

MEMO 3
PRELIMINARY DESIGN OF NITROGEN PROCESSES:
PSA AND MEMBRANE SYSTEMS
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ABSTRACT

The objective of this memo was to conduct a rigorous economic analysis to determine and compare the yearly earnings, the rate of return, and the break-even price of nitrogen for both pressure swing adsorption (PSA) and membrane separation. Both processes were found to be economically favorable compared to purchasing nitrogen from an outside supplier. However, PSA is recommended over membrane separation since it yields a higher yearly earnings and rate of return. The literature search, the selection of process flowsheets, and the completion of the mass and energy balances reported in the previous memos allowed the equipment to be sized and priced. For the economic analysis of this memo, a market price of nitrogen and electricity cost were assumed to be \$.53/100 SCF and \$50/1000 kW-h, respectively. Applying this data to PSA, the net present value (NPV), yearly income, rate of return, and brake-even price were computed to be \$1,536,000, \$283,500, 185.3%, and \$.27/100 SCF, respectively. For membrane separation, the corresponding values were found to be \$1,419,000, \$261,700, 135.1%, and \$.29/100 SCF. These results indicate that pressure swing adsorption is the preferable process. A sensitivity analysis showed that a 10 percent increase in the market price of nitrogen would lead to yearly earnings of \$313,600 (19.8% increase) for membrane separation and \$335,400 (18.31% increase) for PSA. A 10 percent increase in utility costs was found to decrease the yearly earnings by 2.1% for membrane separation and 1.5% for PSA. Furthermore, PSA is expected to be favorable if the capacity is expanded since its cost does not scale linearly with size, which is characteristic of the economics of membrane separation processes.

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I. INTRODUCTION

The purpose of this memo was to complete the preliminary nitrogen-plant design and economic evaluation. The current means of off-site nitrogen supply is economically inefficient due to technological advances in separation techniques. This has led to the consideration of on-site nitrogen production at relatively low costs compared to off-site purchase. The first two memos described the process alternatives, the optimum PSA and membrane process flowsheets, and confirmed their physical and economic feasibility. This correspondence focuses on a rigorous economic analysis to determine and compare the yearly earnings, the rate of return, and the break-even price for the two processes. Also, a sensitivity analysis was conducted to project the effects of changes in market nitrogen price and/or utility cost on these economic parameters. From the results of this analysis, the most economical on-site nitrogen production process was recommended.

The specifications on the nitrogen that is needed for the Technology Division are a 20,000 SCFH capacity and purity of 99 percent. Non-cryogenic processes for nitrogen production were considered because these values are not high enough to demand cryogenic distillation. Pressure swing adsorption receives air at ambient conditions and selectively adsorbs oxygen to produce a continuous nitrogen-rich product stream at the specified temperature and pressure. Gas separation using membranes takes advantage of differences in the permeabilities of oxygen and nitrogen in the membrane interphase to produce a continuous nitrogen-rich raffinate product. The results of a search of the pertinent literature given in the first memo indicated that both of these processes are potentially viable in meeting the specified purity and production capacity. Also, alternative flowsheets were considered and particular ones were chosen due to their potential economic and physical feasibility.

In the second memo, mass and energy balances were carried out to determine the process stream information that is required for equipment sizing and costing. The results confirmed that both processes were physically feasible. Molar flowrates, enthalpies, temperatures, and pressures were determined.

The objective of this final memo was to compute the capital investment and manufacturing costs to determine which of the two processes is more economical. Even though the nitrogen is to be produced for internal use, a brake-even price was calculated to ensure that on-site production is preferable to purchasing the product from an outside supplier. A sensitivity analysis was necessary to estimate the economic implications of changes in variables containing some uncertainty, such as the market price of nitrogen and the utility costs.

The structure of this report is to first discuss the details of pressure swing adsorption and membrane separation to present the theoretical background of the processes. This is followed by a description of the alternative flowsheets (esp. in membrane separation) and to describe the characteristics and operation of the actual processes that were selected. Next, the mass and energy balance results of the previous memo are summarized and are illustrated on the process flowsheets. Finally, the results of the rigorous economic evaluation are discussed, the values of the two processes are compared, and the recommendation of the optimal one is made.

II. BACKGROUND

One alternative process to cryogenic distillation that is capable of producing high purity nitrogen is pressure swing adsorption (PSA). Carbon molecular sieves are employed as the adsorbent because they preferentially adsorb oxygen over nitrogen. The adsorption isotherms of oxygen and nitrogen, which describe their thermodynamic equilibrium coverages, have been found to be quite similar (Shirley et. al, 1997). Thus, pressure swing adsorption of oxygen over nitrogen is a kinetically-controlled process; separation is achieved because the polarities and sizes of the component molecules are different. (Oxygen has the small molecular size).

An optimum PSA process is one that produces a product gas at high purity, maximizes product recovery, and minimizes the adsorbent inventory. Because these objectives are often mutually exclusive, the relative importance of each must be considered and reflected in the process flow diagram. A typical PSA process consists of a sequence of steps that involve adsorption at high pressure and desorption at low pressure. During the adsorption step, the partial pressure of oxygen (the more selectively adsorbed component) should be made to be very high to maximize its coverage. This can be achieved by increasing the total pressure of the bed (pressurization step) and ensuring that the gas is rich in oxygen. On the other hand, desorption requires low oxygen partial pressures. These can be achieved by lowering the total bed pressure (depressurization step) and flowing nitrogen-rich gas through the bed as a purge. In order to have a continuous output of product, multiple beds are needed. The resulting multi-bed process produces oxygen in a cyclic-steady-state.

The original process that incorporated the steps listed above (i.e. pressurization, adsorption, depressurization, and purge) is the Skarstrom cycle, which is mentioned here for purposes of comparison (Sircar, 1989). It involves two adsorption beds. The process is set up so that while one bed is being pressurized and is undergoing adsorption, the other is being purged and depressurized. This process has been found to be very inefficient because it can only produce high purity gas at very low recoveries. For example, it has been shown that for a process producing pure oxygen, a recovery of only 10% was achieved for a product purity of 90% (Sircar, 1989). The low recoveries result during the depressurization and purge steps, in which significant amounts of the less selectively adsorbed component are lost. Modification of these steps is necessary to make PSA an economically viable separation process. Since the invention of the Skarstrom cycle, there have been many advances that have sufficiently improved the efficiency of PSA. The main attempts sought to reduce the amounts of the less selectively adsorbed component lost in the purge and depressurization steps.

One particular modification to the Skarstrom cycle is to implement a pressure equalization step. In this step, void and desorbed gases remaining in the high pressure bed after adsorption are transferred to the low pressure bed until the pressures equalize. This preserves some of the less selectively adsorbed component by keeping it within the overall system instead of venting it, which would make it irrecoverable (Sircar, 1989).

Other modifications to the Skarstrom cycle may be to enable the adsorber to produce two products or to adjust the gas mixture compositions. The latter modification might, for example, create an output purge effluent having the desired product composition. This would be another possible way to increase the product recovery.

Gas permeation is another non-cryogenic separation process that can be used to produce an enriched air stream that is 99% pure in nitrogen. The process takes advantage of the different transport rates of nitrogen and oxygen within the membrane interphase. The degree of separation is determined by a solution-diffusion mechanism that results from the fact that the mobility and concentrations of the components in the membrane are different. A hollow fiber membrane is an appropriate membrane type for this application because it permeates oxygen faster rate than nitrogen.

In the design of an optimum process flow diagram for a membrane separation process, feed preparation and membrane staging are options that must be explored. Because the feed air stream generally contains impurities that could greatly diminish the ability of the membrane to separate the gas, the feed is usually first made to pass through many filters. Staging of the membrane separators increases the capacity of the overall system and therefore is a viable option. However, because economies of scale do not exist, the typical number of stages is kept rather low.

III. DISCUSSION

The purpose of this section is to describe the available processes that can meet the design specifications and to discuss the reasons that led to the selection of particular PSA and membrane process

flowsheets. The Technology Division needs 99 percent pure nitrogen gas for polymer application. This product gas must be delivered at a rate of 20,000 SCFH at 100 psig. In the design, the price of nitrogen that yields a DCF return rate of 15 percent must be calculated, and this price must be compared to the cost of purchasing the nitrogen off-site. The only utility pertaining to both processes is electricity, and its relevant costing was given by the 2005 utility analysis.

PSA and membrane separation processes have many advantages over cryogenically distillation processes. For example, they have a low capital cost and are very cost effective for low to moderate volume demands. However, cryogenic distillation is preferred over these two processes when extremely high purity nitrogen is desired (Hardenburger, 1992). One advantage of PSA processes over membrane separation processes is that they generally achieve a high purity at a lower capital cost (Hardenburger, 1992). Advantages of membrane separation processes over PSA are that there are no moving parts in the process, there is minimal air pre-treatment compared to that necessary for the PSA process, and there is an instantaneous start-up of the process (Spillman *et al.*, 1989).

Next, both the PSA and the membrane separation processes will be analyzed both physically and economically to determine the most optimal arrangement of both processes. This allows the most economically feasible process to be chosen for implementation into the polymerization process.

PRESSURE SWING ADSORPTION PROCESS

This section discusses the chosen PSA process and the assumptions made in the mathematical models that were used to determine the mass and enthalpy of each stream. A rigorous treatment of PSA involves numerical solution of coupled differential equations, which incorporate kinetic and thermodynamic models and appropriate boundary conditions. In this memo, many simplifications were made in order to arrive quickly at molar and energy balances to be used for design. These simplifications include the following:

1. There is no pressure drop between the exit of the compressor and the product outlet
2. Compression of the inlet feed results in no change in temperature
3. The temperature in the exiting waste and product streams is not higher than the feed temperature (i.e. the isosteric heat of adsorption does not lead to any change in enthalpy)
4. All of the water, carbon dioxide, and acetylene present in the feed adsorbs in the first 3-4" of the bed and therefore leave the process only in the waste streams
5. Ninety percent of the argon in the feed leaves in the product stream
6. The feed gas is at ambient temperature and pressure
7. The product stream contains 99% inert gas consisting of nitrogen and argon only (the remainder is only oxygen)
8. The reference enthalpy was taken to be that of an ideal gas at $T=298\text{K}$ and $P=101.325\text{kPa}$ (given in PRO II). The enthalpies of the various streams were found with respect to this point using the Peng-Robinson cubic equation of state.

PSA Process Flowsheet

Air at ambient conditions ($T = 294.26\text{ K}$, $P = 101.325\text{ kPa}$) is fed to an oil flooded screw compressor that has a 60% isentropic efficiency. The compressor increases the pressure of the gas stream to 114.7 psia while maintaining the gas temperature at 70 °F. The air is sent to the adsorbent bed that is operated at high pressure. The first 3-4" of the column serve to remove all of the water (.0717% feed), CO_2 (.0375% feed), and trace acetylene (.0008% feed) that were initially present in the air. When the composition of the oxygen in the effluent begins to approach the specified value of 1% (which occurs as the bed becomes spent) the break point is reached. At this point, the inlet flow is diverted to the other adsorbent bed, which by that time has been depressurized, purged and repressurized (with enriched nitrogen product). The qualitative flowsheet for the PSA process is shown at the top of the next page.

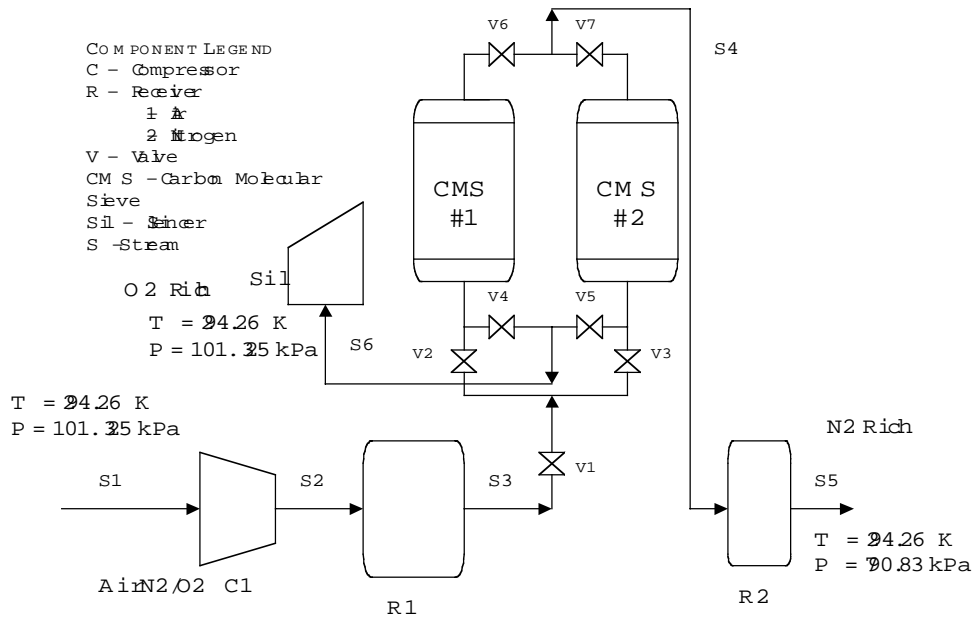


Figure 1: Qualitative Flowsheet of PSA Process

Mass and Energy Balances

In order to solve the material balance, the process was viewed as consisting of three streams; a feed, which carries moles of gas into the process, and waste and product streams, which carry moles out of the process (see Figure 10 on page 14). Because PSA is run in a cyclical steady state, a continuous product stream of enriched nitrogen is produced. Consequently, the amount of entering and exiting moles should be equal over a given period of time.

The total molar flowrate of the entering feed was determined from the specification of the enriched nitrogen product flowrate of 20,000 SCFH (7.02 gmol/sec) and performance data. The supplied performance data is tabulated and plotted below. It enables one to determine the feed-to-product molar flowrate ratio at a specified product purity.

Performance

Mol% O ₂ in N ₂ Product	Air/N ₂ Molar Product Ratio
4.0	1.682
3.0	1.789
2.0	1.938
1.0	2.186
0.8	2.267
0.6	2.317
0.4	2.519
0.2	2.778
0.1	3.048

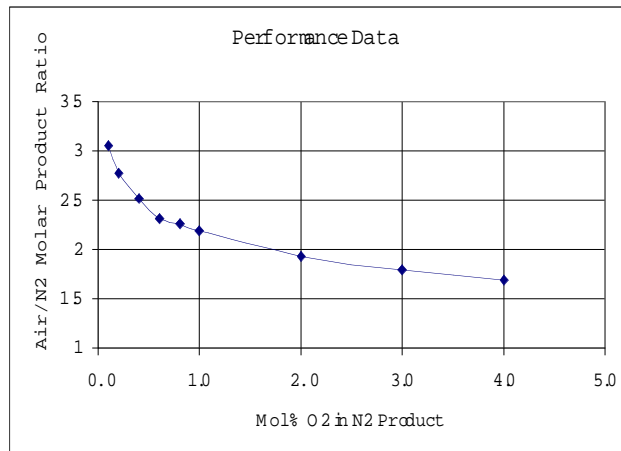


Figure 2: Tabular and Graphical Performance Data

The oxygen composition of the product stream cannot exceed 1.0 mole percent. The feed-to-product molar flowrate ratio corresponding to this oxygen composition is 2.186. This value was used to determine that the total molar flowrate of air to the process is 15.34 gmol/s (see Table 8 page 12). From a total mole balance, the flowrate of the waste stream must be 8.325 gmol/s.

The feed air consists of nitrogen, oxygen, argon, water, acetylene, and carbon dioxide with the following respective mole fractions:

$$\begin{aligned} Y_{f_{N_2}} &= .78 \\ Y_{f_{O_2}} &= .2095 \\ Y_{f_{Ar}} &= .0094 \\ Y_{f_{H_2O}} &= .000717 \\ Y_{f_{Ac}} &= .000008 \\ Y_{f_{CO_2}} &= .000375 \end{aligned}$$

An important specification is that 90% of the argon in the entering feed exits in the product stream. The amount of argon in the feed, .144 gmol/s, was easily calculated from the total feed flowrate and composition. Thus, the molar flowrate of argon in the product stream is 90% of this value (.13 gmol/s). Since the water, carbon dioxide, and acetylene are all assumed to adsorb, the product stream only contains nitrogen, argon, and oxygen. Both the mole fraction of oxygen in the product stream (.01) and the total product flowrate (7.02 gmol/s) have been specified. Thus, it follows that the amount of nitrogen in the product (6.82 gmol/s) and its composition (.972) are also determined.

Solution of the mole balance on the waste gas follows directly from the above information. As stated above, all of the water, carbon dioxide, and acetylene in the feed leave in the waste gas. Thus, the molar flowrates of these components are the feed values (.011, 5.75E-3, and 1.23E-4 gmol/s, respectively). Since the flowrates of oxygen, nitrogen, and argon in both the product and feed are known, then it follows that the difference leaves in the waste stream. Thus, all of the streams have been completely determined. See Table 8 on page 12 for the exact numerical values of the composition and flowrates of all the streams.

The energy balance also utilized a simplified model, which is shown as Figure 11 on page 14. As stated above, all streams of the process are assumed to be at the same temperature. However, the pressures of the streams changed due to compression and led to a difference in the molar enthalpies of the various streams. The enthalpies of the streams were found using PRO II. In the PRO II thermodynamic model used, the enthalpies are calculated with respect to a reference state of 298K and 101.325 kPa (see Assumption 8). The temperature of the streams in the simplified model is 294.26 K (70 °F). The PRO II simulations were made by using a compressor and box (splitter) configuration, which were ran to obtain the enthalpy data. The simulations reported specific enthalpy values, which are located on Table 8 on page 12. These enthalpies were converted to molar enthalpies (J/gmol), and can be found in the stream tables also on page 12.

The analysis of the PSA process yielded reasonable data, despite the many assumptions made. The material balance confirmed that mass was conserved. If the process was treated with more rigorous models that describe the equilibrium, kinetics, and heat effects associated with adsorption, then the isothermal and isobaric assumptions would fail. However, the supplied performance data allowed reasonable data to be generated for quick equipment sizing and costing.

MEMBRANE SEPARATION PROCESS

Material and Energy Balance Discussion

The membrane separation process essentially consists of two unit operations; pressurization and separation. These processes are carried out using an oil flooded screw air compressor and membrane

separators arranged in parallel. There are four process streams for which the mass and energy balances must be satisfied. This process can be seen on page 13 Figure 9.

The process is designed by running simulations on a FORTRAN-based membrane module simulator. The FORTRAN code was altered to solve the mass balance on the separator for every simulation. These changes to the code are shown in Appendix A.2. Additionally, this mass balance is shown to be self-consistent on pages 2.3-2.4 in that Appendix.

Many assumptions were made in order to simplify the calculation of the mass and energy balance and to facilitate the design of the optimum process flowsheet. These assumptions are listed below:

1. The nitrogen and argon are treated as single inert component with identical permeabilities.
2. The oil, water, acetylene, and carbon dioxide in the inlet air permeate (and therefore are not present in the raffinate stream).
3. There is no significant pressure drop across the membrane (i.e. between the feed and the raffinate). Therefore, the pressure of the gas leaving the compressor is the same as that specified for the enriched nitrogen product (raffinate).
4. All streams have a temperature of 294.26 K (70° F). This implies that the compression is carried out isothermally.
5. The enthalpies of the various streams were determined on PRO II, which computed the values with respect to the enthalpy of an ideal gas at 298 K and 101.325 kPa. The Peng Robinson cubic equation of state was used as the thermodynamic model.
6. The permeate gas pressure should be slightly above atmospheric pressure so that it is removed from the process.
7. In addition to the oxygen, the "Fast Gas" in the permeate is composed of the water, carbon dioxide, acetylene, and oils in the feed. (In the FORTRAN code, the fast gas is assumed to be oxygen only).

This process is run with a membrane that has a selectivity of 6 and a feed to permeate pressure ratio of 7.646 (see the discussion below, which describes the origin of these values). The feed flowrate was determined to be 21.09 gmol/sec (see page 2.3). The output of this simulation is found in Figures 2-4 in Appendix A. The FORTRAN generated mass balance is verified in the sample calculations on pages 2.3-2.4 of the Appendix.

In order to solve the energy balance, the temperature, pressure, and enthalpy of every stream must be determined. The entire process can be assumed to be isothermal. The oil screw compressor operates the same as the one used in the PSA process. It isothermally compresses the feed by using an oil bath as a heat sink to remove the heat energy generated by the compressor work. The composition of the stream does not change in the compressor. The molar enthalpy of the feed stream changes from -591.85 to -648.35 J/gmol through the compressor due to pressurization.

Optimum Arrangement of the Process Flowsheet

Selectivity and Feed to Permeability Pressure Ratio

In this memo, attention was given to the optimum arrangement of the process units. For basic compressor cost estimations, the parameters that are assumed to increase the cost of the compressor are the compression ratio and the feed flowrate. Higher values of both of these quantities increase the work that the compressor has to perform, which results in a greater equipment cost. It is assumed that compression costs are the most expensive part of the process.

The main design problem for this process is determining an acceptable feed to permeate pressure ratio and membrane selectivity for the individual membrane separators. Once these parameters are specified, the number of membranes needed for the separation and the necessary feed flowrate can be determined. When the feed flowrate is determined, the compressor can be sized since the compression

work is dependent on this quantity. The work required is also a function of the compression pressure ratio, but it will be shown later that this quantity does not vary the design specifications.

In the code, the user specifies the selectivity, the feed to permeate pressure ratio, the separator flow design pattern (in this case countercurrent), and one arbitrary design specification. Here, that design specification is the mole fraction of the fast gas, oxygen, and is always specified to be .01 or 1 mol% of the raffinate stream. There are certain restrictions on the selectivity and the feed to permeate pressure ratio that can be specified. The following illustrates these.

The permeance, which is the ratio of the permeability of oxygen to the length of the separator, is assumed to be a linear function of the selectivity. This relationship can be seen on page 2.1 of Appendix A. From the plot of permeance vs. selectivity shown on that page, it can be seen that the line crosses the x-axis at a selectivity of approximately 10. This means that the selectivity that is specified cannot be higher than 10 since negative permeances are not feasible.

These simulations also assume that there is no pressure drop across the membrane (i.e. between the feed and raffinate streams). This assumption is made because there is relatively little restriction to the flow across the membrane (similar to gas flow in a pipe). On the other hand, an appreciable pressure drop occurs over the thickness of the membrane (i.e. between the feed and the permeate streams). The pressure drop between these streams is the driving force for mass transfer, and defines the feed to permeate pressure ratio (since the permeate pressure is assumed to be slightly above one atmosphere).

Three Possible Process Flowsheets

Given that there is no pressure drop across the membrane, there are three ways to operate the system. The first is to place the compressor after the membrane. This would cause the feed stream to be "pulled" through the membrane in a vacuum, making the maximum achievable feed or permeate pressure atmospheric. This is not desirable because the feed to permeate pressure ratio would be low ($\cong 1$) and a high feed flowrate would have to be pulled through the membrane to get the desired product amount, regardless of the membrane selectivity. Also the compressor would contaminate whatever is fed to it with oil from the oil bath. If it is placed after the membrane, the oil will contaminate the product. If it is placed before the membrane, the oil will permeate through the membrane and not contaminate the product.

The second option is to place the compressor before the membranes and to pressurize the feed gas to the desired delivery pressure (which assumes no pressure drop across between the feed and raffinate). The selectivity and the feed to permeate pressure ratio are varied until reasonable feed flowrate and membrane areas are obtained. The FORTRAN simulation determines an area factor, represented as Q1, to which the membrane area is proportional. Lower values of Q1 are desirable. It should be noted that the feed to permeate pressure ratio could be adjusted by placing a valve on the permeate stream and to regulate the flow.

A third option would be to place a compressor in front of the membranes to push the feed through at a higher pressure than the desired product pressure. A throttle valve can be used to drop the pressure to the desired value. This arrangement will increase the cost of the compressor due to the increased compression ratio (which increases the work). This may be offset by a reduced feed flowrate, which decreases the amount of required work.

Several simulations were performed where the feed pressure was varied for different selectivities. The purpose of this exercise was to find the optimum pressure ratio at which the system is to be operated. Simulations were performed for selectivities of 2, 6, and 10 and the results can be seen in Figure B1-B3 on pages B1-B3 in Appendix B. Three plots were created from this data and can be seen on these same pages in that Appendix.

The first plot graphs the area factor, Q_1 , against the feed to permeate pressure ratio. It can be seen that the area factor curve follows the same trend for all three selectivities, but is shifted up at higher selectivities. All of the curves appear to be approaching zero as the pressure ratio is increased. From this plot, it appears that the best operating condition is to run at a high pressure ratio and a low selectivity. For example, one might choose to operate at a selectivity of 2.

The second plot shows feed flowrate vs. the feed to permeate pressure ratio. It is desirable to look at this relationship because this will aid in determining the best pressure ratio to minimize compression costs. It can be seen that the feed flowrate decreases with increasing pressure ratio (note the large decrease in feed flow as the selectivity increases from 2 to 6).

The third plot shows the nitrogen permeate flowrate vs. the feed to permeate pressure ratio. This plot is very similar to the previous plot; i.e. the nitrogen permeate flowrate decreases with increasing pressure ratio. The flowrate also shows the same relationship with selectivity as the previous plot. The flowrate decreases with increasing selectivity. From these last two plots, it appears that the optimum operating condition is the one at high pressure ratio and a high selectivity. However, when considering all of the results, it is probably best to operate at an intermediate selectivity and a high pressure ratio. The low selectivity is not an option because it requires enormous feed rates, which will lead to high compression costs. The high selectivity is not as preferable as the intermediate selectivity because the required membrane area is higher (see Figure B4).

From the above discussion, the placement of the compressor can be also be specified. The first option, placing the compressor after the membranes, is eliminated because it is not possible to achieve high pressure ratios with this scheme. The third option can increase the pressure ratio significantly. However, all of the plotted data show that the feed and nitrogen flowrates, and the area factor all tend toward becoming constant functions of the pressure ratio above 7. This is especially true in the case of the feed flowrate. Since the flowrate determines the size (and cost) of the compressor, which is the most expensive part of the process, there is no real benefit to operating at a pressure ratio higher than this. Given these points, the third option is eliminated and the second option is used in this project.

Thus, the second option appears to be the optimum choice. The corresponding pressure ratio is the specified product pressure divided by the permeate pressure (which is slightly above atmospheric pressure). This pressure ratio is 7.646. To ensure that the intermediate selectivity is a valid operating option, a series of simulations were performed by setting the pressure ratio to 7.646 and varying the selectivity. The same plots were created as before. The results of these simulations are in Figures B4-B6 on pages B4-B6 of the Appendix. The qualitative flowsheet for the optimal membrane separation process is shown below.

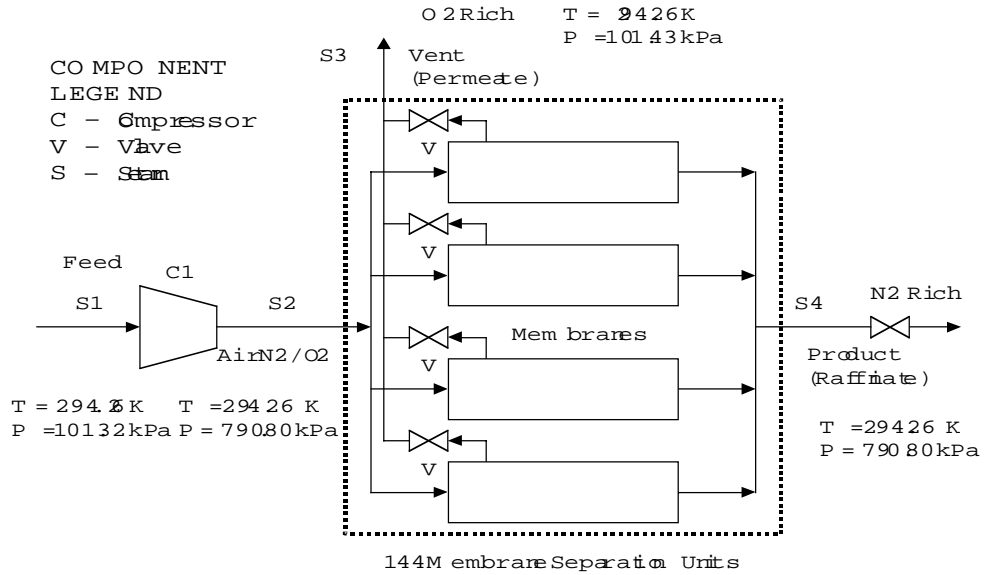


Figure 3: Qualitative Flowsheet for Optimal Membrane Separation Process

The area factor vs. selectivity plot shows that the area factor increases with increasing selectivity. The feed flowrate vs. selectivity and nitrogen permeate flowrate vs. selectivity plots show that the flowrate changes drastically at first (from selectivities of 2 to 4), but begins to level off slightly above these selectivity values. Therefore, it is not advantageous to operate the process at a higher selectivity, since the membrane area will likely be higher and the feed flowrate (necessary compression work) only decreases slightly.

ECONOMIC EVALUATION

Pressure Swing Adsorption Process

The economic analysis for the PSA process was completed and yielded the data shown in Table 1 below. The total onsite investment was found by determining the costs of the carbon molecular sieve, the two vessels, and the compressor. Because ambient air was the feedstock, there were no raw material costs. The manufacturing costs included the components shown in Figure 4 below. This graph indicates that the major contributor was the cost for wages, which includes labor and supervision. The detailed economic calculations can be found in Appendix A.3.

Economic Data for PSA Process	
Total Capital Investment	\$169,300
Utility Cost per year	\$64,000
Manufacturing Cost per year	\$318,500
Estimated Annual Earnings	\$283,500
Estimated Rate of Return	185.3%
Net Present Value	\$1,536,000
Process Nitrogen Price	\$0.27 per 100 SCF

Table 1: Economic Data for PSA Process.

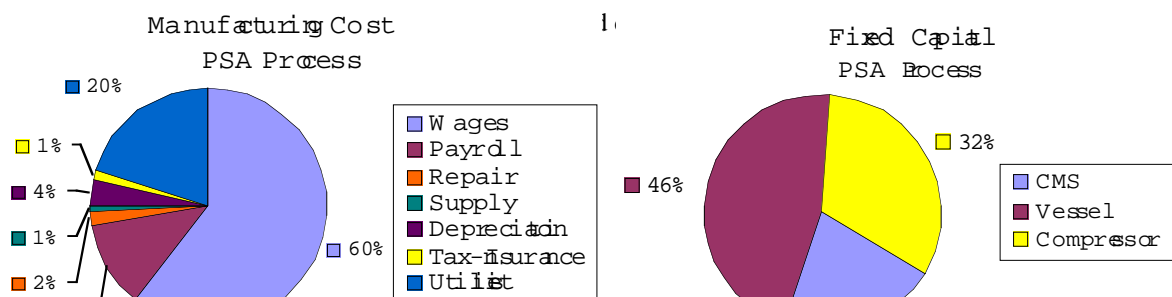


Figure 4: Distribution of Manufacturing Cost and Fixed Capital for PSA Process

There are two uncertain economic parameters that may change; the utility cost and the market price of nitrogen. These costs and prices are increased from 1% to 10% of their assumed values. The response of the calculated economic variables (i.e. yearly earnings, rate of return, and process produced nitrogen price) are plotted over the range of percentage change of the fluctuating variable. This plot for fluctuations in the market price of nitrogen is given below (Fig. 5 page 10).

Variable	Percent Change When Utility Costs Are Increased 10%	Percent Change When The Market Price of Nitrogen is Increased 10%
Yearly Earnings	-1.54%	18.31%
Rate of Return	-1.39%	16.54%
Process Produced Nitrogen Price	1.48%	0%

Table 2. Response of Economic Variables to Changes

Sensitivity of Yearly Earnings, Rate of Return, and Process Produced Nitrogen Price to Fluctuations in Market Price Nitrogen

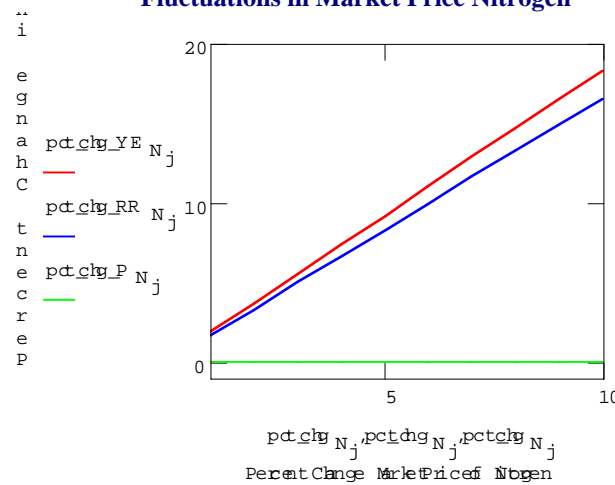


Figure 5: Response of Economic Variables to Changes in the Market Price of Nitrogen

With a 10 percent change in utility costs, the highest change was noticed in annual yearly earnings; nearly 20 percent. This 10% increase in utility cost yielded a 15% change in the rate of return. The parameter that was unaffected by the utility increase was the process price of the nitrogen.

Membrane Separation Process

The economic results of the membrane separation process are shown in Table 3.

Economic Data for Membrane Separation Process	
Total Capital Investment	\$192,266
Utilities per year	\$80,400
Manufacturing cost per year	\$338,200
Estimate of Annual Earnings	\$261,700
Estimate of Rate of Return	135.1%
Net Present Value	\$1,419,000
Process Nitrogen Price	\$0.29 per 100 SCF

Table 3: Economic Evaluation of the Membrane Separation Process

The distribution of these costs can be seen in the following pie chart (Fig. 6).

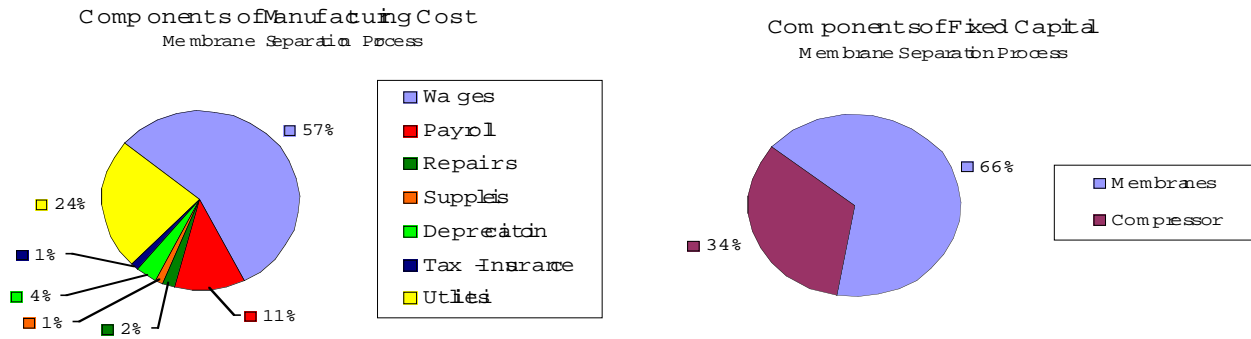


Figure 6: Components of Manufacturing Cost and Fixed Capital for Membrane Process.
 Comments on the Economic Analysis

The major components of the manufacturing cost are wages and utilities. The wage cost cannot be reduced because someone must monitor the process at all times while it is in operation in case there is a malfunction. The utility costs are also fixed and are a function of the compressor power requirements. All other costs are relatively small compared to these two costs. The membranes are the major component of the fixed capital.

Economic Sensitivity Analysis

A similar sensitivity analysis was performed on the membrane separation process economic data. The results are shown below, and the complete analysis can be found in Appendix A.4.

Sensitivity of Yearly Earnings, Rate of Return, and Process Produced Nitrogen Price to Fluctuations in the Market Price of Nitrogen

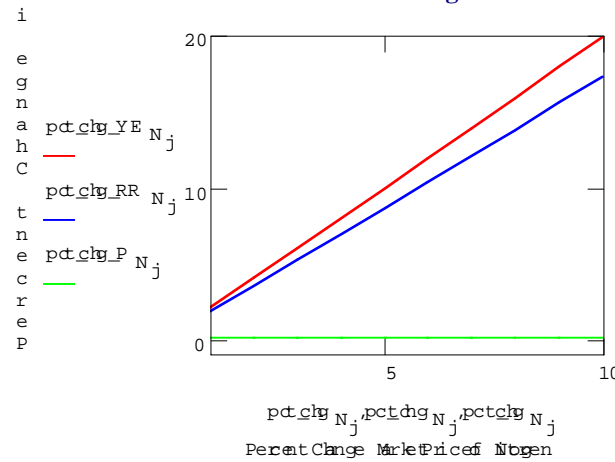


Figure 7: Response of Economic Variables to Changes in the Market Price of Nitrogen

A similar plot for fluctuations in the utility cost can be seen on P.4.12 of Appendix A.4. Plots of the response of a single calculated economic variable versus both of the fluctuating variables can be seen on P. 4.13-14 of Appendix A.4. For example, on P.4.13 the plot of percent change in yearly earnings versus the percent change in fluctuated variables shows that the yearly earnings increase substantially with an increase in the market price of nitrogen and decrease with an increase in utility costs. Responses of the calculated variables to 10% fluctuations are summarized in Table 7.

Variable	Percent Change When Utility Costs Are Increased 10%	Percent Change When The Market Price of Nitrogen is Increased 10%
Yearly Earnings	-2.09%	19.83%
Rate of Return	-1.81%	17.19%
Process Produced Nitrogen Price	1.74%	0%

Table 7: Response of Economic Variables to Changes

The most sensitive variable to fluctuations in utility costs is the process produced nitrogen price. The most sensitive variable to fluctuations in the market price of nitrogen is the yearly earnings. For example, if the market price of nitrogen is increased to \$.58 /100SCF (a 10% increase), the yearly earnings increase to \$313,600.

IV. THE DESIGN

4.1 & 4.2

PRESSURE SWING ADSORPTION PROCESS

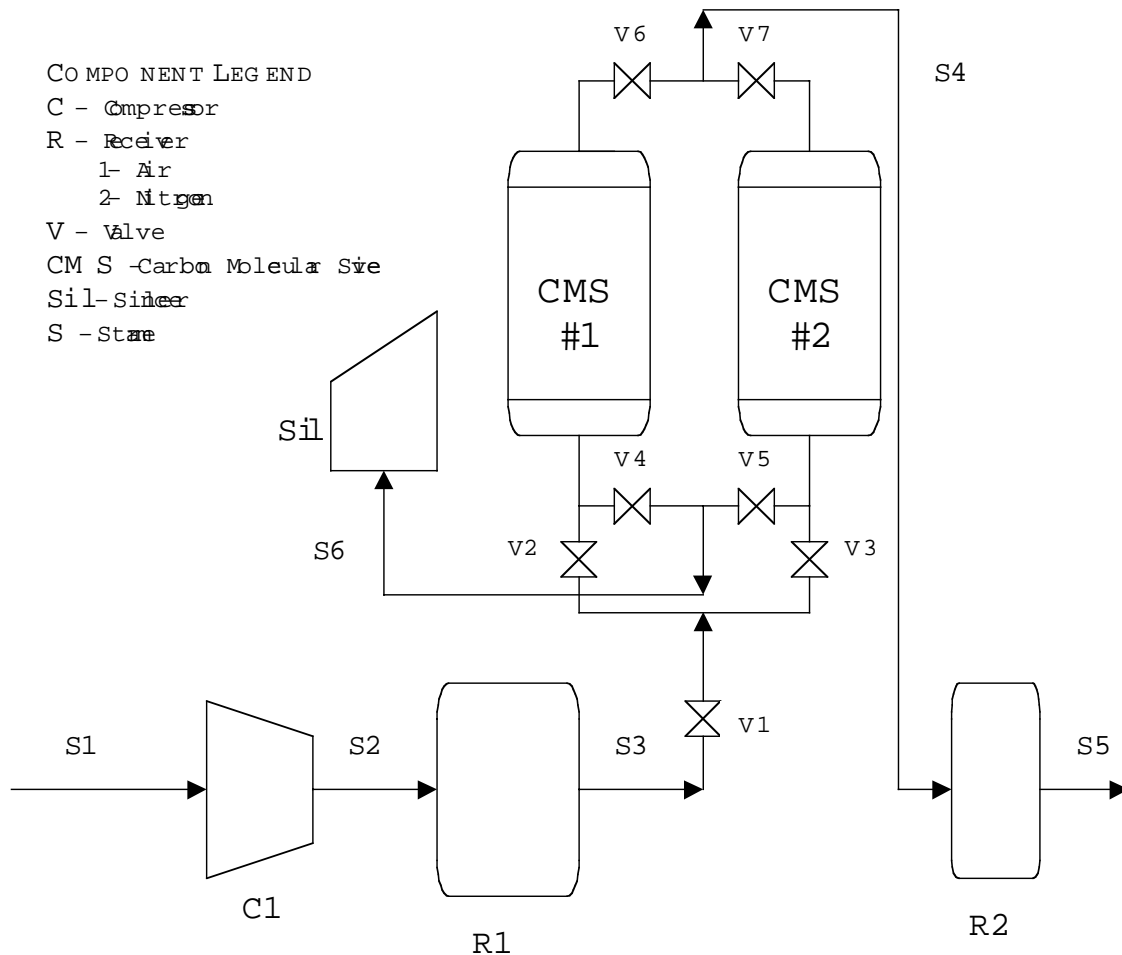


Figure 8: Schematic Component Diagram of PSA Process

STREAM TABLE

stream	Flowrate gmole/sec	Pressure kPa	Temperature K	Compositions (Mole Fractions)						Enthalpy J/gmole	Phase
				N ₂	O ₂	Ar	H ₂ O	CO ₂	Ac		
1	15.34	101.325	294.26	0.78	0.2095	0.0094	7.17x10 ⁻⁴	3.75x10 ⁻⁴	8x10 ⁻⁶	-591.85	G _{as}
2	15.34	790.83	294.26	0.78	0.2095	0.0094	7.17x10 ⁻⁴	3.75x10 ⁻⁴	8x10 ⁻⁶	-648.35	G _{as}
3	15.34	790.83	294.26	0.78	0.2095	0.0094	7.17x10 ⁻⁴	3.75x10 ⁻⁴	8x10 ⁻⁶	-648.35	G _{as}
4	7.02	790.83	294.26	0.972	0.01	0.018	0.0	0.0	0.0	-1293.18	G _{as}
5	7.02	790.83	294.26	0.972	0.01	0.018	0.0	0.0	0.0	-1293.18	G _{as}
6	8.32	101.325	294.26	0.619	0.378	1.73x10 ⁻³	1.32x10 ⁻³	6.91x10 ⁻⁴	1.48x10 ⁻⁵	-45.87	G _{as}

Table 8: Tabular Summary of Mass and Energy Balance Calculations

MEMBRANE SEPARATION PROCESS

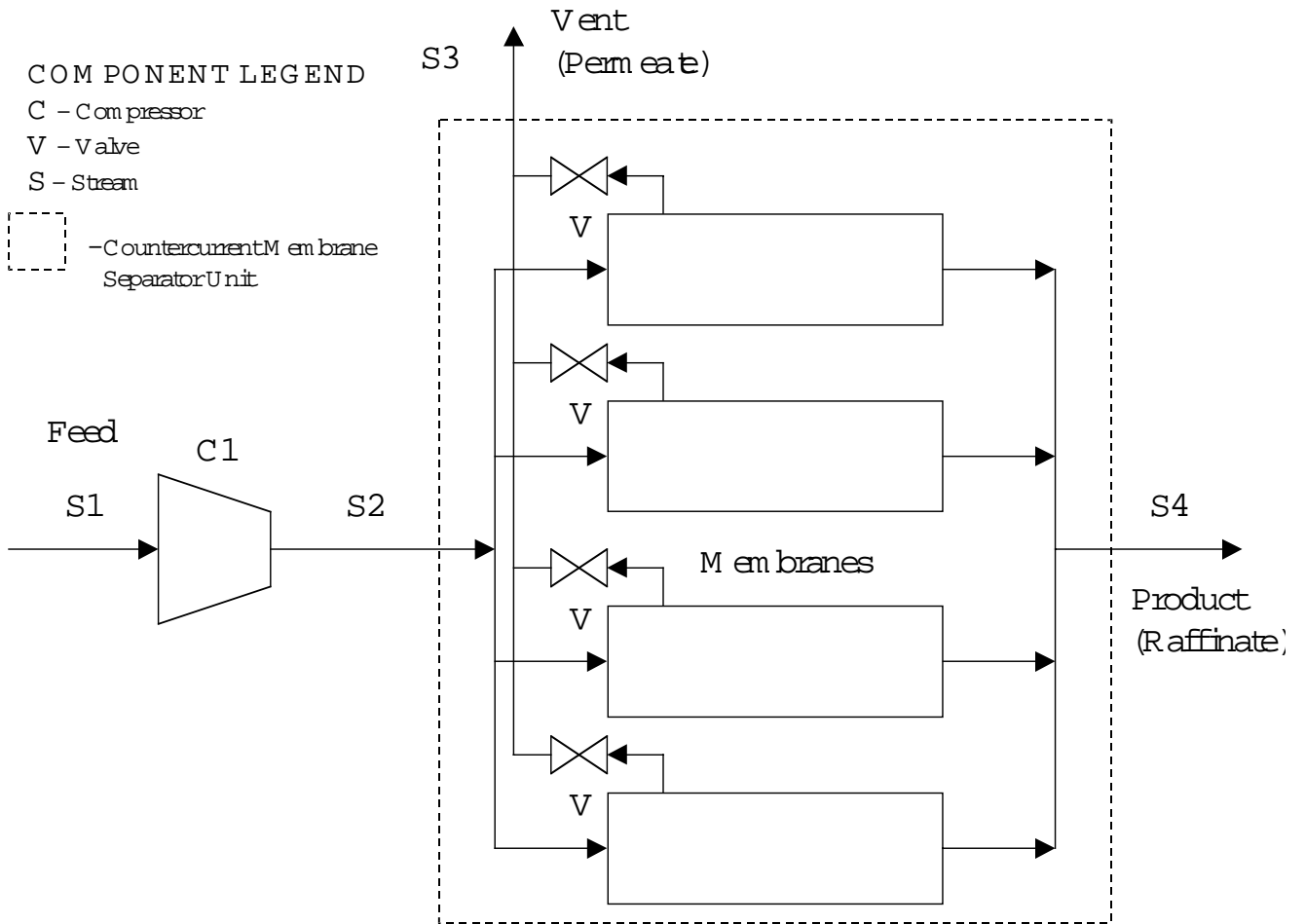


Figure 9: Schematic Component Diagram of Membrane Separation Process.

SCHEMATIC FOR MASS BALANCE CALCULATIONS

Flowrate (F_x) [=] gmol/sec

Temperature (T) [=] K

Pressure (P) [=] kpa

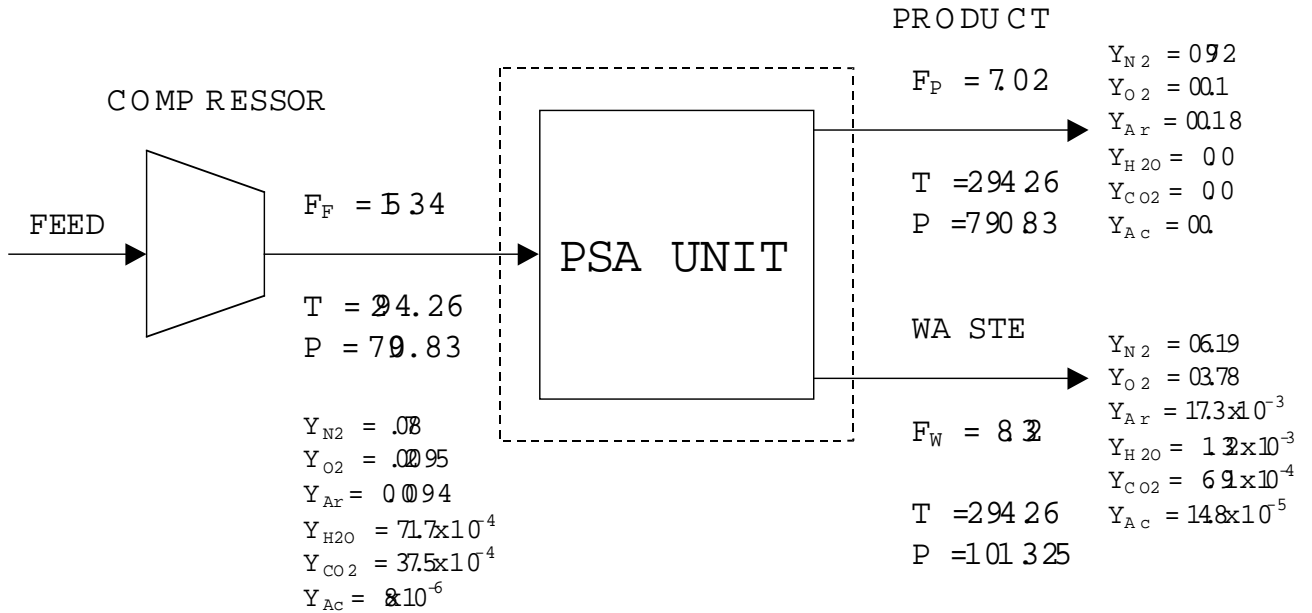


Figure 10: Schematic PSA Unit with Mass Balance Data

SCHEMATIC FOR ENERGY BALANCE CALCULATIONS

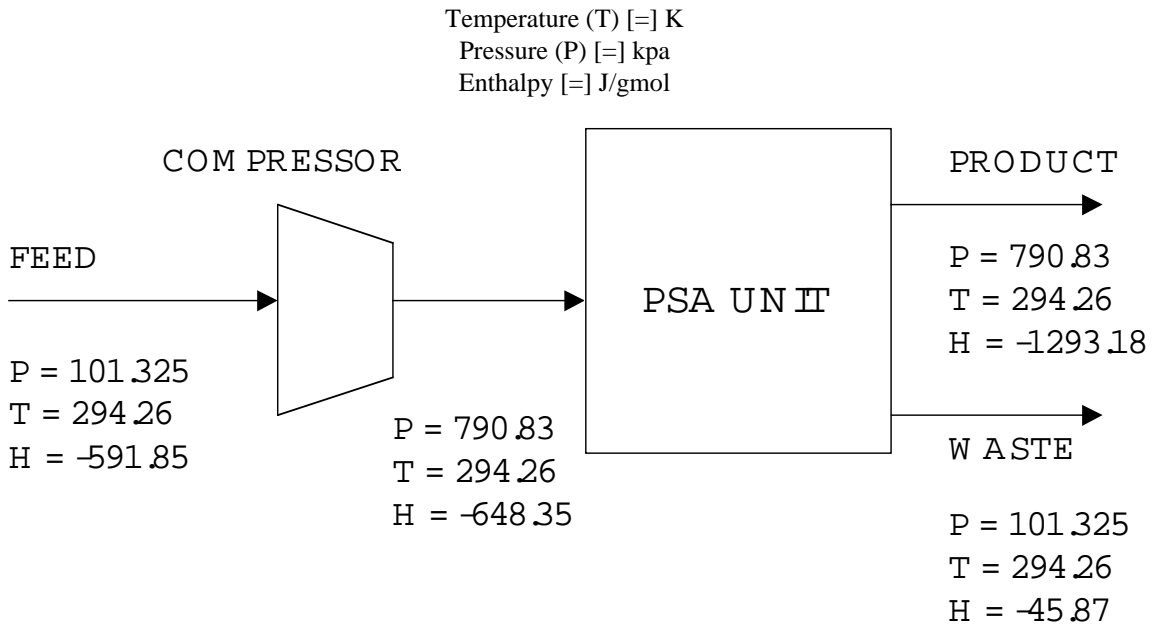


Figure 11: Schematic PSA Unit with Energy Balance Data

MEMBRANE SEPARATION PROCESS

COMPRESSOR BALANCE

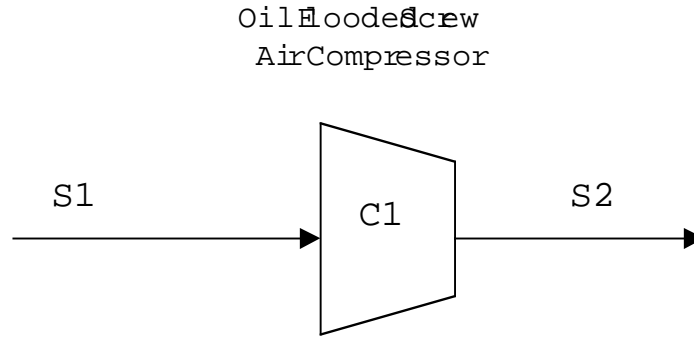


Figure 12: Schematic of Compressor Balance

STREAM TABLE

Stream	Flowrate gmole/sec	Pressure kPa	Enthalpy J/gmol	Temperature K	Composition (Mole Fractions)			Phase
					N ₂	O ₂	Other	
1	21.09	101.32	-591.85	294.26	0.7894	0.2095	0.0011	Gas
2	21.09	790.80	-648.35	294.26	0.7894	0.2095	0.0011	Gas

Table 9: Tabular Summary of Compressor Mass & Energy Balances

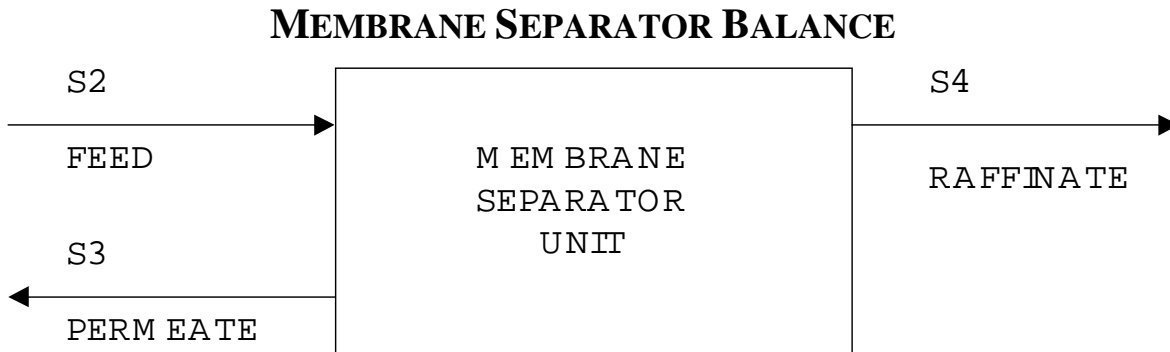


Figure 13: Schematic of Membrane Separator Balance

STREAM TABLE

Stream	Flowrate gmole/sec	Pressure kPa	Enthalpy J/gmol	Temperature K	Composition (Mole Fractions)			Phase
					N ₂	O ₂	Other	
2	21.09	790.80	-648.35	294.26	0.7894	0.2095	0.11	Gas
3	14.07	103.43	-271.06	294.26	0.6910	0.3073	0.0017	Gas
4	7.02	790.80	-1308.69	294.26	0.99	0.01	0.0	Gas

Table 10: Tabular Summary of Membrane Unit Mass & Energy Balances

4.3 Equipment List and Specifications

PSA

Component

Specifications

(1) Oil flooded screw compressor Model

Model Ga160 – Power 160 kW
Processes up to 380 L/s
60% Isentropic Efficiency
Cost: \$45,500

(2) Vessels for CMS

Carbon Steel; P up to 200 psig
L = 11.2 ft D = 2.8 ft.

Carbon Molecular Sieve

45 lbs/ft³ Cost: \$5/lb-cms (2005 Prices)
Performance and Productivity data
located in Figure 2 on page 4.

Piping and Valves, 2 Receivers (Storage)
Silencer

not sized and costed

Membrane Separation

Component

Specifications

(1) Oil flooded screw compressor Model

Model Ga160 – Power 160 kW
Processes up to 380 L/s
60% Isentropic Efficiency
Cost: \$45,500

Membrane Separation Unit

144 Membrane Separation Units
OD Range 325-475 microns
Inter-fiber void volume- 0.5 cm³/cm³
Cost = 350 + 0.6*SA (ft²)

Valves, piping

not sized and costed

4.4 Economic Information

The values of the following economic parameters were computed for both processes. The derivation of the results can be found in Appendix A.

	PSA	Membrane Separation
Total Capital Investment	\$169,300	\$192,266
Utility Cost per year	\$64,000	\$80,400
Manufacturing Cost	\$318,500	\$338,200
Estimate of Annual Earnings	\$283,500	\$261,700
Estimate of Annual Rate of Return	185.3%	135.1%
Net Present Value	\$1,536,000	\$1,419,000

V. CONCLUSIONS AND RECOMMENDATIONS

- Pressure Swing Adsorption is preferred to Membrane Separation.

- Both processes are physically and technically feasible in meeting the product specifications.
- The NPV of PSA and membrane separation are \$1,536,000 and \$1,419,000, respectively.
- The yearly earnings of PSA and membrane separation are \$283,500 and \$261,700, respectively.
- The rate of return of PSA and membrane separation are 185.3 and 135.1%, respectively.
- The break-even price for PSA and membrane separation are \$.27 and \$.29 per 100 SCF, respectively.
- PSA is favored if an expansion of capacity is required.
- The yearly earnings and rate of return were found to be most sensitive to the market price of nitrogen
- The economics should be reconsidered if the market price of nitrogen is expected to change significantly.

VI. ACKNOWLEDGEMENTS

Lorenz T. Biegler – For guidance and support throughout the research and writing.

Bud Kuhn from Atlas-Copco – for his last minute help with compressor costs.

VI. NOMENCLATURE

PSA Calculations

F_p – Product flowrate

F_{in} – Feed flowrate (total)

F_w – Waste Flowrate

FX_{N_2} – Molar Flowrate of Nitrogen

X = f; specifies feed

FX_{Ar} – Molar Flowrate of Argon

X = p; specifies product

FX_{O_2} – Molar Flowrate of Oxygen

X = w; specifies waste

FX_{H_2O} – Molar Flowrate of Water

FX_{Ac} – Molar Flowrate of Acetylene

FX_{CO_2} – Molar Flowrate of Carbon Dioxide

R_{N_2} – Recovery of Nitrogen

Purity – Purity of Nitrogen

$Y_{X_{N_2}}$ – Mole fraction of Nitrogen

x = f; specifies feed

$Y_{X_{Ar}}$ – Mole fraction of Argon

x = p; specifies product

$Y_{X_{O_2}}$ – Mole fraction of Oxygen

x = w; specifies waste

$Y_{X_{H_2O}}$ – Mole fraction of Water

$Y_{X_{Ac}}$ – Mole fraction of Acetylene

$Y_{X_{CO_2}}$ – Mole fraction of Carbon Dioxide

Membrane Calculations

FEED – Feed flowrate (total)

FFN – N_2 flowrate in feed stream

FFO – O_2 flowrate in the feed stream

FFOT – O_2 flowrate in the feed stream

FPN – $N_2 + Ar$ flowrate in permeate stream

FPO – O_2 flowrate in the permeate stream

FR – Raffinate flowrate

FRN – $N_2 + Ar$ flowrate in raffinate stream

FRO – O_2 flowrate in the raffinate stream

FTOT – Permeate flowrate (total)

FTOTP – Flowrate of fast gas in permeate stream

Q1 – Area fraction

R1 – Recovery of fast gas

R2 – Recovery of slow gas

RT – Total recovery in permeate
yN₂ – Mole fraction of N₂ + Ar in permeate stream
yO₂ – Mole fraction of O₂ in permeate stream
yOTH – Mole fraction of “other” in permeate stream
YP – Mole fraction of O₂ + “other” in permeate

VII. BIBLIOGRAPHY

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Preliminary Design of Nitrogen Processes

```
S = 6.0
PR = 7.646
IMEM = 3
IOPT = 5
FEED FLOW RATE= 75924.99198770371
ALL FLOWRATES ARE IN GMOL/HR
NITROGEN FEED FLOWRATE: 59935.1886750933
OXYGEN FEED FLOWRATE: 15906.28582142392
OTHER FEED FLOWRATE: 83.51749118647408
NITROGEN PERMEATE FLOWRATE: 35001.90111681684
OXYGEN PERMEATE FLOWRATE: 15570.0733797004
OTHER PERMEATE FLOWRATE: 83.51749118647408
NITROGEN RAFFINATE FLOWRATE: 25016.8046875
OXYGEN RAFFINATE FLOWRATE: 252.6949920654296
RAFFINATE PRESSURE (PA): 790801.0
PERMEATE PRESSURE (PA): 103426.7590897201
FEED PRESSURE (PA): 790801.0

      YP      .30902
      R1      .98411
      R2      .58318
      RT      .66718
      Q1      .44722
```

Figure 2. Sample FORTRAN Membrane Simulation Output

```
c *****
c This is all code that was added for the simulation
c *****
c This calculates the pressures of all of the streams.
c The raffinate pressure is set to 100 psig.
c This is the same as the feed pressure.
  PRAF=790801 !This is in Pa
  PFEEED=PRAF
  PP=PFEEED/PR
c This solves and displays the mass balance for each separator.
c To solve the mass balance we need to know the feed flow rate.
c We can solve this from a simple mass balance.
c The units are molar flowrates and have units of gmol/hr.
c The mole fractions of nitrogen and 'other' species
c are specified first.
  YFN=.7894
  YFOT=.0011
  FEED=(25269.5)/(1-RT)
  WRITE (5150,*) 'ALL FLOWRATES ARE IN GMOL/HR'
  WRITE (5150,*) 'FEED FLOW RATE= ', FEED
  FRN=.99*25269.5
  FTOTP=RT*FEED*YP
  FFOT=YFOT*FEED
  FFN=YFN*FEED
  FFO=YF*FEED
  FPOT=FFOT
  FPO=FTOTP-FPOT
  FPN=RT*FEED*(1-YP)
  FRO=.01*25269.5
```

Preliminary Design of Nitrogen Processes

```
WRITE (5150,*) 'NITROGEN FEED FLOWRATE: ', FFN
WRITE (5150,*) 'OXYGEN FEED FLOWRATE: ', FFO
WRITE (5150,*) 'OTHER FEED FLOWRATE: ', FFOT
WRITE (5150,*) 'NITROGEN PERMEATE FLOWRATE: ', FPN
WRITE (5150,*) 'OXYGEN PERMEATE FLOWRATE: ', FPO
WRITE (5150,*) 'OTHER PERMEATE FLOWRATE: ', FPOT
WRITE (5150,*) 'NITROGEN RAFFINATE FLOWRATE: ', FRN
WRITE (5150,*) 'OXYGEN RAFFINATE FLOWRATE: ', FRO
WRITE (5150,*) 'RAFFINATE PRESSURE (PA): ', PRAF
WRITE (5150,*) 'PERMEATE PRESSURE (PA): ', PP
WRITE (5150,*) 'FEED PRESSURE (PA): ', PFEED
WRITE(6,10) YP, R1, R2, RT, Q1
WRITE(5150,10) YP, R1, R2, RT, Q1
C *****
```

Figure. 3. Code Added to Solve the Mass Balance for Every Simulation