ECONOMIC EVALUATION OF CO_2 RECOVERY FROM FLUE GAS USING HYDRATES

by

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

JAN 2010

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CERTIFICATION OF APPROVAL

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Approved by,

(Dr Khalik M. Sabil)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2010

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.

MUHAMAD YUSUF BIN AMAT

TABLE OF CONTENTS

ABSTRACT

The purpose of this report is to deliver the progress research work for author's Final Year Research Project 2. This study consists of conceptual design the CO_2 gas separation via hydrate formation and economics evaluation of this process and comparison with other conventional processes. The basis for hydrate process design gathered from several literatures. Then the process is simulated using CHEMCAD process simulation software. There are several important design considerations during simulation. From the simulation results and conceptual design, the economics are evaluated. In general, this research project has potential advantages in terms of economics and environment as long as detailed conceptual design is done.

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1 – PROJECT BACKGROUND

1.1 Introduction

In general, clathrate hydrate or gas hydrate is an inclusion compound of which the cage-like structure formed by hydrogen-bonded water molecules. There is no chemical reaction between water and gas molecules but they are held together by physical bonding. Clathrate hydrates are thermodynamically stable under low-temperature and high-pressure conditions. This cage-like structures, known as cavities can hold relatively small gas molecules (guest) in it. Among the suitable guest molecules for hydrate formation are CO_2, N_2, O_2, H_2, and natural gas components. Three different hydrate structures namely structure I (sI), structure II (sII) and structure H (sH) can be formed depending on the types of cavities that are formed and the distribution of those cavities in a unit cell. **FIGURE 1.1** presents the structures formed from types of cavities and their coordination number.

A variety of applications of gas hydrates has been studied, especially in the field of gas storage and transportation, disposal of CO_2 and gas separation [1]. They are very important in safety issue in oil and gas pipelines, they offer a large unexploited means of energy and they have a significant role in past and future climate change.

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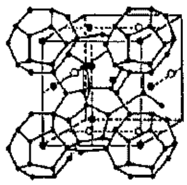
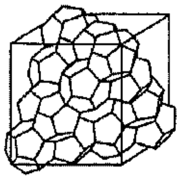
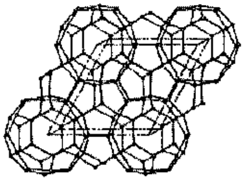
							
1. CAVITY	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^3 5^6 6^3$	$5^{12}6^8$

FIGURE 1.1 Hydrate structures formed from different type of cavities for small and large cage [2].

As previously mentioned, carbon dioxide has been known to be among a number of molecules that can form clathrate hydrate. The existence of CO_2 hydrates dates back to the year 1882, when Wróblewski [1882] reported the clathrate hydrate formation in a system of carbonic acid and water. The hydrate dissociation curve in the range 267 K to 283 K is first published by Villard in 1897 [Villard, 1897].

Later on, Tamman and Krige [1925] measured the hydrate decomposition curve from 230 K to 250 K. Frost and Deaton [1946] determined the dissociation pressure between 273 K and 283 K. Takenouchi and Kennedy [1965] measured the decomposition curve from 4.5 to 200 MPa. Carbon dioxide hydrate was classified as a structure I clathrate for the first time by von Stackelberg & Muller [1954].

As a simple hydrate, carbon dioxide forms structure I hydrate under appropriate pressure and temperature conditions. If all the hydrate cavities are occupied, the chemical formula is $8CO_2.46H_2O$ or $CO_2.5.75H_2O$. [3]

Compilations of hydrate equilibrium conditions of carbon dioxide in pure water can be found in Sloan and Koh [2008]. The phase behaviour of carbon dioxide and water in the hydrate forming region is presented in FIGURE 1.2. As shown in this figure, the hydrate stability region is bounded by the H-I-V, H-L_W-V and H-L_W-L_{CO2}. As such, at any specified temperature, carbon dioxide hydrate will be stable as long as the pressure of the system is higher or equal to the equilibrium pressure of the system. As shown in this figure, carbon dioxide hydrate has two quadruple points, Q_1 and Q_2. The quadruple point Q_1 is a four-phase equilibrium point of I-L_W-H-V and it is located at 273.1 K (-0.05 °C) and 1.256 MPa (about 10 bar). The quadruple point Q_2 is a four phase equilibrium point of L_W-H-L_V-V and is located at 283.0 K (9.85 °C) and 4.499 MPa (44 bar). In literature, the lowest measured equilibrium pressure for carbon dioxide hydrate is at 0.535 kPa and 151.5 K for I-H-V equilibrium point and its value is reported by Miller and Smythe [1970].

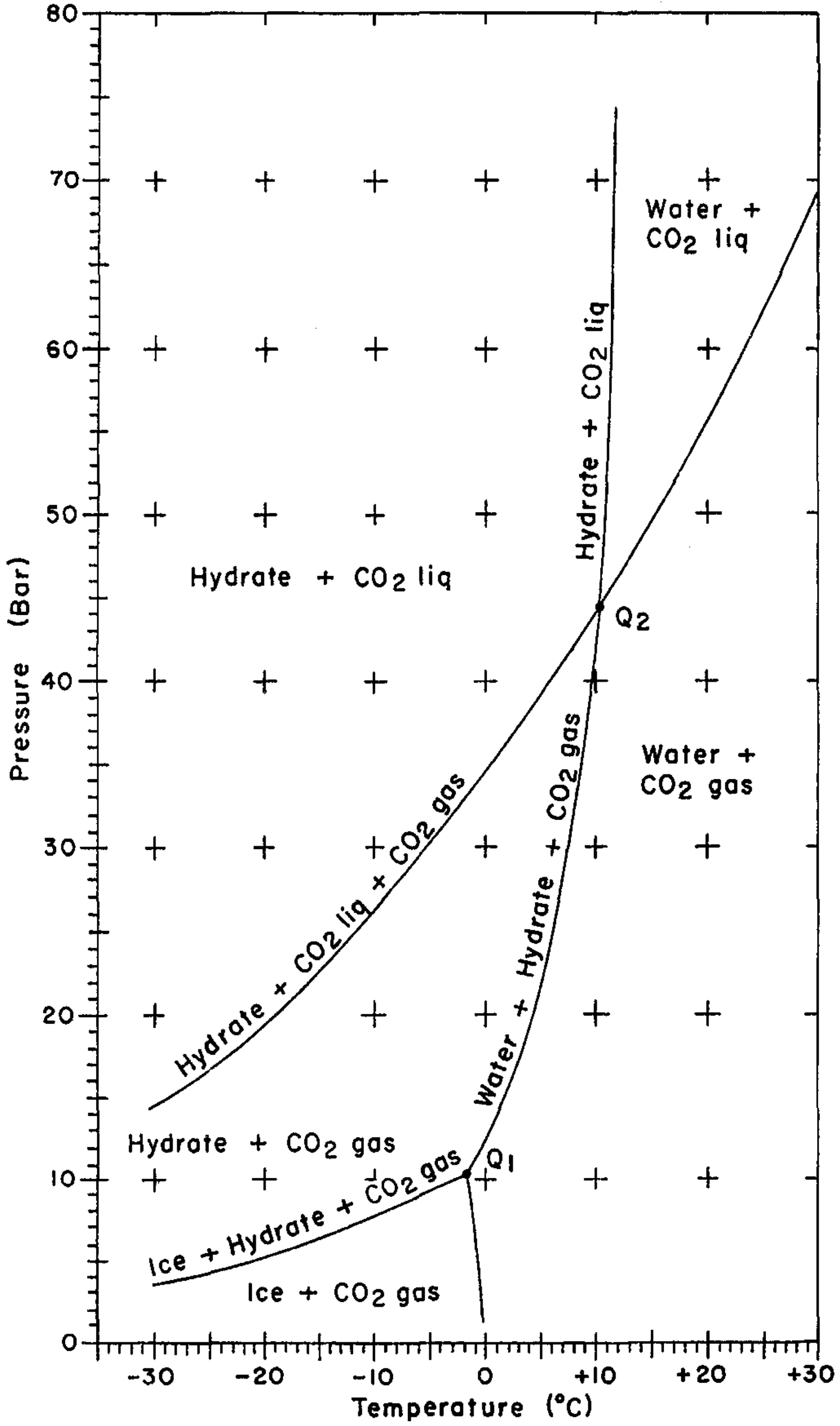


FIGURE 1.2 P-T diagrams for CO_2+N_2 hydrate system as reported by Miller [4]

Concerns on CO_2 as one of the major contributors to greenhouse effects has lead to many studies regarding carbon dioxide recovery and utilization for global sustainability. The main interest in this project is the CO_2 recovery from flue gas (post-combustion) from coal-fired power plant via hydrate formation. Post-combustion capture involves separating CO_2 from flue gas (15-20% CO_2, 5% O_2 and balance N_2). In a conventional power generation station a CO_2 separation and capture unit can be retrofit and carbon dioxide can be separated before letting the flue gas to go out in the atmosphere.

Gas separation process by using hydrates is based on selective partition of the components in the mixture between the gaseous phase and the hydrate phase. Apart from low-temperature and high-pressure conditions requirement, the stability of the hydrates depends on the shape and size of guest molecules, interaction between guest and host molecules, thermodynamic conditions for the hydrate formation would differ in wide range of pressure and temperature depending on the gas molecules. Shiojiri et al. [2004] stated that the separation process is assumed to be conducted in the following three steps; hydrate formation, separation of the solid hydrate from the feed gas and water, and recovery of the enriched gas by dissociation of the hydrate. [1].

The basic phenomenon that explains the reason why hydrates can separate the specified constituent from mixed gases is demonstrated in **FIGURE 1.3**. The constituent is separated as the solid solutions.

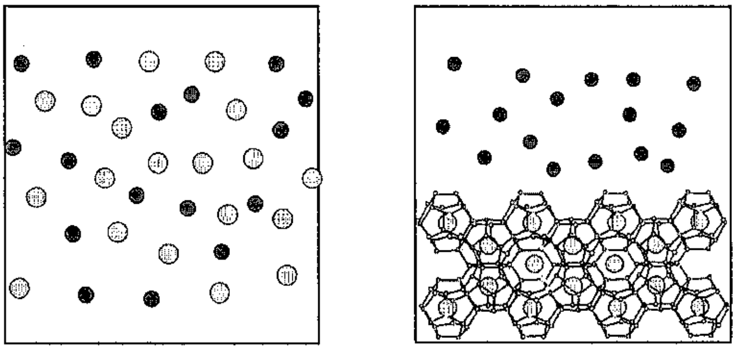


FIGURE 1.3. The separation mechanism of the specified constituent from mixed gases by hydrates. [5]

If the mixed gases were compounded of the components that formed hydrates and the components that could not make hydrates, the former components would be captured in hydrates' cages and the latter components should be left in the mixed gases.

In addition intermolecular force between the gas molecule in the cage and water molecules that surrounding the gas molecule is different among gas components, so the specified constituent exists excessively in the hydrate phase. The mole fraction of each component in hydrate phase depends basically upon the fugacity of each component in the gas phase and the intermolecular potential between the gas molecule and water molecules when they take the hydrate structure. The flue gases from the thermal electric power station contained mainly CO_2, N_2, O_2, and H_2O. Although these components all can make hydrates, but the intermolecular potential is different each other, that enables us to separate CO_2 from other components. The comparison of the intermolecular potential is indicated in **FIGURE 1.4**. The potential well depth of CO_2 is deeper than that of other components and it means that CO_2 makes hydrates in more moderate condition than others. [5]

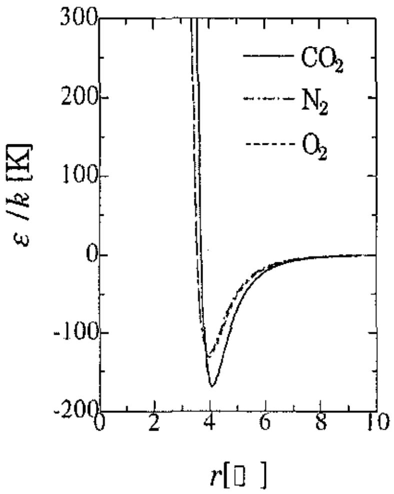


FIGURE 1.4. The intermolecular potentials of CO_2, N_2, and O_2. [5]

Currently, there are many processes developed for removing or isolating a particular gaseous component from a multi-component gaseous stream. These processes include absorption, adsorption, membrane separation etc. and this will be explained later on in Chapter 2 [6]. Praveen et al. [2007] mentioned that the liquid absorption using amines was considered the most promising current method while some other methods are promising but too new for comparison. There is continued interest in the development of less energy intensive processes.

One of the new methods for separating CO_2 from flue gas is through clathrate or gas hydrate formation. When gas hydrate crystals are formed from a mixture of gases the concentration of these gases in the hydrate crystals is different than that in the original gas mixture. This is the basis for the utilization of clathrate hydrate formation decomposition as a separation process [6].

1.2 Problem Statement

Currently, the thermodynamic data for CO_2 hydrate, N_2 hydrate, and CO_2 + N_2 hydrate systems are available though many of them are only for CO_2 hydrate system only. The thermodynamic experimental data for CO_2 + N_2 hydrate system needs to be verified by modeling means. There are only a few proposed conceptual design of this hydrate separation process and there are only available on high level. The detailed process design with material and energy balances with complete streams information are not yet available. The process design simulation also not available and it needs to be optimized as well. The detailed cost estimation also not available and it is needed to produce more accurate costing for economic potential. Therefore, the problem is to produce complete process design with its economics.

1.3 Objectives and Scope of Study

Upon completing the project, a few objectives need to be achieved. The objectives of this research project are as the following:

- To conduct high level thermodynamic analysis of gas hydrate system
- To simulate the proposed hydrate based CO_2 separations with and without additive
- To evaluate the economics for both system with and without additive and thus to study its effect to the economics

CHAPTER 2 – LITERATURE REVIEW

2.1 Hydrate Phase Behavior

Phase equlibria for hydrate formation is the temperature and pressure where microscopic amount of hydrate exist in equilibrium with gas and liquid phase. As reported by Kang and Lee, the three phases H-L-V equilibria of the ternary CO_2-N_2-water system were determined at several different ratios of CO_2 and N_2. The mixed hydrates formed over the wide temperature and pressure ranges of 272-284 K and 15-300 bar largely depending upon the gas-phase compositions. The complete data were demonstrated in **FIGURE 2.1**. As simple hydrates, CO_2 and N_2 form structure I (sI) and structure II (sII), respectively. The structure of mixed hydrates is considered to be either sI or sII depending on the relative ratio of these two different gas molecules occupied in the small and large cavities. As generally expected, all the hydrate formation lines were located between two pure CO_2 and N_2 H-L-V. [7]

With the fundamental information in **FIGURE 2.1** an attempt for developing a new hydrate-based gas separation process was initiated, and its thermodynamic validity was closely examined. One important application of this process is the CO_2 recovery from power plant flue gases containing various concentrations of CO_2. Flue gas from power plant usually consists of 15 to 20 mol % CO_2, 5 to 9 mol % O_2, trace gases, and balance N_2. After suitable pretreatment steps, flue gas can be simplified as ternary CO_2, O_2, and N_2 mixture. [7]

Furthermore, it can be assumed that the treated flue gas is the binary mixture of CO_2 and N_2 because the hydrate formation characteristic of O_2, for example hydrate formation pressure, is nearly the same as that of N_2. In this work, a binary mixture of 17 mol % CO_2 and balance N_2 will be paid special interest for this reason. According to **FIGURE 2.1**, the gas mixtures having concentrations of 17 mol% CO_2 and 83 mol% N_2 can form hydrates with water slightly above 70 bar at temperature of at 273 K. [7]

However, such a high pressure requirement might be regarded as a fatal disadvantage when adopted to the actual process. Therefore, a more favorable condition is to lower the pressure and raise the temperature much higher than 273 K for hydrate formation. But, as shown in **FIGURE 2.1**, when the hydrate formation temperature increases, the corresponding equilibrium pressure also increases. To solve this inherent problem, THF was used as a potential hydrate promoter which enables the operating conditions to shift to milder ones. [7]

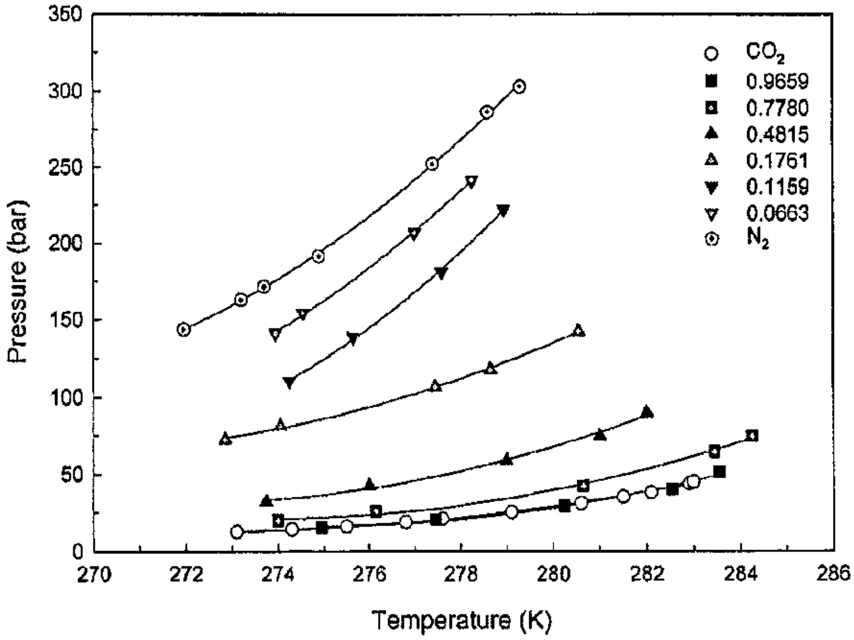


FIGURE 2.1 Hydrate phase equilibria for the CO_2-N_2-H_2O mixture measured at several composition ratios of CO_2 and N_2.

The hydrate-phase compositions were determined at three isotherms of 274, 277, and 280 K, and the results are presented in **FIGURE 2.2**. The relative CO_2 amount in the hydrate phase increased when that in the vapor phase increased. At the vapor composition of 15 mol % CO_2 the corresponding CO_2 composition in the hydrate phase appeared to be about 59, 58, and 39 mol % at three temperatures of 274, 277, and 280 K, respectively. This result indicates that the CO_2 selectivity in the hydrate phase increases when the hydrate formation temperature is lowered. Another sample of 17 mol % CO_2 in the vapor phase shows a similar trend resulting to a little higher selectivity of 63 mol % CO_2 at 274 K. The gas components captured in the hydrate phase can be dissociated and easily recovered simply by either elevating temperature or decreasing the pressure. Only two consecutive steps are required to achieve the recovery of more than 95% CO_2. A new and efficient gas separation/recovery process can be developed using the hydrate formation/dissociation phenomena and more clearly understood through the isothermal *P-x* diagram given in **FIGURE 2.2**. [7]

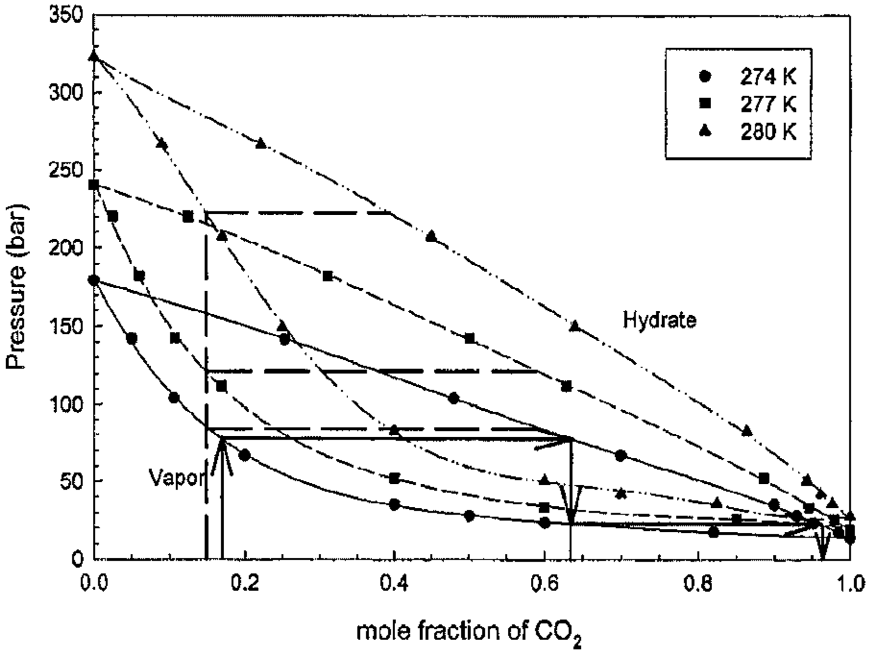


FIGURE 2.2 Pressure-composition diagram of the CO_2-N_2-H_2O mixture measured at three temperatures of 274, 277, and 280 K. Arrow path conceptually illustrates the two-stage separation process for recovering CO_2 from a binary gas mixture.

Another research which has been done by Praveen et al stated that carbon dioxide forms hydrate at much milder condition than nitrogen, and as expected a gas mixture containing CO_2/N_2 takes a middle route. As we can see here, at 0.6 degree centigrade the minimum pressure at which flue gas mixture containing 17% CO_2 and rest nitrogen can form hydrates is 7.7 MPa. [6]

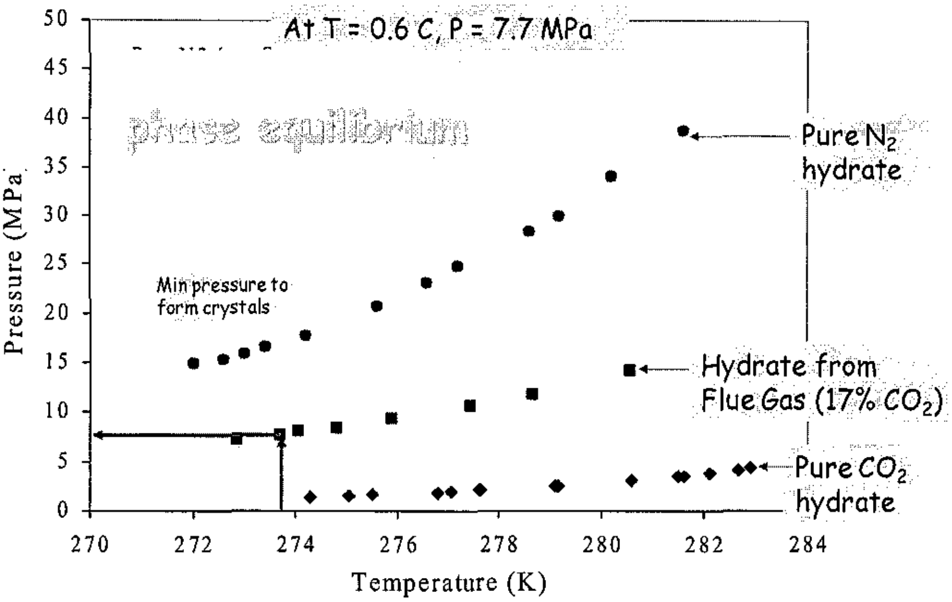


FIGURE 2.3 P-T diagram (H-L_W-V) shows comparison between pure CO_2, pure N_2 and mixture $CO_2 + N_2$ hydrate equilibrium lines [6]

For a substantial hydrate growth we need a driving force, that can be achieved by either performing the experiment at lower temperature or at higher pressure we chose to perform our experiment at higher pressure as we intend to study the kinetics of hydrate formation from liquid water. [6]

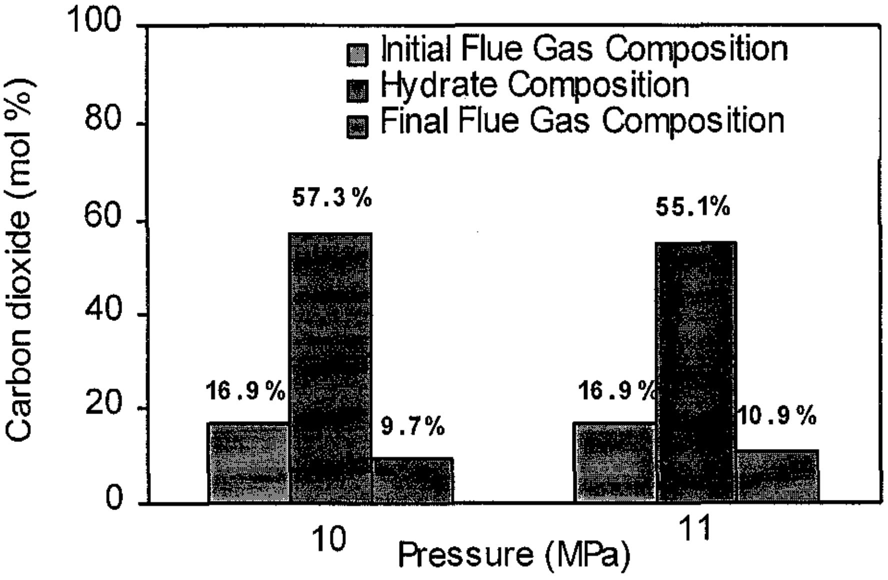


FIGURE 2.4 Carbon dioxide mol composition at 10 and 11 MPa which shows that CO_2 prefers hydrate phase.

From their work, hydrate formation experiments were carried out at 0.6 ^0C and at two pressures 10 MPa and 11 MPa (Peq = 7.7 MPa). One of the results which show the composition of different phases at two different driving forces for a flue gas mixture is shown here in bar graph. With an initial composition of 16.9% CO_2 we end up with 57.3% CO_2 in hydrate phase and 9.7% CO_2 in gaseous phase, at 0.6 degree and 10 MPa, the result shown above is for a single stage. [6]

2.2 Reviews of Several Conventional Processes

Absorption processes are currently the most developed CO_2 removal technology. Absorption systems are continuous scrubbing systems used to remove CO_2 from a gaseous stream. Three main absorption processes available are chemical, physical and hybrid.

CO_2 capture from a power plant is a commercial process nowadays. So far, all commercial CO_2 capture plants use processes based on chemical absorption with a monoethanolamine (MEA) solvent [Klemes and Bulatov, 2005]. Active research is being carried out on new processes and approaches. Technologies such as cryogenic fractionation, membrane separation, and adsorption using molecular sieves to capture the CO_2 from the flue gas of a power plant have been considered but they are even less energy efficient and more expensive than chemical absorption [Herzog, 2001].

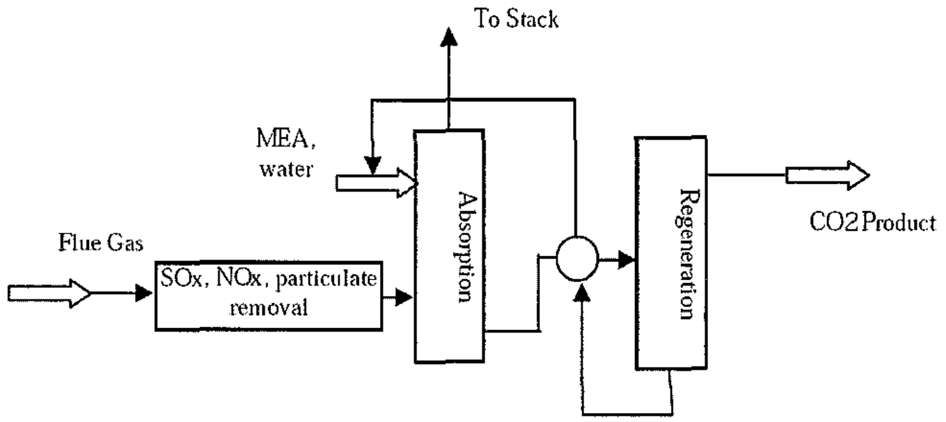


FIGURE 2.5: Chemical Absorption Process

Most conventional coal-burning power plants produce electricity using steam turbines, while most natural gas plants use gas turbines (the excess heat being applied to a second, steam-driven turbine).

Flue gas streams generated by those plants are characterised with low to moderate concentrations of CO_2. For such streams, the current most effective way to capture CO_2 is absorption using a chemical solvent such as monoethanol amine (MEA) or diethanolamine (DEA), ammonia and hot potassium carbonate [Chinn et al., 2004]. Recent research shows that amino-acid salt solutions can be an alternative to amine based solutions [Feron et al., 2004].

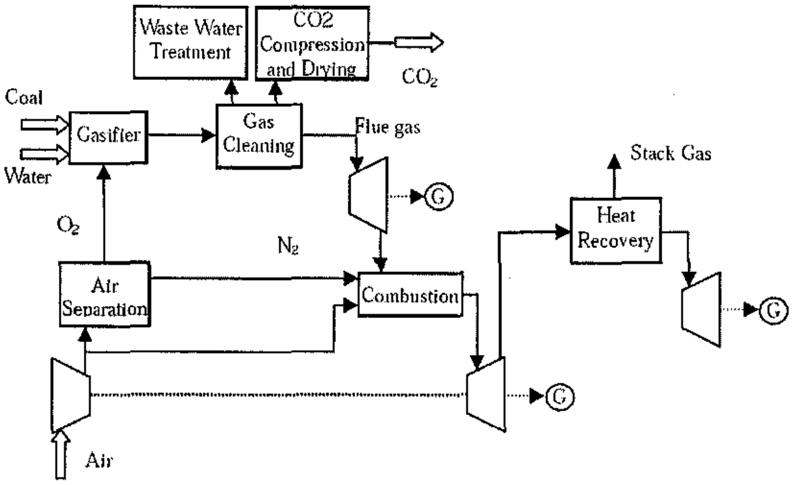


FIGURE 2.6: IGCC power plant with CO_2 removal by means of Selexol scrubbing (IEA, 1998)

Besides chemical absorption of CO_2, the gas can be physically absorbed in a solvent in accordance with Henry's law. By applying heat or reducing pressure or combining both, the gas can be regenerated. Industrial solvents used for this purpose are Selexol (dimethylether of polyethylene glycol) and Rectisol (cold methanol) [Klemes and Bulatov, 2005]. However, they have to be applied at high pressures which can make the process economically prohibitive. At lower pressures, the chemical absorption processes can prove more economical.

For source streams with high concentrations of CO_2, as is the case for the IGCC plant, physical absorption using a solvent like Selexol (dimethylether of polyethylene glycol) or Rectisol (cold methanol) can be less costly than chemical absorption. Increasing external gas pressure and decreasing the temperature improves the absorptive capacity of these solvents. Consequently, applying heat or diminishing the external pressure regenerates the solvents and releases the CO_2 [8].

Physical and chemical absorption currently represent the most developed technical options for CO_2 capture but significant research efforts are being made for more 'exotic' capture technologies. Most of these technologies have been developed for use in other applications and some are used in niche applications. However the answer to the question whether they would be competitive and economically viable for CCS compared to alternative capture techniques (i.e., MEA and physical absorption) in, say, the electric power sector, remains uncertain.

In this research project, hydrate based separation system will be compared with at least one current technology which is amine absorption.

2.3 Proposed Process Design of CO_2 Hydrate-based Separation

There are yet several researches done regarding the CO_2 gas separation via hydrate formation. For instance, the hydrate based gas separation (HBGS) was proposed by Kang and Lee [2000] for the separation of carbon dioxide from flue gas with tetrahydrofuran (THF) as a promoter. The authors claimed that the advantages of this process include high CO_2 recovery from the flue gas, moderate operational temperatures and possibility to treat a large amount of gaseous stream in continuous operations. Another attractive development research is high pressure process for CO_2 separation [Tam et al, 2001] which focuses on the low temperature process, namely SIMTECHE. It is attractive in the first place in terms of its economics finding which shows that SIMTECHE process requires less additional capital cost and the cost of carbon dioxide removal for the SIMTECHE process is also found to be the cheapest if compared to amine and Selexol absorption. These are for the integration of carbon capture system (CCS) in an integrated gasification combined cycle (IGCC) plant [Tam et al., 2001]. Therefore, the mentioned development could provide basis theory and understanding for this research project.

Before the economics of this project are evaluated, the conceptual design for the separation processes must be done beforehand. Three conceptual designs are relevant and available from the literatures.

Design 1

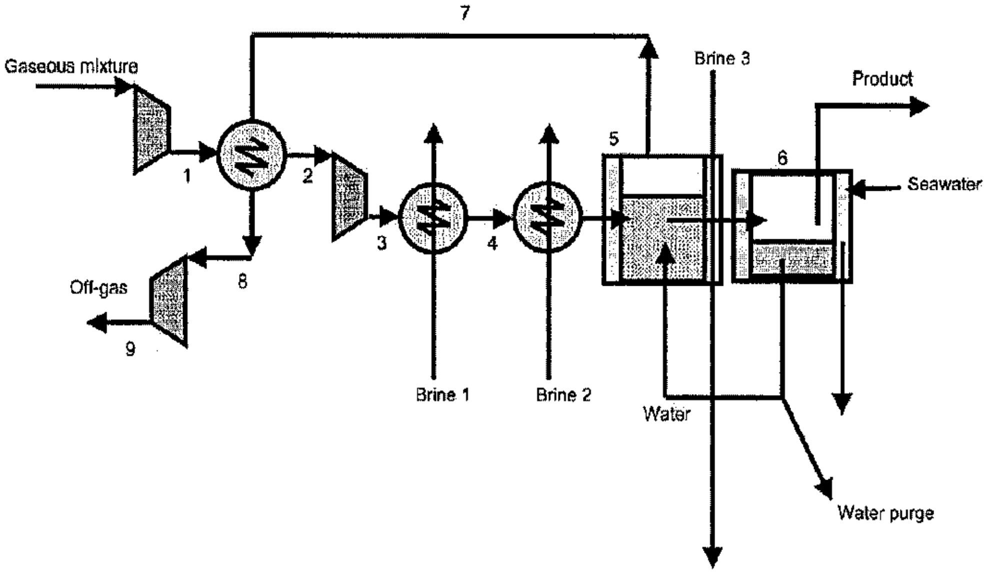


FIGURE 2.7: Process flow diagram for the separation process of CO_2 from the flue gas by using hydrate formation (proposed by H. Tajima et al.) [13]

The separation process of CO_2 from the flue gas of point emission sources such as thermal power plants is considered. The composition of the flue gas is given in **TABLE 2.1**, corresponding to a composition of the flue gas emitted from a typical natural gas-fired thermal power plant after desulfurization and denitration (pre-treatment). Pressure, temperature and flow rate conditions for separating CO_2 is given in **TABLE 2.2**. The total flow rate of the flue gases is 1.0×10^6 N m^3h^{-1}, assuming the treatment of the total emission from a 1000 MW thermal power plant. The hydrate formation condition is set to 274 K, and 140 bar. Since the final pressure after compression is extremely high, a two-stage adiabatic compression of the feed gas is used in this case; 1–20 bar at the first stage, and 20–140 bar at the second stage. After the first compression, the feed gas is cooled to 298 K by the off-gas stream from the hydrate formation unit and cooled down to 274 K after the second compression with a brine stream.

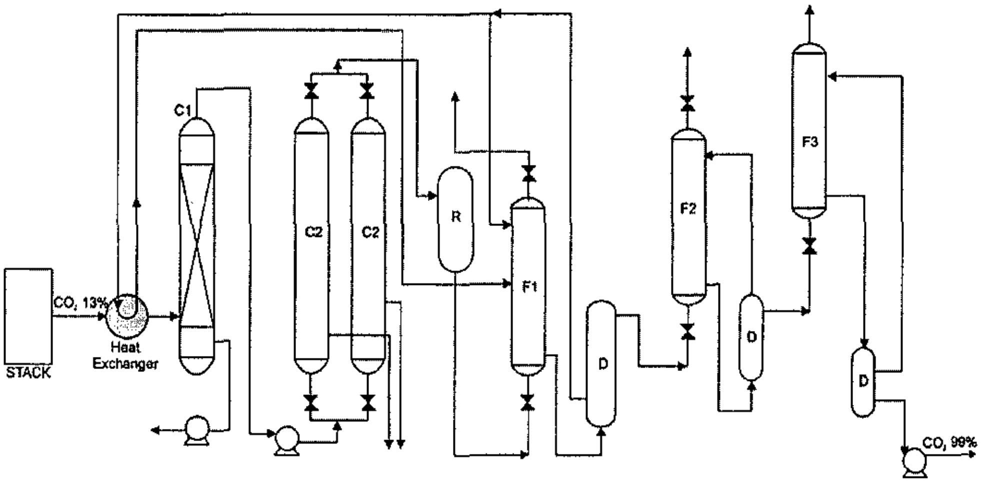
Component	Mole fraction in the feed (–)	Flow rate in the feed (10^3 N m^3/h)	Flow rate in the feed (ton/h)	Flow rate in the product (ton/h)	Flow rate in the off-gas (ton/h)
CO_2	0.10	100	196	186.2	9.8
N_2	0.79	790	988	0	988
O_2	0.04	40	57	0	57
$H_2O(g)$	0.07	70	56	0	56
Total	1.00	1000	1298	186.2	1111.8

TABLE 2.1 Composition of the feed gas for the separation of CO_2.

Pressure and temperature									
i	1	2	3	4	5	6	7	8	9
P_i (bar)	20	20	140	140	140	1.0	140	140	1.0
T_i (K)	776	298	536	298	274	274	274	768	280
Flow rate (ton/h)									
Brine 1	Brine 2	Brine 3	Water	Water purge	Seawater	Product	Off-gas		
5310	813	7466	430	56	6343	186	1112		

TABLE 2.2 Pressure, temperature and flow rate conditions for separating CO_2.

Design 2



C1=precipitator, C2=condenser, D=dissociator, R=reservoir, F1=1st hydrator with 1 mole % THF
F2 and F3=2nd and 3rd hydrator

FIGURE 2.8: Schematic diagram of the hydrate-based CO_2 recovery process (proposed by S.P Kang and Huen Lee)

With the fundamental information from experimental results done by Kang and Lee [2000], an attempt for developing a new hydrate-based gas separation process was initiated. One important application of this process is the CO_2 recovery from power plant flue gases containing various concentrations of CO_2. Flue gas from power plant usually consists of 15 to 20 mol % CO_2, 5 to 9 mol % O_2, trace gases, and balance N_2. After suitable pretreatment steps, flue gas can be simplified as ternary CO_2, O_2, and N_2 mixture.

Furthermore, it can be assumed that the treated flue gas is the binary mixture of CO_2 and N_2 because the hydrate formation characteristic of O_2, for example hydrate formation pressure, is nearly the same as that of N_2. In this work, a binary mixture of 17 mol % CO_2 and balance N_2 will be paid special interest for this reason. The gas mixtures having concentrations of 17 mol% CO_2 and 83 mol% N_2 can form hydrates with water slightly above 70 bar at temperature of at 273 K.

However, such a high pressure requirement might be regarded as a fatal disadvantage when adopted to the actual process. Therefore, a more favorable condition is to lower the pressure and raise the temperature much higher than 273 K for hydrate formation. But, however, when the hydrate formation temperature increases, the corresponding equilibrium pressure also increases [Kang and Lee, 2000]. To solve this inherent problem, THF was used as a potential hydrate promoter which enables the operating conditions to shift to milder ones.

When flue gas containing about 17 mol % CO_2 is introduced to the first hydrator at 280 K and 16.5 bar, the hydrates formed are expected to have a composition of 34.71 mol % CO_2 and 65.39 mol % N_2 in THF-free base. The gas mixture produced by dissociating the hydrates formed in the first hydrator can be fed again into a second hydrator. The next two reactors had better use only water without THF because a larger amount of CO_2 can be recovered to 89.34 mol%at 274 K and 38.7 bar in the second hydrator and 99.67 mol% at 274 K and 28.7 bar in the third hydrator. The hydrate-based CO_2 separation and recovery process developed from the overall experimental results done in this study is schematically demonstrated in **FIGURE 2.8**. The flue gas from a power plant must be first passed to the commercial desulfurization facility for removing SO_X. The pretreated flue gas goes to the first hydrator charged with an aqueous solution containing THF. However, the next two hydrators contain only water. This process makes it possible to recover more than 99 mol % of CO_2 from the flue gas.

This hydrate-based gas recovery process provides several advantages over the conventional ones. First, the operational temperature is low in the range of 273-283 K, and a continuous operation permits this process to treat a large amount of gas stream and to compete with absorption processes. Second, only a small amount of THF is needed together with water and therefore severe corrosion problem can be avoided. Third, the used aqueous solution containing THF can be easily recycled to the hydrator. Several potential candidates of hydrate promoters have been tested and found that THF is the most effective on largely reducing the formation pressure of mixed gas hydrates.

Additional work for optimizing this process with key design data is in progress along with the effect of hydrate promoter on improving process conditions.

Design 3

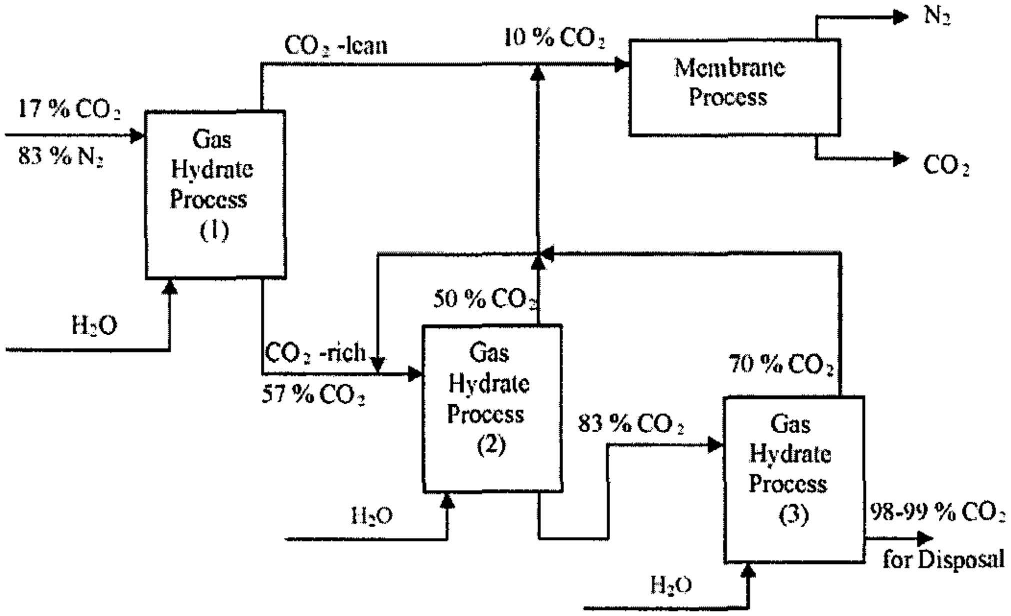


FIGURE 2.9: A hybrid hydrate-membrane process for CO_2 recovery from flue gas (proposed by P. Linga et al.)

The above digaram indicates that following a one-stage hydrate formation-decomposition process for the CO_2/N_2 mixture, a CO_2-rich gas is obtained which contains 57.3% CO_2 at 10MPa. Given that the equilibrium hydrate formation pressure of this gas is about 2.4MPa, a second stage is advocated to obtain a more concentrated CO_2 mixture. The second hydrate formation vessel would operate at a lower pressure compared to the first one since the equilibrium pressure is lower by about 5.3MPa.

Preliminary results indicate that the new CO_2-rich mixture will contain about 83.2% CO_2. Moreover, we envision a hybrid process whereby hydrate formation in three stages is combined with a membrane process. This concept is illustrated in **FIGURE 2.9**. This work is ongoing and another objective is to identify additives to lower the hydrate formation pressures without compromising significantly the separation efficiency. Tetrahydrofuran is one such additive that has been suggested from various sources.

The major disadvantage of the above processes is the high pressure required specially in the first stage. As was mentioned above one way to alleviate this problem for the CO_2/N_2 case is to use THF. The above-illustrated processes show the feasibility of the concept and not the economic viability. Clearly, from an economic viewpoint lower pressures are required which can be achieved by adding proper additives to reduce the hydrate formation pressure at any given temperature without compromising the CO_2 recovery and separation efficiency. Compression costs were calculated for a 500MW conventional power plant, in order to pressurize the flue gas from 0.1 MPa and 70 °C to 10MPa and 1 °C. It was found that four compression stages with intercooling are required [9].

Clearly, this demonstrates the need for additives. The work on additives is ongoing and is the avenue to render the hydrate process economically attractive.

2.4 Economic Evaluation

Allen D. H. (1991) mentioned that the techniques of economic evaluation are tools for us to help ensure that good decisions are made. The author has outlined a systematic guide which is applicable especially for investment of new development projects. These guidelines will be adapted for this research project and implemented as explained later in Chapter 3. Similar to process design, economic evaluation needs a basis, namely cost estimate basis meant for the plant and facilities. This initial information must be provided from the conceptual design stage before developing the cash flow data and eventually evaluating the economics. During economic evaluation stage, values of the appropriate measures such as capital expenditure (CAPEX), operating expenditure (OPEX), net present value (NPV), discounted cash flow rate (DCFR) etc. and sensitivity analysis for changes in important factors contribute to the make-up of the project cash flows must be further investigated [10]. However in this research project, the use of simulation software helps in evaluating the economics provided the right input data of economics such as Chemical Plant Index is inserted.

CHAPTER 3 – METHODOLOGY

In this chapter, the methodology for this research project is presented. The methodology is divided into four main phases and the tools used specifically computer software are mentioned with brief explanation. The Gantt chart with key milestones and work schedule is provided in **APPENDIX A**. Three basis designs are taken. All key properties for key components are noted. Any important properties which are not mentioned in the literature will be assumed appropriately, accordingly.

3.1 Research Methodology

The research works in this project mainly divided into four phases, as described below.

3.1.1 Basis of Design

The feed basis must be known firsthand for both thermodynamic modeling and process simulation. From the literature basis as proposed by Praveen and Kang and Lee, both conclude that the feed composition from the flue gas from power plant usually consists of 15 to 20 mol % CO_2, 5 to 9 mol % O_2, trace gases, and balance N_2. After suitable pretreatment steps, flue gas can be simplified as ternary CO_2, O_2, and N_2 mixture. Furthermore, it can be assumed that the treated flue gas is the binary mixture of CO_2 and N_2 because the hydrate formation characteristic of O_2, for example hydrate formation pressure, is nearly the same as that of N_2. In this work, a binary mixture of 17 mol % CO_2 and balance N_2 will be paid special interest for this reason [66]. The feed basis is 5000 mol/hr. Meanwhile, the product target is hydrate consist of 98-99% CO_2 [6]

3.1.2 Thermodynamic Analysis

Since temperature and pressure play great role for hydrate formation, thermodynamic analysis should be done at the first place to determine the temperature and pressure range of the hydrate process and later on to develop the P-T diagram, P-x or T-x diagram for CO_2-N_2-H_2O system. These values will become inputs to the process simulator that is when simulating the reactor for hydrate formation. The thermodynamics data gathered from the experimental as compiled in Sloan [12] are also compared with the results from the thermodynamic modeling using CSMGem Hydrate Prediction program. This work will help in determining the equilibrium hydrate formation pressure and thus the operating pressure for the hydrate process.

3.1.3 Simulation

After the conceptual design where the separation process flow has been visualized, the process is simulated using computer software namely CHEMCAD. The most crucial part for the simulation is selecting the thermodynamics package of the hydrate. CHEMCAD is used in this project since it has the built-in hydrate prediction tools and capable to detect any hydrate formation in the process streams. Once the simulation is complete, we are able to change the variables of the process to see the effects of some parameters.

There are some important notes to be taken. The first one is the proper selection of unit operations during CHEMCAD simulation such as precipitator, condenser, dissociator, and hydrator. Further investigation should be made to determine the suitable equipments. As usual, several assumptions should be made and the simulation will be in steady-state mode in the early stage of this research.

These are step-by-step procedures for process simulation using CHEMCAD which is basically divided into three main stages.

3.1.3.1 Basis Environment

Within the basis environment, all components inside the hydrate system must be entered – CO_2, N_2, H_2O. Then the thermodynamics properties packages, called as fluid package must be selected properly as this is the crucial part in process simulation and determines how accurate the simulation will be. As studied by Sabil K.M [2009], for the fluid phase, the Peng-Robinson equation of state (EoS) as modified by Stryjek and Vera (PRSV EoS) [1986] combined with Huron-Vidal-Orbey-Sandler mixing rules are used. Meanwhile, the UNIQUAC (Universal Quasi-Chemical Activity Coefficient) model is used to calculate the excess Gibbs free energy. As for hydrate phase, the thermodynamic model is based on the van der Waals and Platteeuw model. In CHEMCAD, not all thermodynamic packages are available for use. Therefore, in this early stage, only the PRSV, UNIQUAC and van der Waals are considered to be used.

3.1.3.2 Simulation Environment

In simulation environment all required unit operations (equipments) are added and for each, sufficient data for inputs must be gathered and entered into the software. The data includes operating conditions like temperature and pressure and also the flow rate (assumed) and compositions of each stream (from literature). Common practice is to simulate the process stage by stage rather than adding all equipments and solve them later on. This is to avoid much simulation problems which is called as troubleshooting. Troubleshooting must be done based on the basic concept of the process. References must be made to clarify that the simulation is a good to go.

3.1.4 Economic Evaluation

Theoretically, the 'straight' economic evaluation is to be done which requires initial information of the projects and development of cash flow data. There are other ways where the cost minimization in equipment selection can be applied and the added values of the project can be analyzed. Furthermore, the complete economic evaluation should consist of uncertainty and risk whereas the sensitivity analysis is done. During economic risk analysis, the subjective probability distributions should be considered with the Monte Carlo simulation. Eventually, the interpretation of results of a project economic risk analysis is to be done.

The computer-aided software which is needed during economic evaluation includes spreadsheet like Microsoft Excel. This software mainly aids to calculate the economic measures like NPV and DCFR. There is also built-in spreadsheet economic template in CHEMCAD which will help calculating the cost of the equipments.

CHAPTER 4 – RESULTS & DISCUSSION

4.1 Phase Diagrams

Phase equalibira data for H-L_w-V phases are gathered from Sloan and Koah, for CO_2 + N_2 hyrate system. The experimental data from Kang and Lee are used for comparison with the modeling using CSMGem. At different CO_2 composition and temperature, the pressure are recorded and presented in a table as in Appendix B. Based from the table, the P-T diagram are plotted as shown in FIGURE 4.1.

Based on the P-T diagram shown, it can be concluded that there are good agreement between experimental data and modeling data with pressure ranging from 1 – 10 MPa since there is no huge deviation. However, the modeling work does not agree with the experimental data for pressure higher than 10 MPa. It also can be concluded that the temperature range from 274 K – 280 K shows good agreement and it is also the preferable range for hydrate formation as the formation of ice must be avoided.

From P-T diagram, the P-x diagram is developed. It is found out that during modeling work, at 279 – 280 K and lower concentration of CO_2, the result from CSMGem gives convergence error in terms of pressure. This represents that the loading composition of CO_2 should not be lower than 0.1 for operation temperature of 279-280 K since the operating pressure cannot be determined from this data. The operating pressure must be higher at about 25% from the equilibrium pressure.

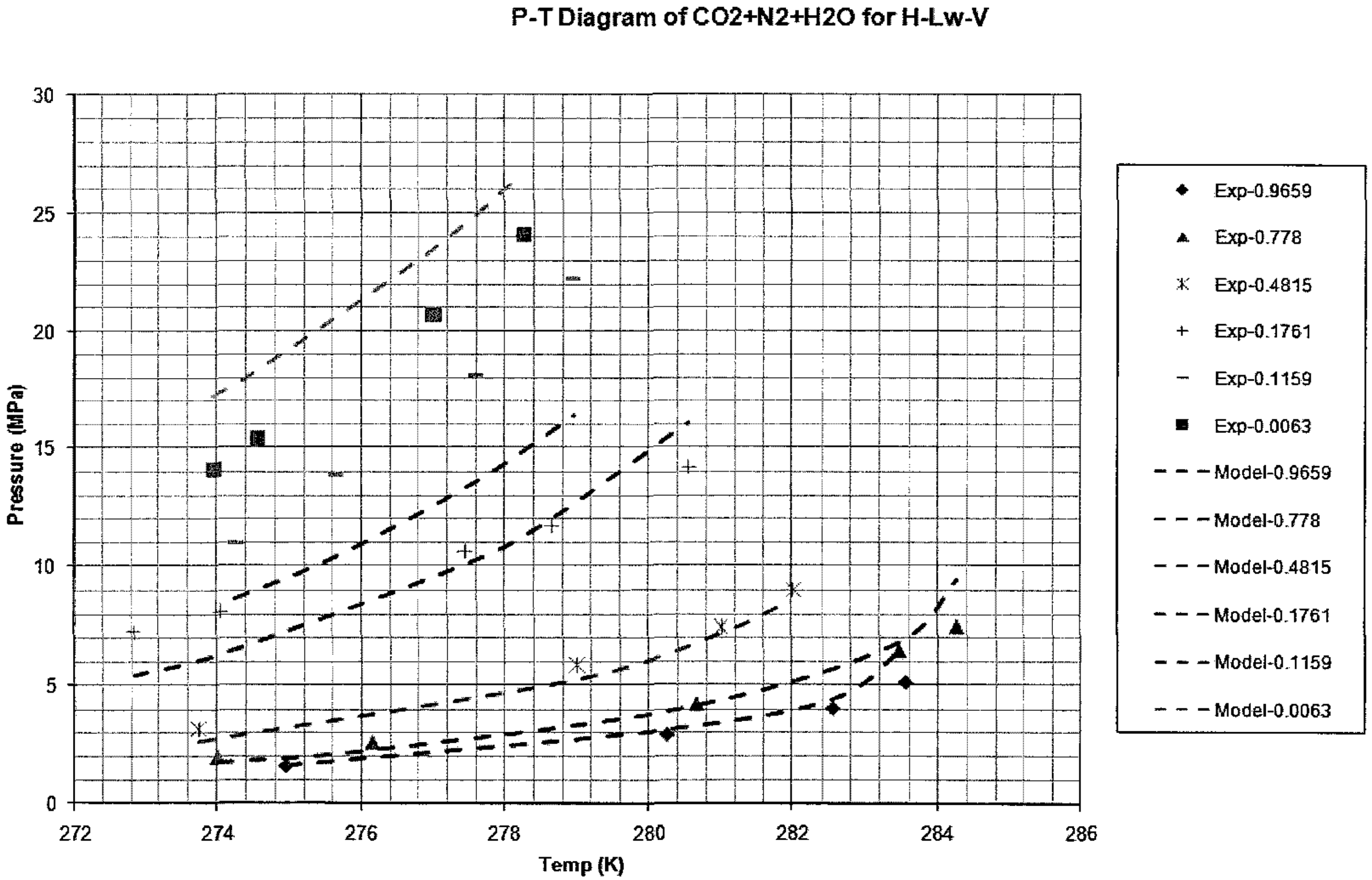


FIGURE 4.1 P-T diagram (H-L_W-V) for $CO_2 + N_2$ hydrate system at different CO_2 compositions

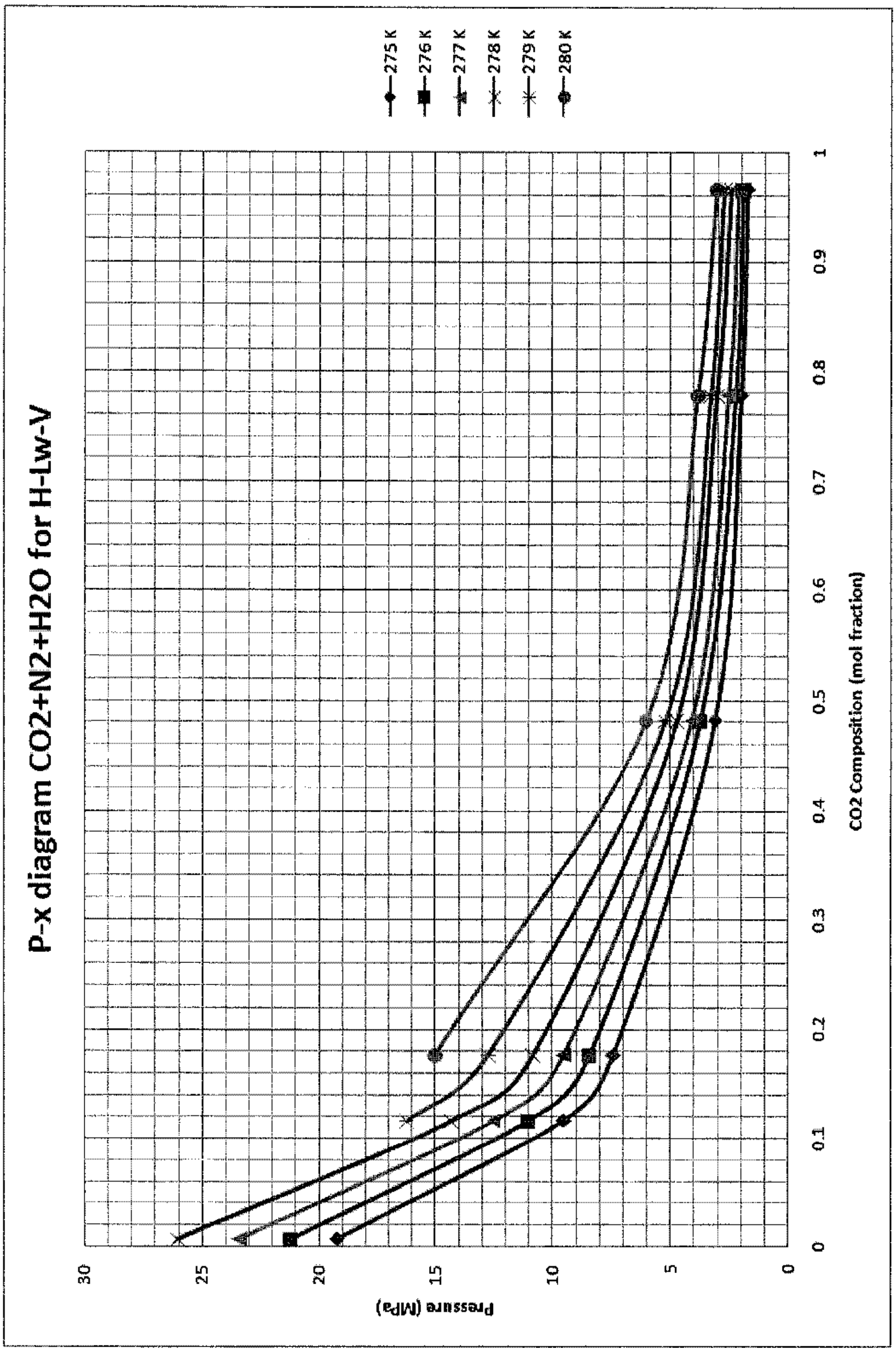


FIGURE 4.2 Pressure-composition diagram for $CO_2 + N_2$ hydrate system (H-L_W-V) for different temperatures.

4.2 Simulation

Process simulation of hydrate process are then developed using CHEMCAD process simulation software. The thermodynamic packages chosen by the software by default after the input of temperature and pressure range are entered are Ideal Vapor Pressure for equilibrium constant, K value and SRK for enthalpy values. Then, the process flow shown is based on the conceptual design of block diagram as proposed by P. Linga (Design 3). The feed and streams composition are shown in Appendix C.

From Appendix C, it can be said that the hydrate are formed after using the built-in CO_2 solid tools to check whether there is hydrate in the streams. The need for compression is a must since the hydrate formation pressure is high. It is also needed to maintain the equilibrium pressure inside the hydrate formation vessel, crystallizer as in the simulation, so that the hydrate will continuously form. Crystallizer is chosen as the major unit operation since the hydrate process needs to be continuous and the liquid water need to be stirred for the physical 'reaction' to occur inside the vessel.

It is no doubt that using the process simulator will lead the simulation to several convergence problems. As for this project, the convergence problem occurred around the crystallizers. The crystallizer module in CHEMCAD namely CRYS module can be used to simulate crystallization or melting processes by cooling or heating. It can also be used as a dissolver where a second solvent stream is added to maintain the outlet stream at a desired concentration level. During input specification, the operation type #1 of three shown below is selected.

0 = No vapor phase (liquid and solid only).

1 = Vapor phase exists; solid formation by boiling off liquid.

2 = Dissolver; calculate solvent flow rate to maintain desired weight fraction of a component (liquid and solid only).

Then the calculation mode #0 of three shown below is selected.

0 = Specify temperature, calculate heat duty.

1 = Specify heat duty, calculate temperature.

2 = Specify vapor flow rate (type = 2, solid formation).

However, the problem is when the input of crystallization stoichiometry has to be entered in order to run the CRYS module. Crystallization stoichiometry is defined similarly to reactions, where negative coefficients refer to liquid precursors (reactants) and positive coefficients refer to crystals (products). As for example:

Component:
$MgSO_4$
H_2O
$MgSO_4.6H_2O$ (Hydrate crystal)

Crystallization equation:

$$1 * MgSO_4 + 6 * H_2O = 1 * MgSO_4 \times 6H_2O$$

The solid crystal must be on the right hand side of the equation whether crystallizing or melting. Thus, data entry for this example:

Coeff.	Component
-1	Magnesium sulfate
-6	Water
1	Hydrate crystal

It is known that during the hydrate process, there is no chemical reaction occurs as there is only the physical reaction between the water and guest molecules. Therefore, there is no crystallization equation for hydrate process. Moreover, the product in this project which is CO_2-N_2-hydrate is not available in the CHEMCAD database. This convergence problem around the CRYS module is the main reason for the CHEMCAD Economics module to not be able to calculate the crystallizer cost automatically. The convergence problem of crystallizer can be seen by the red-coloured label of the crystallizer unit operation shown in FIGURE 4.4 and FIGURE 4.5.

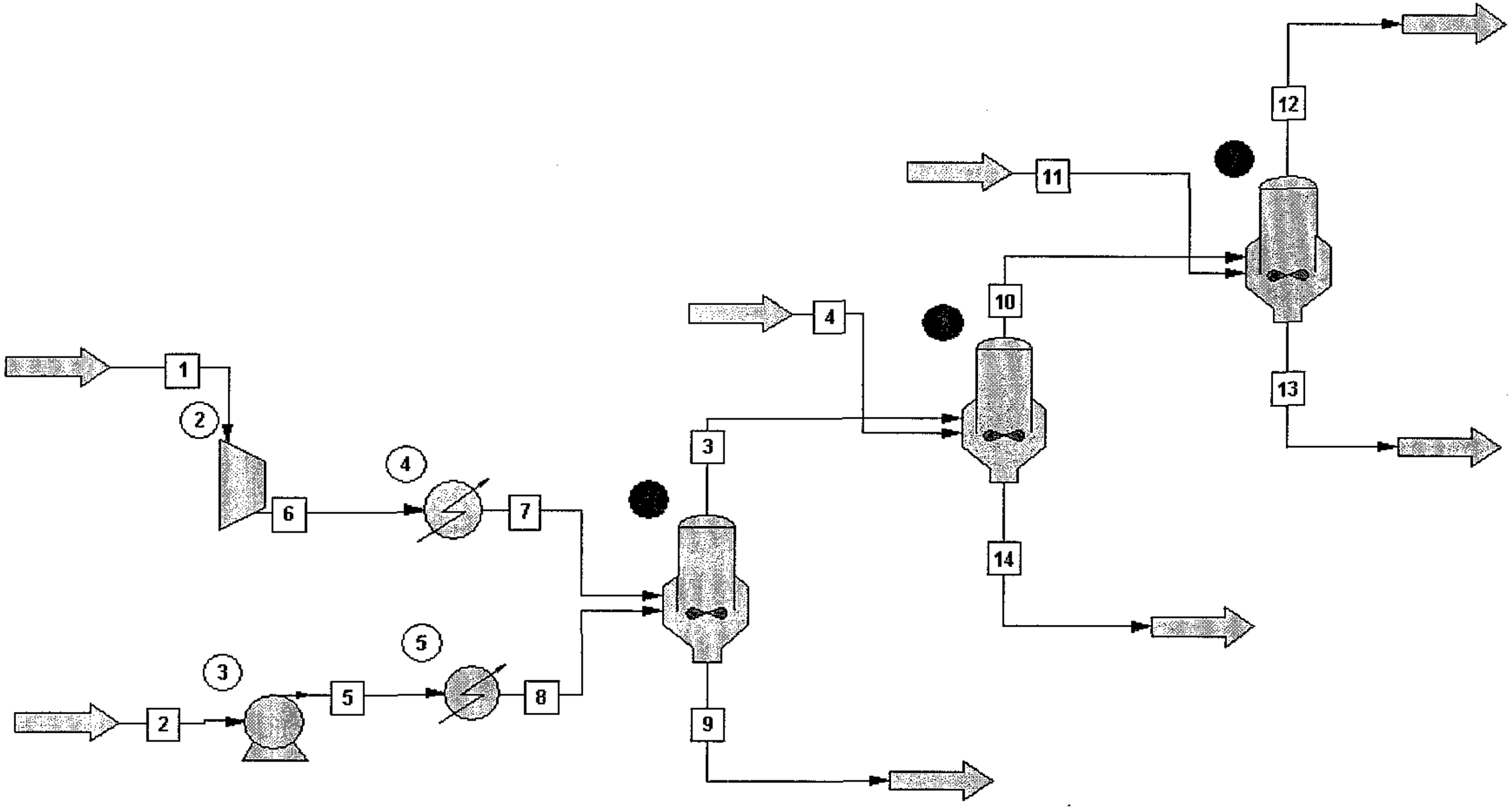


FIGURE 4.3 Preliminary process flow diagram generated from CHEMCAD for the hydrate process

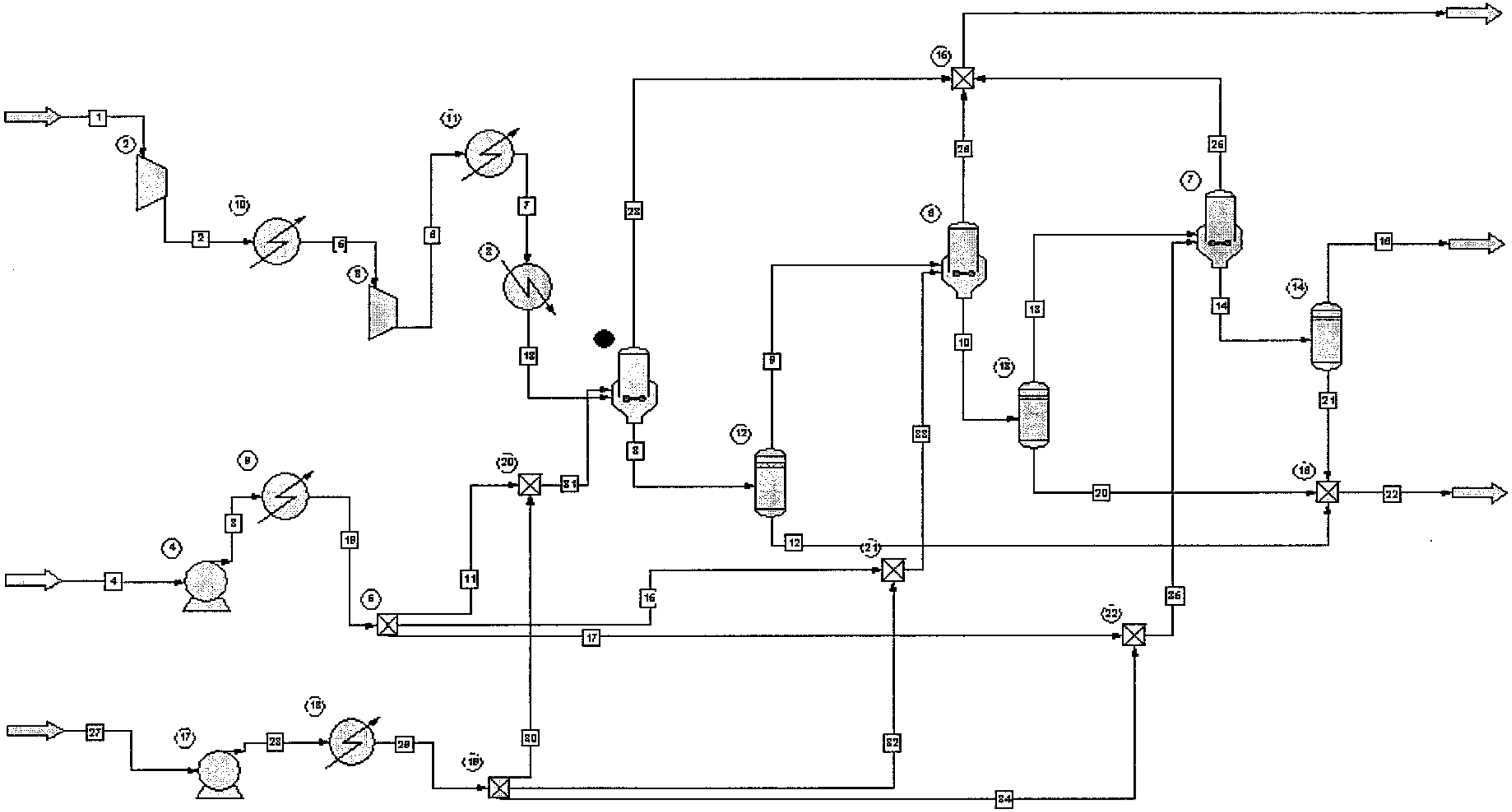


FIGURE 4.4 Complete process flow diagram generated from CHEMCAD for the hydrate process (with 1 mol% THF)

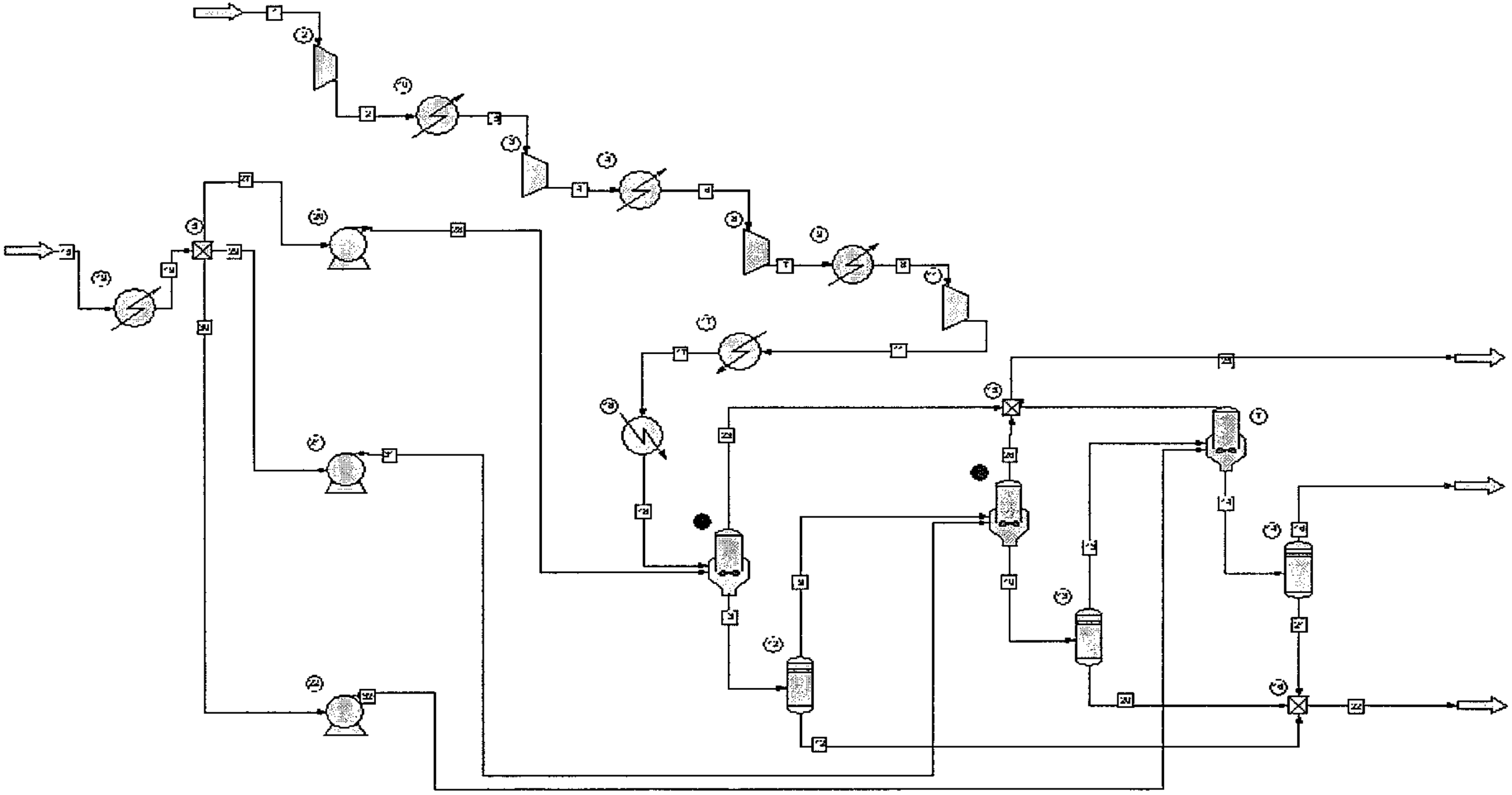


FIGURE 4.5 Complete process flow diagram generated from CHEMCAD for the hydrate process (without THF)

4.3 Mass Balance

The process flow diagram is developed first before the mass balance is done around the major equipments that are crystallizer and dissociator. The mass balance is done by setting the boundary into three major parts at which each part consist of one crystallizer and one dissociator. TABLE 4.1 and TABLE 4.2 show the result of mass balance from process without THF and with 1 mol% THF. The compositions of hydrate streams are not yet calculated. They may be estimated if the hydration number of gas hydrate is known as such in $xCO_2.yN_2.zH_2O$. The composition of each component for each stream is based on the proposed design by P.Linga.

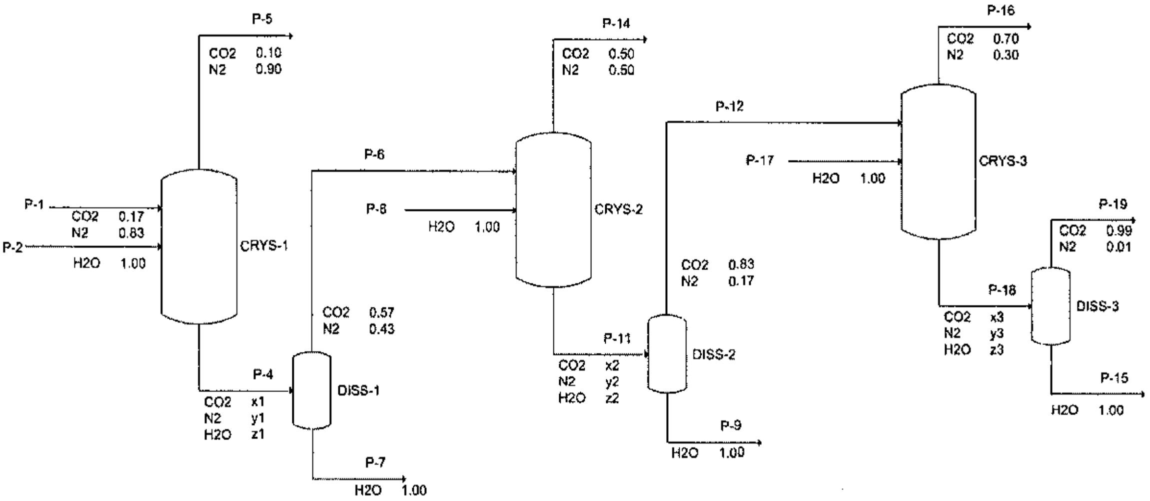


FIGURE 4.6 Process flow diagrams (without THF)

4.3.1 Mass Balance Equation for System Without THF

In this section, the mass balance calculations are done step by step using substitution method. The feed basis are 5,000 mol/hr of flue gas and 10,000 mol/hr of fresh water. The water will be divided and pumped into three crystallizers as appeared in the simulation design. Therefore, it is noted that water supply for each crystallizer = 10000 / 3 = 3333.333 mol/hr.

Overall:

P-1 + P-2 = P-5 + P-6 + P-7 (1)

5000 + 3333.333 = P-5 + P-6 + 3333.333

P-6 + P-8 = P-9 + P-12 + P-14 (2)

P-6 + 3333.333 = 3333.333 + P-12 + P-14

P-12 + P-17 = P-15 + P-16 + P-19 (3)

P-12 + 3333.333 = 3333.333 + P-16 + P-19

1st stage hydrate process:

CO_2:

0.17(P-1) = 0.10(P-5) + 0.57(P-6)

0.17(5000) = 0.10(P-5) + 0.57(P-6)

850 = 0.10(P-5) + 0.57(P-6) (4)

N_2:

0.83(P-1) = 0.90(P-5) + 0.43(P-6)

0.83(5000) = 0.90(P-5) + 0.43(P-6)

4150 = 0.90(P-5) + 0.43(P-6) (5)

H_2O:

1.00(P-2) = 1.00(P-7) (6) balance H_2O can be ignored

P-5 = [850 – 0.57(P-6)] / 0.10 (7)

(7) substituted into (5):

4150 = 0.90 x [{850 – 0.57(P-6)} / 0.10] + 0.43(P-6)

4150 = 9 x [850 – 0.57(P-6)] + 0.43(P-6)

4150 = 7650 – 5.13(P-6) + 0.43(P-6)

-3500 = -4.7(P-6)

P-6 = 744.68 mol/hr

P-5 = [850 – 0.57(744.68)] / 0.10 = **4255.324 mol/hr**

2nd stage hydrate process:

CO_2:

0.57(P-6) = 0.83(P-12) + 0.50(P-14)

0.57(744.68) = 0.83(P-12) + 0.50(P-14)

424.468 = 0.83(P-12) + 0.50(P-14) (8)

N_2:

0.43(P-6) = 0.17(P-12) + 0.50(P-14)

0.43(744.68) = 0.17(P-12) + 0.50(P-14)

320.212 = 0.17(P-12) + 0.50(P-14) (9)

H_2O:

1.00(P-8) = 1.00(P-9) (10) balance H_2O can be ignored

P-14 = [424.468 – 0.83(P-12)] / 0.50 (11)

(11) substituted into (9):

320.212 = 0.17(P-12) + 0.50 x [{424.468 – 0.83(P-12)} / 0.50]

320.212 = 0.17(P-12) + 1 x [424.468 – 0.83(P-12)]

320.212 = 0.17(P-12) + 424.468 – 0.83(P-12)

-104.256 = -0.66(P-12)

P-12 = <u>157.964 mol/hr</u>

P-14 = [420.468 – 0.83(157.964)] / 0.50 = **<u>578.716 mol/hr</u>**

3rd stage hydrate process:

CO_2:

0.83(P-12) = 0.70(P-16) + 0.99(P-19)

0.83(157.964) = 0.70(P-16) + 0.99(P-19)

131.11 = 0.70(P-16) + 0.99(P-19) (12)

N_2:

0.17(P-12) = 0.30(P-16) + 0.01(P-19)

0.17(157.964) = 0.30(P-16) + 0.01(P-19)

26.854 = 0.30(P-16) + 0.01(P-19) (13)

H_2O:

1.00(P-15) = 1.00(P-17) (14) balance H_2O can be ignored

P-16 = [131.11 – 0.99(P-19)] / 0.70 (15)

(15) substituted into (13):

26.854 = 0.30 x [{131.11 – 0.99(P-19)} / 0.70] + 0.01(P-19)

26.854 = 0.43 x [131.11 – 0.99(P-19)] + 0.01(P-19)

26.854 = 56.19 – 0.4257(P-19) + 0.01(P-19)

-29.336 = -0.4157(P-19)

P-19 = <u>70.57 mol/hr</u>

P-16 = [131.11 – 0.99(70.57)] / 0.70 = **<u>87.494 mol/hr</u>**

Hydrates produced

1st stage crystallization: P-4 = P-6 + P-7 = 744.68 + 3333.333 = **<u>4078.01 mol/hr</u>**

2nd stage crystallization: P-11= P-9 + P-12 = 3333.333+157.964 = **<u>3491.294 mol/hr</u>**

3rd stage crystallization: P-18 = P-15 + P-19 = 3333.333 + 70.57 = **<u>3403.9 mol/hr</u>**

All balances calculation is tabulated as below:

	Components	**CO_2**	**N_2**	**H_2O**	**TOTAL**	**REMARKS**
Streams						
P-1	mol fraction	0.17	0.83	0	1	
	flowrate (mol/h)	850	4150	0	5000	
P-2	mol fraction	0	0	1	1	
	flowrate (mol/h)	0	0	3333	3333	
P-4	mol fraction	x1	y1	z1	1	HYDRATE
	flowrate (mol/h)				4078.01	
P-5	mol fraction	0.1	0.9	0	1	
	flowrate (mol/h)	407.801	3670.209	0	4255.324	
P-6	mol fraction	0.57	0.43	0	1	
	flowrate (mol/h)	424.468	320.212	0	744.68	
P-7	mol fraction	0	0	1	1	
	flowrate (mol/h)	0	0	3333	3333	
P-8	mol fraction	0	0	1	1	
	flowrate (mol/h)	0	0	3333	3333	
P-9	mol fraction	0	0	1	1	
	flowrate (mol/h)	0	0	3333	3333	
P-11	mol fraction	x2	y2	z2	1	HYDRATE
	flowrate (mol/h)				3491.294	
P-12	mol fraction	0.83	0.17	0	1	
	flowrate (mol/h)	131.110	26.854	0	157.964	
P-14	mol fraction	0.50	0.50	0	1	
	flowrate (mol/h)	289.358	289.358	0	578.716	
P-15	mol fraction	0	0	1	1	
	flowrate (mol/h)	0	0	3333	3333	
P-16	mol fraction	0.70	0.30	0	1	
	flowrate (mol/h)	61.246	26.248	0	87.494	
P-17	mol fraction	0	0	1	1	
	flowrate (mol/h)	0	0	3333	3333	
P-18	mol fraction	x3	y3	z3	1	HYDRATE
	flowrate (mol/h)				3403.9	
P-19	mol fraction	0.99	0.01	0	1	
	flowrate (mol/h)	69.864	0.706	0	70.57	

TABLE 4.1 Mass balance of hydrate process (without THF)

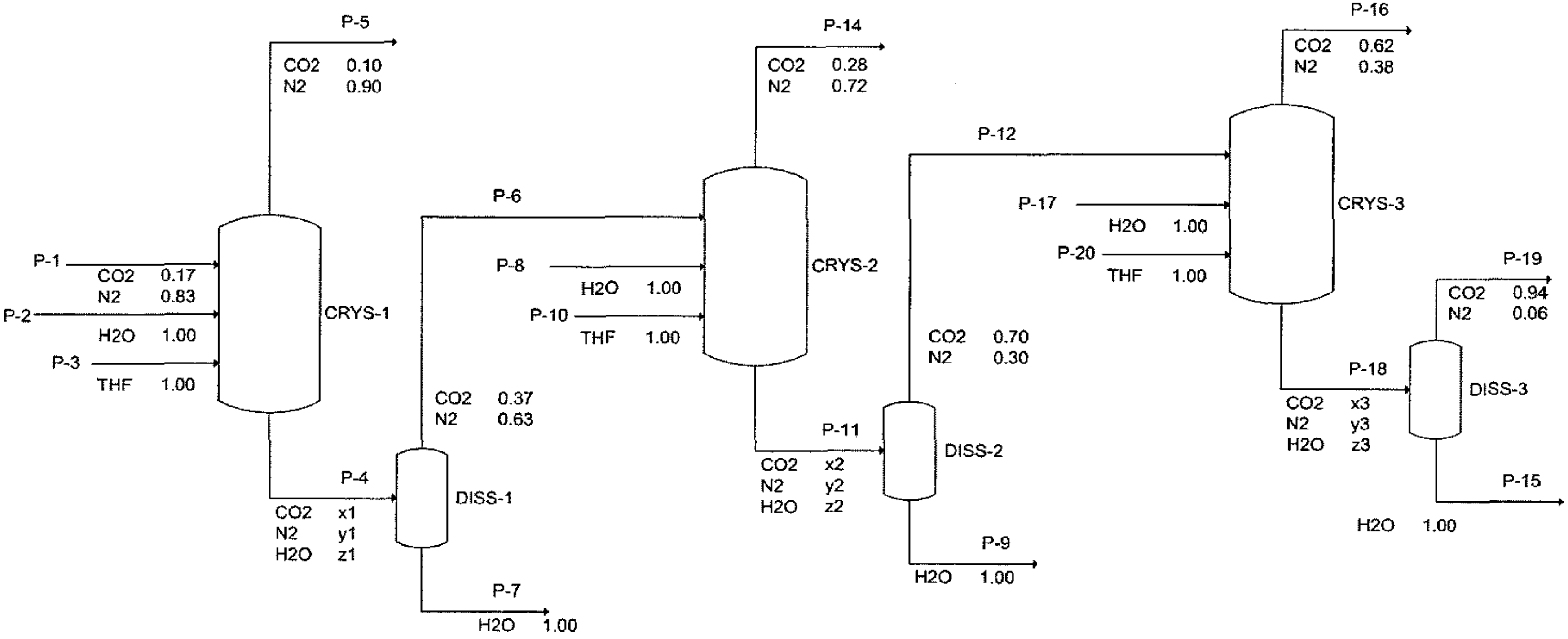


FIGURE 4.7 Process flow diagrams (with THF)

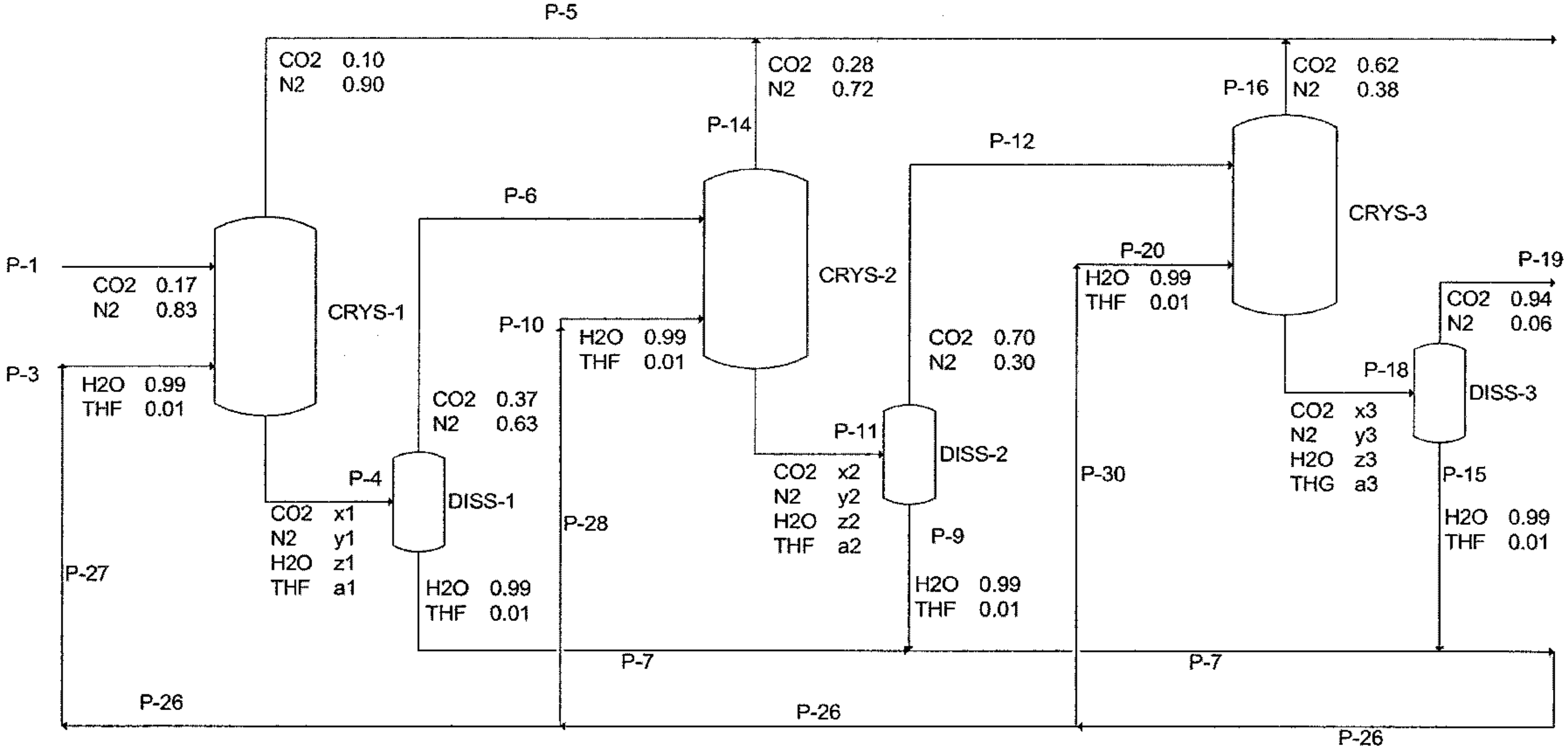


FIGURE 4.8 Process flow diagrams (with THF + recycle streams)

4.3.2 Mass Balance Equation for System With THF

As for system with 1 mol% THF, the mass balances are done using the same substitution method as for system without THF with the same basis of flue gas and fresh water. The difference is only it is assumed in this system the 1-mol% THF is mixed with water before entering the crystallizer. Thus, if 3333.333 mol/hr mixture of water and THF is entering each crystallizer, 1 mol% THF will give 33.333 mol/hr of THF and 99% water will give 3299.999 mol/hr. THF cannot be released into the environment so the after the 3rd stage crystallization, the effluent consist of water and THF will be separated first so that THF can be recycled back to the feed. The recycle stream must be considered in the real design as for safety issue. For the mass balance, the recycle loop is ignored to ease the calculation.

Overall:

P-1 + P-3 = P-5 + P-6 + P-7 (1)

5000 + 3333.333 = P-5 + P-6 + 3333.333

P-6 + P-10 = P-9 + P-12 + P-14 (2)

P-6 + 3333.333 = 3333.333 + P-12 + P-14

P-12 + P-20 = P-15 + P-16 + P-19 (3)

P-12 + 3333.333 = 3333.333 + P-16 + P-19

<u>1st stage hydrate process:</u>

CO_2:

0.17(P-1) = 0.10(P-5) + 0.37(P-6)

0.17(5000) = 0.10(P-5) + 0.37(P-6)

850 = 0.10(P-5) + 0.37(P-6) (4)

N_2:

0.83(P-1) = 0.90(P-5) + 0.63(P-6)

0.83(5000) = 0.90(P-5) + 0.63(P-6)

4150 = 0.90(P-5) + 0.63(P-6) (5)

H_2O:

$0.99(P\text{-}3) = 0.99(P\text{-}7)$ (6) balance of H_2O can be ignored

THF:

$0.01(P\text{-}3) = 0.01(P\text{-}7)$ (7) balance of THF can be ignored

$P\text{-}5 = [\ 850 - 0.37(P\text{-}6)\ ] / 0.10$ (8)

(7) substituted into (5):

$4150 = 0.90 \times [\ \{850 - 0.37(P\text{-}6)\} / 0.10\ ] + 0.63(P\text{-}6)$

$4150 = 9 \times [\ 850 - 0.37(P\text{-}6)\ ] + 0.63(P\text{-}6)$

$4150 = 7650 - 3.33(P\text{-}6) + 0.63(P\text{-}6)$

$-3500 = -2.7(P\text{-}6)$

P-6 = <u>1296.296 mol/hr</u>

P-5 = [850 – 0.37(1296.296)] / 0.10 = **<u>3703.704 mol/hr</u>**

<u>2nd stage hydrate process:</u>

CO_2:

$0.37(P\text{-}6) = 0.70(P\text{-}12) + 0.28(P\text{-}14)$

$0.37(1296.296) = 0.70(P\text{-}12) + 0.28(P\text{-}14)$

479.63 = 0.70(P-12) + 0.28(P-14) (9)

N_2:

$0.63(P\text{-}6) = 0.30(P\text{-}12) + 0.72(P\text{-}14)$

$0.63(1296.296) = 0.30(P\text{-}12) + 0.72(P\text{-}14)$

816.67 = 0.30(P-12) + 0.72(P-14) (10)

H_2O:

$0.99(P\text{-}10) = 0.99(P\text{-}9)$ (11) balance H2O can be ignored

THF:

0.01(P-10) = 0.01(P-9)

P-12 = [479.63 – 0.28(P-14)] / 0.70 (12)

(12) substituted into (10):

816.67 = 0.72(P-14) + 0.30 x [{479.63 – 0.28(P-14)} / 0.70]

816.67 = 0.72(P-14) + 0.43 x [479.63 – 0.28(P-14)]

816.67 = 0.72(P-14) + 206.241 – 0.1204(P-14)

610.429 = 0.5996(P-14)

P-14 = <u>1018.06 mol/hr</u>

P-12 = [479.63 – 0.28(1018.06)] / 0.70 = **<u>278.236 mol/hr</u>**

<u>3rd stage hydrate process:</u>

CO_2:

0.70(P-12) = 0.62(P-16) + 0.94(P-19)

0.70(278.236) = 0.62(P-16) + 0.94(P-19)

194.765 = 0.62(P-16) + 0.94(P-19) (13)

N_2:

0.30(P-12) = 0.38(P-16) + 0.06(P-19)

0.30(278.236) = 0.38(P-16) + 0.06(P-19)

83.471 = 0.38(P-16) + 0.06(P-19) (14)

H_2O:

0.99(P-20) = 0.99(P-15) (15) balance H2O can be ignored

THF:

0.01(P-20) = 0.01(P-15) (16)

P-19 = [194.765 – 0.62(P-16)] / 0.94 (17)

(17) substituted into (14):

83.471 = 0.06 x [{194.765 – 0.62(P-16)} / 0.94] + 0.38(P-16)

83.471 = 0.064 x [194.765 – 0.62(P-16)] + 0.38(P-16)

83.471 = 12.465 – 0.04(P-16) + 0.38(P-16)

71.01 = 0.34(P-16)

P-16 = <u>208.85 mol/hr</u>

P-19 = [194.765 – 0.62(208.85)] / 0.94] = **<u>69.38 mol/hr</u>**

<u>Hydrates produced</u>

1st stage crystallization: P-4 = P-6 + P-7 = 1296.296 + 3333.333 = **<u>4629.629 mol/hr</u>**

2nd stage crystallization: P-11= P-9 + P-12 = 3333.333+278.236 = **<u>3611.569 mol/hr</u>**

3rd stage crystallization: P-18 = P-15 + P-19 = 3333.333 + 69.38 = **<u>3402.713 mol/hr</u>**

All balances calculation is tabulated as below:

	Components	**CO_2**	**N_2**	**H_2O**	**THF**	**TOTAL**	**REMARKS**
Streams							
P-1	mol fraction	0.17	0.83	0	0	1	
	flowrate (mol/h)	850	4150	0	0	5000	
P-3	mol fraction	0	0	0.99	0.01	1	
	flowrate (mol/h)	0	0	3299	33	3333	
P-4	mol fraction	x1	y1	z1	1	1	HYDRATE
	flowrate (mol/h)	[redacted]	[redacted]	[redacted]	[redacted]	4629.629	
P-5	mol fraction	0.1	0.9	0	0	1	
	flowrate (mol/h)	370.3704	3333.334	0	0	3703.704	
P-6	mol fraction	0.37	0.63	0	0	1	
	flowrate (mol/h)	479.62952	816.6665	0	0	1296.296	
P-7	mol fraction	0	0	0.99	0.01	1	
	flowrate (mol/h)	0	0	3299	33	3333	
P-9	mol fraction	0	0	0.99	0.01	1	
	flowrate (mol/h)	0	0	3299	33	3333	
P-10	mol fraction	0	0	0.99	0.01	1	
	flowrate (mol/h)	0	0	3299	33	3333	
P-11	mol fraction	x2	y2	z2	1	1	HYDRATE
	flowrate (mol/h)	[redacted]	[redacted]	[redacted]	[redacted]	3611.569	
P-12	mol fraction	0.7	0.3	0	0	1	
	flowrate (mol/h)	194.7652	83.4708	0	0	278.236	
P-14	mol fraction	0.28	0.72	0	0	1	
	flowrate (mol/h)	285.10608	733.1299	0	0	1018.236	
P-15	mol fraction	0	0	0.99	0.01	1	
	flowrate (mol/h)	0	0	3299	33	3333	
P-16	mol fraction	0.62	0.38	0	0	1	
	flowrate (mol/h)	129.487	79.363	0	0	208.85	
P-18	mol fraction	x3	y3	z3	1	1	HYDRATE
	flowrate (mol/h)	[redacted]	[redacted]	[redacted]	[redacted]	3402.713	
P-19	mol fraction	0.94	0.06	0	0	1	
	flowrate (mol/h)	65.2172	4.1628	0	0	69.38	
P-20	mol fraction	0	0	0.99	0.01	1	
	flowrate (mol/h)	0	0	3299	33	3333	

TABLE 4.2 Mass balance of hydrate process (with THF)

4.4 Economics

Economics template from CHEMCAD maybe adopted in this project to evaluate the economics. As an example, the costing for crystallizer can be estimated as shown below. The costing for other equipments are included in the detailed economic section.

Costing Results

Without THF

```
Preliminary Crystallizers Cost Estimation


Crystallizerr Cost for Equip. 1
Material = Mild steel
fm = 1
External forced circulation
Base cost index = 347.5
Current cost index = 616.6
Purchase cost  = $187672
Installed cost = $187672

Crystallizerr Cost for Equip. 6
Material = Mild steel
fm = 1
External forced circulation
Base cost index = 347.5
Current cost index = 616.6
Purchase cost  = $154381
Installed cost = $293325

Crystallizerr Cost for Equip. 7
Material = Mild steel
fm = 1
External forced circulation
Base cost index = 347.5
Current cost index = 616.6
Purchase cost  = $154788
Installed cost = $294097
```

Total Crystallizers Cost = $187672 + $293325 + $294097 = $775094

With 1 mol% THF

```
Preliminary Crystallizers Cost Estimation

Crystallizerr Cost for Equip. 1
Material = Mild steel
fm = 1
External forced circulation
Base cost index = 347.5
Current cost index = 616.6
Purchase cost  = $187673
Installed cost = $187673

Crystallizerr Cost for Equip. 6
Material = Mild steel
fm = 1
External forced circulation
Base cost index = 347.5
Current cost index = 616.6
Purchase cost  = $154381
Installed cost = $154381

Crystallizerr Cost for Equip. 7
Material = Mild steel
fm = 1
External forced circulation
Base cost index = 347.5
Current cost index = 616.6
Purchase cost  = $154788
Installed cost = $154788
```

Total Crystallizers Cost = $187673 + $154381+ $154788= $496842

Since there is convergence problem around the crystallizer, the CHEMCAD is not able to calculate the cost of crystallizer, therefore using Costing Tool in

CHEMCAD, the costs show above are manually added to the cost of other equipments as calculated by CHEMCAD. Therefore, the total equipments cost for both system will be;

System without THF: `$775,094 + $343,953 = $1,119,037`
System with THF: `$496,842 + $292,750 = $789,592`

From this calculation of crystallizers which is the major part of this hydrate process, it can be preliminary concluded that the cost for system without THF is higher than the system with THF. However, to verify this, the results of detailed economic estimates are shown in the next section and be interpreted.

The cost index or called as Chemical Plant Index (CPI) of the latest must be entered as an input for the software. Then the preliminary costing can be estimated as for both purchase and installed cost. The CPI is varied and **FIGURE 4.9** shows the trend from the earlier years.

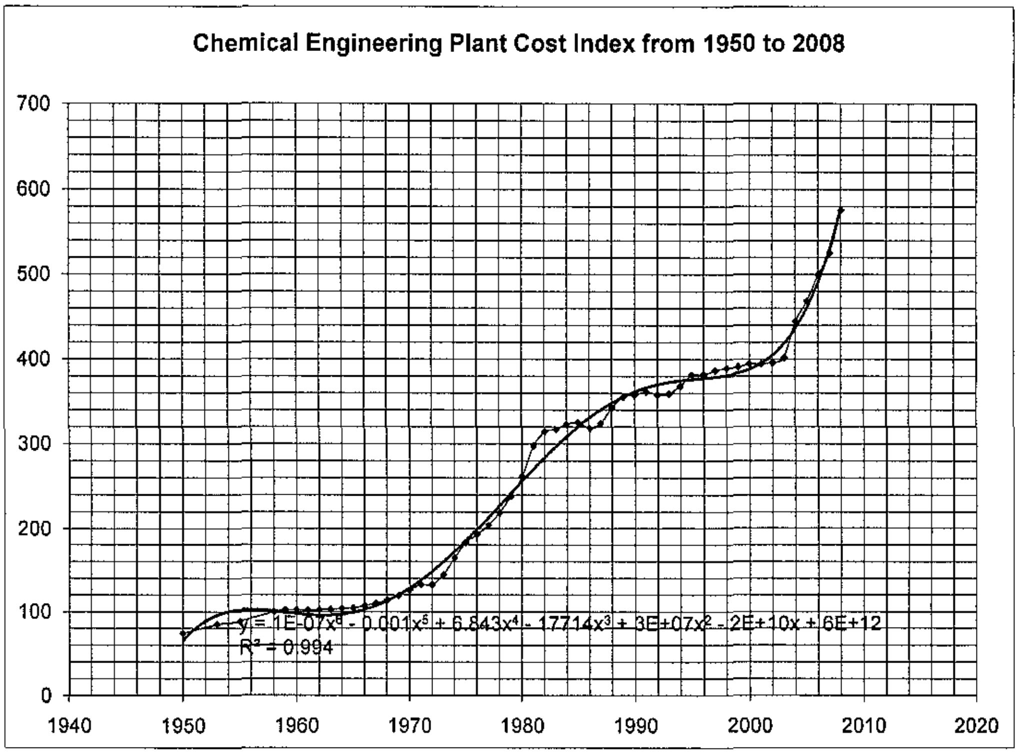


FIGURE 4.9 Trend of Chemical Engineering Plant Cost Index from 1950 to 2008. From the trendline equation generated, the cost index for current or next few years may be estimated.

1/May/2009	Final	509.1	CEPCI
Detailed breakdown for Mar/2009 (Final)			
Equipment			616.6
Heat Exchangers and Tanks			563.2
Process Machinery			597.3
Pipe, valves and fittings			761.0
Process Instruments			385.1
Pumps and Compressors			898.0
Electrical Equipment			459.6
Structural Supports & Misc.			636.1
Construction Labour			325.7
Buildings			494.9
Engineering & Supervision			349.0

TABLE 4.3 Chemical Engineering Plant Cost Index (CEPCI) as in March 2009

In gas capture by hydrate technology, there are only two chemical products: water and hydrate promoter which is tetrahydrofuran (THF). There is nearly no loss of water and THF because THF and water exist in liquid and solid states during the production phase. There might be a very little loss of chemical products that is carried by gas flow. After hydrate dissociation to capture CO_2, the THF and water (in liquid state) will come back to the hydrate crystallizer to begin a new production cycle.

4.5 Detailed Economics Result

This section provides result generated from CHEMCAD simulation based on cost data and process input. Some cost input need to be done manually since the CHEMCAD simulation does not effectively reliable in terms of crystallizer design and operation. For system without THF, there are two cases which the first case deals with negative present value while the second case deals with positive present value which is more preferable in terms of economic. The summary of equipment cost shown does not include the cost of crystallizer which has been manually added beforehand.

System Without THF (Case 1 – Negative Present Value with 10% projected cost increase and 15% projected revenue increase)

Executive Summary	
Total Plant Cost	3692822
Raw Materials Cost	100000
By-product Credit	0
Raw Materials Cost (final?)	110000
Cost to Manufacture	2104262
Product Revenues	2000000
Income before tax	-149262
Income tax	-74631
Income after tax	-74631
Return on Investment	4.92
Length of project (yrs)	10.00
Payout time (yr)	7.76
Rate of Return (%)	8.11

TABLE 4.4 Summary of hydrate process economics (without THF – Case 1)

Summary of Equipment Costs

Unit ID	Unit Name	Unit Type	Equipment Cost
2		Compressors	86,758
3		Compressors	43,007
4		Heat Exchangers	3,734
8		Compressors	35,388
9		Heat Exchangers	4,433
10		Heat Exchangers	2,787
11		Compressors	25,634
12		Drums & Vessels	35,620
13		Drums & Vessels	35,620
14		Drums & Vessels	35,620
17		Heat Exchangers	4,433
18		Heat Exchangers	4,433
19		Heat Exchangers	2,787
20		Pumps	7,168
21		Pumps	7,718
22		Pumps	8,803

TABLE 4.5 Summary of equipment costs (without THF – Case 1)

TOTAL PROJECT COST - DETAILED ESTIMATE

	$/yr
Total Major Equipment Cost	1,119,037
Installation	167,856
Piping	503,567
Instrumentation	111,904
Building & Structure	111,904
Auxillaries	279,759
Outside Lines	167,856
Total Direct Cost	2,461,882
Engineering & Construction	738,564
Contingencies	492,376
Total Plant Cost	3,692,822
MANUFACTURING COST	
Raw Materials	100,000
Credit from By-products	0
Net Raw Materials	110,000
DIRECT EXPENSES	
Utilities	0
Labor	637,200
Supplies	73,856
Maintenance	369,282
Office & Service Overhead	270,000

Laboratory	90,000
Royalties	0
Other Direct Expenses	0
INDIRECT EXPENSES	
Property Taxes	184,641
Depreciation	369,282
Total Manufacturing Cost	2,104,262

TABLE 4.6 Total project cost (without THF – Case 1)

CAPITAL COST ANALYSIS	$/yr
Total New Property (Fixed Capital)	3,692,822
Total Allocated Property	1,292,488
Gross Fixed Investment	4,985,310
Working Capital	690,000
Corporate Capital Allocation	115,000
Gross Investment	5,790,310
Total Revenues	2,000,000
Cost of Goods Manufactured	2,104,262
Cost of Selling Goods	115,000
Total Cost of Goods Sold	2,219,262
SARE (Sales, Admin, R&D Expense)	230,000
Income Before Tax	-149,262
Income Tax	-74,631
Income After Tax	-74,631
Return on Investment, %	4.92

TABLE 4.7 Capital cost analysis (without THF – Case 1)

Year	Income AFIT	Depreciation	Working Capital	Salvage Value	Total Inflow
0	0.0	0.0	0.0	0.0	0.0
1	-74.6	369.3	0.0	0.0	294.7
2	66.5	369.3	0.0	0.0	435.8
3	229.1	369.3	0.0	0.0	598.3
4	416.3	369.3	0.0	0.0	785.6
5	416.3	369.3	0.0	0.0	785.6
6	416.3	369.3	0.0	0.0	785.6
7	416.3	369.3	0.0	0.0	785.6
8	416.3	369.3	0.0	0.0	785.6
9	416.3	369.3	0.0	0.0	785.6
10	416.3	369.3	690.0	73.9	1475.6

Year	Fixed Capital	Working Capital	Startup Expense AFIT	Total Outflow	Cashflow (IN - OUT)
0	3692.8	690.0	277.0	4659.8	-4659.8
1	0.0	0.0	0.0	0.0	294.7
2	0.0	0.0	0.0	0.0	435.8
3	0.0	0.0	0.0	0.0	598.3
4	0.0	0.0	0.0	0.0	785.6
5	0.0	0.0	0.0	0.0	785.6
6	0.0	0.0	0.0	0.0	785.6
7	0.0	0.0	0.0	0.0	785.6
8	0.0	0.0	0.0	0.0	785.6
9	0.0	0.0	0.0	0.0	785.6
10	0.0	0.0	0.0	0.0	1475.6

Payout Time (years)	7.8
Rate of Return (%)	8.1
Present Value ($M)	-849.3

TABLE 4.8 Cash flow (without THF – Case 1)

System Without THF (Case 2 – Positive Present Value with 15% projected cost increase and 20% projected revenue increase)

Executive Summary	
Total Plant Cost	3692822
Raw Materials Cost	100000
By-product Credit	0
Raw Materials Cost (final?)	115000
Cost to Manufacture	2109262
Product Revenues	2000000
Income before tax	-69262
Income tax	-34631
Income after tax	-34631
Return on Investment	8.22
Length of project (yrs)	10.00
Payout time	5.08
Rate of Return (%)	12.88

TABLE 4.9 Summary of hydrate process economics (without THF – Case 2)

Summary of Equipment Costs

Unit ID	Unit Name	Unit Type	Equipment Cost
2		Compressors	86,758
3		Compressors	43,007
4		Heat Exchangers	3,734
8		Compressors	35,388
9		Heat Exchangers	4,433
10		Heat Exchangers	2,787
11		Compressors	25,634
12		Drums & Vessels	35,620
13		Drums & Vessels	35,620
14		Drums & Vessels	35,620
17		Heat Exchangers	4,433
18		Heat Exchangers	4,433
19		Heat Exchangers	2,787
20		Pumps	7,168
21		Pumps	7,718
22		Pumps	8,803

TABLE 4.10 Summary of equipment costs (without THF – Case 2)

TOTAL PROJECT COST - DETAILED ESTIMATE	$/yr
Total Major Equipment Cost	1,119,037
Installation	167,856
Piping	503,567
Instrumentation	111,904
Building & Structure	111,904
Auxillaries	279,759
Outside Lines	167,856
Total Direct Cost	2,461,882
Engineering & Construction	738,564
Contingencies	492,376
Total Plant Cost	3,692,822
MANUFACTURING COST	
Raw Materials	100,000
Credit from By-products	0
Net Raw Materials	115,000
DIRECT EXPENSES	
Utilities	0
Labor	637,200
Supplies	73,856
Maintenance	369,282
Office & Service Overhead	270,000
Laboratory	90,000
Royalties	0
Other Direct Expenses	0
INDIRECT EXPENSES	
Property Taxes	184,641
Depreciation	369,282
Total Manufacturing Cost	2,109,262

TABLE 4.11 Total project cost (without THF – Case 2)

CAPITAL COST ANALYSIS	$/yr
Total New Property (Fixed Capital)	3,692,822
Total Allocated Property	1,292,488
Gross Fixed Investment	4,985,310
Working Capital	720,000
Corporate Capital Allocation	120,000
Gross Investment	5,825,310
Total Revenues	2,000,000
Cost of Goods Manufactured	2,109,262
Cost of Selling Goods	120,000
Total Cost of Goods Sold	2,229,262
SARE (Sales, Admin, R&D Expense)	240,000
Income Before Tax	-69,262
Income Tax	-34,631
Income After Tax	-34,631
Return on Investment, %	8.22

TABLE 4.12 Capital cost analysis (without THF – Case 2)

Year	Income AFIT	Depreciation	Working Capital	Salvage Value	Total Inflow
0	0.0	0.0	0.0	0.0	0.0
1	-34.6	369.3	0.0	0.0	334.7
2	160.7	369.3	0.0	0.0	530.0
3	395.6	369.3	0.0	0.0	764.9
4	678.0	369.3	0.0	0.0	1047.3
5	678.0	369.3	0.0	0.0	1047.3
6	678.0	369.3	0.0	0.0	1047.3
7	678.0	369.3	0.0	0.0	1047.3
8	678.0	369.3	0.0	0.0	1047.3
9	678.0	369.3	0.0	0.0	1047.3
10	678.0	369.3	720.0	73.9	1767.3

Year	Fixed Capital	Working Capital	Startup Expense AFIT	Total Outflow	Cashflow (IN - OUT)
0	3692.8	720.0	277.0	4689.8	-4689.8
1	0.0	0.0	0.0	0.0	334.7
2	0.0	0.0	0.0	0.0	530.0
3	0.0	0.0	0.0	0.0	764.9
4	0.0	0.0	0.0	0.0	1047.3
5	0.0	0.0	0.0	0.0	1047.3
6	0.0	0.0	0.0	0.0	1047.3
7	0.0	0.0	0.0	0.0	1047.3
8	0.0	0.0	0.0	0.0	1047.3
9	0.0	0.0	0.0	0.0	1047.3
10	0.0	0.0	0.0	0.0	1767.3

Payout Time (years)	5.1
Rate of Return (%)	12.9
Present Value ($M)	209.7

TABLE 4.13 Cash flow (without THF – Case 2)

System With 1 mol% THF

Executive Summary	
Total Plant Cost	2605654
Raw Materials Cost	150000
By-product Credit	0
Raw Materials Cost (final?)	165000
Cost to Manufacture	1865727
Product Revenues	2000000
Income before tax	89274
Income tax	44637
Income after tax	44637
Return on Investment	8.95
Length of project (yrs)	10.00
Payout time	5.28
Rate of Return (%)	13.94

TABLE 4.14 Summary of hydrate process economics (with THF)

Summary of Equipment Costs

Unit ID	Unit Name	Unit Type	Equipment Cost
2		Compressors	86,758
3		Compressors	49,644
4		Pumps	6,111
8		Heat Exchangers	3,913
9		Heat Exchangers	3,913
10		Heat Exchangers	3,913
11		Heat Exchangers	3,913
12		Drums & Vessels	35,620
13		Drums & Vessels	35,620
14		Drums & Vessels	35,620
17		Pumps	23,812
18		Heat Exchangers	3,913

TABLE 4.15 Summary of equipment costs (with THF)

TOTAL PROJECT COST - DETAILED ESTIMATE	$/yr
Total Major Equipment Cost	789,592
Installation	118,439
Piping	355,316
Instrumentation	78,959
Building & Structure	78,959
Auxillaries	197,398
Outside Lines	118,439
Total Direct Cost	1,737,102
Engineering & Construction	521,131
Contingencies	347,420
Total Plant Cost	2,605,654
MANUFACTURING COST	
Raw Materials	150,000
Credit from By-products	0
Net Raw Materials	165,000
DIRECT EXPENSES	
Utilities	0
Labor	637,200
Supplies	52,113
Maintenance	260,565
Office & Service Overhead	270,000
Laboratory	90,000
Royalties	0
Other Direct Expenses	0
INDIRECT EXPENSES	
Property Taxes	130,283
Depreciation	260,565
Total Manufacturing Cost	1,865,727

TABLE 4.16 Total project cost (with THF)

CAPITAL COST ANALYSIS	$/yr
Total New Property (Fixed Capital)	2,605,654
Total Allocated Property	911,979
Gross Fixed Investment	3,517,632
Working Capital	690,000
Corporate Capital Allocation	115,000
Gross Investment	4,322,632
Total Revenues	2,000,000
Cost of Goods Manufactured	1,865,727
Cost of Selling Goods	115,000
Total Cost of Goods Sold	1,980,727
SARE (Sales, Admin, R&D Expense)	230,000
Income Before Tax	89,274
Income Tax	44,637
Income After Tax	44,637
Return on Investment, %	8.95

TABLE 4.17 Capital cost analysis (with THF)

Year	Income AFIT	Depreciation	Working Capital	Salvage Value	Total Inflow
0	0.0	0.0	0.0	0.0	0.0
1	44.6	260.6	0.0	0.0	305.2
2	183.0	260.6	0.0	0.0	443.6
3	342.6	260.6	0.0	0.0	603.1
4	526.5	260.6	0.0	0.0	787.0
5	526.5	260.6	0.0	0.0	787.0
6	526.5	260.6	0.0	0.0	787.0
7	526.5	260.6	0.0	0.0	787.0
8	526.5	260.6	0.0	0.0	787.0
9	526.5	260.6	0.0	0.0	787.0
10	526.5	260.6	690.0	52.1	1477.0

Year	Fixed Capital	Working Capital	Startup Expense AFIT	Total Outflow	Cashflow (IN - OUT)
0	2605.7	690.0	195.4	3491.1	-3491.1
1	0.0	0.0	0.0	0.0	305.2
2	0.0	0.0	0.0	0.0	443.6
3	0.0	0.0	0.0	0.0	603.1
4	0.0	0.0	0.0	0.0	787.0
5	0.0	0.0	0.0	0.0	787.0
6	0.0	0.0	0.0	0.0	787.0
7	0.0	0.0	0.0	0.0	787.0
8	0.0	0.0	0.0	0.0	787.0
9	0.0	0.0	0.0	0.0	787.0
10	0.0	0.0	0.0	0.0	1477.0

Payout Time (years)	5.3
Rate of Return (%)	13.9
Present Value ($M)	343.1

TABLE 4.18 Cash flow (with THF)

	System without THF	System with THF
Total major equipments cost ($/yr)	1,119,037	789,592
Total plant cost ($/yr)	3,692,822	2,605,654
Total manufacturing cost ($/yr)	2,104,262	1,865,727
Total capital cost ($/yr)	5,790,310	4,322,632
Payout time (yr)	7.8	5.3
Return on investment (%)	4.92	8.95
Rate of return (%)	8.1	13.9
Present value ($million)	-849.3	343.1

TABLE 4.19 Summary of costs for both systems

From TABLE 4.19, it is shown that the cost for system without THF is higher than the system without THF. The reduction in cost is significantly due to the lower compression requirement at which the hydrate formation pressure is lowered by the addition of THF into the process. The system without THF needs at least four compression stages while for system with THF needs only two compression stages. However, the cost of raw material is increased for system with THF but this does not affect the overall cost of the process since the cost of crystallizers for system without THF is much higher. Significantly, higher pressure affects the design and sizing of the crystallizer vessels. In addition from this result, it can be said that the process with THF is economically feasible if compared to system without THF.

4.5 Concluding Remarks

Based from the literatures, it can be said that the development of this hydrate based CO_2 recovery from the flue gas is still in the early stage. This is probably because the key issue of this hydrate process is to find the lowest possible pressure requirement.

A common problem during simulation is underspecified operating conditions. CHEMCAD is not reliable for process design calculation for hydrate process, but applicable in cost estimation. CHEMCAD is used only to help generate detailed cost estimate. Special process simulation software for hydrate process should be developed so that the detailed and more accurate process design can be developed. This project should also be optimized later on before estimating the cost and then be compared with current conventional process - absorption in MEA

Another challenge is regarding the accuracy of the process simulation. In order to tackle this issue, thorough literature reviews and references should be done properly and thoroughly.

CONCLUSION

As a conclusion, the CO_2 recovery from flue gas via hydrate formation has potential advantages in terms of economics and environmental aspects if it is studied thoroughly. The thermodynamics of $CO_2 + N_2$ hydrate system are verified by modeling means using CSMGem. The process design is done by CHEMCAD and proven not reliable for mass balance of hydrate process, but can help to generate the cost estimates. The costs are estimated and the system with THF is cheaper than the system without THF due to its lower pressure requirement and compression stages.

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APPENDICES

APPENDIX A: FYP 2 Gantt Chart

TITLE: Economic Evaluation of CO_2 Recovery from Flue Gas Using Gas Hydrate

ACTIVITIES	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Phase Diagrams Modeling	■	■	■	■																
Data Gathering	▨																			
Modeling using CSMGem		▨																		
Results Interpretation			▨																	
Deviation Error Analysis				▨																
Process Design					■	■	■													
Manual MEB					▨															
CHEMCAD Simulation						▨														
Problems Identification							▨													
Results Interpretation							▨													
Economics Evaluation								■	■	■										
CHEMCAD Economic Template								▨												
Major Equipment Costing									▨	▨										
Report Writing		■	■	■	■	■	■	■	■	■	■	■	■	■						
Progress report 1		▨	▨	▨	▼															
Progress report 2						▨	▨	▨	▨	▨	▼									
Dissertation (Soft bound)											▨	▨	▨	▼						
Dissertation (Hard bound)															▼					▼
Seminar											▼									
EDX												▼								
Poster Exhibition											▼									
Poster preparation									▨	▨										
Oral Presentation																		▼	▼	
Preparation															▨	▨	▨			
Meetings with SV	■	■	■	■	■	■	■	■	■	■	■	■	■	■						

APPENDIX B1: CO2 + N2 Hydrate Lw-H-V Phase Equilibrium Experimental Data and CSMGem Modeling Result

Hydrate: Nitrogen + carbon dioxide			
Reference: Kang et al. (2001)			
Phases: LW–H–V			
xCO2 (loading)	T (K)	P (MPa)	P CSM (MPa)
0.9659	274.95	1.565	1.5878
	280.25	2.9	3.1158
	282.55	4	4.4028
	283.55	5.115	6.6328
0.778	274	2	1.7375
	276.15	2.6	2.2597
	280.65	4.225	4.1297
	283.45	6.45	6.7807
	284.25	7.445	9.3946
0.4815	273.75	3.195	2.6234
	279	5.867	5.2523
	281	7.449	7.1846
	282	8.975	8.5966
0.1761	272.85	7.24	5.4428
	274.05	8.12	6.3479
	277.45	10.65	10.088
	278.65	11.748	12.023
	280.55	14.22	16.09
0.1159	274.25	11.02	8.6806
	275.65	13.87	10.426
	277.6	18.1	13.573
	278.95	22.23	16.375
0.0063	273.95	14.085	17.216
	274.55	15.4	18.297
	277	20.68	23.477
	278.25	24.12	26.664

APPENDIX B2: CO2 + N2 Hydrate Lw-H-V Pressure-Composition Data for different temperatures

T (K)	x	P
275	0.0063	19.2
	0.1159	9.5
	0.1761	7.4
	0.4815	3.1
	0.778	2
	0.9659	1.7
276	0.0063	21.2
	0.1159	11
	0.1761	8.4
	0.4815	3.7
	0.778	2.2
	0.9659	1.9
277	0.0063	23.4
	0.1159	12.5
	0.1761	9.5
	0.4815	4.1
	0.778	2.5
	0.9659	2.1
278	0.0063	26
	0.1159	14.3
	0.1761	10.8
	0.4815	4.7
	0.778	3
	0.9659	2.4
279	0.0063	
	0.1159	16.2
	0.1761	12.7
	0.4815	5.2
	0.778	3.3
	0.9659	2.7
280	0.0063	
	0.1159	
	0.1761	15
	0.4815	6
	0.778	3.8
	0.9659	3

APPENDIX C1: Streams Composition for CHEMCAD Process Simulation

```
CHEMCAD 6.0.1                                                        Page 1

Job Name: hydrate_process_noTHF   Date: 05/04/2010  Time: 17:12:32

Stream No.                     1             2             3             4
Stream Name
Temp  C                  25.0000*     335.3851        0.6000      129.2060
Pres  MPa                 0.1000*       1.0000        7.5000        2.5000
Enth  MMBtu/h           -0.31708      -0.27028       -3.1723      -0.30229
Vapor mole fraction       1.0000        1.0000       0.00000        1.0000
Total gmol/h           5000.0001     5000.0001    11618.7191     5000.0001
Total g/h            153666.6106   153666.6106   209825.3825   153666.6106
Total std L ft3/hr        6.6780        6.6780        7.4164        6.6780
Total std V scfh         3957.65       3957.65       9196.57       3957.65
Component mole fractions
Carbon Dioxide          0.170000      0.170000      0.001701      0.170000
Nitrogen                0.830000      0.830000      0.000003      0.830000
Water                   0.000000      0.000000      0.998296      0.000000

Stream No.                     5             6             7             8
Stream Name
Temp  C                  25.0000       25.0000      101.7977       25.0000
Pres  MPa                 1.0000        2.5000        5.0000        5.0000
Enth  MMBtu/h           -0.31752      -0.31823      -0.30711      -0.31937
Vapor mole fraction       1.0000        1.0000        1.0000        1.0000
Total gmol/h           5000.0001     5000.0001     5000.0001     5000.0001
Total g/h            153666.6106   153666.6106   153666.6106   153666.6106
Total std L ft3/hr        6.6780        6.6780        6.6780        6.6780
Total std V scfh         3957.65       3957.65       3957.65       3957.65
Component mole fractions
Carbon Dioxide          0.170000      0.170000      0.170000      0.170000
Nitrogen                0.830000      0.830000      0.830000      0.830000
Water                   0.000000      0.000000      0.000000      0.000000
```

```
Stream No.                    9          10           11           12
Stream Name
Temp   C                 0.6000      0.6000      70.7171       0.6000
Pres   MPa               7.5000      5.0000       7.5000       7.5000
Enth   MMBtu/h          0.00000    -0.90037     -0.31277      -3.1723
Vapor mole fraction      1.0000     0.00000       1.0000      0.00000
Total gmol/h             0.0000   3300.0002    5000.0001   11618.7191
Total g/h                0.0000  59449.5037  153666.6106  209825.3825
Total std L ft3/hr       0.0000      2.0994       6.6780       7.4164
Total std V scfh           0.00     2612.05      3957.65      9196.57
Component mole fractions
Carbon Dioxide         0.000000    0.000000     0.170000     0.001701
Nitrogen               0.000000    0.000000     0.830000     0.000003
Water                  0.000000    1.000000     0.000000     0.998296
```

```
CHEMCAD 6.0.1                                                         Page 2

Job Name: hydrate_process_noTHF   Date: 05/04/2010   Time: 17:12:32

Stream No.                      13            14            15            16
Stream Name
Temp  C                     0.6000        0.6000       25.0000*       0.6000
Pres  MPa                   5.0000        2.5000        0.1000*       2.5000
Enth  MMBtu/h              0.00000      -0.92766       -2.7110       0.00000
Vapor mole fraction         1.0000       0.00000       0.00000        1.0000
Total gmol/h                0.0000     3400.0001    10000.0001        0.0000
Total g/h                   0.0000    61251.0000   180150.0000        0.0000
Total std L ft3/hr          0.0000        2.1631        6.3619        0.0000
Total std V scfh              0.00       2691.20       7915.30          0.00
Component mole fractions
Carbon Dioxide            0.000000      0.000000      0.000000      0.000000
Nitrogen                  0.000000      0.000000      0.000000      0.000000
Water                     0.000000      1.000000      1.000000      0.000000

Stream No.                      17            18            19            20
Stream Name
Temp  C                    25.0000        0.6000        0.6000        0.6000
Pres  MPa                   7.5000        7.5000        0.1000        5.0000
Enth  MMBtu/h             -0.32045      -0.32473       -2.7284      -0.90037
Vapor mole fraction         1.0000        1.0000       0.00000       0.00000
Total gmol/h             5000.0001     5000.0001    10000.0001     3300.0002
Total g/h              153666.6106   153666.6106   180150.0000    59449.5037
Total std L ft3/hr          6.6780        6.6780        6.3619        2.0994
Total std V scfh           3957.65       3957.65       7915.30       2612.05
Component mole fractions
Carbon Dioxide            0.170000      0.170000      0.000000      0.000000
Nitrogen                  0.830000      0.830000      0.000000      0.000000
Water                     0.000000      0.000000      1.000000      1.000000
```

```
Stream No.                     21            22            23            24
Stream Name
Temp  C                    0.6000        0.5932        0.6000        0.6000
Pres  MPa                  2.5000        2.5000        7.5000        5.0000
Enth  MMBtu/h            -0.92766       -5.0003      -0.86283       0.00000
Vapor mole fraction       0.00000   5.6888E-006        1.0000        1.0000
Total gmol/h            3400.0001    18318.7182     7687.8036        0.0000
Total g/h              61251.0000   330526.0000   251725.6316        0.0000
Total std L ft3/hr         2.1631       11.6789       10.9005        0.0000
Total std V scfh          2691.20      14499.82       6085.13          0.00
Component mole fractions
Carbon Dioxide           0.000000      0.001079      0.295756      0.000000
Nitrogen                 0.000000      0.000002      0.704104      0.000000
Water                    1.000000      0.998919      0.000141      0.000000
```

```
CHEMCAD 6.0.1                                                      Page 3

Job Name: hydrate_process_noTHF   Date: 05/04/2010   Time: 17:12:32

Stream No.                       25            26            27            28
Stream Name
Temp  C                      0.6000      -23.0756        0.6000        2.8115
Pres  MPa                    2.5000        2.5000        0.1000        7.5000
Enth  MMBtu/h               0.00000      -0.86283      -0.90037      -0.89985
Vapor mole fraction          1.0000       0.99991       0.00000       0.00000
Total gmol/h                 0.0000     7687.8036     3300.0002     3300.0000
Total g/h                    0.0000   251725.6039    59449.5037    59449.4968
Total std L ft3/hr           0.0000       10.9005        2.0994        2.0994
Total std V scfh               0.00       6085.13       2612.05       2612.05
Component mole fractions
Carbon Dioxide             0.000000      0.295756      0.000000      0.000000
Nitrogen                   0.000000      0.704104      0.000000      0.000000
Water                      0.000000      0.000141      1.000000      1.000000

Stream No.                       29            30            31            32
Stream Name
Temp  C                      0.6000        0.6000        2.0643        1.3169
Pres  MPa                    0.1000        0.1000        5.0000        2.5000
Enth  MMBtu/h              -0.90037      -0.92766      -0.90003      -0.92748
Vapor mole fraction         0.00000       0.00000       0.00000       0.00000
Total gmol/h              3300.0002     3400.0001     3300.0000     3400.0001
Total g/h                59449.5037    61251.0000    59449.4968    61251.0000
Total std L ft3/hr           2.0994        2.1631        2.0994        2.1631
Total std V scfh            2612.05       2691.20       2612.05       2691.20
Component mole fractions
Carbon Dioxide             0.000000      0.000000      0.000000      0.000000
Nitrogen                   0.000000      0.000000      0.000000      0.000000
Water                      1.000000      1.000000      1.000000      1.000000
```

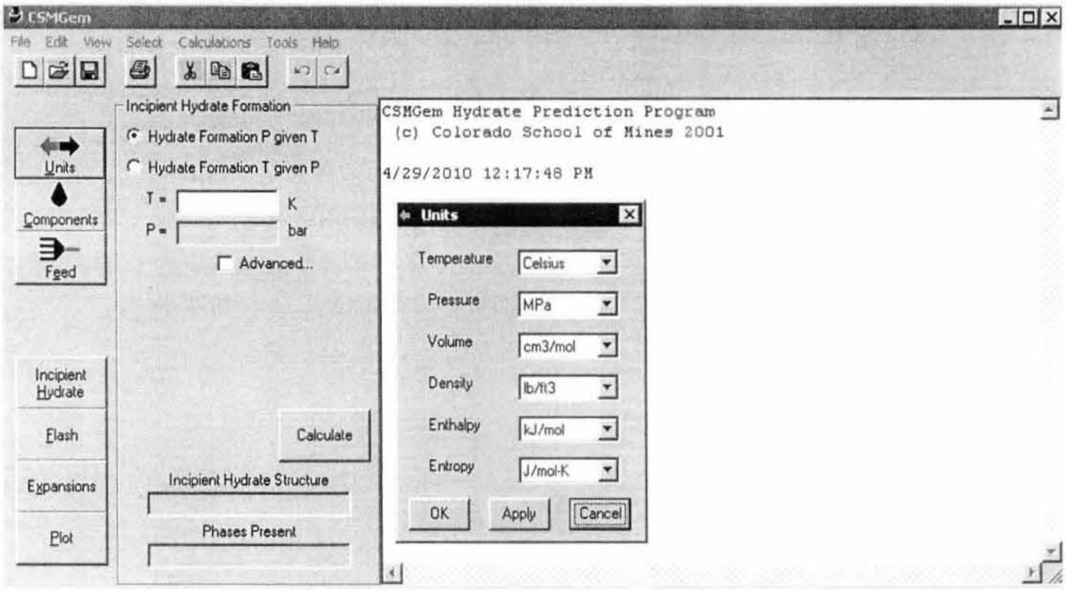
```
CHEMCAD 6.0.1                                                        Page 1

Job Name: hydrate_process_noTHF   Date: 05/04/2010  Time: 17:21:15

Calculation mode : Sequential
Flash algorithm  : Normal

Equipment Calculation Sequence
   2  10  19   3   4   5   8   9  11  17  18  20  21  22   1  12   6  13
   7  14  15  16

No recycle loops in the flowsheet.


Run Time Error and Warning Messages:

*** Equip.   1  ***

Error: CRYS did not converge.
*** Equip.   6  ***

* Error: TPFLASH did not converge.

* Uop     1, Check mass balance.

Stream    3 has two liquid phases.
Stream   12 has two liquid phases.
Stream   22 has two liquid phases.
Stream   26 has two liquid phases.
```

```
CHEMCAD 6.0.1                                                           Page 2

Job Name: hydrate_process_noTHF   Date: 05/04/2010   Time: 17:21:15

Overall Mass Balance       gmol/h                      g/h
                        Input       Output        Input        Output
Carbon Dioxide        850.000     2293.478    37408.499    100936.000
Nitrogen             4150.000     5413.043   116258.104    151641.000
Water               10000.000    18300.001   180150.000    329674.512

Total               15000.000    26006.523   333816.604    582252.000
```

APPENDIX C2: CO2 Solid Tools from CHEMCAD Simulation (Preliminary)

```
CHEMCAD 6.0.1                                                        Page 1

Job Name: hydrate_startup5   Date: 01/26/2010  Time: 23:39:20

CO2 Hydrate Solid Prediction (Valid Range: -210 F to -70 F):

Strm     Temp        Press      Fugacity     Solid Point
         C          MPa          MPa
C
    1     25.0000       0.1000      0.0169    -94.8632
    3      0.6000      10.0000      0.3247    -61.1339
    6    838.9504      10.0000      1.7556    -29.3949
    7      0.6000      10.0000      1.0672    -40.2572
    9      0.6000      10.0000     36.0290     78.8474  * Check CO2 Solid
   10      0.6000       5.0000      0.2753    -63.5658
   12      0.6000       2.5000      0.2727    -63.7036
   13      0.6000       2.5000     42.0726     87.0087  * Check CO2 Solid
   14      0.6000       5.0000     41.7745     86.6276  * Check CO2 Solid
```

APPENDIX D : CSMGem Hydrate Prediction Program Procedural Screenshots



Incipient Hydrate Formation
● Hydrate Formation P given T
○ Hydrate Formation T given P
T = K
P = bar
☐ Advanced...

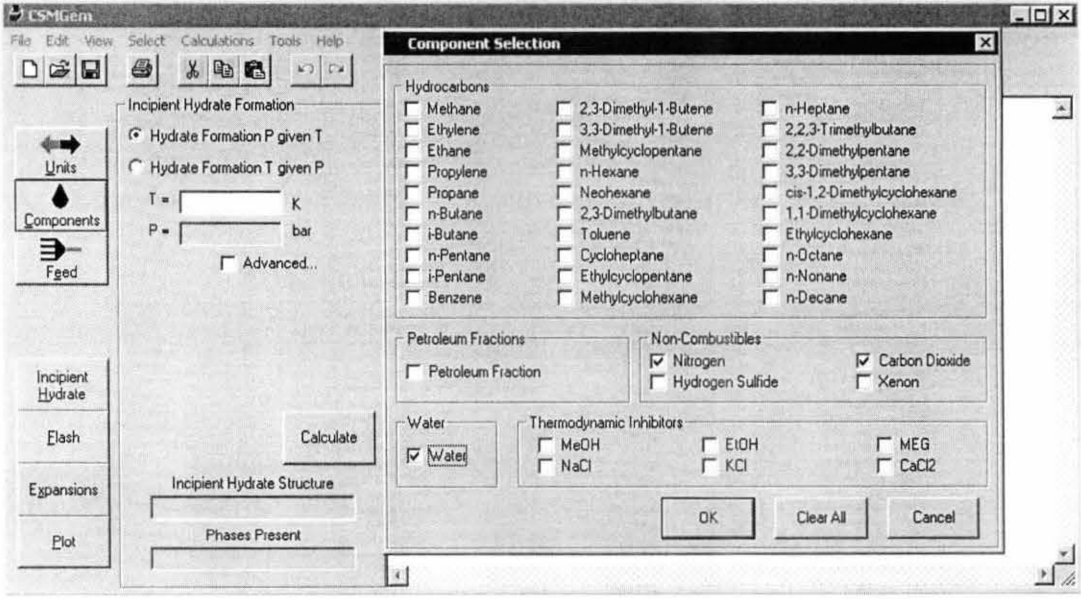
Incipient Hydrate Structure

Phases Present

```
CSMGem Hydrate Prediction Program
 (c) Colorado School of Mines 2001

4/29/2010 12:17:48 PM
```

Temperature: Celsius
Pressure: MPa
Volume: cm3/mol
Density: lb/ft3
Enthalpy: kJ/mol
Entropy: J/mol-K

FIGURE D.1 Units for temperature and pressure can be easily changed.



Incipient Hydrate Formation
● Hydrate Formation P given T
○ Hydrate Formation T given P
T = K
P = bar
☐ Advanced...

Incipient Hydrate Structure

Phases Present

Hydrocarbons
☐ Methane
☐ Ethylene
☐ Ethane
☐ Propylene
☐ Propane
☐ n-Butane
☐ i-Butane
☐ n-Pentane
☐ i-Pentane
☐ Benzene
☐ 2,3-Dimethyl-1-Butene
☐ 3,3-Dimethyl-1-Butene
☐ Methylcyclopentane
☐ n-Hexane
☐ Neohexane
☐ 2,3-Dimethylbutane
☐ Toluene
☐ Cycloheptane
☐ Ethylcyclopentane
☐ Methylcyclohexane
☐ n-Heptane
☐ 2,2,3-Trimethylbutane
☐ 2,2-Dimethylpentane
☐ 3,3-Dimethylpentane
☐ cis-1,2-Dimethylcyclohexane
☐ 1,1-Dimethylcyclohexane
☐ Ethylcyclohexane
☐ n-Octane
☐ n-Nonane
☐ n-Decane

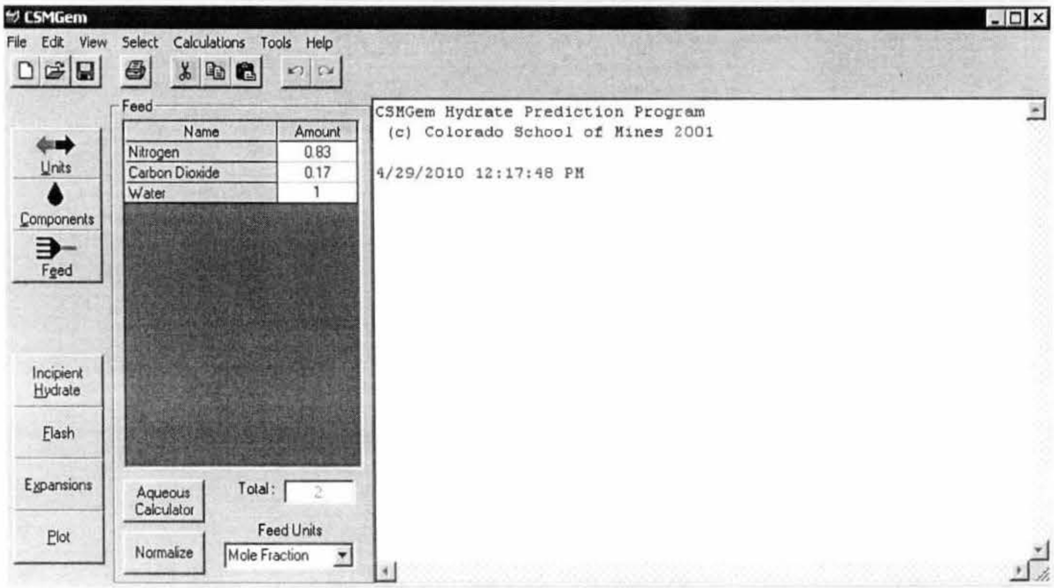
Petroleum Fractions
☐ Petroleum Fraction

Non-Combustibles
☑ Nitrogen
☐ Hydrogen Sulfide
☑ Carbon Dioxide
☐ Xenon

Water
☑ Water

Thermodynamic Inhibitors
☐ MeOH
☐ NaCl
☐ EtOH
☐ KCl
☐ MEG
☐ CaCl2

FIGURE D.2 CO_2, N_2 and water are selected components



Feed

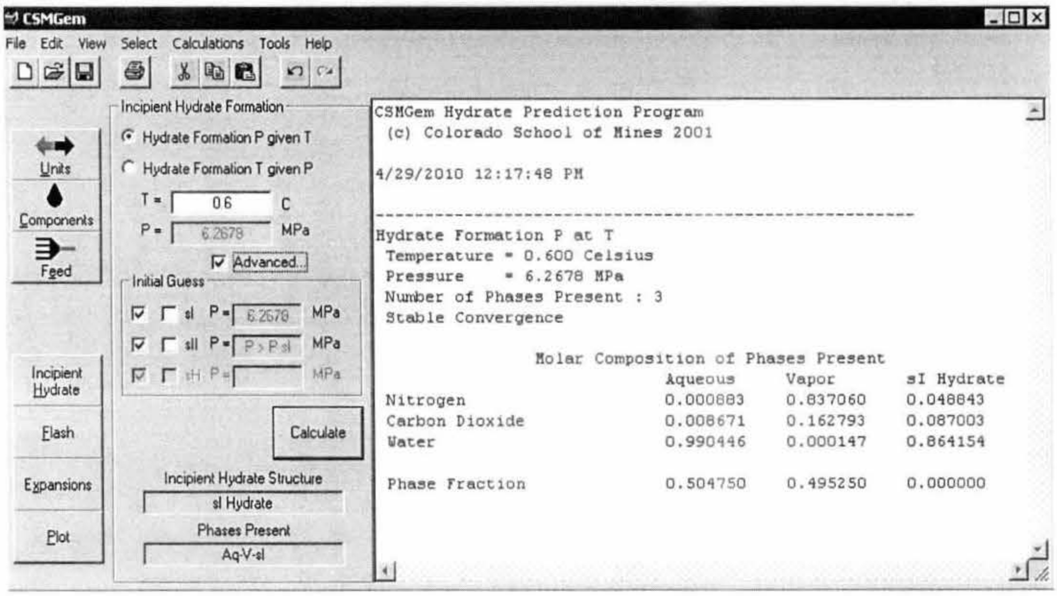
Name	Amount
Nitrogen	0.83
Carbon Dioxide	0.17
Water	1

Total: 2

Feed Units: Mole Fraction

```
CSMGem Hydrate Prediction Program
 (c) Colorado School of Mines 2001

4/29/2010 12:17:48 PM
```

FIGURE D.3 The mol fraction of the feed basis is entered.



Incipient Hydrate Formation

● Hydrate Formation P given T
○ Hydrate Formation T given P

T = 0.6 C
P = 6.2678 MPa

☑ Advanced...

Initial Guess

☑ ☐ sI P = 6.2678 MPa
☑ ☐ sII P = P > P sI MPa
☑ ☐ sH P = MPa

Incipient Hydrate Structure: sI Hydrate

Phases Present: Aq-V-sI

```
CSMGem Hydrate Prediction Program
 (c) Colorado School of Mines 2001

4/29/2010 12:17:48 PM

----------------------------------------------------
Hydrate Formation P at T
 Temperature = 0.600 Celsius
 Pressure    = 6.2678 MPa
 Number of Phases Present : 3
 Stable Convergence

              Molar Composition of Phases Present
                              Aqueous    Vapor      sI Hydrate
 Nitrogen                     0.000883   0.837060   0.048843
 Carbon Dioxide               0.008671   0.162793   0.087003
 Water                        0.990446   0.000147   0.864154

 Phase Fraction               0.504750   0.495250   0.000000
```

FIGURE D.4 Using Incipient Hydrate function, the hydrate formation P given T can be easily calculated by the program and produce the result as shown.

APPENDIX E : CSMGem Results (Raw Data)

```
CSMGem Hydrate Prediction Program
 (c) Colorado School of Mines 2001

3/14/2010 3:07:09 PM

-------------------------------------------------

Hydrate Formation P at T
 Temperature = 0.600 Celsius
 Pressure    = 6.4659 MPa
 Number of Phases Present : 3
 Stable Convergence

                  Molar Composition of Phases Present
                          Aqueous    Vapor     sI Hydrate
 Nitrogen                 0.000916   0.844037   0.050499
 Carbon Dioxide           0.008477   0.155820   0.085473
 Water                    0.990607   0.000143   0.864028

 Phase Fraction           0.672941   0.327059   0.000000

-------------------------------------------------

Hydrate Formation P at T
Temperature = 0.600 Celsius
 Pressure    = 6.4659 MPa
 Number of Phases Present : 3
 Stable Convergence

                  Molar Composition of Phases Present
                           Feed      Aqueous    Vapor     sI Hydrate
 Nitrogen                 0.276667   0.000916   0.844037   0.050499
 Carbon Dioxide           0.056667   0.008477   0.155820   0.085473
 Water                    0.666667   0.990607   0.000143   0.864028

 Phase Fraction                      0.672941   0.327059   0.000000
 Enthalpy (kJ/mol)                   -284.851   -62.885   -252.884

                  Fractional Cage Occupancy of Hydrate Guests
                          sI Hydrate
                           small       large
 Nitrogen                  0.5737      0.2569
 Carbon Dioxide            0.1803      0.6983


-------------------------------------------------
```

```
Hydrate Formation T at P
 Temperature = 3.813 Celsius
 Pressure    = 10.000 MPa
 Number of Phases Present : 3
 Stable Convergence

                Molar Composition of Phases Present
                       Feed       Aqueous    Vapor     sI Hydrate
 Nitrogen              0.276667   0.001258   0.845784   0.057502
 Carbon Dioxide        0.056667   0.009525   0.154082   0.080899
 Water                 0.666667   0.989217   0.000135   0.861599

 Phase Fraction                   0.673890   0.326110   0.000000
 Enthalpy (kJ/mol)                -284.152    -62.433   -252.008

                Fractional Cage Occupancy of Hydrate Guests
                    sI Hydrate
                       small          large
 Nitrogen              0.6371         0.2993
 Carbon Dioxide        0.1687         0.6636


----------------------------------------------------
```

CO_2 = 17%

```
Hydrate Formation P at T
 Temperature = 0.600 Celsius
 Pressure    = 6.2678 MPa
 Number of Phases Present : 3
 Stable Convergence

                Molar Composition of Phases Present
                       Feed       Aqueous    Vapor     sI Hydrate
 Nitrogen              0.415000   0.000883   0.837060   0.048843
 Carbon Dioxide        0.085000   0.008671   0.162793   0.087003
 Water                 0.500000   0.990446   0.000147   0.864154

 Phase Fraction                   0.504750   0.495250   0.000000
 Enthalpy (kJ/mol)                -284.809    -65.626   -252.925

                Fractional Cage Occupancy of Hydrate Guests
                    sI Hydrate
                       small          large
 Nitrogen              0.5619         0.2460
 Carbon Dioxide        0.1877         0.7093


----------------------------------------------------
```

CO2 = 57%

```
Hydrate Formation P at T
 Temperature = 0.600 Celsius
 Pressure    = 5.0109 MPa
 Number of Phases Present : 3
 Stable Convergence

                 Molar Composition of Phases Present
                          Feed      Aqueous    Vapor     sII Hydrate
 Nitrogen                 0.215000  0.000392   0.440515  0.020127
 Carbon Dioxide           0.285000  0.023985   0.559280  0.117125
 Water                    0.500000  0.975623   0.000205  0.862748

 Phase Fraction                     0.512390   0.487610  0.000000
 Enthalpy (kJ/mol)                  -280.568   -222.575  -252.734

                 Fractional Cage Occupancy of Hydrate Guests
                      sII Hydrate
                          small          large
 Nitrogen                 0.1647         0.0671
 Carbon Dioxide           0.6977         0.9125
```

CO2 = 83%

```
Hydrate Formation P at T
 Temperature = 0.600 Celsius
 Pressure    = 1.5870 MPa
 Number of Phases Present : 3
 Stable Convergence

                 Molar Composition of Phases Present
                          Feed      Aqueous    Vapor     sI Hydrate
 Nitrogen                 0.085000  0.000050   0.172424  0.003324
 Carbon Dioxide           0.415000  0.014583   0.827083  0.126483
 Water                    0.500000  0.985367   0.000493  0.870193

 Phase Fraction                     0.507179   0.492821  0.000000
 Enthalpy (kJ/mol)                  -283.431   -327.323  -254.736

                 Fractional Cage Occupancy of Hydrate Guests
                      sI Hydrate
                                 small          large
 Nitrogen                        0.0540         0.0113
 Carbon Dioxide                  0.4902         0.9510
```

```
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 10.000 MPa
 Number of Phases Present : 2
 Stable Convergence

                 Molar Composition of Phases Present
                        Feed       Vapor     sI Hydrate
 Nitrogen               0.415000   0.893856  0.068622
 Carbon Dioxide         0.085000   0.106042  0.069780
 Water                  0.500000   0.000102  0.861599

 Phase Fraction                    0.419733  0.580267
 Enthalpy (kJ/mol)                  -43.472  -252.109

                 Fractional Cage Occupancy of Hydrate Guests
                     sI Hydrate
                        small        large
 Nitrogen               0.6958       0.3787
 Carbon Dioxide         0.1198       0.5810


--------------------------------------------------
P-T Flash
 ** Flash Calculation Error **
 ** T and P Flash
 ** Maximum number of iterations reached.


--------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 5.0000 MPa
 Number of Phases Present : 2
 Stable Convergence

                 Molar Composition of Phases Present
                         Feed      Aqueous    Vapor
 Nitrogen               0.415000   0.000717  0.836067
 Carbon Dioxide         0.085000   0.007509  0.163760
 Water                  0.500000   0.991774  0.000173

 Phase Fraction                    0.504061  0.495939
 Enthalpy (kJ/mol)                 -285.213   -65.870

--------------------------------------------------

P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 2.5000 MPa
```

```
Number of Phases Present : 2
Stable Convergence

                Molar Composition of Phases Present
                    Feed       Aqueous    Vapor
Nitrogen            0.415000   0.000372   0.833402
Carbon Dioxide      0.085000   0.004441   0.166293
Water               0.500000   0.995187   0.000306

Phase Fraction                 0.502265   0.497735
Enthalpy (kJ/mol)              -286.239   -66.606

---------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.0000 MPa
 Number of Phases Present : 2
 Stable Convergence

                Molar Composition of Phases Present
                    Feed       Aqueous    Vapor
Nitrogen            0.415000   0.000849   0.836867
Carbon Dioxide      0.085000   0.008444   0.162982
Water               0.500000   0.990707   0.000151

Phase Fraction                 0.504614   0.495386
Enthalpy (kJ/mol)              -284.888   -65.672

---------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 7.0000 MPa
 Number of Phases Present : 3
 Stable Convergence

                Molar Composition of Phases Present
                    Feed       Aqueous    Vapor       sI Hydrate
Nitrogen            0.415000   0.001004   0.860963    0.054915
Carbon Dioxide      0.085000   0.007966   0.138903    0.081373
Water               0.500000   0.991030   0.000134    0.863712

Phase Fraction                 0.317330   0.467953    0.214717
Enthalpy (kJ/mol)              -284.964   -56.238     -252.782

                Fractional Cage Occupancy of Hydrate Guests
                  sI Hydrate
                    small        large
Nitrogen            0.6032       0.2864
Carbon Dioxide      0.1619       0.6683
```

```
----------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.5000 MPa
 Number of Phases Present : 3
 Stable Convergence

                 Molar Composition of Phases Present
                      Feed      Aqueous    Vapor      sI Hydrate
 Nitrogen            0.415000   0.000922   0.845196   0.050783
 Carbon Dioxide      0.085000   0.008444   0.154662   0.085210
 Water               0.500000   0.990635   0.000142   0.864007

 Phase Fraction                 0.442658   0.486256   0.071085
 Enthalpy (kJ/mol)              -284.859   -62.430   -252.878

                 Fractional Cage Occupancy of Hydrate Guests
                    sI Hydrate
                      small         large
 Nitrogen             0.5757        0.2587
 Carbon Dioxide       0.1791        0.6964


----------------------------------------------------

P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.4000 MPa
 Number of Phases Present : 3
 Stable Convergence

                 Molar Composition of Phases Present
                      Feed      Aqueous    Vapor      sI Hydrate
 Nitrogen            0.415000   0.000905   0.841762   0.049949
 Carbon Dioxide      0.085000   0.008541   0.158094   0.085981
 Water               0.500000   0.990554   0.000144   0.864069

 Phase Fraction                 0.469040   0.490084   0.040876
 Enthalpy (kJ/mol)               -284.837   -63.779   -252.898

                 Fractional Cage Occupancy of Hydrate Guests
                    sI Hydrate
                      small         large
 Nitrogen             0.5698        0.2532
 Carbon Dioxide       0.1827        0.7020


----------------------------------------------------
```

```
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.3000 MPa
 Number of Phases Present : 3
 Stable Convergence

             Molar Composition of Phases Present
                    Feed      Aqueous    Vapor      sI Hydrate
 Nitrogen           0.415000  0.000889  0.838223  0.049113
 Carbon Dioxide     0.085000  0.008639  0.161631  0.086754
 Water              0.500000  0.990472  0.000146  0.864133

 Phase Fraction               0.495957  0.493979  0.010063
 Enthalpy (kJ/mol)            -284.816   -65.169  -252.918

             Fractional Cage Occupancy of Hydrate Guests
                 sI Hydrate
                    small        large
 Nitrogen           0.5639       0.2478
 Carbon Dioxide     0.1865       0.7075


-------------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2000 MPa
 Number of Phases Present : 2
 Stable Convergence

             Molar Composition of Phases Present
                    Feed      Aqueous   Vapor
 Nitrogen           0.415000  0.000875  0.837012
 Carbon Dioxide     0.085000  0.008614  0.162840
 Water              0.500000  0.990511  0.000148

 Phase Fraction               0.504716  0.495284
 Enthalpy (kJ/mol)            -284.829   -65.637

-------------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2500 MPa
 Number of Phases Present : 2
 Stable Convergence

             Molar Composition of Phases Present
                    Feed      Aqueous   Vapor
 Nitrogen           0.415000  0.000881  0.837048
 Carbon Dioxide     0.085000  0.008656  0.162806
 Water              0.500000  0.990463  0.000147
```

```
Phase Fraction                     0.504741   0.495259
Enthalpy (kJ/mol)                  -284.814   -65.629

--------------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2800 MPa
 Number of Phases Present : 3
 Stable Convergence

               Molar Composition of Phases Present
                   Feed        Aqueous    Vapor      sI Hydrate
Nitrogen           0.415000    0.000885   0.837502   0.048945
Carbon Dioxide     0.085000    0.008659   0.162351   0.086909
Water              0.500000    0.990456   0.000146   0.864146

Phase Fraction                 0.501409   0.494767   0.003824
Enthalpy (kJ/mol)              -284.811   -65.452    -252.922

               Fractional Cage Occupancy of Hydrate Guests
                 sI Hydrate
                   small        large
Nitrogen           0.5627       0.2467
Carbon Dioxide     0.1872       0.7086


--------------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2700 MPa
 Number of Phases Present : 3
 Stable Convergence

               Molar Composition of Phases Present
                   Feed        Aqueous    Vapor      sI Hydrate
Nitrogen           0.415000    0.000884   0.837140   0.048861
Carbon Dioxide     0.085000    0.008669   0.162713   0.086986
Water              0.500000    0.990448   0.000147   0.864152

Phase Fraction                 0.504147   0.495163   0.000690
Enthalpy (kJ/mol)              -284.809   -65.595    -252.924

               Fractional Cage Occupancy of Hydrate Guests
                 sI Hydrate
                   small        large
Nitrogen           0.5621       0.2461
Carbon Dioxide     0.1876       0.7092
```

```
---------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2600 MPa
 Number of Phases Present : 2
 Stable Convergence

               Molar Composition of Phases Present
                  Feed       Aqueous    Vapor
 Nitrogen         0.415000   0.000882   0.837055
 Carbon Dioxide   0.085000   0.008664   0.162799
 Water            0.500000   0.990453   0.000147

 Phase Fraction              0.504746   0.495254
 Enthalpy (kJ/mol)           -284.811   -65.627

---------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2650 MPa
 Number of Phases Present : 2
 Stable Convergence

               Molar Composition of Phases Present
                  Feed       Aqueous    Vapor
 Nitrogen         0.415000   0.000883   0.837058
 Carbon Dioxide   0.085000   0.008669   0.162795
 Water            0.500000   0.990448   0.000147

 Phase Fraction              0.504749   0.495251
 Enthalpy (kJ/mol)           -284.809   -65.627

---------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2670 MPa
 Number of Phases Present : 2
 Stable Convergence

               Molar Composition of Phases Present
                  Feed       Aqueous    Vapor
 Nitrogen         0.415000   0.000883   0.837060
 Carbon Dioxide   0.085000   0.008670   0.162794
 Water            0.500000   0.990447   0.000147

 Phase Fraction              0.504749   0.495251
 Enthalpy (kJ/mol)           -284.809   -65.626

---------------------------------------------------
```

```
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2680 MPa
 Number of Phases Present : 3
 Stable Convergence

                Molar Composition of Phases Present
                        Feed       Aqueous    Vapor      sI Hydrate
 Nitrogen               0.415000   0.000883   0.837067   0.048845
 Carbon Dioxide         0.085000   0.008671   0.162786   0.087002
 Water                  0.500000   0.990446   0.000147   0.864154

 Phase Fraction                    0.504694   0.495242   0.000064
 Enthalpy (kJ/mol)                 -284.809   -65.623    -252.925

                Fractional Cage Occupancy of Hydrate Guests
                    sI Hydrate
                        small        large
 Nitrogen               0.5620       0.2460
 Carbon Dioxide         0.1877       0.7093


-----------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 5.0000 MPa
 Number of Phases Present : 2
 Stable Convergence

                Molar Composition of Phases Present
                        Feed       Vapor      sI Hydrate
 Nitrogen               0.215000   0.487819   0.017303
 Carbon Dioxide         0.285000   0.511995   0.120510
 Water                  0.500000   0.000186   0.862187

 Phase Fraction                    0.420170   0.579830
 Enthalpy (kJ/mol)                 -203.804   -252.368

                Fractional Cage Occupancy of Hydrate Guests
                    sI Hydrate
                        small        large
 Nitrogen               0.2756       0.0620
 Carbon Dioxide         0.4705       0.9148

-----------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 2.5000 MPa
 Number of Phases Present : 2
 Stable Convergence
```

```
               Molar Composition of Phases Present
                    Feed        Vapor       sI Hydrate
Nitrogen            0.085000   0.194881   0.004532
Carbon Dioxide      0.415000   0.804793   0.129549
Water               0.500000   0.000326   0.865919

Phase Fraction                 0.422738   0.577262
Enthalpy (kJ/mol)              -318.882   -253.475

               Fractional Cage Occupancy of Hydrate Guests
                 sI Hydrate
                    small          large
Nitrogen            0.0773         0.0144
Carbon Dioxide      0.5637         0.9591



--------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 10.000 MPa
 Number of Phases Present : 2
 Stable Convergence

               Molar Composition of Phases Present
                    Feed        Vapor        sI Hydrate
Nitrogen            0.415000   0.893856   0.068622
Carbon Dioxide      0.085000   0.106042   0.069780
Water               0.500000   0.000102   0.861599

Phase Fraction                 0.419733   0.580267
Enthalpy (kJ/mol)               -43.472   -252.109

               Fractional Cage Occupancy of Hydrate Guests
                 sI Hydrate
                    small          large
Nitrogen            0.6958         0.3787
Carbon Dioxide      0.1198         0.5810


--------------------------------------------------

P-T Flash
 ** Flash Calculation Error **
 ** T and P Flash
 ** Maximum number of iterations reached.


--------------------------------------------------
```

```
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 5.0000 MPa
 Number of Phases Present : 2
 Stable Convergence

               Molar Composition of Phases Present
                        Feed      Aqueous    Vapor
 Nitrogen               0.415000  0.000717   0.836067
 Carbon Dioxide         0.085000  0.007509   0.163760
 Water                  0.500000  0.991774   0.000173

 Phase Fraction                   0.504061   0.495939
 Enthalpy (kJ/mol)                -285.213   -65.870

---------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 2.5000 MPa
 Number of Phases Present : 2
 Stable Convergence

               Molar Composition of Phases Present
                        Feed      Aqueous    Vapor
 Nitrogen               0.415000  0.000372   0.833402
 Carbon Dioxide         0.085000  0.004441   0.166293
 Water                  0.500000  0.995187   0.000306

 Phase Fraction                   0.502265   0.497735
 Enthalpy (kJ/mol)                -286.239   -66.606

---------------------------------------------------

P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.0000 MPa
 Number of Phases Present : 2
 Stable Convergence

               Molar Composition of Phases Present
                        Feed      Aqueous    Vapor
 Nitrogen               0.415000  0.000849   0.836867
 Carbon Dioxide         0.085000  0.008444   0.162982
 Water                  0.500000  0.990707   0.000151

 Phase Fraction                   0.504614   0.495386
 Enthalpy (kJ/mol)                -284.888   -65.672

---------------------------------------------------
```

```
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 7.0000 MPa
 Number of Phases Present : 3
 Stable Convergence

              Molar Composition of Phases Present
                     Feed      Aqueous    Vapor      sI Hydrate
 Nitrogen            0.415000  0.001004  0.860963  0.054915
 Carbon Dioxide      0.085000  0.007966  0.138903  0.081373
 Water               0.500000  0.991030  0.000134  0.863712

 Phase Fraction                0.317330  0.467953  0.214717
 Enthalpy (kJ/mol)              -284.964   -56.238  -252.782

              Fractional Cage Occupancy of Hydrate Guests
                  sI Hydrate
                     small        large
 Nitrogen            0.6032       0.2864
 Carbon Dioxide      0.1619       0.6683


--------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.5000 MPa
 Number of Phases Present : 3
 Stable Convergence

              Molar Composition of Phases Present
                     Feed      Aqueous     Vapor    sI Hydrate
 Nitrogen            0.415000  0.000922  0.845196  0.050783
 Carbon Dioxide      0.085000  0.008444  0.154662  0.085210
 Water               0.500000  0.990635  0.000142  0.864007

 Phase Fraction                0.442658  0.486256  0.071085
 Enthalpy (kJ/mol)             -284.859   -62.430  -252.878

              Fractional Cage Occupancy of Hydrate Guests
                  sI Hydrate
                     small        large
 Nitrogen            0.5757       0.2587
 Carbon Dioxide      0.1791       0.6964

--------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.4000 MPa
 Number of Phases Present : 3
 Stable Convergence
```

```
                 Molar Composition of Phases Present
                          Feed      Aqueous     Vapor     sI Hydrate
Nitrogen                0.415000   0.000905   0.841762   0.049949
Carbon Dioxide          0.085000   0.008541   0.158094   0.085981
Water                   0.500000   0.990554   0.000144   0.864069

Phase Fraction                     0.469040   0.490084   0.040876
Enthalpy (kJ/mol)                  -284.837    -63.779   -252.898

                 Fractional Cage Occupancy of Hydrate Guests
                      sI Hydrate
                          small          large
Nitrogen                  0.5698         0.2532
Carbon Dioxide            0.1827         0.7020


----------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.3000 MPa
 Number of Phases Present : 3
 Stable Convergence

                 Molar Composition of Phases Present
                          Feed      Aqueous     Vapor     sI Hydrate
Nitrogen                0.415000   0.000889   0.838223   0.049113
Carbon Dioxide          0.085000   0.008639   0.161631   0.086754
Water                   0.500000   0.990472   0.000146   0.864133

Phase Fraction                     0.495957   0.493979   0.010063
Enthalpy (kJ/mol)                  -284.816    -65.169   -252.918

                 Fractional Cage Occupancy of Hydrate Guests
                      sI Hydrate
                          small          large
Nitrogen                  0.5639          0.2478
Carbon Dioxide            0.1865         0.7075


----------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2000 MPa
 Number of Phases Present : 2
 Stable Convergence

                 Molar Composition of Phases Present
                          Feed        Aqueous    Vapor
Nitrogen                   0.415000   0.000875   0.837012
```

```
Carbon Dioxide      0.085000   0.008614   0.162840
Water               0.500000   0.990511   0.000148

Phase Fraction                 0.504716   0.495284
Enthalpy (kJ/mol)              -284.829   -65.637

----------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2500 MPa
 Number of Phases Present : 2
 Stable Convergence

            Molar Composition of Phases Present
                     Feed      Aqueous    Vapor
Nitrogen            0.415000   0.000881   0.837048
Carbon Dioxide      0.085000   0.008656   0.162806
Water               0.500000   0.990463   0.000147

Phase Fraction                 0.504741   0.495259
Enthalpy (kJ/mol)              -284.814   -65.629

----------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2800 MPa
 Number of Phases Present : 3
 Stable Convergence

            Molar Composition of Phases Present
                    Feed       Aqueous    Vapor      sI Hydrate
Nitrogen            0.415000   0.000885   0.837502   0.048945
Carbon Dioxide      0.085000   0.008659   0.162351   0.086909
Water               0.500000   0.990456   0.000146   0.864146

Phase Fraction                 0.501409   0.494767   0.003824
Enthalpy (kJ/mol)              -284.811   -65.452    -252.922

            Fractional Cage Occupancy of Hydrate Guests
                  sI Hydrate
                    small       large
Nitrogen            0.5627      0.2467
Carbon Dioxide      0.1872      0.7086


----------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2700 MPa
 Number of Phases Present : 3
```

```
Stable Convergence

                  Molar Composition of Phases Present
                         Feed       Aqueous    Vapor      sI Hydrate
Nitrogen                 0.415000   0.000884   0.837140   0.048861
Carbon Dioxide           0.085000   0.008669   0.162713   0.086986
Water                    0.500000   0.990448   0.000147   0.864152

Phase Fraction                      0.504147   0.495163   0.000690
Enthalpy (kJ/mol)                   -284.809   -65.595    -252.924

                  Fractional Cage Occupancy of Hydrate Guests
                       sI Hydrate
                         small          large
Nitrogen                 0.5621         0.2461
Carbon Dioxide           0.1876         0.7092


----------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2600 MPa
 Number of Phases Present : 2
 Stable Convergence

                  Molar Composition of Phases Present
                         Feed       Aqueous    Vapor
Nitrogen                 0.415000   0.000882   0.837055
Carbon Dioxide           0.085000   0.008664   0.162799
Water                    0.500000   0.990453   0.000147

Phase Fraction                       0.504746   0.495254
Enthalpy (kJ/mol)                    -284.811   -65.627

----------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2650 MPa
 Number of Phases Present : 2
 Stable Convergence

                  Molar Composition of Phases Present
                         Feed       Aqueous    Vapor
Nitrogen                 0.415000   0.000883   0.837058
Carbon Dioxide           0.085000   0.008669   0.162795
Water                    0.500000   0.990448   0.000147

Phase Fraction                      0.504749   0.495251
Enthalpy (kJ/mol)                   -284.809   -65.627
```

```
-----------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2670 MPa
 Number of Phases Present : 2
 Stable Convergence

                  Molar Composition of Phases Present
                           Feed         Aqueous     Vapor
 Nitrogen                  0.415000     0.000883    0.837060
 Carbon Dioxide            0.085000     0.008670    0.162794
 Water                     0.500000     0.990447    0.000147

 Phase Fraction                         0.504749    0.495251
 Enthalpy (kJ/mol)                      -284.809    -65.626

-----------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 6.2680 MPa
 Number of Phases Present : 3
 Stable Convergence

                  Molar Composition of Phases Present
                           Feed         Aqueous     Vapor       sI Hydrate
 Nitrogen                  0.415000     0.000883    0.837067    0.048845
 Carbon Dioxide            0.085000     0.008671    0.162786    0.087002
 Water                     0.500000     0.990446    0.000147    0.864154

 Phase Fraction                         0.504694    0.495242    0.000064
 Enthalpy (kJ/mol)                      -284.809    -65.623     -252.925

                  Fractional Cage Occupancy of Hydrate Guests
                       sI Hydrate
                           small        large
 Nitrogen                  0.5620       0.2460
 Carbon Dioxide            0.1877       0.7093


-----------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 5.0000 MPa
 Number of Phases Present : 2
 Stable Convergence

                  Molar Composition of Phases Present
                           Feed         Vapor       sI Hydrate
 Nitrogen                  0.215000     0.487819    0.017303
 Carbon Dioxide             0.285000     0.511995    0.120510
```

```
Water               0.500000  0.000186  0.862187

Phase Fraction                0.420170  0.579830
Enthalpy (kJ/mol)             -203.804  -252.368

            Fractional Cage Occupancy of Hydrate Guests
                sI Hydrate
                   small        large
Nitrogen           0.2756       0.0620
Carbon Dioxide     0.4705       0.9148


-------------------------------------------------
P-T Flash
 Temperature = 0.600 Celsius
 Pressure    = 2.5000 MPa
 Number of Phases Present : 2
 Stable Convergence

            Molar Composition of Phases Present
                    Feed      Vapor     sI Hydrate
Nitrogen            0.085000  0.194881  0.004532
Carbon Dioxide      0.415000  0.804793  0.129549
Water               0.500000  0.000326  0.865919

Phase Fraction                0.422738  0.577262
Enthalpy (kJ/mol)             -318.882  -253.475

            Fractional Cage Occupancy of Hydrate Guests
                sI Hydrate
                   small        large
Nitrogen           0.0773        0.0144
Carbon Dioxide     0.5637       0.9591


-------------------------------------------------
Hydrate Formation P at T
 Temperature = 280.000 Kelvin
 Pressure    = 151.28 bar
 Number of Phases Present : 3
 Stable Convergence

            Molar Composition of Phases Present
                    Feed      Aqueous   Vapor     sI Hydrate
Nitrogen            0.415000  0.001666  0.838613  0.063911
Carbon Dioxide      0.085000  0.010599  0.161252  0.076489
Water               0.500000  0.987735  0.000135  0.859599

Phase Fraction                0.506141  0.493859  0.000000
Enthalpy (kJ/mol)             -283.414   -65.593  -251.236
```

```
                 Fractional Cage Occupancy of Hydrate Guests
                       sI Hydrate
                            small          large
Nitrogen                    0.6912         0.3396
Carbon Dioxide              0.1563         0.6301
```

```
----------------------------------------------------
```

[This section - to compare with S.P. Kang proposed design]

CO2 = 34.71%
P = 38.7 bar

```
Hydrate Formation P at T
 Temperature = 274.000 Kelvin
 Pressure    = 36.216 bar
 Number of Phases Present : 3
 Stable Convergence

                 Molar Composition of Phases Present
                            Feed        Aqueous     Vapor       sI Hydrate
Nitrogen                    0.326450    0.000418    0.660553    0.024444
Carbon Dioxide              0.173550    0.011893    0.339209    0.109157
Water                       0.500000    0.987689    0.000239    0.866398

Phase Fraction                          0.506113    0.493887    0.000000
Enthalpy (kJ/mol)                       -284.044    -135.065    -253.615

                 Fractional Cage Occupancy of Hydrate Guests
                       sI Hydrate
                            small          large
Nitrogen                    0.3398         0.1030
Carbon Dioxide              0.3296         0.8561
```

```
----------------------------------------------------
```

CO2 = 89.34%
P = 28.7 bar

```
Hydrate Formation P at T
 Temperature = 274.000 Kelvin
 Pressure    = 15.257 bar
 Number of Phases Present : 3
 Stable Convergence

                 Molar Composition of Phases Present
                            Feed        Aqueous     Vapor       sI Hydrate
Nitrogen                    0.053300    0.000030    0.108167    0.001993
```

```
Carbon Dioxide      0.446700  0.015036  0.891311  0.127697
Water               0.500000  0.984933  0.000522  0.870310

Phase Fraction                0.507388  0.492612  0.000000
Enthalpy (kJ/mol)             -283.289  -352.654  -254.759

              Fractional Cage Occupancy of Hydrate Guests
                  sI Hydrate
                    small       large
Nitrogen            0.0328      0.0066
Carbon Dioxide      0.5053      0.9565


----------------------------------------------------
P-T Flash
 Temperature = 274.000 Kelvin
 Pressure    = 28.700 bar
 Number of Phases Present : 2
 Stable Convergence

              Molar Composition of Phases Present
                    Feed      Vapor     sI Hydrate
Nitrogen            0.053300  0.122307  0.002951
Carbon Dioxide      0.446700  0.877394  0.132457
Water               0.500000  0.000300  0.864592

Phase Fraction                0.421839  0.578161
Enthalpy (kJ/mol)             -347.788  -253.069

              Fractional Cage Occupancy of Hydrate Guests
                  sI Hydrate
                    small       large
Nitrogen            0.0520      0.0088
Carbon Dioxide      0.6170      0.9689

----------------------------------------------------
P-T Flash
 Temperature = 274.000 Kelvin
 Pressure    = 38.700 bar
 Number of Phases Present : 3
 Stable Convergence

              Molar Composition of Phases Present
                    Feed      Aqueous   Vapor     sI Hydrate
Nitrogen            0.326450  0.000462  0.686185  0.026778
Carbon Dioxide      0.173550  0.011586  0.313590  0.107111
Water               0.500000  0.987952  0.000225  0.866111

Phase Fraction                0.313877  0.466983  0.219140
Enthalpy (kJ/mol)             -284.115  -124.976  -253.528
```

```
              Fractional Cage Occupancy of Hydrate Guests
                     sI Hydrate
                       small        large
Nitrogen               0.3658       0.1151
Carbon Dioxide         0.3135       0.8436


-----------------------------------------------------
```

[NO HYDRATE FORMED]

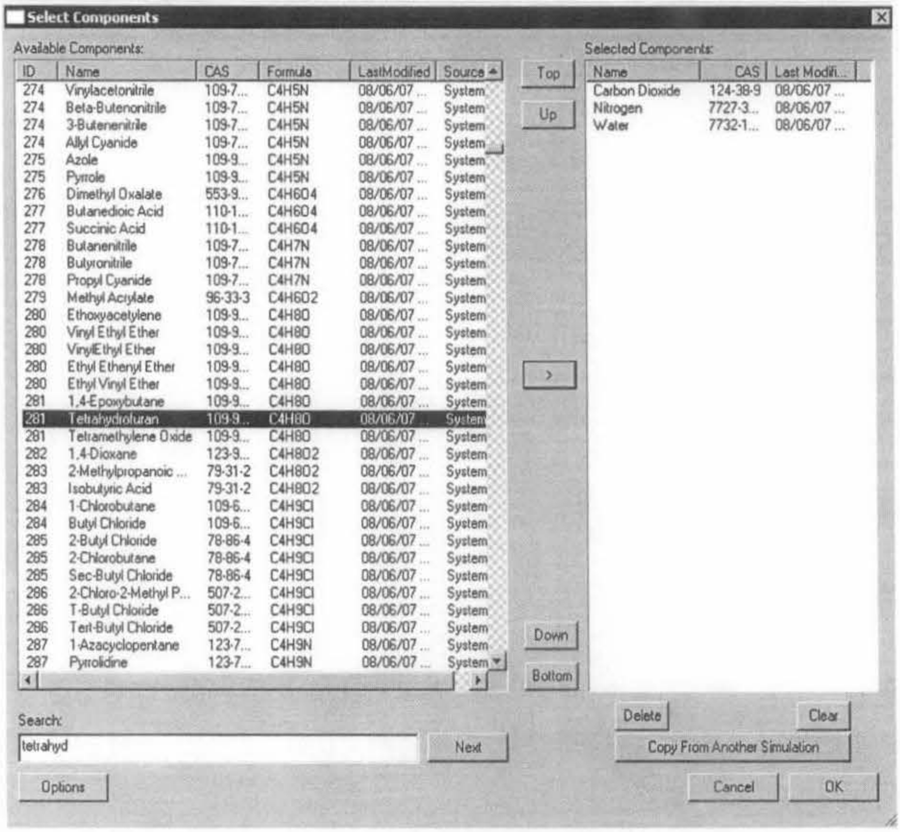
```
P-T Flash
 Temperature = 280.000 Kelvin
 Pressure    = 16.500 bar
 Number of Phases Present : 2
 Stable Convergence

              Molar Composition of Phases Present
                       Feed        Aqueous     Vapor
Nitrogen               0.415000    0.000216    0.831455
Carbon Dioxide         0.085000    0.002474    0.167858
Water                  0.500000    0.997310    0.000687

Phase Fraction                     0.501005    0.498995
Enthalpy (kJ/mol)                  -286.397    -67.014

-----------------------------------------------------
```

CO2 + N2 + H2O + Propane/Methane/Ethane

```
CSMGem Hydrate Prediction Program
 (c) Colorado School of Mines 2001

4/28/2010 7:15:42 PM
-----------------------------------------------------
Hydrate Formation P at T
 Temperature = 0.600 Celsius
 Pressure    = 3.2269 MPa
 Number of Phases Present : 3
 Stable Convergence

              Molar Composition of Phases Present
                       Aqueous     Vapor       sII Hydrate
Propane                0.000021    0.009936    0.045577
Nitrogen               0.000471    0.825905    0.042300
Carbon Dioxide         0.005391    0.163913    0.036424
Water                  0.994118    0.000246    0.875699

Phase Fraction         0.497805    0.502195    0.000000
```

```
--------------------------------------------------
Hydrate Formation P at T
 Temperature = 0.600 Celsius
 Pressure    = 3.2054 MPa
 Number of Phases Present : 3
 Stable Convergence

              Molar Composition of Phases Present
                     Aqueous    Vapor     sII Hydrate
 Propane             0.000021   0.010036   0.045601
 Nitrogen            0.000467   0.824219   0.042022
 Carbon Dioxide      0.005413   0.165497   0.036622
 Water               0.994099   0.000247   0.875755

 Phase Fraction      0.502844   0.497156   0.000000

--------------------------------------------------
Hydrate Formation P at T
 Temperature = 0.600 Celsius
 Pressure    = 6.1162 MPa
 Number of Phases Present : 3
 Stable Convergence

              Molar Composition of Phases Present
                     Aqueous    Vapor     sI Hydrate
 Methane             0.000022   0.010072   0.002788
 Nitrogen            0.000854   0.826872   0.047131
 Carbon Dioxide      0.008538   0.162906   0.085971
 Water               0.990587   0.000149   0.864110

 Phase Fraction      0.504676   0.495324   0.000000

--------------------------------------------------
Hydrate Formation P at T
 Temperature = 0.600 Celsius
 Pressure    = 5.5266 MPa
 Number of Phases Present : 3
 Stable Convergence

              Molar Composition of Phases Present
                     Aqueous    Vapor     sI Hydrate
 Ethane              0.000024   0.010063   0.011576
 Nitrogen            0.000778   0.826421   0.044013
 Carbon Dioxide      0.008000   0.163355   0.079654
 Water               0.991198   0.000161   0.864756

 Phase Fraction      0.504360   0.495640   0.000000

--------------------------------------------------
```

APPENDIX F1 : CHEMCAD Simulation Major Procedural Screenshots



Available Components:

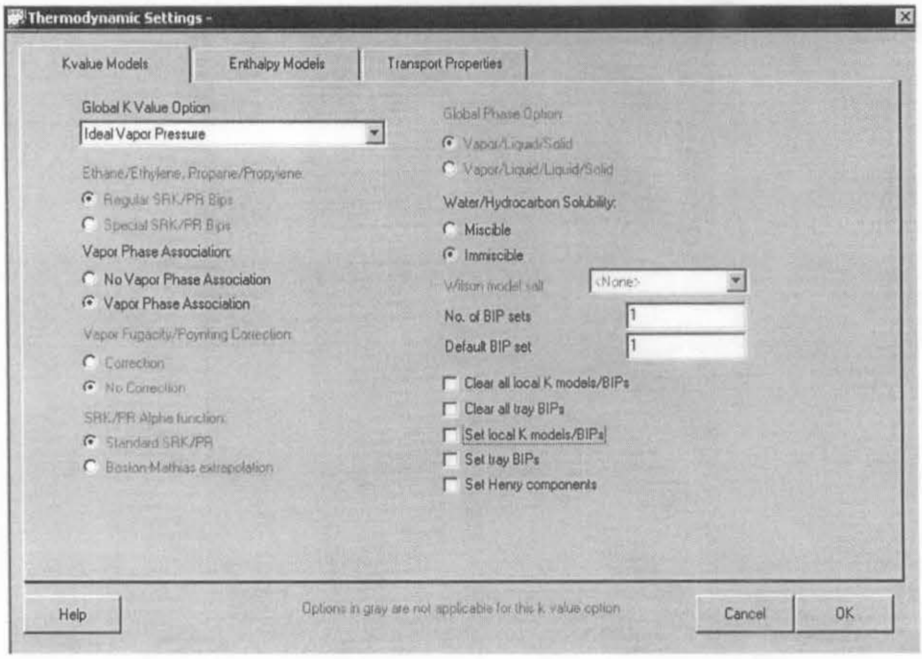
ID	Name	CAS	Formula	LastModified	Source
274	Vinylacetonitrile	109-7...	C4H5N	08/06/07 ...	System
274	Beta-Butenonitrile	109-7...	C4H5N	08/06/07 ...	System
274	3-Butenenitrile	109-7...	C4H5N	08/06/07 ...	System
274	Allyl Cyanide	109-7...	C4H5N	08/06/07 ...	System
275	Azole	109-9...	C4H5N	08/06/07 ...	System
275	Pyrrole	109-9...	C4H5N	08/06/07 ...	System
276	Dimethyl Oxalate	553-9...	C4H6O4	08/06/07 ...	System
277	Butanedioic Acid	110-1...	C4H6O4	08/06/07 ...	System
277	Succinic Acid	110-1...	C4H6O4	08/06/07 ...	System
278	Butanenitrile	109-7...	C4H7N	08/06/07 ...	System
278	Butyronitrile	109-7...	C4H7N	08/06/07 ...	System
278	Propyl Cyanide	109-7...	C4H7N	08/06/07 ...	System
279	Methyl Acrylate	96-33-3	C4H6O2	08/06/07 ...	System
280	Ethoxyacetylene	109-9...	C4H8O	08/06/07 ...	System
280	Vinyl Ethyl Ether	109-9...	C4H8O	08/06/07 ...	System
280	VinylEthyl Ether	109-9...	C4H8O	08/06/07 ...	System
280	Ethyl Ethenyl Ether	109-9...	C4H8O	08/06/07 ...	System
280	Ethyl Vinyl Ether	109-9...	C4H8O	08/06/07 ...	System
281	1,4-Epoxybutane	109-9...	C4H8O	08/06/07 ...	System
281	Tetrahydrofuran	109-9...	C4H8O	08/06/07 ...	System
281	Tetramethylene Oxide	109-9...	C4H8O	08/06/07 ...	System
282	1,4-Dioxane	123-9...	C4H8O2	08/06/07 ...	System
283	2-Methylpropanoic ...	79-31-2	C4H8O2	08/06/07 ...	System
283	Isobutyric Acid	79-31-2	C4H8O2	08/06/07 ...	System
284	1-Chlorobutane	109-6...	C4H9Cl	08/06/07 ...	System
284	Butyl Chloride	109-6...	C4H9Cl	08/06/07 ...	System
285	2-Butyl Chloride	78-86-4	C4H9Cl	08/06/07 ...	System
285	2-Chlorobutane	78-86-4	C4H9Cl	08/06/07 ...	System
285	Sec-Butyl Chloride	78-86-4	C4H9Cl	08/06/07 ...	System
286	2-Chloro-2-Methyl P...	507-2...	C4H9Cl	08/06/07 ...	System
286	T-Butyl Chloride	507-2...	C4H9Cl	08/06/07 ...	System
286	Tert-Butyl Chloride	507-2...	C4H9Cl	08/06/07 ...	System
287	1-Azacyclopentane	123-7...	C4H9N	08/06/07 ...	System
287	Pyrrolidine	123-7...	C4H9N	08/06/07 ...	System

Search: tetrahyd

Selected Components:

Name	CAS	Last Modifi...
Carbon Dioxide	124-38-9	08/06/07 ...
Nitrogen	7727-3...	08/06/07 ...
Water	7732-1...	08/06/07 ...

FIGURE F1.1 Components tab to add component(s) to the simulation.



Global K Value Option: Ideal Vapor Pressure

Ethane/Ethylene, Propane/Propylene:
● Regular SRK/PR Bips
○ Special SRK/PR Bips

Vapor Phase Association:
○ No Vapor Phase Association
● Vapor Phase Association

Vapor Fugacity/Poynting Correction:
○ Correction
● No Correction

SRK/PR Alpha function:
● Standard SRK/PR
○ Boston-Mathias extrapolation

Global Phase Option:
● Vapor/Liquid/Solid
○ Vapor/Liquid/Liquid/Solid

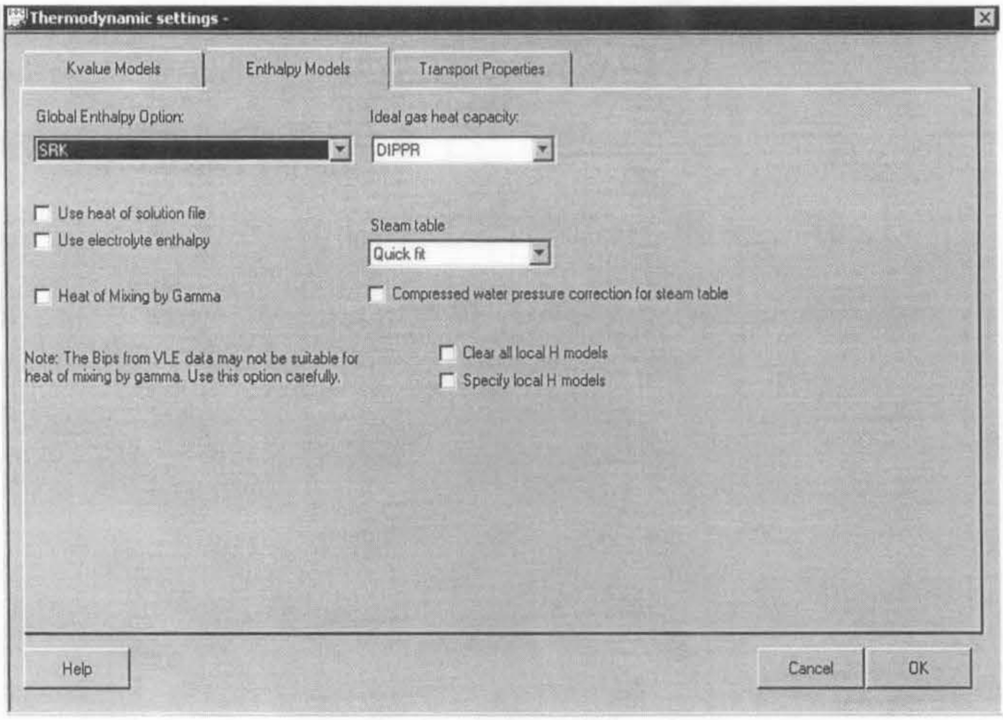
Water/Hydrocarbon Solubility:
○ Miscible
● Immiscible

Wilson model salt: <None>
No. of BIP sets: 1
Default BIP set: 1

☐ Clear all local K models/BIPs
☐ Clear all tray BIPs
☐ Set local K models/BIPs
☐ Set tray BIPs
☐ Set Henry components

Options in gray are not applicable for this k value option

FIGURE F1.2 Thermodynamic package (K Value) setting of the simulation



Global Enthalpy Option: SRK

Ideal gas heat capacity: DIPPR

☐ Use heat of solution file

☐ Use electrolyte enthalpy

Steam table: Quick fit

☐ Heat of Mixing by Gamma

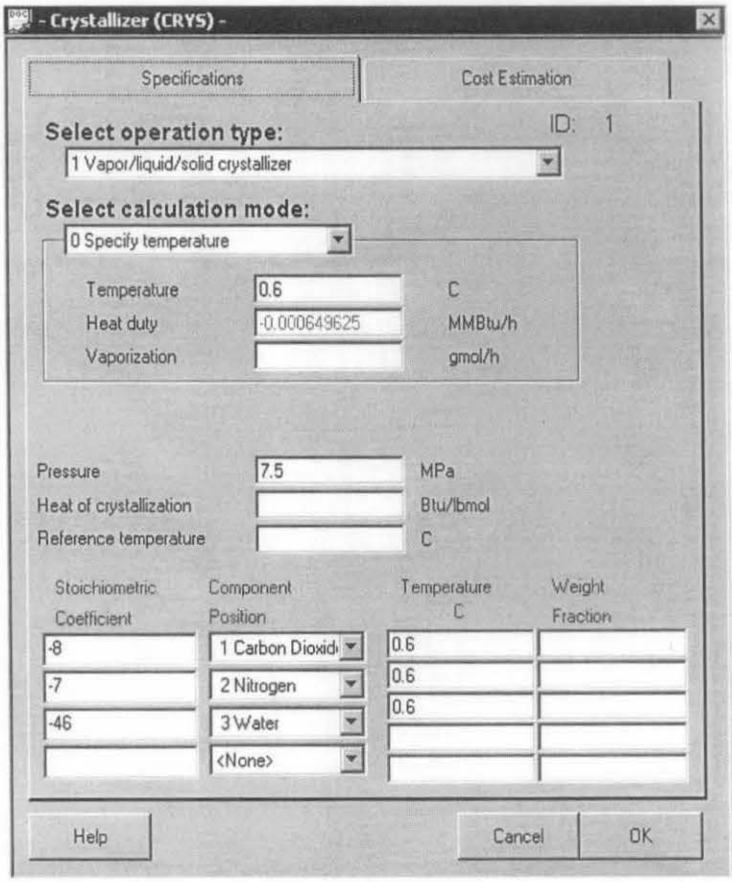
☐ Compressed water pressure correction for steam table

Note: The Bips from VLE data may not be suitable for heat of mixing by gamma. Use this option carefully.

☐ Clear all local H models

☐ Specify local H models

FIGURE F1.3 Thermodynamic package (Enthalpy) setting of the simulation



ID: 1

Select operation type: 1 Vapor/liquid/solid crystallizer

Select calculation mode: 0 Specify temperature

Temperature 0.6 C

Heat duty -0.000649625 MMBtu/h

Vaporization gmol/h

Pressure 7.5 MPa

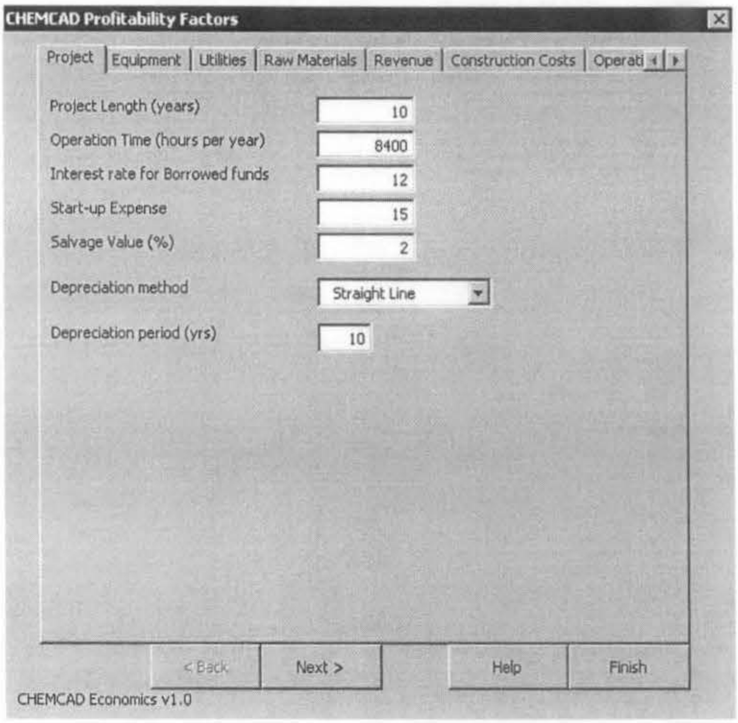
Heat of crystallization Btu/lbmol

Reference temperature C

Stoichiometric Coefficient	Component Position	Temperature C	Weight Fraction
-8	1 Carbon Dioxid	0.6	
-7	2 Nitrogen	0.6	
-46	3 Water	0.6	
	<None>		

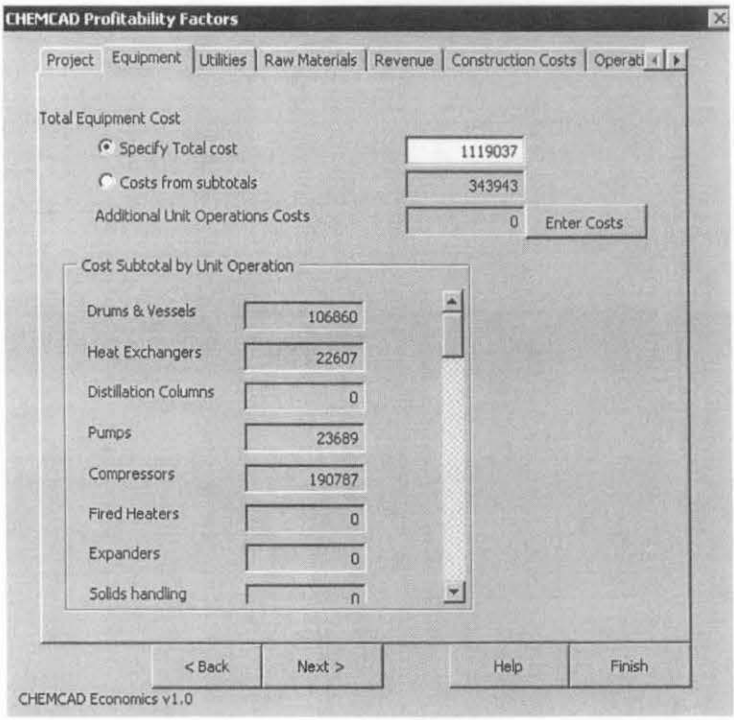
FIGURE F1.4 CRYS Module Input Specification tab

APPENDIX F2 : CHEMCAD Economics Input Procedural Screenshots



Project Length (years): 10
Operation Time (hours per year): 8400
Interest rate for Borrowed funds: 12
Start-up Expense: 15
Salvage Value (%): 2
Depreciation method: Straight Line
Depreciation period (yrs): 10

FIGURE F2.1 Salvage value is set to 2% while the rest is by default.

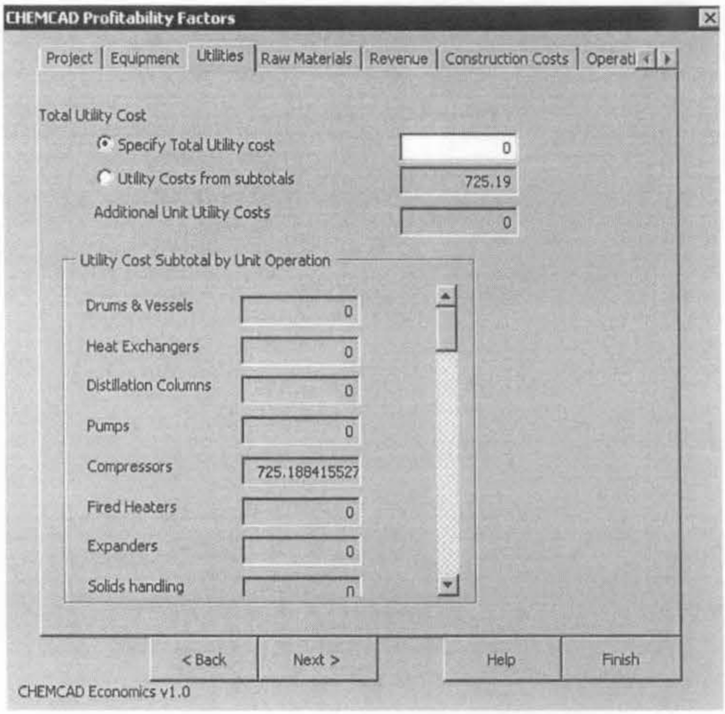


Total Equipment Cost
● Specify Total cost: 1119037
○ Costs from subtotals: 343943
Additional Unit Operations Costs: 0

Cost Subtotal by Unit Operation

Drums & Vessels	106860
Heat Exchangers	22607
Distillation Columns	0
Pumps	23689
Compressors	190787
Fired Heaters	0
Expanders	0
Solids handling	0

FIGURE F2.2 Cost of crystallizer is manually added with cost from subtotals generated by CHEMCAD



Total Utility Cost

● Specify Total Utility cost: 0

○ Utility Costs from subtotals: 725.19

Additional Unit Utility Costs: 0

Utility Cost Subtotal by Unit Operation

Drums & Vessels: 0

Heat Exchangers: 0

Distillation Columns: 0

Pumps: 0

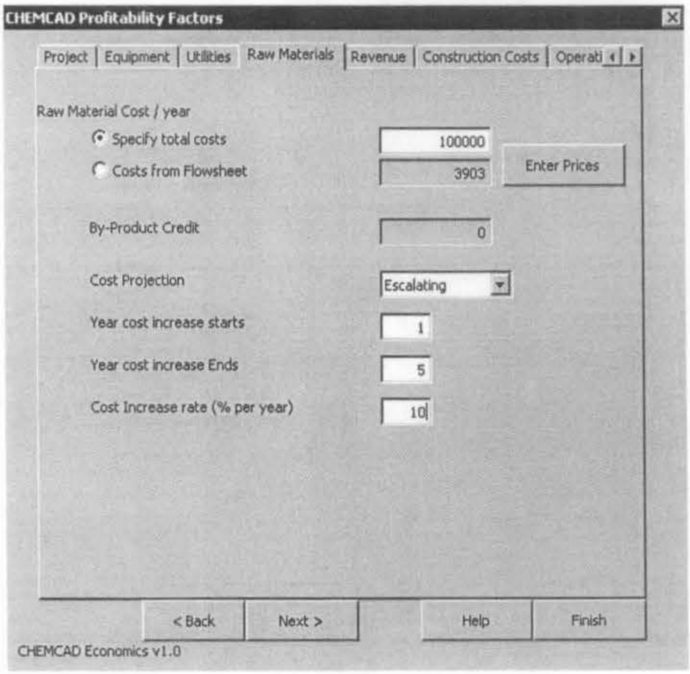
Compressors: 725.188415527

Fired Heaters: 0

Expanders: 0

Solids handling: 0

FIGURE F2.3 Total utility cost is set to zero and not been considered since it will greatly affect the cash flow resulting negative return (one of the simulation accuracy reduction factor)



Raw Material Cost / year

● Specify total costs: 100000

○ Costs from Flowsheet: 3903

By-Product Credit: 0

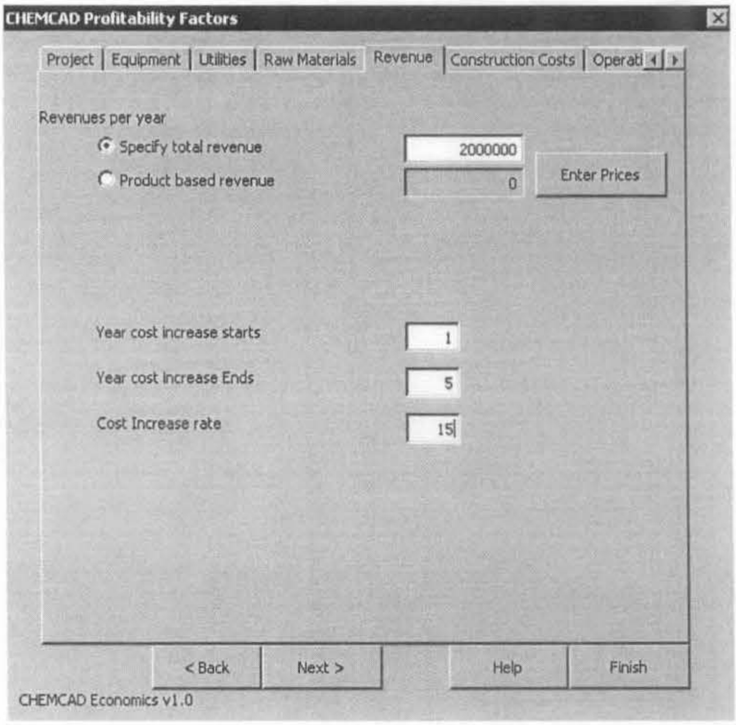
Cost Projection: Escalating

Year cost increase starts: 1

Year cost increase Ends: 5

Cost Increase rate (% per year): 10

FIGURE F2.4 Total costs of raw material are entered with escalating cost projection. Selecting the fixed cost projection will result the negative return in cash flow. The cost increase is set to 10% per year.



Revenues per year

● Specify total revenue 2000000

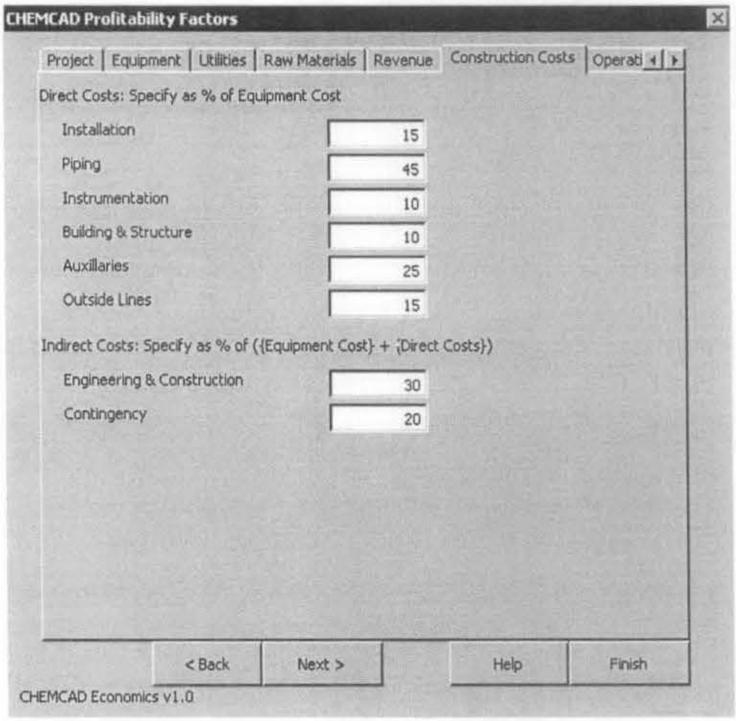
○ Product based revenue 0

Year cost increase starts 1

Year cost increase Ends 5

Cost Increase rate 15

FIGURE F2.5 The estimated revenue is entered. The cost increase rate is set to 15%.



Direct Costs: Specify as % of Equipment Cost

Installation 15

Piping 45

Instrumentation 10

Building & Structure 10

Auxillaries 25

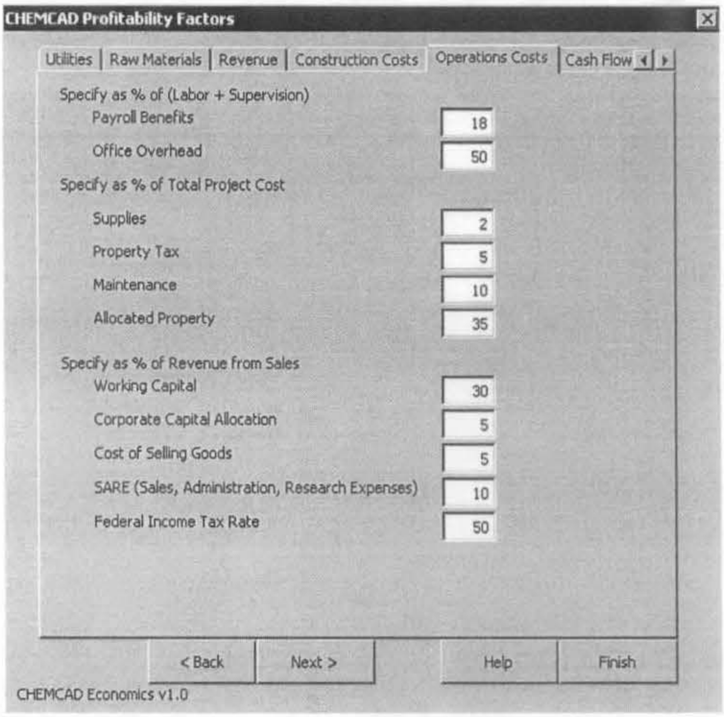
Outside Lines 15

Indirect Costs: Specify as % of ({Equipment Cost} + {Direct Costs})

Engineering & Construction 30

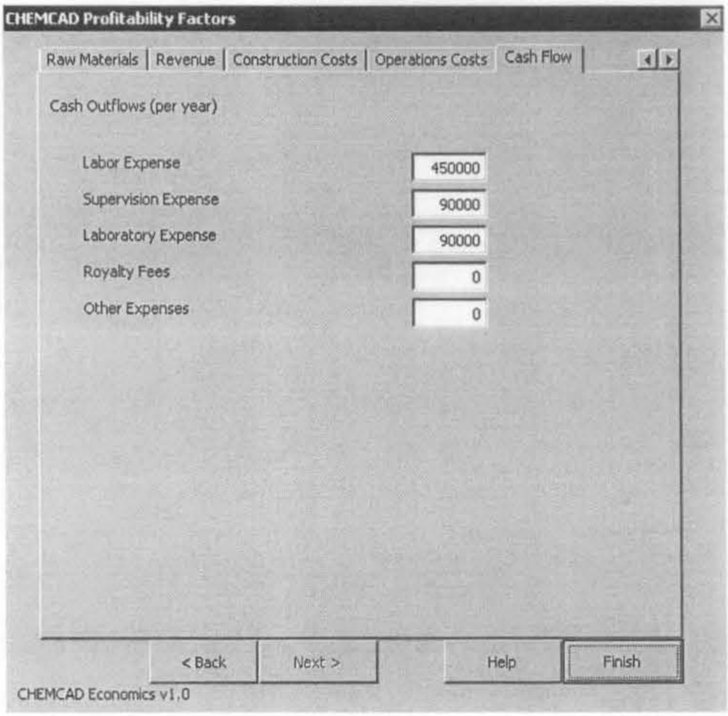
Contingency 20

FIGURE F2.6 All values within this tab are kept as in default.



Specify as % of (Labor + Supervision)
Payroll Benefits 18
Office Overhead 50
Specify as % of Total Project Cost
Supplies 2
Property Tax 5
Maintenance 10
Allocated Property 35
Specify as % of Revenue from Sales
Working Capital 30
Corporate Capital Allocation 5
Cost of Selling Goods 5
SARE (Sales, Administration, Research Expenses) 10
Federal Income Tax Rate 50

FIGURE F2.7 All values within this tab are kept as in default.



Cash Outflows (per year)
Labor Expense 450000
Supervision Expense 90000
Laboratory Expense 90000
Royalty Fees 0
Other Expenses 0

FIGURE F2.8 Labor expense is set to $450,000 and the supervision and laboratory expense are 20% each of the labor expense.