การออพติไมซ์พลังงานของกระบวนการไฮโครทรีตติ้งสำหรับการผลิตกรีนคีเซลจากน้ำมันปาล์ม



บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR) เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ ที่ส่งผ่านทางบัณฑิตวิทยาลัย

The abstract and full text of theses from the academic year 2011 in Chulalongkorn University Intellectual Repository (CUIR) are the thesis authors' files submitted through the University Graduate School.

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต สาขาวิชาวิศวกรรมเคมี กณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย ปีการศึกษา 2557 ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

ENERGY OPTIMIZATION OF A HYDROTREATING PROCESS FOR GREEN DIESEL PRODUCTION FROM PALM OIL

Miss Suwisa Sae-ueng

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Engineering Program in Chemical Engineering Department of Chemical Engineering Faculty of Engineering Chulalongkorn University Academic Year 2014 Copyright of Chulalongkorn University

Thesis Title	ENERGY OPTIMIZATION OF A
	HYDROTREATING PROCESS FOR GREEN
	DIESEL PRODUCTION FROM PALM OIL
Ву	Miss Suwisa Sae-ueng
Field of Study	Chemical Engineering
Thesis Advisor	Professor Dr. Paisan Kittisupakorn

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

> Dean of the Faculty of Engineering (Professor Dr. Bundhit Eua-arporn)

THESIS COMMITTEE	
	Chairman
(Assistant Professor Dr. Kasidit Nootor	ng)
	Thesis Advisor
(Professor Dr. Paisan Kittisupakorn)	
	Examiner
(Dr. Pimporn Ponpesh)	
	External Examiner
(Dr. Wachira Daosud)	าลัย
Cuura oneroph Univ	

สุวิสา แซ่อึ่ง : การออพติไมซ์พลังงานของกระบวนการไฮโครทรีตติ้งสำหรับการผลิตกรีนคีเซล จากน้ำมันปาล์ม (ENERGY OPTIMIZATION OF A HYDROTREATING PROCESS FOR GREEN DIESEL PRODUCTION FROM PALM OIL) อ.ที่ปรึกษาวิทยานิพนธ์ หลัก: ศ. คร. ไพศาล กิตติศุภกร, 132 หน้า.

้งานวิจัยนี้ได้ศึกษาการผลิตกรีนดีเซลจากน้ำมันปาล์มด้วยกระบวนการไฮโดรทรีตติ้งและการ ้ออพติไมซ์พลังงานในกระบวนการ โดยการจำลองกระบวนการด้วยโปรแกรมแอสเพน พลัส ในส่วนแรก ้จะศึกษากระบวนการผลิตกรีนดีเซลจากน้ำมันปาล์มโดยใช้ตัวเร่งปฏิกิริยานิเกิลโมลิบดินัมซัลไฟด์ที่มี แกมมาอะลูมินาเป็นตัวรองรับ จากการจำลองกระบวนการที่เสนอขึ้นนี้พบว่า ค่าผลได้ของกรีนคีเซล ้ความบริสุทธ์ของกรีนดีเซล การกระจายตัวของผลิตภัณฑ์ที่เป็นของเหลว และอัตราการเกิดปฏิกิริยา ใฮโครคืออกซิจีเนชัน ปฏิกิริยาคีการ์บอนิลเลชัน และปฏิกิริยาคีการ์บอกซิลเลชัน มีแนวโน้มเป็นไปตาม ้ผลการทดลอง โดยมีความกลาดเกลื่อนจากผลการทดลองไม่เกิน 2% นอกจากนี้ยังมีการศึกษาการใช้ พลังงานอย่างเหมาะสมของกระบวนการผลิตกรีนดีเซล การลดพลังงานในกระบวนการผลิตกรีนดีเซลนั้น ้สามารถทำได้โดยการใช้เครือข่ายเครื่องแลกเปลี่ยนความร้อน โดยในการวิจัยนี้ได้ศึกษาการออกแบบ ้เครือข่ายเครื่องแลกเปลี่ยนความร้อนออกเป็นสามกลยุทธ์ โคยในกลยุทธ์ที่หนึ่งสามารถลคพลังงานที่ ต้องการใช้ไปได้ 81.79% และกลยุทธ์ที่สองสามารถลดพลังงานไปได้ 80.73% เมื่อเทียบกับกระบวนการ ที่ไม่มีการใช้เครือข่ายเครื่องแลกเปลี่ยนความร้อน ทั้งสองกลยุทธ์นี้ลดการใช้พลังงานลงแตกต่างกัน 1.07% แสดงให้เห็นว่าลำดับของการแลกเปลี่ยนความร้อนนั้นมีผลต่อการลดการใช้พลังงานเนื่องจาก ้งอบเงตงองความแตกต่างของอุณหภูมิน้อยสุดที่จะสามารถแถกเปลี่ยนความร้อนระหว่างกันได้ เมื่อเทียบ ้กับกลยุทธ์ที่สามซึ่งมีการแยกสายร้อนออกเป็นสามสายก่อนการแลกเปลี่ยนพลังงาน ทำให้พลังงานที่ ต้องการใช้ในกระบวนการลดลงไปถึง 89.35% เมื่อเทียบกับกระบวนการที่ไม่มีการใช้เครื่องแลปเปลี่ยน ้ความร้อน จากผลการจำลองกระบวนการที่กล่าวมาข้างต้น แสดงให้เห็นว่ากลยุทธ์การใช้พลังงานที่สามที่ ้นำเสนอในงานวิจัยนี้เป็นกระบวนการที่มีประสิทธิภาพสำหรับการผลิตกรีนดีเซล เมื่อทำการเปรียบเทียบ รากาก่าก่อสร้างเครือข่ายเกรื่องแลกเปลี่ยนความร้อนและหน่วยสาธารณูปโภคแล้ว พบว่ากลยุทธ์ที่สามนั้น ้มีก่าใช้จ่ายต่อปีน้อยที่สุด ดังนั้นกลยุทธ์ที่สามจึงถือเป็นกลยุทธ์ที่กุ้มก่าต่อการลงทุนมากที่สุด ในกรณีที่ ้เกิดกวามดันถดในกระบวนการ จะส่งผลให้กระบวนการต้องการพลังงานเพิ่มขึ้น โดยพลังงานที่เพิ่มขึ้น ส่วนใหญ่มาจากการใช้เครื่องอัคความคัน

ภาควิชา วิศวกรรมเคมี สาขาวิชา วิศวกรรมเคมี ปีการศึกษา 2557

ลายมือชื่อนิสิต	
ลายมือชื่อ อ.ที่ปรึกษาหลัก	

5570568521 : MAJOR CHEMICAL ENGINEERING

KEYWORDS: ENERGY SAVING / HYDRITREATING PROCESS / SIMULATION / GREEN DIESEL PRODUCTION / HEAT INTEGRATION

SUWISA SAE-UENG: ENERGY OPTIMIZATION OF A HYDROTREATING PROCESS FOR GREEN DIESEL PRODUCTION FROM PALM OIL. ADVISOR: PROF. DR. PAISAN KITTISUPAKORN, 132 pp.

This work focus on the hydrotreating process for green diesel production from palm oil and the energy optimization of the process. The process simulations were performed by using Aspen plus program. The green diesel production process from palm oil by using $NiMoS_2/\gamma$ -Al₂O₃ is considered. The results show that the green diesel yield, green diesel purity, liquid product distribution, hydrodeoxygenation (HDO) and decarbonylation (DCO)/decarboxylation (DCO₂) reactions occurring in the process are good agreement with the experimental data. The tolerance allowed is not more than 2%. In addition, the energy optimization for green diesel production process by using the heat exchanger network is studied. To minimize the energy consumption of the process, the energy optimization is divided into 3 strategies. From the energy optimization strategy 1 and 2, the energy consumption of 81.79% and 80.73% are decreased, respectively. The difference of energy saving of strategy 1 and 2 is 1.07%. Thus, the exchanged heat sequence affects on the energy saving due to the boundary of minimum temperature difference of exchanged hot and cold streams. Based on the energy optimization strategy 3, split hot stream, the energy consumption of 89.36% is decreased when compared with the original process. The results suggest that the energy optimization strategy 3 is very promising process for green diesel production. When comparing the cost of heat exchanger network construction and cost of utilities, the energy optimization strategy 3 has the lowest annual cost. Therefore, the energy optimization strategy 3 is the most worthwhile investment. In case of the pressure drop over the process, the compressor is used to increase the pressure that results in the increasing energy requirement.

Department:Chemical EngineeringField of Study:Chemical EngineeringAcademic Year:2014

Student's Signature	
Advisor's Signature	

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to advisor, Professor Dr. Paisan Kittisupakorn, for his excellent guidance, caring, patience, and providing me with an excellent atmosphere for doing research. I would like to thank Assistant Professor Dr. Kasidit Nootong as the chairman, Dr. Pimporn Ponpesh and Dr. Wachira Daosud as the members of the thesis committee for their kind.

Moreover, I would like to acknowledge The Institutional Research Fund (The Thailand Research Fund), Contract No. IRG5780014 and Chulalongkorn University, Contract No. RES_57_411_21_076 for financial supports.

I take this opportunity to record our sincere thanks to Mr. Jutipong Poosumas and all the faculty members of the Department of Chemical Engineering, Chulalongkorn University for their help and encouragement.

Most of all, I am fully indebted to my parents and family for their love, patience, enthusiasm and for pushing me farther than I thought I could go.

จุหาลงกรณ์มหาวิทยาลัย Chulalongkorn University

CONTENTS

Page
THAI ABSTRACTiv
ENGLISH ABSTRACTv
ACKNOWLEDGEMENTSvi
CONTENTSvii
LIST OF TABLES
LIST OF FIGURESxi
CHAPTER 1 INTRODUCTION 1
1.1 Rationale1
1.2 Objective
1.3 Scope of Work
1.4 Expected Outputs
CHAPTER 2 THEORY
2.1 Green diesel
2.2 Green diesel feedstock
2.2.1 Triglycerides
2.3 Fundamentals of hydroconversion processes
2.3.1 Hydrocracking
2.3.2 Hydrotreating
2.4 The reaction of a hydrotreating of vegetable oils
2.4.1 Hydrodeoxygenation15
2.4.2 Decarboxylation16
2.4.3 Decarbonylation16
2.5 Heat Exchanger Network19
2.5.1 What is heat exchanger network?19
2.5.2 The temperature–enthalpy diagram (T–H)
2.5.3 Heat exchanger network design
CHAPTER 3 LITERATURE REVIEWS
3.1 The hydrotreating of vegetable oils

Page CHAPTER 4 SIMULATION 36
4.1 Green diesel production process by using NiMoS ₂ / y -Al ₂ O ₂ catalyst 36
4.1.1 Experimental studies supporting the process simulation 36
4.1.2 Description of process simulation
4.1.2 Description of a green discal production process
4.2 The energy optimization of a green dieser production process
4.2.1 The energy optimization by using heat exchanger network (HEN)44
4.2.2 Energy comparison between the original process and heat-integrated processes
4.2.3 Effect of the minimum temperature difference (ΔT_{min})
4.2.4 The cost estimation for heat exchanger network
4.2.5 Pressure drop consideration for the green diesel production process 45
CHAPTER 5 RESULTS AND DISCUSSION
5.1 Green diesel production process by using NiMoS ₂ /γ-Al ₂ O ₃ catalyst
5.1.1 Process description
5.2 The energy optimization of a green diesel production process
5.2.1 Energy optimization strategy 157
5.2.2 Energy optimization strategy 2
5.2.3 Energy optimization strategy 371
5.2.4 The effect of minimum temperature difference (ΔT_{min})
5.2.5 The cost estimation for heat exchanger network
5.2.6 Pressure drop consideration for the green diesel production process 89
CHAPTER 6 CONCLUSION AND RECOMMENDATION
6.1 Conclusions
6.2 Recommendations
REFERENCES
APPENDIX A IDEAL HEAT CALCULATION FOR HEAT EXCHANGER
NETWORK
APPENDIX B PRESSURE DROP CALCULATION OF THE PROCESS 113

	Page
APPENDIX C COST ESTIMATION FOR HEAT EXCHANGER	
NETWORK	.124
VITA	.132



จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University

LIST OF TABLES

Table 2.1 The differences between petroleum refinery, first generation fuel and second generation fuel. 4
Table 2.2 Properties of the difference types of renewable diesel
Table 2.3 Typical composition of various vegetable oils
Table 2.4 The typical ΔT_{min} values for various types of processes
Table 3.1 The type of oil, reactor, reaction conditions, catalyst, main products and performance of a hydrotreating of vegetable oil
Table 4.1 The palm oil composition used in the simulation study
Table 5.1 Simulation results of the original process. 49
Table 5.2 Equipment summary for the original process. 52
Table 5.3 Comparison between the original process and experimental data. 53
Table 5.4 Heat exchange stream data for the green diesel production process54
Table 5.5 Equipment summary for the energy optimization strategy 1
Table 5.6 Equipment summary for the energy optimization strategy 269
Table 5.7 Equipment summary for the energy optimization strategy 3
Table 5.8 The comparison of performance for green diesel production process with heat exchanger network (HEN). 79
Table 5. 9 The construction cost and operating cost of each strategy
Table 5. 10 The pressure drop for each equipment. 89
Table A.1 The heat exchange stream data with split streams for the green diesel production process. 107
Table B.1 The safety working fiber stress (S _s) of exchanger tube
Table B.2 The tube size (TEMA Standard)
Table B.3 The maximum tubes contained in shell side of heat exchanger
Table C.1 The construction cost factors for heat exchanger
Table C.2 The pressure factors for heat exchanger
Table C.3 Identification numbers for material factor for heat exchanger
Table C.4 The data for calculated cost of heat exchanger network. 130

LIST OF FIGURES

Page
Figure 2.1 Cetane index of the difference types of renewable diesel
Figure 2.2 Net heating value of difference types of renewable diesel
Figure 2.3 Basic structure of triglyceride (Triolein)10
Figure 2.4 Basic structure of fatty acid (Linolenic acid)10
Figure 2.5 Hydrocracking of gas oil into gasoline and diesel on a bifunctional catalyst. 12
Figure 2.6 The reactions occurring in the hydrotreating of triglycerides
Figure 2.7 The reaction pathways during a hydrotreating of triglycerides in palm oil. 18
Figure 2.8 Two extreme designs of heat exchanger network
Figure 2.9 The effect of driving force and heat load on a capital cost
Figure 2.10 General flow system 22
Figure 2.11 A process stream in the T-H diagram. 25
Figure 2.12 T-H diagram in a single heat exchanger unit
Figure 2.13 The composite curves of a process. 28
Figure 4.1 The green diesel production process 38
Figure 4.2 The process structure of green diesel production
Figure 5.1 The process flow diagram for green diesel production process
Figure 5.2 Grid diagram of hot and cold streams
Figure 5.3 The hot composite curve of the process
Figure 5.4 The cold composite curve of the process
Figure 5.5 The composite curves for hot and cold streams at ΔT_{min} of 20°C56
Figure 5.6 The process flow diagram for energy optimization strategy 1
Figure 5.7 The grid representation of the heat exchanger network for energy optimization strategy 1
Figure 5.8 The energy requirement of the original process and optimization strategy 1
Figure 5.9 The process flow diagram for energy optimization strategy 2

Figure 5.10 The grid representation of the heat exchanger network for energy optimization strategy 2
Figure 5.11 The energy requirement of the original process and optimization strategy 2
Figure 5.12 The process flow diagram for energy optimization strategy 373
Figure 5.13 The grid representation of the heat exchanger network for energy optimization strategy 3
Figure 5.14 The energy requirement of the original process and optimization strategy 3
Figure 5.15 The composite curves for hot and cold streams at ΔT_{min} of 10°C80
Figure 5.16 The composite curves for hot and cold streams at ΔT_{min} of 15°C81
Figure 5.17 The composite curves for hot and cold streams at ΔT_{min} of 25°C81
Figure 5.18 The composite curves for hot and cold streams at ΔT_{min} of 30°C82
Figure 5.19 The comparison between utility requirement and the minimum temperature difference (ΔT_{min})
Figure 5.20 The comparison between heat recovery and the minimum temperature difference (ΔT_{min})
Figure 5.21 The comparison between area of heat exchanger and the minimum temperature difference (ΔT_{min})
Figure 5. 22 The comparison of construction cost for each unit
Figure 5. 23 The comparison of operating cost for each unit
Figure 5. 24 The comparison of cost for heat exchanger network
Figure 5.25 The process flow diagram for energy optimization strategy 1 with pressure drop consideration. 90
Figure 5. 26 The process flow diagram for energy optimization strategy 2 with pressure drop consideration. 92
Figure 5. 27 The process flow diagram for energy optimization strategy 3 with pressure drop consideration
Figure 5. 28 The Comparison of energy between the energy optimization strategy 1 with and without pressure drop
Figure 5. 29 The Comparison of energy between the energy optimization strategy 2 with and without pressure drop

Figure 5. 30 The Comparison of energy between the energy optimization str	ategy
3 with and without pressure drop	97
Figure B. 1 Friction factor of fluid in tube side.	123
Figure B. 2 Friction factor of fluid in shell side	123
Figure C.1 The material factor for process equipment.	127



จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University

CHAPTER 1

INTRODUCTION

1.1 Rationale

The growing demand for fuel results in the development of various alternative energy production. A number of countries are looking for alternative energy production. Many types of clean and renewable energy such as solar, wind, geothermal, hydroelectric and biofuels have been proposed to replace the fossil fuel which has limited supply.

Biofuels, one of a clean and renewable fuel, become more and more important in the past 5-10 years and this tendency is expected to continue (Raldov 2005). Therefore, the development of biofuels, is essential for energy production in the future. Biodiesel or fatty acid methyl esters (FAMEs), a first generation of biofuels, can be produced by the transesterification of triglycerides combined with methanol at a temperature range of 65-100°C (Chen, Gong et al. 2013). However, biodiesel has some downsides compared to petroleum diesel as follows (Jain and Sharma 2010, Liu, Sotelo-Boyás et al. 2011, Shin, Lim et al. 2011):

- Sludge formation after long storage.
- Sensitive to hydrolysis.
- Low thermal and oxidation stability because of its high oxygen content.
- High viscosity.
- Low heating value.

All of the disadvantages mentioned above show that biodiesel is still limited in its use. Therefore, an alternative energy that produced from triglycerides has been developed in various methods.

Green diesel, a second generation of biofuel, has similar molecular structure as petroleum diesel. Green diesel overcome the drawbacks of biodiesel and provide a

better diesel properties. In comparison with biodiesel, the advantages of green diesel are (Mikkonen 2008):

- The green diesel product is compatible with existing engines.
- Flexibility with the feedstock.
- Higher cetane number.
- Higher energy density.
- Higher oxidation stability.
- By-products of the process not require additional treatment.
- Better performance in cold weather.

The green diesel has been produced by a hydrotreating of triglycerides in vegetable oils with hydrogen. The hydrotreating process consists of 3 main reactions which are hydrodeoxygenation (HDO), decarbonylation (DCO) and decarboxylation (DCO₂) (Kubička and Kaluža 2010, Faungnawakij and Suriye 2013). Hydrodeoxygenation (HDO) is an exothermic reaction that removes oxygen in the form of water. Decarbonylation (DCO) and decarboxylation (DCO₂) are endothermic reactions that remove oxygen in form of carbonmonoxide, water and carbondioxide, respectively (Snåre, Kubičková et al. 2006, Gong, Shinozaki et al. 2012).

The hydrotreating process of vegetable oils leads to C_{15} - C_{18} primary hydrocarbon products. The range of reactions' temperature is 300-450 °C and pressure above 30 bar (Huber and Corma 2007, Donnis, Gottschalck et al. 2009). The by-products of process are carbonmonoxide, carbondioxide, propane, ethane, methane and water. The catalyst used in the hydrotreating of triglycerides can be divided in two types (Srifa, Faungnawakij et al. 2014):

- Metal catalysts: nickel (Ni), ruthenium (Ru), rhodium (Rh), platinum (Pt), palladium (Pd). These type are favorable to decarbonylation (DCO) and decarboxylation (DCO₂).
- (2) Bimetallic sulfide catalysts: nickel-molybdenum-sulfide (NiMoS₂) supported on alumina (Al₂O₃), cobalt-molybdenum-sulfide (CoMoS₂) supported on alumina (Al₂O₃), nickel-tungstan-sulfide (NiWS₂) supported on alumina (Al₂O₃). They are favorable to hydrodeoxygenation (HDO).

According to the reasons given above, simulation study is needed to predict a result of the process and improve a process efficiency. The main objective of this work aims to simulate and optimize an energy of a hydrotreating process for green diesel production from palm oil.

1.2 Objective

To design and optimize energy of an efficient hydrotreating process for green diesel production from palm oil.

1.3 Scope of Work

1.3.1 Design a green diesel production process.

1.3.1.1 Design a green diesel production from palm oil by using aspen plus simulator. The purity of product, product composition, product yield, amount of hydrogen excess and energy consumption are considered.

1.3.2 Energy optimization of a green diesel production process.

1.3.2.1 Apply the heat exchanger network to the green diesel production process to minimize the overall energy consumption.

1.3.2.3 Compare the developed hydrotreating process with heat exchanger network with an original process.

1.4 Expected Outputs

An efficient energy optimization for a green diesel production process by using the heat integration is expected.

CHAPTER 2

THEORY

2.1 Green diesel

Green diesel, one of the renewable diesels, is produced from biomass such as vegetable oils and fats via catalytic hydrotreating. The green diesel is called as a second generation fuel. The differences between petroleum refinery, first generation fuel and second generation fuel are presented in Table 2.1 (Naik, Goud et al. 2010).

Table 2.1 The differences between petroleum refinery, first generation fuel and second generation fuel.

	Petroleum	First generation	Second generation	
	refinery	fuel	fuel	
Feedstock	Crude petroleum	- Vegetable oils	- Edible oil	
		- Corn	- Non-edible oil	
		- Sugar	- Cheap and abundant	
			waste biomass	
			(Agricultural & forest	
			residue, grass, aquatic	
			biomass and waste	
			hyacinth etc.)	
Product	- CNG	- Biodiesel (FAMEs)	- Hydrotreating oil	
	- LNG	- Corn ethanol	- Bio-oil	
	- Diesel	- Sugar alcohol	- Lignocellulosic	
			ethanol	
			ethanol	

	Petroleum	First generation	Second generation	
	refinery	fuel	fuel	
Product	- Petrol		- Butanol	
	- Kerosene		- Mixed alcohols	
	- Jet fuel			
Problem	- Declining of	- Limited feedstock	- Advance technology	
	petroleum reserve.	(food versus fuel)	still under development	
	- Environmental	- Blended partly with	to reduce the cost of	
	pollution	conventional fuel.	conversion.	
	- Economics and		- High cost of	
	ecological		production.	
	problems.		- Hardly to produce in	
			larger scale.	
Benefit	- Economical	- Environmental	- Non competing with	
	technology.	friendly.	food.	
	- Fit with mostly	- Economics &	- Environmental	
	present diesel	social security	friendly.	
	engine.		- Economics & social	
			security	

Table 2.1 The differences between petroleum refinery, first generation fuel and second generation fuel. (Continued)

The green diesel can be produced from various vegetable oil such as palm oil, jatropha oil, soybean oil, rapeseed oil via catalytic hydrotreating reaction. The hydrotreating process for green diesel production differences from biodiesel because biodiesel is produced via esterification or transesterification reaction. A green diesel also has a difference physical properties as shown in Table 2.2 (Bezergianni and Dimitriadis 2013).

Analysis	Units	White diesel	FAME diesel	Green diesel	Fossil diesel	Diesel s Min	standard /Max
Density	g/ml	0.79	0.855 - 0.9	0.77 – 0.83	0.85	Min 0.8	Max 0.845
Sulfur	mg/kg (ppmwt)	1.54	0-0.012	<10	12		Max 10
Cetane Index		77.23	58.3	50 - 105	54.57	Min 46	
Cetane number			45 -72.7	80 – 99	50	Min 51	
Flash point	°C	116	96 - 188	68- 102	52 - 136	Min 60	Max 170
Water	mg/kg	13	28.5 - 500	42 - 95	0.5		200
MCRT carbon residue	(wt%) %m/m	0.0066	0.02 - 0.3				Max 0.3
Viscosity at 40°C	cSt	3.5	3.89 - 7.9	2.5 – 4.15	2.71	Min 2	Max 4.5
Copper strip corrosion	(3 h in 50 °C)	1b	1	NIVENSIT	<3	Class 1	-
Color	(ASTM)	0		2			-

 Table 2.2 Properties of the difference types of renewable diesel.

Analysis	Units	White diesel	FAME diesel	Green diesel	Fossil diesel	Diesel st Min/	andard Max
HPLC	%wt (%m/m)			<0.1		<1	1
Induction time (oxidation time) at 110°C	h	>22	0.9 – 10.9	>22		Mi	n 6
Distillation 90 vol%	°C	302.6		298 - 342	341	85 - 360	-
Net heating value	MJ/kg	49	37.1 - 40.4	42 - 44	34.97	Min 35	-
CFPP	°C	20	(-13) – 15	>20	-6	-5	+5
Cloud point	°C		(-3) – 17	(-25) – 30	-5	Min -5	Max 12
Pour point	°C	23	(-15) - 16	(-3) – 29	-21	Min -13	Max 10

Table 2.2 Properties of difference types of renewable diesel. (Continued)

จุฬาลงกรณ์มหาวิทยาลัย

Chulalongkorn University

Green diesel mainly consists of $C_{15} - C_{18}$ n-paraffins and free of aromatics, oxygen and sulfur. A green diesel not only has higher cetane index and cetane number than biodiesel (Figure 2.1) but heating value also higher than conventional diesel (Figure 2.2) (Bezergianni and Dimitriadis 2013).



Figure 2.1 Cetane index of the difference types of renewable diesel.



Figure 2.2 Net heating value of difference types of renewable diesel.

The advantages of green diesel are (Mikkonen 2008):

- The product is compatible with existing engines.
- Flexibility with the feedstock.
- Higher cetane number.
- Higher energy density.
- Higher oxidation stability (zero O₂ content).
- It does not increase the emissions of NO_x.
- It does not require water.
- There are not byproducts that require additional treatment (e.g. glycerol).
- The distribution of the renewable diesel does not cause additional pollution since it can be transported through the same pipelines that are currently used for distribution of petrodiesel.
- Better performance in cold weather.



2.2 Green diesel feedstock

2.2.1 Triglycerides

The main structure of vegetable oils and animal fats found in nature makes up from triglycerides. The triglycerides are high molecular weight compound (around 550 to 1050 g/mol) that composed of long chains of fatty acid esters. The side chains of triglyceride consist of saturated, monounsaturated and polyunsaturated. A structure of triglyceride commonly presents in vegetable oils and fats as shown in Figure 2.3 and a structure of fatty acid commonly presents in vegetable oils and fats as shown in Figure 2.4.



Figure 2.3 Basic structure of triglyceride (Triolein).



Linolenic acid

Figure 2.4 Basic structure of fatty acid (Linolenic acid).

Triglycerides can be classified by saturation degree of their side chains. One of the difference point between fats and oils is a melting point. Fats are solid at an ambient temperature but oils are liquid. Fats and oils have many forms of triglycerides such as saturated, unsaturated acids or isomeric. Saturated oils have higher melting point than unsaturated oils and also have better oxidation stability (Alí, El–Alí et al. 2005).

The composition of triglyceride and fatty acid depends on a type of vegetable oil. Typical composition of various vegetable oils can be summarized in Table 2.3 (Sotelo-Boyás, Trejo-Zarraga et al. 2012).

Source	Struc-	Molecular weight (MW)		Typical composition, wt%				
	ture	Fatty acid	Trigly- ceride	Jatro pha	Palm	Canola	Soy bean	Sun flower
Capric	C _{10:0}	172.3	554.8	0.0	0.0	0.6	0.0	0.0
Lauric	C _{12:0}	200.3	639.0	0.0	0.0	0.0	0.0	0.0
Myristic	C _{14:0}	228.4	723.2	0.0	2.5	0.1	0.0	0.0
Palmitic	C _{16:0}	256.4	807.3	15.9	40.8	5.1	11.5	6.5
Palmi- toleic	C _{16:1}	254.4	801.3	0.9	0.0	0.0	0.0	0.2
Stearic	C _{18:0}	284.5	891.5	6.9	3.6	2.1	4.0	5.8
Oleic	C _{18:1}	282.5	885.4	41.1	45.2	57.9	24.5	27.0
Linoleic	C _{18:2}	280.4	879.4	34.7	7.9	24.7	53.0	60.0
Linolenic	C _{18:3}	278.4	873.3	0.3	0.0	7.9	7.0	0.2
Arachidic	C _{20:0}	312.5	975.6	0.0	0.0	0.2	0.0	0.3
Eicosenoic	C _{20:1}	310.5	969.6	0.2	0.0	1.0	0.0	0.0
Behenic	C _{22:0}	340.6	1059.8	0.0	0.0	0.2	0.0	0.0
Erucic	C _{22:1}	338.6	1053.8	0.0	0.0	0.2	0.0	0.0
		Estimated MW:		869.7	847.0	876.9	871.9	876.7

Table 2.3 Typical composition of various vegetable oils.

Note: C_{n:m} describes a fatty acid with n carbon atoms and m double bonds.

2.3 Fundamentals of hydroconversion processes

Hydroprocessing is an important processes in a refinery scheme that contains a set of reactions in which hydrogen is passed through a bifunctional catalyst. This process is used to convert a variety of petroleum fractions into environmental friendly fuel. The reactions that occur in hydroprocessing can be derived in two main types: hydrocracking and hydrotreating.

2.3.1 Hydrocracking

Hydrocracking is a chemical process that used to convert the high-boiling point hydrocarbons from petroleum fractions to more valuable lower-boiling point hydrocarbons such as gasoline, kerosene, jet fuel and diesel fuel. From a catalytic viewpoint, hydrocracking is carried out on acid supports such as amorphous supports (alumino-silicates), silicoaluminophosphates (SAPO) and crystalline supports (zeolites) (Ancheyta, Trejo et al. 2009). For example, a hydrocracking of gas oil component ($C_{26}H_{54}$) into gasoline (C_8H_{18}) and diesel ($C_{18}H_{38}$) is shown in Figure 2.5.



Figure 2.5 Hydrocracking of gas oil into gasoline and diesel on a bifunctional catalyst.

2.3.2 Hydrotreating

Hydrotreating is used to remove about 90% of impurities such as nitrogen, sulfur, oxygen and metals from liquid petroleum fractions. The hydrotreating can be improved the quality of petroleum distillates without significant alteration of the boiling range. This reactions take place on the metal active sites of a catalyst such as NiMo or CoMo in sulfide state supported on γ -Al₂O₃ (Ancheyta, Trejo et al. 2009). Other catalysts have been used in hydrotreating such as supported noble metal catalysts (Lestari, Ma[•]ki-Arvela et al. 2009) and NiMo/ γ -Al₂O₃ catalyst. The NiMo/ γ -Al₂O₃ is generally used in the hydroprocessing process at petroleum refineries. This catalyst has a high hydrogenation activity and mild acidity and this catalyst also appropriate for the hydroconversion of triglycerides into diesel hydrocarbons (Sotelo-Boyás, Liu et al. 2011).



2.4 The reaction of a hydrotreating of vegetable oils

The hydrotreating process (or hydroprocessing process) is used to increase a hydrogen to carbon ratio. This process reduces the boiling point of petroleum fractions and eliminates metal impurities. For green diesel production, the hydrotreating process is focused to produce an alternative diesel that has the properties like a conventional diesel from petroleum refinery.

The green diesel production can be produced by a hydrotreating of triglycerides through three main reactions: hydrodeoxygenation (HDO), decarboxylation (DCO₂) and decarbonylation (DCO). The triglycerides are converted into primary hydrocarbon products (n-paraffins) and by-products (carbonmonoxide, carbondioxide and water). The reactions occurring in the hydrotreating of triglycerides are shown in Figure 2.6.



Figure 2.6 The reactions occurring in the hydrotreating of triglycerides. (adapted from (Veriansyah, Han et al. 2012))

Where:

n	:	Odd number
x, y, z	:	Number of double bonds
=	:	Double bond
-	:	Single bond

2.4.1 Hydrodeoxygenation

Hydrodeoxygenation (HDO) is a hydrogenolysis process for removing oxygen in the form of water from oxygen organic compounds. The carbon atom number of nalkanes that produced from this reaction are corresponding with fatty acids composition in oil source. Equation (2.1) shows a sample of hydrodeoxygenation that relate on green diesel production process.

$$R = H + 3H_2 \xrightarrow{\text{Hydrodeoxygenation}} R = H + H_2O$$
(2.1)

The thermodynamics data at 300°C for linear C₁₇ hydrocarbons from stearic acid (C₁₇H₃₅COOH) indicate that a Gibbs free energy (Δ G) is -86.1 kJ/mol and a standard enthalpy of reaction (Δ H) is -115.0 kJ/mol. The negative value of standard enthalpy of a reaction is indicated that the hydrodeoxygenation is an exothermic reaction. The hydrodeoxygenation reaction for linear C₁₇ hydrocarbons from stearic acid is shown in Equation (2.2).

Chulalongkorn University

$$C_{17}H_{35}COOH + 3H_2 \xrightarrow{Hydrodeoxygenation} C_{18}H_{38} + 2H_2O$$
(2.2)

2.4.2 Decarboxylation

Decarboxylation (DCO₂) is a chemical reaction that removes a carboxyl group and produces carbondioxide as a by-product. Equation (2.3) shows a sample of decarboxylation that relate on green diesel production process.

$$\begin{array}{c} O \\ R \\ OH \end{array} \xrightarrow{\text{Decarboxylation}} R - H + CO_2 \\ \end{array}$$

$$(2.3)$$

Equation (2.4) shows the decarboxylation reaction of a stearic acid. Thermodynamics data at 300°C for linear C₁₇ hydrocarbons from stearic acid (C₁₇H₃₅COOH) indicate that a Gibbs free energy (Δ G) is -83.5 kJ/mol and a standard enthalpy of reaction (Δ H) is 9.2 kJ/mol. The positive value of standard enthalpy of a reaction is indicated that the decarboxylation is an endothermic reaction.

$$C_{17}H_{35}COOH \xrightarrow{Decarboxylation} C_{17}H_{36} + CO_2$$
(2.4)

2.4.3 Decarbonylation

Decarbonylation (DCO) is a chemical reaction that leads to elimination of oxygen to form alkanes and produces CO and water as by-product. The mechanism of a decarbonylation reaction is shown in Equation (2.5).

$$R \to H + H_2 \xrightarrow{\text{Decarbonylation}} R \to H + CO + H_2O$$
(2.5)

Thermodynamics data at 300°C for linear C_{17} hydrocarbons from stearic acid ($C_{17}H_{35}COOH$) indicate that a Gibbs free energy (ΔG) is -7.0 kJ/mol and a standard enthalpy of reaction (ΔH) is 179.1 kJ/mol. The positive value of standard enthalpy of a reaction is indicated that the decarbonylation is an endothermic reaction. The decarbonylation reaction for linear C_{17} hydrocarbons from stearic acid is shown in Equation (2.6).

$$C_{17}H_{35}COOH + H_2 \xrightarrow{Decarbonylation} C_{17}H_{36} + CO + H_2O$$
(2.6)

All of hydrotreating reactions: hydrodeoxygenation, decarboxylation and decarbonylation have a negative value of a Gibbs free energy at the specified conditions. Thus, all three reactions can be occurred under the thermodynamics principle. However, without catalyst presence in the process, the rate of reactions will be low and reactions may take a longer reaction time (Sotelo-Boyás, Trejo-Zarraga et al. 2012). The catalyst is a substance that increases the rate of chemical reaction. For green diesel production, the catalyst is usually presented in the solid phase that packed inside the reactor. The catalyst plays the important role for a hydrotreating process that specifies the state of main condition in the process (such as temperature, pressure, reaction phase, hydrogen to oil ratio etc).

The general condition for hydrotreating process are 300 to 450°C, pressure above 30 bar. Figure 2.7 shows a probable mechanism in which triglycerides are converted into linear n-paraffins. In this case, the palm oil is considered to be composed by triolein, tripalmitin and trilinolein (Guzman, Torres et al. 2010).



Figure 2.7 The reaction pathways during a hydrotreating of triglycerides in palm oil.

2.5 Heat Exchanger Network

2.5.1 What is heat exchanger network?

A heat exchanger network is one of the method that conserve an energy in the process and minimize an energy requirement from external sources or utilities. A heat exchanger network can transfer heat between the hot and cold streams. The objectives of heat exchanger network can be described as follows:

- To heat and cool process streams from initial temperatures to specified target temperatures.
- To reduce an energy from utilities such as heater and cooler.
- To minimize the number of heating and cooling unit.

The additional heat exchangers for recovering heat from the hot or cold streams would invariably increase the capital cost but it reduce the cost of utilities. Figure 2.8a shows the maximum operating cost and the maximum utility cost. On the other hand, if all the hot and cold streams are used for heating and cooling duties and the utilities take care of only those extreme duties that cannot be met by mutual exchange of heat from the streams as presented in Figure 2.8b, this structure causes the maximum heat recovery at a minimum energy cost, having minimum hot and cold utility requirements. However, this structure has some drawbacks such as higher capital cost, higher process complexity and complicated process start-up.

There is an actual optimum that lies between these two extreme design of heat exchanger network, and the total annual cost should be minimized (total annual cost are the sum of annual utility cost and annualized capital cost such as an annual deterioration, plus interest).

The driving forces and the effects of heat load are two basic thermodynamic effects that influence capital costs, as depicted in Figure 2.9. The capital cost increases with reduced driving forces, but decreases with reduced heat load.



Figure 2.8 Two extreme designs of heat exchanger network (a) Maximum capital cost (b) Maximum heat recovery.



Figure 2.9 The effect of driving force and heat load on a capital cost.

A heat exchanger network is designed to handle the heat available. The hot process streams can be used to meet heating demand and the cold process streams can be used to meet cooling demand. Matching heating and cooling duties in the process streams consequently reduce the hot and cold utilities usage.

The recovery of energy not only improve economy by reducing the energy cost, but also reduce the operating costs. Thus, the heat exchanger network design is a key aspect of chemical process that should be considered to save the energy (Coker 2015).

2.5.2 The temperature-enthalpy diagram (T-H)



Figure 2.10 General flow system

From a general flow system as shown in Figure 2.10, this is one inlet and one outlet stream. The total energy, mass inlet (\dot{m}_{in}) and mass outlet (\dot{m}_{out}) of the system, the general energy balance is:

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W} + \dot{m}_{in} \left(u + \frac{P}{\rho} + \frac{1}{2}V^2 + gz \right)_{in} - \dot{m}_{out} \left(u + \frac{P}{\rho} + \frac{1}{2}V^2 + gz \right)_{out}$$
(2.7)

Where:

 ρ = Fluid density (mass/volume)

The specific enthalpy (energy/mass), h is:

$$h = u + \frac{p}{\rho} \tag{2.8}$$

The energy balance equation becomes:

$$\frac{dE_{sys}}{dt} = \dot{Q} - \dot{W} + \dot{m}_{in} \left(h + \frac{1}{2} V^2 + gz \right)_{in} - \dot{m}_{out} \left(h + \frac{1}{2} V^2 + gz \right)_{out}$$
(2.9)

For steady state operation,

$$rac{dE_{system}}{dt}=0$$
 , $\dot{m}=\dot{m_{in}}=\dot{m}_{out}$

So, the Equation (2.9) after re-arranging becomes:

$$\dot{Q} = \dot{W} + \dot{m} \left[\left(h + \frac{1}{2} V^2 + gz \right)_{out} - \left(h + \frac{1}{2} V^2 + gz \right)_{in} \right]$$
(2.10)

Assuming work done, w, kinetic energy and potential energy of the streams are negligible:

$$\dot{Q} = \dot{m}[h_{out} - h_{in}] = \Delta \dot{H}$$
(2.11)

Where:

$$\Delta \dot{H} = \dot{m}CpdT \tag{2.12}$$

and

$$CP = \dot{m}Cp \tag{2.13}$$
The heat flow through the system is:

$$\dot{Q} = \Delta \dot{H} = CP \cdot dT \tag{2.14}$$

Where:

 $\Delta \dot{H} = \text{Heat content (kW)}.$ CP = Heat capacity flow rate (KW/°C). $dT = \text{Temperature change for stream (°C)} = (T_{out} - T_{in}), (T_{target} - T_{supply}).$

Where CP is assumed to be constant for a stream that requires heating from a supply temperature (T_s) to a target temperature (T_t) . The total heat added will be equal to the stream enthalpy change as shown in Equation (2.15).

$$Q = CP \int_{T_s}^{T_t} dT = CP(T_t - T_s) = \Delta H$$
(2.15)

The differentiation of Equation (2.15) provides the slope of the line representing the stream that shows in Equation (2.16).

$$\frac{dT}{dQ} = \frac{1}{CP}$$
(2.16)

The CP can also be calculated from:

$$CP = \frac{dQ}{dT} = \frac{dH}{dT} = \frac{\Delta H}{(T_t - T_s)}$$
(2.17)

In the heat exchanger, the heat flow is defined by:

$$Q = UA\Delta T_{LMTD} \tag{2.18}$$

Where:

U = Overall heat transfer coefficient (kW/m^2K) .

A = Heat transfer area (m^2) .

 ΔT_{LMTD} = Log mean temperature difference (K).

Figure 2.11 shows that the T-H diagram can be used to represent heat exchange. Where the phase transition occurs, the latent heat is used instead of CP to calculate the stream duties. The energy in term of the latent heat is:

$$\dot{Q} = \dot{m}\lambda \tag{2.19}$$

Where:

 \dot{m} = Mass flow rate (kg/s)

 λ = Latent heat (kJ/kg)



Figure 2.11 A process stream in the T-H diagram.

2.5.3 Heat exchanger network design

2.5.3.1 Minimum temperature difference (ΔT_{min})

For the design of heat exchanger network, the temperature difference between hot and cold stream must greater than ΔT_{min} in every contact point along the length of heat exchanger. ΔT_{min} can be shown in Equation (2.20) and the typical ΔT_{min} values from experience-based (Linnhoff 1998) are shown in Table 2.4.

$$T_H - T_C \ge \Delta T_{min} \tag{2.20}$$

Where:

 T_H = Hot stream temperature.

 T_C = Cold stream temperature.

Table 2.4 The typical ΔT_{min} values for various types of processes.

No.	Industrial Sector	Experience ΔT_{min} values	
1	Oil refining	20-40°C	
2	Petrochemical	10-20°C	
3	Chemical	10-20°C	
4	Low temperature processes	3-5°C	

Figure 2.12 shows the hot stream and cold stream in term of temperature and enthalpy. The minimum temperature difference between hot and cold streams is defined as ΔT_{min} .



Figure 2.12 T-H diagram in a single heat exchanger unit.

Chulalongkorn University

2.5.3.2 Construction of composite curves

The composite curves show the relation between temperature and enthalpy (T-H) that include the enthalpy of hot streams in a process and the enthalpy of cold streams in a process. The enthalpy of hot and cold stream are plotted in the same diagram. Figure 2.13 shows the composite curve in a process. The hot and cold pinch temperature is defined by the closest point between hot and cold composite curve and a middle of hot and cold pinch temperature is called pinch temperature. The ΔT_{min} can be evaluated by the temperature difference between hot pinch temperature and cold pinch temperature. The interception enthalpy of hot composite curve and cold composite curve represent the possibility range that can be recoverd the heat in a process. $Q_{H,min}$ and $Q_{C,min}$ are

the minimum heat required from external utilities. The composite curves can be guided a target of energy recovery and energy added in the process.





จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University

CHAPTER 3

LITERATURE REVIEWS

This chapter showed the review of research that related to the hydrotreating of vegetable oils process with various catalysts.

3.1 The hydrotreating of vegetable oils

The first study about a hydrotreating of vegetable oils was presented by (Nunes 1984). He used rhodium and ruthenium supported catalysts in a batch reactor with soybean oil feedstock. Two years later, (Nunes, Brodzki et al. 1986) reported that the temperature of the hydrotreating of soy bean oil was observed to begin at about 400°C. They used bifunctional catalyst at this temperature and observed the decarbonylation/decarboxylation of fatty acids to take place with a marked hydrogenolysis on a catalyst. The overall conversion is 83 wt% including the gas fraction of carbonmonoxide, carbondioxide, methane, ethane, propane, butane and yielding mainly normal paraffins under favorable conditions of pressure and temperature. Since then, many types of catalysts have been used to crack the long chain of hydrocarbons of vegetable oils to produce short chain of hydrocarbons.

(Charusiri and Vitidsant 2005) worked at a temperature range of 400 to 430°C in a 70 cm³ batch micro-reactor with reaction time from 30 to 90 min over sulfated zirconia catalyst and the range of hydrogen pressures between 10 and 30 bar. They reported that a maximum conversion to gasoline occurred at a lower limit (10 bar). They found that the longer reaction times (than 90 min) favored a light gases and aromatics production. The production of liquid hydrocarbons consisting of gasoline was occurred at high temperature. The conclusion of this research, they found that the initial hydrogen pressure was responsible for the catalytic cracking step. The hydrocracking and hydrogenation were possible for the cracking and rearrangement to yield light

hydrocarbon molecules. In the next year, (Charusiri, Yongchareon et al. 2006) studied about the catalytic conversion of waste cooking vegetable oil at the temperature range of 380 to 430°C and hydrogen pressure about 10 to 20 bar with reaction time from 45 to 90 min. In this case, they used zeolite HZSM-5, sulfated zirconia and a hybrid catalyst HZSM-5-sulfated zirconia. The result showed that the hybrid catalyst provided a higher conversion to gasoline fuel with a yield of 26.57 wt% at 430°C. In the hydrotreating process, the three parallel reactions consisted of hydrogenation, hydrodeoxygenation and decarboxylation of carboxylic acids. The hydrodeoxygenation produced n-paraffins with an even number of carbon atom such as $n-C_{16}$ and $n-C_{18}$. The carbon atom number of n-paraffins corresponded to the side chains of the fatty acids in the triglycerides.

(Hancsók, Krár et al. 2007) studied the isomerization of pre-hydrogenated sunflower oil for diesel production. In this case, they used Pt/HZSM-22/ γ -Al₂O₃ catalysts over catalysts containing 0.25–1.1% platinum on HZSM-22. They worked at temperatures of 280 to 370°C, total pressures of 35 to 80 bar and liquid hourly space velocities (LHSV) of 1.0 to 4.0 h⁻¹. They found a yield of liquid products higher than 90% with cold filter plugging point (CFPP) in between -18 and -14°C, the range of cetane number between 81–84 and the ratio of iso-paraffins to n-paraffins was in the range of 3.7:1–4.7:1 under favorable conditions. This catalyst provided a good quality of green diesel fuel. The green diesel from this experiment not only provided a high cetane number, but also provided a low freezing point.

Some studies conducted by (Nasikin, Susanto et al. 2009), the production of biogasoline from palm oil by simultaneous cracking and hydrogenation reactions over NiMo/zeolite catalyst. The experiment used a batch reactor with atmospheric pressure in presence of hydrogen, temperature at 300 and 320°C, a feed per catalyst ratio of 75 wt/wt with the reaction times were 1, 1.5 and 2 hours for each temperature. The experimental result produced biogasoline that contained C_8 to C_{10} with a volumetric yield of 11.93%. The green diesel was obtained with 13.1% volumetric yield. In the same year, (Simacek, Kubicka et al. 2009) worked at various temperature between 260 to 340°C, pressure under 70 bar in a laboratory continuous flow reactor. The hydrotreating of rapeseed oil can be converted into diesel fuel with using a different

concentrations of NiO and MoO_3 of three NiMo/alumina catalysts (such as A (3.8 and 15.7 wt%), B (2.6 and 15.7 wt%) and C (2.6 and 8.8 wt%)), respectively. An organic liquid product was obtained only hydrocarbons as same as diesel fuel compositions that found in the nature.

In 2010, (Kikhtyanin, Rubanov et al. 2010) tested siliconaluminophosphates materials (SAPO) in the hydroconversion of sunflower oil on Pd/SAPO-31 catalysts. They used a bifunctional catalysts for single-stage production of hydrocarbons in the diesel fuel range. A sunflower oil transformed to hydrocarbons product at a temperature between 320 to 360° C. The main product components were identified as C₁₇ and C₁₈ n-paraffins and iso-paraffins. The catalyst exhibited a high initial activity for the hydroconversion of the feed and provided a good isomerization activity, but this catalyst deactivation occurred after several hours of operation.

(Murata, Liu et al. 2010) studied a renewable green diesel (alkanes type) by hydrotreated a jatropha oil at standard hydrotreating conditions (temperature of 270 to 300°C and pressure of 20 bar) with Pt/H-ZSM-5 and rhenium-modified Pt/H-ZSM-5 catalysts. The production of hydrocarbons (C_{15} – C_{18} paraffins) cannot produced by the non-modified Pt/H-ZSM-5 catalysts at a high oil per catalyst ratio but the rheniummodified Pt/H-ZSM-5 catalysts were found more effective for a hydrotreating of jatropha oil process at a high oil per catalyst ratio of 10. The conversion was up to 80% and the selectivity of C_{18} was up to 70%. The deoxygenation activity of a catalyst was improved with the addition of rhenium.

(Sotelo-Boyás, Liu et al. 2011) worked about the hydrocracking of rapeseed oil on three different types of a bifunctional catalysts are Pt/H-Y, Pt/H-ZSM-5 and sulfide NiMo/ γ -Al₂O₃. They worked at a temperature range of 300 to 400°C and an initial hydrogen pressure from 50 to 110 bar in a batch reactor. To prevent a high degree of cracking, the reaction time was limited to 3 hours. Among the three catalysts, NiMo/ γ -Al₂O₃ gave a highest yield of liquid hydrocarbons in the boiling range of diesel fraction and provided mainly n-paraffins from C₁₅ to C₁₈. Therefore, this catalyst produced a diesel with high cetane number but poor cold flow properties. The both zeolitic catalysts produced more iso-paraffins than n-paraffins in the boiling range of C₅ to C₂₂. The Ptzeolite catalysts had a strong catalytic activity for cracking and hydrogenation reactions.

(Liu, Sotelo-Boyás et al. 2011) studied about the production of biohydrogenated diesel from a hydrotreating of vegetable oils using Ni-Mo based catalysts in a high pressure fixed bed flow reactor at the temperature of 350° C under hydrogen pressure at 40 bar. They used a jatropha curcas L. oil as a feedstock and converted into paraffins by one step hydrotreatment process. The production of hydrocarbons had a high melting point and poor cold properties (a pour point higher than 20° C). The Ni-Mo based catalysts supported on zeolites (such as Ni-Mo/H-Y or Ni-Mo/H-ZSM5) produced a large amount of gasoline hydrocarbons. The Ni-Mo/SiO₂ catalyst favored n-C₁₈H₃₈, n-C₁₇H₃₆, n-C₁₆H₃₄ and n-C₁₅H₃₂ production.

In the next year, (Liu, Sotelo-Boyás et al. 2012) worked on the production of bio-hydrogenated diesel by hydrotreatment of high-acid-value waste cooking oil over ruthenium catalyst supported on Al-polyoxocation-pillared montmorillonite at the temperature of 350°C and hydrogen pressure at 20 bar. The triglycerides and free fatty acids in waste cooking oil concurrently deoxygenated. The main products were n- $C_{18}H_{38}$, n- $C_{17}H_{36}$, n- $C_{16}H_{34}$ and n- $C_{15}H_{32}$ with a conversion of 98.9 wt%

A cleaner process for hydrocracking of jatropha oil into green diesel was presented by (Liu, Liu et al. 2013). They used a new green Ni-HPW/Al₂O₃ catalyst in a fixed-bed reactor. They worked on the reaction conditions at 360°C, pressure of 33 bar, liquid hourly space velocity (LHSV) of 1 h⁻¹ and hydrogen per oil ratio of 600 Nm³/m³. The experiment observed that the higher reaction temperatures favored the decarboxylation and decarbonylation reactions in a hydrotreating process and favored an oxygen removal from the products. A jatropha oil was transformed into hydrocarbons with a conversion of 99.85% and a selectivity of 85.52% of n-C₁₅ to n-C₁₈ fractions. The new Ni-HPW/Al₂O₃ catalyst had great potential for green diesel production.

A commercially-viable, one-step process for green diesel production from soybean oil on Pt/SAPO-11 catalyst was conducted by (Herskowitz, Landau et al. 2013). In this experiment a trickle-bed reactor was used. They worked on the temperature of 375 to 380°C, hydrogen pressure of 30.4 bar (30 atm) and liquid hourly space velocities (LHSV) of 1 h⁻¹. The steady-state operation was reached after about 150 hours. The renewable diesel fuel (isodiesel) that produced in this study was improved the properties. The catalyst performed a hydrodeoxygenation to water, decarboxylation to carbondioxide and decarbonylation to carbonmonoxide. The result of this study were measured over the period of 150 to 650 hours. The organic liquid and water yield varied over a narrow range of 85–86 wt% and 7–8 wt%, respectively.

(Srifa, Faungnawakij et al. 2014) studied the production of bio-hydrogenated diesel by catalytic hydrotreating of palm oil over NiMoS₂/ γ -Al₂O₃ catalyst in continuous flow fixed bed reactor. They found the optimal hydrotreating conditions from the temperature of 270 to 420°C, hydrogen pressure of 15 to 80 bar, liquid hourly space velocity (LHSV) of 0.25 to 5 h⁻¹ and hydrogen per oil ratio of 250 to 2000 Nm³/m³. The greatest of hydrotreating conditions were: temperature at 300°C, pressure of 30 to 50 bar, liquid hourly space velocity (LHSV) of 1 to 2 h⁻¹ and hydrogen per oil ratio of 750 to 1000 Nm³/m³. The result of this experiment provided 90.0% of product yield and more than 95.5% of n-alkanes content. The main compositions of liquid product were the n-alkane of C₁₆ and C₁₈. The NiMoS₂/ γ -Al₂O₃ catalyst had a high selective hydrodeoxygenation reaction. They found that the temperature strongly affected to the reaction pathways while the higher hydrogen pressure favored a hydrodeoxygenation reaction.

In addition, there are many research about a hydrotreating of vegetable oil in the different oil sources, reactor type, reaction conditions, catalysts, main products and performance were summarized in Table 3.1.

Table 3.1 The type of oil, reactor, reaction conditions, catalyst, main products and performance of a hydrotreating of vegetable oil

(Adapted from several references).

O il	Dogetor	Reaction		Main		
source	type	conditions	Catalyst	products	Performance	Ref.
Soybean	Batch	T=400°C	NiMo/	C15-C18	Conversion:92.9%	(Veriansyah,
		P=9.2MPa	γ -Al ₂ O ₃	n-paraffins	Yield C ₁₅ -C ₁₈ :	Han et al. 2012)
		t=1 h			64.45 wt %	
		Cat./oil weight	Pd/y-Al ₂ O ₃	C15-C17	Conversion:91.9%	_
		ratio = 0.044, 0.088		n-paraffins	Yield C ₁₅ -C ₁₇ :	
					79.22 wt%	
			CoMo/	C15-C17	Conversion:78.9%	_
			γ -Al ₂ O ₃	n-paraffins	Yield C ₁₅ -C ₁₇ :	
					33.67 wt%	
			Ni/	C15-C17	Conversion:60.8%	_
			Al ₂ O ₃ -SiO ₂	n-paraffins	Yield C ₁₅ -C ₁₇ :	
					39.24 wt%	
			Pt/y-Al ₂ O ₃	C15-C17	Conversion:39.7%	_
				n-paraffins	Yield: 32.00 wt%	
			Ru/y-Al ₂ O ₃	C15-C17	Conversion:39.7%	_
				n-paraffins	Yield: 32.00 wt%	
	Batch	T=350°C	Ni/Al ₂ O ₃	\geq C ₁₈	Conversion: 68%	(Morgan, Santillan-
		P=0.7 MPa			$Yield \ge C_{18}:$	Jimenez et
		t=4 h			51.20 wt%	al. 2012)
		Stirring rate =	NiAl/LDH	C8-C17	Conversion :74%	_
		1000 rpm			Yield C ₈ -C ₁₇ :	
					52.90 wt%	
			MgAl/LDH	C8-C17	Conversion: 72%	_
					Yield C ₈ -C ₁₇ :	
					47.80 wt%	

Table 3.1 The type of oil, reactor, reaction conditions, catalyst, main products andperformance of a hydrotreating of vegetable oil

Oil	Reactor	Reaction		Main	D 4	D (
source	type	conditions	Catalyst	products	Performance	Kef.
Rapeseed	Fixed bed	T=340°C	NiMo/	C ₁₅ -C ₁₈	Conversion:93%	(Mikulec, Cyengroš et
		P=4.0 MPa	γ -Al ₂ O ₃	n-paraffins	Yield C ₁₅ -C ₁₈	al. 2010)
		LHSV=1 h-1			n-paraffins:	
		H ₂ /oil ratio =			54.52 wt%	
		500-1000 Nm ³ /m ³				
Sun-	Fixed	T=350-370°C	NiMo/	C15-C18	Yield:	(Kovacs, Kasza et al
flower	bea	P=2-4 MPa	Al ₂ O ₃ -F	n-paraffins	73.2-75.6 wt%	2011)
		LHSV=1.0 h ⁻¹				
		H ₂ /oil ratio=				
		500 Nm ³ /m ³				
	Fixed bed	T=380°C	CoMo/Al ₂ O ₃	C14-C19	Conversion: 100%	(Krár, Kovacs et
		P=4-6 MPa		n-paraffins	Yield: 73.7-73.9%	al. 2010)
		LHSV=1.0 h ⁻¹				
		H ₂ /oil ratio=				
		500-600 Nm ³ /m ³				
Palm	Fixed	T=350°C	NiMo/Al ₂ O ₃	C16-C18	Molar yield: 100%	(Guzman, Torres et al
	(nilot	P=4-9 MPa		n-paraffins		2010)
	(pilot	LHSV=2 h ⁻¹				
	Plant)	TOS=0-14 days				

(Adapted from several references). (Continued)

CHAPTER 4

SIMULATION

The simulation of green diesel production was performed using Aspen Plus program. The procedures of the process simulation consist in defining chemical components and thermodynamical models, selecting and specifying operating equipment and operating conditions. The pseudo simulating components were created by UNIFAC thermodynamic properties. The UNIFAC model was used to predict some binary interaction parameters that were not available in a databank of the simulation.

The simulation study is divided into two main parts. Firstly, the green diesel production process from palm oil by using NiMoS₂/ γ -Al₂O₃ catalyst will be designed. Second, the energy optimization of a green diesel production process will be designed.

4.1 Green diesel production process by using NiMoS₂/γ-Al₂O₃ catalyst

In this work, we studied the green diesel production from the hydrotreating of palm oil and hydrogen with $NiMoS_2/\gamma$ -Al₂O₃ catalyst. Mass and energy balance for each unit, as well as operating conditions, were obtained. The existing pressure drop in different equipment was neglected in the present study.

4.1.1 Experimental studies supporting the process simulation

The simulation study was based on an experimental of (Srifa, Faungnawakij et al. 2014). They investigated the catalytic hydrotreating of palm oil over NiMoS₂/ γ -Al₂O₃ catalyst at various temperatures (270, 300, 330, 360, 390, 420°C), pressures (15, 30, 50, 80 bar), and hydrogen per oil ratios (250, 500, 750, 1000, 1500, 2000 N(cm³/cm³)). The continuous flow fixed bed reactor was used to produce a green diesel. Their results showed that a good quality green diesel was produce at 300°C, with pressure of 30 bar, a 1000 N(cm³/cm³) of hydrogen per oil ratio. The effect of dominant

hydrotreating parameters (temperature, pressure, hydrogen per oil ratio) can be described as follows:

(1) Effect of hydrotreating temperature

The reaction temperature has been identified as one of dominant parameters on the catalyst performance and catalyst deactivation (Yang, Wang et al. 2013). In this section, they studied the effect of temperature in the range of 270 to 420°C with a fixed other operating condition. At the temperature of 270°C, the organic liquid product became solidified at room temperature. Their result was consistent to those of (Simacek, Kubicka et al. 2009). The increasing temperature from 270 to 300°C increased the product yield. On the other hand, the promotion of isomerization, cracking and cyclization reactions were occurred at the temperature of 330 to 420°C. At 330 to 420°C, the product yield was decreased. The results confirmed that the hydrotreating temperature of 300° C was successful to convert triglyceride to n-alkane for palm oil via NiMoS₂/ γ -Al₂O₃ catalyst.

(2) Effect of hydrotreating pressure

The pressure was strong effect to deoxygenation, isomerization and cracking reactions. At the pressure of 15 bar, the liquid product remained small amount of fatty acids that indicated the incomplete transformation of free fatty acids to n-alkane. The low conversion was observed at the pressure of 20 bar similarly to (Kubic ka, Šimác ek et al. 2009) and (Anand and Sinha 2012). The increasing pressure from 15 to 80 bar slightly increased the product yield. The pressure did not significant effect on the conversion of triglycerides.

(3) Effect of hydrogen per oil ratio

The hydrogen per oil ratio defines to the ratio of hydrogen feed to the liquid feed. The hydrogen per oil ratio showed a small impact on the conversion. The increasing hydrogen per oil ratio from 250 to 1500 N(cm³/cm³) improved the product yield. At the hydrogen per oil ratio of 250 N(cm³/cm³), the product was separated into two layer at room temperature. However, the hydrogen per oil ratio of 2000 N(cm³/cm³)

reduced the product yield due to the decreasing of decarbonylation (DCO) and decarboxylation (DCO₂) reactions.

Hydrodeoxygenation (HDO) was a major reaction pathway, whereas decarbonylation (DCO) and decarboxylation (DCO₂) were minor reaction pathways. The palm oil use in their experiment was composed mainly C_{16} and C_{18} fatty acids. Therefore, the main composition of liquid products were C_{16} and C_{18} n-alkane due to high selective hydrodeoxygenation reaction of NiMoS₂/ γ -Al₂O₃ catalyst.

4.1.2 Description of process simulation

The green diesel production process will be designed under the theoretical concepts and computational methods that describe, represent and simulate the functioning of real-world process.

The green diesel production is produced by the hydrotreating process of palm oil with hydrogen via $NiMoS_2/\gamma$ -Al₂O₃ catalyst. The hydrotreating process for green diesel production is shown in Figure 4.1.



Figure 4.1 The green diesel production process

The simulation study can be divided into four main parts that consists of reactor feed preparation system, reactor system, phase separation system and recycle system. Figure 4.2 shows the process structure of green diesel production (Turton, Bailie et al. 2009).



Figure 4.2 The process structure of green diesel production

(1) Reactor feed preparation system

The reactor feed preparation system provides the suitable operating conditions (temperature, pressure, phase etc.). This section also mix the multiple feed streams and/or recycle streams before feeding to the reactor. The green diesel production process is produced by palm oil and hydrogen. The palm oil and hydrogen used in this process are adjusted temperature and pressure as required in the reactor. The palm oil composition used in this simulation is described by its content of fatty acids as it is shown in Table 4.1.

Component	Name of component	Mass fraction
FFA FFA1 C16:0	Palmitic acid	42.2%
FFA2 C18:1	Oleic acid	46.3%
FFA3 C18:2	Linoleic acid	11.5%

Table 4.1 The palm oil composition used in the simulation study

(2) Reactor system

The palm oil and hydrogen from the reactor feed preparation system are mixed and fed into a fixed bed reactor with the suitable operating conditions. In this section, the reaction temperature, pressure and hydrogen per oil ratio will be considered.

The reactions occurred in the reactor are divided into two parts. Firstly, the triglycerides are converted to fatty acids. Second, the fatty acids are converted to n-alkanes. In this work, the palm oil is considered to be composed by trilinolein, tripalmitin and triolein. As first step, free fatty acids are formed by scission of propane from the glycerol backbone of the triglyceride molecules in presence of hydrogen. The three moles of linoleic acid, palmitic acid and oleic acid are formed. In the second step, the unsaturated fatty acids are converted to saturated fatty acids by the hydrogenation. Then, the hydrodeoxygenation (HDO), decarbonylation (DCO) and decarboxylation (DCO₂) are occurred to eliminate oxygen. The hydrodeoxygenation (HDO) removes the oxygen. This reaction keeps the same carbon atoms as in the original fatty acids whereas the decarbonylation (DCO) and decarboxylation (DCO₂) form n-alkane that have one carbon atom less than the original fatty acids. All of reactions for the green diesel production process are shown in Equations (4.1) to (4.12).

$$C_{57}H_{98}O_6 + 3H_2 \leftrightarrow 3C_{17}H_{31}COOH + C_3H_8 \tag{4.1}$$

(Trilinolein + Hydrogen \leftrightarrow Linoleic acid + Propane)

$$C_{51}H_{98}O_6 + 3H_2 \leftrightarrow 3C_{15}H_{31}COOH + C_3H_8 \tag{4.2}$$

(Tripalmitin + Hydrogen \leftrightarrow Palmitic acid + Propane)

$$C_{57}H_{104}O_6 + 3H_2 \leftrightarrow 3C_{17}H_{33}COOH + C_3H_8 \tag{4.3}$$

(Triolein + Hydrogen \leftrightarrow Oleic acid + Propane)

$$C_{17}H_{31}COOH + 2H_2 \leftrightarrow C_{17}H_{35}COOH$$
 (4.4)

(Linoleic acid + Hydrogen \leftrightarrow Stearic acid)

$$C_{17}H_{33}COOH + H_2 \leftrightarrow C_{17}H_{35}COOH$$
 (4.5)

$$C_{15}H_{31}COOH + 3 H_2 \leftrightarrow C_{16}H_{34} + 2 H_2O$$
(4.6)

(Palmitic acid + Hydrogen \leftrightarrow Hexadecane + Water)

$$C_{17}H_{35}COOH + 3 H_2 \leftrightarrow C_{18}H_{38} + 2 H_2O \tag{4.7}$$

(Stearic acid + Hydrogen
$$\leftrightarrow$$
 Octadecane + Water)

$$C_{15}H_{31}COOH + H_2 \leftrightarrow C_{15}H_{32} + H_2O + CO \tag{4.8}$$

(Palmitic acid + Hydrogen \leftrightarrow Pentadecane + Water + Carbonmonoxide)

$$C_{17}H_{35}COOH + H_2 \leftrightarrow C_{17}H_{36} + H_2O + CO$$
(4.9)

(Stearic acid + Hydrogen ↔ Heptadecane + Water + Carbonmonoxide)

$$C_{15}H_{31}COOH \leftrightarrow C_{15}H_{32} + CO_2$$
 (4.10)

(Palmitic acid \leftrightarrow Pentadecane + Carbondioxide)

$$C_{17}H_{35}COOH \leftrightarrow C_{17}H_{36} + CO_2$$
 (4.11)

(Stearic acid \leftrightarrow Heptadecane + Water + Carbonmonoxide)

$$C_3H_8 + H_2 \leftrightarrow CH_4 + C_2H_6$$
 (4.12)
(Propane + Hydrogen \leftrightarrow Methane + Ethane)

Where:

Equations (4.1) to (4.3) are the hydrogenolysis reaction. Equations (4.4) to (4.5) are the hydrogenation reaction. Equations (4.6) to (4.7) are the hydrodeoxygenation reaction (HDO). Equations (4.8) to (4.9) are the decarbonylation reaction (DCO). Equations (4.10) to (4.11) are the decarboxylation reaction (DCO₂). Equation (4.12) is the side reaction.

(3) Phase separation system

All of components from the reactor are separated by phase separation system. In this section, the various compounds can be separated from each other by phase separator. In the green diesel production process, all of product from the reactor can be defined as a gases (carbonmonoxide, carbondioxide, methane, ethane, propane, hydrogen), a polar liquid (water) and non-polar liquid (green diesel). As the first step, the gases and liquids will be separated. In the second, the polar and non-polar liquid will be separated. The purity of green diesel, the product yield and the distribution of hydrodeoxygenation (HDO), decarbonylation (DCO) and decarboxylation (DCO₂) are defined in Equations (4.13) to (4.16), respectively.

$$Purity (\%) = \frac{Mass of n-alkane (n-C_{15}to n-C_{18}) in product stream}{Total mass in product stream} \times 100$$
(4.13)

Product yield (%) =
$$\frac{\text{Total mass of } n-\text{alkane} (n-C_{15} \text{to } n-C_{18}) \text{ in product}}{\text{Total mass of fatty acid } (C_{15} \text{to } C_{18}) \text{ in feed}} \times 100 \quad (4.14)$$

$$HDO(\%) = \frac{Total \ mol \ of \ n-alkane \ (n-C_{16} and \ n-C_{18}) \ in \ product}{Total \ mol \ of \ fatty \ acid \ (C_{15} to \ C_{18}) \ in \ feed} \times 100$$
(4.15)

$$DCO/DCO_2 (\%) = \frac{Total \ mol \ of \ n-alkane \ (n-C_{15} \ and \ n-C_{17}) \ in \ product}{Total \ mol \ of \ fatty \ acid \ (C_{15} \ to \ C_{18}) \ in \ feed} \times 100$$
(4.16)

(4) Recycle system

The recycle system is used to recycle the excess hydrogen. In this work, the recycle system increases a hydrogen volume that corresponding with hydrogen per oil ratio required in the green diesel production process.

In some case, the unit operations such as heater, cooler, pump and compressor are required to recondition the recycle stream before feeding to the reactor feed preparation system.

4.2 The energy optimization of a green diesel production process

The energy consumption is one of the key factor in various industrial process that affects to operating cost. Thus, the energy optimization must be considered.

4.2.1 The energy optimization by using heat exchanger network (HEN)

In this section, the heat exchanger network (HEN) is used to minimize the energy consumption. A heat exchanger network is designed to handle the heat available. The hot process streams can be used to meet heating demand and the cold process streams can be used to meet cooling demand. Matching heating and cooling duties in the process streams consequently reduce the hot and cold utilities usage. A heat exchanger network can improve the energy efficiency of green diesel production process.

4.2.2 Energy comparison between the original process and heat-integrated processes

This section will compare the energy consumption of the original process and heat-integrated processes. The energy consumption of each processes will be summarized and analyzed the energy saving efficiency.

4.2.3 Effect of the minimum temperature difference (ΔT_{min})

The minimum temperature difference (ΔT_{min}) affects to the heat recovery, cold utility requirement and hot utility requirement of the process. This section will compare the minimum temperature difference (ΔT_{min}) from 10°C to 30°C.

4.2.4 The cost estimation for heat exchanger network

A number of heat exchanger affect to the investment of the process. This section will compare the construction and operation cost of original process, energy optimization strategy 1, 2 and 3.

4.2.5 Pressure drop consideration for the green diesel production process

The pressure drop affects to the required energy of the process. The comparison between the green diesel production process with and without pressure drop will be considered.



CHAPTER 5

RESULTS AND DISCUSSION

In this chapter, the results and discussion of simulation studies of green diesel production is presented. The processes were simulated by using Aspen Plus program. From this simulation studies, the results of product purity, product composition, product yield and energy requirement are interested. This simulation study is divided into two main parts that consist of the green diesel production process by using NiMoS2/ γ -Al₂O₃ catalyst and the energy optimization of a green diesel production process by heat exchanger network (HEN).

5.1 Green diesel production process by using NiMoS₂/γ-Al₂O₃ catalyst

5.1.1 Process description

The process flow diagram for a green diesel production process is shown in Figure 5.1, in which 200,000 metric tons per year of green diesel is produced. Due to the simplicity of the process, an operating factor greater than 0.91 (8,000 hours per year) is used.

A palm oil, Stream 1, which consists of trilinolein 11.5 wt%, tripalmitin 42.2 wt% and triolein 46.3 wt% is pumped to 30 bar by P-101 and heated to 300°C by H-101, respectively. A hydrogen, Stream 4, is reduced pressure to 30 bar by V-101 and heated to 300°C by H-102. Both stream (palm oil and fresh hydrogen) are mixed with recycled hydrogen, Stream 18. The hydrogen per oil ratio before fed to the reactor is 1000:1 by volume. After that, the palm oil and hydrogen is fed to the reactor, R-201.

The reactor, R-201, is fixed bed reactor that operated isothermally at the temperature of 300°C and pressure of 30 bar. The hydrogenolysis, hydrogenation, hydrodeoxygenation (HDO), decarbonylation (DCO), decarboxylation (DCO₂) and

side reaction are occurred. The product from reactor is cooled by H-301 before fed to flash drum, D-301.

The flash drum, D-301, is used to separate gases and liquid product. The gases, Stream 10, consist of unreacted hydrogen and light gas (methane, ethane, carbonmonoxide, carbondioxide). The gases of 99.5 wt% are recycled back to the front end of the process. The liquid product, Stream 11, is degased by expansion, EP-301, before sent to flash drum, D-302, to remove trace amounts of light gases. The liquid product from flash drum, D-302, is sent to decanter to separate primary product (nonpolar liquid phase) and water (polar liquid phase).

Stream summaries, equipment summaries are presented in Tables 5.1 to 5.2, respectively.





Figure 5.1 The process flow diagram for green diesel production process.

	1	2	3	4	5	6	7
Temperature (°C)	30.00	31.00	300.00	30.00	34.40	300.00	300.10
Pressure (bar)	1.01	30.00	30.00	138.00	30.00	30.00	30.00
Vapor fraction	0.00	0.00	0.00	1.00	1.00	1.00	0.998
Mass flow (kg/hr)	29399.70	29399.70	29399.70	1067.37	1067.37	1067.37	253535.38
Volume flow	17.05	17.06	22.25	105 02	450.20	850 05	25800 11
(cum/hr)	17.95	17.90	25.55	105.05	439.30	830.03	55800.44
Enthalpy (Gcal/hr)	-18.16	-18.14	-13.73	0.04	0.04	1.02	-177.01
Mass flow (kg/hr)							
H_2	0	0	0	1067.37	1067.37	1067.37	29486.76
СО	0	0	0	0	0	0	54129.93
CH_4	0	0	0	0	0	0	46494.93
C_2H_6	0	0	0	0	0	0	61958.94
CO_2	0	0	0	0	0	0	30217.67
C_3H_8	0	0	0	0	0	0	0
H_2O	0	0	0	0	0	0	1844.03
$C_{15}H_{32}$	0	0	0	0	0	0	1.20
$C_{16}H_{34}$	0	0	0	0	0	0	1.63
$C_{17}H_{36}$	0	0	0	0	0	0	0.24
$C_{18}H_{38}$	0	0	0	0	0	0	0.35
$C_{16}H_{32}O_2$	0	0	0	0	0	0	0
$C_{18}H_{32}O_2$	0	0	0	ยาลย 0	0	0	0
$C_{18}H_{34}O_2$	0	0	ORN U 0	VERSIT ₀	0	0	0
TG2	12409.79	12409.79	12409.79	0	0	0	12409.79
TG1	3379.39	3379.39	3379.39	0	0	0	3379.39
TG3	13610.52	13610.52	13610.52	0	0	0	13610.52

 Table 5.1 Simulation results of the original process.

Table 5.1 Simulation results of the original process. (Continued)

	8	9	10	11	12	13	14
Temperature (°C)	300.00	50.00	50.00	50.00	39.90	39.90	39.90
Pressure (bar)	30.00	30.00	30.00	30.00	1.01	1.01	1.01
Vapor fraction	1.00	0.985	1.00	0.00	0.156	1.00	0.00
Mass flow (kg/hr)	253535.38	253535.38	224145.18	29390.20	29390.20	1369.29	28020.91
Volume flow (cum/hr)	35623.49	19732.09	19689.40	42.70	1360.18	1323.42	36.76
Enthalpy (Gcal/hr)	-182.30	-237.10	-212.17	-24.93	-24.93	-1.676	-23.31
Mass flow (kg/hr)							
H_2	0	0	0	0	0	0	0
СО	28558.61	28558.61	28558.61	< 0.001	< 0.001	< 0.001	trace
CH ₄	54456.88	54456.88	54395.38	61.50	61.50	60.36	1.14
C_2H_6	47049.77	47049.77	46716.43	333.34	333.34	297.30	36.04
CO_2	62998.92	62998.92	62264.11	734.81	734.81	615.33	119.48
C_3H_8	30731.38	30731.38	30354.17	377.21	377.21	315.17	62.04
H ₂ O	0	0	0	0	0	0	0
$C_{15}H_{32}$	4951.57	4951.57	1853.04	3098.53	3098.53	81.02	3017.51
$C_{16}H_{34}$	2205.18	2205.18	1.21	2203.98	2203.98	0.04	2203.94
C ₁₇ H ₃₆	8094.41	8094.41	1.64	8092.78	8092.78	0.05	8092.74
C ₁₈ H ₃₈	3119.06	3119.06	0.24	3118.82	3118.82	0.01	3118.82
$C_{16}H_{32}O_2$	11369.59	11369.59	0.35	11369.24	11369.24	0.01	11369.25
$C_{18}H_{32}O_2$	0	0	0	0	0	0	0
$C_{18}H_{34}O_2$	0	0	0	0	0	0	0
TG2	0	0	0	0	0	0	0
TG1	0	0	0	0	0	0	0
TG3	0	0	0	0	0	0	0

15 19 16 17 18 39.90 39.90 50.00 300.00 50.00 Temperature (°C) 1.01 1.01 30.00 30.00 30.00 Pressure (bar) 0.00 0.00 1.00 1.00 1.00 Vapor fraction 25000.38 3020.53 223068.31 223068.31 1076.87 Mass flow (kg/hr) Volume flow 33.66 3.10 19594.81 34924.58 94.59 (cum/hr) -1.02 -11.88 -11.43 -211.15 -164.31 Enthalpy (Gcal/hr) Mass flow (kg/hr) 0 0 0 0 0 H_2 28421.41 28419.40 137.21 CO trace trace 0.90 0.24 54134.05 54129.93 261.33 CH_4 46491.99 35.10 0.94 46494.93 224.44 C_2H_6 118.34 1.14 61964.97 61958.94 299.14 CO_2 5.51 30208.34 30217.67 C_3H_8 56.53 145.83 0 0 0 0 0 H_2O 4.77 3012.74 1844.14 1844.03 8.90 $C_{15}H_{32}$ 2203.94 < 0.001 1.20 1.20 0.01 $C_{16}H_{34}$ 8092.74 < 0.001 1.63 1.63 0.01 $C_{17}H_{36}$ 3118.82 trace 0.24 0.24 0.00 $C_{18}H_{38} \\$ 11369.25 0.35 0.35 0.00 trace $C_{16}H_{32}O_2$ 0 0 0 0 0 $C_{18}H_{32}O_2$ 0 0 0 0 0 $C_{18}H_{34}O_2$ 0 0 0 0 0 TG2 0 0 0 0 0 TG1 0 0 0 0 0 TG3

Table 5.1 Simulation results of the original process. (Continued)

Pump	P-101A/B			
Flow (kg/hr)	29399.70			
Volumetric flow (m ³ /hr)	17.95			
Power (shaft) (kW)	28.66			
Efficiency	0.50			
Temperature (in) (°C)	30.00			
Temperature (out) (°C)	31.00			
Pressure (in) (bar)	1.01			
Pressure(out) (bar)	30.00			
Pressure reducing unit	V-101	EP-301		
Pressure (in) (bar)	138.00	30.00		
Pressure (out) (bar)	30.00	1.01		
Power (kW)		-60.40		
Reactor	R-201	~		
Temperature (°C)	300.00	No.		
Pressure (bar)	30.00			
Duty (kW)	-6142.59			
Orientation	Vertical			
	Fixed bed			
Туре	isothermal			
	reactor			
Heaters	H-101	H-102	H-301	H-401
Temperature (in) (°C)	31.00	34.40	300.00	50.00
Temperature (out) (°C)	300.00	300.00	50.00	300.00
Pressure (bar)	30.00	30.00	30.00	30.00
Duty (kW)	5128.93	1142.43	-63741.28	54496.92

 Table 5.2 Equipment summary for the original process.

Vessels	D-301	D-302	D-303	
Temperature (°C)	50.00	42.84	42.84	
Pressure (bar)	30.00	1.01	1.01	
Vapor fraction	0.99	0.16	-	
Orientation	Vertical	Vertical	Horizontal	

Table 5.2 Equipment summary for the original process. (Continued)

Under this condition, the purity of green diesel and green diesel yield are 99.2% and 88.3%, respectively. For the NiMoS₂/ γ -Al₂O₃ catalyst, the hydrodeoxygenation (HDO) is favorer than decarbonylation (DCO) and decarboxylation (DCO₂). Therefore, the main composition of liquid product is n-C₁₆ and n-C₁₈ due to high selective hydrodeoxygenation (HDO) reaction. The comparison between original process and experimental data is shows in Table 5.3. The overall energy requirement of the original process is 124,509.56 kW. However, the overall energy requirement for green diesel production process can be reduced by using heat exchanger network (HEN).

	(Srifa, Faungnawakij	This work	Difference
	et al. 2014)		
Raw material	Palm oil	Palm oil	-
Liquid product composition	(%)		
$C_{15}H_{32}$	7.98	8.90	0.92
$C_{16}H_{34}$	30.78	32.65	1.87
C17H36	13.45	12.58	-0.87
C ₁₈ H ₃₈	47.79	45.87	-1.92
Product purity (%)	-	99.20	-
Product yield (%)	89.80	88.25	-1.55
HDO (%)	77.78	77.50	-0.28
DCO/DCO ₂ (%)	22.22	22.50	0.28

Table 5.3 Comparison between the original process and experimental data.

Table 5.3 shows the details of the original process compared with experimental data. The tolerance allowed is not more than 2% and the results of original process correspond with the experimental data.

5.2 The energy optimization of a green diesel production process

Efficiency energy utilization can reduce the cost of the process. To minimize the energy consumption of the green diesel production process, the heat exchanger network (HEN) is considered. In the original process, the product stream from the reactor is used to pre-heat palm oil feed stream, hydrogen feed stream and recycled hydrogen stream. Table 5.4 shows the heat exchange stream data for the green diesel production process.

					Heat
		Supply	Target	Input O	capacity
Stream	Туре	temperature	temperature (°C)		flow rate,
		(°C)		(K VV)	CP*
					(kW/°C)
Hot	H-1	300.00	50.00	-63741.30	254.97
Cold	C-1	31.00	300.00	5128.93	19.07
Cold	C-2	34.40	300.00	1142.43	4.30
Cold	C-3	50.00	300.00	54496.90	217.99

Table 5.4 Heat exchange stream data for the green diesel production process.

* Heat capacity flow rate in this table not depend on the temperature.

From Table 5.4, the hot stream has a CP of 255 kW/°C and is cooled from 300°C to 50°C and losses of 63,741.30 kW. The cold streams are heated from 31°C to 300°C, 34.4°C to 300°C and 50°C to 300°C with the CP of 19 kW/°C, 4 kW/°C and 218 kW/°C and loss of 5,129 kW, 1,142 kW and 54,496.9 kW, respectively. The grid diagram of interval temperature versus heat capacity flow rate of hot and cold streams is presented in Figure 5.2. The construction of the hot composite curve and cold composite curve are shown in Figure 5.3 and Figure 5.4.



Figure 5.2 Grid diagram of hot and cold streams.



Figure 5.3 The hot composite curve of the process.



Figure 5.4 The cold composite curve of the process.

The composite curves can be used to illustrate the minimum energy target of the process. The composite curves of hot and cold streams with the minimum temperature difference (ΔT_{min}) of 20°C is presented in Figure 5.5.



Figure 5.5 The composite curves for hot and cold streams at ΔT_{min} of 20°C.

As illustrated in Figure 5.5, the maximum heat recovery, minimum cold utility requirement and minimum hot utility requirement are around 56,269, 7,137 and 4,461 kW, respectively.

In this section, the energy optimization of a green diesel production process is divided into 3 strategies.

5.2.1 Energy optimization strategy 1

In this strategy, the product, Stream 10, is used to exchange the energy with recycled hydrogen stream, hydrogen feed stream and palm oil feed stream, respectively. The minimum temperature difference is set at 20°C.

Through this strategy, 25,000 kg/h of green diesel with purity of 99.2% are obtained with the total energy consumption of 22,654.65 kW. The yield of the process is 88.25%. The unit operation consists of pump, valve, reactor, heat exchanger, expansion, flash drum and decanter.

The process flow diagram of energy optimization strategy 1 is shown in Figure 5.6. The grid diagram of the heat exchanger network for energy optimization strategy 1 and the energy requirement of the original process and optimization strategy 1 are presented in Figures 5.7 and 5.8, respectively. From this strategy, the heat of 81.80% is saved when compares with the original process. The equipment of this strategy is summarized in Table 5.5.










Figure 5.8 The energy requirement of the original process and optimization strategy 1.

จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University

Pump	P-101A/B		
Flow (kg/hr)	29399.70		
Volumetric flow (m ³ /hr)	17.95		
Power (shaft) (kW)	28.66		
Efficiency	0.50		
Temperature (in) (°C)	30.00		
Temperature (out) (°C)	31.00		
Pressure (in) (bar)	1.01		
Pressure(out) (bar)	30.00		
Pressure reducing unit	V-101	EP-301	
Pressure (in) (bar)	138.00	30.00	
Pressure (out) (bar)	30.00	1.01	
Power (kW)		-60.40	
Reactor	R-201		
Temperature (°C)	300.00	20	
Pressure (bar)	30.00		
Duty (kW)	-6142.38		
Orientation	Vertical		
	Fixed bed		
Туре	isothermal		
	reactor		

Table 5.5 Equipment summary for the energy optimization strategy 1.

Heat exchanger	E-101	E-102	E-301	
Туре	Shell and tubeSh	ell and tubeS	hell and tube	
Area (m ²)	26.18	6.21	1869.64	
Duty (kW)	863.12	205.26	50005.10	
Temperature (°C)				
Hot stream (in)	101.43	102.31	300.00	
Hot stream (out)	97.69	101.43	102.31	
Cold stream (in)	30.96	34.36	50.00	
Cold stream (out)	81.43	82.31	280.00	
Heaters	H-101	H-102	H-301	H-401
Temperature (in) (°C)	81.43	82.31	97.70	280.00
Temperature (out) (°C)	300.00	300.00	50.00	300.00
Pressure (bar)	30.00	30.00	30.00	30.00
Duty (kW)	4265.80	937.16	-12815.30	4636.38
Vessels	D-301	D-302	D-303	
Temperature (°C)	50.00	42.84	42.84	
Pressure (bar)	30.00	1.01	1.01	
Vapor fraction	0.99	0.16	-	
Orientation	Vertical	Vertical	Horizontal	

 Table 5.5 Equipment summary for the energy optimization strategy 1. (Continued)

5.2.2 Energy optimization strategy 2

This strategy is similar to the optimization strategy 1 but the sequence of heat exchanger is changed. The product, Stream 10, is used to exchange the energy with palm oil feed stream, hydrogen feed stream and recycled hydrogen stream, respectively. The minimum temperature difference is set at 20°C.

In this process, 25,000 kg/h of green diesel with purity of 99.2% is produced. The product yield of this process is the same as for energy optimization strategy 1. The unit operation of this strategy consists of pump, valve, reactor, heat exchanger, expansion, flash drum and decanter. The energy consumption of this process is 23,987.54 kW. The heat of 80.73% is saved when compares with the original process. The difference of energy saving of strategy 1 and strategy 2 is 1.07%. The heat recovery of energy optimization strategy 1 is better than energy optimization strategy 2 due to the boundary of minimum temperature difference of hot and cold streams. Thus, the exchanged heat sequence affects on the energy saving.

The process flow diagram for energy optimization strategy 2 is shown in Figure 5.9. The grid diagram of the heat exchanger network for energy optimization strategy 2 and the energy requirement of the original process and optimization strategy 2 are presented in Figures 5.10 and 5.11, respectively. The equipment of this strategy is summarized in Table 5.6.

Chulalongkorn University













the original process and optimization strategy 2.



Pump	P-101A/B		
Flow (kg/hr)	29399.70		
Volumetric flow (m ³ /hr)	17.95		
Power (shaft) (kW)	28.66		
Efficiency	0.50		
Temperature (in) (°C)	30.00		
Temperature (out) (°C)	31.00		
Pressure (in) (bar)	1.01		
Pressure(out) (bar)	30.00		
Pressure reducing unit	V-101	EP-301	
Pressure (in) (bar)	138.00	30.00	
Pressure (out) (bar)	30.00	1.01	
Power (kW)		-60.40	
Reactor	R-201		
Temperature (°C)	300.00	20	
Pressure (bar)	30.00		
Duty (kW)	-6142.38		
Orientation	Vertical		
	Fixed bed		
Туре	isothermal		
	reactor		

Table 5.6 Equipment summary for the energy optimization strategy 2.

Heat exchanger	E-101	E-102	E-301	
Туре	Shell & tube	Shell & tube	Shell & tube	
Area (m ²)	60.66	12.72	1662.11	
Duty (kW)	4703.04	974.26	44729.40	
Temperature (°C)				
Hot stream (in)	300.00	281.53	277.68	
Hot stream (out)	281.53	277.68	100.58	
Cold stream (in)	30.96	34.36	50.00	
Cold stream (out)	280.00	261.00	257.00	
Heaters	H-101	H-102	H-301	H-401
Temperature (in) (°C)	280.00	261.00	100.58	257.00
Temperature (out) (°C)	300.00	300.00	50.00	300.00
Pressure (bar)	30.00	30.00	30.00	30.00
Duty (kW)	425.89	168.16	-13481.40	9912.09
Vessels	D-301	D-302	D-303	
Temperature (°C)	50.00	42.84	42.84	
Pressure (bar)	30.00	1.01	1.01	
Vapor fraction	0.99	0.16	-	
Orientation	Vertical	Vertical	Horizontal	

Table 5.6 Equipment summary for the energy optimization strategy 2. (Continued)

5.2.3 Energy optimization strategy 3

To minimize the energy consumption in the process, the heat exchanger network is used to exchange the heat from hot and cold streams. In this strategy, the product, Stream 10, is split to three streams in order to exchange with cold stream. The first stream, Stream 11, is used to exchange the energy with palm oil feed stream. The second stream, Stream 13, is used to exchange the energy with hydrogen feed stream and the last stream, Stream 15, is used to exchange the energy with recycled hydrogen stream. The minimum temperature difference is set at 20°C.

In this process, 25,000 kg/h of green diesel with purity of 99.2% is produced. The product yield of this process is 88.25%. The energy consumption of this process is 13,253.88 kW. When compare with the original process, 89.36% of energy is saved. In this process, the unit operation consists of pump, valve, reactor, heat exchanger, expansion, flash drum and decanter.

Comparison of strategy 3 with the strategy 1 and 2, the highest energy saving efficiency is energy optimization strategy 3 due to each split hot streams can be exchanged the energy at a maximum temperature of hot stream. The driving forces of the strategy 3 is high due to the great temperature difference between hot and cold streams in this process.

In the energy optimization strategy 1 and 2, the driving forces of the strategy 1 and 2 are lower than the strategy 3 due to the lower temperature difference between hot and cold streams in this process. The hot stream temperature is decreased rapidly when the hot stream is used to meet heating demand with minimum temperature difference (ΔT_{min}) of 20°C. Therefore, the energy exchange is limited under the minimum temperature difference between hot and cold stream that results in the energy cannot be fully exchanged even if the streams have a sufficient energy.

The process flow diagram for energy optimization strategy 3 is shown in Figure 5.12. The grid diagram of the heat exchanger network for energy optimization strategy 3 and the energy requirement of the original process and optimization strategy 3 are presented in Figures 5.13 and 5.14, respectively. The equipment summary of this strategy is presented in Table 5.7 and the comparison of performance for a green diesel production process with heat-integrated, energy optimization strategy 1, 2 and 3, is presented in Table 5.8.



จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University













the original process and optimization strategy 3.



Pump	P-101A/B		
Flow (kg/hr)	29399.70		
Volumetric flow (m ³ /hr)	17.95		
Power (shaft) (kW)	28.66		
Efficiency	0.50		
Temperature (in) (°C)	30.00		
Temperature (out) (°C)	31.00		
Pressure (in) (bar)	1.01		
Pressure(out) (bar)	30.00		
Pressure reducing unit	V-101	EP-301	
Pressure (in) (bar)	138.00	30.00	
Pressure (out) (bar)	30.00	1.01	
Power (kW)		-60.40	
Reactor	R-201		
Temperature (°C)	300.00		
Pressure (bar)	30.00		
Duty (kW)	-6142.38		
Orientation	Vertical		
	Fixed bed		
Туре	isothermal		
	reactor		

Table 5.7 Equipment summary for the energy optimization strategy 3.

Heat exchanger	E-101	E-102	E-301	
Туре	Shell & tube	Shell & tube	Shell & tube	
Area (m ²)	327.88	16.95	3067.65	
Duty (kW)	4703.04	1056.17	49838.50	
Temperature (°C)				
Hot stream (in)	300.00	300.00	300.00	
Hot stream (out)	52.81	217.188	71.23	
Cold stream (in)	30.96	34.36	50.00	
Cold stream (out)	280.00	280.00	280.00	
Heaters	H-101	H-102	H-301	H-401
Temperature (in) (°C)	280.00	280.00	77.3	280.00
Temperature (out) (°C)	300.00	300.00	50.00	300.00
Pressure (bar)	30.00	30.00	30.00	30.00
Duty (kW)	425.89	86.25	-8119.61	4622.13
Vessels	D-301	D-302	D-303	
Temperature (°C)	50.00	42.84	42.84	
Pressure (bar)	30.00	1.01	1.01	
Vapor fraction	0.99	0.16	-	
Orientation	Vertical	Vertical	Horizontal	

Table 5.7 Equipment summary for the energy optimization strategy 3. (Continued)

	Original	Strategy 1	Strategy 2	Strategy 3
Hydrogen to oil feed volume ratio	1005.84	1011.24	1011.24	1003.71
Green diesel purity (wt%)	99.20	99.20	99.20	99.20
Green diesel yield (%)	88.25	88.25	88.25	88.25
H-101, heat duty (kW)	5128.93	4265.80	425.89	425.89
H-102, heat duty (kW)	1142.43	937.16	168.16	86.25
H-301, heat duty (kW)	-67341.3	-12815.30	-13481.40	-8119.61
H-401, heat duty (kW)	54496.9	4636.38	9912.09	4622.13
Cold utility requirement (kW)	63741.30	12815.30	13481.40	8119.61
Hot utility requirement (kW)	60768.26	9839.34	10506.14	5134.27
Heat recovery (kW)		102146.97	100813.40	111195.42
Total energy requirement (kW)	124509.56	22654.64	23987.54	13253.88
Heating requirement reduce (%)		83.81	82.71	91.55
Cooling requirement reduce (%)		80.97	78.85	87.26
Energy saving (%)	0	81.80	80.73	89.36
Productivity (kg green diesel/h)	25000	25000	25000	25000
Number of unit operation	gkorn Un	IVERSITY		
Pump	1	1	1	1
Valve	1	1	1	1
Reactor	1	1	1	1
Heat exchanger	4	7	7	7
Expansion	1	1	1	1
Flash drum	2	2	2	2
Decanter	1	1	1	1
Total unit operation	11	14	14	14

Table 5.8 The comparison of performance for green diesel production process withheat exchanger network (HEN).

As summarized in Table 5.8, it can be seen that the heat integrated processes require lower energy consumption than the original process. The heating requirement are reduced by 84%, 83% and 92% and the cooling requirement are reduced by 81%, 79% and 87% for the energy optimization strategy 1, strategy 2 and strategy 3, respectively. The results show that the great strategy for minimum energy usage is the strategy 3. The strategy 3 can be reduced 111,195 kW of energy usage in the process. Thus, the heat exchanger network can be reduced heat of the process and improved the efficiency of energy usage.

5.2.4 The effect of minimum temperature difference (ΔT_{min})

The minimum temperature difference (ΔT_{min}) fixes the relative position of the hot and cold composite curves. Figures 5.15 to 5.18 show the composite curves of the process with the minimum temperature difference of 10°C, 15°C, 25°C and 30°C, respectively. (The composite curves of the process with the minimum temperature difference of 20°C is shown in Figure 5.5.)



Figure 5.15 The composite curves for hot and cold streams at ΔT_{min} of 10°C.



Figure 5.16 The composite curves for hot and cold streams at ΔT_{min} of 15°C.



Figure 5.17 The composite curves for hot and cold streams at ΔT_{min} of 25°C.



Figure 5.18 The composite curves for hot and cold streams at ΔT_{min} of 30°C.

The minimum temperature difference (ΔT_{min}) affects the utility requirement, heat recovery and area of heat exchanger. In this section, the effect of minimum temperature difference (ΔT_{min}) is considered under the greatest strategy, energy optimization strategy 3. The comparison between utility requirement, heat recovery and area of heat exchanger and the minimum temperature difference (ΔT_{min}) from 10°C to 30°C are shown in Figures 5.19 to 5.21, respectively.



Figure 5.19 The comparison between utility requirement and the minimum temperature difference (ΔT_{min}).



Figure 5.20 The comparison between heat recovery

and the minimum temperature difference (ΔT_{min}).



Figure 5.21 The comparison between area of heat exchanger and the minimum temperature difference (ΔT_{min}).

As illustrated in Figures 5.19 to 5.21, it can be seen that the increasing of minimum temperature difference (ΔT_{min}) from 10°C to 30°C affects to the utility requirement and heat recovery of the process linearly that can be expressed by Equations (5.1) and (5.2) with high coefficient of determination (R-square). The utility requirement increases and the heat recovery decreases when the minimum temperature difference (ΔT_{min}) increases. The area of heat exchanger network decreases exponentially when the minimum temperature difference (ΔT_{min}) increases from 10°C to 30°C that can be expressed by Equation (5.3).

$$Total utility requirement = 482.71\Delta T_{min} + 2973$$
(5.1)

$$R^2 = 1.0000$$

$$Total heat recovery = 241.36\Delta T_{min} + 60768$$
(5.2)

 $R^2 = 1.0000$

 $Total heat exchanger area = 137127\Delta T_{min}^{-1.075}$ (5.3)

$$R^2 = 0.9998$$

จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University

5.2.5 The cost estimation for heat exchanger network

The heat exchanger network can be reduced the energy consumption of the process. However, the reduced energy result in the increasing construction cost of heat exchanger network. In this part, the heat exchanger is made from carbon steel. The construction cost and operating cost of heat exchanger network are considered. The construction cost and operating cost of original process, energy optimization strategy 1, 2 and 3 are presented in Table 5.9.

	Original	Strategy 1	Strategy 2	Strategy 3
Construction cost	Q			
(Baht)				
Heat exchanger				
E-101		816,000	979,200	1,924,400
E-102		744,600	754,800	771,800
E-301		7,174,000	6,630,000	12,580,000
Heaters/Cooler				
H-101	907,800	897,600	754,800	754,800
H-102	181,560	179,520	153,680	132,600
H-401	2,437,800	1,278,400	1,734,000	1,247,800
H-301	3,236,800	2,206,600	2,240,600	1,924,400
Total construction cos	6,763,960 6,763	13,296,720	13,247,080	19,335,800
Operating cost				
(Baht/year)				
U-101	54,680,000	45,480,000	4,544,000	4,544,000
U-102	12,176,000	9,992,000	1,792,000	920,000
U-401	580,976,000	49,424,000	105,672,000	49,272,000
U-301	23,968,000	4,816,000	5,072,000	3,056,000
Total operating cost	671,800,000	109,712,000	117,080,000	57,792,000

Table 5.9 The construction cost and operating cost of each strategy.

As summarized in Table 5.9, it can be seen that the heat integrated processes require higher construction cost than the original process. However, the operating cost of heat integrated processes are lower than the original process. The highest construction cost is energy optimization strategy 3. However, the operating cost of energy optimization strategy 3 is less than other strategy. The comparison of construction cost and operating cost for are shown in Figures 5.22 and 5.23, respectively.



■ Original process Strategy 1 □ Strategy 2 ■ Strategy 3

Figure 5. 22 The comparison of construction cost for each unit.



Figure 5. 23 The comparison of operating cost for each unit.

In case of 10 years plant life consideration, the average construction cost of original process, energy optimization strategy 1, 2 and 3 are 676,396, 1,329,672, 1,324,708 and 1,933,580 baht per year, respectively. The operating cost of original process, energy optimization strategy 1, 2 and 3 are constant at 671,800,000, 109,712,000, 117,080,000 and 57,792,000 baht per year, respectively. The total cost of heat exchanger network for 10-year plant life is presented in Figure 5.24.



Figure 5. 24 The comparison of cost for heat exchanger network

As presented in Figure 4, it can be seen that the lowest cost is the energy optimization strategy 3. Therefore, the energy optimization strategy 3 is the most worthwhile investment.



5.2.6 Pressure drop consideration for the green diesel production process

In this part, the pressure drop in green diesel production process is considered. The pressure drop for each equipment is approximated in order to study the effect of pressure drop in the process. The pressure drop for each equipment is defined in Table 5.9.

The process flow diagram of the energy optimization strategy 1, 2 and 3 with pressure drop consideration are shown in Figures 5.22, 5.23 and 5.24, respectively. The comparison of total energy requirement between the energy optimization strategy 1, 2 and 3 with pressure drop consideration and the energy optimization strategy 1, 2 and 3 without pressure drop consideration are shown in Figures 5.25, 5.26 and 5.27, respectively. In this work, the compressor is added to the process in order to compress a recycled hydrogen to the required process condition. The energy of strategy 1, 2 and 3 with pressure drop consideration are increased around 7,217 kW, 4,381 kW and 11,241 kW when compared with the energy optimization strategy 1, 2 and 3, respectively. It can be seen that the pressure drop in the equipment result in the increasing energy of the process.

Tuno		Press	Pressure drop (ΔP),bar		Calculated	Poforonco	
Туре		Strategy 1	Strategy 2	Strategy 3	method	Reference	
Reactor		8 85	8 85	8 85	Ergun's	(Silla 2003)	
Treactor		0.00	0.00	0.00		(51114 2003)	
Heat					Kern's	(Walas 1000)	
exchanger					method	(w alas 1990)	
E-101	Tube	0.48	0.73	0.04			
	Shell	0.014	0.02	0.06			
E-102	Tube	0.97	0.54	0.06			
	Shell	0.0004	0.0004	0.02			
E-301	Tube	0.27	0.33	0.30			
	Shell	0.39	0.40	0.52			
Elech duran		0.0005	0.0005	0.0025	0.0025		(Sulzer-
Flash drum		0.0025	0.0025	0.0025		Chemtech)	

 Table 5. 10 The pressure drop for each equipment.


























Figure 5. 28 The Comparison of energy between the energy optimization strategy 1 with and without pressure drop.



Figure 5. 29 The Comparison of energy between the energy optimization strategy 2 with and without pressure drop.



Figure 5. 30 The Comparison of energy between the energy optimization strategy 3 with and without pressure drop.



CHAPTER 6

CONCLUSION AND RECOMMENDATION

6.1 Conclusions

The green diesel production process by using NiMoS₂/ γ -Al₂O₃ catalyst is simulated. A palm oil is used as a raw material that consists of trilinolein (11.5%), tripalmitin (42.2%) and triolein (46.3%). The condition for this process is 1000:1 of hydrogen to oil volume feed ratio, reaction temperature of 300°C and pressure of 30 bar. This condition provides the green diesel purity of 99.2 wt%, green diesel yield of 88.25%. The hydrodeoxygenation (HDO) and decarbonylation (DCO)/decarboxylation (DCO₂) distribution are 77.50% and 22.50%, respectively. The liquid product composition are 8.90%, 32.65%, 12.58% and 45.87% of n-C₁₅, n-C₁₆, n-C₁₇ and n-C₁₈, respectively. The green diesel production capacity of this process is 200,000 metric tons per year with 8,000 of working hours per year. The results of this simulation study are good agreement with the experimental data. The tolerance allowed is not more than 2%. The energy consumption of 124,510 kW is used in this process.

To minimize the energy consumption of the green diesel production process, the heat exchanger network (HEN) is considered. The three energy optimization strategy are designed. All of the energy optimization strategies can keep the quality of green diesel product. The energy optimization strategy 1 and 2 can decrease the energy consumption of 81.80% and 80.73%, respectively. It indicated that the exchanged heat sequence affects on the energy saving. Based on the energy optimization strategy 3, the energy consumption of 89.36% is decreased. The energy saving of strategy 3 is greatest due to each split hot streams can be exchanged the energy with the maximum driving force. In this work, the construction and operating cost are considered. When considering the cost of construction and operation, it can be seen that the energy optimization strategy 3 is the most worthwhile investment.

The minimum temperature difference (ΔT_{min}) affects to the utility requirement, heat recovery and area of heat exchanger of the process. The utility requirement increases and the heat recovery decreases linearly when the minimum temperature difference (ΔT_{min}) increases. The area of heat exchanger network decreases exponentially when the minimum temperature difference (ΔT_{min}) increases. The pressure drop of each equipment results in the increasing energy requirement of the process.

6.2 Recommendations

In this work, the objectives only focus on the quality of green diesel product and energy consumption of the process. However, the economic feasibility, investment and operational costs and intensive equipment design should be considered.

All of the recommendations are provided the perfection of green diesel production process simulation.



REFERENCES

Alí, M. F., et al. (2005). Handbook of Industrial Chemistry, McGraw-Hill.

Anand, M. and A. K. Sinha (2012). "Temperature-dependent reaction pathways for the anomalous hydrocracking of triglycerides in the presence of sulfided Co–Mocatalyst." <u>Bioresour Technol</u> **126**: 148-155.

Ancheyta, J., et al. (2009). <u>Asphaltenes: Chemical Transformation during</u> <u>Hydroprocessing of Heavy Oils</u>. New York, CRC Press

Bezergianni, S. and A. Dimitriadis (2013). "Comparison between different types of renewable diesel." <u>Renewable and Sustainable Energy Reviews</u> **21**: 110-116.

Charusiri, W. and T. Vitidsant (2005). "Kinetic Study of Used Vegetable Oil to Liquid Fuels over Sulfated Zirconia." <u>Energy & Fuels</u> **19**: 1738-1789.

Charusiri, W., et al. (2006). "Conversion of used vegetable oils to liquid fuels and chemical over HZSM-5, sulfated zircinia and hybrid catalysts." <u>Korean Journal of Chemical Engineering</u> **23**: 349-355.

Chen, N., et al. (2013). "Effects of Si/Al ratio and Pt loading on Pt/SAPO-11 catalysts in hydroconversion of Jatropha oil." <u>Applied Catalysis A: General</u> **466**: 105-115.

Coker, A. K. (2015). "Process Integration and Heat Exchanger Networks." 491-622.

Donnis, B., et al. (2009). "Hydroprocessing of Bio-Oils and Oxygenates to Hydrocarbons, Understanding the Reaction Routes." <u>Topics in Catalysis</u> **52**: 229-240.

Evans, F. L. J. (1997). <u>Equipment Design Handbook for Refineries and Chemical Plant</u>. New York, Gulf Pub. Co.

Faungnawakij, K. and K. Suriye (2013). "Chapter 4 - current catalytic processes with hybrid materials and composites for heterogeneous catalysis.": 79-104.

Gong, S., et al. (2012). "Role of support in hydrotreatment of jatropha oil over sulfided NiMo catalysts." <u>Industrial & Engineering Chemistry</u> **51**: 13953-13960.

Guzman, A., et al. (2010). "Hydroprocessing of crude palm oil at pilot plant scale." <u>Catalysis Today</u> **156**(1-2): 38-43.

Hancsók, J., et al. (2007). "Investigation of the production of high cetane number bio gas oil from pre-hydrogenated vegetable oils over Pt/HZSM-22/Al2O3." <u>Microporous and Mesoporous Materials</u> **101**(1-2): 148-152.

Herskowitz, M., et al. (2013). "A commeicially-viable, one-step process for production of green diesel from soybean oil on Pt/SAPO-11." <u>Fuel</u> **111**: 157-164.

Huber, G. W. and A. Corma (2007). "Synergies between Bio- and Oil Refineries for the Production of Fuels from Biomass." <u>Angewandte Chemie International Edition</u> **46**: 7184-7201.

Jain, S. and M. P. Sharma (2010). "Stability of biodiesel and its blends, a review." <u>Renewable and Sustainable Energy Reviews</u> 14: 667-678.

Kern, D. Q. (1965). Process Heat Transfer. New York, McGraw-Hill Book Co.

Kikhtyanin, O. V., et al. (2010). "Hydroconversion of sunflower oil on Pd/SAPO-31 catalyst." <u>Fuel **89**</u>: 3085-3092.

Kovacs, S., et al. (2011). "Fuel production by hydrotreating of triglycerides on NiMo/Al2O3/F catalyst." <u>Chemical Engineering Journal</u> **176-177**: 237-243.

Krár, M., et al. (2010). "Fuel Purpose Hydrotreating of Sunflower Oil on CoMo/Al₂O₃. Catalyst." <u>Bioresour Technol</u> **101**: 9287-9293.

Kubic ka, D., et al. (2009). "Transformation of vegetable oils into hydrocarbons over mesoporous-alumina-supported CoMo catalysts." <u>Topics in Catalysis</u> **52**: 161-168.

Kubička, D. and L. Kaluža (2010). "Deoxygenation of vegetable oils over sulfided Ni, Mo and NiMo catalysts." <u>Applied Catalysis A: General</u> **372**: 199-208.

Lestari, S., et al. (2009). "Catalytic Deoxygenation of Stearic Acid in a Continuous Reactor over a Mesoporous Carbon Supported Pd Catalyst." <u>Energy & Fuels</u> **23**: 3842-3845.

Linnhoff, B. and E. Hindmarsh (1983). "The pinch design method for heat exchanger networks." <u>Chemical Engineering Science</u> **38**: 745-763.

Linnhoff, M. (1998). "Introduction to Pinch Technology." from <u>www.ou.edu/class/che-</u> <u>design/a-design/Introduction%20to%20Pinch%20Technology-LinnhoffMarch.pdf</u>.

Liu, C., et al. (2013). "A cleaner process for hydrocracking of jatropha oil into green diesel." Journal of the Taiwan Institute of Chemical Engineers **44**(2): 221-227.

Liu, Y., et al. (2011). "Hydrotreatment of Vegetable Oils to Produce Bio-Hydrogenated Diesel and Liquefied Petroleum Gas Fuel over Catalysts Containing Sulfided Ni–Mo and Solid Acids." <u>Energy & Fuels</u> **25**(10): 4675-4685.

Liu, Y., et al. (2012). "Production of Biohydrogenated Diesel by Hydrotreatment of High-Acid-Value Waste Cooking Oil over Ruthenium Catalyst Supported on Alpolyoxocation-Pillared Montmorillonite." <u>Catalysts</u> **2**: 171-190.

Ludwig, E. E. (1997). <u>Applied Process Design for Chemical and Petrochemical Plants</u>. Houston, Gulf Pub. Co.

Mandal, D., et al. (2013). "Void fraction and effective thermal conductivity of binary particulate bed." <u>Fusion Engineering and Design</u> **88**(4): 216-225.

Mikkonen, S. (2008). "Second-generation renewable diesel offers advantages." <u>Hydrocarbon Processing</u> **87**: 63-66.

Mikulec, J., et al. (2010). "Second Generation Diesel Fuel from Renewable Sources." Journal of Cleaner Production 18: 917-926.

Morgan, T., et al. (2012). "Catalytic Deoxygenation of Triglycerides to Hydrocarbons over Supported Nickel Catalysts." <u>Chemical Engineering Journal</u> **189-190**: 346-355.

Murata, K., et al. (2010). "Production of Synthetic Diesel by Hydrotreatment of Jatropha Oils Using Pt–Re/H-ZSM-5 Catalyst." <u>Energy & Fuels</u> **24**(4): 2404-2409.

Naik, S. N., et al. (2010). "Production of first and second generation biofuels: A comprehensive review." <u>Renewable and Sustainable Energy Reviews</u> **14**: 578-597.

Nasikin, M., et al. (2009). "Biogasoline from Palm Oil by Simultaneous Cracking and Hydrogenation Reaction over NiMo/zeolite catalyst." <u>World Applied Sciences Journal</u> **5**: 74-79.

Nunes, P. P. (1984). Hydrocraquage de l'huile de soja sur des catalyseurs au rhodium et au ruthenium supportes. Paris, Université Pierre et Marie Curie

Nunes, P. P., et al. (1986). "Soybean Oil Hydrocracking under Pressure: Process and General Aspect of the Transformation." <u>Revue de L'Institute Francais du Pétrole</u> **41**: 421-431.

Raldov, W. (2005). <u>Bio-Refining Workshop</u>. Proceedings of the First International Conference, Washington D.C. .

Shin, H. Y., et al. (2011). "Thermal decomposition and stability of fatty acid methyl esters in supercritical methanol." Journal of Analytical and Applied Pyrolysis **92**: 332–338.

Chulalongkorn University

Silla, H. (2003). <u>Chemical process engineering design and economics</u>. New York, Marcel Dekker.

Simacek, P., et al. (2009). "Hydroprocessed rapeseed oil as a source of hydrocarbonbased biodiesel." <u>Fuel</u> **88**: 456-460.

Snåre, M., et al. (2006). "Heterogeneous catalytic deoxygenation of stearic acid for production of biodiesel." <u>Industrial & Engineering Chemistry Research</u> **45**: 5708-5715.

Sotelo-Boyás, R., et al. (2011). "Renewable Diesel Production from the Hydrotreating of Rapeseed Oil with Pt/Zeolite and NiMo/Al2O3Catalysts." <u>Industrial & Engineering</u> <u>Chemistry Research</u> **50**(5): 2791-2799.

Sotelo-Boyás, R., et al. (2012). "Hydroconversion of Triglycerides into Green Liquid Fuels." 187-216.

Srifa, A., et al. (2014). "Production of bio-hydrogenated diesel by catalytic hydrotreating of palm oil over NiMoS2/gamma-Al2O3 catalyst." <u>Bioresour Technol</u> **158**: 81-90.

Sulzer-Chemtech. "Gas/Liquid Seperation Technology." 2015, from <u>http://www.sulzer.com/ms/-</u> /media/Documents/ProductsAndServices/Separation_Technology/Mist_Eliminators/B rochures/Gas_Liquid_Separation_Technology.pdf.

Turton, R., et al. (2009). <u>Analysis, Synthesis, and Design of Chemical Processes</u>, Prentice hall.

Ghulalongkorn University

Veriansyah, B., et al. (2012). "Production of renewable diesel by hydroprocessing of soybean oil: Effect of catalysts." <u>Fuel</u> **94**: 578-585.

Walas, S. M. (1990). <u>Chemical process equipment selection and design</u>. Boston, Butterworth-Heinemann.

Yang, Y., et al. (2013). "Hydrotreating of C18 fatty acids to hydrocarbons on sulphided NiW/SiO₂–Al₂O₃." <u>Fuel Processing Technology</u> **116**: 165-174.





จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University

APPENDIX A

IDEAL HEAT CALCULATION FOR

HEAT EXCHANGER NETWORK

This section shows the ideal heat calculation for heat exchanger network with a constant heat capacity flow rate (CP). The heat exchange stream data for the green diesel production process is shown in Table 5.4. In this case, the hot stream of the process is split into 3 streams in order to exchange the maximum energy. The heat exchange stream data with split streams are presented in Table A.1.

Table A.1 The heat exchange stream data with split streams for the green diesel production process.

Stream	No.	Туре	Supply temperature (°C)	Target temperature (°C)	Q (kW)	Heat capacity flow rate, CP* (kW/°C)
Hot	1	H-1	300.00	50.00	4766.78	19.07
Hot	2	H-2	300.00	50.00	55755.05	223.02
Hot	3	H-3	300.00	50.00	3220.68	12.88
Cold	4	C-1	31.00	300.00	5128.93	19.07
Cold	5	C-2	34.40	300.00	1142.43	4.30
Cold	6	C-3	50.00	300.00	54496.90	217.99

From the composition curves shown in Figure 5.5, the minimum temperature difference is set to 20°C. The pinch temperature, the hot pinch temperature and the cold pinch temperature are 290°C, 300°C and 280°C, respectively.

Conceptual network design (Linnhoff and Hindmarsh 1983)

Step 1: Stream 1 is matched with stream 4.

Stream 1 transfers the amount of heat to bring stream 4 to its pinch temperature. The amount of heat in stream 4 from the initial temperature to its pinch temperature is:

$$\Delta H_{ex} = CP\Delta T$$

= 19.07 × (280 - 31)
= 4748.43 kW

The amount of heat in stream 1 from the pinch temperature to its target temperature is:

$$\Delta H_{ex} = CP\Delta T$$

= 19.07 × (300 - 50)
= 4767.50 kW

A cooler is required in stream 1 as the remaining heat load is:

$$\Delta H_{cold} = 4767.50 - 4748.43 = 19.07 \, kW$$

The intermediate temperatures in the streams are:

In stream 1:

iulalongkorn Univers

1 - 10 10

$$\Delta H_{ex} = CP\Delta T$$

$$\frac{4748.43}{19.07} = (300 - T)$$
$$T = 51^{\circ}C$$

The cooler load is 19.07 kW. Thus, the target temperature is:

$$\Delta H_{ex} = CP\Delta T$$

$$\frac{19.07}{19.07} = (51 - T)$$

$$T = 50^{\circ}C$$

The heater is required in stream 4 as the remaining heat load is:

$$\Delta H_{Hot} = 5128.93 - 4748.43 = 380.50 \, kW$$

Thus, the target temperature is:

$$\Delta H_{ex} = CP\Delta T$$

 $\frac{380.50}{19.07} = (T - 280)$
 $T = 300^{\circ}\text{C}$

Step 2: Stream 2 is matched with stream 6.

Stream 2 transfers the amount of heat to bring stream 6 to its pinch temperature. The amount of heat in stream 6 from the initial temperature to its pinch temperature is:

$$\Delta H_{ex} = CP\Delta T$$

= 217.99 × (280 - 50)
= 50137.70 kW

The amount of heat in stream 2 from the pinch temperature to its target temperature is:

$$\Delta H_{ex} = CP\Delta T$$

= 223.02 × (300 - 50)
= 55755.00 kW

A cooler is required in stream 2 as the remaining heat load is:

$$\Delta H_{cold} = 55755.00 - 50137.70 = 5617.30 \, kW$$

The intermediate temperatures in the streams are:

In stream 2:

$$\Delta H_{ex} = CP\Delta T$$

$$\frac{50137.70}{223.02} = (300 - T)$$

$$T = 75.19^{\circ}C$$

The cooler load is 5617.30 kW. Thus, the target temperature is:

$$\Delta H_{ex} = CP\Delta T$$

 $\frac{5617.30}{223.02} = (75.19 - T)$
 $T = 50^{\circ}C$

The heater is required in stream 6 as the remaining heat load is:

 $\Delta H_{Hot} = 54496.90 - 50137.7 = 4359.20 \, kW$

Thus, the target temperature is:

 $\Delta H_{ex} = CP\Delta T$ $\frac{4359.20}{217.99} = (T - 280)$

 $T = 300^{\circ}C$

Step 3: Stream 3 is matched with stream 5.

Stream 3 transfers the amount of heat to bring stream 5 to its pinch temperature. The amount of heat in stream 5 from the initial temperature to its pinch temperature is:

$$\Delta H_{ex} = CP\Delta T$$

= 4.30 × (280 - 34.4)
= 1056.08 kW

The amount of heat in stream 3 from the pinch temperature to its target temperature is:

$$\Delta H_{ex} = CP\Delta T$$
$$= 12.88 \times (300 - 50)$$
$$= 3220 \ kW$$

A cooler is required in stream 3 as the remaining heat load is:

$$\Delta H_{cold} = 3220 - 1056.08 = 2163.92 \, kW$$

The intermediate temperatures in the streams are:

In stream 3:

$$\Delta H_{ex} = CP\Delta T$$

$$\frac{1056.08}{12.88} = (300 - T)$$

$$T = 218.01^{\circ}C$$

The cooler load is 2163.92 kW. Thus, the target temperature is:

$$\Delta H_{ex} = CP\Delta T$$

 $\frac{2163.92}{12.88} = (218.01 - T)$
 $T = 50^{\circ}C$

The heater is required in stream 5 as the remaining heat load is:

$$\Delta H_{Hot} = 1142.43 - 1056.08 = 86.35 \, kW$$

Thus, the target temperature is:

$$\Delta H_{ex} = CP\Delta T$$
$$\frac{86.35}{4.30} = (T - 280)$$
$$T = 300^{\circ}\text{C}$$

It is noted that the results of this network is an ideal calculation with a constant heat capacity flow rate (CP). Thus, the calculated heat of this network is not equal to the network strategy that calculated from real physical properties by Aspen plus. However, the trend of ideal calculation is corresponding with the results from Aspen plus. This ideal calculation can be used to guild the further heat exchanger network design.



APPENDIX B

PRESSURE DROP CALCULATION OF THE PROCESS

In this work, the pressure drop calculation is divided into 2 parts. Firstly, the pressure drop in a reactor is considered. Secondly, the pressure drop on heat exchanger is considered.

1. Pressure drop calculation for the fixed bed reactor

In this section, the pressure drop calculation is divided into 8 steps as follows (Silla 2003):

Step 1: Calculate the bed volume (V_B) from equation (B.1).

$$V_B = \frac{V_{V}}{s_{CL}} \tag{B.1}$$

Where:

 V'_V = Volumetric flow rate of fresh feed of limiting reactant (kg/m³)

 S'_{CL} = Space velocity (h⁻¹) $V_B = \frac{17.945}{1}$ $V_B = 17.9450 m^3$

Step 2: Calculate bed area (A_B) from equation (B.2).

$$V_V = v'_s A_B \tag{B.2}$$

Where:

 V_V = Volumetric flow rate of gas inlet (m³/h)

 v'_s = Superficial velocity, $v'_s \approx 1.0$ (m/s)

$$A_B = \frac{23434}{1}$$

 $A_B = 6.5094 \ m^2$

Step 3: Calculate the reactor diameter (D) from equation (B.3). Round off D in 6 inch (0.152 m) increments, starting at 30 inch (0.762 m). If D is less than 30 inch, use standard pipe.

$$A_B = \frac{\pi D^2}{4}$$
(B.3)
 $D = 2.8796 \ m = 9.4450 \ ft$
Round off D = 9.5 ft = 2.8956 m

Step 4: After rounding off D, calculate the actual bed area from equation (B.3).

$$A_B = \frac{\pi (2.8956^2)}{4}$$
$$A_B = 6.5852 \ m^2$$

Step 5: Calculate the actual superfacial velocity (V_S) from equation (B.2).

$$v_s = \frac{23434}{6.5852}$$

$$v_s = 0.9885 \frac{m}{s} = 3.2430 \frac{ft}{s} = 11675.2030 \frac{ft}{h}$$

Step 6: Calculate the bed length (L_B) from equation (B.4).

$$L_B = \frac{V_B}{A_B} \tag{B.4}$$

 $(L_B \text{ minimum} = 1/2D = 4.75 \text{ ft}, L_B \text{ maximum} = 25 \text{ ft})$

$$L_B = \frac{17.945}{6.5852}$$
$$L_B = 2.7250 \ m = 8.940 \ ft$$

Step 7: Calculate the reactor length (L_R) from equation (B.5). Round off L_R in 3 inch (0.25 ft) increments (for example: 5.0, 5.25, 5.50, 5.75 etc.).

$$L_R = L_B + L'_I \tag{B.5}$$

Where:

$$L'_{I} = 3 ft$$

 $L_{R} = 8.940 + 3$
 $L_{R} = 11.940 ft$
Round off $L_{R} = 12 ft = 3.6576 m$

Step 8: Calculate the reactor pressure drop (ΔP) from equation (B.6).

$$\frac{\Delta P}{L} = 150 \frac{\mu G}{kg\rho D^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} + 1.75 \frac{G^2}{kg\rho D} \frac{(1-\varepsilon)}{\varepsilon^3}$$
(B.6)

So,

 $\Delta P = 128.351 \, psi = 8.85 \, bar$

Where:

 $\Delta P = Pressure drop (lb/in², psi)$

L = Depth of the packed bed (ft)

 $G = \rho V =$ Mass velocity (lb/hr-ft²) = 5165.11 lb/hr-ft²

V = Superficial linear velocity (ft/hr) = 11675.203 ft/h

 ρ = Fluid density (lb/ft³) = 0.4424 lb/ft³

 μ = Fluid viscosity (lb/hr-ft) = 0.8891 lb/hr-ft

D = Effective particle diameter (ft) = 0.00328 ft

(Srifa, Faungnawakij et al. 2014)

 ε = Interparticle void fraction (dimensionless) = 0.455

(Mandal, Sathiyamoorthy et al. 2013)

g = Gravitational constant (4.17 x 10^8 lb-ft/lb-hr²)

 $k = Conversion factor (144 in^2/ft^2)$

จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University

2. Pressure drop calculation for the heat exchanger

Type of heat exchanger: Shell and tube

Heat duty (Q): 1056.17 kW

Heat transfer area (A): 16.95 m²

Heat transfer coefficient (U): 846.62 W/m²-°C

Shell side information:

Flow rate	$W_{shell} = 1067.37 \text{ kg/h}$
Pressure (in)	P ₁ = 3000 kPa (30 bar)
Temperature (in)	$T_1 = 34.4 \ ^{o}C$
Temperature (out)	$T_2 = 280 \ ^{o}C$
Fluid density	$ \rho_{shell} = 2.3239 \text{ kg/m}^3 $
Fluid viscosity	$\mu_{shell} = 0.0091 \text{ cP}$
Tube side information:	
Flow rate	W _{tube} = 12810.6 kg/h
Pressure (in)	$P_2 = 3000 \text{ kPa} (30 \text{ bar})$
Pressure (in) CHUI Temperature (in)	$P_2 = 3000 \text{ kPa} (30 \text{ bar})$ $t_1 = 300 \text{ °C}$
Pressure (in) Temperature (in) Temperature (out)	$P_2 = 3000 \text{ kPa} (30 \text{ bar})$ $t_1 = 300 \text{ °C}$ $t_2 = 217.19 \text{ °C}$
Pressure (in) Temperature (in) Temperature (out) Fluid density	$P_2 = 3000 \text{ kPa} (30 \text{ bar})$ $t_1 = 300 \text{ °C}$ $t_2 = 217.19 \text{ °C}$ $\rho_{tube} = 7.127 \text{ kg/m}^3$
Pressure (in) Temperature (in) Temperature (out) Fluid density Fluid viscosity	$P_{2} = 3000 \text{ kPa (30 bar)}$ $t_{1} = 300 \text{ °C}$ $t_{2} = 217.19 \text{ °C}$ $\rho_{tube} = 7.127 \text{ kg/m}^{3}$ $\mu_{tube} = 0.0201 \text{ cP}$

Log Mean Temperature Difference (LMTD): 73.6 °C

In this case, the fixed tube sheet type of heat exchanger and $\Delta 20X24$ TEMA Steel tube is considered.

Identify the thickness of tube:

Safety working pressure $P_s = 3x1.25 3.75$ MPa

Safety working fiber stress $S_s = 99.5 \text{ N/mm}^2$ (From Table B.1)

Corrosion Allowance C = 1.3 mm

Minimum safe thickness $t_m = \frac{d_0}{2.3} \left(\frac{P_s}{S_s} + \frac{1}{30} \right) + C = \frac{20}{2.3} \left(\frac{3.75}{99.5} + \frac{1}{30} \right) + 1.3$

$$t_m = 1.918 \ mm$$

Thickness of tube $t_m = 2.108 \text{ mm}$ (From Table B.2)

Tube inside diameter $(d_i) = 15.784 \text{ mm}$ (From Table B.2)

Identify the length of tube:

Tube length $L_T = 2000 \text{ mm}$

Effective tube length $L_{eff} = 2000 - 75 = 1925 \text{ mm}$

Identify the total number of tubes:

Number of tube pass $n_{TP} = 1$

Number of tubes $=\frac{318310A}{d_o L_{eff}} = \frac{318310(16.95)}{(20)(1925)} = 140.139$ Number of tubes per pass $n_{TPP} = \frac{140.139}{1} = 141$

Total number of tubes $n_T = 141$

Identify the shell nominal diameter:

Shell diameter (D) = 400 mm (From Table B.3)

Check the ratio between tube length and shell diameter:

 $L_T/D = 2000/400 = 5$ (between 2.5 – 8)

Identify the baffles detail:

Type: Segmental

Percent baffles cut (P_{BC}): 25

Baffle spacing $(P_B) = 1xD = 400 \text{ mm}$

The tube side details are:

Tube side mass velocity (G_i) =
$$\frac{353.68W_{tube}}{n_{TPP}d_i^2} = \frac{(353.68)(12810.6)}{(141)(15.784^2)} = 128.98 \frac{kg}{m^2} \cdot s$$

Tube side velocity (V_i) = $\frac{G_i}{\rho_{tube}} = \frac{128.98}{7.127} = 18.097 m/s$
Tube side Reynolds' number (Re_i) = $\frac{d_iG_i}{\mu_{tube}} = \frac{(15.784)(128.98)}{0.0201} = 101138.169$

Tube side friction factor $(j_f) = 0.0027$ (From Figure B.1)

Thus, the tube side pressure drop (ΔP_i) is:

$$\Delta P_{i} = 10^{-3} n_{TP} \left[8j_{f} \left(\frac{L_{T}}{d_{i}} \right) + 2.5 \right] \left(\frac{\rho_{i} V_{i}^{2}}{2} \right)$$

$$\Delta P_{i} = 10^{-3} (1) \left[8(0.0027) \left(\frac{2000}{15.784} \right) + 2.5 \right] \left(\frac{(7.127)(18.0977^{2})}{2} \right)$$

$$\Delta P_{i} = 6.1122 \ kPa$$

$$\Delta P_{i} = 0.06 \ bar$$

The shell side details are:

Shell side mass velocity (G_o) = $\frac{277.8W_{shell}P_T}{DiP_BC'} = \frac{(277.8)(1067.37)(24)}{(400)(400)(4)}$

hulalongkorn University

$$G_0 = 11.119 \ \frac{kg}{m^2} \, s$$

Where:

 P_T = Tube pitch = 24 mm

C' = Tube clearance = P_T - $d_o = 24 - 20 = 4 \text{ mm}$

d_o = Tube outside diameter (mm)

Shell side equivalent diameter (d_e) = $\frac{1.10}{d_0} (P_T^2 - 0.971d_0^2)$

$$d_e = \frac{1.10}{20} \left[(24^2 - 0.971(20^2)) \right] = 10.32 \, mm$$

Shell side velocity (V₀) = $\frac{G_0}{\rho_{shell}} = \frac{11.119}{2.3239} = 4.785 \ m/s$

Shell side Reynolds' number (Re_o) = $\frac{d_e G_o}{\mu_{shell}} = \frac{(10.32)(11.119)}{0.0091} = 12609.679$

Shell side friction factor $(J_f) = 0.048$ (From Figure B.2)

Thus, the shell side pressure drop (ΔP_i) is:

$$\Delta P_{i} = 8 \times 10^{-3} J_{f} \left(\frac{D_{i}}{d_{e}}\right) \left(\frac{L_{T}}{P_{B}}\right) \left(\frac{\rho_{shell}V_{0}^{2}}{2}\right)$$

$$\Delta P_{i} = 8 \times 10^{-3} (0.048) \left(\frac{400}{10.32}\right) \left(\frac{2000}{400}\right) \left(\frac{2.3239 \times 4.784^{2}}{2}\right)$$

$$\Delta P_{i} = 1.979 \ kPa$$

$$\Delta P_{i} = 0.02 \ bar$$

Table B.1 The safety working fiber stress (S_s) of exchanger tube.

Tubing material	CHULALONGKORN Temperature (°C)							
Tuoning material	50	100	150	200	250	300	350	
Carbon steel	125.2	120	115	109.8	104.5	99.5	94	

Sizo (mm)	PWC	Thickness (mm)	Inlet diameter	
Size (IIIII)	BwG	Thickness (mm)	(mm)	
	10	3.403	13.194	
	12	2.768	14.464	
20	14	2.108	15.784	
20	16	1.651	16.698	
	18	1.244	17.512	
	20	0.889	18.222	
	10	3.403	15.194	
	12	2.768	16.464	
22	14	2.108	17.784	
	16	1.651	18.698	
	20	0.889	20.222	
	8	4.191	16.618	
	10	3.403	18.194	
	12	2.768	19.464	
25	14	2.108	20.784	
	16	1.651	21.698	
	18	1.244	22.512	
	20	0.889	23.222	
	8	4.191	23.618	
	10	3.403	25.194	
	12	2.768	26.464	
32	14	2.108	27.784	
	16	1.651	28.698	
	18	1.244	29.512	
	20	0.889	30.222	

Table B.2 The tube size (TEMA Standard) (Kern 1965).

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $
$\begin{array}{c c c c c c c c c c c c c c c c c c c $
$\begin{array}{cccccccccccccccccccccccccccccccccccc$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $
$\begin{array}{c c c c c c c c c c c c c c c c c c c $
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $
$\begin{array}{c c c c c c c c c c c c c c c c c c c $
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $
$\begin{array}{c c c c c c c c c c c c c c c c c c c $
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $
$\begin{array}{c c c c c c c c c c c c c c c c c c c $
$\begin{array}{c c c c c c c c c c c c c c c c c c c $
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
6-F 614 546 470 424 334 296 252 212 164 136 104 74 54 46 24 14 6-U 562 488 426 356 304 252 206 168 130 100 68 42 30 30 30 252 206 168 130 100 68 42 30 30 30 30 252 206 168 130 100 68 42 30 3
6-U 562 488 426 356 304 252 206 168 130 100 68 42 30 8-F 598 532 454 400 316 286 242 202 160 128 94 72 50 44 8-U 540 464 404 340 290 238 190 154 118 90 58 38 24 120X24
8-F 598 532 454 400 316 286 242 202 160 128 94 72 50 44 8-U 540 464 404 340 290 238 190 154 118 90 58 38 24
2-0 540 464 404 340 290 238 190 154 118 90 56 36 24
1-F 934 845 749 657 553 481 413 341 277 224 177 137 97 81 52 32 2-F 914 824 718 640 526 460 394 324 270 220 165 124 90 76 52 26 2-F 914 624 718 640 526 460 394 324 270 220 165 124 90 76 52 26
2-F 914 824 718 640 526 460 394 324 270 220 166 124 90 76 52 26
2-U 654 //8 688 586 506 436 362 304 242 188 142 100 72 52 30 12
4-F 886 780 688 600 480 432 370 308 246 204 158 116 82 68 40 20
6-F 866 766 676 580 468 420 356 302 240 192 150 108 76 68 36 20
6-U 820 718 632 534 458 392 322 268 210 160 118 80 56
8-F 838 748 648 560 456 408 346 292 234 188 142 108 70 60
8-U 792 692 608 512 438 374 306 254 194 146 106 70 48
□25X32
1-F 596 522 465 406 341 300 260 213 177 138 112 81 61 48 32 21
2-F 5/4 518 460 398 326 288 252 208 166 132 112 76 56 45 52 10 241 526 464 406 356 304 256 214 190 134 100 76 58 38 22 12
4-F 562 488 432 380 300 278 238 192 158 128 96 68 52 40 26 14
4-U 500 440 384 336 286 238 198 166 122 90 66 50 32 16
6-F 544 484 420 368 294 268 226 184 152 122 90 68 48 38 24
5-U 478 420 362 316 268 224 182 152 110 80 60 42 8.E 532 472 414 258 296 296 400 448 448 448 446 43
8-U 456 396 344 300 254 206 170 142 98 70 50 34

Table B.3 The maximum tubes contained in shell side of heat exchanger (Evans 1997).

*n-X: n = number of tube pass, X = F/fixed tube sheet, U/u-bend.



Figure B. 1 Friction factor of fluid in tube side (Ludwig 1997).



Figure B. 2 Friction factor of fluid in shell side (Ludwig 1997).

APPENDIX C

COST ESTIMATION FOR HEAT EXCHANGER NETWORK

In this part, the example of construction and operating cost for heat exchanger and utility are considered. The construction cost of heat exchangers are calculated by CAPCOST program (Turton, Bailie et al. 2009). The utilities supplement consist of Dowtherm-A and water that are circulated in the system. The natural gas is used as a fuel for thermal oil boiler.

In this case, the heat exchanger, H-101, of the energy optimization strategy 3 is considered. The Dowtherm-A is exchanged energy with palm oil feed stream (Stream no. 3). The cost estimation for heat exchanger can be calculated as follows:

1. The construction cost of heat exchanger

The data for the construction cost of the equipment, at ambient operating pressure and using carbon steel construction, C_p^0 , were fitted to the following equation:

$$\log_{10}C_p^0 = K_1 + K_2 \log_{10}(A) + K_3 [\log_{10}(A)]^2$$
(C.1)

Where:

A = Heat transfer area (m²)

 $K_1, K_2, K_3 = Construction cost factors (From Table C.1)$

Exchanger Type	K ₁	K 2	K 3
Double Pipe	3.3444	0.2745	-0.0472
Multiple Pipe	2.7652	0.7282	0.0783
Fixed tube, sheet, or U tube	4.3247	-0.303	0.1634
Floating Head	4.8306	-0.8509	0.3187
Bayonet	4.2768	-0.0495	0.1431
Kettle Reboiler	4.4646	-0.5277	0.3955

 Table C.1 The construction cost factors for heat exchanger.

For H-101, the heat transfer area is 12.797 m^2 and K₁, K₂, K₃ are 4.3247, -0.303 and 0.1634, respectively.

Thus, the construction cost of the equipment on September, 2001 (CEPCI=397) is:

$$C_p^0 = \$15471.19$$

The pressure factor, F_p , for the remaining process equipment are given by the following form:

$$log_{10}F_p = C_1 + C_2 log_{10}(P) + C_3 [log_{10}(P)]^2$$
(C.2)

Where:

P = Pressure (barg)

 C_1 , C_2 , C_3 = Pressure correlations (From Table C.2)

Exchanger Type	C ₁	C ₂	C ₃
Double Pipe	13.1467	-12.6574	3.0705
40 barg $< P < 100$ barg	0.6072	-0.912	0.3327
P < 40 barg	0	0	0
Multiple Pipe	13.1467	-12.6574	3.0705
40 barg $< P < 100$ barg	0.6072	-0.912	0.3327
P < 40 barg	0	0	0
Fixed tube, sheet, or U tube	0.03881	-0.11272	0.08183
tubes only > 5 barg	-0.00164	-0.00627	0.0123
Floating Head	0.03881	-0.11272	0.08183
tubes only > 5 barg	-0.00164	-0.00627	0.0123

Table C.2 The pressure factors for heat exchanger.

For H-101, the pressure correlations C_1 , C_2 , C_3 are -0.00164, -0.00627 and 0.0123, respectively.

Thus, the pressure factor is:

$$F_p = 1.0$$

The material factor, F_M , for heat exchanger is given in Figure C.1, with the appropriate identification number listed in Table C.3.

จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University



Figure C.1 The material factor for process equipment.

	Shell - CS	CS	Cu	CS	SS	CS	Ni	CS	Ti
Exchanger Type	Tube - CS	Cu	Cu	SS	SS	Ni	Ni	Ti	Ti
Double Pipe	1.00	1.35	1.69	1.81	2.73	2.68	3.73	4.63	11.38
Multiple Pipe	1.00	1.35	1.69	1.81	2.73	2.68	3.73	4.63	11.38
Fixed tube sheet,	1.00	1 25	1 60	1 0 1	2 72	260	2 72	1 62	11 20
or U tube	1.00	1.55	1.09	1.81	2.75	2.08	5.75	4.05	11.38
Floating Head	1.00	1.35	1.69	1.81	2.73	2.68	3.73	4.63	11.38
Bayonet	1.00	1.35	1.69	1.81	2.73	2.68	3.73	4.63	11.38
Kettle Reboiler	1.00	1.35	1.69	1.81	2.73	2.68	3.73	4.63	11.38
Scraped Wall	1.00	1.35	1.69	1.81	2.73	2.68	3.73	4.63	11.38
Spiral Tube	1.00	1.35	1.69	1.81	2.73	2.68	3.73	4.63	11.38

Table C.3 Identification numbers for material factor for heat exchanger.

Thus, the material factor, F_M , is:

$$F_{M} = 1.0$$

The construction cost of heat exchanger, at operating pressure and using carbon steel construction, C_p^1 , is:

$$C_p^1 = C_p^0 F_P F_M \tag{C.3}$$

Thus,

$$C_p^1 = \$15471.19$$

In 2015, the CEPCI is 568.7 (preliminary March, 2015). Thus, the construction cost of heat exchanger is:

$$Construction \ cost = \frac{CEPCI(2015)}{CEPCI(2001)} \times C_p^1$$
(C.4)

The construction cost of heat exchanger, H-101, is around \$22200. Thus, the construction cost is 754,800 Baht (34 baht/\$)

2. The utility cost of heat exchanger

2.1 Dowtherm-A supplement

From H-101, the input heat duty (Q) is:

Q = 1,453,196.305 Btu/h (425.89 kW)

A natural gas $1 \text{ m}^3/\text{h}$ provides the energy of 35325.48 Btu/h.

In this heat exchanger, the required natural gas is $41.137 \text{ m}^3/\text{h}$.

The cost of natural gas is 13.7962 Baht/m³.

Thus, the total cost of natural gas used in heat exchanger, H-101, is 568 Baht/h.

The process is operated 8,000 working hours per year.

Thus, the total cost of natural gas is 4,544,000 Baht per year.

2.2 Water supplement

The input heat duty of heat exchanger, H-301 (From energy optimization strategy 3), is:

The cost of cooling water supplement is \$0.384/GJ.

Thus, the total cost of utility requirement is \$11.2245/h or 381.63 Baht/h.

The process is operated 8,000 working hours per year.

Thus, the total cost of cooling water is 3,056,000 Baht per year.

In this work, the data for cost calculation of heat exchanger network is presented in Table C.4.

	Energy optimization strategy 1					
-	H-101	H-102	H-401	H-301		
Heat duty (kW)	4265.80	937.16	4636.38	-12815.30		
Area (m ²)	42.71	9.33	133.86	423.34		
Туре	Shell & Tube	Double pipe	Shell & Tube	Shell & Tube		
Supplement	Dowtherm-A	Dowtherm-A	Dowtherm-A	Water		
Tube side:						
Temperature (in) (°C)	81.43	82.31	280.00	97.70		
Temperature (out) (°C)	300.00	300.00	300.00	50.00		
Pressure (bar)	30.00	30.00	30.00	30.00		
Shell side:						
Temperature (in) (°C)	350.00	350.00	350.00	30.00		
Temperature (out) (°C)	310.00	312.99	312.40	39.90		
Pressure (bar)	5.437	5.437	5.437	1.013		

 Table C.4 The data for calculated cost of heat exchanger network.

จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University

	Energy optimization strategy 2					
	H-101	H-102	H-401	H-301		
Heat duty (kW)	425.89	168.16	9912.09	-13481.40		
Area (m ²)	12.80	4.31	266.89	434.89		
Туре	Shell & Tube	Double pipe	Shell & Tube	Shell & Tube		
Supplement	Dowtherm-A	Dowtherm-A	Dowtherm-A	Water		
Tube side:						
Temperature (in) (°C)	280.00	261.00	257.00	100.58		
Temperature (out) (°C)	300.00	300.00	300.00	50.00		
Pressure (bar)	30.00	30.00	30.00	30.00		
Shell side:						
Temperature (in) (°C)	350.00	350.00	350.00	30.00		
Temperature (out) (°C)	310.00	303.12	294.59	40.40		
Pressure (bar)	5.437	5.437	5.437	1.013		
		Energy optimization	zation strategy 3			
	H-101	H-102	H-401	H-301		
Heat duty (kW)	425.89	86.25	4622.13	-8119.61		
Area (m ²)	12.80	2.25	125.21	327.72		
Туре	Shell & Tube	Double pipe	Shell & Tube	Shell & Tube		
Supplement	Dowtherm-A	Dowtherm-A	Dowtherm-A	Water		
Tube side:						
Temperature (in) (°C)	280.00	280.00	280.00	77.30		
Temperature (out) (°C)	300.00	300.00	300.00	50.00		
Pressure (bar)	30.00	30.00	30.00	30.00		
Shell side:						
Temperature (in) (°C)	350.00	350.00	350.00	30.00		
Temperature (out) (°C)	310.00	310.16	317.34	36.31		
Pressure (bar)	5.437	5.437	5.437	1.013		

 Table C.4 The data for calculated cost of heat exchanger network. (Continued)
VITA

Miss Suwisa Sae-ueng was born in May 28, 1991 in Betong, Yala, Thailand. She received the Bachelor's Degree in Chemical Engineering from Faculty of Engineering, Price of Songkla University in 2012. Afterward, she strated her Master's Degree in Chemical Engineering since October 2012.



จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University