

M.SC. THESIS

Upgradation of High CO₂-Content Natural Gas by Low-
Temperature Distillation

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DEDICATION

This thesis is dedicated to

My Parents

(for their continuous moral, emotional, and financial support)

and

My Supervisor, Dr. Muhammad Faheem

(whose accomplishments are a source of motivation for me)

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First and foremost, I am beholden to Allah Almighty and the last Holy Prophet, Muhammad (PBUH), for providing the perfect and true teachings of life.

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ABSTRACT

High CO₂ content in natural gas reduces the overall calorific value and creates handling and transportation problems. In the low-temperature distillation process for CO₂ removal from natural gas, methane is recovered as the top product, whereas CO₂ and heavy hydrocarbons are recovered from the bottoms of a series of distillation columns. The principle challenges in the design and operation of this process include the high energy requirements to meet liquid natural gas (LNG) feed specifications, minimizing the total utility requirements, and avoiding CO₂ solidification.

In this study, pinch analysis was performed for a 6-column, low-temperature distillation process to identify opportunities for heat integration in the process and to reduce energy consumption and utility requirements while maintaining methane recovery and purity. A comparison indicated that the heat-integrated process offers 19.8% reduction in total energy requirements, 16.9% reduction in greenhouse gas emissions due to utilities, 24.4% reduction in total heat-transfer area, and 9.9% cost savings relative to the reference process.

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CHAPTER 1

INTRODUCTION

The ever-increasing global energy demand has led to a strong dependence on fossil fuels including coal, petroleum, and natural gas.¹ The untreated natural gas contains many impurities including water, hydrogen sulfide, carbon dioxide, and higher ($C_3 - C_6$) hydrocarbons. Non-hydrocarbon impurities significantly reduce the calorific value of natural gas, increase the gas volume and transportation cost, and cause pipeline corrosion.² Up to 40% of known natural gas reserves are sour and many of them have CO_2 content above 10%.³⁻⁴ Exploitation of these low-quality natural gas reserves presents unique technological and economic challenges.

Current technologies for CO_2 removal from natural gas include physical and chemical absorption,⁵ pressure-swing adsorption,⁶ membrane separation,⁷ and low-temperature distillation (LTD).⁸⁻⁹ The selection of sweetening process depends on the CO_2 content of natural gas. For example, absorption and adsorption processes are economical for purification of low CO_2 -content feeds. However, for sweetening of high CO_2 -content natural gas, these processes require large quantities of solvent or adsorbent, and consequently large amounts of energy for their regeneration.¹⁰ Similarly, the trade-off between the permeability (that is, production rate) and the selectivity (that is, product purity) of membranes limits their practical applications, especially for the removal of large quantities of CO_2 .¹¹ On the other hand, the LTD process becomes economical for upgradation of high CO_2 -content natural gas.¹² Its advantages include recovery of high-purity liquid CO_2 at moderate pressures, precluding the corrosive amine-based solvents, and reduced process footprint and hydrocarbon inventories.¹³ The principle challenges in the design and operation of LTD processes for natural gas

purification include high energy requirements to meet liquid natural gas (LNG) feed specifications, minimizing the total utility requirements, and avoiding the solidification of CO₂ and the formation of CO₂/CH₄ and CO₂/C₂H₆ azeotropes.

Low-temperature CO₂/CH₄ separation processes operate below the triple point temperature of CO₂ (-56.5 °C),¹⁴ making CO₂ solidification inside the system a major design and operational concern. Such processes must either be able to handle the formation of a solid phase inside process equipment or completely avoid CO₂ solidification. Examples of the former group include the CFZ™ process,¹⁵ and the Cryocell® process.¹⁶ Examples of the latter group include the Sprex® process,¹⁷ and the Ryan–Holmes process.¹⁸ In the Sprex® process, bulk removal of CO₂ and H₂S takes place in a high-pressure, low-temperature distillation column while the remaining CO₂ is removed using a traditional amine-based solvent. On the other hand, the Ryan–Holmes process is essentially an extractive distillation process where a heavy hydrocarbon entrainer is used to cause CO₂ freezing point depression, allowing the process to be operated well below the normal CO₂ solidification temperature.¹⁹ When excessive solvent loss and reducing energy requirements are major concerns, butane and pentane are more efficient solvents than propane.²⁰ Another advantage of introducing a heavy hydrocarbon entrainer is that the formation of CO₂/CH₄ and CO₂/C₂H₆ azeotropes is avoided.²¹

Despite its significant advantages, the LTD process is highly energy intensive. In a typical amine-based sweetening process, steam consumption for solvent regeneration accounts for over 80% of the total energy demand of the process.¹² On the other hand, the LTD process requires electrical energy to drive the refrigeration cycle. Since electrical energy is considerably more expensive than thermal energy, heat integration of cold streams is especially critical for improving the overall energy efficiency of the LTD process.

Pinch analysis is a pragmatic and well-developed methodology for optimal design and retrofit of energy systems and heat exchanger networks.²²⁻²³ It offers a systematic approach to identify the maximum energy recovery or the minimum energy requirement (MER) in a counter-current heat exchange setup. Since the MER limit can sometimes lead to impractically large heat transfer area requirements, the objective of pinch analysis, for all practical purposes, is to minimize the total annualized cost (TAC) of the process.²⁴

In this study, pinch analysis is performed for a 6-column LTD process to identify opportunities for heat integration in the process and to reduce energy consumption and utility requirements while maintaining methane recovery and purity. The heat exchanger network (HEN) is analyzed and reconfigured using a combined composite curve diagram to minimize the TAC of the process. The heat-integrated process is then compared with the reference process in terms of total energy requirements and greenhouse gas emissions.

CHAPTER 2

PROCESS DESCRIPTION

Figure 2.1 shows an Aspen Plus® representation of the LTD process flowsheet. The overall process can be divided into four sections, namely CO₂ bulk removal section, heavy hydrocarbons' separation section, natural gas treatment section, and LNG feed treatment section. Preconditioning, precooling and refrigeration systems are excluded from this study.

After preconditioning and precooling, 24,800 kmol/h natural gas feed (Table 2.1) enters the CO₂ bulk removal section at -10 °C and 7 MPa . It is fed to a distillation column (COL101) for the bulk removal of CO₂ after depressurization to 4 MPa (VLV101). In this column, the CO₂ content is reduced from 50.6% to 10.6% whereas the methane purity is increased from 39.7% to 86.3%. The methane-rich top stream (S201) is sent to the natural gas treatment section. The bottoms stream (S102) contains most of the CO₂ and heavy hydrocarbons and is sent to the heavy hydrocarbons' separation section.

The heavy hydrocarbons' separation section contains a sequence of three distillation columns for the recovery of CO₂, propane, and butanes, respectively. CO₂-rich bottoms stream from the CO₂ bulk removal section (S102) is fed to the first distillation column (COL102) after depressurization to 3 MPa (VLV102). The top product of this column is 94.3% pure CO₂ which can be used for enhanced oil recovery. The bottoms product is rich in hydrocarbons and is fed to the second distillation column (COL103) after depressurization to 1.6 MPa (VLV103). This column recovers essentially all propane and leftover CO₂ in the top product. The bottoms product is further depressurized to 1 MPa (VLV104) and fed to the butane recovery column (COL104). A mixture of i-butane and n-butane with traces of heavy hydrocarbons is recovered

Table 2.1. Chemical composition of the natural gas feed²⁵

Component	Mole fraction
Methane	0.3974
Ethane	0.0350
Propane	0.0240
i-Butane	0.0090
n-Butane	0.0090
i-Pentane	0.0060
n-Pentane	0.0060
n-Hexane	0.0020
Carbon dioxide	0.5065
Nitrogen	0.0050

Table 2.2. Distillation column data from the converged process simulation model

	COL101	COL102	COL103	COL104	COL201	COL301
Theoretical stages ¹	19	62	62	77	14	62
Feed stage from top	4	34	20	20	1 / 4	11 / 62
Pressure (MPa)	4.0	3.0	1.6	1.0	4.0	4.0
Reflux ratio	1.70	1.52	2.57	2.65	1.27	1.53
Condenser temp. (°C)	-68.1	-6.5	49.2	74.1	-85.2	-87.9
Reboiler temp. (°C)	7.8	108.2	117.4	124.5	3.4	3.0
Condenser duty (MW)	-48.2	-54.7	-6.4	-4.9	-16.8	-10.3
Reboiler duty (MW)	40.4	87.8	7.5	6.0	15.4	9.7

¹ Including condenser and reboiler

hydrocarbons (S205) are combined with the recycle solvent (S111) coming from the heavy hydrocarbons' separation section.

The LNG feed treatment section uses a similar recycle loop. The methane-rich top stream from the natural gas treatment section (S301) goes to the extractive distillation column

Table 2.3. Process stream conditions and flow rates from the converged process simulation model. Flow rates have been rounded to the nearest integer.

Stream ID	T (°C)	P (MPa)	F (kmol/h)	Stream ID	T (°C)	P (MPa)	F (kmol/h)
FEED	-10.0	7.0	24,800	S204	-43.5	0.1	3,550
S101	-26.9	4.0	24,800	PRG201	-43.5	0.1	1,765
S102	7.8	4.0	13,380	S205	-43.5	0.1	1,785
S103	-3.4	3.0	13,380	S206	-43.1	1.0	1,785
CO2	-6.5	3.0	11,997	S207	-39.7	1.0	1,817
S104	108.2	3.0	1,384	S208	-38.4	4.0	1817
S105	82.6	1.6	1,384	SLK201	-38.4	4.0	2
PROPANE	49.2	1.6	645	S209	-38.4	4.0	1,815
S106	117.4	1.6	739	S301	-85.2	4.0	9,684
S107	95.4	1.0	739	S302	-85.2	4.0	9,684
BUTANE	74.1	1.0	390	CH4	-87.9	4.0	9,372
S108	124.5	1.0	349	S303	3.0	4.0	1,145
PENTANE	124.5	1.0	287	S304	-14.7	0.1	1,145
S109	124.5	1.0	63	PRG301	-14.7	0.1	343
S110	124.5	1.0	63	S305	-14.7	0.1	802
S111	124.5	1.0	31	S306	-14.2	1.0	802
S112	124.5	1.0	31	S307	-8.2	1.0	833
S201	-68.1	4.0	11,420	S308	-6.5	4.0	833
S202	-68.1	4.0	11,420	SLK301	-6.5	4.0	1
S203	3.4	4.0	3,550	S309	-6.5	4.0	833

(COL301) where its methane purity is increased to 98.7% while CO₂ content is reduced to 50 ppm to meet LNG feed specifications.²⁶

A steady state simulation model for the LTD process has been developed and validated against published data²⁵ using Aspen Plus® V10 with Peng–Robinson equation of state. Data for all distillation columns are listed in Table 2.2. Temperatures, pressures, and flow rates of

Table 2.4. Distillation column product compositions from the converged process simulation model

	COL101		COL102		COL103	
	Top	Bottom	Top	Bottom	Top	Bottom
Methane	0.8630	3 ppm	4 ppm			
Ethane	0.0199	0.0480	0.0535	1 ppm	1 ppm	
Propane	0.0002	0.0444	0.0038	0.3960	0.8500	
i-Butane	3 ppm	0.0167		0.1614	0.0797	0.2327
n-Butane	1 ppm	0.0167		0.1614	0.0059	0.2971
i-Pentane		0.0111		0.1076		0.2015
n-Pentane		0.0111		0.1076		0.2015
n-Hexane		0.0037		0.0359		0.0672
Carbon dioxide	0.1060	0.8483	0.9427	0.0300	0.0644	
Nitrogen	0.0109					

	COL104		COL201		COL301	
	Top	Bottom	Top	Bottom	Top	Bottom
Methane			0.9774	0.1110	0.9867	0.1931
Ethane			0.0006	0.0723		0.0063
Propane	1 ppm		6 ppm	0.0012		0.0001
i-Butane	0.4414			50 ppm		4 ppm
n-Butane	0.5582	0.0060	1 ppm	0.0004		0.0008
i-Pentane	0.0004	0.4257	0.0001	0.0944		0.1604
n-Pentane	39 ppm	0.4262	0.0001	0.1524		0.2395
n-Hexane		0.1421	30 ppm	0.2357		0.3193
Carbon dioxide			0.0090	0.3324	50 ppm	0.0803
Nitrogen			0.0128		0.0132	0.0002

all streams are listed in Table 2.3. Table 2.4 provides the top and bottom product compositions for all distillation columns.

CHAPTER 3

METHODOLOGY

Pinch analysis of the LTD process has been performed using Aspen Energy Analyzer® V10. In the first step, thermal data for all heat exchangers is extracted from the steady state reference model. This includes information about inlet and outlet temperatures, flow rates, and heat capacities of the process and utility streams involved (Table 3.1). Because of the wide range of temperatures involved, the process requires 3 cold utilities (that is, air, refrigerant-1, and refrigerant-4) and 2 hot utilities (that is, low- and medium-pressure steam). This information is then used to construct a combined composite curve diagram (Figure 3.1). Because the pinch temperature is below ambient, a minimum temperature difference of 5 °C is selected.²⁷

Table 3.1. Operating temperatures (°C) of all heat exchangers in the reference model

Unit Operation	Utility	Process Stream		Utility	
		Inlet	Outlet	Inlet	Outlet
Condenser@COL101	Refrigerant-4	-40.8	-68.1	-103.0	-102.0
Condenser@COL102	Refrigerant-1	-6.2	-6.5	-25.0	-24.0
Condenser@COL103	Air	54.4	49.2	30.0	35.0
Condenser@COL104	Air	74.6	74.1	30.0	35.0
Condenser@COL201	Refrigerant-4	-82.2	-85.2	-103.0	-102.0
Condenser@COL301	Refrigerant-4	-87.7	-87.9	-103.0	-102.0
Reboiler@COL101	LP steam	6.1	7.8	125.0	124.0
Reboiler@COL102	LP steam	78.0	108.2	125.0	124.0
Reboiler@COL103	MP steam	111.3	117.4	175.0	174.0
Reboiler@COL104	MP steam	122.2	124.5	175.0	174.0
Reboiler@COL201	LP steam	-42.8	3.4	125.0	124.0
Reboiler@COL301	LP steam	-78.4	3.0	125.0	124.0

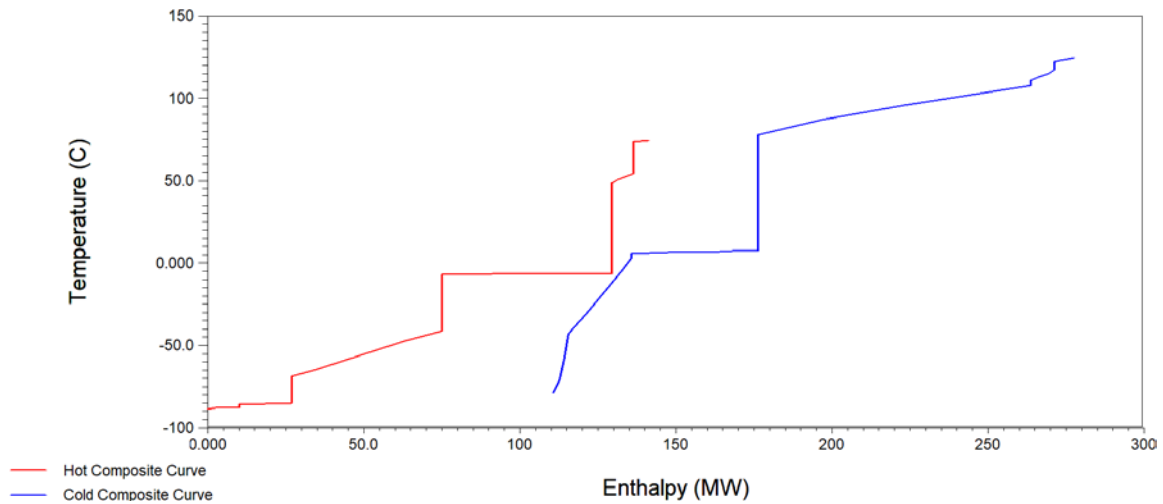


Figure 3.1. Combined composite curves for the low-temperature distillation process with $\Delta T_{\min} = 5\text{ }^{\circ}\text{C}$

Figure 3.1 provides a counter-current picture of the total heat transfer in the process and can be used to identify energy targets of the process. Since heat recovery is possible only in the zone where the hot and cold composite curves overlap, this region represents the potential for maximum energy recovery through process-to-process heat transfer. The hot composite curve extending below the lowest overlap temperature represents the minimum cold utility requirements for the process. Similarly, the cold composite curve extending above the highest overlap temperature represents the minimum hot utility requirements for the process. A summary of potential energy savings and minimum cold and hot utility requirements is presented in Table 3.2.

In the next step, several near-optimal HEN designs are generated using the built-in optimization algorithm of Aspen Energy Analyzer®. The ultimate objective of the optimization is to minimize the TAC of the process while energy targets of the process are treated as constraints. In the last step, the alternative HEN designs are compared and the one with minimum TAC is selected.

Table 3.2. Potential benefits of heat integration in the low-temperature distillation process

	Reference Model	Target	Reduction Potential	Savings (%)
Cold utilities (MW)	141.3	110.7	30.6	21.6
Hot utilities (MW)	166.8	136.3	30.6	18.3
Total utilities (MW)	308.1	247.0	61.1	19.8
Cold utilities (million \$/year)	25.0	22.4	2.6	10.4
Hot utilities (million \$/year)	10.1	8.2	1.9	18.8
Total utilities (million \$/year)	35.1	30.6	4.5	12.8
Greenhouse gases (ton/h)	65.6	54.5	11.10	16.9

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Pinch Analysis

The initial heat exchanger network for the LTD process has all its cooling and heating requirements satisfied by utility streams. Figure 4.1 shows a grid diagram of this heat exchanger network. In the middle of the diagram, hot and cold process streams are shown in red and blue colors, respectively. The cold and hot utilities follow the same color coding and are shown on the top and the bottom of the diagram, respectively. Heat exchangers in blue and red marking require cold and hot utilities, respectively. Operating temperatures and duties of all heat exchangers are also shown on the HEN diagram.

Aspen Energy Analyzer® has been used to create design alternatives for the heat exchanger network following the steps outlined in Chapter 3. Such process-to-process heat exchangers are shown in grey color (Figure 4.2). The alternative HEN designs are compared and the one with minimum TAC is selected. This optimal design (Figure 4.2) requires addition of 4 new heat exchangers to the process, elimination of 2 existing heat exchangers, and modification (that is, reduction in heat transfer area) of another 4 existing heat exchangers.

Table 4.1 provides an area-based comparison of the existing and modified heat exchanger networks. In summary, heat exchangers eliminated from the existing network represent a total heat transfer area of 4,385 m². Another 1,398 m² heat transfer area is reduced through modification of existing heat exchangers. Finally, 1,094 m² new heat transfer area is added in 4 new heat exchangers with an estimated capital cost of 0.34 million dollars. As a result of these modifications, the total heat transfer area requirement is reduced by 24.4%.

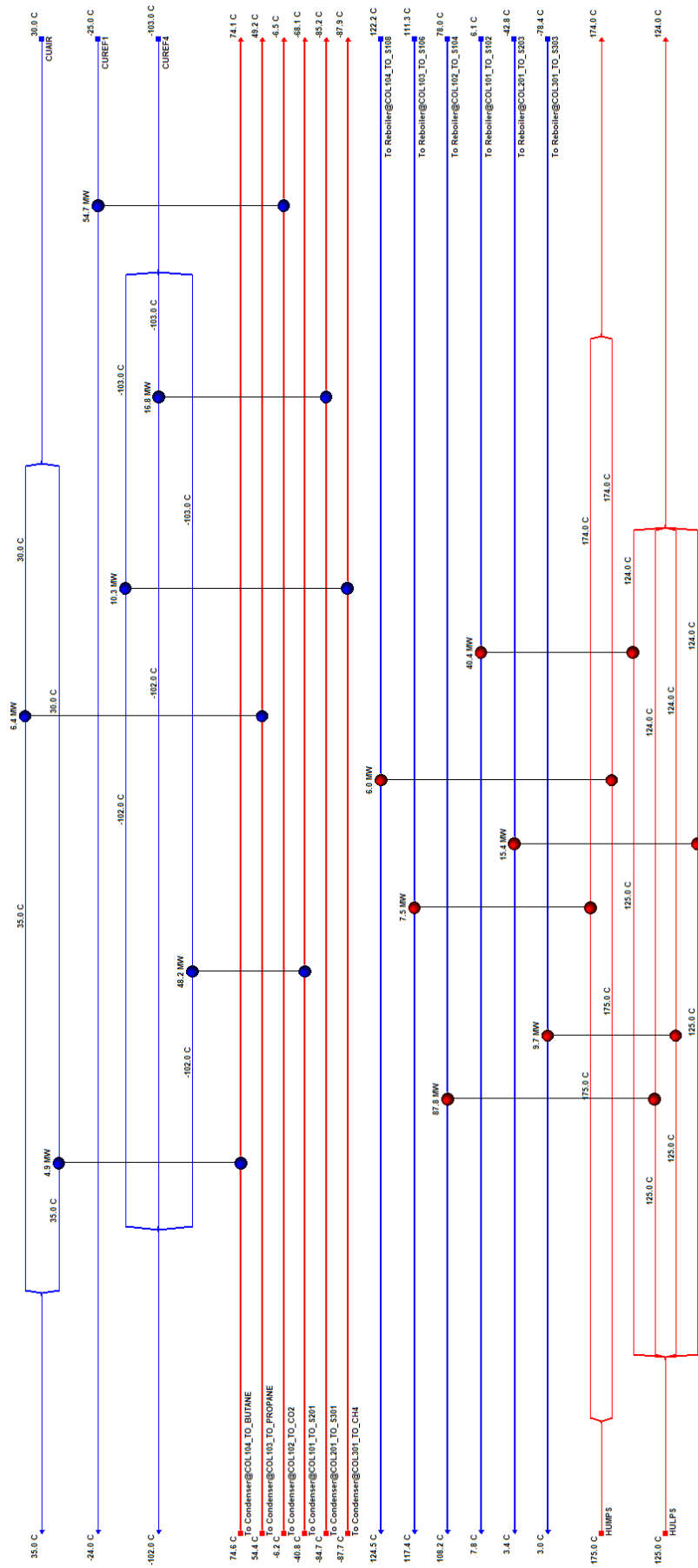


Figure 4.1. Heat exchanger network (HEN) diagram for the reference model

Table 4.1. Comparison of heat exchanger areas (m^2) for the reference and updated models

Heat Exchanger	Reference Model	Updated Model
Condenser@COL101	1,721	1,721
Condenser@COL102	3,260	1,971
Condenser@COL103	3,294	---
Condenser@COL104	1,091	---
Condenser@COL201	5,522	5,522
Condenser@COL301	785	785
Reboiler@COL101	127	98
Reboiler@COL102	3,063	3,077
Reboiler@COL103	85	85
Reboiler@COL104	63	63
Reboiler@COL201	69	26
Reboiler@COL301	45	9
E-100	---	617
E-101	---	309
E-102	---	132
E-103	---	36
Total heat-transfer area	19,124	14,450
Reduction (%)	---	24.4

As shown in Table 4.2, the requirement for air (cold utility) can be fully reduced to zero and the corresponding heat exchangers eliminated from the process. In addition, the utility requirements for refrigerant-1 (cold utility) and low-pressure steam (hot utility) can be reduced by 35.2% and 19.9%, respectively. However, refrigerant-4 (cold utility) and medium-pressure steam (hot utility) are required beyond the overlapping zone on the combined composite curve diagram (Figure 3.1) and are therefore unaffected by this heat integration. The total cold and hot utility requirements are reduced by 21.6% and 18.3%, respectively. The overall reduction in utility requirements is approximately 61 MW, representing 19.8% reduction relative to the

Table 4.2. Comparison of utility loads (MW) for the reference and updated models

Utility	Reference Model	Updated Model	Savings (%)
Air	11.3	0.0	100.0
Refrigerant-1	54.7	35.4	35.2
Refrigerant-4	75.3	75.3	0.0
LP steam	153.4	122.8	19.9
MP steam	13.4	13.4	0.0
Cold utilities	141.3	110.7	21.6
Hot utilities	166.8	136.3	18.3
Total utilities	308.1	247.0	19.8

reference model. This corresponds to an estimated saving of over 4 million dollars per year in direct operating costs.

Finally, we have evaluated the impact of heat integration on environmental footprint of the process. All utilities can ultimately be expressed in terms of greenhouse gas emissions associated with their generation, operation, and reuse. The greenhouse gas emissions corresponding to utility requirements for the reference model are estimated to be 65.6 ton/h. The reduction in utility requirements in the heat-integrated design reduces this value to 54.5 ton/h, representing a decrease of 16.9% (Table 3.2).

4.2. CO₂ Solidification

CO₂ solidification is a potential problem for the LTD process. It can choke the process equipment resulting in decreased efficiency and potentially unsafe operation. The possibility of CO₂ solidification is high in the CO₂ bulk removal section (COL101), natural gas treatment section (COL201), and LNG feed treatment section (COL301) because of low operating temperatures. The operating temperatures in the heavy hydrocarbons' separation section are considerably higher and do not allow CO₂ freeze-out.

TFREEZ utility of Aspen Plus® was used to investigate the possibility of CO₂ solidification with respect to its liquid-phase mole fraction for the vulnerable distillation columns. Figure 4.3 shows the column profiles of difference between stage temperatures and the corresponding CO₂ solidification temperatures. For the CO₂ bulk removal column (COL101), the operating margin is 23.9 °C for the top tray (stage 2) and gradually increases to 65.7 °C for the last tray (stage 18). However, the condenser of this column (stage 1) is operating only 1.2 °C above the estimated CO₂ solidification temperature. For the distillation column COL201 in the natural gas treatment section, the lowest operating margins are between 9.2 °C and 9.7 °C in the middle section of the column. Because of the very low concentration of CO₂, the operating margin for the distillation column COL301 in the LNG feed treatment section is above 50 °C for most of the length of the column. The lowest operating margin (12.3 °C) is observed on the last tray (stage 61) immediately above the reboiler.

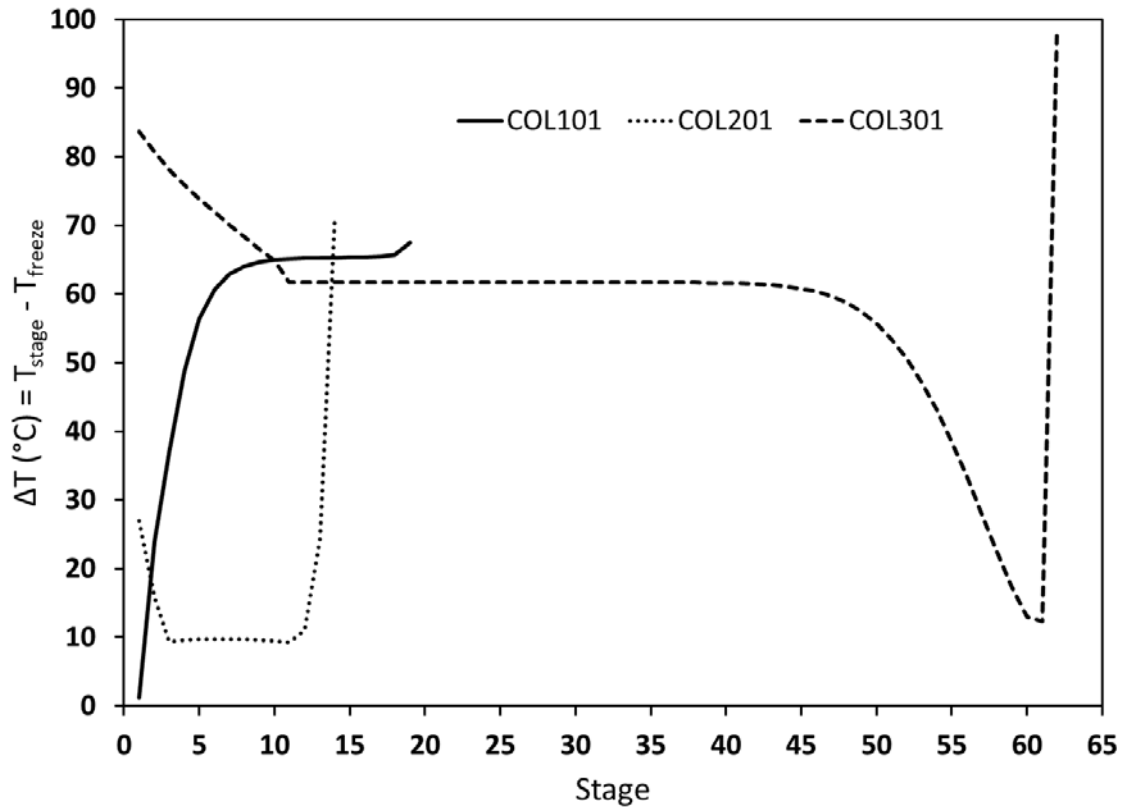


Figure 4.3. CO₂ solidification in distillation columns

Because of the significant operating margins, we conclude that under the proposed operating conditions, CO₂ solidification is not a concern on any tray in any distillation column. The only point in the whole LTD process where the system operates very close to the estimated CO₂ solidification temperature is the condenser of the main distillation column (COL101). As shown in Table 3.1, the process stream enters this condenser at -40.8°C and leaves at -68.1°C . The estimated CO₂ solidification temperature at this composition is -69.3°C . Because of the very low temperatures involved, even a small operating margin can provide considerable operational flexibility. Moreover, handling CO₂ solidification in a heat exchanger is considerably less complicated, both technically and economically, than on a distillation column tray.

CHAPTER 5

CONCLUSIONS

The low-temperature distillation process to recover methane from low-quality raw natural gas is an energy intensive process and requires large cold and hot utility loads. The overall energy efficiency of this process can be improved through an improved heat exchanger network design, where process-to-process heat exchange is implemented at a higher priority than process-to-utility heat exchange. Pinch analysis can be used to analyze the existing heat exchanger network to identify opportunities for heat integration and energy targets of the process. The information can then be used for optimal design and retrofit of energy systems and heat exchanger networks. For the 6-column, low-temperature distillation process described here, pinch analysis shows that by addition of 4 new process-to-process heat exchangers at an estimated capital investment of 0.34 million dollars, the overall utility requirements can be reduced by 19.8% representing a reduction of over 4 million dollars in direct operational cost per year.

The safety of the low-temperature distillation process has also been explored in terms of potential of CO₂ solidification in distillation columns. Since the operating margin at all distillation column trays is at least 9 °C, we conclude that CO₂ solidification is not a significant design and operational concern.

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