การประเมินคาร์บอนไดออกไซด์ที่จับได้และไฮโดรเจนเหลือทิ้งเพื่อเป็นสารตั้งต้นที่มีศักยภาพในการ ผลิตเมทานอล



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 ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2560
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

EVALUATION OF CAPTURED CO_2 AND WASTE H_2 AS POTENTIAL FEEDSTOCK FOR METHANOL PRODUCTION



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 2017

Copyright of Chulalongkorn University

Thesis Title	EVALUATION	OF CAPTURED (CO ₂ AND	WASTE H ₂ AS
	POTENTIAL	FEEDSTOCK	FOR	METHANOL
	PRODUCTION			
Ву	Miss Kankanit	Kitsahawong		
Field of Study	Chemical Engineering			
Thesis Advisor	Professor Suttichai Assabumrungrat, Ph.D.			
Thesis Co-Advisor	Pongtorn Cha	aroensuppanimi	t, Ph.D.	
Accepted by the Faculty	of Engineering	g, Chulalongkorr	n Univers	sity in Partial
Fulfillment of the Requirements	for the Maste	er's Degree		
	8 D	ean of the Facu	ılty of Er	ngineering
(Associate Professor Su	IIIn S			
THESIS COMMITTEE	1/3004			
THESIS CONTINUE FEE				
<u> </u>		Chairman		
(Associate Professor Ta	watchai Charii	npanitkul, D.Eng	į.)	
		Thesis Advi	isor	
(Professor Suttichai Ass	abumrungrat,	Ph.D.)		
จหาลงเ		Thesis Co-	Advisor	
(Pongtorn Charoensupp				
		Examiner		
(Palang Bumroongsakul	sawat, Ph.D.)			
		External Ex	aminer	
(Assistant Professor Wo				

Thesis Title

กันต์กนิษฐ์ กิจสหวงศ์ : การประเมินคาร์บอนไดออกไซด์ที่จับได้และไฮโดรเจนเหลือทิ้ง เพื่อ เป็นสารตั้งต้นที่มีศักยภาพในการผลิตเมทานอล (EVALUATION OF CAPTURED ${\rm CO_2}$ AND WASTE ${\rm H_2}$ AS POTENTIAL FEEDSTOCK FOR METHANOL PRODUCTION) อ.ที่ ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร.สุทธิชัย อัสสะบำรุงรัตน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร. พงศ์ธร เจริญศุภนิมิตร, 93 หน้า.

ภาวะเรือนกระจกเป็นปัญหาสำคัญที่เกิดจากการปลดปล่อยก๊าซเรือนกระจกซึ่งส่วนใหญ่ เป็นก๊าซคาร์บอนไดออกไซด์ดังนั้นการนำคาร์บอนไดออกไซด์กลับมาใช้จึงเป็นทางเลือกที่ดีสำหรับการ ลดการปลดปล่อก๊าซคาร์บอนไดออกไซด์โดยที่นำไฮโดรเจนเหลือทิ้งจากการผลิตโซเดียมเมทอกไซด์ ขนาดต่างๆมาทำปฏิกิริยากับก๊าซคาร์คาร์บอนไดออกไซด์ผ่านปฏิกิริยาคาร์บอนไดออกไซด์ไฮโดรจีเน ชันเพื่อผลิตเป็นเมทานอลซึ่งสามารถป้อนกลับเป็นสารตั้งต้นของการผลิตโซเดียมเมทอกไซด์ได้ ซึ่งผล การจากการจำลองกระบวนการพบว่าเมทานอลที่สมารถผลิตได้คิดเป็นร้อยละ 16.3 ของปริมาณเมทานอลที่ต้องการใช้ในการผลิตโซเดียมเมทอกไซด์ และกระบวนการผลิตเมทานอลสามารถดึง คาร์บอนไดออกไซด์ไปใช้ได้ 1.34 กิโลกรัม ต่อ การผลิตเมทานอล 1 กิโลกรัมในทุกๆกำลังการผลิต อย่างไรก็ตามความเป็นไปได้ทางเศรษฐศาสตร์ของกระบวนการผลิตเมทานอลขึ้นอยู่กับกำลังการผลิต โดยการผลิตเมทานอลจะสามารถให้ประโยชน์จากการลดการซื้อเมทานอลเข้ามาใช้ในกระบวนการผลิตโซเดียมเมทอกไซด์มม่อกำลังการผลิตโซเดียมเมทอกไซด์มากกว่ากำลังการผลิตที่มีอยู่ในปัจจุบัน 9.5 เท่า โดยได้รับผลประโยชน์ในปีที่ 17 (P.O. period = 16.9) และมีดัชนีกำไรเมื่อสิ้นสุดปีที่ 20 ใกล้เคียง 1 (PI = 1.02) กำลังการผลิตที่มากขึ้นจะช่วยทำให้การผลิตเมทานอลมีความเป็นได้ทาง เศรษฐศาสตร์มากขึ้น หรืออีกทางเลือกที่น่าสนใจคือกาารผลิตสารที่มีราคาสูงกว่าเมทานอลซึ่งหลาย ชนิดสามารถผลิตได้จากเมทานอล

ภาควิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต
สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อ อ.ที่ปรึกษาหลัก
ปีการศึกษา	2560	ลายมือชื่อ อ.ที่ปรึกษาร่วม

5870114521 : MAJOR CHEMICAL ENGINEERING

KEYWORDS:

KANKANIT KITSAHAWONG: EVALUATION OF CAPTURED CO_2 AND WASTE H_2 AS POTENTIAL FEEDSTOCK FOR METHANOL PRODUCTION. ADVISOR: PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D., CO-ADVISOR: PONGTORN CHAROENSUPPANIMIT, Ph.D., 93 pp.

Global warming is the critical issue that is the result of Greenhouse Gases (GHGs) emission. Carbon dioxide (CO_2) is concerned to be major GHGs. Thus, Carbon dioxide utilization is the promising pathway to reduce the emission of CO_2 . To utilize CO_2 , waste hydrogen from sodium methoxide production is used to produce methanol which can be recycled as reactant of sodium methoxide synthesis. Carbon dioxide hydrogenation process is used for produce methanol from CO_2 and waste H_2 from various size of sodium methoxide production process. In every size of methanol production process, methanol which produce from the process is 16.3% of required methanol for sodium methoxide process and CO_2 is consumed 1.34 kg per 1 kg of methanol which is produced from process. However, the economic feasibility of methanol process is depended on size of process. The process start to be profitable at 9.5 folds of present actual sodium methoxide production capacity with 17 years payback period (P.O. period = 16.9) and profitability at the 20^{th} years of project near to 1 (PI = 1.02). The larger capacity or production of more valuable product from methanol may be improve the economic feasibility of process.

Department:	Chemical Engineering	Student's Signature
Field of Study:	Chemical Engineering	Advisor's Signature
Academic Year:	2017	Co-Advisor's Signature

ACKNOWLEDGEMENTS

First, I would like to express my sincere gratitude and appreciation to my thesis advisor, Prof. Dr. Suttichai Assabumrungrat for his encouraging guidance, invaluable suggestions, and useful discussions throughout my graduated research. In addition, I would like to extend my greatest gratitude towards Dr. Pongtorn Charoensuppanimit, my thesis co-advisor for his generosity in providing continuously support and encouragement over the year, without his concernedness, this thesis could not be completed. Their advices are always worthwhile and without them this work could not be possible.

Special thanks belong to Assoc. Dr. Tawatchai Charinpanitkul as Chairman as well as Dr. Palang Bumroongsakulsawat and Asst. Prof. Worapon Kiatkittipong as members of thesis committee for their valuable guidance and revision throughout my research.

I also wish to express special thanks to Department of Chemical technology, Faculty of Science, Chulalongkorn University for providing the ASPEN program license.

My most sincere thanks are given to the Ratchadapisek Sompoch Endowment Fund (2016), Chulalongkorn University (CU-59-003-IC).

I wish to give special thanks to the whole students of Center Excellence on Catalysis and Catalytic Reaction Engineering for their good spirit shared, joyful workplace and wonderful times.

Finally, I would like to express the highest gratitude to my family, especially my father and my mother for their unconditional love, inspiration, encouragement and financial support during this research.

CONTENTS

	Page
THAI ABSTRACT	iv
ENGLISH ABSTRACT	V
ACKNOWLEDGEMENTS	Vi
CONTENTS	Vii
LIST OF TABLES	X
LIST OF FIGURES	X
CHAPTER 1 INTRODUCTION	1
1.1 Statement of the problem	
1.2 Objective	3
1.3 Scope of work	
1.4 Hypothesis	3
CHAPTER 2 THEORY AND BACKGROUND	
2.1 CO ₂ management	4
2.1.1 CO ₂ capture technology	4
2.1.2 CO ₂ capture and storage (CCS)	6
2.1.3 CO ₂ capture and utilization (CCU)	7
2.2 methanol	10
CHAPTER 3 LITERATURE REVIEW	11
3.1 CO ₂ Hydrogenation	11
3.2 Hydrogen source	14
3.2.1 Hydrogen from propane dehydrogenation	14
3.2.2 Hydrogen from sodium methoxide production	14

	Page
3.3 Sodium methoxide production	15
3.4 CO ₂ Utilization evaluation methods	15
3.5 Economic analysis	16
CHAPTER 4 METHODOLOGY	18
4.1 Design scope	18
4.2 Feedstock estimation	19
4.3 Process description	20
4.3.1 Multi-stages compressor design	21
4.3.2 Reactor design	22
4.3.3 Flash separation unit design	22
4.3.4 Stabilizer and methanol purification column	22
4.4 Evaluation of CO ₂ utilization	22
4.5 Economics analysis	23
CHAPTER 5 RESULT AND DISCUSSION	24
5.1 Simulation of methanol production using ASPEN PLUS	
5.2 Evaluation of carbon dioxide utilization	38
5.3 Economic feasibility	39
CHAPTER 6 CONCLUSION	44
REFERENCES	46
APPENDIX A VERIFICATION OF RATE EQUATIONS	53
APPENDIX B CALCULATION OF METHANOL REQUIRED FOR SODIUM METHOXIDE	
PRODUCTION PLANT AND FEED AMOUNT FOR METHANOL PRODUCTION	56
B.1 Calculation of feed amount of BRZ capacity	56

	Page
B.2 Calculation of feed amount of BRZ x 5 capacity	56
B.3 Calculation of feed amount of BRZ x 7.5 capacity	57
B.4 Calculation of feed amount of BRZ x 9.5 capacity	58
APPENDIX C EQUIPMENT SPECIFICATION	59
C.1 Utilities specification	59
C.2 Compressor Specifications	59
C.3 Heater and cooler specifications	60
C.4 Reactor Specifications	60
C.5 Flash drum specifications	61
C.6 Distillation column specifications	62
APPENDIX D CALCULATION OF NET CO2 EMISSION AND CARBON EFFICIENCY	63
D.1 Net CO ₂ Emission and carbon efficiency of BRZ size	63
D.2 Net CO ₂ Emission and carbon efficiency of BRZ x 5 size	64
D.3 Net CO ₂ Emission and carbon efficiency of BRZ x 7.5 size	66
D.4 Net CO ₂ Emission and carbon efficiency of BRZ x 9.5 size	67
APPENDIX E ECONOMIC ANALYSIS RESULT	70
E.1 Nomenclature of variables in economic analysis result	70
E.2 Economic analysis result of BRZ size	70
E.3 Economic analysis result of BRZ x 5 size	76
E.4 Economic analysis result of BRZ x 7.5 size	82
E.5 Economic analysis result of BRZ x 9.5 size	88
VITA	93

LIST OF TABLES

Table 2.1 Summary of CO ₂ capture technologies [6, 16]	5
Table 2.2 Physical and chemical properties of methanol [25]	10
Table 3.1 List of catalyst types and conditions for CO_2 hydrogenation to methanol production [28-31]	11
Table 3.2 Kinetics of CO ₂ hydrogenation for methanol products on various catalysts.	12
Table 3.3 Sources of CO ₂ and hydrogen for CO ₂ hydrogenation to produce methanol	13
Table 3.4 the size of sodium methoxide production	15
Table 4.1 Hydrogen waste flow rate from NaOCH3 catalyst production	20
Table 4.2 Cost of raw material and selling price of product	
Table 5.1 Feed condition	24
Table 5.2 Stream result of BRZ size	25
Table 5.3 Stream result of BRZ x 5 size	28
Table 5.4 Stream result of BRZ x 7.5 size	31
Table 5.5 Stream result of BRZ x 9.5 size	34
Table 5.6 Percentages of methanol yield to amount of methanol which want to	
use by the sodium methoxide production	37
Table 5.7 Net CO ₂ utilization	38
Table 5.8 Net CO ₂ emission of various studies	39
Table 5.9 Carbon efficiency of methanol production process	39
Table 5.10 Economic analysis result	40
Table 5.11 Other products from methanol and their price	43

LIST OF FIGURES

Figure 2.1 Schematic of CO ₂ Managements Route	4
Figure 2.2 Diagram of CO ₂ capture and sequestration (CCS) [17]	6
Figure 2.3 Example of products from carbon dioxide [19]	8
Figure 2.4 Molecular structure of methanol [24]	10
Figure 4.1 Scope of work	18
Figure 4.2 Process flow sheet for methanol production	21
Figure 5.1 Relationship between methanol yield and amount of methanol	
required for the sodium methoxide production	37
Figure 5.2 Trend of Total capital cost, total operating cost, and total product	
sales	41
Figure 5.3 Equipment cost of unit operation	41
Figure 5.4 Trend of compressor construction cost and methanol purification unit	
(B10) construction cost	42

ี จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University

CHAPTER 1

INTRODUCTION

1.1 Statement of the problem

Nowadays, the climate change as a result of the global warming is a critical issue that has gained its attention worldwide. Such issue may result from the emissions of greenhouse gases (GHG) such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF_6) [1]. Among these GHG, CO_2 accounts for more than 70% of the total GHG emissions [2]. According to National Oceanic and Atmospheric Administration (NOAA), atmospheric concentration of CO_2 had increased from 381 ppm in 2006 to 402 ppm in 2016 [3].

Industrialized-based countries attempt to come up with agreements in order to solve such concern. For example, in 2015, Paris Agreement aim to holding the global temperature rising to well below 2 °C compare to pre-industrial levels and try to continue to limit of global temperature rising to 1.5 °C compare to pre-industrial levels in year 2023 [4]. Similarly, environmental and public health authority in Thailand aims to decrease about 7 to 20 percent of the total GHG emissions from energy and transportation sectors before year 2020 [5].

For the past centuries, many researchers have been attempting to develop feasible technologies that enable reduction of the CO_2 emissions [6]. There are two major technologies that effectively decrease CO_2 emissions: Carbon dioxide Capture and Storage (CCS), and Carbon dioxide Capture and Utilization (CCU). CCS is the technology which CO_2 is collected, compressed, and sequestered in underground geological storage. However, major problems found in the CCS are 1) limitation of storage volume [7] 2) its expensive operation cost that may not worth the capital investment [6, 8] and 3) its effect that may relate to more frequent with earthquake earthquakes such as in the US [9]. Therefore, the CCU is more preferred, and will be focused in this study.

According to CCU, CO_2 is considered as one-carbon atom feedstock that reacts with hydrogen gas (H_2) to produce others chemical products [7, 8]. However, the major problem in CCU exists as H_2 is conventionally produced from the non-stainable via natural gas steam reforming. To remedy this, biogas may be more suitable as an input for the H_2 production.

Nevertheless, utilization of H_2 produced from biogas may be hindered by one constraint; that is its large amount of CO_2 constituent. In fact, the purpose of this study is to evaluate chemical processes that can consume CO_2 from external sources and produce more valuable chemical products. If the feedstock has a large amount of preexisting CO_2 , the CO_2 from external sources may not be fully utilized. Thus, a high purity source of H_2 is preferred which leads to considerations of using renewable hydrogen and waste hydrogen as feedstock.

Since, renewable hydrogen has high production cost that may not be feasible [10, 11]. Industrial waste hydrogen is another alternative that will be scrutinized in this study. Some industries such as propane dehydration, and sodium methoxide production release a large amount of H_2 [12, 13]. The reuse of such H_2 waste may satisfy the objective of the sustainable CO_2 utilization.

As mentioned above, waste H_2 is released from the sodium methoxide production process. Sodium methoxide is a catalyst utilized in biodiesel productions. In 2016, the global biodiesel production was about 90 million liters/day and Thailand alone synthesized approximately 3.4 million liters/day [14, 15]. As considered by the number of biodiesel productions, they can be justified that waste H_2 was produced in a large quantity. Consequently, benefit may be gained from the conversion of such problematic CO_2 and the zero-value H_2 waste through chemical reactions in order to produce more valuable products. This definitely not only helps solve the environmental problems but also adds value to the CO_2 and H_2 waste.

In this work, methanol production is selected as a chemical process that utilizes H_2 waste from sodium methoxide production. The CO_2 from external sources is consumed in the methanol production process via CO_2 hydrogenation in order to

reduce the CO_2 emissions. Also noted that methanol production process is chosen for the evaluation due to one major reason; the obtained methanol may be recycled to the sodium methoxide production process. This should contribute to a reduction in raw material cost since the methoxide production uses methanol as a reactant.

1.2 Objective

The aim of this work is to evaluate the potential of wasted H_2 and captured CO_2 as feedstock for methanol production through CO_2 hydrogenation reaction. The produced methanol is then recycled to the sodium methoxide production. The process evaluation is conducted using a process simulator namely Aspen Plus.

1.3 Scope of work

- 1. Quantify the amount of H_2 waste released from NaOCH $_3$ production. Further details regarding the H_2 waste estimation is given in Chapter 4.
- 2. Analyze the methanol production process using Aspen Plus. The analyzed process converts CO_2 and H_2 through CO_2 hydrogenation using H_2 waste obtained from sodium methoxide production process and CO_2 from external sources.
- 3. Evaluate the economics of methanol production process that benefits a future feasibility study.

1.4 Hypothesis

The conversion of waste H_2 and a greenhouse gas such as CO_2 via CO_2 hydrogenation leads to an economically feasible process capable of reducing the CO_2 emissions as well as producing a more valuable product such as methanol.

CHAPTER 2

THEORY AND BACKGROUND

This chapter describes about the theoretical background relevant to this research. Carbon dioxide (${\rm CO_2}$) management, and methanol properties and its production are provided in this chapter 2.

2.1 CO₂ management

There are two main approaches for the reduction of CO_2 emission including 1) CO_2 Capture and Storage (CCS) and 2) CO_2 Capture and Utilization (CCU). In fact, the first step of both approaches is similar; CO_2 is captured. However, the step after CO_2 capture is different depending upon how the captured CO_2 is managed. The CO_2 management schematic is summarized and depicted in Figure 2.1

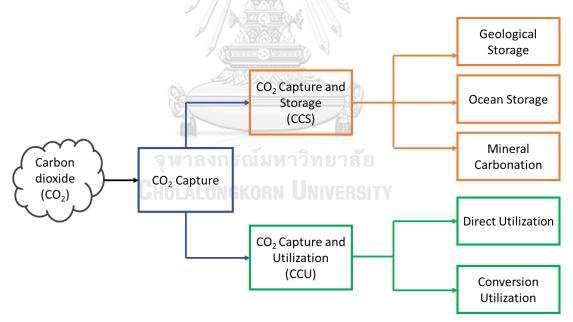


Figure 2.1 Schematic of CO₂ Managements Route

2.1.1 CO₂ capture technology

The CO_2 capture technique can be partitioned into 3 categories including preconversion, post-conversion, and oxy-fuel combustion captures. Pre-conversion capture is the technique which CO_2 is captured from a mixture of reactants before

moving into a reactor, for example, CO_2 captured from syngas before burning H_2 in IGCC and CO_2 captured from syngas before being fed to ammonia production processes. In post-combustion capture, CO_2 is separated after the reaction is completed. The example of this type of capture is CO_2 captured from flue gas produced from burning of fossil fuel. Finally, the oxy-fuel combustion is a technique that an air separation unit is required. After combusting with pure oxygen, the obtained flue gas contains only CO_2 and CO_2 and CO_3 and $CO_$

Separation processes are important for CO_2 capture. Technologies for CO_2 capture are not only centered on developments of chemical solvents that dissolve CO_2 but also developments of unit operations that can effectively separate the CO_2 . The summary of CO_2 capture technologies is provided in Table 1

Table 2.1 Summary of CO₂ capture technologies [6, 16]

Process	Chemicals/Unit Operation	Usage
Absorption	Amine solution, Selexol	Pre-conversion, Post-conversion
High temperature	Metal oxide as oxygen	Pre-conversion, Post-conversion,
solid looping	carrier	Oxy-fuel combustion
Solid sorbents	Amine-based sorbent, Alkaline earth metal-based or carbonate sorbent	Pre-conversion, Post-conversion, Oxy-fuel combustion
Cryogenic	Cooler and compressor	Post-conversion, Oxy-fuel combustion
Membranes	Polymeric membrane	Pre-conversion, Post-conversion, Oxy-fuel combustion

From the list in Table 1, absorption is the only technology that is fully developed. For example, in 2015, demonstration plant of CO_2 capture and sequestration project were achieved at the rate of 1 Mt CO_2 /yr. [16]

2.1.2 CO₂ capture and storage (CCS)

In CO_2 capture and storage (CCS), after CO_2 is captured, CO_2 will be stored in technological potential storages such as geological storage, ocean storage, and mineral carbonation [6]. The diagram of CO_2 storage is shown in figure 2.1

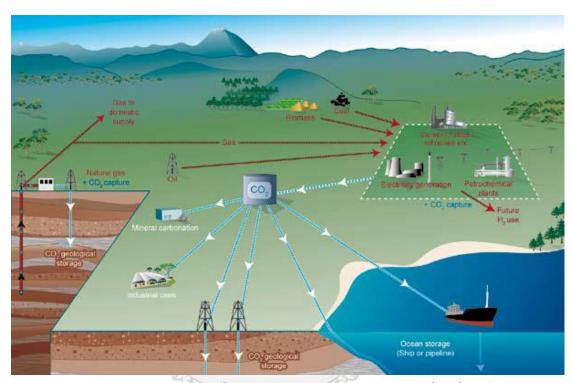


Figure 2.2 Diagram of CO₂ capture and sequestration (CCS) [17]

In geological storage, the captured CO_2 are compressed and sequestered in storages such as petroleum fields, deep saline formation, and unminable coal beds. For storing underneath the ocean floor, gas is shipped or delivered through pipelines for direct injection of CO_2 . Finally, mineral carbonation is the fixation of CO_2 ; CO_2 reacts with metal oxide to form carbonate compounds, such as, MgCO₃ and MgCO₃ [17].

Also noted that, the mineral carbonation process may be perceived as the CCU approach since more valuable products are obtained.

However, a main limitation of CCS is its expensive operation cost of compression of CO_2 before sequestration. Another constraint is formation leakage that may occur in both geological storage and ocean storages. Moreover, CO_2 sequestration

in geological storage may cause adverse effect which may relate to earthquake particularly in the US [6, 18].

2.1.3 CO₂ capture and utilization (CCU)

Carbon dioxide capture and utilization (CCU) may be more superior to the CCS as far as the sustainability is concerned because CO_2 can be reprocessed to form more valuable products. There are two types of CO_2 utilization: direct utilization and conversion utilization.

Direct utilization means CO_2 is used directly: there is no conversion of CO_2 to other products. For example, in food industry, CO_2 is used as supercritical solvent for flavors extraction or used in carbonated drinks [6].

Utilization conversion of CO_2 is the utilization that CO_2 is converted to more valuable products by biological and chemical processes.

Conversion of CO_2 via biological process is focused on biofuel production from microalgae. Waste gas contains CO_2 is fed directly to the microalgae. However, the production cost of biofuels from microalgae appears to be high [6].

In the transformation of CO_2 via chemical process, CO_2 is considered as one-carbon-atom source. The potential products which can be produced from CO_2 are shown in figure 2.3.

CHULALONGKORN UNIVERSITY

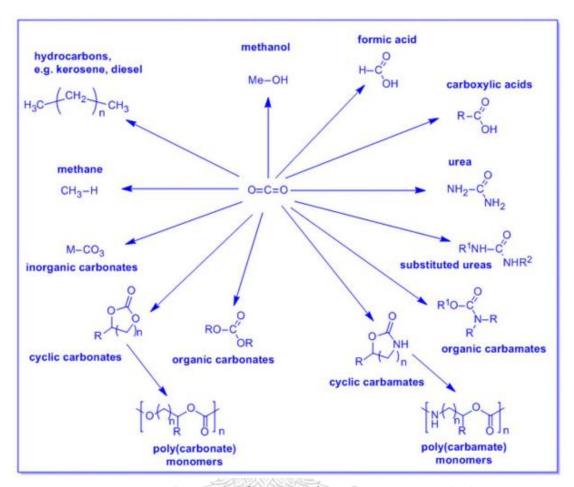


Figure 2.3 Example of products from carbon dioxide [19]

According to Figure 2.3 the major products obtained from the conversion of CO_2 are urea, methanol, organic carbonates, cyclic carbonates, as well as, organic and cyclic carbamates. The following section is dedicated to providing the chemical reactions that converts CO_2 to more valuable products.

Urea production from CO₂

Urea production from CO_2 is started form CO_2 and ammonia. The two-step reaction and side reaction are listed as following [20].

1st step:
$$2NH_3 + CO_2 \leftrightarrow NH_2COONH_4$$
 (1)

$$2^{\text{nd}}$$
 step: $NH_2COONH_4 \leftrightarrow NH_2CONH_2 + H_2O$ (2)

Side reaction: $2NH_2CONH_2 \leftrightarrow NH_2CONHCONH_2 + NH_3$ (3)

• Methanol production from CO₂

The synthesis of methanol from CO_2 is the reaction between CO_2 and H_2 with copper-based catalysts as given in the following reaction [21].

$$CO_2$$
 Hydrogenation: $CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$ (4)

The side reactions of CO_2 hydrogenation are Reverse Water Gas Shift (RWGS) reaction and methanol dehydration reaction respectively [21].

RWGS Reaction:
$$CO_2 + H_2 \longleftrightarrow CO + H_2O$$
 (5)

CH₃OH dehydration:
$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$$
 (6)

• Organic carbonates and Cyclic carbonates

Organic carbonates can be produced in various ways. One way of low toxic synthesis is transesterification of urea. The 1^{st} step is urea synthesis and the 2^{nd} step is transesterification of urea as provided in the following equations [22]

urea synthesis:
$$CO_2 + 2NH_3 \longleftrightarrow NH_2CONH_2 + H_2O$$
 (7)

Transesterification:
$$NH_2CONH_2 + ROH \longleftrightarrow ROCOOR + NH_3$$
 (8)

Cyclic carbonates can be synthesized from epoxides or alcohols as given in the following reaction [23]

Epoxide reactant:
$$2ROH + CO_2 \rightarrow (RO)_2C = O + H_2O$$
 (10)

Organic carbamates and Cyclic carbamates

Organic carbamates can be synthesized by two-step reaction. First, CO_2 reacts with amine to form carbamic acid. Then carbamic acid reacts with alcohol to form carbamates as shown in following equation [23].

The 1st step:
$$RNH_2 + CO_2 \rightarrow RNHCOOH$$
 (11)

The
$$2^{nd}$$
 step: RNHCOOH + R'OH \rightarrow RNHCOOR' + H₂O (12)

There are many ways to synthesize cyclic carbamates from CO_2 . One example of cyclic carbamate synthesis is the reaction of aziridines with CO_2 as shown in reaction (13) [23].

Cyclic carbamates:
$$R$$
 $+ co_2 \xrightarrow{cat} O$ R $+ co_2 \xrightarrow{R} R$ (13)

2.2 methanol

In atmospheric pressure and room temperature, methanol is colorless liquid. Molecular structure of methanol is shown in figure 2.4. Physical and chemical properties of methanol are listed in table 2.2.

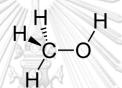


Figure 2.4 Molecular structure of methanol [24]

Table 2.2 Physical and chemical properties of methanol [25]

Properties	Methanol	
Formula	CH₃OH	
Molecular weight	32.04 g/mole	
Appearance	No color liquid,	
Odor	Alcohol like	
Melting point	-97.8 °C	
Boiling point	64.5 °C	
Specific gravity	0.7915 (water = 1)	
Vapor pressure	12.3 kPa (at 20 °C)	
Solubility	Easy to solute in water	
Classification (National Fire Protection	Health:1, Flammability: 3, Reactivity:0,	
Association)*	and no specific hazard	

^{*}NFPA 704 defined the degree of hazard of chemical products. Degree of health hazard at level 1 means this chemical can make some of eyes, respiratory tract, and skin irritation. Degree of flammability hazard at level 3 mean this chemical have flash point between 22.8 °C and 37.8 °C. Degree of reactivity hazard at level 0 means this chemical do not sensitive to thermal or mechanical shock at normal or elevated temperature and pressure.[26]

CHAPTER 3

LITERATURE REVIEW

This chapter is a review of relevant literature about the CO_2 hydrogenation reaction to produce methanol. The review of reactant source is provided herein. Novelty of this study will be given in this chapter.

3.1 CO₂ Hydrogenation

With regard to the objective of CO_2 utilization, CO_2 hydrogenation is one of the effective method for CO_2 utilization. Although CO_2 may be converted to various products, production of methanol from CO_2 is chosen since the production process of methanol is potentially feasible and further modification of the process is easily developed as provided in the following examples.

In Iceland, waste CO_2 reacts with H_2 from water electrolysis using geometric energy. Capacity of a demonstration plant is about 10 tons/day. Moreover, a demonstration plant with a capacity of about 10000 tons/year has been planned to be constructed in Japan. Reactants are obtained from CO_2 waste from other production plant and H_2 from photoelectrolysis. [27]

In methanol production process, a typical catalyst used in ${\rm CO_2}$ hydrogenation process in order to produce methanol is copper-based. Various catalyst types and conditions for methanol synthesis are listed in table 3.1

Table 3.1 List of catalyst types and conditions for CO_2 hydrogenation to methanol production [28-31]

Catalyest	Temperature	Pressure	CO ₂ Conversion	Methanol
Catalyst	(°C)	(bar)	(%)	Selectivity (%)
Cu/Ga/ZrO ₂	250	20	13.7	75.6
Cu/Zn/ZrO ₂	220	80	21.0	68.0
Pd/Zn/CNTs	250	30	6.30	99.6
Cu/ZnO/Al ₂ O ₃	170	50	25.9	72.9

To produce methanol, the best catalyst of CO_2 hydrogenation to produce methanol appears to be $Cu/ZnO/Al_2O_3$ since the catalyst has highest CO_2 conversion and methanol selectivity. At temperature and pressure around 200 $^{\circ}C$ and 50 bars, CO_2 hydrogenation follow the CAMERE pathway. [32]

The CAMERE pathway contains two step including reverse water shift reaction and carbon monoxide hydrogenation. [32]

RWGS Reaction:
$$CO_2 + H_2 \longleftrightarrow CO + H_2O$$
 (3.1)

CO Hydrogenation:
$$CO + 2H_2 \longleftrightarrow CH_3OH$$
 (3.2)

$$CO_2$$
 Hydrogenation: $CO_2 + 3H_2 \longleftrightarrow CH_3OH + H_2O$ (3.3)

The rate equations of reaction kinetics are different depending upon components in each catalyst. The rate equations of ${\rm CO_2}$ hydrogenation are listed in Table 3.2

Table 3.2 Kinetics of CO₂ hydrogenation for methanol products on various catalysts.

$r_{CH_3OH} = \frac{k_1 p_{CO_2} p_{H_2} (1 - p_{CH_3OH} p_{H_2O} / (K_1^* p_{CO_2} p_{H_2}^3)}{p_{CO_2} + K_{H_2O} p_{CO_2} p_{H_2O} + K'' p_{H_2O}}$
$PCO_2 \cdot H_2OPCO_2PH_2O \cdot HPH_2O$
RMNIINDIND
$r_{RWGS} = \frac{k_2 p_{H_2} p_{CO_2} (1 - p_{CO} p_{H_2O} K_3^* / (p_{CO_2} p_{H_2})}{p_{CO_2} + K_{H_2O} p_{CO_2} p_{H_2O} + K'' p_{H_2O}}$
r_{MeOH}
$= \frac{K_a p_{CO_2} p_{H_2} [1 - (1/K^*) (p_{H_2O} p_{CH_3OH} / p_{H_2}^3 p_{CO_2})]}{(1 + (K_{H_2O} / K_8 K_9 K_{H_2}) (p_{H_2O} / p_{H_2}) + \sqrt{K_{H_2} p_{H_2}} + K_{H_2O} p_{H_2O})^3}$
(1 (H ₂ 0)H ₂ 0)H ₂ 0)H ₂ 0)H ₂ 0)H ₂ 00H ₂ 0)
$= \frac{k'_{1}p_{CO_{2}}[1 - K_{3}^{*}(p_{H_{2}O}p_{CO}/p_{CO_{2}}p_{H_{2}})]}{(1 + (K_{H_{2}O}/K_{8}K_{9}K_{H_{2}})(p_{H_{2}O}/p_{H_{2}}) + \sqrt{K_{H_{2}}p_{H_{2}}} + K_{H_{2}O}p_{H_{2}O})}$
$-\frac{1}{\left(1+\left(K_{H_{2}O}/K_{8}K_{9}K_{H_{2}}\right)\left(p_{H_{2}O}/p_{H_{2}}\right)+\sqrt{K_{H_{2}}p_{H_{2}}}+K_{H_{2}O}p_{H_{2}O}\right)}$
$K_a = k'_{5a}K'_2K_3K_4K_{H_2}$
$r_{CO} = \frac{k_A K_{CO} K_{H_2}^2 K_{CH,CO} (P_{H_2}^2 P_{CO} - P_{CH_3OH} / K_{PA})}{(1 + K_{CO} P_{CO}) (1 + K_{H_2}^{0.5} P_{H_2}^{0.5} + K_{H_2O} P_{H_2O})}$
rausa
$= \frac{k_B K_{CO_2} K_{H_2}^{0.5} (P_{CO_2} P_{H_2} - P_{CO} P_{H_2O} / K_{PB}) / P_{H_2}^{0.5}}{(1 + K_{CO} P_{CO}) (1 + K_{H_2}^{0.5} P_{H_2}^{0.5} + K_{H_2O} P_{H_2O}) (1 + K_{CO_2} P_{CO_2})}$

H.W. Lim et		$r_{CO_2} = \frac{k_C K_{CO_2} K_{H_2} K_{CH,CO_2} (P_{CO_2} P_{H_2}^3 - P_{CH_3OH} P_{H_2O} / K_{PC}) / P_{H_2}^2}{(1 + K_{H_2}^{0.5} P_{H_2}^{0.5} + K_{H_2O} P_{H_2O}) (1 + K_{CO_2} P_{CO_2})}$
al., 2009	$Cu/ZnO/Al_2O_3/ZrO_2$	$k_{DME}K_{CH_{3}OH}^{2}\left(C_{CH_{3}OH}^{2}-\left((C_{H_{2}O}C_{DME})/K_{P,DME}\right)\right)$
(cont.)		$r_{DME} = \frac{R_{DME} R_{H_3OH} \left(S_{CH_3OH} - \left(S_{H_2O} S_{DME} \right) R_{P,DME} \right) \right)}{\left(1 + 2\sqrt{K_{CH_3OH} C_{CH_3OH}} + K_{H_2O} C_{H_2O} \right)^4}$
E.S. Van-Dal		
and Chakib	Cu/750/ALO	$r_{CH_3OH} = \frac{k_1 P_{CO_2} P_{H_2} - k_6 P_{H_2O} P_{CH_3OH} P_{H_2}^{-2}}{\left(1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O}\right)^3}$
Bouallou	Cu/ZnO/Al ₂ O ₃	$r_{RWGS} = \frac{k_5 P_{CO_2} - k_7 P_{H_2O} P_{CO} P_{H_2}^{-1}}{1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O}}$
[35]		$r_{RWGS} = \frac{1}{1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O}}$

Studies that CO_2 and H_2 were obtained from different sources have been conducted for CO_2 hydrogenation to methanol. These studies are collected and provided as shown in Table 3.3

Table 3.3 Sources of CO_2 and hydrogen for CO_2 hydrogenation to produce methanol

CO ₂ source	Hydrogen source	Reference
By-product of fermentation	Water electrolysis	[11]
process	water electrolysis	[11]
Flue gas of coal power plant	Water electrolysis	[35]
(Captured CO ₂)	water electrotysis	[55]
Captured CO ₂	Purchase	[36]
Captured CO ₂	CO ₂ /steam mixed reforming	[37]
CHULALONGK	ORN UNIVERSITY	

Type of a reactor chosen in this work is plug flow model (PFR). A simple plug flow [35, 36] and a multi-tubular plug flow [11, 37] are used in this study.

From Table 3.3, the method that mostly used to produce hydrogen is water electrolysis. Electricity for the electrolysis is produced from a renewable energy such as wind or solar power. Although a renewable energy does not produce CO_2 the cost of water electrolysis appears to be more expensive when compared to the conventional steam reforming of natural gas [11]. As a result, a trade-off is unavoidable since one alternative is more expensive where as another produce CO_2 as a by-product.

Thus, in this research H_2 released as industrial waste will be used as feedstock for CO_2 hydrogenation process in order to produce methanol.

3.2 Hydrogen source

Although the hydrogen source may be a main barrier for CO₂ hydrogenation process specifically for methanol production, some industries release hydrogen as waste such as propane dehydrogenation and sodium methoxide production processes.

3.2.1 Hydrogen from propane dehydrogenation

Propane dehydrogenation (PDH) is the important step for preparing the propylene monomer. The reaction of propane dehydration is shown as a following equation

Propane Dehydrogenation:
$$C_3H_8 \rightarrow C_3H_6 + H_2$$
 (3.4)

The conditions for this reaction are 437-477 $^{\circ}\text{C}$ and 1.1 bar with Pt-based catalyst [38].

3.2.2 Hydrogen from sodium methoxide production

Sodium methoxide (NaOCH₃) can be used widely in various application. One application of NaOCH₃ which is focus of this work is the compound is use as a catalyst for biodiesel production. Methanol reacts with sodium metal to produce high purity sodium methoxide as expressed in the following equation.

Sodium methoxide synthesis:
$$2Na + 2CH_3OH \rightarrow 2NaOCH_3 + H_2$$
 (3.5)

The suitable temperature range of this equation is between 80 to 86 °C[13].

When compared to PDH, H₂ waste from NaOCH₃ production is more attractive in this case since methanol obtained from a main process in this study could be used and compensate some methanol feed for the NaOCH₃ production. Further, as the higher use of renewable energy is gaining its attention, sodium methoxide production

plant in Brazil is planned to be expanded [39]. As such, the H_2 waste from NaOCH $_3$ production is by far the most attractive source for H_2 feedstock.

3.3 Sodium methoxide production

As mentioned above, Sodium methoxide can be produced from methanol and sodium metal which afterwards releases hydrogen as waste. This process was patented by E. I. Du Pont De Nemours And Company in 1997 [13]. This dry-production process may still be in-use for sodium methoxide production according to recent publication of EnviroCat [40] and the patent about sodium methoxide production in year 2002 [41]. Therefore, the BRZ in Table 3.4 is served as a based case of NaOCH₃ production that will be used to estimate the amount of H₂ released as waste. Such waste will be used to react with external CO₂ in accordance with the objective of this work: CO₂ utilization

Further, in order to conduct a feasibility analysis, the capacities of sodium methoxide production are established as the four set-up listed in table 3.4. These four set-ups are constructed since the author would like to determine the cut-off size that would make this process economically feasible.

Table 3.4 the size of sodium methoxide production

Name	Company	Country	Capacity (ton/year)	References
BRZ	Dupont, JBS	Brazil	3.00 × 10 ⁴	[39]
BRZ x 5	Assume	ed size	1.50×10^5	-
BRZ x 7.5	Assume	ed size	2.25 x 10 ⁵	-
BRZ x 9.5	Assume	ed size	2.85 x 10 ⁵	-

3.4 CO₂ Utilization evaluation methods

There are several methods to evaluate CO_2 utilization in a process. There are three methods used in the literature [37, 42, 43].

Evaluation of CO_2 utilization in the first method is determined based on CO_2 flow rate. the net CO_2 emission can be calculated by the following equation

Net
$$CO_2$$
 emission = $\sum_{n=1}^{i} CO_{2_{outlet}} - \sum_{n=1}^{i} CO_{2_{inlet}}$ (3.6)

Direct ${\rm CO_2}$ released from a process and indirect ${\rm CO_2}$ computed from plant's energy input such as electricity are accounted for $\sum_n^i {\rm CO_2}_{outlet}$. [42]

Evaluation of CO_2 utilization in the second method is computed based on dimensionless expression. Carbon efficiency is one of the example of this method. expression for determination of Carbon efficiency is given in Equation (3.7) [37]

Carbon efficiency =
$$\frac{Total \, moles \, of \, C \, atom \, in \, output \, product}{Total \, moles \, of \, C \, atom \, inlet \, flow+Total \, moles \, of \, C \, atom \, in \, energy \, used} \quad (3.7)$$

Evaluation of CO_2 in the third method is estimated based on potential factors of input and output. In life-cycle assessment (LCA) study, Global warming potential (GWP) of input and output material are used to calculated carbon footprints (GW) as shown in equation (3.8) [43].

$$GW = \sum_{i} m_{i} GWP_{i} \quad (3.8)$$

In this research, Net ${\rm CO_2}$ emission and carbon efficiency might be calculated for evaluation of ${\rm CO_2}$ utilization.

3.5 Economic analysis ULALONGKORN UNIVERSITY

Net present value (NPV) is the promising method to evaluate the economic feasibility of the production process. At NPV \geq 0, it means that the project is payback.

From Matzen et al. [11], the methanol selling price and hydrogen production cost from water electrolysis would be varied. The result of net present value (NPV) after 10 years of project show that the hydrogen production cost would be around 0.4-0.7 \$/kg with methanol price in year 2015 and sell oxygen by-product from electrolysis process.

Moreover, Pérez-Fortes, M., et al. [36] found that hydrogen price should be decrease about 2.5 times or methanol selling price increase about 2 times of present price NPV will be equal to zero for the 20 years of project.

In this study, H_2 is considered as waste and the price of H_2 is zero. CO_2 is assumed that it is bought from plant which release CO_2 such as ethanol production plant (0.7537 tons per 1 m³ of ethanol product [44]). Net present value is used to compare the economic feasibility of each production size in Table 3.4.



CHAPTER 4

METHODOLOGY

This chapter is divided in to 5 parts including Design scope, feedstock estimation, process description, evaluation of ${\rm CO_2}$ utilization and a method for economics evaluation.

4.1 Design scope

A scope of this work encompassed in the dotted square is depicted in Figure 4.1. As mentioned previously, the need exists for a chemical process suitable for the CO_2 capture and utilization (CCU) approach. As such, the methanol production process is selected and thoroughly investigated. The highlight of this work is that captured CO_2 and H_2 waste from other processes are utilized as feedstock for the methanol production. Details about the feedstock and the feedstock estimations are given in Section 4.2 and 4.3 respectively.

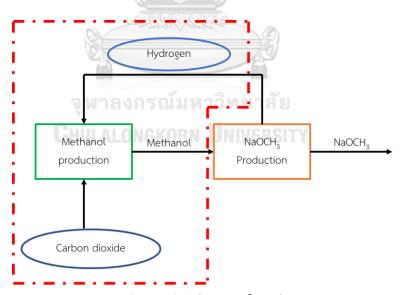


Figure 4.1 Scope of work

4.2 Feedstock estimation

There are two potential feedstock that meet the research objective. Such objective is that the feedstock are renewable such as captured CO_2 and H_2 obtained as waste from other processes.

The H_2 feedstock for the methanol production is received as waste from another process. In fact, a high purity H_2 in the feedstock is preferred since the preexisting CO_2 , if contained in the H_2 feedstock, would decrease the conversion of CO_2 obtained externally. Accordingly, the H_2 waste obtained from NaOCH $_3$ production is considered since it meets the purpose of this work. To underline this, first, the exhaust released from the NaOCH $_3$ production contains high purity H_2 that is not currently feasible for further usage. Second, methanol is also a raw material for NaOCH $_3$ production that may be recycled and leads to a reduction of raw material cost.

For CO_2 , the gas is available and obtained from external sources such as exhausts from fermentation processes [45]. The price of CO_2 is assumed to be the commercial grade CO_2 . Required feed amount of CO_2 is calculated based on stoichiometric ratio in a reaction of CO_2 hydrogenation, and is determined relative to the available waste H_2 obtained from NaOCH₃ production.

Since quantitative data of H_2 waste from the NaOCH $_3$ productions are not available, the H_2 waste estimates are determined by assuming that every NaOCH $_3$ productions plant uses the process condition which is shown in patent [13].

Steps involved in the H_2 waste estimations are given as follow.

- Mass of sodium used for production of NaOCH₃ is estimated from mass balance that 0.445 kg of sodium metal are used for producing 1 kg of NaOCH₃ [13]
- ullet The amounts of required methanol and released H₂ are estimated from stoichiometric ratio. If 2 moles of sodium metal are used, 2 moles of methanol are required and 1 mole of H₂ is generated.

As a result, required amounts of CO_2 and H_2 waste were determined and listed in Table 4.1. Details about Table 4.1, for example, how each capacity comes from are explained in Chapter 3, section 3.3.

Amount of CO2 in Table 4.1 are calculated from stoichiometric ratio of equation (3.3) and the feed ratio of CO_2 :H₂ is 1:3.

Table 4.1 Hydrogen waste flow rate from NaOCH₃ catalyst production

Size	Capacity of NaOCH ₃ (t/year)	Methanol required for NaOCH ₃ production (t/day)	Waste Hydrogen flow rate (t/day)	Stoichiometrically required CO ₂ (t/day)
BRZ	3.00 x 10 ⁴	51.6	1.61	11.8
BRZ x 5	1.50×10^5	258	8.06	59.1
BRZ x 7.5	2.25 x 10 ⁵	387	12.1	88.7
BRZ x 9.5	2.85 x 10 ⁵	490	15.3	112

Please note that the methanol amounts required for $NaOCH_3$ production given in Table 4.1 are constructed for comparative purposes used in further discussion in Table 5.6 in Chapter 5.

4.3 Process description

The process flowsheet of methanol production process in this study is listed in Figure 4.2.

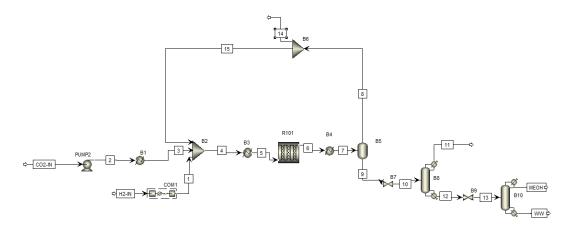


Figure 4.2 Process flow sheet for methanol production

Feed hydrogen is compressed in multi-stage compressors COM1 to 50 bars. While, feed $\rm CO_2$ is pumped to 50 bar in PUMP2 and evaporated to gas phase by heater B1. Then the compressed gases are delivered and mixed with a recycled stream 15 in a mixer B1. The mixed stream 4 is heated to 250 °C in the heater B3. Reactor R101 is in plug flow model with the rate equation of reaction kinetics which shown in Appendix A. The reactor effluence is cooled down in a cooler B4. The cooled products pass through a flash separator to remove the recycle gas from product stream. The gas stream 8 is split to a purge stream 14 at ratio of 0.01%. This purge stream is required for purge some of components that may be accumulated in the system because of no exit point [46]. Liquid stream from flash separation is reduced pressure to 15 bars and then sent to stabilizer column (B8) to remove the light gas such as $\rm CO_2$, $\rm CO$, $\rm H_2$. Liquid stream 12 is decreased pressure to atmospheric pressure and then sent to a distillation column to recover methanol in column B10. The product purity is designed to be 99.95 wt% methanol.

Design criteria of equipment would be listed as below. The results of equipment design are shown in Appendix C.

4.3.1 Multi-stages compressor design

Each compressor is designed to have equal compression ratio in every stage because this design gives the minimum required power input [47].

4.3.2 Reactor design

Methanol production reactor is designed by its concentration profile. The length of reactor is chosen from the minimum length where the reaction reaches chemical equilibrium as indicated by composition plateau as shown in Appendix C.4. Geometry of reactor is designed with a recommended aspect ratio of L/D = 5.

4.3.3 Flash separation unit design

Flash separation unit is designed to be operated adiabatically at a constant pressure of 50 bars. Size and geometry of flash drum are designed using ASPEN PLUS program. The vertical drum was chosen with an aspect ratio of L/D = 3.4.

4.3.4 Stabilizer and methanol purification column

Stabilizer column is utilized the light gases removal, so the condenser of this unit has to be a partial condenser. For the methanol purification column, its reflux is condense using a total condenser. Diameter and height of column are designed using ASPEN PLUS.

4.4 Evaluation of CO₂ utilization

In this research, net CO_2 emission and carbon efficiency is used to evaluate the CO_2 utilization.

Net CO_2 emission is calculate based on CO_2 fed into the process and CO_2 released from the process by 1) the process stream (or waste) and 2) by the utility usage that potentially produce CO_2 . Net CO_2 emission is calculated using Equation 3.6 mentioned in the previous chapter.

Net
$$CO_2$$
 emission = $\sum_{n}^{i} CO_{2outlet} - \sum_{n}^{i} CO_{2inlet}$ (3.6)

Carbon efficiency is expressed as given in equation (3.7).

Carbon efficiency =
$$\frac{Total\ moles\ of\ C\ atom\ in\ output\ product}{Total\ moles\ of\ C\ atom\ inlet\ flow+Total\ moles\ of\ C\ atom\ in\ energy\ used}\ (3.7)$$

According to Equation 3.7, the total moles of C atom in energy used include the total moles of C generated from fuel burning for heating units. The total moles of C are estimated from electricity used as the process utility.

Further details regarding the calculation of ${\rm CO_2}$ utilization are provided in Appendix D.

4.5 Economics analysis

In this study, sizes and costs of all equipment in methanol production process are obtained from Economics Evaluator in ASPEN PLUS. The estimated cost of raw material and selling price of the product are given in Table 4.2.

Table 4.2 Cost of raw material and selling price of product

Туре	Grade	Price (\$/t)
Liquid carbon dioxide	- Industrial	20 [48]
Methanol	Industrial	350 [49]



CHAPTER 5

RESULT AND DISCUSSION

Explanation and discussion of results from this study are included in this chapter. Three major highlights contained in this chapter includes simulation of methanol production using ASPEN PLUS, evaluation of CO2 utilization, and economic feasibility analysis.

5.1 Simulation of methanol production using ASPEN PLUS

Methanol production in this study is simulated using ASPEN PLUS. Feeds condition are provided in Table 5.1.

Table 5.1 Feed condition

Feed	Conditions	References
Liquid CO ₂	Pressure: 18 barg Vapor fraction: 0	[45]
H ₂	Pressure: 14.3 bar Temperature: 83 °C	[13]

According to the simulated results obtained from the process depicted in figure 4.2, stream results of each capacity in Table 4.1 are shown in Tables 5.2-5.5. Table 5.6 summarizes, for each capacity, the percentages of methanol yield relative to the required amount of methanol for the sodium methoxide production.

Table 5.2 Stream result of BRZ size

Mass Fraction	LINIT	1	2	3	4	5	9	7
CO		0.00	0.00	0.00	0.0226	0.0226	0.0226	0.0226
WATER		0.00	0.00	0.00	0.00822	0.00822	0.0999	0.0999
СНЗОН		0.00	0.00	0.00	0.0613	0.0613	0.224	0.224
Н2		1.00	0.00	0.00	0.400	0.400	0.369	0.369
CO2		0.00	1.00	1.00	0.508	0.508	0.284	0.284
Mass Flow	KG/HR	2.79	493	493	2.18E+03	2.18E+03	2.18E+03	2.18E+03
Temperature	೦ೢ	108	-16.6	14.3	55.8	250	250	55.0
Pressure	BAR	50.0	20.0	50.0	20.0	50.0	50.0	50.0
Enthalpy Flow KCAL/SEC	KCAL/SEC	5.44	-303	-295	-715	-533	-578	-812

9.05E-05 3.09E-08 3.90E-07 0.362 0.637 -303 15.3 550 162 12 0.00449 0.04127 0.0605 0.448 0.446 10.6 15.0 108 5.44 11 8.48E-05 0.00114 0.00851 0.356 0.634 55.6 15.0 -387 560 10 8.48E-05 0.00114 0.00851 0.356 0.634 55.0 50.0 -387 990 0 1.62E+03 0.0304 0.0826 0.0111 0.496 0.380 55.0 50.0 -425 ∞ KCAL/SEC KG/HR L N O BAR ပ **Enthalpy Flow** Mass Fraction Temperature Mass Flow Pressure CH30H WATER C02 0 H2

9.05E-05

550

1.33

-295

3.90E-07

3.09E-08

13

0.362

0.637

Table 5.2 Stream result of BRZ size (Cont'd)

0.000143 0.000244 4.86E-08 6.14E-07 MEOH 9666.0 63.5 1.03 -425 349 H2-IN 0.00 0.00 0.00 1.00 0.00 83.0 14.3 -812 67.7 CO2-IN -20.8 0.00 19.0 0.00 0.00 0.00 1.00 -578 493 1.62E+03 0.0304 0.0825 0.0111 0.496 0.380 55.0 50.0 -533 15 0.0825 0.0304 0.0111 0.496 0.162 0.380 -715 55.0 50.0 14 KCAL/SEC KG/HR FIND BAR ပ **Enthalpy Flow** Mass Fraction **Temperature** Mass Flow Pressure CH30H WATER C02 0 H2

1.30E-31

 \gtrsim

0.00679

0.993

1.16E-30

3.88E-22

201

1.33

-387

107

Table 5.2 Stream result of BRZ size (Cont'd)

Table 5.3 Stream result of BRZ \times 5 size

Mass Fraction	LINO	1	2	33	4	2	9	7
00		0.00	0.00	0.00	0.0188	0.0188	0.0188	0.0188
WATER		0.00	0.00	0.00	0.00804	0.00804	0.0913	0.0913
СНЗОН		0.00	0.00	0.00	0.0600	0.0600	0.208	0.208
H2		1.00	0.00	0.00	0.386	0.386	0.358	0.358
CO2		0.00	1.00	1.00	0.527	0.527	0.324	0.324
Mass Flow	KG/HR	339	2.46E+03	2.46E+03	1.20E+04	1.20E+04	1.20E+04	1.20E+04
Temperature	٥٫	108	-16.6	14.3	55.8	250	250	55.0
Pressure	BAR	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Enthalpy Flow	KCAL/SEC	27.2	-1.52E+03	-1.48E+03	-4.05E+03	-3.08E+03	-3.30E+03	-4.54E+03

Table 5.3 Stream result of BRZ \times 5 size (Cont'd)

Mass Fraction	UNIT	8	6	10	11	12	13	
00		0.0245	7.22E-05	7.22E-05	0.00393	2.72E-08	2.72E-08	
WATER		0.0105	0.356	0.356	0.0325	0.362	0.362	
СНЗОН		0.0783	0.633	0.633	0.369	0.638	0.638	
Н2		0.467	0.00114	0.00114	0.0619	4.00E-07	4.00E-07	
CO2		0.419	0.00991	0.00991	0.533	0.000111	0.000111	
Mass Flow	KG/HR	9.18E+03	2.80E+03	2.80E+03	51.5	2.75E+03	2.75E+03	
Temperature	్ర	55.0	55.0	55.6	101	162	81.1	
Pressure	BAR	50.0	50.0	15.0	15.0	15.3	1.33	
Enthalpy Flow	KCAL/SEC	-2.60E+03	-1.93E+03	-1.93E+03	-25.3	-1.83E+03	-1.83E+03	

H2-IN 0.00 0.00 0.00 1.00 CO2-IN 0.00 0.00 0.00 0.00 0.0245 0.0105 0.0783 0.467 15 0.0245 0.0783 0.0105 0.467 14 **Table 5.3** Stream result of BRZ \times 5 size (Cont'd) LIND Mass Fraction CH30H WATER 0 H2

-1.03E+03 2.41E-22 5.68E-32 0.00235 6.59E-31 0.998 1.33 \gtrsim 266 108 0.000174 1.75E+03 0.000256 4.27E-08 6.28E-07 9666.0 MEOH 63.4 1.03 -857 0.00 339 83.0 14.3 18.6 -1.52E+03 2.46E+03 -20.8 1.00 19.0 -2.60E+03 9.18E+03 0.419 55.0 50.0 -0.260 0.918 0.419 55.0 50.0 KCAL/SEC KG/HR BAR ပ **Enthalpy Flow Temperature** Mass Flow Pressure CO2

Table 5.4 Stream result of BRZ \times 7.5 size

Mass Fraction	UNIT	1	2	3	4	5	9	7
OO		0	0	0	0.0174	0.0174	0.0174	0.0174
WATER		0	0	0	8.59E-03	8.59E-03	0.0858	0.0858
СНЗОН		0	0	0	0.0641	0.0641	0.201	0.201
Н2		1	0	0	0.411	0.411	0.385	0.385
CO2		0	\vdash	1	0.499	0.499	0.310	0.310
Mass Flow	KG/HR	508	3.70E+03	3.70E+03	1.94E+04	1.94E+04	1.94E+04	1.94E+04
Temperature	ు	108	-16.6	14.3	55.6	250	250	55.0
Pressure	BAR	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Enthalpy Flow	KCAL/SEC	40.8	-2.28E+03	-2.21E+03	-6.25E+03	-4.60E+03	-4.93E+03	-6.99E+03

-2.75E+03 4.12E+03 9.63E-05 2.31E-08 3.94E-07 0.638 0.362 15.3 162 12 3.35E-03 0.0611 0.0387 0.426 0.471 -37.9 78.6 15.0 106 11 -2.90E+03 4.20E+03 6.26E-05 1.14E-03 8.90E-03 0.634 0.356 55.6 15.0 10 -2.90E+03 4.20E+03 6.26E-05 1.14E-03 8.90E-03 0.356 0.634 55.0 50.0 0 -4.08E+03 1.52E+04 0.0818 0.0222 0.0110 0.491 0.394 55.0 50.0 ω KCAL/SEC KG/HR L N O BAR ပ **Enthalpy Flow** Mass Fraction Temperature Mass Flow Pressure **CH30H** WATER CO2 0 H2

-2.75E+03

1.33

4.12E+03

81.1

9.63E-05

3.94E-07

0.638

0.362

2.31E-08

13

Table 5.4 Stream result of BRZ \times 7.5 size (Cont'd)

-1.29E+06 0.9995901 2.63E+03 3.62E-08 2.58E-04 6.18E-07 1.51E-04 MEOH 63.5 1.03 H2-IN 0.508 83.0 14.3 27.9 0 0 0 0 -2.28E+06 3.70E+03 CO2-IN -20.8 19.0 0 0 0 0 -4.08E+06 1.52E+04 0.0818 0.0222 0.0110 0.394 0.491 55.0 50.0 15 -408.2571 1.51883 0.0818 0.0222 0.0110 0.394 0.491 55.0 50.0 KCAL/SEC KG/HR L N O BAR ပ **Enthalpy Flow** Mass Fraction Temperature Mass Flow Pressure **CH30H** WATER CO2 0 H2

0.9978813

2.12E-03

6.14E-31

1.96E-22

1.50

4.51E-32

≫

-1.54E+06

1.33

107

Table 5.4 Stream result of BRZ \times 7.5 size (Cont'd)

Table 5.5 Stream result of BRZ \times 9.5 size

Mass Fraction	LINIT	1	2	3	4	5	9	7
OO		0.00	0.00	0.00	0.0160	0.0160	0.0160	0.0160
WATER		0.00	0.00	0.00	0.00843	0.00843	0.0854	0.0854
СНЗОН		0.00	0.00	0.00	0.0629	0.0629	0.200	0.200
H2		1.00	0.00	0.00	0.403	0.403	0.377	0.377
CO2		0.00	1.00	1.00	0.510	0.510	0.322	0.322
Mass Flow	KG/HR	643	4.68E+03	4.68E+03	2.46E+04	2.46E+04	2.46E+04	2.46E+04
Temperature	J _o	108	-16.8	14.3	55.7	250	250	55.0
Pressure	BAR	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Enthalpy Flow	KCAL/SEC	51.6	-2.89E+03	-2.80E+03	-8.09E+03	-6.02E+03	-6.44E+03	-9.02E+03

0.000104 5.22E+03 2.19E-08 3.97E-07 0.638 0.362 15.3 162 12 0.00317 0.0355 0.0615 0.397 0.503 98.7 15.0 104 5.32E+03 5.87E-05 0.00943 0.00114 0.356 0.633 55.6 15.0 10 5.32E+03 5.87E-05 0.00114 0.00943 0.356 0.633 50.0 55.0 0 1.93E+04 0.0204 0.0802 0.0107 0.408 0.480 50.0 55.0 ω KG/HR LNO BAR ပ Mass Fraction **Temperature** Mass Flow Pressure CH30H WATER CO2 0 H2

-3.48E+03

-3.48E+03

-48.1

-3.68E+03

-3.68E+03

-5.34E+03

KCAL/SEC

Enthalpy Flow

1.33

81.1

0.000104

3.97E-07

0.638

2.19E-08

13

0.362

5.22E+03

Table 5.5 Stream result of BRZ \times 9.5 size (Cont'd)

Table 5.5 Stream result of BRZ \times 9.5 size (Cont'd)

Mass Fraction	UNIT	14	15	CO2-IN	H2-IN	МЕОН	WW
00		0.0204	0.0204	0.00	0.00	3.45E-08	1.10E-31
WATER		0.0107	0.0107	0.00	0.00	0.000241	0.991
СНЗОН		0.0802	0.0802	0.00	0.00	9666.0	0.00887
Н2		0.480	0.480	0.00	1.00	6.26E-07	1.37E-30
CO2		0.408	0.408	1.00	0.00	0.000164	5.28E-22
Mass Flow	KG/HR	1.93	1.93E+04	4.68E+03	643	3.32E+03	1.91E+03
Temperature	ఎం	55.0	55.0	-20.8	83.0	63.4	107
Pressure	BAR	50.0	50.0	19.0	14.3	1.03	1.33
Enthalpy Flow	KCAL/SEC	-0.533	-5.34E+03	-2.89E+03	35.4	-1.62E+03	-1.96E+03

Table 5.6 Percentages of methanol yield to amount of methanol which want to use by the sodium methoxide production

C:	Methanol required for	Methanol yield	Compensation
Size	NaOCH ₃ production (t/day)	(t/day)	percentages (%)
BRZ	51.6	8.38	16.2
BRZ x 5	258	42.0	16.3
BRZ x 7.5	387	63.1	16.3
BRZ x 9.5	490	79.7	16.3

According to Table 5.6, the compensation percentages are not affected by the size of the plant (e.g. BRZx5 and etc.). Further, the correctness of this simulation work is confirmed by the linear correlation in Figure 5.1 since the results are consistent with 1) mass balance constraint that larger $NaOCH_3$ production would require more methanol and release more waste H_2 and 2) the trend in Figure 5.2 in linear fashion as each capacity is merely a linear scale-up from the based case.

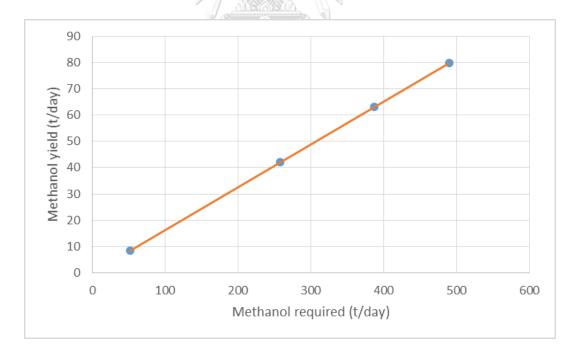


Figure 5.1 Relationship between methanol yield and amount of methanol required for the sodium methoxide production

5.2 Evaluation of carbon dioxide utilization

According to previous chapter, net CO_2 emission is used to evaluate carbon dioxide utilization of methanol production process.

Table 5.7 shows flow of carbon dioxide into the process, direct and indirect carbon dioxide exiting the process and net ${\rm CO_2}$ emission.

Table 5.7 Net CO₂ utilization

	Methanol	Inlet	Ou	tlet	Net CO ₂
Size	flow rate	Inlet CO ₂	Direct outlet	Indirect	emissions
	(kg/h)	(kg/h)	(kg/h)	outlet (kg/h)	(kg/kg _{MeOH})
BRZ	349	493	4.78	19.6	-1.34
BRZ x 5	1.75E+03	2.46E+03	27.8	98.0	-1.33
BRZ x 7.5	2.63E+03	3.70E+03	40.0	147	-1.34
BRZ x 9.5	3.32E+03	4.68E+03	50.4	186	-1.34

From above table, net CO_2 emission of methanol production process is lower than zero. As mentioned in equation 3.6, if this value is lower than zero, it certainly means that the process utilizes CO_2 .

Moreover, the result from table 5.7 suggests that net CO_2 emissions in each size of process are equal and consistent with results from Table 5.6. This means that the capacity of the process does not affect the CO_2 utilization capacity of the process.

In this study, the major outlet of CO_2 from the process is indirect CO_2 emission. This result shows that the CO_2 emission of the process mainly comes from the energy usage in the methanol production.

When compare to previous works in the literature, net ${\rm CO_2}$ emission of this study is comparable to them as presented in Table 5.8

Table 5.8 Net CO₂ emission of various studies

Processes	Net CO ₂ emission (kg/kg _{MeOH})
This study	1.34
Matzen, M., et al. (2015) [11]	1.30
Pérez-Fortes, M., et al. (2016) [36]	1.23

In terms of CO_2 efficiency, efficiencies obtained from this study seem to be higher than the process in Zhang, C., et al. (2016) [37] about 6% given in Table 5.9. Such minute difference may result from the higher recycled portion of CO_2 across the reactor [37].

Table 5.9 Carbon efficiency of methanol production process

Name	Recycle Ratio	Carbon efficiency
BRZ*	0.99	0.94
BRZ x 5*	0.99	0.94
BRZ x 7.5*	0.99	0.94
BRZ x 9.5*	0.99	0.94
Zhang, C., et al. (2016) [37]	0.95	0.89

^{*}Recycle ratio (this study) = (stream 15)/(stream 8)

5.3 Economic feasibility ใส่งกรณ์มหาวิทยาลัย

The economic evaluation of methanol production processes are evaluated by ASPEN PLUS Economics evaluator. Parameters used in the evaluator are shown in Appendix E. The result of evaluation are used to compare the feasibility of each production size with a fixed 20 years project lifetime. The economic analysis results are shown in Table 5.10.

Table 5.10 Economic analysis result

	BRZ	BRZ x 5	BRZ x 7.5	BRZ x 9.5
Total Capital Cost [USD]	8.79E+06	1.48E+07	1.81E+07	1.96E+07
Total Operating Cost [USD/Year]	2.05E+06	3.42E+06	4.37E+06	5.06E+06
Total Raw Materials Cost	9.52E+04	4.76E+05	7.14E+05	9.04E+05
[USD/Year]	7.5ZL104	4.702103	7.146105	7.046103
Total Product Sales [USD/Year]	1.07E+06	5.38E+06	8.06E+06	1.02E+07
Total Utilities Cost [USD/Year]	2.24E+05	9.14E+05	1.46E+06	1.83E+06
Equipment Cost [USD]	1.27E+06	2.69E+06	3.40E+06	3.94E+06
P.O. Period [Year]	· ·	-	-	16.9
NPV (Net Present Value)	-1.29E+07	-5.49E+06	-2.40E+06	1.13E+06
(20 years)	-1.296+07	-3.470+00	-2.400+00	1.136+00
PI (Profitability Index) (20 years)	0.324	0.846	0.948	1.02

From Table 5.10, the methanol production processes which have capacity lower than BRZ \times 9.5 do not have a payout period (P.O. period).

Payout period (or payback period) is defined as the length of time that the process can give the profit which overcomes the investment cost [50]. From the result, the processes which have no P.O. period does not make profit in 20-year period.

Profitability index for each capacity is shown in Table 5.10. This index is the ratio of benefit to cost [50]. If it has higher value than 1, the process would be profitable. In the same way of P.O. period, the small capacity appears to be unprofitable. These methanol production process start to be profitable at the process size of BRZ \times 9.5 with the PI near to 1 (1.02). Thus, the cut-off point for this CO₂ hydrogenation process that would make such process economically feasible is at 9.5 folds of the based case.

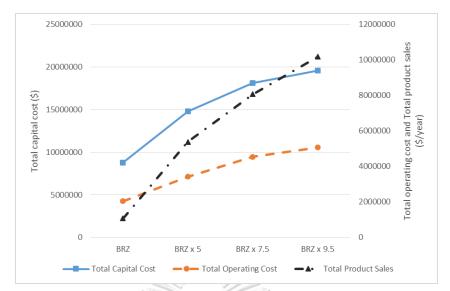


Figure 5.2 Trend of Total capital cost, total operating cost, and total product sales

According to Figure 5.2, the increasing rate of the total product sales as a function of the production size appears to be higher than those rate of total capital cost and total operating cost. This explains the results obtained previously that the process becomes more feasible when the capacity is higher.

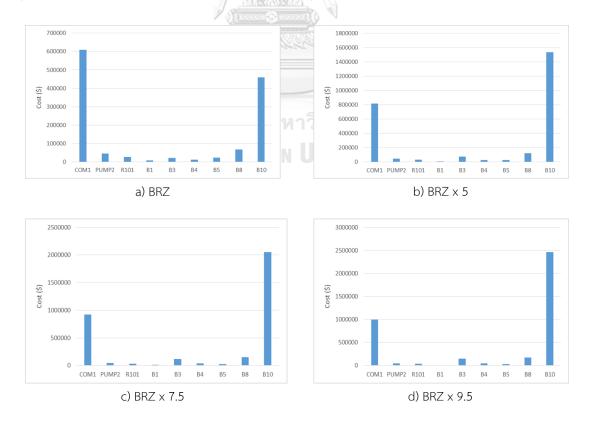


Figure 5.3 Equipment cost of unit operation

Equipment costs of unit operations are shown in figure 5.3. The main cost of equipment is in gas compressor (COM1) and methanol purification unit. This observation is apparent, especially in the large capacity of methanol production, the equipment cost of methanol purification unit is relatively higher than others unit.

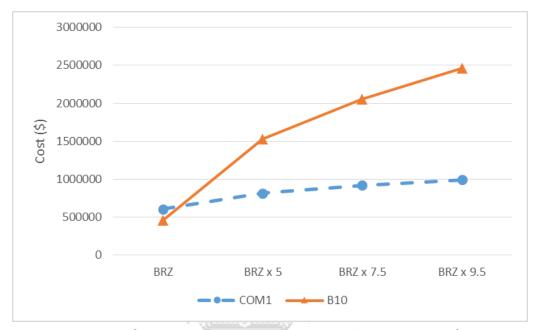


Figure 5.4 Trend of compressor construction cost and methanol purification unit
(B10) construction cost

Figure 5.4 shows the increasing rate of compressor construction cost and methanol purification unit (B10) construction cost, which are the major equipment costs of methanol production. Although the cost of compressor in the based case is lower than B10, the increasing rate of B10 is greater than the compressor. Thus, the equipment cost of methanol production appears to depend on B10 when the production size is greater than 5 times of the based case.

In summary, the amount of hydrogen from present capacity of sodium methoxide (the capacity labeled with BRZ) cannot make the methanol production process feasible. The obtained results suggest that the methanol production from H_2 waste could truly compensate the sodium methoxide plant in the 17^{th} year (where the process becomes profitable) at the capacity of 9.5 folds of the current Brazil's production capacity.

However, the feasibility of such methanol production may be improved as the sodium methoxide production capacity increase is planned according to the factsheet released by DuPont [39].

In fact, the suggestion made above agrees in the same way as the conventional methanol production plant (natural gas as feedstock) that the capacity of methanol production is currently around 5000 t/day and tends to increase in order to inprove its economic feasibility because of the increase feedstock for Methanol-to-Olefin (MTO) process [51].

Another way for making this process economically feasible is that since methanol is used as a precursor for producing other chemicals [52-54], production of more expensive products such as DME, DMC and others provided in Table 5.11 may result in an improved profitability. This could be a focus and recommendation for a future work.

Table 5.11 Other products from methanol and their price

Products	Prices (\$/mt)	Reference
Methyl tertiary butyl ether (MTBE)	650	[55]
Dimethyl ether (DME)	700	[56]
Formic acid	житаивт 7 35	[57]
Propylene	RN UNIVE 952 Y	[58]
Ethylene	1133	[59]
Dimethyl carbonate (DMC)	1200	[60]

CHAPTER 6

CONCLUSION

In order to utilize carbon dioxide, low-pressure hydrogen waste from sodium methoxide production is used to produce methanol based on the assumption that the produced methanol could compensate some methanol fed to the sodium methoxide production process.

The methanol production by CO_2 hydrogenation process from waste H_2 which was simulated in this work has four capacity set-ups including one based case (BRZ) and other three assumed cases (BRZ \times 5, BRZ \times 7.5, and BRZ \times 9.5).

First, from mass balance, every capacity of methanol production produces about 16.3% of the required amount of methanol for sodium methoxide production process; the process size does not affect the percentage of supportive methanol relative to the amount required as feedstock for the sodium methoxide production process.

Second, the result from the evaluation of CO_2 utilization shows that methanol production process from waste H_2 may consume carbon dioxide at 1.34 kg/kg_{CH3OH}. The highest amount of CO_2 released from the process is indirect CO_2 from utilities usage. In the same way of mass balance, the CO_2 utilization capacity does not depend on methanol production capacity.

Finally, from economic analysis results, CO_2 hydrogenation process becomes more feasible when the capacity is higher. The cut-off point that make the process to be economically feasible is at 9.5 folds of the based case.

At the cut-off point, the methanol production process has a profitability index near to 1 (PI = 1.02) at the end of the 20^{th} year and can truly compensate some fed methanol to the sodium methoxide plant at year 17^{th} . Further, according to the economic analysis, the feasibility of the process may be improved as the sodium methoxide production capacity increases.

For the future work, another way to make this process more feasible is to produce more valuable products which uses methanol as a precursor such as dimethyl ether (DME), and dimethyl carbonate (DMC), etc.



REFERENCES

- 1. UN, KYOTO PROTOCOL TO THE UNITED NATIONS FRAMEWORK CONVENTION ON CLIMATE CHANGE. 1998.
- 2. IPCC, Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment. 2014, New York: Cambridge University Press.
- 3. NOAA. *Trends in Atmospheric Carbon Dioxide*. 2016 [cited 2017 April 23]; Available from: https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html.
- 4. UN, PARIS AGREEMENT. 2015.
- 5. TGO, สาระสำคัญความตกลงปารีส. 2015.
- 6. Cuéllar-Franca, R.M. and A. Azapagic, *Carbon capture, storage and utilisation technologies: A critical analysis and comparison of their life cycle environmental impacts.* Journal of CO2 Utilization, 2015. **9**: p. 82-102.
- 7. Taheri Najafabadi, A., CO2 chemical conversion to useful products: an engineering insight to the latest advances toward sustainability. International Journal of Energy Research, 2013. 37(6): p. 485-499.
- 8. Isahak, W.N.R.W., et al., *The formation of a series of carbonates from carbon dioxide: Capturing and utilisation.* Renewable and Sustainable Energy Reviews, 2015. **47**: p. 93-106.
- Zoback, M.D. and S.M. Gorelick, Earthquake triggering and large-scale geologic storage of carbon dioxide. Proceedings of the National Academy of Sciences, 2012. 109(26): p. 10164-10168.
- 10. Environnement, N. Biogas composition. 2009 [cited 2017 April 23].
- 11. Matzen, M., M. Alhajji, and Y. Demirel, *Chemical storage of wind energy by renewable methanol production: Feasibility analysis using a multi-criteria decision matrix.* Energy, 2015. **93**: p. 343-353.
- 12. HMC. *Production*. [cited 2017 April 23]; Available from: http://www.hmcpolymers.com/production.
- 13. Tse, S.W., Continuous process for sodium methylate. 1997, Google Patents.

- 14. DOEB, ปริมาณการผลิตน้ำมันไบโอดีเซลประเภทเมทิลเอสเตอร์ของกรดไขมัน. 2017.
- 15. PLATT. World biodiesel production/consumption to rise 14% by 2020:

 OECD/FAO. 2016 [cited 2017 April 23]; Available from:

 http://www.platts.com/latest-news/agriculture/london/world-biodiesel-productionconsumption-to-rise-26485632.
- 16. Abanades, J., et al., *Emerging CO 2 capture systems.* International Journal of Greenhouse Gas Control, 2015. **40**: p. 126-166.
- 17. IPCC, IPCC Special Report on Carbon Dioxide Capture and Storage. 2005, Intergovernmental Panel on Climate Change.
- 18. C2ES. CARBON CAPTURE USE AND STORAGE. [cited 2017 May 26]; Available from: https://www.c2es.org/technology/factsheet/CCS.
- 19. Styring, P.J., Daan; Coninck, Heleen de; Reith, Hans; Armstrong, Katy *Carbon Capture and Utilisation in the green economy*. 2011, Energy Research Centre of the Netherlands, University of Sheffield.
- J. C. Copplestone, C.M.K. AMMONIA AND UREA PRODUCTION. [cited 2017 May 26].
- 21. Lim, H.-W., et al., Modeling of the Kinetics for Methanol Synthesis using Cu/ZnO/Al2O3/ZrO2 Catalyst: Influence of Carbon Dioxide during Hydrogenation. Industrial & Engineering Chemistry Research, 2009. **48**(23): p. 10448-10455.
- 22. Sakakura, T. and K. Kohno, *The synthesis of organic carbonates from carbon dioxide*. Chemical Communications, 2009(11): p. 1312-1330.
- 23. Omae, I., Recent developments in carbon dioxide utilization for the production of organic chemicals. Coordination Chemistry Reviews, 2012. **256**(13–14): p. 1384-1405.
- 24. wikipedia. *methanol*. [cited 2017 May 26]; Available from: https://en.wikipedia.org/wiki/Methanol.
- 25. ScienceLab.com. *Material Safety Data Sheet Methyl alcohol MSDS*. [cited 2017 May 26]; Available from: www.sciencelab.com/msds.php?msdsId=9927227.

- 26. NFPA, NFPA 704, Standard System for the Identification of the Hazards of Materials for Emergency Response. 2011: National Fire Protection Association.
- 27. Goeppert, A., et al., *Recycling of carbon dioxide to methanol and derived* products closing the loop. Chemical Society Reviews, 2014. **43**(23): p. 7995-8048.
- 28. Liang, X.-L., et al., *Carbon nanotube-supported Pd–ZnO catalyst for hydrogenation of CO2 to methanol.* Applied Catalysis B: Environmental, 2009. **88**(3–4): p. 315-322.
- 29. Liu, X.-M., G.Q. Lu, and Z.-F. Yan, *Nanocrystalline zirconia as catalyst support in methanol synthesis.* Applied Catalysis A: General, 2005. **279**(1–2): p. 241-245.
- 30. Liu, Y., et al., Efficient Conversion of Carbon Dioxide to Methanol Using Copper Catalyst by a New Low-temperature Hydrogenation Process.

 Chemistry Letters, 2007. **36**(9): p. 1182-1183.
- 31. Słoczy**ń**ski, J., et al., *Catalytic activity of the M/(3ZnO·ZrO2) system (M = Cu, Ag, Au) in the hydrogenation of CO2 to methanol.* Applied Catalysis A: General, 2004. **278**(1): p. 11-23.
- 32. Jadhav, S.G., et al., *Catalytic carbon dioxide hydrogenation to methanol: A review of recent studies.* Chemical Engineering Research and Design, 2014. **92**(11): p. 2557-2567.
- 33. Mochalin, V.P., G.I. Lin, and A.Y. Rozovsky, *KINETIC-MODEL OF THE PROCESS OF METHANOL SYNTHESIS ON THE SNM-1 CATALYST.* 1984(1): p. 11-13.
- 34. Bussche, K.M.V. and G.F. Froment, A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al2O3Catalyst. Journal of Catalysis, 1996. **161**(1): p. 1-10.
- 35. Van-Dal, É.S. and C. Bouallou, *Design and simulation of a methanol production plant from CO2 hydrogenation.* Journal of Cleaner Production, 2013. **57**: p. 38-45.
- 36. Pérez-Fortes, M., et al., *Methanol synthesis using captured CO2 as raw material: Techno-economic and environmental assessment.* Applied Energy, 2016. **161**: p. 718-732.

- 37. Zhang, C., et al., Efficient utilization of carbon dioxide in a gas-to-methanol process composed of CO2/steam-mixed reforming and methanol synthesis.

 Journal of CO2 Utilization, 2016. 16: p. 1-7.
- 38. Hou, K. and R. Hughes, *A comparative simulation analysis of propane dehydrogenation in composite and microporous membrane reactors.* Journal of Chemical Technology & Biotechnology, 2003. **78**(1): p. 35-41.
- 39. Fernanda, B.d. *DuPont, JBS kick off sodium methylate production eyeing local biodiesel market*. 2010 [cited 2017 November 5]; Available from:

 http://www.bnamericas.com/en/news/petrochemicals/DuPont, JBS kick off sodium methylate production eyeing local biodiesel market.
- 40. EnviroCat. FINE CHEMISTRY SECTOR. [cited 2017 November 5]; Available from: http://www.envirocat.fr/en/34-Sodium_methylate/37-Fine_chemistry.
- 41. Ely, W.B. and C.A. Renner, *Production of alcoholates*. 2002, Google Patents.
- 42. Frauzem, R., et al., *Sustainable Process Design.* Computer Aided Chemical Engineering, 2015. **36**: p. 175-195.
- 43. von der Assen, N., J. Jung, and A. Bardow, *Life-cycle assessment of carbon dioxide capture and utilization: avoiding the pitfalls.* Energy & Environmental Science, 2013. **6**(9): p. 2721-2734.
- 44. USEPA, Greenhouse gas emissions estimation methodologies for biogenic emissions from selected source categories: Solid waste disposal, wastewater treatment, ethanol fermentation. 2010, USEPA Washington, DC.
- 45. ASCO. CO2 Recovery. 2017 [cited 2017 November 12]; Available from:

 http://www.ascoco2.com/fileadmin/PDF_Download/PDF_Produkte/PDF_CO2_Produktion_und_Rueckgewinnung/en/CO2_By-Product_Recovery_Systems.pdf.
- 46. Dimian, A.C., C.S. Bildea, and A.A. Kiss, *Integrated Design and Simulation of Chemical Processes*. 2014: Elsevier Science.
- 47. Coker, A.K., Chapter 18 Compression Equipment (Including Fans), in Ludwig's Applied Process Design for Chemical and Petrochemical Plants (Fourth Edition). 2015, Gulf Professional Publishing: Boston. p. 729-978.
- 48. Rushing, S. *Carbon Dioxide Apps Are Key In Ethanol Project Developments*.

 2011 [cited 2017 November 10]; Available from:

- http://www.ethanolproducer.com/articles/7674/carbon-dioxide-apps-are-key-in-ethanol-project-developments.
- 49. Methanex. Methanex Monthly Average Regional Posted Contract Price
 History. 2017 [cited 2017 November 10]; Available from:

 https://www.methanex.com/sites/default/files/methanol-price/MxAvgPrice_Oct%2027%2C%202017.pdf.
- 50. Al-Malah, K.I.M., *Aspen Process Economic Analyzer (APEA)*, in *Aspen Plus*®. 2016, John Wiley & Sons, Inc. p. 523-564.
- 51. Aasberg-Petersen, K., et al., *Large scale methanol production from natural* gas. Haldor Topsoe, 2008. **22**.
- 52. Iwasita, T., *Electrocatalysis of methanol oxidation.* Electrochimica Acta, 2002. **47**(22): p. 3663-3674.
- 53. Rihko-Struckmann, L.K., et al., *Assessment of methanol synthesis utilizing exhaust CO2 for chemical storage of electrical energy.* Industrial & Engineering Chemistry Research, 2010. **49**(21): p. 11073-11078.
- 54. UOP. *Methanol to Olefins*. 2014 [cited 2017 November 14]; Available from: http://www.petrochemconclave.com/presentation/2014/Mr.JGregor.pdf.
- 55. BORICA. *Acrylic World Newsletter-Nov. 2017*. 2017 [cited 2017 November 14]; Available from: http://www.borica.com/Hymer/hymer_newsletter.aspx.
- 56. Fasihi, M. and C. Breyer, *Synthetic Methanol and Dimethyl Ether Production* based on Hybrid PV-Wind Power Plants. 2017.
- 57. ICIS. CHEMICAL PROFILE: Formic acid. 2006 [cited 2017 November 13];

 Available from:

 https://www.icis.com/resources/news/2006/07/26/2015258/chemical-profile-formic-acid/.
- 58. PLATT. *PLATTS GLOBAL PROPYLENE PRICE INDEX*. 2017 [cited 2017 November 14].
- 59. PLATT. *PLATTS GLOBAL ETHYLENE PRICE INDEX*. 2017; Available from: https://www.platts.com/news-feature/2014/petrochemicals/pgpi/ethylene.

- 60. Kongpanna, P., *DESIGN AND EVALUATION OF DIMETHYL CARBONATE PRODUCTION FROM CARBON DIOXIDE*, in *Department of Chemical Engineering*. 2015, Chulalongkorn University.
- 61. DEDE. หมวดที่ 7 : มอเตอร์และตัวขับ (Motor & Drive) [cited 2017 November 17]; Available from:
 http://www2.dede.go.th/bhrd/old/web_display/websemple/Industrial(PDF)/Bay21%20High%20Efficiency%20Motors.pdf.
- 62. EURELECTRIC, Efficiency in Electricity Generation. 2003.





APPENDIX A VERIFICATION OF RATE EQUATIONS

Rate equations which are used in this study is found in from ref. The equation in form of LHHW and its parameter is shown by following equations and Table A1

$$r_{CH_3OH} = \frac{k_1 P_{CO_2} P_{H_2} - k_6 P_{H_2O} P_{CH_3OH} P_{H_2}^{-2}}{\left(1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O}\right)^3}$$

$$r_{RWGS} = \frac{k_5 P_{CO_2} - k_7 P_{H_2O} P_{CO} P_{H_2}^{-1}}{1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O}}$$
(A2)

$$r_{RWGS} = \frac{k_5 P_{CO_2} - k_7 P_{H_2O} P_{CO} P_{H_2}^{-1}}{1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O}} \tag{A2}$$

Table A1 Kinetics parameter for reaction set of CO₂ hydrogenation

i-th reaction	A _i	B _i
k1	-29.87	4811.2
k2	8.147	0
k3	-6.452	2068.4
k4	-34.95	14928.9
k5	4.804	-11797.5
k6	17.55	-2249.8
k7	0.1310	-7023.5

The parameters k_i in equation A1 and A2 are in the form of

$$\ln k_i = A_i + \frac{B_i}{T} \tag{A3}$$

These equation are verified by compared its concentration and temperature profile with experimental result from the other research [34]. The comparison of concentration and temperature profile are shown in Figure A1 and A2

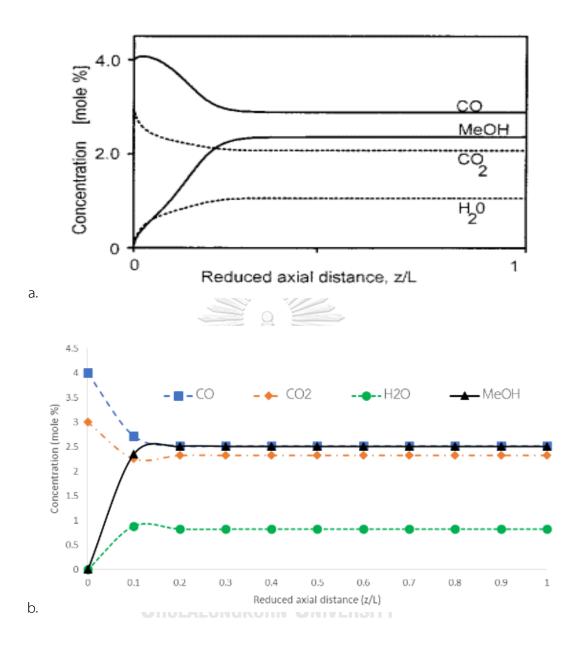


Figure A1 a. Concentration profile from experimental result [34] b. Concentration profile from simulation result of ASPEN PLUS program

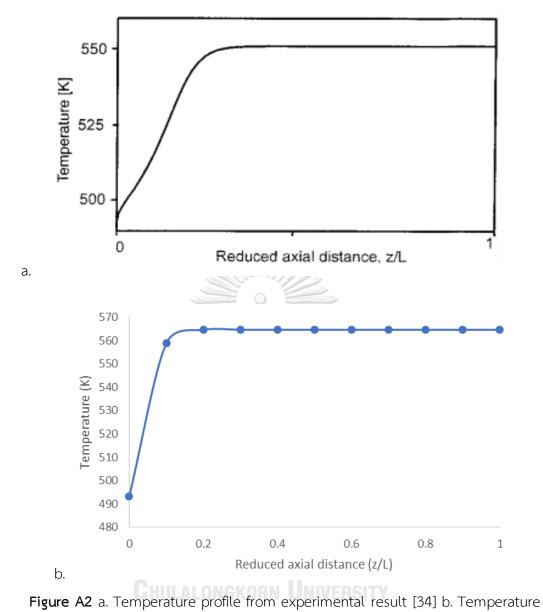


Figure A2 a. Temperature profile from experimental result [34] b. Temperature profile from simulation result of ASPEN PLUS program

APPENDIX B CALCULATION OF METHANOL REQUIRED FOR SODIUM METHOXIDE PRODUCTION PLANT AND FEED AMOUNT FOR METHANOL PRODUCTION

B.1 Calculation of feed amount of BRZ capacity

B.2 Calculation of feed amount of BRZ x 5 capacity

Sodium methoxide capacity =
$$1.50 \times 10^5$$
 $t_{NaOCH3}/year.$ (Section 3.3)
Sodium methoxide yield = $\frac{1 \text{ kg}_{NaOCH3}}{0.445 \text{ kg}_{Na}}$ [13]

B.3 Calculation of feed amount of BRZ x 7.5 capacity

B.4 Calculation of feed amount of BRZ \times 9.5 capacity

APPENDIX C EQUIPMENT SPECIFICATION

C.1 Utilities specification

Table C1 Utilities specification

Name	HOT-OIL	LP-STEAM	MP-STEAM	R-W
Utility type	OIL	STEAM	STEAM	WATER
Calculated inlet pressure [bar]	-	2.32	8.93	1.01
Specified inlet temperature [C]	280	125	175	35
Specified outlet temperature [C]	250	124	174	50

C.2 Compressor Specifications

Table C2 Multi-stages compressor design specifications

	Inlet Pressure (bar)	Inlet Temperature (°C)	Number of stages	Pressure ratio	Cooler Utility
COM1 (for H ₂)	14.0	86.0	3.00	1.51	R-W

Table C3 Size of compressor in

Name กลงกรณ์มห	Net work required (kW)			
BRZULALONGKORN	UNIVERSITY 48.7			
BRZ x 5	243			
BRZ x 7.5	365			
BRZ x 9.5	462			

C.3 Heater and cooler specifications

Table C4 Size of Heater and Cooler

Nama	l leste	1 14:1:4.	Туре	Duty	Area (m²)
Name Unit		Utility		(kcal/s)	
	B1	LP-STEAM	Heater	8.83	0.373
BRZ	В3	HOT-OIL	Heater	181	41.5
	В4	R-W	Cooler	-235	10.9
BRZ x 5	B1	LP-STEAM	Heater	44.2	1.87
	В3	HOT-OIL	Heater	970	222
	В4	R-W	Cooler	-1.24E+03	57.3
	B1	LP-STEAM	Heater	66.2	2.80
BRZ x 7.5	B3	HOT-OIL	Heater	1.98E+03	452
	B4	R-W	Cooler	-2.37E+03	110
BRZ x 9.5	B1	LP-STEAM	Heater	84.1	3.55
	В3	HOT-OIL	Heater	2.07E+03	473
	B4	R-W	Cooler	-2.57E+03	119

C.4 Reactor Specifications

Table C5 Catalyst Properties

Catalyst type ONGKORN	UNIVERSI Cu/ZnO/Al ₂ O ₃
Density (kg/m³)	1775
Porosity	0.5

Table C6 Size of Reactor

Name	Unit	Diameter (m)	Length (m)	L/D
BRZ	R101	0.50	2.50	5.00
BRZ x 5	R101	0.70	3.50	5.00
BRZ x 7.5	R101	0.75	3.75	5.00
BRZ x 9.5	R101	0.80	4.00	5.00

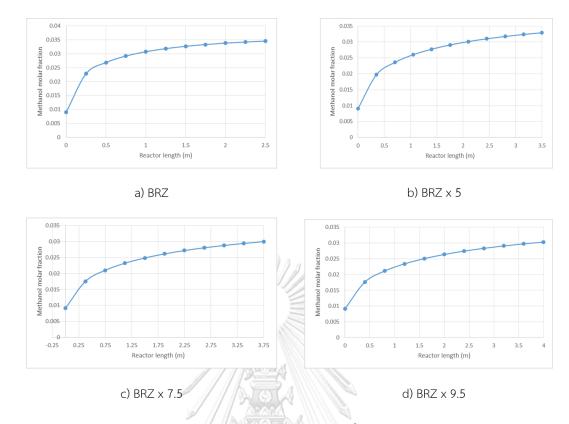


Figure C1 Reactor profile

C.5 Flash drum specifications

Table C7 Size of flash drum

	Unit	Diameter (m)	Height (m)	L/D
BRZ	B4	1.07	3.66	3.43
BRZ x 5	B4	ALUNG 1.07 W	7EKST 3.66	3.43
BRZ x 7.5	В4	1.07	3.66	3.43
BRZ x 9.5	B4	1.07	3.66	3.43

C.6 Distillation column specifications

Table C8 Distillation column specification

1.154	Candanaar	Doboilos	Reflux	Ctosoo	Feed	Condenser
Unit	Condenser	Reboiler	ratio	Stages	stage	pressure (bar)
B8	Partial	Kettle	5	3	2	15.0
ВО	vapor	Rettle	5)	2	15.0
B10	Total	Kettle	2	20	15	1.03

Table C9 Size of distillation column

Name	Unit	Condenser duty (kcal/sec)	Reboiler duty (kcal/sec)	Height (m)	Diameter (m)
BRZ	В8	-7.41	22.7	4.88	0.914
DITZ	B10	-79.3	69.3	19.5	4.42
BRZ x 5	В8	-36.4	112	4.88	1.83
DNZ X 3	B10	-398	348	19.5	9.91
BRZ x 7.5	В8	-54.8	169	4.88	2.29
DNZ X 1.3	B10	-597	522	19.5	12.0
BRZ x 9.5	В8	-69.5	214	4.88	2.95
DNZ X 9.3	B10	-753	658	19.5	13.6

CHULALONGKORN UNIVERSITY

APPENDIX D CALCULATION OF NET CO2 EMISSION AND CARBON EFFICIENCY

D.1 Net CO₂ Emission and carbon efficiency of BRZ size

Methanol Yield 349 kg_{CH3OH}/h

Inlet CO₂ 493 kg_{CO2}/h

Direct Outlet CO₂ 4.78 kg_{CO2}/h

Indirect Outlet CO₂

Basis: Motor efficiency 0.9 [61]

> Electricity production efficiency 0.5 [62]

9052 kcal/m³_{NG} [62] Natural gas used for Electricity production =

CO₂ Emission per natural gas used $1.85 \text{ kg}_{\text{CO}2}/\text{m}^3_{\text{NG}}$

COM1

Net work required (from Simulation result)

48.7 kW Work required 0.9×0.5

108 kW

$$= \frac{108 \times 10^{3} \text{J}}{\text{s}} \times \frac{0.24 \text{ cal}}{1 \text{ J}}$$
= 25.8 kcal/s

25.8 kcal/s

 $\frac{25.8 \text{ kcal}}{1 \text{ s}} \times \frac{1 \text{ m}_{\text{NG}}^3}{9052 \text{ kcal}}$ Natural gas required

0.00285

 m^3_{NG}/s

 $\frac{0.00285 \ m_{NG}^3}{1 \ s} \times \frac{1.85 \ \text{kg}_{\text{CO}_2}}{1 \ \text{m}_{\text{NG}}^3}$ CO₂ emission

 $5.28 \times 10^{-3} \, \text{kg}_{\text{CO}2}/\text{s}$

PUMP2

Net work required 1.54 kW (from Simulation result)

1.54 kWWork required 0.9×0.5 3.42 kW

$$= \frac{3.42 \times 10^{3} J}{s} \times \frac{0.24 \text{ cal}}{1 \text{ J}}$$

$$= 0.816 \text{ kcal/s}$$
Natural gas required
$$= \frac{0.816 \text{ kcal}}{1 \text{ s}} \times \frac{1 \text{ m}_{NG}^{3}}{9052 \text{ kcal}}$$

$$= 9.02 \times 10^{-5} \text{ m}_{NG}^{3}/s \times \frac{1.85 \text{ kg}_{CO_{2}}}{1 \text{ m}_{NG}^{3}}$$

$$= \frac{9.02 \times 10^{-5} \text{ m}_{NG}^{3}/s}{1 \text{ m}_{NG}^{3}} \times \frac{1.85 \text{ kg}_{CO_{2}}}{1 \text{ m}_{NG}^{3}}$$

$$= 1.67 \times 10^{-4} \text{ kg}_{CO_{2}}/s$$
Indirect CO₂ outlet
$$= (5.28 \times 10^{-3} \text{ kg}_{CO_{2}}/s) + (1.67 \times 10^{-4} \text{ kg}_{CO_{2}}/s)$$

$$= \frac{5.44 \times 10^{-3} \text{ kg}_{CO_{2}}}{1 \text{ s}} \times \frac{60 \text{ s}}{1 \text{ h}} = 19.6 \text{ kg}_{CO_{2}}/h$$

$$\text{Net CO}_{2} \text{ emission} = \sum_{n}^{i} co_{2}_{outlet} - \sum_{n}^{i} co_{2}_{inlet} \quad (3.6)$$

$$\text{Net CO}_{2} \text{ emission} = \begin{pmatrix} 4.78 + 19.6 \text{ kg}_{CO_{2}}/h \\ 349 \text{ kg}_{CH_{3}OH}/h \end{pmatrix} - \begin{pmatrix} 493 \text{ kg}_{CO_{2}}/h \\ 349 \text{ kg}_{CH_{3}OH}/h \end{pmatrix}$$

$$= -1.34 \text{ kg}_{CO_{2}}/\text{kg}_{CH_{3}OH}$$

$$\text{Carbon efficiency} = \frac{349 \text{ kg}_{CH_{3}OH}/h}{(493 \text{ kg}_{CO_{2}}/h + 19.6 \text{ kg}_{CO_{2}}/h)}$$

$$= 0.94$$

D.2 Net CO₂ Emission and carbon efficiency of BRZ x 5 size

Methanol Yield = 1.75×10^3 kg_{CH3OH}/h

Inlet CO_2 = 2.46 x 10^3 kg_{CO2}/h

Direct Outlet CO_2 = 27.8 kg_{CO2}/h

Indirect Outlet CO₂

Basis: Motor efficiency = 0.9 [61]

Electricity production efficiency = 0.5 [62]

Natural gas used for Electricity production = $9052 \text{ kcaV/m}^3_{NG}$ [62]

 CO_2 Emission per natural gas used = $1.85 \text{ kg}_{CO_2}/\text{m}^3_{NG}$

COM1

Net work required = 243 kW (from Simulation result)

$$\text{Work required} = \frac{0.9 \times 0.5}{0.9 \times 0.5} \\ = 541 \text{ kW} \\ = \frac{541 \times 10^3}{\text{s}} \times \frac{0.24 \text{ cal}}{1 \text{ J}} \\ = 129 \text{ kcal/s} \\ \text{Natural gas required} = \frac{129 \text{ kcal}}{1 \text{ s}} \times \frac{1 \text{ m}_{NG}^2}{9052 \text{ kcal}} \\ = 0.0143 \frac{m_{NG}^2}{1 \text{ m}_{NG}^2} \times \frac{1.85 \text{ kg}_{\text{CO}_2}}{1 \text{ m}_{NG}^2} \\ = 0.0264 \text{ kg}_{\text{CO}_2}/\text{s} \\ \text{O2 emission} = \frac{0.0264 \text{ kg}_{\text{CO}_2}/\text{s}}{1 \text{ m}_{NG}^2} \times \frac{1.85 \text{ kg}_{\text{CO}_2}}{1 \text{ m}_{NG}^2} \\ = \frac{7.69 \text{ kW}}{0.9 \times 0.5} \\ = 17.1 \text{ kW} \\ = \frac{17.1 \times 10^3}{1 \text{ s}} \times \frac{0.24 \text{ cal}}{1 \text{ J}} \\ = 4.08 \text{ kcal/s} \\ \text{Natural gas required} = \frac{4.08 \text{ kcal}}{1 \text{ s}} \times \frac{1 \text{ m}_{NG}^2}{9052 \text{ kcal}} \\ = \frac{4.08 \text{ kcal/s}}{1 \text{ s}} \times \frac{10^{-4} \text{ m}_{NG}^2}{1 \text{ m}_{NG}^2} \times \frac{10^{-4} \text{ m}_{NG}^2}{1 \text{ m}_{NG}^2} \\ \text{CO}_2 \text{ emission} = \frac{9.02 \times 10^{-4} \text{ m}_{NG}^2}{1 \text{ s}} \times \frac{1.85 \text{ kg}_{\text{CO}_2}}{1 \text{ m}_{NG}^2} \\ = \frac{8.34 \times 10^4 \text{ kg}_{\text{CO}_2}/\text{s}}{1 \text{ s}} \times \frac{10^{-4} \text{ kg}_{\text{CO}_2}/\text{s}}{1 \text{ m}_{NG}^2} \\ \text{Indirect CO}_2 \text{ outlet} = \frac{0.0272 \text{ kg}_{\text{CO}_2}}{1 \text{ s}} \times \frac{60 \text{ s}}{1 \text{ h}} = 98.0 \text{ kg}_{\text{CO}_2}/\text{h}} \\ \text{Net CO}_2 \text{ emission} = \frac{(27.8 + 98.0 \text{ kg}_{\text{CO}_2}/\text{s}) + (3.6)}{1.75 \times 10^3 \text{ kg}_{\text{CH}_3}\text{OH}/\text{h}} - \left(\frac{2.46 \times 10^3 \text{ kg}_{\text{CO}_2}/\text{h}}{1.75 \times 10^3 \text{ kg}_{\text{CH}_3}\text{OH}/\text{h}}\right) \\ = -1.33 \text{ kg}_{\text{CO}_2}/\text{kg}_{\text{CH}_3}\text{OH}} \\ = -1.33 \text{ kg}_{\text{CO}_2}/\text{kg}_{\text{CH}_3}\text{OH}/\text{h}}$$

243~kW

Carbon efficiency =
$$\frac{1.75 \times 10^{3} \text{ kg}_{\text{CH}_{3}\text{OH}}/\text{h}}{(2.46 \times 10^{3} \text{ kg}_{\text{CO}_{2}}/\text{h} + 98.0 \text{ kg}_{\text{CO}_{2}}/\text{h})}$$
= 0.94

D.3 Net CO_2 Emission and carbon efficiency of BRZ x 7.5 size

Methanol Yield = 2.63×10^3 kg_{CH3OH}/h Inlet CO₂ = 3.70×10^3 kg_{CO2}/h Direct Outlet CO₂ = 37.6 kg_{CO2}/h

Indirect Outlet CO₂

Basis: Motor efficiency = 0.9 [61]

Electricity production efficiency = 0.5 [62]

Natural gas used for Electricity production = 9052 kcal/m³_{NG} [62]

 CO_2 Emission per natural gas used = $1.85 \text{ kg}_{CO_2}/\text{m}^3_{NG}$

COM1

Net work required = 365 kW (from Simulation result)

Work required $= \frac{365 \text{ kW}}{0.9 \times 0.5}$ = 811 kW

$$\frac{811\times10^{3}J}{s}\times\frac{0.24 \text{ cal}}{1 \text{ J}}$$

$$= 194 \text{ kcal/s}$$

Natural gas required = $\frac{194 \text{ kcal}}{1 \text{ s}} \times \frac{1 \text{ m}_{NG}^3}{9052 \text{ kcal}}$

0.0214 m^3_{NG}/s

CO₂ emission = $\frac{0.0214 \, m_{NG}^3}{1 \, s} \times \frac{1.85 \, \text{kg}_{\text{CO}_2}}{1 \, m_{\text{NG}}^3}$

= 0.0396 kg_{CO2}/s

PUMP2

Net work required = 11.5 kW (from Simulation result)

Work required = $\frac{11.5 \, kW}{0.9 \times 0.5}$

$$= 25.6 \text{ kW}$$

$$= \frac{25.6 \times 10^{3} \text{J}}{\text{s}} \times \frac{0.24 \text{ cal}}{1 \text{ J}}$$

$$= 6.12 \text{ kcal/s}$$
Natural gas required
$$= \frac{6.12 \text{ kcal}}{1 \text{ s}} \times \frac{1 \text{ m}_{\text{NG}}^{3}}{9052 \text{ kcal}}$$

$$= 6.76 \times 10^{-4} \text{ m}_{\text{NG}}^{3}/\text{s}$$

$$= 6.76 \times 10^{-4} \text{ m}_{\text{NG}}^{3}/\text{s}$$

$$= 1.25 \times 10^{-3} \text{ kg}_{\text{CO}2}/\text{s}$$
Indirect CO₂ outlet
$$= (0.0396 \text{ kg}_{\text{CO}2}/\text{s}) + (1.25 \times 10^{-3} \text{ kg}_{\text{CO}2}/\text{s})$$

$$= \frac{0.0409 \text{ kg}_{\text{CO}2}}{1 \text{ s}} \times \frac{60 \text{ s}}{1 \text{ h}} = 147 \text{ kg}_{\text{CO}2}/\text{h}$$

$$= \frac{0.0409 \text{ kg}_{\text{CO}2}}{1 \text{ s}} \times \frac{60 \text{ s}}{1 \text{ h}} = 147 \text{ kg}_{\text{CO}2}/\text{h}$$

$$= \frac{37.6 + 147 \text{ kg}_{\text{CO}2}/\text{h}}{2.63 \times 10^{3} \text{ kg}_{\text{CH}_3\text{OH}}/\text{h}} - \frac{3.70 \times 10^{3} \text{ kg}_{\text{CH}_3\text{OH}}/\text{h}}{2.63 \times 10^{3} \text{ kg}_{\text{CH}_3\text{OH}}/\text{h}}$$

$$= -1.34 \text{ kg}_{\text{CO}2}/\text{kg}_{\text{CH}_3\text{OH}}$$

$$= -1.34 \text{ kg}_{\text{CO}2}/\text{kg}_{\text{CH}_3\text{OH}}/\text{h}$$

D.4 Net CO₂ Emission and carbon efficiency of BRZ x 9.5 size

Methanol Yield = 3.32×10^3 kg_{CH3OH}/h

Inlet CO_2 = 4.68×10^3 kg_{CO2}/h

Direct Outlet CO_2 = 50.4 kg_{CO2}/h

Indirect Outlet CO₂

Basis: Motor efficiency = 0.9 [61]

Electricity production efficiency = 0.5 [62]

Natural gas used for Electricity production = 9052 kcal/m³_{NG} [62]

 CO_2 Emission per natural gas used = 1.85 kg_{CO2}/m³_{NG}

COM1

Net work required = 462 kW (from Simulation result)

Work required =
$$\frac{0.9 \times 0.5}{0.9 \times 0.5}$$
 = 1.03×10^3 kW = $\frac{1.03 \times 10^6}{s} \times \frac{0.24 \text{ cal}}{1 \text{ J}}$ = 245 kcal/s Natural gas required = $\frac{245 \text{ kcal}}{1 \text{ s}} \times \frac{1 \text{ m}_{NG}^3}{9052 \text{ kcal}}$ = 0.0271 m $_{NC}^3$ /s $\times \frac{1.85 \text{ kg}_{O2}}{1 \text{ m}_{NG}^3}$ = $0.0271 \frac{m_{NG}^3}{s} \times \frac{1.85 \text{ kg}_{O2}}{1 \text{ m}_{NG}^3}$ = $0.0502 \text{ kg}_{CO}/\text{s}$ where $\frac{13.8 \text{ kW}}{0.9 \times 0.5}$ = $0.0502 \text{ kg}_{CO}/\text{s}$ where $\frac{13.8 \text{ kW}}{0.9 \times 0.5}$ = $\frac{30.7 \times 10^3 \text{ J}}{s} \times \frac{0.24 \text{ cal}}{1 \text{ J}}$ = 7.34 kcal/s Natural gas required = $\frac{7.34 \text{ kcal/s}}{1 \text{ s}} \times \frac{1.0 \text{ m}_{NG}^3}{9052 \text{ kcal}}$ = $\frac{7.34 \text{ kcal/s}}{1 \text{ m}_{NG}^3} \times \frac{1.85 \text{ kg}_{CO}}{1 \text{ m}_{NG}^3}$ Natural gas required = $\frac{7.34 \text{ kcal/s}}{1 \text{ s}} \times \frac{10.4 \text{ m}_{NG}^3}{9052 \text{ kcal}}$ = $\frac{1.50 \times 10^{-3} \text{ kg}_{CO}}{1 \text{ m}_{NG}^3}$ = $\frac{1.50 \times 10^{-3} \text{ kg}_{CO}}{1 \text{ m}_{NG}^3}$ = $\frac{1.50 \times 10^{-3} \text{ kg}_{CO}/\text{s}}{1 \text{ m}_{NG}^3}$ = $\frac{0.0517 \text{ kg}_{CO}}{1 \text{ s}} \times \frac{60 \text{ s}}{1 \text{ h}} = 186 \text{ kg}_{CO}/\text{h}$ Net CO_2 emission = $\frac{1}{s} \frac{c}{s} O_2 \frac{c_{outlet}}{s} - \frac{1}{s} \frac{c}{s} O_2 \frac{c_{intet}}{s}$ (3.6) Net CO_2 emission = $\frac{(50.4 + 186 \text{ kg}_{CO}/\text{h}}{3.32 \times 10^3 \text{ kg}_{CH_3}\text{OH}/\text{h}} - \frac{(4.86 \times 10^3 \text{ kg}_{CO_3}/\text{h}}{3.32 \times 10^3 \text{ kg}_{CH_3}\text{OH}/\text{h}}$

= -1.34 kg_{CO2}/kg_{CH3OH}

Carbon efficiency = $\frac{3.32\times10^3 \text{ kg}_{\text{CH}_3\text{OH}}/\text{h}}{\left(4.86\times10^3 \text{ kg}_{\text{CO}_2}/\text{h}+186 \text{ kg}_{\text{CO}_2}/\text{h}\right)}$

= 0.94



APPENDIX E ECONOMIC ANALYSIS RESULT

E.1 Nomenclature of variables in economic analysis result

Table E1 Nomenclature of variables in economic analysis result

DEP	Depreciation expense
Е	Earnings before Taxes
TAX	Taxes
NE	Net earnings
TED	Total earnings
TEX	Total expenses (excludes taxes and depreciation)
CF	Cash flow
PV	Present value
NPV	Net present value

E.2 Economic analysis result of BRZ size

TW (Number of Weeks per Period)	Weeks/period	52
T (Number of Periods for Analysis)	Period	20
DTEPC (Duration of EPC Phase)	Period	0.442308
DT (Duration of EPC Phase and Startup)	Period	0.826923
WORKP (Working Capital Percentage)	Percent/period	5
OPCHG (Operating Charges)	Percent/period	25
PLANTOVH (Plant Overhead)	Percent/period	50
CAPT (Total Project Cost)	Cost	8.79E+06
RAWT (Total Raw Material Cost)	Cost/period	95209.4
PRODT (Total Product Sales)	Cost/period	1.07E+06
OPMT (Total Operating Labor and Maintenance	Cost/period	912541
Cost)		
UTILT (Total Utilities Cost)	Cost/period	223687
ROR (Desired Rate of Return/Interest Rate)	Percent/period	20

AF (ROR Annuity Factor)		5
TAXR (Tax Rate)	Percent/period	40
IF (ROR Interest Factor)		1.2
ECONLIFE (Economic Life of Project)	Period	20
SALVAL (Salvage Value (Percent of Initial Capital	Percent	20
Cost))		
DEPMETH (Depreciation Method)		Straight
		Line
DEPMETHN (Depreciation Method Id)		1
ESCAP (Project Capital Escalation)	Percent/period	5
ESPROD (Products Escalation)	Percent/period	5
ESRAW (Raw Material Escalation)	Percent/period	3.5
ESLAB (Operating and Maintenance Labor	Percent/period	3
Escalation)		
ESUT (Utilities Escalation)	Percent/period	3
START (Start Period for Plant Startup)	Period	1
DESRET (Desired Return on Project for Sales	Percent/Period	10.5
Forecasting)	9	
END (End Period for Economic Life of Project)	Period	20
GA (G and A Expenses)	Percent/Period	8
DTEP (Duration of EP Phase before Start of	Period	0.211538
Construction)		
OP (Total Operating Labor Cost)	Cost/period	832770
MT (Total Maintenance Cost)	Cost/period	79770.6

Operating Costs (Cost/Period) Utilities Maintenance 87167.5 89782.5 84628.6 98107.8 45822.1 95250.3 Cost Operating Labor Cost Materials Raw Working Capital Cumulative Capital Cost Expenses (Cost/Period) Capital Cost Unescalated Cumulative Capital Cost Economic analysis result of BRZ size (Capital Costs) CAP (Cost/Period) (Products Sale Sales) SP Year ∞

Overhead

Plant

Operating Charges Economic analysis result of BRZ size (Cont'd)

	Sale		PANAGRA	es (Cost/Period)	(100)				Operating Costs (Cost/Period)	(Dost/Period)		
	(Cost/Period)				Ò			Ó				
ear	SP	CAP	Unescalated		() ii+c	S CLINA V	Day	Operating	() () () () () () () () () () () () () (, to 000	+4 10
	(Products	(Capital	Cumulative	Capitat Cor+	Califacine Cost	Sills Sills	4 + 4 + 4 + 4 + 4 + 4 + 4 + 4 + 4 + 4 +	Labor	ואומוו ורבו ומו וכת	Utilities	Characters	r di il
	Sales)	Costs)	Capital Cost	1605	Capital Cost	Capital	ואומותוומנא	Cost	7607		כוומוצתא	Overliead
11	1832100		8789450		9228920		139003	1152750	110421	309635	288187	631585
12	1923700		8789450		9228920		143868	1187330	113734	318924	296833	650532
13	2019890		8789450		9228920		148903	1222950	117146	328491	305738	670048
14	2120880		8789450		9228920		154115	1259640	120660	338346	314910	690150
15	2226930		8789450		9228920		159509	1297430	124280	348496	324357	710854
16	2338270		8789450		9228920		165092	1336350	128008	358951	334088	732180
17	2455190		8789450		9228920		170870	1376440	131849	369720	344110	754145
18	2577940		8789450		9228920		176850	1417740	135804	380812	354434	776770
19	2706840		8789450		9228920		183040	1460270	139878	392236	365067	800073
20	2842180		8789450		9228920		189447	1504080	144075	404003	376019	824075

Economic analysis result of BRZ size (Cont'd)

	Operating Costs (Cost/Period)	ng Costs Period)				Revenue (Cost/Period)	st/Period)			Presen (Cost/	Present Value (Cost/Period)
Year	Subtotal Operating Costs	G and A Costs	DEP	E	ΤΑΧ	ΞZ	TED	TEX	CF	<u>~</u>	NPV
0	0	0	0	0	0	0	0	0	0	0	0
1	1089310	87145.1	351578	-11023700	0	-11023700	-10672200	10866800	-10672200	-8893460	-8893460
2	2012340	160987	351578	-1343920	0	-1343920	-992344	2173330	-992344	-689128	-9582590
3	2073220	165858	351578	-1350620	0	-1350620	-999045	2239080	-999045	-578151	-10160700
4	2135950	170876	351578	-1356360	0	-1356360	-1004790	2306820	-1004790	-484561	-10645300
5	2200570	176046	351578	-1361060	0	-1361060	-1009480	2376620	-1009480	-405687	-11051000
9	2267150	181372	351578	-1364610	0	-1364610	-1013030	2448530	-1013030	-339262	-11390300
7	2335750	186860	351578	-1366920	0	-1366920	-1015340	2522610	-1015340	-283364	-11673600
∞	2406430	192515	351578	-1367890	0	-1367890	-1016310	2598950	-1016310	-236362	-11910000
6	2479250	198340	351578	-1367400	0	-1367400	-1015830	2677590	-1015830	-196874	-12106900
10	2554280	204342	351578	-1365340	0	-1365340	-1013770	2758620	-1013770	-163729	-12270600

Economic analysis result of BRZ size (Cont'd)

	Operating Costs (Cost/Period)	Costs iod)				Revenue (Cost/Period)	'eriod)			Presen (Cost/	Present Value (Cost/Period)
Year	Subtotal Operating Costs	G and A Costs	DEP	Ш	TAX	Ш Z	TED	TEX	CF	A	ΛΦV
11	631585	2631580	210526	351578	-1361590	0	-1361590	-1010010	2842110	-1010010	-135935
12	650532	2711220	216898	351578	-1355990	0	-1355990	-1004420	2928120	-1004420	-112652
13	670048	2793280	223462	351578	-1348430	0	-1348430	-996852	3016740	-996852	-93169.7
14	690150	2877820	230226	351578	-1338740	0	-1338740	-987164	3108050	-987164	-76886.8
15	710854	2964930	237194	351578	-1326770	0	-1326770	-975194	3202120	-975194	-63295.4
16	732180	3054670	244374	351578	-1312350	0	-1312350	-960772	3299040	-960772	-51966.2
17	754145	3147140	251771	351578	-1295300	0	-1295300	-943722	3398910	-943722	-42536.6
18	776770	3242400	259392	351578	-1275430	0	-1275430	-923852	3501800	-923852	-34700.8
19	800073	3340560	267245	351578	-1252540	0	-1252540	-900964	3607810	-900964	-28200.9
20	824075	3441690	275335	351578	-1226420	0	-1226420	-874844	3717030	1322520	-22819.5
									P.O. period (year)	d (year)	0
									Profitability index	y index	0.324204

E.3 Economic analysis result of BRZ \times 5 size

,	<u> </u>	<u> </u>
TW (Number of Weeks per Period)	Weeks/period	52
T (Number of Periods for Analysis)	Period	20
DTEPC (Duration of EPC Phase)	Period	0.557692
DT (Duration of EPC Phase and Startup)	Period	0.942308
WORKP (Working Capital Percentage)	Percent/period	5
OPCHG (Operating Charges)	Percent/period	25
PLANTOVH (Plant Overhead)	Percent/period	50
CAPT (Total Project Cost)	Cost	1.48E+07
RAWT (Total Raw Material Cost)	Cost/period	476047
PRODT (Total Product Sales)	Cost/period	5.38E+06
OPMT (Total Operating Labor and Maintenance	Cost/period	1.05E+06
Cost)		
UTILT (Total Utilities Cost)	Cost/period	913890
ROR (Desired Rate of Return/Interest Rate)	Percent/period	20
AF (ROR Annuity Factor)		5
TAXR (Tax Rate)	Percent/period	40
IF (ROR Interest Factor)		1.2
ECONLIFE (Economic Life of Project)	Period	20
SALVAL (Salvage Value (Percent of Initial Capital	Percent	20
Cost))		
DEDMETH (Depresisting Mathed)		Straight
DEPMETH (Depreciation Method)		Line
DEPMETHN (Depreciation Method Id)		1
ESCAP (Project Capital Escalation)	Percent/period	5
ESPROD (Products Escalation)	Percent/period	5
ESRAW (Raw Material Escalation)	Percent/period	3.5
ESLAB (Operating and Maintenance Labor	Percent/period	3
Escalation)		
	1	1

ESUT (Utilities Escalation)	Percent/period	3
START (Start Period for Plant Startup)	Period	1
DESRET (Desired Return on Project for Sales	Percent/Period	10.5
Forecasting)		
END (End Period for Economic Life of Project)	Period	20
GA (G and A Expenses)	Percent/Period	8
DTEP (Duration of EP Phase before Start of	Period	0.211538
Construction)		
OP (Total Operating Labor Cost)	Cost/period	832770
MT (Total Maintenance Cost)	Cost/period	212576



Operating Charges 94847.7 Operating Costs (Cost/Period) Utilities Maintenance 96844.5 Cost Operating Labor Cost Materials Raw Working Capital Cumulative Capital Cost Expenses (Cost/Period) Capital Cost Unescalated Cumulative Capital Cost (Capital Costs) CAP (Products (Cost/Period) Sales) Sale SP Year ∞

Overhead

Plant

 Economic analysis result of BRZ \times 5 size

Economic analysis result of BRZ \times 5 size (Cont'd)

	Sale) ()	as (Cos+/Dar	(70)			Ĉ) stac pater	(Locited/tach)		
0)	(Cost/Period)		בואטאיז		(noi			Ď.	Operating Costs (Costs Ferrou)	COST/FEIIOU,		
	SP	CAP	Unescalated	1.1	Cumulative	1 ()		Operating	() () () () () ()		+	+ S
	(Products	(Capital	Cumulative	Capitat Cost	Capital	working Capital	Kaw	Labor	Maintenance	Utilities	Operating	riant O m
	Sales)	Costs)	Capital Cost	1605	Cost	Capital	Materiars	Cost	1602		כוומוצמא	כאת: המט
	9194090		14764400		15502700		695013	1152750	294254	1265040	288187	723501
	9653800		14764400		15502700		719339	1187330	303082	1302990	296833	745206
	10136500		14764400		15502700		744516	1222950	312174	1342080	305738	767563
	10643300		14764400		15502700		770574	1259640	321540	1382340	314910	790589
	11175500		14764400		15502700		797544	1297430	331186	1423810	324357	814307
	11734300		14764400		15502700		825458	1336350	341121	1466520	334088	838736
	12321000		14764400		15502700		854349	1376440	351355	1510520	344110	863898
	12937000		14764400		15502700		884251	1417740	361896	1555840	354434	889815
	13583900		14764400		15502700		915200	1460270	372752	1602510	365067	916510
	14263100		14764400		15502700		947232	1504080	383935	1650590	376019	944005

Economic analysis result of BRZ \times 5 size (Cont'd)

	Operating Costs (Cost/Period)	ng Costs Period)				Revenue (Cost/Period)	Period)			Presen (Cost/	Present Value (Cost/Period)
Year	Subtotal Operating Costs	G and A Costs	DEP	Ш	TAX	ШZ	TED	TEX	CF	2	NP.
0	0	0	0	0	0	0	0	0	0	0	0
1	1443480	115478	590577	-18101700	0	-18101700	-17511100	17836700	-17511100	-14592600	-14592600
2	3363880	269110	590577	1703030	681211	1021820	1612390	3632990	1612390	1119720	-13472900
3	3467350	277388	590577	1887610	755045	1132570	1723140	3744730	1723140	997190	-12475700
4	3574010	285920	590577	2083570	833427	1250140	1840720	3859930	1840720	887692	-11588000
5	3683960	294717	590577	2291520	916609	1374910	1965490	3978670	1965490	789887	-10798100
9	3797300	303784	590577	2512150	1004860	1507290	2097870	4101090	2097870	702571	-10095500
7	3914150	313132	590577	2746150	1098460	1647690	2238260	4227280	2238260	624659	-9470870
∞	4034600	322768	590577	2994260	1197700	1796550	2387130	4357370	2387130	555171	-8915700
6	4158770	332702	590577	3257260	1302900	1954360	2544930	4491480	2544930	493225	-8422470
10	4286780	342942	590577	3535980	1414390	2121590	2712160	4629720	2712160	438030	-7984440

Economic analysis result of BRZ \times 5 size (Cont'd)

	Operating Costs (Cost/Period)	Costs iod)				Revenue (Cost/Period)	'eriod)			Presen (Cost/	Present Value (Cost/Period)
	Subtotal Operating Costs	G and A Costs	DEP	Ш	TAX	ШZ	TED	TEX	CF	2	AdN N
	4418740	353499	590577	3831280	1532510	2298770	2889340	4772240	2889340	388871	-7595570
_	4554780	364382	590577	4144060	1657620	2486440	3077010	4919160	3077010	345107	-7250470
_	4695020	375602	590577	4475290	1790120	2685170	3275750	5070620	3275750	306164	-6944300
	4839590	387167	590577	4825980	1930390	2895590	3486160	5226760	3486160	271525	-6672780
_	4988630	399091	590577	5197180	2078870	3118310	3708880	5387720	3708880	240727	-6432050
_	5142280	411382	590577	5590010	2236010	3354010	3944590	5553660	3944590	213354	-6218690
	5300670	424054	590577	0995009	2402260	3603390	4193970	5724730	4193970	189036	-6029660
_	5463970	437117	590577	6445350	2578140	3867210	4457790	5901080	4457790	167439	-5862220
	5632310	450585	590577	6910390	2764160	4146240	4736810	6082890	4736810	148266	-5713950
	5805850	464468	590577	7402160	2960860	4441300	5031870	6270320	8722980	131252	-5486420
l									P.O. period (year)	d (year)	0
									Profitability index	y index	0.846

E.4 Economic analysis result of BRZ \times 7.5 size

TW (Number of Weeks per Period)	Weeks/period	52
T (Number of Periods for Analysis)	Period	20
DTEPC (Duration of EPC Phase)	Period	0.596154
DT (Duration of EPC Phase and Startup)	Period	0.980769
WORKP (Working Capital Percentage)	Percent/period	5
OPCHG (Operating Charges)	Percent/period	25
PLANTOVH (Plant Overhead)	Percent/period	50
CAPT (Total Project Cost)	Cost	1.81E+07
RAWT (Total Raw Material Cost)	Cost/period	714070
PRODT (Total Product Sales)	Cost/period	8.06E+06
OPMT (Total Operating Labor and Maintenance Cost)	Cost/period	1.11E+06
UTILT (Total Utilities Cost)	Cost/period	1.46E+06
ROR (Desired Rate of Return/Interest Rate)	Percent/period	20
AF (ROR Annuity Factor)		5
TAXR (Tax Rate)	Percent/period	40
IF (ROR Interest Factor)		1.2
ECONLIFE (Economic Life of Project)	Period	20
SALVAL (Salvage Value (Percent of Initial Capital	Percent	20
Cost)) GHULALONGKORN UNIVERSI	TY	
DEPMETH (Depreciation Method)		Straight
		Line
DEPMETHN (Depreciation Method Id)		1
ESCAP (Project Capital Escalation)	Percent/period	5
ESPROD (Products Escalation)	Percent/period	5
ESRAW (Raw Material Escalation)	Percent/period	3.5
ESLAB (Operating and Maintenance Labor Escalation)	Percent/period	3
ESUT (Utilities Escalation)	Percent/period	3
START (Start Period for Plant Startup)	Period	1

DESRET (Desired Return on Project for Sales	Percent/Period	10.5
Forecasting)		
END (End Period for Economic Life of Project)	Period	20
GA (G and A Expenses)	Percent/Period	8
DTEP (Duration of EP Phase before Start of	Period	0.211538
Construction)		
OP (Total Operating Labor Cost)	Cost/period	832770
MT (Total Maintenance Cost)	Cost/period	278321



Operating Charges 86600.1 Operating Costs (Cost/Period) Utilities Maintenance Cost Operating Labor Cost Materials Raw Working Capital Cumulative Capital Cost Expenses (Cost/Period) Capital Cost Unescalated Cumulative Capital Cost (Capital Costs) CAP (Cost/Period) (Products Sales) Sale SP Year ~ ∞

Overhead

Plant

Economic analysis result of BRZ \times 7.5 size

Economic analysis result of BRZ \times 7.5 size (Cont'd)

	Sale		Fxnens	Expenses (Cost/Period)	riod)				Operating Costs (Cost/Period)	(Cost/Period		
	(Cost/Period)				(n)				واجام الأسام			
/ear	SP (Products	CAP	Unescalated	Capital	Cumulative	Working	Raw	Operating	Maintenance	(;; ;; ;	Operating	Plant
	Sales)	(Capitat Costs)	Capital Cost	Cost	Capital Cost	Capital	Materials	Labor Cost	Cost	Others	Charges	Overhead
11	13782600		18063600		18966800		1042520	1152750	385261	2024440	288187	769005
12	14471800		18063600		18966800		1079010	1187330	396818	2085170	296833	792075
13	15195300		18063600		18966800		1116770	1222950	408723	2147730	305738	815837
14	15955100		18063600		18966800		1155860	1259640	420985	2212160	314910	840312
15	16752900		18063600		18966800		1196320	1297430	433614	2278520	324357	865521
16	17590500		18063600		18966800		1238190	1336350	446623	2346880	334088	891487
17	18470000		18063600		18966800		1281520	1376440	460021	2417290	344110	918232
18	19393500		18063600		18966800		1326380	1417740	473822	2489800	354434	945779
19	20363200		18063600		18966800		1372800	1460270	488037	2564500	365067	974152
20	21381400		18063600		18966800		1420850	1504080	502678	2641430	376019	1003380

Economic analysis result of BRZ imes 7.5 size (Cont'd)

La	(Cost/Period)				Revenue (Cost/Period)	/Period)			Presen (Cost/	Present Value (Cost/Period)
	G and A Costs	DEP	Ш	TAX	Ш Z	TED	TEX	CF	≥	^dN
	0	0	0	0	0	0	0	0	0	0
	134933	722544	-2.23E+07	0	-2.23E+07	-2.16E+07	2.17E+07	-2.16E+07	-1.80E+07	-1.80E+07
	344440	722544	3.51E+06	1.40E+06	2.11E+06	2.83E+06	4.65E+06	2.83E+06	1.97E+06	-1.60E+07
	355079	722544	3.81E+06	1.53E+06	2.29E+06	3.01E+06	4.79E+06	3.01E+06	1.74E+06	-1.43E+07
-	366048	722544	4.13E+06	1.65E+06	2.48E+06	3.20E+06	4.94E+06	3.20E+06	1.54E+06	-1.27E+07
5 4.72E+06	377357	722544	4.47E+06	1.79E+06	2.68E+06	3.40E+06	5.09E+06	3.40E+06	1.37E+06	-1.14E+07
6 4.86E+06	389017	722544	4.82E+06	1.93E+06	2.89E+06	3.62E+06	5.25E+06	3.62E+06	1.21E+06	-1.01E+07
7 5.01E+06	401039	722544	5.20E+06	2.08E+06	3.12E+06	3.84E+06	5.41E+06	3.84E+06	1.07E+06	-9.08E+06
8 5.17E+06	413433	722544	5.60E+06	2.24E+06	3.36E+06	4.08E+06	5.58E+06	4.08E+06	949756	-8.13E+06
9 5.33E+06	426213	722544	6.02E+06	2.41E+06	3.61E+06	4.34E+06	5.75E+06	4.34E+06	840626	-7.29E+06
10 5.49E+06	439388	722544	6.47E+06	2.59E+06	3.88E+06	4.61E+06	5.93E+06	4.61E+06	743856	-6.54E+06

Economic analysis result of BRZ \times 7.5 size (Cont'd)

	Operating Costs (Cost/Period)	Costs riod)				Revenue (Cost/Period)	eriod)			Presen (Cost/	Present Value (Cost/Period)
Year	Subtotal Operating Costs	G and A Costs	DEP	Э	TAX	Ш Z	TED	TEX	CF	≥	NPV
11	5.66E+06	452973	722544	6.94E+06	2.78E+06	4.17E+06	4.89E+06	6.12E+06	4.89E+06	658070	-5.88E+06
12	5.84E+06	466979	722544	7.45E+06	2.98E+06	4.47E+06	5.19E+06	6.30E+06	5.19E+06	582042	-5.30E+06
13	6.02E+06	481420	722544	7.97E+06	3.19E+06	4.78E+06	5.51E+06	6.50E+06	5.51E+06	514680	-4.79E+06
14	6.20E+06	496309	722544	8.53E+06	3.41E+06	5.12E+06	5.84E+06	6.70E+06	5.84E+06	455012	-4.33E+06
15	6.40E+06	511661	722544	9.12E+06	3.65E+06	5.47E+06	6.20E+06	6.91E+06	6.20E+06	402173	-3.93E+06
16	6.59E+06	527489	722544	9.75E+06	3.90E+06	5.85E+06	6.57E+06	7.12E+06	6.57E+06	355393	-3.57E+06
17	6.80E+06	543809	722544	1.04E+07	4.16E+06	6.24E+06	6.97E+06	7.34E+06	6.97E+06	313989	-3.26E+06
18	7.01E+06	560636	722544	1.11E+07	4.44E+06	6.66E+06	7.38E+06	7.57E+06	7.38E+06	277350	-2.98E+06
19	7.22E+06	577986	722544	1.18E+07	4.74E+06	7.10E+06	7.83E+06	7.80E+06	7.83E+06	244937	-2.74E+06
20	7.45E+06	595874	722544	1.26E+07	5.05E+06	7.57E+06	8.29E+06	8.04E+06	1.28E+07	216270	-2.40E+06
									P.O. period (year)	d (year)	0
									Profitability index	y index	0.936

E.5 Economic analysis result of BRZ x 9.5 size

TW (Number of Weeks per Period)	Weeks/period	52
T (Number of Periods for Analysis)	Period	20
DTEPC (Duration of EPC Phase)	Period	0.634615
DT (Duration of EPC Phase and Startup)	Period	1.01923
WORKP (Working Capital Percentage)	Percent/period	5
OPCHG (Operating Charges)	Percent/period	25
PLANTOVH (Plant Overhead)	Percent/period	50
CAPT (Total Project Cost)	Cost	1.96E+07
RAWT (Total Raw Material Cost)	Cost/period	904488
PRODT (Total Product Sales)	Cost/period	1.02E+07
OPMT (Total Operating Labor and Maintenance	Cost/period	1.16E+06
Cost)		
UTILT (Total Utilities Cost)	Cost/period	1.83E+06
ROR (Desired Rate of Return/Interest Rate)	Percent/period	20
AF (ROR Annuity Factor)		5
TAXR (Tax Rate)	Percent/period	40
IF (ROR Interest Factor)		1.2
ECONLIFE (Economic Life of Project)	Period	20
SALVAL (Salvage Value (Percent of Initial Capital	Percent	20
Cost))		
DEPMETH (Depreciation Method)		Straight
		Line
DEPMETHN (Depreciation Method Id)		1
ESCAP (Project Capital Escalation)	Percent/period	5
ESPROD (Products Escalation)	Percent/period	5
ESRAW (Raw Material Escalation)	Percent/period	3.5
ESLAB (Operating and Maintenance Labor	Percent/period	3
Escalation)		

ESUT (Utilities Escalation)	Percent/period	3
START (Start Period for Plant Startup)	Period	1
DESRET (Desired Return on Project for Sales	Percent/Period	10.5
Forecasting)		
END (End Period for Economic Life of Project)	Period	20
GA (G and A Expenses)	Percent/Period	8
DTEP (Duration of EP Phase before Start of	Period	0.211538
Construction)		
OP (Total Operating Labor Cost)	Cost/period	832770
MT (Total Maintenance Cost)	Cost/period	329821



Overhead 218768 616696 736368 758459 781212 635197 654253 694097 714920 673881 Plant 0 Operating Charges 78352.4 227498 279793 234322 241352 248593 271644 220871 263732 256051 0 Operating Costs (Cost/Period) 1.94E+06 2.00E+06 2.06E+06 2.12E+06 2.19E + 062.39E+06 2.46E+06 2.25E+06 2.32E+06 689665 Utilities 0 Maintenance 371216 360404 382353 393823 405638 443252 124127 349907 417807 430341 Cost 0 Operating 1.05E+06 1.09E + 061.12E + 061.02E+06 313410 965409 883486 066606 937290 994371 Labor Cost 0 1.23E + 061.28E+06 1.00E+06 1.04E+06 1.07E+06 1.11E + 061.15E + 061.19E + 06968910 Materials 342053 Raw 0 1.03E+06Working Capital 0 Cumulative 2.05E+07 Capital Cost 0 Expenses (Cost/Period) 2.05E+07 Capital Cost 0 Unescalated Cumulative Capital Cost 1.96E+07 1.96E+07 1.96E + 071.96E+07 1.96E + 071.96E+07 1.96E+07 1.96E + 071.96E+07 1.96E+07 0 2.16E+07 (Capital Costs) CAP 0 SP (Products (Cost/Period) 1.30E+07 1.36E+07 1.43E + 071.24E+07 1.50E+07 1.58E+07 1.66E+07 1.10E+07 1.18E+07 Sales) Sale 0 0 Year 10 0 2 4 2 9 ∞ 6

Economic analysis result of BRZ x 9.5 size

Economic analysis result of BRZ \times 9.5 size (Cont'd)

	Sale		, aga,	Expanses (Cost/Dariod)	(Locina				Operating Costs (Cost/Deriod)	(Poinod/toc)		
	(Cost/Period)		ב אלטל א	10000 000					Operating Costs			
Year	SP	CAP	Unescalated	Lations	0, ii+ch 1 can 1	p ci./hc///	Down	Operating	مرم دمن +مند ۱۸		Duckting.	+ac 0
	(Products	(Capital	Cumulative	Capital	Cultidative	NO L	4 d v v	Labor	ואומוו ונכן ומווכב	Utilities	Cheraturis	רמוונ
	Sales)	Costs)	Capital Cost	1807	Capital Cost	Capitat	Materials	Cost	1800		Charges	Overnead
11	1.74E+07		1.96E+07		2.05E+07		1.32E+06	1.15E+06	456549	2.54E+06	288187	804649
12	1.83E+07		1.96E+07		2.05E+07		1.37E+06	1.19E+06	470246	2.61E+06	296833	828788
13	1.92E+07		1.96E+07		2.05E+07		1.41E+06	1.22E+06	484353	2.69E+06	305738	853652
14	2.01E+07		1.96E+07		2.05E+07		1.46E+06	1.26E+06	498883	2.77E+06	314910	879261
15	2.11E+07		1.96E+07		2.05E+07		1.52E+06	1.30E+06	513850	2.86E+06	324357	905639
16	2.22E+07		1.96E+07		2.05E+07		1.57E+06	1.34E+06	529265	2.94E+06	334088	932808
17	2.33E+07		1.96E+07		2.05E+07		1.62E+06	1.38E+06	545143	3.03E+06	344110	960793
18	2.45E+07		1.96E+07		2.05E+07		1.68E+06	1.42E+06	561498	3.12E+06	354434	989616
19	2.57E+07		1.96E+07		2.05E+07		1.74E+06	1.46E+06	578343	3.21E+06	365067	1.02E+06
20	2.70E+07		1.96E+07		2.05E+07		1.80E+06	1.50E+06	595693	3.31E+06	376019	1.05E+06

1.02

Profitability index

Economic analysis result of BRZ $\times\,9.5$ size (Cont'd)

Present Value (Cost/Period)	ΛdN	-3.45E+06	-2.68E+06	-1.99E+06	-1.39E+06	-859290	-389638	24837.3	390553	713189	1.13E+06	16.9
Presen (Cost/	À	874903	772839	682549	602693	532079	469652	414475	365716	322636	284583	d (year)
	CF	6.50E+06	6.89E+06	7.30E+06	7.74E+06	8.20E+06	8.68E+06	9.20E+06	9.74E+06	1.03E+07	1.58E+07	P.O. period (year)
	TEX	7.08E+06	7.30E+06	7.53E+06	7.76E+06	8.00E+06	8.25E+06	8.51E+06	8.77E+06	9.05E+06	9.33E+06	
eriod)	TED	6.50E+06	6.89E+06	7.30E+06	7.74E+06	8.20E+06	8.68E+06	9.20E+06	9.74E+06	1.03E+07	1.09E+07	
Revenue (Cost/Period)	ШZ	5.72E+06	6.11E+06	6.52E+06	6.96E+06	7.42E+06	7.90E+06	8.41E+06	8.95E+06	9.52E+06	1.01E+07	
	TAX	3.81E+06	4.07E+06	4.35E+06	4.64E+06	4.94E+06	5.27E+06	5.61E+06	5.97E+06	6.35E+06	6.75E+06	
	E	9.53E+06	1.02E+07	1.09E+07	1.16E+07	1.24E+07	1.32E+07	1.40E+07	1.49E+07	1.59E+07	1.69E+07	
	DEP	782616	782616	782616	782616	782616	782616	782616	782616	782616	782616	
Costs riod)	G and A Costs	524745	541015	557792	575092	592930	611324	630291	649849	670017	690813	
Operating Costs (Cost/Period)	Subtotal Operating Costs	6.56E+06	6.76E+06	6.97E+06	7.19E+06	7.41E+06	7.64E+06	7.88E+06	8.12E+06	8.38E+06	8.64E+06	
	Year	11	12	13	14	15	16	17	18	19	20	

VITA

Miss Kankanit Kitsahawong was born on June 23rd, 1993 in Bangkok Thailand. In 2011, she graduated a high school Bodindecha (Sing Singhaseni) School, Bangkok. She received the Bachelor's Degree of Chemical Technology from Department of Chemical Technology, Faculty of Science, Chulalongkorn University in 2015. During 4 years under graduated study, she found that she wanted to know well in Chemical Engineering field. Thus, she continued her Master's degree in Chemical Engineering, Chulalongkorn University under the supervision of Prof. Sutthichai Assabumrungrat and her co-advisor Dr. Pongtorn Charoensuppanimit.

Although she had some rough time in graduated study, she got a kind and worthy advice from her advisor and her co-advisor. Then, she learnt more about works and life.

Finally, for 2 years and half of master degree life, she got many lesson from many people and had grown up to be a better person.

จุฬาลงกรณ์มหาวิทยาลัย Chulalongkorn University