CERTIFICATION OF APPROVAL

Phase Separation of Methane and CO_2 using Pressure and Temperature Manipulation

by

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Approved by,

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CERTIFICATION OF ORIGINALITY

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

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MUNEER AHMAD B. NAZIR DEEN

ABSTRACT

This report constitutes of, as the title for this project suggests, separation of carbon dioxide and methane by manipulating temperature and pressure. The objectives of this project are mainly; to simulate both mixture in a separator and observe its vapor and solid compositions after separated, secondly; to study the possibilities of forming gas hydrate for methane and carbon dioxide to establish equilibrium conditions third; study the effect of temperature and pressure governing the formation of gas and hydrate and finally to compared and discuss the results obtained and recommend any improvement. The methods of separation in the industry are mainly adsorption, membrane and temperature and pressure method. The scope of study in this project is to separate carbon dioxide and methane by just manipulating temperature and pressure. Focus of the project will be on different types of fluid packages and phase equilibrium. The outcome expected from this project is to see the ability of temperature and pressure work to separate carbon dioxide into solid form and methane into vapor form.

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Yours Sincerely,
Muneer Ahmad b. Nazir Deen

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Natural gas is a naturally occurring gas mixture of light hydrocarbons consisting primarily of methane but including significant quantities of methane, ethane, butane, propane, carbon dioxide, nitrogen, helium and hydrogen sulfide. It is found in oil fields and natural gas fields and coal beds. Extensive processing needs to be carried out before the natural gas can be used as a fuel. Almost all materials must be removed to obtain methane.

Natural gas is clean burning and emits lower levels of potentially harmful byproducts into the air. We require energy constantly, to heat our homes, cook our food and generate our electricity. It is this need for energy that has elevated natural gas to such a level of importance in our society and in our lives.

Carbon dioxide, CO_2 is a chemical compound composed of two oxygen atoms covalently bonded to a single carbon atom. Joseph Black, a Scottish chemist and physician first identified carbon dioxide n the 1750s. At room temperature carbon dioxide is an odorless, colorless gas which is faintly acidic and non-flammable.

Although carbon dioxide mainly consists in the gaseous form, it also has a solid and a liquid form. Liquid carbon dioxide mainly exists when carbon dioxide is dissolved in water. Carbon dioxide is only water-soluble, when pressure is maintained. After pressure drops the carbon dioxide gas will try to escape into the air. This event is characterized by the CO_2 bubbles forming into water [9].

Property	Value
Molecular weight	44.01
Specific gravity	1.53 at 21 °C
Critical density	468 kg/m^3
Stability	High
Melting point	Temperature < -78 °C
Boiling point	Pressure < 415.8 kPa
Solubility in water	0.9 vol/vol at 20 °C

Table 1: Properties of CO_2 [Source: http://www.lenntech.com/carbon-dioxide.htm]

Carbon dioxide does not exist in liquid form at atmospheric pressure at any temperature. The pressure-temperature phase diagram of CO_2 shows that liquid carbon dioxide at 20°C requires a pressure at 30 atm. The lowest pressure at which liquid CO_2 exist is at the triple point, namely 5.11 atm at -56.6 °C
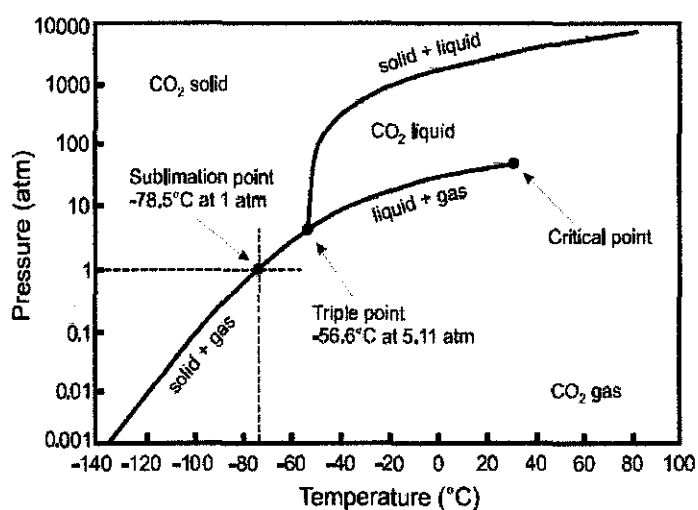
Figure 1: Pressure-Temperature Phase diagram of CO_2 (Source: Prof Shakhashiri)

There are three principal commercial sources for carbon dioxide. High-purity carbon dioxide is produced from some wells. The gas is obtained as a byproduct of chemical manufacture, as in the fermentation of grain to make alcohol and the burning of limestone to make lime. It is also manufactured directly by burning carbonaceous fuels. For commercial use it is available as a liquid under high pressure in steel cylinders, as a low-temperature liquid at lower pressures, and as the solid dry ice.

Carbon dioxide has varied commercial uses. Its greatest use as a chemical is in the production of carbonated beverages such as soda water. Formed by the action of yeast or baking powder, carbon dioxide causes the rising of bread dough. The compound is also used in water softening, in the manufacture of aspirin and lead paint pigments, and in the Solvay process for the preparation of sodium carbonate. In some fire extinguishers carbon dioxide is expelled through a nozzle and settles on the flame, smothering it. It also has numerous nonchemical uses. It is used as a pressurizing medium and propellant, e.g. in aerosol cans of food, in fire extinguishers, in target pistols, and for inflating life rafts. Because it is relatively inert, it is used to provide a nonreactive atmosphere, e.g. for packaging foods, such as coffee, that can be spoiled by oxidation during storage. Solid carbon dioxide, known as dry ice, is used as a refrigerating agent.

Methane is a colorless, odorless gas with a wide distribution in nature. It is the principal component of natural gas, a mixture containing about 75% CH_4, 15% ethane (C_2H_6), and 5% other hydrocarbons, such as propane (C_3H_8) and butane (C_4H_{10}). It was first discovered by Alessandro Volta in 1776 that noticed bubbles rising from a pond and found that these bubbles could be ignited with a naked flame. At room temperature, methane is a gas less dense than air. It melts at -183°C and boils at -164 °C. It is not very soluble in water. Methane is combustible, and mixtures of about 5 to 15 percent in air are explosive [10].

Natural sources of methane are dominated by wetlands. Where soils are waterlogged and oxygen concentrations are low or zero, a group of microorganisms called methanogens may produce large amounts of methane as they respire carbon dioxide to derive energy.

Wetland methane emissions are thought to comprise around 80 percent of the total natural methane source, with methane release from termites, methane hydrates (frozen deposits of methane), and the emission from the oceans also being important. Total annual methane emissions from natural sources are estimated to be around 250 million tones. A paper by Frank Keppler in 2006 suggested that vegetation may also be an important natural source of methane. His study indicated that up to a third of natural methane emissions may actually arise from this source. If true, then the current estimate for wetland methane emissions is likely to be an overestimate, but the true magnitude of the newly-discovered vegetation source is still uncertain.

1.2 Background

Field development planning is one of the core business processes in the upstream oil and gas industry. Before a discovered field can be developed and its hydrocarbon produced, proper evaluation and planning of the subsurface reservoirs and surface facilities are necessary to ensure that the field development plan is not only economical to undertake, but also flexible enough to cater for any deviation from the original plan during implementation as a result of inherent uncertainties in the reservoirs over the production life span of the field.

One of the biggest issues in the oil and gas industry today in Malaysia's field is the presence of high carbon dioxide, CO_2 in its reservoirs. In a study recently made (Dr. Nasir and A.Rahman), the average of CO_2 in the fields of peninsular Malaysia is between 28% and 66%. Whereas in the East of Malaysia the highest contain of CO_2 ever achieved is 87%. Since the content level of CO_2 is beyond the gas specification required for gas sales, therefore the gas will be process and pre-treated to obtain minimum contain of CO_2 [13]

High CO_2 in hydrocarbon faces many challenges and issues. Some of them are economic issues in developing optimal solution to meet gas demand. For CO_2 separation, the technology is not fully ready to deal with very high CO_2 content coupled with very high flow rate and the CO_2 transportation by pipeline are also high in cost. Besides that, CO_2 disposal is another issue because it is important to meet the Enhance Oil Recovery (EOR) requirement that has been fixed.

In the past few years the price for natural gas used as fuel and chemical feedstock has been steadily increasing. The desire to sell the increasing amount of natural gas has lead to some extent to the exploration of new and forbidding areas for additional supplies of gas. However some newer fields contain gas having only 25% to 40% methane. The remaining mixture of acid gas that is CO_2 has up to 60% to 75%. CO_2 acts as diluents that lower the heat content of the natural gas to the point that it may never burn [1].

In addition, in the presence of water, these components render the gas very corrosive in nature. It is desirable to remove acid gases to produce a sweet and concentrated methane gas. Separation of carbon dioxide and methane is not an ease separation. Basically the process can be separated into four classes;

      i.   Absorption by physical solvents

     ii.   Absorption by chemical solvents

    iii.   Adsorption by solids and;

    iv.   Distillation.

The specification for pipeline quality gas typically calls for a maximum of 2% to 4% carbon dioxide and specification for an LNG plant typically require less than 100ppm of carbon dioxide [1].

1.3 Objective and Scope of Study

The main objective highlighted in this project is to determine the separation of Carbon dioxide and Methane by just manipulating temperature and pressure with and without the presence of water.

Other objectives are as follows:
- To study phase equilibrium for CO_2 and methane.
- To simulate both mixture in a separator and observe its vapor and solid compositions after separated.
- To study the possibilities of forming gas hydrate for methane and carbon dioxide to establish equilibrium conditions.
- The study the effect of temperature and pressure governing the formation of gas and hydrate
- To compared and discuss the results obtained and recommend any improvement.

As discussed in the problem statement, CO_2 contain in the reservoir is high in Malaysia. Therefore the solution for this issue is to reduce contain of the CO_2 by removing or separating CO_2 from the components of hydrocarbon in a form that is the best for the environment as well as to the economic potential.

There are three common methods of separation used in the industry, there are:
  i. Membrane technology
  ii. Adsorption technology
  iii. Temperature and pressure manipulation

To achieve the objective of this project as mentioned, the scope of study will be focused on the temperature and pressure manipulation method of separation.

CHAPTER 2

LITERATURE REVIEW

2.1 Separation of CO_2 and CH_4

Phase separation is said to be one of the most promising ways of separating acid gases particularly carbon dioxide from methane. However it is important to know and understand the pressure and temperature condition in getting the right separation. Different temperature, pressure and even composition of both carbon dioxide and methane will develop different phases of mixture. For instance, phases that probably exist are solid phase, liquid phase, vapor-liquid phase, vapor phase and supercritical phase.

Understanding the function of pressure and temperature is vital since they may also cause some effects to the system during separation. For example, increasing pressure for a separator make result in warmer operating temperatures and a consequent increase in solubility of carbon dioxide thus narrowing the range of conditions at which solid carbon dioxide forms. Besides that, additional increase in pressure will also cause the carbon dioxide-methane to reach and surpass its critical conditions.

This will cause the vapor and liquid phase of mixture indistinguishable from one another and therefore cannot be separated. Separating acid gases, particularly carbon dioxide from methane by using phase separation method would separate the mixed stream to produce a liquid carbon dioxide stream an enriched methane stream. This process should be carried out at a higher pressure than the critical pressure of methane.
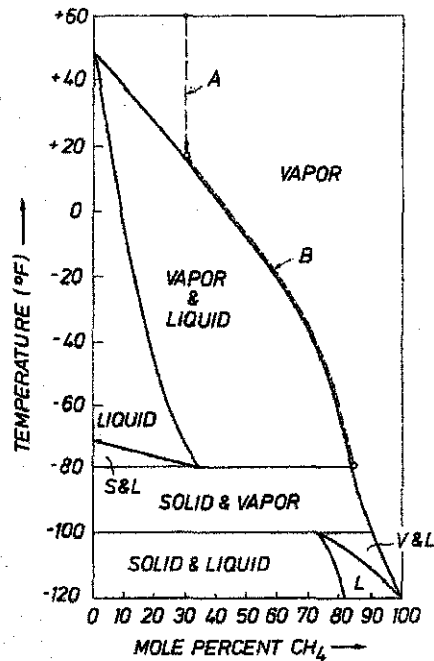
Figure 2: Binary phase diagram for methane and carbon dioxide as a function of temperature at 650psia (Donnelly H. G. and Katz D. L.)

This diagram shows region of solid carbon dioxide, liquid only, vapor only, vapor and liquid existing together and regions having solids existing with either vapor or liquid. FIG. 1 shows that there is a region of carbon dioxide solids formation which would cause problems. For example, cooling a 30% methane – 70% carbon dioxide mixture initially at 60°F. At line "A" in FIG. 1 will cause liquid to form beginning at about 15°F.

At this point vapor-liquid equilibrium may take place. In the methane enriching section, the vapor in equilibrium with the liquid would increase in methane content along line "B". As the temperature lowered to -80°F, solid carbon dioxide begin to form. Therefore, further methane enrichment of the vapor products stream cannot be achieved without the formation of solid carbon dioxide [1].

The product methane stream in the illustration could have as much as 15% carbon dioxide remaining in it. However, it is possible to avoid the formation of carbon dioxide solids by raising the pressure.
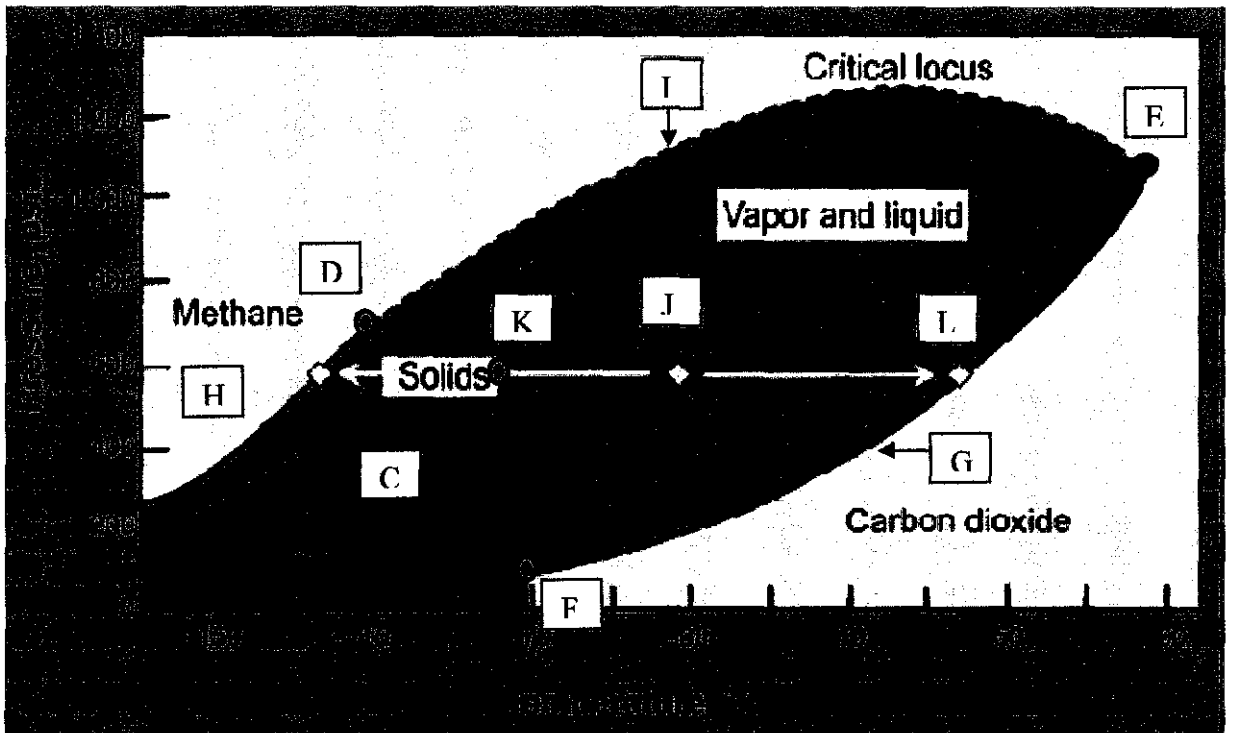
Figure 3: Carbon dioxide freezing envelope and critical pressure of gas mixture
(Source: Karen Bybee 2008)

Area "C" shows the carbon dioxide freezing envelope a pressure-temperature phase diagram. On this diagram, the methane critical point is shown at "D" and the carbon critical point is shown at "E". The carbon dioxide triple point at which solid, liquid and gaseous carbon dioxide are in equilibrium is shown as "F". Curve "G" between points "E" and "F" is the carbon dioxide vapor-liquid equilibrium or vapor pressure line.

The curve of "H" between point "D" and the vapor graph's pressure ordinate line is the methane vapor pressure line. Any separation of mixtures containing only methane and carbon dioxide must take place below the dashed critical pressure line "I" and yet above the carbon dioxide solidification area "C". For instance, methane-carbon dioxide mixture having a composition which places at point "J" may produce two streams having the compositions associated with points "K" and "L".

Point "K" shows that a enriched methane streams which exists in equilibrium at about -80°F and 670 psia. It would be more preferable if the separation could be carried to lower temperature since the methane content in the product stream would be higher. However, the carbon dioxide solidification region "C" falls in the way at the chosen pressure. One might select a higher pressure to avoid the upper end of area "C", but the critical pressure line "I" then becomes the limiting factor in effecting the separation [14].

2.2 Hydrates

One of the most promising methods for the removal of carbon dioxide is the gas hydrates method. Hydrates are ice-like solids that form when a sufficient amount of water and hydrate former are present in proper combination of temperature and pressure, where hydrates dissociation is favored by low temperature and high pressure depending on the thermodynamics of the system. Clathrate compounds are crystalline materials formed by a physical interaction between host molecules and relatively light guest molecules.

Guest molecules are either non-polar or slightly polar in nature. Depending on the chemical properties of the host molecules, clathrate compounds can be divided into two categories: aqueous and non-aqueous. Clathrate compounds in which the host molecules are water belong to aqueous. Gas-phase guest molecules generally form non-aqueous clathrates. Macroscopically, hydrates are similar in appearance to ice.

Methane and carbon dioxide clathrates occur naturally at temperature above freezing point of water, up to 30^0C, under pressure of 0.1MPa -100MPa. Gas hydrates can be converted back to gas and water easily by applying heat to the solid hydrate. This property can be exploited to separate carbon dioxide and methane in hydrates form.

One of the potential applications of gas hydrates is to sequester carbon dioxide in the deep ocean. The replacement of methane with carbon dioxide in gas hydrates may draw an innovative procedure for natural gas production. By injecting carbon dioxide to methane hydrates fields, methane dissociation from hydrates sediments can be facilitated while the formation rate carbon dioxide hydrate can be largely increased and therefore the physical fixation of carbon dioxide molecules to hydrate cavities can be easily achieved. To analyze this complex thermodynamics phenomenon, the complete phase behavior of the carbon dioxide and methane mixture in aqueous solution must be first investigated to understand the overall reformation mechanism occurring in the deep sea floor [3].

2.3 Peng-Robinson equation of states

Peng Robinson modified the attractive term mainly to improve the prediction of liquid density in comparison with Soave-Redlich-Kwong equation of states. This equation is given by [15]:

$$\left(P + \frac{a_c \alpha}{V_m (V_m + b)}\right)(V_m - b) = RT$$

(2-1)

P   = pressure

a_c = empirical constant

V_m = molar volume

b   = empirical constant

R   = ideal gas constant

T   = temperature

With

$$\alpha = 0.457235 \frac{R^2 T_c^2}{P_c}$$

(2-2)

and

$$b = 0.077796 \frac{RT_c}{P_c}$$

(2-3)

They used a similar form of α as proposed by Soave,

$$\alpha = (1 + (0.480 + 1.574\omega - 0.176\omega^2)(1 - T_r^{0.5}))^2$$

(2-4)

But used vapor-pressure data from the normal boiling point to critical point and correlated m as:

$$m = 0.37464 + 1.5422\omega - 0.26992\omega^2$$

(2-5)

The investigator later expands this expression to give the relationship:

$$m = 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3$$

(2-6)

Peng-Robinson equation exhibits performance similar to the Soave-Redlich-Kwong equation, although it is generally superior in predicting the liquid densities of many materials, especially non-polar one. Both Soave-Redlich-Kwong and Peng-Robinson is possible candidate for the calculation of hydrate phase equilibrium as long as solid phase does not play significant role.

2.4 K-factor method

K-factor originated with Carson and Katz (1942) although additional data and charts have been reported since then. One of the ironies of this method is that original charts of Carson and Kartz (1942) have been uncertain.

The K-factor is defined as the distribution of the component between the hydrate and the gas:

$$K_i = \frac{y_i}{s_i}$$

(2-7)

Where y_i and s_i are the mole fraction of components i in the vapor and hydrate, respectively. Those mole fractions are on a water-free basis and water is not included in the calculations. It is assumed that sufficient water is present to form hydrate. A chart is available for each of the component commonly encountered in natural gas that is: methane, ethane, propane, carbon dioxide and etc.

The evaluation of K value for CH4 and CO2 can be done using the proposed formula given by Sloan, 1997 as:

$$\ln(Kvsi) = A + B.T + C.\prod + D.T^{-1} + E.\prod{}^{-1} + F.\prod.T + G.T^2 + H.\prod{}^2 + I.\prod.T^{-1} + J.\ln(\prod.T^{-1}) + K.(\prod{}^{-2}) + L.T.\prod{}^{-1} + M.T^2.\prod{}^{-1} + N.\prod.T^{-2} + O.T.\prod{}^{-3} + P.T^3 + Q.\prod{}^3.T^{-2} + R.T^4$$

(2-8)

Where, $\prod$ =   Pressure, psia
       T =   Temperature, °F

Table 2: Parameter and Accuracy of Prediction of Equation 2.19 (Sloan, 1997)

Component	CH_4	CO_2
A	1.63636	9.0242
B	0	0
C	0	0
D	31.6621	-207.033
E	-49.3534	0
F	-0.00000531	4.66E-05
G	0	-0.006992
H	0	-2.89E-06
I	0.128525	-0.006223
J	-0.78338	0
K	0	0
L	0	0
M	0	0.27098
N	-5.3569	0
O	0	0
P	-0.00000023	8.82E-05
Q	-0.00000002	2.55E-06
R	0	0
Correlation Coefficient	0.999	0.996

Table 2 presents the parameters of Equation with an indication of the correlation coefficient. The Kvsi-value charts or equations are used to determine the temperature or pressure of three-phase (Lw-H-V) hydrate formation above $0^{\circ}C$ [12]

Calculation Algorithms

The K-charts are usually used in three methods:

1. Given the temperature and pressure, calculate the composition of the coexisting phases

2. Given the temperature, calculate the pressure at which the hydrate form and the composition of the hydrate

3. Given the pressure, calculate the temperature at which the hydrate form and the composition of the hydrate.

Flash

The first type of calculation is basically a flash. In this type of calculation, the objective is to calculate the amount of the phases present in equilibrium mixture and to determine the composition of the coexisting phases. The temperature, pressure and compositions are input parameters.

The objective function to be solved, in the Rachford-Rich-form is:

$$f(V) = \sum \frac{z_i(1 - K_i)}{1 + V(K_i - 1)}$$

(2-9)

Where z_i is the composition of the feed on a water-free basis. An interactive procedure is used to be solve for the vapor phase fraction, V. Such that the function must equal to zero. Once you have calculated the phase fraction, the vapor phase compositions can be calculated as follows:

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)}$$

(2-10)

And from the vapor phase, the composition of the solid is calculated from:

$$s_i = \frac{y_i}{K_i}$$

(2-11)

Incipient solid formation

The other two methods are incipient solid formation points and are basically equivalent to a dew point. This is the standard hydrate calculation. The purpose of this calculation is to answer the question, "Given the temperature and the composition of the gas, at what pressure will a hydrate form?" a similar calculation is to estimate the temperature at which hydrate will form given the pressure and the composition. The execution of these calculations is similar.

The objectives functions to be solved are:

$$f1(T) = 1 - \sum \frac{yi}{Ki}$$

$$f2(T) = 1 - \sum \frac{yi}{Ki}$$

(2-12), (2-13)

Depending on whether to calculate the pressure or the temperature, the appropriate function, either Equation is selected. Iterations are performed on the unknown variable until the summation is equal to unity. Therefore to use the first equation, the pressure is known and iterations are on the temperature.

CHAPTER 3

METHODOLOGY

For this project the tools that will be used are HYSIS and Icon software. The project will focused on simulation. The estimated work flow throughout this project is summarized in the schematic flow diagram as shown below:

```
                          ┌──────────────┐
                          │   Problem    │
                          │Identification│
                          └──────┬───────┘
                                 ▼
┌──────────────────┐     ┌──────────────┐     ┌──────────────────┐
│ Literature review│◄────│              │────►│Information obtained│
│ (journals, library,│    │   Research   │     │ based on problem  │
│ internets, articled and│ │              │     │    statement      │
│       etc        │     └──────┬───────┘     └──────────────────┘
└──────────────────┘            ▼
              ┌──────────────────────────────────────┐
              │ Set constraints and criteria for simulation │
              └──────────────────┬───────────────────┘
                                 ▼
              ┌──────────────────────────────────────┐
              │          Simulation handling          │
              └──────────────────┬───────────────────┘
                                 ▼
                          ◇ Analysis ◇
                                 ▼
              ┌──────────────────────────────────────┐
              │ Final decision (recommendation and conclusin) │
              └──────────────────┬───────────────────┘
                                 ▼
                        (  Project completed  )
```
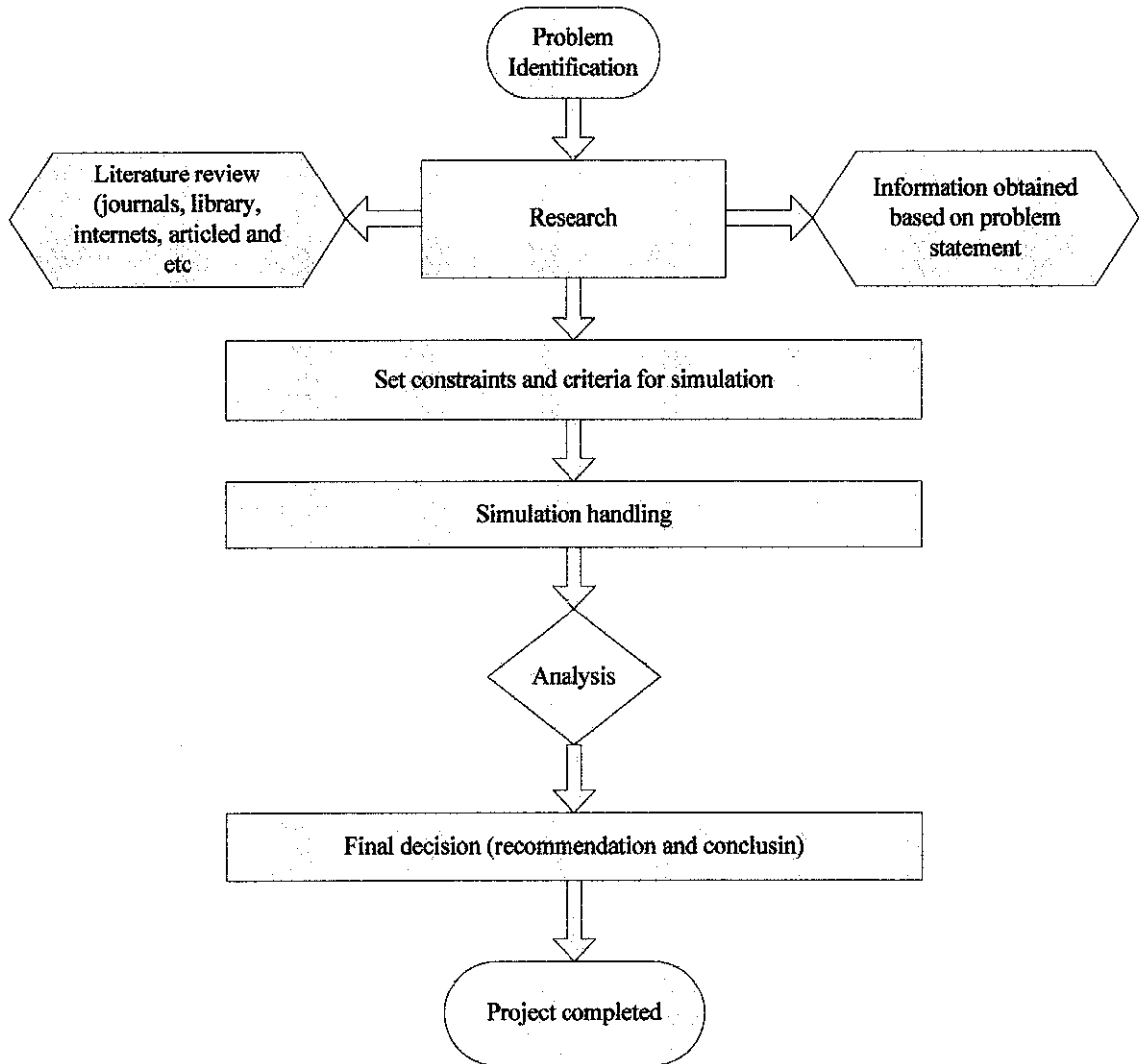
Figure 4: Schematic flow of project.

Basically the focus in this report will be more on the research development of this project. Where many literature review, such as engineering books, journal related to the topic, internet findings, articles and etc are used to understand the nature of this project and understand the fundamental in developing this project.

As mentioned earlier this project basically involves simulation in obtaining the end results of this project. Simulations are used to obtain data related to the topic. There are few criteria needed to start the simulation. The main reason is to make sure the methodology used could optimize the end result of this project.

The main methods used are:
    a) Simulation using ICON software
    b) Spreadsheet, Excel

3.1 Study on Clathrates based on Literature review

Hydrates were studied to ensure the properties that affect its formation building. Understanding the technology used in the hydrate formation in the past and the current has been studied to see the potential usage of the research.

3.2 Study on previous research on Removal of Carbon Dioxide from Natural Gas by using Gas Hydrate by Vu Thi Huong

A study on the equilibrium of methane and carbon dioxide has been carried out using PETRONAS Sim and K-Chart method by determining the operating properties and conditions which initiates the hydrate formation. Same approach but different tools were used to obtain the operating conditions. The newly used tool is Icon which replaces the PETRONAS Sim software [8].

3.3 Temperature and Pressure Formation Simulation ICON

As mentioned, Icon was used in the simulation to obtain initial operating conditions. Advanced Peng-Robinson was chosen as the property package for the calculation of hydrate formation temperature and pressure due its ability to suite with all fluid properties in natural gas. The components chosen were Carbon dioxide, Methane and water. Hand calculations were done with water gas ratio (WGR) 1, 3, 5.75 and 7.

The steps used to obtain the pressure formation value at different Water-Gas ratio are as in Figure 5.

Data recorded should as follow:

Table 3: Hydrate temperature and pressure formation (ICON), WGR: 1

Hydrate temperature and pressure formation WGR: 1			
CH$_4$ %	CO$_2$%	T (^{o}C)	P (kPa)
1	0	-10	
		-8	
		-6	
		-4	
		-2	
		0	
		2	
		4	
		6	
		8	
		10	

Hydrate temperature and pressure formation WGR: 1			
CH$_4$ %	CO$_2$%	T ($^\circ$C)	P (kPa)
0.9	0.1	-10	
		-8	
		-6	
		-4	
		-2	
		0	
		2	
		4	
		6	
		8	
		10	

The yellow box is the info needed from the ICON simulation. The step continues with using the same temperature but different fraction of methane and carbon dioxide to: 0.8:0.2, 0.7:0.3 and 0.6:04. Next was to increase the Water-Gas ration to 3, 5.75 and 7.

3.4 Flow chart of ICON Simulation Methodology

```
                    ┌─────────────┐
                    │    Start    │
                    └─────────────┘
                           │
                           ▼
┌──────────────────────────────────────────────────────────┐
│  Property Package : Choose Advanced Peng-Robinson and      │
│         Natural Gas Processing for chemical system          │
│         categories.                                         │
│         In components: add CH4, CO2 and H20                 │
└──────────────────────────────────────────────────────────┘
                           │
                           ▼
┌──────────────────────────────────────────────────────────┐
│        Add a stream and connect it with Hydrate utilities   │
└──────────────────────────────────────────────────────────┘
                           │
                           ▼
┌──────────────────────────────────────────────────────────┐
│     Compute CH4, CO2 and H20 fraction (hand calculation)    │
└──────────────────────────────────────────────────────────┘
                           │
                           ▼
┌──────────────────────────────────────────────────────────┐
│   Input CH4, CO2 and H20 fraction and designed temperature  │
└──────────────────────────────────────────────────────────┘
                           │
                           ▼
┌──────────────────────────────────────────────────────────┐
│       Output hydrate pressure formation (from ICON)         │
└──────────────────────────────────────────────────────────┘
                           │
                           ▼
                    ┌─────────────┐
                    │     End     │
                    └─────────────┘
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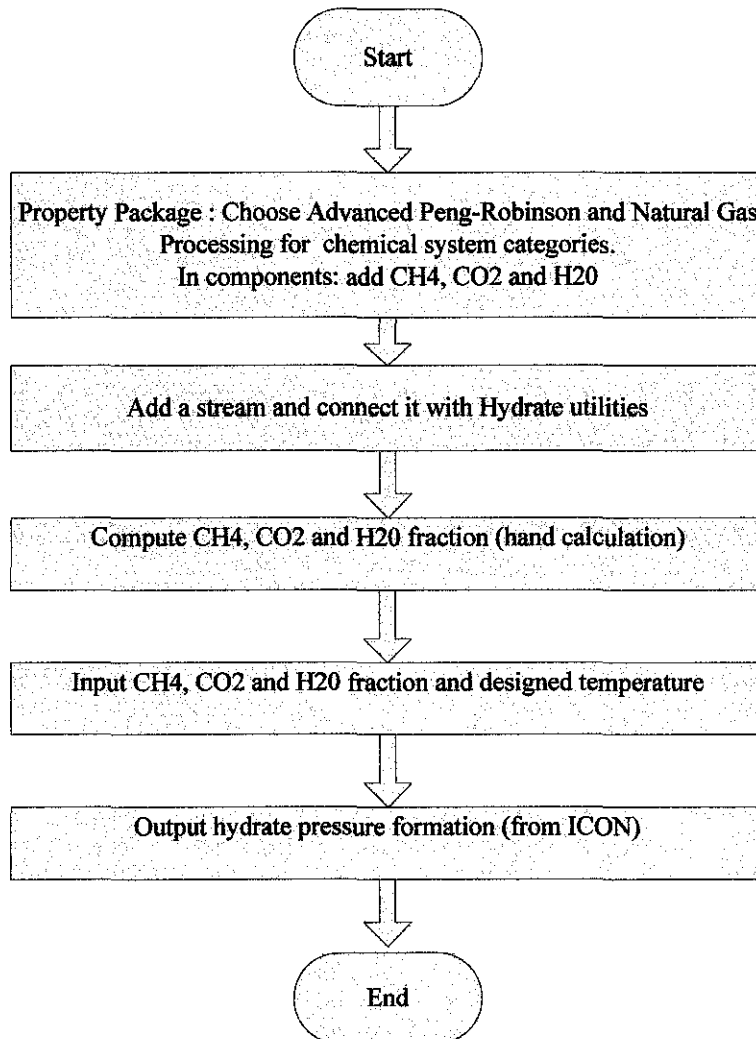
Figure 5: Simulation steps to obtain temperature and pressure dissociation in ICON

3.5 Temperature and Pressure Formation K-Factor Method

For this method, equation 2-1 was used to obtain K factor. This method could only determine the pressure of hydrate formation with temperature above 0°C. This is because the Kvsi value charts or equation are used to determine the temperature or pressure of three phase (Lw-H-V) hydrate formation. This method has limitations too where the K value charts has limited range of temperatures above the ice-point.

Table 4: Phase compositions of Methane and Carbon dioxide at 2°C and at pressure hydrate formation (80% feed impurity), K-Chart method.

Pressure (kPa)	Vapor fraction, y	Solid fraction, x	CO2 vapor, y %	CH4 vapor, y%	CO2 solid, x%	CH4 solid, x%
	0.99	0.01				
	0.84	0.16				
	0.70	0.30				
	0.53	0.47				
	.041	0.59				
	0.32	0.68				
	0.24	0.76				
	0.12	0.88				
	0.07	0.93				
	0.01	0.99				

Above is the table of sample to be completed to get the Pressure hydrate formation range and the fraction of vapor and solid for each component of methane and carbon dioxide. This method is continued with different temperature: 4°C , 6°C , 8°C and 10°C .

3.6 Flow Chart of K-Chart Methodology

Start

Input gas composition of CH4, CO2 : z1 and z2 accordingly

Input temperature, T

Assume a value for pressure, P

Calculate K values for CH4 and CO2 from eq. 2-8

Calculate V from eq. 2-9

$0 < V < 1$

No

Yes

Calculate vapor and solid fraction of CH4 and CO2 from eq 2-10 & 2-11

End
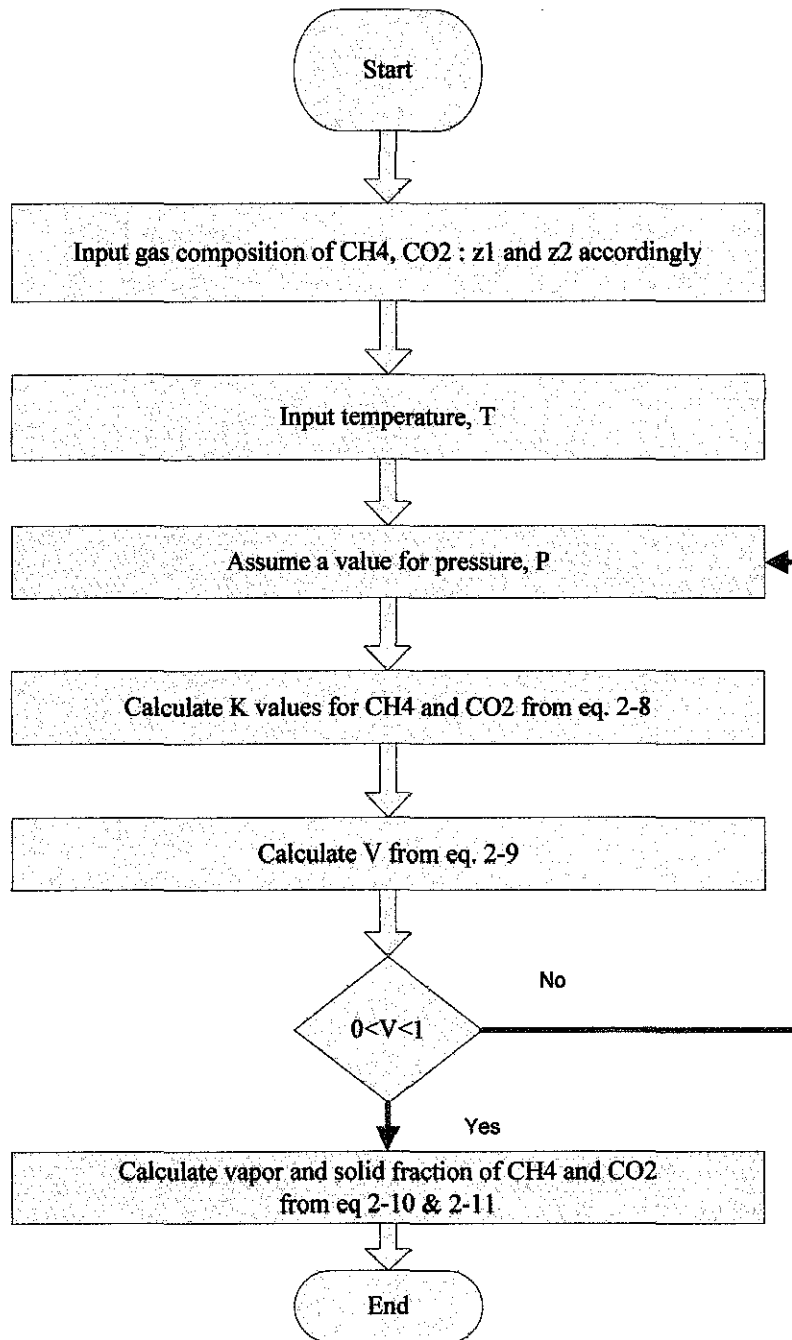
Figure 6: Calculation steps to obtain hydrate equilibrium composition using K-factor method

3.7 Analysis

The results of the simulation will be presented and discuss in detail in chapter 4. The focus of the discussion would be on few factors such as:

i. Effect of temperature on pressure formation of methane and carbon dioxide hydrate

ii. Effect of Water-Gas ratio in feed on pressure formation of methane and carbon dioxide hydrate

iii. Effect of pressure hydrate phase equilibrium composition of methane and carbon dioxide mixture hydrate

CHAPTER 4

RESULTS AND DISCUSSIONS

This section presents the data obtained from ICON Simulation and K-factor method which comprises of studies on effect of temperature on pressure formation of CO2 and CH4 hydrate, effect of water-gas ratio in feed on pressure formation of CH4 and CO2 hydrate, effect of temperature on hydrate phase equilibrium composition of CH4 and CO2 mixture hydrate.

4.1 Effect of temperature on Pressure Formation of CH4 and CO2 hydrate

Here are some of the result from a simple simulation created base on different temperature and Water-Gas Ratio. The ICON simulation resulted to obtain pressure formation hydrates.
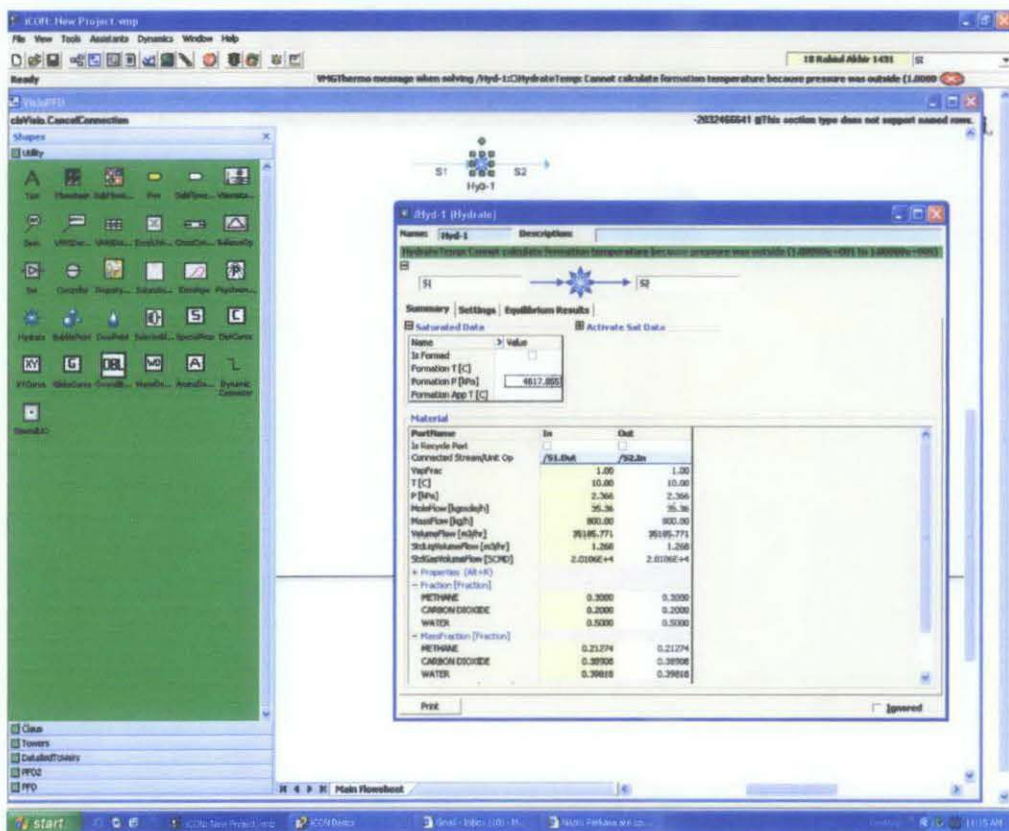
Figure 7: ICON simulation for Hydrate formation

According to Vu, *Figure* 8 has shown the plot of formation pressure if hydrate versus temperature at various CO2 concentrations. The positive slopes of the plots shows that at higher temperature, larger pressures were needed to form hydrate. Plus, as the temperature increases from negative to positive, the phase equilibrium changes from I-H-V (Ice-Hydrate-Vapor) to Lw-H-V (Liquid water-Hydrate-Vapor).

This is observed from the graph which shows the slope before $0°C$ is smaller to its increment after $0°C$. The change in slope P-T curves can only be explained by the change of phase equilibrium. Based on *Figure 8*, the change in phase equilibrium has occurred at $0°C$. This finding can be proven correct by *Figure* 9 (Makogon 1997) where the turning points (quadruple point) if CH4 and CO2 for P-T Hydrate formation are at 0 $°C$.
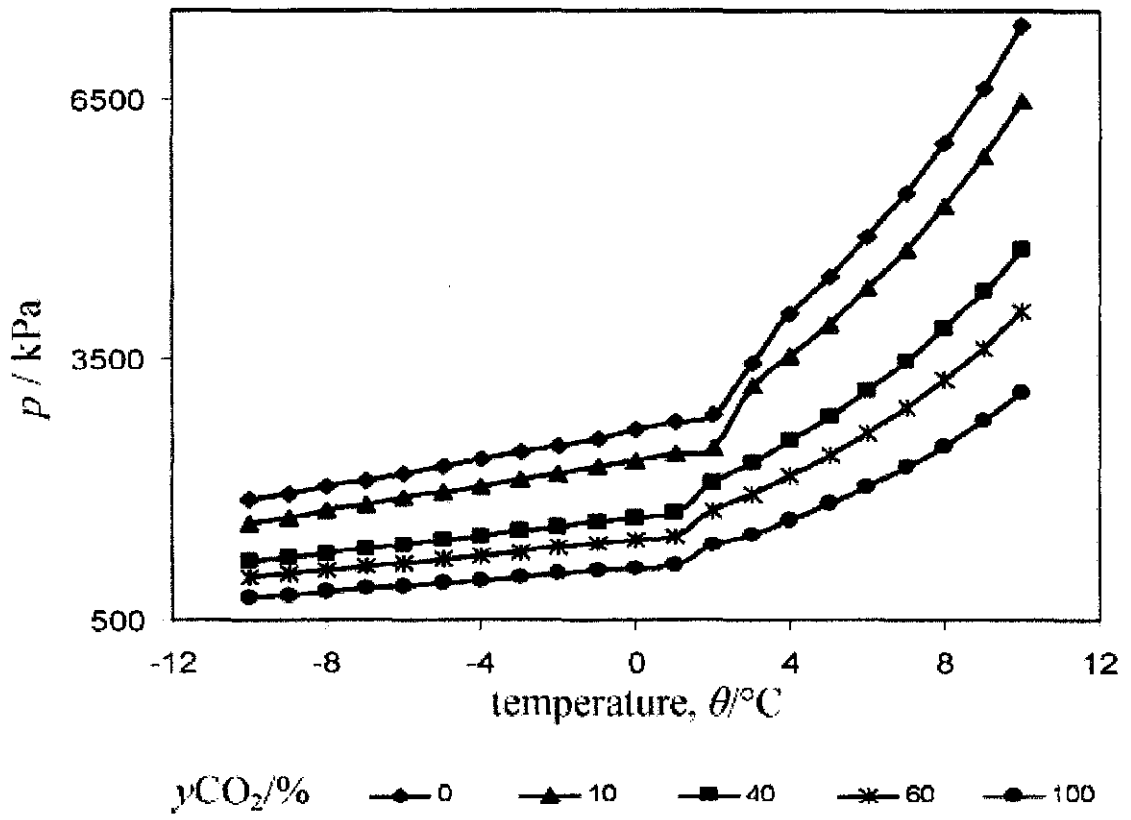
Figure 8: Pressure formation versus Temperature for methane and carbon dioxide hydrate at different carbon dioxide content (WGR: 5.75) [8]
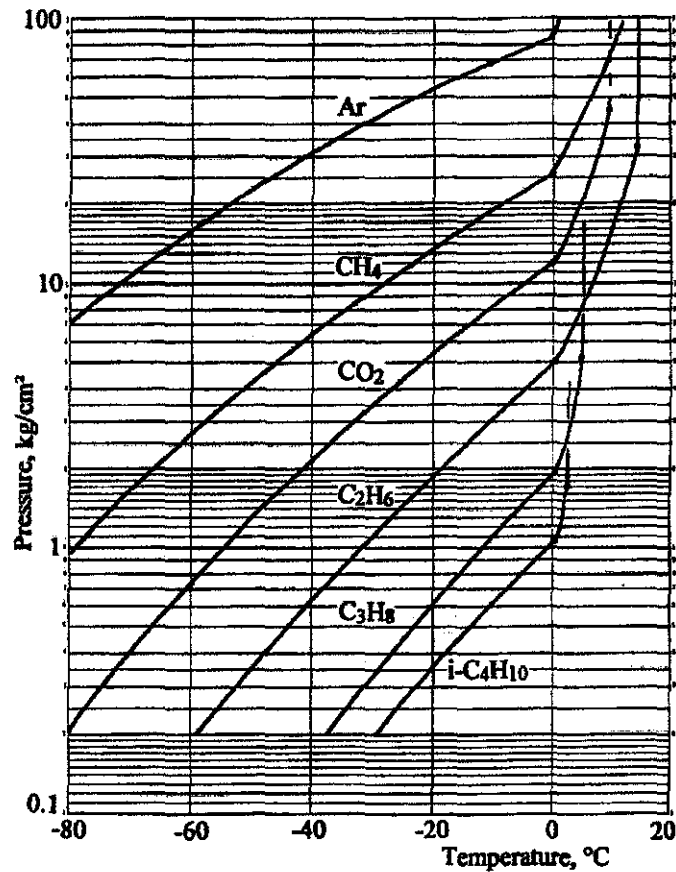
Figure 9: Hydrate formation with different gases at T< 0°C (Makogon 1997)

Figure 10 shows the plot of formation pressure of hydrate versus temperature at various CH_4 compositions; which ranged from 60%, 70%, 80%, 90% and 100%. The pressure data are obtained from ICON simulation by varying the temperature from -10°C to 10°C. The positive slopes of the plots prove that a higher temperature requires larger pressure for hydrate formation. It is also can be seen that the increase in formation pressure with respect to the increase in temperature is smaller before the temperature of 0°C.

This is observed from the graph which shows the slope of P-T curves can only be explained by the change of phase equilibrium changes from I-H-V (Ice-Hydrate-Vapor) to L_w-H-V (Liquid water-Hydrate-Vapor). Based on *Figure 10*, the change in phase equilibrium has occurred at 0°C. This shows that the turning points of CH_4 and CO_2 for P-T hydrate formation are at 0°C. All the data are attached in the *Appendix A*

Table 5: Hydrate temperature and pressure formation (ICON), WGR: 5.75

(CH4:1, CO2:0)

Hydrate temperature and pressure formation WGR: 5.75			
CH$_4$ %	CO$_2$%	T (°C)	P (kPa)
1	0	-10	1901.514
		-8	2049.653
		-6	2203.595
		-4	2363.06
		-2	2527.717
		0	2697.19
		2	3323.647
		4	4041.401
		6	4916.77
		8	5991.517
		10	7322.652

Table 6: Hydrate temperature and pressure formation (ICON), WGR: 5.75

(CH4:0.9, CO2:0.1)

Hydrate temperature and pressure formation WGR: 5.75			
CH$_4$ %	CO$_2$%	T (°C)	P (kPa)
0.9	0.1	-10	1629.591
		-8	1778.058
		-6	1919.86
		-4	2060.001
		-2	2204.819
		0	2353.985
		2	2903.566
		4	3539.379
		6	4317.034
		8	5274.937
		10	6466.237

Table 7: Hydrate temperature and pressure formation (ICON), WGR: 5.75
(CH4:0.8, CO2:0.2)

Hydrate temperature and pressure formation WGR: 5.75			
CH$_4$ %	CO$_2$%	T (°C)	P (kPa)
0.8	0.2	-10	1416.282
		-8	1544.721
		-6	1680.059
		-4	1822.192
		-2	1954.724
		0	2088.006
		2	2576.485
		4	3145.843
		6	3843.709
		8	4705.588
		10	5781.237

Table 8: Hydrate temperature and pressure formation (ICON), WGR: 5.75
(CH4:0.7, CO2:0.3)

Hydrate temperature and pressure formation WGR: 5.75			
CH$_4$ %	CO$_2$%	T (°C)	P (kPa)
0.7	0.3	-10	1286.774
		-8	1403.207
		-6	1525.813
		-4	1639.37
		-2	1756.268
		0	1876.816
		2	2315.947
		4	2830.721
		6	3462.649
		8	4244.681
		10	5223.587

Table 9: Hydrate temperature and pressure formation (ICON), WGR: 5.75

(CH4:0.6, CO2:0.4)

Hydrate temperature and pressure formation WGR: 5.75			
CH$_4$ %	CO$_2$%	T (^{o}C)	P (kPa)
0.6	0.4	-10	1190.845
		-8	1286.206
		-6	1385.54
		-4	1488.683
		-2	1595.434
		0	1705.561
		2	2104.206
		4	2573.589
		6	3150.384
		8	3865.293
		10	4762.416
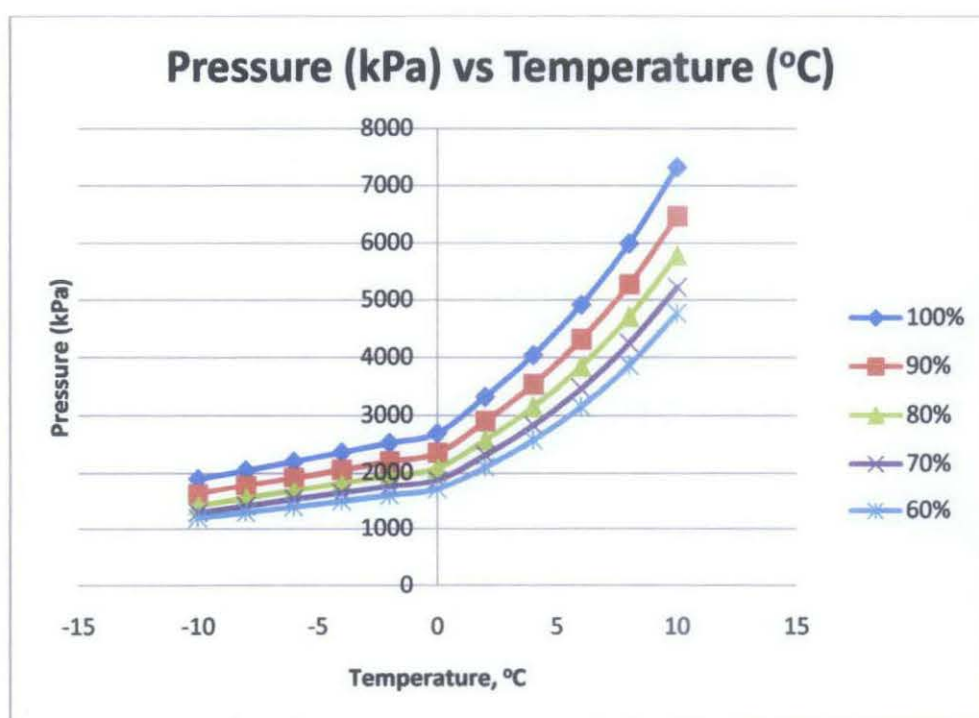
Figure 10: Pressure formation versus temperature for Methane and Carbon dioxide hydrate at different Methane content (WGR=5.75)

4.2 Effect of Water-Gas-Ratio (WGR) in Feed on Pressure Formation of CH4 and CO2 hydrate

According to Ayesha, a study carried on effect of WGR, on Delta pressure, kPa versus temperature °C at different WGR show that WGR: 7 which are greater than 5.75 have a positive curve upwards. As for delta P for WGRs of 1 and 3 are negative. This shows that the higher the WGR in the feed stream the higher the pressure required forming hydrate. This also shows that the higher the percentage of CH4, the less sensitive it is to WGR [16].
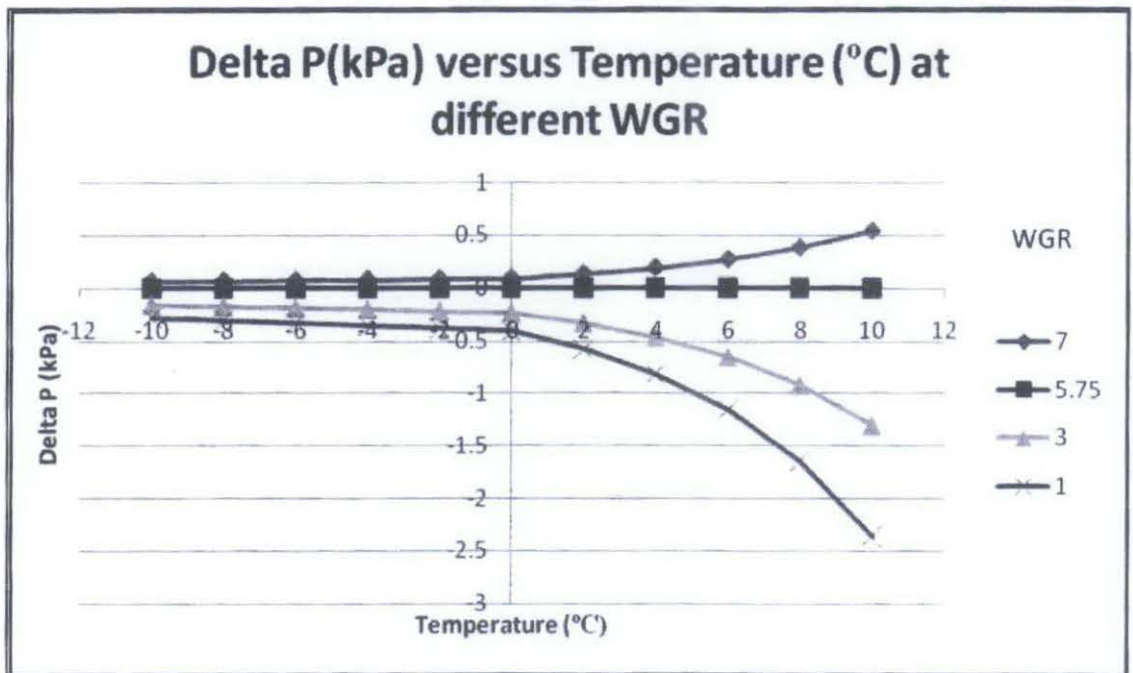
Figure 11: Delta P formation at various WGR to Pressure formation at 5.75 WGR versus temperature. (Source: Ayesha 2008)

4.3 Effect of Pressure on Hydrate Phase Equilibrium Composition of Methane and Carbon dioxide using K-factor method.

Table 10 show the pressure hydrate formation for Methane and carbon dioxide at various range of composition which ranged from 100: 0 %, 90:10%, 80:20%, 70:30% and 60:40%. At this composition different range of temperature used to see the composition of vapor and solid. The ranges of temperature used are $0^{\circ}C$, $-2^{\circ}C$, $-4^{\circ}C$, $-6^{\circ}C$, $-8^{\circ}C$ and $-10^{\circ}C$

Table 10: Phase composition of Methane and Carbon dioxide at $-6^{\circ}C$ with Pressure Formation Hydrate

P (kPa)	CH_4	CO_2	y, CH_4	y, CO_2	s, CH_4	s, CO_2
1322	1	0	1	0	1	0
697	0.9	0.1	0.971443	0.028557	0.828557	0.171443
487	0.8	0.2	0.913166	0.086834	0.686834	0.313166
407	0.7	0.3	0.832471	0.167529	0.567529	0.432471
364	0.6	0.4	0.735841	0.264159	0.464159	0.535841

From the temperature $0^{\circ}C$ to $-6^{\circ}C$, the pressure formation hydrate decrease gradually and the vapor fraction for methane and solid fraction for carbon dioxide increase gradually. This proves that the research carried out by Sloan does prove the logic for this simulation. The other data of the simulation is in **Appendix B**.

However at the condition of -8°C the vapor fraction of methane and solid in carbon dioxide start to reduce as shown in *Table 11*

Table 11: Phase composition of Methane and Carbon dioxide at -8°C with Pressure Formation Hydrate

P (kPa)	CH_4	CO_2	y, CH_4	y, CO_2	s, CH_4	s, CO_2
989	1	0	0.999858	0	1.000142	0
236	0.9	0.1	1.359165	0.024718	0.440835	0.175282
183	0.8	0.2	1.165003	0.089009	0.434997	0.310991
162	0.7	0.3	0.986731	0.180655	0.413269	0.419345
151	0.6	0.4	0.825	0.286701	0.375	0.513299

The reasons that might cause this effect are due to the range of pressure formation hydrate and temperature exceeds the limits or its range. This is due the phase equilibrium of both methane and carbon dioxide which has certain range of temperature and pressure that cause the change of composition of both vapor and solid. However there is another opinion that this k-factor method does not converge up to - 8°C. At -10°C, the k-factor method can be used at all. This is due the formula used were not able to converge even the pressure of formation hydrate.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Basically the separation of carbon dioxide and methane is a very important process in the current industry since it involves money and environment. Many technologies have been introduced to separate carbon dioxide and methane to optimize the separation for higher liquid carbon dioxide and higher vapor methane, however very few that focuses on the temperature and pressure manipulation. The base of the study is to understand the basic theory of phase equilibrium.

In the formation of gas hydrate, the temperature is directly proportional to pressure. Therefore, the formation of gas hydrate at a higher temperature requires higher pressure. The phase equilibrium turning point is at $0^{o}C$ applies to Carbon dioxide-Methane mixture. However, the effect of temperature to mixture content is more applicable using ICON.

Same temperature and gas composition that is methane, the higher the WGR gives a higher pressure requirement to form gas hydrate. In this study, a WGR of 1 yields lowest pressure hydrate formation and WGR of 7 gives highest formation pressure. The composition of gas mixture plays a major role in for the increment in pressure needed to form hydrate when WGR increases. This can be shown where pure methane composition in the gas mixture is not affected by WGR. The effect of WGR on hydrate is not a significant as temperature and pressure has.

For the K-factor method, as the temperature decrease with proportional with pressure the composition for vapor methane and solid carbon dioxide increase gradually. However there are ranges of optimal temperature to give the best condition to achieve the wanted results. At temperatures that are much lower, this method can be used due the equation cant converge to obtain result.

This could help to achieve the objective of this project which are first; to simulate both mixture in a separator and observe its vapor and solid compositions after separated, secondly; to study the possibilities of forming gas hydrate for methane and carbon dioxide to establish equilibrium conditions third; study the effect of temperature and pressure governing the formation of gas and hydrate and finally to compared and discuss the results obtained and recommend any improvement

RECOMMENDATION

There are a few recommendations to improve and upgrade from this research since the study has shown a positive result in the ideal effects of methane-carbon dioxide equilibrium for hydrate formation.

Here are some suggestions for the future:

- Introduce other components to the study the effect on methane-carbon dioxide equilibrium conditions. This could help to consider the effect of other hydrocarbon and non-hydrocarbon effect toward pressure and temperature of hydrate.

- To also discover the effect of hydrate formation its disadvantages.

- Determine the optimum conditions of hydrate formation and phase equilibrium of methane and carbon dioxide mixture by using other options.

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Appendix A

Table: Hydrate temperature and pressure formation (ICON), WGR: 1

(CH4:1, CO2:0)

Hydrate temperature and pressure formation WGR: 1			
CH$_4$ %	CO$_2$%	T (^{o}C)	P (kPa)
1	0	-10	1901.514
		-8	2049.653
		-6	2203.595
		-4	2363.06
		-2	2527.717
		0	2697.19
		2	3323.647
		4	4041.401
		6	4916.77
		8	5991.517
		10	7322.652

Table: Hydrate temperature and pressure formation (ICON), WGR: 1

(CH4:0.9, CO2:0.1)

Hydrate temperature and pressure formation WGR: 1			
CH$_4$ %	CO$_2$%	T (^{o}C)	P (kPa)
0.9	0.1	-10	1599.791
		-8	1745.718
		-6	1893.825
		-4	2032.68
		-2	2176.215
		0	2324.106
		2	2863.061
		4	3486.435
		6	4248.2
		8	5185.953
		10	6351.984

Table: Hydrate temperature and pressure formation (ICON), WGR: 1

(CH4:0.8, CO2:0.2)

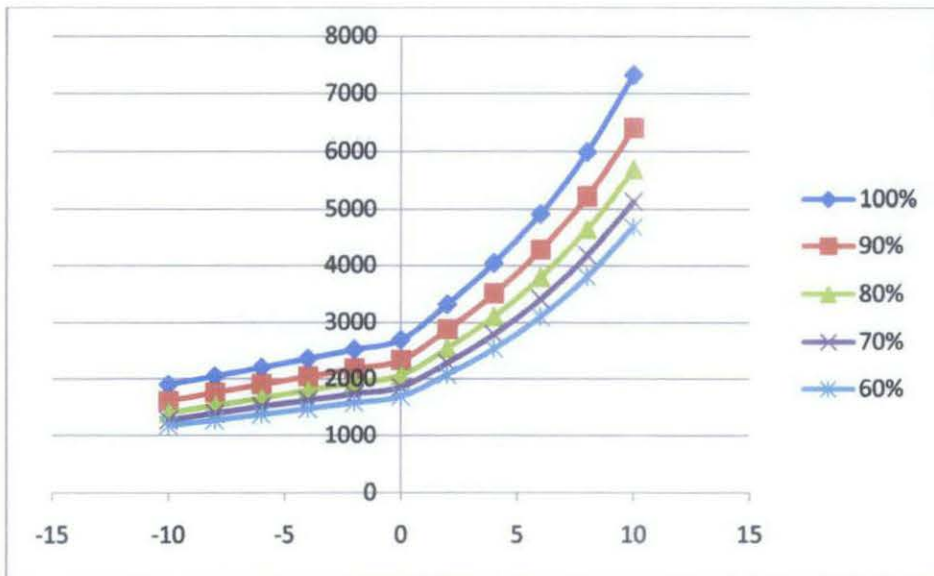| Hydrate temperature and pressure formation WGR: 1			
CH$_4$ %	CO$_2$%	T (^{o}C)	P (kPa)
0.8	0.2	-10	1389.435
		-8	1515.599
		-6	1648.554
		-4	1788.2
		-2	1918.42
		0	2050.024
		2	2524.563
		4	3077.167
		6	3753.292
		8	4587.149
		10	5627.07

Table: Hydrate temperature and pressure formation (ICON), WGR: 1

(CH4:0.7, CO2:0.3)

Hydrate temperature and pressure formation WGR: 1			
CH$_4$ %	CO$_2$%	T (^{o}C)	P (kPa)
0.7	0.3	-10	1265.324
		-8	1379.962
		-6	1494.413
		-4	1605.728
		-2	1720.944
		0	1839.81
		2	2265.011
		4	2762.681
		6	3372.117
		8	4124.739
		10	5065.545

Table: Hydrate temperature and pressure formation (ICON), WGR: 1

(CH4:0.6, CO2:0.4)

Hydrate temperature and pressure formation WGR: 1			
CH$_4$ %	CO$_2$%	T (^{o}C)	P (kPa)
0.6	0.4	-10	1165.922
		-8	1259.819
		-6	1357.67
		-4	1459.317
		-2	1564.565
		0	1673.187
		2	2059.389
		4	2513.213
		6	3069.307
		8	3756.784
		10	4617.855
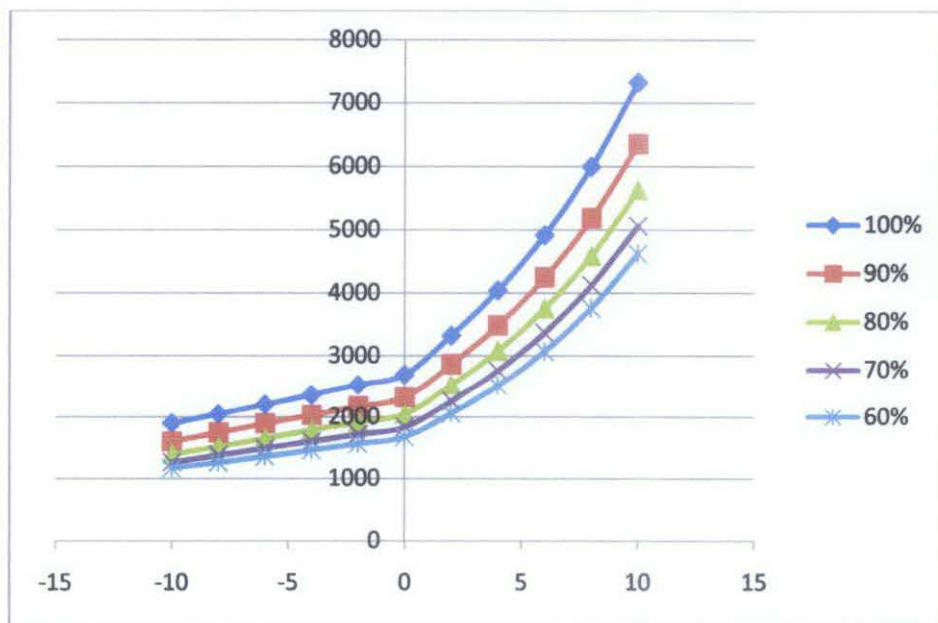
Figure: Pressure formation versus temperature for Methane and Carbon dioxide hydrate at different Methane content (WGR=1)

Table: Hydrate temperature and pressure formation (ICON), WGR: 3

(CH4:1, CO2:0)

Hydrate temperature and pressure formation WGR: 3			
CH$_4$ %	CO$_2$%	T ($^{\circ}$C)	P (kPa)
1	0	-10	1901.514
		-8	2049.653
		-6	2203.595
		-4	2363.06
		-2	2527.717
		0	2697.19
		2	3323.647
		4	4041.401
		6	4916.77
		8	5991.517
		10	7322.652

Table: Hydrate temperature and pressure formation (ICON), WGR: 3

(CH4:0.9, CO2:0.1)

Hydrate temperature and pressure formation WGR: 3			
CH$_4$ %	CO$_2$%	T ($^{\circ}$C)	P (kPa)
0.9	0.1	-10	1612.655
		-8	1759.676
		-6	1905.222
		-4	2044.633
		-2	2188.722
		0	2337.163
		2	2880.834
		4	3509.767
		6	4278.665
		8	5225.513

		10	6403.003

Table: Hydrate temperature and pressure formation (ICON), WGR: 3

(CH4:0.8, CO2:0.2)

Hydrate temperature and pressure formation WGR: 3			
CH$_4$ %	CO$_2$%	T (°C)	P (kPa)
0.8	0.2	-10	1400.803
		-8	1527.928
		-6	1661.891
		-4	1802.59
		-2	1933.968
		0	2066.287
		2	2546.85
		4	3106.729
		6	3792.332
		8	4638.46
		10	5694.102

Table: Hydrate temperature and pressure formation (ICON), WGR: 3

(CH4:0.7, CO2:0.3)

Hydrate temperature and pressure formation WGR: 3			
CH$_4$ %	CO$_2$%	T (°C)	P (kPa)
0.7	0.3	-10	1274.299
		-8	1389.687
		-6	1507.896
		-4	1619.921
		-2	1735.846
		0	1855.424
		2	2286.523
		4	2791.456
		6	3410.47

| | | 8 | 4175.657 |
| | | 10 | 5132.804 |

Table: Hydrate temperature and pressure formation (ICON), WGR: 3

(CH4:0.6, CO2:0.4)

Hydrate temperature and pressure formation WGR: 3			
CH$_4$ %	CO$_2$%	T ($^{\circ}$C)	P (kPa)
0.6	0.4	-10	1176.31
		-8	1270.82
		-6	1369.293
		-4	1471.566
		-2	1577.444
		0	1686.698
		2	2078.086
		4	2538.402
		6	3103.145
		8	3802.098
		10	4678.292

Figure: Pressure formation versus temperature for Methane and Carbon dioxide hydrate at different Methane content (WGR=3)

Table: Hydrate temperature and pressure formation (ICON), WGR: 7
(CH4:1, CO2:0)

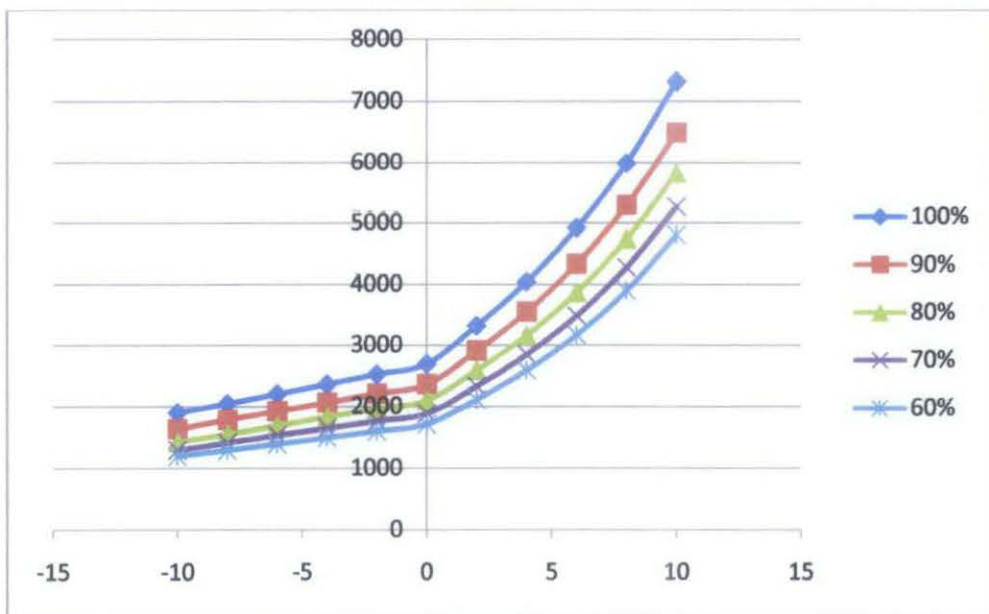| Hydrate temperature and pressure formation WGR: 7			
CH$_4$ %	CO$_2$%	T ($^\circ$C)	P (kPa)
1	0	-10	1901.514
		-8	2049.653
		-6	2203.595
		-4	2363.06
		-2	2527.717
		0	2697.19
		2	3323.647
		4	4041.401
		6	4916.77
		8	5991.517
		10	7322.652

Table: Hydrate temperature and pressure formation (ICON), WGR: 7
(CH4:0.9, CO2:0.1)

Hydrate temperature and pressure formation WGR: 7			
CH$_4$ %	CO$_2$%	T ($^\circ$C)	P (kPa)
0.9	0.1	-10	1637.002
		-8	1786.105
		-6	1926.139
		-4	2066.599
		-2	2211.737
		0	2361.221
		2	2913.28
		4	3551.958
		6	4333.228

		8	5295.66
		10	6492.575

Table: Hydrate temperature and pressure formation (ICON), WGR: 7
(CH4:0.8, CO2:0.2)

Hydrate temperature and pressure formation WGR: 7			
CH$_4$ %	CO$_2$%	T ($^{\circ}$C)	P (kPa)
0.8	0.2	-10	1423.249
		-8	1552.28
		-6	1688.238
		-4	1831.019
		-2	1963.908
		0	2097.62
		2	2589.55
		4	3163.013
		6	3866.148
		8	4734.749
		10	5818.878

Table: Hydrate temperature and pressure formation (ICON), WGR: 7
(CH4:0.7, CO2:0.3)

Hydrate temperature and pressure formation WGR: 7			
CH$_4$ %	CO$_2$%	T ($^{\circ}$C)	P (kPa)
0.7	0.3	-10	1292.484
		-8	1409.394
		-6	1532.5
		-4	1648.165
		-2	1765.502
		0	1886.489
		2	2329.226

		4	2848.397
		6	3486.071
		8	4275.545
		10	5264.009

Table: Hydrate temperature and pressure formation (ICON), WGR: 7

(CH4:0.6, CO2:0.4)

Hydrate temperature and pressure formation WGR: 7			
CH$_4$ %	CO$_2$%	T (°C)	P (kPa)
0.6	0.4	-10	1197.535
		-8	1293.285
		-6	1393.013
		-4	1496.553
		-2	1603.703
		0	1714.23
		2	2116.21
		4	2589.748
		6	3172.061
		8	3894.233
		10	4800.845

Figure: Pressure formation versus temperature for Methane and Carbon dioxide hydrate at different Methane content (WGR=7)

Appendix B

Table: Phase composition of Methane and Carbon dioxide at 0°C with Pressure Formation Hydrate

P (kPa)	CH₄	CO₂	y, CH₄	y, CO₂	s, CH₄	s, CO₂
2670	1	0	1.000083	0	0.999917	0
2402	0.9	0.1	0.955257	0.065811	0.844743	0.134189
2147	0.8	0.2	0.897708	0.139422	0.702292	0.260578
1925	0.7	0.3	0.823801	0.22225	0.576199	0.37775
1744	0.6	0.4	0.733608	0.314376	0.466392	0.485624

Table: Phase composition of Methane and Carbon dioxide at -2°C with Pressure Formation Hydrate

P (kPa)	CH₄	CO₂	y, CH₄	y, CO₂	s, CH₄	s, CO₂
2154	1	0	1.000257	0	0.999743	0
1862	0.9	0.1	0.983519	0.056756	0.816481	0.143244
1593	0.8	0.2	0.944839	0.124097	0.655161	0.275903
1380	0.7	0.3	0.876614	0.204142	0.523386	0.395858
1223	0.6	0.4	0.783093	0.296401	0.416907	0.503599

Table: Phase composition of Methane and Carbon dioxide at -4°C with Pressure Formation Hydrate

P (kPa)	CH₄	CO₂	y, CH₄	y, CO₂	s, CH₄	s, CO₂
1708	1	0	0.999793	0	1.000207	0
1313	0.9	0.1	1.058729	0.042576	0.741271	0.157424
1014	0.8	0.2	1.048066	0.102773	0.551934	0.297227
837	0.7	0.3	0.970315	0.182009	0.429685	0.417991
732	0.6	0.4	0.857317	0.276072	0.342683	0.523928