Methane production from reforming of glycerol

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A Report Submitted in Partial Fulfillment of the Requirements
for the Degree of Bachelor of Engineering (Petrochemical Engineering)
Department of Chemical Engineering, Faculty of Engineering,
King Mongkut's Institute of Technology Ladkrabang
Academic Year 2019

การผลิตมีเทนจากการรีฟอร์มมิงของกลีเซอรอล

ชวิศ ธุระมะฉายา

ปริญญานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตร

วิศวกรรมศาสตรบัณฑิต สาขาวิชาวิศวกรรมปิโตรเคมี

ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์

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ปีการศึกษา 2562

Title	Methane production through reforming of glycerol
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Field of Study	Petrochemical Engineering
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Accepted by the Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang in Partial Fulfillment of the Requirements for the Degree of Bachelor of Engineering (Petrochemical Engineering).

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Abstract

This work aims to study the methane production from renewable resource. Since methane is an essential chemical that can be used as fuel for power generation and raw materials for many chemical industries. Among various renewable resources, glycerol as highly produced from biodiesel production is much interest because it is low cost and can convert into other products. In this work, the model of methane production through dry reforming of glycerol was presented. Thermodynamic analysis was performed to determine gas product composition which can be calculated from minimization of Gibbs free energy. The impact of operating conditions, i.e., reformer temperature, carbon dioxide to glycerol molar ratio (CGR) and reformer pressure on methane production is investigated. The simulation results indicated that decreases in temperature and CGR and an increase in pressure can increase methane molar flow rate. In addition, the simulation results indicated that the highest methane production can be provided when the reformer is operated at temperature of 600 K, CGR of 0.5 and pressure of 4 atm. However, gas product obtained from reformer contains high amount of steam, the flash drum is applied in the system. After gas product is removed steam by flash drum operated at 323 K and 1 atm, the final methane molar flow rate of 0.804 kmol/hr with purity of 41 mol% can be provided.

Keywords: Methane, Glycerol, Dry reforming, Process simulation

เรื่อง การผลิตมีเทนจากการรีฟอร์มมิงของกลีเซอรอล

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บทคัดย่อ

โครงงานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการผลิตก๊าซมีเทนจากแหล่งพลังงานหมุนเวียน เนื่องจากมีเทนเป็นสารเคมีที่จำเป็นที่สามารถนำไปใช้เป็นเชื้อเพลิงในการผลิตกระแสไฟฟ้าและเป็นสารตั้งต้นสำหรับอุตสาหกรรมเคมีต่างๆ ในบรรดาทรัพยากรหมุนเวียนที่หลากหลาย กลีเซอรอลซึ่งถูกผลิตจากกระบวนการไบโอดีเซลเป็นปริมาณมากจึงเป็นที่สนใจเนื่องจากเป็นสารที่มีต้นทุนต่ำและสามารถเปลี่ยนเป็นผลิตภัณฑ์อื่นได้ ในโครงงานนี้ได้นำเสนอแบบจำลองกระบวนการผลิตมีเทนผ่านการรีฟอร์มมิงโดยใช้แก๊สคาร์บอนไดออกไซด์ (dry reforming) ในการศึกษาจะใช้การวิเคราะห์ทางอุณหพลศาสตร์เพื่อหาองค์ประกอบของแก๊สผลิตภัณฑ์ที่คำนวนได้จากพลังงานอิสระกิบส์ที่น้อยที่สุด ในโครงงานนี้ได้ทำการศึกษาผลกระทบของอุณหภูมิของรีฟอร์มเมอร์ อัตราส่วนโดยโมลระหว่างคาร์บอนไดออกไซด์และกลีเซอรอล และความดันของรีฟอร์มเมอร์ ที่มีต่อการผลิตแก๊สมีเทน ผลการจำลองกระบวนการบ่งบอกว่าการลดลงของอุณหภูมิของรีฟอร์เมอร์และอัตราส่วนโดยโมลระหว่างคาร์บอนไดออกไซด์และกลีเซอรอล รวมถึงการเพิ่มขึ้นของความดันของเครื่องรีฟอร์มเมอร์จะส่งผลให้อัตราการไหลของแก๊สมีเทนมีค่าเพิ่มขึ้น นอกจากนี้ผลของการจำลองแสดงให้เห็นว่าเมื่อเครื่องรีฟอร์มเมอร์ดำเนินงานที่อุณหภูมิ 600 เคลวิน ความดัน 4 บรรยากาศ ด้วยการป้อนอัตราส่วนโดยโมลระหว่างคาร์บอนไดออกไซด์และกลีเซอรอลเท่ากับ 0.5 จะได้อัตราการไหลของก๊าซมีเทนสูงที่สุด อย่างไรก็ตามแก๊สผลิตภัณฑ์ที่ได้จากเครื่องรีฟอร์มเมอร์ประกอบไปด้วยไอน้ำจำนวนมาก เครื่องแยก (flash drum) จึงถูกนำใช้เพื่อแยกน้ำออกจากแก๊สผลิตภัณฑ์ หลังจากไอน้ำถูกแยกออกโดยเครื่องแยกที่อุณหภูมิ 323 เคลวิน และความดัน 1 บรรยากาศ พบว่าสุดท้ายแล้วจะได้อัตราการไหลของก๊าซมีเทนอยู่ที่ 0.804 กิโลโมลต่อชั่วโมง ซึ่งมีความบริสุทธ์เท่ากับ 41 เปอร์เซ็นต์โดยโมล

คำสำคัญ: มีเทน, กลีเซอรอล, การรีฟอร์มมิ่งแบบแห้ง, การจำลองกระบวนการ

Acknowledgements

For this project, I am thankful my advisor, Assist.Prof.Dr.Yaneeporn Patcharavorachot for introduction to interesting project, helping, advising, and discussion throughout the work until completed. Moreover, I would like to thank my family and professor that not mentioned but educate, encourage and support me.

Finally, if the project has some mistake, I apologize.

Mr.Chawit Thuramachaya

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CHAPTER I

INTRODUCTION

1.1 Background

Methane is hydrocarbon compound that can be found in natural gas around 70 percent. Methane are commonly used as fuel for power generation and heat production in industrial plants. In addition, methane can be used as fuel for vehicles in Thailand known as "Natural gas for vehicle (NGV)". Moreover, methane can be used as raw materials for many chemical industries, such as fertilizer, ammonia, urea and methanol production [1].

In Thailand, natural gas can be produced 4,042 million cubic feet per day. This is around 80 percent, and another is imported from aboard. In 2013, Thailand consumed 4,568 million cubic feet of natural gas per day in average [2] which has more natural gas consumption than the production per days due to higher natural gas usage. The use of alternative energy to replace natural gas is an important issue. Biodiesel which can be synthesized through transesterification from vegetable oil is one of alternative fuels used in Thailand. The main by-product of transesterification is glycerol [3]. When the biodiesel production is growing, the amount of crude glycerol is also greater. Glycerol has low price in which is commonly used for pharmacy and cosmetic industry. But glycerol used in these industries must be purified which leads to higher production cost. Besides that, glycerol can be produced hydrogen, methane and synthesis gas through reforming processes [4].

Glycerol dry reforming is one of the most promising methods for converting into other products. The use of carbon dioxide in the reaction is reusing carbon dioxide as the greenhouse gas. Besides synthesis gas produced from glycerol dry reforming, it is found that methane can be generated through glycerol dry reforming operated under an appropriate condition [4].

1.2 Objective

To investigate methane production from glycerol dry reforming

1.3 Scopes of Work

1.3.1 Design methane production process by using Aspen Plus simulator

1.3.2 Study the effect of reformer operation on methane production

The studied parameters are:

- Carbon dioxide to glycerol molar ratio (CGR): 0.5-5
- Reformer temperature: 600 – 1000 K
- Reformer pressure: 1 – 4 atm

1.4 Expected Outputs

1.4.1 The suitable operating condition of glycerol dry reforming that providing the highest methane production can be obtained.

1.4.2 The obtained results can be guideline for operation in the real application.

CHAPTER II

LITERATURE REVIEW

2.1 Methane

Methane (CH_4) as a molecular structure shown in Figure 2.1 is a colorless, odorless gas and highly flammable gas with a wide distribution in nature. It is the major component of natural gas, a mixture containing about 75% methane, 15% ethane and 5% other hydrocarbons, such as propane and butane. Methane is one of several gases including carbon dioxide, nitrous oxide and fluorinated gases that leads to global climate change [5].

The physical and chemical properties of methane [6] are shown below:

Formula weight: 16.04
Specific gravity: 0.415^{-164}
Melting point: -182.6 ^{o}C
Boiling point: -161.4 ^{o}C

In chemical industry methane is a raw material to produce methanol, formaldehyde, nitromethane, chloroform and carbon tetrachloride. The common use of methane is as a fuel. The combustion of methane is highly exothermic. Methane from natural gas is used directly to heat homes and commercial buildings and used for generation of electricity [7].

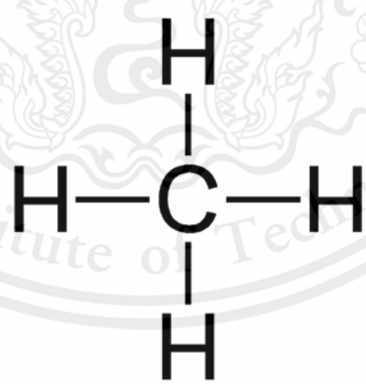

Figure 2.1 Molecular structure of Methane.

2.2 Methane production from glycerol

2.2.1 Glycerol

Crude glycerol is a by-product of the biodiesel production process. The crude glycerol has many contaminants, so the price is quite low. The use of glycerol in the industry process should be pure glycerol. But the cost of purification process of crude glycerol is quite high. Currently, many researchers have focused on the adding value of crude glycerol by using crude glycerol to produce hydrogen [8]. In addition to hydrogen production, glycerol can be also used for producing methane.

The molecular structure of glycerol is shown in Figure 2.2 and the physical and chemical properties [6] of glycerol can be listed as:

Formula weight: 92.09
Specific gravity: $1.250^{50/4}$
Melting point: 17.9 ^{o}C
Boiling point: 290 ^{o}C

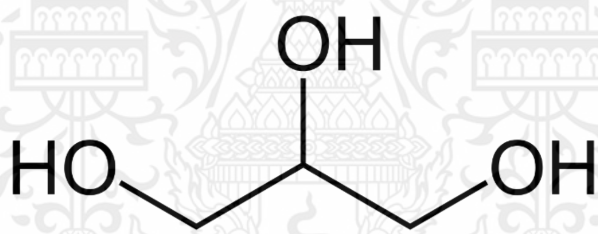

Figure 2.2 Molecular structure of glycerol.

2.2.2 Reforming of glycerol

In general, there are many reforming processes used for converting glycerol to other products. They are included steam reforming [9], dry reforming [4], partial oxidation [10] and autothermal reforming [11]. Each reforming process has different features and offers difference in advantages. This work aims to produce methane from glycerol through dry reforming because the use of carbon dioxide as agent can reuse carbon dioxide as greenhouse gas. The possible reactions occur in glycerol dry reforming as shown below [4]:

Glycerol dry reforming

$$C_3H_8O_3 + CO_2 \rightarrow 4CO + 3H_2 + H_2O \quad (2.1)$$

Glycerol decomposition

$$C_3H_8O_3 \rightleftharpoons 4H_2 + 3CO \quad \Delta H = 251.18 \text{ kJ/mol} \quad (2.2)$$

Methanation

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad \Delta H = -206.11 \text{ kJ/mol} \quad (2.3)$$

$$CO_2 + 4H_2 \rightleftharpoons 2CH_4 + 2CO \quad \Delta H = -164.94 \text{ kJ/mol} \quad (2.4)$$

Methane dry reforming

$$CO_2 + CH_4 \rightleftharpoons 2H_2 + 2CO \quad \Delta H = 247.28 \text{ kJ/mol} \quad (2.5)$$

Water-gas shift

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \quad \Delta H = -41.17 \text{ kJ/mol} \quad (2.6)$$

$$C + H_2O \rightleftharpoons H_2 + CO \quad \Delta H = 131.26 \text{ kJ/mol} \quad (2.7)$$

Coke formation

$$CH_4 \rightleftharpoons 2H_2 + C \quad \Delta H = 74.85 \text{ kJ/mol} \quad (2.8)$$

$$2CO \rightleftharpoons CO_2 + C \quad \Delta H = -172.43 \text{ kJ/mol} \quad (2.9)$$

$$2H_2 + CO_2 \rightleftharpoons C + 2H_2O \quad \Delta H = -90.09 \text{ kJ/mol} \quad (2.10)$$

2.3 Literature review

Patcharavorachot et al. [12] studied the hydrogen production from glycerol through steam reforming by using supercritical water as agent. They performed the simulation by using Aspen Plus simulator. Although their study focused on hydrogen production, it can be observed that the suitable operation for producing methane is at temperature of 500^{o}C and pressure of 240 atm. The product of methane as 22 mole% can be produced when the steam to glycerol molar ratio is set as 99. In addition, this study proposed the use of flash separation to remove water from the gas product obtained from reformer to get more content of the desired product.

Xiadong Wang et. al [4] presented thermodynamic analysis of glycerol dry reforming to produce hydrogen by using the method of Gibbs free energy minimization. Considering the methane production in their study, it was found that the suitable operation for producing methane is temperature of 600 K at atmospheric pressure. Under this operating condition, 0.8 moles of methane can be produced when the carbon dioxide to glycerol ratio of 0.

CHAPTER III

RESEARCH METHODOLOGY

This chapter presents the process description of methane production from glycerol dry reforming designed in Aspen Plus simulator. In addition, the solution approach for calculating gas composition from the reformer is explained.

Figure 3.1 shows the flowsheet of methane production from glycerol through dry reforming. The flowsheet is designed in the Aspen Plus simulator. Firstly, glycerol (GLY) is preheated in heater (HEAT1) whereas carbon dioxide (CO2) is preheated in heater (HEAT2). When glycerol and carbon dioxide are fed to the reformer (REFORM), there are possible reactions occurred in the reformer as mention in Section 2.2. Table 3.1 lists model and specification of each unit operations used in the simulation.

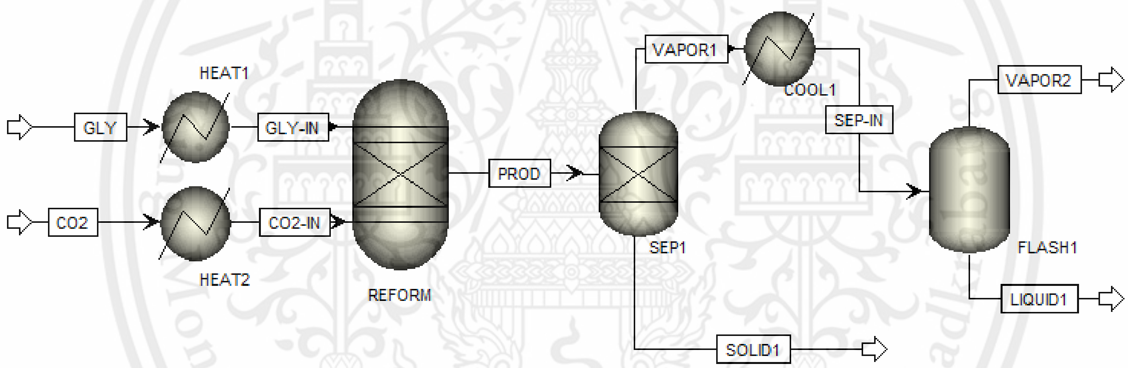

Figure 3.1 The flowsheet of methane production from glycerol dry reforming designed in Aspen Plus simulator.

The possible reactions occurred in the reformer are shown below:

$C_3H_8O_3 + CO_2 \rightarrow 4CO + 3H_2 + H_2O$		(3.1)
$C_3H_8O_3 \rightleftharpoons 4H_2 + 3CO$	$\Delta H = 251.18$ kJ/mol	(3.2)
$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	$\Delta H = -206.11$ kJ/mol	(3.3)
$CO_2 + 4H_2 \rightleftharpoons 2CH_4 + 2CO$	$\Delta H = -164.94$ kJ/mol	(3.4)
$CO_2 + CH_4 \rightleftharpoons 2H_2 + 2CO$	$\Delta H = 247.28$ kJ/mol	(3.5)
$CO + H_2O \rightleftharpoons H_2 + CO_2$	$\Delta H = -41.17$ kJ/mol	(3.6)
$C + H_2O \rightleftharpoons H_2 + CO$	$\Delta H = 131.26$ kJ/mol	(3.7)
$CH_4 \rightleftharpoons 2H_2 + C$	$\Delta H = 74.85$ kJ/mol	(3.8)
$2CO \rightleftharpoons CO_2 + C$	$\Delta H = -172.43$ kJ/mol	(3.9)
$2H_2 + CO_2 \rightleftharpoons C + 2H_2O$	$\Delta H = -90.09$ kJ/mol	(3.10)

Table 3.1 Model and specification of each unit operations used in this work

Name	Model	Base case operating condition	Variable
HEAT1	Heater	573 K	-
HEAT2	Heater	573 K	-
REFORM	Reformer	800 K 1 atm	600 – 1000 K 1 – 4 atm
SEP1	Separator	Split fraction = 1	-
COOL1	COOLER	573 K 1 atm	-
FLASH1	Flash drum	323 K 1 atm	-

In the simulation, glycerol and carbon dioxide are fed into the system with equal molar flow rate as 1 kmol/hr and this indicates that carbon dioxide to glycerol molar ratio or CGR in based case as 1. When the operating condition of all unit models are specified as Table 3.1, the gas product at equilibrium can be calculated by Gibbs free energy minimization. The equation of state used in calculation is PENG-ROB.

In this work, the operating condition of reformer on methane production is determined. The change in CGR means the molar flow rate of carbon dioxide stream (CO2) is adjusted between 0.5 and 5. When the influences of reformer temperature and pressure on methane production are investigated, it means the temperature and pressure in reformer (REFORM) are varied according to Table 3.1. The product (PROD) from the reformer is further sent to separator (SEP1) to separate solid carbon from the product. Next, the gas stream (VAPOR1) is sent to the cooler (COOL1) to reduce stream temperature before sending to flash drum (FLASH1). Flash drum is used to remove water from gas product. In order to purify methane, the operation in flash drum is operated at 323 K and 1 atm.

CHAPTER IV

RESULTS AND DISCUSSION

This chapter presents the influences of operating conditions (i.e., reformer temperature, carbon dioxide to glycerol molar ratio (CGR) and reformer pressure) on molar flow rates of product exited from reformer (PROD stream in Figure 3.1).

4.1 Effect of temperature on gas product

Figures 4.1-4.5 show molar flow rates of methane, carbon dioxide, carbon monoxide, hydrogen and steam as a function of CGR and reformer temperature at atmospheric pressure. In order to study the impact of CGR and reformer temperature, CGR is varied between 0.5 and 5 whereas reformer temperature is adjusted between 600 and 1000 K. As seen in Figure 4.1, molar flow rate of methane can be improved when reformer operates at lower temperature and CGR. This is because decreasing temperature leads to the reactions in Eqs. (3.3) and (3.4) forward to product side and thus, the molar flow rate of methane is increased. In addition, a decrease of CGR or less carbon dioxide content fed to the system will promote the reversion of reaction in Eq. (3.5). Thus, the amount of methane is higher.

Like methane production, the lower temperature operation causes increase in carbon dioxide and steam, as shown in Figures 4.2 and 4.5. In contrast, decreasing reformer temperature can shift the endothermic reaction (i.e., Eqs. (3.2), (3.7) and (3.8)) to reactant side. Therefore, the molar flow rate of carbon monoxide and hydrogen decrease as seen in Figures 4.3 and 4.4.

From the simulation result, it can be concluded that the suitable reformer operation for methane production is 600 K and CGR of 0.5. Because at this operating condition, the reformer can provide the highest methane amount whereas there is no carbon monoxide is in the gas product.

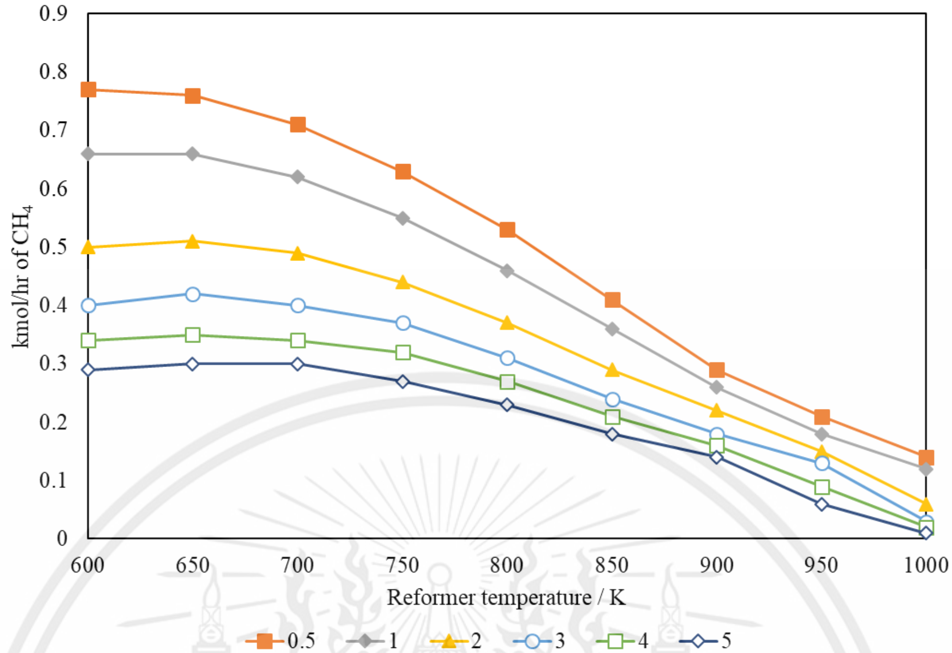

Figure 4.1 Moles of methane as a function of CGR and temperature at atmospheric pressure

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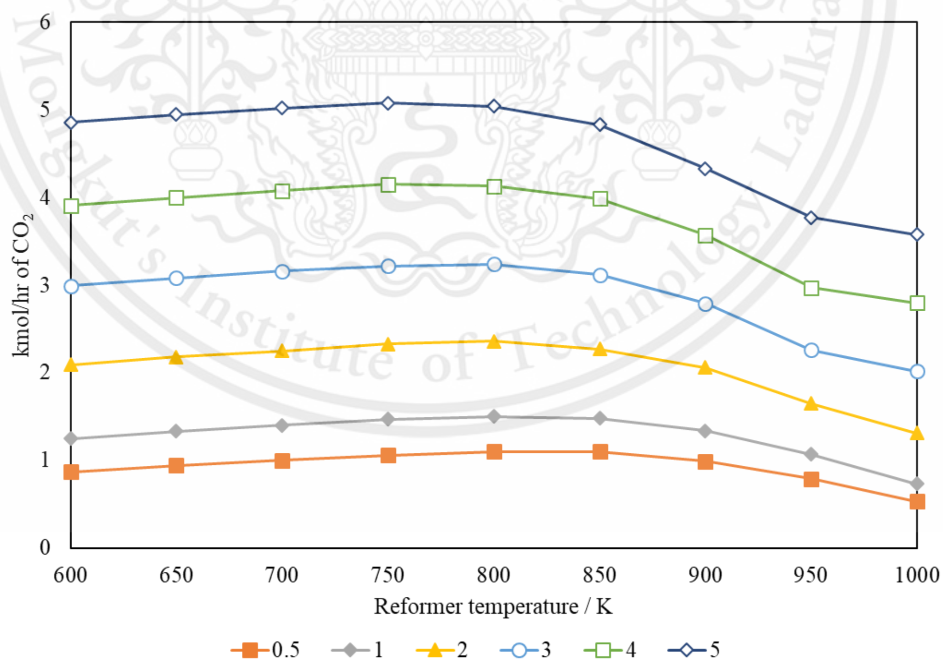

Figure 4.2 Moles of carbon dioxide as a function of CGR and temperature at atmospheric pressure.

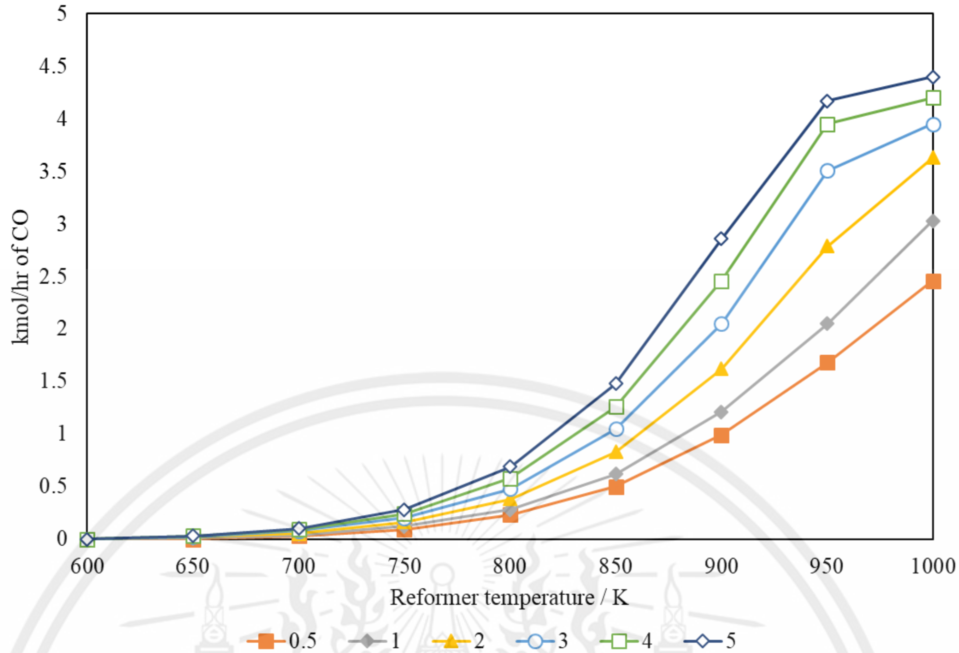

Figure 4.3 Moles of carbon monoxide as a function of CGR and temperature at atmospheric pressure.

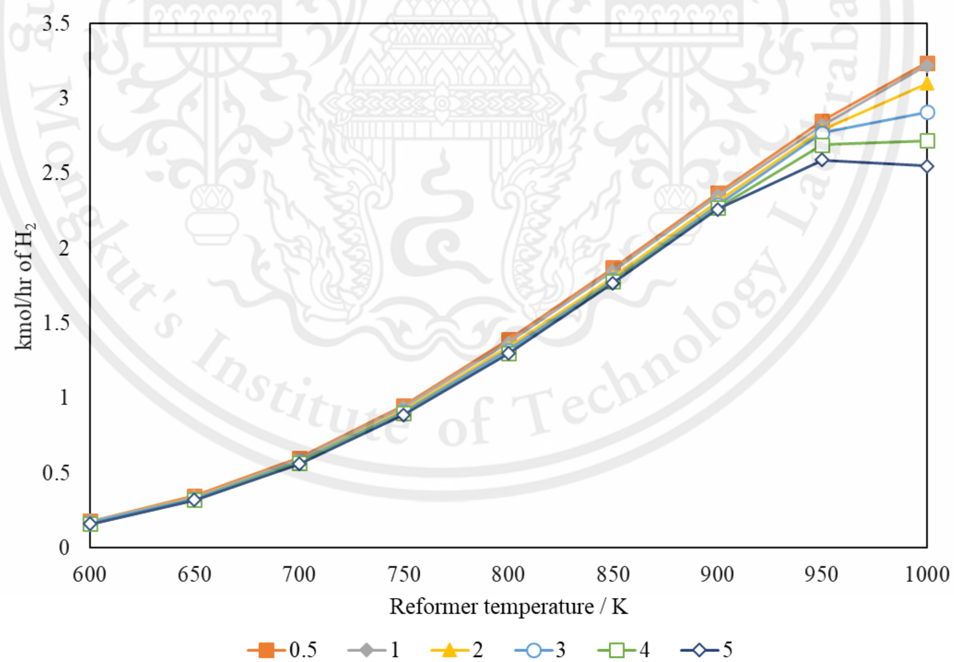

Figure 4.4 Moles of hydrogen as a function of CGR and temperature at atmospheric pressure.

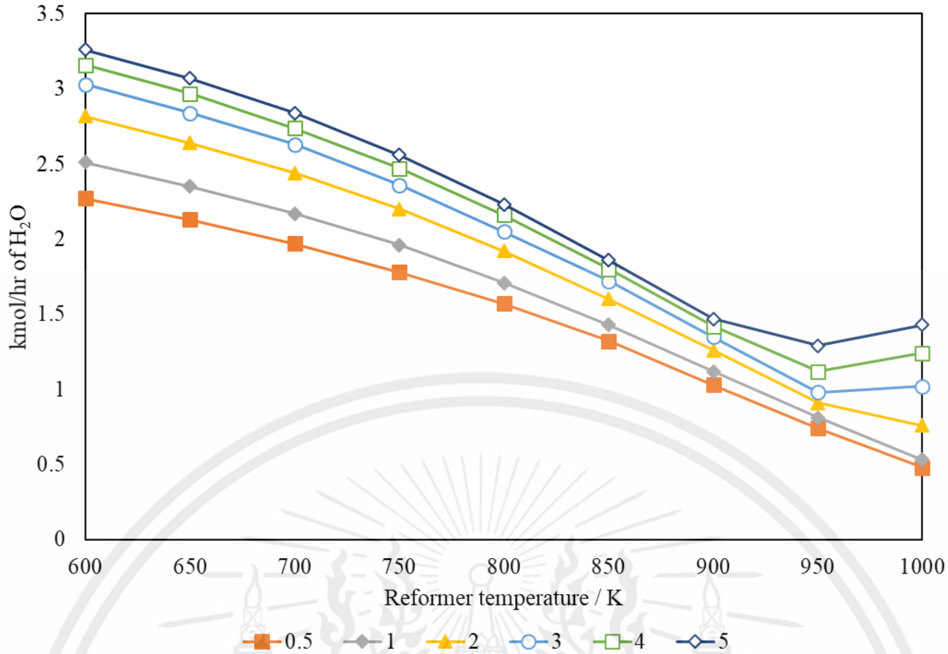

Figure 4.5 Moles of steam as a function of CGR and temperature at atmospheric pressure.

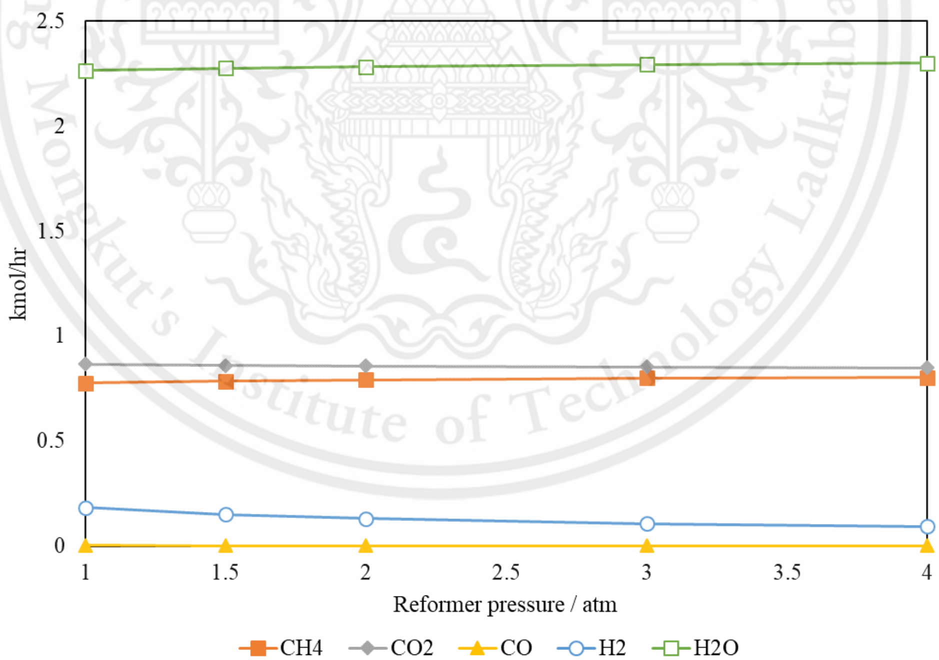

Figure 4.6 Moles of methane, carbon dioxide, carbon monoxide, hydrogen and steam as a function of reformer pressure at reformer temperature of 600 K and CGR of 0.5.

4.2 Effect of pressure on gas product

Figure 4.6 show effect of reformer pressure on gas product when the reformer operates at temperature of 600 K and CGR of 0.5. From the simulation results, it can be seen that the higher pressure operation can slightly improve the molar flow rate of methane. Therefore, the pressure of 4 atm is selected as suitable operating condition.

4.3 Gas product composition

From the study on methane production as functions of operating conditions, it is found that the suitable operating conditions are temperature of 600 K, CGR of 0.5 and pressure of 4 atm. Under these operating conditions, the gas product from reformer (PROD stream) consists of carbon dioxide, steam, hydrogen, carbon monoxide, carbon and methane as 0.850, 2.300, 0.093, 0.001, 1.845 and 0.804 kmol/hr, respectively. After sending the gas product to separator, carbon is removed and then, the stream of SEP-IN is composed of carbon dioxide, steam, hydrogen, carbon monoxide and methane as 0.850, 2.300, 0.093, 0.001 and 0.804 kmol/hr, respectively. To improve purity of methane, water will be removed by flash drum which operated at 323 K and 1 atm. Finally, the methane product (VAPOR2 stream) of 0.804 kmol/hr with purity of 41 mol% can be obtained. Tables 4.1 and 4.2 summarize composition of gas product in each stream.

Table 4.1 Molar flow rate of gas product in stream PROD, SEP-IN, LIQUID1 and VAPOR2

Mole Flow	PROD	SEP-IN	LIQUID1	VAPOR2
GLY	0.000	0.000	0.000	0.000
CO_2	0.850	0.850	0.000	0.850
H_2O	2.300	2.300	2.089	0.211
H_2	0.093	0.093	0.000	0.093
CO	0.001	0.001	0.000	0.001
C	1.845	0.000	0.000	0.000
CH_4	0.804	0.804	0.000	0.804

Table 4.2 Mole fraction of gas product in stream PROD, SEP-IN, LIQUID1 and VAPOR2

Mole fraction	**PROD**	**SEP-IN**	**LIQUID1**	**VAPOR2**
GLY	0.000	0.000	0.000	0.000
CO_2	0.144	0.210	0.000	0.434
H_2O	0.390	0.568	1.000	0.108
H_2	0.016	0.023	0.000	0.047
CO	0.000	0.000	0.000	0.001
C	0.313	0.000	0.000	0.000
CH_4	0.136	0.199	0.000	0.410

CHAPTER V

CONCLUSION

This work presents the study on methane production through dry reforming of glycerol. Thermodynamic analysis was performed to determine gas product composition which can be calculated from minimization of Gibbs free energy. Effect of reformer temperature, CGR and reformer pressure on methane production is investigated. The simulation results showed that decreases in temperature and CGR and an increase in pressure can improve methane molar flow rate. The simulation results indicated that the reformer should be operated at temperature of 600 K, CGR of 0.5 and pressure of 4 atm However, gas product obtained from reformer contains high amount of water, the flash drum is included in the system. Finally, the methane product of 0.804 kmol/hr with purity of 41 mol% can be provided after passing flash drum operated at 323 K and 1 atm.

5.2 Recommendations

5.2.1 The installation of CO_2 removal process by may be considered to improve the amount of methane.

5.2.2 The energy analysis should be considered.

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APPENDIX A

SIMULATION RESULTS

Table. A.1 The simulation results of the glycerol dry reforming at temperature of 600 K and pressure of 1 atm

CGR	Molar flowrate (kmol/hr)				
	CH_4	CO_2	CO	H_2	H_2O
0.5	0.770	0.870	0.000	0.180	2.270
1	0.660	1.250	0.000	0.180	2.510
2	0.500	2.090	0.000	0.170	2.820
3	0.400	2.990	0.000	0.170	3.030
4	0.340	3.910	0.000	0.160	3.160
5	0.290	4.860	0.000	0.160	3.260

Table. A.2 The simulation results of the glycerol dry reforming at temperature of 650 K and pressure of 1 atm

CGR	Molar flowrate (kmol/hr)				
	CH_4	CO_2	CO	H_2	H_2O
0.5	0.760	0.940	0.000	0.350	2.130
1	0.660	1.330	0.010	0.340	2.350
2	0.510	2.180	0.020	0.340	2.640
3	0.420	3.080	0.020	0.330	2.840
4	0.350	4.000	0.030	0.320	2.970
5	0.300	4.950	0.030	0.320	3.070

Table. A.3 The simulation results of the glycerol dry reforming at temperature of 700 K and pressure of 1 atm

CGR	**Molar flowrate (kmol/hr)**				
	CH_4	**CO_2**	**CO**	**H_2**	**H_2O**
0.5	0.710	1.000	0.030	0.600	1.970
1	0.620	1.400	0.040	0.590	2.170
2	0.490	2.250	0.050	0.580	2.440
3	0.400	3.160	0.080	0.580	2.630
4	0.340	4.080	0.090	0.570	2.740
5	0.300	5.020	0.100	0.560	2.840

Table. A.4 The simulation results of the glycerol dry reforming at temperature of 750 K and pressure of 1 atm

CGR	**Molar flowrate (kmol/hr)**				
	CH_4	**CO_2**	**CO**	**H_2**	**H_2O**
0.5	0.630	1.060	0.090	0.950	1.780
1	0.550	1.470	0.120	0.940	1.960
2	0.440	2.330	0.160	0.920	2.200
3	0.370	3.220	0.200	0.910	2.360
4	0.320	4.150	0.240	0.900	2.470
5	0.270	5.080	0.280	0.890	2.560

Table. A.5 The simulation results of the glycerol dry reforming at temperature of 800 K and pressure of 1 atm

CGR	Molar flowrate (kmol/hr)				
	CH_4	CO_2	CO	H_2	H_2O
0.5	0.530	1.100	0.230	1.390	1.570
1	0.460	1.500	0.280	1.370	1.710
2	0.370	2.360	0.380	1.340	1.920
3	0.310	3.240	0.480	1.320	2.050
4	0.270	4.130	0.580	1.300	2.160
5	0.230	5.040	0.690	1.300	2.230

Table. A.6 The simulation results of the glycerol dry reforming at temperature of 850 K and pressure of 1 atm

CGR	Molar flowrate (kmol/hr)				
	CH_4	CO_2	CO	H_2	H_2O
0.5	0.410	1.100	0.500	1.870	1.320
1	0.360	1.480	0.620	1.850	1.430
2	0.290	2.270	0.830	1.810	1.600
3	0.240	3.120	1.050	1.790	1.720
4	0.210	3.990	1.260	1.780	1.800
5	0.180	4.830	1.480	1.770	1.860

Table. A.7 The simulation results of the glycerol dry reforming at temperature of 900 K and pressure of 1 atm

CGR	Molar flowrate (kmol/hr)				
	CH_4	**CO_2**	**CO**	**H_2**	**H_2O**
0.5	0.290	0.990	0.990	2.370	1.030
1	0.260	1.340	1.210	2.350	1.120
2	0.220	2.060	1.620	2.310	1.260
3	0.180	2.790	2.050	2.290	1.350
4	0.160	3.570	2.460	2.270	1.420
5	0.140	4.330	2.860	2.260	1.470

Table. A.8 The simulation results of the glycerol dry reforming at temperature of 950 K and pressure of 1 atm

CGR	Molar flowrate (kmol/hr)				
	CH_4	**CO_2**	**CO**	**H_2**	**H_2O**
0.5	0.210	0.790	1.680	2.850	0.740
1	0.180	1.070	2.050	2.820	0.810
2	0.150	1.650	2.790	2.790	0.910
3	0.130	2.260	3.510	2.770	0.980
4	0.090	2.970	3.950	2.690	1.120
5	0.060	3.770	4.170	2.590	1.290

Table. A.9 The simulation results of the glycerol dry reforming at temperature of 1000 K and pressure of 1 atm

CGR	**Molar flowrate (kmol/hr)**				
	CH_4	**CO_2**	**CO**	**H_2**	**H_2O**
0.5	0.140	0.530	2.460	3.240	0.480
1	0.120	0.730	3.030	3.220	0.530
2	0.060	1.310	3.630	3.100	0.760
3	0.030	2.020	3.950	2.910	1.020
4	0.020	2.800	4.200	2.720	1.240
5	0.010	3.580	4.400	2.550	1.430

Table. A.10 The simulation results of the glycerol dry reforming at temperature of 600 K and CGR of 0.5

Pressure (atm)	**Molar flowrate (kmol/hr)**				
	CH_4	**CO_2**	**CO**	**H_2**	**H_2O**
1	0.775	0.866	0.002	0.184	2.265
1.5	0.786	0.861	0.002	0.151	2.277
2	0.793	0.857	0.002	0.131	2.284
3	0.800	0.853	0.001	0.107	2.293
4	0.804	0.850	0.001	0.093	2.300

Table. A.11 The simulation results of each stream at suitable condition as molar flowrate (temperature of 600 K, pressure of 1 atm and CGR of 0.5)

Molar flowrate (kmol/hr)	**PROD**	**SEP-IN**	**LIQUID1**	**VAPOR2**
GLY	0.000	0.000	0.000	0.000
CO_2	0.850	0.850	0.000	0.850
H_2O	2.300	2.300	2.089	0.211
H_2	0.093	0.093	0.000	0.093
CO	0.001	0.001	0.000	0.001
C	1.845	0.000	0.000	0.000
CH_4	0.804	0.804	0.000	0.804

Table. A.12 The simulation results of each stream at suitable condition as mole fraction (temperature of 600 K, pressure of 1 atm and CGR of 0.5)

Mole fraction	**PROD**	**SEP-IN**	**LIQUID1**	**VAPOR2**
GLY	0.000	0.000	0.000	0.000
CO_2	0.144	0.210	0.000	0.434
H_2O	0.390	0.568	1.000	0.108
H_2	0.016	0.023	0.000	0.047
CO	0.000	0.000	0.000	0.001
C	0.313	0.000	0.000	0.000
CH_4	0.136	0.199	0.000	0.410

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