	Carbon steel	Carbon steel
②	C.S.	Brass
③	C.S.	Stainless steel
④	S.S.	S.S.

Pressure factors

1–10 bar	× 1.0
10–20	× 1.1
20–30	× 1.25
30–50	× 1.3
50–70	× 1.5

Type factors

Floating head	× 1.0
Fixed tube sheet	× 0.8
U tube	× 0.85
Kettle	× 1.3

Figure 6.3*a*, *b*. Shell and tube heat exchangers. Time base mid-2004
Purchased cost = (bare cost from figure) × Type factor × Pressure factor

The shell and tube heat exchangers are costed using the above graph and tables:

1) Pretreatment Water Cooler

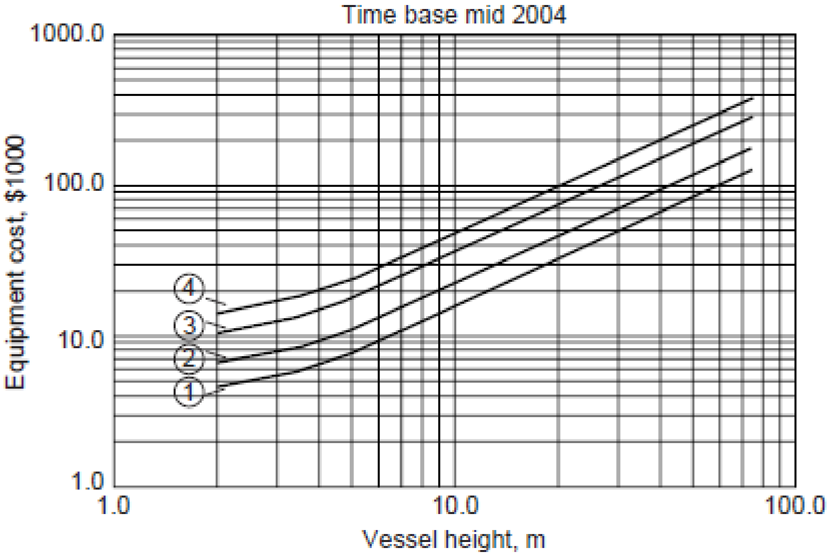
   Area = 70m$^{2;}$ $24480

2) Pre-Cooler Membrane

   Area = 130m^2; $30000

3) Post-Cooler Membrane

   Area = 80m^2; $25000



(*b*) US dollars

Diameter, m	
①—0.5	③—2.0
②—1.0	④—3.0

Material factors	
C.S.	× 1.0
S.S.	× 2.0
Monel	× 3.4
S.S. clad	× 1.5
Monel clad	× 2.1

Pressure factors	
1–5 bar	× 1.0
5–10	× 1.1
10–20	× 1.2
20–30	× 1.4
30–40	× 1.6
40–50	× 1.8
50–60	× 2.2

Temperature up to 300°C

Figure 6.5*a*, *b*. Vertical pressure vessels. Time base mid-2004.
Purchased cost = (bare cost from figure) × Material factor × Pressure factor

The separating vessels and adsorber vessel are costed using above graphs and tables

1) Pretreatment Vessel

   $9100

2) Cold Box Separator

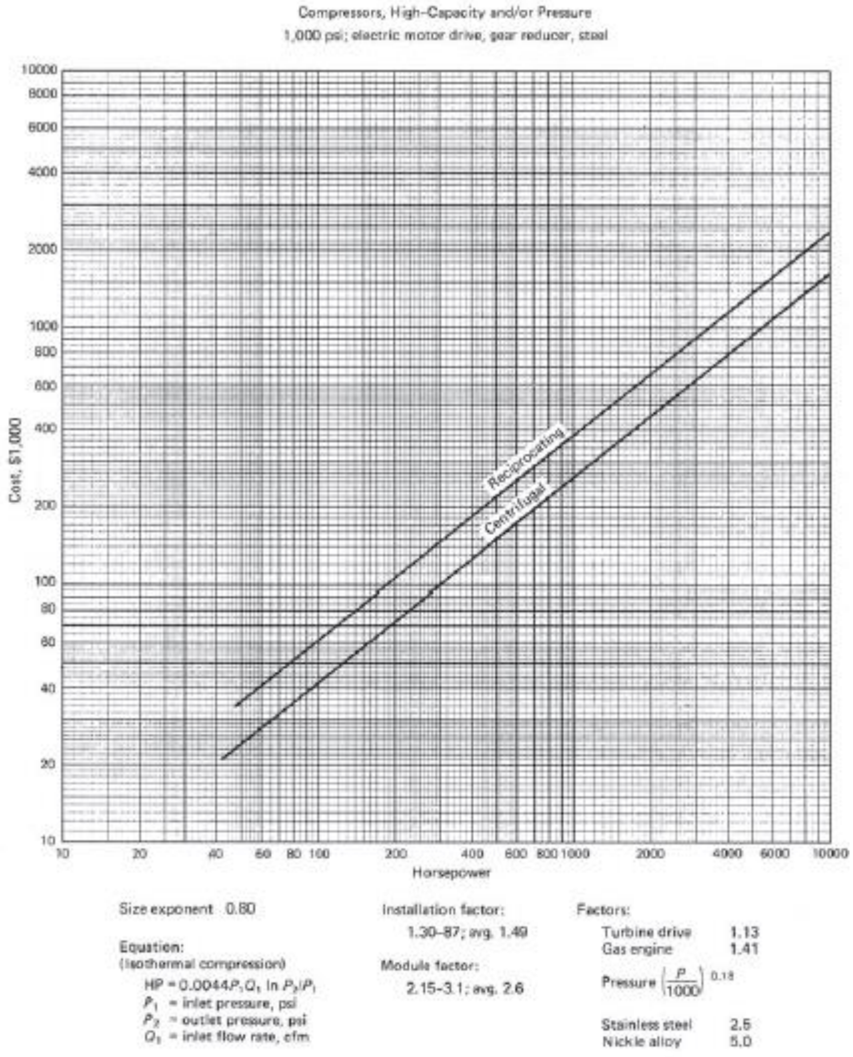
   $15600

3) Adsorber

   Vessel = $18600

   Adsorbent = $16800

   Adsorber Total = $35400



Compressor [15]

Costing of compressors is done using above graph

Pre-compressor = $230,000

Post compressor = $270,000

Cold Box

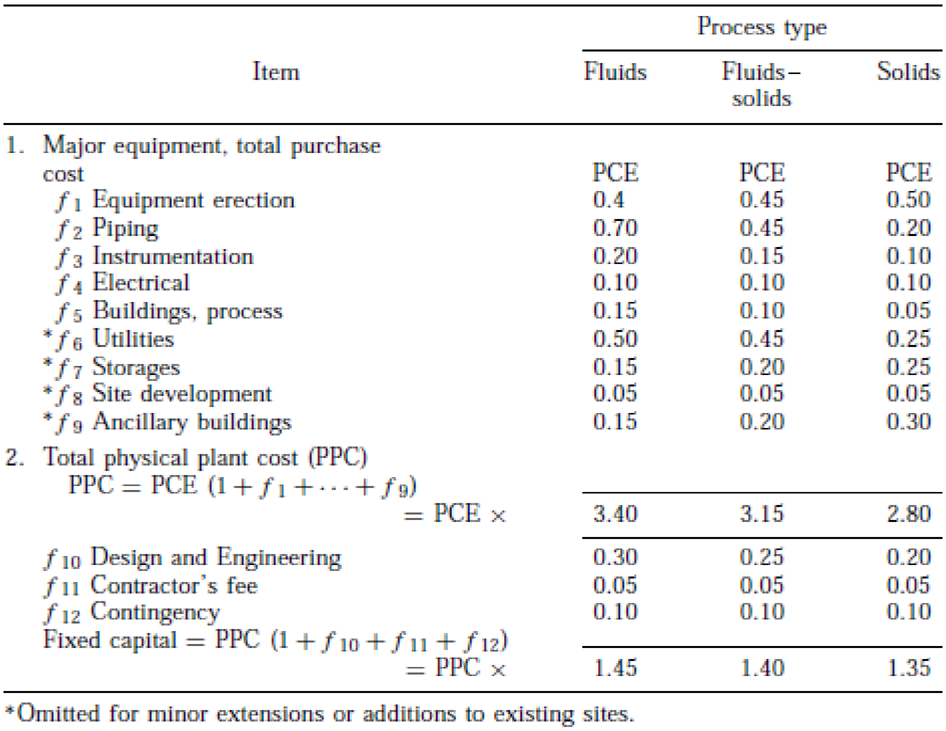
Cost = $1,000,000 (calculated from linde’s manual)

Membrane

Cost = 6671m^2 x $(3.3)^2$ x $5/$ft^2$ = $363250

Using the tables below the purchase cost of equipment, physical plant cost, fixed capital and operating cost are calculated.

Table 6.1. Typical factors for estimation of project fixed capital cost

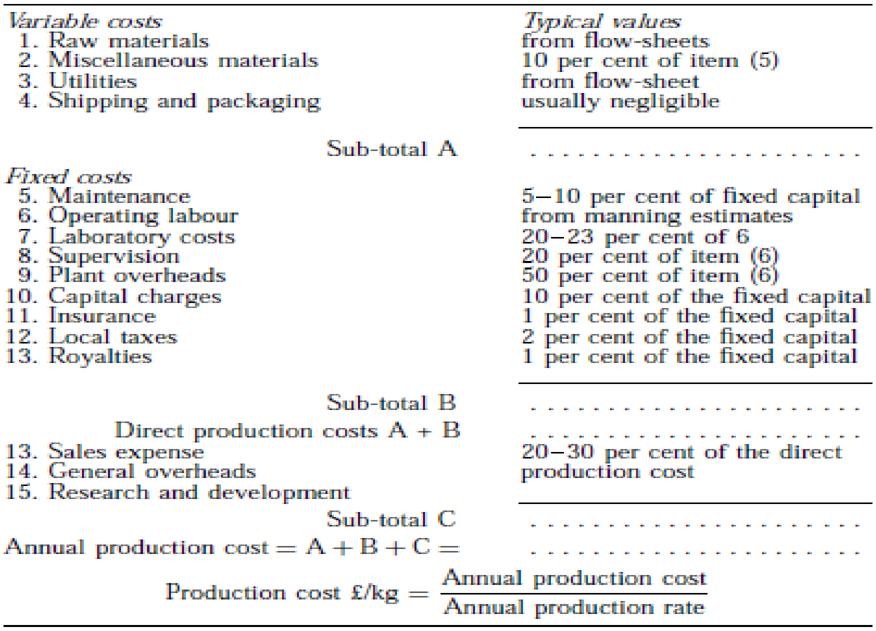


Item	Process type		
	Fluids	Fluids–solids	Solids
1. Major equipment, total purchase cost	PCE	PCE	PCE
f_1 Equipment erection	0.4	0.45	0.50
f_2 Piping	0.70	0.45	0.20
f_3 Instrumentation	0.20	0.15	0.10
f_4 Electrical	0.10	0.10	0.10
f_5 Buildings, process	0.15	0.10	0.05
* f_6 Utilities	0.50	0.45	0.25
* f_7 Storages	0.15	0.20	0.25
* f_8 Site development	0.05	0.05	0.05
* f_9 Ancillary buildings	0.15	0.20	0.30
2. Total physical plant cost (PPC)			
$PPC = PCE(1 + f_1 + \cdots + f_9)$			
$= PCE \times$	3.40	3.15	2.80
f_{10} Design and Engineering	0.30	0.25	0.20
f_{11} Contractor's fee	0.05	0.05	0.05
f_{12} Contingency	0.10	0.10	0.10
Fixed capital $= PPC(1 + f_{10} + f_{11} + f_{12})$			
$= PPC \times$	1.45	1.40	1.35

*Omitted for minor extensions or additions to existing sites.

Since our plant is an extension to a current facility, the factors with asterisk are not included in our calculations

Table 6.6. Summary of production costs



Variable costs	*Typical values*
1. Raw materials	from flow-sheets
2. Miscellaneous materials	10 per cent of item (5)
3. Utilities	from flow-sheet
4. Shipping and packaging	usually negligible
Sub-total A	. . . .
Fixed costs	
5. Maintenance	5–10 per cent of fixed capital
6. Operating labour	from manning estimates
7. Laboratory costs	20–23 per cent of 6
8. Supervision	20 per cent of item (6)
9. Plant overheads	50 per cent of item (6)
10. Capital charges	10 per cent of the fixed capital
11. Insurance	1 per cent of the fixed capital
12. Local taxes	2 per cent of the fixed capital
13. Royalties	1 per cent of the fixed capital
Sub-total B	. . . .
Direct production costs A + B	. . . .
13. Sales expense	20–30 per cent of the direct production cost
14. General overheads	
15. Research and development	
Sub-total C	. . . .
Annual production cost = A + B + C =	. . . .

$$\text{Production cost £/kg} = \frac{\text{Annual production cost}}{\text{Annual production rate}}$$

7.2 Cost Summary:

Table 21 Cost summary for Cryogenic separation

CRYOGENIC	
Equipment	**Cost ($)**
Separator	9100
2 Adsorbers	70800
Water Cooler	24480
Cold Box + Plate fin heat exchanger	1000000
Separator	15600
Steam Heater	8100
Physical Cost of Equipment(PCE)	˜1100000
Physical Plant Cost(PPC)	˜2800000
Fixed capital	˜4100000
Operating Cost/Year	˜500000

Table 22 -Cost summary for Membrane separation

MEMBRANE	
Equipment	**Cost ($)**
Separator	9100
2 Adsorbers	70800
3 Water Coolers	80000
2 Compressors	500000
Membrane Modules	360000
Steam Heater	8100
Physical Cost of Equipment(PCE)	˜1020000
Physical Plant Cost(PPC)	˜2450000
Fixed capital	˜3550000
Operating Cost/Year	˜340000

7.3 Comparison

Table 23 Comparison of Cryogenic and Membrane separation

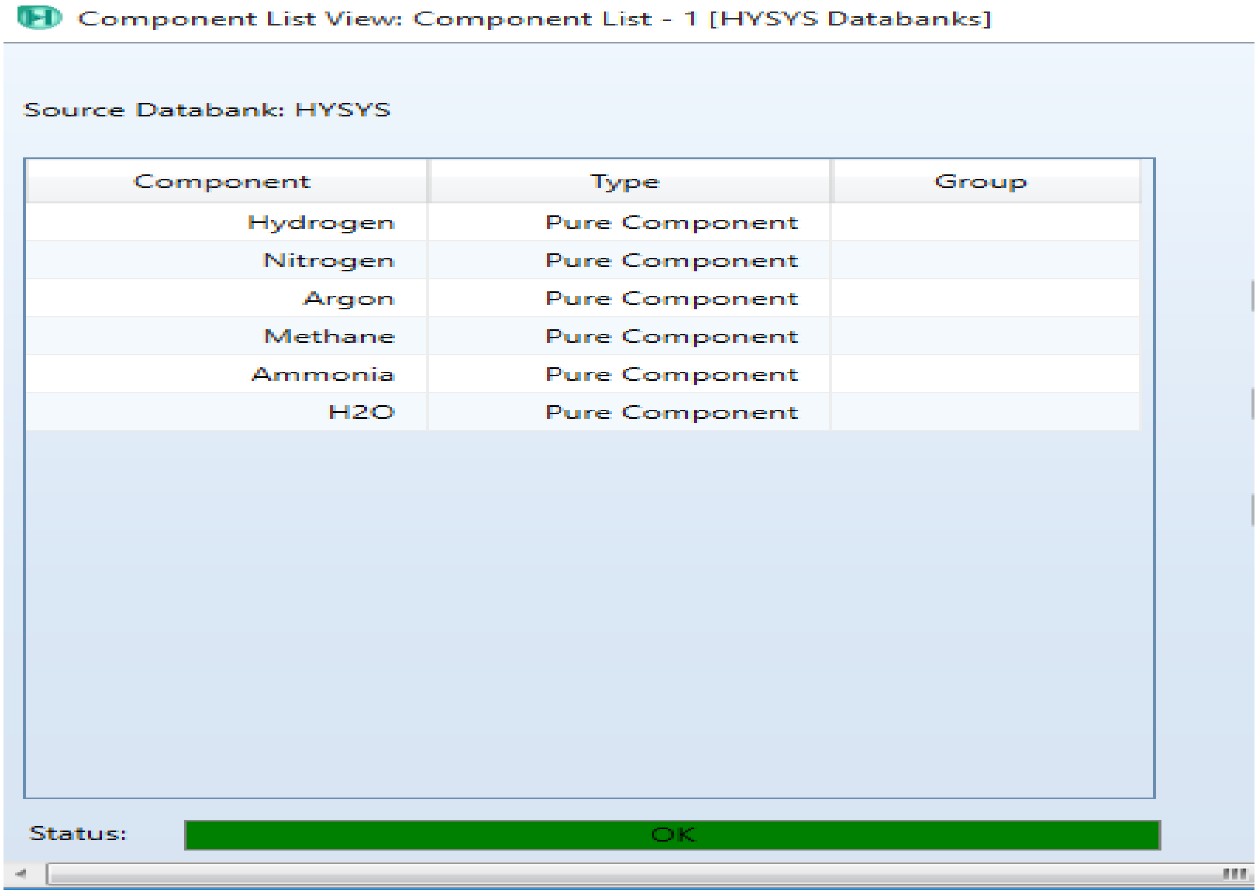
Process	**Linde's Cryogenic**	**PRISM Membrane**
Recovery %	94	85
Purity %	91	93.7
By-product recovery	Yes	Difficult
Ease of Expansion	Low	High
Fixed Capital Cost $	~ 4.1 million	~3.5 million
Operating Cost $/year	~500000	~340000
Replacement	Lifetime Warranty	12-18 months warranty, replacement after 2 years

After careful and detailed analysis of both the technologies and comparing them on various levels, we came to a conclusion that PRISM Membrane Technology has a comparatively lower initial investment and operating costs but foreseeing this in to future we realize that the replacement cost after every two years is not feasible and cryogenic is a more effective option in the long run. Hence, our further study of Simulation, Instrumentation & Process Control and HAZOP Analysis has been focused on the Linde's Cryogenic Process only.

Chapter 8: Simulation

Once a process is designed, it is usually simulated to check its realistic nature and to test it in different environments. We carried out the simulation of our cryogenic process in Aspen Hysys. It is a chemical process simulator software used for simulating and modelling chemical processes and plants mathematically. We carried out a steady state simulation and confirmed our manual calculations from with those of Hysys related to material and energy balances.

Firstly, we model the properties of our chemical process. We select the different components to be added in the simulation, in our case hydrogen, nitrogen, ammonia, water, argon and methane as pure components.



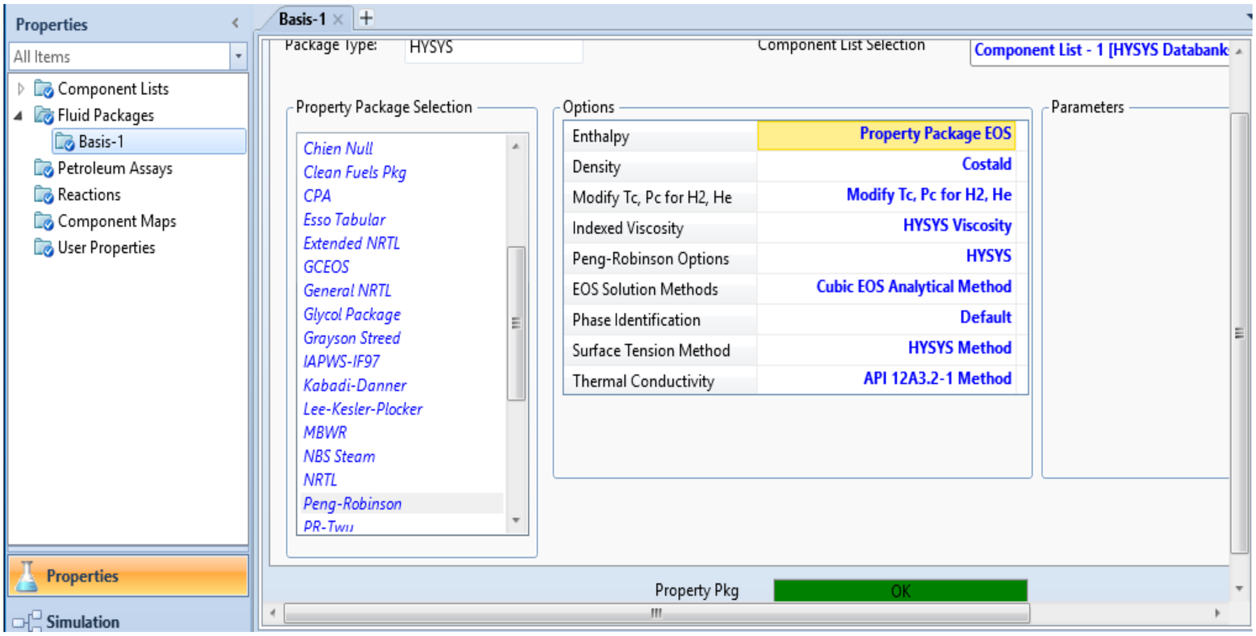
Component List View: Component List - 1 [HYSYS Databanks]

Source Databank: HYSYS

Component	Type	Group
Hydrogen	Pure Component	
Nitrogen	Pure Component	
Argon	Pure Component	
Methane	Pure Component	
Ammonia	Pure Component	
H2O	Pure Component	

Status: OK

Once the components are selected, we select a fluid package to model the properties of the components selected. We chose Peng Robinson property package as it supports all the components involved in our system.



Package Type: HYSYS

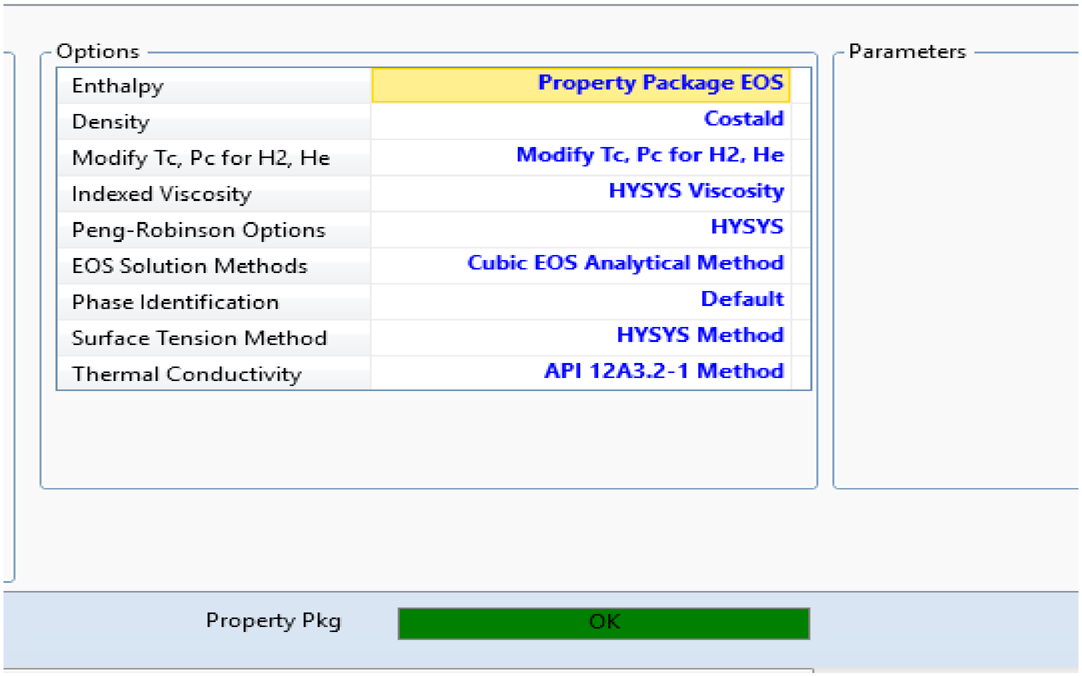
Component List Selection: Component List - 1 [HYSYS Databank

Property Package Selection:
- Chien Null
- Clean Fuels Pkg
- CPA
- Esso Tabular
- Extended NRTL
- GCEOS
- General NRTL
- Glycol Package
- Grayson Streed
- IAPWS-IF97
- Kabadi-Danner
- Lee-Kesler-Plocker
- MBWR
- NBS Steam
- NRTL
- Peng-Robinson
- PR-Twu

Options

Enthalpy	Property Package EOS
Density	Costald
Modify Tc, Pc for H2, He	Modify Tc, Pc for H2, He
Indexed Viscosity	HYSYS Viscosity
Peng-Robinson Options	HYSYS
EOS Solution Methods	Cubic EOS Analytical Method
Phase Identification	Default
Surface Tension Method	HYSYS Method
Thermal Conductivity	API 12A3.2-1 Method

Property Pkg: OK

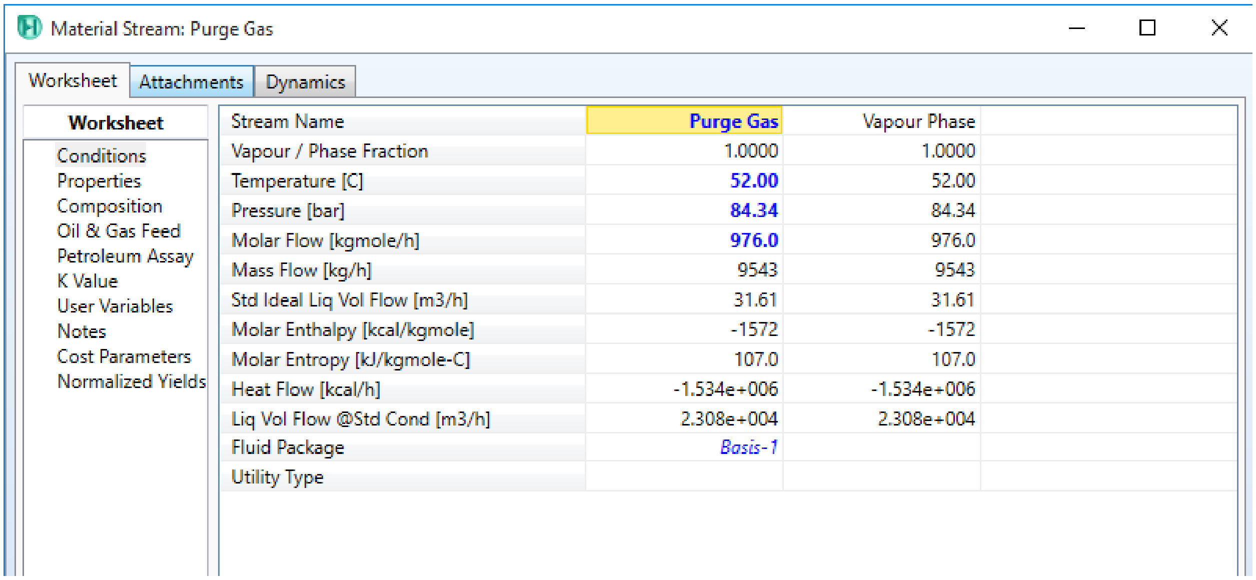


Options

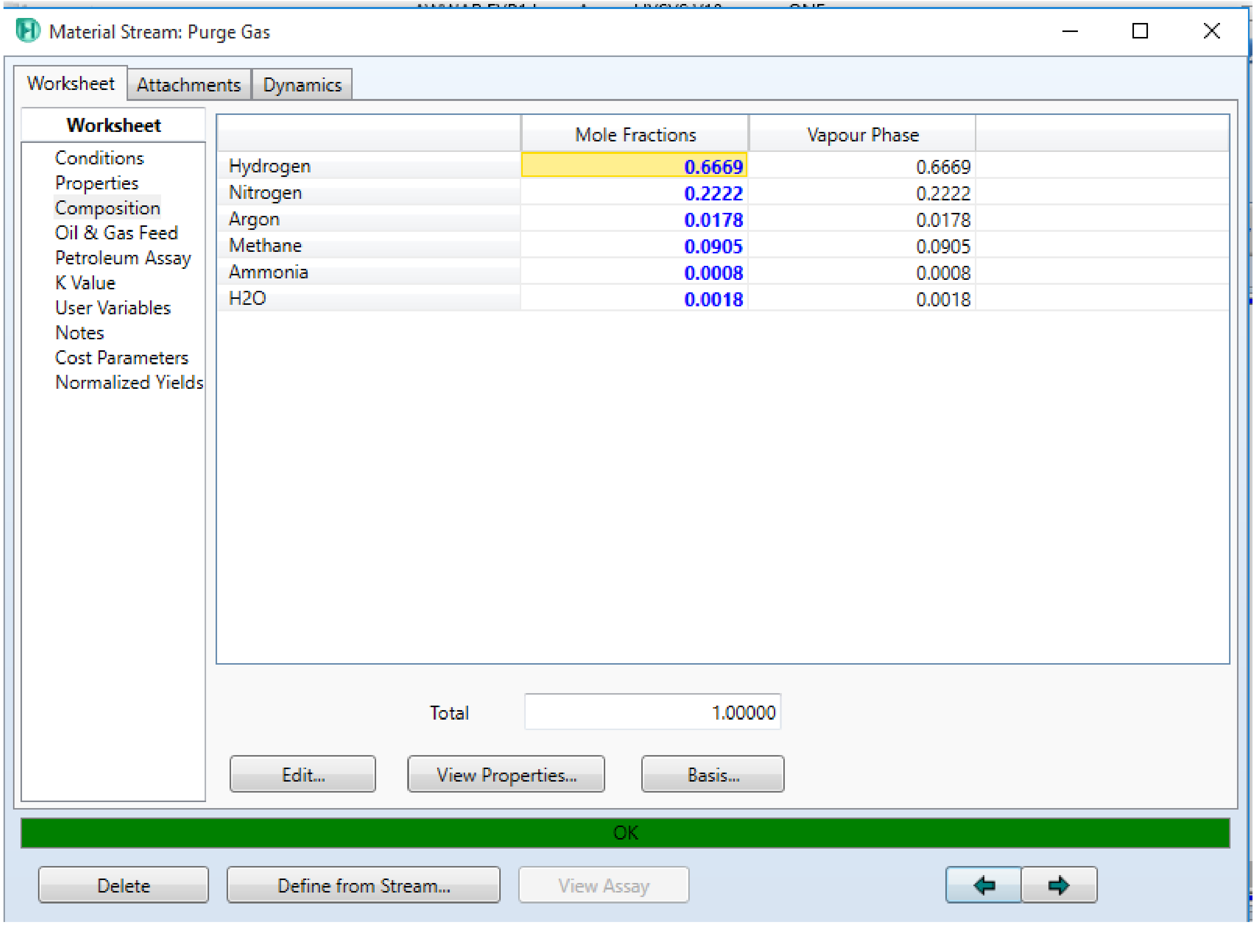
Enthalpy	Property Package EOS
Density	Costald
Modify Tc, Pc for H2, He	Modify Tc, Pc for H2, He
Indexed Viscosity	HYSYS Viscosity
Peng-Robinson Options	HYSYS
EOS Solution Methods	Cubic EOS Analytical Method
Phase Identification	Default
Surface Tension Method	HYSYS Method
Thermal Conductivity	API 12A3.2-1 Method

Property Pkg: OK

After that we move into the simulation environment to actually model our process. We create a material stream 'Purge Gas' at following conditions and composition.



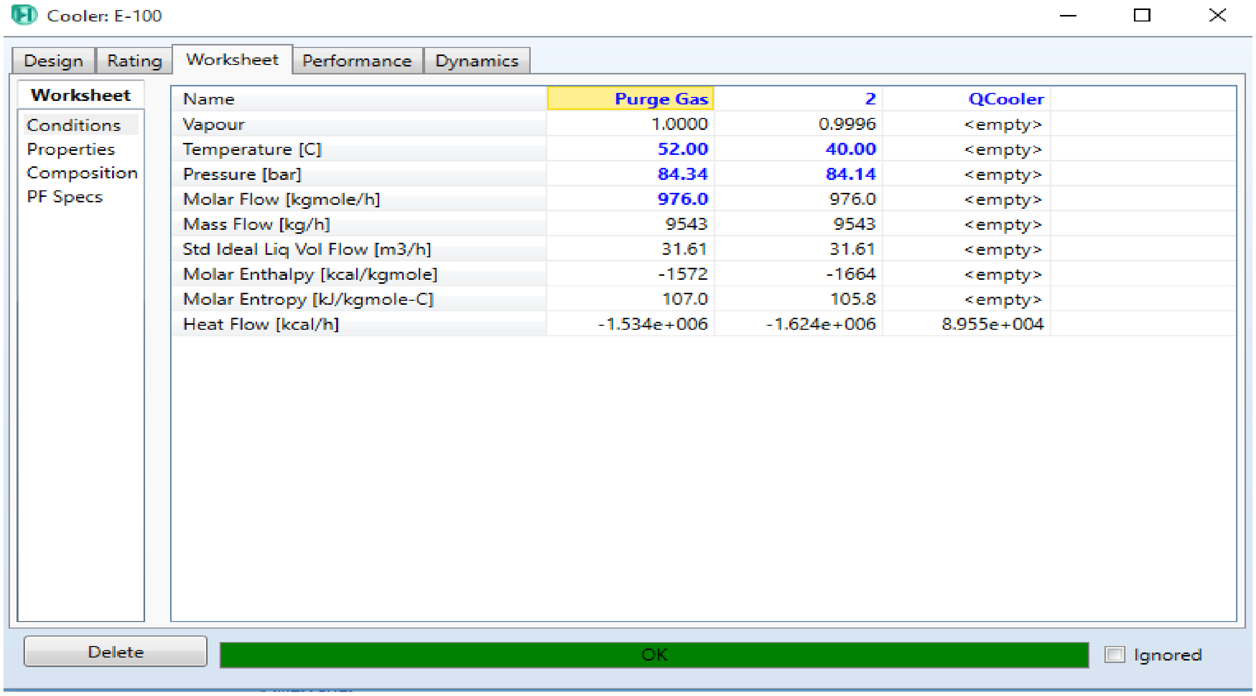
Stream Name	Purge Gas	Vapour Phase
Vapour / Phase Fraction	1.0000	1.0000
Temperature [C]	52.00	52.00
Pressure [bar]	84.34	84.34
Molar Flow [kgmole/h]	976.0	976.0
Mass Flow [kg/h]	9543	9543
Std Ideal Liq Vol Flow [m3/h]	31.61	31.61
Molar Enthalpy [kcal/kgmole]	-1572	-1572
Molar Entropy [kJ/kgmole-C]	107.0	107.0
Heat Flow [kcal/h]	-1.534e+006	-1.534e+006
Liq Vol Flow @Std Cond [m3/h]	2.308e+004	2.308e+004
Fluid Package	*Basis-1*	
Utility Type		



	Mole Fractions	Vapour Phase
Hydrogen	0.6669	0.6669
Nitrogen	0.2222	0.2222
Argon	0.0178	0.0178
Methane	0.0905	0.0905
Ammonia	0.0008	0.0008
H2O	0.0018	0.0018

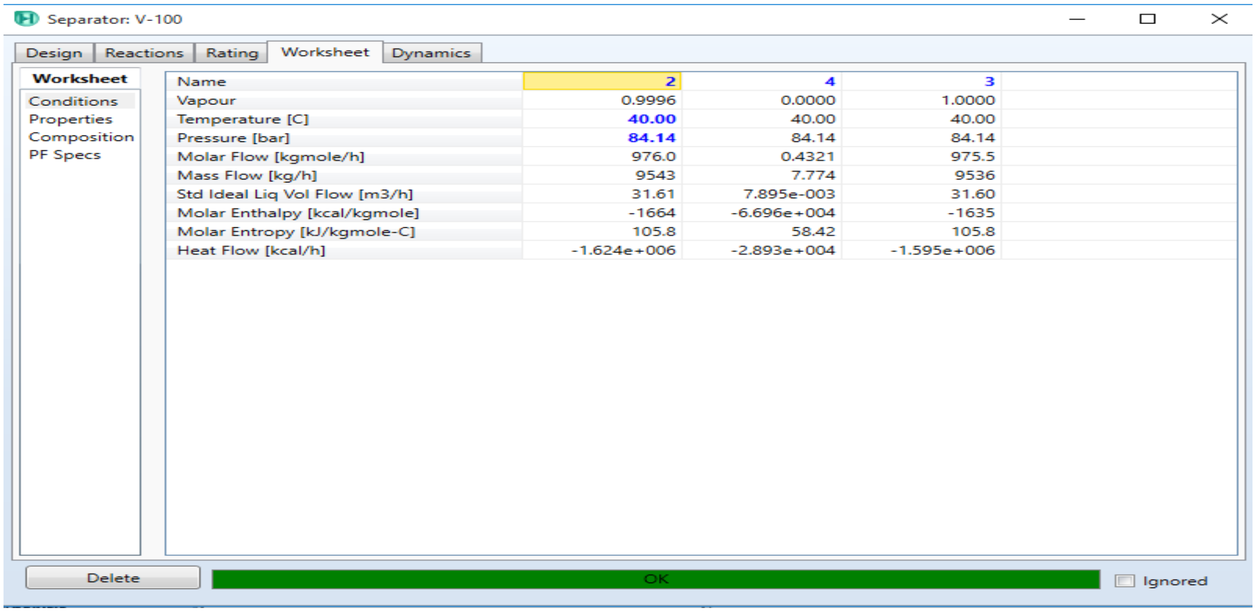
Total 1.00000

Now a cooler is added from the model pallet and this stream is made its inlet. The outlet temperature is given as 40°C and pressure drop of 0.2bar. An energy stream is also defined for the cooler E-100.



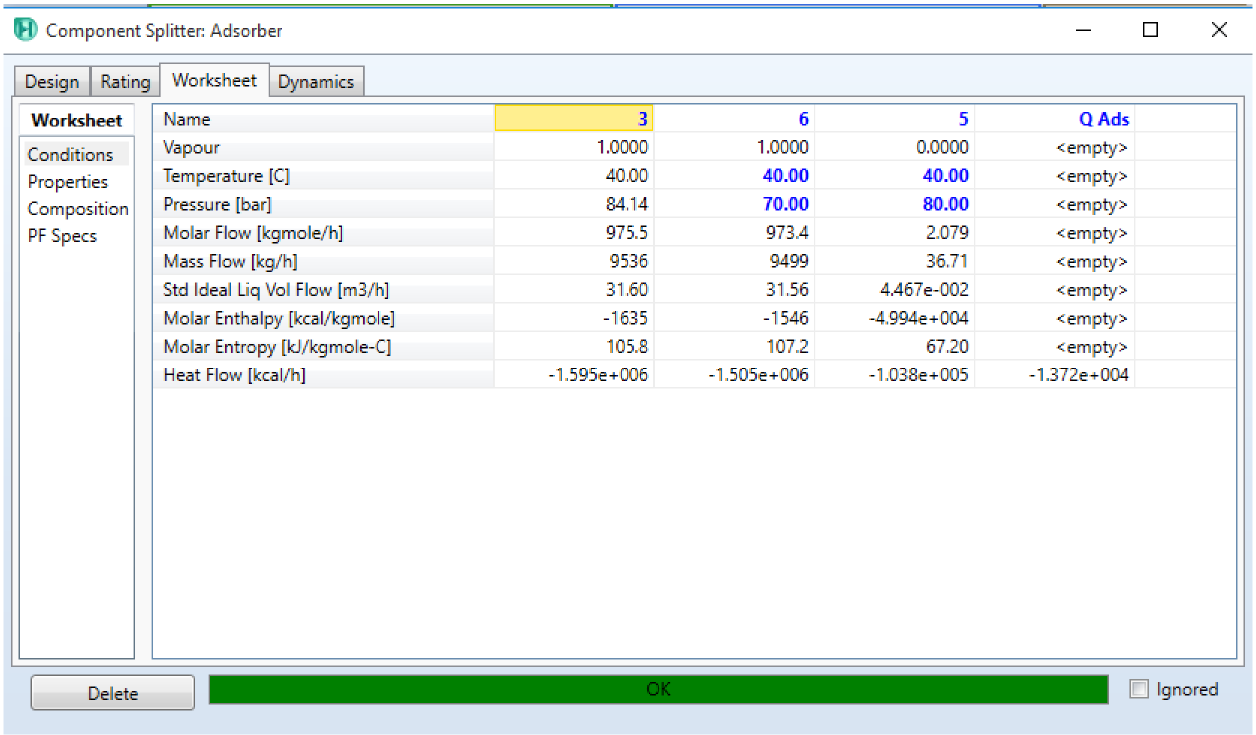
Name	**Purge Gas**	**2**	**QCooler**
Vapour	1.0000	0.9996	<empty>
Temperature [C]	**52.00**	**40.00**	<empty>
Pressure [bar]	**84.34**	**84.14**	<empty>
Molar Flow [kgmole/h]	**976.0**	976.0	<empty>
Mass Flow [kg/h]	9543	9543	<empty>
Std Ideal Liq Vol Flow [m3/h]	31.61	31.61	<empty>
Molar Enthalpy [kcal/kgmole]	-1572	-1664	<empty>
Molar Entropy [kJ/kgmole-C]	107.0	105.8	<empty>
Heat Flow [kcal/h]	-1.534e+006	-1.624e+006	8.955e+004

The cooler causes the ammonia and water to partly liquify and so the liquid part is separated in a two-phase separator added next with the inlet defined as the outlet of cooler. The specifications of the separating vessel V-100 are as follows:



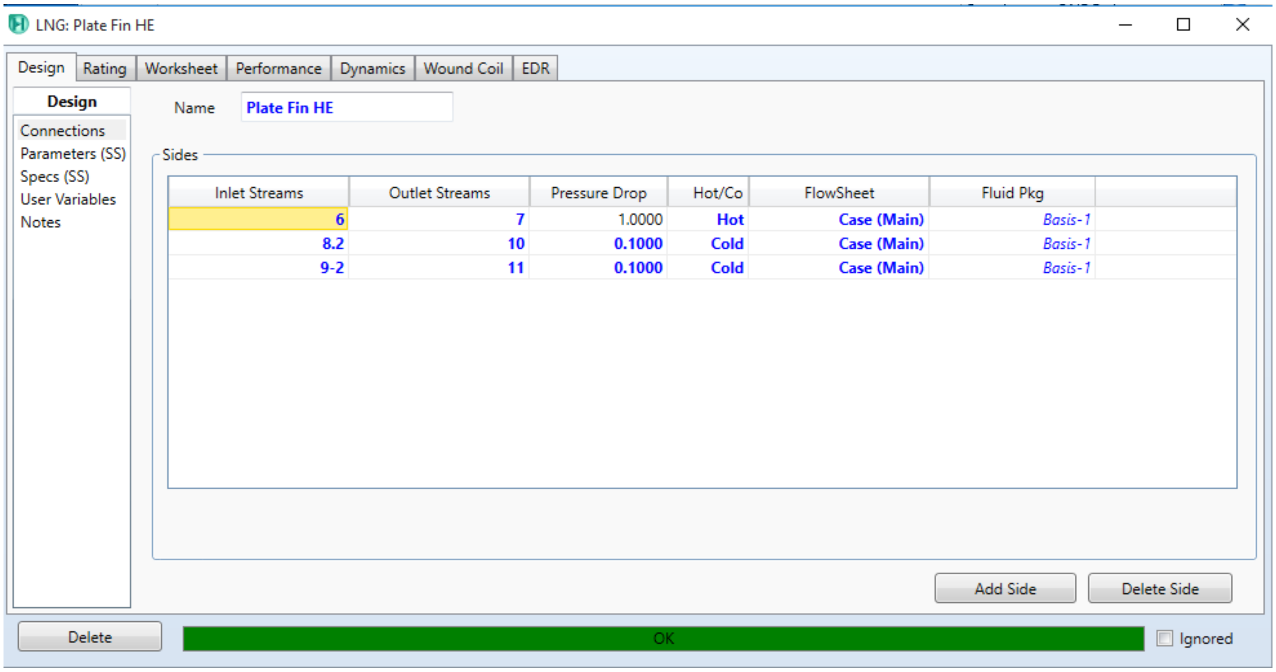
Name	**2**	**4**	**3**
Vapour	0.9996	0.0000	1.0000
Temperature [C]	**40.00**	40.00	40.00
Pressure [bar]	**84.14**	84.14	84.14
Molar Flow [kgmole/h]	976.0	0.4321	975.5
Mass Flow [kg/h]	9543	7.774	9536
Std Ideal Liq Vol Flow [m3/h]	31.61	7.895e-003	31.60
Molar Enthalpy [kcal/kgmole]	-1664	-6.696e+004	-1635
Molar Entropy [kJ/kgmole-C]	105.8	58.42	105.8
Heat Flow [kcal/h]	-1.624e+006	-2.893e+004	-1.595e+006

Now the gaseous outlet of separator is then sent to an adsorber. Adsorber is not directly available in Hysys hence it is modelled with a component splitter. The remaining ammonia and water are completely separated from the gas stream. Specifications of the Adsorber are as shown:



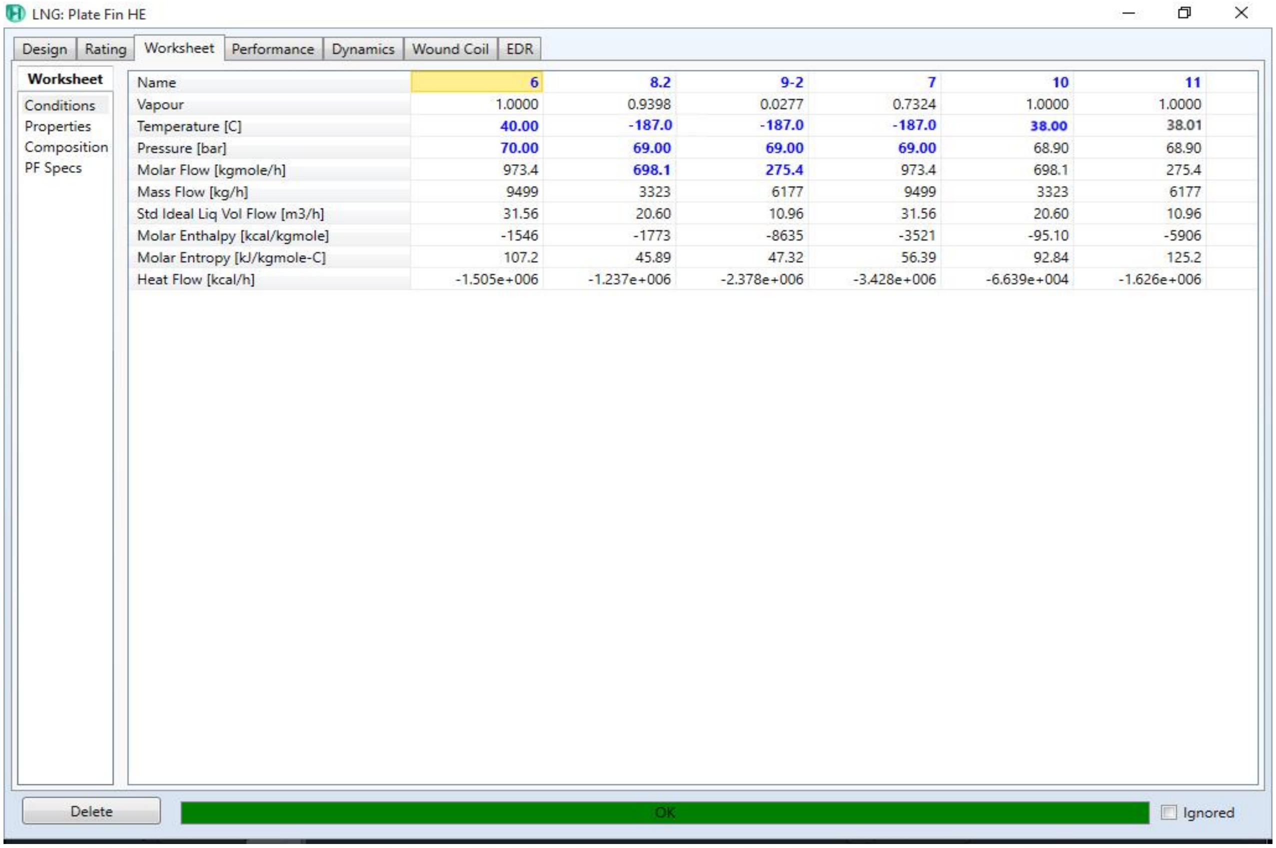
Name	3	6	5	Q Ads
Vapour	1.0000	1.0000	0.0000	<empty>
Temperature [C]	40.00	40.00	40.00	<empty>
Pressure [bar]	84.14	70.00	80.00	<empty>
Molar Flow [kgmole/h]	975.5	973.4	2.079	<empty>
Mass Flow [kg/h]	9536	9499	36.71	<empty>
Std Ideal Liq Vol Flow [m3/h]	31.60	31.56	4.467e-002	<empty>
Molar Enthalpy [kcal/kgmole]	-1635	-1546	-4.994e+004	<empty>
Molar Entropy [kJ/kgmole-C]	105.8	107.2	67.20	<empty>
Heat Flow [kcal/h]	-1.595e+006	-1.505e+006	-1.038e+005	-1.372e+004

After this pretreatment, the main cryogenic process starts. Since we required that the two outlet streams of the separator in the cold box cool this incoming gas we modelled the plate fin heat exchanger with the 'LNG Exchanger' which allows multiple heating and cooling streams. The stream is cooled down to -187°C and the specifications of this heat exchanger are as follows:



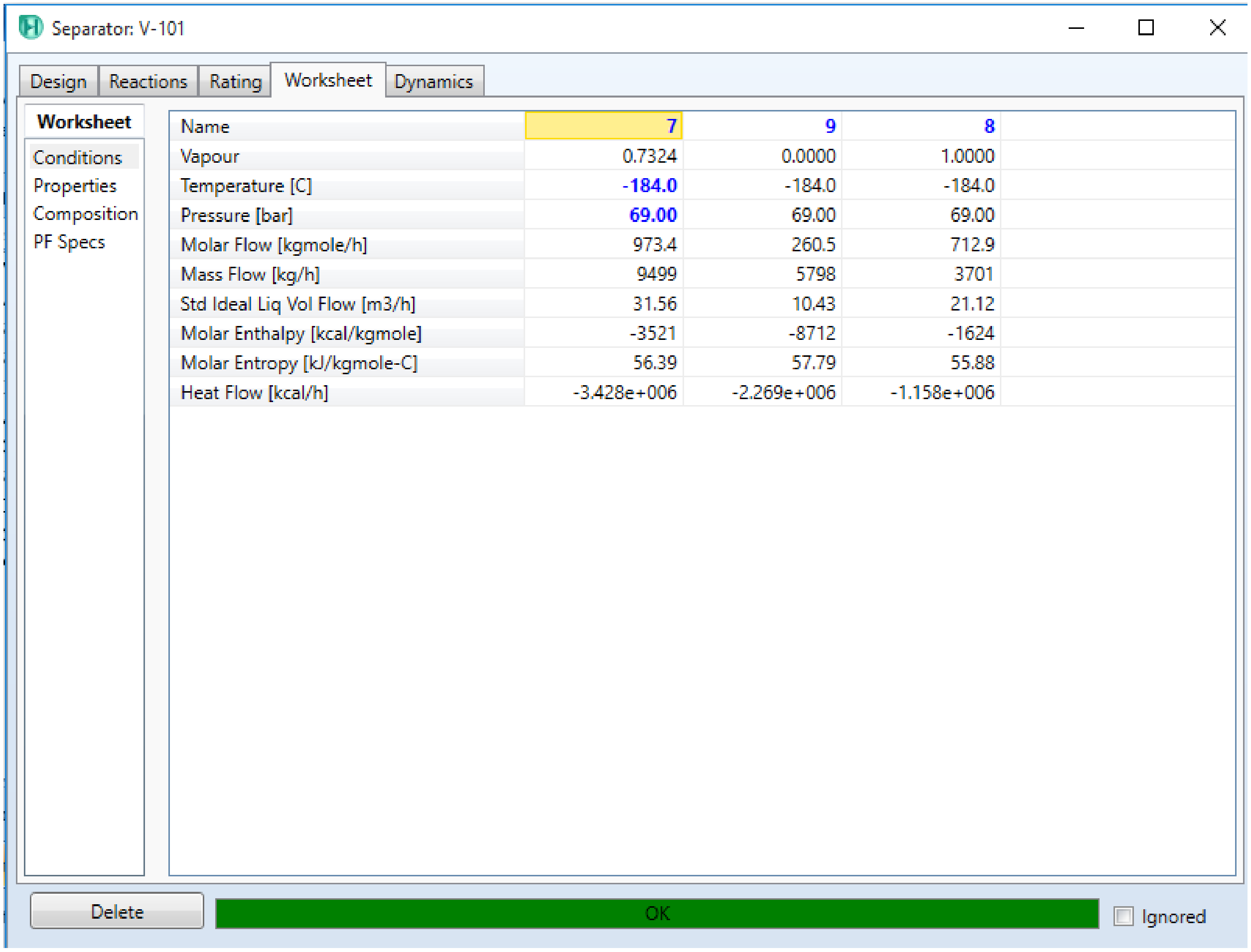
Name: Plate Fin HE

Inlet Streams	Outlet Streams	Pressure Drop	Hot/Co	FlowSheet	Fluid Pkg
6	7	1.0000	Hot	Case (Main)	Basis-1
8.2	10	0.1000	Cold	Case (Main)	Basis-1
9-2	11	0.1000	Cold	Case (Main)	Basis-1



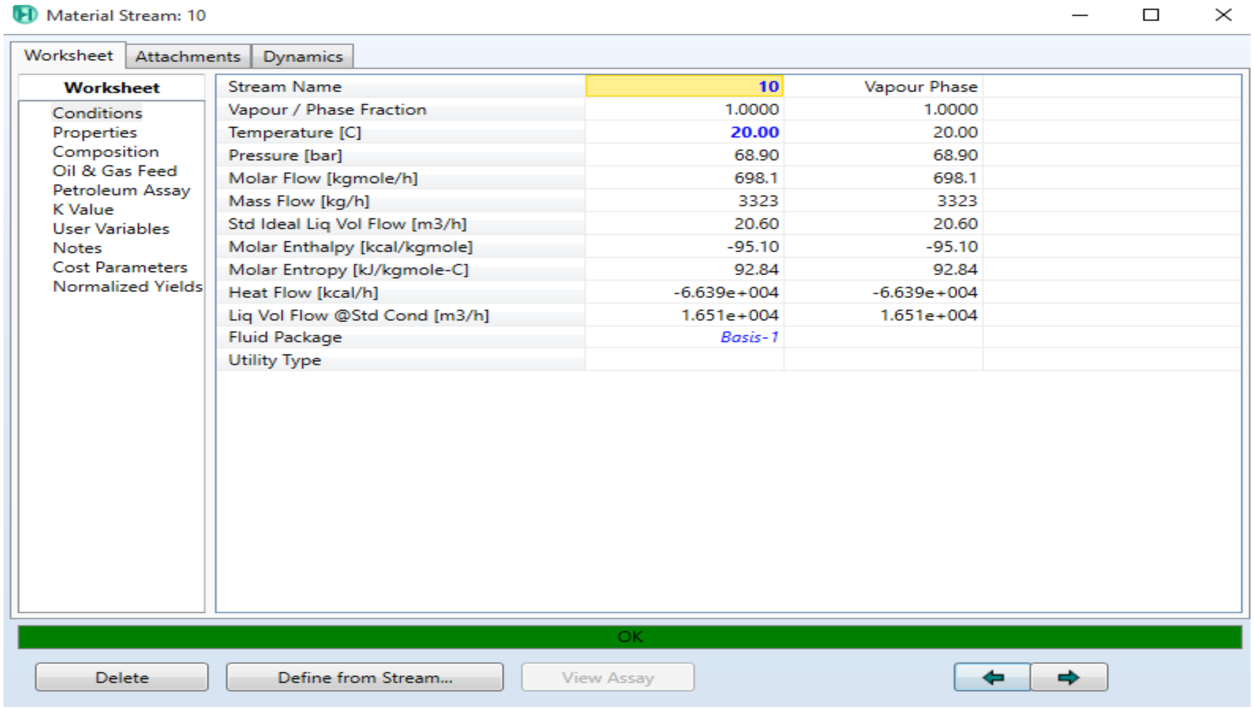
Name	6	8.2	9-2	7	10	11
Vapour	1.0000	0.9398	0.0277	0.7324	1.0000	1.0000
Temperature [C]	40.00	-187.0	-187.0	-187.0	38.00	38.01
Pressure [bar]	70.00	69.00	69.00	69.00	68.90	68.90
Molar Flow [kgmole/h]	973.4	698.1	275.4	973.4	698.1	275.4
Mass Flow [kg/h]	9499	3323	6177	9499	3323	6177
Std Ideal Liq Vol Flow [m3/h]	31.56	20.60	10.96	31.56	20.60	10.96
Molar Enthalpy [kcal/kgmole]	-1546	-1773	-8635	-3521	-95.10	-5906
Molar Entropy [kJ/kgmole-C]	107.2	45.89	47.32	56.39	92.84	125.2
Heat Flow [kcal/h]	-1.505e+006	-1.237e+006	-2.378e+006	-3.428e+006	-6.639e+004	-1.626e+006

The cooled and partly liquified stream enters a separating vessel inside the cold box modelled by a two-phase separator V-101. The details are shown below:

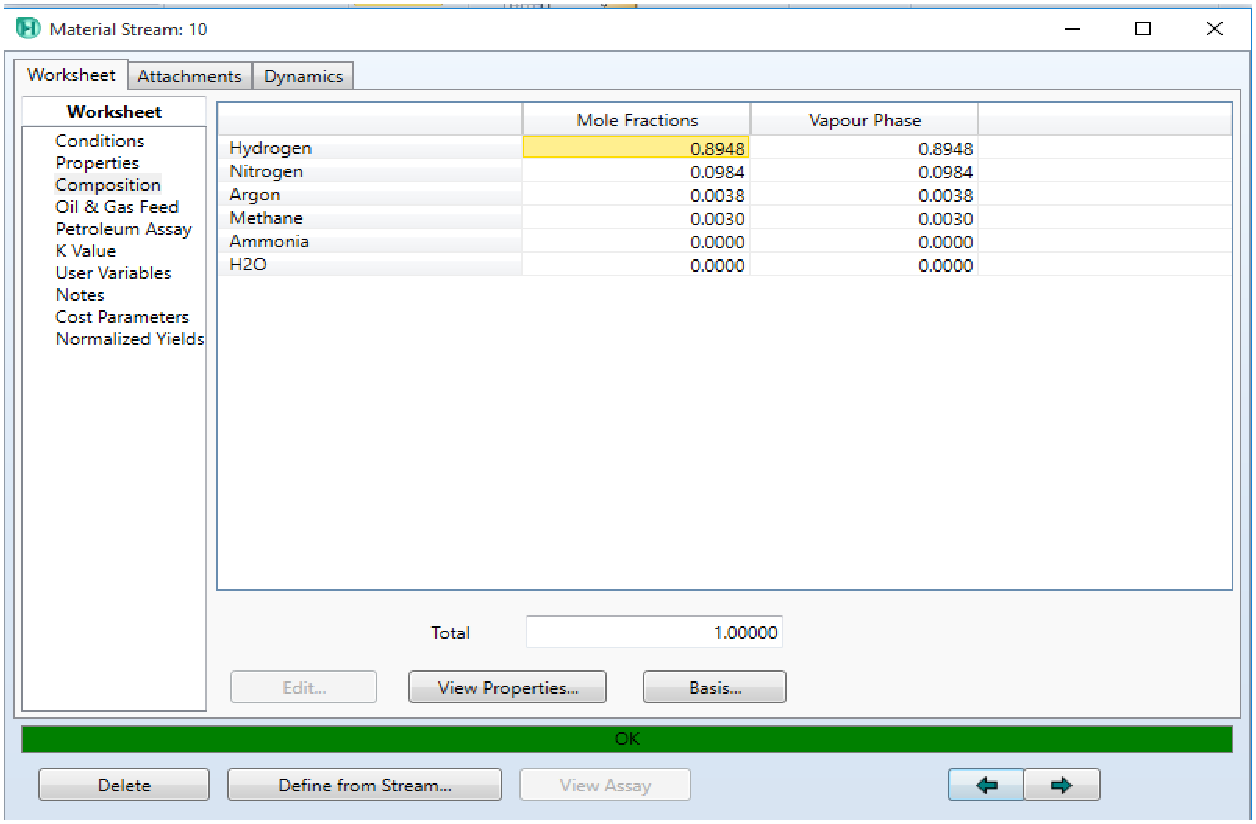


Name	7	9	8
Vapour	0.7324	0.0000	1.0000
Temperature [C]	-184.0	-184.0	-184.0
Pressure [bar]	69.00	69.00	69.00
Molar Flow [kgmole/h]	973.4	260.5	712.9
Mass Flow [kg/h]	9499	5798	3701
Std Ideal Liq Vol Flow [m3/h]	31.56	10.43	21.12
Molar Enthalpy [kcal/kgmole]	-3521	-8712	-1624
Molar Entropy [kJ/kgmole-C]	56.39	57.79	55.88
Heat Flow [kcal/h]	-3.428e+006	-2.269e+006	-1.158e+006

The outlets of this separator enter the Cold box exchanger to cool the incoming stream. In the process of doing so, these streams themselves are heated to product specifications of 38°C and leave the cold box. The liquid outlet 9 changes to 11 to be used a fuel gas while the gaseous outlet 8 is heated to product hydrogen, stream 10 leaving the cold box. The product details are as follows:



Stream Name	10	Vapour Phase
Vapour / Phase Fraction	1.0000	1.0000
Temperature [C]	20.00	20.00
Pressure [bar]	68.90	68.90
Molar Flow [kgmole/h]	698.1	698.1
Mass Flow [kg/h]	3323	3323
Std Ideal Liq Vol Flow [m3/h]	20.60	20.60
Molar Enthalpy [kcal/kgmole]	-95.10	-95.10
Molar Entropy [kJ/kgmole-C]	92.84	92.84
Heat Flow [kcal/h]	-6.639e+004	-6.639e+004
Liq Vol Flow @Std Cond [m3/h]	1.651e+004	1.651e+004
Fluid Package	*Basis-1*	
Utility Type		



	Mole Fractions	Vapour Phase
Hydrogen	0.8948	0.8948
Nitrogen	0.0984	0.0984
Argon	0.0038	0.0038
Methane	0.0030	0.0030
Ammonia	0.0000	0.0000
H2O	0.0000	0.0000

Total 1.00000

This composition table shows an 89.5% pure hydrogen recovered as product which is approximately equal to our manual calculation of 91% pure product hydrogen gas to be recycled back into the synthesis loop.

The overall Simualtion of our process is shown below:

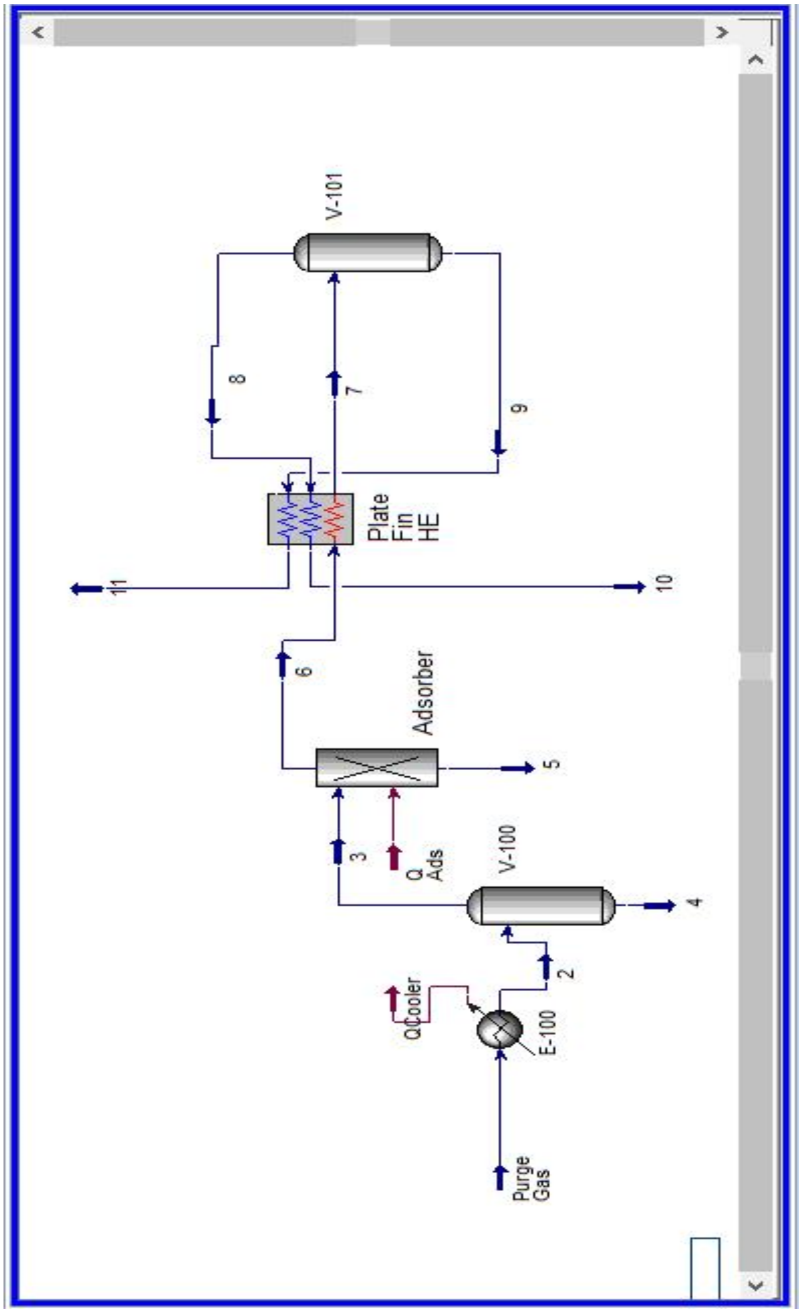


Figure 11 Aspen HYSYS Simulation of Cryogenic Distillation

Chapter 9: Instrumentation and Process Control

Instrumentation and process control is a vital part of any chemical or industrial process occurring nowadays. It adds to safety of the process apart from the automation it imparts and gives more stability and productivity to a designed process. It deals with the measurement and control of process variables to ensure they are in the optimum and safe range. Examples of process variables include temperature, pressure, flow, level, pH, speed etc.

Control loops are the fundamental part of any industrial control system. It consists of a group of components working together to achieve and maintain a measured variable to its desired set point. There are two types of control loops: Open control loop and Closed control loop. Open control loop is one where the controller actions are independent of the process outputs while in closed control loop, also called feedback control loop, the controller responds to changes in the output process variable.

There are generally three main types of controllers; P (proportional), PI (proportional integral) and PID (proportional integral derivative). P controllers give an output proportional to the error, PI give an output to sum of proportional and integral part of error while PID have an added response to the derivative of the error as well. P controllers always give an output with a slight set-off. PI have fluctuations and gradually eliminate the error while PID have a very fast response. In our study we have used PI controllers to as they are mostly applied in the industry. Following are brief examples of how IPC is applied to our system.

9.1 Level Controller

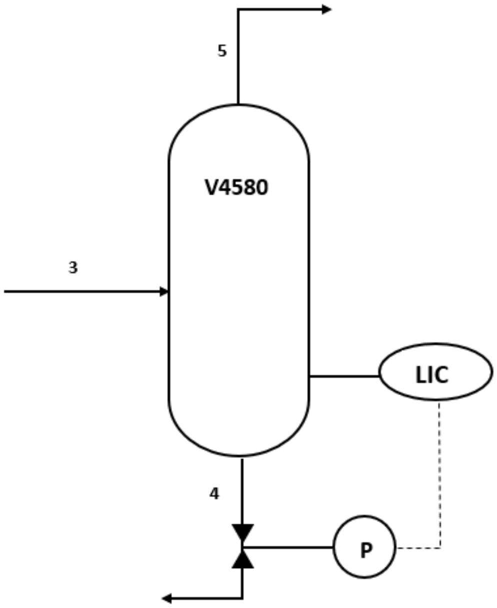


Figure 12 Level Controller

In this fist example, we consider a separating vessel in the pretreatment section. This two-phase separator basically removes the condensed water and ammonia from the purge gas. In the vessel, it is highly important to maintain a certain level in the vessel to achieve efficient separation and proper functioning of the vessel. Therefore, a control loop is developed to maintain this desired liquid level.

Firstly, a measuring element is installed which measures the level in the vessel. Then a transmitter gives this signal to the controller. The controller then gives a corresponding output in the form pf pneumatic pressure on the valve which controls its opening. Hence the level is maintained. In case the level increases above the set point, the controller give an output as such the valve opening is increased so that more flow can occur and the level is brought back to the desired set point.

9.2 Temperature Controller

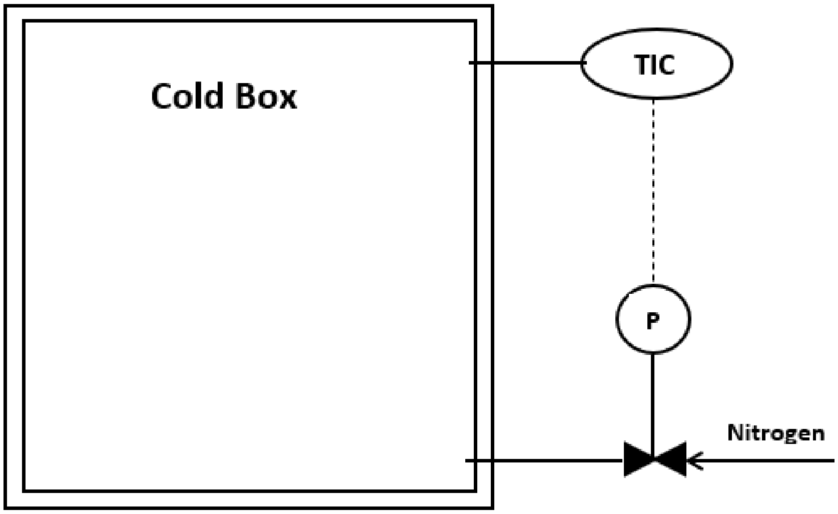


Figure 13 Temperature Control System

This is an example of how controls are applied to maintaining proper cryogenic temperatures in the cold box. The cold box has an internal environment of cold nitrogen gas at around -180°C. The nitrogen is basically is a closed refrigeration loop where the cold box is basically the evaporator part of the secondary circuit. A temperature measuring device like a thermocouple is used to measure the internal temperature of the cold box. It then sends this signal to the controller which checks whether the temperature is above or below the set point. If it is above the set point, the controller output will be as such the opening of valve is increased to allow more refrigerant nitrogen into the box to lower the temperature back to the setpoint.

9.3 Flow-Temperature-Level Controller:

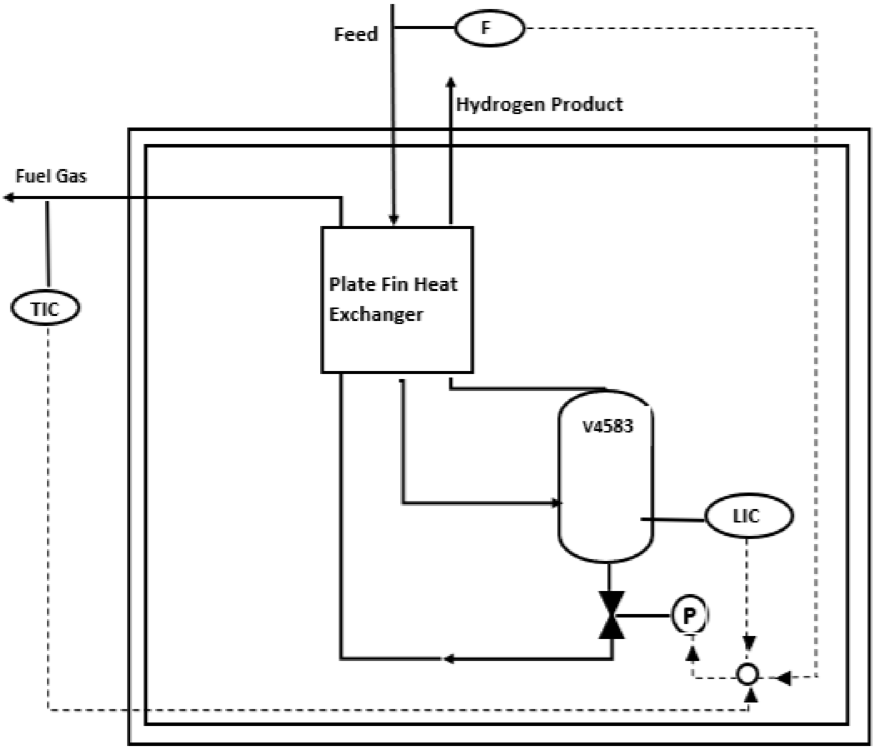


Figure 14 Complete control system in Cold Box

This last example is of a slightly more complex control loop. Again, the equipment is the cold box. The process variable is basically the flow of fuel from the separating vessel. This output is adjusted by multiple factors. So, three control loops are combined to give an enhanced and a well-controlled output. The signals from the flow sensor of the feed, temperature sensor of outlet fuel gas and level sensor of the separating vessel are sent to a controller. The controller combines the error and gives a compromised output so that the flow is as such that all these three variables are controlled. Considering separately, the controller allows more flow thorough the valve by increasing its opening when the level in the vessel increases, or when the flow of feed increases so that extra flow is compensated, or when the temperature of fuel gas decreases so that it is not cooled to below set point. This is a multi-variable control loop designed specifically for our process.

Chapter 10: HAZOP Analysis

Hazard and Operability study is carried out on different lines and vessels to assess different risks that may arise in the plant.

10.1 Two phase separator: Stream no 2

INTENTION: To separate liquid and gaseous phases based on density

Table 24 Hazop analysis on two-phase separator

Process parameter	**Guide word**	**Possible causes**	**Consequences**	**Actions**
Temperature	More of	(1) Less flow rate of cooling water in heat exchanger (2) Appropriate LMTD is not achieved in heat exchanger	Water will not condense completely and will get to the adsorber column and deteriorate the adsorbent.	(1)Check for the temperatures and flow rates of streams in heat exchanger. (2) Install TCV in line 2
	Less of	(1) More flow rate of cooling water in heat exchanger (2) Appropriate LMTD is not achieved in heat exchanger	More power is being consumed without any good reason	(1) Check for the temperatures and flow rates of streams in heat exchanger.

				(2) Install TCV in line 2
Flow	None	Purge gas is not coming from the loop because of failure in splitter valve	The continuous process will be stopped	Check the splitter which splits the purge and recycle gas.
	More of	More percentage is coming in purge stream than specified because of improper functioning of splitter valve.	Separator will be overfilled	Same as above
	Less of	Less percentage is coming in purge stream than specified because of improper functioning of splitter valve.	Expected output would not be obtained from the plant	Same as above

10.2 Plate and fin heat exchanger: Stream no 7

INTENTION: To cool down the coming gases and liquefying most of them

Table 25 Hazop analysis on Plate and fin heat exchanger

Process parameter	**Guide word**	**Possible causes**	**Consequences**	**Actions**
Temperature	More of	(1) Fouling in exchanger (2) Nitrogen environment is not maintained properly	All fuel gases will not be condensed and hence cannot be separated from hydrogen up to the mark.	(1) Check for the nitrogen valve. (2) Check for the flows and fouling in plate and fin heat exchanger
	Less of	(1) More nitrogen is released in the atmosphere. (2) Proper LMTD and flow rates are not being achieved.	More hydrogen will be condensed due to which required purity will not be achieved.	Same as above
Flow	None	(1) Blockage in any of the previous lines (2) Purge gas is not coming to HRU	The continuous process will be stopped	(1) Check all the previous valves. (2) Check the splitter valve in ammonia loop.

	More of	More flow is coming from ammonia loop.	Pressure inside the separator will increase and required purity will not be achieved.	Same as above.
	Less of	Less flow is coming from ammonia loop.	Pressure inside the separator will decrease and required purity will not be achieved.	Same as above
	Part of	Less percentage of hydrogen in the stream due to varying natural gas feed composition	Required ammonia will not be formed and therefore percentage recovery of H_2 will be dropped.	Maintain the feed composition and check for any problem in steam reforming.

10.3 Adsorber: Stream no 5

INTENTION: To adsorb and hence separate out ammonia from the stream

Table 26 Hazop analysis on adsorber

Process parameter	**Guide word**	**Possible causes**	**Consequences**	**Actions**
Flow	None	(1) Complete blockage of flow n adsorber due to extremely dense packing. (2) Purge gas is not coming to HRU	The continuous process will be stopped	(1) Check the void spacing in adsorber. (2) Check for the splitter valve in ammonia loop.
	More of	(1) More void spacing in adsorber than required. (2) high pressure than deigned	Heat transfer in the plate and fin heat exchanger will not be appropriate.	Same as above
	Less of	(1) High pressure drop in adsorber (2) Fouling in pipes	(1) Gases will take more time to liquefy in the exchanger.	(1) Check the void spacing in adsorber. (2) Cleaning of pipes.
	As well as	Ammonia is not completely adsorbed and is present in this	Pipes of cold box will be blocked completely	Check the adsorber. Check whether

		stream due to inefficiency of adsorption column.	due to the freezing of ammonia at such low temperatures.	adsorber is being operated under design conditions or not.
Pressure	More of	More void spacing in adsorber than required.	Improper cooling in cold box due to deviation than designed conditions.	Check the void spacing in adsorber.
	Less of	High pressure drop in adsorber	Same as above	Check the void spacing in adsorber.

Conclusions

- Linde's Cryogenic Process recovers approximately 15000 Nm^3/hr while Membranes recover 13500 Nm^3/hr. On average, they save around $1million/year by Natural Gas saving. [7]
- Cryogenic System has a higher initial investment and operating costs than Membrane System due to maintenance of extremely low temperatures.
- Overall analysis shows, Cryogenic separation is indeed a more effective technology and a more economical process in the long run.

References

[1] https://petrowiki.org/Separator_sizing

[2] https://www.researchgate.net/publication/301625110_ENERGY_SAVING_BY_PURGE_GAS_RECOVERY_UNIT

[3] https://www.linde-engineering.com/en/images/Brochure%20-%20Purge%20gas%20recovery_tcm19-486079.pdf

[4] https://membraneinsider.com/wp-content/uploads/2015/08/prism_membranesystems_for_ammonia_plants.pdf

[5] https://scialert.net/fulltextmobile/?doi=jas.2005.459.464

[6] https://www.ogj.com/articles/print/volume-88/issue-3/in-this-issue/gas-processing/h2-recovery-processes-compared.html

[7] https://www.researchgate.net/profile/Palash_Bhowmik/publication/269984394_Economic_Aspects_of_Setting_up_Purge_Gas_Recovery_Unit_PGRU_with_Ammonia_Production_Process/links/549aa49f0cf2d6581ab21f35/Economic-Aspects-of-Setting-up-Purge-Gas-Recovery-Unit-PGRU-with-Ammonia-Production-Process.pdf

[8] https://www.linde-engineering.com/en/images/30160_LE_Manufacturing_PFHE_brochure_update_RZ_VIEW_tcm19-406598.pdf

[9] http://mimoza.marmara.edu.tr/~zehra.can/ENVE401/5.%20Adsorption%20Column%20Design.pdf

[10] https://www.bre.com/PDF/Advantages-of-Brazed-Heat-Exchangers-in-the-Gas-Processing-Industry.pdf

[11] https://www.seas.upenn.edu/~dlewin/FOCAPD_2004/LECTURE_06_Equipment_Sizing_and_Capital_Cost_Estimation.pdf

[12] https://www.airproducts.co.kr/~/media/Files/PDF/industries/membranes-supply-options-brochure-advanced-prism-membrane-systems.pdf

[13] https://www.linde-engineering.com/zh/images/P_3_2_e_12_150dpi_tcm112-5772.pdf

[14] http://dl4a.org/uploads/pdf/Coulson%20Richardson%27s%20Chemical%20Engineering%20Vol.6%20Chemical%20Engineering%20Design%204th%20Edition.pdf

[15] https://www.scribd.com/document/392007315/1989-Bookmatter-ChemicalEngineeringEconomics

[16] HRU Linde Manual from FFC

[17] http://www.essentialchemicalindustry.org/chemicals/ammonia.html

[18] Chemical Process Technology by JACOB A. MOULIJN MICHIEL MAKKEE ANNELIES E. VAN DIEPEN, 2nd edition

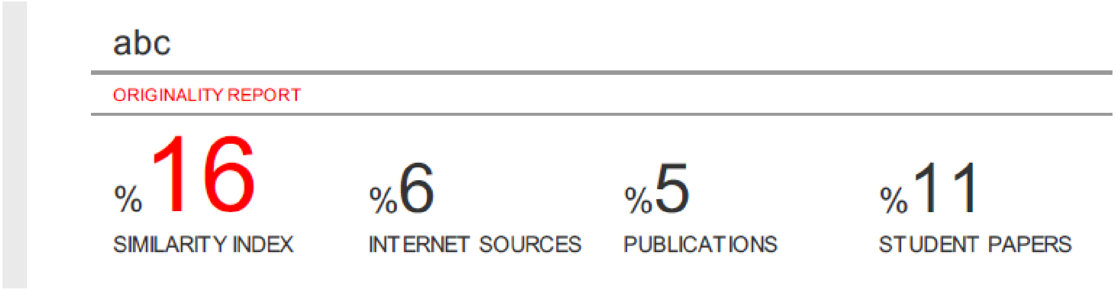
[19] https://education.jlab.org/itselemental/ele001.html

[20] http://thermopedia.com/content/1121/

[21] http://www.thermopedia.com/content/1036/

[22] https://www.mechanicalbooster.com/2018/03/reciprocating-air-compressor.html

[23] https://www.mech4study.com/2017/11/centrifugal-compressor.html



abc

ORIGINALITY REPORT

%16	%6	%5	%11
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS