Simulation of Membrane Technology for CO_2 Removal for cross-flow model using ASPEN HYSYS software

by

LE HOAN

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

Dr. Lau Kok Keong

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

LE HOAN

ABSTRACT

There are nearly 40% of the world gas reservoir contains high level of CO_2 and H_2S that pose obstacles to development. Due to the high CO_2 content, up to 13 trillion cubic feet of high CO_2-NG gas fields remain undeveloped in Malaysia. Therefore, development of CO_2-NG separation techniques will enable monetization of high CO_2-NG gas fields in Malaysia and to position PETRONAS the competitive edge for international fields' acquisition. Many technologies have been developed for CO_2 removal such as adsorption, absorption, cryogenic distillation but membrane is the most optimized technology.

In order to complete the existing simulation for the membrane in HYSYS software, the temperature change between the inlet and outlet stream needs to be considered. The reason that causes the temperature change is Joule-Thomson effect. By studying the Joule-Thomson effect, the author can apply all the mathematical equations into the HYSYS program to simulate the membrane. With the membrane simulation in HYSYS, the chemical engineers will easily see the temperature change as well as other properties (composition of CO_2 content) in the outlet streams.

ACKNOWLEDGEMENT

First and foremost, I would like to thank my supervisor, Dr. Lau Kok Keong, who gives me the guidance and advice needed in the process of doing Final Year Project. The time spent and endless support that he has given to me is highly appreciated.

A special thank goes out to Mr. Faizan for his time and help in solving many issues regarding the temperature effect as well as the user unit operation in HYSYS software.

Last but not least, I would like to express my sincere gratitude towards Mr. Faudzi Mat Isa from PETRONAS Carigali Sdn. Bhd. for giving me precious advices and data that helps me a lot in doing the final year project.

CHAPTER 1: PROJECT BACKGROUND

1.1 BACKGROUND OF STUDY

Membrane systems have become a tried and accepted natural gas treating technology with distinct advantages in a variety of processing applications. From the earliest units producing below 10 MM SCFD treated gas, systems are now in place to produce upward of 250 MM SCFD. Although most units have been installed onshore, some offshore facilities do exist, and many more are planned. These systems, as well as those in the Middle East and elsewhere, exploit the reliability and minimum manpower requirements of membranes.

There are two effects may allow condensation within the membrane. First, because CO2 and the lighter hydrocarbons permeate faster than the heavy hydrocarbons, the gas becomes heavier and therefore its dew point increases through the membrane. Second the gas cools down as a result of the Joule-Thomson effect, as it passes through the membrane. Condensation is prevented by achieving a predetermined dew point before membrane and then heating the gas to provide a sufficient margin of superheat.

The cross flow model in membrane assumes there is no mixing at both high and low pressure side of the membrane. It approximates the spiral wound membrane that is using in most of the plants nowadays.

1.2 PROBLEM STATEMENT

Development of high CO_2 fields offshore will indisputably give masses of new challenges for those who need to deal with it. Malaysia is known to be one of the countries which have high carbon dioxide (CO_2) gas fields in the world. Due to its high CO_2 content fields (10% - 80% CO_2) makes most of the gas fields remain undeveloped. As for Malaysia the resources have to be developed timely to sustain supply to meet the increasing gas demand. Consequently, significant removal of CO_2 offshore is required to meet low design limits for CO_2 (6%- 10% CO_2 design limit) onshore. The development of these high CO_2 gas fields requires high capital due to CO_2 capture, transportation and storage & utilization.

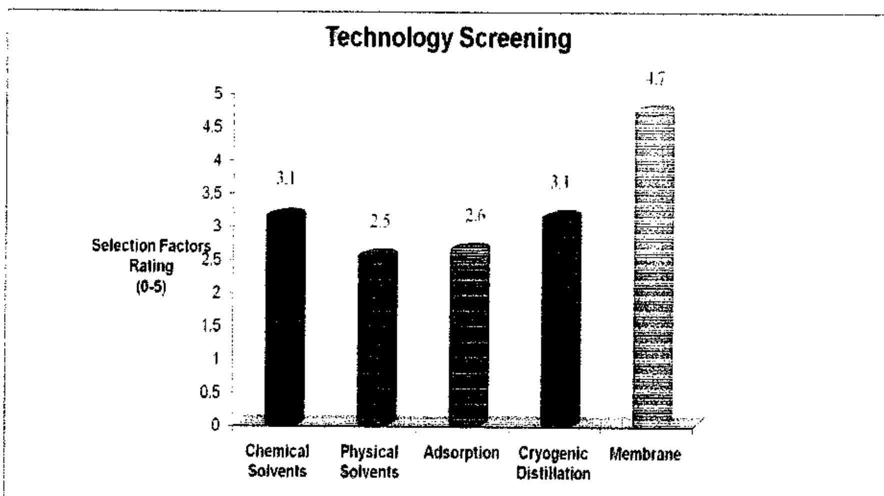


Figure 1: Technology Screening for CO_2 Removal

According to the technology screening above, membrane is the most optimized solution for CO_2 removal (2).

The Joule-Thomson effect is the change in temperature of a fluid upon expansion (i.e., pressure decrease) in a steady flow process involving no heat transfer or work (i.e., at constant enthalpy). This occurs in "throttling" type processes such as adiabatic flow through a process such as adiabatic flow through a porous plug or an expansion valve. The need to understand the Joule-Thomson effect through the membrane and how to calculate Joule-Thomson coefficient is really important. This is the only reason that can change the temperature between the feed and the permeate stream. It has a significant influence on the temperature change through the membrane.

Currently, there is no well-catered membrane simulation in any software. In iCON software that was developed by PETRONAS, there is a membrane simulation. However, this model is very simple, restricted to use and impossible to demonstrate the membrane performance in the industry.

Since it becomes popular day by day because of its advantage, the need to have a useful and flexible membrane simulation that can be used in the industry is critical.

1.3 OBJECTIVE AND SCOPE OF ACTIVITY

The main objectives of this project are:

- Study on the Joule-Thomson effect through the membrane with all the mathematical equations
- To design a Membrane Simulation for cross-flow model
- To solve the complex differential equation in HYSYS

In order to achieve the objectives, research on journals need to be carried out by collecting all technical data regarding the cross flow model for membrane and learning on how to use the following software:

- HYSYS process simulation software
- Visual Basic 6.0
- Visual Basic. NET
- MATLAB
- C# program

CHAPTER 2: LITERATURE REVIEW

2.1 Membrane Technology

Semi-permeable membranes are a mature technology that has been applied in natural gas processing for over 20 years. Membranes are currently used for CO2 removal from natural gas at processing rates from 1 MMSCFD to 250 MMSCFD. New units are in design or construction to handle volumes up to 500 MMSCFD. It has been recognized for many years that nonporous polymer films exhibit a higher permeability toward some gases than towards others. The mechanism for gas separation is independent of membrane configuration and is based on the principle that certain gases permeate more rapidly than others (Figure 2).

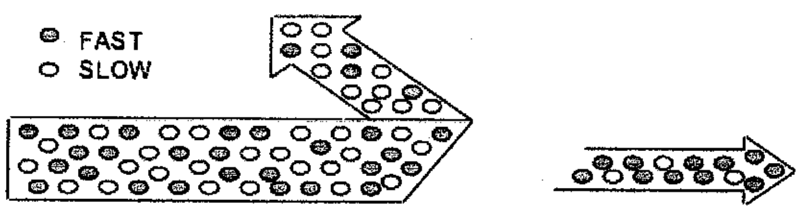


Figure 2: Thin Semi-Permeable Barriers that Selectively Separate Some Compounds from Others

"Permeability" is a measure of the rate at which gases pass through the membrane. "Selectivity" refers to the relative rates of permeation among gas components. The permeation rate for a given gas component is determined by the molecule's size, its solubility in the membrane polymer and the operating conditions of the separation. Selectivity allows a gas mixture of two or more components, of varying permeability, to be separated into two streams, one enriched in the more permeable components and the other enriched in the less permeable components.

2.1.1 Membrane Configuration [1]

The technical breakthrough in the application of membranes to natural gas separation came with the development of a process for preparing cellulose acetate in a state which retains its selective characteristics but at greatly increased permeation rates than were previously achieved. The new membrane was called asymmetric and was first cast into a flat sheet. The major portion of the asymmetric membrane is an open-pore, sponge-like support structure through which the gases flow without restriction. All the selectivity takes place in the thin, non-porous polymer layer at the top. Asymmetric membranes are made out of a single material. The permeability and selectivity characteristics of asymmetric membranes are functions of the casting solution composition, film casting conditions and post-treatment, and are relatively independent of total membrane thickness, though this parameter is closely controlled in the manufacturing process.

Methods were later developed to incorporate this asymmetric membrane structure for gas separation in a hollow fiber configuration rather than a flat sheet. Hollow fibers have a greater packing density (membrane area per packaging volume) than flat sheets, but typically have lower permeation rates. Both configurations of cellulose acetate membranes have their individual advantages and disadvantages.

2.1.2 Types of Membrane [1]

In order for membranes to be used in a commercial separation system they must be packaged in a manner that supports the membrane and facilitates handling of the two product gas streams. These packages are generally referred to as elements or bundles. The most common types of membrane elements in use today for natural gas separation are of the spiral - wound type and the hollow-fiber type.

Spiral - wound elements, as shown in Figure 3, consist of one or more membrane leaves. Each leaf contains two membrane layers separated by a rigid, porous, fluid-conductive material called the permeate spacer. The spacer facilitates the flow of the permeate gas, an end product of the separation. Another spacer, the high pressure feed spacer, separates one membrane leaf from another and facilitates the flow of the high pressure stream linearly along the element. The membrane leaves are wound around a perforated hollow tube, known as the permeate tube, through which permeate is removed. The membrane leaves are sealed with an adhesive on three sides to separate the feed gas from the permeate gas, while the fourth side is open to the permeate tube.

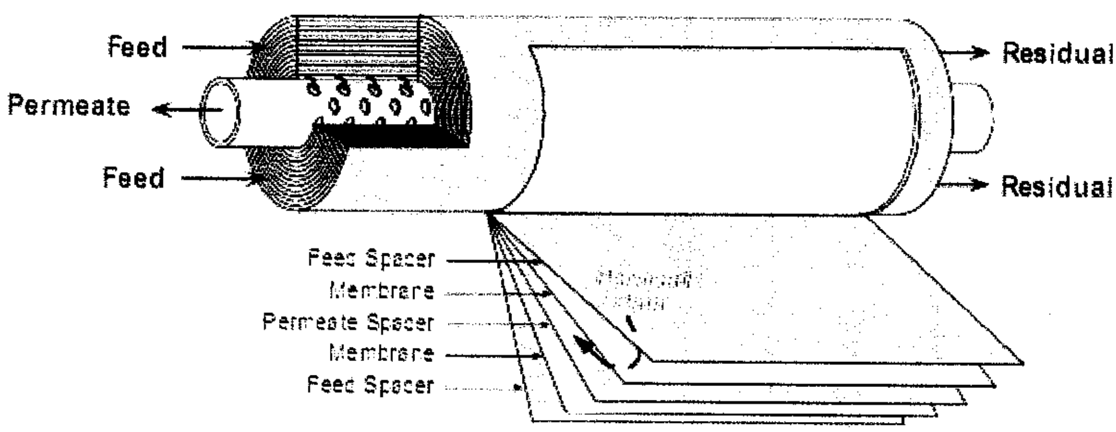


Figure 3: Spiral-Wound Membrane

The operation of the spiral-wound element can best be explained by means of an example. In order to separate carbon dioxide from a natural gas, the feed mixture enters the pressure vessel (tube) at high pressure and is introduced into the element via the feed spacer. The more permeable CO_2 and H_2O rapidly pass through the membrane into the permeate spacer, where they are concentrated as a low pressure gas stream. This low pressure CO_2 gas stream flows radially through the element in the permeate spacer channel and is continuously enriched by additional CO_2 entering from other sections of the membrane. When the low pressure CO_2 reaches the permeate tube at the center of the element, the gas is removed in one or both directions. The high pressure residual gas mixture remains in the feed spacer channel, losing more and more of the carbon dioxide and being enriched in hydrocarbon gases as it flows through the element, and exits at the opposite end of the element.

To construct hollow fiber elements, very fine hollow fibers are wrapped around a central tube in a highly dense pattern. The feed natural gas flows over and between the fibers and the fast components permeate into the middle of the hollow fiber. The wrapping pattern used to make the element is such that both open ends of the fiber terminate at a permeate pot on one side of the element. The permeate gas travels within the fibers until it reaches the permeate pot, where it mixes with permeate gas from other fibers. A permeate pipe allows the collected gases to exit the element. An illustration is shown in Figure 8.

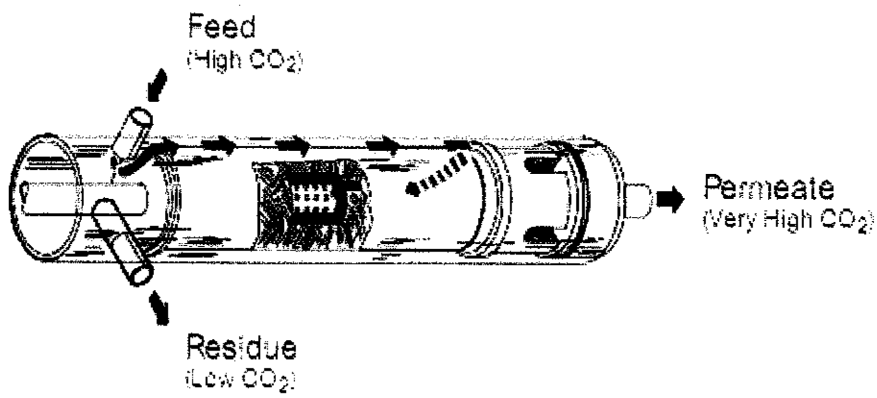


Figure 4: Hollow-Fiber Membrane

As the feed gas passes over the fibers, the components that do not permeate eventually reach the center tube in the element, which is perforated like the spiral-wound permeate tube. In this case, however, the central tube is for residual gas collection, not permeate collection. Many optimizations are possible for either element configuration. For hollow fibers, an important parameter is adjusting fiber diameter – finer fibers give higher packing density while larger fibers have lower permeate pressure drop and so use the feed-to-permeate-side pressure drop driving force more efficiently. While each element type has its own advantages, the mechanism for gas separation is independent of the membrane configuration and is based on the principle that certain gases permeate more rapidly than others. This is due to the combination of diffusion and solubility differences, whereby a gas mixture of two or more gases of varying permeability may be separated into two streams, one enriched in the more permeable components and the other enriched in the less permeable components.

2.1.3 Cross-Flow Model for gas separation by Membranes [8]

In this case, the longitudinal velocity of the high-pressure or reject stream is large enough that this gas stream is in plug flow and flows parallel to the membrane. On the low-pressure side the permeate stream is almost pulled into vacuum, so that the flow is essentially perpendicular to the membrane.

This model assumes no mixing in the permeate side as well as no mixing on the high pressure side. Hence, the permeate composition at any point along the membrane is determined by the relatives rates of permeation of the feed components at that point. This cross-flow pattern approximates that in an actual spiral wound membrane separator with a high-flux asymmetric membrane resting on a porous felt support

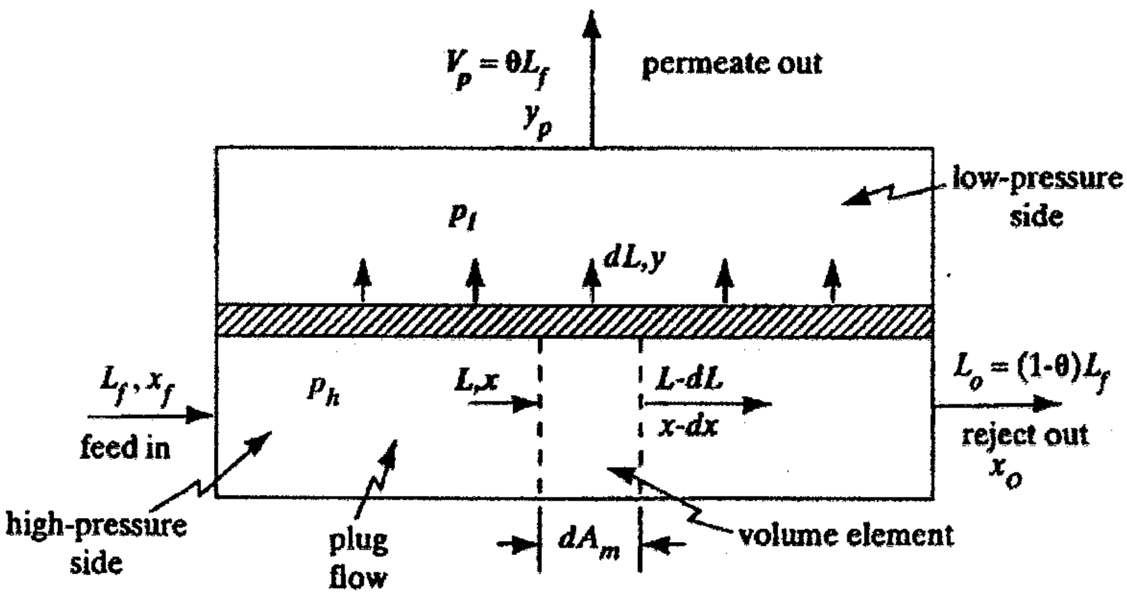


Figure 5: Process Flow Diagram for Cross Flow Model

The local permeation rate over a differential membrane area dA_m at any point in the stage is:

$$ydV = \frac{P'_A}{t}\left[p_h x - p_l y\right]dA_m \,(*)$$

$$(1-y)dV = \frac{P'_B}{t}\left[p_h(1-x) - p_l(1-y)\right]dA_m \,(**)$$

Where dL=dV and is the total flow rate permeating through the area dA_m. Dividing (*) by (**) gives

$$\frac{y}{1-y} = \frac{\alpha^*\left[x - (p_l/p_h)y\right]}{(1-x) - (p_l/p_h)(1-y)}$$

This equation relates to the permeate composition y to the reject composition x at a point along the path.

Weller and Steiner (W3,W4) used some ingenious transformations and were able to obtain an analytical solution to the three equations as follows:

$$\frac{(1-\theta^*)(1-x)}{(1-x_f)} = \left(\frac{u_f - E/D}{u - E/D}\right)^R \left(\frac{u_f - \alpha^* + F}{u - \alpha^* + F}\right)^S \left(\frac{u_f - F}{u - F}\right)^T$$

Where

$$\theta^* = 1 - \frac{L}{L_f}$$

$$i = \frac{x}{1-x}$$

$$u = -Di + (D^2 i^2 + 2Ei + F^2)^{0.5}$$

$$D = 0.5\left[\frac{(1-\alpha^*)p_l}{p_h} + \alpha^*\right]$$

$$E = \frac{\alpha^*}{2} - DF$$

$$F = -0.5\left[\frac{(1-\alpha^*)p_l}{p_h} - 1\right]$$

$$R = \frac{1}{2D-1}$$

$$S = \frac{\alpha^*(D-1)+F}{(2D-1)(\alpha^*/2-F)}$$

$$T = \frac{1}{1-D-E/F}$$

The term u_f is the value of u at $i = i_f = x_f / (1-x_f)$. The value of θ^* is the fraction permeated up to the value of x in (*). At the outlet where $x = x_o$, the value of θ^* is equal to θ, the total fraction permeated. The composition of the exit permeate stream is y_p and is calculated from the overall material balance.

The total membrane area was obtained by Weller and Steiner (W3,W4) using some additional transformations above to give:

$$A_m = \frac{tL_f}{p_h P'_B} \int_{i_o}^{i_f} \frac{(1-\theta^*)(1-x)di}{(f_i - i)\left[\frac{1}{1+i} - \frac{p_l}{p_h}\left(\frac{1}{1+f_i}\right)\right]}$$

Where $f_i = (Di - F) + (D^2 i^2 + 2Ei + F^2)^{0.5}$

Values of θ^* can be obtained from the equation above. The integral can be calculated numerically. The term i_f is the value of I at the feed x_f and i_o is the value of i at the outlet x_o. A shortcut approximation of the area without using a numerical integration, available from Weller and Steiner (W3), has a maximum error of about 20%.

2.1.4 Membrane Flow Scheme [3]

A single stage unit is the simplest application of membrane technology for CO2 removal from natural gas. As shown in Figure 10, a feed stream, which has been pretreated, enters the membrane module, preferably at high system pressure and high partial pressure of CO2. High- pressure residue is delivered for further processing or to the sales gas pipeline. Low-pressure permeate is vented, incinerated, or put to use as a low-to-medium BTU fuel gas. There are no moving parts, so the system works with minimal attention from an operator. As long as the feed stream is free of contaminants, the elements should easily last five years or more, making the system extremely reliable and inexpensive to operate.

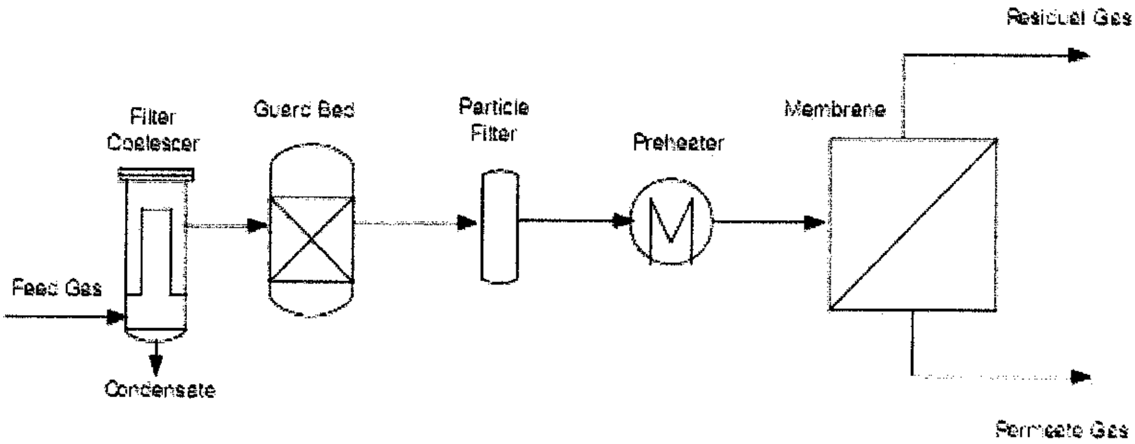


Figure 6: Single-stage Flow Scheme

No membrane acts as a perfect separator, however. Some of the slower gases will permeate the membrane, resulting in hydrocarbon loss. This is the principle drawback to single-stage membrane systems. In order to recover hydrocarbons that would otherwise be lost in the permeate stream, a two-stage system can be employed (Figure).

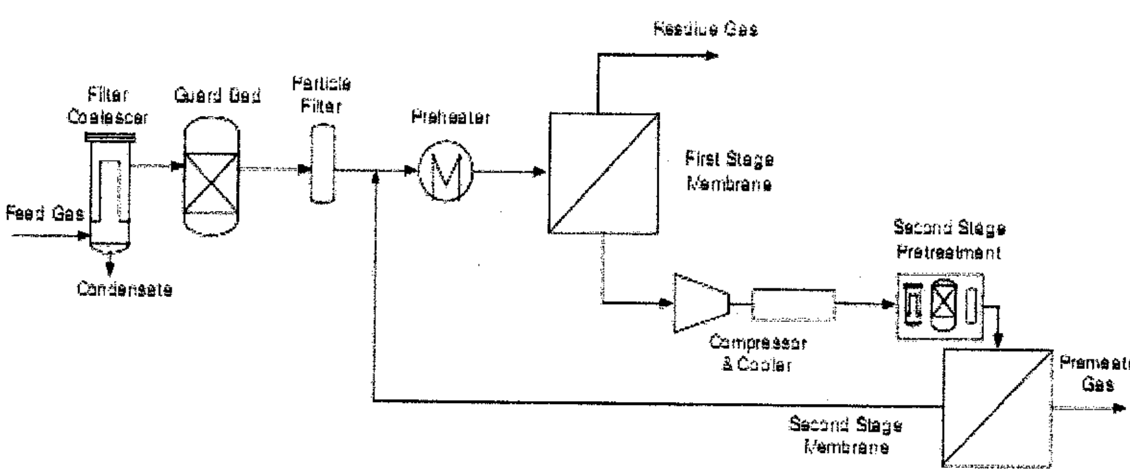


Figure 7: Two Stage Flow Scheme

The permeate from the first stage, which may be moderately rich in hydrocarbons, is compressed, cooled and sent to a second stage of pretreatment to remove entrained lube oil and provide temperature control. A second stage membrane is then used to remove CO2 from the stream prior to recycling the residue gas to the first stage membrane.

2.2 Joule Thomson Effect through the Membrane (7)

Figure 8: Schematic representation of the principle of the Joule-Thomson Effect

Joule-Thomson effect is known as a special phenomenon in gas separation. This occurs if a gas is expanded across a membrane, as in the case of a gas permeation process. In the case of such an adiabatic expansion of a real gas, the temperature may change to a large extent dependent on the type of gas and the pressure applied (for ideal gases the temperature does not change). In turn, this temperature change may have a large influence on the permeation properties, i.e., if the temperature decreases generally the flux decreases and the selectivity increases. The principle will be demonstrated by a simple experiment as shown schematically in figure:

A gas passes a membrane from the high pressure side (subscript 1) to the low pressure side (subscript 2). This process is assumed to occur adiabatically, i.e. the whole system has been isolated and no heat transfer occurs (q=0). The internal energy change of this process is equal to:

$$\Delta U = U_2 - U_1 = -P_2V_2 + P_1V_1$$

$$\rightarrow U_1 + P_1V_1 = U_2 + P_2V_2$$

$$\rightarrow H_1 = H_2$$

This implies that this process occur isenthalpic. The temperature change in this process is expressed by the differential equation ($\left(\partial T / \partial P\right)_H$ which is called the Joule-Thomson coefficient μ_{JT}. If the enthalpy of a gas H is considered to be dependent on T and P then the total differential of H is given by

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

Furthermore, $\left(\frac{\partial H}{\partial T}\right)_P = c_p$ (1)

And $\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T$ (2)

For the enthalpy change of a reversible process we can write

$$dH = V\,dP + T\,dS$$

Differentiation with respect to P at constant temperature gives

$$\left(\frac{\partial H}{\partial P}\right)_T = V + T\left(\frac{\partial S}{\partial P}\right)_T \quad (3)$$

From the Maxwell's relations we have:

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad (4)$$

From (1), (2), (3), (4) we have:

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu_{JT} = -\frac{1}{c_P}\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]$$

Depending on the relative magnitude of the two terms between brackets the gas is either cooled or warmed upon pressurizing. Some values of Joule Thomson coefficient of various gases are given in table below.

Table 1: Joule Thomson coefficient of various gases at 1bar and 298K

gas	μ_{JT} (K/bar)
He	-0.06
CO	0.01
H_2	0.03
O_2	0.30
N_2	0.25
CH_4	0.70
CO_2	1.10

It can be seen clearly that temperature decrease in gas separation depends on the type of gas. Hydrogen will give a small temperature difference only but carbon dioxide may give a tremendous temperature decrease at high applied pressure. It is clear that in the latter case, the separation performance is affected as well and that the Joule-Thomson effect should be taken into account when carbon dioxide is removed at a high pressure.

2.3 Create an Extension in Visual Basic 6.0 [4]

2.3.1 Create the Extension Definition File (EDF):

The EDF can be created from View Editor in HYSYS:

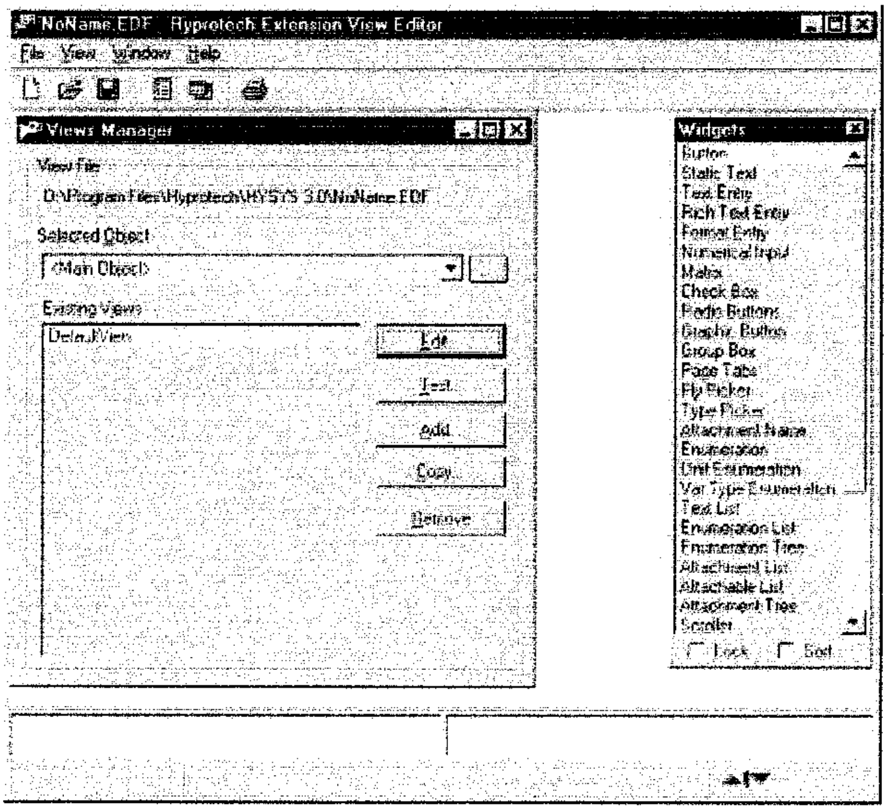


Figure 9: View Editor in HYSYS

The EDF contains important information about an extension that is required by the extension's container in HYSYS. Specifically, it contains information about the variables that the extension own (that are managed by the container), and it may also contain one or more property views for the object.

For each extension, CLSID or a ProgID must be provided. Other information that can be provided at this point includes: the extension description, from which the engineer identifies the extension within HYSYS, the extension type and the number of property views.

Once the preliminary definition information is provided, the engineer specifies the variables that the object owns and that are visible to the user. These variables are of the following types:

- Numeric: These variables represent numerical quantities and have a Variable Type that allows HYSYS to manage Unit Conversions for the user and might have zero, one or two dimensions. They can also trigger the steady state solver when they are changed. If this is the case, the variable operates like other HYSYS variables in that the solver performs consistency checking when values are changed.

- Text: These variables represent a string and might be zero or one dimensional.

- Message: These variables are usually associated with buttons in a property view. Messages are sent through the VariableChanged method of an extension.

Numeric Variables and Text Variables may or may not be persistent. If they are, their values are stored when the Simulation Case containing the extension is saved.

2.3.2 Create the Object Property View

A property view for the extension is not necessary, but quite often if the engineer wants the user to be able to interact with the object. The View Editor can be used to create property views for the object.

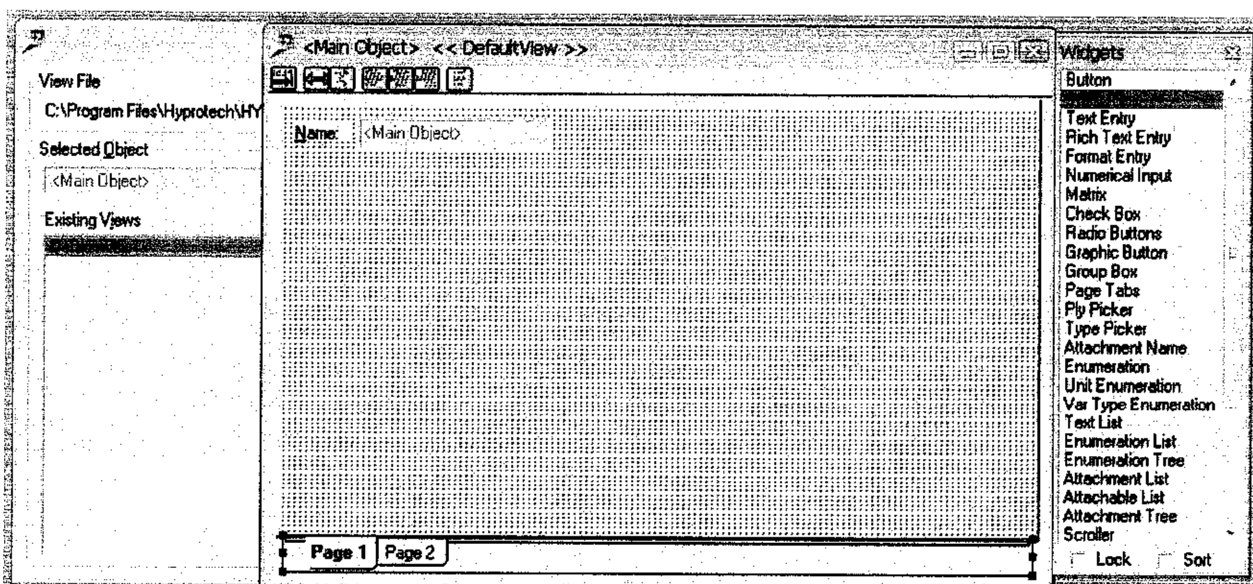


Figure 10: Object Property View

Views are created by adding the widgets to the DefaultView form. Select a widget with the secondary mouse button, drag it onto the DefaultView form, and drop it. The engineer can then position the widget to his liking. Double-click the widget to access its Properties property view, from which the engineer can specify detailed information for the widget. If necessary, the engineer can associate a variable with the widget.

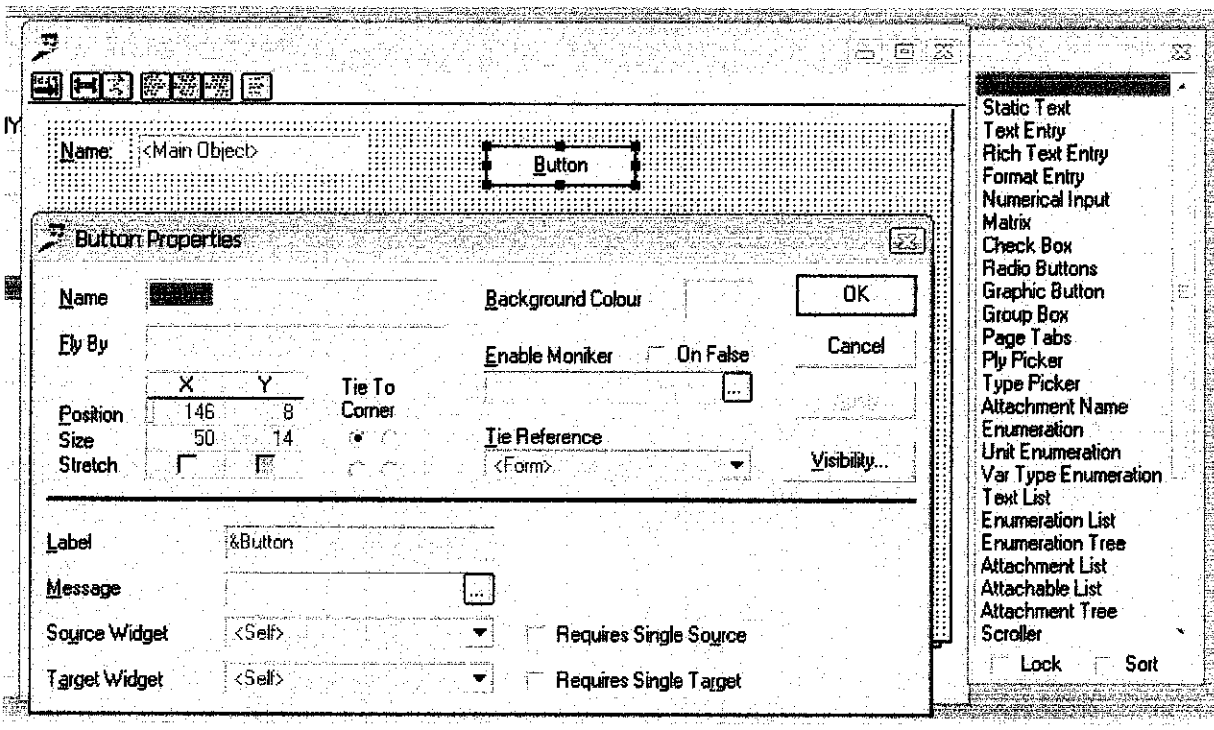


Figure 11: Button Properties

Each DefaultView must have a unique name. The object's default property view must be called DefaultView as it is the property view HYSYS attempts to open when the object is instantiated, provided the functionality of the OnView method is not overridden.

2.3.3 Implement the Required Methods

To implement an extension in VB.NET, the engineer must first create a Class Library project. In the project, the engineer must then add a reference to the HYSYS Interoperability Library (Aspentech.HYSYS.Interop.dll) which can be found in the root directory of the install location for Aspen HYSYS 2006.

Next, the engineer must create a class that implements the required interfaces. For example, an Extension Unit Operation must implement the ExtensionObject interface and the ExtensionUnitOperation interface.

The class should have the appropriate attributes from the System.Runtime.InteropServices namespace required to export a class to COM. These include but are not limited to ComVisible, ClassInterface, GuidAttribute, and ProgIdAttribute. ComVisible must be set to true; Class Interface is recommend to be set to AutoDispatch which is the default; GuidAttribute represents the CLSID and will be generated if not specified (its highly recommend that the engineer specify this manually); ProgIDAttribute is optional unless the engineer refer to this class using the ProgID in the Extension Definition.

2.3.4 Register the Extension

The engineer can register extensions on the Extensions tab of the Session Preferences property view.

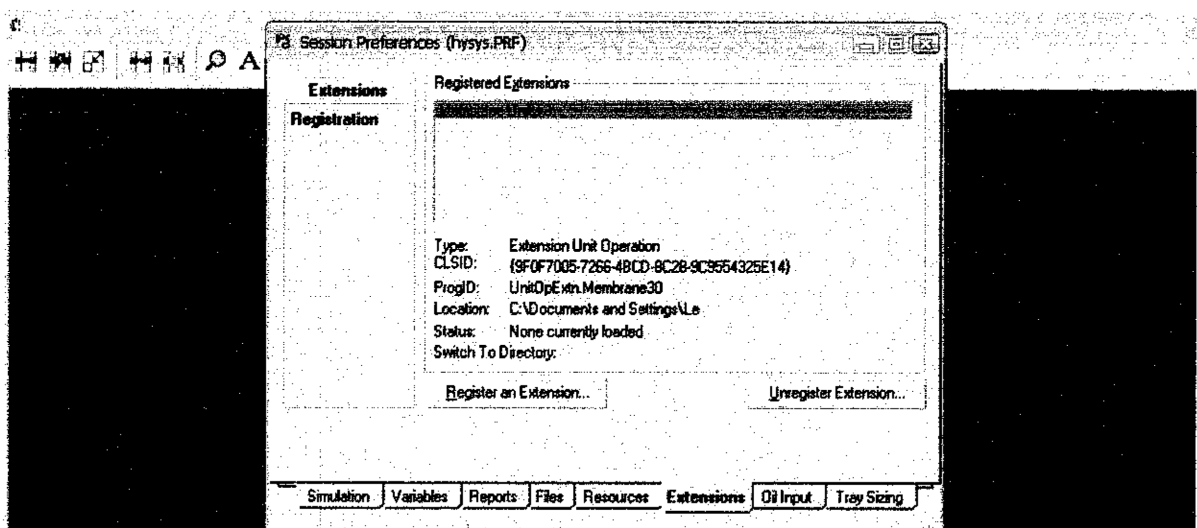


Figure 12: Register the Extension

2.3.5 Debug the Extension

To debug the extension, the engineer can set breakpoints on just about any line the class. Initially, the engineer should probably set a breakpoint on the Initialize method. Then set HYSYS.exe as the external program in the Project Properties Debug page.

The engineer can debug the extension in Microsoft Visual Studio 2003 or 2005 by setting breakpoints in the code and by attaching to running copy of HYSYS from the Attach to Process dialog from the Tool menu. When attaching the extension to running HYSYS case, ensure that the engineer selects the managed code debug option and not native code debug option. The engineer can also start HYSYS from Microsoft Visual

Studio by specifying the path of the HYSYS executable file in the Start external program field on the Debug tab of the Project Settings property view.
The engineer can load the extension by starting HYSYS and creating an instance of the extension. HYSYS creates a container, and this container then calls the Initialize method of that extension. The engineer can also use the System.Diagnostic.Debug.Print method in .NET to print information to the Output Debug view while the extension runs.

2.3.6 Distribute the Extension

Once the engineer is confident that the extension is behaving properly, the engineer can create an ActiveX DLL file. DLL stands for Dynamic-link library.
The end result of this step is an extension that the engineer can distribute without exposing any proprietary information or methods.
Finally, to distribute the extension, the engineer must provide the DLL file, the EDF file and any other files required by the extension. The engineer must register the extension on each individual machine that uses the extension calculations.

CHAPTER 3: METHODOLOGY

Literature review

(Books, journals, articles etc.)

Research

Problem

Identification

Selection and derivation of the correct equations that can be used for Membrane

- Assumption should be known
- What are the temperature and pressure – range for these equations
- Find the properties changes through the membrane.

Create the Extension Definition File (EDF) using View Editor in HYSYS

- Understand on how to create the property view of the membrane simulation in HYSYS

Create the Dynamic Linked Library (DLL), CLS (Class) and VBP (Visual Basic Project) files using Visual Basic 6.0

- These files contain the derived analytic equations for the property changes through the membrane
- Link with the EDF variables.

Final stage: Study on different membrane configuration

- Different membrane can be two membranes in series or recycle of permeate stream or hybrid system which includes the membrane and amine.

CHAPTER 4: RESULT AND DISCUSSION

4.1 RESULT

4.1.1 Find analytical equation for temperature change through the Membrane [5]

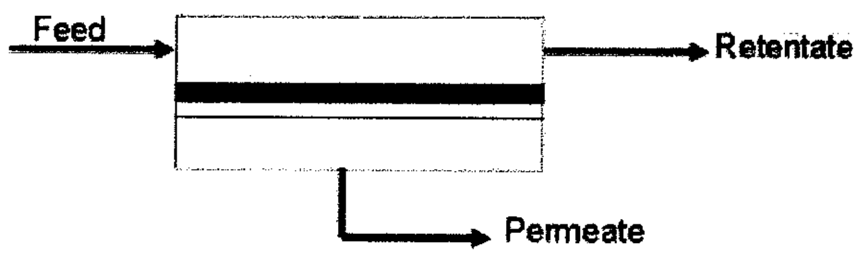


Figure 13: Membrane

An analytical equation has been found to calculate the permeate temperature based on the Joule Thomson coefficient.

$$T_2 = T_1 - \mu_{JT}\Delta P \quad (5)$$

Where: T_1: *Feed Temperature*

T_2: *Permeate Temperature*

μ_{JT} : *Joule- Thomson coefficient*

ΔP : *Pressure Loss through the Membrane*

The derived formula for Joule-Thomson coefficient:

$$\mu_{JT} = \frac{RT^2}{\rho C_{m,p}}\left(\frac{\partial Z}{\partial T}\right)_P \quad (6)$$

Molar heat capacity at constant P: $C_{m,p}$

$$C_{m,p} = \frac{C_P}{M} = \frac{C_{PI} - RT(T\phi'' + 2\phi')}{M} \quad (7)$$

Where: *C_{PI}: Ideal heat molar capacity*

ϕ', ϕ'': First and second derivatives of the gas fugacity coefficient

The first derivative of the compression factor with respect to temperature is:

$$Z' = \frac{R(TZ)^2 \sum_{n=13}^{58} C_n^{*'} D_n^* + pZ(TZ_0' - Z_1)}{R(TZ)^2 + pTZ_1} \quad (8)$$

Where:

$$Z = 1 + B\rho_m - \rho_r \sum_{n=13}^{18} C_n^* + \sum_{n=13}^{58} C_n^* D_n^* \quad (9)$$

$$Z_0 = B - K^3 \sum_{n=13}^{18} C_n^* \quad (10)$$

$$Z_0' = B' - K^3 \sum_{n=13}^{18} C_n^{*'} \quad (11)$$

$$Z_1 = Z_0 + \sum_{n=13}^{58} C_n^* D_{1n}. \quad (12)$$

ρ_m: Gas mixture molar density

ρ_r: Reduced density

B: Second virial coefficient

C_n^*: Temperature – Composition dependent coefficient

Therefore, the final analytical formula for Joule-Thomson coefficient is:

$$\mu_{JT} = \frac{RT^2}{\rho} \times \frac{M}{C_{PI} - RT(T\phi'' + 2\phi')} \times \left[\frac{R(TZ)^2 \sum_{n=13}^{58} C_n^* D_n^* + \rho Z(TZ_0' - Z_1)}{R(TZ)^2 + \rho T Z_1} \right] \quad (13)$$

From (5): Permeate temperature is: $T_2 = T_1 - \mu_{JT} \Delta P$

4.1.2 Procedure for Input – Output parameters in HYSYS

Input parameters—constant:

• Molar gas constant (R = 8314.51 J/(kmol K))

• Natural gas equation of state parameters (a_n, b_n , c_n , k_n, u_n, g_n , q_n , f_n, s_n, w_n; n = 1, 2, ..., 58)

Input parameters—time varying:

• Absolute pressure: p [MPa]

• Absolute temperature: T [K]

• Molar fractions of the natural gas mixture: yi ; i = 1, 2,..., N

Calculation sequence:

1. Molar mass of a gas mixture M

2. Mixture size parameter K, second virial coefficient B, and temperature dependent coefficient C_n^*

3. Compression factor Z (Eq. (9))

4. Molar density ρ_m and reduced density ρ_r

5. Coefficients D_n^*

6. Specific volume v

7. 1st and 2nd derivative of the second virial coefficient B

8. 1st and 2nd derivative of the coefficient C_n^*

9. 1st derivative of the comparison factor Z (Eqn(8))

10. 1st and 2nd derivative of the fugacity Φ'and Φ''

11. Ideal molar heat capacity of a gas mixture: c_{pI}

12. Joule-Thomson coefficient μ_{JT} (Eq. (13))

4.1.3 Create the Extension Definition File using View Editor in HYSYS

- Create the Object:

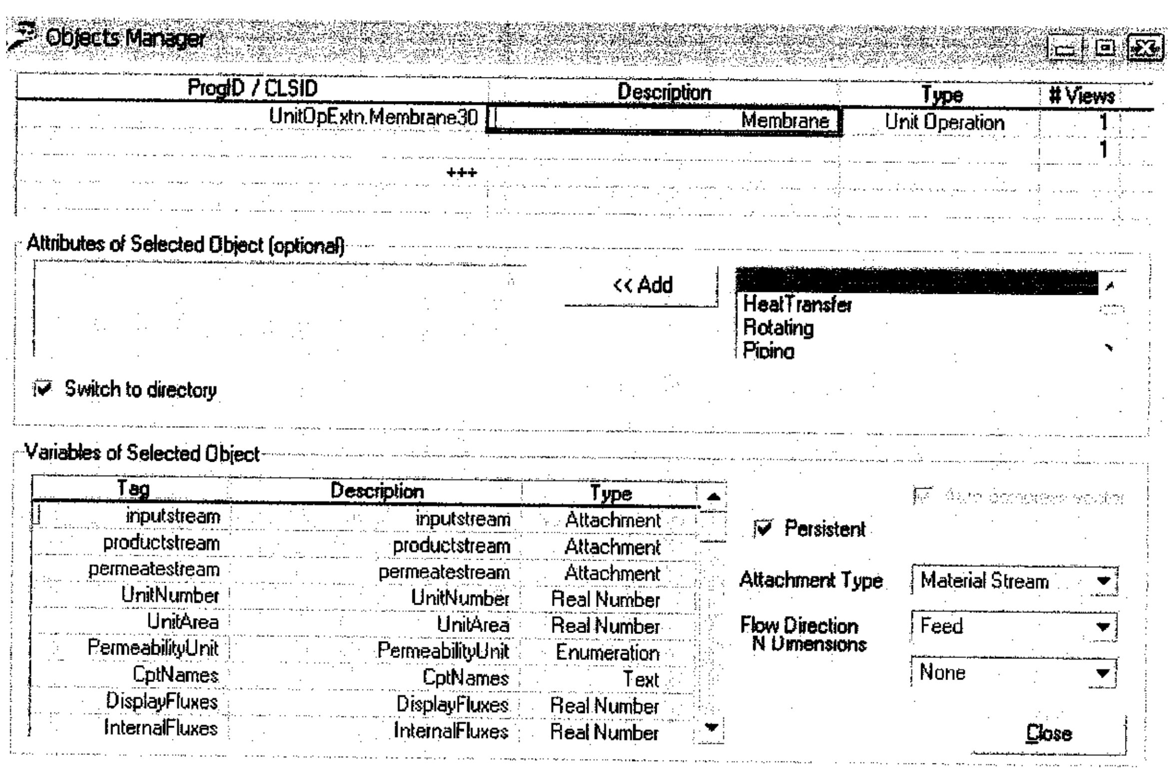


Figure 14: Object Manager

The object is named as membrane with the ProgID/CLSID is UnitOpExtn.Membrane30 and Unit Operation Type with many variables that are related to the input, product and permeate streams.

- Create the EDF:

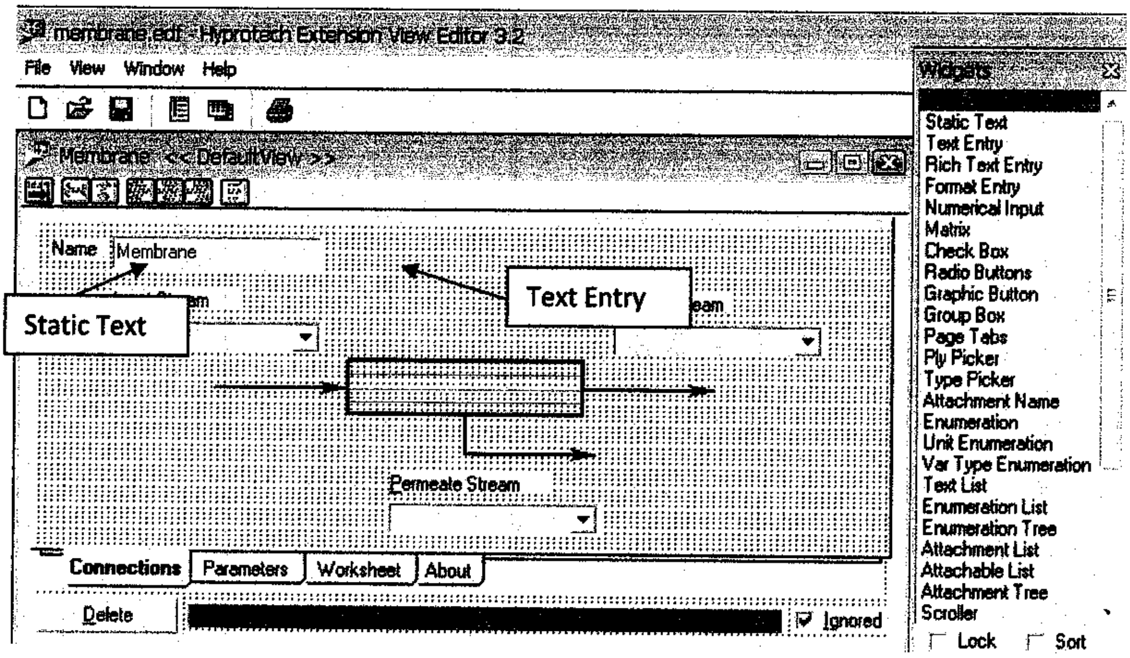


Figure 15: Created Extension Definition File

This above picture illustrates the Extension Definition File for the Membrane that the author has successfully created.

In order to create the EDF, firstly the author needs to add the widgets to the Default View which includes the Static Text, Text Entry, Attachment Name, Check Box, Button, Matrix, and Page Tabs. The EDF contains of 3 streams which are Input Stream, Output Stream and Permeate Stream with the Form Background as picture.

The attachment name properties for three streams will look like this:

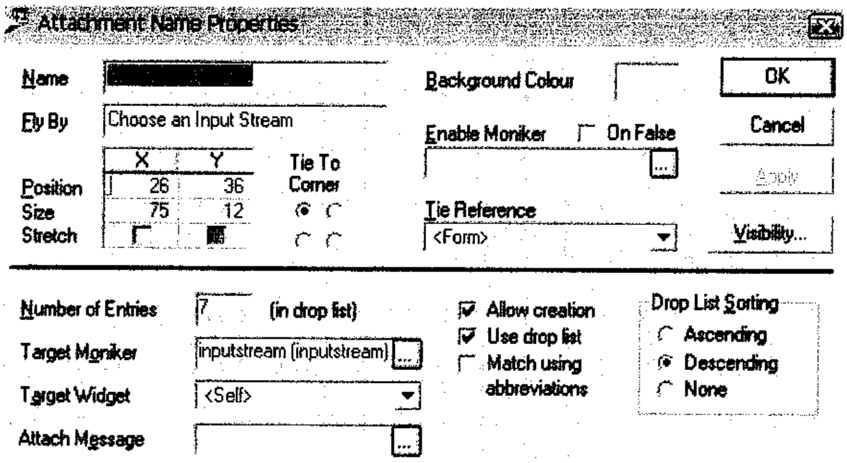


Figure 16: Attachment Name Properties

There are four main tabs of the default view in the membrane which are Connection, Parameters, Worksheet and About.

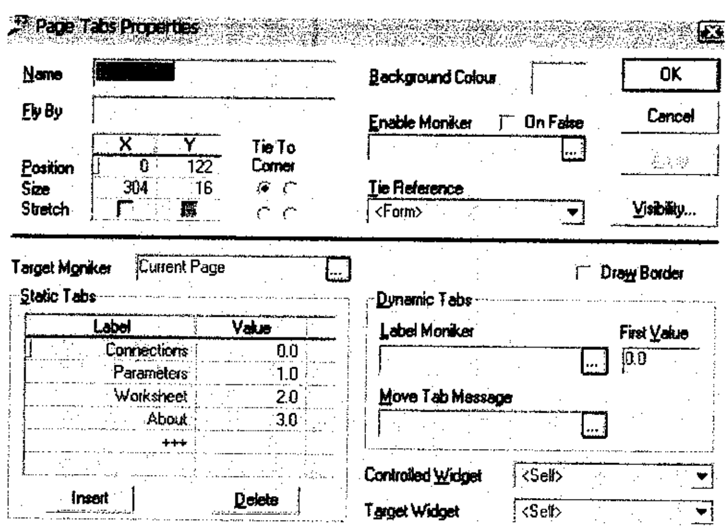


Figure 17: Page Tabs Properties

4.1.4 Create the Visual Basic Files

The function of the Visual Basic Files is to put the derived analytical equations for the property changes and link with the variables in the Extension Definition File in HYSYS. First, the author put the code in the Visual Basic Project file.

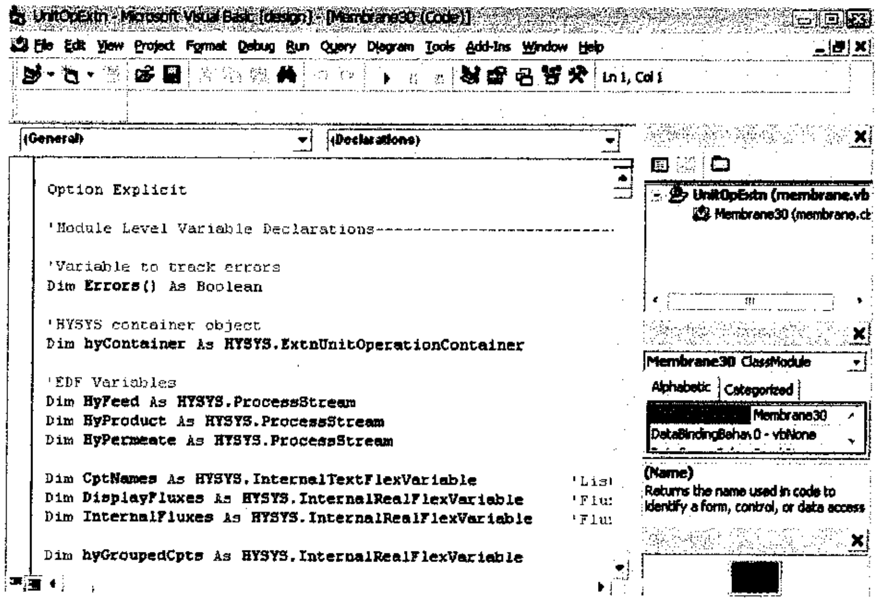


Figure 18: Example of Code

After completing, the author made the Dynamic Linked Library (DLL) file from the VBP file so that it can be used in the HYSYS. This DLL file is for the HYSYS to register the Extension Unit Operation in the next step.

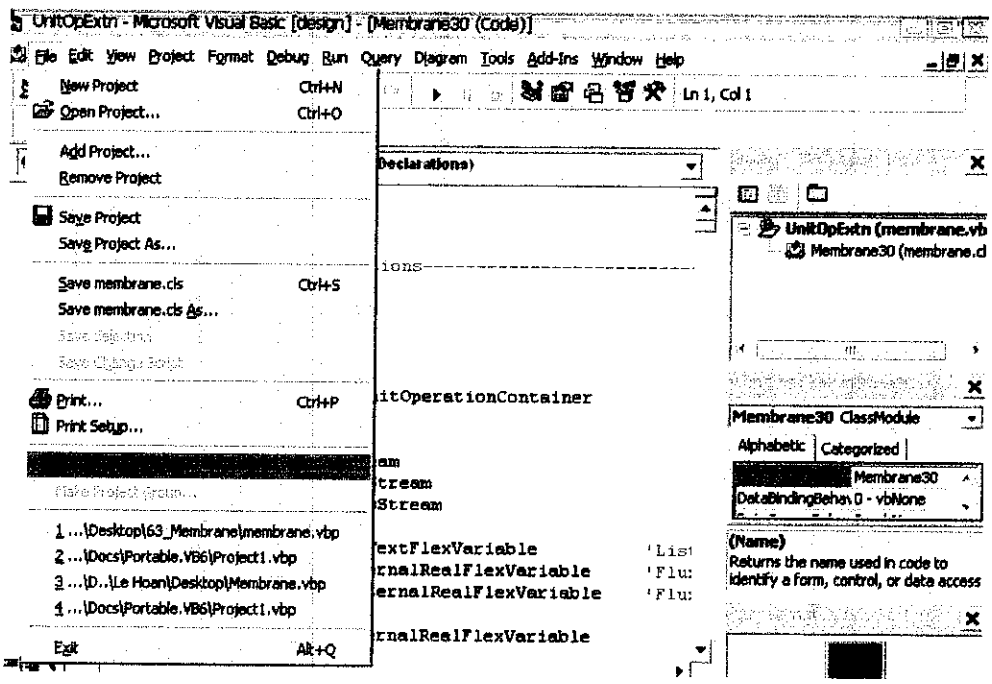


Figure 19: Make Membrane DLL file

4.1.5. Register and Distribute the Extension in HYSYS

Registeration of the Membrane Extension in HYSYS:

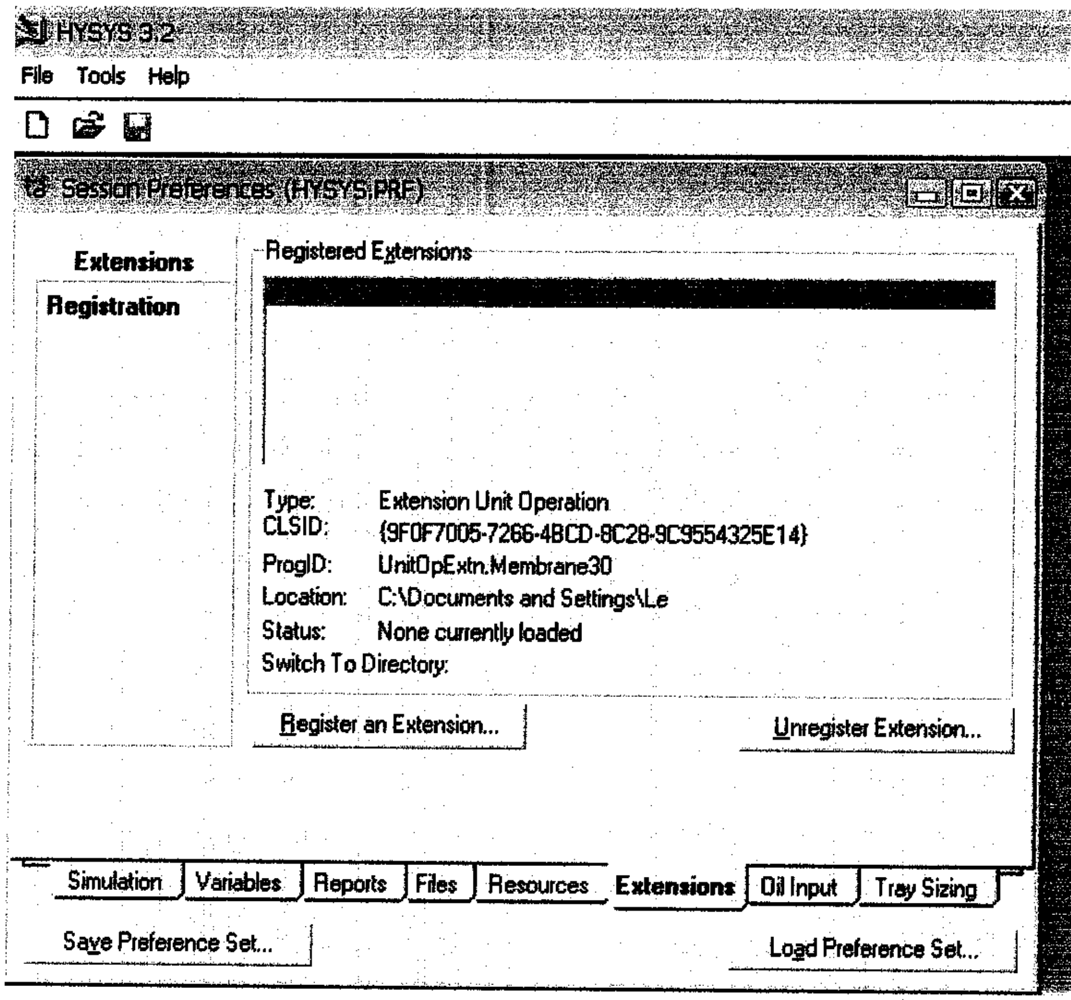


Figure 20: Registeration of the Membrane Extension

After registering the Extension (Membrane) in HYSYS, the property view of the simulation is like below:

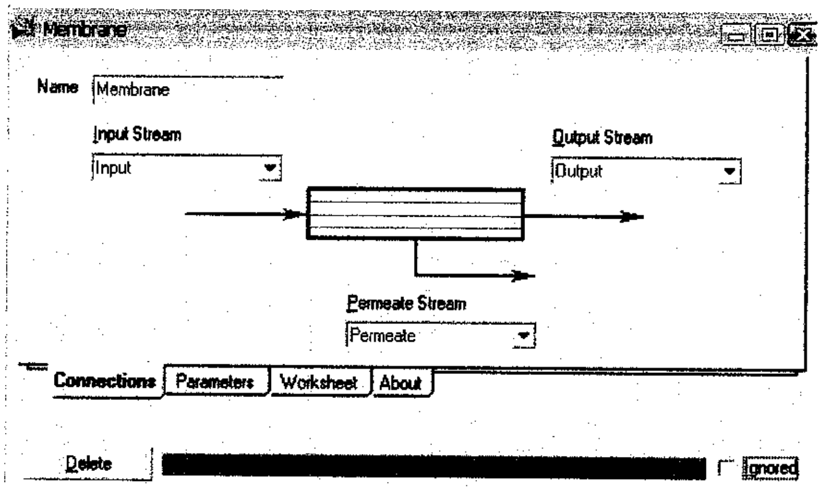


Figure 21: Property View in HYSYS

The Process Flow Diagram:

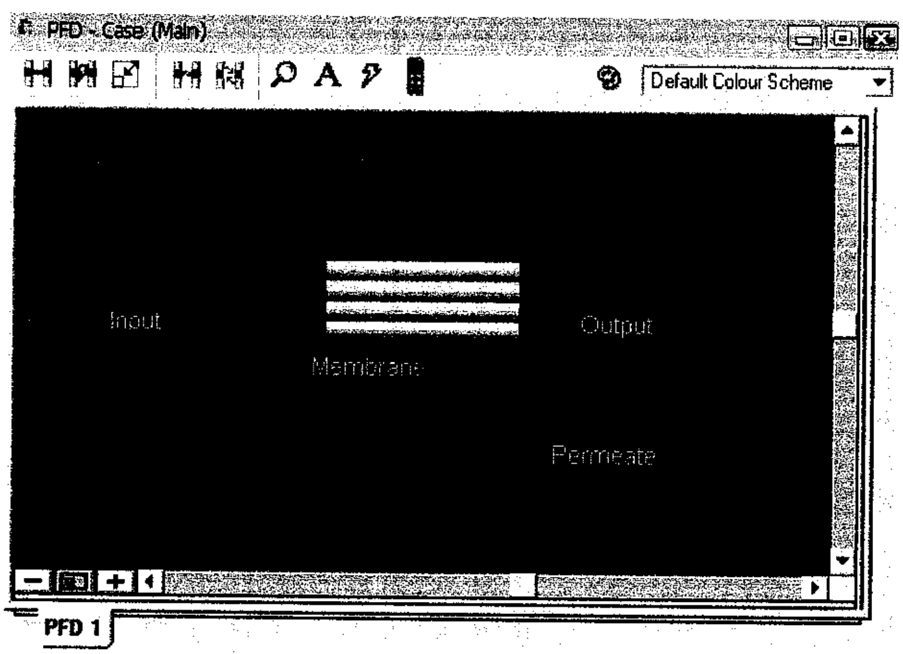


Figure 22: PFD in HYSYS

Testing Result:

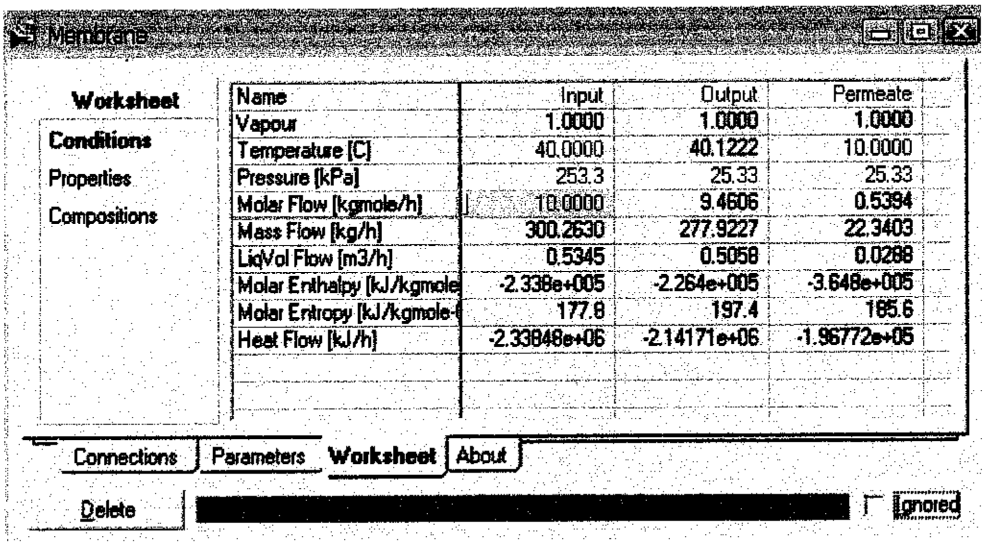


Figure 23: Conditions

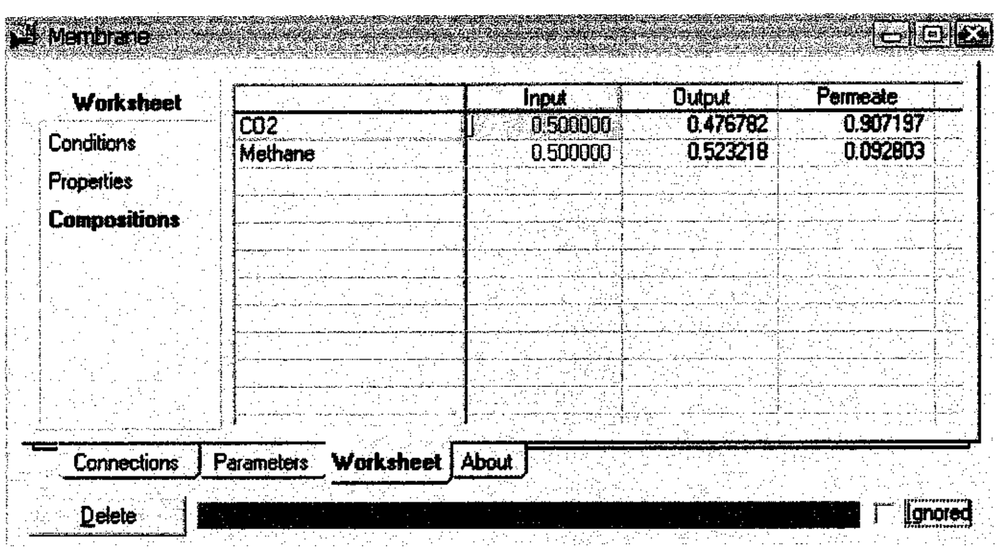


Figure 24: Compositions

4.1.6 Validation for the calculation of flow rate and composition

Validation is a critical part to see whether the membrane simulation is working properly or not. In order to do that, the author has taken the 10 sample experiment datum from literature and compares the measurements with the estimates from the HYSYS. Below here is the table for the comparison.

Table 2: Comparison

Data set	Measurements from Experiments						Estimates from HYSYS	
	L_f (m^3/s)	P (MPa)	x_f	γ_o	θ_o	y_p	θ_o	y_p
1	0.0331	3.7557	0.0523	0.0272	0.3762	0.1318	0.3738	0.1308
2	0.0318	2.3767	0.0528	0.0429	0.2887	0.1564	0.2546	0.1628
3	0.0331	3.8427	0.1161	0.0267	0.4059	0.2676	0.4412	0.2701
4	0.0466	3.2041	0.1213	0.0318	0.3310	0.3345	0.2961	0.3350
5	0.0695	4.8589	0.1234	0.0210	0.3538	0.3319	0.3090	0.3605
6	0.0692	3.9626	0.1241	0.0258	0.2796	0.3732	0.2926	0.3932
7	0.0370	3.2386	0.1272	0.0315	0.3628	0.3212	0.3621	0.3245
8	0.0774	4.8589	0.1298	0.0210	0.3051	0.3766	0.3018	0.3931
9	0.0672	3.8936	0.1339	0.0262	0.2537	0.4081	0.2728	0.4124
10	0.0367	3.8936	0.2134	0.0262	0.5000	0.4115	0.5045	0.4155

Where:

L_f: Feed gas flowrate

γ_o: Ratio of permeate pressure to feed pressure

x_f: Mole fraction of CO_2 in the feed stream

y_p: Mole fraction of CO_2 in the outlet stream

θ_o: Ratio of permeate flow to feed flow

The data consists of CO_2/CH_4 which is generated from the original multi-components (N_2 and hydrocarbons) as the slower permeating component (CH4). The predictions are less accurate than those obtained from the simulation data. This is expected since the experimental system has complications that are not present in simulation:

- The separation is multi-component
- There are differences in operating conditions that are not completely reflected in the experimental data sets (e.g., temperature variations)
- The approximate model does not account for non-ideal effects such as concentration polarization, flow channeling, CO2 plasticization.

4.1.7 Call Visual Basic Function from Matlab

In order to solve the complex differential equations in HYSYS, the author must need the help from Matlab function. Therefore, a solution to link the Matlab with Visual Basic.Net needs to be figured out. First, a new Class Library must be created in the Visual Basic.Net

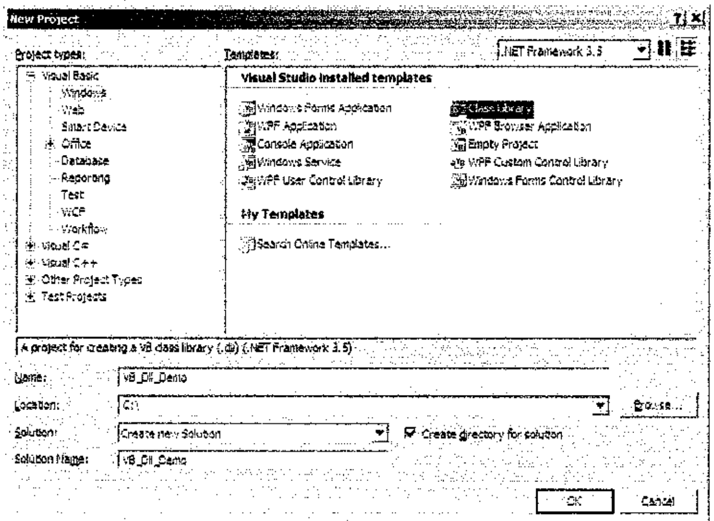


Figure 25: Class Library

In the public function, for this demo, the author is adding two numbers together:

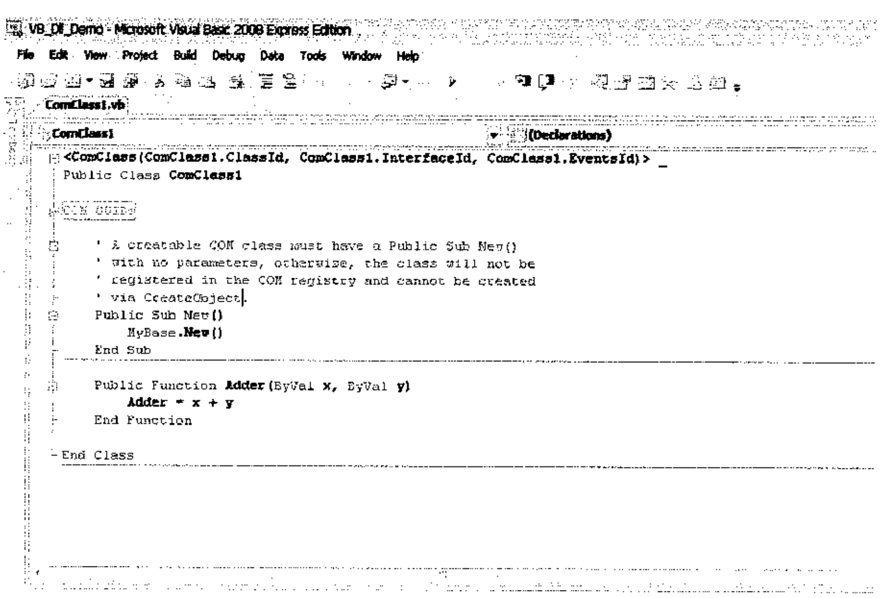


Figure 26: Function in Visual Basic.Net

After this, the author creates an M-file from Matlab that can execute the function Adder in the Visual Basic.Net

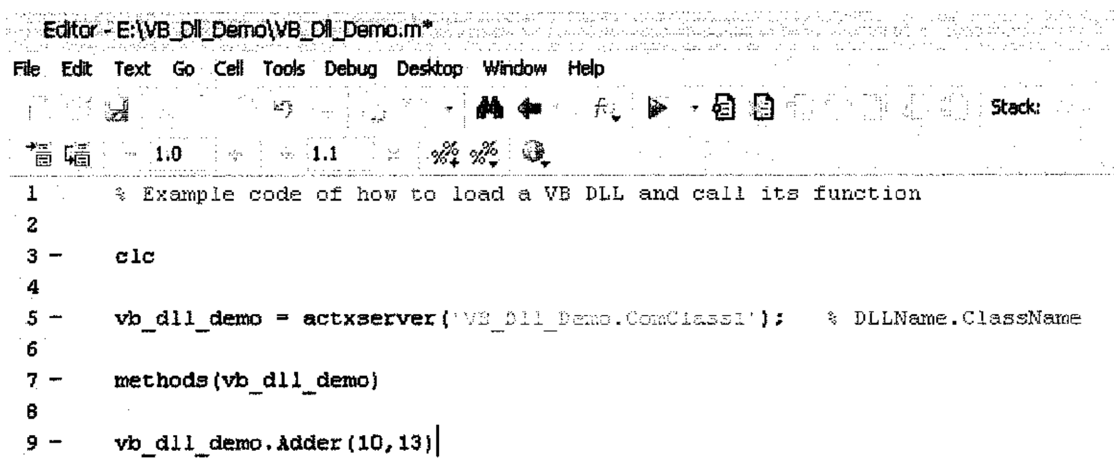


Figure 27: M-file

4.2 DISCUSSION

The procedure for calculating the temperature change through the Membrane is quite complicated when programming in HYSYS since the author needs to key in a lot of input parameters and calculations. There is still a simple solution for temperature effect which does not base on the Joule-Thomson coefficient as well as the compressibility factor. However, the result from this solution is not as accurate as the solution above.

The author still needs to do more validation to see whether the simulation gives the correct result of every variable or not. In order to do that, a lot of experiments must be done soon. For the pressure loss calculation, the author has to solve the differential equation which could not be done by using Visual Basic but Matlab program. For doing that, the author has to create the m-file which contains the differential equation solution and link the file with Visual Basic. Net or C# program. If this most difficult work can be done in the near future, the author can proceed with the membrane simulation in HYSYS.

Since the Visual Basic.Net can be linked with Matlab (as described above), the only left problem is how to program in Visual Basic.Net which relate to the Extension Unit Operation in HYSYS. It takes time to learn how to program in the new software. Therefore, the author has not completed this part yet.

CHAPTER 5: CONCLUSION AND WAY FORWARD

Last semester, the author only concentrated on the temperature effect cross the membrane by using the Joule-Thomson coefficient and how to put it in the User Unit Operation in HYSYS. However, in order to determine the temperature effect, the author needs to find the pressure loss through the membrane for cross flow model. In other words, an analytical equation for pressure loss calculation is needed to put in HYSYS. It will lead to the relationship between the active membrane area which is provided by the supplier and the permeate pressure.

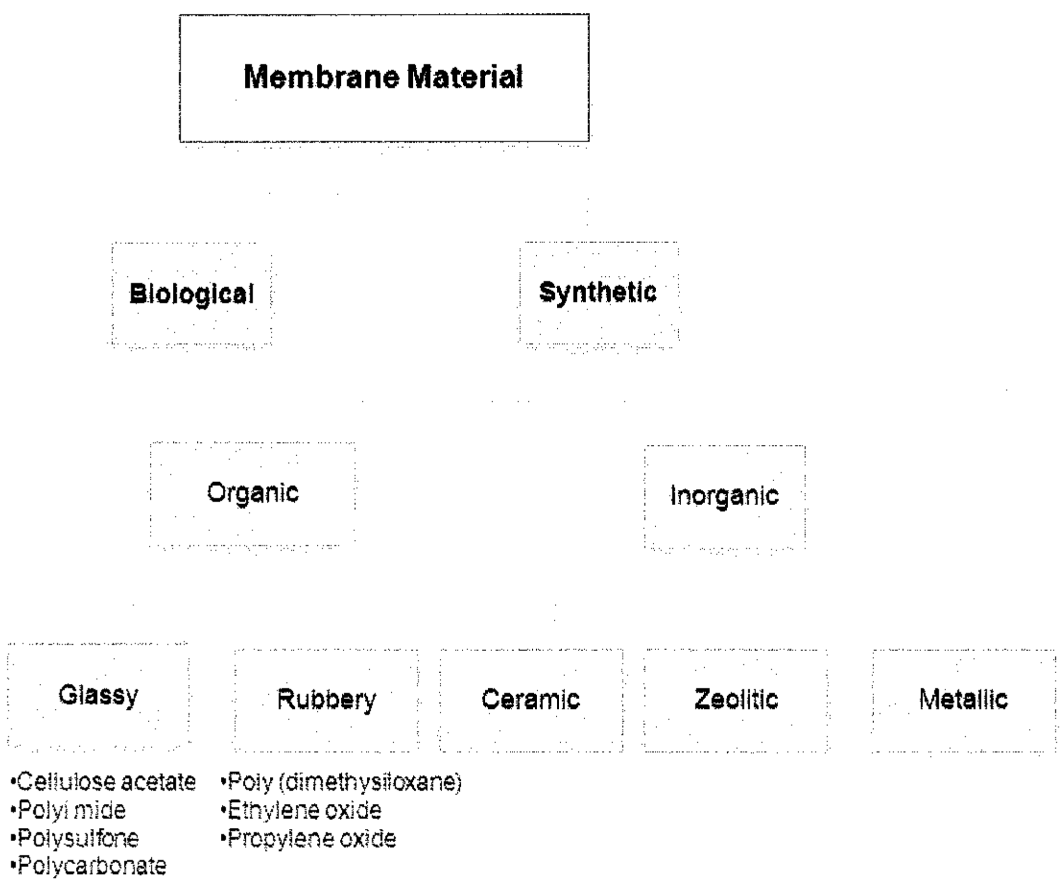
Basically, the membrane simulation is built successfully without the pressure loss calculation. This is the main concern at the moment. The author is able to link the Matlab file with Visual Basic.Net and C# program. In other words, the VB.Net (or C#) files can be executed in the Matlab. Therefore, learning programming in Visual Basic. Net or C# to link with the EDF variables and others is critical in order to complete the membrane simulation for cross flow model.

After getting all the needed equations, the author will put it in the Extension Unit Operation in HYSYS to see the effect of the membrane simulation. The membrane simulation will help the engineers to predict the properties of the outlet stream if using two membranes in series or hybrid system (membrane + amine) so that it can be applied in the real industry.

In conclusion, this project is a good starting point to develop a well-catered membrane simulation in the near future. Since everything can be put in the code, it is very flexible to use. When a useful membrane simulation is built successfully in the future, PETRONAS will save the time, money while dealing with membrane performance.

APPENDICES

Appendix A: Membrane Material



Appendix B: Summary of Selection Factors

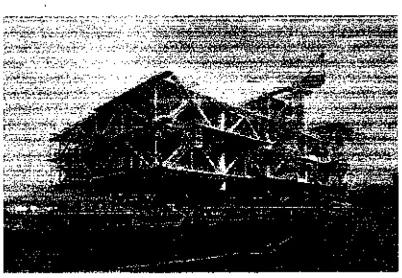
5=Best	Chemical Solvents	Physical Solvents	Adsorption	Cryogenic Distillation	Membranes
CAPEX	3	2	3	1	**5**
OPEX	2	2	2	2	**5**
Operating Flexibility	4	3	2	3	**4**
Reliability	4	3	3	5	**5**
Expandability	2	2	2	2	**5**
Environment Friendly	1	2	4	4	**5**
Weight	3	2	2	3	**5**
Footprint	3	2	2	2	**5**
CO_2 Removal Efficiency	4	3	3	4	**4**
CO_2 Purity	5	4	3	5	**4**
Averages	**3.1**	**2.5**	**2.6**	**3.1**	**4.7**

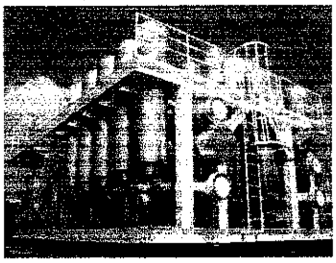
APPENDIX C: LIST OF IMPORTANT DAYS

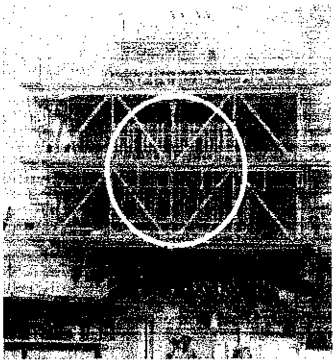
- Submission of progress report 1	26/08/2010
- Submission of progress report 2	15/10/2010
- Poster presentation and Seminar – preEDX	11-12/10/2010
- EDX	25-26/10/2010
- Final report (soft)	08/11/2010
- Final presentation	29/11/2010 – 10/12/2010
- Final report (hard)	17/12/2010

APPENDIX D: CHALLENGES FOR CO2 REMOVAL

- *Limitation of weight and space*
- *Reduction in capital investment and maintenance cost*
- *Low requirement of manning*
- *Reduction in energy consumption*
- *Uncertainty in CO_2 percentage (to establish operating boundary)*







APPENDIX E: PROJECTS UNDERTAKEN USING MEMBRANE SYSTEM FOR CO2 REMOVAL BY PETRONAS