INVESTIGATION OF OPTIMAL COMPOSITION OF MIXED-REFRIGERANT IN ORC

MISS JINSASIPAK KUNNATHUMSATHID

A SPECIAL RESEARCH PROJECT SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF ENGINEERING (CHEMICAL ENGINEERING)
FACULTY OF ENGINEERING
KING MONGKUT'S UNIVERSITY OF TECHNOLOGY THONBURI
2010

Investigation of Optimal Composition of Mixed-Refrigerant in ORC

Ms. Jinsasipak Kunnathumsathid B.Eng. (Chemical Engineering)

A Special Research Project Submitted in Partial Fulfillment

of the Requirements for

The Degree of Master of Engineering (Chemical Engineering)

Faculty of Engineering

King Mongkut's University of Technology Thonburi

2010

Special Research Project Committee

.... (Assoc. Prof. Suvit Tia, Ph.D.)	Chairman of Special Research Project Committee
.... (Asst. Prof. Bunyaphat Suphanit, Ph.D.)	Member and Special Research Project Advisor
.... (Lect. Wimolsiri Pridasawas, Ph.D.)	Member and Special Research Project Co-Advisor
.... (Lect. Annop Nopharatana, Ph.D.)	Member

Special Research Project Title	Investigation of Optimal Composition of Mixed-Refrigerant in ORC
Special Research Project Credits	6
Candidate	Ms. Jinsasipak Kunnathumsathid
Special Research Project Advisors	Asst. Prof. Dr. Bunyaphat Suphanit Dr. Wimolsiri Pridasawas
Program	Master of Engineering
Field of Study	Chemical Engineering
Department	Chemical Engineering
Faculty	Engineering
B.E.	2553

Abstract

This work compared the capabilities of the Organic Rankine Cycle (ORC) operating under saturated and superheated conditions. Furthermore, a guideline for using a single and mixed-working fluid in an ORC was suggested. The potential of applying mixed-working fluid in an ORC was explored and the optimal composition of the selected working fluids was determined. In this study, the recovery of medium grade energy from a biogas-fueled internal combustion engine (ICE) was considered. The stack temperature, acid dew point and mass flow rate of the exhaust gas supplied to an ORC were 400°C, 110°C and 4,582.83 kg/hr, respectively. The model development of 16 working fluids, consisting of 13 hydrocarbons and 3 halocarbons were carried out by using Aspen Plus V.7.1. For a single working fluid, all selected hydrocarbons and halocarbons were investigated whereas only hydrocarbons were studied in case of the mixed-working fluid because the halocarbons showed much lower potential to generate work when compared to the hydrocarbons. There were two objective functions being considered, i.e. maximizing net work output and maximizing profit. The key optimization parameters were the mass flow rate of the working fluid, the compositions of the selected working fluids, the turbine inlet pressure, the turbine outlet pressure and the superheating temperature. The optimization results revealed that pure toluene and a mixture of toluene and n-tetradecane (C14) operating under saturated condition were the most favorable alternative for the single working fluid and mixed-working fluid, respectively. When consider the profit gained from pure toluene and a toluene-C14 mixture, it was found that the profit gained from a toluene-C14 mixture was higher than that obtained by pure toluene. In consequence, it can be concluded that a mixture of 97.29 %wt toluene and 2.71 %wt n-tetradecane was the best working fluid under the condition in this study.

Keywords: Biogas-Fueled Internal Combustion Engine/ Organic Rankine Cycle/ Working Fluid Selection/ Mixed-Working Fluid

หัวข้อโครงการศึกษาวิจัย	การศึกษาองค์ประกอบของสารทำความเย็นชนิดต่าง ๆ ที่เหมาะสมใน Organic Rankine Cycle (ORC)
หน่วยกิต	6
ผู้เขียน	นางสาวจิณณ์ศศิภักด์ คุณธรรมสถิต
อาจารย์ที่ปรึกษา	ผศ.ดร.บุญยพัต สุภานิช
อาจารย์ที่ปรึกษาร่วม	ดร.วิมลศิริ ปรีดาสวัสดิ์
หลักสูตร	วิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชา	วิศวกรรมเคมี
ภาควิชา	วิศวกรรมเคมี
คณะ	วิศวกรรมศาสตร์
พ.ศ.	2553

บทคัดย่อ

งานวิจัยนี้ได้ดำเนินการเปรียบเทียบความสามารถสูงสุดของสารทำงานแต่ละตัว ในวัฏจักรแรงคินซึ่งทำงานภายใต้สภาวะไอร้อนอิ่มตัว และไอร้อนยวดยิ่ง ซึ่งมีการนำพลังงานคุณภาพระดับกลางจากเครื่องสันดาปภายในที่ใช้ก๊าซชีวภาพเป็นเชื้อเพลิงกลับมาใช้ใหม่ ก๊าซไอเสียที่ใช้เป็นแหล่งความร้อนของระบบ ORC มีอุณหภูมิ 400°C อุณหภูมิอิ่มตัว 110°C และอัตราการไหล 4,582.83 กิโลกรัมต่อชั่วโมง นอกจากนี้ยังมีการศึกษาศักยภาพของสารทำงานแบบผสมที่ใช้ในวัฏจักรแรงคิน และหาสัดส่วนองค์ประกอบที่เหมาะสมของสารทำงานแบบผสมที่ผ่านการคัดเลือก ในงานวิจัยนี้ได้ศึกษาสารทำงาน 16 ชนิด ซึ่งประกอบไปด้วยสารประกอบไฮโดรคาร์บอน 13 ชนิด และสารฮาโลคาร์บอน 3 ชนิด โดยสร้างแบบจำลองวัฏจักรแรงคินโดยใช้โปรแกรม Aspen Plus เวอร์ชัน 7.1 สำหรับกลุ่มสารทำงานบริสุทธิ์ สารประกอบไฮโดรคาร์บอนและฮาโลคาร์บอนทั้งหมดจะถูกพิจารณาเปรียบเทียบประสิทธิภาพในวัฏจักรแรงคิน แต่ในกรณีของสารทำงานแบบสารผสม มีการพิจาณาเฉพาะแค่สารประกอบไฮโดรคาร์บอนเท่านั้น เนื่องจากวัฏจักรแรงคินที่ใช้สารประกอบฮาโลคาร์บอนมีประสิทธิภาพต่ำกว่าวัฏจักรแรงคินที่ใช้สารประกอบไฮโดรคาร์บอนเป็นอย่างมาก ในการหาสภาวะที่เหมาะสม พิจารณาจากเกณฑ์ 2 แบบ คือ หาสภาวะที่ผลิตไฟฟ้าได้มากที่สุด และ หาสภาวะที่ได้กำไรจากการปฏิบัติงานสูงสุด โดยตัวแปรสำคัญที่มีผลต่อสภาวะที่เหมาะสม ได้แก่ อัตราการไหลของสารทำงาน องค์ประกอบของสารชนิดต่างๆ ในสารทำงานแบบผสม ความดันขาเข้ากังหัน ความดันขาออกจากกังหัน และอุณหภูมิของไอร้อนยวดยิ่งจากหม้อต้ม จากผลการจำลองที่ได้ พบว่าสารทำงานแบบบริสุทธิ์ และสารทำงานแบบผสมที่ทำกำไรได้มากที่สุด ได้แก่ โทลูอีนบริสุทธิ์ และสารผสมระหว่างโทลูอีนกับเตตระเดคเคน ที่ทำงานภายใต้สภาวะไออิ่มตัว อย่างไรก็ตามเมื่อพิจารณาโดยรวม

พบว่าสารผสมระหว่างโทลูอีนร้อยละ 97.29 โดยน้ำหนัก กับเตตระเดคเคนร้อยละ 2.71 โดยน้ำหนัก มีศักยภาพมากที่สุดภายใต้สภาวะในการศึกษานี้

คำสำคัญ: เครื่องยนต์สันดาปภายในที่ใช้ก๊าซชีวภาพเป็นเชื้อเพลิง/ วัฏจักรแรงคิน/ การเลือกสารทำงาน/ สารทำงานแบบผสม

ACKNOWLEDGEMENTS

Foremost, the author would like to express profound gratitude to advisor and co-advisor of this thesis, Asst. Prof. Dr. Bunyaphat Suphanit and Dr. Wimolsiri Pridasawas for the technical support, valuable guidance and revision that enabled her to complete this work successfully. The author also greatly appreciates the committee members, Assoc. Prof. Dr. Suvit Tia and Dr. Annop Nopharatana for technical instructions and constructive comments to help her to improve her work.

Also, the author owes her deepest gratitude to the Chemical Engineering Practice School (ChEPS) for providing a full-scholarship for the master degree. Moreover, the author is highly grateful to the staffs of the Chemical Engineering Practice School (ChEPS) particularly Mrs. Chadaporn, who helped the author with some administrative issues. Lastly, this thesis would not have been possible without direct and indirect assistance from many people including the author's family and friends.

CONTENTS

	PAGE
ENGLISH ABSTRACT	ii
THAI ABSTRACT	iii
ACKNOWLEDGEMENTS	v
CONTENTS	vi
LIST OF TABLES	viii
LIST OF FIGURES	xi
NOMENCLATURES	xv
CHAPTER	
1. INTRODUCTION	**1**
1.1 Background	1
1.2 Objectives	2
1.3 Scopes of work	2
1.4 Expected results	2
2. THEORIES AND LITERATURE REVIEW	**3**
2.1 Principle of Organic Rankine Cycle (ORC)	3
2.2 The preliminary selection of working fluid	6
2.3 The differences in characteristics between an ORC with a pure fluid and an ORC with mixed-working fluid	8
2.4 Literature review	9
3. METHODOLOGY	**15**
3.1 Methodology	15
3.1.1 Study theory and review literatures relating to the ORC and collect information	15
3.1.2 Selection of working fluids used in an ORC	16
3.1.3 Develop the ORC simulation model using Aspen Plus V.7.1 based on different operating conditions and fluid compositions	18
3.1.4 Process Optimization	22
3.1.5 Analyze and conclude the results	23
4. RESULTS AND DISCUSSION	**24**
4.1 Maximization of net work output	24
4.1.1 Saturated condition	24
4.1.1.1 Sensitivity analysis	24
4.1.1.2 Optimization results from maximizing net work output	27
4.1.1.2.1 Single working fluids	27
4.1.1.2.2 Mixed-working fluids	37
4.1.2 Superheated condition	42

4.1.2.1	Sensitivity analysis	42
4.1.2.2	Optimization results from maximizing net work output	47
4.1.2.2.1	Single working fluids	47
4.1.2.2.2	Mixed-working fluids	60
4.2	Maximization of profit	65
5. CONCLUSION AND RECOMMENDATIONS		**69**
5.1	Conclusion	69
5.2	Recommendations	70
REFERENCES		**71**
APPENDIX		**73**
A	Stream and equipment input data	73
B	Optimization results	77
C	Cost estimation	96
CURRICULUM VITAE		**100**

LIST OF TABLES

TABLE		PAGE
3.1	The conditions and feed composition of the exhaust gas.	16
3.2	Preselected single working fluid.	17
3.3	Selected single working fluids.	18
3.4	Optimization variables in various design scenarios.	22
4.1	Arrangement of the net work output and the TAC per net work output.	36
4.2	Comparison of the optimization results between single and mixed-working fluids operating under saturated condition.	38
4.3	Contribution of changes in turbine and pump work on an increase in the net work output and the thermal efficiency of an ORC operating under saturated condition using mixed-working fluid.	42
4.4	Comparison between the optimization results of an ORC operating under superheated condition and saturated condition using various n-paraffin compounds as a working fluid.	50
4.5	Comparison between the optimization results of an ORC operating under superheated and saturated condition using various aromatic compounds as a working fluid.	53
4.6	Comparison between the optimization results of an ORC operating under superheated and saturated condition using various hydrocarbons containing six carbon atoms with different molecular structure as a working fluid.	55
4.7	Comparison between the optimization results of an ORC operating under superheated and saturated condition using halocarbons as a working fluid.	58
4.8	Comparison of the optimization results between single and mixed-working fluids operating under superheated condition.	60
4.9	Contribution of changes in turbine and pump work on an increase in the net work output and thermal efficiency of an ORC operating under superheated condition using mixed-working fluid.	62
4.10	Comparison of an increase in the net work output and thermal efficiency of an ORC using single working fluid and mixed-working fluid operating under saturated and superheated condition.	64
4.11	The maximum profit gained from an ORC operating under saturated and superheated condition.	65
4.12	The maximum profit gained from an ORC operating under saturated condition.	67

4.13 Comparison between the simulation results of pure toluene and the mixture of toluene and n-tetradecane operating under saturated condition at the same operating pressure of 1.348 MPa. 68
A.1 Stream input data of an ORC operating under saturated and superheated condition. 74
A.2 Equipment input data of pump and turbine of an ORC operating under saturated condition and superheated condition. 75
A.3 Equipment input data of boilers and condensers of an ORC operating under saturated condition. 75
A.4 Equipment input data of boilers and condensers of an ORC operating under superheated condition. 75
A.5 The design specifications for controlling the concerned parameters in case of an ORC employing the single working fluid operating under saturated and superheated condition. 75
A.6 The design specifications for controlling the concerned parameters in case of an ORC employing the mixed-working fluid operating under saturated and superheated condition. 76
B.1 Optimization results from maximizing net work output of n-paraffin compounds operating under saturated condition. 78
B.2 Optimization results from maximizing net work output of aromatic compounds operating under saturated condition. 80
B.3 Optimization results from maximizing net work output of hydrocarbons containing six carbon atoms with different molecular structures operating under saturated condition. 81
B.4 Optimization results from maximizing net work output of halocarbons operating under saturated condition. 82
B.5 Temperature-enthalpy data of all single working fluids operating under saturated condition from maximizing net work output. 83
B.6 Optimization results from maximizing net work output of mixtures operating under saturated condition. 84
B.7 Temperature-enthalpy data of all mixed-working fluids operating under saturated condition from maximizing net work output. 85
B.8 Optimization results from maximizing net work output of n-paraffin compounds operating under superheated condition. 86
B.9 Optimization results from maximizing net work output of aromatic compounds operating under superheated condition. 88
B.10 Optimization results from maximizing net work output of hydrocarbons containing six carbon atoms with different molecular structures operating under superheated condition. 89
B.11 Optimization results from maximizing net work output of halocarbons operating under superheated condition. 90
B.12 Temperature-enthalpy data of all single working fluids operating under superheated condition from maximizing net work output. 91

B.13 Optimization results from maximizing net work output of mixtures operating under superheated condition. 92
B.14 Temperature-enthalpy data of all mixed-working fluids operating under superheated condition from maximizing net work output. 93
B.15 Optimization results from maximizing profit of pure toluene operating under saturated condition. 94
B.16 Optimization results from maximizing profit of mixture of toluene and n-tetradecane operating under saturated condition. 95
C.1 Cost coefficient for purchase cost calculation. 97
C.2 Pressure coefficient for calculating pressure factor. 98

LIST OF FIGURES

FIGURE		PAGE
2.1	Schematics of T-S diagrams for water and an organic compound.	3
2.2	Schematics of an ORC configuration.	4
2.3	Temperature-entropy diagram of ideal (s) and non-ideal (a) ORC.	4
2.4	Schematics of (a) isentropic, (b) wet and (c) dry working fluids.	7
2.5	Schematic of T-ΔH diagram used for pinch point analysis in the evaporator.	8
3.1	Methodology for investigating of optimal composition of mixed-working fluid in an ORC.	15
3.2	Development of an ORC simulation model.	19
3.3	The simulation model of an ORC in the Aspen Plus V.7.1 for the saturated operation.	20
3.4	The simulation model of an ORC in Aspen Plus V.7.1 for the superheated operation.	21
4.1	Effect of the turbine inlet pressure and the mass flow rate of n-octane on the net work output in an ORC operating under the saturated condition.	25
4.2	Effect of the turbine inlet pressure and mass flow rate of n-octane on the thermal efficiency in an ORC operating under saturated condition.	25
4.3	Pressure-enthalpy diagram of n-octane.	26
4.4	Relationship between the turbine inlet pressure and the turbine work output in an ORC operating under saturated condition and using 1,000 kg/hr of n-octane as a working fluid.	26
4.5	Net work output obtained from an ORC operating under saturated condition using various n-paraffin compounds as a working fluid.	28
4.6	Thermal efficiency of an ORC operating under saturated condition using various n-paraffin compounds as a working fluid.	28
4.7	Temperature-enthalpy diagrams of various n-paraffin compounds operating under saturated condition.	29
4.8	Net work output obtained from an ORC operating under saturated condition using various aromatic compounds as a working fluid.	30
4.9	Thermal efficiency of an ORC operating under saturated condition using various aromatic compounds as a working fluid.	31
4.10	Temperature-enthalpy diagrams of various aromatic compounds operating under saturated condition.	31
4.11	Net work output obtained from an ORC operating under saturated condition using various hydrocarbons containing six carbon atoms with different molecular structures as a working fluid.	32

4.12 Thermal efficiency of an ORC operating under saturated condition using the various hydrocarbons containing six carbon atoms with different molecular structures as a working fluid. 33

4.13 Temperature-enthalpy diagrams of various hydrocarbons containing six carbon atoms with different molecular structures operating under saturated condition. 33

4.14 Net work output obtained from an ORC operating under saturated condition using various halocarbons as a working fluid. 34

4.15 Thermal efficiency of an ORC operating under saturated condition using various halocarbons as a working fluid. 34

4.16 Temperature-enthalpy diagrams of various halocarbons operating under saturated condition. 35

4.17 Net work output obtained from an ORC operating under saturated condition using single hydrocarbons and halocarbons as a working fluid. 36

4.18 Thermal efficiency of an ORC operating under saturated condition using single hydrocarbons and halocarbons as a working fluid. 37

4.19 Temperature-enthalpy diagrams of pure component and the optimal fluid mixture when consider all hydrocarbons operating under saturated condition. 39

4.20 Temperature-enthalpy diagrams of pure component and the optimal fluid mixture when consider n-paraffin compounds operating under saturated condition. 40

4.21 Temperature-enthalpy diagrams of pure component and the optimal fluid mixture when consider all aromatic compounds operating under the saturated condition. 40

4.22 Comparison of the net work output obtained from pure component and the optimal fluid mixture operating under saturated condition. 41

4.23 Comparison of the thermal efficiency obtained from pure component and the optimal fluid mixture operating under saturated condition. 41

4.24 Effects of the superheating temperature on the specific turbine work output and the mass flow rate of R-245fa used in an ORC operating under superheated condition at 3.64 MPa. 43

4.25 Effects of the superheating temperature on the work generated from turbine and the work requirement for pump in an ORC operating under superheated condition at 3.64 MPa using R-245fa as a working fluid. 44

4.26 Effects of the superheating temperature on the net work output and thermal efficiency of an ORC operating under superheated condition at 3.64 MPa using R-245fa as a working fluid. 44

4.27 Effects of the turbine inlet pressure on the specific turbine work output and the mass flow rate of R-245fa used in an ORC operating under superheated condition at 210°C. 45

4.28 Effects of the turbine inlet pressure on the work generated from turbine and the work requirement for pump in an ORC operating under superheated condition at 210°C and using R-245fa as a working fluid. 46

4.29 Effects of the turbine inlet pressure on the net work output and thermal efficiency of an ORC operating under superheated condition at 210°C using R-245fa as a working fluid. 46

4.30 Net work output obtained from an ORC operating under superheated condition using various n-paraffin compounds as a working fluid. 48

4.31 Thermal efficiency of an ORC operating under superheated condition using various n-paraffin compounds as a working fluid. 49

4.32 Temperature-enthalpy diagrams of various n-paraffin compounds operating under superheated condition. 49

4.33 Net work output obtained from an ORC operating under superheated condition using various aromatic compounds as a working fluid. 51

4.34 Thermal efficiency of an ORC operating under superheated condition using various aromatic compounds as a working fluid. 51

4.35 Temperature-enthalpy diagrams of various aromatic compounds operating under superheated condition. 52

4.36 Net work output obtained from an ORC operating under superheated condition using various hydrocarbons containing six carbon atoms with different molecular structure as a working fluid. 54

4.37 Thermal efficiency of an ORC operating under superheated condition using various hydrocarbons containing six carbon atoms with different molecular structure as a working fluid. 54

4.38 Temperature-enthalpy diagrams of various hydrocarbons containing six carbon atoms with different molecular structure operating under the superheated condition. 55

4.39 Net work output obtained from an ORC operating under superheated condition using various halocarbons as a working fluid. 56

4.40 Thermal efficiency of an ORC operating under superheated condition using various halocarbons as a working fluid. 57

4.41 Temperature-enthalpy diagrams of various halocarbons operating under superheated condition. 57

4.42 Net work output obtained from an ORC operating under superheated condition using single hydrocarbons and halocarbons as a working fluid. 58

4.43 Thermal efficiency of an ORC operating under superheated condition using single hydrocarbons and halocarbons as a working fluid. 59

4.44 Temperature-enthalpy diagrams of pure component and the optimal fluid mixture when consider all hydrocarbons operating under superheated condition. 61
4.45 Temperature-enthalpy diagrams of pure component and the optimal fluid mixture when consider all n-paraffin compounds operating under superheated condition. 61
4.46 Temperature-enthalpy diagrams of pure component and the optimal fluid mixture when consider all aromatic compounds operating under the superheated condition. 62
4.47 Comparison of the net work output obtained from pure component and the optimal fluid mixture operating under superheated condition. 63
4.48 Comparison of the thermal efficiency obtained from pure component and the optimal fluid mixture operating under superheated condition. 64
4.49 Relationship between the electricity selling price and profit gained from an ORC. 66

NOMENCLATURES

A	Area
CFCs	Chlorofluorocarbons
CW	Cooling water
C_P	Specific heat capacity
EB	Ethylbenzene
HCFCs	Hydrochlorofluorocarbons
ΔH_T	Enthalpy change between the turbine inlet and outlet
ICE	Internal combustion engine
M_{WF}	Mass flow rate of working fluid
n-PB	n-Propylbenzene
ORC	Organic Rankine Cycle
P_C	Critical pressure
P_{Elec}	Electricity selling price
P_{evap}	Evaporating pressure
$P_{T,in}$	Turbine inlet pressure
$P_{T,out}$	Turbine outlet pressure
ΔP	Pressure drop
Q	Heat duty
Sat.	Saturated condition
SPH.	Superheated condition
TAC	Total annualized cost
T_B	Normal boiling point
T_C	Critical temperature
T_{evap}	Evaporating temperature
$T_{evap,i}$	Initial evaporating temperature
$T_{evap,f}$	final evaporating temperature
$T_{g,out}$	Flue gas outlet temperature
T_{SPH}	Superheating temperature
$\Delta T_{boilers}$	Temperature difference between the heat sink and heat source at any point of phase transition internal boilers
$\Delta T_{condensers}$	Temperature difference between the heat sink and heat source at any point of phase transition internal condensers
$\Delta T_{hot\text{-}cold}$	Minimum temperature approach
$V_{frac,T}$	Vapor fraction at turbine inlet
$\hat{V}_{T,in}$	Specific volume of gas entering the turbine
W_{net}	Net work output
W_P	Work requirement for pump
W_T	Work generated from turbine
$X_{T,out}$	Molar liquid fraction at turbine outlet
X_i	Mass fraction of component i
η	Thermal efficiency