

**SUSTAINABLE PROCESS DESIGN FOR LIGNOCELLULOSIC-BASED
BIOETHANOL USING LIFE CYCLE ASSESSMENT TECHNIQUE**



Mr. Pongsawat Tansutapanich

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
2010


530005

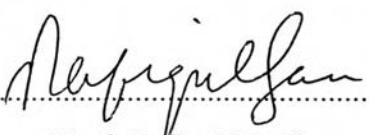
Thesis Title: Sustainable Process Design for Lignocellulosic-based Bioethanol using Life Cycle Assessment Technique
By: Pongsawat Tansutapanich
Program: Petroleum Technology
Thesis Advisors: Asst. Prof. Pomthong Malakul
Prof. Rafiqul Gani

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



..... Dean
(Asst. Prof. Pomthong Malakul)

Thesis Committee:


.....
(Asst. Prof. Pomthong Malakul)


.....
(Prof. Rafiqul Gani)


.....
(Asst. Prof. Kitipat Siemanond)


.....
(Assoc. Prof. Thumrongrut Mungcharoen)

ABSTRACT

5173007063: Petroleum Technology Program

Pongsawat Tansutapanich: Sustainable Process Design for Lignocellulosic-based Bioethanol using Life Cycle Assessment Technique

Thesis Advisors: Asst. Prof. Pomthong Malakul and Prof. Rafiqul Gani, 115 pp.

Keywords: Sustainable Process Design/ Life Cycle Assessment/ Lignocellulosic Bioethanol/ Sustainability Analysis

This study focused on the sustainable process design of a bioethanol conversion process using lignocellulosic biomass as a raw material for fuel ethanol (99.5 wt%) production. The process simulator, PRO/II 8.2, was used to generate the base case design of the bioethanol conversion process using sugarcane bagasse as a feedstock. The sustainability analysis tool, SustainPro, was used in the analysis of indicators, sustainability metrics, and safety indices, which are further analyzed to provide directions for improvements. The life cycle environmental burdens associated with the bioethanol conversion process was performed by using Life Cycle Assessment software, SimaPro 7.0 with the CML 2 baseline 2000 and Eco-indicator 95 method, to quantify the impacts in various categories such as global warming, acidification, eutrophication, and energy resources. Four new design alternatives were generated based on suggestions from SustainPro, both in the process aspect (Alternatives 1, 2, 3, and 4) and the energy efficiency aspect (Alternative 5). The comparison between base case and new design alternatives was conducted to indicate the improvement for sustainability. Using the heat integrated design, Alternative 5 was shown to be the best option as seen from the lowest impact in all categories studied. The results showed that the greenhouse gas emission mainly come from the recovery and pre-treatment stage in the bioethanol conversion process.

บทคัดย่อ

พงศวัฒน์ ต้นสุตะพานิช : การออกแบบกระบวนการผลิตเอทานอลจากวัสดุประเภทลิกโนเซลลูโลสอย่างยั่งยืนโดยใช้เทคนิคการประเมินวัฏจักรชีวิต (Sustainable Process Design for Lignocellulosic-based Bioethanol using Life Cycle Assessment Technique) อ. ที่ปรึกษา : ผศ. ดร. ปมทอง มาลากุล ณ อยุธยา และ ศ. ดร. ราฟีก กานี 115 หน้า

งานวิจัยนี้มุ่งเน้นการศึกษาการออกแบบอย่างยั่งยืนสำหรับกระบวนการเปลี่ยนชีวมวลประเภทลิกโนเซลลูโลสเป็นเอทานอลสำหรับใช้เป็นเชื้อเพลิง (เกรด 99.5 % โดยมวล) อย่างยั่งยืนโดยใช้โปรแกรม PRO/II 8.2 ในการจำลองแบบจำลองพื้นฐานสำหรับกระบวนการเปลี่ยนเอทานอลโดยใช้กากอ้อยเป็นสารตั้งต้น โปรแกรมวิเคราะห์ความยั่งยืน SustainPro ถูกนำมาประยุกต์ใช้ในการวิเคราะห์ตัวชี้วัดด้านความยั่งยืน และตัวชี้วัดด้านความปลอดภัย เพื่อนำมาวิเคราะห์หาแนวทางปรับปรุงแบบจำลองให้ดีขึ้น และทำการประเมินผลกระทบด้านสิ่งแวดล้อมของกระบวนการเปลี่ยนเอทานอลโดยใช้เทคนิคการประเมินวัฏจักรชีวิตด้วยโปรแกรม SimaPro 7.0 และวิธี CML 2 baseline 2000 และ Eco-indicator 95 เพื่อประเมินผลกระทบต่อสิ่งแวดล้อมในด้านต่างๆ เช่น ภาวะโลกร้อน ภาวะความเป็นกรด ภาวะแหล่งน้ำเปลี่ยนสี และการใช้พลังงานเป็นต้น นอกจากนี้แบบจำลองทางเลือกใหม่จำนวนสี่แบบได้ถูกสร้างขึ้นจากผลการวิเคราะห์ของโปรแกรม SustainPro ทั้งในเชิงกระบวนการ (แบบจำลองทางเลือกที่หนึ่ง สอง สาม และสี่) และเชิงประสิทธิภาพการใช้พลังงาน (แบบจำลองที่ห้า) และทำการเปรียบเทียบระหว่างแบบจำลองพื้นฐานกับแบบจำลองทางเลือกเพื่อแสดงให้เห็นว่าการปรับปรุงกระบวนการให้ยั่งยืนขึ้นเพียงใด ผลการศึกษาแสดงให้เห็นว่าแบบจำลองทางเลือกที่ห้าเป็นแบบจำลองที่ดีที่สุดโดยมีผลกระทบต่อสิ่งแวดล้อมน้อยที่สุดในทุกๆ ด้านที่สนใจในการศึกษานี้ และผลการศึกษายังแสดงให้เห็นว่า การปล่อยก๊าซเรือนกระจกส่วนใหญ่ปล่อยเกิดจากขั้นตอนการทำให้เอทานอลบริสุทธิ์ และขั้นตอนการย่อยเฮมิเซลลูโลสไปเป็นน้ำตาลเบื้องต้นในกระบวนการเปลี่ยนเอทานอล

ACKNOWLEDGEMENTS

This work would not have been possible without the assistance of the following individuals:

First and foremost, I sincerely appreciate Asst. Prof. Pomthong Malakul and Prof. Rafiqul Gani, my advisor for providing invaluable knowledge, creative comments, untouchable experience in classroom, and kind support throughout this research work.

I would like to thank Asst. Prof. Kitipat Siemanond and Assoc. Prof. Thumrongrut Mungcharoen for being my thesis committee. Their suggestions and comments are very beneficial for me and this work.

I would like to acknowledge to Dr. Ana Carvalho and Mr. Merlin Morales for the excellent supporting regarding PRO/II and SustainPro with patience and total availability to help. I would like to express my appreciation to Mr. Seksan Papong for the help for running SimaPro.

This thesis work is funded by the Petroleum and Petrochemical College, Chulalongkorn University; and the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand; Computer Aided Process Engineering Center, Technical University of Denmark. I would also like to give my appreciation TRE associations who have kindly provided valuable data for this project.

I greatly appreciate all PPC staffs and my friends who gave me support and encouragement.

Finally, I am deeply indebted to my family for their love, understanding, encouragement, and support for me at all time.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	xi
List of Figures	xiv
 CHAPTER	
I INTRODUCTION	1
 II LITERATURE REVIEW	
2.1 Petroleum Outlook in Thailand	3
2.1.1 Crude Oil Market	3
2.1.2 Oil Potentials, Supply, Demand, and Consumption	4
2.1.3 Petroleum Products	5
2.1.4 Uses of Petroleum Products	6
2.2 The use of ethanol as fuel	6
2.2.1 Ethanol as a Transportation Fuel and Additive	7
2.2.1 Ethanol as Fuel in Thailand	9
2.3 Bioethanol	10
2.3.1 Raw Materials	10
2.3.2 Process Overview	10
2.4 Lignocellulosic-based derive Ethanol	11
2.4.1 Lignocellulosic Biomass	11
2.4.2 Potential of Cellulosic Materials in Thailand	15
2.4.3 Ethanol Plant in Thailand	16

CHAPTER	PAGE
2.4.3.1 TRE Ethanol Production	17
2.5 Sustainability Analysis	18
2.5.1 Sustainable Development	18
2.5.2 SustainPro	19
2.5.2.1 Collect Steady-state Data	20
2.5.2.2 Flowsheet Decomposition	20
2.5.2.3 Calculation of Indicators, Sustainability Metrics and Safety Indices	21
2.5.2.4 Indicator Sensitivity Analysis (ISA) Algorithm	27
2.5.2.5 Operational sensitivity analysis	28
2.5.2.5 Generation of new design alternatives	28
2.5.3 Sustainability Analysis Study on Bioethanol	28
2.5.3.1 Process Simulation	28
2.5.3.1 Sustainability Aanalysis	30
2.6 Life Cycle Assessment (LCA)	30
2.6.1 Overview	30
2.6.2 Definition of LCA	32
2.6.3 LCA's Methodology	32
2.6.3.1 Goal and Scope Definition	32
2.6.3.2 Inventory Analysis	32
2.6.3.3 LCIA	33
2.6.3.4 Interpretation	33
2.5.4 LCA Studies on bioethanol	34
III EXPERIMENTAL	38
3.1 Materials and Equipments	38
3.1.1 Equipment	38
3.2.1 Software	38
3.2 Methodology	38

CHAPTER	PAGE
3.2.1 Preparation	38
3.2.2 Modeling	38
3.2.3 Sustainability Analysis	39
3.2.3.1 Collection of Steady State Data	39
3.2.3.2 Flowsheet Decomposition	39
3.2.3.3 Calculation of Indicators, Sustainability Metrics and Safety Indices	39
3.2.3.4 Indicator Eensitivity Analysis	39
3.2.3.5 Operational Sensitivity Analysis	39
3.2.4 Life Cycle Assessment	39
3.2.4.1 Defining (Goal and Scope)	39
3.2.4.2 Inventory Analysis	40
3.2.4.3 Impact Assessment	40
3.2.4.4 Interpretation	41
3.2.5 Re-modeling	41
3.2.5.1 Generating New Design Alternative	41
3.2.5.2 Sustainability Analysis of Alternatives	41
3.2.5.3 Life Cycle Assessment of Alternatives	41
3.2.6 Comparing	41
3.2.6.1 Indicators	41
3.2.6.2 Sustainability Metrics	41
3.2.6.3 WAR Algorithm	41
3.2.6.2 Safety Indices	41
3.2.6.3 Life Cycle Assessment	41
 IV RESULTS AND DISCUSSION	 42
4.1 Base Case Design	42
4.1.1 Process Simulation of Base Case Design	42
4.1.1.1 TRE Design	42

CHAPTER	PAGE
4.1.1.2 Base Case Design	43
4.1.2 Sustainability Analysis	44
4.1.2.1 Indicator Results	44
4.1.2.2 Sensitivity Analysis Results	46
4.1.2.3 Sustainability Metrics Results	48
4.1.2.4 WAR Algorithm Results	49
4.1.2.5 Safety Indices Results	49
4.1.3 Life Cycle Assessment	50
4.1.3.1 Life Cycle Inventory of Bioethanol Conversion Process	50
4.1.3.2 Life Cycle Energy Analysis	56
4.1.3.3 Life Cycle Impact Assessment	56
4.2 Generation of New Design Alternatives	58
4.2.1 Process Aspect	58
4.2.1.1 Evaporator Platform	59
4.2.1.2 Distillation Platform	61
4.2.2 Energy Efficiency Aspect	62
4.2.2.1 Heat Integration	62
4.3 Comparison Between Base Case and Alternatives	64
4.3.1 Energy Consumption	64
4.3.2 Sustainability Analysis	65
4.3.2.1 Indicators	65
4.3.2.2 Sustainability Metrics	67
4.3.2.3 WAR Algorithm	68
4.3.2.4 Safety Indices	69
4.3.3 Life Cycle Assessment	70

CHAPTER		PAGE
V	CONCLUSIONS AND RECOMMENDATIONS	76
	REFERENCES	79
	APPENDICES	84
	Appendix A Components Considered in PRO/II	84
	Appendix B Chemical Reactions Implemented in PRO/II	85
	Appendix C Bioethanol Conversion Process Flowsheet Implemented in PRO/II	86
	Appendix D Stream Summary of The Base Case Design	92
	Appendix E Stage Model and Result from GAMS of Alternative-4	101
	Appendix F Life Cycle Inventory Analysis of New Design Alternatives	104
	Appendix G Life Cycle Impact Assessment of New Design Alternatives	113
	CURRICULUM VITAE	115

LIST OF TABLES

TABLE	PAGE	
2.1	Energy parameters for ethanol, isooctane, gasoline, and diesel	7
2.2	World's ethanol producers	8
2.3	Contents of cellulose, hemicellulose, and lignin in common lignocellulosic materials	13
2.4	Potential of lignocellulosic materials in Thailand	15
2.5	Contents of cellulose, hemicellulose, and lignin in Thai-based- lignocellulosic materials	16
2.6	List of ethanol plants in Thailand	17
2.7	List of safety indices and their sources	24
2.8	The sustainability metrics considered in SustainPro	26
2.9	The environmental impact factor is WAR algorithm	26
2.10	The comparison of indicators betewwn base case design and new design	30
2.11	Greenhouse gas emission comparison	34
2.12	The comparison of GHG emission from difference sources	36
3.1	Source of data of base case simulation	38
3.2	Sources of inventory data of Bioethanol conversion	40
4.1	List of the most sensitive indicators for the open-paths	44
4.2	List of most sensitive indicators for the close-paths	45
4.3	Details of high potential paths for improvement	45
4.4	Scores from the indicators sensitivity analysis algorithm	46
4.5	Sensitivity analysis of OP 554	47
4.6	Sensitivity analysis of OP 555	47
4.7	Sensitivity analysis of C2	47
4.8	Sensitivity analysis of C58	47

TABLE	PAGE
4.9 Sustainability metrics results of base case design	48
4.10 WAR algorithm results of base case design obtained through ICAS	49
4.11 Safety indices for the bioethanol conversion process	50
4.12 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in pretreatment stage	52
4.13 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in neutralization stage	53
4.14 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in fermentation stage	53
4.15 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in recovery stage	54
4.16 Partitioning fraction between mass and water removed allocation	54
4.17 Results of the inventory analysis per one kilogram ethanol 99.5 wt% production in biogas and cogeneration stage	55
4.18 Environmental impact of bioethanol conversion process per one kilogram ethanol 99.5 wt%	57
4.19 Environmental impact of bioethanol conversion process per one megajoule ethanol 99.5 wt%	57
4.20 Comparison of operating condition and duty between base case and Alternative-1	60
4.21 Comparison of duty between the base case and Alternative-2	60
4.22 Comparison of duty between the base case and Alternative-3	61
4.23 Comparison of duty between the base case and Alternative-4	62
4.24 Properties of hot and cold stream in Alternative-3	63
4.25 Properties of potential heat supplied in Alternative-3	63

TABLE	PAGE
4.26 Comparison of total energy consumption between the base case and alternatives	65
4.27 Comparison of indicators of alternatives corresponding to the same OP 554 of the base case design	66
4.28 Comparison of indicators of alternatives corresponding to the same OP 555 of the base case design	66
4.29 Comparison of sustainability metrics between the base case and alternatives	68
4.30 Comparison of WAR algorithm between the base case and alternatives	68
4.31 Safety indices of Alternative 4 and 5	69

LIST OF FIGURES

FIGURE	PAGE
2.1 Total primary energy supply in Thailand.	3
2.2 Thailand's oil demand in barrel per day.	4
2.3 Crude oil import sources.	4
2.4 Thairoil refining process and products.	5
2.5 Petroleum product uses in Thailand.	6
2.6 Gasohol consumption in Thailand.	9
2.7 General process scheme for ethanol production.	11
2.8 Composition of lignocellulosic materials.	12
2.9 The US annual biomass resource potential.	14
2.10 The US biomass scenario.	14
2.11 The main operations of TRE plant.	18
2.12 Sustainable development concept.	19
2.13 The systematic methodology in SustainPro.	20
2.14 Example of the sustainability metrics.	25
2.15 The target improvement for the indicators.	27
2.16 Lignocellulosic-based bioethanol process flow sheet.	29
2.17 Life cycle of biofuels.	31
2.18 Life cycle assessment framework.	33
2.19 Greenhouse gas emission of ethanol from sugarcane.	35
2.20 The comparison (between allocation factor) of CO ₂ equivalent emission for ethanol production and main process involved	36
3.1 System boundary for bioethanol conversion process.	39
4.1 The main operations of TRE process.	42
4.2 Four stages of process life cycle.	51
4.3 System boundary of bioethanol conversion process.	51

FIGURE	PAGE
4.4 Distribution of environmental impacts classified stage by stage.	58
4.5 Grid diagram of hot and cold stream in Alternative-4	63
4.6 Grid diagram of hot and cold stream in Alternative-5	64
4.7 Comparison of net energy ratio from bioethanol conversion process between the base case and alternatives.	70
4.8 Comparison of the greenhouse effect (gCO ₂ -equivalent) generated from bioethanol conversion process between the base case and alternatives per one kilogram of bioethanol.	71
4.9 Comparison of the greenhouse effect (gCO ₂ -equivalent) generated from bioethanol conversion process between the base case and alternatives per one megajoule of bioethanol.	71
4.10 Comparison of the acidification (gSO ₂ -equivalent) generated from bioethanol conversion process between the base case and alternatives per one kilogram of bioethanol.	72
4.11 Comparison of the acidification (mgSO ₂ -equivalent) generated from bioethanol conversion process between the base case and alternatives per one megajoule of bioethanol.	73
4.12 Comparison of the eutrophication (gPO ₄ --equivalent) generated from bioethanol conversion process between the base case and alternatives per one kilogram of bioethanol.	73
4.13 Comparison of the eutrophication (mgPO ₄ --equivalent) generated from bioethanol conversion process between the base case and alternatives per one megajoule of bioethanol.	74
4.14 Comparison of the energy resources (MJ LHV) from bioethanol conversion process between the base case and alternatives per one kilogram of bioethanol.	74

FIGURE	PAGE
4.15 Comparison of the energy resources (kJ LHV) from bioethanol conversion process between the base case and alternatives per one megajoule of bioethanol.	75