

DESIGN AND INTEGRATION ANALYSIS OF CRYOGENIC AIR SEPARATION

UNIT

A Thesis

by

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ABSTRACT

Industrial Gas market is expected to grow to \$106 billion from \$76 billion by 2022 parallel to the global energy and chemical production sector growth. Air separation is one of the major technologies utilized within this industry to supply Nitrogen, Oxygen and Inert gasses for various industrial applications. Cryogenic separation has emerged as a technology of choice for high capacity and high purity units, but it is also known for its high energy intensive characteristic. Cryogenic air separation units (CASU) utilize electricity to produce refrigeration for liquefaction and separation of air components, operating near temperatures as low as 78 K and consuming around 200kWh/ton oxygen product. Even 1% increase in efficiency can result in millions of dollars of energy savings annually.

CASU technology inherits tight heat integration with approach temperatures of up to $\sim 1^{\circ}\text{C}$ in the heat exchangers due to refrigeration at very low temperatures. This work is intended to systematically study and analyze the dependence of energy usage of this technology on process design, utilize the insights of this analysis to develop a framework for design improvement and operation of the plant, and develop heat integration map of the unit operations. Benchmarking of this heat integration is performed using pinch analysis. As part of the work, sensitivity analysis of the complex thermally coupled sequential distillation system is also presented. Well established benchmarking and targeting techniques pioneered by Dr. El- Halwagi are used to investigate the 'big picture' without getting into heat exchanger network details. The novel insight presented

by this research is the dependence of enthalpy flow into the separation section on the product recoveries. A unique way to assess heat flow by dissecting the process into smaller control volume helps in overall enthalpy balance which helps in estimating important process parameters. This helps in reducing the handles available for process modification. Finally, a case study is presented where the implementation of control volume approach and resultant process improvement is demonstrated.

DEDICATION

This work is dedicated to my parents Dr. Renu Goel and Dr. Nirankar Goel who gave me the strength to believe in myself and encouraged me to pursue my dreams. Without their sacrifices, I wouldn't be where I am today.

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CONTRIBUTORS AND FUNDING SOURCES

Contributors

This work was supervised by a thesis committee consisting of Dr. Mahmoud El-Halwagi [advisor] and Dr. Ahmad Hilaly of Artie Mcferrin Department of Chemical Engineering and Dr. Hisham Nasr-El-Din of Harold Vance Department of Petroleum Engineering.

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NOMENCLATURE

CASU	Cryogenic Air Separation Unit
CAPEX	Capital Expenditure
GAN	Gaseous Nitrogen
GOX	Gaseous Oxygen
HP	High Pressure
HEN	Heat Exchange Network
KW	Kilo Watts
LAR	Liquid Argon
LOX	Liquid Oxygen
LP	Low Pressure
MJ	Mega Joules
N ₂	Nitrogen
PFD	Process Flow Diagram
PPM	Parts Per Million
PSIA	Pounds per Square Inch
T-T	Tangent to Tangent length
XIC	Concentration Indicator and Controller

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1. INTRODUCTION

Air constituents of majorly Nitrogen, Oxygen, and Argon along with few other trace gases. These three major constituents are used in various processes and applications in a multiple industries. Nitrogen is used as inert gas in oil, gas and petrochemical plants, oxygen is used in pharmaceutical, metal and feed for production of chemicals like Methanol, Vinyl Acetate etc. Argon is used as inert gas in arc welding and cutting, light bulbs manufacturing. The industrial gas market is growing at fast pace and expected to grow to \$106 billion by 2022 [2]. Hence production of these gasses via separation of air components is expected to increase as well. With increasing demand and production, it is equally important to not only utilize the most economical path way but also most efficient, sustainable, safe and energy efficient process. Large scale production typically works on cryogenic process. Cryogenic Air Separation Units (CASU) are highly energy intensive. Energy demands of the order of 200 kWh per ton of Oxygen product has been reported [3]. At such high level of electricity consumption, a small improvement in process efficiency or yields may have a substantial financial impact. Researchers have been working on improving the process and its control systems for many years and have helped this technology to evolve significantly. From a detailed patent and literature review it was observed that the design for CASU has been modified numerous times. This provides the motivation that the designs in use are not optimal and might still be much farther away from the actual optimal energy targets. Consequently, in this work we propose to apply targeting and benchmarking techniques to analyze the

process design, understand the complexities and propose improvements that are not only incremental but as close to target as possible. For a given amount of power consumption, it will be demonstrated that multiple product yields are possible by process modification.

1.1. Properties of Air

Air is a mixture of many elements in gaseous form along with various suspended impurities like dust particles organic matter and other pollutants. Water is also present in air which we know as humidity. The major components are however, Nitrogen, Oxygen and Argon. A detailed composition of air is shown in table 1.1 as per data in [28] [33].

Table 1.1 Typical composition of fresh air

Components	Fraction of air	Components	Fraction of air
Nitrogen	78.09%	Methane	1-2 vppm
Oxygen	20.95%	Acetylene	<1 vppm
Argon	0.93%	Krypton	1.14 vppm
Carbon dioxide	350 vppm	Nitrous oxide	0.5 vppm
Carbon monoxide	3-4 vppm	Hydrogen	0.5 vppm
Neon	18 vppm	Ozone	0.4 vppm
Helium	5.2 vppm	Xenon	0.087 vppm

1.1.1. Thermodynamic Properties

The main components of air which take part in distillation are Nitrogen, Oxygen and Argon. Nitrogen is the lightest component while Oxygen is heaviest. Boiling points of the three components at various pressures of interest are given in Table 1.2.

Table 1.2 Boiling points for major air components

Component	Normal Boiling Point	Boiling Point (20 psia)	Boiling Point (85 psia)
Nitrogen	77.42	80.14	96.12
Argon	87.33	90.35	108.0
Oxygen	90.18	93.22	111.0

The critical point of air is 132.5 K and 549.08 psia. So, air can be liquefied only at temperatures below 132.5 K. Once liquefied, the air has to be distilled. It is easier to separate the components at lower pressure distillation column as observable in the xy-VLE charts in figure 1.1 below.

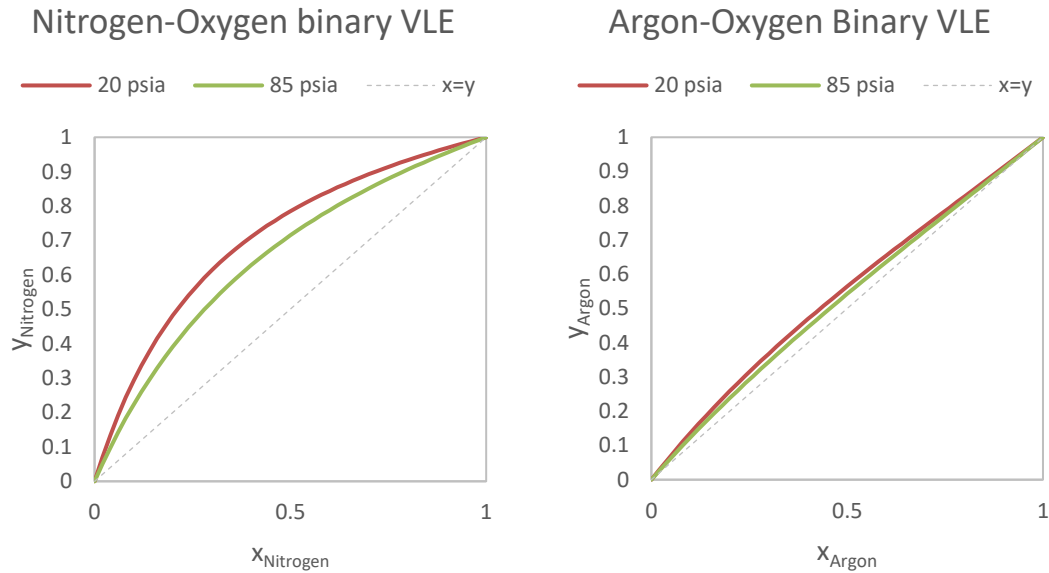


Figure 1.1 Binary vapor-liquid equilibrium (VLE) data for air components

1.1.2. Air Contaminants and their Removal

Air contains a variety of components in trace amounts. For any process to operate reliability and safely, it is very important to consider the physical behaviors, concentration and exit route for each of these components. For a continuous process, if these components are not controlled in the feed and if they do not have an exit route, they can gradually build up and deteriorate equipment performance as well as pose a safety hazard. For analysis in this research, the feed air is assumed pre-treated.

1.1.2.1. Hydrocarbons

Hydrocarbons like Methane, Ethane as well as heavier species will condense on low temperatures and would eventually accumulate in the system or freeze on the surface of heat exchangers. Since the heaviest fraction is taken out from LP column bottom as liquid oxygen, these hydrocarbons will be most concentrated in that stream. Hence it is recommended that the concentration of HCs in liquid Oxygen stream is limited to 450 ppm “methane equivalent” which corresponds to 1% of LEL. [11].

1.1.2.2. CO₂ and N₂O

CO₂ and N₂O are reported to cause plugging issues in the CASU unit [11]. Since they form solid solution hence, as a best practice of plant operation, their concentration should be limited to less than 50% of their solubility in liquid and gas stream.

1.2. Safety Considerations in Air Processing

In addition to the operational risks of concentration, low temperature condensation and deposition of components that may affect process reliability and safety, the CASU process has four major hazards: rapid oxidation, embrittlement, pressure excursions due to vaporizing liquid and oxygen enriched or deficient atmosphere [11]. Oxygen is a very hazardous compound and has capacity to cause explosions due to rapid oxidation. The oxygen processing lines need special surface preparation to eliminate any possibility of foreign particles hitting the pipe walls and initiating ignition. The air separation industry has recognized these are special hazards and pay special attention to them.

1.3. Air Separation Technologies

The process of separation of air components can be mainly classified in two major categories, namely, cryogenic processes and non-cryogenic processes. As the name suggests, cryogenic processes operate in sub-zero temperatures and high pressure where air is compressed, cooled, liquefied and then separated using fractionation. On the other hand, non-cryogenic processes utilize adsorbents, chemicals and polymeric membranes to perform the separation. Based on the scale of production, required product purities, type of product required (Nitrogen, Oxygen, both, both + Argon), different technologies and their configurations are selected on case by case basis.

Cryogenic processes are mostly used for high purity and high rate of production for example, Oxygen for coal/petcoke gasification unit, methanol production units, Vinyl Acetate Monomer (VAM) production and Nitrogen for ammonia production, refinery inert gas production, semiconductor manufacturing, and food processing industry.

2. CRYOGENIC AIR SEPARATION PROCESS

2.1. Technology Evolution

The research undertaken in this thesis project build upon the Praxair's design of CASU. During the literature survey, it was observed that there has been substantial modification proposed by Praxair in the technology design. In patent filed in 1993 [8], three columns were used in series, thermally coupled to each other. The heavy stream was progressively transferred to the next column in series. Although the process yields are not disclosed, one can easily figure out that the process is highly capital intensive. In the patent filed in year 2003 [9], a double column arrangement operating at high and low pressure and thermally coupled to each other was disclosed but with an additional intermediate pressure column which pre-fractionates the feed. The technology disclosed in 2008 patent [10] is one of the most commonly used commercial design. The process used in this research as a base case for various analyses is also based the same. Most of the commercial industrial gas producers use the two column arrangement with a third column to produce Argon product. The processes vary slightly in terms of operation parameter, heat exchange network and pressure profiles, but the overarching theme remains the same.

2.1.1. Single Column Design

It is worth mentioning that the first air separation process was much elementary in nature and had just one column operating at lower pressure ranges. Carl von Linde first developed air liquefaction process where the compressed air was cooled by

countercurrent flow of cold vapors. In 1902, he constructed single column distillation system where pure Oxygen could be separated from air by rectifying the liquid air in the column. The Nitrogen produced from this process was impure with high Oxygen concentrations. This is because the single column process did not have any reflux stream to knock back the Oxygen in the vapor. It was only in 1910 when the double column process was developed which both pure Nitrogen and Oxygen could be produced.

2.2. Dual Column Design - Process Description

Dual column process produces nitrogen liquid at high pressure which is then used as reflux in low pressure column. This research is based on dual column process which is depicted in figure 2.1. Ambient air is taken as the feed to the unit. Since air contains many other components in addition to the component of interest, namely Oxygen, Nitrogen and Argon, a pre-treatment process is required to bring the quality suitable for Cryogenic processing. The first step in any air separation plant is filtering, compressing, drying and cooling the incoming air feed. This pretreatment process helps in removing moisture, dust and particulate matter, heavy hydrocarbons which liquefy on cooling and tend to freeze inside the cryogenic equipment. The pre-treatment process involves compressing the air to a pressure of 87.5 psia, then cooled using chillers to condense out the water vapor. Some of the cooling is provided by cooling water. The low temperature chillers are often operated on waste nitrogen product stream as a cooling medium. After the compression and cooling, the dried gas goes for filtration and absorption process to remove Carbon dioxide and residual water vapors, hydrocarbons. It is important to remove these components as they can freeze and deposit on the surface

of low temperature equipment, deteriorating their performance. For example heat exchangers or distillation column tray/packing fouling severely reduces their performance efficiency. Molecular sieves are often deployed for this task.

Post compression and purification, the air feed is split into three streams, one fraction is further compressed to 1600 psia using a booster compressor and cooled using cooling water followed by cooling in HP heat exchanger by using high pressure pumped liquid oxygen (Pumped-LOX) product stream and a fraction of waste nitrogen stream. The resultant air feed stream is in liquid/dense phase which is expanded in a turbine to 87.5 psia and fed to HP column. Another fraction of the compressed and purified air feed stream is cooled in LP heat exchanger and fed to the HP column bottom. This stream is in the temperature range of 100-125 K and provides the heat duty to the HP column. A third and final fraction of the purified and compressed air feed stream is processed through heat pump using cooling water exchanger and LP heat exchanger as heat sink to produce the remaining refrigeration for the system. This stream is fed to LP column's rectification stages.

HP column with its two feed streams one being liquid/dense and other relatively warm produces pure nitrogen (99.99 mol%) at the top and crude oxygen enriched liquid. These Nitrogen vapors are condensed in the condenser/reboiler heat exchanger installed inside the LP column sump. This arrangement thermally couples the two columns. HP column pressure is set such that the condensing temperature of Nitrogen vapors is slightly above the reboiling temperature of oxygen product in LP column bottom. The Nitrogen liquid produced is used as a reflux for both HP and LP column. HP column

bottom stream enriched in Oxygen is then sent as a feed to LP column. Before this stream is introduced to LP column it is routed through subcooler. A part of subcooled stream provides Argon condenser duty which increases the vapor fraction of the stream as it enters the column.

LP column receives feed from HP column bottom and cooled gas feed from heat pump arrangement outlet. Additionally, some fraction of liquid/dense feed is also sent to LP column. This column receives reboiling duty by condensing HP column overhead vapors in the submerged HP condenser/LP reboiler heat exchanger. The reflux to this column is the remaining fraction of Nitrogen produced in HP column, which is subcooled before its introduction to LP column. Subcooling helps in reducing the flashing of the stream upon pressure reduction to LP column conditions. The LP column produces pure Oxygen product (99.7-99.8 mole %) in the bottom in liquid phase, and pure Nitrogen product (99.99 mole %) at the top. An Argon rich side stream is extracted from LP column (around the stages which are rich in Argon but extremely lean in Nitrogen) and fed to Argon column (super fractionator) where a part of incoming Argon is extracted as a liquid product. The remaining liquid, mainly containing Oxygen, is transferred back to LP column. It is extremely important that the Argon feed has minimal Nitrogen contamination, to maintain the Argon product purity.

All the unrecovered air components, which is largely Nitrogen, is purged out of the system as waste Nitrogen rich product stream which plays major role in heat integration. Essentially, all the product streams leaving the system are brought to ambient temperature, except Argon liquid and LIN (if applicable). This is implemented

in multiple heat exchange zone described above as LP and HP heat exchangers and the subcooler. Nitrogen gas product, GAN, is the lowest temperature stream, which is used to subcool the Nitrogen reflux stream to LP column along with the waste nitrogen rich stream.

Any cooling above temperatures of 304 K can be achieved by using cooling water and air as the cold utility, but there is no other cold utility in the system. This means that any cooling required within the process has to be generated by the refrigeration system i.e. the turbines and expanders within the process.

As described above, the Oxygen product can be produced at high pressure in this process by pumping the Oxygen liquid before it is vaporized. This eliminates the need of gas compression post vaporization which results in CAPEX savings. Also, compression of Oxygen poses additional safety issues. This type of process is called Pumped-LOX process. In order to vaporize the high pressure liquid oxygen, air feed pressure plays an important role as well [25]. Air pressure depends on required GOX pressure and its location relative to the critical pressure. As mentioned by Bruce et al. in [25], above critical point, higher air pressures in general give better heat exchange thermodynamically.

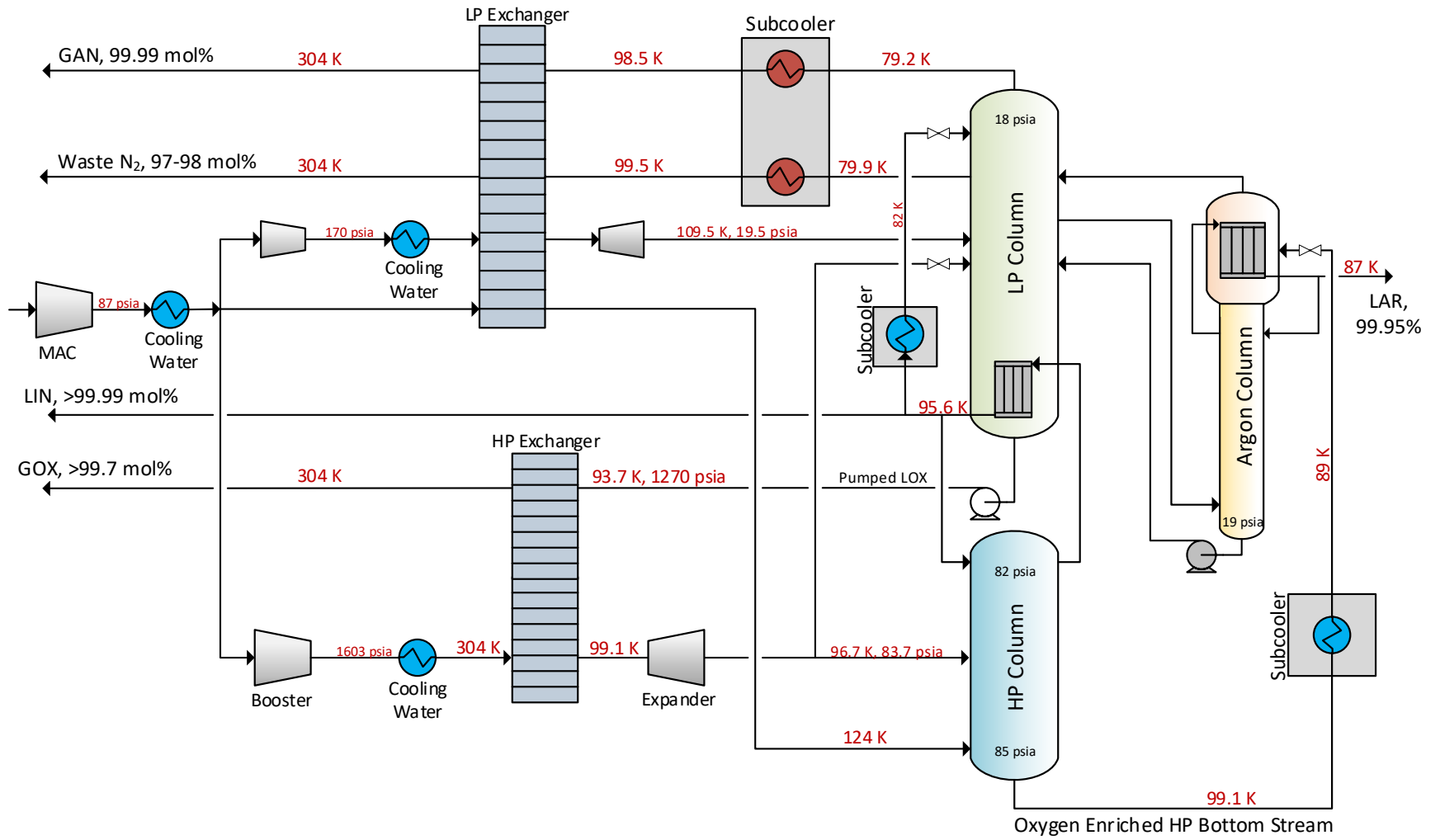


Figure 2.1 Air separation unit - Process Flow Diagram (PFD)

3. PROCESS SIMULATION

3.1. Thermodynamic Property Package

Replicating the actual behavior of fluids in various unit operations critically depends on accuracy of vapor liquid equilibrium and hence the thermodynamic property package used. Especially in this case, where the temperatures are as low as 80K, it is very important that proper package is used for the properties. Industrial gas producers like Praxair, Linde etc. develop or modify their thermos packages based on the operational experience and their in house research and development work. It is recognized that this information is highly confidential for each company which they develop by collecting multiple data points from plant operation. For academic purpose, the next best substitute is untuned version of known property methods that nearly match the actual process. From literature survey it was found that Peng–Robinsons equation of state, modified by Stryjek and Vera and using Lee–Kessler vapor pressures (PRSV-LK) is well suited for academic studies [15] [16] [17].

3.2. Simulation and Analysis Tools

The steady state simulation model is built in Aspen HYSYS. This choice was made based on ease of use, availability of cryogenic plate type heat exchanger model, availability of thermodynamic package, provision for integration with other software and references available in published research. For thermal pinch analysis, a spreadsheet developed by IChemE, which is available on open platform is used.

3.3. Pressure Drop in Equipment

Choosing the optimal configuration of CASU distillation column and its mass transfer components is not only important for the separation performance, but vital to keep capital and operating costs minimal. Structured packing is now the accepted industry standard for cryogenic air separation application. They provides a large surface area per volume, which maximizes the contact area for vapor and liquid while maintaining adequate superficial velocities. They produce enhanced mass transfer performance and creates substantially lower pressure drop as compared to conventional distillation trays.

Air Products and Chemicals demonstrated the improvements in improvements due to structured packing in their patent [24], where it is suggested that the pressure drop is in the range of 0.2 to 0.5 inches of liquid per theoretical stage. As compared to a typical value of 1.5 inch liquid for a tray. They also demonstrated that the increase in theoretical trays for structured packing application does not have the expected energy penalty due to increased pressure drop. This is because of increased separation efficiency and hence recovery of products. Height equivalent to theoretical plate (HETP) is reported in the range of 7 to 9 inches [29], which can be used to calculate the column T-T length.

4. SENSITIVITY ANALYSIS

The CASU technology has many process variables and design variables that can be manipulated to modify the process performance. Some of these need to be optimized while some act as handles to control the performance. Each unit operation itself can have multiple configurations and operating conditions. For example, distillation column feed locations, feed quality and rate etc. will affect the separation and efficiency of the column. The product streams affect the heat integration, hence the feed quality (figure 4.1). So to understand the effect of these variables on the performance, sensitivity analysis was performed on each such handle individually.

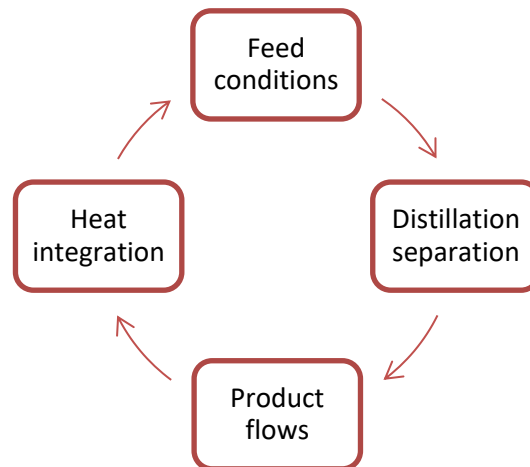


Figure 4.1 Interdependence of separation and heat integration

4.1. HP Column Design and Sensitivity Analysis

The high pressure column primarily does the job of separating the Nitrogen from a part of the air feed and producing liquid nitrogen stream which is used as reflux in the low pressure column. A liquid/dense phase stream is fed at an intermediate stage in addition to vapor feed stream at the bottom. This column does not have any external

reboiling duty and works on the enthalpy provided by the vapor phase feed received at the bottom. The condensation duty is provided by LP column bottom boiling liquid.

As for a typical distillation column, putting in more heat duty improves the separation. So was observed in the HP column. Fixing the specification of the HP column distillate stream at 99.99% Nitrogen, increased duty to the column in the form of higher feed temperature improves the separation yield as shown in figure 4.2.

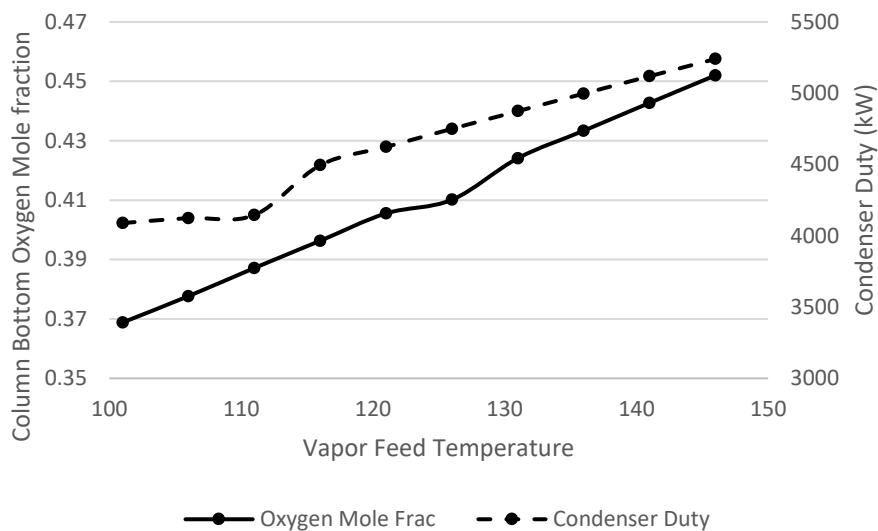


Figure 4.2 Feed temperature (heat duty) sensitivity at fixed distillate purity

The column did not show much sensitivity for change in liquid/dense phase feed location and based on sensitivity analysis, its location was fixed at 50th theoretical stage. Also, the number of theoretical stages in the column can be changed in view of CAPEX vs OPEX tradeoff. Based on literature, a 62 theoretical stage column was selected. The pressure of this column is tied to the LP column bottom. It should be high enough so that Nitrogen condensation temperature in HP column is higher than Oxygen reboiling temperature at low pressure. Figure 4.3 shows effect of number of trays on separation.

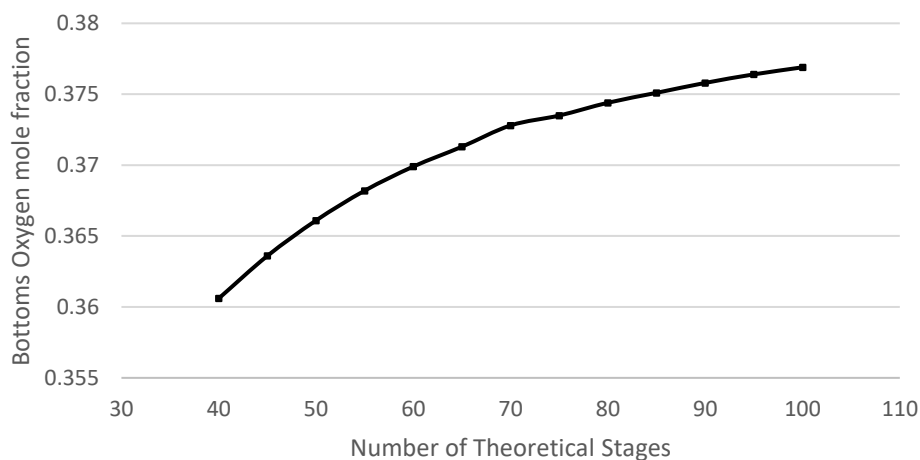


Figure 4.3 HP column number of theoretical stages vs Oxygen product purity, at fixed distillate composition

4.1.1. HP Column Reboiling Design Modification

Since it was observed that the gas phase air feed entering at the bottom of the column is 78% nitrogen while the bottom product stream of HP column is ~60-65% Nitrogen, the feed entering at the bottom stage might be contaminating the bottom liquid product. A case study was performed to check if there is some improvement in separation of the column performance when the reboiling activity is performed separately and the air feed location is changed from bottom most stage to a few stages above it, as shown in figure 4.4. The study showed no improvement in the separation as the loss of stripping action of vapors in the few stages dominated the minor improvements in Nitrogen concentration in vapor due to reboiling. Essentially, the air is not hot enough to provide generate substantial vapor between bottom most stage and the gas feed entry stage. Benefit of this configuration can be realized if substantially hot air (~300K) were used as a feed to HP column.

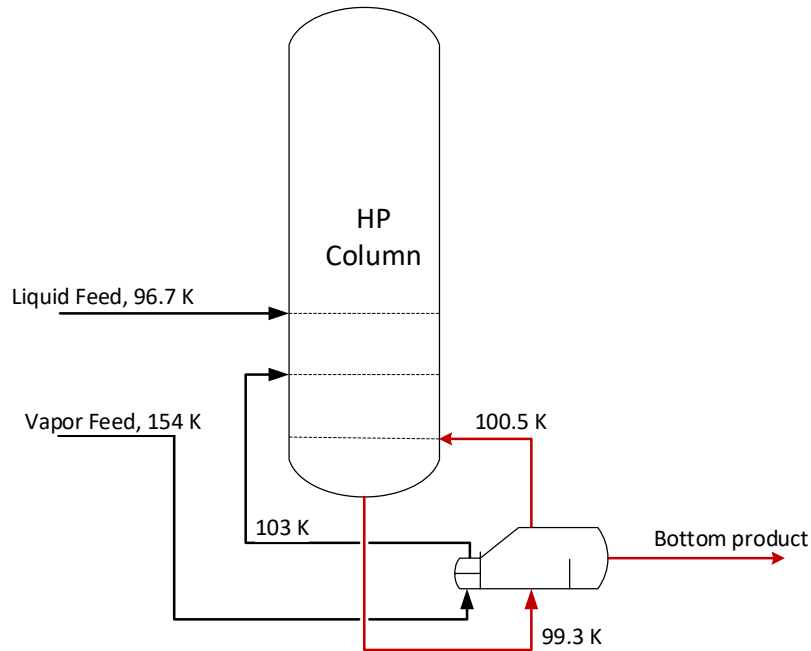


Figure 4.4 HP column design modification case study

4.1.2. HP Column Heat Duty Sensitivity

As discussed before, the HP column in base case design does not have any external reboiling duty. However, the hotter the gas phase air feed to the column, the more vapor traffic will be there in the column, and hence a better separation would take place if adequate condensing duty is provided for increased reflux. The major changes that would occur due this manipulation are higher Nitrogen reflux to LP column and lower flow rate of oxygen enriched stream: This improved separation in HP column reduces the separation efforts required in LP column. It is observed that Oxygen and Nitrogen production increases from LP column while the waste nitrogen production is reduced. Argon production changes negligibly.

While the above improvements are favorable for the process efficiency, increased reboiling duty to LP column has its own effects. Higher heat input to LP column will require increased cooling/condensing duty. The increased reflux to LP column does not pacify this because it is simply a compensation for reduced oxygen enriched stream flow. The net liquid to the LP column from HP column is still the same as before, only the composition and splits have changed. Since the oxygen enriched stream plays a critical role in heat integration, it is important to see the effect of reduced flow of this stream.

Moreover, if we assume a control volume around LP column, the net heat input to the column increased. Enthalpy analysis, discussed in later section, will demonstrate that LP column reboiling has to be restricted based on amount of cooling/refrigeration available for a stable operation of column.

4.2. Argon Column Design and Sensitivity Analysis

The Argon enriched gas feed from LP column is processed in Argon column to recover pure Argon product. The Oxygen along with unrecovered Argon is sent back to the LP column which adds to the liquid flow. Argon column also does not have any reboiler and all the enthalpy is entering along with the gas feed at the bottom stage. The condensing duty to Argon column is obtained by vaporizing a part of subcooled and flashed HP bottoms (Oxygen enriched) stream. As shown in figure 4.5, the condensed liquid is partially used as reflux and remaining is drawn out as LAR product.

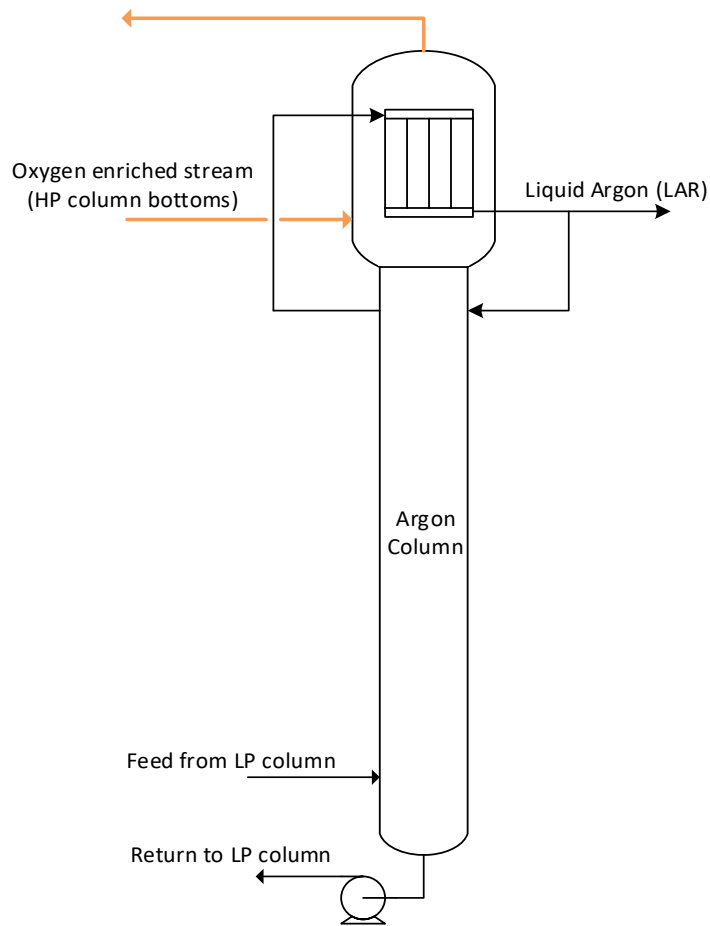


Figure 4.5 Argon column schematic

4.2.1. Argon Purification Section Design Variations

In some designs, it is observed that Argon purification is done in two steps, similar to the configuration shown in figure 4.6. The side draw from LP column is processed in Crude Argon column where Argon with any trace Nitrogen quantity is separated from Oxygen. This is the more difficult separation and requires large number theoretical stages. The Crude Argon produced as distillate is then fed to the Pure Argon column where any Nitrogen that may have accompanied feed is purged out from the top

section. Pure Argon product is collected from the column bottom. This particular arrangement improves the resilience of the process against Nitrogen entrainment in the LP column side draw but at higher capital cost. If the LP column has sufficient theoretical stages, Nitrogen free Argon feed can be produced.

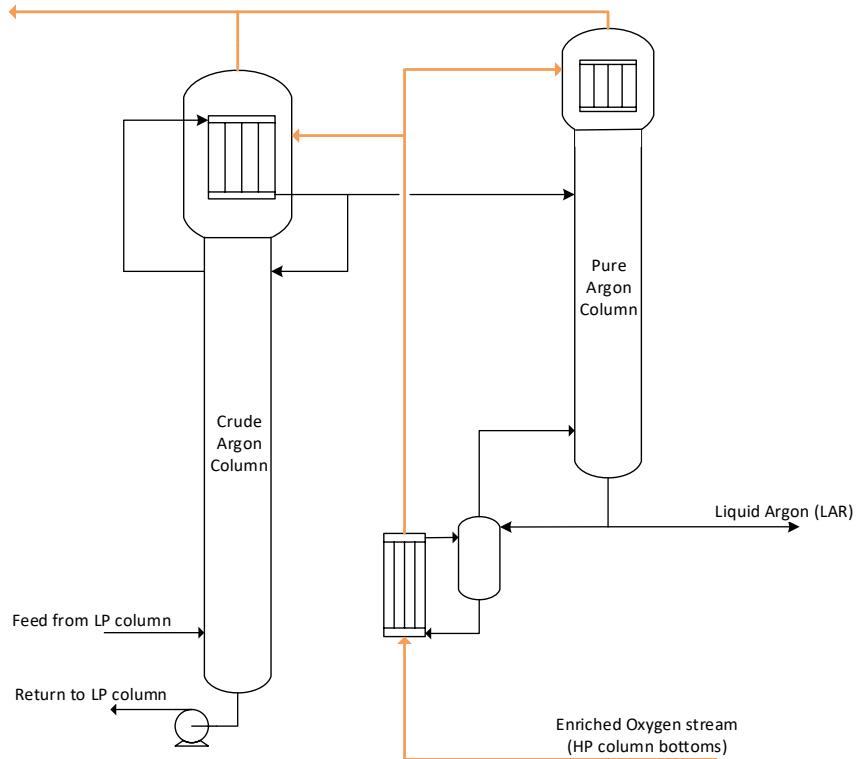


Figure 4.6 Two column Argon purification process

4.2.1.1. Heat Balance of Two Arrangements:

Since the net amount of Argon feed in vapor phase is same, and since all of it has to condense to either form Argon product or liquid recycle back to LP column, the overall heat balance remain constant for a given feed rate. In absence of external reboiling duty, the total enthalpy balance remain the same. Any reboiling duty to Pure Argon column is provided by HP bottom stream.

For a given feed quality and rate, the design handles available is the number of theoretical stages. This is because the top purity requirement is fixed based on Argon product purity specification, hence there's no degree of freedom left. The only parameter that will change by changing number of theoretical stages is the amount of Argon that can be recovered from the feed. A sensitivity analysis was performed for this and it was found that recovery improves only up to a certain increment in number of stages (figure 4.7). In other words, recovery starts to decrease drastically after a threshold value of number of theoretical stages in column. This analysis helps determine the optimum number of stages for the column, found 85 in this case.

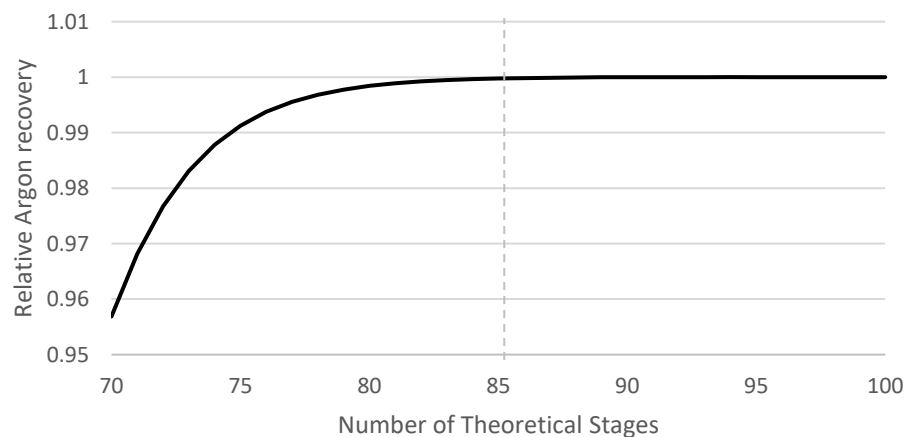


Figure 4.7 Argon column number of theoretical stages vs product recovery

4.3. LP Column Design and Sensitivity Analysis

The low pressure column is the unit operation where the actual separation of Oxygen occurs. This is a complex column with multiple feed streams and multiple sections of varying vapor-liquid traffic (figure 4.8). Since the column operates at low pressure, it harnesses the improved vapor liquid equilibrium of Oxygen, Argon and

Nitrogen. As observed earlier, it is easy to separate these components at low pressure than high pressure.

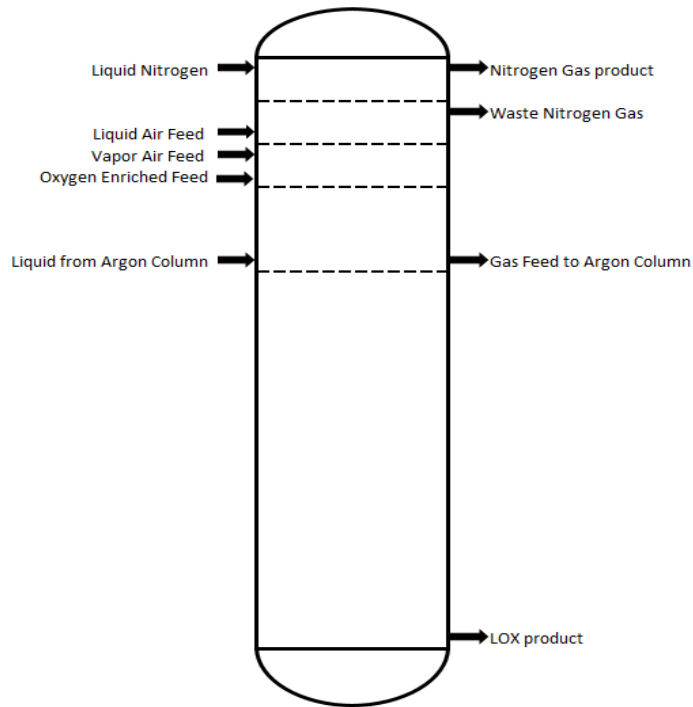


Figure 4.8 Low pressure column feed and product streams with relative locations

The LP column receives Oxygen enriched feed from HP column bottom, a fraction of liquid/dense phase air feed coming from HP heat exchanger and a refrigerated cold air supply from the heat pump section. These feed streams bring certain amount of enthalpy with them and hence provide cooling to the column at corresponding stages of their entry. This is important because the entry of these streams change the vapor liquid traffic in the column, hence the separation of components. In addition to that, there is a 99.99% pure Nitrogen reflux coming from the HP column condenser, after getting subcooled by exiting product streams. The reboiling duty is provided by HP column

condenser-LP column reboiler heat exchanger, which is typically submerged in the LP column sump. Linde mentions various advances in the condenser equipment over the years [23], two of such arrangements are shown in figure 4.9.

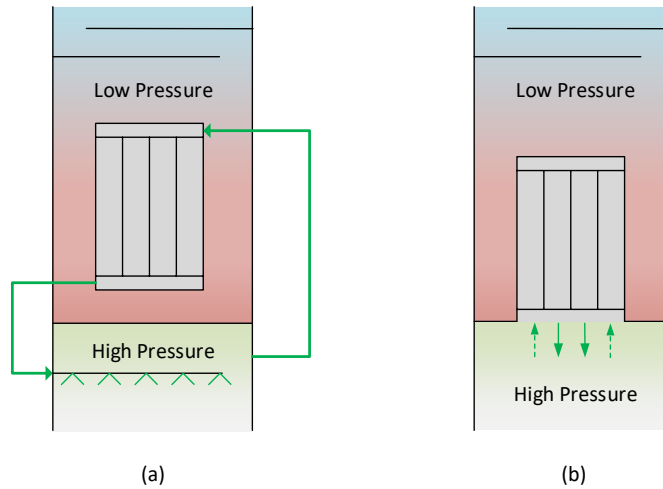


Figure 4.9 Schematic of Condenser/Reboiler heat exchanger arrangements

One of the configurations of LP column used in the research (Case 1, described in section 5) is shown below as an example of typical LP column feed distribution.

Table 4.1 An example of LP column feed distribution

Feed stream	Theoretical Stage	Rate (kmol/h)	% Total Feed
Liquid Nitrogen	1	1425	(28%)
Air feed (liquid/dense)	12	1169	(23%)
LP air feed (vapor)	13	538	(11%)
O2 enriched feed	18	1881	(38%)
Argon Column liquid	31	900	(recycle)

Since the separation of the Nitrogen and Argon is easy, it takes only a few stages in the top section of the column to produce waste nitrogen stream (~98%) and pure Nitrogen gas product from the air feed. A major portion of the column, in the bottom

section, is used for Oxygen-Argon separation since these are close boiling molecules. Sensitivity analysis comes handy to decide the exact locations for each stream. Figure 4.10 shows composition profile inside the LP column. As can be observed, Nitrogen is quickly stripped off the air feed in the top section. It is also worth noticing that Argon concentration peaks in mid-section of the column where it is most beneficial to draw out the feed for Argon purification section as long as Nitrogen concentration is within tolerable limits. The middle section works to strip off any Nitrogen going towards the bottom section and also to rectify the vapor going up to minimize the Argon and Oxygen losses with waste Nitrogen stream. The bottom section and also to rectify the vapor going up to minimize the Argon and Oxygen losses with waste Nitrogen stream.

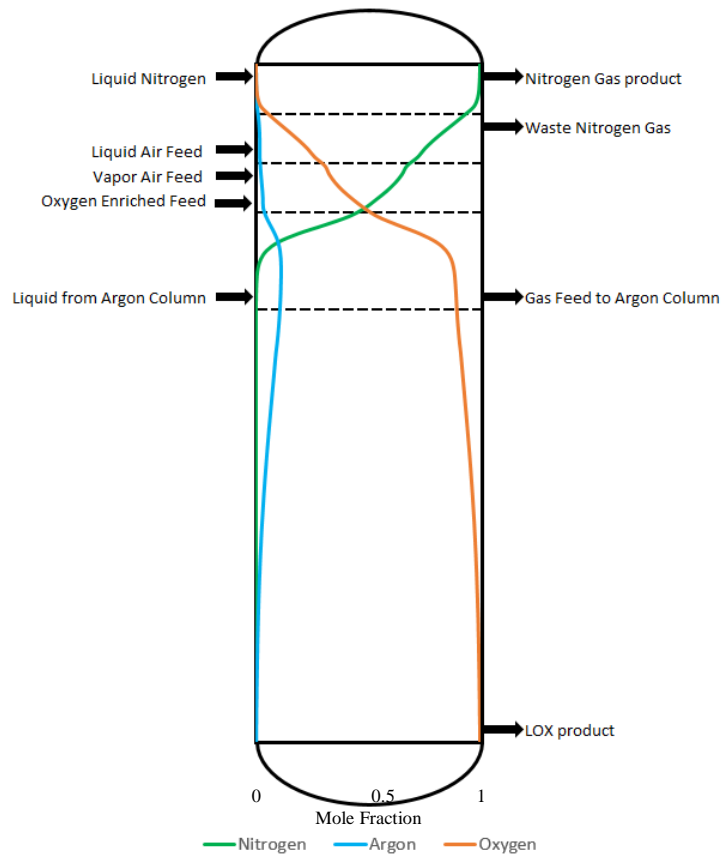


Figure 4.10 Composition profile of LP column

4.3.1. Waste Nitrogen Draw-off Location

A major portion of the feed goes out of the system as waste nitrogen stream, which constitutes of mainly nitrogen (97-98 mole %) along with unrecovered Oxygen and Argon. Any Argon or Oxygen that exits via this route is a loss, hence it is important to limit their concentration in this stream. The liquid reflux through the top portion of the column rectifies the vapors going up which will eventually exit as waste nitrogen or GAN. There should be sufficient number of theoretical stages between the air feed inlet and the waste nitrogen draw stage to make allow proper rectification of vapors. This requires moving the vapor draw stage upwards. But this reduces the number of stages available to purify the remaining vapors before they reach the top. This trade off needs to be balanced critically by studying the sensitivity of this stage location (figure 4.11). For the design used in this research, stage 7 was found to be optimal. It is to be noted that the air feed location was assumed fixed. Shifting air feed location down to facilitate separation in top section would affect the Oxygen-Argon separation, hence might result in higher total number of theoretical stages required in column.

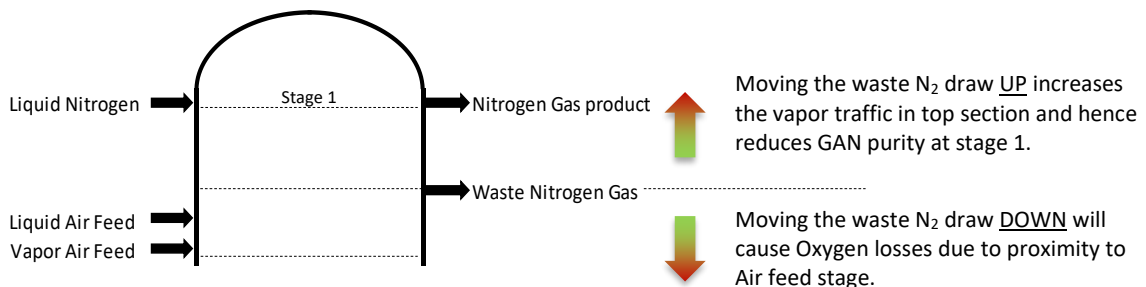


Figure 4.11 Waste nitrogen product draw off stage location

Furthermore, it was seen that amount of waste Nitrogen can be optimized. The amount of Nitrogen not taken out as GAN will eventually exit as with the waste stream. Also, the more the vapors in the top section (stage 1 to stage 7), the harder it is to rectify them with the limited amount of reflux. Hence, we observed waste nitrogen is a handle to control the GAN purity. If GAN purity goes down, waste Nitrogen draw should be increased. This was implemented in the simulation model as shown in figure 4.12. It was also observed that the bottom section of the column was not affected by this manipulation.

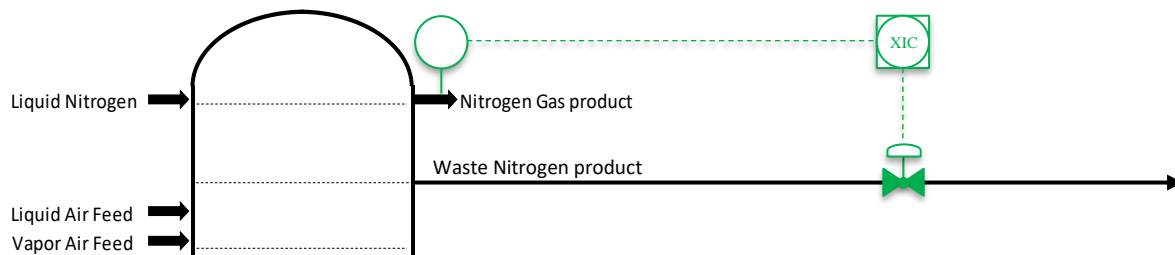


Figure 4.12 GAN purity control handle. Waste nitrogen flow is manipulated to control GAN purity.

4.3.2. Oxygen Enriched Feed Stream Conditions' Sensitivity Analysis

As vapor fraction of this stream increases, the column basically has more vapor traffic than what the limited reflux can rectify. This causes an increase in the Oxygen and Argon concentration in waste nitrogen stream. It is important to capture these Oxygen and Argon molecules in order to separate them in the stripping section of the column to produce pure products. On the other hand, the too little vapor fraction of this stream cause over refluxing of the column, which cause contamination of Oxygen product by Argon as well as contamination of Argon feed by Nitrogen.

4.3.3. Argon Feed Rate Sensitivity

The Argon column feed from LP column and the liquid from Argon column back to LP column is a long recycle loop. The flowrate of argon column feed is another parameter which is available to operator and can potentially affect the performance. Obviously, the rate will affect the capital costs for Argon recovery and purification section. Higher flow means fatter distillation column. To see how much improvement does the Argon column feed rate has on Argon recovery and what effect it has on LP column separation performance, the argon column feed rate sensitivity analysis was performed.

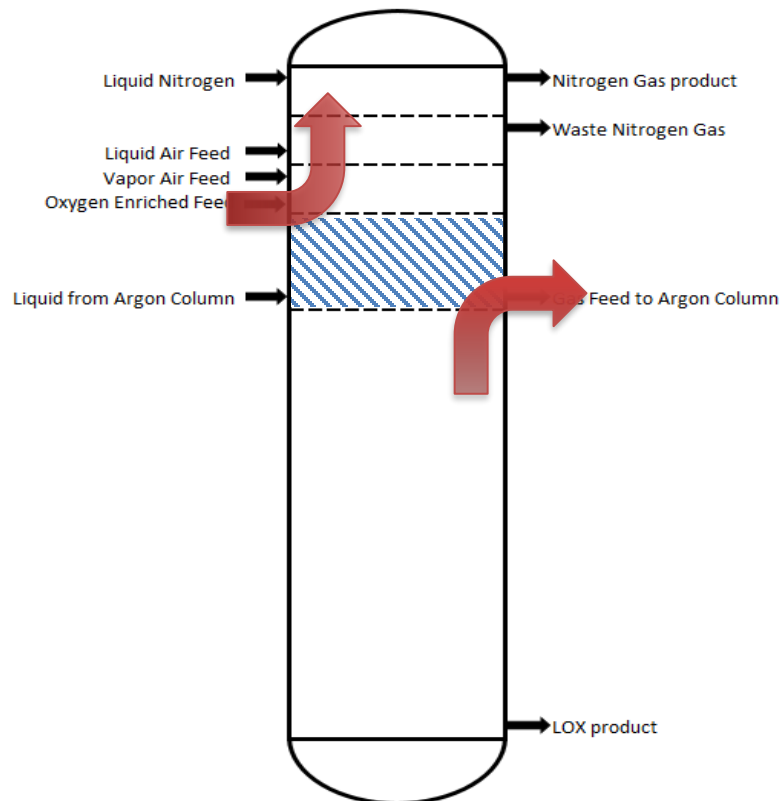


Figure 4.13 Enthalpy balance w.r.t. Argon feed loop

When more Argon feed is withdrawn from the column, since it is in gas phase, it takes a lot of enthalpy out with it. The liquid return from the Argon column bottom is having much less enthalpy because of the loss of latent heat of vaporization. Also, the vapors going up the column are now reduced while the liquid going down the column increases. The delta enthalpy around the theoretical stage of Argon feed and liquid return is approximately = (Enthalpy of vapors – Enthalpy of liquid). This heat goes out of the Argon column as the condenser duty (and some with the LAR). But, it is interesting to note that the condenser duty is provided by the oxygen enriched HP bottom stream which is routed to the LP column. So, on an overall scenario, the enthalpy comes back into the column, only now it comes at a different location, depicted in figure 4.13.

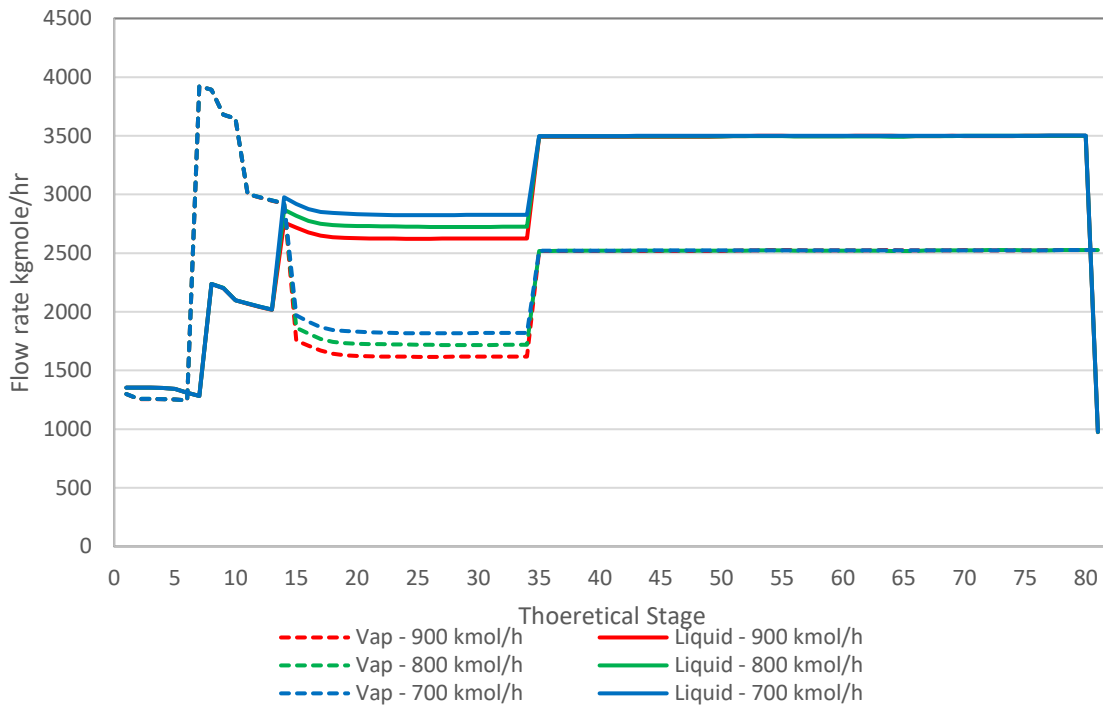


Figure 4.14 Effect of Argon feed rate on LP column traffic

The vapor fraction of oxygen enriched stream increases due to this heat absorbed from argon condenser. This increases the vapor traffic in the column and compensates for the reduced vapor from the Argon feed stage. Similarly, the reduced liquid fraction of oxygen enriched stream is a compensation of increased liquid flow due to liquid returning from Argon column. This can be seen from figure 4.14 as well. As more flow is pulled out of the LP column for Argon feed (around stage 35), the more vapor and liquid traffic drops in that section of the column.

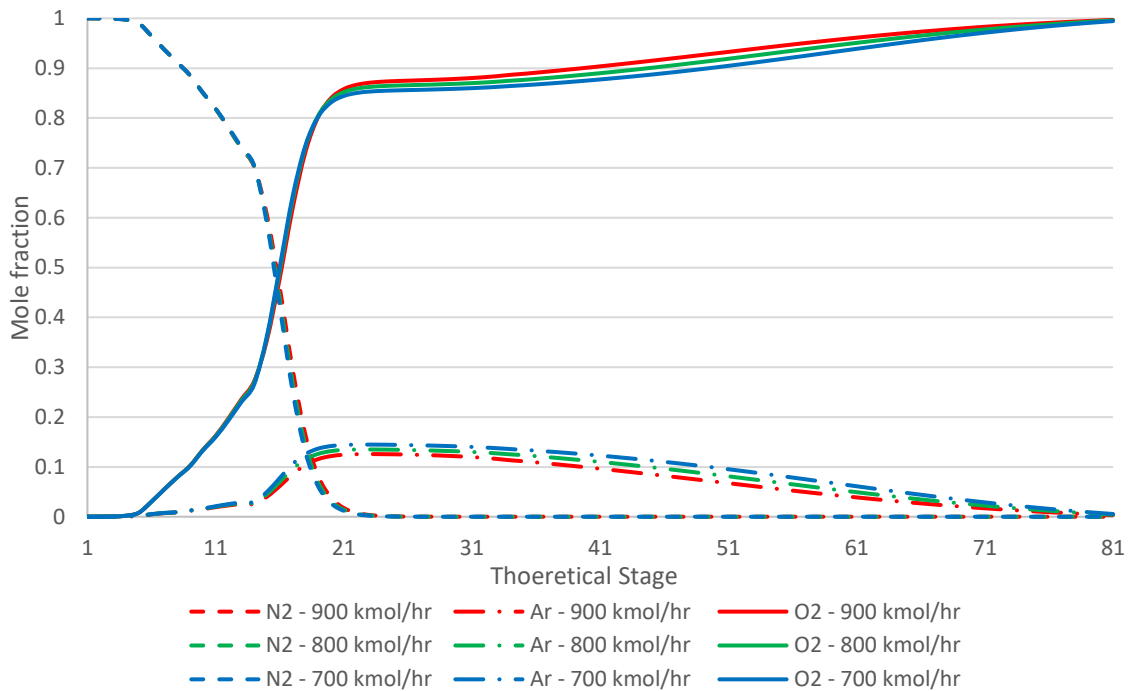


Figure 4.15 Effect of Argon feed rate on LP column profile

Due to change in internal vapor and liquid streams, the composition profile of the LP also gets modified. With increased Argon column feed, there is more reflux to the bottom section of LP column, hence Oxygen concentration increases and Argon

concentration is suppressed. It is worth noting that for higher flow rate of Argon feed, the concentration of Argon in the stream is lower. Hence the absolute amount of Argon going out of the LP column for recovery in Argon column is balanced. The top section of the column does not get disturbed much as evident in the data plotted in figure 4.15.

4.3.4. Oxygen-Argon Separation

A major section of the LP column is utilized for Oxygen and Argon separation. Argon feed is withdrawn near stage 32 and the returning liquid is put back below the same stage. The exact location can be optimized by performing the sensitivity analysis. If the column has excess reflux/liquid traffic/refrigeration it is reflected in Oxygen purity. Argon starts to contaminate the LOX. Hence this portion is limited by the reboiling duty. LOX purity can be controlled by controlling reboiling duty. This is one of the factors that fixes the amount of reboiling duty in LP column.

5. ENERGY AND INTEGRATION ANALYSIS

Since CASU technology is highly energy intensive, each design modification should be evaluated not only on yield improvement but also on overall energy consumption and self-sufficiency in providing required refrigeration to the cold sections of the process. In this context, benchmarking approaches are vital and can help quantify the true capability limits of the manufacturing assets. As per pinch methodology described by Dr. El-Halwagi's [1], the focus is on "Big Picture" at the very beginning of analyses. This means that before we make changes to the process for manipulating a specific utility consumption and demands, for a given process, we can actually get energy targets using pinch analysis. This analyses provides minimum heating and cooling utility targets irrespective of the detailed design and heat exchange network (HEN). This helps in keeping the focus on bigger issues during the analysis phase. One does not have to worry about the detailed design of heat exchange network because irrespective of how simple or complex the network is, irrespective of the number of heat exchangers utilized, the minimum amount of heating and cooling utilities as identified in pinch analysis would have to be supplied to the process.

The CASU process has high level of integration and multiple streams exchange heat in the actual flowsheet. To simplify the investigation, thermal pinch analysis is done whenever a major change is made to the process. If the utility targets obtained from thermal pinch analysis does not show any cold utility requirement (error tolerance of +/- 0.5% of total process refrigeration duty) then it is indicative of the fact that a suitable HEN can be developed to achieve those targets. The complexity of the HEN and hence

the capital cost associated with it might vary and should also be evaluated. One of the advantages with the CASU process is that the heat exchangers utilized are plate type exchangers which can handle multiple hot and cold streams in various channels based on temperature and area requirements.

Moreover, various enthalpy balance envelopes are created to analyze the overall heat inflow or outflow. While analyzing the heat flow within the process, it was observed that some heat transfers operations are just internal to the process and can be eliminated to in some selected contexts, making the analysis easier.

5.1. Effect of Subcooling HP Bottom Stream

Oxygen enriched HP bottom stream when flashed to operating pressure of LP column has a boiling temperature lower than the Argon condensation temperature. Hence the stream is used as a cooling media for extracting the Argon condensation duty. As learned in the sensitivity analysis, the vapor fraction of this stream is extremely important for LP column operation. Hence to reduce the amount of vaporization of this stream, it is subcooled via Waste Nitrogen stream and GAN stream straight out of the LP column. The HP bottom stream is at temperature higher than 100 K hence it is feasible to exchange heat to warmer hot end temperatures of subcooler. The subcooled HP bottom stream when flashed has now lower vapor fraction and hence can provide adequate duty to Argon column without excessive vaporization. The figure 5.1 shows how the ‘low quality cooling’ of GAN and waste nitrogen beyond the Argon condensation temperature is converted to ‘high quality cooling’ that can be used to condense Argon column vapors.

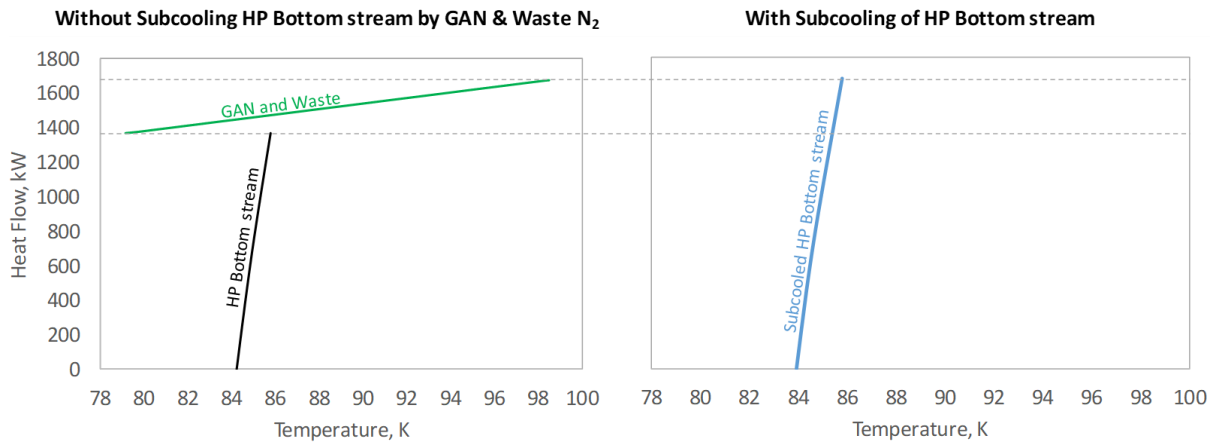


Figure 5.1 Effect of Subcooling the HP Bottom stream to maintain post Argon condenser vapor fraction

5.2. Thermal Pinch Analysis

Thermal pinch analysis is a critical step in this study as it helps in evaluating various modifications in the process without actually delving into the detailed heat integration and network design. The following example will illustrate the utility of the pinch analysis. It is to be noted that for temperatures above 304 K, it was assumed that ambient air or cooling water will be utilized for all the heating cooling. Hence the pinch analysis was performed for heat exchange below 304 K. Furthermore, all the effluent streams were heated to 304 K except liquid Argon and liquid Nitrogen (if applicable). The compressor outlets were cooled to 304 K using cooling water and then only the process streams were used to provide further cooling.

Preliminary design was developed by following the data presented in Praxair patent [10]. Since the patent discloses only limited process data, various design details and process parameters were set by insights gained from sensitivity analysis. Mainly, air

feed stream conditions, split and processing were modelled using the disclosed process data.

5.2.1. Pinch Analysis Case Study

In the base case simulation model (Case 1), the product yields obtained for Oxygen and Argon were low. Since the difficult separation is that of Oxygen and Argon from the air, it can be commented that the process performance was low. One of the identified reasons was inadequate vapor flow in stripping section. Using the knowledge acquired from previously performed sensitivity analysis, to improve the process, some additional heat duty was provided to the LP column which enabled higher separation in the stripping section resulting in higher vapors available for Argon column feed and improved yields. This duty was provided by increasing the gas air feed temperature to HP column. Note that HP column bottom Nitrogen concentration was kept constant during this analysis hence the Nitrogen reflux purity increased from 99.99% to 100%. It was observed that HP bottom stream was not able to provide required condensing duty to Argon condenser. In other terms, the LP column could not converge if the HP bottom stream was allowed to absorb all the heat from argon condenser. Hence the Argon condenser was delinked from this stream in the hope that there might be some other stream in the process which could provide cooling. This is where the utility of pinch analysis proves the critical utility. When the composite curves for both the cases were plotted, it was observed that for Case 2, there is net cold utility demand. This means that there is shortage of cooling at Argon condensation temperature. Furthermore, the cold process streams that required to be heated as per pinch analysis were also not cold

enough to even subcool the high pressure HP bottom liquid. Hence neither the direct heat exchange with Argon condenser nor the subcooling of HP bottoms stream at high pressure is possible.

Table 5.1 Product yields for base case and manipulated case

Molar Yields	Case 1	Case 2
Oxygen yield	17.66	20.26
GAN yield	42.79	36.12
LAR yield	0.091	0.73
Waste N ₂ yield	39.03	42.47
LIN yield	0.43	0.43
Air Feed temperature	102 °C	150 °C
Argon Yield	Low	High
External Refrigeration	No	Yes

Yield results and composite curves from thermal pinch analysis for both the cases are presented in table 5.1 and figures 5.2 and 5.3 respectively. For both the cases, product specifications were maintained the same at Nitrogen product > 99.95 mol %, Oxygen product > 99.6 mol% and Argon product > 99.9 mol%.

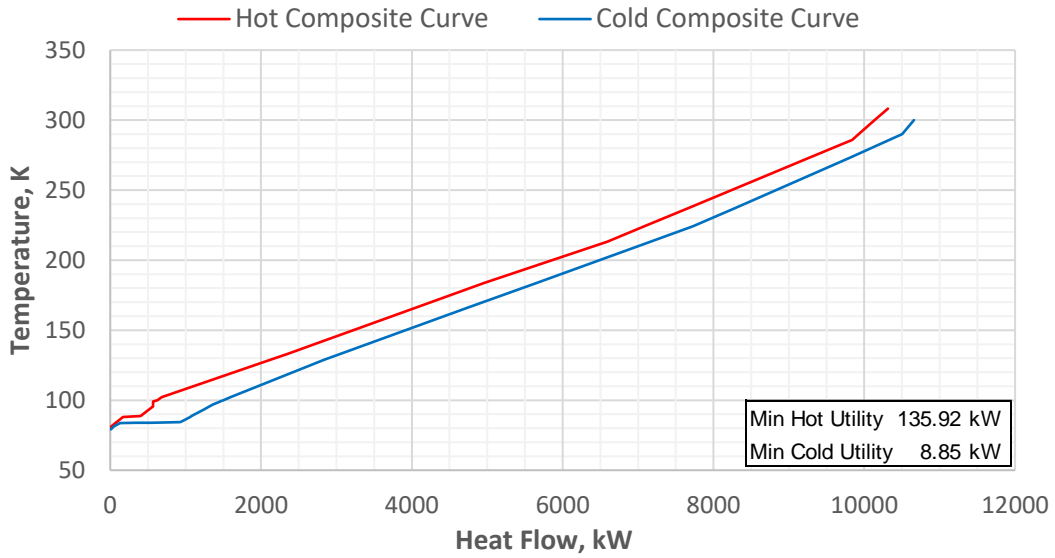


Figure 5.2 Hot and cold composite curves for Case 1 with $T_{\min} = 1.5$ K

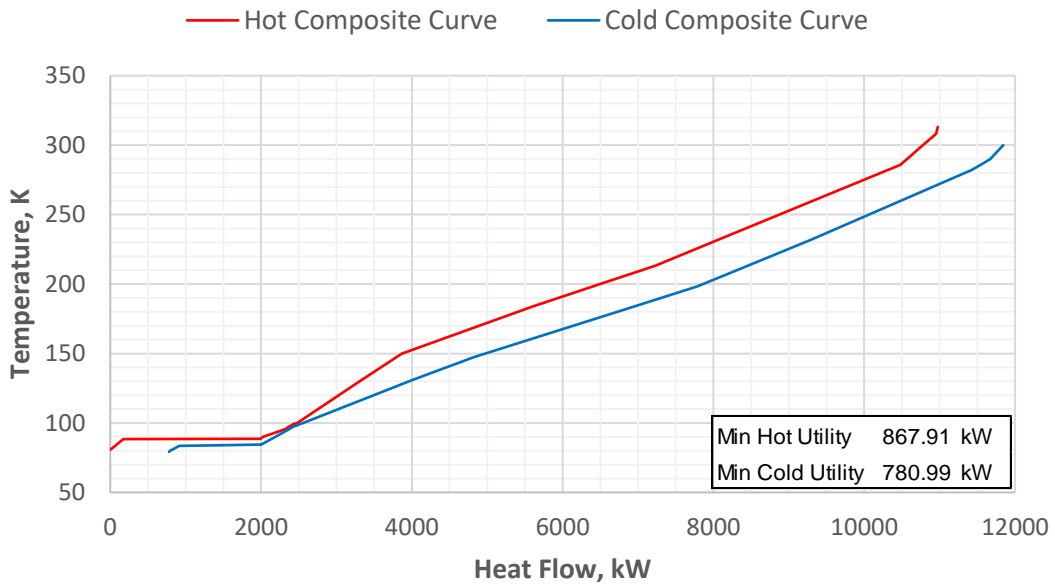


Figure 5.3 Hot and cold composite curves for Case 2 with $T_{\min} = 1.5$ K

From above case study, the two major learning were,

- 1) Yields are improved by improving vapor traffic in the stripping section of LP column.
- 2) A corresponding amount of cooling should be arranged for the separation section if additional heat is supplied as shown in figure 5.4.

The second insight helped in visualization and development of the enthalpy envelopes around the process. Furthermore, it was realized that each modified flowsheet should be scrutinized by the pinch analysis.

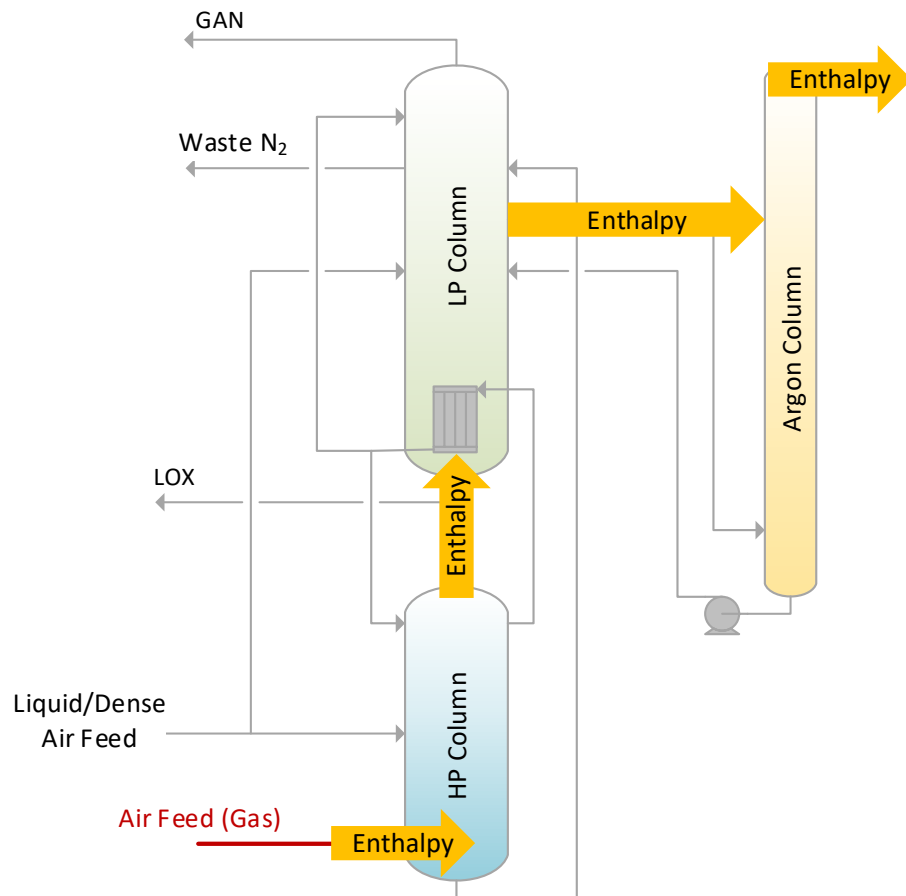


Figure 5.4 Heat flow with air feed temperature change in Case 1 and 2

5.2.2. Thermal Analysis of Single Low Pressure Column Design

As part of due diligence a design based on single low pressure column was also studied. Some academic studies have explored and claimed a single column based process which is capable to produce Nitrogen and Oxygen yields comparable to dual column system [30][31][32]. However, we found that the assumption of neglecting Argon made in these studies challenge the credibility of results. Since we know that separation of just the Nitrogen from Oxygen is much easier than Nitrogen & Argon from Oxygen, and that Argon is major contaminant in Oxygen product, the distillation duties calculated by neglecting Argon would be unrealistic. Hence, we tried to develop a case study where air consists of Nitrogen, Oxygen and Argon. The feed streams, conditions and flows are kept the same as base case model. Liquid Oxygen and GAN product are produced from the LP column along with waste nitrogen and LAR from Argon column. Heat integration is done in similar fashion, where LOX is used to liquefy the air. Except LAR, all the products are gas and leave the process at 304K. Reflux for the column is produced by a heat pump arrangement where column vapors are compressed to such a pressure that their condensation temperature is higher than column bottom reboiling temperature. The condensed Nitrogen vapors are then expanded in a turbine to further remove some enthalpy from the stream. The resultant liquid is put back as reflux while the gas produced from flashing is taken out as GAN. Figure 5.5 shows the process flow diagram of the process. Argon condenser was assumed to be operated with external refrigeration during the simulation with the understanding that a suitable stream would be found for this application during heat integration. Similarly, all the product streams

were directly heated to 304 K with the understanding that actual exchange will be worked out during heat integration. This is a time saving technique and implementation of the idea ‘Big picture first, details later’, pioneered by Dr. El-Halwagi.

The single column process also requires heating of column near stage 20 in order to converge the simulation. This is achieved by providing heat to the column via internal process stream rather than providing heat from outside. The heat exchange can be incorporated in heat integration analysis and during detailed HEN development.

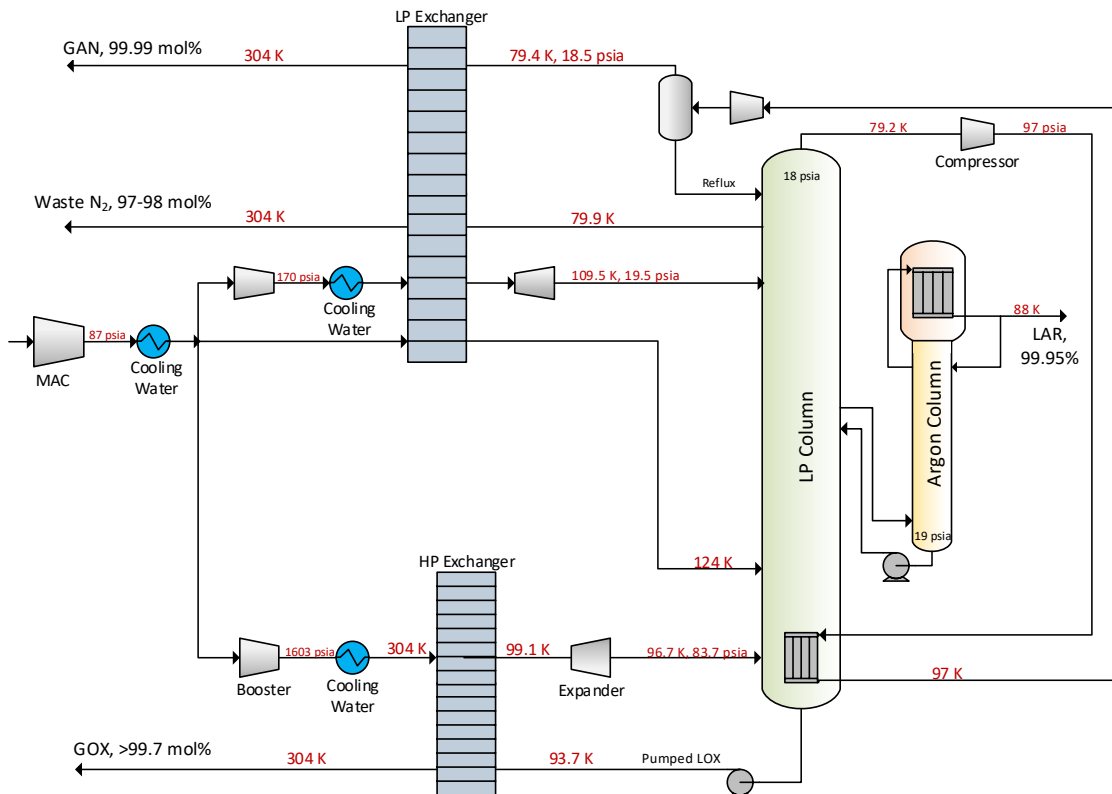


Figure 5.5 Single column design PFD

It is found from the pinch analysis that there is shortage of refrigeration in the system, also visible from composite curves in figure 5.6. Specifically, there is no process

stream that can provide the refrigeration for Argon condensation. If we apply the concept of enthalpy envelope, explained in next section, it can be seen that there is net increase in inlet enthalpy because of energy added by heat pump compressor, but there is no addition of corresponding refrigeration. Hence the shortfall is reflected in thermal pinch analysis.

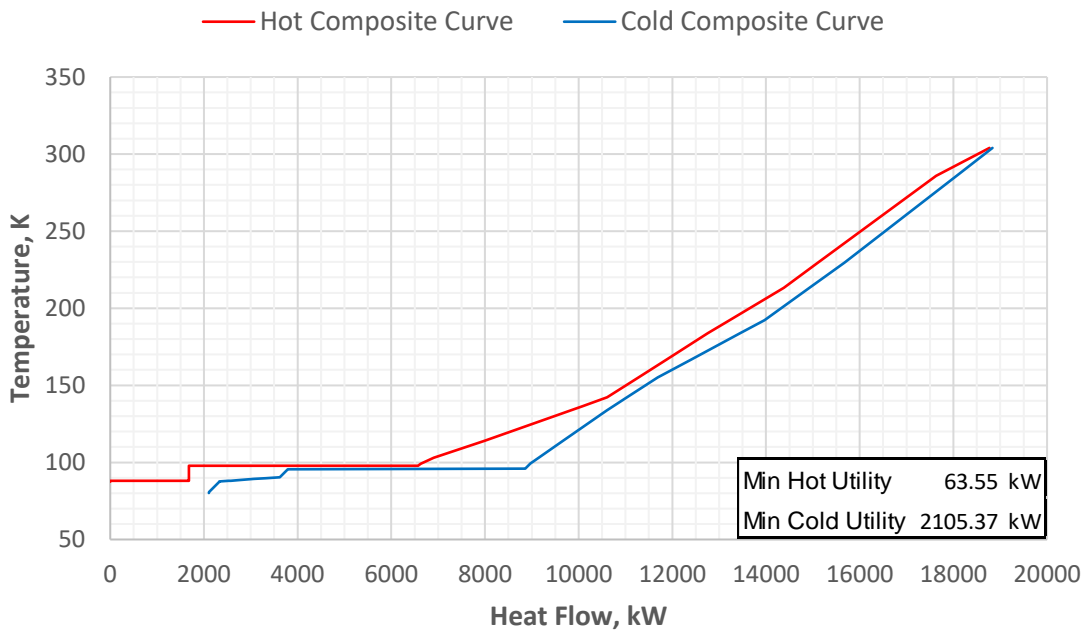


Figure 5.6 Thermal pinch analysis of single low pressure design

If we suppose the 2100 kW of cooling at 80-85 K range can be provided by external refrigeration, a quick economic analysis shows that 48 m³/hour of liquid Nitrogen will be required which can cost around \$12,000 per hour. This includes just the cost of refrigerant without consideration of transportation and other capital investment. Moreover, the best refrigerant for this service would be liquid Nitrogen which can be produced in-house. So it is better to produce this refrigeration within the process, by

utilizing heat pump or liquefying a higher fraction of air. High pressure liquid feed air can be subcooled via GAN and waste nitrogen product and then used as a refrigerant for Argon condenser after it is flashed. This can be further investigated and a more optimized single column design can be produced, but the energy efficiency is still questionable.

5.3. Concept of Enthalpy Envelope

The idea behind the enthalpy envelope is that the enthalpy entering the control volume should be equal to the enthalpy exiting it. There might be multiple exchanges happening inside the envelope/control volume, but the total enthalpy inlet/outlet should be the same. This means that if for a given air feed, the recoveries of Oxygen, Nitrogen and Argon are fixed and since the pressure profile of the unit is kept constant, the total enthalpy of the product streams can be calculated. This total enthalpy should be matched by the feed air supplied to the separation section, as depicted in figure 5.7.

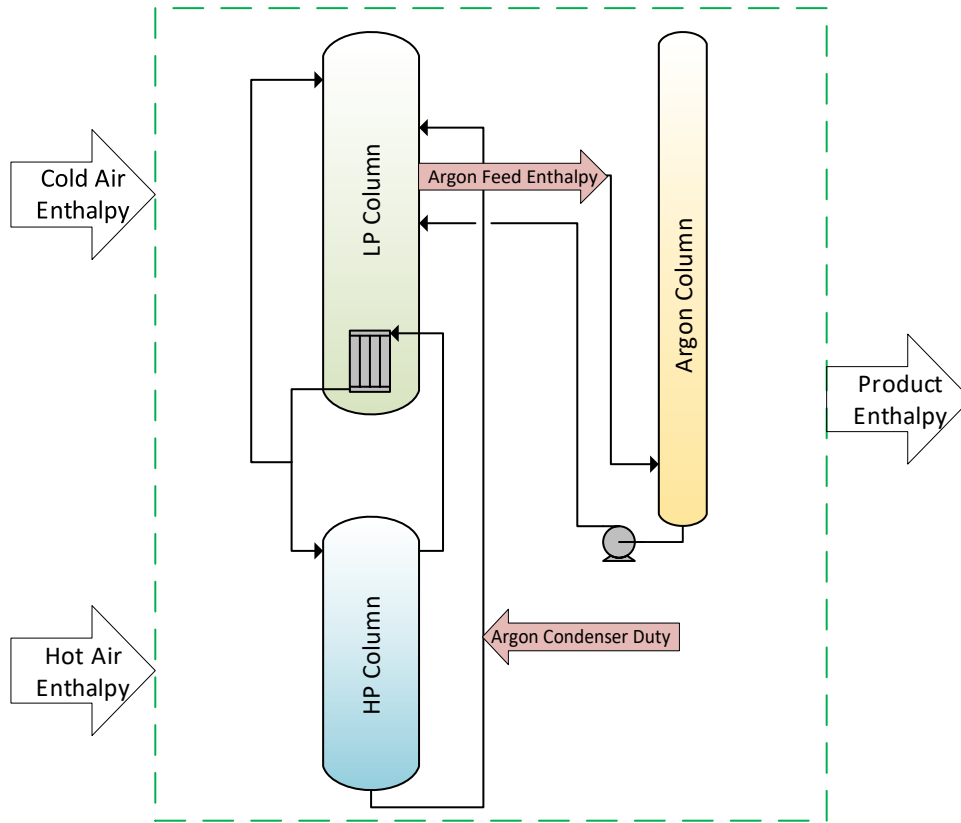


Figure 5.7 Concept of enthalpy envelope

The benefit of this analysis is that the complex and integrated system can be dissected into two sub systems. One is the separation section consisting of the three distillation columns, shown in figure 5.8. The second is the heat exchange section where air is compressed, cooled and a fraction is liquefied while the product streams are heated to ambient temperature. This dissection helps in understanding the relation of separation system with the feed conditions. For a given feed condition, there will be an optimal separation performance inside the envelope.

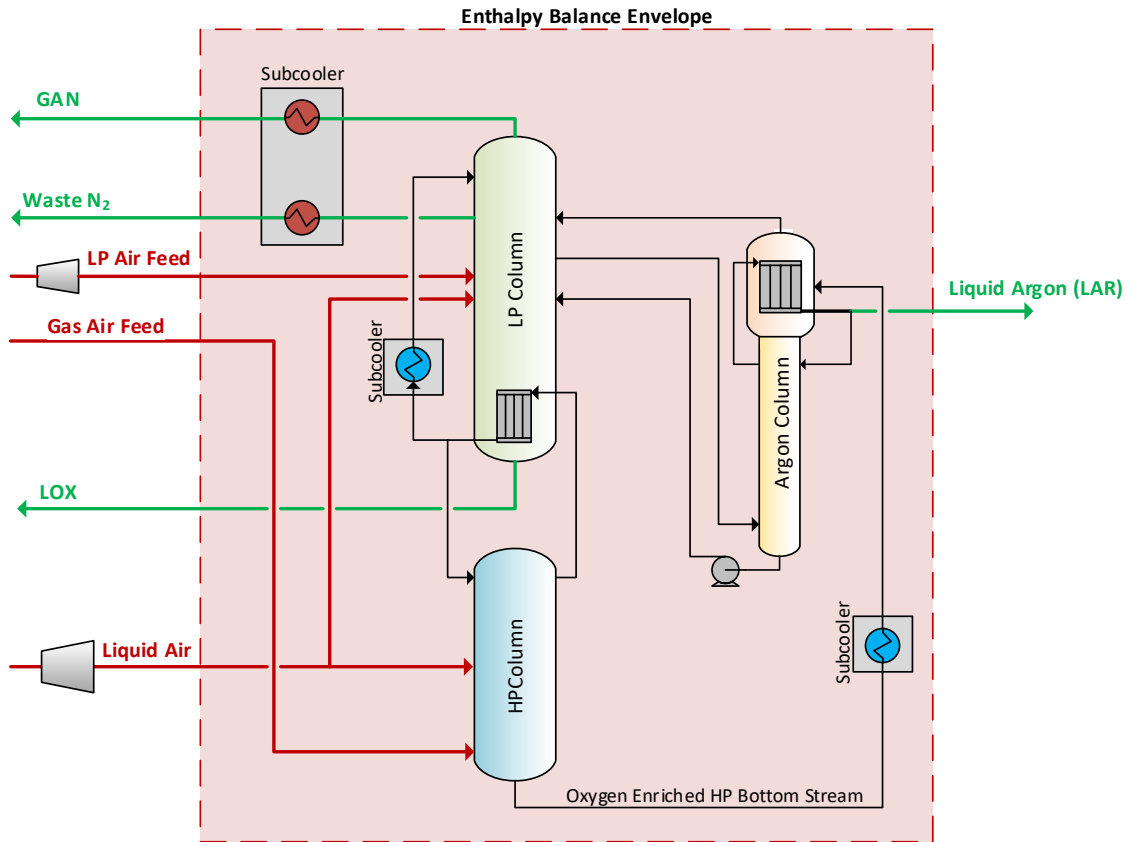


Figure 5.8 Actual enthalpy balance envelope for CASU process with inlet and outlet streams

5.4. Case Study of Same Inlet Enthalpy With Three Different Product Distributions

The above concept of enthalpy envelope was applied to three cases with same inlet enthalpy to the envelope i.e. separation section has same net enthalpy, but the product split of the cases are significantly different. The total 5036 kgmol/hr of air feed is split into three portions. The first portion of 1623 kgmole/hr is compressed, boosted, liquefied in HP heat exchanger and expanded in a turbine, then is fed partially to HP column (454kgmol/hr) and remaining to LP column. A second portion of air feed (HP Air, 2875 kgmol/hr) is simply compressed to HP column pressure and cooled to 103 K

before it is fed to HP column bottom stage. The last portion named as LP Air, is cooled to 109.5 K using heat pump arrangement where it is compressed, cooled with water exchanger, further cooled via effluent product streams in LP heat exchanger and finally expanded in a turbine. The stream is expanded to LP column pressure and fed in the top section of the tower. Additionally, external heat duty of 555 kW is provided to LP column to enhance the stripping section performance. This is practically feasible by installing second heat exchanger in the LP column sump. In Case C, it will be demonstrated that this duty can also be provided by increasing HP air stream temperature to 124K. Providing the enthalpy via HP Air feed not only provides additional duty to the LP column but also improves separation in HP column which then affects the heat integration.

5.4.1. System Configuration Used in Case Studies

All the three cases use same configuration of unit operation i.e. the pressure profile of the whole process was the same as has been described in PFD. The HP column was modelled with 62 theoretical stages. Argon column was modelled as 85 staged column. LP column consists of 81 stages with Waste N₂ drawn from stage 7, flashed liquid/dense phase air feed at stage 9, LP Air feed at stage 10 and Oxygen enriched HP bottom stream fed at stage 14. Argon feed was drawn from vapors above stage 34 and the returning liquid from Argon column were fed on stage 34.

5.4.2. Results

It is observed that the three cases show quite different yields of the products. Case C has highest yields for GAN and GOX products of all the cases and the least amount of Waste N₂ is produced. Case B produced higher amount of Argon as compared to Case A & C.

	Units	Liquid Air	LP Air	HP Air	External Duty	Total	
Feed Enthalpy Entering the Envelope for Case A & B							
Flow	kgmole/hr	1623.0	538.0	2875.0		5036.0	
Molar Enthalpy	kJ/kgmole	-11143.5	-5430.5	-5869.9			
Stream Enthalpy	MJ/hr	-18085.8	-2921.6	-16875.9	1996.0	-35887.3	
Feed Enthalpy Entering the Envelope for Case C							
Flow	kgmole/hr	1623.0	538.0	2875.0		5036.0	
Molar Enthalpy	kJ/kgmole	-11143.5	-5430.5	-5175.8			
Stream Enthalpy	MJ/hr	-18085.8	-2921.6	-14880.4	0.0	-35887.8	100.0%

	Units	GAN	Waste N2	Argon	GOX	LIN	Total	
Case A Exit Enthalpy								
Flow	kgmole/hr	1299.2	2709.3	31.9	973.9	21.7	5036.0	
Molar Enthalpy	kJ/kgmole	-5765.1	-5767.6	-10866.8	-12544.6	-11713.0		
Stream Enthalpy	MJ/hr	-7490.2	-15626.0	-346.7	-12216.7	-254.2	-35933.8	100.1%
Case B Exit Enthalpy								
Flow	kgmole/hr	1421.1	2590.9	33.6	990.4	0.0	5036.0	
Molar Enthalpy	kJ/kgmole	-5765.1	-5756.2	-10866.8	-12543.2	-11713.0		
Stream Enthalpy	MJ/hr	-8192.6	-14913.5	-365.0	-12423.4	0.0	-35894.6	100.0%
Case C Exit Enthalpy								
Flow	kgmole/hr	1603.0	2399.0	31.8	1002.2	0.0	5036.0	
Molar Enthalpy	kJ/kgmole	-5765.1	-5724.7	-10866.8	-12543.4	-11713.0		
Stream Enthalpy	MJ/hr	-9241.6	-13733.6	-345.0	-12571.1	0.0	-35891.3	100.0%

Table 5.2 Enthalpy inflow and outflow for cases A, B and C

Pinch analysis was also performed for all the three cases with an approach temperature of T_{\min} of 1.5 K, shown in figures 5.9, 5.10 and 5.11.

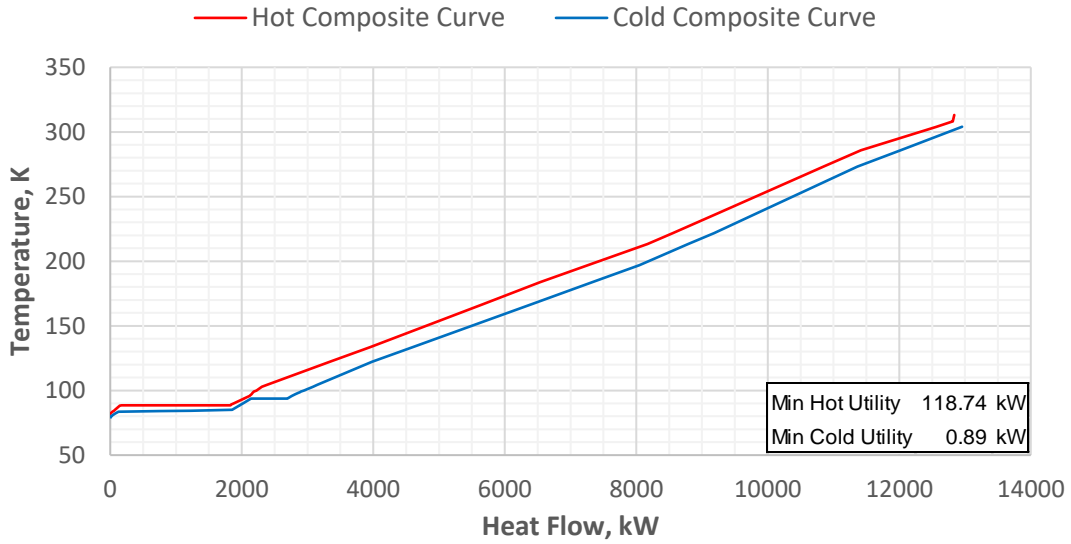


Figure 5.9 Case A thermal pinch analysis

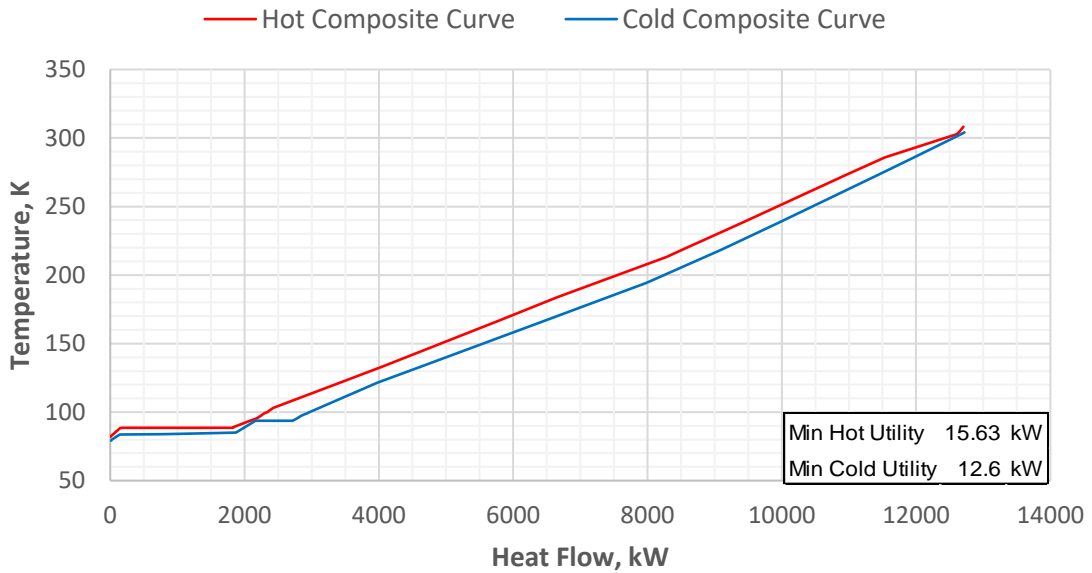


Figure 5.10 Case B thermal pinch analysis

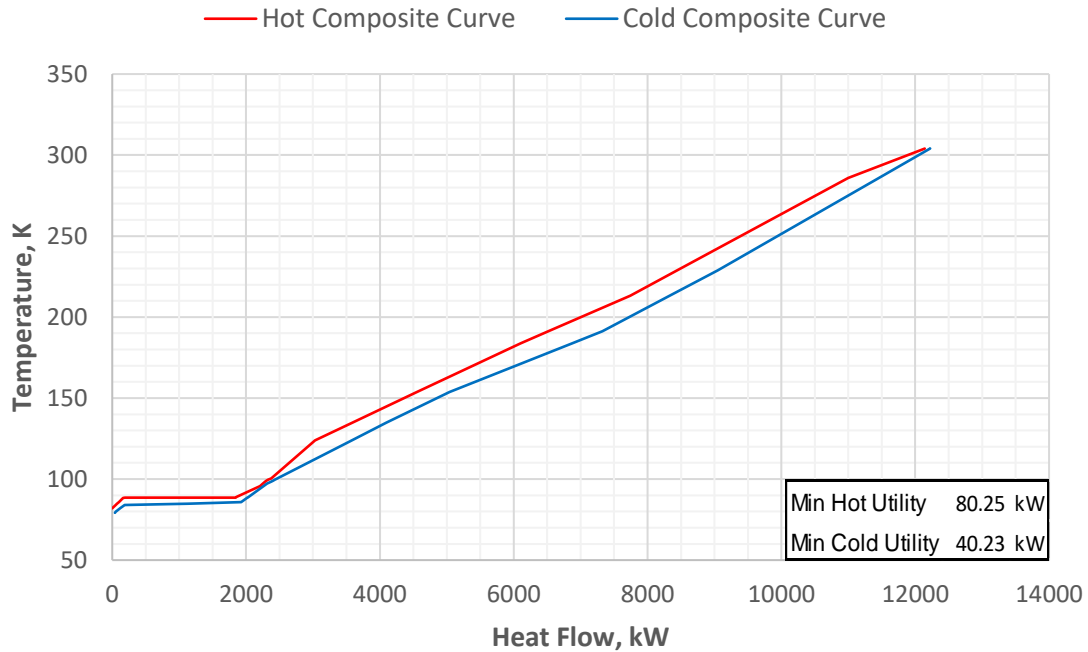


Figure 5.11 Case C thermal pinch analysis

Cases A did not require any significant external cold utility while Case B and Case C showed 12.6 kW and 40 kW refrigeration requirement respectively. This can be eliminated by fine tuning subcooling temperatures and producing a little extra refrigeration in heat pump systems.

5.5. Design Analysis Framework

As a culmination of all the sensitivity analyses the concept of enthalpy envelope was developed. Similarly, the concept of enthalpy envelope helped in developing even larger macroscopic insights. Since the pressure profile of the system is kept constant and the product purity specifications (composition) are also constant, the molar enthalpy of

the streams get fixed. If the recoveries, and hence the flowrates, of the products are fixed then the net enthalpy exiting the system can be calculated. This can help in back calculating feed stream conditions. Since it is known that the HP feed air temperature is a handle to change inlet enthalpy to the system, it can be modified to match the inlet and outlet heat flow through envelope. Once the outer balance is satisfied, one can delve into detailed designing of the process using results of macroscopic analysis.

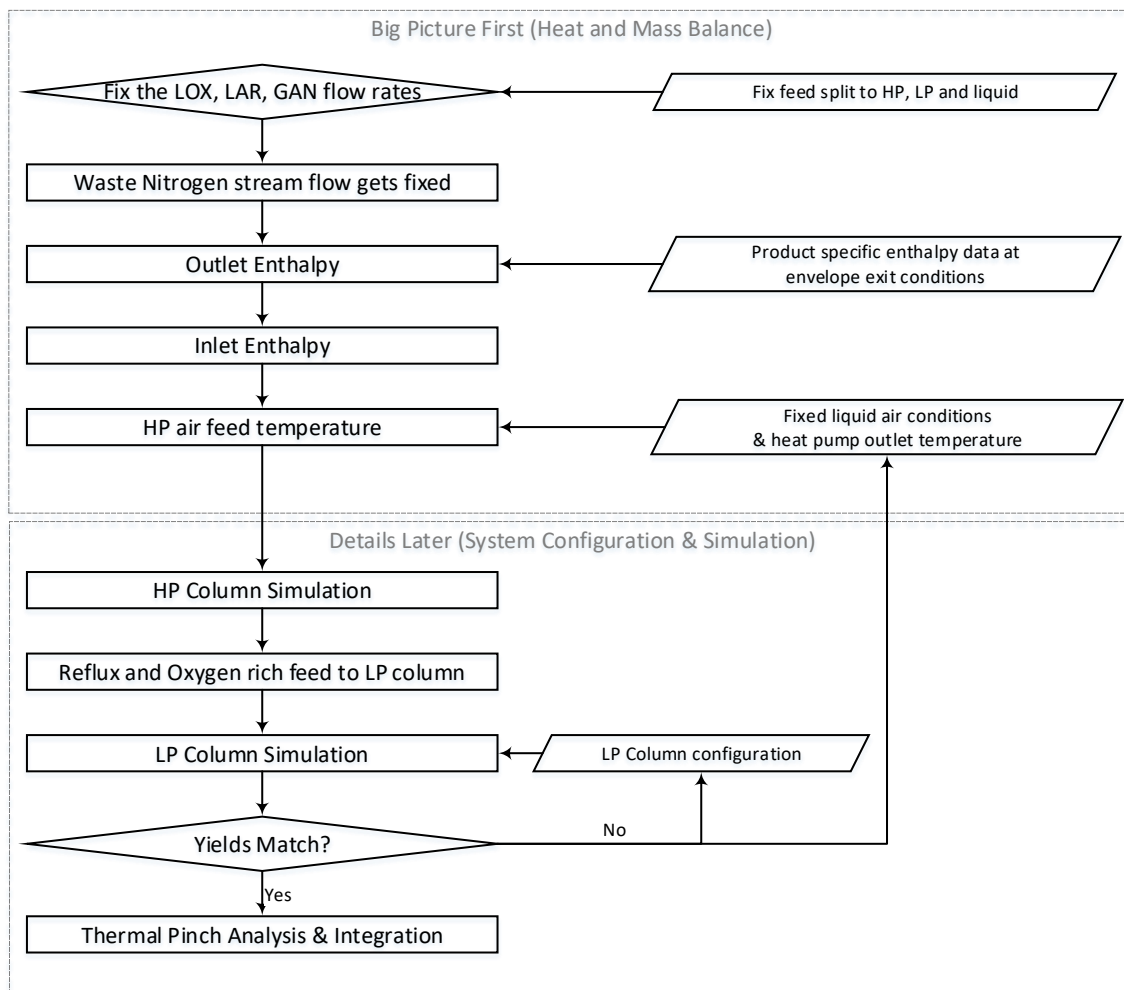


Figure 5.12 Framework to analyze CASU design

6. CONCLUSION

Cryogenic air separation process was manipulated in this research and multiple flowsheets were developed toward improving the yields. In the scenario considered, the net power consumption in the compressors in the same as the feed flow and pressure profile is not changed. The two cases, namely 1 & 2, presented in section 5.2 and the cases A, B, C presented in section 5.4 shows that for a given feed, the separation section performance can be modified and improved drastically, by changing the feed temperature, location of feed stages in LP column, reboiling energy to LP column, and subcooler outlet temperatures for subcooled Nitrogen reflux and HP bottom product stream. From these insights, a framework was developed to systematically analyze the CASU process and calculate macroscopic parameters without delving into convoluted detailed designing of mass and heat integration.

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