

Proper Validation of Freezing Prediction Results from Process Simulation

by

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CERTIFICATION OF APPROVAL

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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.

INTAN ELLINA BINTI NORAZMI

ABSTRACT

The motivation of the work is to increase the knowledge about thermodynamic modeling of freeze outs in natural gas systems and a deeper understanding of the phase behavior of natural gas mixtures, due to the problems experienced in cryogenic natural gas process-plants. Critical components in natural gas mixtures introduce a risk of forming a solid coating and plugging the process equipment. Hence, it is relevant to examine methane rich binary mixtures containing components with high risk of freezing. Due to their high triple point temperatures, carbon dioxide, benzene and cyclohexane are regarded as the most critical components. Due to time constraint, the scope of study is narrowed down to methane rich binary mixture with carbon dioxide as the main critical component.

This study was carried out by applying a simulation tool called HYSYS, where the equation of state method which is the Soave-Redlich-Kwong equation is implemented. To investigate the reliability and accuracy of the equation of state method, experimental data from the literature is used as a foundation for validation. The outcome is that the BIAS and average absolute deviation (AAD) of all three papers under study is within the satisfying degree of accuracy. Thus it validate that the data from simulation is reliable and is able to reduce the dependency of experimental procedure that is more costly.

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ABBREVIATION AND NOMENCLATURE

a_w	= water activity
$a.a.T.d.$	= average of absolute temperature difference
$a.a.p.e$	= average of absolute percentage error on pressure
C_{ji}	= Langmuir adsorption constant
C_p	= molar heat capacity
f_i	= fugacity of gas component in a gas mixture
H	= molar enthalpy
k_{ij}	= binary interaction coefficient
K^{vs}	= vapor/solid equilibrium ratio
M_{air}	= molecular weight of air
M_i	= molecular weight of electrolyte i
M_j	= molecular weight of thermodynamic inhibitor j
MW_i	= molecular weight of component i in a gas mixture
n	= number of data points
n_i	= number of cavities of type i per water molecules
p	= pressure of the system
p_c	= critical pressure
p_{pc}	= pseudocritical pressure
p_{pr}	= pseudoreduced pressure
p_r^v	= reduced vapor pressure
p_w^v	= vapor pressure of water
R	= universal gas constant
s_i	= mol fraction of component i in solid phase
T	= temperature of the system
T_c	= critical temperature

T_{pc}	= pseudocritical temperature
T_{pr}	= pseudoreduced temperature
T_r	= reduced temperature
T_0	= reference temperature
V	= molar volume
y_i	= mol fraction of component i in vapor phase
x_i	= concentration of electrolyte i
x_j	= concentration of thermodynamic inhibitor j
Δ	= difference in properties
ϕ	= fugacity coefficient
γ	= gas specific gravity
μ	= chemical potential
μ_w^l	= viscosity of liquid water
ω	= acentric factor

CHAPTER 1

INTRODUCTION

1.1 Project background

Cryogenic processes are expanding currently due to the process and material technology advancement which make these solutions economically feasible. In natural gas processing, the liquefied natural gas (LNG) solution is usually compared to the traditional piping solution. Producers are more interested for a global market where they can sell their product with the highest profit, thus the LNG and liquid petroleum gas (LPG) concepts become more interesting considering the transport distance to different markets.

The main advantage with the LNG concept is the energy density, which leads to minimal storage requirements where the volume of 1m³ LNG at atmospheric pressure equals to about 614m³ of natural gas at the same pressure (Lavik, 2009). The natural gas with a satisfactory composition is liquefied at a temperature about -162°C and consists mainly of methane (85-95%) in addition to some fractions of other to some fractions other hydrocarbons and traces of nitrogen and carbon dioxide.

These solutions require new processes and equipment developed, for mixtures in which the behaviour is unknown. However, the most important part of these concepts, both LNG and the developing solutions are the liquefaction process, where the natural gas gets cooled down. The only difference is the temperature, at which the different petroleum gases are liquefied, and the extent of the separation process, in which the LNG involves separation of methane from heavier alkenes; this is the main process which requires the low operation temperatures, when refining LNG.

In regards of these low temperature processes of natural gas there is a serious issue when the components in the feed stream precipitates. This is especially critical for carbon dioxide and various hydrocarbons components, due to their high triple point temperature. These components introduce a risk of forming freeze such in Figure 1.



Figure 1: Freeze formation inside pipeline (Products, 2012)

1.2 Problem Statement

Among the critical heavy hydrocarbons are benzene and cyclohexane, components which creates a great risk of freeze outs. These components introduce a risk of forming solid coating on process equipment such as heat exchangers, process piping and valves, in which can lead to blockage and further expensive shutdown of the production. Freezing is a potential and serious problem starting at the production wellhead through the last point in the customer delivery system.

The presence of freeze can not only shut off pipeline but can also alter measurement. If ice forms on the rim of orifice plate, the flow measurement will be in error as a result of the reduced orifice diameter. If freeze forms in the instrumentation supply lines, controllers will cease to function causing a loss of control of the system. Freeze can block off sensing ports and other vital instrument readings (Fish, 2005).

All of these potential issues will ultimately affect the overall operation of natural gas and may have major impact on the profitability of the company. Thus some cost investment is done to make experiment in order to determine the condition where freeze might occur.

Another source of information is computer simulations of natural gas systems. The accurate prediction of freeze formation is required in process simulation which will be the focus of this project. Thus, proper validation of process simulation with existing experimental data needs to be carried out.

1.3 Objective

This research project focuses on the following objectives:

- 1) Improve and extend the knowledge about freeze outs with the focus on modelling and predictions of freeze out parameter
- 2) To validate the freeze out parameter prediction from simulation with experimental data from previous research

1.4 Scope of Study

In this paper, due to time constraint, the study will mainly focuses at developing a HYSYS simulation of the critical components in binary methane rich mixture, due to the composition of natural gas systems. The main component discussed will be freeze out of carbon dioxide which has the highest triple point temperature of the critical components. Issue regarding water and hydrate formation are excluded.

Analysis and validation of the simulation results is against the experimental data obtained from journals.

CHAPTER 2

LITERATURE REVIEW

2.1 Cryogenic Processing Plant

Natural gas processing has developed over the last 2 decades from lean-oil technology to cryogenics to separate methane from heavier components present in the gas streams. Cryogenic processing has been proved to reduce capital and operating costs of recovering natural gas liquids (NGL's). Cryogenic fractionation, however, encounters potential problems when more than about 5 % CO₂ is present in the gas stream. When a gas containing large quantities of CO₂ encounters the process conditions of a cryogenic demethanizer, the CO₂ may freeze, thereby plugging the trays or packing and preventing tower operation (Haut & Thomas, 1989).

2.2 Solid CO₂ Formation

The component which represents the highest risk of precipitation in natural gas systems is definitely carbon dioxide, both due to the high triple point and the concentrations of carbon dioxide in natural gas. Hence, it is regarded as a critical component in many cryogenic processes in the industry and there exist several studies concerning both freeze outs from vapor and liquid phase in binary mixtures with methane.

There are actually two modes for formation of solid CO₂ in gas processing systems. In one, the CO₂ content of a liquid can exceed its solubility limit, in which case carbon dioxide precipitates or crystallizes from the liquid solution. In the other, the CO₂ content of a vapour can exceed the solubility limit, on which case solid CO₂ is formed by desublimation or frosting (Eggeman & Chafin, 2003).

2.2.1 Phase behavior

In order to handle and discuss both the experimental data and the results from the simulations, it is necessary to have good understanding of the phase behavior for the mixtures under investigation. For the binary system consisting of carbon dioxide and methane, a qualitative phase diagram is presented in figure 2. From the Gibbs phase rule it is indicated that in a two phase binary system, the degrees of freedom is two; thus the two phase locus is shown by an area in the phase diagram. Similar are the degree of freedom one in a three-phase binary system, and the three-phase locus is indicated with a line in the phase diagram.

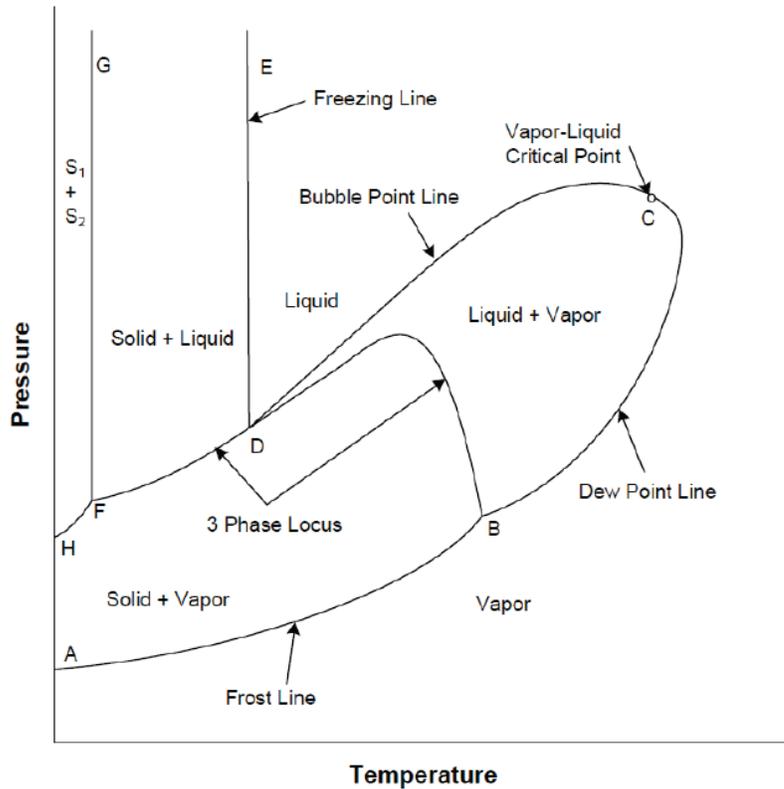


Figure 2: Qualitative Pressure-Temperature Diagram for the Methane-Carbon Dioxide Binary System (Hlavinka & Hernandez)

There are two basic methods for precipitation of solid carbon dioxide in the methane binary system. First, when the carbon dioxide content in a liquid exceeds the solubility limit of the liquid phase, this is indicated by the freezing line (DE) in figure 2 and described by Solid-Liquid equilibrium. A phenomenon that can affect this precipitation

method is super-cooling of the liquid phase, which occurs when the precipitation of the solute happens at a lower temperature than the true thermodynamic Solid-Liquid equilibrium point.

Next method of solid deposition is if the carbon dioxide content exceeds the solubility limit of the gas phase. Hence, the solid formation is described by the solid-vapor equilibrium, this is indicated by the frost line (AB) in the phase diagram.

Most of the experimental data gathered are based on three-phase experiments, where the solubility of carbon dioxide in the three-phase locus, indicated by the line (BDF). However, the lines FH and FG are also indicating three-phase lines, but at these conditions there will be a solid methane phase present, thus it is an irrelevant temperature area in the scope of natural gas processing. Solid carbon dioxide formed between the three-phase locus (BDF) and the frost line (AB) will be dissolved in the liquid phase until the temperatures drops to below the freezing line (DE). The interesting areas regarding freeze out of carbon dioxide in natural gas system is at low carbon dioxide concentrations, and considering that the point (B) is the triple point for pure carbon dioxide and the point (F) is the triple point for pure methane, is the DF line the most interesting of the three phase locus. A change in the overall composition will not affect these lines, BD and DF, due to degrees of freedom these are fixed in a pressure temperature diagram. However, the lines AB, BC, CD, DE, and point C will be affected by an overall change in composition.

2.3 Aspen HYSYS

The utility integrates with Aspen HYSYS and aids in the evaluation of CO₂freeze potential for natural gas processing plants. It predicts both vapor and liquid phase CO₂freezing temperatures for process streams, heat exchangers, expanders, and columns(Engineering).

2.3.1 Technical Superiority

The utility uses a combination of equation of state (Soave-Redlich-Kwong) and activity coefficient based Non-Random-Two-Liquid (NRTL) models for its predictions. The models are tuned with a comprehensive set of critically reviewed experimental data. Its CO₂ freeze prediction is believed to be the most accurate, publicly available for complex mixtures typical of the natural gas processing industry. And where other calculation methods fail mathematically and can report incorrect freezing temperatures, Aspen have developed solution methods that avoid these typical pitfalls.

2.3.2 Ease of Use

The utility is a custom user operation extension and is very easy to install and use within HYSYS. It is similar in design to that of all of the standard simulation unit operations and may be used in any version of HYSYS version 3.1 or later. Simply pick a process stream (either single phase or two phase), a column, a heat exchanger, and so on and the utility will immediately calculate the appropriate CO₂ freeze information.

2.3.3 Benefits

The ability within a given process simulation to rapidly and conveniently check numerous process streams and unit operations for areas where CO₂ freezing may be of concern. This not only saves time, but also ensures that no problematic areas go unnoticed during the design phase of a project. Confidence in more reliable predictions may allow a plant operator to increase NGL recoveries by reducing its operating CO₂ freeze margins.

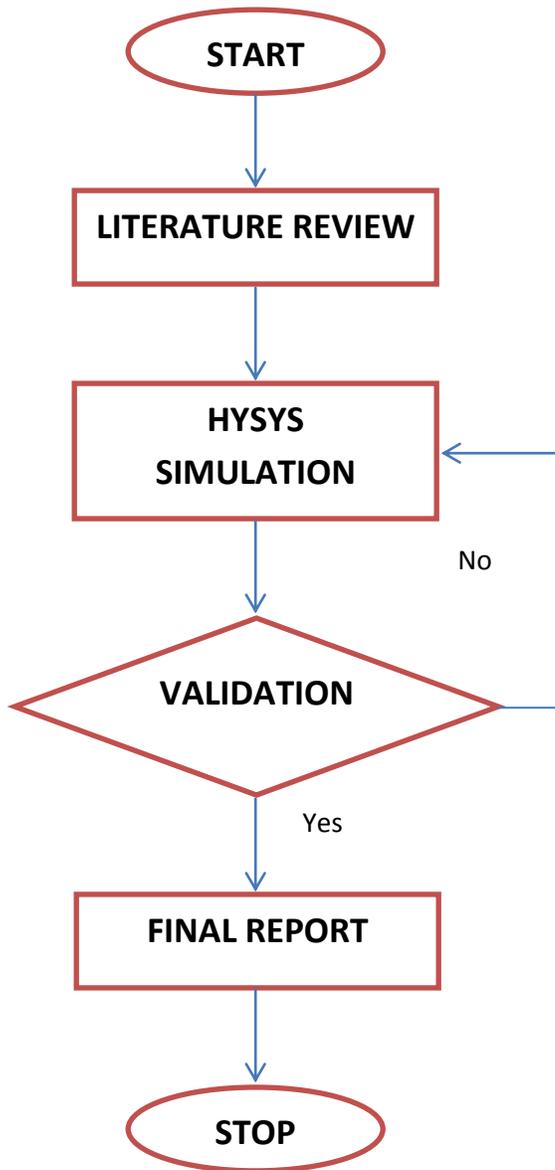
2.3.4 Licensees

Clients who have already licensed the utility: ConocoPhillips, Marathon Oil, Mustang Engineering, Black & Veatch, and others(Engineering).

CHAPTER 3

METHODOLOGY

3.1 Process Flow Chart



-
- Literature review
-
- Introduction on freeze formation on natural gas flow line
-
- Fundamental studies from references and journals
-
- Develop analysis method for the project
-
- Identify suitable parameters and solving methods
-
- Determine mathematical model
-
- Simulation analysis
-
- Recommendation on process application

Figure 3: Project Flow

3.2 Gantt Chart

Timelines for FYP 1

Table 1: Gantt Chart FYP1

no	Details/week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	
1	First meeting with coordinator and supervisors								Mid-semester break								
2	Preliminary research work																
3	Submission of extended proposal																
4	Proposal defense																
5	Project work continues																
6	Submission of interim draft report																
7	Submission of interim report																

Timelines for FYP 2

Table 2: Gantt Chart FYP 2

no	Details/week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15	
1	Project work continuation	█	█	█	█	█	█	█	Mid-semester break									
2	Submission of progress report									█								
3	Project work continuation									█	█	█	█	█				
4	Pre-SEDEX												█					
5	Submission of draft report													█				
6	Submission of dissertation (soft bound)														█			
7	Submission of technical paper														█			
8	Oral presentation																█	
9	Submission of project dissertation (hard bound)																	█

3.3 Project Activities And Key Milestone

Table 3 Activities that have been carried out during FYP 1

Week No	Activities	Description
1-2	Introduction to project	<ul style="list-style-type: none"> - Meeting with Coordinator and Supervisor. - Assigned project title by Supervisor. - Identifying the problem statement. - Identifying objectives and scope of study.
3-4	Software familiarization	<ul style="list-style-type: none"> - Learning how to use the simulator. - Doing some exercise to get familiarize with the function of the software.
5-8	Literature review on project title	<ul style="list-style-type: none"> - Performing some research on related journals and articles. - Executing analysis on the case studies
9	Proposal defense	<ul style="list-style-type: none"> - Oral presentation evaluated by Supervisor and Internal Examiner. - Weaknesses and suggestion for improvement of the project will be highlight.
10-12	Project research continue	<ul style="list-style-type: none"> - Continue research on case studies
13-14	Submission of Interim Draft Report and Interim Report	<ul style="list-style-type: none"> - Submitting draft report to Supervisor for room of improvement and weakness identifying.

Table 4 Activities that have been carried out during FYP 2

Week No	Activities	Description
1-7	Project work continuation	<ul style="list-style-type: none"> - Meeting with Coordinator and Supervisor. - Continue on experimental data suitability study - Try to simulate existing data
8	Submission of progress report	<ul style="list-style-type: none"> - To report on project progress and result obtained so far
11	Pre-SEDEX	<ul style="list-style-type: none"> - Prepared and design a poster covering the introduction and result obtained from simulation and validation with experimental data - Present to internal examiner - Weaknesses and suggestion for improvement of the project will be highlight.
12	Submission of draft report	<ul style="list-style-type: none"> - Submission to supervisor
13	Submission of dissertation (soft bound) and technical paper	<ul style="list-style-type: none"> - Submission of 3 copies of soft bound dissertation and 1 copy in CD to coordinator
14-15	Oral presentation and Submission of project dissertation (hard bound)	<ul style="list-style-type: none"> - Yet to be performed

3.4 Tool/Software Required

The software required to conduct this project are;

- HYSYS
- Techplot
- Digitize It
- Endnote
- Microsoft Office (Word & Excel)

3.5 Phase Equilibrium

The equilibrium condition between different phases in a multi-component system are reached when the exchange of substance between the phases have reached a constant value, meaning that the mass transfer from one phase to another is equal in each direction. For a system in a non-equilibrium condition, the mass transfer between the phases will try to establish a new equilibrium condition. This phase equilibrium condition is, dependent on several variables, including temperature, pressure, composition and the chemical nature of the substances. However, the driving force for this mass transfer taking place is dependent on how far the system is from the thermodynamic equilibrium. Phase equilibrium studies are focusing on the relation between these parameters, in which can be used to describe the systems of interest. The functionality of these models which are used to calculate the thermodynamic and physical properties are crucial to the accuracy of the result.

3.5.1 Thermodynamic Equilibrium

The freezing phenomena is addressed in the phase changes in a fluid, thus it is important to consider the thermodynamic mechanisms for understanding the freeze out subject complete. The phase equilibrium criteria are developed from the principle of conservation of energy and the second law of thermodynamics. The next subchapters give a short introduction to the properties and parameters used for describe and investigate phase equilibriums in fluids (Lavik, 2009).

3.5.1.1 Gibbs Free Energy

When investigating phase equilibrium, it is appropriate to use the Gibbs function, which is defined as:

$$G = H - TS = U + pV - TS \quad (1)$$

By using the law of thermodynamics and Gibbs in differential form, the following function is derived:

$$dG = Vdp + SdT \leq 0 \quad (2)$$

All processes carried through at a specific temperature and pressure ($dT= 0$ and $dp= 0$), are bounded by:

$$dG]_{T,p} \leq 0 \quad (3)$$

This inequality indicates that the Gibbs function of a system, at specific temperature and pressure, decreases through an irreversible process. Each step in such a process results in a reduction of the Gibbs function, and brings the system closer to equilibrium, where equilibrium is achieved at the time the process reach a minimum value of the Gibbs function:

$$dG]_{T,p} = 0 \quad (4)$$

Equation above establishes a relationship between the properties of a system at equilibrium. The way the system has reached the equilibrium condition is not important, but as soon equilibrium condition is achieved, at a specific temperature and pressure, no further spontaneous changes can take place. When we use this equation we specify the temperature and pressure, but it is not necessary to further specify how the system achieves the equilibrium state (Lavik, 2009).

3.5.1.2 Fugacity

The use of chemical potential in equilibrium calculations will often lead to computational difficulties, when the chemical potential at some states approach minus infinity. Thus for some systems it may be more convenient to use fugacity instead of chemical potential, the fugacity function behaves in many cases better, and may be evaluated as:

$$\mu = g = RT \ln (f) \quad (5)$$

Fugacity has the same notation as pressure, and in ideal gas systems it generally plays the same role as the pressure. Since ideal gas behavior is achieved when the pressure goes to zero, the constant term can be determined by the requirement showing that the fugacity of a pure component is equal to the pressure in the limit of zero pressure. Mathematically described:

$$\lim_{p \rightarrow 0} \frac{f}{p} = 1 \quad (6)$$

These two equations completely define the fugacity function; the phase equilibrium criterion is described as:

$$f_1^1 = f_1^2 \quad (7)$$

Thus for a multiphase, multi-component system the fugacity for a component must be the same in all phases in order to achieve equilibrium (Lavik, 2009).

3.5.2 Equation of State

Since the ideal gas law is not applicable on natural gas mixtures, the use of equations of state are necessary for being able to calculate the state of a fluid or fluid mixture at given conditions. The equation of state method is important for designing of processes in chemical engineering, and it is assumed that it will have a growing role in phase equilibrium studies of fluids and fluid mixtures.

Traditional use of equations of state was mainly for pure components, the development of these models has allowed the equations to describe mixtures as well. At first they were only used for nonpolar mixtures, but as the development continued they were able to calculate phase equilibria for both non-polar and polar mixtures. The advantages by using equations of state for calculating phase equilibria are many; they can be used over a wide range of temperature and pressure, applicable for multi-component mixtures, consisting of light gases and heavy liquids.

The progress of the computational power and statistical development has allowed the equations of state to take consideration to molecular behavior that applies for real fluids and mixtures. Thus the accuracy of the underlying model is improved.

For describing natural gas systems the Soave-Redlich-Kwong (SRK) is widely used in the chemical process industry. The focus is on equation of state based on the van der Waals equation of state.

3.5.2.1 Van der Waals equation of state (vdW)

The van der Waals equation of state was the first equation capable of representing vapor-liquid coexistence, and it were proposed in 1873. The expression is as followed:

$$Z = \frac{V}{V-b} - \frac{a}{RTV} \quad (8)$$

Where Z is indicating the compressibility factor ($Z = pVRT$). In both expressions is T the temperature, V is volume, p is the pressure, and R is the molar universal gas constant. The parameter a is representing the attractive forces between the molecules, and the parameter b is representing the co-volume occupied by the molecules, thus if the molecules are treated as hard spheres with a diameter, σ ; the expression for the co-volume are expressed by $b = 2\pi N\sigma^3/3$.

The a and b parameters is a function of the critical properties of the fluid. Because of the functionality of the van der Waals regarding the description of the contribution of repulsive and attractive intermolecular interactions, it is consider to be an “hard sphere (repulsive) + attractive” term equation of state. It is capable of describing the vapour and liquid phases and phase transitions in a qualitative manner, but is seldom sufficient accurate for phase equilibrium calculations. The compressibility factor which applies for all fluids, are $Z_c = 0.375$. In contrast, the real value for various hydrocarbons is in between 0.24 and 0.29. The van der Waals equation of state has been succeeded by several more accurate equations; the equations further presented in this work are regarded as modifications of the van der Waals equation (Lavik, 2009).

3.5.2.2 Redlich-Kwong equation of state (RK)

The modification to the van der Waals equation of state by adding a temperature dependent attractive term is regarded as one of the most important improvements. The Redlich-Kwong equation of state is expressed by:

$$Z = \frac{V}{V-b} - \frac{a}{RT^{1.5}(V+b)} \quad (9)$$

For pure substances, the equation parameters a and b are usually expressed as,

$$a = 0.4278R^2T_c^{2.5}/p_c$$

$$b = 0.0867 RT_c/p_c$$

By applying mixing rules to the equation parameters a and b , the Redlich-Kwong equation of state can be used for describing mixtures. It has been showed that by treating the interaction parameters as empirical parameters have led to a substantial improvement of the description of the fugacity in gas mixtures. In addition, the accuracy of the critical properties for binary mixtures can be increased by adjusting the value of the interaction parameter in the mixing rule for the a term (Lavik, 2009).

3.5.2.3 Soave-Redlich-Kwong equation of state (SRK)

By replacing the temperature dependent attractive term ($a T^{1.5}$), in the Redlich-Kwong equation, with a more general temperature dependent term $a(T)$, Soave (1972) made a significant improvement to the Redlich-Kwong equation:

$$Z = \frac{V}{V-b} - \frac{a(T)}{RT(V+b)} \quad (10)$$

Where

$$a(T) = 0.4274 \left(\frac{R^2 T_c^2}{p_c} \right) \left\{ 1 + k \left[1 - \frac{T}{T_c} \right]^{0.5} \right\}^2$$

$$m = 0.480 + 1.57\omega - 0.176\omega^2$$

$$b = 0.08664 \frac{RT_c}{p_c}$$

and ω is the acentric factor.

As mentioned Soave-Redlich-Kwong equations of state widely used in the industry. It has many advantages regarding describing binary and multi component systems. It is accurately representing the correlation between temperature, pressure and phase

compositions. The only requirements necessary is the critical properties and acentric factors for the generalized parameters, and little computational time is needed to get accurate phase equilibrium correlations. The restriction of the quality of the result is the estimation of the vapor pressure, since the description of saturated liquid volumes is over predicted compared to experimental data (Lavik, 2009).

3.6 Experimental Data from Literature

The experimental studies on the subject of phase equilibrium including a solid phase in light hydrocarbon systems were mainly done between the 50th-70th decades. However, the current understanding of solid-fluid equilibrium in hydrocarbon dominant mixtures is limited to a number of binary and ternary systems. A selection of these experimental sources are further investigated and evaluated, exclusively the binary systems including methane as the dominant component. The most important selection criterion for this type of experimental data, are the concentration of the solute component, in which should represent the concentration in real natural gas. Thus it has been focused on low solute concentration, especially of the critical hydrocarbons in methane binary mixtures.

The experimental data evaluated in this study are presented in table 5 and table 6, and this forms the foundation of the investigation related to the accuracy and behavior of the simulation tools. As stated earlier, this study focuses on the following component; carbon dioxide (CO₂). Three literature papers are selected to be the basis of experimental data:

- 1) Author : Dr. Fred Kurata
Title : Solubility of Solid Carbon Dioxide in Pure Light Hydrocarbon and Mixtures of Light Hydrocarbons(Kurata, 1974)
- 2) Author : G.M. Agrawal and R.J. Leverman
Title : Phase Behavior of the Methane Carbon Dioxide System in the Solid-Vapor Region(Agrawal & Leverman, 1974)
- 3) Author : T.T. Le and M.A. Trebble

Title : Measurement of Carbon Dioxide Freezing in Mixtures of Methane, Ethane, and Nitrogen in the Solid-Vapor Equilibrium Region (Le & Trebble, 2007)

Table 5: Solid-Liquid experiment of binary system liquid methane

Author	No. of Point	Mole Fraction		Temperature (K)		Pressure (bars)		Experimental Method
		Min	Max	Min	Max	Min	Max	
Kurata	20	0.0016	0.90	129.6	214.16	3.57	48.18	Spectroscopy

Table 6: Solid-Vapor experiment of binary system liquid methane

Author	No. of Point	Mole Fraction		Temperature (K)		Pressure (bars)		Experimental Method
		Min	Max	Min	Max	Min	Max	
Agraval	42	0.0012	0.1067	137.5	198.1	1.72	27.85	Visual Synthetic
Le	55	0.01	0.0293	168.6	187.7	9.62	30.08	Visual Synthetic

The full tabulated experimental data is attached in appendix section. A total of 117 data point will be simulated in HYSYS simulation. In the simulation, the mole fraction and pressure will be maintained according to literature as above, and the parameter under study will be the temperature at freeze start to form.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Solid-Liquid Equilibrium for Binary CH₄ and CO₂ Systems.

The experimental data used as references for the binary interaction parameter study for the solid-liquid system are the high quality experimental data from the work done by Kurata (Kurata, 1974). This was published in 1974 by Dr. Fred Kurata, which got the task to present all available information about the solubility of carbon dioxide in light hydrocarbons in one publication, and it is regarded as one of the most reliable low temperature sources. Hence, the SLE calculation will be compared against the sources available, which constitute a comprehensive selection of experimental data.

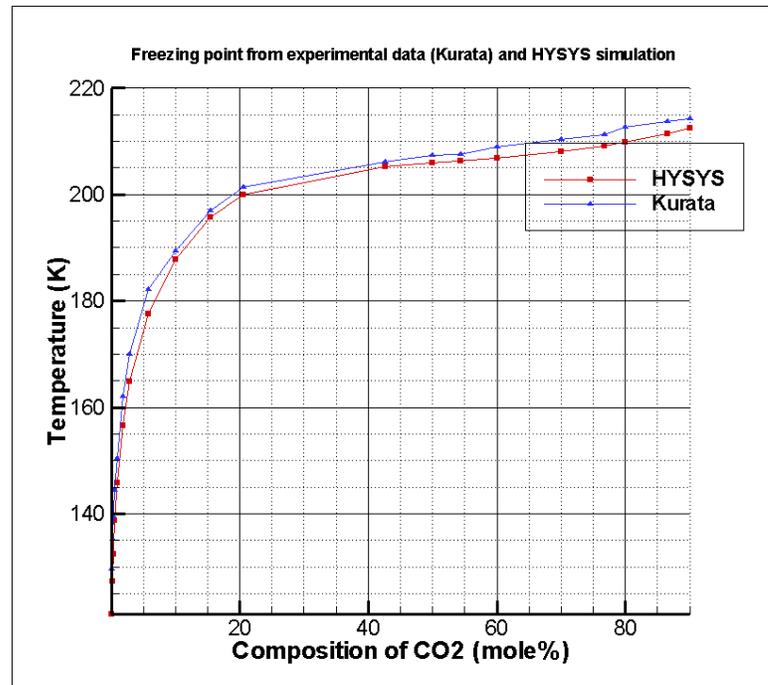


Figure 4: Formation of CO₂ Freeze in liquid CH₄, predictions and experimental points from Kurata

Figure 4 is presenting the experimental data gathered from Kurata, and the simulations carried through with HYSYS. Regarding the accuracy of the HYSYS predictions compared to the whole dataset from Kurata, which consists of freezing point

temperatures for carbon dioxide concentrations from 0.16 to 90 mole %, the consistency are quite decent; the predicted temperatures are overall a little lower than the experimental results

Compared to the experimental dataset from Kurata, the average absolute deviation is calculated to 3.51 K, and a maximum absolute deviation of 8.45 K. The deviation tends to increase in the low temperature area; from a temperature of 180 K to 130 K (referring to the sample numbers 13-20 in appendix A1) it predicts a temperature at least 4 K lower than the reference temperature, thus the large absolute deviation. HYSYS is under predicting the freezing point temperatures especially in the upper temperature range, however, the simulations give good results in the lower temperature range.

4.2 Solid-Vapor Equilibrium for Binary CH₄ and CO₂ Systems.

For solid-vapor equilibrium (SVE) systems, it is harder to obtain experimental data; freeze out of carbon dioxide in SVE systems has not been studied as much as SLE systems. For freezing points study in vapor-solid systems has the sources of Agrawal and Le.

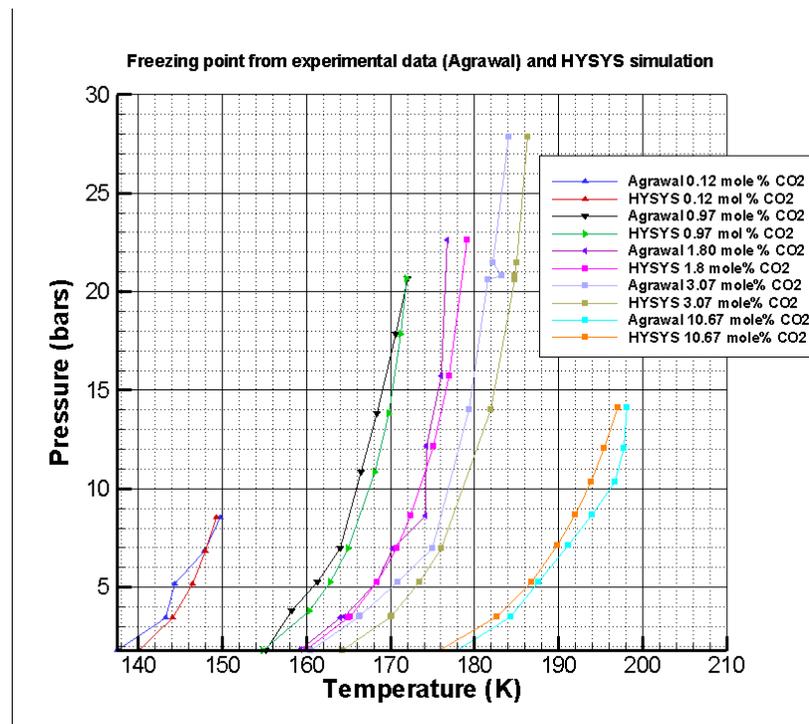


Figure 5: Formation of CO₂ Freeze in solid CH₄, predictions and experimental points from Agrawal

Considering figure 5, HYSYS calculate in general temperatures below the experimental points from Agrawal, except for the data series including a carbon dioxide content of 10.7 mole %. The dataset exists of methane-carbon dioxide compositions at different pressures, and has a carbon dioxide content of respectively (from right to left), 0.12%, 0.97%, 1.8%, 3.07% and 10.7%. The predictions from the HYSYS simulator, gives an average absolute deviation of 1.69 K and a max absolute average of 4.34 K.

The experimental dataset from Le includes freezing point temperatures for three different compositions of the binary mixture consisting of methane-carbon dioxide, respectively (from left to right) with 1.0, 1.91 and 2.93 mole % carbon dioxide content.

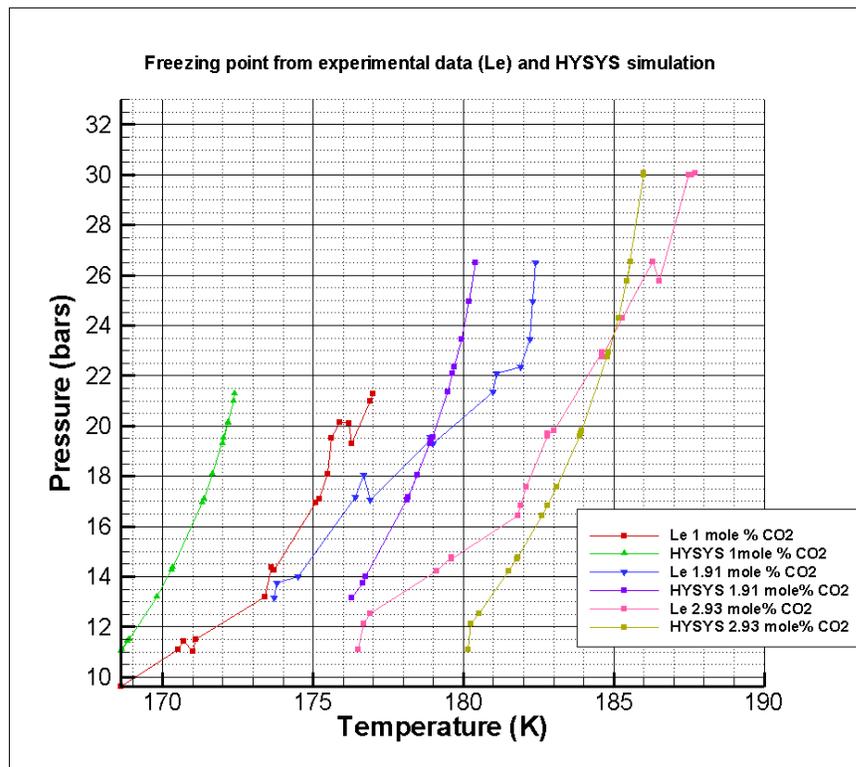


Figure 6: Formation of CO2 Freeze in solid CH4, predictions and experimental points from Le

The agreement between predicted and experimental data from this dataset is about the same as the data from Agrawal. From studying figure 6 it looks like the deviation is much larger than the deviation in figure 5, but considering the different temperature intervals the result is more or less similar.

4.3 Comparison of experimental data and different simulation models

When analyzing the results, the emphasis is first of all, the accuracy of the results. Next, in which temperature interval the deviations are highest and if there are any conditions where the simulations fails to describe the system of interest. This is done with the intentions to investigate whether it is the experimental results or the calculation methods used which are causing deviations. The method used for comparison of predicted and experimental freezing points is average absolute deviation (AAD) and BIAS, described beneath.

$$\text{AAD: average of } \text{ABS}(T_{\text{calc}} - T_{\text{exp}}) \quad (11)$$

$$\text{BIAS : average of } (T_{\text{calc}} - T_{\text{exp}})$$

Where a negative BIAS value indicates the calculated results predicts in average a lower freezing point temperature than the experimental dataset. For predictions where the BIAS and AAD values are equal, the entire predicted dataset are either, over or under predicting the freezing point temperatures. Regarding the accuracy of the predictions, there are both insecurity related to the experimental results and in the thermodynamic models, in form of component properties and the description of the vapor pressure.

The information presented in table 7 and 8, shows an overview over the accuracy of the results generated regarding freezing point temperatures of the methane rich binary mixtures investigated. All the raw data are presented in table form in the appendix, and the column on the right hand side specify the appendix number.

Table 7: Solid-Liquid experiment of binary system liquid methane

Author	No. of Point	Mole Fraction		Temperature (K)		Pressure (bars)		Experimental Method	HYSYS simulation		Appendix
		Min	Max	Min	Max	Min	Max		BIAS (K)	AAD (K)	
Kurata	20	0.0016	0.90	129.6	214.16	3.57	48.18	Spectroscopy	-3.51	3.51	A1

Table 8: Solid-Vapor experiment of binary system liquid methane

Author	No. of Point	Mole Fraction		Temperature (K)		Pressure (bars)		Experimental Method	HYSYS simulation		Appendix
		Min	Max	Min	Max	Min	Max		BIAS (K)	AAD (K)	
Agraval	42	0.0012	0.1067	137.5	198.1	1.72	27.85	Visual Synthetic	0.89	1.69	A2
Le	55	0.01	0.0293	168.6	187.7	9.62	30.08	Visual Synthetic	-0.73	2.13	A3

As described earlier, the HYSYS model is capable of predicting carbon dioxide freeze outs. However, it seems to predict crystallization from the vapor phase better than from the liquid phase.

From table 7 and 8, it is confirmed the equation of state used which is the SRK predicts the freezing points with a satisfying degree of accuracy when compared with experimental data base on literature review where values of BIAS and AAD below 4 K is within satisfying value (Lavik V. F., 2009). It is also worth mentioning that the data obtained from simulation data is reliable thus can reduce the dependency on experimental procedures which consume more cost than simulation.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In cryogenic processes for deep LNG recovery, accurate prediction of dry ice formation conditions is important. A good knowledge of phase behavior and thorough understanding of dry ice formation can prevent severe operational problems. It is important to use the right and accurate equation of state within simulation software to generate the correct freeze curve. Accuracy can be determined by comparing simulation result with experimental result from literature.

For the simulations carried through in HYSYS, the Soave-Redlich-Kwong equation of state selected. It is also recognized from previously work, that these equations of state are widely used for describing the fluid phases in solid-fluid equilibrium calculations, and the prediction of freezing point temperatures.

Base on the simulation carried out, the BIAS and AAD of all three papers simulated is within the acceptable level of accuracy thus validated the simulation data. This validation show reliability in simulation prediction thus reduce the dependency on experimental data that consume more cost.

5.2 Recommendation

Since there is a lack in time, the scope of study is narrowed to binary mixture of methane with carbon dioxide. As a recommendation, the research can be furthered by simulating other two critical components which is benzene and cyclohexane

Other than that, further study can be done on multi-component mixture, similar to real natural gas mixtures.

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APPENDIX

A1: Comparison of simulation and experimental data from Kurata

Table 9: Comparison of simulation and experimental data from Kurata

Sample no.	Composition, mole %		Pressure (bars)	Temp (K)	Temp (K)	(Tcalc - Texp)	ABS	Pressure (bar)
	CH4	CO2						
1	10	90	20.79	214.3	212.47	-1.83	1.83	23
2	13.5	86.5	24.31	213.7	211.42	-2.28	2.28	28
3	20	80	30.14	212.6	209.79	-2.81	2.81	35
4	23.2	76.8	36.39	211.2	209.15	-2.05	2.05	39
5	30	70	39.37	210.4	207.99	-2.41	2.41	44
6	40	60	43.57	209	206.75	-2.25	2.25	47
7	45.7	54.3	46.47	207.6	206.24	-1.36	1.36	48
8	50	50	46.93	207.3	205.89	-1.41	1.41	48
9	57.4	42.6	48.18	206.2	205.28	-0.92	0.92	48
10	79.5	20.5	48.18	201.3	199.96	-1.34	1.34	48
11	84.61	15.39	45.18	196.9	195.71	-1.19	1.19	48
12	89.92	10.08	39.54	189.3	187.84	-1.46	1.46	48
13	94.15	5.85	32.91	182.2	177.49	-4.71	4.71	43
14	97.06	2.94	22.35	169.9	164.83	-5.07	5.07	34
15	98.17	1.83	16.7	162	156.6	-5.4	5.4	30
16	99.07	0.93	10.53	150.4	145.76	-4.64	4.64	22
17	99.42	0.58	8.08	144.5	138.85	-5.65	5.65	18
18	99.63	0.37	6.29	139.4	132.47	-6.93	6.93	15
19	99.75	0.25	5.07	135.2	127.24	-7.96	7.96	13
20	99.84	0.16	3.57	129.6	121.15	-8.45	8.45	10
					BIAS/AAD	-3.506	3.506	
					MIN	-8.45	0.92	
					MAX	-0.92	8.45	

A2: Comparison of simulation and experimental data from Agraval

Table 10: Comparison of simulation and experimental data from Agraval

Sample no.	Composition, mole %		Pressure (bars)	Temp (K)	Temp (K)	(Tcalc - Texp)	ABS
	CH4	CO2					
					HYSYS Simulation		
1	99.88	0.12	1.79	137.54	140.11	2.57	2.57
2			3.45	143.21	144.06	0.85	0.85
3			5.17	144.32	146.44	2.12	2.12
4			6.83	147.82	148.03	0.21	0.21
5			8.55	149.76	149.24	-0.52	0.52
6	99.03	0.97	1.79	155.15	154.78	-0.37	0.37
7			3.79	158.21	160.41	2.20	2.20
8			5.24	161.26	162.86	1.60	1.60
9			6.96	163.98	164.99	1.01	1.01
10			10.82	166.48	168.17	1.69	1.69
11			13.79	168.37	169.78	1.41	1.41
12			17.86	170.59	171.28	0.69	0.69
13			20.68	172.04	171.97	-0.07	0.07
14	98.20	1.80	1.72	158.21	159.42	1.21	1.21
15			1.86	159.32	160.03	0.71	0.71
16			3.45	163.98	165.00	1.02	1.02
17			3.52	164.54	165.16	0.62	0.62
18			5.24	168.37	168.42	0.05	0.05
19			6.96	170.32	170.73	0.41	0.41
20			8.62	174.15	172.45	-1.70	1.70
21			12.13	174.26	175.09	0.83	0.83
22			15.72	176.04	176.95	0.91	0.91
23			22.61	176.76	179.08	2.32	2.32
24	96.93	3.07	1.72	159.59	163.93	4.34	4.34
25			1.79	160.43	164.26	3.83	3.83
26			3.52	166.21	170.04	3.83	3.83
27			3.55	166.43	170.12	3.69	3.69

28			5.24	170.82	173.52	2.70	2.70
29			6.96	174.98	176.01	1.03	1.03
30			14.00	179.37	181.91	2.54	2.54
31			20.62	181.59	184.74	3.15	3.15
32			20.82	183.21	184.81	1.60	1.60
33			21.44	182.15	184.99	2.84	2.84
34			27.85	184.04	186.35	2.31	2.31
35	89.33	10.67	1.72	177.71	175.53	-2.18	2.18
36			3.52	184.32	182.64	-1.68	1.68
37			5.24	187.65	186.74	-0.91	0.91
38			7.10	191.21	189.91	-1.30	1.30
39			8.69	193.98	192.03	-1.95	1.95
40			10.34	196.65	193.84	-2.81	2.81
41			12.07	197.71	195.44	-2.27	2.27
42			14.13	198.09	197.04	-1.05	1.05
					BIAS/AAD	0.89	1.69
					Min	-2.81	0.05
					Maz	4.34	4.34

A3: Comparison of simulation and experimental data from Le

Table 11: Comparison of simulation and experimental data from Le

Sample no.	Composition, mole %		Pressure (bars)	Temp (K)	Temp (K)	(Tcalc - Texp)	ABS
	CH4	CO2					
1	99.00	1.00	9.62	168.60	167.64	-0.96	0.96
2			11.10	170.50	168.64	-1.86	1.86
3			11.41	170.70	168.83	-1.87	1.87
4			11.04	171.00	168.60	-2.40	2.40
5			11.49	171.10	168.88	-2.22	2.22
6			13.19	173.40	169.79	-3.61	3.61
7			14.35	173.60	170.33	-3.27	3.27
8			14.26	173.70	170.29	-3.41	3.41
9			16.94	175.10	171.31	-3.79	3.79
10			17.08	175.20	171.38	-3.82	3.82
11			18.09	175.50	171.66	-3.84	3.84
12			19.52	175.60	172.03	-3.57	3.57
13			20.13	175.90	172.17	-3.73	3.73
14			20.09	176.20	172.16	-4.04	4.04
15			19.31	176.30	171.98	-4.32	4.32
16			20.99	176.90	172.35	-4.55	4.55
17			21.29	177.00	172.40	-4.60	4.60
21	98.09	1.91	13.14	173.70	176.30	2.60	2.60
22			13.76	173.80	176.64	2.84	2.84
23			13.99	174.50	176.76	2.26	2.26
24			17.16	176.40	178.17	1.77	1.77
25			18.03	176.70	178.48	1.78	1.78
26			17.05	176.90	178.12	1.22	1.22
27			19.44	178.90	178.94	0.04	0.04
28			19.55	178.90	178.98	0.08	0.08
29			19.30	179.00	178.90	-0.10	0.10
30			21.35	181.00	179.47	-1.53	1.53
31			22.07	181.10	179.64	-1.46	1.46
32			22.35	181.90	179.70	-2.20	2.20

33			23.45	182.20	179.93	-2.27	2.27
34			24.97	182.30	180.19	-2.11	2.11
35			26.51	182.40	180.39	-2.01	2.01
36	97.07	2.93	11.09	176.50	180.15	3.65	3.65
37			12.13	176.70	180.24	3.54	3.54
38			12.53	176.90	180.51	3.61	3.61
39			14.21	179.10	181.51	2.41	2.41
40			14.77	179.60	181.81	2.21	2.21
41			14.70	179.60	181.77	2.17	2.17
42			16.44	181.80	182.62	0.82	0.82
43			16.84	181.90	182.80	0.90	0.90
44			17.58	182.10	183.11	1.01	1.01
45			19.58	182.80	183.86	1.06	1.06
46			19.71	182.80	183.90	1.10	1.10
47			19.82	183.00	183.94	0.94	0.94
48			22.92	184.60	184.83	0.23	0.23
49			22.74	184.60	184.79	0.19	0.19
50			24.28	185.30	185.15	-0.15	0.15
51			26.52	186.30	185.57	-0.73	0.73
52			25.77	186.50	185.44	-1.06	1.06
53			29.98	187.50	185.98	-1.52	1.52
54			30.00	187.60	185.99	-1.61	1.61
55			30.08	187.70	185.99	-1.71	1.71
					BIAS/AAD	-0.73	2.13
					Min	-4.60	0.04
					Maz	3.65	4.60