NTNU – Trondheim
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A systematic Design Methodology for Multicomponent Membrane Systems

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Masters thesis

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MASTER THESIS

for

Student Opeyemi Bamigbetan

Spring 2015

A Systematic Design Methodology for Multicomponent Membrane Systems

En systematisk metodikk for multikomponente membran-systemer

Background and objective

Gas separation membranes represent a promising technology for post-combustion carbon capture. The driving force for membrane systems is the partial pressure difference between the feed and the permeate stream. The purity of the product, in this case CO_2, and the extent of separation depend on membrane properties such as selectivity and permeability in addition to available membrane area and the partial pressure differential. Designing cost-optimal membrane processes is thus a complex task, since there are quite a few parameters to tune. SINTEF Energy Research is developing a systematic graphical methodology for designing cost-optimal membrane processes with similarities to Pinch Analysis and the concept of an Attainable Region.

A specialization project in the fall 2014 developed a program for multicomponent membrane systems based on a model from the literature. This program was tested and compared with values from the literature for both binary and multicomponent systems. The Attainable Region methodology is based on the assumption that the feed consists of 2 components only, so even though results with remarkable small deviations were produced during the project, the application of the graphical method for the multicomponent model is restricted.

The main objective of this Master thesis project is to extend the synthesis methodology for membrane based separation processes to a broader range of applications.

The following tasks are to be considered:

1. Extend the synthesis methodology for multiple components. The McCabe-Thiele stage-wise visual method originally developed for distillation processes unfortunately only works for binary systems. Ways to extend this for multi-component systems should be explored.
2. The methodology for membrane system design is currently set up for post-combustion capture systems. The methodology should be modified for application to more generic cases (e.g. for biogas clean-up, H_2 separation, etc.)
3. The developed methodology does not work, in its present form, for cases where there is a sweep gas stream on the permeate side. Possibilities to extend the methodology to include sweep gas should be explored.

Within 14 days of receiving the written text on the master thesis, the candidate shall submit a research plan for his project to the department.

When the thesis is evaluated, emphasis is put on processing of the results, and that they are presented in tabular and/or graphic form in a clear manner, and that they are analyzed carefully.

The thesis should be formulated as a research report with summary both in English and Norwegian, conclusion, literature references, table of contents etc. During the preparation of the text, the candidate should make an effort to produce a well-structured and easily readable report. In order to ease the evaluation of the thesis, it is important that the cross-references are correct. In the making of the report, strong emphasis should be placed on both a thorough discussion of the results and an orderly presentation.

The candidate is requested to initiate and keep close contact with his/her academic supervisor(s) throughout the working period. The candidate must follow the rules and regulations of NTNU as well as passive directions given by the Department of Energy and Process Engineering.

Risk assessment of the candidate's work shall be carried out according to the department's procedures. The risk assessment must be documented and included as part of the final report. Events related to the candidate's work adversely affecting the health, safety or security, must be documented and included as part of the final report. If the documentation on risk assessment represents a large number of pages, the full version is to be submitted electronically to the supervisor and an excerpt is included in the report.

Pursuant to "Regulations concerning the supplementary provisions to the technology study program/Master of Science" at NTNU §20, the Department reserves the permission to utilize all the results and data for teaching and research purposes as well as in future publications.

The final report is to be submitted digitally in DAIM. An executive summary of the thesis including title, student's name, supervisor's name, year, department name, and NTNU's logo and name, shall be submitted to the department as a separate pdf file. Based on an agreement with the supervisor, the final report and other material and documents may be given to the supervisor in digital format.

☐ Work to be done in lab (Water power lab, Fluids engineering lab, Thermal engineering lab)
☐ Field work

Department of Energy and Process Engineering, 13 January 2015

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Abstract

Fossil fuel predominantly dominates the world energy supply. With energy demand set to increase, especially for developing countries, CO_2 emissions tax and the environmental impact of high CO_2 concentration in the atmosphere emphasises the need for a cost effective solution to CO_2 emissions capture. Existing CO_2 capture technologies are expensive, giving an opportunity for a new technology. Membrane technology is emerging has the alternative solution in the CO_2 capture market.

Finding the right design and configuration for a membrane system is difficult and time consuming. A simple way has been developed which makes use of a graphical representation of stages of membrane system with cost curve for optimization. This method for systematic membrane design has been tested and seen to be a useful tool in the early design phase of a membrane system. This report develops this methodology in two main areas. First, it extends the graphical methodology from a binary feed to a ternary feed by the development of new design concepts. Secondly, it expands the application of the methodology to more industries other than CO_2 post combustion capture by incorporating different process scenarios into the methodology.

Acknowledgement

I wish to express my sincere thanks to my supervisor, Professor Truls Gunderson, for his guidance throughout the period of writing my thesis.

I am also grateful to my co-supervisor, Rahul Anantharaman, SINTEF Energy Research for sharing his knowledge, expertise and providing valuable support on my thesis topic.

To my friends, family and all who directly or indirectly made this journey a memorable one. I say a big thank you.

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Chapter 1

1. Background and Motivation

1.1. Introduction

Designing a membrane system with optimal performance at minimum cost can be very challenging. A high degree of freedom leads to various possibilities for the configuration of the system. Choosing the most cost effective and operationally optimal configuration out of these many possible configurations requires a systematic approach to designing the system. This systematic approach should factor in it multiple variables as a combined simple target function “cost”. It should present the ability to perform design analysis that reflects a trade-off between this function “cost” and another variable function as desired. The membrane system with conflicting effects of energy and area with respect to cost should therefore optimize as a cost-based engineering process (Zhang et al., 2013). It should enable a designer to make qualitative and quantitative decisions at the early design phase of the membrane system. It should assist to inform a designer of the practicality of his design, its potential cost and the design options available to him early enough in the development process.

The principles of a systematic approach to solving systems of multi-variable functions have been applied to membrane technology. The method involves the use of a graphical methodology for the synthesis of membrane systems for CO_2 capture applications. It enables the user or the system designer to visualize the entire system in a series of plots. These plots depicts the distribution of cost across multiple stages of a membrane system against a particular function value, in this case CO_2 purity. This graphical design methodology have been used in the analysis of three process plants; Cement Plant, Coal based and Natural Gas based Power plants for post combustion CO_2 capture. The cost, complexity of the membrane system, details of components per stage, CO_2 purity and Carbon Capture Ratio (CCR) achieved for the process plants were determined at optimal point by the use of this graphical methodology for membrane design. The design methodology is simple and easy to use. It was direct in approach and reveals information about the system including the possibilities for stream recycle. The graphical design methodology enabled optimization of the system to achieve a desired minimum cost or in some cases a simplification of the system by a reduction of the number of stages.

The graphical design methodology for membrane systems was developed by Lindqvist and Anantharaman (2014). The design methodology is in its early phase but has shown potential as a tool for analysing and predicting the most cost effective solutions for post combustion CO_2 capture. This methodology has areas for possible improvement. A last year specialization project was dedicated to research into improvements towards expanding the application of the graphical design methodology. It included applying the method to designing membrane systems for Coal and Natural Gas power plants. It also involved research into multicomponent feed solutions to improve on the assumption of the initial design of a binary component feed. This report will present further research into possible improvements of the design methodology in the areas of graphical representation of a multicomponent feed stream and the expansion of the graphical design methodology for application in other separation processes utilizing membrane technology for separation.

1.2. Motivation

Reducing greenhouse gas is probably the most significant challenge in combating global climate change. CO_2 is the main greenhouse gas emitted through the activities of humans. Though naturally present in the atmosphere, human activities alters the carbon cycle leading to increase of CO_2 in the atmosphere. The atmospheric CO_2 concentration has steadily increased since the industrial revolution. This increase is attributed to the consumption of fossil fuels such as coal, oil and natural gas (Wei et al., 2012). It is reported by IPCC (Bernstein et al., 2007) that CO_2 from fossil fuel contributes about 57% of all anthropogenic greenhouse gases emissions. This sadly is bound to increase with global energy demand set to climb especially in developing countries.

Carbon capture and storage (CCS) is the way forward if energy is to be extracted from fossil fuel with protection for the environment. Several technologies under CCS have been developed to control and capture CO_2 emissions. One of such technologies is the use of polymer membranes. Geankoplis (2003) noted that the use of membranes for separation is becoming increasingly important in the process industry. Existing technology for CO_2 capture require very high investment and leads to loss of the process plant efficiency (Metz et al., 2005). This increases the need for a more energy-efficient and cost effective capture technology. Chemical absorption processes like solvent monoethanolamide (MEA), has been the most used capture technology around the world for post combustion processes (Blomen et al., 2009). This method requires high energy due to the regeneration of the solvent. It also suffers degradation of the solvent due to secondary reactions.

With more regulations set to come in an attempt to force down emissions, there is an urgent need to have a technology that is competitive both in terms of cost and in terms of effectiveness. Due to the low fraction of CO_2 in the exhaust gas of most commercial processes, the application of membrane technology based on existing membrane material is not straightforward. This is so because multiple stages of membranes will be required to achieve set targets of purity and Carbon Capture Ratio (CCR). The number of stages with their operating conditions then becomes the important question to determine the cost of the membrane system. If not properly designed, the cost will be unnecessarily high and uncompetitive with other methods of CO_2 capture and CO_2 avoidance tax.

Being a relatively new technology with respect to the few areas of existing applications, the possibility of cost savings exists in the design phase of a membrane system. This is particularly so as a membrane system requires the right balance between operational conditions and cost. Most methods of designing membrane systems involve a trial and error approach due to the complexity of finding the right configuration of a membrane at minimum cost (Lindqvist & Anantharaman, 2014). It is for this reason a systematic methodology was developed by Lindqvist and Anantharaman (2014). This systematic methodology uses a graphical representation to assist a designer in making decisions as to how the membrane system will be configured at minimum cost. The methodology being in its early stage requires further development to enable accurate application to physical processes and a generic methodology for membrane separation not only focused on CO_2 post combustion capture but rather for all separation processes.

Several effort have gone into the benefits of having a systematic approach to designing membrane systems. Glasser et al. (2009) investigated the importance of having an energy efficient plant integrated with a carbon capture technology. They concluded that there is a need to adopt a systematic approach to evaluate and compare processes to find the optimal cost saving alternative. Also, research into the effects of designing an energy efficient process with CO_2 capture technology was done by Anantharaman et al. (2013). After evaluation of different process integration methods with a focus on a systematic approach, it was clear to them that there is potential savings from it.

1.3. Focus of the work

For the graphical design method to be a true representation of a physical system, it is important that the approximations and assumptions made are as few as possible and a true representation of physical systems. The graphical design method developed by Lindqvist and Anantharaman (2014) has an assumption of a binary feed composition. This assumption is made possible because the combination of CO_2 and N_2 constitute over 80% of the total feed composition to the post combustion membrane system. However, for a more accurate analysis and estimation, the feed composition considered should reflect the actual composition or as close as possible to ensure the accuracy of the system. It is therefore necessary to consider more than a binary feed composition. The new graphical design method proposed in this report utilizes a ternary feed composition.

With the success of the graphical design methodology in designing and analysing different process plants for CO_2 capture post combustion, it will be interesting to broaden the application to other process systems such as pre-combustion processes, biogas clean up, H_2 separation and many more. A more generic approach in the design will be required to enable its application to other industries and processes. A new design approach is therefore needed, though with the same idea and representation, but with a broader scope. This report will demonstrate research into the expansion of the methodology to enable application to other separation processes with membrane technology.

The model used by the binary and ternary feed composition also had an assumption of no sweep gas stream. Since the driving force for the purity of CO_2 is the partial pressure difference of the feed and permeate side, a sweep gas on the permeate side will improve this driving force and enhance a purer CO_2 out from the system. Is it therefore necessary to investigate further the benefits of extending the developed graphical design to include sweep gas stream.

1.4. Structure of the Thesis

In its presentation of ideas, proposed designs and analysis of data, this report will have the following structure. Following this introduction there will be a literature review in Chapter 2 divided into three sections. The first will be a review of the existing graphical design methods for binary component membrane system. This section will include notable works on systematic design methods for membrane systems. The second section of the literature review will focus on multicomponent feed membrane systems. The last section will be a review of the application of graphical design methods in providing solutions to engineering designs. In Chapter 3, there will be a presentation of the theories behind the binary graphical design method, the multicomponent model for membrane separation and some fundamentals about membrane technology. In Chapter 4, there will be a presentation of the proposed concepts for a graphical methodology for design of membrane systems with a ternary feed composition. Chapter 5 will explain modifications to the developed methodology to incorporate other separation systems and make the method more generic. This report will conclude with a summary of results and ideas. Finally, there is presentation of recommendations for further studies. Each chapter will start with by a brief introduction.

Chapter 2

2. Literature review

2.1. Introduction

Designing membranes for post combustion capture has over the years improved in methods and techniques used. Lonsdale (1982) highlighted the growth of membrane technology over the years with an overview of references and important works leading to the present state of development of membrane technology. Gin and Noble (2011) looked into the possible future and the next type of membranes for separation. Their focus was on membrane materials. The focus of this report is on the structure and configuration of the membrane as a system of separation and not on the membrane material.

This question arises, "given a membrane type, how can a membrane system be designed to meet the required specifications in the most cost effective way". Glasser et al. (2009) tried to answer this question. They investigated the importance of having an energy efficient plant integrated with carbon capture. They concluded that there is a need to adopt a systems approach to evaluate and compare processes to find the optimal cost saving alternative. Anantharaman et al. (2013) had also investigated the role played by process synthesis and process integration towards reduction in investment costs and improvement in efficiency of capture technology. Therefore, an answer to the question above would be to approach the design in a systematic manner while optimizing its variables within set constraints to minimize cost as done in process synthesis. Some have made this systematic design method to membrane technology. The different ideas will be discussed with a focus on the idea of a systematic design using a graphical method by Lindqvist and Anantharaman (2014).

2.2. The Graphical Design Methodology

SINTEF Energy Research group has developed a graphical design methodology for membrane technology for post combustion CO_2 capture. It is a novel idea using the concept of process synthesis to design a membrane separation system that will achieve the required CO_2 purity in a cost effective way. The method has been applied to evaluate membrane system for a cement process plant (Lindqvist et al., 2013) and for Coal based and Natural Gas based power plant in last year specialization project prior to this thesis. This approach uses a graphical display to visualize an attainable region in which membrane stages can operate while taken into consideration the optimal cost. The number of stages and operating points of each membrane stage can be identified using an approach similar to the McCabe Thiele binary distillation diagram.

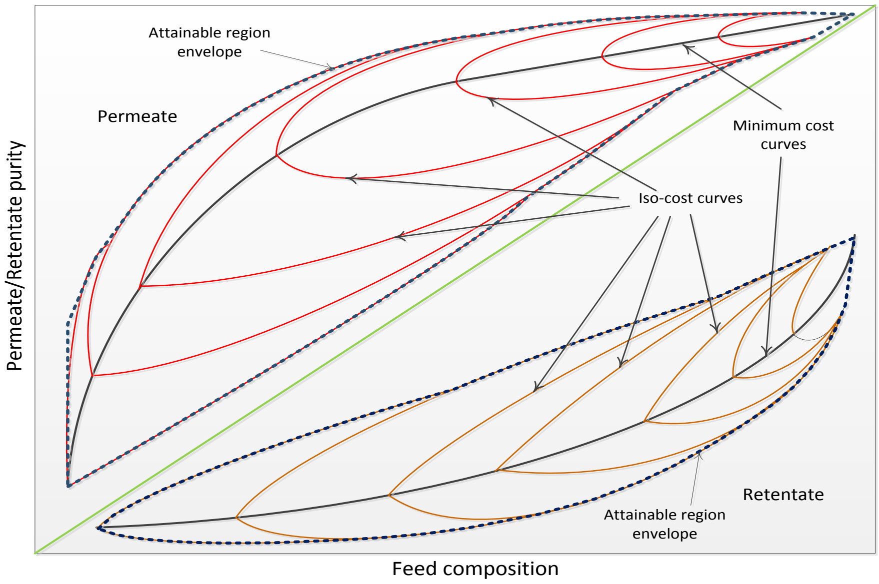


Figure 2-1: Concentration versus minimum and iso-cost curves for a given membrane and CCR (Lindqvist & Anantharaman, 2014)

The graph in Figure 2-1 shows a completed graphical plot. This graph will be used to design and estimate the number of stages, details about each stages and the overall cost of the membrane system. The attainable region indicates all possible solution to the membrane type for both the permeate and the retentate side of the membrane. Details of how this graphical design works will be explained in Chapter 3.

2.3. The Trial and Error Method

In systems of multiple variables, it is quite common to use a trial and error method to determine the optimal solution for a given function, in most cases a cost function. The limitation to this method apart from being exhaustive is that it is difficult to pre-determine a capture cost ratio CCR with a set purity at minimum cost. A compromise will have to be made to one of the requirements.

This trial and error method was used by Merkel et al. (2013) in determining optimal membrane properties that reduces the minimum energy for CO_2 capture while investigating the impact of a selective exhaust gas recycle with membrane configuration. Kundu et al. (2014) similar to Merkel et al. (2013) during their investigation into the effectiveness of hybrid membrane systems compared with absorption with amines for post-combustion CO_2 capture, used several single stage and multistage membrane system configuration to evaluate performances and minimize cost. Scholes et al. (2014) utilized the trial and error methodology by comparing three distinct process designs and simulation to evaluate the performance and cost related to each. These methods do not approach design of a membrane system by systematically analysing the attainable region possible for the process conditions and developing the process design that will achieve the minimum cost.

2.4. The Multiple Configuration Method

Research done by Lee et al. (1995) investigated the effects of variables such as pressure, feed flow rate, and CO_2 feed composition. Membrane modules were tested on field for separation of CO_2 from low-quality natural gas (Lababidi et al., 1996). They optimized three configurations of membrane systems using their developed mathematical model. Wang et al. (2007) were the first to use auto-controlling of permeate gas flux that improved the operational flexibility and adaptability of membrane processes. Optimization of gas processing cost for the membrane unit as done by Datta and Sen (2006) showed that by adjusting the number of modules in each stage and the compressor power, the optimal configuration can be achieved for a certain range of CO_2 feed gas composition and minimum capture cost. Hao et al. (2008) identified the best membrane configuration that will give the minimum capture cost by focusing on upgrading low-quality natural gas. They evaluated various system configurations and found the most economical processes for the system design.

Qi and Henson (2000), proposed a design strategy for membrane networks separating multicomponent gas mixtures based on an approximate permeator model and mixed-integer nonlinear programming (MINLP). A permeator system superstructure is used to enable a large number of possible network configurations. This allowed permeate feed-side pressure to be fixed. The MINLP minimized the total annual process cost by simultaneously optimizing the permeator configuration and operating conditions. The study was conducted on separation of acid gases (CO_2 and H_2S) from crude natural gas. The strategy was to evaluate multiple system designs with varying number of components while area is allowed to change continuously or discretely. The results showed that the MINLP strategy is an effective tool for preliminary design of multistage, multicomponent gas membrane systems, including those components with very low mole fraction.

2.5. Multicomponent Membrane Design

Though a lot of research goes into design model for gas separation, most of it are dedicated to binary feed components for its simplicity. Only few reports exist for calculations for multicomponent gas separation by permeation (Shindo et al., 1985). Unfortunately, in most practical applications, there will be more than two components for separation. The influence of the other components, though probably with relatively small mole fractions, does play a role in changing the partial pressures of the more important gases and as such cannot be neglected for designing membrane systems. In addition, having a model as close to practical applications is important to the development of a systematic methodology for membrane design.

Two decades ago, Pettersen and Lien (1994) presented a robust method for designing membranes modules for multicomponent gas separation. The method provides a simple algebraic solution to membrane calculations. The method was developed by making an analogy to heat exchanger systems with both being a rate-governed process. Similarities between the heat transfer flux and temperature driving force of heat exchanger systems with rate of permeation and the partial pressure differential of membrane systems were made in the model. The model was simplified to algebraic equations using the Paterson approximation to the logarithmic mean (Paterson, 1984). This eases the challenge of developing computer programs to solve the equations. The results showed that product purity was predicted to within 2% deviation to numerical and experimental results from literature. The work of Pettersen and Lien (1994) is the model used in this thesis for all ternary graphical representations. The model will be explained in Chapter 3.

Shindo et al. (1985), presented calculation methods for multicomponent gas separation by permeation. Different flow patterns such as cocurrent flow, counter current flow, cross flow, perfect mixing and one-side mixing were considered. Equations were derived for each type of flow pattern, though different flow pattern had similar equations valid between them. Their results were based on both polymeric membranes and micro porous glass membrane.

2.6. Graphical Solutions to Engineering Design

Graphical design is the methodology of visual communication, and problem solving using type, space and image. As already discussed, Lindqvist and Anantharaman (2014) used this graphical design methodology and applied it to systematic design of membrane systems. Graphical designs as a method to solve engineering challenges in an easy and visual way that has been in existence for a long time. Lindqvist and Anantharaman (2014) graphic design is very similar to the design concept by Mccabe and Thiele (1925) for distillation processes in that it visually represents the attainable regions and a user can systematically describe the required steps to achieve a specified function. The McCabe–Thiele method is a simple and instructive way for analysis of binary distillation. The composition at each theoretical tray is completely determined by the mole fraction of one of the two components under certain assumptions.

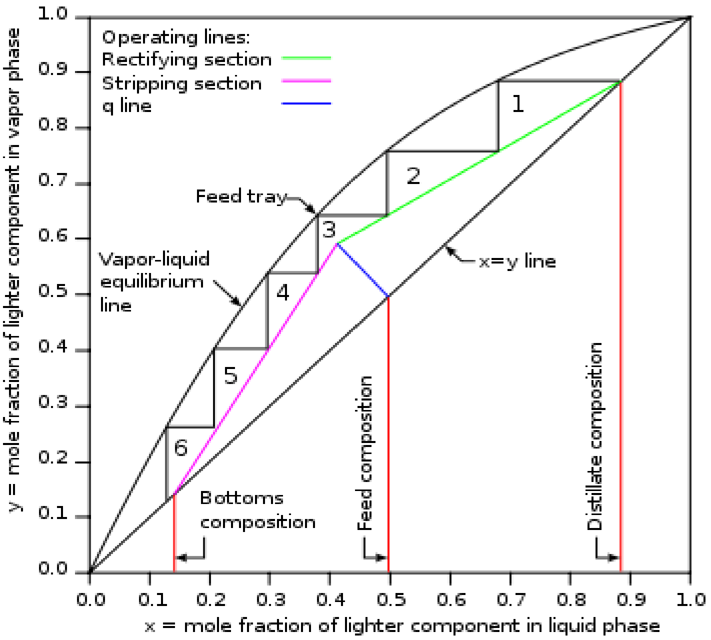


Figure 2-2: McCabe-Thiele method illustration

Olan-Acosta et al. (2014) used the graphical design method to solve quaternary systems in simultaneous chemical and physical liquid–liquid equilibrium (reaction–separation process). Using two projection diagrams with rectangular coordinates, they were able to represent the reactive phase equilibrium data and the stage-by-stage calculation.

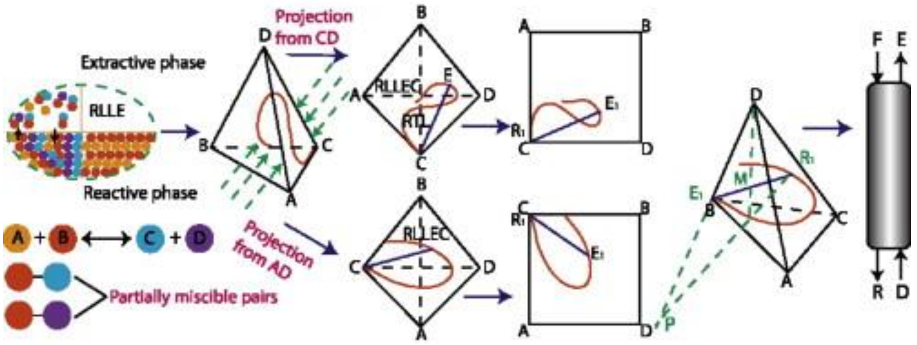


Figure 2-3: Graphical design method for quaternary systems in simultaneous chemical and physical liquid–liquid equilibrium (Olan-Acosta et al., 2014)

According to their report, this graphical method in Figure 2-3 allowed estimation of the number of reactive theoretical stages, the limits of the solvent to feed ratio, the extent of reaction and the conversion. They were able to compare results obtained from the graphical method to that in simulation software and it showed good agreement. Their key conclusion was that the graphical method made it easy to implement.

Alwi et al. (2014) expanded on the established graphical tools of composite curves, grand composite curves and balanced composite curves in order to simultaneously target multiple utilities and perform heat allocation between the utilities and the individual process streams. The method was called STEP (Stream Temperature versus Enthalpy Plot). It is depicted in the graph in Figure 2-4. They concluded that their method yielded accurate variable-temperature utility targets.

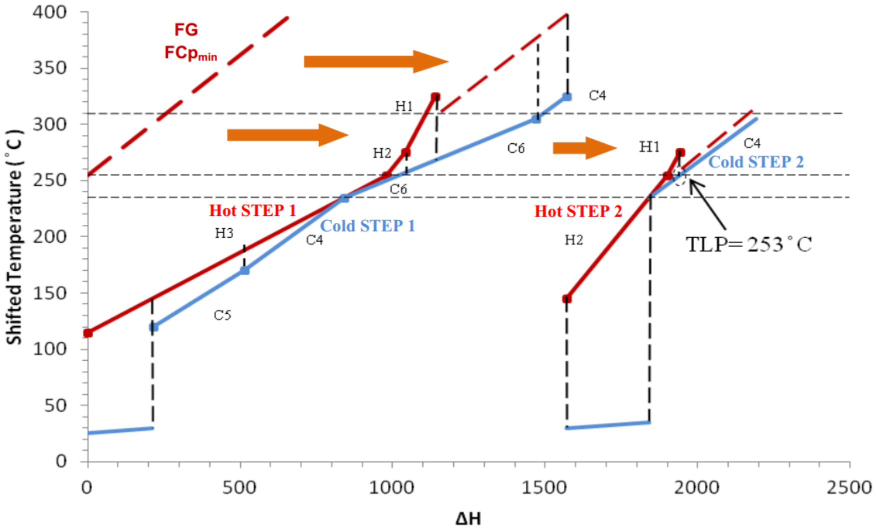


Figure 2-4: Graphical Method for Simultaneous Targeting and Design (Alwi et al., 2014)

Picon-Nunez et al. (2013) presented the application of a graphical tool for the preliminary design of heat exchangers. The graphical design tool was developed for shell and tube heat exchangers and then applied for spiral and welded compact exchangers. According to the presentation the tool depicts a design space as shown in Figure 2-5 which relating to the design by Lindqvist and Anantharaman (2014) can be referred to as an attainable region where a number of combinations of geometrical parameters meet the heat duty and allowable pressure drops.

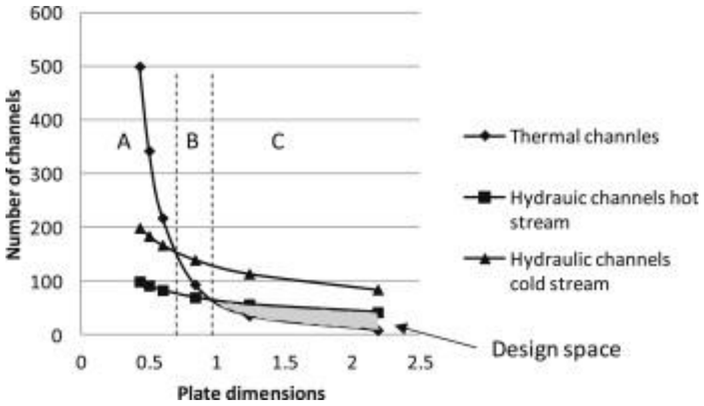


Figure 2-5: Parameter plot for the design of compabloc exchangers (Picon-Nunez et al., 2013)

They concluded that the use of graphical plots could reduce significantly the complexity of design and give engineers a practical tool that guides and narrows the search for optimal solution. In their report, the design space represents the area where the dimensions of the heat exchanger meets, and as such defines the design possibilities for the heat exchanger. Though applied differently, it is interesting to note the use of the principle of attainable region as it applies and discussed in later Chapters of this report.

Abraham et al. (2009) in their report presented a graphical approach to visualizing optimal operating conditions based upon estimated proportion of items within specification limits. Their focus was on the ability of the graphical design to offer users visual comparisons of competing sets of optimal operating conditions, to assess assumptions violations and the opportunity to observe the shape of response distribution as it relates to stated specification limits. They concluded that their graphical method was informative in estimation of deviation from desired target value and within specified limits. The visual summary of distribution of these deviations showed the costs associated with different operating conditions and enabled determination of a better alternative. They also concluded that by the graphical examination of different solutions for robust design problems, they were able to visualize and understand better the trade-offs between different solutions and what impact this would have on performance and hence cost.

Chapter 3

3. Theory of Membranes and the Design Methodology

3.1. Introduction

Lindqvist and Anantharaman (2014) had developed a systematic graphical approach to designing a membrane system for use in post combustion CO_2 capture. The concept, which is a novel idea, estimates the design cost and configuration of a membrane system. In this chapter, the fundamentals of membrane technology and the calculation model used for multicomponent feed will be discussed. A description of the program developed in Visual Basic code will be presented. A step-by-step guide will be given on how to use the graphical design methodology.

3.2. Theory of Membrane Separation

3.2.1. What is a membrane?

A membrane is an interphase that separates two phases and restricts the transport of various chemical species in a rather specific manner (Strathmann, 1981). This definition applies to a whole range of synthetic membranes not discussed in this project. More specific and of interest to this project are membranes classified under gas permeation. These membranes follows the Solution – Diffusion Model as it applies to reverse osmosis and pervaporation. It involves molecule diffusion in non-porous or dense polymer films such as rubber or polyamide.

The membrane functions as a semipermeable material that restricts or control the rate of hydrodynamic flow of various molecules between either two liquid, two gases or a liquid and a gas (Geankoplis, 2003). The membrane technology is possible because some substances pass through membranes at different speed than others. This speed is a function of the difference in partial pressure of the substance over the membrane. The partial pressure is dependent on the permeability, which is a function of the material solubility of the membrane.

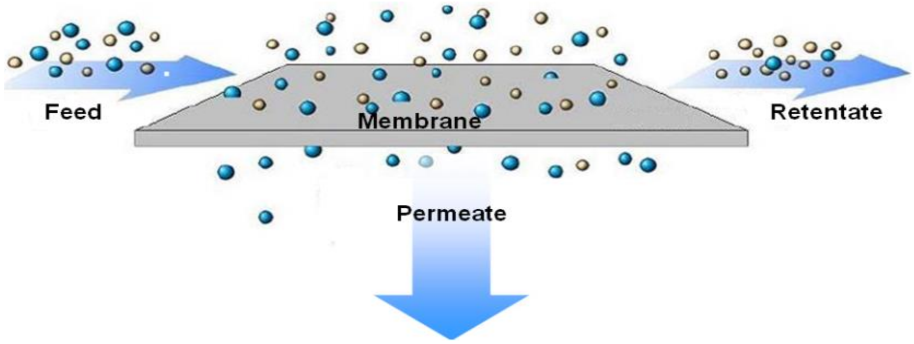


Figure 3-1: A simple membrane process (Schmeling et al., 2010)

3.2.2. Classification of membranes

Membranes are classified into two broad types

1. Porous membranes: These are used for separation processes such as;
    a. Gas diffusion
    b. Microfiltration
    c. Ultrafiltration
    d. Reverse osmosis
    e. Dialysis
2. Non-porous membranes: The molecules are adsorbed by the membrane material and flow under a thermodynamic potential. Such potentials can be:
    a. Gradient of vapour pressure
    b. Pressure gradient used in gas permeation
    c. Temperature gradient
    d. Concentration gradient
    e. Gradient in electric potential

Of interest to this project is the non-porous gas permeation membrane.

3.2.3. How does non-porous gas permeation membranes work?

For separation to occur through a membrane there needs to be a driving force across the membrane from the feed side to the permeate side. The driving force for this instance will be the partial pressure difference of CO_2 across the membrane. The ability of CO_2 to move through the membrane is determined by the diffusivity and concentration of CO_2 on both sides of the membrane. It is a slow process. How pure CO_2 is at the permeate side is a function of membrane properties such as the selectivity of the membrane, the permeability of the components, and the size of the membrane. Gas separation in dense polymeric membrane is based on the different solubility of gases. This makes gases travel through the membrane at different speeds, hence its mechanism (Ahmed et al., 2012).

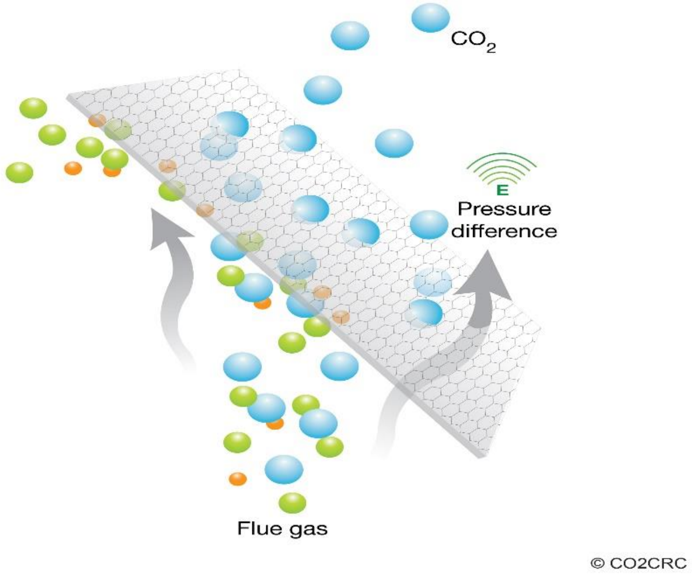


Figure 3-2: CO_2 Partial Pressure Difference as Driving Force. (CO_2CRC, 2012)

3.2.4. Types of membranes and permeability relationship for non-porous gas separation

The ability of molecules to flow through a membrane, its permeation flux, is related to the thickness of the membrane. The permeation flux is inversely proportional to the thickness. To have a membrane with a high permeation flux will require a very thin membrane. Membranes are usually of thickness 500-1000Å with a support of a porous material. Membranes are more permeable at higher temperatures, but these temperatures often destroy the material of the membrane.

3.2.5. Types of gas permeation equipment

There are three basic types of membrane equipment. The types are based on how the membrane material is applied for separation. They could be either:

1. Flat membrane: Easy to fabricate. Can be stacked up to increase area. Compared to other types it has a smaller membrane area per unit separator volume
2. Spiral-wound membranes: Has a significant increase in membrane area per unit volume. It consist of four sheets wrapped round a perforated tube for permeate flow. The sheets are a layer of top sheet for open separator grid for the feed, a membrane, a porous backing for the membrane and another membrane.

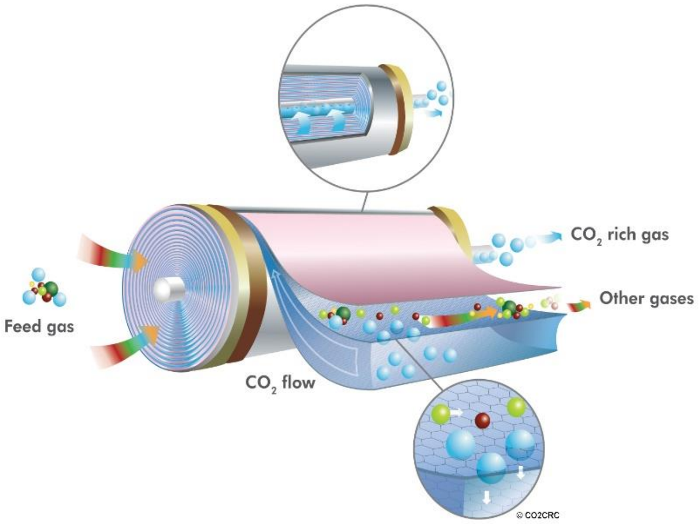


Figure 3-3: A Typical Spiral Wound Membrane for CO_2 capture (CO_2CRC, 2012)

3. Hollow-fibre membrane: This has the highest membrane area per unit volume. It is designed like a shell and tube heat exchanger. High-pressure feed enters at the shell side and leaves at the opposite end. The membrane in hollow fibres is closed at one end. Permeate gas flows through the membrane counter currently and leaves at a collection chamber. (Geankoplis, 2003)

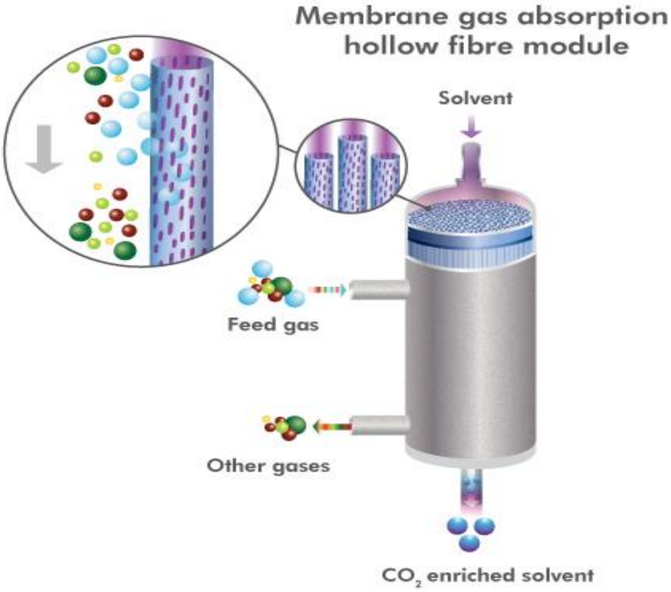


Figure 3-4: A Typical Hollow-fibre Membrane for CO_2 capture (CO_2CRC, 2012)

3.2.6. Types of flow in gas permeation

There are four effective types of flow in gas permeation.

a. Complete-mixing model
b. Cross-flow model: This flow model is considered in this report
c. Counter current flow
d. Concurrent flow

These are illustrated in Figure 3-5

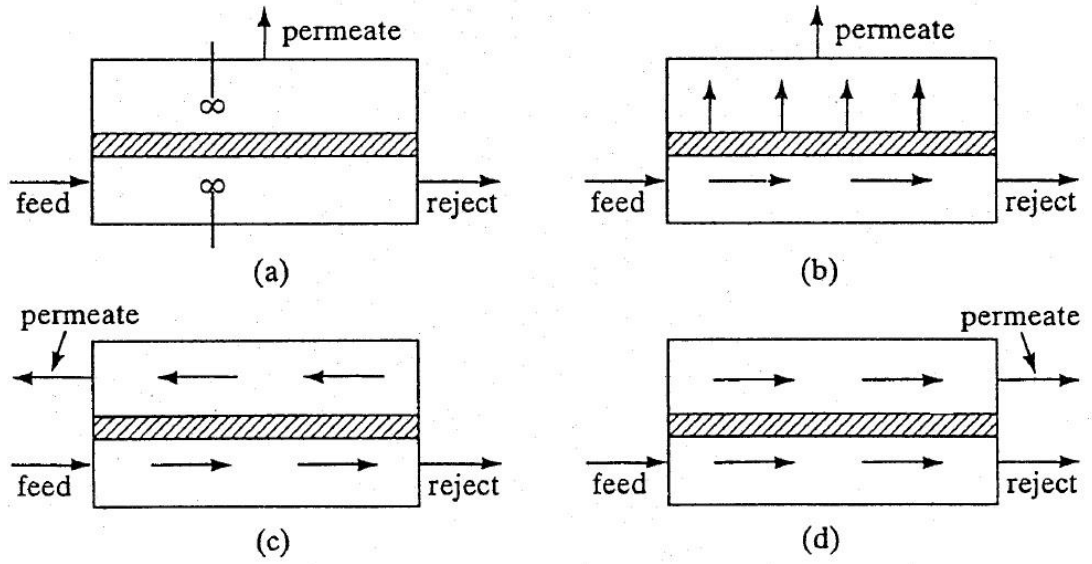


Figure 3-5: Types of flow in gas permeation (Geankoplis, 2003)

3.3. Membrane Model for Multiple Components Feed

The extension of the graphical design methodology for ternary feed component requires a new model for evaluation of the parameters of separation. The new model developed by Pettersen and Lien (1994). The model is a multicomponent feed model for calculation of the parameters of a membrane separation. One of the focus of the last year semester project was to confirm the applicability of this model and compare with existing model. This model has been shown to be consistent with the model for binary feed component by Weller and Steiner (1950) within a certain range. The Pettersen and Lien (1994) will therefore be used for all calculations in the ternary graphical design methodology.

The model is described as follows:

A dimensionless permeation factor R, is defined as

$$R = \frac{AP_f Q_i}{n_f} \tag{1}$$

Equations 2 and 3 below relates the flow rate of a permeating component of a membrane module to the heat transfer rate of a heat exchanger.

$$Heat\ Transfer = UA\Delta T_{lm} \tag{2}$$

$$\int dn_i = Q_i A \Delta P_{lm,i} \tag{3}$$

Equation 3 is known as Fick's Law of diffusion.

The variable Q_i representing permeation constant is used instead of the permeability constant because of its dependence on the overall membrane thickness. Information about effective thickness of membranes in commercially available gas separation membranes is not readily available. Parameter ΔP_{lm} is defined by assuming counter current flow relation with logarithmic mean defined in Equation 3

$$\Delta P_{lm,i} = \frac{(p_{f,i} - p_{p,i}) - (p_{r,i} - p_{pc,i})}{ln\frac{(p_{f,i} - p_{p,i})}{(p_{r,i} - p_{pc,i})}} \tag{4}$$

Where

A	Membrane Area	m^2
n	Flow rate	$m^3/_s$
nc	Number of components	$Dimensionless$
P	Pressure	Pa
p_i	Partial pressure of component i	Pa
Q_i	Overall permeability constant	$\left(m^3(STP)/_{m^2hbar}\right)$
R	Permeation factor	$Dimensionless$
x_i	Mole fraction of component i at high pressure side	$Dimensionless$
y_i	Mole fraction of component i at low pressure side	$Dimensionless$
δ	Trans-membrane pressure ratio defined as $^{P_p}/_{P_f}$	$Dimensionless$
θ	Cut ratio, defined as $^{n_p}/_{n_f}$	$Dimensionless$
$\Delta P_{lm,i}$	Logarithmic mean partial pressure difference	Pa
$\Delta P_{Ar,i}$	Arithmetical mean partial pressure difference	Pa

$\Delta P_{Gm,i}$	Geometric mean partial pressure difference	Pa
z	Defined as x_i	$Dimensionless$
p, f, r, pc	Permeate, Feed, Retentate, Permeate Closed end	

Component material balance over a membrane is given as:

$$n_f x_{f,i} = n_p y_{p,i} + n_r x_{r,i} \qquad 5\ 1$$

Solution-diffusion theory shows that permeation of individual component in a mixture is independent of other component but dependent on the components partial pressure.

Therefore it is seen that:

$$\int dn_i = n_p y_{p,i} \qquad 6$$

The effects of pressure drop in a hollow fibre can be considered negligible. Therefore

$$P_{pc} \approx P_p \qquad 7$$

Following the derivations of Pettersen and Lien (1994) accordingly, the following equations represents an entire membrane model.

$$\frac{y_{p,i}}{y_{p,i+1}} = \frac{Q_i(x_i - \delta y_{p,i})}{Q_{i+1}(x_{i+1} - \delta y_{p,i+1})} \qquad i = 1, \dots, nc - 1 \qquad 8$$

$$n_f \theta y_{p,i} = Q_i A \Delta P_{lm,i} \qquad i = 1, \dots, nc \qquad 9$$

$$x_{f,i} = \theta y_{p,i} + (1 - \theta) x_{r,i} \qquad i = 1, \dots, nc - 1 \qquad 10$$

$$\sum_{i=1}^{nc} x_{f,i} = 1 \ \sum_{i=1}^{nc} x_{r,i} = 1 \ \sum_{i=1}^{nc} y_{p,i} = 1 \ \sum_{i=1}^{nc} y_{pc,i} = 1 \qquad 11$$

Paterson (1984) approximation to logarithmic mean was used to simplify the Equations 8, 9, 10 and 11 into one implicit algebraic equation with one unknown, the stage-cut rate. This is under the assumption that all input variables and membrane parameters are specified.

The following equations are derived from Equation 9 using this approximation

$$\frac{\theta y_{p,i}}{R} = \frac{1}{3} \Delta P_{Ar,i} + \frac{2}{3} \Delta P_{Gm,i} \qquad 12$$

$$\Delta P_{Ar,i} = \frac{1}{2}\left[\left(x_{f,i} - \delta y_{p,i}\right) + \left(x_{r,i} - \delta y_{pc,i}\right)\right] \qquad 13$$

$$\Delta P_{Gm,i} = \sqrt{(x_{f,i} - \delta y_{p,i})(x_{f,i} - \delta y_{pc,i})} \qquad 14$$

The retentate molar fraction in Equation 13 is substituted with Equation 10. By using the approximation in Equation 7 and rearranging the expression with respect to $y_{p,i}$, the following is obtained

$$y_{p,i} = \frac{-BB_i\sqrt{(BB_i)^2 - 4AA_iCC_i}}{2AA_i} \qquad 15$$

Where

$$AA_I = \frac{\delta}{3}\left(\frac{2\theta}{R} - \delta\right) + \frac{\theta}{3(1-\theta)}\left(\frac{\theta}{R} + \frac{\theta}{12(1-\theta)} - \delta\right) + \left(\frac{\theta}{R}\right)^2 \qquad 16$$

$$BB_I = \frac{z}{3}\left(1 + \frac{1}{1-\theta}\right)\left(\delta - \frac{\theta}{R}\right) + \frac{\theta z}{18(1-\theta}\left(7 - \frac{1}{1-\theta}\right) \qquad 17$$

$$CC_i = \left(\frac{z}{6(1-\theta)}\right)^2 (\theta^2 + 12\theta - 12) \qquad 18$$

Equation 15 gives the permeate mole fraction of any component in the feed. The equation is a function of feed and operating conditions. The stage-cut rate is found by solving the following equation:

$$\sum_{i=1}^{nc} y_{p,i}(\theta) = 1 \qquad 19$$

Equation 19 only has one solution for $\theta\epsilon(0{,}1)$. The following is also valid for solving Equation 19:

$$\lim_{\theta - 1}\sum_{i=1}^{nc} y_{p,i}(\theta) = 0 \qquad 20$$

All equations are derived by Pettersen and Lien (1994). Equations 15, 16, 17, 18 and 19 forms the main equations for the written code used in Chapter 4.

3.3.1. General Assumptions for the Membrane Model

1. Membrane considered was homogenous and symmetric in its structure
2. It does not carry any charge
3. Model flow pattern used is the cross-flow pattern
4. The feed stream is in plug flow
5. Pressure drop across the flow within the feed stream area and permeate stream area are negligible
6. No mixing in the permeate and feed sides
7. Water vapour is assumed to be an inert gas and adds to the N_2 mole fraction in the composition according to Saltonstall (1987)
8. No sweep gas.+

3.4. The Graphical Methodology for Membrane Design

3.4.1. The Attainable Region

The attainable region as defined by Glasser and Hildebrandt (1997) is “the set of all physically realizable outcomes using only the processes of reaction and mixing in steady-state systems for some given feed”. When applied to reactor system, it is the set of all possible outputs of a chemical reaction, given the feed and the reaction kinetics. With this, the best combination within certain operating constraints can be deduced at its optimal reactor structure (Mulenga & Chimwani, 2013).

The graphical design methodology for membrane system utilizes the concept of an attainable region. Process conditions and variables is combined together as a single variable “cost”, which is minimized at reasonable process complexity. The principle is applied in creation of a region in which regardless of changes in process conditions and feed stream, all possible outcome converges in a defined space when plotted of a graph. Within this space, a designer will be in a position to synthesize the optimal membrane system, making trade-offs between cost and system complexity as he desires. By having an attainable region the conventional methods of trial and error or choosing from a few alternatives is eliminated.

The Lindqvist and Anantharaman (2014) graphical methodology is based on the Weller and Steiner (1950) model for binary feed composition for gas separation in membranes. It consist of graphical plots of minimum cost curve and iso-cost curves coupled to form an attainable region. These plots are used to draw stages of the membrane process in such a way as to minimize the overall cost by taking advantage of the lowest cost path to achieve the desired CO_2 purity. A Visual Basic Code that works with a User Interface of a Microsoft Excel Sheet generates the graphical plots.

3.4.2. The Visual Basic Code

The code is Microsoft Visual Basic for Application. It is used to perform all calculations needed for the generation of the plots. Included with the code is an optimizer (Microsoft Excel Solver Function) for solving to minimum cost by varying the trade-off between area and pressure ratio. This report will present an improved version of the code with respect to ternary feed composition.

The code is sectioned into programming functions as follows:

- The main function
- The Weller and Steiner equations
- The control functions to solve the Weller and Steiner equations
- The input and output sub-functions
- The cost calculations
- The CO_2 capture cost optimizer
- The graphical representation
- Others: power consumption calculations, error handlers, data types and definitions, numerical integration sub-function, data counters, unit conversions etc.

The main function controls the sequence of execution of the program. It starts and ends the program, calls all other sub-functions and evaluates the path the program runs based on user specified data. The input section of the input and output sub-functions accepts all user specified data, all data constants and determines the correctness and completeness of the data required to run the program. The data is retrieved both from the excel sheets and from the data specified within the program. The output section formats and displays all results as calculated by the program. The result displayed is in excel worksheet. The equations for calculating the membrane properties are written in the Weller and Steiner equations sub-function. There are several control functions attached to the Weller and Steiner equations that adjust values in order to attain a solution equal to the user specification.

The cost calculations sub-section evaluates different cost parameters based on the calculated membrane process properties such as pressure ratio, area, plant operating parameters such as number of operating hours, maintenance percentage cost and equipment specific cost such as cost of membrane unit per unit area and cost of installed turbo machinery per unit Kilowatt. The CO_2 capture cost optimizer sub-section utilizes the solver tool installed with Microsoft Office Excel to evaluate the minimum cost possible by varying pressure ratio and area.

The graphical representation sub-section draws the minimum cost curve line and the iso-curves for the user specified range. The program also has many other sub-sections to handle different scenarios as needed within the program.

3.4.3. User Data Requirement

All data required from a user of the program is entered at the excel sheet interface. Incorrect data would result in the program running but not converging returning a message. Incomplete data is quickly detected and will prompt an instruction to complete the data as required. If the user inputs a specification that is outside a possible solution as defined by the attainable region for such membrane properties, the program will run but also display a non-converging error. The data required by the program is divided into the following sections:

- Process conditions
  - Components and their mole fraction
  - Molar mass
  - Temperature
  - Feed flow rate
  - Feed and Permeate side Pressure
- Membrane Properties
  - Permeance
  - Selectivity
- Specifications
  - Selection of parameter and their data range:
    - Product purity
    - Stage cut
    - Carbon Capture Ratio
    - Area
- Other Inputs
  - Convergence Tolerance
  - Numerical Integration data

- Feed Composition Case Study
    - Data range
- Solver Parameter
    - Solver target, constraint and variable
- Cost Parameters
    - All cost associated with a membrane system

3.4.4. How the Graphical Design Methodology works

What is a stage?

A stage consists of a membrane, an intercooler, compressor and expander, and a vacuum pump. These are considered for all technical and cost calculations.

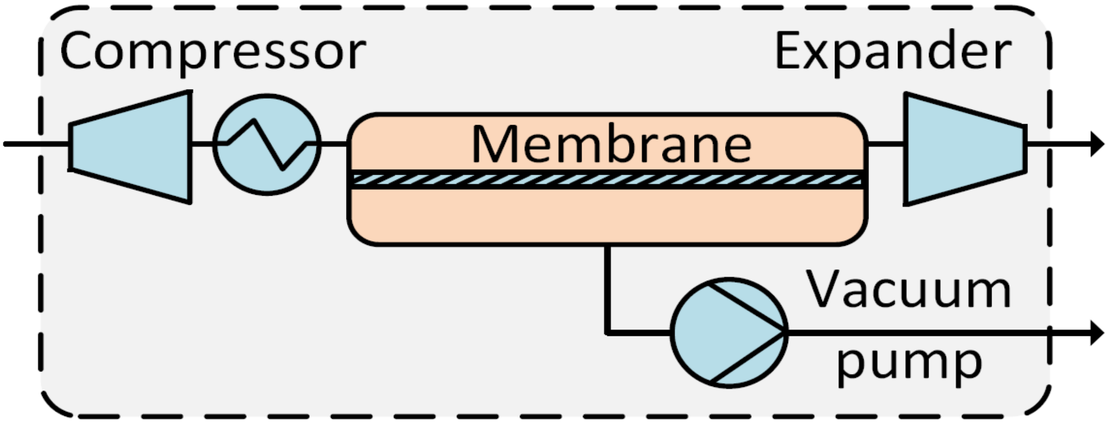


Figure 3-6: A membrane stage as considered in by the SINTEF Energy Research group (Lindqvist et al., 2013)

The following is a systematic procedure on how the program runs

Preparation:

The following data is required before the start of the graphical design methodology.

- The process conditions of the plant
    - Flue gas flowrate
    - Flue gas composition and their mole fractions
    - Temperature and pressure of flue gas
    - Cost parameters
- Membrane properties
    - Selectivity

  - Permeability of each component in membrane
- Desired CO_2 Capture Ratio
- Target Purity

Typical process conditions for the plant can be gotten from literature and/or an existing plant. The physical properties of the membrane such as selectivity and permeability of a membrane is determined and fixed. This will form a membrane type. Robeson (2008) investigated the possible outcomes for CO_2 separation from N_2 and came up with the upper bounds for their separation. Figure 3-7 shows that there is a limit to the permeability of CO_2 as a compromise of the selectivity (Alpha) of the material.

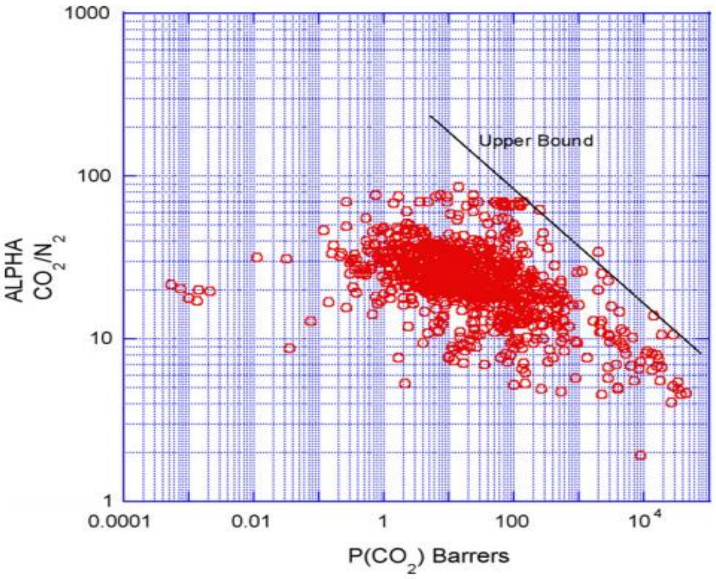


Figure 3-7: Upper bound correlation for CO_2/N_2 separation (Robeson, 2008)

Multiple membrane types of different properties can be superimposed on a graph to analyse a configuration of stages with different membrane properties. The required Carbon Capture Ratio is also determined and fixed. There is a compromise between the energy cost, CO_2 capture ratio and the permeate purity. Figure 3-8 shows the relationship between capture cost, permeate purity and the desired CCR. At higher CCR, the permeate purity of CO_2 reduces.

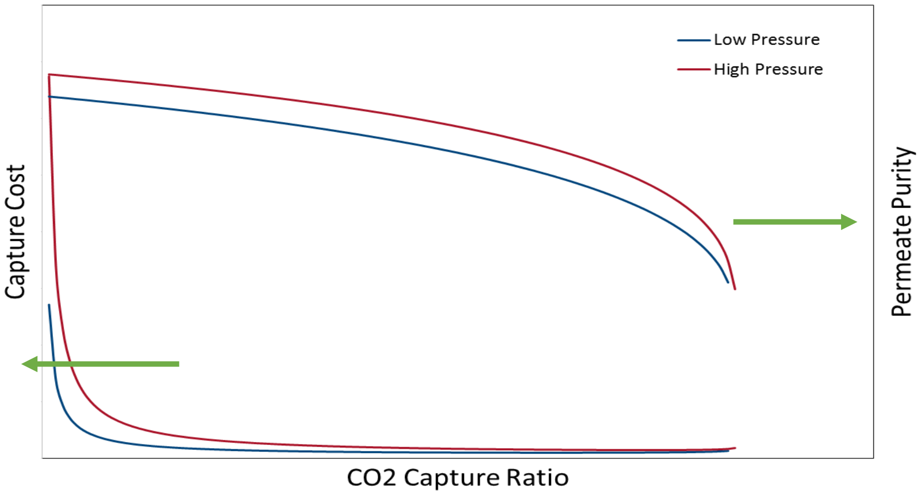


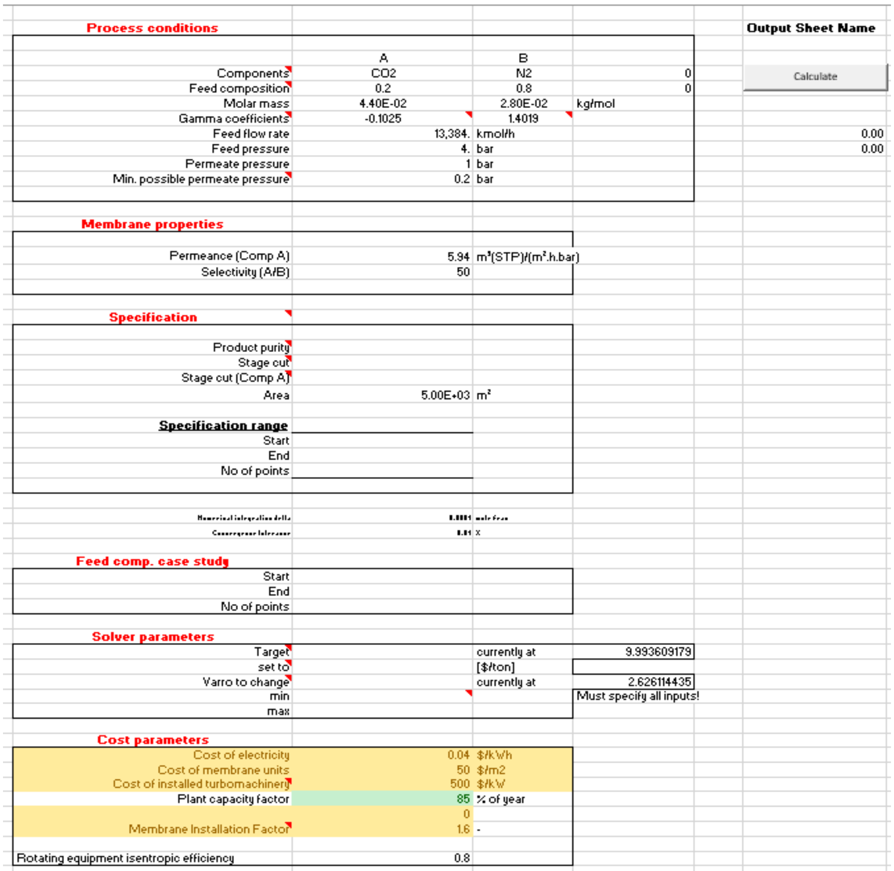
Figure 3-8: Relationship between Capture Cost, Permeate Purity with CCR

The program generates the values used in Figure 3-8. All required data (cost, process conditions, membrane properties) are entered into the excel sheet. Specification is selected as CO_2 Capture Ratio (CCR) with a range of 0.01 to 0.99. The program is executed. Values generated are used to plot Figure 3-8. A CCR that will give a reasonable permeate purity at minimum cost is selected.

The required data to start the graphical design methodology is now complete.

Step 1:

Values (cost, process conditions, membrane properties, etc.) are entered in the excel sheet for the code. Cost is specified as target and pressure ratio as variable for the optimizer. The minimum function is selected and it sets the optimizer to calculate for lowest possible cost. Minimum and maximum values are also selected for the variable of the optimizer. Feed condition case study range from 0.01 – 1 representing the CO_2 mole fraction is specified. The program is executed to generate permeate/retentate purity corresponding to the CO_2 feed composition. Figure 3-9: Screen Shot of User Interface



Process conditions

	A	B	
Components	CO2	N2	0
Feed composition	0.2	0.8	0
Molar mass	4.40E-02	2.80E-02	kg/mol
Gamma coefficients	-0.1025	1.4019	
Feed flow rate	13,384.	kmol/h	
Feed pressure	4.	bar	
Permeate pressure	1	bar	
Min. possible permeate pressure	0.2	bar	

0.00
0.00

Membrane properties

Permeance (Comp A)	5.94	m^3(STP)/(m^2.h.bar)
Selectivity (A/B)	50	

Specification

Product purity		
Stage cut		
Stage cut (Comp A)		
Area	5.00E+03	m^2
Specification range		
Start		
End		
No of points		

Feed comp. case study

Start	
End	
No of points	

Solver parameters

Target		currently at	9.993609179
set to		[$/ton]	
Varro to change		currently at	2.626114435
min			Must specify all inputs!
max			

Cost parameters

Cost of electricity	0.04	$/kWh
Cost of membrane units	50	$/m2
Cost of installed turbomachinery	500	$/kW
Plant capacity factor	85	% of year
	0	
Membrane Installation Factor	1.6	-
Rotating equipment isentropic efficiency	0.8	

Figure 3-9: Screen Shot of User Interface

Step 2:

The graph of permeate/retentate purity versus CO_2 feed composition is plotted using the values generated by the code. The curve plotted as permeate/retentate purity on the Figure 2-10 is called the Minimum Cost Curve. A diagonal line is drawn across the graph. This line represents points on the graph where permeate purity equals feed composition. This will be used to indicate the start of subsequent stages. The retentate purity curve can be used to examine the possibility of retentate stream recycle.

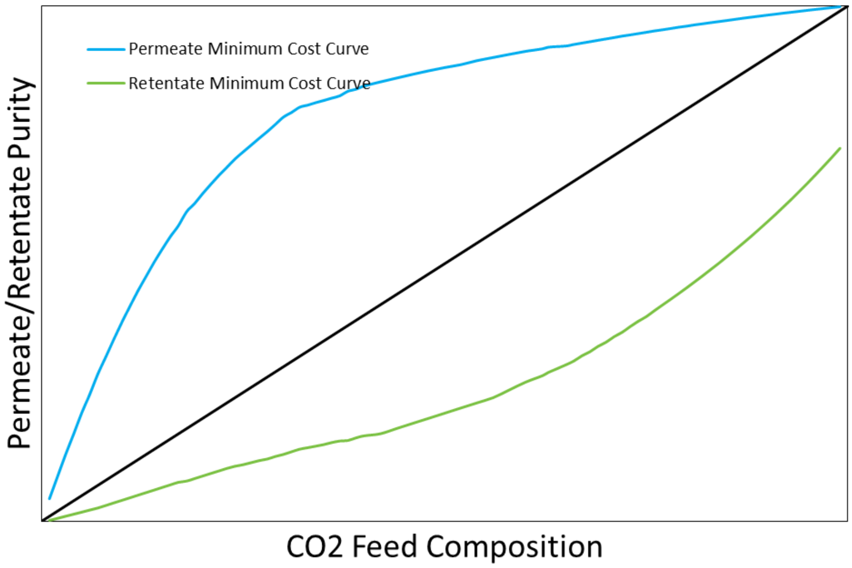


Figure 3-10: Plot of permeate/retentate purity against CO_2 feed composition

Step 3:

Across the permeate purity minimum cost curve, there exist minimum cost regions in which for a given cost value, there will be two different permeate purity. Intervals of minimum cost curve values are selected as specification in the program. The program is then executed for a range of feed composition to visualize all possible purity achievable at that specified cost. The purity values generated are in duplicates. This is expected as there will be two solutions for every feed composition. One solution for high-pressure ratio with a small membrane area and the other low pressure ratio with a large membrane area. The values are plotted on the same graph in Figure 3-10 as shown in Figure 3-11.

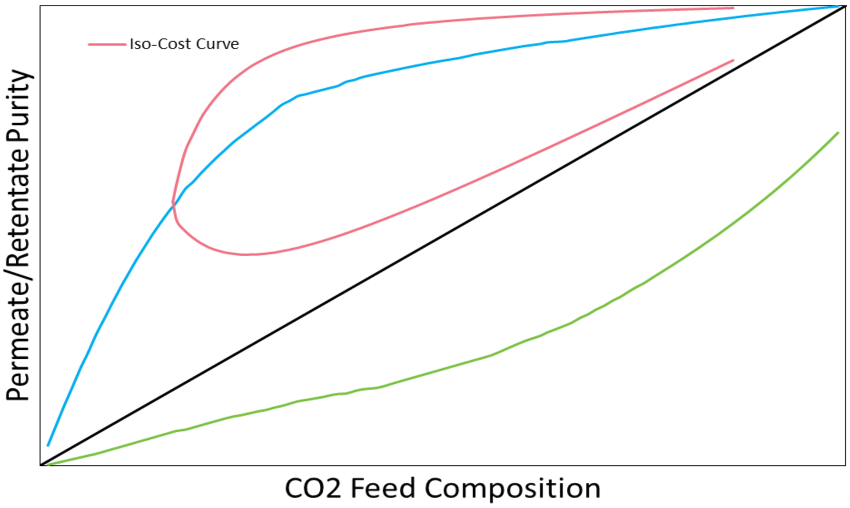


Figure 3-11: The Iso-Cost Curve

The curves drawn is called the iso-curve. It represent two possible solutions at every feed composition due to the energy-area trade-off. Selecting cost values at progressive intervals and repeating Step 3 will create plots on the graph with a certain region in which a membrane with certain selectivity and CCR can operate at minimum cost. This process can be repeated for progressive intervals of minimum cost value. The different cost intervals together will form an envelope. This region is the attainable region envelope. The completed graphical representation will look like Figure 3-12.

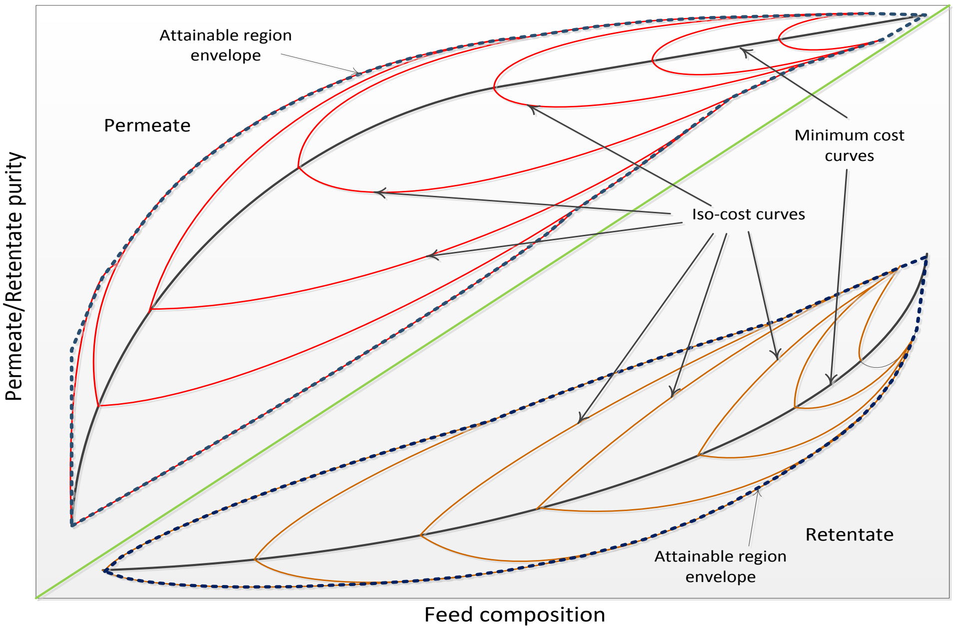


Figure 3-12: Purity at minimum cost versus feed composition with the iso-curves (Lindqvist & Anantharaman, 2014)

3.4.5. Determining number of stages and its operating conditions

To determine the number of stages and its operating conditions necessary to achieve a particular permeate purity, the following steps are taken

Preparation:

The flue gas CO_2 composition for the process plant to be examined is specified. This will form the starting point for the analysis.

Step 1:

A vertical line is drawn from the CO_2 feed composition of the process plant to meet the minimum cost curve at the permeate side. This is a single stage of a membrane. The permeate purity achieved at this stage is at minimum cost possible. Above or below this point is a trade-off of area or pressure and will represent a higher cost for the stage. A horizontal line is then drawn to meet the diagonal line. Points on the diagonal line are equal for both abscissa and ordinal. As such, the permeate purity achieved in the first stage is now the feed composition of CO_2 for the second stage.

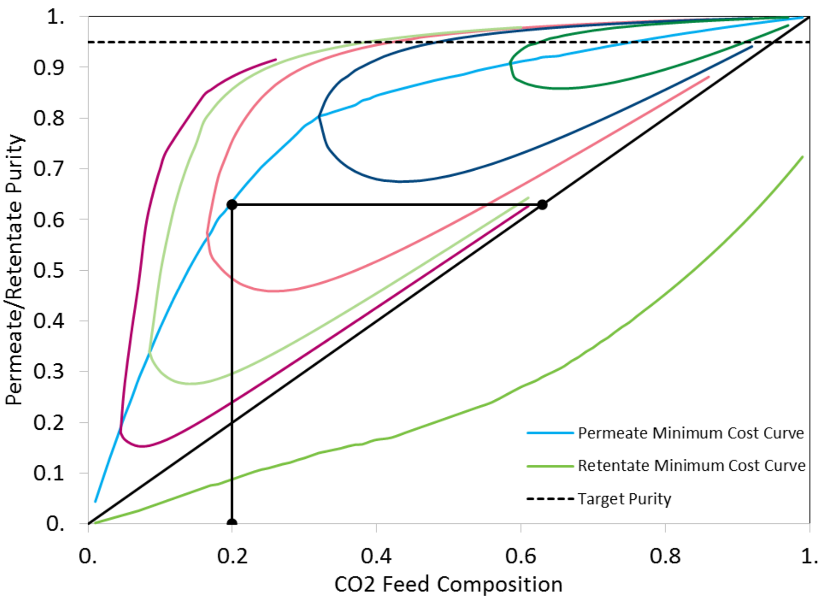


Figure 3-13: A single stage represented by a vertical line at CO_2 feed composition 0.2

Step 2:

The process in Step 1 is repeated until the vertical line reaches the permeate purity required. The number of vertical lines represents the number of stages. In this illustration in Figure 3-14, there are three stages of the membrane system. The region each stage lies in represents the cost for that stage. An accurate cost is evaluated by running the code with the new feed composition and optimized purity value. From the second stage, drawing the vertical line downwards to the retentate curve will indicate the retentate purity. This will be evaluated to determine the possibility of retentate stream recycle.

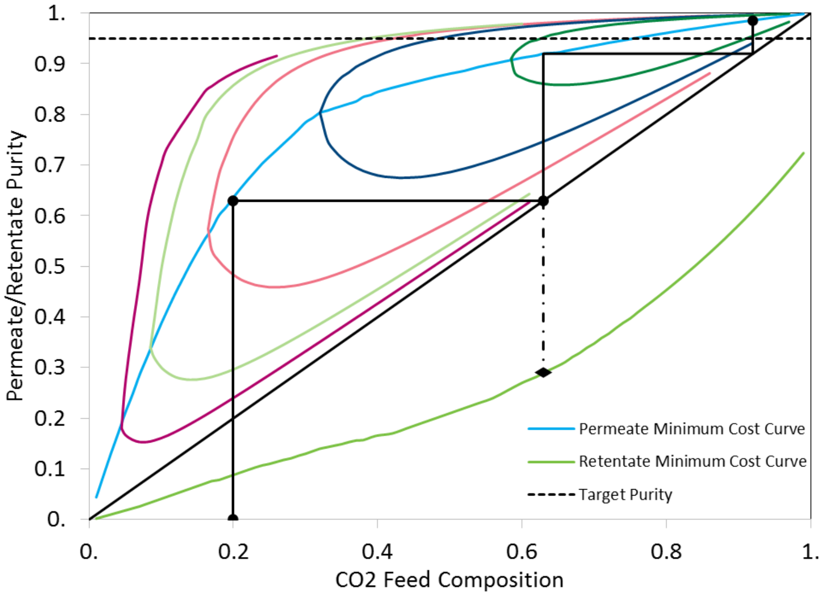


Figure 3-14: 3 stages complete graphical representation at minimum cost.

Step 3 (Improvement):

If it is desired to have a certain number of stages, the vertical lines can be adjusted beyond the minimum cost to obtain a higher purity at each stage in order to have the desired CO_2 purity based on a certain number of stages. This is important in order to reduce the complexity of the membrane system. Figure 3-15**Error! Reference source not found.** is an illustration of how the three stages membrane system can be converted to a two-stage system. The first stage cost will be higher than the previous design as this falls into a region away from the minimum cost curve. For practical applications, this implies that the pressure ratio will be higher in order to achieve the purity. By having the first stage with higher purity, stage two can be started at a feed purity higher than before and closer to the target mark. Starting stage two at higher purity level provides the opportunity to reach the target purity level and still remain in the region of the smaller iso-curve. This permits an entire stage (stage 3) in the system to be removed at reasonable cost increase to the previous two stages. A cost analysis is required to determine if this improvement will have a savings. Improvement on the complexity of the membrane system is already achieved.

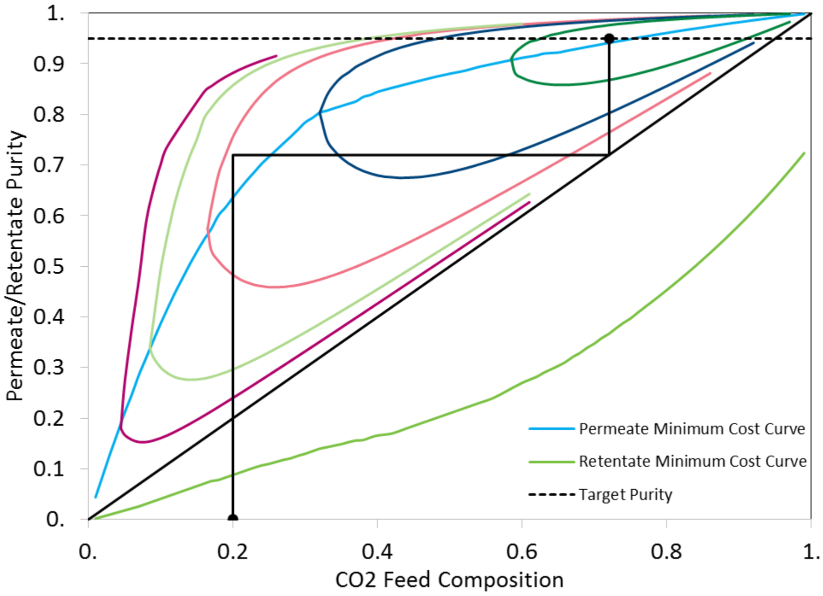


Figure 3-15: 2 stages graphical representation at minimum cost

This opportunity to visually analyse a membrane system, determine the complexity, number of stages, cost required per stage, necessary pressure ratios, determine possibilities for stream recycle, calculate overall cost and also make improvements and compromise at the design stage of a membrane system is the key motivation to the graphical approach to systematic design of membrane systems.

It is simple, clear and an easy to use tool. Although its assumption of a binary feed composition might simplify a multicomponent flue gas stream, this method can provide a first look at how and what would be required to start designing a membrane system.

Chapter 4

4. The Ternary Component Graphical Design Methodology

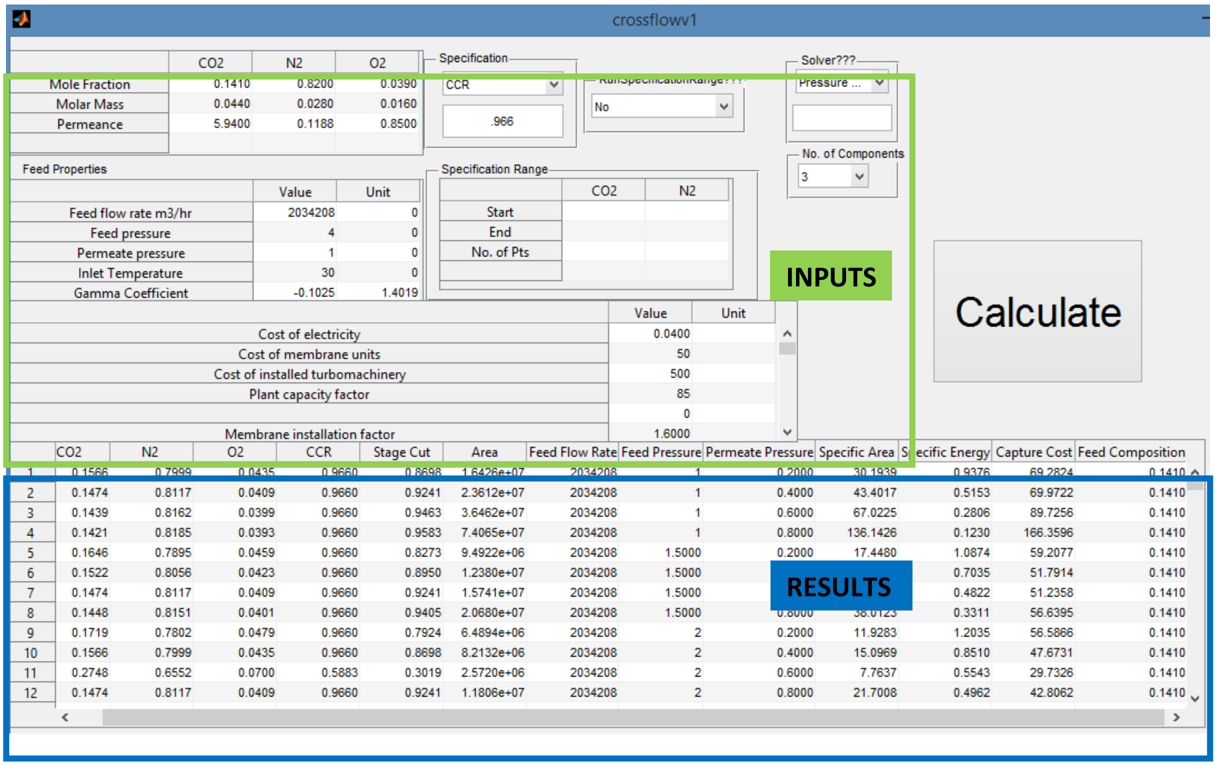
4.1. Introduction

The main challenge of the ternary graphical methodology and any attempt to have a design methodology beyond the binary design system is the difficulty in predicting the values of the mole fractions of the other components (N_2 and O_2) after the first membrane stage. In the binary design methodology, this was not a challenge, as a '1' less the mole fraction of CO_2 easily determines the mole fraction of the second component. However, this is not possible in a ternary system. The mole fractions of at least two of the component has to be explicitly determined by the multicomponent membrane model by Pettersen and Lien (1994). '1' less the first two mole fractions obviously can get the third. This difficulty will suggest that a graphical representation will be in a three dimensional form to be able to capture all possibilities of outcomes. While this is possible conceptually, it is unrealistic as a tool for analysing membrane systems, as it is complex to visualize easily such a three dimensional surface plot. For this reason, for ease of visualization and use, it is important to keep the graphical design methodology to a two dimensional system.

This chapter will present two graphical design methodology for ternary feed membrane system. It will describe the steps to follow to use this new methodology and its application to an actual process plant. For the ternary design methodology, a new program is written using a more robust programming tool with multi-paradigm numerical computing environment MATLAB (matrix laboratory). The description of how the program functions with a flow chart will be given. At the end of the chapter, there will be a summary of the work done.

4.2. The MATLAB Program

A MATLAB program was used to re-write the multicomponent model by Pettersen and Lien (1994). The previous code developed using the Microsoft Visual Basic for Applications was not sufficient in handling optimization challenges for which MATLAB has dedicated tools. The new code utilizes the "Guide" function of MATLAB that enables a graphical user interface for input and output data. The structure of the code is similar to that as described in Chapter 3 with the exception of the model used, which is for multicomponent and not binary and the optimization methods. Every other section of the code utilizes the same principles as already described in theory just with a MATLAB syntax.



crossflowv1

	CO2	N2	O2
Mole Fraction	0.1410	0.8200	0.0390
Molar Mass	0.0440	0.0280	0.0160
Permeance	5.9400	0.1188	0.8500

Specification: CCR
.966

RunSpecificationRange???: No

Solver???: Pressure ...

No. of Components: 3

Feed Properties

	Value	Unit
Feed flow rate m3/hr	2034208	0
Feed pressure	4	0
Permeate pressure	1	0
Inlet Temperature	30	0
Gamma Coefficient	-0.1025	1.4019

Specification Range

	CO2	N2
Start		
End		
No. of Pts		

	Value	Unit
Cost of electricity	0.0400	
Cost of membrane units	50	
Cost of installed turbomachinery	500	
Plant capacity factor	85	
	0	
Membrane installation factor	1.6000	

	CO2	N2	O2	CCR	Stage Cut	Area	Feed Flow Rate	Feed Pressure	Permeate Pressure	Specific Area	Specific Energy	Capture Cost	Feed Composition
1	0.1566	0.7999	0.0435	0.9660	0.8698	1.6426e+07	2034208	1	0.2000	30.1939	0.9376	69.2824	0.1410
2	0.1474	0.8117	0.0409	0.9660	0.9241	2.3612e+07	2034208	1	0.4000	43.4017	0.5153	69.9722	0.1410
3	0.1439	0.8162	0.0399	0.9660	0.9463	3.6462e+07	2034208	1	0.6000	67.0225	0.2806	89.7256	0.1410
4	0.1421	0.8185	0.0393	0.9660	0.9583	7.4065e+07	2034208	1	0.8000	136.1426	0.1230	166.3596	0.1410
5	0.1646	0.7895	0.0459	0.9660	0.8273	9.4922e+06	2034208	1.5000	0.2000	17.4480	1.0874	59.2077	0.1410
6	0.1522	0.8056	0.0423	0.9660	0.8950	1.2380e+07	2034208	1.5000	[illegible]	[illegible]	0.7035	51.7914	0.1410
7	0.1474	0.8117	0.0409	0.9660	0.9241	1.5741e+07	2034208	1.5000	[illegible]	[illegible]	0.4822	51.2358	0.1410
8	0.1448	0.8151	0.0401	0.9660	0.9405	2.0680e+07	2034208	1.5000	0.8000	38.0123	0.3311	56.6395	0.1410
9	0.1719	0.7802	0.0479	0.9660	0.7924	6.4894e+06	2034208	2	0.2000	11.9283	1.2035	56.5866	0.1410
10	0.1566	0.7999	0.0435	0.9660	0.8698	8.2132e+06	2034208	2	0.4000	15.0969	0.8510	47.6731	0.1410
11	0.2748	0.6552	0.0700	0.5883	0.3019	2.5720e+06	2034208	2	0.6000	7.7637	0.5543	29.7326	0.1410
12	0.1474	0.8117	0.0409	0.9660	0.9241	1.1806e+07	2034208	2	0.8000	21.7008	0.4962	42.8062	0.1410

Figure 4-1: Screen Shot of Graphical User Interface for MATLAB Code

Figure 4-1 shows the developed MATLAB graphical user interface GUI for the ternary component design methodology. This program is used for all calculations in the development of the graphical design solutions in this chapter. The GUI is divided into two main sections: The Inputs section and the Results section.

The MATLAB program follows a simple process for evaluation of the membrane parameters. It accepts user inputs, after which it processes the inputs by evaluation of the Pettersen and Lien (1994) equation. It then checks the user specification for tolerance, adjusts the membrane area if necessary, and finally prints the result. Figure 4-2 shows the flowchart of the MATLAB program.

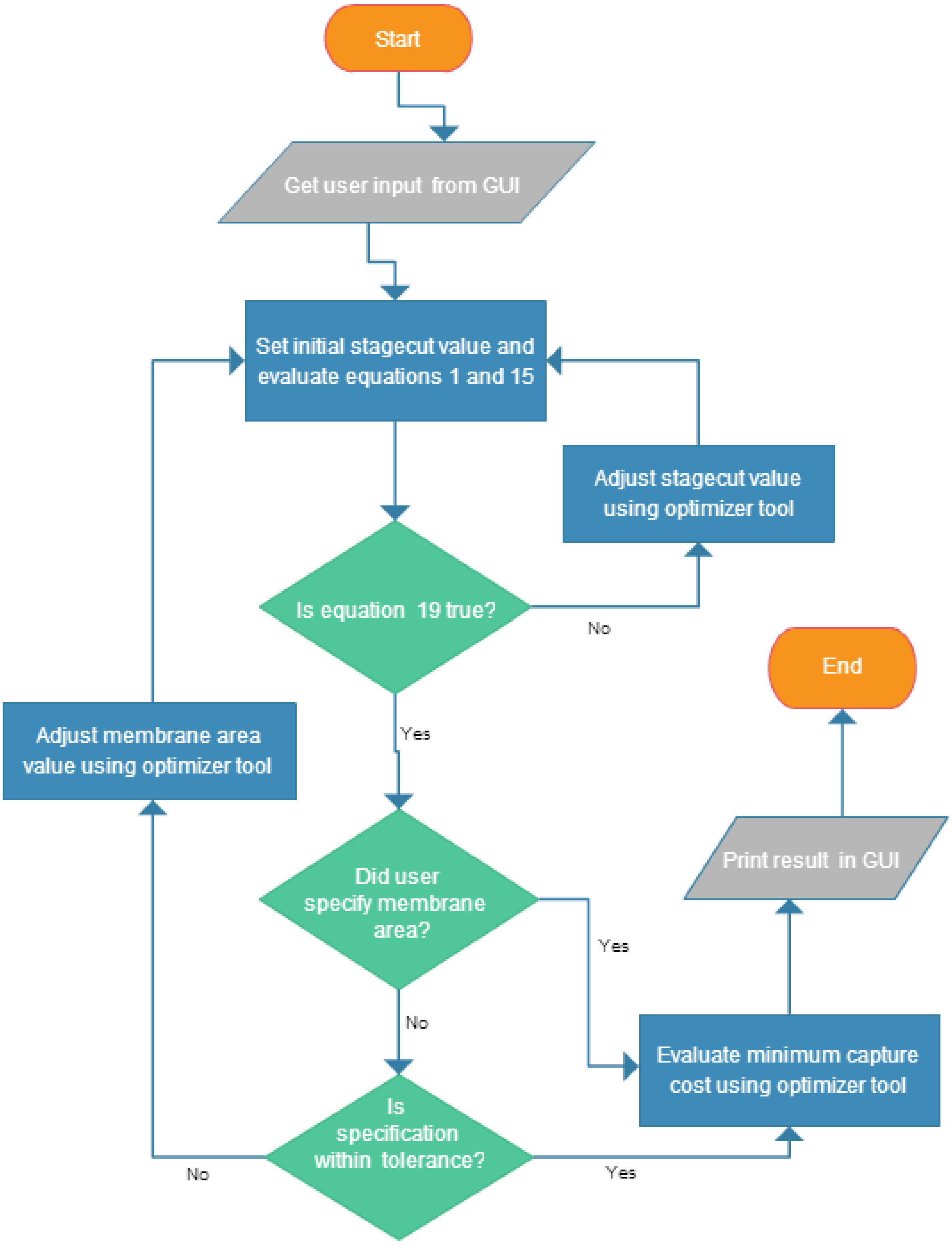


Figure 4-2: Flowchart of MATLAB program

4.3. Design Approach 1

The new graph for a ternary approach cannot retain the axis of the previous binary methodology. The axis is redefined to be CO_2 Feed/Purity plotted against N_2 Feed/Purity. The introduction of N_2 Feed/Purity on the horizontal axis is to ensure that every point described by the plot has the required information for the mole fraction in the stream for both feed and exit of membrane. The feed and purity values of a particular component is combined to an axis for simplicity. This is possible as the axis are of the same scale. Figure 4-3 shows the adjustments to the axis of the binary design methodology to accommodate for the ternary design. The figure to the left is the binary design methodology graph, while the right is the new ternary design graph

Figure 4-3: Change in Axis representation. N_2 added to horizontal axis

As considered in the binary feed composition graphical design, certain specifications will be required at the start of the design.

- The overall Carbon Capture Ratio required (CCR)
- The CO_2 purity target
- The membrane property permeance of each component
- The process plant conditions
  - Flue gas composition
  - Flowrate
  - Exit Temperature

The following procedure will be followed to utilize the Design Approach 1

4.3.1. Step 1: Determine the CCR/stage

At the beginning of the design stage, the number of stages in the final design is unknown. Since the number of stages affects the overall CCR, it is necessary to make an informed guess of the final number of stages. Usually, and from previous designs, it is safe to assume a 3-stage membrane system. This will imply that an overall CCR target of 90% will require a CCR/stage of 96.6% if three stages is to be the final design.

Optimization of the desired CCR at certain cost bracket can be done similar to as done in the binary feed composition as illustrated in Figure 4-4. However, local regulations can also affect what will be the overall CCR and the designer will have to start with that requirement.

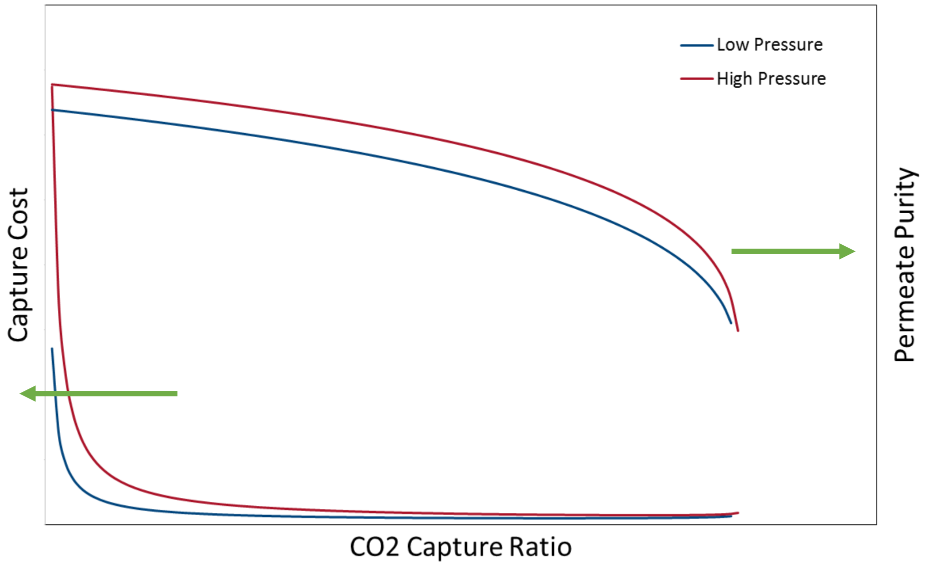


Figure 4-4: Relationship between Capture Cost, Permeate Purity with CCR

4.3.2. Step 2: Plot the minimum cost/stage curve

In the binary feed composition graphical design, the first plot drawn is the minimum cost curve that represents the purity achieved at lowest cost for every possible feed composition. In a ternary feed composition, for every CO_2 feed there will be a multiple possible combinations of the remaining mole fractions of N_2 and O_2. With the new defined axis for ternary feed composition graphical design, a plot for all possible outcome will represent a variable point region below the middle diagonal line. As discussed in the introduction to this chapter, this variable point region is better represented in a three dimensional surface plot, but that is not easy to visualize. A simple compromise is then made to focus only on the particular feed composition from the process plant. This compromise introduces the idea of a stage-by-stage approach to designing the optimal solution to the membrane system.

The compromise made to the design permits visualization of a lower boundary line at which point any purity level below it will indicate a higher cost. In this compromise, rather than plot for all feed composition, a plot is made for only feed composition of the desired process plant. Figure 4-5 is an illustration.

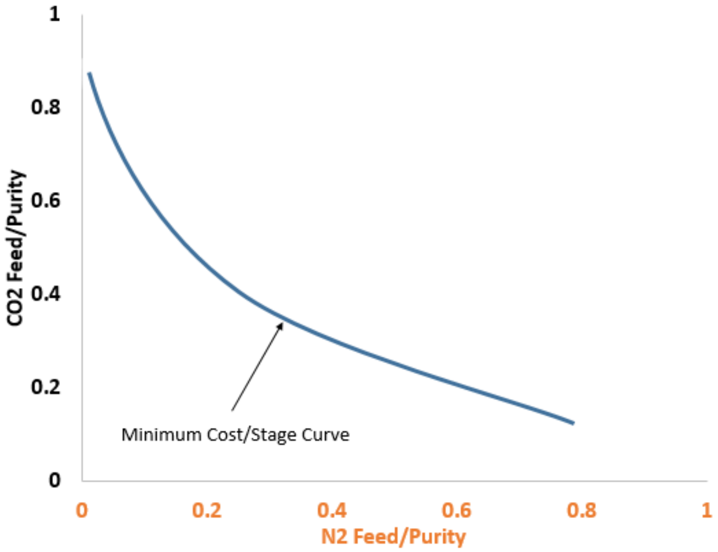


Figure 4-5: Minimum Cost per stage curve. Design Approach 1

Figure 4-5 is a plot of the minimum cost/stage curve. The curve indicates a pathway from the feed composition to achieving the target purity of CO_2. The curve is made up of small increments of CO_2 purity increase representing individual stages. These stages are optimized for minimum cost, as such, only a small increase in the purity of CO_2 is achieved. The importance of this curve is the representation of the lower boundary line below which purity is either attainable with a higher cost or is unattainable. The region below the minimum cost/stage curve is not important to the membrane system designer as it is a worse solution as compared to the region above it

4.3.3. Step 3: Plot the maximum cost/stage curve

The purity achieved does not continuously increase with increase in the cost of the membrane stage. A limit defines the maximum attainable purity, such that any further increase in cost for a membrane stage will not yield a corresponding increase in purity of CO_2. This limit is defined as the maximum cost/stage curve. Since the driving force for the purity is the partial pressure of CO_2, for the purpose of this design methodology, the maximum purity attainable is set by the pressure ratio across the membrane sides. The cost at this point is the maximum cost/stage.

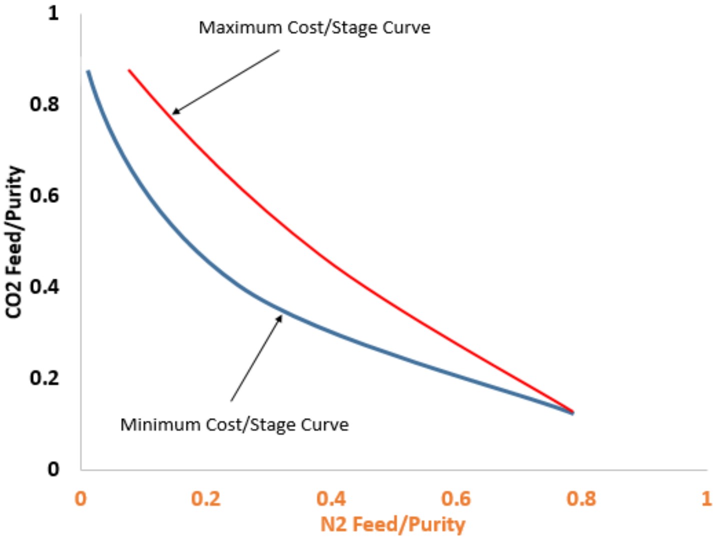


Figure 4-6: Maximum cost/stage curve

Figure 4-6 shows the maximum cost/stage curve in red. When this curve is combined with the minimum cost/stage curve, they enclose the attainable region of all possible outcomes of a membrane system for a process plant. This is shown in Figure 4-7. Regardless of the configuration, the solution to the design will lie within the two curves shaded green in Figure 4-7. Worthy of note is that the minimum cost/stage curve and the maximum cost/stage curve does not represent the minimum or maximum overall cost of the membrane system. The cost optimization is done per stage. The overall cost of a membrane system is determined by the choices made by the designer from the plots. This is illustrated in the next step.

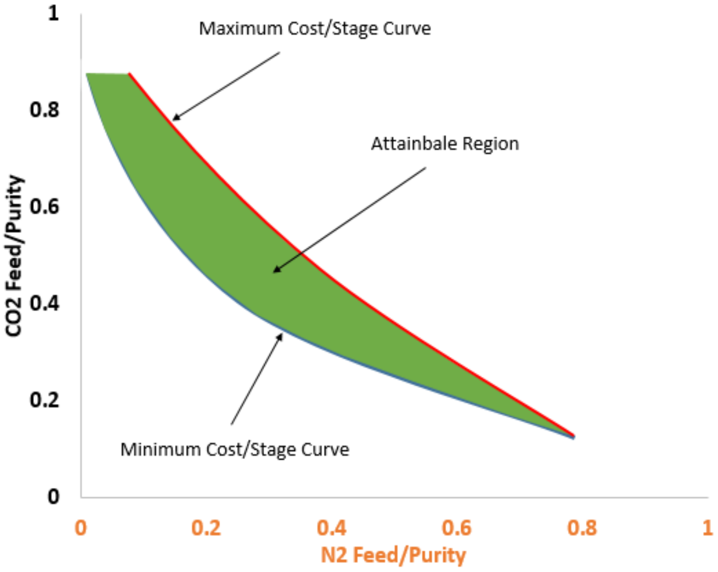


Figure 4-7: The attainable Region for Ternary Graphical Design Approach 1

4.3.4. Step 4: Design the Membrane System

Determining how the membrane system is designed is the choice of the designing engineer. The plots that describes the attainable region of the membrane serves as a guide to make these decisions in a cost optimal way. It also allows the designer to know the possibilities with different membrane system configurations. For every stage, there is a wide range of outcomes from the minimum cost to the maximum cost. However, the cost distribution is not evenly split across the range of outcomes. As the maximum cost/stage gets closer, an optimal solution is reached that achieves a reasonable cost for the stage matched with high purity.

Designing the membrane system involves two activities:

1. Plotting all outcomes between the minimum and maximum per stage curves.
2. Marking out the cost distribution.

The first activity enables visualization of the CO_2 and N_2 purity. While the CO_2 purity is of most importance as it is the target component, the N_2 purity is also of significance, as it is needed for the start of the next stage. This need to know the N_2 purity is essentially the main difference of the ternary to the binary design methodology. It also constitute the main challenge in having a graphical design concept. A plot is drawn from the minimum to the maximum cost/stage curve. This plot represents the possible purity outcomes across gradually increasing cost.

The second activity marks the plot at intervals with a cost. The designer will have to decide at what purity is of reasonable cost, above which cost increase becomes too high for the added benefits of purity. Figure 4-8 shows the two activities of Step 4.

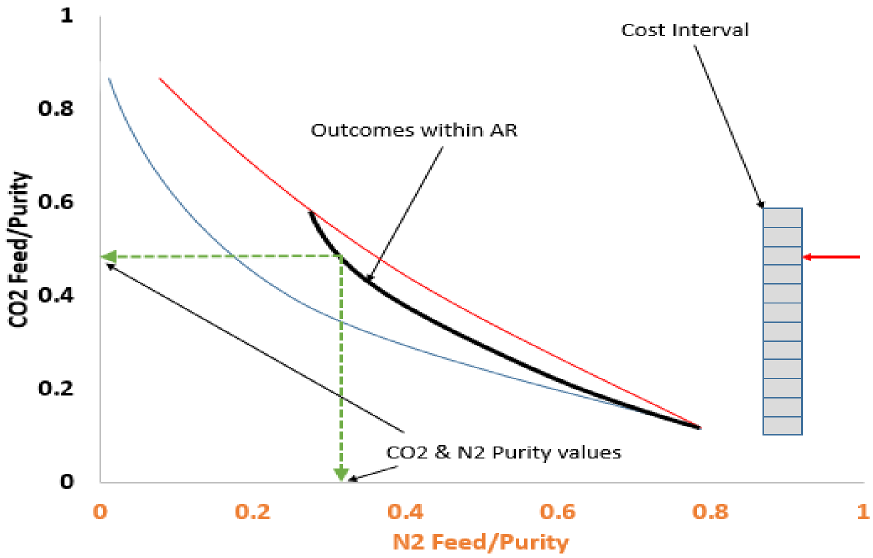


Figure 4-8: Plot of possible outcomes and the cost interval

Figure 4-8 shows the two activities completed. The black curve within the attainable region (AR) is the plot of all possible outcome between the minimum and maximum cost/stage. The curve is used to indicate the CO_2 and N_2 purity. Beside the curves is a cost section marking out the cost intervals. From the cost interval, the cost fluctuations across the CO_2 purity is visualized. This fluctuation is due to the rate of change of the cost of membrane area and of compressor work.

Once the designing engineer decides on what best fits his membrane system at minimum cost, the membrane stage design is completed. In this example, the red arrow marks the optimal solution for the first stage. At that point on the plots, the cost is with a reasonable CO_2 purity. The corresponding N_2 purity is indicated by the green dotted arrows from the possible outcome curve within the attainable region in Figure 4-8. The information for the next stage is now available. Interesting to note is that the two subsequent cost interval above the optimal solution are considered to show a rapid increase in the cost with little gain on CO_2 purity. Therefore, though with higher purity, they are not the cost optimal solution.

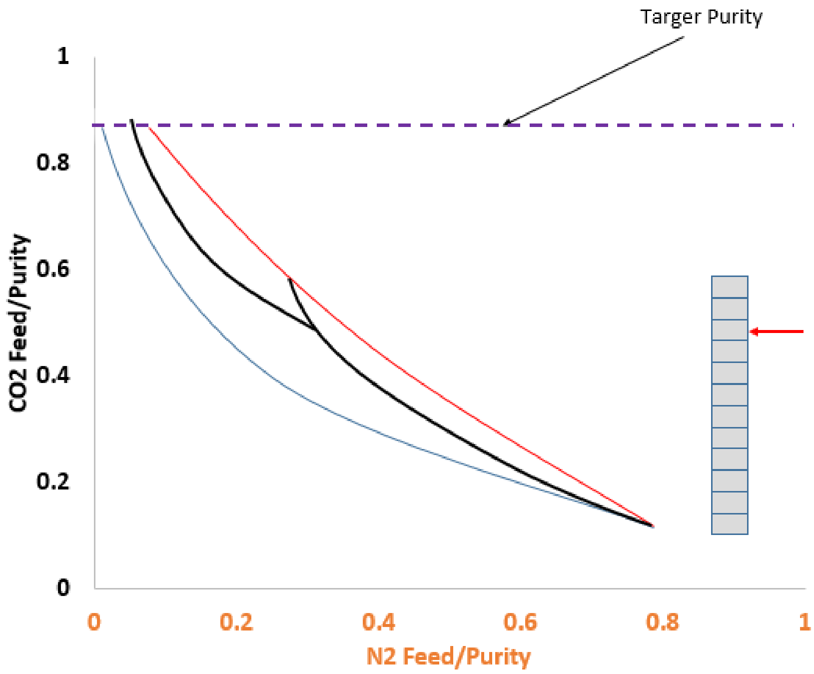


Figure 4-9: Completed membrane design with two stages

The Figure 4-9 shows a completed illustration of the graphical design methodology for ternary feed. The second stage of the design meets the target purity. The cost evaluation here is just as required to meet the target specification. If the optimization of the first stage had been properly done, the optimal cost for the membrane system is then determined by the addition of the first stage cost indicated by the red arrow in Figure 4-9 and the cost to reach the target purity of the second stage.

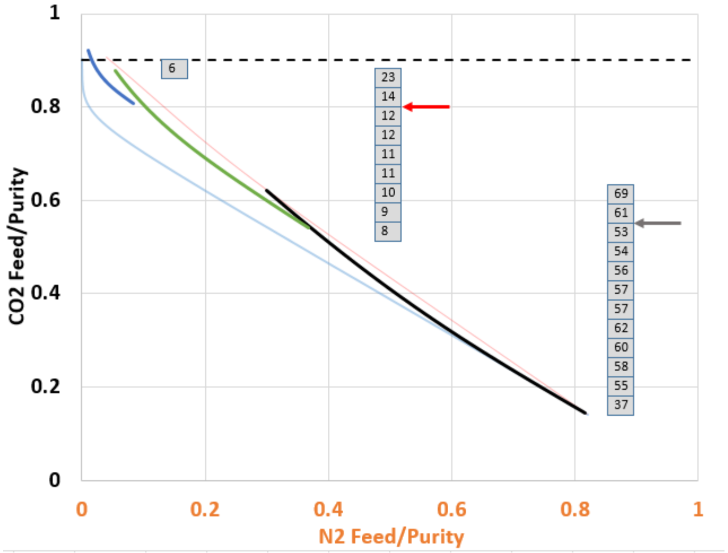


Figure 4-10: Ternary Membrane Design for Coal Power Plant

The Figure 4-10 shows a completed membrane system design with the ternary design methodology for actual plant parameters. The parameters are:

Table 4-1: Coal Power Plant Specification and Parameters

Type of Plant	**Coal Power Plant**
CO_2 Purity Target	90%
CCR Overall Target	90%
Feed Composition	**Mole Fraction**
CO_2	14.1%
N_2	82.1%
O_2	3.8%
Membrane Properties	**Permeance**
CO_2	5.94
N_2	0.1188
O_2	0.85

The steps are followed as described in the procedure. Stage 1 of the design is optimized at the cost of 53 \$/ton indicated by the grey arrow. Cost here is defined as the capture cost/ton of CO_2. Any further increase in purity leads to a significant increase in cost. Stage 2 of the design is optimized at a cost of 12 \$/ton indicated by the red arrow with the plot of all possibilities of Stage 2 being the green curve. Again, a higher purity will require a significantly higher cost. Even at the highest possible cost, Stage 2 is unable to achieve the required CO_2 purity of 90%. Another stage will therefore be required. The required purities for the start of Stage 3 is determined. The plot of all possibilities is shown by the blue curve. Here, the target purity is achieved. The engineer needs only to select the solution that meets the CO_2 purity requirement. This is at a cost of 6 \$/ton.

The membrane system design is completed. Looking at the cost distribution of the first and second stages, there is very little room for a better optimization. Stage 1 is obviously optimized fully. The cost is higher in both directions of CO_2 purity. Stage 2 however shows some promise as a lower CO_2 purity could give a better cost. However, this would imply a lower starting purity for the next stage, and hence a higher cost to reach CO_2 purity of 90%. The designing engineer will have to make the decisions of which would be the better solution, both in terms of cost and complexity of the membrane system. Adaptability to existing systems in the process plant will also be considered in the making the decision.

4.3.5. Membrane Properties Evaluation

The design methodology of Approach 1 defines a certain area between the two extreme curves as the attainable region of a membrane. This region is the workable area of a membrane within which a feasible solution to the membrane design exist. Outside of this region, there exist either no solution or a solution with a significantly higher cost with a worse CO_2 purity. The size of this region therefore defines the flexibility of the designing engineer in shaping his membrane system. A wider attainable region will indicate a greater flexibility and good opportunity to optimize and minimize cost. A narrower attainable region will indicate little chance for optimization. With a very narrow attainable region, the engineer simply accepts the available solution as no significant cost different exist between minimum and maximum cost/stage.

With this behaviour of the graphical design methodology, it is therefore possible to conduct an evaluation of different membrane material properties solely for the purpose of visualizing which has the greater possibility for optimization. This is important in the membrane industry, as membrane material technology is still in the early stages of development. Knowing what type membrane properties shows flexibility to save cost will be important for the development of the membrane material. An illustration is shown of two membrane types.

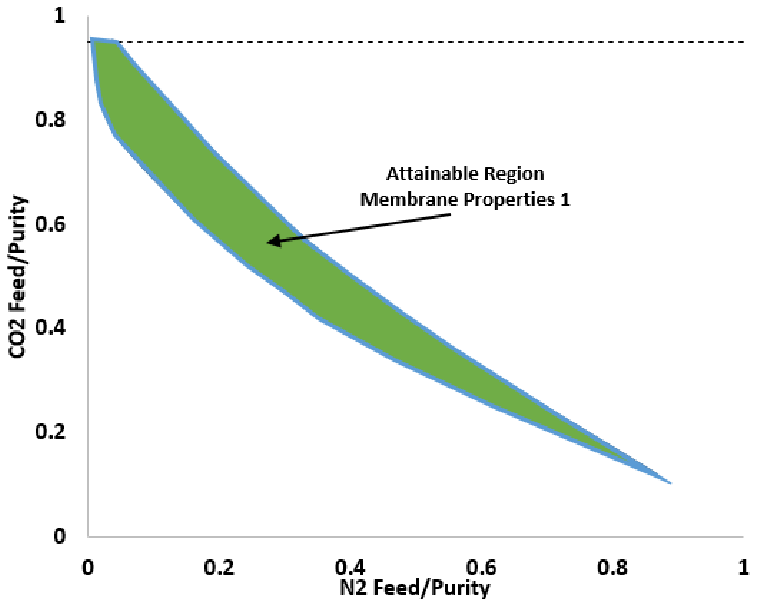


Figure 4-11: Attainable Regions of low selectivity membrane

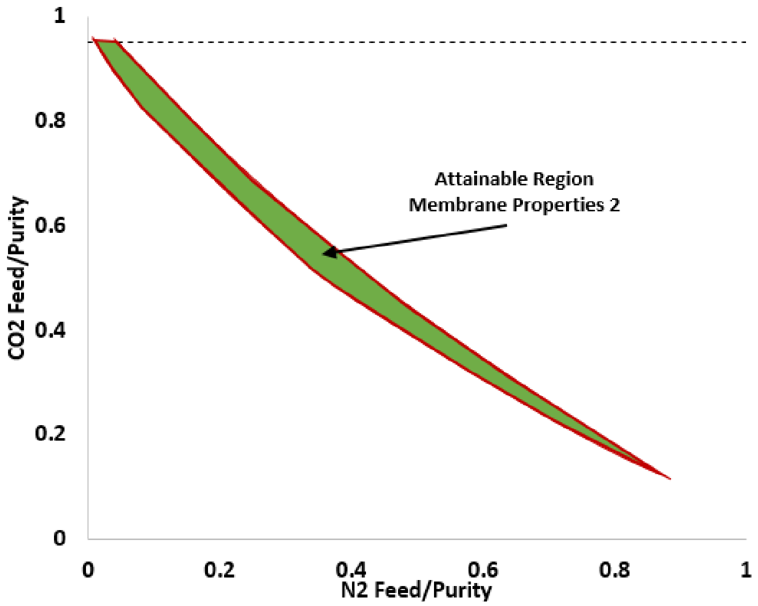


Figure 4-12: Attainable Regions of high selectivity membrane

The first plot in Figure 4-11 has a larger attainable region than Figure 4-12. The membrane property of permeance and their selectivity (relative permeance) between the components determines how large the attainable region will be. A membrane where the selectivity CO_2/N_2 and CO_2/O_2 permeance ratio is low will have a broader attainable region than a membrane with high selectivity. This implies that membrane materials with high selectivity will not have a high degree of flexibility for design optimization as the difference between the minimum and maximum overall cost will not be much. It will also imply that the opportunity to increase or decrease the number of stages will be limited for highly selective membrane material type.

4.3.6. Design Summary

Design Approach 1 simplifies the ternary graphical design methodology from a potential three-dimensional surface plot to a two dimensional plot by utilizing an axis of plot for both CO_2 purity and feed. It then adds the second axis as another component N_2. It establishes an attainable region by plots of the minimum and maximum cost/stage. This region defines the possible outcome of all purity at a reasonable cost. By dividing the possible outcomes of purity into cost intervals, the design approach enables optimization of the membrane stage by comparisons of cost and purity values. Finally, the design also assists in evaluation of the flexibility for optimization of a membrane material type by definition of the size of the attainable region.

4.3.7. Limitations of the Design

The main challenge with utilizing this design approach is the narrow size of the attainable region in some membrane material type. While this will indicate little flexibility to the design, any form of optimization available will be very difficult to visualize. Another challenge is the stage-by-stage solution to designing. Unlike the Lindqvist and Anantharaman (2014) design where the graphical plots are completed before the actual design and optimization process, this design will require optimization for each stage before the next plot is made. Finally, due to the new axis of plot, there is difficulty to have a region of constant cost known as the iso-cost curve in binary graphical design methodology. Cost are simply defined by intervals.

4.4. Design Approach 2

The first approach highlighted the difficulty in finding a methodology where the possible outcomes within the attainable region can be depicted across all possible feed composition. This challenge made the graphical methodology to be presented in stage-wise curves where optimization is done before moving to the next stage. However, the approach retained a single graph for the plots. Since the analysis of this graph is done stage-wise, it presents an opportunity to focus on graphical solutions with a stage-wise optimization rather than a system-wise optimization.

The following approach attempts a graphical solution with a focus on stage-by-stage optimization. This approach takes advantage of a secondary axis for the introduction of a cost curve corresponding to all possible purity outcomes from a stage. By having the purity and cost curve plot on the same graph, the designer is able to visualize the trade-off between the CO_2 purity and cost, making it easy to decide at which purity will be the most cost efficient. This approach is illustrated in the following steps.

Again, as considered in approach 1, the following will be required at the start of the design

- The overall Carbon Capture Ratio required (CCR)
- The CO_2 purity target
- The membrane property permeance of each component
- The process plant conditions

4.4.1. Step 1: Determine the CCR/stage

The activities here are identical to that of Design Approach 1 Step 1. A desired CCR can be determine by a plot of capture cost versus CO_2 Capture Ratio or set by regulations for overall CCR and then back calculated to CCR for each stage.

4.4.2. Step 2: Plot the purity curve between cost boundaries

The cost boundaries here defines the attainable region for the membrane. It represents the solutions possible by changing the variables that constitute the cost, that is, the pressure ratio and area. The attainable region itself will not be visible in this approach. The plot will only be for values defined within the attainable region. This simplification is possible as the analysis per stage allows a closer look into the behaviour of the membrane with varying cost function.

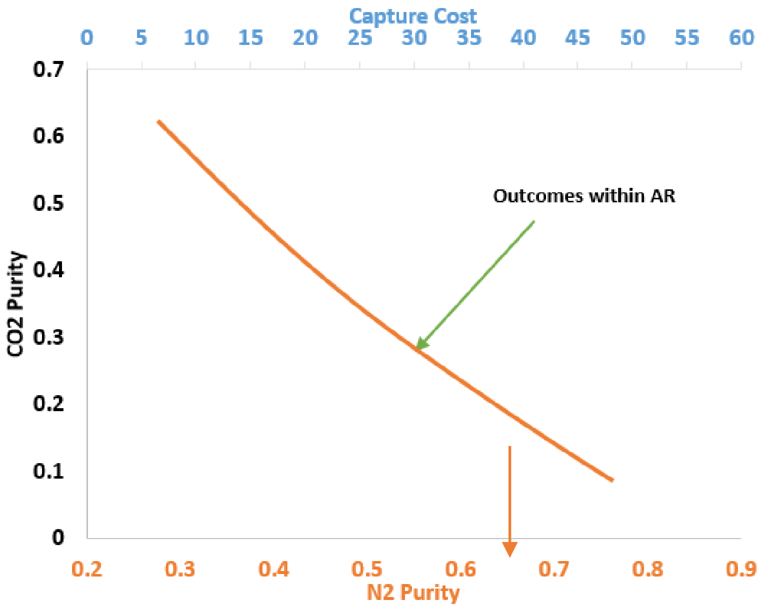


Figure 4-13: Purity outcomes within Attainable Region (AR)

Figure 4-13 is a similar depiction as illustrated in Step 4 of Approach 1. The purity of CO_2 on the vertical axis is plotted against the purity of N_2 on the horizontal. The initial starting point is the feed from the plant or a feed from a previous membrane separation. The curve is a plot of all possible purity attainable between two cost boundaries. The cost boundaries are defined by the two extremes of the pressure ratios (lowest possible pressure ratio and highest practicable at which point no significant changes to purity) of the membrane system.

4.4.3. Step 3: Plot the cost curve between the cost boundaries

The cost curve data is from the same calculation results as Step 2. Rather than the CO_2 purity versus the N_2 purity plot, it will be the CO_2 purity versus the Capture Cost plot. The boundaries are set same as Step 2. The axis of plot is set on the secondary horizontal axis of the graph. This allows superimposition of the cost curve on the purity curve.

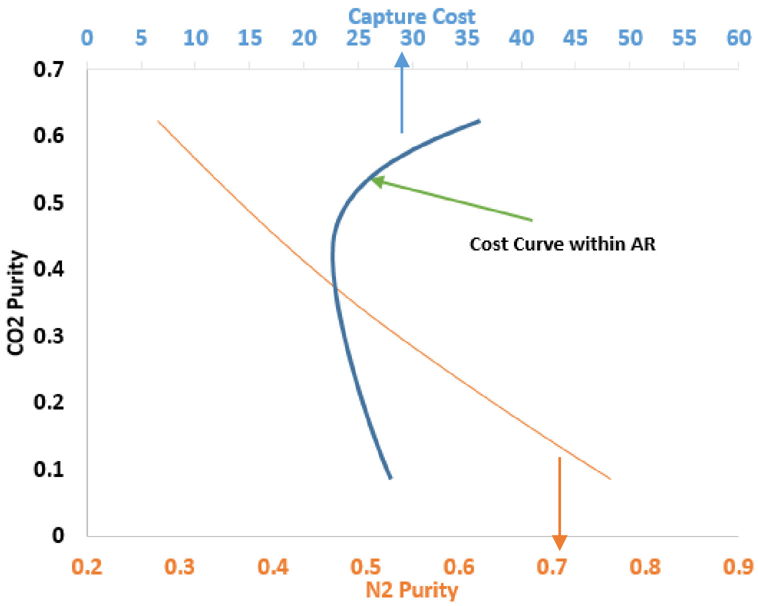


Figure 4-14: Cost curve of outcomes within the AR

The Figure 4-14 represents the combinations of the two plots of purity and cost. The cost curve varies along the purity of CO_2 enabling visualization of the cost at every outcome.

4.4.4. Step 4: Optimization

After plotting the curves for purity and cost, the next step is the optimization and design step. These two curves allows the design engineer to visualize the cost distribution across all possible solutions for the membrane stage. This permits selection of a desired CO_2 purity corresponding to a reasonable cost. The undulating section of the cost curve in Figure 4-15 shows a region of the membrane system where the cost of membrane area vary inversely with the cost of compression. The magnitudes of these cost changes non-linearly across a wide range of purity giving the opportunity to maximize the purity achieved without a significant increase in cost.

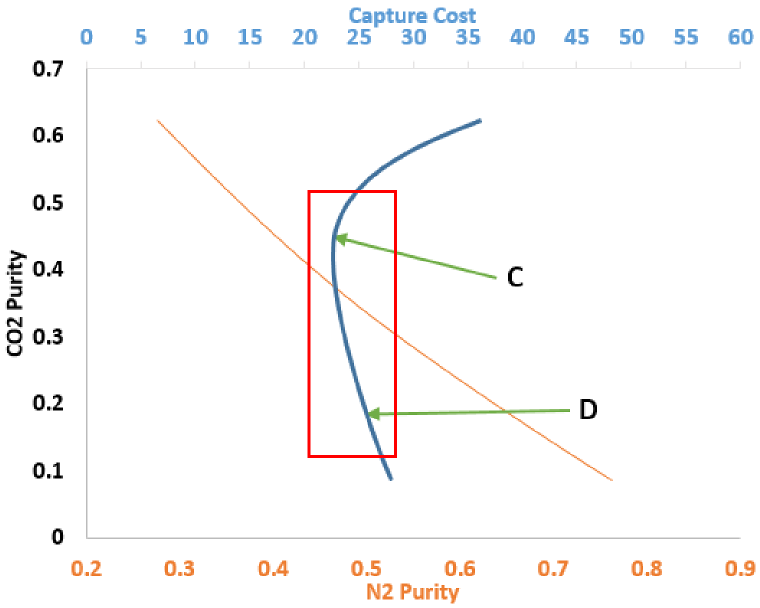


Figure 4-15: Optimization region

The region in the Figure 4-15 marked with a red rectangle, shows that there are regions of higher purity with lower cost marked ‘C’ as compared to the region ‘D’. These occurs when the magnitude of cost for the area is significantly higher than that of compression at region ‘D’. As the compressor pressure ratio is increased, the area will decrease and the purity increases. The overall cost of the stage does not necessarily increase. At region ‘C’ the rate of increase of the cost of compression is lower than the rate of decrease of the cost of membrane area. This leads to a lower overall membrane stage cost at region ‘C’. This is not always the case as will be seen in practical example later

In the process of optimization, the designer will take into consideration the effect of his decisions on the current stage to the subsequent stages in the membrane system. Always, the aim is to optimize fully the purity at the first stage as it often has the best region for optimization. This is also observed in the previous binary graphical design methodology for membrane design. The cost savings is high in the first and second stage as they often have a higher opportunity for increase in purity with little additional cost. The designer also considers that the chances of have more than the required number of membrane stages increases if the first stage is not properly optimized. That is a low purity can lead to more than required number of stages, which will prevent attainment of the carbon capture ratio. Due to the ability to have a closer look at the optimization for a stage-wise approach to membrane design, the need to go back and forth in order to find the best or minimum overall cost as done in the previous binary design methodology is minimized. If this stage wise approach is implemented correctly, there is an opportunity to get it right the first design try, giving a system with achieved purity and capture ratio at minimum possible cost and complexity.

4.4.5. Step 5: Prepare for the next membrane stage

One of the good features of this design approach is that since the purity curve comprises purity of both the CO_2 and N_2, it is easy to have the necessary information of the mole fractions of the composition after this membrane stage, and used in the next membrane stage. After the designer visually selects the point in the optimization process, a straight horizontal line meeting the purity curve will enable determination of the purity of both CO_2 and N_2.

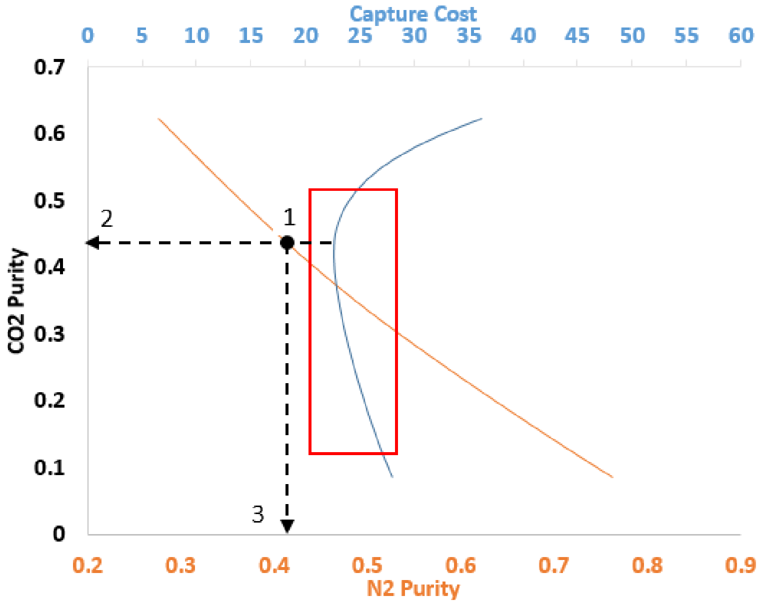


Figure 4-16: Purity of optimal solution

Point 1 on Figure 4-16 indicates the corresponding point of the designers optimized cost on the purity curve. Further extension of the line horizontal and vertically will mark the purity of CO_2 and N_2 as shown by points 2 and 3 respectively. These values are required for the start of the next membrane stage.

Once the optimized cost, purity of CO_2 and N_2 are determined, the membrane stage design is complete. The purity information is used as the new start composition for the next stage. The steps as described above is repeated until the target values of purity is achieved. There is a possibility of repeating the process if the optimization was not initially well done or there is a need to adjust a stage to meet certain conditions. Any change to a previous stage will require recalculation and optimization of the subsequent stages.

For a practical example, the following data is used

Table 4-2: Coal Power Plant Specification and Parameters

Type of Plant	**Coal Power Plant**
CO_2 Purity Target	90%
CCR Overall Target	90%
Feed Composition	**Mole Fraction**
CO_2	14.1%
N_2	82.1%
O_2	3.8%
Membrane Properties	**Permeance**
CO_2	5.94
N_2	0.1188
O_2	0.85

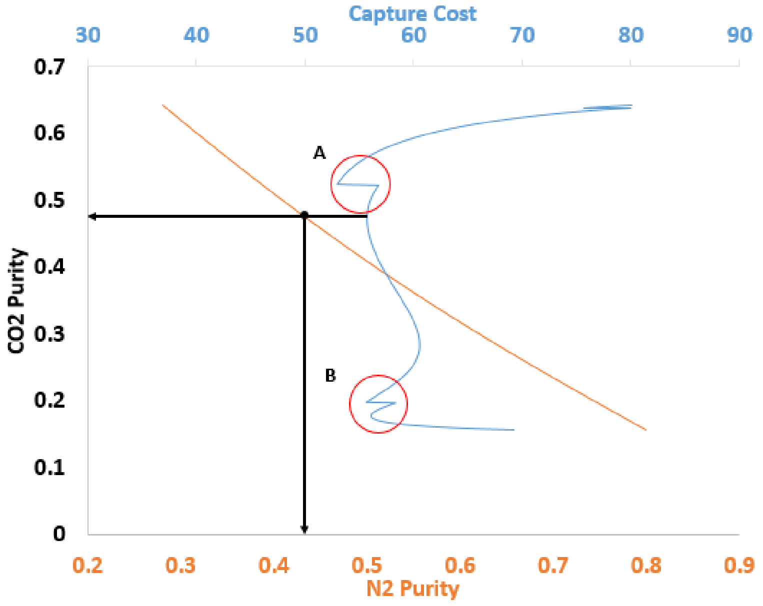


Figure 4-17: Stage 1

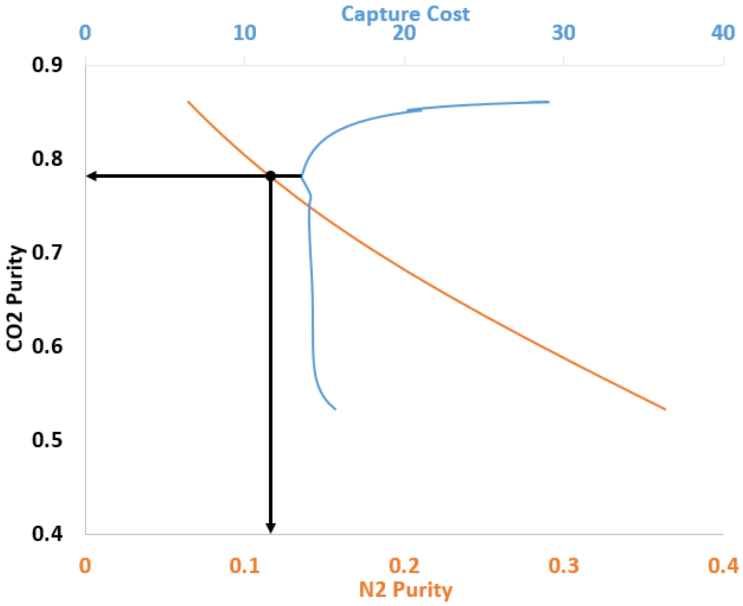


Figure 4-18: Stage 2

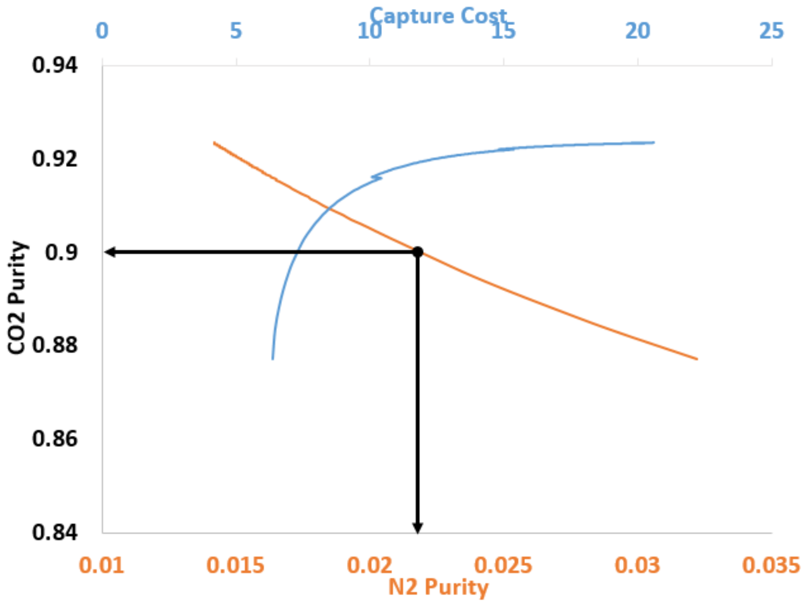


Figure 4-19: Stage 3

The three figures Figure 4-17, Figure 4-18 and Figure 4-19 represents the graphs for stages 1, 2 and 3 of the membrane system. The noise shown as indicated by ‘A’ and ‘B’ in the Figure 4-17 represents the point of change in the number of compressor stages. The third figure shows that the required purity of CO_2 of 90% is achieved. The number of stages also meets the requirements to enable a CCR of 90%. Looking at the third stage of the membrane system, the designer has the ability to visualize that the target purity of 90% is achieved with relatively low pressure ratio in the stage. This will suggest the possibility to further optimize the membrane system to two stages. However, on looking for opportunities to increase the purity in the previous two stages, it is clear to the designer that the cost curve beyond the optimized points for the first and second stage increases with a high slope. This is more obvious in the second stage. This will possibly lead to an even higher cost than the three-stage solution. The two-stage solution is ruled out easily as not being a better low cost solution.

Nevertheless, there is opportunity to balance the third stage with a higher cost and lower the cost in the first and second stage. Since purity target in achieved quickly in the third stage, the cost of the third stage may not justify the effort of separation. Some of the cost can be spread out to the previous stages. This may or may not lead to a lower cost. The designer has to consider the necessity of it and make these decisions. Integration to other processes in the plant might also affect how the designer distributes the workload and hence cost in each stage.

4.4.6. Design Summary

This approach focuses on the stage-wise optimization of a membrane system. Rather than defining an attainable region, it makes only plots within the attainable region. This gives a closer look at the plots of both purity and cost curves for ease of determining the most optimal solution to the stage. Due to the detailed approach, it presents an opportunity to visualize quickly further overall optimization of the membrane system. The cost curves shows the rate of increase in magnitude with respect to the purity of CO_2.

4.4.7. Limitations of the Design

Similar to Approach 1, unlike the Lindqvist and Anantharaman (2014) design where the graphical plots are completed before the actual design and optimization process, this design methodology will require optimization for each stage before the next plot is made.

Chapter 5

5. Expansion of the Graphical Design Methodology (Binary Feed)

5.1. Introduction

The application of the graphical design methodology for binary feed by Lindqvist and Anantharaman (2014) is in the CO_2 post combustion separation. The methodology is hence limited for use in power plants, cement plants and similar process plants were CO_2 is a by-product of a combustion process with its removal due to emission restrictions. However, the membrane technology has a very broad area of application beyond post combustion CO_2 capture. It is widely used in the food technology, biotechnology and pharmaceutical industries.

There is a continuous increase in the global demand for membrane technology. It is estimated to be worth approximately 15.6 billion USD in 2012. New development and improvement in membrane material science and process technology has led to increase in global demand and emergence of new applications. The market is expected to increase by around 8% annually in few years, with a forecast of 21.22 billion USD in 2016 and further 25 billion USD in 2018 (Intelligence, 2013).

The opportunities for membrane technology is therefore large and ever growing. The graphical methodology can provide design solutions to the different applications of membrane technology. However, with the current methodology, there is a need to adapt the method of applying the graphical design to a more generic and robust system. This will enable its use in all membrane technology application without a need to change the basic principle of design in the graph or the code that it runs on.

Making the graphical design methodology a generic system for membrane system synthesis will require elimination of all parts of the method that uniquely links it to a post combustion CO_2 capture. It will also involve considerations for different possible process scenario that were not considered in the existing method. It will not be practical to consider all unique scenarios of every available application of the technology. However, there are certain applications with specific features that represent other common scenarios different from the existing method.

Two of such applications are considered. These are:

- Biogas Clean-up
- H_2 Separation

Biogas Clean-up

With the current energy crises, there is a need to seek alternative sources of energy aside the conventional fossil fuels. In order to have long-term sustainable development across the world, the continuous dependence of fossil fuel with the associated environmental impart will have to reduce. This leads to opportunities for renewable energy resources like biogas. Biogas is a renewable energy source for natural gas. It is considered as one of the best alternatives for fossil fuels. (Imam et al., 2013)

Biogas typically refers to a mixture of different gases produced by the breakdown of organic matter in the absence of oxygen. Biogas can be produced from raw materials such as agricultural waste, manure, municipal waste, plant material, sewage, green waste or food waste. Biogas is a colourless, flammable gas produced via anaerobic digestion of these raw materials, to give mainly methane, carbon dioxide and traces of other gases such as nitrogen, hydrogen, ammonia, hydrogen sulphide, water vapour etc. It is smokeless, hygienic and more convenient to use than other solid fuels.

To use biogas as a conventional fuel, it has to be cleaned and upgraded. Cleaning requires removal of water and hydrogen sulphide. Upgrading requires removal of CO_2 to improve the calorific value. It is in this biogas upgrade that membrane technology has found application. In the case of biogas, we would need a selective membrane that will have a large permeability difference between CO_2 and CH_4. (Hagen et al., 2001)

Hydrogen (H_2) Separation

The application of membrane technology has presented a pathway for hydrogen separation economically. Membranes are now available in the commercial market for hydrogen separation. The application of membranes in H_2 separation exist in different stages of H_2 use. Membranes are used in both hydrogen production and as proposed for the future in hydrogen transportation in existing natural gas pipelines.

H_2 is a valuable material generally produced by the reactions of metals and strong acids. It is consumed in billions of cubic meters per day by various industries especially in the petroleum industry as hydrodealkylation, hydrodesulphurization and hydrocracking (Paglieri & Way, 2002). Hydrogen is also considered as a potential alternative energy source that can help to reduce the dependence on oil and gas. Hydrogen technologies are important to solving problems related to the energy and environmental sectors (Milciuviene et al., 2006). It differs from conventional energy sources like the oil and gas because it is potentially inexhaustible, and is an environmentally friendly sustainable resource. There is an increase in the demand for it and this therefore motivates research into the production processes of hydrogen in which H_2 separation is of significance. The success of many of the hydrogen technology like fuel cell technology is dependent on the purity of hydrogen to a high degree of 99.99% (Shao et al., 2009).

The pressure swing adsorption method is most commonly used method of separation in hydrogen processes (Linde, 2010). This method is rather energy intensive due to the high volume of adsorbent used in the separation process and it records waste of H_2 in the regeneration process thereby reducing the overall efficiency of the system. Therefore, the use of membrane technology has great opportunities in H_2 separation and could if proper research is done in optimization, be the best method to meet the growing demand for pure hydrogen.

The above applications for membrane technology adds two unique process scenarios that are not considered in the post combustion CO_2 capture. They are:

- High pressure feed
- Retentate side cascade

5.2. High pressure feed

Unlike in the post combustion CO_2 capture were the process plant exit pressure is approximately 1 bar, other process scenarios will vary in the exit pressure of the plant to the membrane system. High pressure in this case will serve as a positive to the separation system as it reduces the cost of compression of the feed stream. Nevertheless, this poses a new challenge to the graphical design methodology.

The graphical design methodology works on an assumption related to the pressure of the stream to each membrane stage. This pressure is corrected and it will always be at about 1 bar at the start of each stage. This corresponds to the feed stream pressure at the inlet to the membrane system. To take advantage of the high pressure feed membrane system, the first stage of the membrane system will have a feed pressure greater than 1 bar. The subsequent stages will maintain a feed pressure of 1 bar. The difference in feed pressure of the first stage to the subsequent stages hinders the use of just one minimum cost curve for the membrane design. To make the graphical design methodology more generic, the high-pressure feed to the first stage will have a different minimum cost curve superimposed on the other. This is illustrated in Figure 5-1.

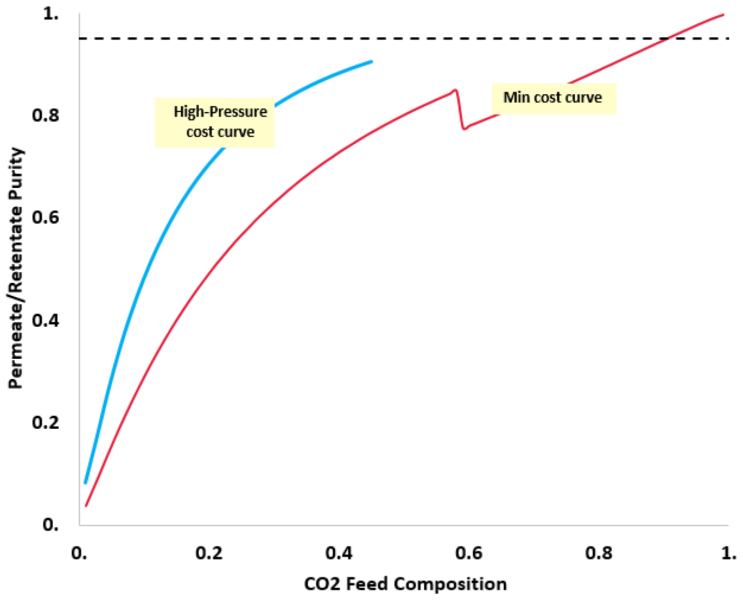


Figure 5-1: Normal and High Pressure minimum cost curve

Figure 5-1 shows both the high-pressure cost curve and the min cost curve. The high-pressure cost curve does not need to be fully drawn for all CO_2 feed. Since it is only required for the first stage cost analysis, it is drawn so much as to cover the first stage CO_2 composition. Determining the number of stages and their operating conditions is the same as described is theory in Chapter 2. However, for the first stage, the high-pressure cost curve is used rather than the min cost curve. Subsequent stages are analysed with the min cost curve. Figure 5-2 shows a completed graphical design with a high-pressure feed to the membrane system. The same principles for optimizing the overall cost and number of stages as described in Chapter 2 applies.

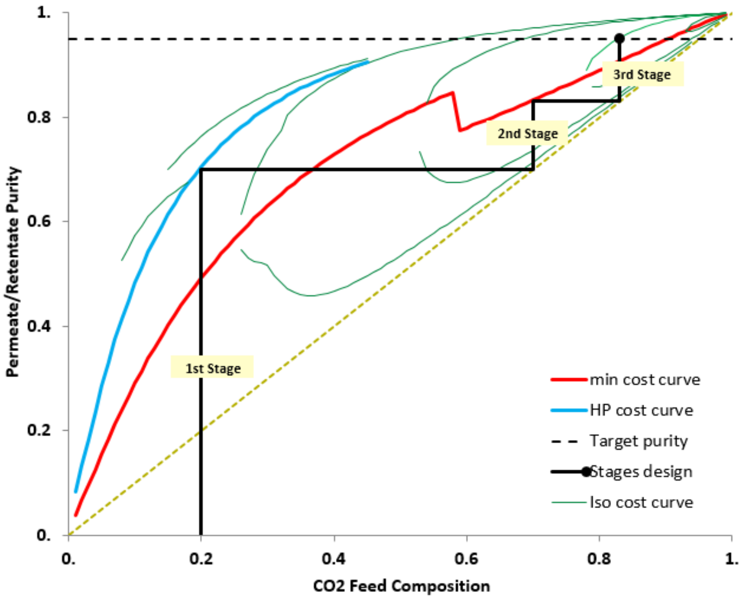


Figure 5-2: Completed Design with High Pressure Feed Stream

5.3. Retentate Side Cascade

So far, the described membrane separation processes have had the component of interest with the higher permeance. This ensures that the permeate side of the membrane will always be the feed to the next membrane stage as shown in Figure 5-3. This can be referred to as a permeate side cascade. The component that diffuses fastest to the permeate side is determined by the selectivity of the membrane material (the component permeance). Obviously, the membrane material can be equally selectable to the other component, but such material can be limited by existing technology. Therefore, it is necessary to consider a design methodology for a scenario where the important component has a lower permeance. An example is the biogas clean-up.

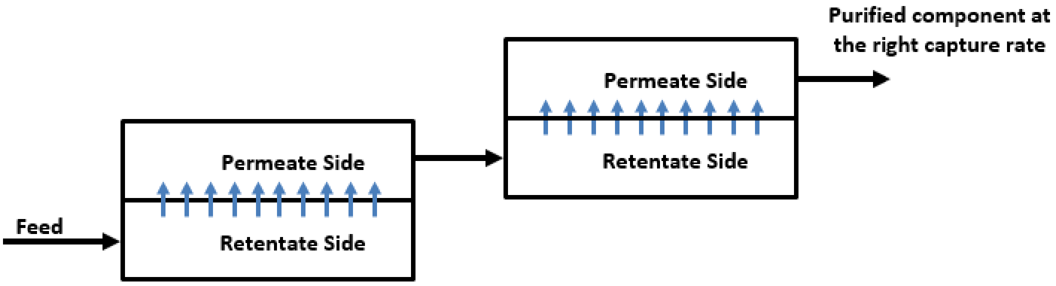


Figure 5-3: Permeate side cascade

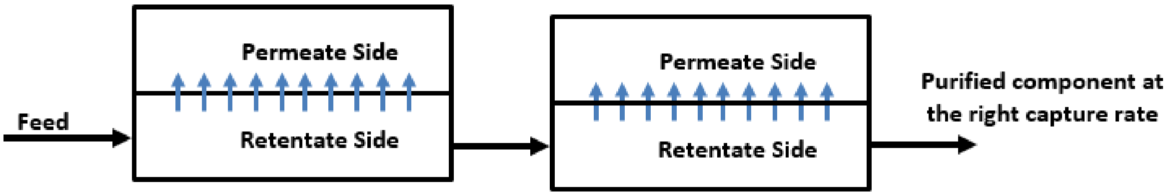


Figure 5-4: Retentate side cascade

The challenge here is that CH_4 which is the component of interest in a biogas plant has a permeance lower than that of CO_2 for certain common membrane material. This means that the bulk of CH_4 will be on the retentate side of the membrane. Therefore, the next stage of the membrane system will have to take its feed from the output of the retentate side. This is called retentate side cascade and is illustrated in the Figure 5-4. The capture rate of the membrane stage is usually defined by the volume of the important component captured on the permeate side to the feed volume. If the component of interest is on the retentate side, the capture ratio will be defined by the volume of the important component captured on the retentate side to the volume of the feed as seen in the equation below. This requires a minor adjustment to the specification section of the program to effect the new capture ratio definition.

$$Capture\ Ratio(Stagecut) = \frac{Volume\ fraction\ of\ Component\ (CH_4)\ on\ Retentate\ Side}{Volume\ fraction\ of\ Component\ \ (CH_4)\ on\ Feed\ Stream}$$

The more important challenge here is the graphical representation. As mentioned in the theory in Chapter 3, the graphical design methodology already has provisions for retentate side evaluation. However, how to use this provision had not been developed and applied. This is discussed next.

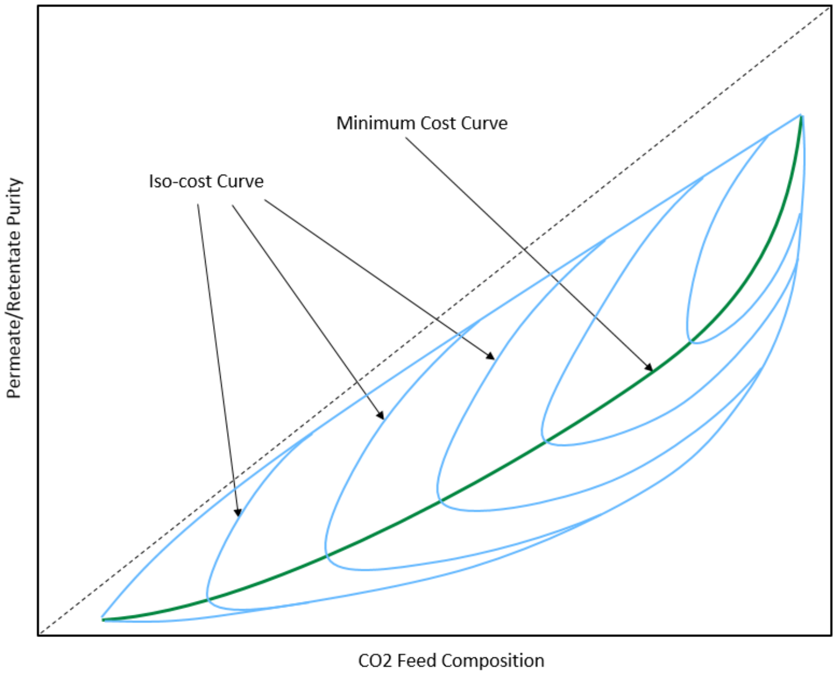


Figure 5-5: Retentate side curves of Iso-cost curve and Min cost curve

Figure 5-5 is an illustration of the developed methodology by Lindqvist and Anantharaman (2014) for the retentate side cascade. The iso-cost curves and minimum cost curve are similar to that for permeate side cascade but plotted with retentate purity of CO_2. For a binary feed assumption, the mole fraction of CH_4 is 1 less the mole fraction of CO_2. This will imply that on the axis for CH_4, the purity will increase in opposite direction to that of CO_2. This is deliberate for consistency in the design methodology. The analysis of the stages will then be from right to left. The methodology is the same as explained in Chapter 2. Optimization of the membrane system will require a trade-off on each stage for higher purity at a higher cost. The iso-cost curve will serve as guide in determining the best stages for optimization. An example of optimized membrane system for a retentate side cascade is shown in Figure 5-6.

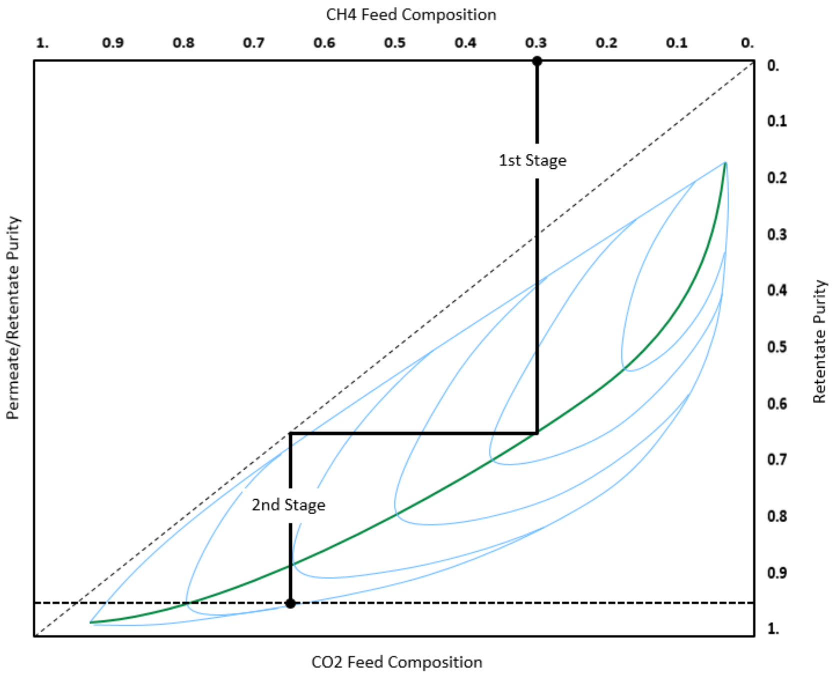


Figure 5-6: Completed retentate side cascade. 2 membrane stages

5.4. Sweep Gas Consideration

One of the main challenges in implementing membrane technology is the cost of energy required to generate a sufficient partial pressure difference across the membrane. Typically, the required partial pressure difference is achieved by either the compression of the feed side, the use of a vacuum on the permeate side or the combination of both. With this, a total pressure difference is created across the membrane. This total pressure difference will enable the partial pressure of CO_2 on the feed side to drive it across to the permeate side. This is not the only method to have a partial pressure differential of CO_2 across the membrane.

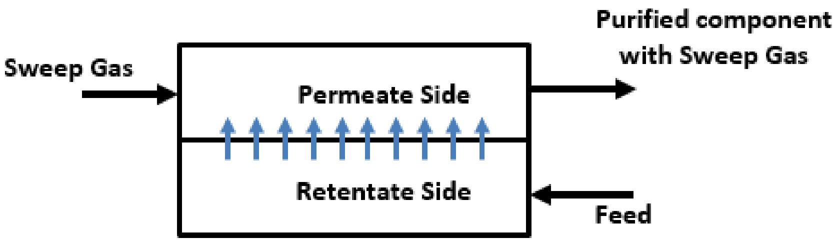


Figure 5-7: Use of Sweep gas illustration

The use of a sweep gas provides an opportunity to have this partial pressure for CO_2 without the need for a high-cost compression or vacuuming system. Merkel et al. (2010) had focused on improved membrane technology in combination with the use of incoming combustion air as sweep gas to generate driving force. The driving force for the transmembrane permeation is achieved by having a sweep gas on the permeate side of the membrane. This reduces the mole fraction and hence the partial pressure of the permeant below that on the feed side of the membrane. With the use of a sweep gas (usually air), it will be possible to have the total pressure of both sides of the membrane system to be the same or even higher on the permeate side. It can also be combined with compression or vacuum system for a combined effect.

The graphical design methodology for both the binary and ternary feed is based on models by Weller and Steiner (1950) and Pettersen and Lien (1994) respectively. The models do not consider a sweep gas in the permeate side of the membrane. Therefore, implementation of a sweep gas to the existing graphical design methodology will require an adaptation of the models or a complete replacement of the model with a new model that considers a sweep gas. Unfortunately, there is not much literature on membrane models with sweep gas. Franz et al. (2013) did an investigation into the influence of sweep gas on CO_2/N_2 membranes for post-combustion capture. They made use of the simulation tool Aspen Plus® software (Aspen Tech Inc.) for their evaluation.

Important to the graphical design methodology is the impact of the sweep gas to the visual representation of membrane system. At this point it is important to mention that both models by Weller and Steiner (1950) and Pettersen and Lien (1994) for the binary and multicomponent feed system are applicable to the Lindqvist and Anantharaman (2014) graphical design methodology for membrane systems. The graphical design methodology in this case is independent of the model used for evaluation. Therefore, any model operating within the same assumptions can be used with the graphical design methodology remaining the same. However, the sweep gas introduces changes to the whole capture process as O_2 permeation is affected leading to an increase in the required air flow rate and membrane area (Franz et al., 2013).

Other changes to the membrane system by the sweep gas is the possible elimination of compression and vacuum cost. One of the important concept of the graphical design methodology highlighted by Lindqvist and Anantharaman (2014) is the elimination of the two design parameters (installed membrane area and the pressure ratio) and, in their place use cost as a design parameter. This significantly simplifies the synthesis of a membrane system. It also ensures the inclusion of additional cost factors, such as that needed to provide a sweep gas, does not affect in any way the methodology of the graphical design.

Without a working model for the implementation of the sweep gas, it will remain inconclusive for now its impact on the graphical design methodology. However, the independence of the methodology on membrane models, the simplification of all design parameters as a single function of cost, and the visual representation of the membrane system by the relationship of cost and purity will suggest that the graphical design methodology can be extended for the synthesis of a membrane system with sweep gas.

5.5. Other Changes to Design Methodology

There are minor changes to the existing methodology that converts it to a generic methodology. The terminologies used by the existing design is as used in CO_2 post combustion capture. This will be changed to terms more suitable to be applied in every situation

Carbon Capture Ratio (CCR)

The carbon capture ratio CCR is in reference to carbon capture and storage in CO_2 producing process plant. The term is a measure of volume of CO_2 removed compared with the volume of CO_2 fed into the membrane system. This is equivalent to the stage-cut of the component of interest. As explained in the retentate side cascade, the stage cut calculation is not always on the permeate side of the membrane. Therefore, for a generic definition applicable to all process condition or composition, the stage-cut of the component of interest is appropriate rather than the CCR.

Axis Titles

The horizontal and vertical axis of the graphical design methodology are both defined by the feed and purity of CO_2 respectively. CO_2 being the component with the higher permeance is used to plot the curves in the graph. Therefore, the component that permeates faster as decided by the membrane material selection defines what is used to plot the curves. This component is called 'component A'. In the retentate side cascade, for ease of visualization, secondary axis is introduced to represent the direction of increase of 'component B', as in the case CH_4 separation.

5.6. Summary

Two possible scenarios were considered for the expansion of the graphical design methodology for binary feed. Processes with high pressure feed were incorporated with alterations to the design curves by including a new cost curve for high pressure on the first stage. For processes that requires the retentate side cascade, the Lindqvist and Anantharaman (2014) design methodology was developed with the stage cut of component of interest (Component B) adjusted within the code, to apply for the retentate side. Finally, the terminologies with attributes to CO_2 post combustion capture were changed to more generic terms.

5.7. Limitations of the Design

The high-pressure cost curve is only applicable to the first stage of the membrane system in this design methodology. It will require a stage-by-stage approach to the design methodology if high-pressure feed is to be considered for every stage, maintaining a system design as originally done for the binary graphical design methodology requires a compromise. This compromise requires having the high-pressure cost curve only on the first stage. This may or may not be considered a limitation, as maximizing the high-pressure on the first stage reduces the complexity of the membrane design (lower number of stages).

Chapter 6

6. Conclusions and Recommendations

6.1. Conclusion

The graphical design methodology has been improved on two separate platforms. The first was the extension of the design methodology from a binary feed to a ternary feed. Two design approaches were proposed as a solution to the graphical representation for ternary feed towards the optimal design of membrane systems. Both proposed design enabled a design engineer or any user to make decisions regarding how the membrane system will be configured at the best cost. They visually represented stages of the membrane system with information about the feed and exit conditions easily acquired from the plots. The use of any of the design approach will assist in making a more precise estimation of the design configuration and cost of a membrane system.

Secondly, this report expanded the application of the existing graphical design methodology for binary feed applied for CO_2 post combustion capture to other processes utilizing membrane technology. Graphical design methodologies were proposed for two process scenarios of high-pressure feed and retentate side cascade, which were not considered before. The proposed methodologies, if correctly applied, will enable the application of the graphical design methodology to more processes using membrane technology.

6.2. Recommendations

The graphical design methodology depends on the accuracy of both the model for the membrane separation and the code that evaluates the mathematics of the model. The robustness of the coding language determines the ability to have accurate results useful for the graphical design plots. The behaviour of the model used in this report suggests a need for further investigation into optimization tools where minimization of costs are determined. An option will be the inclusion of certain constraints to the feed or permeate side pressure thereby limiting the variables of the model. The applicability of this will have to be investigated.

Also interesting for further studies will be the use of sweep gas. Though the opportunity for cost reduction is debatable considering the complications of introducing a sweep gas, the principle suggests possible gains. A new model may be required for this, after which a graphical design methodology can be developed or the existing graphical methodologies adapted to include the use of sweep gas.

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