DESIGN AND OPTIMIZATION OF CRYOGENIC PROCESS

.

.

Juthathip Thasai

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Master of Science The Petroleum and Petrochemical College, Chulalongkorn University in Academic Partnership with The University of Michigan, The University of Oklahoma, Case Western Reserve University and Institut Français du Pétrole

2015

Thesis Title:	Design and Optimization of Cryogenic Process
By:	Juthathip Thasai
Program:	Petrochemical Technology
Thesis Advisor:	Asst. Prof. Kitipat Siemanond

Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

..... College Dean

(Asst. Prof. Pomthong Malakul)

Thesis Committee:

÷

Kitipat Siemanad

(Asst. Prof. Kitipat Siemanond)

inthe

(Assoc. Prof. Thirasak Rirksombon)

RungRoj Q2.

(Dr. Rungroj Chuvaree)

ABSTRACT

5671007063: Petrochemical Technology Program
Juthathip Thasai: Design and Optimization of Cryogenic Process.
Thesis Advisors: Asst. Prof. Kitipat Siemanond 115 pp.
Keywords: Cryogenic process/ Refrigeration system/ Exergy/ Pinch/
Mathematical Programming

Refrigeration system is widely used in the industry, especially in cryogenic process. The main problem of refrigeration system is high energy consumption from shaft work resulting in high operation cost. To minimize the amount of shaft work, it is accomplished by a combination of pinch and exergy analysis. The strength of pinch analysis is graphical representation by using simple diagrams of composite curves and grand composite curve for process modifications. However, limitation of pinch analysis is that it only deals with thermal system, not including power or shaft work. Exergy analysis is a tool to utilize power or shaft work and identify thermodynamic imperfection of process. Both strengths are combined to help improve process efficiency. In this study, this methodology is applied for case study of LNG to improve processes such a reducing shaft work and increasing the exergy efficiency. Furthermore, the cascade refrigeration system is designed by mathematical programming.

σ

บทคัดย่อ

จุฑาทิพย์ ท่าทราย : การออกแบบและหาค่าสภาวะที่เหมาะสมที่สุดของกระบวนการที่ ดำเนินการภายใต้อุณหภูมิที่ต่ำ (Design and Optimization of Cryogenic Process) อ. ที่ปรึกษา : ผศ. คร. กิติพัฒน์ สีมานนท์ 115 หน้า

ในปัจจุบันระบบทำความเย็นใช้กันอย่างแพร่หลายในโรงงานอุตสาหกรรม โดยเฉพาะ ้อย่างยิ่งกระบวนการที่ดำเนินการภายใต้อุณหภูมิที่ต่ำ ปัญหาหลักที่พบในระบบทำความเย็นคือ ค่า ้ดำเนินการของกระบวนการที่ดำเนินการภายใต้อุณหภูมิที่ต่ำนั้นจะขึ้นกับงานที่เครื่องอัดอากาศ ต้องการ ดังนั้นการถดงานที่เครื่องอัดอากาศต้องการเป็นผลช่วยถดด่าดำเนินการได้ งานวิงัยนี้ได้ เสนอวิธีการที่ใช้การออกแบบกระบวนการเพื่อลุคความค้องการของงานโคยใช้ระบบอนรักษ์ พลังงาน (Pinch Analysis) และ เอ็กเซอร์จี (Exergy) ในการวิเคราะห์ ซึ่งข้อคีของการใช้ Pinch Analysis คือการแสดงผลที่เข้าใจได้ง่ายโดยการใช้เส้นโค้งคอมโพสิท (Composite Curve)ในการ ปรับปรุงกระบวนการ อย่างไรก็ตาม Pinch Analysis มีข้อจำกัดเนื่องจาก Pinch Analysis จะ พิจารณาแค่ปริมาณความร้อน ซึ่งในกระบวนการคำเนินการภายใต้อุณหภูมิที่ต่ำนั้นงานก็เป็นตัว แปรสำคัญเช่นกัน คังนั้น Exergy Analysis จึงถูกใช้เป็นเครื่องมือในการออกแบบ เนื่องจาก เอ็ก เซอร์จีมีความสัมพันธ์กับงาน การนำจุดเด่นของทั้ง Pinch Analysis และ Exergy Analysis จึงช่วย กระบวนการมีประสิทธิภาพที่ดีขึ้นทั้งยังลดความต้องการของพลังงานและงาน ดังนั้นงานวิจัยนี้ได้ ใช้หลักการคังกล่าวมาประยุกต์ใช้ในการออกแบบกับกรณีศึกษาของการเปลี่ยนสถานะกำซ ธรรมชาติให้กลายเป็นก๊าซธรรมชาติเหลว นอกจากนั้นได้นำโปรแกรมทางคณิตศาสตร์ (General Algebraic Modelling System; GAMS) มาใช้ในการออกแบบโครงสร้างเครือข่ายเครื่องแลกเปลี่ยน ความร้อนอย่างมีประสิทธิภาพและลดความต้องการของงาน

0

ACKNOWLEDGEMENTS

This thesis could not have been completed without the participation of the following individuals and organizations. This thesis work was partially supported by the Ratchadapisek Sompoch Endowmant Fund (2013), Chulalongkorn University (CU-56-900-FC) and Thailand Research Fund (IRG5780012).

First of all, the author, Ms. Juthathip Thasai would like to express the gratitude to the Petroleum and Petrochemical College, Chulalongkorn University, The center of Excellence on Petrochemical and Materials Technology, PETROMAT and Government Budget Fund for funding support.

I would like to express the greatest pleasure and the deepest appreciation to Asst. Prof. Kitipat Siemanond, my supervisor, for providing invaluable knowledge. Throughout my research work in the last year of Master degree, he has been a great mentor and a marvellous scholar of great enthusiasm, insights, constant encouragement, and considerations. The suggestions and comments on methodology of design and optimization of cryogenic process are very valuable to this thesis.

My gratitude also extends to Assoc. Prof. Thirasak Rirksomboon, and Dr. Rungroj Chuvaree for serving on my examination committee. Their suggestions and comments are very beneficial for me and this thesis.

My two-year study at the Petroleum and Petrochemical College, Chulalongkorn University, is very meaningful to me. I appreciate and thank all my friends, my colleagues for constantly encouraging and supporting throughout my entire studies.

Most of all, I would like to express my sincere and deepest gratitude to my parents for their tender love, understanding, generous encouragement and financial and moral support to me all the times.

o

TABLE OF CONTENTS

		PAGE
Title Page		i
Abstract (in English)		iii
Abstract (in Thai)		iv
Acknowledgements		v
Table of Contents		vi
List of Tables		ix
List of Figures		x
List of Abbreviations		xiii
List of Symbols		XV

1

-

CHAPTER

ø

I INTRODUCTION

Π	LITERATURE REVIEW	3
	2.1 Refrigeration System	4
	2.2 The Subambient Processes	7
	2.2.1 Process of Natural Gas Liquefaction	9
	2.2.1.1 Single Mixed Refrigerant Process	9
	2.2.1.2 Propane-Precooled Mixed Refrigerant Process	10
	2.2.1.3 Multistage Cascade Refrigeration Cycle Proces	ssll
	2.2.1.4 Single State Mixed Refrigerant Process	12
	2.2.1.5 New LNG Scheme	12
	2.2.1.6 GCL Concept	13
	2.2.1.7 cLNG	14
	2.3 Fundamental Principles	14
	2.3.1 Pinch Technology	15
	2.3.2 Exergy Analysis	16
	2.3.2.1 Exergy Analysis of Heat Recovery Systems	19
	2.3.2.1.1 Exergy of Process Streams	19

CHAPTER

PAGE

		1 A 1	
		2.3.2.1.2 Exergy of Heat	20
۰		2.3.2.2 The Application of Exergy Analysis	21
		2.4 Methods and Tools for Cryogenic Process	24
		2.4.1 Shaft Work Targeting	25
		2.4.2 Heuristic Rules to Support Subambient Process Design	29
		2.4.3 The ExPAnD Methodology	30
		2.4.4 New Graphical Representation of Exergy	30
		2.4.4.1 Exergetic Temperature	32
		2.5 Mathematical Programming	34
	Ш	METHODOLOGY	37
		3.1 Materials and Equipment	37
		3.1.1 Equipment	37
		3.1.2 Software	37
		3.2 Research Procedures	37
		3.2.1 Shaft Work Targeting	37
		3.2.2 The ExPAnD Method with Novel Exergy Diagram	38
		3.2.3 Mathematical Programming	39
	IV	RESULTS AND DISCUSSION	40
		4.1 Improved Case by Shaft Work Targeting Technique	42
		4.2 Improved Case by the Extended Pinch Analysis and	
		Design Methodology and Novel Exergy Diagram	47
		4.3 Improved Case by Mathematical Programming	53
		4.3.1 Heat Exchanger Network Synthesis	57
		4.3.1.1 The Result of HEN Synthesis	61
		4.3.1.2 Model Validation by PROII	62
		4.3.2 HEN Retrofit	62
		4.3.2.1 The Result of HEN Retrofit	63

-

PTE	R		PAC
V	CONCLUSI	ONS AND RECOMMENDATIONS	75
	5.1 Conclusi	on	75
	5.2 Recomm	endation	77
	REFERENC	ES	78
	APPENDIC	ES	81
	Appendix A	HEN Synthesis	81
	Appendix B	The Multistage Cascade Refrigeration of LNG	
		Process Flowsheet and Stream Condition in PROII	90
	Appendix C	HEN Retrofit	94
	CURRICUL	UM VITAE	115

CHAPTER

•

GE

LIST OF TABLES

TABLE		PAGE
4.1	The LNG compositions and other assumption	40
4.2	Initial stream data of multistage cascade refrigeration of	
	LNG process	41
4.3	Compared between value from simulation and shaft work	
	targeting	45
4.4	Exergy data of base case multistage cascade refrigeration of	
	LNG process	51
4.5	Comparison the methodology to estimate exergy destruction.	53
4.6	The stream data for mathematical optimization	54
4.7	The area in term of lumped parameter with overall heat	
	transfer coefficient of base case multistage cascade	
	refrigeration of LNG process	65
4.8	The area in term of lumped parameter with overall heat	
	transfer coefficient of improved case multistage cascade	
	refrigeration of LNG process	65
4.9	The result of HEN validation from mathematical	
	programming	66
4.10	The result of HEN validation's solution	67
4.11	The retrofitted exchanger area compared to original	
	exchanger area of case 1 (new exchangers ≥ 20)	68
4.12	The retrofitted exchanger area compared to original	
	exchanger area of case 1 (new exchangers ≥ 10)	69
5.1	The results between base case and improved case (1C case)	76
5.2	The exergetic efficiency of compressor and expander in each	
	method	76

.

σ

LIST OF FIGURES

FIGURE

2.1	Interaction between three main components.	3
2.2	Grand composite curve (GCC) of subambient processes.	4
2.3	A simple refrigeration cycle flow diagram.	4
2.4	P-H diagram of simple refrigeration cycle.	5
2.5	Schematic of natural gas pretreatment process.	8
2.6	Single-pressure mixed refrigerant natural gas liquefaction	
	process (Chiu et al., 1980).	9
2.7	Propane-precooled mixed refrigerant natural gas liquefaction	
	process (Chiu et al., 1980).	10
2.8	Cascade refrigeration cycle that show only one stage for	
	each refrigerant cycle (Kanoğlu, 2002).	11
2.9	Single-state mixed refrigerant (Remeljej et al., 2004).	12
2.10	New LNG (Foglietta, 1999).	13
2.11	The GCL concept (Remeljej et al., 2004).	13
2.12	The cLNG process (Remeljej et al., 2004).	14
2.13	The composite curve of process (Alejandro, 2014).	16
2.14	The exegy balance that obtained maximum work from	
	system.	18
2.15	The exegy balance that required minimum work.	18
2.16	Classification of exergy (Aspelund et al., 2007).	19
2.17	Exergy-Enthalpy diagram with decomposition of	
	thermomechanical exergy E TM (Gundersen et al., 2013).	19
2.18	Dimensionless exergy of heat temperature diagram	
	(Gundersen et al., 2013).	20
2.19	(a) The system used in development of minimum work	
	required for liquefaction of natural gas. (b) The system that	
	is equivalent to the system given in (a) (Kanoğlu, 2002).	24

σ

-

FIGURE		PAGE
2.20	The design of chemical processes (Linnhoff et al., 1990).	25
2.21	The onion diagram of subambient process (Linnhoff et	
	<i>al.</i> ,1990).	25
2.22	Changes in shaft work are directly related to changes in the	
	shaded area (Linnhoff et al., 1990).	27
2.23	The EGCCs representation (Linnhoff et al., 1994).	28
2.24	Overall exergy balance for a subambient plant (Linnhoff et	
	<i>al.</i> , 1994).	28
2.25	ECCs diagram (Gundersen et al., 2012).	31
2.26	Comparison between exergetic temperature, regular	
	temperature and Carnot factor (Gundersen et al., 2013).	33
2.27	$T^{E^{T}} - \dot{E}^{T}$ diagram below T ₀ (Gundersen <i>et al.</i> , 2012).	34
4.1	Natural gas cooling curve.	42
4.2	(a) Base case multistage cascade refrigeration of LNG	
	process in PROII. (b) Scheme of multistage cascade	
	refrigeration of LNG process.	43
4.3	(a) The flow diagram of work or exergy losses $(\sigma T_o)_{HEN}$ (b)	
	ECCs of base case multistage cascade refrigeration of LNG	
	process.	44
4.4	ECCs of improved multistage cascade refrigeration of LNG	
	process.	45
4.5	Process change by using ECCs.	45
4.6	(a) ECCs of changed process condition. (b) ECCs of	
	improved cold stream condition.	46
4.7	CCs of base case multistage cascade refrigeration of LNG	
	process.	47
4.8	CCs of alternative 1A multistage cascade refrigeration of	
	LNG process.	48

-

0

xi

FIGURE		
1.0	CCs of alternative 1P multistage accords refrigeration of	
4.7	LNC	40
	LNG process.	48
4.10	CCs of alternative 1C multistage cascade refrigeration of	
	LNG process.	49
4.11	(a) CCs for the base case multistage cascade refrigeration of	
	LNG process. (b) Exergy diagram for the base case	
	multistage cascade refrigeration of LNG process.	50
4.12	Exergy diagram for the alternative 1A multistage cascade	
	refrigeration of LNG process.	52
4.13	Exergy diagram for the alternative 1B multistage cascade	
	refrigeration of LNG process.	52
4.14	Exergy diagram for the improved multistage cascade	
	refrigeration of LNG process.	53
4.15	A simple stage-wise model (Yee and Grossman, 1990).	55
4.16	HEN of base case multistage cascade refrigeration of LNG	
	process.	56
o 4.17	A simple refrigeration cycle.	57
4.18	HEN of improved case multistage cascade refrigeration of	
	LNG process from Mathematical programming.	70
4.19	The result of HEN of improved case validation from	
	Mathematical programming	71
4 20	The result of HEN of improved cased validation's solution	72
4.20	The result of retrefitted LEN of ease 1 (new evaluation >	12
4.21	The result of refrontied HEW of case 1 (new exchangers \geq	70
1 2 2	20).	13
4.22	The result of retrofitted HEN of case 1 (new exchangers \geq	
	10).	74

EI/

. .

-

xii

LIST OF ABBREVIATIONS

С	Cold streams
Cl	Methane
C2	Ethylene
C3	Propane
CCs	Composite curve
CO ₂	Carbon dioxide
СОР	Coefficient of performance
EA	Exergy analysis
ECCs	Exergy composite curve
EGCCs	Exergy grand composite curve
EMAT	Exchanger minimum approach temperature
ExPAnD	Extended Pinch Analysis and Design Methodology
GAMS	General Algebraic Modeling System
GCCs	Grand composite curve
Н	Hot streams
H_2S	Hydrogen sulfide
HCFC	Hydrochlorofluorocarbon
HEN	Heat exchanger network
Hg	Mercury
HRAT	Heat recovery approach temperature
HRS	Heat recovery system
iC4	Iso - butane
iC5	Iso - Pentane
LNG	Liquefied natural gas
MDEA	Methyldiethanolamine
MILP	Mixed-integer linear programming
MINLP	Mixed-integer nonlinear programming
N ₂	Nitrogen
nC4	Normal – butane

	NG	Natural gas
	NLP	Nonlinear programming
	OPD	Ozone depletion potential
	Р	Absolute pressure
	P ₀	Ambient pressure
	PA	Pinch analysis
	Т	Absolute temperature
	T ₀	Ambient temperature
	ТАС	Total cost associated in heat exchanger network
	TEG	Triethylene glycol
	$TH_{i,IN}$	Supply temperature of hot process stream i
	T _{min}	Minimum temperature
	W	Approximately shaft work

LIST OF SYMBOLS

$(\sigma T_0)_{HEN}$	Exergy lose due to heat transfer equivalent to shaft work
Ė ^P	Pressure based exergy
ĖQ	Exergy of heat
Ė ^T	Temperature based exergy
Ė TM	Thermo – mechanical exergy
Ŵ _{rev}	Work in reversible process
Ŵu	Useful work
\dot{Q}_{0}	Heat rejected
Š _{gen}	Entropy generation
Ė _{in}	Incoming exery stream
Ėout	Outing exergy stream
Ė _{Deficit,} min	Minimum exergy deficitt
Ė _{Destruction,} min	Minimum exergy destruction
Ė _{Rejection,} min	Minimum exergy rejection
E _{Requirement,} min	Minimum exergy requirement
Ė _{Surplus,min}	Minimum exergy surplus
İ _e	Exergy destruction in ethane
İ _m	Exergy destruction in methane
İ _n	Exergy destruction in natural gas
İ _p	Exergy destruction in propane
m _e	Mass flowrate in ethane
m _m	Mass flowrate in methane
m'n _n	Mass flowrate in natural gas
m _p	Mass flowrate in propane
$T^{E^{T}}$	Temperature based exergetic temperature
Ŵ _{1,2,3}	Amount of power for supplying in each cycle namely 1,2 and 3
Ŵ _{actual}	Actual work
Ŵ _{min}	Minimum work

σ

$\Omega_{i,j}$	Upper bound of heat content for heat exchanger
CCU _i	Cost of cooling utility <i>cu</i>
CFHX _{i,j}	Fixed charges for exchanger $i - j$
CW _{i,j}	Cost of work consumption of compressor
C_p	Average molar heat capacity
FC _i	Heat capacity of cold process stream j
FH _i	Heat capacity of hot process stream i
FW _{i,j}	Heat capacity of stream between compressor $i - j$
Ż	Heat absorbed
$T^{E^{P}}$	Pressure based exergetic temperature
TCU _{CU,IN}	Inlet temperature of cooling utility cu
TCU _{cu,OUT}	Outlet temperature of cooling utility cu
$TC_{j,IN}$	Supply temperature of cold process stream j
TH _{i,OUT}	Target temperature of hot process stream i
dthu _j	Temperature approach for match of heating utility hu and cold
	process stream j
dtcu _{i,cu}	Temperature approach for match between cooling utility cu and
	hot process stream i
$dt_{i,j,k}$	Temperature approach for match $i - j$ at the feft of heat exchanger
qhu _j	Heat exchanged between hot utility hu and cold process stream j
qcu _{i,cu}	Heat exchanged between cold utility cu and hot process stream i
$q_{i,j,k}$	Heat exchanged between hot process stream iand cold process
	stream j in stage k
th _{i,k}	Temperature of hot process stream i at "hot end" of stage k
tc _{j,k}	Temperature of cold process stream j at "hot end" of stage k
zhu _j	Existence of an exchanger for match between heating utility and
	cold process stream j
	stream i
zcu _{i,cu}	Existence of an exchanger for match between cooling utility cu
	and hot process

Ø

Z _{i,j,k}	Existence of an exchanger for match $i - j$ in stage k
η_c	Carnot factor
ΔT_{lm}	Log mean temperature difference
Δe	Change of exergy
ΔEx_p	Process receive exergy
$\Delta E x_r$	Refrigeration system supply exergy
ΔW	Reduction in shaft work
А	Area
CHU_j	Cost of heating utility
e	Exergy of process stream per unit mass
E _{CV}	Energy in control volume
Edestruction, I	Exergy destruction
h	Enthalpy per unit mass
Н	Enthalpy
h*	Enthalpy of ideal gas $(P_0 = 0)$
\mathbf{h}_0	Enthalpy per unit mass at dead state
m	Mass flowrate
Р	Absolute pressure
P ₀	Ambient pressure
P _C	Critical pressure
P ^{vap}	Vapor pressure
Q	Heat duty
R	Gas constant
S	Entropy per unit mass
S	Entropy
s ₀	Enthalpy per unit mass at dead state
S _{gen}	Generated entropy
Т	Absolute temperature
T ₀	Ambient temperature
T _C	Critical temperature
U	Overall heat transfer coefficient

.

σ

W, Wc, W _{shaft}	Shaft work
Ŵ _{min}	Minimum work input to cycle
Z	Compressibility factor
ε, η_{ex}	Exergy efficiency
η	Compressor's isentropic efficiency
ω	Acentric factor
EMAT	Minimum-approach temperature difference
ST	Number of stage (often chosen as maximum between number of
	hot and cold streams)
k	Specific heat ratio
Г	Upper bound for temperature difference
κ	Dimensionless parameter

÷

o