Economic Potential of Carbon Dioxide Capture by Hydrate Formation
and
Comparison of Energy Consumption of CO_2 Capture Methods

By

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

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FINAL YEAR PROJECT II

DISSERTATION REPORT

UNIVERSITI TEKNOLOGI PETRONAS
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CERTIFICATION OF APPROVAL

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Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS
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SEPTEMBER 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, and the original work is produced on my own except as specified in the references and acknowledgement, and it has not been undertaken or done by unspecified sources or person.

Produced by,

MOHD AZFAR BIN MD JAAFAR

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ABSTRACT

This document is regarding on the works on the project of simulation of a hydrate reactor for the process of capturing CO_2 gas in a mixed gas stream containing CO_2 and methane. The objective of the project is to simulate the reactor in order to see the energy consumption of the process as an overall. Included in this project is the background, the scope of work, the objective, the methodology and the results of the overall project.

The project main results are to see the economic potential of the process based on levels stated by Douglas (1988) as well as to see the energy consumption of the overall process. The discussions and analysis of the project results are also included, as well as the conclusion and recommendations on further studies regarding the subject of hydrate technology.

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CHAPTER 1

PROJECT BACKGROUND

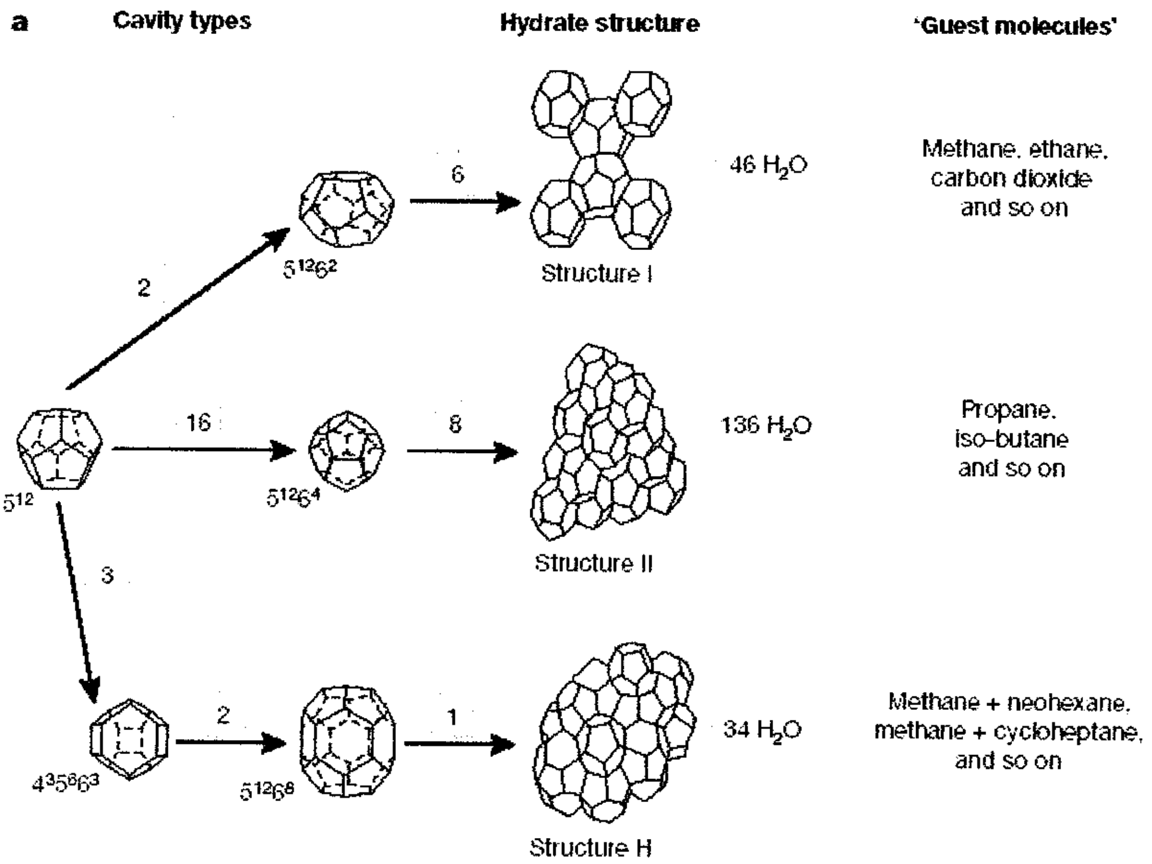
1.1. Background of Study

Hydrate compounds form when molecules, like water, crystallize and 'trap' another molecule as crystallization proceeds. The crystallized molecules are known as the main molecules while the trapped molecules are usually known as secondary molecules. It can also be viewed as a cage, since the main molecules actually form a cage around the secondary molecule. As mentioned earlier, the main molecules or host molecules are water molecules while the caged molecules or guest molecules are usually of non-polar gas or weakly polar gas origin. Since carbon dioxide (CO_2) is a quadra polar gas, CO_2 can also form hydrates with water.

As for the bonds, the main water molecules will form hydrogen bonds as crystallization occurs. The gas molecules trapped inside the crystals however form van der Waals bonds with the main molecules. Therefore, hydrates are not chemical compounds (no covalent bonds).

The crystals are made of lattice structures. Therefore, different types of lattice structures can be formed depending on the size of the secondary molecule.

For CO_2 hydrates, the structures are simple hydrates made of lattice structure of Type I (sI). Type I hydrates consist of 46 water molecules that made up the lattice structure of the crystal. This lattice structure has one large cavity and 2 smaller cavities, or empty spaces, in its structure. The large cavity has the tetradecaherdon ($5^{12}6^{2}$) shape while the small cavities have the pentagonal dodecahedron (5^{12}) shape (Sabil, Azmi, and Mukhtar, 2011). According to Sloan and Koh (2008), CO_2 hydrates with all its cavities filled will have 46 water molecules and 8 CO_2 molecules, or 5.75 water molecules for every molecule of CO_2.



b

Hydrate crystal structure	I		II		H		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Description	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Number of cavities per unit cell	2	6	16	8	3	2	1
Average cavity radius (Å)	3.95	4.33	3.91	4.73	3.91†	4.06†	5.71†
Coordination number*	20	24	20	28	20	20	36
Number of waters per unit cell	46		136		34		

*Number of oxygens at the periphery of each cavity.

†Estimates of structure H cavities from geometric models.

Figure 1-1 Lattice structures of Hydrates

Hydrate formation is especially undesirable in industry since it can cause pipeline clogging. Therefore, hydrates in processing plants, especially in natural gas processing plants, is not preferred. However, there have been studies suggesting that hydrate formation can be a potential new method of gas separation, especially where CO_2 separation is concerned. This report is to propose a feasibility study on whether this method is viable in industry.

1.2. Scope of Study and Problem Statement

1.2.1. Scope of Study

This project focuses on cost estimation per energy used for the separation of CO_2 from natural gases by hydrate formation and whether this method is comparable with using amines usually utilized in the natural gas processing industry. This is mainly because a lot of natural gas reservoirs nowadays contain high levels of CO_2 (20% and above), which lower the heating value of the natural gas and cause corrosion to equipments during processing. Therefore, CO_2 separation is highly important in natural gas processing. Current conventional method of using amine solution such as MDEA has proved to be efficient, but requires a lot of energy to operate especially during regeneration. Thus, a more feasible and cost effective method is being sought by researchers, like the use of membranes, ionic liquids, solid supports, mixed amine solutions and membrane-amine hybrid. Hydrate formation is also seen as one of the potential method of gas separation of the future.

Since there are no definitive technologies having established for this method of CO2 capture in the large scale, this project will attempt to create a simulation of the technology itself based on experimental data gathered from known sources. This is to acquire as much possible and accurate information as possible for this project.

1.2.2. Problem Statement and Identification

a) How much energy does CO_2 capture from natural gas by hydrate formation unit consume?

Energy is a very important resource, especially considering that more and energy source are becoming scarce. Therefore, there is a need to ensure that energy will utilized in the most efficient way. Not only that, what we want is to use the most minimal amount of energy for the work we require to do. CO_2 separation has always been one of the most energy consuming processes in any kind of industry. In natural gas purification, separating CO_2 is vital since this will determine the grade and eventually the price of the natural gas. Basically, more energy consumption leads to higher cost of separation, which then causes the price of natural gas to be high as to cater to the process cost. Researchers and engineers everywhere are currently trying to find other methods that are less costly. Capture of CO_2 by hydrates is one the many alternatives currently being considered by experts. Since hydrates utilize water as feed, this reduces costs. By right, with accordance to this knowledge, the economic potential should be positive, and therefore this process is a viable alternative for capturing CO_2. However, to fully see the overall cost of the process, it is important to determine the costing of the equipments, or capital cost and the operating cost. However, for this process, determining the equipment cost will be a challenge, as there are no definitive process train that are currently in use, and there are actual reactor design applicable in the industry. Therefore, it is better to rely on the operating cost since it is important overall when it comes to running a plant. The operating cost is usually associated with the energy usage in any processes. Having said that, energy consumption is a good indicator to determine the operating cost as energy and cost are always proportional to each other. Therefore, this work focuses on determining the energy consumption by simulating the process. This energy consumption is to be our yardstick in determining whether this process is viable to be utilized in the industry or not.

b) Is the method comparable to the methods of CO_2 capture conventionally used in the natural gas processing and LNG industries in terms of cost and energy?

The conventional method used in natural gas refineries are absorption by amine. Other methods include pressure swing adsorption, and the use of Benfield solutions. In some cases, even cryogenic separation is applied. This project aims at comparing the cost of CO_2 separation between hydrates and the conventional method practiced in the industry. This is merely to check whether hydrates are economically competitive should this method be implemented in large scale. Again, we are depending on the energy consumption as our baseline, as it is a more reliable method of comparing. This is because operating cost depends on the utilities cost which can differ with accordance to places and it will not be a reliable method of comparison.

1.2.3. Objective of the Proposed Project

- To estimate the energy consumption of a CO2 capture unit that utilizes the hydrate formation method via energy usage. To do an economic potential analysis on the process.

- To compare the cost of CO2 capture by hydrate formation with the conventionally used method of using amine solution. The basis of the comparison, however, would be by the energy consumed per kg CO_2 captured. This is because energy usage is proportional to the cost incurred

.

CHAPTER 2

LITERATURE REVIEW

Literature reviews regarding cost estimation for CO2 capture by hydrate in a CO2 – natural gas mixtures are very scarce. Their simulation is for six stages of crystallization, meaning that there are six crystallizers. The pressure range is from 7.5 bar to 50 bar. For this project, the number of stages and pressure range will be based on the experimental results. In estimating the cost of equipments, Duc suggested using methods presented in Douglas (1988). This project will use similar methods based on Seider et al. (2010). Other costs such as utilities and maintenance will be calculated as a function of total cost equipment.

The key to this simulation is to estimate the best path for the hydrate based gas separation that is available and to be put into the simulation. Choosing the right path can substantially reduce cost (both running and capital costs) and therefore leads to a more prospective future for hydrate based gas separation. For instance, Duc, Chauvy and Herri (2007) uses 6 stages of separation for their simulation. However, decreasing the number of stages while at the same time increasing the rate of CO2 formation into hydrates is the main target. This leads to another obstacle, that is to choose the best data in which to simulate. In order to set the separartion stages, thermodynamic data is needed, so as to see and set the best configuration and operating conditions along the separation train.

Anothert literature by Dabrowski, Windmeier and Oellrich (2009) evaluates hydrate based gas separation of CO2 in a mixed biogas to be evaluated with accordance to its enegy consumption. This method require the estimation of energy based on Langmuir's equation, as suggested by Dabrowski.. This literature is a good example of comparing technologies of CO2 capture and removal, since it evaluates in terms of energy, therefore making the basis of comparison the same. Plus, energy itself is a factor of cost especially in the processing industry, thus the method of making comparison by energy evaluation can give a plausible result. Shown below is the separation stages along with its operating conditions :

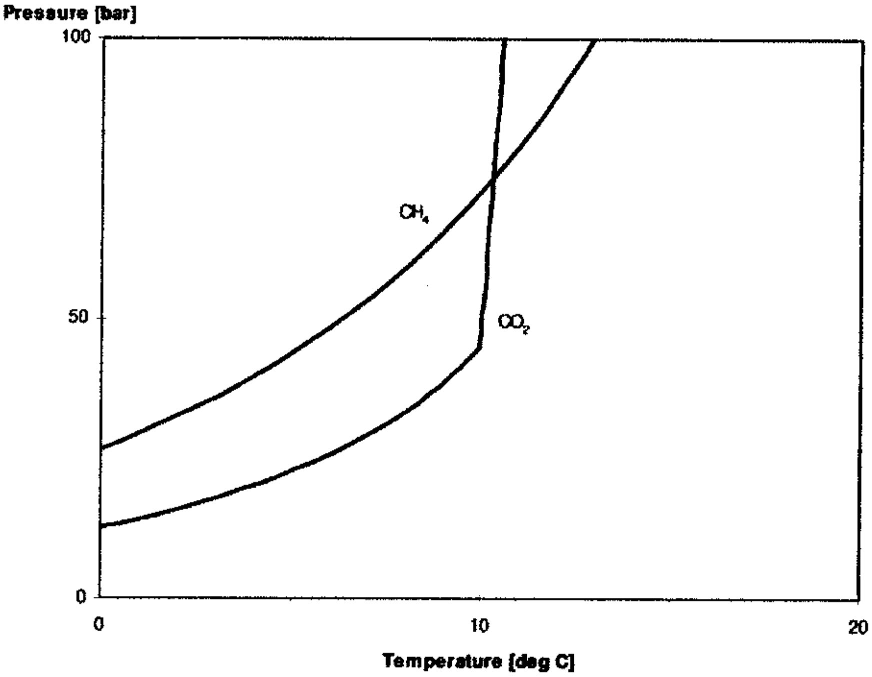


Figure 2-1 Hydrate formation phase diagram for a CO$_2$ – CH$_4$ mixture systems

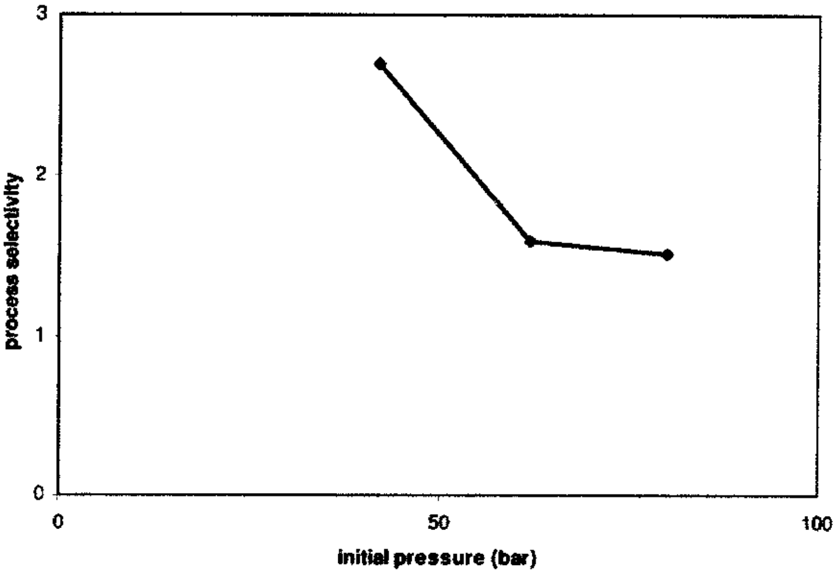


Figure 2-2 Process selectivity against initial pressure graph

There are a few experimental data than be used for simulation purposes. van Denderen, Ineke, and Golombok (2009) have ran an experiment regarding CO2 capture in CO2 – natural gas mixtures. The data acquired is as shown below:

Figure 2-1 depicts the hydrate formation phase diagram between pure methane and CO2 while figure 4 shows the selectivity of the hydrate formation given different initial pressures. Figure 3 is a prominent data, since it shows whether formation of CH4 hydrates or CO2 hydrates are more preferable at varying initial pressures. van Denderen defines the process selectivity as

$$Process\ selectivity, \chi = \frac{\eta_{CO_2(g)} / \eta_{CH_4(g)}}{\eta_{CO_2(f)} / \eta_{CH_4(f)}}$$

Based from this formula, it can be concluded that

$\chi < 1$: favor CH4 hydrates formation

$\chi = 1$: favor no particular hydrate formation

$\chi > 1$: favor CO2 hydrate formation

From figure 3, it is noted that CO2 hydrate formation is within the region of 40 to 90 bar. This data can be used in the simulation program later on. Also noted was that the pressure region for CO2 hydrate formation is the normal operating pressure found in most LNG plants.

van Denderen also concluded that for CO2 – CH4 mixture containing 25% of CO2, a total of 80 minutes is needed for the CO2 concentration to reach equilibrium at 15% at the initial pressure of 40 bar. van Denderen highlights that in the experiment, CO2 hydrates' kinetics are faster, leading to faster removal of CO2 as hydrates rather than the rate of hydrate formation of CH_4. This is important because it will affect which of the components of the mixture is actually being removed.

Currently, it is suggested that van Denderen's data is used to help set the feed conditions as to maximize selectivity. As for the process design, it has been determine that the process is continuous, and that kinetics data should follow that of continuous hydrate reactors. As of 2011, three designs of continuous hydrate reactors have been fabricated and tested. The three are: i) Continuous Kenics-type static mixer hydrate reactor, ii) jet hydrate reactor, and iii) vortex and impinging stream reactor (VIR). The problem with these reactors is that they are mainly tested for hydrate formation of pure CO_2 systems, and not mixtures of CO_2 and CH_4. Another problem is that all these reactors are have only been tested on a pilot scale, therefore the data from these tests might be obsolete when tested in larger scale. For that, certain assumptions will need to be done to ensure the simulation works are at a steady state.

As previously stated, the reactor designs are still in the making and not completed fully yet. Therefore, another method is to use enthalpy and equilibrium data that have been derived via modelling, such as modelling of enthalpy of dissociation and hydration number from Clapeyron equation (Anderson, 2003). The method of analysis employed in this modelling uses the latest data available at the time and also directly uses the Clapeyron equation, thus taking account of CO_2solubility into water phase. Interestingly, Anderson's derivation shows that there is relation between equilibrium pressure and temperature, the hydrate numbers, and the amount of CO_2 that dissolves into the water phase (this amount is interrelated amount of CO_2 captured). Also, since Anderson's model is based on the equilibrium data, note that the hydration number is not constant. Hydration numbers are the stoichiometry number at which the amount of water molecules will be needed to capture one CO_2 molecule. Anderson's results in the following figure:-

Enthalpy change ΔH and hydration number n for reaction (I) and temperature T and pressure p for mole fraction x of CO_2

T/K	p/MPa	(dp/dT) / $(MPa \cdot K^{-1})$	$x(CO_2)$	ΔH_{lv} / $(kJ \cdot mol^{-1})$	ΔH_v / $(kJ \cdot mol^{-1})$	ΔH_l / $(kJ \cdot mol^{-1})$	n
274.15	1.377	0.167 ± 0.005	0.0162	60.1 ± 1.8	2.42	62.5 ± 1.8	6.4 ± 0.3
275.15	1.556	0.192 ± 0.006	0.0174	60.1 ± 1.8	2.60	62.7 ± 1.8	6.5 ± 0.3
276.15	1.760	0.216 ± 0.006	0.0187	58.7 ± 1.8	2.71	61.4 ± 1.8	6.2 ± 0.3
277.15	1.989	0.243 ± 0.007	0.0200	57.3 ± 1.8	2.80	60.0 ± 1.8	6.0 ± 0.3
278.15	2.249	0.279 ± 0.008	0.0214	56.4 ± 1.8	2.94	59.3 ± 1.8	5.9 ± 0.3
279.15	2.550	0.326 ± 0.010	0.0228	56.1 ± 1.8	3.13	59.2 ± 1.8	5.9 ± 0.3
280.15	2.906	0.389 ± 0.011	0.0244	56.1 ± 1.8	3.38	59.5 ± 1.8	5.9 ± 0.3
281.15	3.335	0.472 ± 0.021	0.0261	55.8 ± 2.4	3.62	59.4 ± 2.4	5.9 ± 0.3
282.15	3.858	0.579 ± 0.035	0.0279	54.5 ± 3.0	3.74	58.2 ± 3.0	5.7 ± 0.3

Figure 2-3 Results showcasing relations between equilibrium temperature and pressure and the subsequent effects on the enthalpy and hydration numbers.

Anderson argued that since hydrate formation depends on the gas molecules filling the empty spaces in the lattices, the fact is that the lattices will not be actually full unless at very, very high pressures. This argument shows that hydrate formation thermodynamics are not easily derived.

Yang, Martinez, Currier, Spencer accepted Anderson's argument in their paper regarding kinetics of CO_2 hydrates a continuous flow reactor. Yang et al. (2011) studies the various factors that might have an effect in hydrate formation in the reactors. Their involvement with SIMTECHE that is trying to design a continuous flow reactor for hydrate themselves, shows that this paper is important in understanding the fundamentals in designing continuous flow reactors. Accordingly, Yang et al. (2011) provides the most substantial and current foundings in the hydrate research, therefore making its data the most up to date.

Included in this paper the quantative analysis of the slurry concentration, as well as effects of flow, heat, and operating conditions for suitable hydrate formations. Yang et al. (2011) offers data that might be truly useful in determining the outcome of this project.

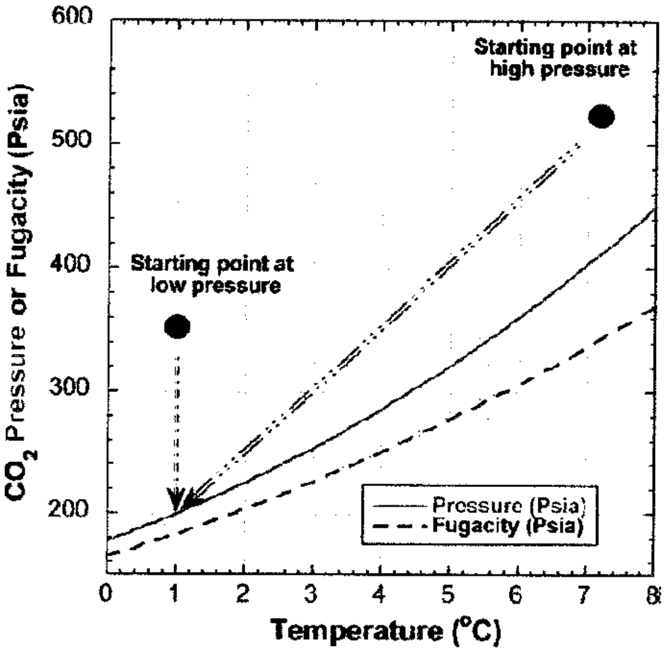


Figure 2-4 Yang et al. (2011) data regarding hydrate equilibrium.

Yang stated that the higher the inlet pressure and the lower the inlet temperature, the better the hydrate formation rate in a continuous hydrate reactor.

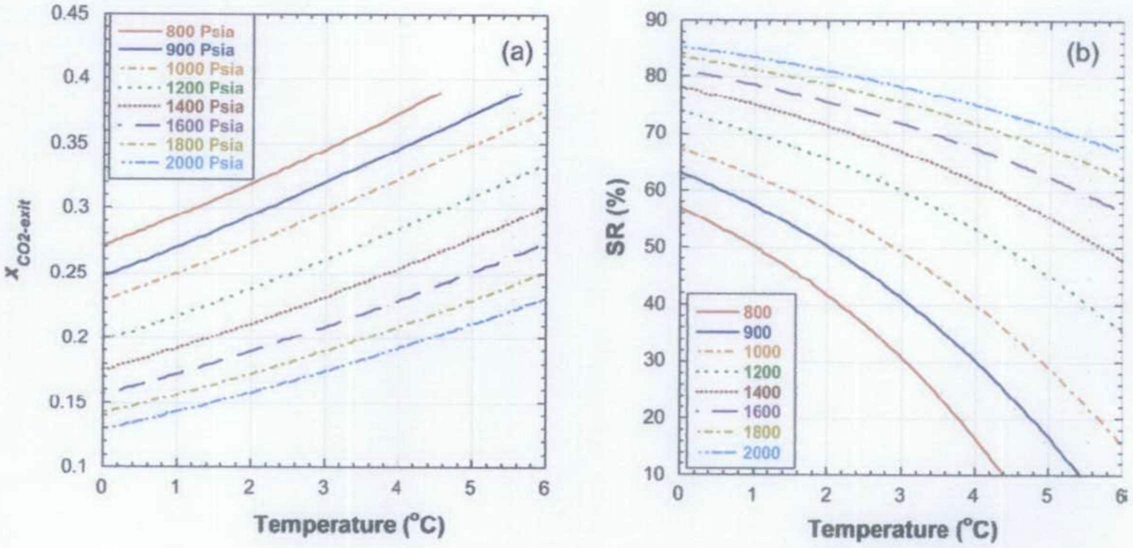


Figure 2-5 (a) Effects of pressure on achievable and outlet concentration of CO2 at reactor exit for CO2 – Ar mixture at equilibrium. (b) The SR for a $H_2 - CO_2$ mixture.

Yang et al. also defined the separation ratio as to measure the effective separation done in the system. The equation is as below:-

$$Separation\ Ratio, SR = 1 - \frac{\chi_{CO_2\,exit}/\left(1-\chi_{CO_2\,exit}\right)}{\chi_{CO_2\,in}/\left(1-\chi_{CO_2\,in}\right)}$$

X_{CO_2} exit and in refers to the fraction of CO_2 present in the end product and the feed.

Another interesting argument is that Duc et al. (2006) did not simulate based on reactors, but rather only on kinetics and thermodynamics data that was experimented by themselves. Therefore, for this project as well, there is no need to do the simulation by looking at the specific pilot reactors, but rather on the thermodynamics data provided in other studies or experimented by ourselves.

Another limitation to this simulation is the fact that kinetics involving CO_2 hydrates' flow properties cannot be simulated properly. So far, the only extensive data of flow properties involving CO_2 hydrates and water is given also by Yang et al. (2011). Based on the data, there is a need to keep the flow velocity at a relatively 0.3 m/s, by which then the flow will be annular and steady. This is important since hydrates are the main reason of pipe clogging in natural gas processing plants. However, as stated beforehand, the flow properties cannot be extensively be simulated. In this case, the assumption for the simulation is that the flow is already at a constant velocity of 0.3 m/s, and that there are no plugging of pipes.

CHAPTER 3

METHODOLOGY

3.1. Tools

The main tool to be used is software that focuses on calculations. The preferred software to be used is Microsoft Excel (either the 2007 version or the 2010 version). For simulation works, HYSIS will be used. PRO II might also be used as both softwares are widely used and recognized as a good simulation tool.

3.2. Research Methodolgy

The research methodology will focus on the methods to be used in estimating the costs of using hydrate formation as a potential gas separation method. Figure 1 will showcase the research methodology proposed for this project.

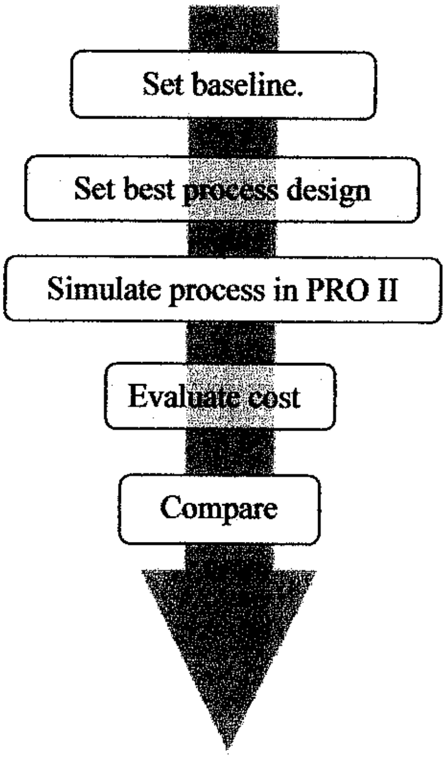


Figure 3-1: Research Methodology

i) Setting baseline

Baseline is the starting point of the project. A case study is made that will fulfill the project's objective.

The proposed baseline is:-

Gas flowrate = 1,000 kmol/hr of mixed gas
Concentration = 20% CO2; 80% CH4
Design Pressure = 30 bar
Design temperature = 35°C
Objective = 90% purity of CH4
Water feed flowrate = 6.5 times the amount of mol CO_2 in feed. (For this simulation water feed is set at 1300 kmol/hr)

This baseline is opted as the feed, while the operating conditions and the simulation train and the number of stages shall be discussed in the current works.

It is proposed that the project follows van Denderen, Ineke and Golombok (2009) for its thermodynamic data with Azmi, Mukhtar and Sabil (2011) as supplement data.

As of current updates, the thermodynamics data offered by Yang et al. (2011) seems like another viable option for this simulation to follow. Yang et al. (2011) also provides the quantative analysis of a hydrate reactor without having to run experiments, which should be handy when working with simulation.

The simulation is to be done in PRO II.

The conventional process in which comparisons will be made is chosen. The chosen process is removal of CO2 by MDEA solution.

ii) Select best process design

This is to select the best number of stages along with the operating conditions. Also, there is also the need to choose suitable overall process path along with other equipments in the process. Simulate the separation and acquire data for evaluation in the next stage from the simulation. At this stage it is also possible to simulate different paths in order to plot stages against cost.

Currently, the thermodynamics data have already been acquired. As of now, the project is at this stage. More on the updates will be covered in the current works section.

iii) Simulation steps in PRO II

Simulation is done in order to see the power consumption of a hydrate unit. PRO II is selected based on its easiness to use and it also has a user friendly interphase. PRO II also allows manual addition of chemical compounds. Below is graphical method on how PRO II is used in order to simulate the hydration unit.

Step 1: Starting PRO II

a) Go to Start Menu
b) Select 'All Programs'
c) Select SIMSCI. It will open into 2 subfolders. Select PRO II 9.0. Select the icon PRO II 9.0.

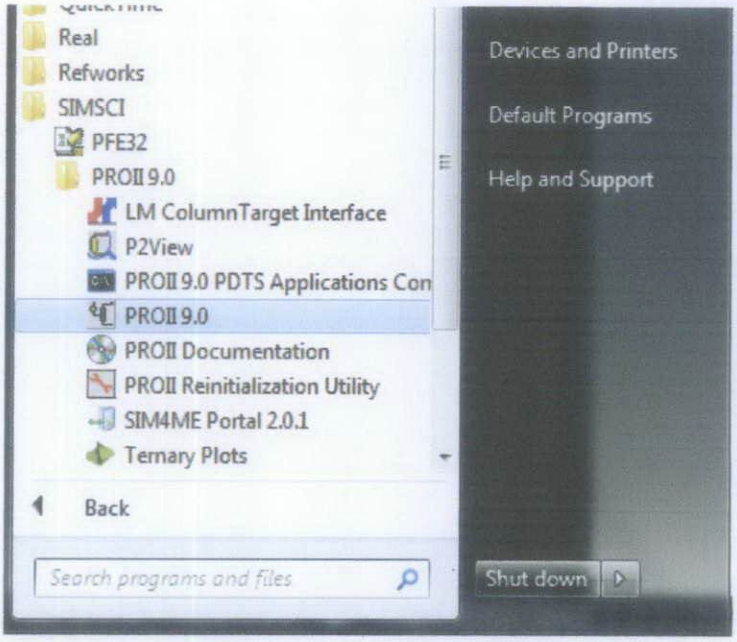
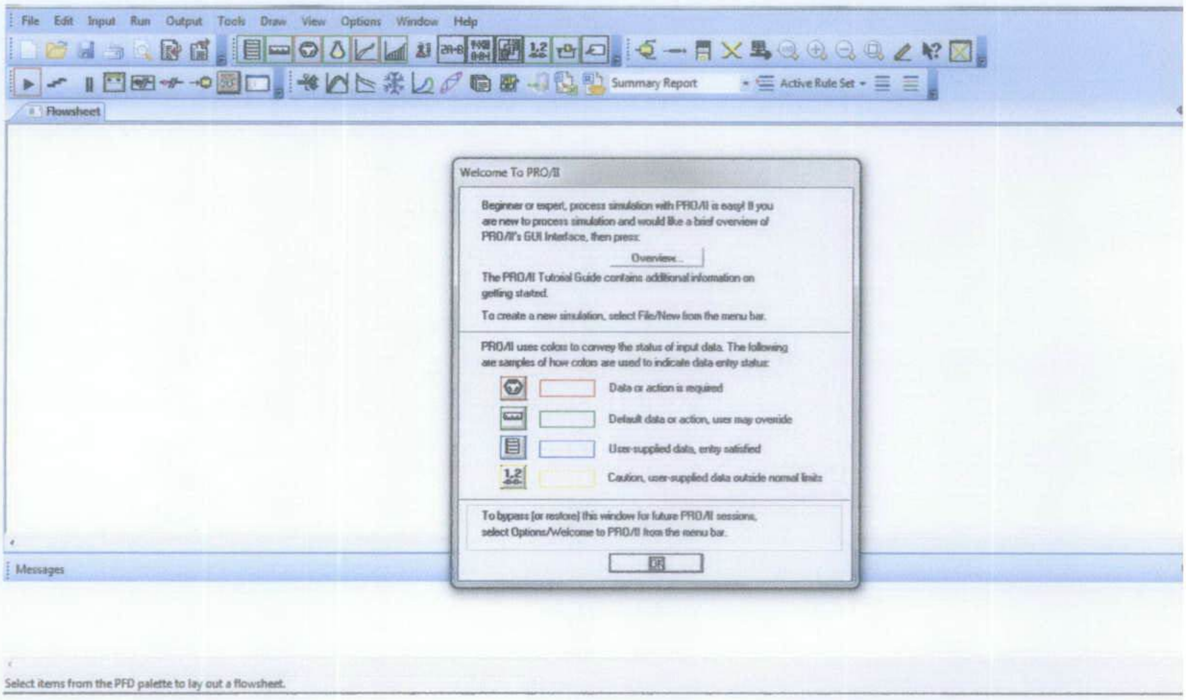


Figure 3-2 Start Menu

d) Wait for program to load. Once load is finished the interface will be as shown below.



Beginner or expert, process simulation with PRO/II is easy! If you are new to process simulation and would like a brief overview of PRO/II's GUI Interface, then press:

The PRO/II Tutorial Guide contains additional information on getting started.

To create a new simulation, select File/New from the menu bar.

PRO/II uses colors to convey the status of input data. The following are samples of how colors are used to indicate data entry status:

Data or action is required

Default data or action, user may override

User-supplied data, entry satisfied

Caution, user-supplied data outside normal limits

To bypass (or restore) this window for future PRO/II sessions, select Options/Welcome to PRO/II from the menu bar.

Select items from the PFD palette to lay out a flowsheet.

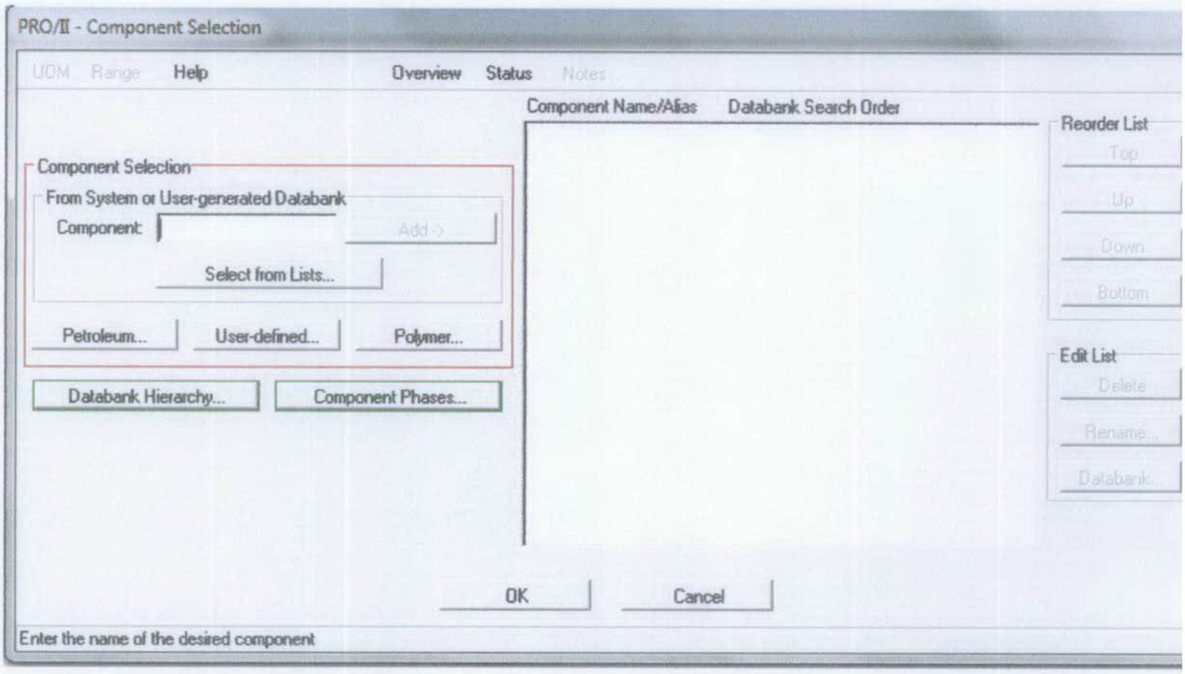
Figure 3-3 Starting interface for PRO II. The initial interface also gives a brief outlook on how to use PRO II.

Step 2: Define chemical compounds and thermodynamic package

a) Click at the icon.

b) The enter compound interface will pop up, as shown below.

c) To select thermodynamic package, click icon. This project uses the Peng-Robinson thermodynamic package as it is the default package for most simulations. Also, there are not many literature regarding the suitable thermodynamic package for simulation of hydrate formation. Click Modify on the thermodynamic property entry window to set all thermodynamic package calculations to Peng-Robinson.



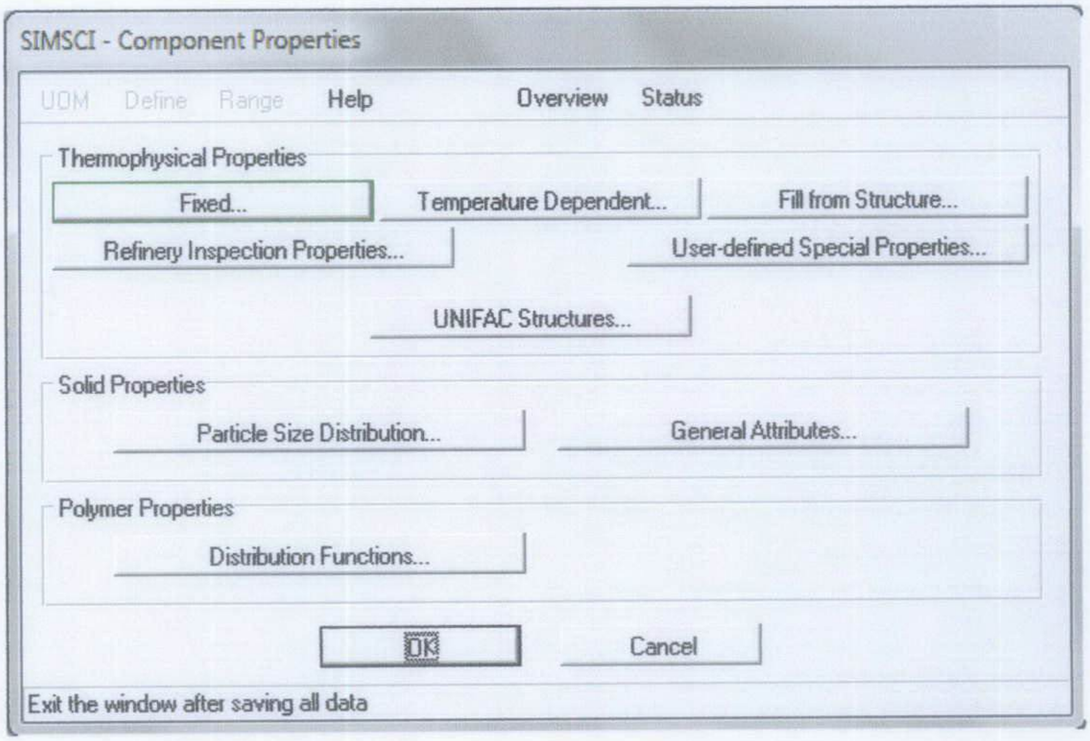
Enter the name of the desired component

Figure 3-4 Interface for entering the chemical compounds for simulation.

d) To select known chemical compounds, click "Select from Lists". For CH_4, CO_2, and water, these compounds can be selected from the list. For CO_2 hydrate, we will have to define the compound ourselves. Select "User-defined" to do this. Name the new compound as CO2HYDRATE Next, while selecting CO2HYDRATE, click on the Component Phases and define the CO2HYDRATE as solid. The step for chemical compounds selection now ends.

Step 3: Defining chemical compounds' parameters

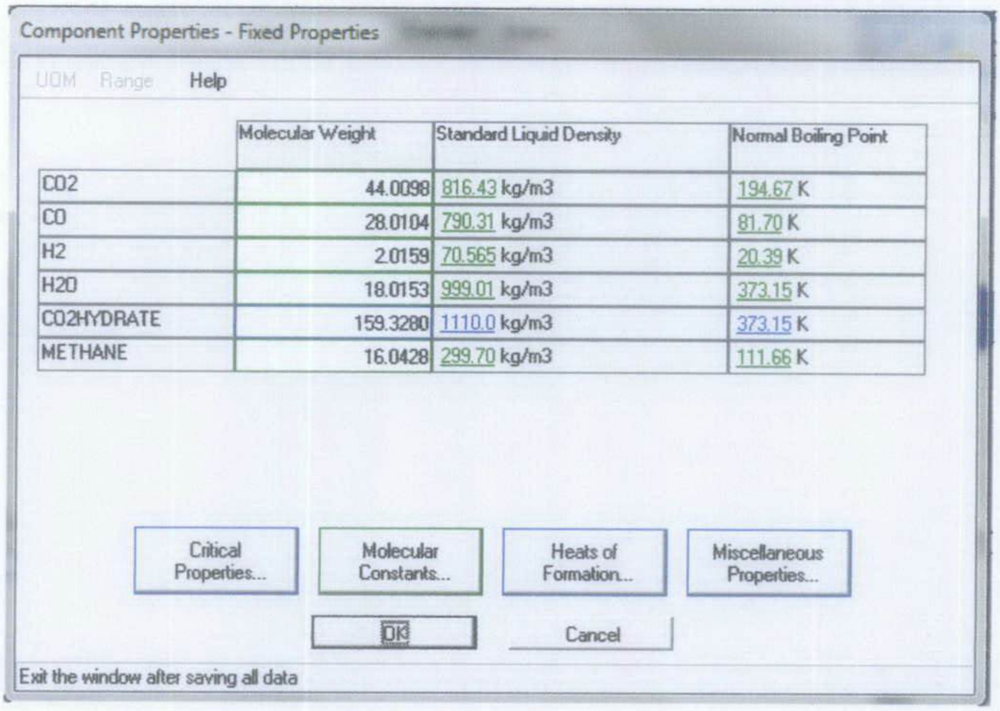
a) Press the icon to enter the CO2HYDRATE parameters. The interface to enter parameters for CO2HYDRATE will be as below:



Exit the window after saving all data

Figure 3-5 Interface for entering Component Properties

b) To enter fixed parameters (non-temperature dependent) press "Fixed". Enter data as below.



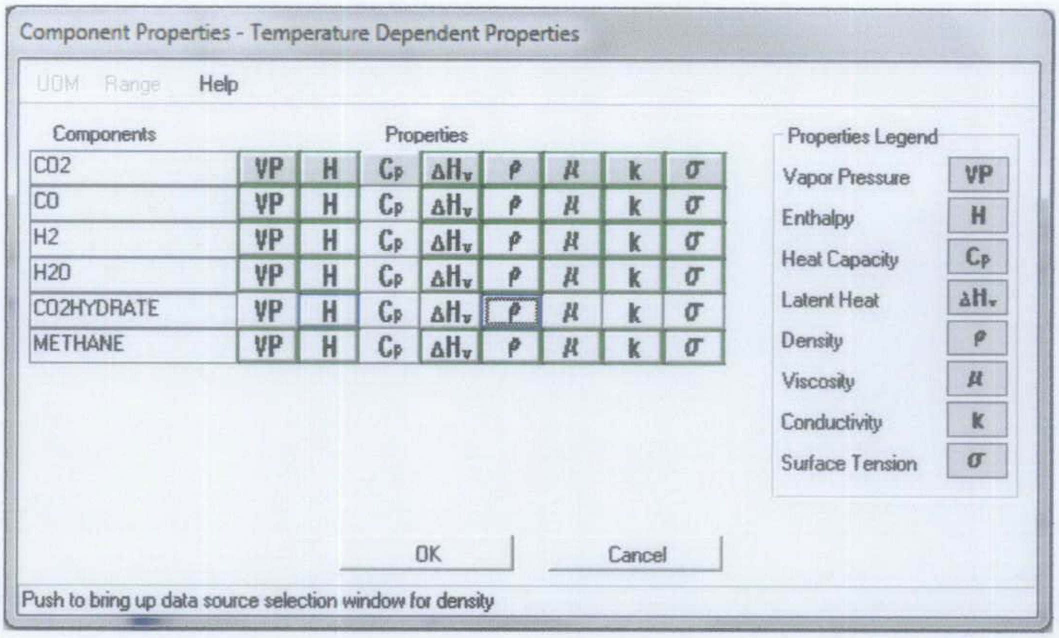
	Molecular Weight	Standard Liquid Density	Normal Boiling Point
CO2	44.0098	816.43 kg/m3	194.67 K
CO	28.0104	790.31 kg/m3	81.70 K
H2	2.0159	70.565 kg/m3	20.39 K
H2O	18.0153	999.01 kg/m3	373.15 K
CO2HYDRATE	159.3280	1110.0 kg/m3	373.15 K
METHANE	16.0428	299.70 kg/m3	111.66 K

Figure 3-6 Fixed data entry window

c) Enter heat of formation, $\Delta H_f°$ as 1.82×10^6 kJ/kg-mole for CO2HYDRATE.

d) Enter standard Gibbs energy of formation, $\Delta G_f°$ as 1.743×10^6 kJ/kg-mole for CO2HYDRATE.

e) Click OK. Now proceed to "Temperature Dependent". Enter Solid Enthalpy of CO2HYDRATE. To enter Solid enthalpy data, see below:



Push to bring up data source selection window for density

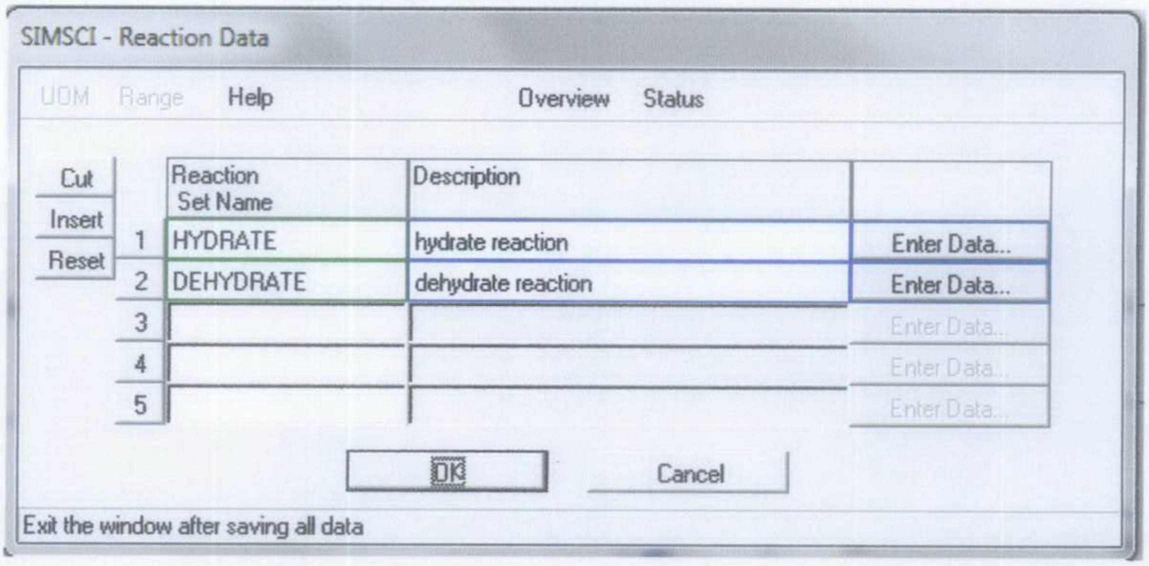
Figure 3-7 Temperature dependent entry window

Click H and then click Solid to enter data. The data entered here is the data $\Delta H_{I\text{-}V}$ from Anderson (2003), but without the pressure. Then, the data for the reaction of CO2HYDRATE can be entered.

Step 4: Entering reaction data.

a) Click 2A+B icon. The window for entering the hydration reaction will pop out.

b) Define two reactions as below:



	Reaction Set Name	Description
1	HYDRATE	hydrate reaction
2	DEHYDRATE	dehydrate reaction
3		
4		
5		

Exit the window after saving all data

Figure 3-8 Reaction data window entry

c) Enter data for hydrate reaction and dehydrate reaction as follows:

Table 3-1 Reaction properties for CO_2 hydrate

Property/Paramater	Value
Heat of reaction	~62.5 kJ/mol at 3MPa
Intrinsic rate of reaction	1.83 x 10^8 mol/(m^2•Pa-s)
Intrinsic activation energy	102.88 kJ/mol

The heat of reaction is taken to be the negative value of the heat of disocciation given by Anderson (2003). The hydration number will also be assumed to be 6.4 mol H_2O/mol CO_2.

The intrinsic data is given by Clark and Bishnoi (2001). However, it is reported by Yang et al. (2011) that this data might not be coincide with other reported properties of CO_2 hydrate reaction data. It was, however, hypothesized by Yang et al. (2011) that the interphase contact of the system tested by Clark and Bishnoi (2001) and Yang et.al (2011) might have an effect to the differences. Another rate of reaction is given by Bergeron and Servio (2008). For Bergeron and Servio (2008), the rate is given as 1.83 x 10^{-8} m/s at 275.5 K and 3,047 kPa. However, no activation energy is given, and only three data are reported. By graphing this graph, the activation energy and pre-exponential constant are found to be highly different than

Clark and Bishnoi (2001). Another data that we can use is by Yang et al. (2011), but the data includes implicit operational variable into the pre-exponential factor, A and the activation energy, E. Also, Yang remarked that E is dependent upon the flow properties and velocity of the system.

Another assumption is that this is an ideal gas mixture, and therefore, the gases will act like individual gas components, and therefore, all the properties for the CO_2 hydration reaction is valid as long as only CO_2 gas reacts with water within the inlet gas mixture. This assumption is also based on that the selectivity of CO_2 forming hydrates are higher than that of CH_4. The selectivity, as van Denderen (2009) remarked, is affected by the inlet pressure. The data by van Denderen however, is only limited until 80 bar, while the system will utilize a much higher pressure in order to increase the reaction rate. Since there are not many available data regarding the process selectivity at this pressure, it is assumed that the selectivity is still towards CO_2 hydrates.

As for the separation of the solid hydrate, it is assumed that the hydrate's density is higher than water and therefore it will settle down in the reactor. This is simulated in the simulation via flash with solid separator. The reason as to why excess water is flashed out of the gas stream is to reduce the effects of hydration of gases in the pipeline. In other words, it is implied that the hydration will only occur in the hydrate reactors/formers under controlled conditions.

Step 5: Start the simulation.

a) To start the simulation, the process unit can be selected from the column on the left. The tabs on the side of the column represents different column options with different process units.

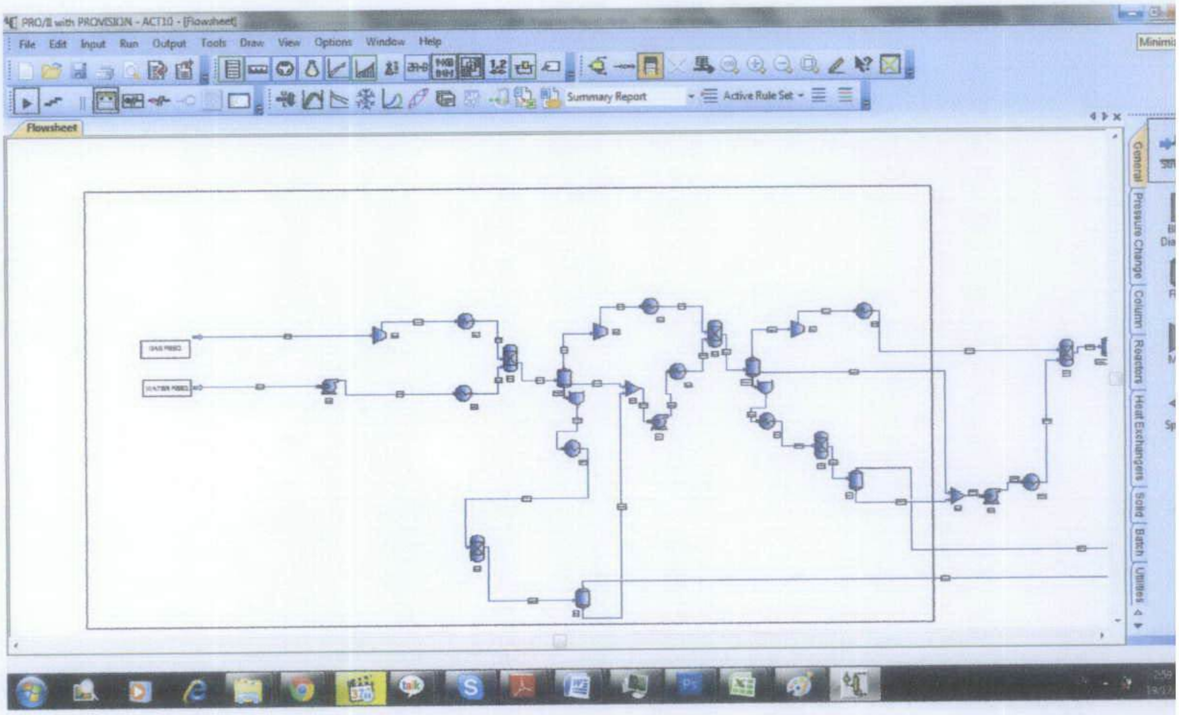


Figure 3-9 Full interface of the PRO II simulation software

b) For the simulation of a hydration unit, it is determined that a single hydration unit will consist of the following:-

- Compressors
- Pumps
- Heat exchanger
- Hydrate reactor
- Flash with solid separator
- Dehydrate reactor/vessel

c) The hydrate reactor's operating conditions are as tabulated

Table 3-2 Hydrator inlet conditions in the reactor

Operating Conditions	**Value**
Temperature (mixed gas and water)	10°C – set at inlet stream temperature at stream heat exchanger.
Pressure (gas)	80 bar – set at gas compressor before reactor inlet.
Pressure (water)	80 bar – set at water pump before reactor inlet.

[It is assumed as well that the hydration reaction is uniform throughout the reactor. The the driving force of the reaction, in truth, is the equilibrium of hydrate-vapor(gas)-water of CO_2 and its hydrate and the excess water. However, due to limitations of the software, it is not possible to enter the full equilibrium data. Although the are works showcasing modelling of the phase equilibria by Klauda and Sandler(2003) even for gas mixtures, it seems that the data from Klauda and Sandler are deemed unusable for this project. We also cannot simulate it as Gibbs reactor as a result of data lacking in the Gibbs properties of CO_2 hydrate.Therefore, in this simulation, we attempted to control the reactor conditions so as to simulate the reaction reaching equilibrium. Since the reaction of hydration is exothermic, coolant jackets are therefore assumed to be utilized to keep the reactor in a cooled condition.Accordingly, we assumed the reactor to be an adiabatic reactor, with all the excess heat assumed to be absorbed by a cooling jacket. The temperature of the outlet gas and temperature within the reactor is assumed to be equal at 1°C. The equilibrium pressure according to Yang et al. (2011) data, is around 13.6 bar (1.36 MPa), and this pressure is put as the outlet pressure of the reactor. Here, we are manually entering the equilibrium in order to satisfy the reaction equilibrium.]

d) Next, assume all other equipments to have the same pressure drop of 68 kPa.

e) For the dehydration of CO2HYDRATE, set the reactor conditions as below

Table 3-3 Dehydrator inlet conditions for dehydrators

Operating Conditions	Value
Temperature	30°C – set at inlet stream temperature at stream heat exchanger. The temperature rise within the reactor is 20°C.
Pressure	No pressure setting (assumed the same as stream inlet pressure).

[In actual, the dehydrator is meant to be a pressure vessel in which to heat up the CO_2 hydrate and let the it dissociate under controlled conditions.]

f) Repeatedly simulate the process by stage until the amount of CO_2 gas in feed is reduced to at least 10 mol% of total molar gas in the product stream.

iv) Evaluating energy consumption

The energy consumption data will be taken from the simulation and analyzed accordingly using Microsoft Excel. The energy taken from the simulation as our data is the adiabatic duty of the reactor. The reactor adiabatic duty is taken since we believe that there are no energy loss from the reactor.

On another note, it is also important to be able to discern the economic potential of the process. On that note, we will be depending on Douglas (1988) to to do this evaluation.

According Douglas (1988), there are four levels of cost evaluation, with each level corresponding to certain percentages of error and accuracy The problem here is that cost evaluation cannot be done extensively as of now due to the inability to design the reactor. However, rooms for improvement are available should we take the reactor as a normal pressure vessel and evaluate on it from there. As of now, we can only do the economic potential for the first level, which caters to around 30% error. However this is deemed acceptable since this project aims to quantify the cost in a systematic manner, as such to provide a groundbreak for further analysis in the future.

v) Compare

Simulate the process again, this time utilizing the CO2 removal by amine. Calculate associated costs and compare. The basis of comparison will be energy consumed to capture 1 kg of CO2 removal.

CHAPTER 4

RESULT ANALYSIS AND DISCUSSION

This section is regarding current results that was obtained for this project.

4.1. Simulation results

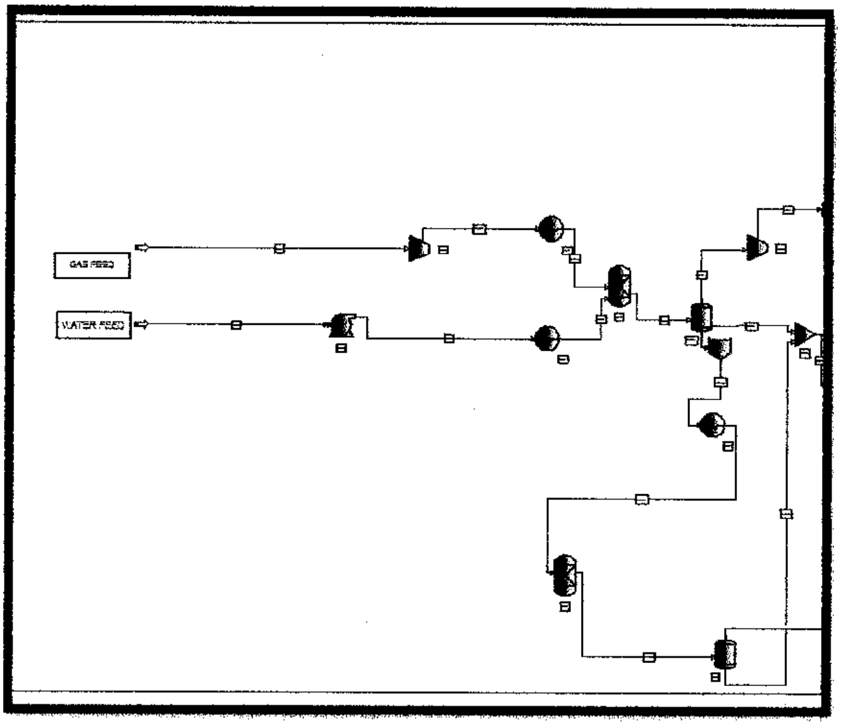


Figure 4-1 A single hydrate capture unit

Based on the report, the total energy utilized by the hydrate capture unit is 9.92 x 10^7 kJ/hr, or 2.75 x 10^4 kW. If we based this on a single year having a total of 330 days of operation, then the total annual energy consumption is 7.58 x 10^{11} kWh.

The breakdown of the energy consumption are as follow

Table 4-1 Percentage of energy consumed by equipment

Equipment	Percentage of energy consumed
Compressor	3.4%
Dehydrator	43.4%
Hydrator	43.6%
Flash	0.7%
Hx	8.6%
Pump	0.3%

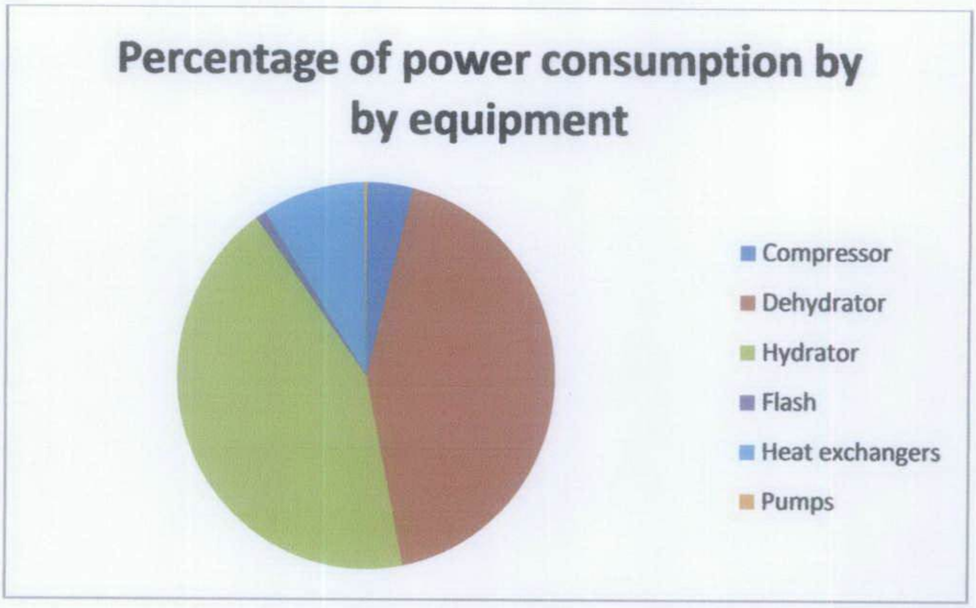


Figure 4-2 Pie chart of energy consumed by equipment

The achievable purity of CH_4 is 99.97 mol% (~99.69% by weight) with CO_2 content at the outlet is 0.0095 mol% (~0.024% by weight). However, it is noted that there are a little water moist, but only as low as 0.0183mol%, or 357.423 ppm. This low amount of moisture can be absorbed via glycol, should it be necessary to do so. Since the gas has low amount of CO_2 and water moisture, the gas can be transported via pipelines.

As for the simulated process itself, the process utilizes two stage hydration units. Below is the table indicating percentage removal by stages.

Table 4-2 Percentage of CO2 removal by stage

Stages	Percentage removal of inlet CO_2
Stage 1	79.75%
Stage 2	99.81%

Both reactors are simulated at the same temperature and pressure as well as the same feed conditions of feed gas and water, albeit different composition for the gas inlet.

In order to minimize the water usage of the system, it is assumed that water is recycled at every stage and also at the end of the stage whereas the water is recycled back as feed. This was not, however, simulated into the simulation process.

The calculation amount of energy consumed to remove a mol of CO_2 by hydrate formation will result in 9.811 MJ of energy consumed per kg CO_2 (taking only the energy for hydration and dehydration equipment). In other words, the power consumption is 0.065 kW per kmol CO_2 captured.

An interesting point for this simulation is that we only assume that there two compounds within the natural gas mixture. This is done as to minimize assumption on having multiple amount of assumptions, which can render the simulation invalid. A valid scenario is that we assumed that the feed gas is already a treated natural gas but still with high CO_2 content, which has been supplied to a gas sweetening plant to remove the excess CO_2 for further processing.

With this much assumption, it is possible that this simulation have high possibilities of error, especially when it comes to the thermodynamics and flow dynamics of the simulation. There are no data as well to correlate or verify whether this simulation is correct. Therefore, we cannot actually determine the accuracy of the simulation, nor estimate the error.

4.2. Economic Potential Analysis

There are multiple uses of the clean natural gas in both industrial and domestic area. However, the main use of natural gas is to supply energy, and therefore it is best to assume the product will be used for energy production as well. Therefore, the price for the end product will be taken as the average price of natural gas utility in Malaysia, which is RM 16.07 / MMBTU.

To estimate the cost, it recommended that it to be done by levels, as per Douglas (1988) has stated. However, it cannot be done without knowing the fragmented cost of a single natural gas processing plant by units. This is because we only simulate a unit within the natural gas processing plant itself, notably only on the CO_2 capture/separation unit. We can also assume the units as a single natural gas sweetening plant, instead of a full fledged natural gas processing plant.According to Douglas (1988), for the first level of cost estimation, we need only estimate the difference between the annual sales of the end product with the annual cost of feed. If we assume the whole unit as only a gas sweetening plant, then the cost of feed will only be treated natural gas with high CO_2 content and water. In short, water is almost free, and therefore can be set to zero cost (we can take water from rive, or even the sea, as suggested by several studies on using brine as a medium (including van Denderen et.al (2009) for CO_2 capture as hydrates).

In Malaysia, there are no wellhead pricelist due to all natural gas being processed first-hand by PETRONAS. Accordingly, the price of processed natural gas given by GAS Malaysia in 2003 is RM 0.49/m^3. However, since the gas we are buying is that of lower quality, the price should be extensively lower than the price given by GAS Malaysia. To ease the calculation method, we assume the price of such gas to be half of the original price, that is RM 0.25/m^3. The summary of the feed prices as assumed in this project is tabulated below.

Table 4-3 Summary table of assumed prices for feed and product

Item	**Price**
Water feed	Free
Natural gas feed	RM 0.25/m^3
Natural gas product	RM 16.07/MMBTU

Total annual feed cost = RM 44,379,704.44/year.

Total annual sales of product = RM 85,103,485.03 /year.

Therefore, for first level economic potential of the unit = RM 40,723,780.59. For the first level economic potential to be positive means that this hydration unit (acting as a gas sweetening plant) is for now considered as a good investment since it has a very good potential. However, there are higher levels of economic potential which can actually affect the unit's economy as a whole.

As for the utility cost, According to Seider (2010), the utility cost of plant can be estimated to be around 10% of total sales. Based on this, we calculated the utility cost to be RM 8,510,348.50/year. However, Seider also note that if the utilities are used as the feed itself, it can result invalid results of the rule above. Therefore, depending on the water source of the feed, this estimation may or may not be valid.

The reason as to why this rule is being used in estimating the utility cost is because the lack of data in searching for utility costing per unit use in Malaysia. Though the data can be searched in the internet, the fact remains that we do not know

However, if this hydration unit is integrated into a natural gas processing plant, the utility cost will be different, and may even be lower depending on the optimization of the utility usage (including usage of heat exchanger networks and as such).

A summary concerning the all the associated estimated costs are tabulated below.

Table 4-4 Tabulation of estimated annual cost for feed and utility

Cost	Value
Total annual feed cost	RM 44,379,704.44/year.
Annual utility cost	RM 8,510,348.50/year.

Note that this estimation are likely to have a maximum 30% error, as remarked by Douglas (1988). However, the simulation itself is likely to have a large error, due to many unknown properties only being assumed. Therefore, this cost estimation is at best 50% correct.

4.3. Comparison of the Hydrate Method and Amine Scrubbing.

For this, we can either compare the whole unit energy consumption against each other, or we can basically just compare the energy used to capture a mol of CO_2 gas of both methods. Technically, the method with the lower energy consumed per mol CO_2 captured is the lower cost technology since less expenditure will be spent on utilities. In doing so, we are assuming that the operating expenditure in terms of manpower and maintenance to be similar for both methods. We are also assuming that energy used for other equipments in the methods (for instance, pumps, compressors and heat exchangers for streams) to be similar to each other too.

We are able to do this since both methods have similar power consumption percentage, that is, most of the energy consumed in CO_2 capture or scrubbing by amine is in the absorber and stripper. As for CO_2 capture by hydrate, similar situation occurred, and therefore, by calculating energy consumption on only the two equipments for both methods, we are already comparing most of the energy consumed for both methods.

Øi (2007) concluded that energy consumption of amine scrubbing for a power plant amine scrubber unit is around 3.65 MJ/kg CO_2. As for CO_2 capture by hydrate energy consumption, it is found out that the energy consumed is around 9.811 MJ/kg CO_2. That is nearly 3 times the energy consumption of amine scrubbing. But then, Øi (2007) only simulated CO_2 capture by amine for a flue gas, and the difference in operating parameters might have contributed to the large difference. This may play into effect especially since we are dealing with gas-phase chemicals.Another possible explanation would be that the simulation of the hydration unit in this work itself is wrong. But, as explained earlier, the lack of supporting data makes it hard to discern the accuracy of the simulation.

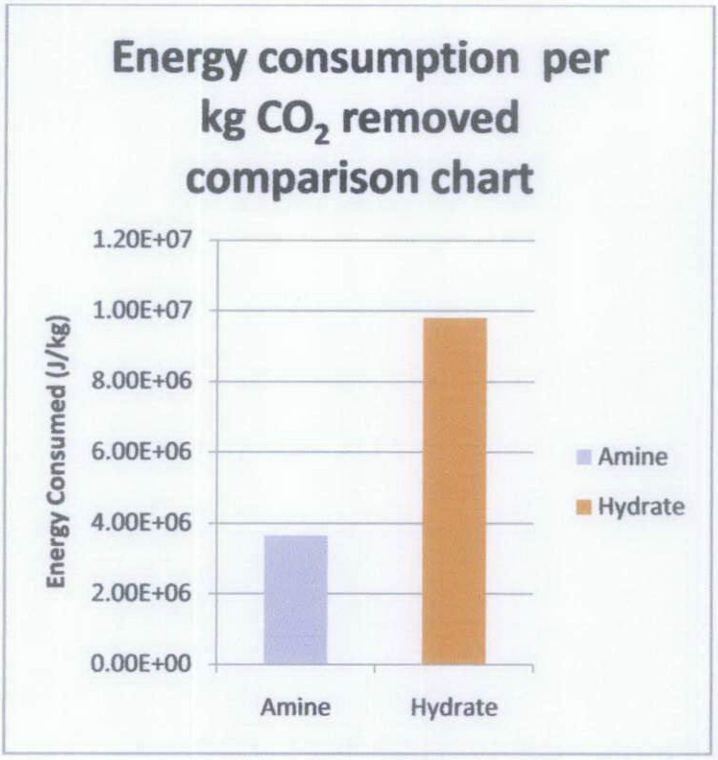


Figure 4-3 Bar chart showcasing the comparison of energy consumed for each method of CO_2 capture.

One other possibility is the extreme operating conditions of the hydrate former itself. Hydrate formers/reactors within the simulation require high pressure, up to even 80 bar, and a cool temperature as low as 10°C to 1°C. This requires a lot of work and cooling energy. Plus, with the hydrate reaction itself releasing energy, and yet needing the reactor to cool down means that massive amounts of energy are needed to take all the heat released by reaction as well as the heat within the system itself. For CO_2 capture by amine the highest energy requirement is mainly for regenerating the amine.From this data, it seems like CO_2 capture by hydrate is by far the more energy demanding method, and therefore, seems unlikely to be able to be used as a CO_2 capture unit in a natural gas processing plant.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1. Conclusion

Based on this findings, we can conclude that the current CO_2 hydrate technology still requires massive amount of energy, compared to that of the conventional methods used in the industry for CO_2 capture. This can be seen when the energy consumed to capture 1 kg of CO_2 for amine scrubbing is lower than that of CO_2 capture by hydrate. Based on the results, it seems like CO_2 capture by hydrates will never be able to compete against other conventional processes unless significant findings are reported. This can be considered as a challenge to researches to prove whether CO_2 hydrates can actually be used as a CO_2 capture method in the future.

The major difficulty regarding the project was to simulate the hydration unit. This is because there are generalized properties of CO_2 hydrates available yet. In addition, hydrates are

Even though CO_2 capture by hydrates seemed like a prospective business, based on the cost estimation data, the technology itself have never been tested in a large-scale pilot plant. The limitations of understanding hydrate properties might be the reason as to why this technology cannot be implemented yet. Since cost and energy are directly related to each other, the estimation reported may well be highly off compared to the actual. However, this cannot be verified unless a large-scale pilot hydrate unit is to be tested. Note that capital costs are not reported due to inability to design a reactor. Estimations can be done, but will require more literature review on designing a hydrate reactor.

Still, CO_2 hydrate technology is currently being researched as means of CO_2 storing via hydrate sequestration. This itself might be a new utilization of CO_2 hydrate, other than for separation and capture purposes. Another currently reseached utilization of CO_2 hydrates is for displacement of CH_4 hydrates by introducing CO_2. In a simpler term, this research is on releasing CH_4 from its hydrates by displacing them with CO_2 and forming CO_2 hydrates. Both technology might define the engineering and industrial world in the near future.

5.2. Recommendations

The recommendations are as below:-

- It is recommended that the next step of this project to be changed to experimental work. There are limited data regarding hydrates and simulation work requires a lot of guessworks. This may lead to inconclusive results. Duc et.al (2007) did both experimental and simulation works to reduce error on simulating the hydration unit.
- The project should change focus to latest research on CO_2 hydrates. A few current research on hydrates are the availability of CO_2 hydrates as means to displace CH_4 hydrates, as well as reseraches on reducing phase equilibria of CO_2. There are also kinetics study on hydrates, as well as the use of hydrate to capture CO_2 from flue gas.
- An interesting study on hydrate will be the modelling of hydrate-water flow to see the effects of hydrates have on flows. Yang et al. (2011) observed that the water and gas flow properties affects the hydration unit as well.
- It is also recommended that should Universiti Teknologi PETRONAS (UTP) are interested in studying hydrates, a hydrate reactor should be designed and be tested. There are a few reactor designs that can be used as a model. A notable design would be the jet reactor design by Smzycek et al. (2008) and also the VIR design by Bai et al. (2009).

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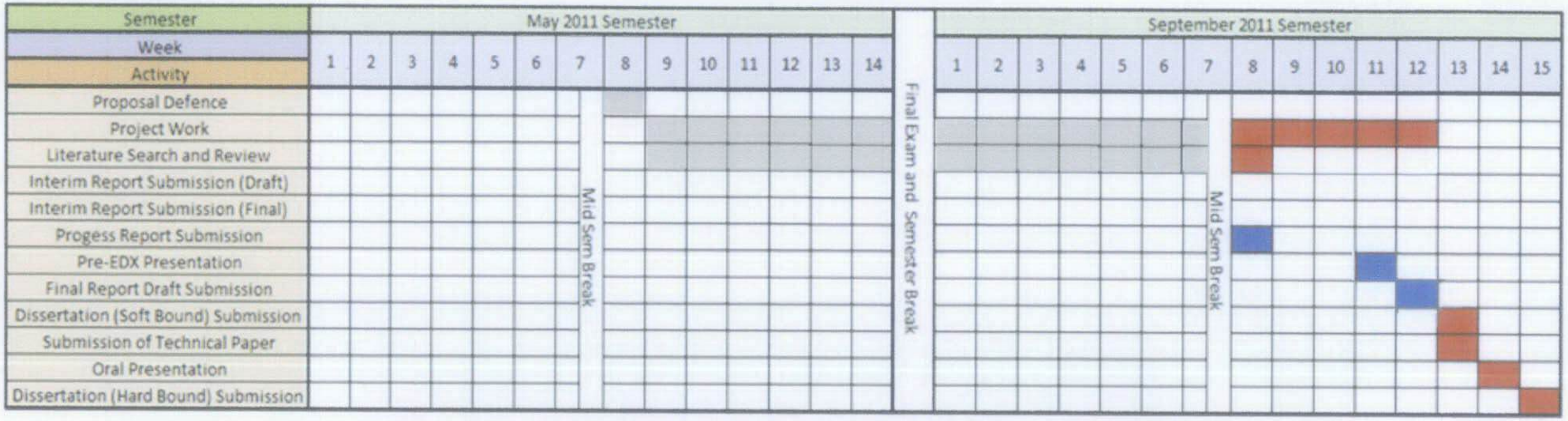
APPENDIX



Semester	May 2011 Semester															Final Exam and Semester Break	September 2011 Semester															
Week	1	2	3	4	5	6	7	Mid Sem Break	8	9	10	11	12	13	14		1	2	3	4	5	6	7	Mid Sem Break	8	9	10	11	12	13	14	15
Activity																																
Proposal Defence									▨																							
Project Work										▨	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨		🟥	🟥	🟥	🟥	🟥			
Literature Search and Review										▨	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨		🟥							
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Figure A-1-1 Project Gantt chart with current works

Project planning and timeline is showcased in the Gantt chart below. The activities and timelines follow the course outline for Final Year Project (FYP) I and II.

Legend

▨	Finished Phase
🟦	Current Works
🟥	Future and Important Works Planned