Clathrate Hydrates in Refrigeration System

by

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

JULY 2010

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ABSTRACT

Refrigeration is an important system that is use in daily life and industry process. Using hydrates to replace current refrigerant would greatly reduce the environmental issues by reducing the usage of environment threatening substance. Hydrates have a potential to be a good replacement for refrigerant because of its two phase behavior and have a high latent heat. Current researches regarding hydrates as refrigerant involve secondary refrigeration system. For main refrigeration system, hydrate is mix with fluorocarbon which can contribute to global warming. Elimination of fluorocarbon is the main priority, thus replacing them with non-threatening substance, Tetrahydrofuran. Manual calculation is made in order to calculate the mass and energy balance and coefficient of performance (COP). Results obtain shows that the designs can achieve 0.87 and 1.42 of COP. Typical refrigeration system produce 3.0 COP and hydrate mix with fluorocarbon can produce COP of 8.0. The value of COP shows that although the design made pass the minimum value of COP to operate, which is 0.8, the systems does not provide better efficiency in cooling. However, being a non-threatening system towards the environment would be a good reason to modify and enhance the system so that it would provide better efficiency in cooling besides the advantage of environmental friendly.

ACKNOWLEDGEMENT

First and foremost, I would like to express my appreciation and gratefulness to Allah, for His blessing and for giving me the strength and health to do this project until it is completed. I am heartily thankful to my family for the moral support, encouragement and care. I owe my deepest gratitude to Dr. Khalik Mohamad Sabil, the supervisor for Final Year Project 1 and Final Year Project 2, for his most valuable guidance, support and constructive criticism throughout this project.

This thesis would not have been possible unless Universiti Teknologi PETRONAS (UTP) provide me with a good environment and facilities to complete this project. Also, I would like to take this opportunity to thank to the Chemical Engineering Department of Universiti Teknologi PETRONAS (UTP) for offering this subject, Final Year Project. It gave me an opportunity to show characteristic of being a researcher and learn about the importance in writing a journal.

Lastly I am indebted to my many of my colleagues who support me, who were very informative and helpful, and to everyone who provided valuable information that assisted directly or indirectly in completing this project.

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CHAPTER 1: INTRODUCTION

1.1 BACKGROUND OF STUDY

Refrigeration is one of the most important processes whether for industry or daily life needs. From the definition, refrigeration is a process of removing heat from an enclosed space or from a substance and moving it to a place where it is unobjectionable [1]. The refrigeration process is meant to lower and maintaining the temperature of the enclosed space. The driving force of this process is the temperature gradient.

The process of exchanging heat from the enclosed space to the heat sink is carry out by substance/fluid which is called refrigerant. Refrigerant is a substance that has a high latent heat preferably a substance that can undergo phase change so it would produce better efficiency in cooling [2]. Currently, refrigeration system main refrigerant is fluorocarbon. However, the usage of fluorocarbon had proven that they can cause harm towards environment. Researches had been made to overcome this problem by identifying different substance to be use as refrigerant. Two phase secondary refrigerant (TPSR) is identified to be one of the best solutions since TPSR refrigerant have high latent heat. Among the TPSR used currently is the hydrates compound. However, the hydrates compound in this context is used as the secondary refrigerant.

Secondary refrigeration system is one of the best current methods to reduce the usage of fluorocarbons. Secondary refrigeration system creates another loop inside the main cooling system. The secondary loop replaces the evaporator in the main loop. The purpose of this loop is to reduce the load of the main refrigerant, which is mainly the fluorocarbon. By going through secondary cooling/heat exchange between the main refrigerant and the secondary refrigerant, total of fluorocarbon emission towards the atmosphere could be reduce. The advantages of this system are [3]:

- Amount of primary refrigerant used can be minimized.
- Pressure losses in vapor compression cycle – increasing cycle efficiency

- Hazardous primary refrigerant is possible to be used.
- Breakdowns can be repaired in the primary system while the secondary system cooling capability is maintain.

As listed above, the secondary refrigeration system possess significant advantages compared to typical refrigeration system. Using hydrates as secondary refrigerant is a good way to overcome the environment issues that refrigeration process possess. However, the advantage in hydrates properties is not fully optimized since the hydrates have a very high latent heat. The hydrates compound would produce even better result in refrigerating if it acts as the primary refrigerant.

Clathrate Hydrates used as primary refrigerant would produce better and higher efficiency of refrigeration system. Hydrates-based refrigeration system has a high potential to produce higher efficiency system because [4]:

- The heat of formation/dissociation of hydrate substance is several times larger compared to any fluorocarbon base refrigerant used in conventional vapor-compression refrigeration system.
- The compressor power required for the system is greatly reduce; when guest gas and liquid water are mixed and compressed together, the heat generated is absorbed by water having a large heat capacity, so the compression process in the refrigeration cycle should produce isothermal compression process.

Current hydrate-base refrigerant refrigeration system design available use mixture of HFC 32 + cyclopentane [4]. In this project, the elimination of fluorocarbon compound would be the main concern in choosing the right mixture of hydrates as refrigerant.

For the time being, this project would use CO_2 hydrates + tetrahydrofuran as the hydrates-based refrigerant. The main concern in choosing this substance is its low temperature of formation (around 15^oC). Choosing the cooling material for formation reactor would be a problem. Further details regarding this matter would be discussed in other section. The process design flow would be quite similar with the one suggested by

T.Ogawa et al [5]. Material and energy balance would be done throughout the system to ensure the capabilities of the CO_2 hydrates + tetrahydrofuran mixture act as refrigerant.

Other than that, few calculations regarding this system will be made. Among them is the calculation of compressor and pump power required. The coefficient of performance of this system would also be determined. Parameters used in this paper would be taken from [4] and [6].

1.2 PROBLEM STATEMENT

Using hydrates as refrigerant is a great solution to overcome the problem especially regarding environmental issues for current refrigeration system. A lot of research had been done regarding the behavior of hydrates acts as the refrigerant to make this system practical. However, up till now, refrigeration system design involving hydrates are only limited to use hydrates as secondary refrigerant. One of the main problems for current design is the refrigerant use still contain fluorocarbon that can cause environmental issues. As for this project, elimination of fluorocarbon in the refrigerant would be the main concern.

1.3 SIGNIFICANT OF PROJECT

In order to fulfill the requirement of Kyoto Protocol and to maintain the balance of nature, refrigeration system using hydrates as refrigerant must be optimize and commercialize. The success outcome of this project would be beneficial to all mankind and to the environment as well. As the use of CFC and HFC in refrigeration system could be reduced, the risk of ozone layer to be depleted could be reduced as well. This would overcome the problem of global warming that the earth experienced now.

1.4 OBJECTIVE AND SCOPE OF STUDY

The objectives of this research are:

1. To design refrigeration system using few hydrates as refrigerant.

2. To optimize the properties of hydrates in the refrigeration system by replacing the fluorocarbon in the substance with other substance which less environmental threatening such as tetrahydrofuran.

3. To calculate the mass and energy balance of the hydrates refrigeration system using manual calculation and compare the COP value with current refrigeration system.

The scope of this project is to calculate the mass and energy balance of hydrates refrigeration system by using manual calculation and also to ensure the possibility to use the suggested mixture as refrigerant. The calculation would involve various types of hydrates in order to identify the significance of the hydrates towards the refrigeration system.

CHAPTER 2: LITERATURE REVIEW

2.1 HYDRATES COMPONENT

Hydrates are crystalline compound formed in mixture of water and non- or low polar molecule (eg: methane, ethane, propane, carbon dioxide nitrogen and etc.) when subjected to appropriate pressure and temperature. This hydrogen bond creates a cage structure (known as cavities) and these cavities must be filled with guest molecule. In this case, it seems like the water is solidifying at temperature higher that the freezing point of water. The size and structure depends on the guest molecule. Currently, 3 structures of hydrates had been identified (structure I, II and H). The density of hydrates component is smaller than ice [14].

2.1.1 TYPICAL GAS HYDRATES PHASE BEHAVIOR

Gas hydrates can be said acting like a solution with gas being the solute and water being the solvent. However, the two main constituents are not chemically bonded. A typical phase diagram is presented below (for a mixture of water and light pure hydrocarbon) [11].

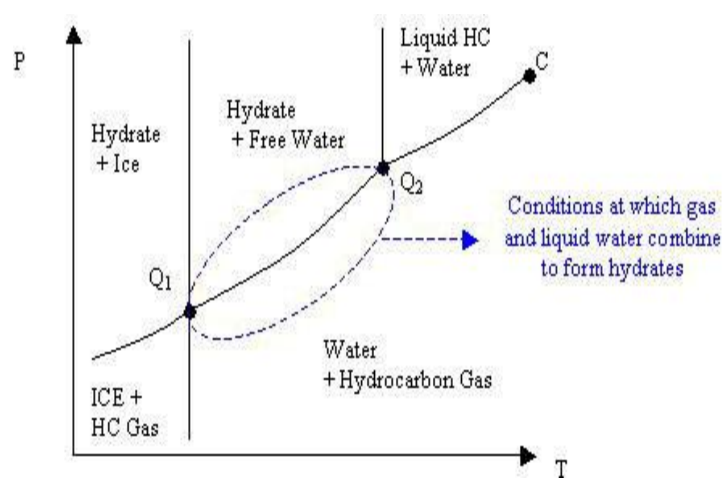

Figure 1 PHASE DIAGRAM FOR A WATER/HYDROCARBON (HC) SYSTEM

From the diagram, the behaviors of typical gas hydrates that can be identified are:

- Hydrate formation favored by low temperature and high pressure.
- Point C: The three phase critical point represents the condition where the liquid and gas hydrocarbon merge into a single hydrocarbon phase in equilibrium with liquid water.
- Point Q_2: The upper quadruple point, where four phases (liquid water, liquid hydrocarbon, gaseous hydrocarbon, and solid hydrate) are found in equilibrium.
- Point Q_1: The lower quadruple point typically occurs at 0 °C (ice freezing point) where four phases (ice, hydrate, liquid water, and hydrocarbon gas) are found in equilibrium.

The most important line in the diagram above is the segment Q_1Q_2 equilibrium line. The line represents the condition for a hydrates component to form and dissociate. When focusing in that zone, the diagram can be simplified like figure 2.

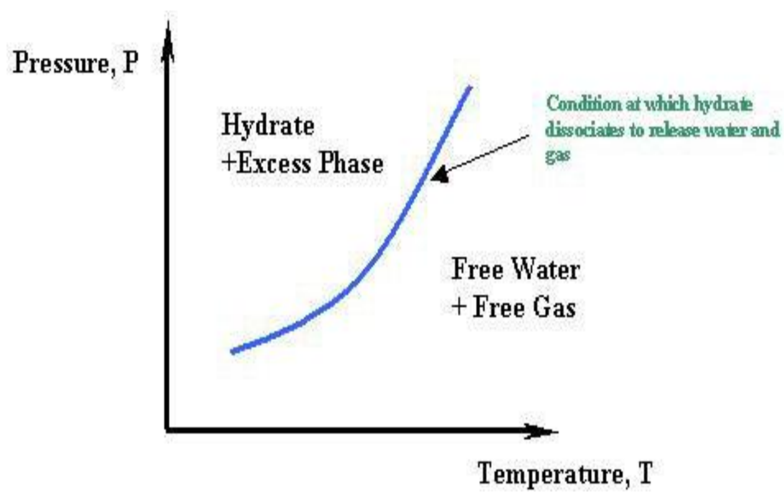

Figure 2 PHASE BEHAVIOR OF WATER/HYDROCARBON SYSTEM (Q1Q2 SEGMENT)

There are three methods to determine the phase behavior to create the formation and dissociation line. The first two methods of prediction were proposed by Katz known as Gas Gravity Method and the K_i-value Method. Both methods allow the calculation of P-T equilibrium curves for three phases; liquid water, hydrates and natural gas. However, these methods only provide qualitative understanding on the equilibrium line. The third method is Statistical Mechanics. It is recognize as the most accurate calculation.

2.1.2 SUMMARY ON RULES OF HYDRATION FORMATION:

In order for hydrates component to form between hydrocarbon gas and water molecules, certain rules need to be achieves [12]. The rules are:

1. Presence of water around the guest component.
2. Low temperature (below temperature of freezing point).
3. High operating pressure.
4. High velocity, agitation or pressure pulsations (preferable, can serve as formation catalyst)

For this project, the hydrates that will be focus on are carbon dioxide hydrates and propane hydrates. Study of both substance behaviors will be done thoroughly in order to fit the refrigeration process. From previous research, the carbon dioxide and propane phase behavior can be summarize in the below section. In this project, the concern is to design the refrigeration system so that the hydrates can operate in optimum condition without any difficulties encountered. Both hydrates will be tested out to run as a refrigerant in the system. Simulation of the designs will be compared to see the outcome. In order to accomplish the design, 2 major criteria must be taken into account; the latent heat of melting and the flowing condition of the slurry (so that it won't scrap and brush the heat exchanger or pipe) [5].

2.1.3 CO_2 PHASE BEHAVIOR

Carbon dioxide hydrates will be the primary concern in this project. Studies had shown that carbon dioxide hydrates is a suitable replacement of current refrigerant. CO_2 hydrates slurries is a two phase fluid compose of hydrates crystals in a liquid phase. Acting as a two phase fluid gives CO_2 hydrates a high latent heat of melting (high heat exchange rate) makes it preferable to be replaced as refrigerant. In addition, using co2 hydrates is said can lower the operating cost since the gas hydrates is easier and cheaper to produce using simple gas injection.

The phase behavior of CO_2 hydrates can be seen clearly in the P-T diagram below [10]. As shown, CO_2 hydrates equilibrium diagram fulfill the similarity with the typical hydrates compound phase behavior. The critical temperature is 284 K (11^oC), where beyond that temperature, the CO_2 hydrates compound will reach the region of instability. No hydrates compound between carbon dioxide and water will be formed beyond this temperature

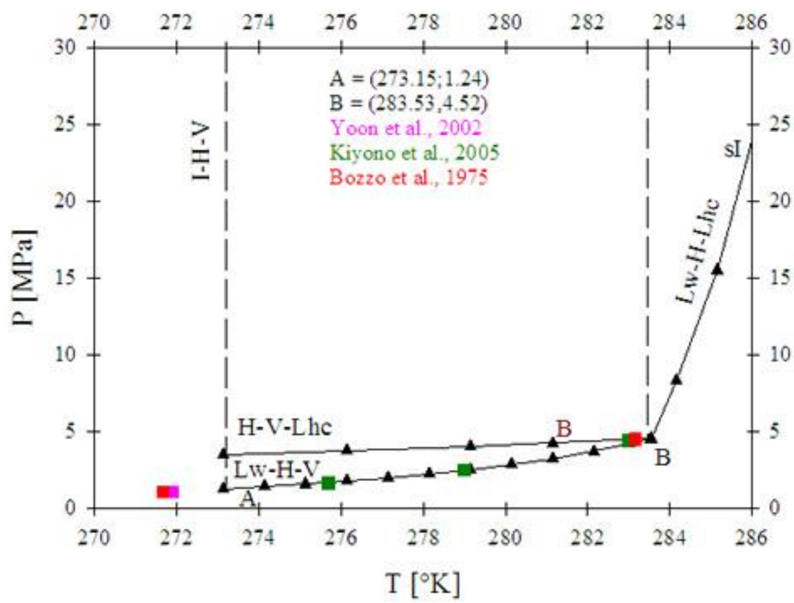

Figure 3 CO2 EQUILIBRIUM DIAGRAM

Notation: I = ice, Lw = liquid water, V = vapor or gas, and Lhc = liquid hydrocarbon (carbon dioxide).

2.1.4 PROPANE PHASE BEHAVIOR

Propane hydrates will also be tested out for this refrigeration system. This to identify the difference of effects towards the system using two different type of hydrates compound. The formation and dissociation method is similar, however the phase behavior, condition of formation and dissociation would be different. We can see on the phase diagram of propane hydrates [7].

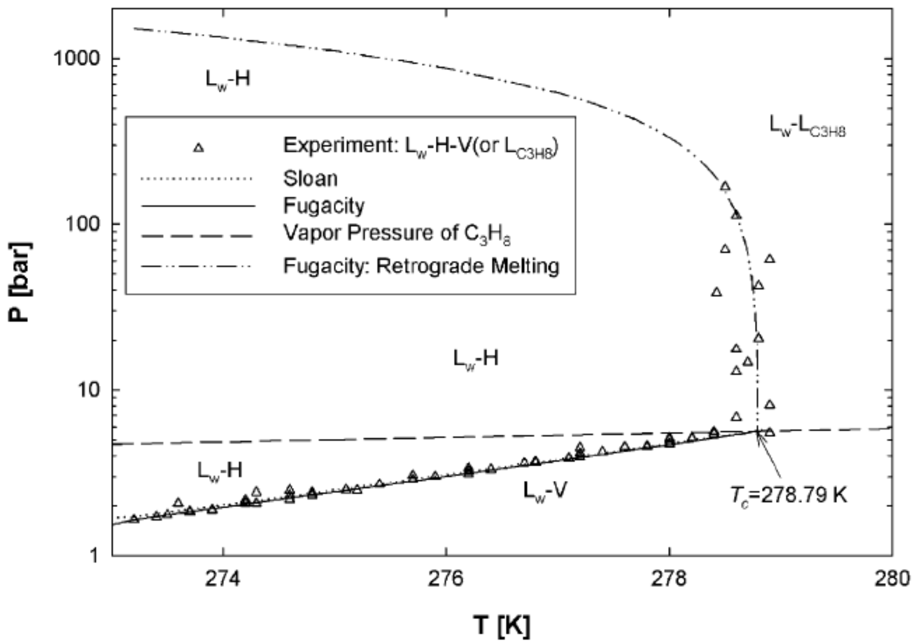

Figure 4 PROPANE EQUILIBRIUM DIAGRAM

2.1.5 TWO PHASE SUBSTANCE

Two phase substance had been identified to have much more advantages compared to single phase substance when acting as the secondary refrigerant. As for example, the cooling capacity of an ice slurry (two phase) is four to six times higher compare to conventional chiller water (single phase) depending on the ice fraction [9]. Also, the same refrigerant system that uses two phase refrigerant could reduce the pipe line diameter compared to single phase refrigerant.

In this project, hydrates would be use as the two phase refrigerant. The advantages of using hydrates compound as refrigerant are lower pumping power, smaller pipe size, excellent heat transfer properties, and good material compatibility compared to conventional single phase secondary refrigerant. In addition, the fluid cost would be cheaper. However, there are some disadvantages such as low critical temperature (example for CO_2 is 284K) and the availability of the component.

In order to be an efficient two phase fluid as a refrigerant, the compound must fulfill other kind of condition. [8]:

1. Pressure and temperature condition must adapt to the refrigeration application. For example, CO_2 hydrates compound is stable at 3MPa at temperature condition of 280K.
2. High fraction in solid particles (20%- 30%) containing large cold source and provide stable temperature levels; a solid fraction model was developed to estimate global amount of hydrates from the thermodynamic equilibrium condition.
3. Appropriate flowing conditions preserving efficient heat transfers.

2.2 HYDRATES AS SECONDARY REFRIGERANT

Hydrates substance is known to be suitable to act as refrigerant only if it use in a secondary loop. Using hydrates compound as a refrigerant is a good step in order to reduce the problem cause towards environment. According to the phase behavior, the hydrates compound could not form at atmospheric pressure and normal temperature. So, it is not suitable to use the compound as the primary refrigerant. However, current research had prove that hydrates compound could be fully utilize its potential if it being use as primary refrigerant in a single loop. The detail of the flow diagram and the solution to overcome the formation condition will be explained in next section.

Secondary refrigerant run as the refrigerant for secondary loop in the primary system in order to reduce the load of heat exchange in the primary system [3]. The secondary loop is installed in exchange of the evaporator in the primary system [9]. The diagram of the secondary loop can be seen in figure below.

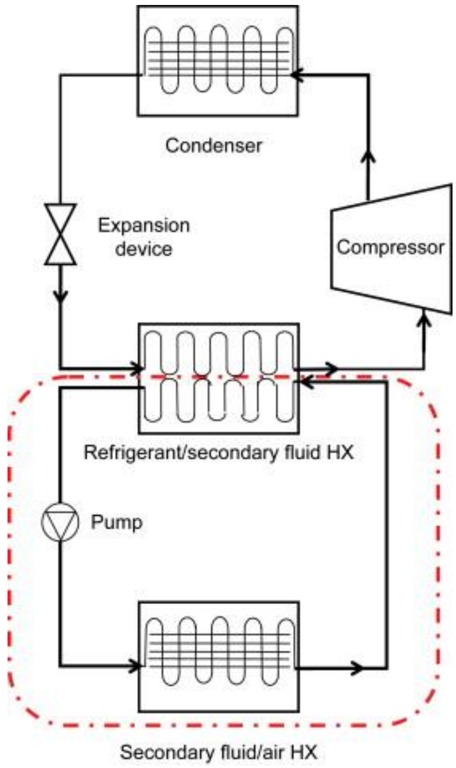

Figure 5 SECONDARY LOOP SYSTEM

In the secondary loop refrigeration system, we can use many other types of refrigerant besides the current refrigeration system that use HFC and CFC since the loop is isolated from the primary loop. So, we can use flammable substance, hazardous substance or in this case, hydrates compound as refrigerant. One of the advantages is it reduces the amount of refrigerant charge and refrigerant leakage. We can see that the secondary refrigeration system did not fully eliminate the usage of fluorocarbon; however it only reduces its usage in the primary loop. The system is however easy to maintain and service. In addition, by installing additional pump towards the secondary loop, the length of pipe used can be reduced. . Secondary refrigerant which is usually water reduces the exergy of the system due to the usage of circulation pump in the loop.

An experimental loop had been design in order to study the application of CO_2 hydrates towards refrigeration system [6]. The design is shown in figure below where most of the system is being put in the temperature controlled room in order to maintain the temperature below the critical temperature of CO_2 hydrates.

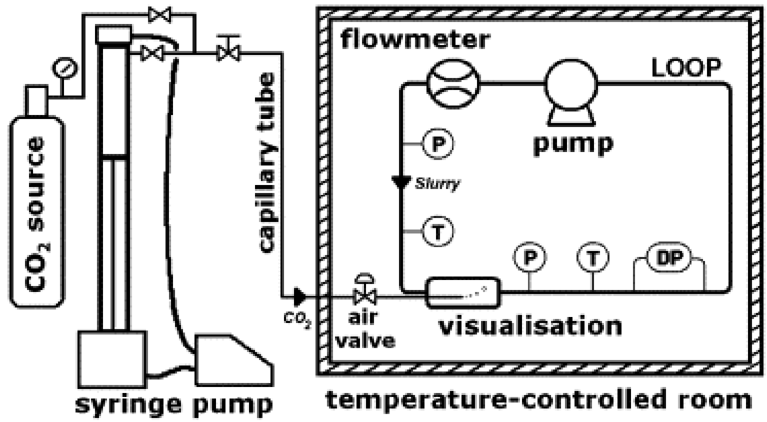

Figure 6 EXPERIMENTAL CO2 HYDRATES REFRIGERATION SYSTEM

The design consisted of stainless pipe and controlled CO_2 injection (using syringe pump, a regulation air-valve and a capillary tube). The flow is ensured by a micro pump (control the effective volume of the co2 source cylinder) and measured by the electronic volumetric flow meter. A differential pressure gauge is installed on a linear part of the circuit in order to measure pressure drops generated by the slurry. The design is also equip with thermocouple located at various position in order to observer the temperature around the loop. Maintaining the loop temperature below the critical temperature point of CO2 hydrates is important as the CO2 hydrates will go into unstable region above that temperature.

Although using hydrates as secondary refrigerants gives promising results towards reducing the usage of fluorocarbon, the hydrates capability in acting as refrigerant is not fully optimize. Having a high latent heat compared to typical refrigerant, hydrates compound could produce a better system of cooling if it being use as a main refrigerant in a single loop. In this project, calculations based on mass and energy of a hydrate single cooling system will be identified and prove to be practical.

2.3 HYDRATES COMPOUND AS MAIN REFRIGERANT

The potential of hydrates to be used as refrigerant is identified more than just as secondary refrigerant. Using the hydrates compound is more functional as main refrigerant instead of just using it as secondary cooling system. This is because of the high latent heat cause from formation and dissociation of the compound. Recent research had proved that hydrates can be use as main refrigerant. However, due to the low temperature required for formation, it is not suitable for the compound to be use alone (eg: pure CO_2 hydrates). From the latest research, the compound is mixed with typical fluorocarbon to increase its temperature of formation to room temperature. However, this is not what we want try to achieve. The purpose of this project is to totally eliminate the usage of fluorocarbon. Due to that, in this paper, the possibility of hydrates compound mixed with non-fluorocarbon compound (e.g.: tetrahydrofuran) will be identified. The process flow diagram for single loop hydrate based refrigerant is shown below [4]:

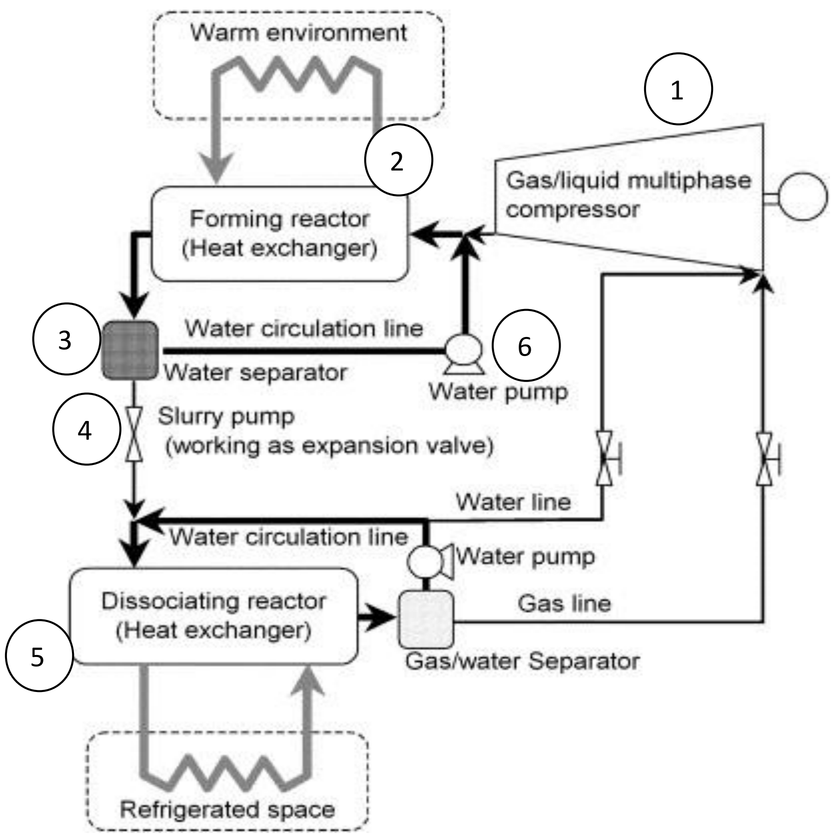

Figure 7 HYDRATE-BASED REFRIGERANT SYSTEM

The system consists of 6 major equipments. Number 1 is the compressor. The compressor used in this system is a multiphase compressor where guest gas and water are mixed and compressed. The number 2 equipment is the forming reactor which is basically the place where hydrates is formed at its temperature and pressure. Number 3 is the water separator for dewatering the slurries. It is basically the equipment to control the concentration of the slurries. Number 4 is the slurry pump act as the slurry conveyer. Number 5 is the dissociating reactor where the cooling process for the targeted space happens. Number 6 is the pump circulating water use to improve the fluidity of the hydrate slurry while flowing.

This system will be studied and be use for this project although the substance will be different. Changes towards the system will be made if necessary.

CHAPTER 3: METHODOLOGY

3.1 EVALUATE CLATHRATE HYDRATES BEHAVIOR

Before designing the refrigeration system, first, understanding the hydrates compound is critical. Literature review must be done base on previous research in order to get full understanding on the hydrates compound. Among the information that need to be fully understand are:

- Formation condition
- Phase behavior
- Enthalpy of dissociation

The formation condition of the hydrates compound must first be identified. The temperature and the pressure for the substance to form must be known. This is a priority to ensure that the system will be circulated with the hydrates compound throughout the system. In order to know the formation condition, the phase behavior of the compound will be studied. The phase behavior of the compound is clearly stated in the equilibrium diagram where information such as critical temperature, phase region and required temperature and pressure are there.

Data for the mixture compound that will be use can be obtained from past researches and experiments. As for now, the important variable needed is the hydration number of the substance, the temperature and pressure for forming the hydrates substance.

Another important thing that needs to be known is the cooling material to absorb the heat release from the formation process. This is critical since the forming temperature will not be near the room temperature. Choosing the suitable cooling material is important as it will determine the relevancy and possibility of this system.

3.2 DATA GATHERING

The project concerns on modeling the process of refrigeration using CO_2 – THF – Water mixture. All parameter involves in the calculation will be gather base on other research and literature. No experimental work is being done while modeling this project. In order to obtain the perfect data for this project, cross reference is important. This would bring us to the most accurate data obtain by experimental work.

The most important data needed is the formation chemical equation. The formation of CO_2 –THF-Water is represented by the chemical equation below, obtain from [6].

$$CO_2 + 0.5THF + 8.5H_2O \rightleftarrows CO_2 \times 0.5THF \times 8.5H_2O \ \{\text{theoretical mixed } CO_2\text{−THF hydrate}\}$$

From this data, we could determine the ratio needed for our feed streams. Based on the theoretical equation above, we could extract that the ratio needed to form the hydrates compound base on molar for CO_2: THF: Water is 2:1:17. This data would lead us throughout the whole mass and energy balance for this project.

For the resulting hydrates, the compositions of the hydrates in terms of moles contain 9% of CO_2 and 5% of THF. The composition is chosen based on the temperature and pressure needed to produce hydrates at around room temperature. Based on the graph pressure versus temperature, the suitable value to produce the hydrates is at 1.5MPa and 290K [16].

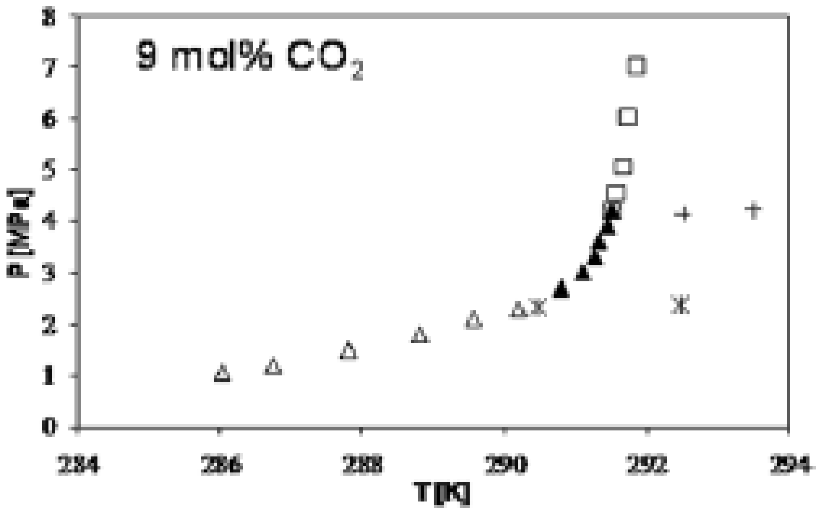

Figure 8 P-T DIAGRAM OF CO2-THF-H2O [16]

This temperature and pressure would be use in the system. Although we could not achieve the temperature desired (20-25 Celsius), 15°C would be good enough in order to make this system possible to run. Using this composition, a 15°C of cooling water is needed for supply in order to remove the heat produce from the formation. Removal of heat is necessary in order to encourage the formation.

Hydrate conversion could not be determined directly. Since the experimental work is not possible in this project, the hydrate conversion model will be use in order to know the mol produce with the given amount of feed. The conversion formula is given as follow [6].

$$n_{\mathrm{h}} = \frac{n_{\mathrm{CO_2,tot}} - \sigma_{\mathrm{CO_2,H_2O}} n_{\mathrm{H_2O,tot}} - \sigma_{\mathrm{CO_2,THF}} n_{\mathrm{THF,tot}} - \dfrac{P_{\mathrm{CO_2}}}{ZRT}\left(V_{\mathrm{tot}} - \dfrac{n_{\mathrm{H_2O,tot}} M_{\mathrm{eqH_2O}} + n_{\mathrm{THF,tot}} M_{\mathrm{eqTHF}}}{\rho_{\mathrm{liq}}}\right)}{1 - \dfrac{c}{a}\sigma_{\mathrm{CO_2,H_2O}} - \dfrac{b}{a}\sigma_{\mathrm{CO_2,THF}} + \dfrac{P_{\mathrm{CO_2}}}{ZRT}\left(\dfrac{\frac{c}{a} M_{\mathrm{eqH_2O}} + \frac{b}{a} M_{\mathrm{eqTHF}}}{\rho_{\mathrm{liq}}} - \dfrac{M_{\mathrm{h}}}{\rho_{\mathrm{h}}}\right)}$$

Based on this equation, the mass balance around the formation reaction would be possible. The parameter needed to complete the equation need to find from experimental work or literature review. Some of the parameters are thermodynamic parameters that can be obtained from various table and diagram.

For the feed stream, we would assume mass flow of THF as 100kg/hr. Using the mol ratio obtain from the theoretical chemical equation (mol ratio for CO_2: THF: Water = 2: 1: 17); we would have 90.2kg/hr for carbon dioxide and 306.34kg/hr for water stream.

Solubility of carbon dioxide is also needed. Base on the solubility table of carbon dioxide in water. We would get; Solubility of CO_2 in water = 0.1782g/100g H_2O []. For the solubility of CO2 in THF, there is no literature review or experimental work regarding this. So, we would make an assumption that CO2 does not solute in THF, which will get us; solubility of CO2 in THF = 0 [6].

Next, the data that need to be obtained is the density. Density of each substance at standard temperature and pressure can be obtained from physical properties; Density of CO2 = 1.98 kg/m3, density of water = 998 kg/m3, density of THF = 889.2 kg/m^3. Density of each substance at operating pressure is also needed (1.5Mpa). This would give us density for; CO2 = 1068 kg/m3 (liquid), H2O = 1004 kg/m3. For density of THF at 1.5Mpa, the density would be no much difference at the standard state. The density could be obtained from the table below.

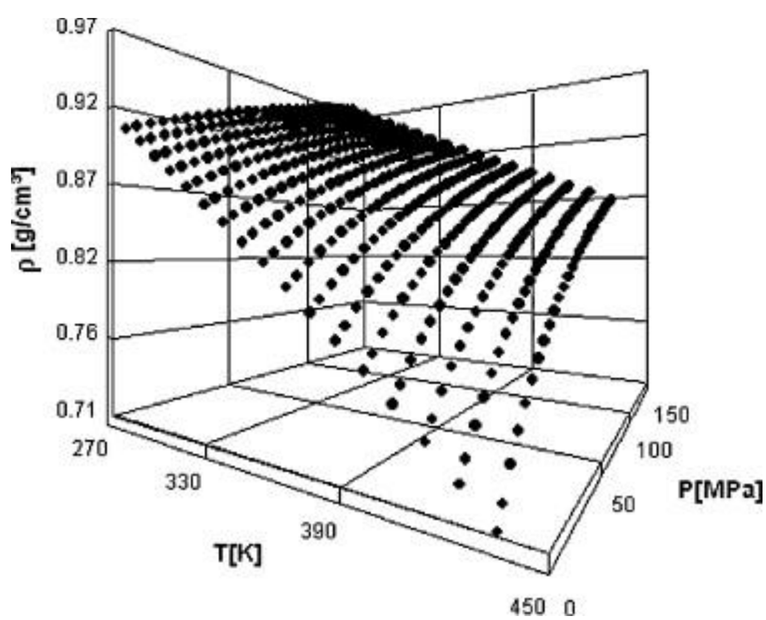

Figure 9 DENSITY OF THF

Based on the graph, we could see that the density of THF at 1.5Mpa and 290K is still around 890kg/m3.

Molar mass is important in any mass balance process. Due to that, each substance molar mass must be obtained in order to complete the parameter needed. Based on the physical properties of each substance, we get; Molar mass of water = 18 kg/kmol, molar mass of CO2 = 44 kg/kmol, molar mass of THF = 72.11kg/kmol.

From the hydrate conversion formula, the stoichiometry value is also needed. Based on the theoretical chemical equation and assume that the hydrates is structure II hydrates, we could get the value; a= 16, b= 8, c= 136.

As stated previously, we assume that CO2 does not solute in THF. This will lead us to the next assumption which is the density of THF-CO2 is equal to density of THF alone. From literature, we get that density of CO2-water is 1000kg/m3. This value is important in order to calculate the value of liquid density, ρ_{liq}. The equation is given below [6]:

$$\rho_{\mathrm{liq}} = \frac{1}{\frac{(1 - wt_{\mathrm{THF}})}{\rho_{\mathrm{CO_2-H_2O}}} + \frac{wt_{\mathrm{THF}}}{\rho_{\mathrm{CO_2-THF}}}}$$

The last parameter needed in order to calculate the formation of hydrate is the density of the hydrates and the molar weight of the hydrate. From literature review [6], we could get; ρ_h = 1195.89 kg/m3 and M_h = 0.233 kg/kmol.

3.3 CONCEPTUAL DESIGN

Next, study on the conceptual design of the refrigeration system will be made. Among the tasks that need to be done in this part is:

- Study on previous refrigeration cycle
- Identify the basis of design condition

Previous design is important as it acts as the basis of the designing process. The system will be fully analyzed and modifications that need to be done will be taken note. For this project, the refrigeration system will be study and the system will be modified base on the phase behavior of the hydrates used. The system identified in the previous research will be fully utilized in modification of the current refrigeration system.

The design that will be use throughout the project will be taken from previous research. No additional equipment will be installed since the priority is to calculate the COP of the system.

By using the system design, the mass and energy balance will be calculated. A few concerns are notice regarding this design. The use of multiphase compressor would produce a complex calculation regarding the work load. However, we could reduce the complexity by reducing the pressure ratio of inlet and outlet.

3.4 CALCULATION

For this project, manual calculation will be done. No simulation software will be use as for now since there are limitations towards hydrates compound. Most of the simulation software does not provide a precise data regarding the hydrates compound. Due to that, manual calculation is chosen.

The first and important calculations that need to be done are the mass and energy balance. Up to this date, the project is currently undergoing this process. Data regarding the compound (CO_2 hydrates + tetrahydrofuran) must be obtained from previous researches and experiments. This data will be used to calculate the total energy and mass balance of this system. The mass and energy balance is crucial since it will help in determining the coefficient of performance for this system.

Along that, calculation for the power of multiphase compressor and pump will be done. This is also important as these results will help to improve the efficiency of the system and cost to run the system. More detail calculation will be included in the next report since this stage is currently in progress.

3.5 GANTT CHART

Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Project Work																				
#Data gathering																				
#Calculation																				
#Improvement of system																				
Submission of Progress Report 1																				
Submission of Progress Report 2																				
Poster/Pre-EDX																				
EDX																				
Submission of Final Report																				
Final Oral Presentation																				
Submission of Hardbound Copies																				

Figure 10 PROJECT'S GANTT CHART

The Gantt chart of this project is shown at the table above. Currently, the project is still on the right pace. Calculation part will be done until completion before improvement of the system is made.

CHAPTER 4: RESULT AND DISCUSSION

Calculation include in this project is done manually by using Microsoft Excel software. Using the data obtain from literature review and process design made earlier, the mass and energy balance is summarize in table below.

4.1 DESIGN 1: NORMAL REFRIGERATION SYSTEM.

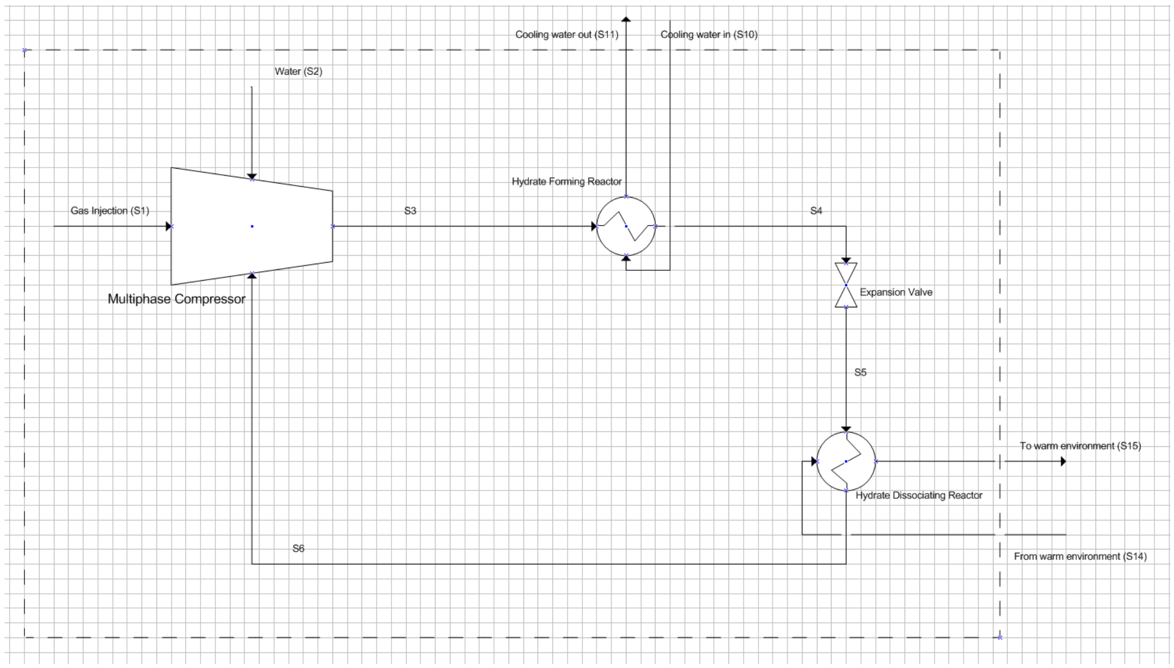

Figure 11 PROCESS DESIGN 1

	S1	S2	S3	S4	S5
Upstream	Gas Injector	Water Supply	Compressor	Forming Reactor	Expansion valve
Downstream	Compressor	Compressor	Forming Reactor	Expansion Valve	Dissociating Reactor
T(C)	25.000	25.000	25.000	15.000	10.800
P(bar)	1.000	1.000	15.000	15.000	0.030
Massflow/Composition (Kg/hr)					
THF	72.110		72.110		
CO_2	88.000		88.000		
Water		306.000	306.000	449.310	451.662

Hydrates		0.000		16.800	14.448
Total	160.110	306.000	466.110	466.110	466.110

	S6	S10	S11	S14	S15
Upstream	Dissociating Reactor	Water Supply	Forming Reactor	Water Supply	Dissociating Reactor
Downstream	Compressor	Forming Reactor	Water Supply	Dissociating Reactor	Water Supply
T(C)	10.800	15.000	14.000	8.680	7.000
P(bar)	0.030	15.000	15.000	0.030	0.030
Massflow/Composition (Kg/hr)					
THF	72.11				
CO_2	88				
Water	306.000	1033.000	1033.000	1000.000	1000.000
Hydrates					
Total	466.110	1033.000	1033.000	1000.000	1000.000

Table 1 Design 1 Stream Summary

4.2 DETAIL CALCULATION FOR DESIGN 1

Feed

Using the mol ratio basis for THF: CO_2: Water which is 1:2:17, we take the flow rate for stream 1 with 72.11 kg/hr THF and 88 kg/hr CO_2. For stream 2, the flow rate of water is 306 kg/hr. the temperature and pressure for both stream is set at room condition which is 25^{o}C and 1 bar.

Compressor

The compressor is used to pressurize the component to its forming condition. Earlier, the optimum forming pressure and temperature has been identify as 1.5MPa (15 bar) and 15^{o}C. In order to pressurize the component to 15 bar, certain amount of power is needed. The power value is important in order to calculate the total work consumption for the whole system.

To calculate the work produce by the compressor equation can be obtain from literature review. The pressure ratio for compressor in this system is 15 (P2/P1), which is not so high. Calculation of compressor work is divided into 2 (because the compressor used is multiphase compressor); work consumes by gas and work consumes by water + guest component. Before the calculation is made, certain parameters based on the type of compressor must be known. For this project, the compressor has the efficiency as below [4]:

Adiabatic efficiency	75%
Motor efficiency	94%
Inverter efficiency	96%
Efficiency for pumping liquids	85%

The other parameter that needs to be known is the specific heat, mass flow and density. The data is tabulated in table below:

Data	Value	Condition
Specific heat of water(KJ/Kg)	104.86	1bar
Specific heat of CO_2 (KJ/Kg)	257.7	1500 bar
	234	1 bar
Mass flow THF (Kg/hr)	72.11	
Mass flow CO_2 (Kg/hr)	88	
Mass flow of water (Kg/hr)	306	
Density of water Kg/m^3	998	STP
Density of THF kg/m^3	889.2	STP

Table 2 Compressor Work Parameters

To calculate work consume by gas, the equation below is used [4]:

$$\dot{W}_g = \frac{1}{\eta_I}\frac{1}{\eta_M}\frac{1}{\eta_c}\dot{m}_g \times \sum_{i=1}^{n}\left[h_g\left(T''_{(i+1)}, P_{(i+1)}\right) - h_g\left(T_{(i)}, P_{(i)}\right)\right],$$

By plugging in the number into the equation we obtain the work consume by gas which is 3081.56 KJ/hr.

To calculate works consume by water + gas component, the equation below is used [4]:

$$\dot{W}_{\mathrm{w}} + \dot{W}_{\mathrm{gl}} = \frac{1}{\eta_{\mathrm{p}}}\left(\frac{\dot{m}_{\mathrm{w}}}{\rho_{\mathrm{w}}} + \frac{\dot{m}_{\mathrm{gl}}}{\rho_{\mathrm{gl}}}\right)(P_2 - P_1),$$

By plugging in the number into the equation we obtain the work consume by liquid + guest component which is 638.58 KJ/hr. By adding up both works, we obtain the total work consume by the compressor which is 3720.14 KJ/hr.

<u>Hydrate Forming Reactor</u>

At the hydrate forming reactor, the hydrates is form by cooling the 15 bar component streams from 25^{o}C to 15^{o}C. At that temperature and pressure, hydrate started to form. In order to know the mass flow of the hydrate formed, certain parameters need to be known. Most of the parameters are obtained from internet (eg: density, molar mass and solubility). Specific parameters is obtain from previous research and study based on experiments. The parameters are tabulated in table below:

Data	Value
Mass flow THF (Kg/hr)	72.11
Mass flow CO_2 (Kg/hr)	88
Mass flow of Water (Kg/hr)	306
Mol CO_2	2
Mol of Water	17
Mol of THF	1
Solubility of CO_2 in THF (g/100g H2O)	0
Solubility of CO_2 in water (g/100g H2O)	0.1782
Pressure of CO_2	1500
Constant R	8.314
Temperature (F)	298
Volume total (m3)	46

Density of CO_2	1.98
	1068
Density of water Kg/m^3	998
	1004
Density of THF kg/m^3	889.2
Density of CO_2 -THF(Kg/m3)	889.2
Density of CO_2 -Water(Kg/m3)	1000
Molar Mass of water (Kg/kmol)	18
Molar Mass of CO_2 (Kg/hr)	44
Molar Mass of THF (Kg/kmol)	72.11
Weight fraction of THF	0.15
P_{liq}	975.68
Constant A	16
Constant B	8
Constant C	136
P_h (Kg/m3)	1195.89
M_h (Kg/kmol)	0.233

Table 3 Hydrate Forming Parameters

Mass flow rate of hydrate formed could not be identify or calculated in precise. Only experimenting would able to get the exact data. However, based on previous research [6], theoretical molar flow rate formula has been develop in order to estimate the molar flow produce given the feed composition and formation condition. By plugging in the parameter in the equation below, we obtained the molar flow rate of hydrates formed which is 72.06 mol/hr.

$$n_{\mathrm{h}} = \frac{n_{\mathrm{CO_2,tot}} - \sigma_{\mathrm{CO_2,H_2O}} n_{\mathrm{H_2O,tot}} - \sigma_{\mathrm{CO_2,THF}} n_{\mathrm{THF,tot}} - \dfrac{P_{\mathrm{CO_2}}}{ZRT}\left(V_{\mathrm{tot}} - \dfrac{n_{\mathrm{H_2O,tot}} M_{\mathrm{eqH_2O}} + n_{\mathrm{THF,tot}} M_{\mathrm{eqTHF}}}{\rho_{\mathrm{liq}}}\right)}{1 - \dfrac{c}{a}\sigma_{\mathrm{CO_2,H_2O}} - \dfrac{b}{a}\sigma_{\mathrm{CO_2,THF}} + \dfrac{P_{\mathrm{CO_2}}}{ZRT}\left(\dfrac{\frac{c}{a} M_{\mathrm{eqH_2O}} + \frac{b}{a} M_{\mathrm{eqTHF}}}{\rho_{\mathrm{liq}}} - \dfrac{M_{\mathrm{h}}}{\rho_{\mathrm{h}}}\right)}$$

From the mol flow obtain we can find the mass flow rate of hydrate in stream 4 by multiplying the mol flow rate with molar mass. The value obtain is 16.8 kg/hr. by assuming the mass is conserve, we may obtain the flow rate of water which is 449.31 kg/hr.

In the formation reactor, there is work consume which is the work done by the cooling water to cool down the component to 15^{o}C. In order to calculate the value, we need to identify the heat of formation for this substance. From literature review, CO_2-THF-H_2O substance has the heat of formation around 60 Kj/kmol. By multiplying the value with molar flow rate, we could get the work consume by the substance in order to cool down which is 4323.661 KJ/hr.

To calculate the mass flow rate of needed cooling water, we need to target the cooling water return temperature. Since we r using a low temperature cooling water, which is 15^{o}C we could not have big temperature difference. So, temperature difference around 1^{o}C is chosen. By using heat formula which is:

$$Q = mCp\Delta T$$

The value obtain for mass flow rate of water is 1033 Kg/hr for both stream 10 and stream 11.

Expansion Valve

Expansion valve is used mainly to reduce the pressure of the substance. Having 15 bar of pressure would be inconvenient, as higher pressure would increase the cost of piping and dissociation process. Thus, expansion valve is used to reduce the pressure from 15 bar to 0.03 bar. To determine the working medium temperature, we interpolate the phase equilibrium graph. Based on the graph we obtain the value of temperature is 10.8^{o}C. However, by reducing the pressure, the hydrate is likely to reduce in molar flow rate. There is no accurate way to calculate the loss of hydrate since there is no experimental work involve. Due to that, we use the ratio of hydrate loss base on previous research [4] using hydrate as refrigerant. The loss is approximately 14%. By multiplying 86% to the mass in, we get the mass out of expansion valve which is 14.45 Kg/hr. Technically, the hydrate will loss towards the surrounding. However in this project, we assume there is now refrigerant loss throughout the whole system. Thus we assume the hydrate loss is converted back into water. This make the mass flow of water is 451.662 Kg/hr.

Dissociation Reactor

Dissociation is where the cooling process happens. When the hydrate is dissociated to its original compound, it would produce work of cooling. From literature review, we could obtain the heat of dissociation for CO2-THF-Water compound, which is 113.66 Kj/kmol. In order to calculate the work produce by the compound, it is just multiplying the heat of dissociation and molar flow rate of the hydrate. By doing so, we could obtain the value of work which is 7043.792 Kj/hr.

In order to see clearly the cooling process, we set the target temperature of cooling $7^{o}C$. By running the cooling water with 200kg/hr of mass flow rate, we need $8.68^{o}C$ (using the same heat equation: Q=mCpdT). We could see that the cooling process is not practical. However in order to identify the efficiency of the system, we need to calculate the COP (coefficient of performance).

Calculation of COP

COP is the best way in order to determine the performance of a cooling system. In order for a cooling system to have a good efficiency, the COP value must not less than 0.8. If the value of COP is less than 0.8, the system is considered not practical to be used. The calculation of COP is using the below equation:

$$COP = \frac{Work\,\mathrm{Pr}oduce}{Work\,Consume}$$

Work produce of the system is only from the dissociation reactor. Converting 7043.792 Kj/hr to KW, we obtain the value of power is 1.95 KW.

For work consume, we have to work that need to be considered; work consume by compressor and work consume by cooling water at formation reactor. By adding 4323.661 Kj/hr and 3720 Kj/hr, we obtain the power consume is 2.234 KW.

By plugging in the value into the equation of COP, we obtain the COP value which is 0.87. The system is clearly possible to run, although it has the minimum value of COP for efficient system. In order to perform better cooling, certain modification must be made into the design. The detail of the modification is discussed in next topic.

4.3 DESIGN 2: WITH WATER RECIRCULATION LOOP.

For the 2nd design, the process flow design and material stream is shown below:

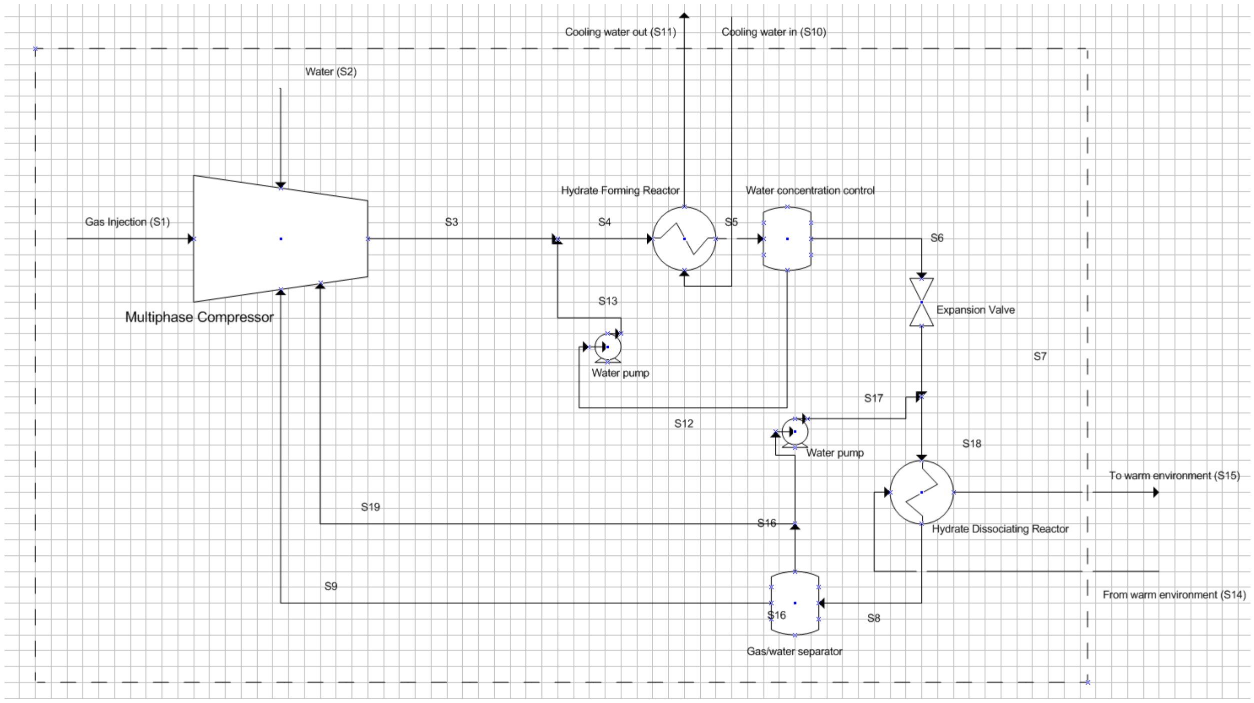

Figure 12 PROCESS DESIGN 2

	S1	S2	S3	S4	S5
Upstream	Gas Injector	Water Supply	Compressor	Mixer	Forming Reactor
Downstream	Compressor	Compressor	Mixer	Forming Reactor	Water conc. Control
T(C)	25.000	25.000	25.000	25.000	15.000
P(bar)	1.000	1.000	15.000	15.000	15.000
Massflow/Composition (Kg/hr)					
THF	72.110		72.110	72.110	

CO_2	88.000		88.000	88.000	
Water		306.000	306.000	5385.600	5266.040
Hydrates					279.670
Total	160.110	306.000	466.110	5545.710	5545.710

	S6	S7	S8	S9	S10
Upstream	Water conc. Control	Expansion Valve	Dissociating Reactor	Separator	Water Supply
Downstream	Expansion Valve	Mixer	Separator	Compressor	Forming Reactor
T(C)	15.000	10.800	10.800	10.800	15.000
P(bar)	15.000	0.030	0.030	0.030	0.030
Massflow/Composition (Kg/hr)					
THF			72.110	72.110	
CO_2			88.000	88.000	
Water	186.440	225.594	376.192		18414.760
Hydrates	279.670	240.516			
Total	466.110	466.110	536.302	160.110	18414.760

	S11	S12	S13	S14	S15
Upstream	Forming Reactor	Water conc. Control	Pump 1	Water Supply	Dissociating Reactor
Downstream	Water Supply	Pump 1	Mixer	Dissociating Reactor	Water Supply
T(C)	14.000	15.000	15.000	37.900	10.000
P(bar)	0.030	15.000	15.000	15.000	15.000
Massflow/Composition (Kg/hr)					
THF					
CO_2					
Water	18414.760	5079.600	5079.600	1000.000	1000.000
Hydrates					
Total	18414.760	5079.600	5079.600	1000.000	1000.000

	S16	S17	S18	S19
Upstream	Separator	Pump 2	Mixer	Separator
Downstream	Pump 2	Mixer	Dissociating Reactor	Compressor
T(C)	10.800	10.800	10.800	10.800
P(bar)	0.030	0.030	0.030	0.030
Massflow/Composition (Kg/hr)				
THF				
CO_2				
Water	150.598	150.598	376.192	306.000
Hydrates			240.516	
Total	150.598	150.598	616.708	306.000

Table 4 Design 2 Stream Summary

4.4 DETAIL CALCULATION OF DESIGN 2

For this design, there is 2 additional equipment and 2 pumps added. The calculation on compressor, formation reactor, expansion valve and dissociation reactor is similar to the first design, although the value is different. Detail calculation will be shown regarding the 2 newly add equipment which is the water concentration control and water separator.

Water concentration control

Water concentration main purpose is to control the mass fraction of the hydrate. This is possible by adding a loop of water circulation. For this system, we try to maintain the mass fraction of the hydrate to be 0.6. Previous design shows us that without water circulation, the mass fraction of hydrate is 0.03. The expected hydrate mass flow rate can be calculated by multiplying the mass fraction with total flow rate. This would give us value of hydrate mass flow rate is 279.67 Kg/hr. Having this flow rate, we must estimate how much water flow rate need to be circulate in the loop in order to produce 279.67 Kg/hr. By calculating the ratio of expected hydrate flow rate with current flow rate we obtain 16.6. So, the amount of water needed for circulation loop is 1660% more than the feed water input. By multiplying it, we get 5079.6 Kg/hr of water. This amount of water would enhance the formation of hydrate, thus increasing the flow rate in order to achieve the mass fraction of hydrate 0.6.

Water Separator

Before the stream enters the dissociation reactor, the stream must be added some amount of water. In order to get the output of the dissociation having same composition as the compressor inlet, the ratio of hydrate and water must be similar with the ratio of gas and water input. The ratio is calculated to be around 0.35. For stream 7 to have ratio of 0.35, 150.598 Kg/hr of water must be added. After the dissociation process is complete, the stream enters the separator to separate water and gas content. 150.598 Kg/hr of water is recycled back to dissociation reactor and 306 Kg/hr of water is send back to the compressor. CO_2 and THF are also being sent back to the compressor.

Pump Work

For water circulation and water separation process, pump is added. Pump consumes work, thus contributing towards the COP value. For water pump calculation, the formula used is as below:

$$P_h = q \rho g h / (3.6\ 10^6)$$

Where

P_h = power (kW)

q = flow capacity (m^3/h)

ρ = density of fluid (kg/m^3)

g = gravity (9.81 m/s^2)

h = differential head (m)

The differential head or friction head loss could not be calculated since detail of pipe such as length and diameter does not include in this project. Thus, we assume the differential head to be 5m. Since both pumps are pumping water, the density of the fluid is taken as 1000 kg/m^3 (water density).

i) Pump 1

For pump 1, the flow capacity is 18.414 m^3/hr. Plugging in the value into the equation gives us the power of the pump which is 0.42 KW.

ii) Pump 2

For pump 2, the flow capacity is 1 m^3/hr. Putting the value inside the equation will tell us the power of pump which is 0.02 KW.

Thus, total work consume by both pump is 0.44 KW. Getting this value, we can calculate the COP for this system.

<u>Calculation of COP</u>

For this design, the COP is expected to be higher than the previous design. The work produce in this system is 32.54 KW. The work consume is total of work done by compressor, cooling water in formation reactor and pump, giving the value of 22.88 KW. Putting both values in the COP formula, we would obtain the COP of the system which is 1.42. This system gives much better performance. We can see that from stream 14 and 15. By using 1000 Kg/hr of water flow rate, we obtain 27.9 temperature differences.

4.5 REVIEW ON THE COP VALUE

From the calculation above, we already obtain the value of COP for both design 1 and design 2 which are 0.87 and 1.42. In comparison, it is proven that having the concentration of hydrate controlled in the stream would enhance the cooling process. Based on literature review, it is shown that the value of minimum COP needed is 0.8. Thus, both of the designs have passed the requirement, making it possible to be run. To compare to other system that use fluorocarbon as part of the substance [4], we can simply compare the COP value. For system that uses hydrate + HFC [4], the value of COP is determined to be 8.0. Typical refrigeration system non-hydrate has the COP of average 3.0. Using COP as comparison, we could see that hydrate + THF system produce lesser COP. Although this system would eliminate all environmental issue, it gives less efficient cooling process. Modification must be made in order to increase its COP, thus making this system possible to compete with current refrigeration system.

CHAPTER 5: CONCLUSION

Previous research had shown that clathrate hydrates compound is suitable to be use as refrigerant. In fact, using the hydrates compound as the refrigerant would greatly reduce the environmental issues that the world is currently going. However, the substance use in the hydrates mixture still contains fluorocarbon properties that we hope to fully eliminate. Using CO2 + tetrahydrofuran would eliminate this problem. Producing a commercialize refrigeration system using hydrates as refrigerant would hopefully could eliminate the usage of CFC, HFC and other environmental threatening substance. Optimizing the hydrate condition to work as the refrigerant would reduce the cost to operate and install the equipment thus creating a new revolution towards refrigeration industry. As the calculation had been done, the COP of the system shows that this system is possible to be use as replacement of current system. Having COP at 0.87 and 1.42, this system is proven it could reduce the environmental issues while having considerable efficiency of a refrigeration system.

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