การผลิตเมทานอลจากทรัพยากรหมุนเวียน

จัดทำโดย

ณิศรา พาณิชย์กิตติกุล

อาจารย์ที่ปรึกษา

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ปริญญานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตร
วิศวกรรมศาสตร์บัณฑิต สาขาวิชาวิศวกรรมปิโตรเคมี
ภาควิชาวิศวกรรมเคมี คณะวิศวกรรมศาสตร์
สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง
ปีการศึกษา 2563

Title	Methanol production from renewable resource
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Field of Study	Petrochemical Engineering
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Accepted by the School 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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Methanol Production from Renewable Resource

Submitted by

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Advisor

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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, School of Engineering,
King Mongkut's Institute of Technology Ladkrabang
Academic Year 2020

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Abstract

This project aims to investigate the methanol production from renewable resources. The renewable resources studied in this project is biomass and the selected biomass is bagasse because it is a by-product from sugar industrial processes. In this project, the study on methanol production from syngas produced from bagasse gasification is performed through Aspen Plus simulation software version 9. The effect of operating conditions in gasification process and methanol production process is determined to obtain the large amount of methanol with high purity. Firstly, the influence of gasifier temperature, gasifier pressure and steam to biomass mass ratio on syngas production is studied. The simulation results show that the syngas production increases with increasing gasifier temperature and steam to biomass mass ratio and will be decreased when the gasifier pressure increases. From the simulation, it is found that the optimal operating conditions in gasification process are at temperature of 700 ° C, pressure of 1 bar and the steam to biomass mass ratio is 0.6. Next, the effect of temperature and pressure of methanol reactor is investigated. The simulation results show that the methanol production decreases with an increase in methanol reactor temperature, but it can be increased when the methanol reactor pressure is higher. However, to reduce the cost in energy consumption, the optimal pressure is suggested as 50 bar while the optimal temperature is 220 ° C. Finally, the produced methanol is purified by using distillation which found that the methanol has purity around 96%.

Keywords: Methanol, Process simulation, Syngas, Hydrogen, Biomass

เรื่อง	การผลิตเมทานอลจากทรัพยากรหมุนเวียน
โดย	นางสาว ณิศรา พาณิชย์กิตติกุล
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สังกัด	คณะวิศวกรรมศาสตร์

บทคัดย่อ

โครงงานนี้มุ่งเน้นศึกษากระบวนการผลิตเมทานอลจากทรัพยากรหมุนเวียน ซึ่งทรัพยากรหมุนเวียนที่นำมาศึกษาในโครงงานนี้คือชีวมวล และชีวมวลที่ได้เลือกมาคือชานอ้อย เนื่องจากเป็นผลพลอยได้ที่เหลือจากกระบวนการทางอุตสาหกรรมผลิตน้ำตาล ในโครงงานได้ทำการศึกษากระบวนการผลิตเมทานอลจากแก๊สสังเคราะห์ที่ผลิตจากกระบวนการแก๊สซิฟิเคชั่นของชานอ้อยโดยใช้ซอฟต์แวร์สำเร็จรูป Aspen Plus เวอร์ชั่น 9 ซึ่งจะพิจารณาผลของสภาวะการดำเนินงานในกระบวนการแก๊สซิฟิเคชั่นและกระบวนการผลิตเมทานอลเพื่อให้ปริมาณของเมทานอลมากที่สุดและมีความบริสุทธิ์มากที่สุด โครงงานนี้เริ่มทำการศึกษาผลของอุณหภูมิและความดันในเตาแก๊สซิฟายเออร์และสัดส่วนโดยมวลของไอน้ำต่อชีวมวลที่ป้อนเข้าเตาแก๊สซิฟายเออร์ที่มีต่อการผลิตแก๊สสังเคราะห์ ผลการจำลองกระบวนการแสดงให้เห็นว่าการผลิตแก๊สสังเคราะห์เพิ่มขึ้นตามการเพิ่มขึ้นของอุณหูภมิในเตาแก๊สซิฟายเออร์และสัดส่วนโดยมวลไอน้ำต่อชีวมวล แต่จะมีค่าลดลงเมื่อความดันในเตาแก๊สซิฟายเออร์เพิ่มขึ้น จากการจำลองกระบวนการพบว่าสภาวะการดำเนินงานที่เหมาะสมของกระบวนการแก๊สซิฟิเคชั่น คือ ที่อุณหภูมิ 700 องศาเซลเซียส ความดัน 1 บาร์ และสัดส่วนโดยมวลของไอน้ำต่อชีวมวลมีค่าเท่ากับ 0.6 จากนั้นได้ทำการศึกษาผลของอุณหภูมิและความดันของเครื่องปฏิกรณ์ผลิตเมทานอล จากการจำลองกระบวนการพบว่าปริมาณของเมทานอลจะลดลงเมื่อมีการเพิ่มอุณหภูมิของเครื่องปฏิกรณ์ผลิตเมทานอล แต่การผลิตเมทานอลจะมีค่าเพิ่มขึ้นเมื่อความดันของเครื่องปฏิกรณ์ผลิตเมทานอลเพิ่มขึ้น อย่างไรก็ตามเพื่อเป็นการลดค่าใช้จ่ายทางด้านพลังงาน ความดันที่เหมาะสมของเครื่องปฏิกรณ์ผลิตเมทานอลคือ 50 บาร์ ส่วนอุณหภูมิที่เหมาะสม คือที่ 220 องศาเซลเซียส สุดท้ายเมทานอลที่ผลิตได้จะถูกทำให้บริสุทธิ์โดยการกลั่น ซึ่งทำให้ได้เมทานอลที่มีความบริสุทธ์ร้อยละ 96

คำสำคัญ: เมทานอล, การจำลองกระบวนการ, ซินแก๊ส, ไฮโดรเจน, ชีวมวล

Acknowledgements

This project can be accomplished with the kindness of my advisor Assoc.Prof.Dr.Yaneeporn Patcharavorachot who are advises, guides and tells me what needs to be improved, as well as conveys useful knowledge to me.

Thank you to all teachers from the Department of Chemical Engineering, King Mongkut's Institute of Technology Ladkrabang, who have provided knowledge to apply and solve problems that are extremely useful in completing project.

Thank you to my family for supporting and encouraging my project to be successful.

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

Nitsara Panichkittikul

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NOMENCLATURE

S/B	Steam to biomass mass ratio
E_a	Activation energy
r	Rate of reaction
k	Rate constant

CHAPTER I

INTRODUCTION

1.1 Background

Nowadays, the energy consumption in transportation sector is higher; however, the energy generated from fossil fuels has been limited. In Thailand, there is a large number of uses of automobiles or motorcycles in transportation. These vehicles need to be powered by petroleum fuel, 95 percent will use gasoline-diesel fuel, and another 5 percent will use LPG-NGV gas fuels[1]. The situation of fuel used in Thailand has been estimated to be around 148 million liters of finished oil per day, which is a huge amount[1]. According to the Ministry of Energy in January 2019, Thailand imported 179 million liters of crude oil per day whereas finished oil was imported 11.7 million liters per day[1]. Besides the limited amount of fossil fuels, there are environmental issue encountered from using fossil fuels, such as global warming, climate change, air pollution and acid rain[2]. Moreover, the fossil fuels take millions of years to transform. Therefore, in recent years, many researchers focused on the use of renewable energy to replace fossil fuels.

Thailand is an agricultural country and thus, there is a lot of agricultural waste such as rice husk, bagasse and palm shell. This is referred to biomass. Biomass is one of renewable energy that has been interested in many researchers since 2012[3]. In general, there are different methods for converting biomass into energy. Biomass can be burned to produce energy in form of heat and electricity; however, the biomass combustion has low energy conversion[4]. If the energy production in form of chemical is concerned, the biomass conversion through pyrolysis or gasification become more potential method. Pyrolysis is the biomass conversion in the absence of oxygen in which the bio-oil is the main product[5]. Although bio-oil can be used as the transportation fuel, there is a difficulty in downstream process. Gasification is another method to convert biomass into combustible or syngas by using gasifying agent. The syngas can be transformed into valuable chemicals or biofuels. Since biomass can provide more than 10% of the global energy supply and this makes it one of the leading potential viable renewable energy resources[6]. Therefore, many researchers have developed clean and sustainable technologies to use the biomass as feedstock for biofuel production.

Biofuels can be divided into two categories: (1) liquid biofuels that are used in the transportation and (2) gaseous biofuels that are used for heat and power production. Most biofuels are in liquid form for easy transportation. There are four main types of biofuels that are currently used: ethanol, biodiesel, methanol, and butanol. This project focuses on methanol production because methanol can be used in several applications. Methanol is a component in many industries such as adhesives, plastics, and paints and as a fuel or additive. Methanol can be used potentially as transportation fuel, alone or mixed with gasoline and it can also be used in the automotive field in the development of fuel cell vehicles. In addition, methanol is considered a suitable substance to promote the transition from fossil fuel to renewable sources both on the basis of its intrinsic chemical-physical properties and on its ability to be produced by biomass technology[7]. When methanol is produced from syngas derived from biomass gasification, it may be called that clean methanol.

In the methanol production, high amount of water always contaminates in the product. To provide the purified methanol, the separation process should be included in the production process. Among various separators (e.g., membrane, evaporation, and freezing crystallization), the distillation is focused on this project since it is an efficient method to remove water from methanol.

As mentioned above, this project aims to study methanol production from syngas produced from biomass gasification. Bagasse is considered as feedstock for gasification process. Methanol that obtained from the production process is purified by using distillation. This study is performed through the simulation by using Aspen Plus simulation software version 9.

1.2 Objective

To determine the optimal operating condition of methanol production from bagasse gasification.

1.3 Scopes of Work

1.3.1 Design methanol production process that includes biomass gasification, methanol synthesis and distillation by using Aspen Plus simulation software version 9. The feedstock that used in the gasification is bagasse.

1.3.2 Validate the simulation results with the experimental data from the literature.

1.3.3 Study the effect of operating conditions of gasification process on syngas production. The parameters are examined as follows:

- gasifier temperature (600 – 1100 °C)
- gasifier pressure (1 – 15 bar)
- steam to biomass mass ratio (0.1 – 3.0)

1.3.4 Study the effect of operating conditions of methanol synthesis on methanol production. The parameters are examined as follows:

- reactor temperature (220 – 300 °C)
- reactor pressure (50 – 50 bar)

1.3.5 Determine the optimal operating conditions of each process that provide the highest purity of methanol production.

1.4 Expected Outputs

1.4.1 The process model of methanol production from syngas produced from bagasse gasification can be obtained and used by other researchers.

1.4.2 The optimal operating conditions with the highest purity of methanol production can be provided. The obtained results can be guideline for methanol production from syngas produced from bagasse gasification.

CHAPTER II

LITERATURE REVIEW

2.1 Renewable energy

Renewable energy is a natural clean energy that can be renewable and reusable without limits. It tends to replace fossil fuels for the future. There are many types of renewable energy such as solar energy, wind energy, geothermal energy, biomass energy and hydroelectric energy.

2.2 Biomass

Biomass[8] is an organic substance that is a natural energy storage source and can be used to produce energy. Biomass has different sources such as agricultural crops, agricultural residues, wood and wood residues, or other waste from industry and communities. For example: rice husk is obtained by milling paddy, bagasse is obtained from the production of sugar, wood residues are mostly obtained from rubber or eucalyptus wood processing and some from the plantation, palm residues are obtained from the extraction of crude palm oil or from fresh palm fruit, cassava is obtained from the production of tapioca starch, corn cobs are obtained by milling corn to remove the kernels, endocarp and shell of coconut are obtained by peeling the coconut to produce coconut milk and coconut oil and yeast is obtained from the production of alcohol.

2.2.1 The process of converting biomass into various forms of energy

2.2.1.1 Combustion

When the biomass is burned, the heat will be released according to the heating value of the biomass. The heat obtained by combustion can be used to produce steam at high temperatures and pressures. This steam is then used to drive the steam turbines to generate electricity further. Examples of this type of biomass are agricultural residues and wood residues.

2.2.1.2 Gasification

This process can convert biomass into fuel gases. The reaction that takes place is the partial oxidation of biomass to steam, oxygen, or air. The resulting fuel gases is composed according to the type and properties of the biomass used as a precursor. The main components of fuel gases consist of carbon monoxide and hydrogen, with some methane and carbon dioxide. Other products include tar and ash.

2.2.1.3 Fermentation

This process is the use of biomass to ferment with bacteria in anaerobic conditions. Biomass is degraded and broken down to form biogas containing methane and carbon dioxide. Methane is used as a fuel in engines for generating electricity.

2.2.2 Analyses of biomass

The composition of biomass or general matter is divided into 3 main parts:

2.2.2.1 Moisture

Moisture[9] refers to the amount of water available. Most biomass has relatively high moisture because it is agricultural production. If biomass is taken as energy by combustion, moisture should not exceed 25 percent[10].

2.2.2.2 Combustible substance

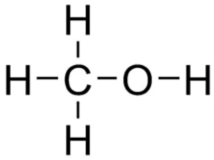
The combustion substance[9] is divided into two parts such as volatiles matter and fixed carbon volatiles matter. Therefore, any biomass with high volatiles matter indicates that it is easily combustible.

2.2.2.3 Non-combustible substance

The non-combustible substance[9] is ash. Most biomass contains about 1-3 percent of the ashes, except for husks and rice straw that there will be about 10-20 percent of the ashes, which will have enough burning and removal problems.

2.3 Methanol

Methanol[11] or methyl alcohol has the molecular formula of CH_4O or CH_3OH as shown in Figure 2.1. Methanol is a clear, volatile liquid, a by-product of petrochemical refining and is commonly used as a solvent in the furniture industry, such as wood paints, varnishes, paint remover and uses as a natural fuel. The physical toxicity can be considered very toxic and very severe. It can be absorbed through skin and breath. The inhaled person will have respiratory irritation, causing bronchial and throat inflammation, irritation of the conjunctiva. If inhaled heavily, it can lead to abdominal pain, dizziness, nausea, vomiting, muscle spasms, difficulty breathing, and vision is impaired and can lead to blindness. But if you drink it, methanol will react with chemical substances in the body to turn into formaldehyde (formaldehyde), which is very toxic, resulting in nausea, vomiting, diarrhea, and blurred vision which affects the optic nerve that can lead to blindness, kidney inflammation. More importantly, it also affects the respiratory system, which eventually fatal.



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}O{-}H}$$

Figure 2.1 Molecular structure of Methanol

If methanol is burned with the air, carbon dioxide and water will be gotten, as shown in equation below:

$$2CH_3OH+3O_2 \rightarrow 2CO_2+4H_2O \tag{2-1}$$

The flames obtained from the burning were almost invisible. Therefore, be careful if methanol is used as fuel.

2.3.1 Safety data sheet of methanol

The chemical and physical properties of methanol are shown below:

Molecular weight:	32.042 g/mol
Boiling point:	64.7 °C or 148.3 °F at 760 mmHg
Melting point:	-97.6 °C or -143.7 °F at 760 mmHg
Flash point:	Closed vessel: 12 °C or 54 °F
	Open vessel: 15.6 °C or 60.1 °F
Auto ignition temperature:	470 °C or 878 °F

2.3.2 Methanol synthesis

In the past, methanol was a by-product of wood spirit, which was very small and could not be manufactured for industrial purposes. Thereafter, industrial methanol production was started in Germany by BASF Company, which used syngas as a reactant. Synthetic gas is composed of carbon monoxide and hydrogen, which is processed through a chemical process and the reaction of process is an exothermic process which is 91.15 kJ / mol at temperature 320-380 Celsius degree and pressure 350 bar. The reaction required the chromium oxide zinc oxide catalyst. The process is high pressure process Nowadays, industrial production uses ICI technology, which is a low-pressure process. Copper zinc oxide catalyst was used at temperature 250-280 Celsius degree and pressure 50-80 bar with water gas shift reaction as a side reaction.

CO hydrogenation reaction

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H = -90.77\ kJ/mol \qquad (2\text{-}2)$$

CO_2 hydrogenation reaction

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H = -49.16\ kJ/mol \qquad (2\text{-}3)$$

Water gas shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41.21\ kJ/mol \qquad (2\text{-}4)$$

2.3.3 Applications of methanol production

The use of methanol as fuel is used in two characteristics:

- M85, which is obtained by mixing 85% methanol with 15% gasoline, is used for light engines.
- M100 contains 100% methanol, used for heavy engines.

Methanol can be used as a fuel for internal combustion engines, according to Eq. 2-1. However, the use of methanol as fuel has its drawback: it goes on to erode some aluminum and metals. The advantage of methanol is that it is quite easy to store. Storage of liquefied methanol is much easier than storing hydrogen or natural gas and other advantages are biodegradable and half-life short in groundwater.

Other applications of methanol

- Methanol is a common laboratory solvent. It is useful for HPLC and UV/VIS spectroscopy due to its low UV cutoff.
- Methanol is used as an antifreeze in pipelines and windshield washer fluid.
- Methanol is used in the production of hydrocarbons, olefins, and some aromatic compounds.
- Methanol is the feedstock for manufacture of other chemicals. About 40% of methanol is converted to formaldehyde and then the formaldehyde uses in the paint, adhesive and wood furniture coating industry.
- About 65% of the methanol is used for the production of acetic acid, methyl and vinyl acetates, methyl methacrylate, methylamines, methyl tertiary butyl ether (MTBE), fuel additives.

- The other chemical derivatives of methanol include acetic acid and dimethyl ether (DME). DME can be mixed with liquefied petroleum gas (LPG) for home heating and cooking and can be used as a diesel replacement transportation fuel.

2.4 Syngas

Syngas, or synthesis gas, is the mixture of hydrogen, carbon monoxide and carbon dioxide. It can be used as an intermediate for the production of synthetic natural gas (SNG), ammonia and methanol. Syngas is also used to produce synthetic petroleum as a fuel and lubricant in the production of gasoline. Syngas burns well and is frequently used in internal combustion engines, but only has the density of energy less than natural gas. Moreover, syngas can be used as fuel in solid oxide fuel cells to generate electricity. Syngas can be produced from several raw materials containing carbon and hydrogen such as fossil fuels include natural gas, coal, petroleum and can also be produced from renewable energy, including biomass, waste and others. In general, there are many technologies used for syngas production as described below:

2.4.1 Thermochemical process

It is a process that can produce syngas by a chemical reaction using heat from a main raw material as hydrocarbon compounds. The examples of syngas production through thermochemical processes are steam reforming and gasification.

2.4.2 Electrochemical process

If only hydrogen is needed, electricity is used to separate the water and then, hydrogen and oxygen can be produced. This method is called water electrolysis. In case of syngas production, the co-electrolysis of water and carbon dioxide can provide the mixture of hydrogen and carbon monoxide.

2.4.3 Biochemical process

This process can produce syngas production based on the photosynthesis process of small organisms such as microorganisms and blue-green algae. This method is less popular because of its low efficiency. Its productivity is limited by the intensity of the received light.

2.5 Gasification Process

Gasification[12] is a technology for converting biomass into energy in the form of fuel gases by using a thermal-chemical process. When heating biomass in combination with the technique of limiting the amount of air, oxygen, steam to achieve a regulated state of proportional oxygen that is lower than the amount that causes the fuel to complete combustion causing biomass to break down into hydrocarbon compounds in solid and gas form containing carbon monoxide (CO), hydrogen (H_2), methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2) and other gases are called producer gas.

The gasification[8] process from biomass is an incomplete combustion process. The chemical reactions that take place are complex and can produce many products or gases, depending on the nature of the biomass and the limiting techniques. The products obtained from this process are not only fuel gas. There are also solids and impurities that cannot be completely burned such as char, ash, tar, and steam.

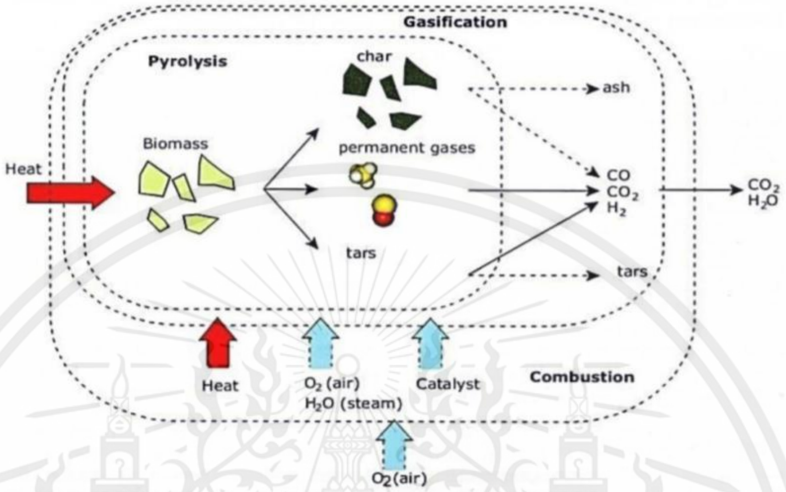


Figure 2.2 Gasification process from biomass

The gasification process is a chemical process that converts carbon-based materials, such as biomass, coal into synthetic fuel gases or chemical precursors in chemical process, where there are several chemical reactions that are associated. These include pyrolysis, partial oxidation, and hydrogenation. When comparing the combustion process that converts carbon-based materials into exhaust gas and thermal energy, but gasification processes is a collection of energy in the form of chemical bonds and thus produce products that can be used to provide energy. The difference between gasification process and combustion process is the gasification process has a reduction reaction that is an endothermic reaction, but the combustion process has only an oxidation reaction that is exothermic reaction.

The result of this process is the syngas that can be used to generate electricity or used in other manufacturing industries, so waste or biomass is no longer useless but become feedstocks for gasifiers.

2.5.1 Components of gasification process

The gasification process mainly consists of the following processes:

2.5.1.1 Drying and preheat zone

Since natural fresh wood has a moisture content of 30 - 60% and some fuels can have a humidity of up to 90%, each kilogram of moisture contained in the fuel requires at least 2,260 kJ of energy from the gasification process to evaporate the water which requires large amounts of energy to dry the fuel, results in low reducing reaction temperatures, resulting in poor heat and quality gas product. Therefore, in most gasification systems, there is a demand for fuel with a moisture value in the range of 10 - 20%.

The process begins when the fuel enters the gasification system and gets heat from the combustion process, causing the water in the biomass to break down the bonds and convert to vapor phase and then the temperature increase is not high enough to cause the decomposition of the volatile substance as equation 2-5.

$$\text{Biomass} + \text{Heat} \rightarrow \text{Dry biomass} + \text{Water} \qquad (2\text{-}5)$$

The zone at the top is responsible for drying and evaporating water from the raw material with heat. In the temperature range from about 40-200 Celsius degree, the temperature can reduce the humidity by approximately 5 percent, and the moisture content of the suitable raw materials for use should be lower than 30 percent to keep the fuel material dry and easy to ignite.

2.5.1.2 Pyrolysis zone

It is a thermal process to separate large hydrocarbon molecules that are in the biomass into gases with smaller molecules without reacting with air, gases or reagents. The temperature in this zone is approximately 200-600 Celsius degree. The remaining solids from this process are carbon in the form of coal.

2.5.1.3 Combustion or oxidation zone

It is a zone that produces heat to transmit heat to other zones in the gasifier furnace. In this zone, combustion or oxidation reactions occur. The raw materials or carbon charcoal from the pyrolysis zone are burned to form carbon dioxide and heat. The resulting heat is directly transferred to the reduction zone and to the pyrolysis zone and to the drying zone.

Char partial combustion:

$$C + 0.5O_2 \rightarrow CO \qquad \Delta H = -111 \text{ kJ/mol} \qquad (2\text{-}6)$$

C combustion:

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -394 \text{ kJ/mol} \qquad (2\text{-}7)$$

CO partial combustion:

$$CO + 0.5O_2 \rightarrow CO_2 \qquad \Delta H = -284 \text{ kJ/mol} \qquad (2\text{-}8)$$

Methane combustion:

$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$ $\Delta H = -803$ kJ/mol (2-9)

H_2 partial combustion:

$H_2 + 0.5O_2 \rightarrow H_2O$ $\Delta H = -242$ kJ/mol (2-10)

2.5.1.4 Reduction zone

It is a zone[10] that produces syngas consisting of carbon monoxide and hydrogen as the main products. By the process of converting carbon to syngas, the reaction takes place in the temperature range of approximately 800-1000 Celsius degree of combustion under the condition of limiting the air volume, which carbon, and tar to break into syngas.

Boudouard reaction:

$C + CO_2 \leftrightarrow 2CO$ $\Delta H = +172$ kJ/mol (2-11)

Water gas reaction:

$C + H_2O \leftrightarrow CO + H_2$ $\Delta H = +131$ kJ/mol (2-12)

Hydrogenation reaction:

$C + 2H_2 \leftrightarrow CH_4$ $\Delta H = -74.8$ kJ/mol (2-13)

Water gas shift reaction:

$CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H = -41.2$ kJ/mol (2-14)

Methanation reaction:

$2CO + 2H_2 \rightarrow CH_4 + CO_2$ $\Delta H = -247$ kJ/mol (2-15)

$CO + 3H_2 \leftrightarrow CH_4 + H_2O$ $\Delta H = -206$ kJ/mol (2-16)

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ $\Delta H = -165$ kJ/mol (2-17)

Reforming reaction:

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ $\Delta H = +206$ kJ/mol (2-18)

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$ $\Delta H = -36$ kJ/mol (2-19)

2.5.2 Benefits of Gasification Process

2.5.2.1 Energy

After the biomass is taken through the gas system, biomass gas, which has flammable properties, can be used as energy in various forms.

- Thermal energy	To take advantage of direct thermal energy Used to drive machines
- Electric energy	Used as fuel for the engine to generate electricity.

2.5.2.2 Agriculture

The ashes from the gasification process contain a large amount of carbon, which, when used as fertilizer, helps to retain water and nutrients in the soil, which improves soil integrity.

2.5.2.3 Environment

- Make use of agricultural waste efficiently
- Reduce the amount of greenhouse gas emissions and the problem of smog from burning of agricultural waste materials in the open air

2.6 Distillation

The distillation process is used to separate the mixture from each other. It is based on the difference in the volatility of substances. When heating the mixture, the substances with lower boiling points are highly concentrated in the vapor phase that has come out at the upper of the distillation column. Through condensation, the desired product substance is distilled in a liquid state as needed. The mixture to be distilled is placed in a reboiler at the base of the distillation column. The difficulty of distillation depends on several factors, such as the difference in boiling point of various substances in the mixture and vapor pressure characteristics. If each substance in the mixture has a different boiling point, it can be easily separated.

At the beginning of the distillation process, this will heat the mixture in the boiler. When the mixture reaches a high enough temperature, it will evaporate. The vapors of this mixture pass through the trays inside the column. A fractional distillation occurs within each of those layers. The vapor of substances that leave the top layer of the column has a large concentration of substances with lower boiling points. This is alcohol, and inside the re-boiling pot, there will be more and more concentrations of substances with higher boiling points. The vapor of alcohol leaving the top of the column is condensed by a condenser with water as a heat transfer. The high purity alcohol in liquid phase is passed from the condenser to the feedback accommodation. Before entering the valve that feeds the substance back into the column, this valve can control the flow of alcohol back into the top of the column. It is called reflux and can be controlled to allow alcohol to flow out into the product at the top of column.

The vapor pressure of a mixture is the pressure balance of the molecules of the substance that moves away from the surface of the liquid and moves back to equilibrium at a certain temperature. The vapor pressure can be changed by increasing or decreasing the thermal energy that is fed to the substance. The vapor pressure is associated with the boiling point of the substance, i.e., when the vapor pressure of the substance is equal to the pressure of the environment, it can be said that the substance is boiling. That is the difficulty of boiling the substance depends on volatility. Substances with a high vapor ability boil at lower temperatures than substances with low vapor ability. The vapor pressure and boiling point of the mixture depend on the concentration of each substance in the mixture. Distillation can be performed due to the different volatility of the components in the mixtures.

2.7 Literature review

L.F. Calvo et al.[13] studied the gasification of rice straw in a fluidized-bed gasifier for syngas application in close-coupled boiler-gasifier systems. From the research, the suitable condition of gasification process was at temperature in a range of 700 and 850 Celsius degree. In the gasification process, a mixture of alumina-silicate and magnesium oxide was used as bed media to prevent bed agglomeration during the rice straw gasification. The stoichiometric air-fuel ratio for rice straw was 4.28 and air supplied was 7-25% of that necessary for stoichiometric combustion. Under the experimental conditions used, a high-quality syngas with higher heating value of 5.14 MJ Nm^{-3}, low tar content, hot gas efficiency of 61% and cold gas efficiency of 52% was produced. The obtained results proved that rice straw may be used as fuel.

F.J. Gutiérrez Ortiz et al.[14] studied the methanol synthesis from syngas obtained by supercritical water reforming of glycerol. The process of methanol synthesis operated at temperature of 250 °C and pressure of 85 atm. The important conditions for methanol production include temperature of reforming, water-to-glycerol mass ratio and the purge ratio in the methanol synthesis loop. From the research, the process operated at the temperature of reforming with 1000 °C and pressure of reforming of 240 atm, water-to-glycerol mass ratio of 1.68 and purge ratio of 0.2 to achieve the highest overall process efficiency in terms of total net power and methanol production.

G.H. Graaf et al.[15] studied kinetics of low-pressure methanol synthesis. The Cu-Zn-Al catalyst was used in methanol production. The kinetics data of experiment was described by Langmuir-Hinshelwood mechanism. The temperature that suitable for kinetics data was 210 – 245 °C. According to the results of the experiment, Methanol can form from CO hydrogenation reaction, CO_2 hydrogenation and water gas shift reaction in low-pressure methanol synthesis.

Y. Zhang et al.[16] studied the process simulation and optimization of methanol production coupled to tri-reforming process. The Peng Robinson equation of state is selected as thermodynamic method. From the experiment, they tested the results of product composition using Peng Robinson equation of state with the Boston-Mathias modification (PR-BM). There was no difference in the results compared to Peng Robinson equation of state. The effect of operating conditions of tri-reforming that include temperature, pressure and CH_4/flue gas ratio were studied. The optimal operating condition for methanol production from tri-reforming process was temperature of 850 °C, pressure of 1 atm and CH_4/flue gas ratio of 0.4. From the experiment, the tri-reforming process can integrate with methanol synthesis to provide an economical solution for the treatment and utilization of carbon dioxide in flue gas.

CHAPTER III

RESEARCH METHODOLOGY

This chapter presents the process description of methanol production from syngas produced from bagasse gasification. Section 3.1 presents the modeling of methanol production from bagasse gasification. Section 3.2 presents the simulation approach.

3.1 Modeling of methanol production from bagasse gasification

3.1.1 Modeling of gasification process of syngas production

The gasification process is designed in Aspen Plus simulation software version 9 as shown in Figure 3.1. In this project, the bagasse is considered as feedstock. The biomass is specified as non-conventional components in Aspen Plus simulator. Therefore, the ultimate and proximate analysis of bagasse as given in Table 3.1 is defined in the simulation. Firstly, biomass is devolatized[17] in decomposition unit where converts the non-conventional component of biomass into conventional components (C, H_2, N_2, S). Next, the conventional component is delivered to gasification unit. In the gasification unit, biomass will react with gasifying agent (steam) where many possible chemical reactions can be carried out as follows:

Char partial combustion:

$C + 0.5O_2 \rightarrow CO$ $\Delta H = -111$ kJ/mol (3-1)

C combustion:

$C + O_2 \rightarrow CO_2$ $\Delta H = -394$ kJ/mol (3-2)

CO partial combustion:

$CO + 0.5O_2 \rightarrow CO_2$ $\Delta H = -284$ kJ/mol (3-3)

Methane combustion:

$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$ $\Delta H = -803$ kJ/mol (3-4)

H_2 partial combustion:

$H_2 + 0.5O_2 \rightarrow H_2O$ $\Delta H = -242$ kJ/mol (3-5)

Boudouard reaction:

$C + CO_2 \leftrightarrow 2CO$ $\Delta H = +172$ kJ/mol (3-6)

Water gas reaction:

$C + H_2O \leftrightarrow CO + H_2$ $\Delta H = +131$ kJ/mol (3-7)

Hydrogenation reaction:

$C + 2H_2 \leftrightarrow CH_4$ $\Delta H = -74.8$ kJ/mol (3-8)

Water gas shift reaction:

$CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H = -41.2$ kJ/mol (3-9)

Methanation reaction:

$$2CO + 2H_2 \rightarrow CH_4 + CO_2 \qquad \Delta H = -247\ kJ/mol \qquad (3\text{-}10)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H = -206\ kJ/mol \qquad (3\text{-}11)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H = -165\ kJ/mol \qquad (3\text{-}12)$$

Reforming reaction:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H = +206\ kJ/mol \qquad (3\text{-}13)$$

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \qquad \Delta H = -36\ kJ/mol \qquad (3\text{-}14)$$

After the chemical reactions accomplish, there are many products provided that include carbon monoxide, carbon dioxide, methane, hydrogen, oxygen, nitrogen, water, sulfur, and ash. Cyclone is used to remove ash from gas product. Then, nitrogen and methane are separated through flash. Finally, the syngas consisting of hydrogen, carbon monoxide and carbon dioxide can be provided.

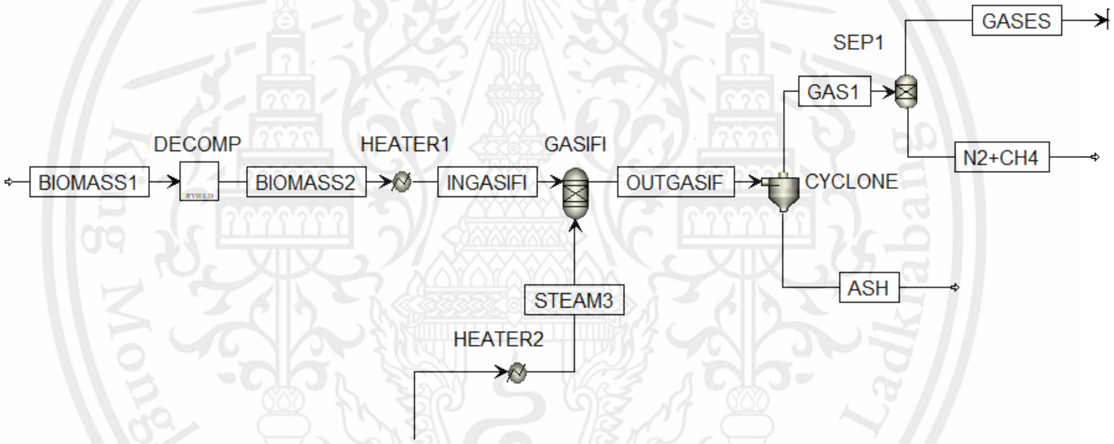


Figure 3.1 Diagram of syngas production from bagasse gasification

Table 3.1 Biomass composition (Ultimate analysis and Proximate analysis)[17]

Ultimate Analysis	**Composition (%)**
Carbon	49.80
Hydrogen	6.00
Oxygen	43.90
Nitrogen	0.20
Sulphur	0.06
Proximate Analysis	**Composition (%)**
Volatile matter	85.50
Fixed Carbon	12.40
Ash	2.10

3.1.2 Validation of simulation results with experimental data

In order to confirm that the proposed process model designed in Aspen Plus simulation can provide appropriate results, the simulation results of gasification are compared with the experimental results of Arpit Shukla et al.[18] In their work, sugarcane bagasse was considered as feedstock which has the ultimate and proximate analysis according to Table 3.2. In their experiment, the gasifier was operated at temperature of 850 °C, pressure of 1 atm and steam to biomass mass ratio of 0.5.

Table 3.2 Ultimate and proximate analysis of sugarcane bagasse[18]

Ultimate Analysis	**Composition (%)**
Carbon	49.20
Hydrogen	4.70
Oxygen	43.00
Nitrogen	0.20
Sulphur	0.04
Chlorine	0.16
Ash	2.70
Proximate Analysis	**Composition (%)**
Volatile matter	75.72
Fixed Carbon	11.71
Ash	2.20
Moisture	10.30

3.1.3 Investigation on effect of operating conditions in bagasse gasification

In bagasse gasification, the effects of important parameters that include gasifier temperature, gasifier pressure and steam to biomass mass ratio on syngas production are studied. The parameters considered are listed in Table 3.3.

Table 3.3 Parameters and operating conditions of bagasse gasification

Parameter	**Operating condition**
Gasifier temperature	600 – 1,100 °C
Gasifier pressure	1 – 15 bar
Steam to biomass mass ratio	0.1 - 3.0

3.1.4 Modeling of methanol synthesis of methanol production

From Section 3.1.3, under the optimal operating condition of gasification process, the suitable composition of syngas can be provided. The obtained syngas is used as reactant for methanol production. The methanol production process is further designed through Aspen Plus simulator as shown in Figure 3.2. Since the methanol production process operates at high pressure, the syngas obtained from gasification process must be sent to compressor to increase pressure before entering to the methanol production process. When the pressurized syngas is sent to the methanol production unit, there are three chemical reactions occurred as follows:

Reaction A: CO hydrogenation reaction

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H = -90.77 \text{ kJ/mol} \qquad (3\text{-}15)$$

Reaction B: CO_2 hydrogenation reaction

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H = -49.16 \text{ kJ/mol} \qquad (3\text{-}16)$$

Reaction C: Water gas shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41.21 \text{ kJ/mol} \qquad (3\text{-}17)$$

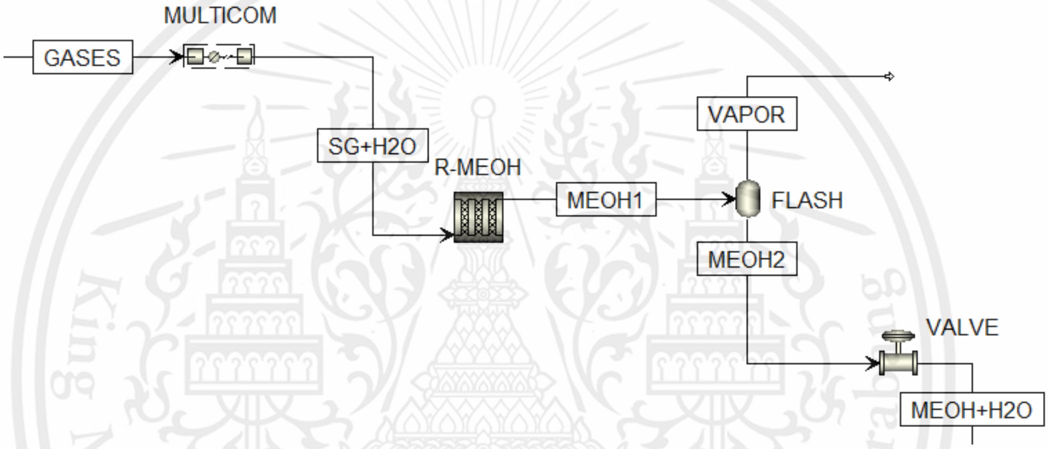


Figure 3.2 Diagram of methanol production from syngas

3.1.5 Investigation on effect of operating conditions in methanol production

In methanol synthesis, the influences of important parameters that include temperature and pressure of methanol reactor on methanol production are studied. The parameters examined are shown in Table 3.4.

Table 3.4 Parameters and operating conditions of methanol production

Parameter	Operating condition
Methanol reactor temperature	220 - 300 °C
Methanol reactor pressure	50 – 150 bar

3.1.6 Purification of methanol production by using distillation

The products exited from methanol production unit consist of not only methanol but also carbon monoxide, carbon dioxide, hydrogen, and water. Therefore, the distillation column is introduced to provide the purified methanol. Figure 3.3 shows the purification process designed in Aspen Plus simulator. In order to provide the purified methanol, carbon monoxide, carbon dioxide and hydrogen are firstly removed through flash drum. Further, water is separated from methanol by using distillation. Water from distillation can be recycled and mixed with steam at the mixer to be used as a gasifying agent in the gasification process. Figure 3.4 shows the overall process of methanol production from bagasse gasification.

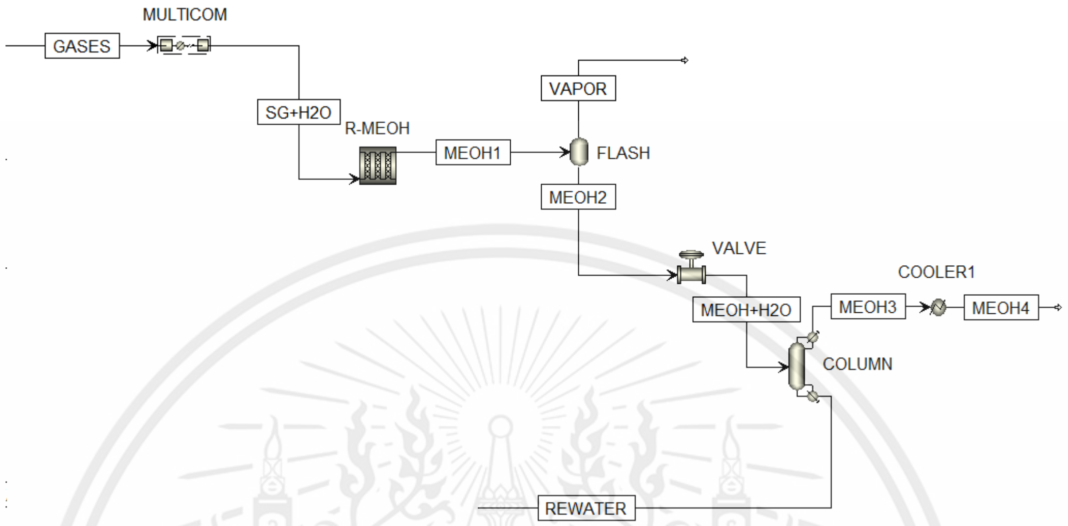


Figure 3.3 Diagram of distillation (Column)

3.1.7 Optimal operating conditions of methanol production from bagasse gasification.

From above studies, the optimal conditions in bagasse gasification and methanol production process that provide the maximum methanol production is determined.

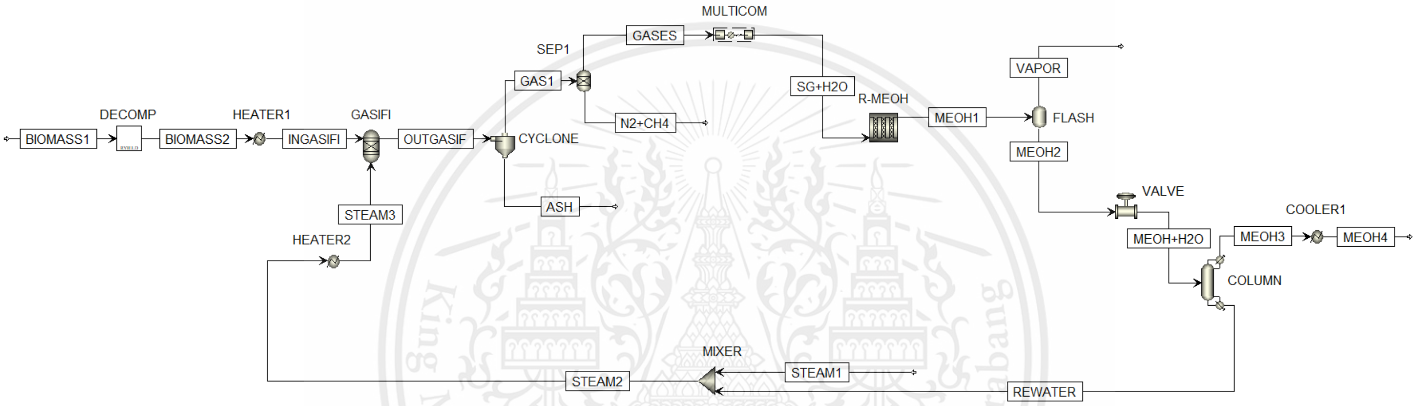


Figure 3.4 Diagram of methanol production from bagasse gasification

3.2 Simulation approach

The Aspen Plus simulation software version 9 is used to simulate the methanol production from syngas produced from bagasse gasification. The Peng-Robinson equation of state with Boston-Mathias modifications[16] is used in the simulation. Firstly, the compositions of bagasse as listed in Table 3.1 are specified corresponding with steam to biomass mass ratio[19]. Further, the operating conditions and specifications of each unit operation in gasification process, methanol synthesis and distillation as listed in Table 3.9 – Table 3.15 are specified. In gasification process, the equilibrium gas compositions can be calculated by the minimum Gibbs free energy method. While, the methanol production can be calculated by kinetic data[20] as shown below:

The rate equations of methanol synthesis as shown below:

$$\text{Reaction A:}\quad r_A = k_A \frac{K_{CO}\left[f_{CO}f_{H_2}^{3/2} - f_{CH_3OH}/\left(K_A\sqrt{H_2}\right)\right]}{\left(1+K_{CO}f_{CO}+K_{CO_2}f_{CO_2}\right)\left[\sqrt{f_{H_2}}+\left(K_{H_2O}/\sqrt{K_H}\right)f_{H_2O}\right]} \tag{3-18}$$

$$\text{Reaction B:}\quad r_B = k_B \frac{K_{CO_2}\left[f_{CO_2}f_{H_2} - f_{H_2O}f_{CO}/K_B\right]}{\left(1+K_{CO}f_{CO}+K_{CO_2}f_{CO_2}\right)\left[\sqrt{f_{H_2}}+\left(K_{H_2O}/\sqrt{K_H}\right)f_{H_2O}\right]} \tag{3-19}$$

$$\text{Reaction C:}\quad r_C = k_C \frac{K_{CO_2}\left[f_{CO_2}f_{H_2}^{3/2} - f_{H_2O}f_{CH_3OH}/\left(f_{H_2}^{3/2}K_C\right)\right]}{\left(1+K_{CO}f_{CO}+K_{CO_2}f_{CO_2}\right)\left[\sqrt{f_{H_2}}+\left(K_{H_2O}/\sqrt{K_H}\right)f_{H_2O}\right]} \tag{3-20}$$

The Langmuir–Hinshelwood expression that explains the kinetic data of the catalyst that was used in the methanol synthesis.

$$r = \frac{(\text{kinetic factor})(\text{driving force expression})}{\text{adsorption term}}$$

$$\text{kinetic factor} = kT^n e^{-E_a/RT}$$

The reacting phase is vapor phase, and the rate basis is weight of catalyst.

Table 3.5 Kinetic for methanol synthesis

Reaction	**k**	**n**	**E_a (J/kmol)**
A	4.0638×10^{-6}	0	1.1695×10^{7}
B	9.0421×10^{8}	0	1.1286×10^{8}
C	1.5188×10^{-33}	0	2.6601×10^{8}

The driving force of reactions for methanol synthesis as shown below:

Reaction A: $$\text{Reaction A: } K_{CO}f_{CO}f_{H_2}^{3/2}-\frac{K_{CO}}{K_A}f_{CH_3OH}f_{H_2}^{1/2}\left[Pa^{3/2}\right] \tag{3-21}$$

Reaction B: $$\text{Reaction B: } K_{CO_2}f_{CO_2}f_{H_2}^{3/2}-\frac{K_{CO_2}}{K_B}f_{H_2O}f_{CH_3OH}\left[Pa^{3/2}\right] \tag{3-22}$$

Reaction C: $$\text{Reaction C: } K_{CO_2}f_{CO_2}f_{H_2}-\frac{K_{CO_2}}{K_C}f_{H_2O}f_{CO}[Pa] \tag{3-23}$$

Table 3.6 Driving force of methanol synthesis

Reaction	**Term 1**		**Term 2**	
	A	**B**	**A**	**B**
A	-23.20	14225	28.895	2385
B	-22.48	9777	-28.12	15062
C	-22.48	9777	23.974	3222

The adsorption term of reaction for methanol synthesis as shown below:

$$\sqrt{f_{H_2}}+\frac{K_{H_2O}}{\sqrt{K_H}}f_{H_2O}+K_{CO}f_{CO}\sqrt{f_{H_2}}+\frac{K_{CO}K_{H_2O}}{\sqrt{K_H}}f_{CO}f_{H_2O}+K_{CO_2}f_{CO_2}\sqrt{f_{H_2}}+\frac{K_{CO_2}K_{H_2O}}{\sqrt{K_H}}f_{CO_2}f_{H_2O}$$

Table 3.7 Exponent of adsorption term for methanol synthesis

Component	Term 1	Term 2	Term 3	Term 4	Term 5	Term 6
H_2	0.5	0	0.5	0	0.5	0
H_2O	0	1	0	1	0	1
CO	0	0	1	1	0	0
CO_2	0	0	0	0	1	1

Table 3.8 Constants of adsorption term for methanol synthesis

Term no.	1	2	3	4	5	6
Coefficient A	0	-26.1568	-23.2006	-49.3574	-22.4827	-48.6395
Coefficient B	0	13842	14225	28067	9777	23619
Coefficient C	0	0	0	0	0	0
Coefficient D	0	0	0	0	0	0

Table 3.9 Operating condition of each unit models in syngas production from bagasse gasification

Unit operation	Unit model	Range of condition	
		Temperature (°C)	Temperature (°C)
DECOMP	Reactor (RYield)	25	25
HEATER1	Exchanger (Heater)	700	700
GASIFI	Reactor (RGibbs)	600 – 1,100	600 – 1,100
HEATTER2	Exchanger (Heater)	500	500
CYCLONE	Splitter (SSplit)	-	-
SEP1	Separator (Sep)	-	-

Table 3.10 Specification of CYCLONE (GAS1 stream)

Substream Name	Specification	Value
MIXED	Split fraction	1
CISOLID	Split fraction	0

Table 3.11 Specification of CYCLONE (ASH stream)

Substream Name	Specification	Value
NC	Split fraction	1

Table 3.12 Specification of SEP1 (N2+CH4 stream)

Component ID	Specification	Value
CH4	Split fraction	1
N2	Split fraction	1

Table 3.13 Operating condition of each unit models in methanol production from syngas produced from bagasse gasification

Unit operation	Unit model	Range of condition	
		Temperature (°C)	Temperature (°C)
MULTICOM	Pressure changer (MCompr)	220 - 300	50 - 150
R-MEOH	Reactor (RPlug)	220 - 300	50 - 150
FLASH	Separator (Flash2)	25	50
VALVE	Pressure changer (Valve)	-	1
COLUMN	Column (RadFrac)	65	1
COOLER1	Exchanger (Heater)	25	1
MIXER	Mixer	-	1

Table 3.14 Specification of methanol reactor

Unit operation	Type	Diameter (meter)	Length (meter)	Number of tubes	Residence time (hour)
Reactor (R-MEOH)	Plug flow reactor	0.06	12	81	0.0538

Table 3.15 Specification of distillation (Column)

Number of stages			50	
Condenser			Partial-Vapor	
Feed stage			33	
Reflux ratio			0.764855	
Start Stage	**End Stage**	**Tray/Packing Type**	**Tray/Spacing/Section Packed Height (meter)**	**Diameter (meter)**
2	32	SIEVE	0.6096	0.2565
33	49	SIEVE	0.6906	0.2699

CHAPTER IV

SIMULATION RESULTS AND DISCUSSION

In this project, the methanol production from syngas produced through the bagasse gasification is designed and simulated by using Aspen Plus simulation software version 9. This chapter is divided into 5 sections. Firstly, the comparison between the simulation results and the experimental results is shown in Section 4.1. The effect of operating conditions in gasification on syngas production is discussed in Section 4.2. Further, Section 4.3 presents the effects of operating conditions in methanol synthesis on methanol production. The purification of methanol by using distillation is presented in Section 4.4. Finally, the optimal operating conditions of methanol production from bagasse gasification is shown in section 4.5.

4.1 Comparison results between simulation and experiment

In order to confirm that the proposed process model designed in Aspen Plus simulator can provide appropriate results, the simulation results of gasification are compared with the experimental results of Arpit Shukla et al.[18] In their work, bagasse which has the ultimate and proximate analysis according to Table 3.2 is fed to gasifier operated at temperature of 850 °C and an atmospheric pressure of 1. Table 4.1 presents the comparison results obtained from experiment and simulation. It can be seen that under the same feedstock and same operating condition with the experiment, the simulation results of hydrogen and carbon monoxide agree with the experimental results. While the amount of carbon dioxide is deviated from the experimental result due to increasing in methane.

Table 4.1 The comparison of syngas production from bagasse between experimental results from the literature[18] and simulation results in this study.

Gas composition (%)	Experimental results[18]	Simulation results
CO	36.6900	35.4100
CO_2	14.2300	17.1900
H_2	34.3800	35.4400
CH_4	0.0197	1.1762
O_2	0.0000	0.0000
N_2	0.2150	0.2257
H_2O	14.4075	10.5396
S	0.0225	0.0237

4.2 Effects of operating conditions in gasification on syngas production

This section presents the influences of operating conditions in gasification (i.e., gasifier temperature, gasifier pressure and steam to biomass mass ratio) on syngas production.

4.2.1 Effect of gasifier temperature on syngas production

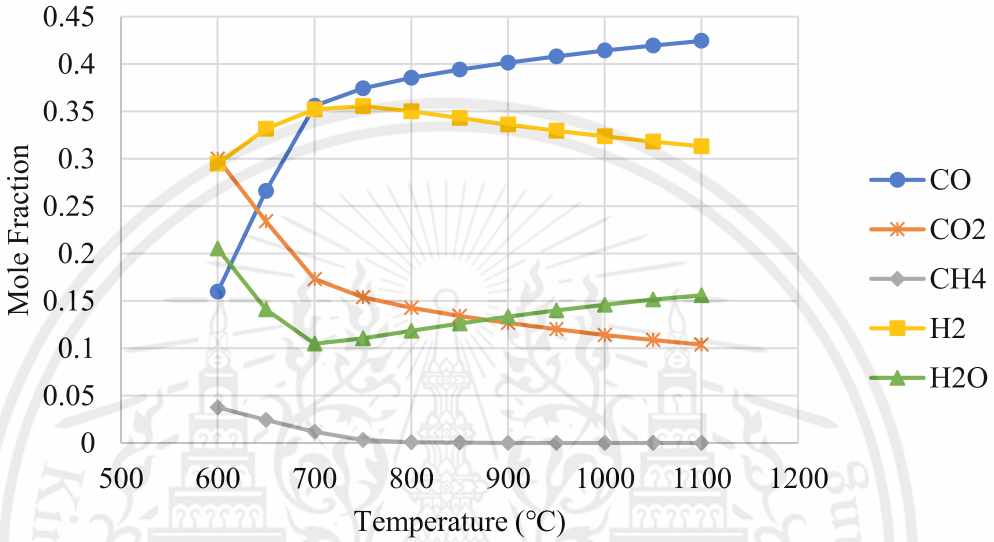


Figure 4.1 Effect of gasifier temperature on syngas composition at gasifier pressure of 1 bar and steam to biomass mass ratio of 0.6.

Figure 4.1 shows the effect of gasifier temperature on syngas composition. In this study, the gasifier temperature is varied between 600 and 1,100 °C whereas the gasifier pressure and steam to biomass mass ratio are fixed as 1 bar and 0.6, respectively. As seen in Figure 4.1, increasing gasifier temperature can increase mole fraction of carbon monoxide and hydrogen whereas mole fraction of carbon dioxide, methane and water decrease. This is because high temperature operation can shift the endothermic reactions that include Boudouard reaction (Equation (2-11)), water-gas reaction (Equation (2-12)) and reforming reaction (Equation (2-18)) forward and thus, the carbon monoxide and hydrogen are higher while carbon dioxide, methane and water are lower. However, the simulation results show that the mole fraction of hydrogen is dropped when gasifier operates at temperature above 700 °C. This is due to water gas shift reaction[21] (Equation (2-4)). From the simulation, it implies that the optimal gasifier temperature is 700 °C.

4.2.2 Effect of gasifier pressure on syngas production

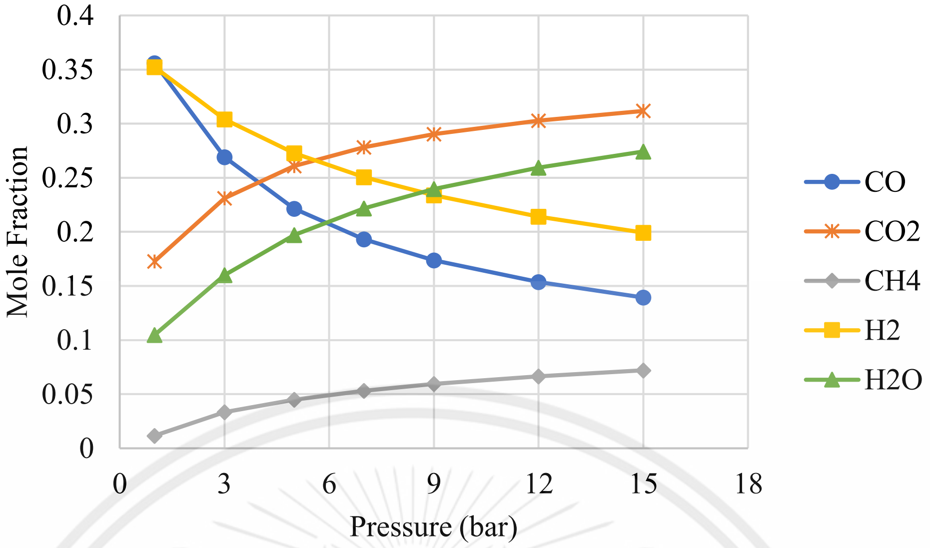


Figure 4.2 Effect of gasifier pressure on syngas composition at gasifier temperature of 700 °C and steam to biomass mass ratio of 0.6.

In this section, the effect of gasifier pressure on syngas production is studied as shown in Figure 4.2. The gasifier pressure is adjusted in range of 1 to 15 bar whereas the gasifier temperature and steam to biomass mass ratio are 700 °C and 0.6, respectively. The simulation results as shown in Figure 4.2 indicate that mole fraction of carbon dioxide, methane and water increase when the gasifier pressure is increased. At the same time, increasing gasifier pressure will reduce mole fraction of carbon monoxide and hydrogen. This can be described by Le Châtelier's principle in which higher pressure operation can shift the chemical equilibrium to the lower number of gaseous moles side. In contrast to high pressure operation, the lower pressure operation leads to the shifting of the chemical equilibrium to the greater number of gaseous moles side. Considering the chemical reaction involved in gasification (Equations (2-6), (2-13), (2-15), (2-16), (2-17), (2-18) and (2-19)), it is found that the number of moles in reactant side is more than that of product side and thus, the reaction will move forward. This causes an increase in carbon monoxide and hydrogen. From the simulation results, it is clearly shown that the gasifier pressure should be maintained between 1 and 2 bar because this will reduce the energy consumption to increase the pressure of the gasifier and the composition of the syngas is still abundant.

4.2.3 Effect of steam to biomass mass ratio on syngas production

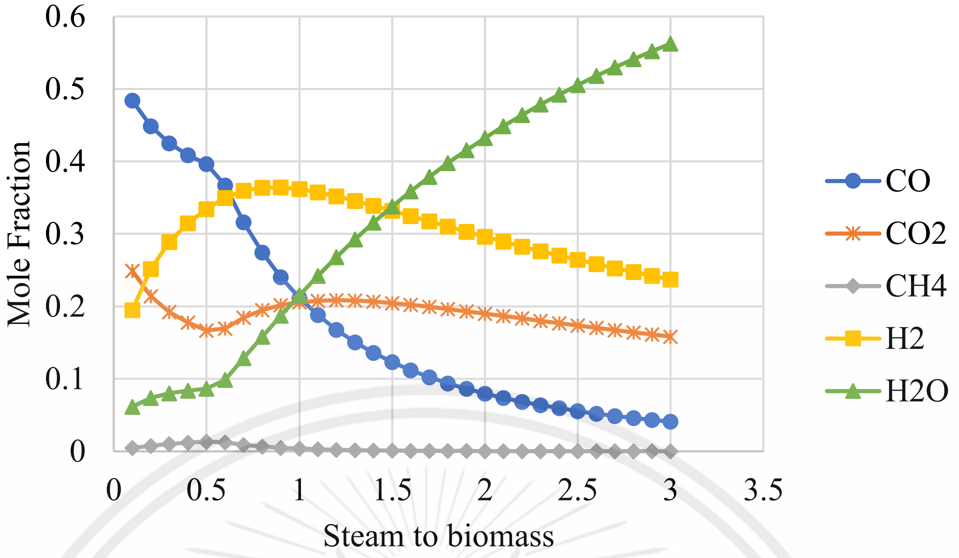


Figure 4.3 Effect of steam to biomass mass ratio on syngas composition at gasifier temperature of 700 °C and gasifier pressure of 1 bar.

Figure 4.3 shows syngas production as a function of steam to biomass mass ratio when gasifier is operated at temperature of 700 °C and pressure of 1 bar. Increasing steam to biomass mass ratio in a range of 0.1-3.0 cause an increase in mole fraction of carbon dioxide and hydrogen. However, mole fraction of carbon monoxide and methane decrease with increasing steam to biomass mass ratio. When higher steam or reactant is added in gasification process, the chemical equilibrium that include water gas reaction (Equation (2-12)), water gas shift reaction (Equation (2-14)) and reforming reaction (Equation (2-18)) move forward, resulting in an increase in product and a decrease in reactant. From the simulation results, it can be seen that the mole fraction of hydrogen will increase at initial and will decrease when steam to biomass mass ratio above 0.8. When more steam is fed, this will lower the gasifier temperature because the steam temperature is lower than the gasifier temperature. As a result, the chemical reaction of the water gas reaction that is endothermic reaction was reversed, resulting in reduced hydrogen. Therefore, it can be concluded that the optimal syngas composition can be provided at steam to biomass mass ratio of 0.6.

4.3 Effects of operating conditions in methanol synthesis on methanol production

This section presents the influences of temperature and pressure in methanol production unit on methanol production.

4.3.1 Effect of temperature on methanol production

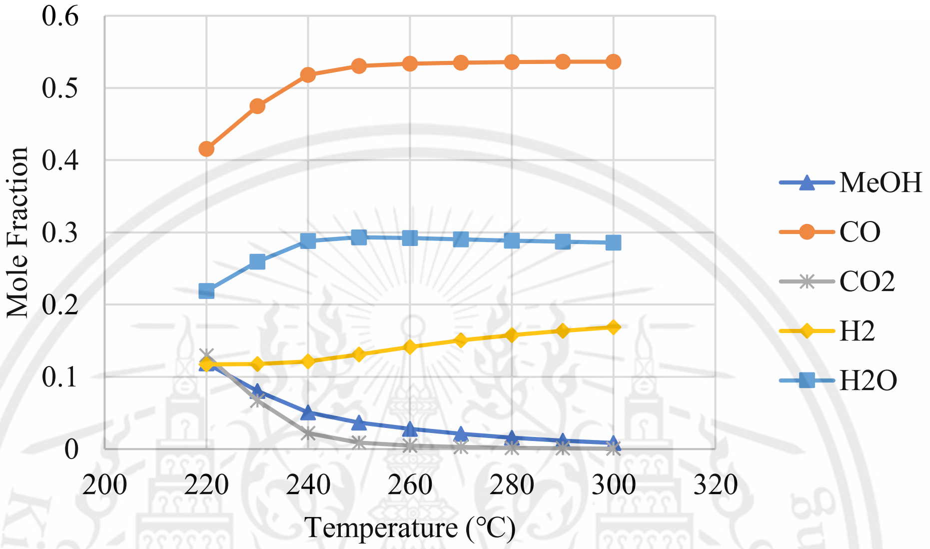


Figure 4.4 Effect of temperature on methanol synthesis at pressure of 50 bar.

Figure 4.4 shows methanol production at different methanol reactor temperature when the methanol reactor pressure is kept constant as 50 bar. When the methanol reactor temperature is increased from 220 to 300 °C, it can be seen in Figure 4.4 that mole fraction of methanol decreases whereas mole fraction of carbon monoxide and hydrogen increase. Considering the chemical reactions in methanol synthesis that include CO hydrogenation reaction (Equation (2-2)) and CO_2 hydrogenation reactions (Equation (2-3)) are exothermic reaction and reversible reaction in which the chemical equilibrium will shift backward to reactant side. This result in an increase in reactant that is carbon monoxide and hydrogen whereas the product as methanol is decreased. Beside CO and CO_2 hydrogenation, water gas shift reaction is involved. From the simulation results, it is found that the temperature of methanol synthesis should be 220 °C since the highest amount of methanol can be provided.

4.3.2 Effect of pressure on methanol production

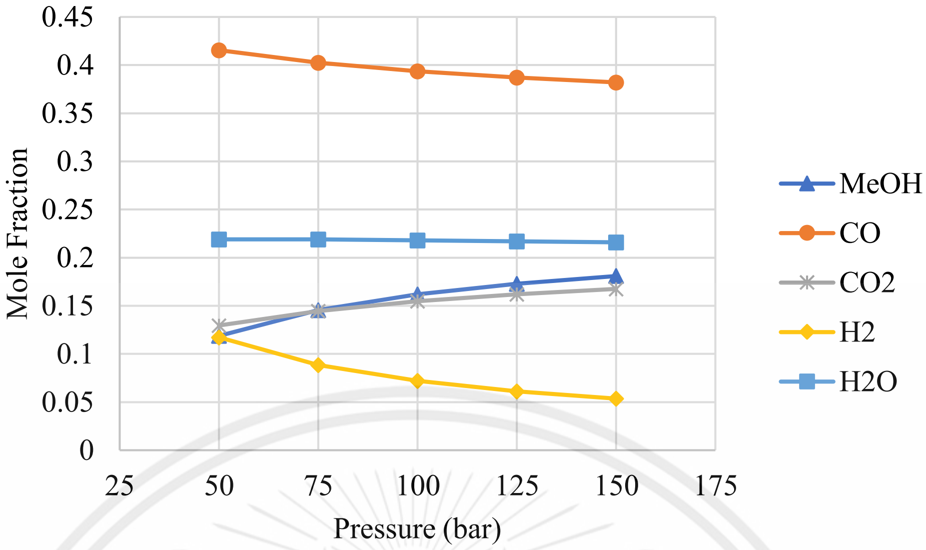


Figure 4.5 Effect of pressure on methanol synthesis at temperature of 220 °C.

Figure 4.5 shows the effect of methanol reactor pressure varied between 50 and 150 bar on methanol production when the reactor is operated at reactor temperature 220 °C. It is found that mole fraction of methanol will be enhanced when the pressure of methanol synthesis is increased. At the same time, mole fraction of carbon monoxide and hydrogen decrease. This can be described by Le Châtelier's principle as present in Section 4.2.2. Considering the chemical reactions in methanol synthesis that include CO hydrogenation reaction (Equation (2-2)) and CO_2 hydrogenation reaction (Equation (2-3)), it can be seen that the number of moles in reactant side is more than that of product side and thus, the reaction will move forward. Although the high-pressure operation can improve the methanol production, the amount of methanol is an insignificant increase. Therefore, the methanol reactor pressure should be 50 bar because this will reduce the energy consumption to increase the pressure of the reactor and the composition of the syngas used as reactant to produce methanol is still abundant.

4.4 Purification of methanol by using distillation

From Section 4.2 and 4.3, it is found that 35% methanol can be provided when the gasifier operates at temperature of 700 °C, pressure of 1 bar and steam to biomass mass ratio of 0.6 and the temperature and pressure of methanol production unit are temperature of 220 °C and pressure of 50 bar. It is observed that the methanol is still contaminated with water. Therefore, the distillation is further installed to remove water from methanol.

Figure 4.6 shows the mass flow rate of methanol before removing water (MEOH+H2O stream) and after removing water (MEOH4 stream). From the simulation results, it is found that the amount of methanol in MEOH4 stream is slightly reduced compared with MEOH+H2O stream. In contrast to mass flow rate, the purity of methanol can be improved when the distillation is installed in the process (Figure 4.7). The simulation result shows that the purity of methanol obtained from distillation is 96% with an error of 3% compared to the experiment[22].

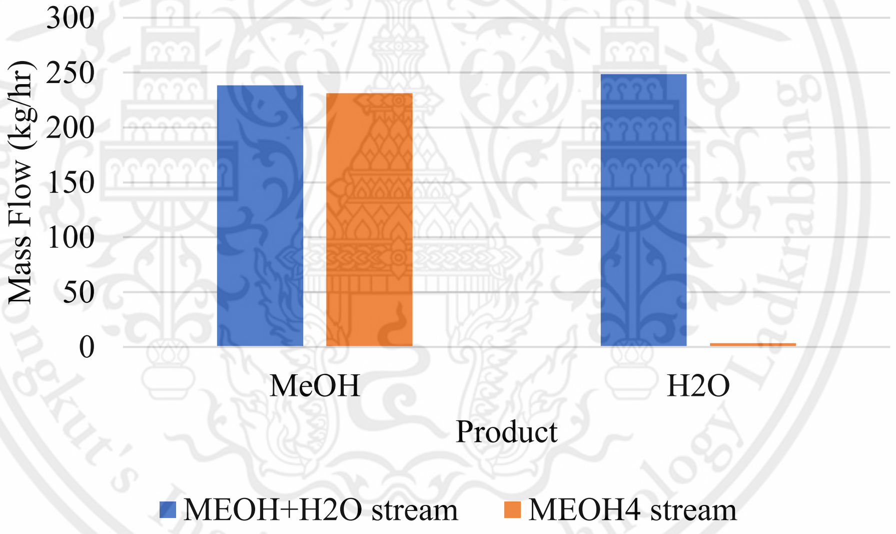


Figure 4.6 Amount of methanol after removing water.

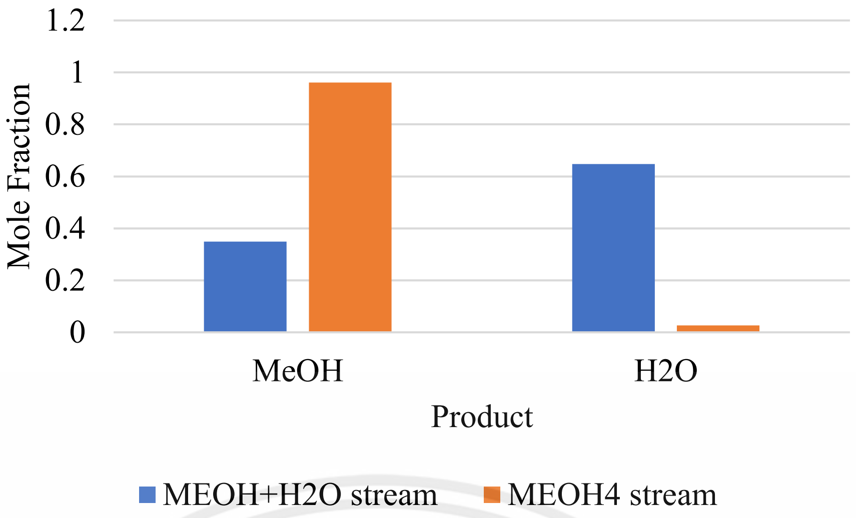


Figure 4.7 Purity of methanol after removing water.

4.5 Optimal operating conditions of methanol production from bagasse gasification

From the investigation on bagasse gasification for syngas production, it can provide the optimal operating conditions of bagasse gasification as shown in Table 4.2. Under the operating conditions, the maximum syngas composition consisting of 35.44% hydrogen and 35.41% carbon monoxide can be obtained.

Table 4.2 Optimal operating conditions of bagasse gasification

Parameter	**Operating condition**
Gasifier temperature (^{o}C)	700
Gasifier pressure (bar)	1
Steam to biomass mass ratio	0.6

When the syngas obtained from gasification process is used as feed for methanol production, the effect of temperature and pressure in methanol reactor on methanol production is further determined. Table 4.3 shows the optimal operating conditions of methanol reactor in which 35% methanol can be provide. The methanol purity can be improved through the distillation column. Under the specification of distillation column as shown in Table 3.15, it can provide the methanol purity of 96%.

Table 4.3 Optimal operating conditions of methanol production

Parameter	**Operating condition**
Methanol reactor temperature (^{o}C)	220
Methanol reactor pressure (bar)	50

CHAPTER V

CONCLUSION

5.1 Conclusion

In this project, the methanol production from syngas produced from bagasse gasification is designed and simulated through the Aspen Plus simulation software version 9 program. The simulation is performed to determine the optimal operating conditions in bagasse gasification and methanol production process. The amount of syngas composition is calculated through the minimum Gibbs free energy method. The thermodynamic equation that used is Peng-Robinson equation of state with Boston-Mathias modifications. The methanol production can be calculated by using kinetic data from literature. The operating conditions of bagasse gasification are determined with the wider range of gasifier temperature, gasifier pressure and steam to biomass mass ratio. The simulation results showed the bagasse gasification should be operated at temperature of 700 °C, pressure of 1 bar, and steam to biomass mass ratio of 0.6. Under the operating conditions, the maximum syngas composition consisting of 35.44% hydrogen and 35.41% carbon monoxide can be provided. Further, the operating conditions of methanol production process are studied and found that the methanol production unit should be operated at temperature 220 °C and pressure 50 bar to provide the maximum methanol production. In order to provide higher methanol purity, the methanol is purified by using distillation. The simulation result indicates that the final methanol has a purity of 96%.

5.2 Recommendations

5.2.1 Heat integration for all equipment in the process should be considered.

5.2.2 Economic analysis should be considered

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APPENDIX

APPENDIX A
Gasification process simulation results

Table A.1 The simulation results of gasifier temperature in bagasse gasification at gasifier pressure of 1 bar and steam to biomass mass ratio of 0.6

Temperature (°C)	**Mole Fraction**					
	CO	**CO_2**	**CH_4**	**H_2**	**O_2**	**H_2O**
600	0.1597	0.3001	0.0375	0.2948	6.56E-25	0.2050
650	0.2661	0.2341	0.0243	0.3317	9.80E-24	0.1411
700	0.3560	0.1728	0.0117	0.3522	1.32E-22	0.1048
750	0.3744	0.1540	0.0031	0.3556	2.87E-21	0.1106
800	0.3854	0.1427	0.0008	0.3502	5.14E-20	0.1184
850	0.3941	0.1341	0.0002	0.3430	7.26E-19	0.1261
900	0.4015	0.1266	7.75E-05	0.3360	8.19E-18	0.1333
950	0.4082	0.1200	2.74E-05	0.3295	7.56E-17	0.1399
1000	0.4141	0.1140	1.05E-05	0.3235	5.84E-16	0.1458
1050	0.4195	0.1086	4.36E-06	0.3182	3.82E-15	0.1512
1100	0.4244	0.1038	1.93E-06	0.3133	2.21E-14	0.1561

Table A.2 The simulation results of gasifier pressure in bagasse gasification at gasifier temperature of 700 °C and steam to biomass mass ratio of 0.6

Pressure (bar)	**Mole Fraction**					
	CO	**CO_2**	**CH_4**	**H_2**	**O_2**	**H_2O**
1	0.3560	0.1728	0.0117	0.3522	1.32E-22	0.1048
3	0.2690	0.2310	0.0335	0.3039	1.37E-22	0.1599
5	0.2213	0.2608	0.0450	0.2728	1.55E-22	0.1972
7	0.1931	0.2783	0.0532	0.2507	1.65E-22	0.2217
9	0.1739	0.2903	0.0594	0.2337	1.73E-22	0.2396
12	0.1537	0.3029	0.0666	0.2142	1.80E-22	0.2594
15	0.1393	0.3117	0.0721	0.1993	1.85E-22	0.2743

Table A.3 The simulation results of steam to biomass mass ratio in bagasse gasification at gasifier temperature of 700 °C, gasifier pressure of 1 bar

S/B	**Mole Fraction**					
	CO	**CO_2**	**CH_4**	**H_2**	**O_2**	**H_2O**
0.1	0.4839	0.2489	0.0046	0.1951	1.48E-22	0.0615
0.2	0.4484	0.2138	0.0077	0.2518	1.27E-22	0.0736
0.3	0.4251	0.1921	0.0101	0.2888	1.14E-22	0.0800
0.4	0.4086	0.1775	0.0120	0.3148	1.05E-22	0.0838
0.5	0.3963	0.1670	0.0135	0.3342	9.92E-23	0.0863
0.6	0.3671	0.1693	0.0125	0.3497	1.10E-22	0.0988
0.7	0.3159	0.1845	0.0090	0.3596	1.91E-22	0.1286
0.8	0.2744	0.1948	0.0066	0.3638	2.82E-22	0.1582
0.9	0.2402	0.2015	0.0049	0.3641	3.93E-22	0.1872
1.0	0.2118	0.2056	0.0037	0.3617	5.27E-22	0.2152
1.1	0.1880	0.2078	0.0028	0.3575	6.83E-22	0.2421
1.2	0.1678	0.2084	0.0021	0.3520	8.62E-22	0.2679
1.3	0.1506	0.2079	0.0017	0.3457	1.06E-21	0.2924
1.4	0.1359	0.2065	0.0013	0.3389	1.29E-21	0.3157
1.5	0.1231	0.2046	0.0010	0.3319	1.54E-21	0.3379
1.6	0.1120	0.2021	0.0008	0.3246	1.82E-21	0.3589
1.7	0.1024	0.1994	0.0007	0.3174	2.12E-21	0.3788
1.8	0.0939	0.1964	0.0006	0.3101	2.45E-21	0.3977
1.9	0.0864	0.1933	0.0005	0.3030	2.80E-21	0.4155
2.0	0.0797	0.1900	0.0004	0.2961	3.18E-21	0.4325
2.1	0.0738	0.1867	0.0003	0.2893	3.58E-21	0.4486
2.2	0.0685	0.1834	0.0003	0.2827	4.01E-21	0.4639
2.3	0.0638	0.1801	0.0002	0.2763	4.46E-21	0.4784
2.4	0.0595	0.1769	0.0002	0.2701	4.94E-21	0.4922
2.5	0.0556	0.1736	0.0002	0.2642	5.45E-21	0.5054
2.6	0.0521	0.1704	0.0001	0.2584	5.98E-21	0.5179
2.7	0.0489	0.1673	0.0001	0.2528	6.54E-21	0.5298
2.8	0.0460	0.1643	0.0001	0.2474	7.12E-21	0.5412
2.9	0.0434	0.1613	0.0001	0.2422	7.73E-21	0.5521
3.0	0.0409	0.1584	0.0001	0.2372	8.37E-21	0.5625

APPENDIX B
Methanol synthesis simulation results

Table B.1 The simulation results of temperature in methanol synthesis at pressure of 50 bar

Temperature (°C)	**Mole Fraction**				
	CH_3OH	**CO**	**CO_2**	**H_2**	**H_2O**
220	0.1188	0.4155	0.1296	0.1173	0.2189
230	0.0804	0.4750	0.0673	0.1178	0.2596
240	0.0506	0.5180	0.0221	0.1213	0.2880
250	0.0365	0.5303	0.0088	0.1311	0.2934
260	0.0279	0.5335	0.0049	0.1413	0.2924
270	0.0210	0.5351	0.0028	0.1504	0.2906
280	0.0157	0.5359	0.0016	0.1579	0.2888
290	0.0116	0.5363	0.0009	0.1640	0.2872
300	0.0085	0.5365	0.0006	0.1687	0.2858

Table B.2 The simulation results of pressure in methanol synthesis at temperature of 220 °C

Pressure (bar)	**Mole Fraction**				
	CH_3OH	**CO**	**CO_2**	**H_2**	**H_2O**
50	0.1188	0.4155	0.1296	0.1173	0.2189
75	0.1454	0.4025	0.1445	0.0886	0.2190
100	0.1618	0.3935	0.1547	0.0720	0.2180
125	0.1729	0.3870	0.1620	0.0612	0.2169
150	0.1809	0.3820	0.1676	0.0536	0.2159

Table B.3 The simulation results of methanol production before being purified by using distillation

Mass Flows (kg/hr)	**MEOH+H2O stream**
	490.8897
CO	0.0875
CO_2	3.7261
H_2	0.0024
H_2O	248.6640
CH_3OH	238.4098
Mole Fraction	
CO	0.0001
CO_2	0.0040
H_2	5.46E-05
H_2O	0.6470
CH_3OH	0.3488

APPENDIX C
Result of maximum methanol production

Table C.1 The simulation results of bagasse gasification at gasifier temperature of 700 °C, gasifier pressure of 1 bar and steam to biomass mass ratio of 0.6

Mass Flows (kg/hr)	**INGASIFI stream**	**STEAM3 stream**	**OUTGASIF stream**
	1000.0000	630.3845	1630.3845
BIOMASS	0.0000	0.0000	0.0000
ASH	21.0000	0.0000	21.0000
C	508.0000	0.0000	0.0000
CO	0.0000	3.05E-88	784.1910
CO_2	0.0000	1.96E-56	598.0555
CH_4	0.0000	0.0000	14.9199
H_2	6.4000	1.23E-86	56.4888
O_2	459.0000	0.0000	3.33E-19
N_2	5.0000	0.0000	5.0000
H_2O	0.0000	623.3029	150.1293
S	0.6000	0.0000	0.6000
Mole Fractions			
C	0.0000	0.0000	0.0000
CO	0.0000	3.13E-91	0.3541
CO_2	0.0000	1.28E-59	0.1719
CH_4	0.0000	0.0000	0.0118
H_2	0.1792	1.75E-88	0.3544
O_2	0.8097	0.0000	1.32E-22
N_2	0.0101	0.0000	0.0023
H_2O	0.0000	0.9937	0.1054
S	0.0011	0.0000	0.0002

Table C.2 The simulation results of methanol synthesis at temperature of 220 °C and pressure of 50 bar

Mass Flows (kg/hr)	**SG+H2O stream**	**MEOH1 stream**
	1588.8647	1588.8647
CO	784.1910	726.8230
CO_2	598.0555	356.1849
H_2	56.4888	14.9946
H_2O	150.1293	249.1383
CH_3OH	0.0000	241.7238
Mole Fractions		
CO	0.3592	0.4128
CO_2	0.1744	0.1288
H_2	0.3595	0.1183
H_2O	0.1069	0.2200
CH_3OH	1.90E-09	0.1200

Table C.3 The simulation results of purified methanol by using distillation

Mass Flows (kg/hr)	**MEOH+H2O stream**	**MEOH4 stream**
	490.8897	238.7441
CO	0.0875	0.0875
CO_2	3.7261	3.7261
H_2	0.0024	0.0024
H_2O	248.6640	3.6002
CH_3OH	238.4098	231.3279
Mole Fractions		
CO	0.0001	0.0004
CO_2	0.0040	0.0113
H_2	5.46E-05	0.0002
H_2O	0.6470	0.0266
CH_3OH	0.3488	0.9615

BIOGRAHPY

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