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KELANTAN

Modeling of Bio-Methanol Production from Chicken Manure using Aspen Plus® Simulation

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A report submitted in fulfilment of the requirement for the degree of Bachelor of Applied Science (Bioindustrial Technology) with Honours

Faculty of Bioengineering and Technology

Universiti Malaysia Kelantan

2019

DECLARATION

I hereby declare that the work embodied in this Report is the result of the original research and has not been submitted for a higher degree to any universities or institutions.

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I certify that the report of this final year entitled " Modeling of Bio-Methanol Production from Chicken Manure using Aspen Plus® Simulation" by Nor Effi Afizal bin Norisman, Matric Number F15A0114 has been examined and all the correction recommended by examiner has been done for the degree of Bachelor of Applied Science (Bioindustrial Technology) with Honours, Faculty of Bioengineering and Technology, Universiti Malaysia Kelantan.

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ACKNOWLEDGEMENT

Firstly, would like to express my sincere appreciation to my supervisor, Dr Nik Nurul Anis Binti Nik Yusoff for her valuable advice, patience, understanding, leading and guidance for a bio-methanol production from chicken manure by using Aspen plus. Under her guidance and support, I have managed to complete my thesis successfully

I am very thankful to my friends, Puteri Nur'Ain binti Norazlisham and my course mates for their invaluable information, encouragement and continuous support until completion of my thesis. We have the hard time together in discussing, modelling and simulation of process flow diagram, and supporting each other until today, all of us have finished our final year project.

Last but not least, my sincere thanks to my lovely family. Their love and unconditional support is my driving force upon completion of my study. As I was doing final year project, I spent less time with them, yet they were understand of my work and continuously giving me a lots of care and support.

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LIST OF ABBREVIATIONS

PFD	Process Flow Diagram
Cu	Copper
H	Hydrogen
C	Carbon
H_2O	Water
K_A	Kinetic
N	Nitrogen
S	Sulphur
O	Oxygen
MAN	Manure
CRISPS	Combustion Reduction Integrated Pyrolysis System

LIST OF SYMBOLS

Atm	Atmosphere
°C	Degree Celcius
Ft	Foot
kg	Kilogram
K	Kelvin
L	Litre
g	Gram
Bar	Pressure
Mol	Molarity
Rpm	Revolution per minute
%	Percentage
$	US Dollar
Kw	Kilowatt

MODELING BIO-METHANOL DARI NAJIS AYAM MENGGUNAKAN SIMULASI ASPEN PLUS®

ABSTRAK

Methanol dianggap sumber tenaga alternatif kerana pelbagai kegunaan dan oktanen yang tinggi. Sebagai bahan bakar, ia mengeluarkan pelepasan yang rendah, dan menunjukkan prestasi tinggi dan risiko mudah terbakar yang rendah. Selain itu, dari kajian terdahulu ia hanya dibandingkan dengan proses yang sama. Dalam penyelidikan ini, tiga proses bio-metanol berterusan dengan kapasiti pengeluaran 50,000 kg setahun, termasuk pengegasan, pirolisis dan pengegasan bersepadu dan pirolisis menggunakan kotoran ayam sebagai bahan mentah, telah disimulasikan dalam Aspen Plus®. Proses ekonomi dianalisis dengan menggunakan Penaksir Kos Dalam Aspen. Proses gasifikasi dan pirolisis bersepadu yang menggunakan baja ayam mempunyai jumlah pelaburan modal tertinggi, tetapi proses superkritikal adalah keseluruhan yang paling ekonomik, yang menyediakan kos pengeluaran yang lebih rendah dan nilai bersih bersih yang lebih tinggi dan kadar pulangan aliran tunai yang didiskaunkan. Manakala kos pembuatan khusus dan kos pelaburan tertentu dikira pada lingkungan US $ 312,000 dan 1500-2800 kW-1. Selain itu, kos pelaburan infrastruktur dianggarkan berjumlah AS $ 6,012,000 juta dengan kos khusus untuk satu unit dalam lingkungan US $ 1800-3500 kW-1. Hasil yang diperoleh adalah setanding dengan kajian lain.

Kata kunci: Najis ayam, Aspen Plus®**,** simulasi.

MODELING OF BIO-METHANOL PRODUCTION FROM CHICKEN MANURE USING ASPEN PLUS® SIMULATION

ABSTRACT

Methanol was considered an alternative energy source due to its various applicability and high octane. As a fuel, it releases low emissions, and shows high performance and low risk of flammability. Other than that, from previous study it's just compare with the same processes. In this research, three continuous bio-methanol processes with production capacity of 50,000 kg per year, including gasification, pyrolysis and integrated gasification and pyrolysis using chicken manure as the raw material, were simulated in Aspen Plus®. Process economics were analyzed using Aspen In-Plant Cost Estimator. The integrated gasification and pyrolysis process using chicken manure had the highest total capital investment, but the supercritical process was the most economically feasible overall, providing a lower manufacturing cost and higher net present value and a discounted cash flow rate of return. While the specific manufacturing cost and the specific investment cost were calculated at the range of US$ 312,000 and 1500–2800 kW−1, respectively. Furthermore, the infrastructure investment cost was estimated to be in the US $ 6,012,000 million with the specific cost for one unit in the range of US$ 1800–3500 kW−1. The results obtained are comparable with other studies.

Keywords: Chicken manure, Aspen Plus®**,** simulation.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Chicken manure is a heterogeneous mixture of which is come from chicken droppings, waste beddings, waste food, and feathers from the coops. Chicken manure is characterized by high nitrogen, phosphorus and ash content which makes it a (Hussien, 2017). Chicken manure also was high in concentration of phosphorous found in the soil. The local use for farmer in chicken manure for fertilizer applications of chicken manure is no longer an option because wastes can be managed by transporting and renewable into usable energy (Kelleher, 2002). Thermochemical conversion techniques such as pyrolysis and gasification can convert the chicken manure into bio-methanol production, which can be further processed to fuels or directly used for power and help reduce the on fossil fuels that has been use recently. Other than that, converting the chicken manure will decrease greenhouse gases produced and generate energy in a carbon neutral process (Kumar, 2009).

Process simulation studies for determining process characteristics and their dependence on design operating variables and lastly simulate fo economical. Basically, Aspen Plus® simulation is based on a flowsheet simulation which can predict the entire chemical process using basic engineering relationships. The simulation starts from the raw material to the final finished product which symbolically represented by different icons. Each icon stands for a unit operation, chemical process, input and output material stream, input and output energy stream, or input/output electric signal (Kamal, 2016). Notably, Aspen Plus® simulation has been used extensively in renewable energy production (Nejadfomeshi, 2013). Then, Aspen Plus® simulation is suitable method for this bio-methanol production.

Today diesel powered vehicles represents about one to third of the vehicles sold in Europe and the United States and it is being predicted that the sales of diesel run automotive will rise from 4% in 2004 to 11% by 2012. As an alternative for petrol diesel in the transportation sector, biodiesel can easily become the crucial solution for environmental problems. First, it does not require any engine modification, second it reduces greenhouse gas (GHG) emission substantially and finally it also improves lubricity. These factors had make biodiesel usage more adaptable and attractive to current energy scenario, which are to ensure energy security, environmental sustainability and also to boost rural development by shifting of power from petrol to agroindustry simultaneously (Masjuki,2013). Then, renewable energy sources play a major role in reducing the dependencies on fossil fuels. It's can help to supply energy for electrical power generation and transportation sectors such as wind, hydro, solar, biomass, biofuel, geothermal and ocean energy are amongst the renewable energy resources. These natural power sources offer alternative means that can simultaneously save the environment and reduce reliance on fossil fuels (Energy Information and Administration, 2018). Biomass, proven as potential biomass carbon resource as it can be change from a solid phase into a chemical which is in liquids form that can be used as biofuels. The example of biofuel was bio-oil, bio-ethanol, bio-methanol, bio-char, syngas and bio-diesel (Paula *et al.*, 2013)

Amongst the biofuels, bio-methanol has the best potential as a biofuel for power generation because its come from form energy production. Other than that, methanol is suitable for downstream processes, such as fuel cell-powered vehicles, because it can be easily degraded to carbon dioxide and hydrogen. Then, it will produce steam. Methanol is the simple organic liquid hydrogen carrier that acts as a hydrogen storage compound. It’s also a good automotive fuel because of physical and chemical composition and characteristics of methanol (Eppinger *et al.*, 2017).

There are several new processes and acceptable processes for the production of bio-methanol, such as pyrolysis, gasification, biosynthesis, electrolysis and photo electrochemical processes (Shamsul *et al.*, 2014). However, only pyrolysis and gasification processes will be employed in this study. Pyrolysis technology is more suitable for the big scale production of methanol for diesel engines and gas turbine applications. Furthermore, cost gasification processes were very effective preferred for the production of gaseous fuel (Bridgwater, 2011). Direct combustion of manure is inefficient compared to pyrolysis and gasification. Due to high moisture and ash content, manure has very low heating value in its solid state compared to gas liquid products of gasification. The higher heating value of syngas allows a more stable, more efficient, and energy denser combustion and thus more efficient energy production. Thermochemical conversion methods such as gasification and pyrolysis are industrially viable options with high throughput compared to bio-chemical conversion methods such as anaerobic digestion due to the high thermochemical reaction rates. In this project, pyrolysis, gasification and integrated pyrolysis and gasification was selected for bio-methanol production.

In this project, chicken manure waste had a great potential as a bio-methanol production due to directly used for power, and thus help reduce dependence on fossil fuels by using thermochemical conversion techniques which is pyrolysis and gasification. Pyrolysis is a processed whereby chicken manure was heated in the absence of air. The process results liquid, solid and gaseous fractions, mainly gases, bio-oil and char. Then, gasification was a process that chicken manure was broken down into combustible gas, volatiles and ash. Main products of gasification are synthesis gas, char and tars. This two process content depend on the feedstock, oxidizing agent and the condition of process. For the last process are integrated between pyrolysis and gasification. Main product of this process was bio-oil, char and gases. In the preliminary study, have reported waste from chicken manure was used in the production of methane (Hussien, 2017).

1.2 Problem statement

Continuous increase in chicken meat consumption calls for the chicken unprecede dense chicken production and associated waste production (Hussien, 2017). The chicken farms produce large amounts of chicken manure that can no longer be directly used as a fertilizer due to concerns of land pollution and water bodies eutrophication. To solve this issue waste from chicken manure can be converted the economic value of chicken manure into fuel to help foster energy security and energy sustainability.

All of the recent production of bio-methanol has been widely designed by the simulation approaches but most of them were not ended with the commercialization phase

(Abdelaziz *et al.*, 2014). The simulation tool has been widely used for industry purpose especially for petroleum and chemical industries. The capital investment on scaling up the production will be decreased by doing the simulation first before the establishment of the industry. It is important to know exactly how the process going because clearer picture of the process will make the simulation tool could be used much easier for screening, selection, and strategic planning of production flow depend on preliminary economic analyses and environmental impact.

The gasification process and pyrolysis process has been highlighted in this study is one of the thermochemical conversions where the biomass will be heated with sufficient amount of oxygen to produce the synthetic gas with a mixture of carbon monoxide and hydrogen. The synthetic gas produce were lower in calorific value in which it has a wide future to be used as a fuels for transportation. The gasification process also has become a modern process where they can convert all types of biomass such as liquid, gaseous and solid into the liquid fuels. The by-product produced from this process is tar and ammonia. One of study claimed that the high grade of synthetic gas is often characterized by low N_2, high H_2 content, low tar levels and high heating value (Doherty et al., 2013).

Recent studies have proved that chicken manure have a potential to be used as bio-methanol production by using gasification. However, the process performance of bio-methanol production was expensive, long residence time and no change in product gas content. This research aims to investigate the potential of chicken manure waste in three different process which is gasification, pyrolysis and combination process. This is due to previous study only use one process which is gasification instead of doing other additional process that can researcher analyze which process is much better in chicken manure simulation only used one process which is gasification.

The studies are simulated by the Aspen Plus® simulation because the availability of the reactor that can be used for gasification process and pyrolysis process compared to another simulator programs such as Super Pro Designer which is are more limited in their unit procedure. This simulation also has been widely used by many researchers for the prediction of the chemical composition of the gas produced in function of gasification process. Since the Aspen Plus® simulation has a large database of the chemical compounds, it will be applicable to stimulate the bio-methanol production which involves the chemical and thermodynamic reactions. The simulation also requires the economic assessment in order to estimate the cost and profit that will be gained after the scaling up process. It also would be used to evaluate which feedstock much worth in the production of bio-methanol.

1.3 Objectives

This research is purposed to achieve the following objectives:

1. To simulate the difference processes of bio-methanol production from chicken manure using Aspen Plus®simulation.
2. To evaluate and compare the profitability for the difference processes based on economic assessment.

1.4 Scope of Study

In this study, the scope will be divided into three sections. Firstly, is the literature review on each process. The selection of operating mode and raw materials, operating conditions such as process time, temperature, reaction kinetic and pressure required for each unit procedure, and parameters which include efficiency and productivity were able to be determined. Secondly, is about the process model, development and simulation by using Aspen Plus®simulation.as there have three different processes. The last one is on economic evaluation which included capital expenditure, operating expenditure, payback time.

1.5 Significance of Study

The significant of this study is to differentiate between 3 processes in bio-methanol production which is pyrolysis, gasification and combination. To get the most suitable process for bio-methanol production. Besides that, the Aspen Plus simulation will be used to obtained the production and economical evaluation. The constant will be fixed and purity is assumed up to 70%.

CHAPTER 2

LITERATURE REVIEW

2.1 Bio-methanol

Methanol is a simplest alcohol compared to ethanol. It is conventionally produced from methane (natural gas) with a chemical formula CH3OH. Methanol can be produced from lignocellulose renewable sources, municipal wastes, carbon dioxide and sewage sludge. Regardless of the bio-methanol technologies that were used to produce bio-methanol, need to undergo several treatments in which normally involves the pre-treatment, gasification, gas reformation and methanol synthesis. The chemical catalyst that commonly used in the reactor for methanol synthesis is copper oxide, zinc oxide or chromium oxide. The synthetic gas produce after the gasification process plays a major role as an intermediate in production of methanol.

Natural gas approximately 78% of the total cost of methanol production in Western European methanol full plant production. In fact, the total cost of methanol production from carbon dioxide was higher which is 500–600 €. However, the cost of producing methanol from biomass is approximately 300–400 € of methanol (Lundgren *et al.*, 2013). Then, biomass processing is the most cost effective of the processes that have been developed for the production of methanol from renewable sources. The production cost of bio-methanol is lower than that of light oil, which is used in power stations (Bula, 2012).

The enormous amount of fossil fuels burned worldwide is increasing the production of acid rain and photochemical smog, which are continuously increasing the amount of atmospheric carbon dioxide that is resulting in global warming. A parallel problem is the depletion of fossil fuels, although in recent year new oil resources have been discovered. The partial or complete substitution of fossil fuels with the direct or indirect use of solar energy is the most attractive option for stabilizing Earth's climate. The other possible option is nuclear energy, but this choice presents serious drawbacks. Nuclear fuels are non-renewable energy resources, and also if a plant failure were to occur, large amounts of radioactive material could be released into the environment. In addition, nuclear waste remains radioactive for thousands of years, and its storage is very complex and dangerous. The use of renewable biofuel is attractive because it is based on solar energy, and it reduces carbon dioxide by photosynthesis. The combustion of biomass-derived fuels does not increase the total global CO2. Moreover, liquid fuel, in particular ethanol and methanol, represents an alternative to petroleum fuels for different engines and is easy to store and manage. The carbon cycle of bio-methanol is shown in Fig. 2.1, adapted from (Olah *et al.*, 2006).

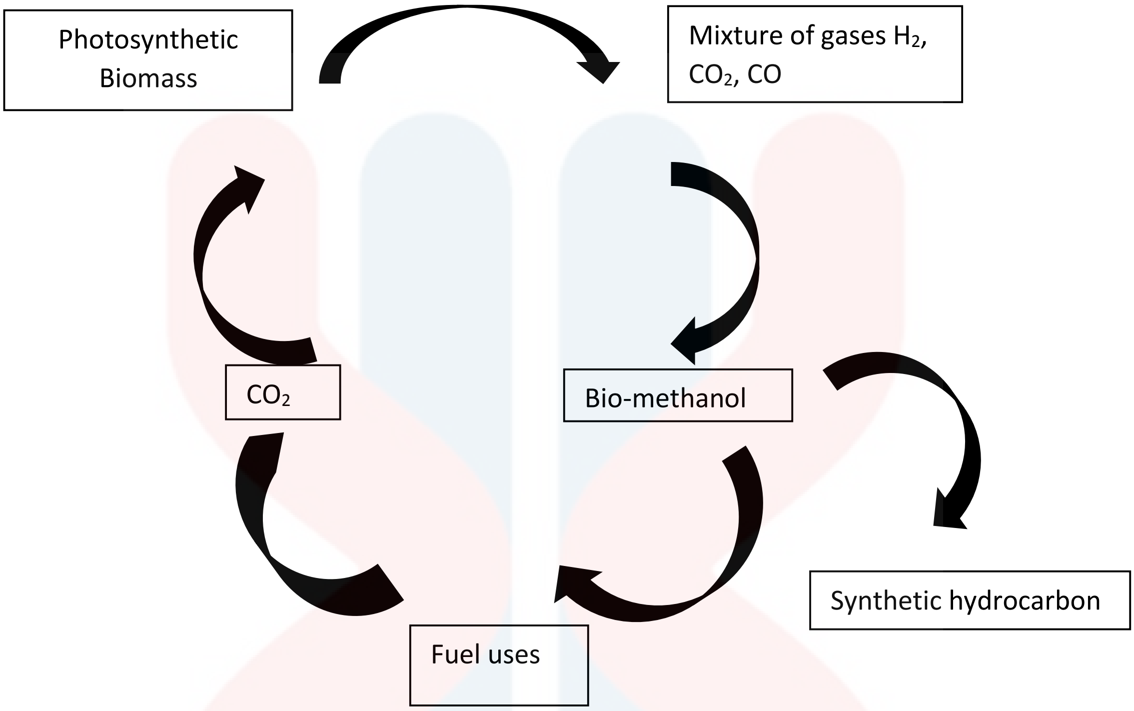


Figure 2.1: The carbon cycle of bio-methanol.

Source: Olah *et al.* (2006).

Figure 2.1 shows the million metric tons for methanol demand as much as 90% of the total of demand and as such access to low cost feedstocks is key to overall methanol economics. The primary feedstock for methanol has been natural gas, representing as much as 85% of installed global capacity and historically methanol production primarily existed in Europe and North America. Other regions with access to low cost natural gas have also seen a surge in methanol capacity additions, such as the Middle East, Africa and South America. With the growth in Asia demand for methanol and the country's rich coal reserves, the industry has seen a sharp rise in coal based methanol production beginning in the early 2000. Currently coal based methanol capacity represents around 35% of installed global capacity. So, it's can be assume methanol demand rapidly increase used from 2010 to 2020.

In 2001, approximately 6.5 billion tons of carbon was emitted into the atmosphere as carbon dioxide and approximately 38% of this was emitted during the production of electricity. The consumption of electricity, which increases significantly every year, is projected to increase by 44% from 2006 to 2030. By 2050, road transportation is expected to be the largest contributor to greenhouse emissions. In Europe, the renewable energy target for 2010 was approximately 6.75% of the transport fuels sold, and this target will likely increase to 12% in 2020. If this trend continues, the renewable energy target for the transport fuels sold should reach 30% by 2025. Compared with the gasoline and fossil diesel demands, biofuels are expected to constitute 80% of the total demand (Ben-Iwo *et al.*, 2016).

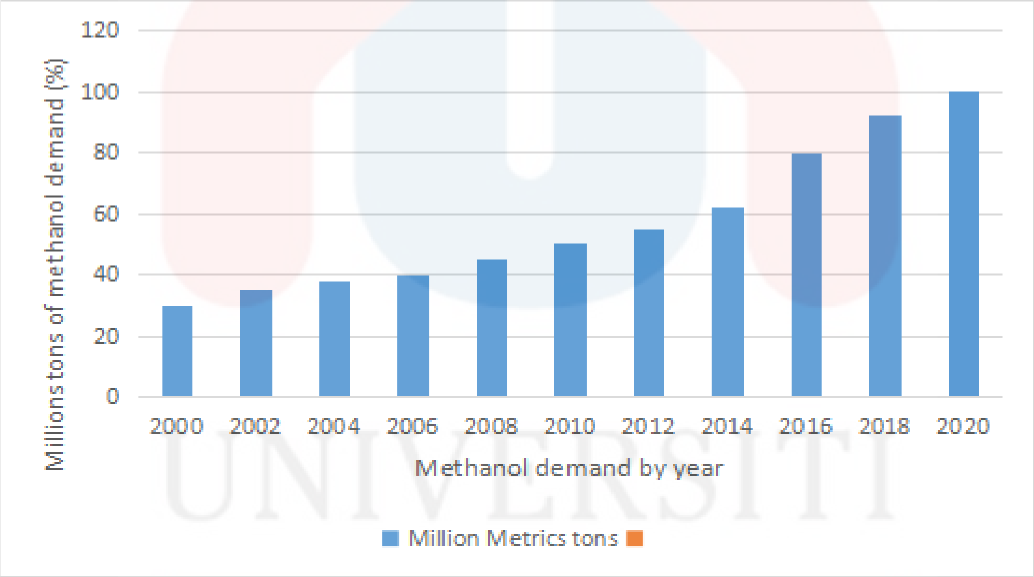


Figure 2.2: World Methanol Demand.

Source: Marc (2016).

2.1(a) Bio-methanol Sources

The production of bio-methanol can be finish from varieties of biomass. Biomass refers to organic and carbonaceous materials that store sunlight via photosynthesis in the form of mass energy which in chemical energy. Biomass can be divided into five main categories which is wood from natural forests, agricultural residue, energy crops (i.e., those cultivated exclusively for fuel production), urban solid waste/sewage, and food waste, as illustrated in Figure 2.3, adapted from (Shamsul *et al.*, 2014).

Biomass used as feedstock for biofuel production can be classified as first, second, and third generation biofuel. First generation biofuels are those produced directly from food crops. For example, crops such as wheat and sugar have been used in bioethanol production by fermentation, and oilseed rape has been one of the main raw materials in biodiesel synthesis. Second generation biofuels its was improvement from the first generation of biofuel , primarily because it's were produced from nonfood crops. The example were wood, organic waste, food crop waste, and specific biomass crops. Finally, third generation biofuels were a big improvements in their production plant, which is increasing the total yield of the process. The use of second and third generation biofuels helps to decrease the amount of food products devoted to fuel production, helps to decrease greenhouse gas emissions, and increases the selection of possible feedstock (Pirola *et al*.,2018). Figure 2.3 show the bio-methanol sources that has been used.

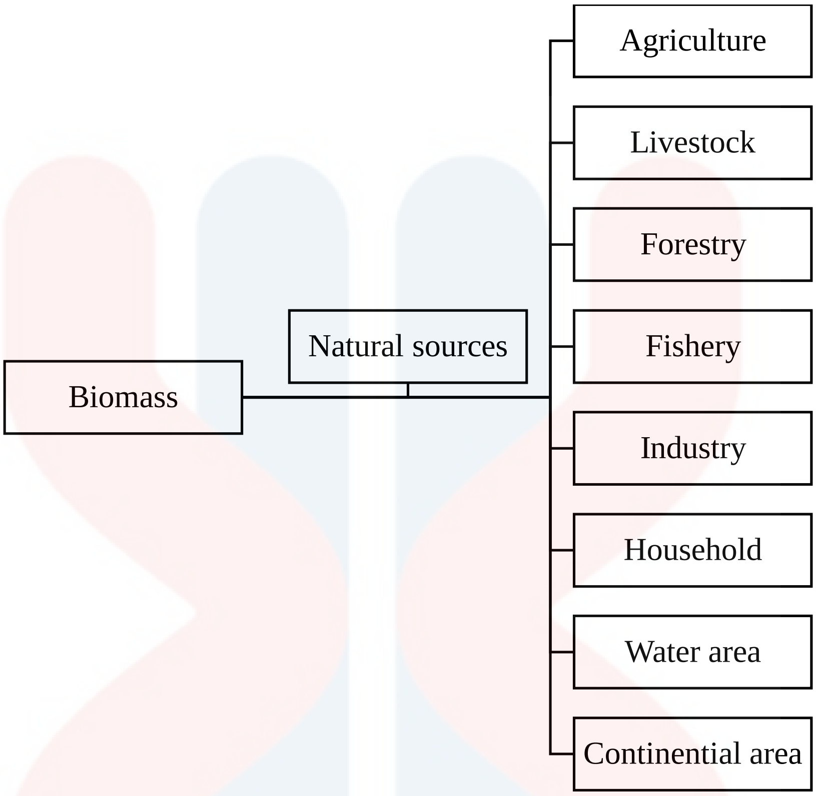


Figure 2.3: Types of Biomass Used for Bio-methanol Production.

Source: Shamsul *et al.*, (2014).

The poultry industry is growing rapidly along with human consumption, which results in large quantities of animal wastes to be treated. Inappropriate management of manure may cause numerous undesirable consequences. Moreover, ammonia and greenhouse gases, methane and carbon dioxide, emitted from the waste storage units cause air pollution problems (Böjti *et al.*, 2017).

2.2 Chicken Manure

Chicken manure is a heterogeneous mixture of chicken droppings, waste beddings, waste food, and feathers from the coops. Chicken manure is characterized by high nitrogen, phosphorus and ash content which makes it a lower grade feed compared to conventional biomass such as wood (Hussein et al. 2017). Poultry litter compared to the other wastes from animals produced in confinement systems presents some advantages due to inclusion of the material used as litter which raises the carbon concentrations. Table 2.2 shows the chemical composition data of animal wastes with regards to their potential for use as fuel for thermochemical processes.

Table 2.1: The comparison of mean composition of animal manure.

Parameters %	Cattle Manure	Horse Manure	Pig Manure	Hen Manure	Poultry Litter
Volatiles	53.1	-	73.0	-	48.8
Fixed Carbon	4.6	-	3.4	-	-
Ash	42.3	10.9	23.6	10.6	34.3
Moisture	24.6	19.0	-	39.7	19.3
Cellulose	32.7	37.8	16.6	-	-
Hemicellulose	24.5	32.4	-	-	-
Lignin	42.8	19.6	1.6	-	-
C	21.9	-	12.3	24.8	27.8

H	3.6	-	1.7	3.8	5.7
N	2.3	-	0.9	7.3	4.3
O	20.8	-	-	17.0	-
S	1.1	-	0.1	3.0	1.1

Source: Maerere (2001).

It should be noted that the chemical composition of the various animal wastes is variable considering that many factors affect its composition, namely: diet and age, race, climate conditions, production level and others. In the case of poultry litter, highlighted are other factors such as litter material used to serve as bedding for the birds, the use of acclimatization in aviaries, such as ventilation and exhaustion, the number of reuses, management during production and management of wastes on the property. Poultry litter presents high reactivity and can be used as fuel biomass because it is rich in volatile material. Furthermore, it can be observed that the poultry litter has a low amount of fixed carbon, therefore combustion in the solid phase may become insignificant. This occurs due to high volatile of the compounds in this phase, requiring lower temperatures for the thermal processes. However, moisture of the litter is the most important parameter and must always be correlated with the content of volatile material in order to establish the optimum firing temperatures. Based on this, (Abelha, 2012) identified that at a humidity of 11% the ignition temperature for an adequate thermal process would be 580 °C for 2 s, while for in natural litter with 20% humidity, this value rose to 620 °C for 8 s. This is important since it indicates greater energy consumption to release the energy content of poultry litter, meaning higher costs, more sophisticated equipment and loss in the energy balance.

Although literature regarding the use of poultry litter as a fuel is still very incipient, its viability as biomass may be verified. This considers that there is knowledge of its composition, purpose of use, the concern of not generating pollutants, harmful emissions and unwanted ash resulting from poorly sized processes. Energy conversion of poultry litter may occur via thermochemical transformations such as direct combustion, gasification and pyrolysis (Dalólio *et al.*, 2017).

2.3 Model Development for Bio-methanol Production

2.3(a) Gasification Process

Gasification is the thermochemical process of converting a solid or liquid raw material into a gas with fuel characteristics, by its partial oxidation at intermediate temperatures. The thermochemical reactions occur at temperatures above those recommended in fast pyrolysis processes and below those recommended in combustion processes. In the gasification process restricted amounts of oxygen are supplied in its pure form or simply as atmospheric air, depending on the final use of the gas. The material may also be gasified in the presence of controlled amounts of superheated steam. This steam is the gasification agent needed to produce a gas mixture known as synthesis gas, rich in hydrogen and carbon monoxide. In general, the produced synthesis gas has many practical applications, from combustion in internal combustion engines and gas turbines for the generation of mechanical and electric energy, as well as direct heat generation (Dalólio *et al.*, 2017). Considerable studies have been carried out on biomass gasification on the catalytic effects, and thermochemical parameters such as temperature, heating rate, gasifier type and feedstock (Hussein *et al.*, 2017).

2.3(b) Pyrolysis Process

Pyrolysis may be defined as the thermal degradation of organic material in the partial or total absence of an oxidizing agent, or even in an environment with an oxygen concentration capable of preventing intensive gasification of organic material. It can be split between slow and fast pyrolysis, where that which modifies each process are the heating rates during the biomass decay time and the temperatures used. Fast pyrolysis takes place at elevated temperatures, around 900 °C, producing fuel gas and small amounts of charcoal, about 10%. Slow pyrolysis usually occurs within the temperature range of 300–450 °C, until beginning the gasification system with the aim of producing charcoal, bio-oil and synthesis gas. In this process there is greater coal production, with the higher concentration of carbon (Dalólio et al., 2017).

2.3(c) Integrated Gasification and Pyrolysis Process.

The model of the integrated biomass pyrolysis and gasification process consisting of pyrolysis, gasification, auto-thermal reformer (ATR) and water gas shift reactor, is developed in Aspen plus simulation, as explained in their previous work. Firstly, the biomass is going in pyrolysis, and some volatile components. After that, hydrogen, carbon monoxide, light hydrocarbons and bio-oil are released. The remaining char is further used as a gasification process. Finally, the product gas from both the pyrolysis and gasification units is combined and moved to ATR to remove tar before it is sent to adjust the H_2/CO ratio at the water gas shift reactor. Delivering the oxygen at approximately atmospheric pressure. The pyrolysis of rice straw feedstock is explained by an empirical model. During pyrolysis, some volatile components are removed and char is remained. The raw pyrolysis gas containing volatile components is later cooled down to the temperature of 150 ^oC to separate the bio-oil, which is assumed to be a mixture of phenol and water, from the pyrolysis gas. The remaining char is used as a gasification process to produce additional synthesis gas which is mixed with pyrolysis gas afterward. Normally, the operating temperature of the pyrolysis reactor is controlled in a range of 400-700 ^oC. The gasification model is divided into two parts; the first one is the combined pyrolysis and oxidation reactions, which are relatively fast and the thermodynamic equilibrium is assumed, and the second one describes the low reaction rate of char gasification reactions which the reaction kinetic is therefore considered. In this study, it is supplied to the gasifier until 98% of char conversion is achieved. The operating condition is set at 780 ^oC and 1 atm. Moreover, a thermal self-sufficient operation is considered. The H_2/CO ratio of synthesis gas is adjusted to be a value of two which is essential for the synthesis of several chemicals. In the water gas shift reactor, steam is supplied as a reactant of the water gas shift reaction. To determine the product gas composition, the chemical equilibrium of this reaction is assumed. Lastly, the production of bio-methanol will be produce. (Karittha, 2017).

2.4 Kinetic Reaction in Bio-methanol Production

Process model requires kinetics of reaction as it provides parameters useful to predict extent of the reaction at any time under particular conditions. Various kinetic studies have been conducted to describe the kinetics of bio-methanol production using different catalysts and process gasification. The kinetics data collected are normally dependent on predetermined factors such as types of reactor used, feedstock, and types of catalysts used, as well as reaction conditions such as reaction temperature and catalyst concentration (Hernandez *et al.*, 2018). The equation from 2.1 to 2.2 show the major representative governing reactions (considering C to represent the biomass) that occur during gasification (Hussein *et al.* 2017), whereas Table 2.2 gave the kinetics for the methanol synthesis (Kempegowda, 2012).

Water gas shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$ (2.1)

Water gas reaction: $C + H_2O \leftrightarrow CO + H_2$ (2.2)

Table 2.2: Kinetics used for the methanol synthesis.

Kinetic Parameters	Reaction Type	Reference
K_A= 1.16 X 10^{-9} EXP $\left[\frac{-7.01\times10^3}{R}\left(\frac{1}{T}-\frac{1}{523}\right)\right]$	CO hydrogenation reaction	Jansen W,2007
K_B= 2.82 X 10^{-5} EXP $\left[\frac{-2.7\times10^2}{R}\left(\frac{1}{T}-\frac{1}{523}\right)\right]$	Water gas shift reaction	Dry ME, High quality diesel via the Fischer–Tropsch process, 2002
K_C= 1.15 X 10^{-6} EXP $\left[\frac{-1.19\times10^2}{R}\left(\frac{1}{T}-\frac{1}{523}\right)\right]$	CO2 hydrogenation reaction	Dong Y and Steinberg M, Hynol, 2009
K_{CO}= 4.96 X 10^{-8} EXP $\left[\frac{9.93\times10^3}{R}\left(\frac{1}{T}-\frac{1}{523}\right)\right]$	CO shift reaction	Vamvuka D, 2010
K_{CH30H}= 1.41 X 10^{-3} EXP $\left[\frac{6.05\times10^3}{R}\left(\frac{1}{T}-\frac{1}{523}\right)\right]$	Methanol synthesis	Newsome D.S., 1980

Source: Kempegowda (2012).

2.5 Simulation using Aspen Plus® Software

Aspen Plus® is a problem-oriented process simulation program that is used to facilitate the physical, chemical and biological calculations. It is often exploited to model chemical processes that involve solid, liquid and gaseous streams under defined condition by using mass and energy balance equations and phase equilibrium database. Over the years Aspen Plus® has made model creation and upgradation easier and small sections of complex and integrated systems can be created and tested as separate modules before they are integrated. Aspen Plus® is multipurpose and is used to simulate variety of processes, for example, methanol synthesis, indirect coal liquefaction processes, integrated coal gasification combined cycle (IGCC) power plants, atmospheric fluidized-bed combustor processes, compartment fluidized-bed coal gasifiers, coal hydrogasification processes and coal gasification simulation. Modelling biomass gasification, pyrolysis and integrated gasification and pyrolysis on Aspen Plus® platform has gained momentum in recent years (Kaushal *et al.*, 2017). Since to conduct the trial plant is very costly and many test needed to predict the optimal condition for maximizing the yield of bio-methanol, Aspen Plus® is become a beneficial tool in determining the parameter that can affect the bio-methanol production.

2.5(a) Economic Evaluation of Bio-methanol Production

Thomas (2008) evaluated the costs involved in producing 500,000 ton per year of bio-methanol from. Consequently, the main focus of this work was to investigate the feasibility of methanol production from animal manure combined with co-generation by utilization of a SOEC. Two cases were chosen: A farm scale plant processing 18,500 ton/year and a large scale plant processing 500,000 ton/year. Different process schemes were investigated on the large scale plant using either a steam reformer or catalytic partial oxidation reactor to convert biogas into a more desirable synthesis gas, which could be synthesized into methanol. On farm scale, only partial oxidation was considered due to the fast kinetics and therefore a more compact and simple system. For all plants the possibility of using a SOEC to add H2 and CO was present. All scenarios presented have been based on a 2010 level regarding the electricity price. As it has been shown, especially the large scale plant based on partial oxidation is sensitive to the electricity price. Future production prices have been estimated by changing the electricity price from the 2010 level, to the projected prices presented for the two 2050 levels from table 10.5 on page 66. The results are shown in table 12.1. The production price of the farm scale plant increases by approximately 12 %. Due to the increase and the higher sensitivity on the electricity price for the large scale POX based schemes, the production price increases by more than 20 %. It is now evident, that at 2050 levels the production price is almost identical for the two large scale plants.

Table 2.3: Optimization results without SOEC.

	Farm Scale	**Large Scale Pox**	**Large Scale Sr**
Total Annual Expenditure (Kg/Year)	2,908,977	27,198,580	28,276,238
Annual Methanol Production (Kg/Year)	706,495	14,368,320	11.825,417
Methanol Price (Usd/Ton)	735.26	338.02	426.99
Co_2 Purge (%)	80	80	72

Source: Thomas (2008).

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

Aspen Plus® simulator is a convenient and powerful tool for determining process characteristics and their dependence on design and operating variables particularly in bio-methanol production (Nasir *et al.* 2013). In this study, Aspen Plus® version 12.1 was used as computer aided simulation software to model the three difference processes involved in producing bio-methanol such as gasification, pyrolysis and integrated pyrolysis and hydrogasification using chicken manure as a feedstock.

Process simulations were started with the determination of the chemical components and selection of suitable thermodynamic model. Subsequently, unit operations, operating conditions, input conditions and plant capacity must be specified. Most of the property data of components were available in the software library. However, if certain component property was unavailable in the simulator library, registration of the component can be made by introducing the component as a new chemical component (Nasir *et al.*, 2013). Next, process economics were analyzed using Aspen In-Plant Cost Estimator, since it has been used for over 30 years in commercial plants and engineering designs, and provides more accurate estimation (Seider *et al.*, 2004). The plant annual capacity was specified at 50,000 kg per year of bio-methanol production based on 8000 operating hours per year.

3.1(a) Composition of Chicken Manure

As can be seen in Table 3.1, the composition of chicken manure was taken from Hussein et al. (2017). Chicken manure was modelled according to the proximate and ultimate analysis. Proximate analysis were volatile matter, ash content and fixed carbon of chicken manure composition gave 65.56 wt% dry, 21.65 wt% dry and 12.8 wt% dry, respectively. Besides, proximate analysis gave the valuable information of chicken manure in terms of combustion and gasification. On the other hand, the ultimate analysis contains of carbon, hydrogen, nitrogen and oxygen compositions. It can be found that the highest composition was observed in carbon (35.59 wt% dry), whereas the sulfur gave the lowest composition amounted 1.45% wt% dry. Basically, the ultimate analysis is crucial in estimating the ultimate environmental impact and heating values of certain biomass. In this study, bio-methanol was considered as the product of gasification, pyrolysis or integrated pyrolysis and hydrogasification reactions.

Table 3.1 Composition of Chicken Manure using proximate and ultimate analysis.

Types Of Analysis	Items	Weight Dry (%)
Proximate	Volatile content	65.56
	Ash Content 550 °C	21.65
	Fixed Carbon	12.8
Ultimate	Carbon	35.59
	Hydrogen	4.57
	Nitrogen	4.98
	Sulfur	1.45
	Oxygen	35.52
	HHV (in MJ/kg)	13.15

Source: (Hussien et al. 2017).

3.1(b) Reaction Kinetic Model

As described earlier, there are three bio-methanol production processes were simulated using chicken feedstock as feedstock. The first process, named pyrolysis, the second process, named gasification and third process, named integrated pyrolysis and hydrogasification. The reactions were summarized in Table 3.2.

Table 3.2: Summarized Reaction Kinetic Model.

Types Of Reaction	Reactions	Kinetic Parameters	Reference
Gasification	400-550°C ,500kPa	k_A= 1.16 x 10^{-9} exp $\left[\frac{-7.01\times10^{3}}{R}\left(\frac{1}{T}-\frac{1}{523}\right)\right]$	Jansen W,2007
Pyrolysis	500-700 °C, 100-200kPa	k_A= 1.16 x 10^{-9} exp $\left[\frac{-7.01\times10^{3}}{R}\left(\frac{1}{T}-\frac{1}{523}\right)\right]$	Jansen W,2007
Integrated Pyrolysis And Hydrogasification	500-700 °C, 5000kPa	k_B= 2.82 x 0^{-5} exp 1 $\left[\frac{-2.7\times10^{2}}{R}\left(\frac{1}{T}-\frac{1}{523}\right)\right]$	Dry ME, High quality diesel via the Fischer–Tropsch process, 2002

3.2 Process Design of Bio-methanol Production using Aspen Plus®

Figure 3.1 to Figure 3.9 were the simulation procedures for the base case simulation of bio-methanol production using Aspen Plus® software version 12.1 namely gasification process. Table 3.3 gave the details of different reactions involved in bio-methanol production.

Figure 3.1: Selection of unit operation.

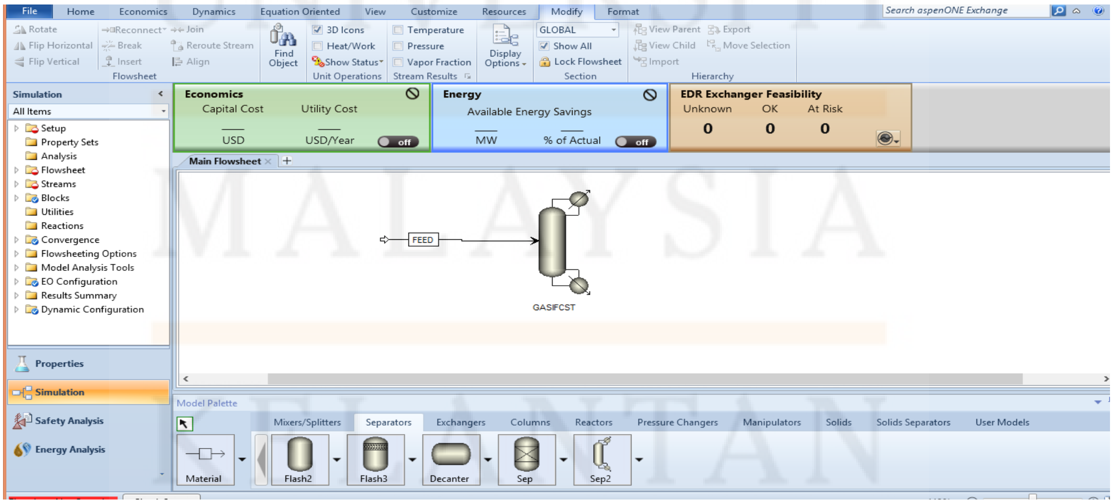
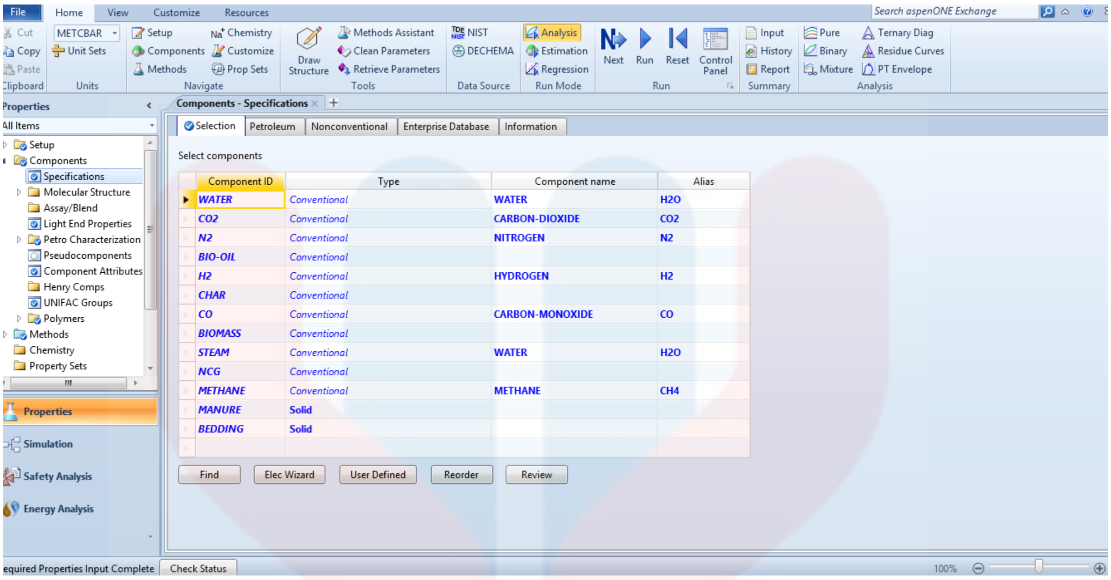


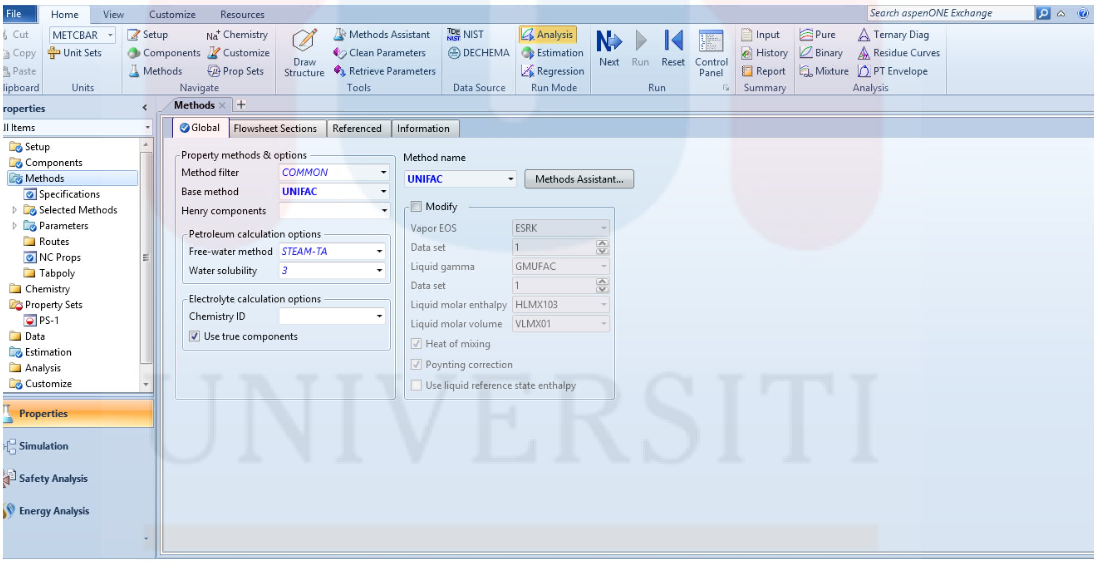
Figure 3.2: Stream added to gasification reactor (GASIFCST).



Select components

Component ID	Type	Component name	Alias
WATER	Conventional	WATER	H2O
CO2	Conventional	CARBON-DIOXIDE	CO2
N2	Conventional	NITROGEN	N2
BIO-OIL	Conventional		
H2	Conventional	HYDROGEN	H2
CHAR	Conventional		
CO	Conventional	CARBON-MONOXIDE	CO
BIOMASS	Conventional		
STEAM	Conventional	WATER	H2O
NCG	Conventional		
METHANE	Conventional	METHANE	CH4
MANURE	Solid		
BEDDING	Solid		

Figure 3.3: Selection of component involved in the simulation.



Property methods & options

Method filter: COMMON

Base method: UNIFAC

Henry components:

Petroleum calculation options

Free-water method: STEAM-TA

Water solubility: 3

Electrolyte calculation options

Chemistry ID:

☑ Use true components

Method name: UNIFAC

☐ Modify

Vapor EOS: ESRK

Data set: 1

Liquid gamma: GMUFAC

Data set: 1

Liquid molar enthalpy: HLMX103

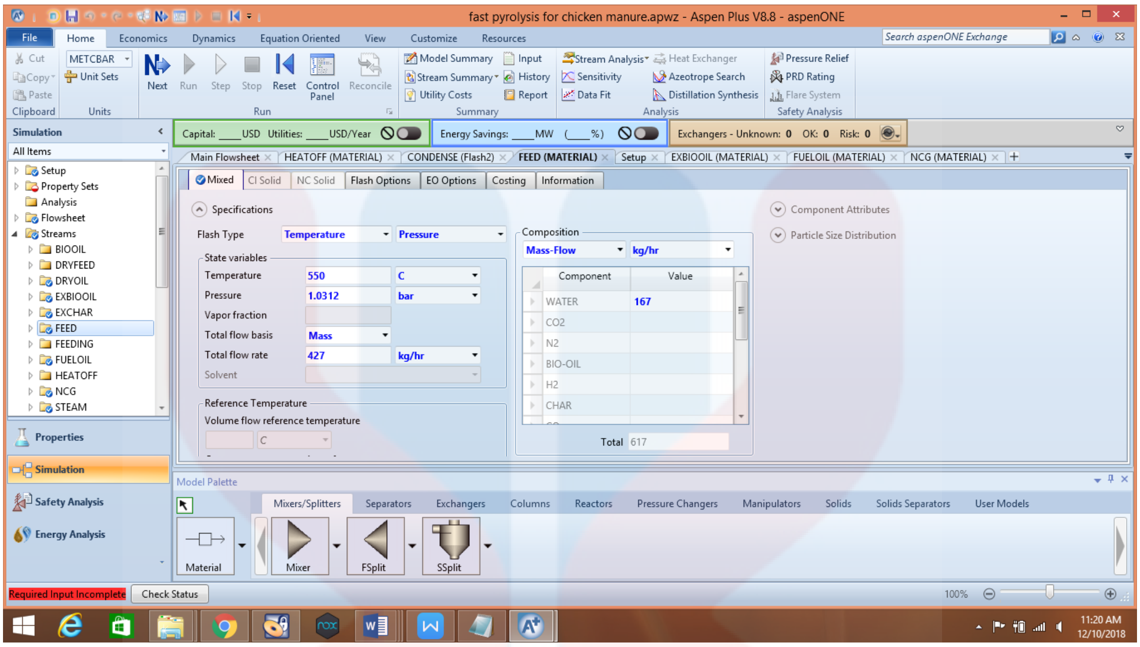
Liquid molar volume: VLMX01

☑ Heat of mixing

☑ Poynting correction

☐ Use liquid reference state enthalpy

Figure 3.4: Property method added to the simulation.


fast pyrolysis for chicken manure.apwz - Aspen Plus V8.8 - aspenONE

FEED (MATERIAL) – Mixed

Specifications

Flash Type: Temperature, Pressure

State variables

Temperature	550	C
Pressure	1.0312	bar
Vapor fraction		
Total flow basis	Mass	
Total flow rate	427	kg/hr
Solvent		

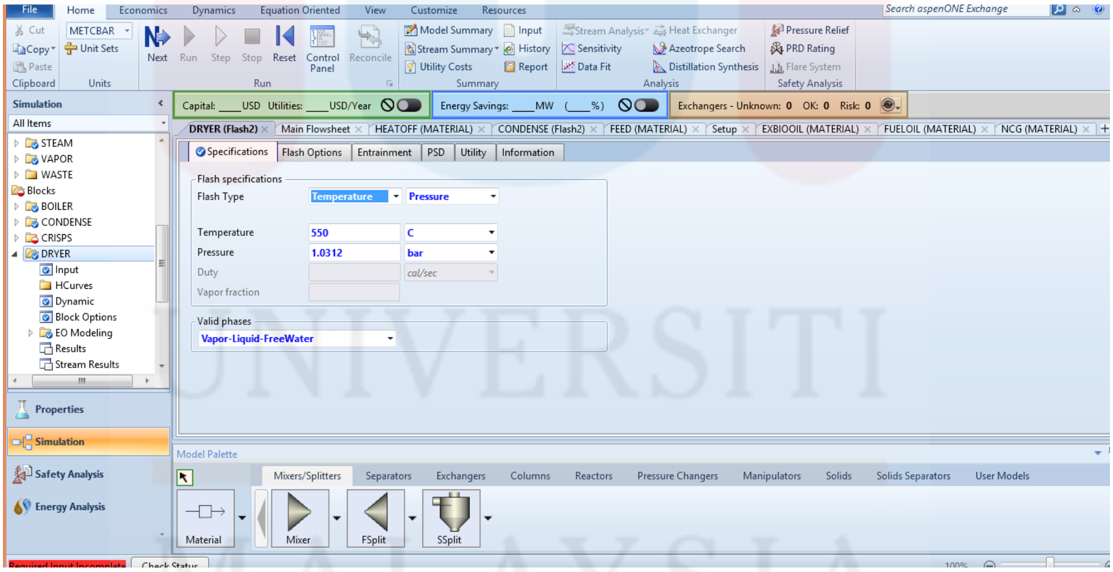
Composition: Mass-Flow, kg/hr

Component	Value
WATER	167
CO2	
N2	
BIO-OIL	
H2	
CHAR	

Total 617

Required Input Incomplete

Figure 3.5 Specification for stream properties.


DRYER (Flash2) – Specifications

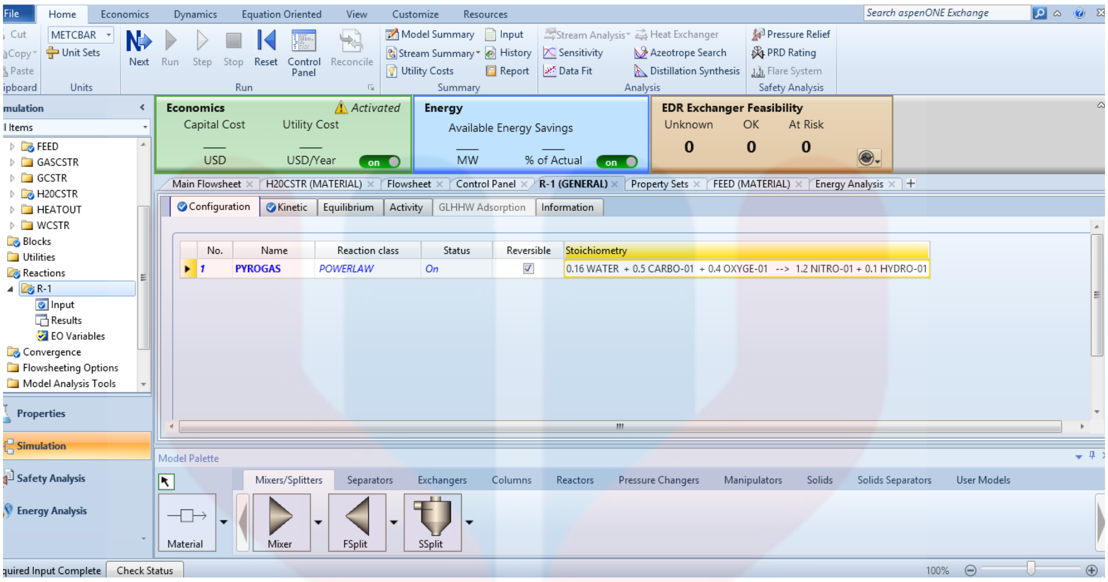
Flash specifications

Flash Type: Temperature, Pressure

Temperature	550	C
Pressure	1.0312	bar
Duty		cal/sec
Vapor fraction		

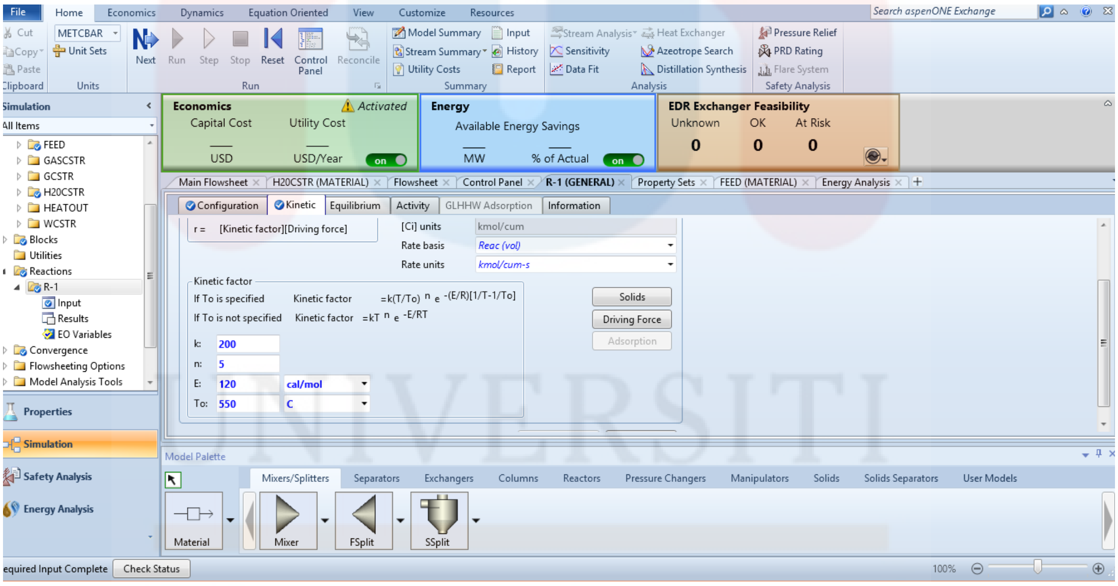
Valid phases: Vapor-Liquid-FreeWater

Figure 3.6: Specification for GASIFCST equipment.



No.	Name	Reaction class	Status	Reversible	Stoichiometry
1	PYROGAS	POWERLAW	On	☑	0.16 WATER + 0.5 CARBO-01 + 0.4 OXYGE-01 --> 1.2 NITRO-01 + 0.1 HYDRO-01

Figure 3.7: Reaction for simulation process.



r = [Kinetic factor][Driving force]

[Ci] units: kmol/cum

Rate basis: Reac (vol)

Rate units: kmol/cum-s

Kinetic factor

If To is specified Kinetic factor $=k(T/To)^{n} e^{-(E/R)[1/T-1/To]}$

If To is not specified Kinetic factor $=kT^{n} e^{-E/RT}$

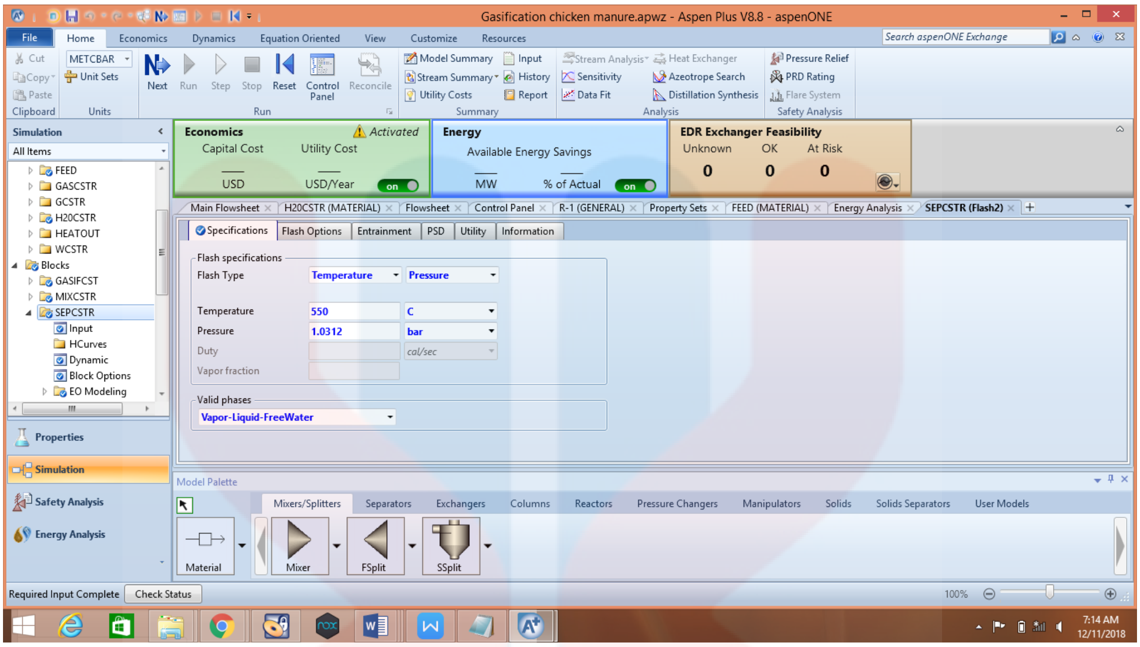
k: 200

n: 5

E: 120 cal/mol

To: 550 C

Figure 3.8: Reaction kinetic expression for reaction involved.



Flash specifications
Flash Type: Temperature, Pressure
Temperature: 550 C
Pressure: 1.0312 bar
Duty: cal/sec
Vapor fraction:
Valid phases: Vapor-Liquid-FreeWater

Figure 3.9: Specification for separator (SEPCSTR).

3.2(a) Gasification Process

Figure 3.10 shows the flowsheet of bio-methanol plant by gasification process. Beginning at the left, the chicken manure and water were mixed in the mixer and the products were fed into the gasification reactor with the operating temperature and pressure, 550 °C and 500kPa, respectively. The gasification reactor mainly continuous stirred tank reactor was selected to carry out the gasification reaction. Then, the gasification products were fed into a separator (SEPCSTR) to separate the methanol from the water, which methanol was finally obtained as distillate.

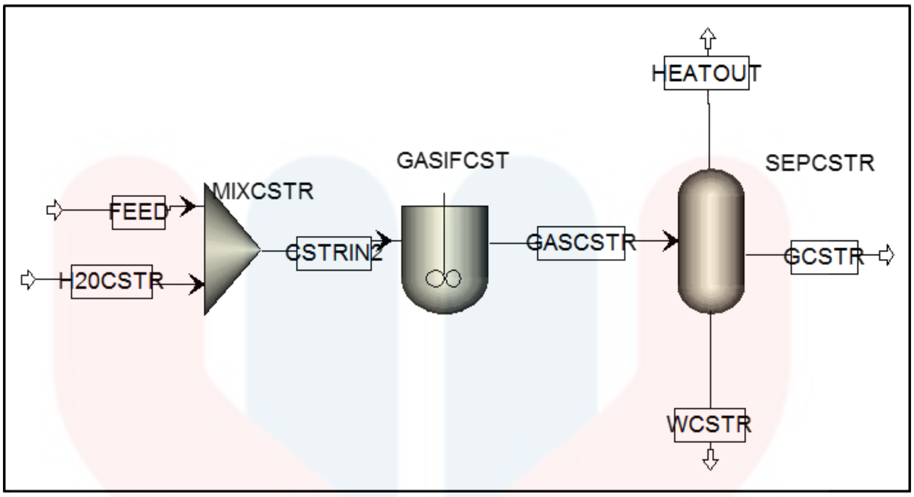


Figure 3.10: Flowsheet of bio-methanol plant by gasification process using chicken manure.

3.2(b) Pyrolysis Process

A detailed of pyrolysis process of bio-methanol production was given in Figure 3.11. Beginning at the left, the chicken manure and water were mixed in the mixer and the products were fed into the dryer reactor with the operating temperature and pressure, 500 °C and 200kPa, respectively. From here its begin the heat to ensure self-sufficient a fraction of bio-oil was combusted. After that, the feeding will store first and enter Combustion Reduction Integrated Pyrolysis system (CRISPS) because this system avoid external energy use for the endothermic pyrolysis reactions. Then, its going to non-condensable gas (NCG). The NCG were heated using combustion gases from the CRISPS. After that, the stream is split for use as a fluidizing gas for the pyrolysis reactor. Lastly, the pyrolysis products were fed into a Condense to separate the methanol from the water, which methanol was finally obtained as distillate.

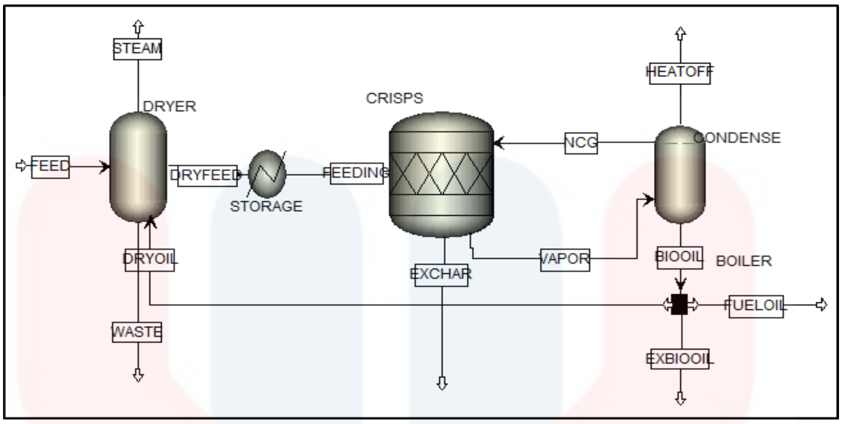


Figure 3.11: Flowsheet of bio-methanol plant by pyrolysis process using chicken manure.

3.2(c) Integrated Gasification and Pyrolysis Process

A detailed process model using Aspen Plus has been developed as shown in Fig. 3.12 to produce high quality hydrogen-rich syngas and CHP. Figure 3 shows the schematic diagram of gasification process using chicken manure. Beginning at the top, feed (chicken manure) will enter the reactor. The products of pyrolysis of organic waste in the temperature range 500–700◦C consist of methane-rich gas called pyro gas, bio-oil consisting of various organic compounds, and char.4 A portion of the char and pyro gas will be burnt. The other parts of the pyro gas [CO_2 (19.6%), CO (35%), CH_4 (20.4%), H_2 (16.3%), C_2H_4 (8.7%)] together with recycled off-gases from the methanol process, and combined with crude glycerol waste from the first generation biodiesel factories as well as condensed bio-oil mixed with char from the pyrolysis, are hydro-gasified at 800 ◦ C to produce hydrogen-rich gas. For the last stage, methanol process proposed in this study produces methanol by a catalytic process at low temperature and pressure, as described in the previous section. Several types of methanol synthesis reactors are used in production plants. Then its go through separator for production of methanol.

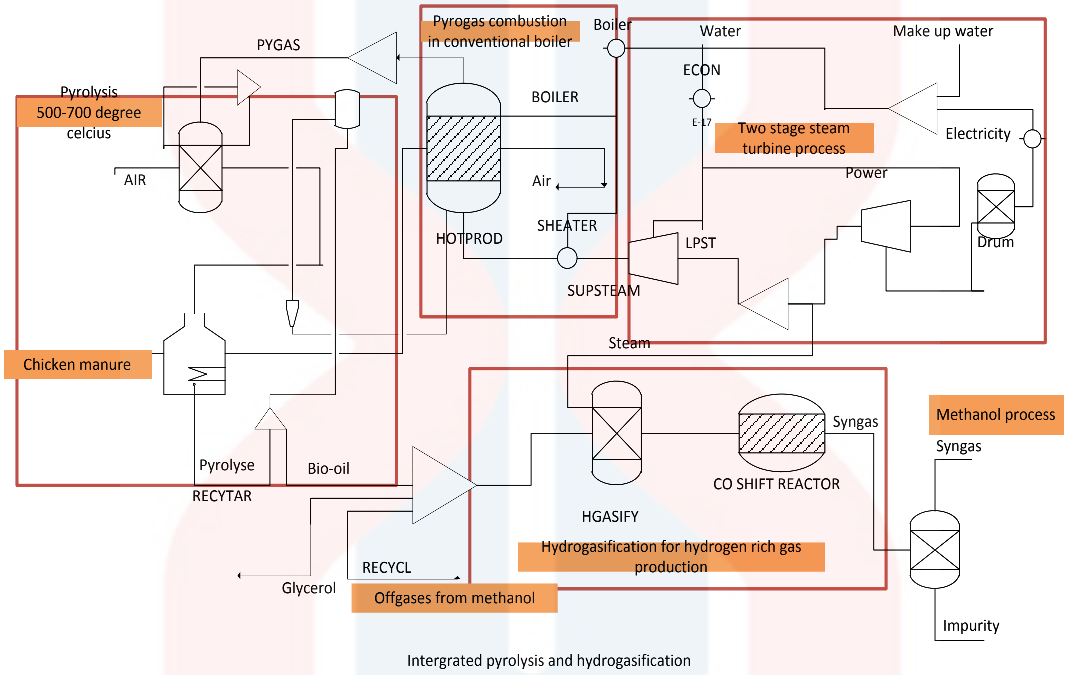


Figure 3.12: Flowsheet of bio-methanol plant by integrated gasification and pyrolysis process using chicken manure.

3.3 Economic Assessment

Since each process was capable of producing bio-methanol, it was of interest to conduct an economic assessment to determine process viability and determine if any one process was advantageous over the others. As with the sizing calculations, all the economic calculations were performed using Aspen In-Plant Cost Estimator, since it has been used for over 30 years in commercial plants and engineering designs, and provides more accurate estimation (Seider *et al.*, 2004). With this cost estimating software, users can develop detailed designs, estimates, and schedules with minimal project outlines.

Other than that, its can help company reduce risk and uncertainty when undergoing capital and maintenance projects with the brochure (Lee *et al.*, 2011).

3.4 Methodology Development

Figure 3.13 summarized the flow chart for the development of bio-methanol production. Three stages were categorized namely stage 1 for gathering the crucial information, stage 2 for flow sheeting of three different processes using Aspen Plus® software version 12.1 and lastly, stage 3 for analyze the process which based on economic evaluation.

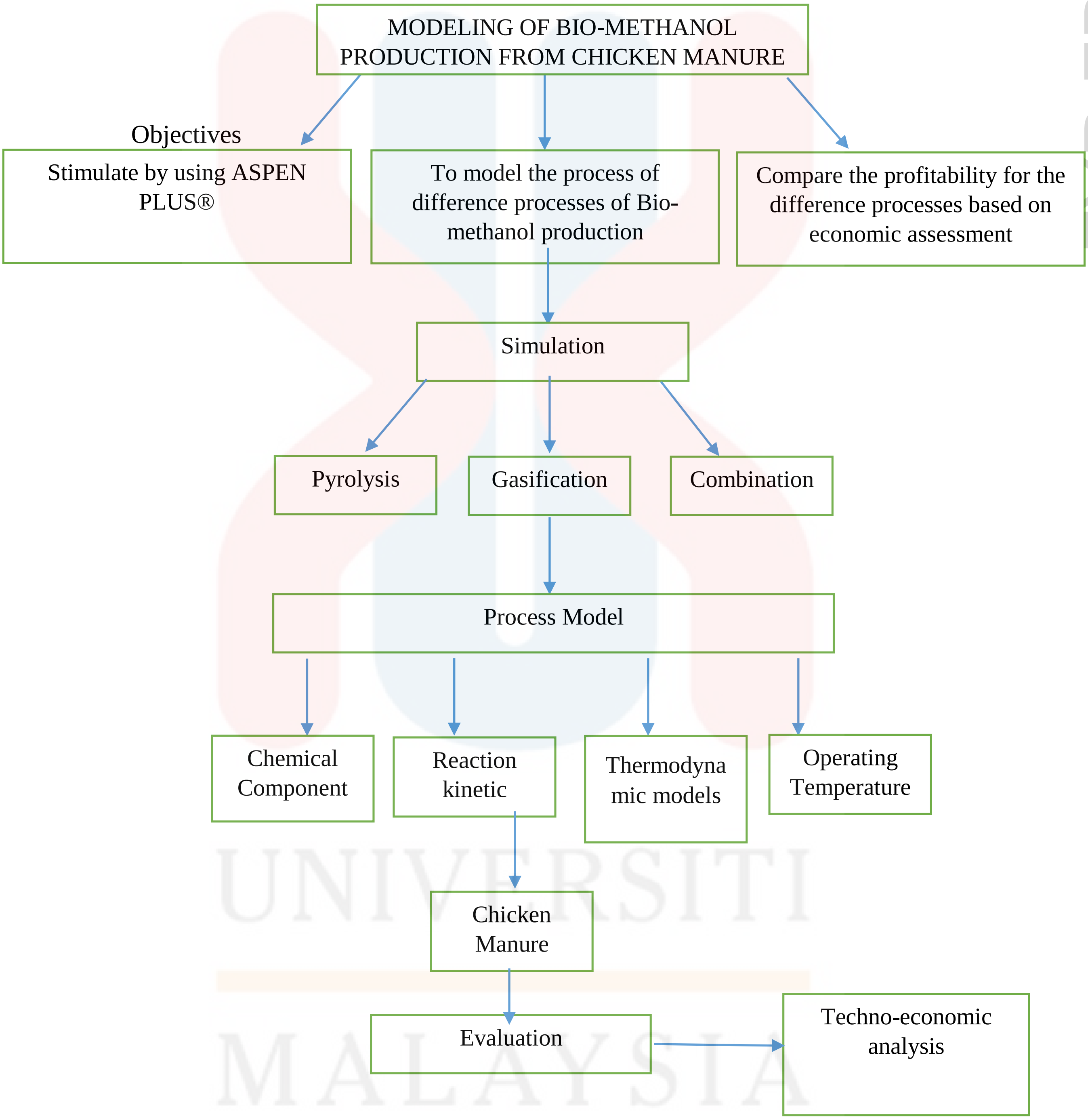


Figure 3.13: Summarized the flow chart for the development of bio-methanol production.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Operating Mode

Among batch process and continuous process, batch process was selected as the operating mode. In batch process, scheduling data is needed in order to obtain the plant batch time and stream flows are shown as per-batch. In continuous process, scheduling is not necessary, therefore plant batch time cannot be calculated and stream flows are shown as per-hour basis.

Batch process was chosen as production of bio-methanol from chicken manure by using three different processes which is gasification, pyrolysis and integrated pyrolysis and gasification. In batch process, equipment and machines handling is easier compared to continuous process which not allowed stopping or pausing when the production occurs.

4.2 Bio-methanol experiments

This experiments were performed on samples of chicken manure to provide key data for the Aspen Plus® model. All of three processes were provided with this chicken manure data. Results from the ultimate and proximate analysis of these feedstocks (listed in 2.5.1) show that the manure are consistent with data on other lignocellulosic biomass. A higher yield of bio-oil fast pyrolysis were produced from the chicken manure yield of 54 wt%, while gasification of the chicken manure produced a higher yield of syngas, especially CO and CO_2, resulting in a lower bio-oil yield of 41 wt%. Then, for the intergrated the most higher bio-oil produce which is 60 wt%.

Table 4.1: Yield distribution of components for 3 process in bio-methanol of chicken manure.

	Yield Distribution (Wt%)		
Components	Gasification	Pyrolysis	Integrated
Bio-Char	0	21.88	19.76
Water	12.08	14.25	16.30
Organic Pyrolysis Oil	0	40.13	45.16
Total Liquids	40.60	54.38	70.42
Co_2	19.60	14.84	10.12
Co	9.02	8.18	5.4
H_2	0.01	0.01	0.01

CH_4	0.94	0.71	0.98

4.3 Development of Aspen Plus® model

All of this three processes are a complex process comprising highly complex reaction steps that cannot be found in the Aspen Plus® database, so the reactants and products were modeled using a simplified chemical system which is consistent with both the atomic composition and heating value (enthalpy) of the bio-oil. The biomass feed stocks in question were defined as non-conventional components in Aspen Plus® using the experimentally determined ultimate and proximate analyses and HHV values. However, the complexity of pyrolysis oil makes it difficult to define the composition of the oil in a simulation, especially since there is no readily available thermodynamic data for most pyrolysis oil compounds. Therefore, a single representative compound, acrolein, with similar stoichiometry and HHV to the pyrolysis oils derived from the equine waste was chosen as the surrogate compound. Yan and Zhang (1999) had also previously assumed that the chemical formula of bio-oil could be described by conventional components as surrogates. The HHV of acrolein and that measured for the bio-oil produced from the equine waste were in agreement within 0.4e 2.6% . Similarly, quinone was assigned as a surrogate compound for the bio-char coproduct. Despite their fit, the drawback in selecting these surrogate compounds is the neglect of nitrogen and sulfur due to their small effects in the material and energy balances, hence the potential exits that these may under represent the true emissions profile upon combustion.

The overall stoichiometric reactions for the gasification, pyrolysis and integrated of the surrogate compounds based on yield values depicted in Table 4.1 were established as follows:

$$100\mathrm{MAN} \nearrow 0.72\mathrm{Biooil} + 0.20\mathrm{Char} + 0.79\mathrm{H_2O} + 0.34\mathrm{CO_2} + 0.29\mathrm{CO} + 0.004\mathrm{H_2} + 0.04\mathrm{CH_4};$$

$$\Delta H^0{}_r = -0.11\mathrm{MJ/kg} \qquad (1)$$

Where, MAN is a chicken manure respectively. It must be noted that the molecular weight is assigned in Aspen Plus® as 1 kg/k mol. Therefore, for example, 100 k mol Manure 100 kg Manure which yields 0.72 k mol bio-oil (acrolein).

4.4 Overall mass and energy balance

The material and energy flows for the pyrolysis, gasification and integrated system are summarized in Table 4.4 respectively. By using reactions in Equations (1) are exothermic, however the overall energy balance of the pyrolysis process is endothermic due to the heat required to raise the biomass temperatures to 480 ^{o}C which is not recovered when the products are condensed. Other than that, energy balance for integrated and gasification were higher which is recovered when the products are condensed. This result is consistent with that of other systems reported in the literature. Energy recovery in the products is predicted at 91% of the incoming biomass from three process, slightly higher. Energy losses could be accounted. Comparison of the results obtained using the surrogate compound enthalpies with the measured enthalpies suggested that the surrogate compounds selection was a good fit. Furthermore, there are a big different for gasification no boi oil because limited of unit procedure and just produce syngas for overall. For gasification process, actually its need to go through pyrolysis, if only gasification is being used the production bio-methanol will not success. Lastly, the higher energy flow was integrated pyrolysis and gasification because it has complete unit procedure.

Table 4.2: Mass balance of three processes system from Aspen Plus®.

	Gasification	**Pyrolysis**	**Integrated**
Input			
Total flow rate in (kg/hr)	429	1215	1648
Moisture in	39%	46%	50%
Ash in	5%	5%	5%
Biomass drying and feeding			
Biofuel used (kg/hr)	/	75	90
CRISPS			
Bio-oil produced	/	197	208
Bio-char produced	/	178	185
CSTR (wt%)			
CO_2	19.6	/	10.12
CO	9.02	/	5.4
Hot water generation (kg/hr)			
Fuel flow in each chamber	/	/	/
Bio-oil flow in each chamber	/	1.86	1.86

4.5 Techno-economic analysis

Economic analyses were conducted for the three process scales: pyrolysis, gasification and integrated pyrolysis and gasification. Using the mass and energy balances obtained from the Aspen Plus® model, each major piece of equipment was sized. Overall Total Installed Capital (TIC) is detailed in Table 4.5. Operating cost were determined from the material and energy balances obtained from Aspen Plus®. In this techno-economic analysis, the most higher total installed cost was integrated process. This happen because there are many operation and unit procedure in the processes, while the lower installed cost was gasification process. Unlike most biomass to power projects, the feedstock costs are insignificant for this project because the manure is produced on site while it costs $6.80/m3 to dispose of after its use. However, the economics are based on the revenue achieved through the elimination of disposal costs and diesel fuel displacement.

Based on the capital and operating costs described above, neither the gasification, pyrolysis nor the integrated process proves economical because the annual revenue is less than the annual cost of production. Then, operating cost of the year for integrated process was the most higher because of high utilities, high labor cost and annual production cost. Lastly for annual saving of the year, integrated was the highest but its only 5% different from pyrolysis process.

Table 4.3: Overall total installed capital.

	Gasification	Pyrolysis	Integrated
Total installed cost	2,260,000	3,463,000	6,012,000
Operating cost $/year			
Feedstock	0	0	0
Utilities	17,000	35,000	58,000
Labor, supplies and overheads	201,000	253,000	367,000
Administration	33,000	50,000	83,000
Depreciation	226,000	346,000	420,000
Annual production cost	477,000	684,000	890,178
Annual saving $/year			
Manure disposal	22,000	61,000	90,000
Diesel displacement	0	191,000	300,000
Co-product credits	6000	18,000	25,000
Annual revenue	110,000	268,000	312,000

4.6 Methanol Production Price

The methanol price is calculated from the results presented above and the annual production of methanol presented in table 4.3. Even though the gasification based on continuous stirred-tank reactor (CSTR) has the lowest annual production cost, the production of methanol is lower as well. The low production of methanol is caused by the large amount of gas purged, in order to heat the steam reformer. The purge fraction is 30 % in the steam re-forming configuration compared to only 0.2 % in the plant based on partial oxidation, hence a better conversion to methanol can be achieved in the integrated pyrolysis and gasification configuration.

Table 4.4: Total production and price of methanol.

	Gasification	Pyrolysis	Integrated
Annual methanol production, (kg/year)	2,040,240	8,635,711	16,327,131
Methanol price, USD/ton	687,03	476,56	418,57

4.7 Cost Sensitivity

In order to find those parameters, which affect the methanol price the most in the three cases, a sensitivity analysis have been made. The parameters of interest are the interest rate, electricity price, heat price and the costs involved in upgrading of biogas. The analysis is carried out by evaluating the methanol price by changing the parameters

10 %. The results are presented in normalized values around the base numbers presented in table 4.4 on the above.

The sensitivity of the parameters on gasification plant is presented in figure 4.1. From the figure is can be seen, that the interest rate and electricity price are the most sensitive parameters. Even though the interest rate has an influence on all expenditures involving the investment, corresponding to 51 % of the total annual costs, it all most have the same influence as the electricity price, which only has a 35 % share of the costs. As previously stated the heat sales is not included on gasification plant.

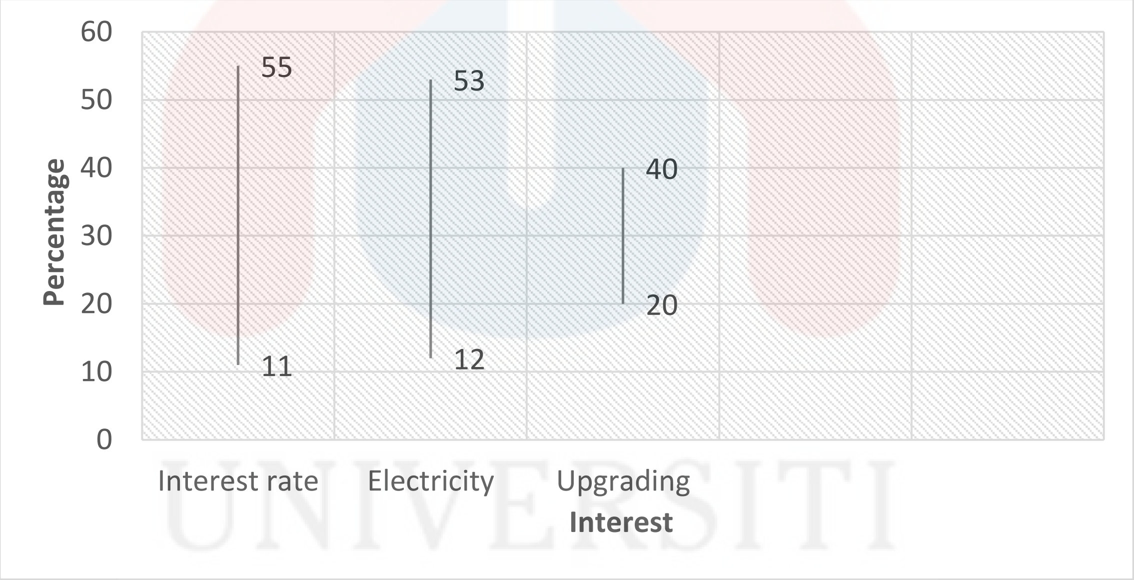
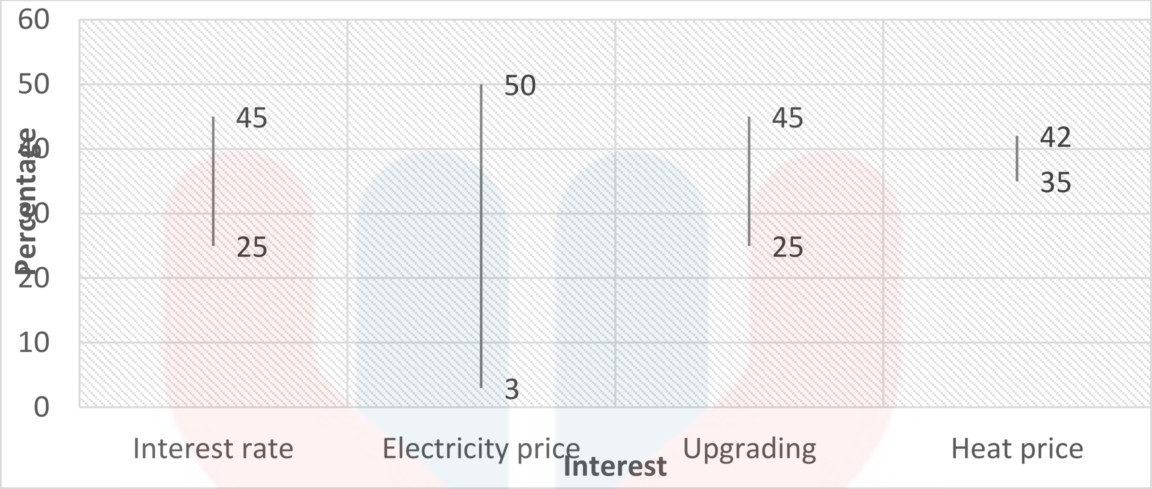


Figure 4.1: Sensitivity analysis of the Gasification plant.

Figure 4.2 in the sensitivity analysis, is the large scale plant based on pyrolysis. Again the electricity is the most sensitive parameter. However, is it now less significant, compared to the partial oxidation plant, due to a lower electricity consumption regarding the electrolysis unit. It follows, that by lowering the electricity price, only a 3 % reduction in methanol production price can be achieved.



4.2: Sensitivity analysis of the Pyrolysis plant.

Lastly, the influence of the sensitivity parameters for the pyrolysis plant is shown in figure 4.3. As expected the electricity price is the most sensitive parameter involved, due to additional unit procedure use. By decreasing the electricity price by 10 %, the methanol production price can be reduced by 6 %. Comparing 4.1 and 4.3 it is shown, that the interest rate is now less dominant and the influence of upgrading costs is almost unchanged. Furthermore, the figure indicates, that the sensitivity of both interest rate and upgrading price is almost the same.

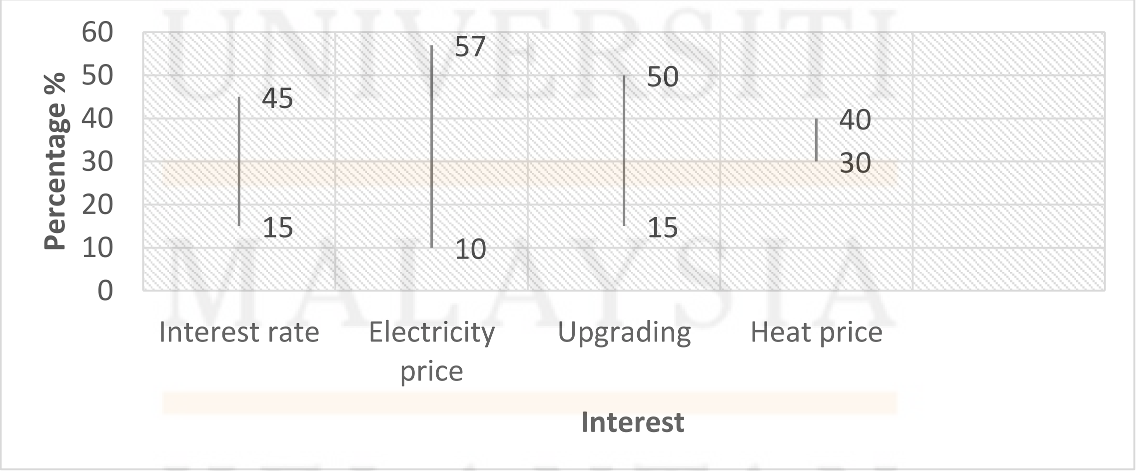


Figure 4.3: Sensitivity analysis of the integrated pyrolysis and gasification plant.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

In conclusion, production of bio-methanol from chicken manure by using 3 process: First gasification process (dealing with continuous stirred tank reactor (CSTR) process. Second process, involves pyrolysis through bio-oil steam reforming process. For the last process is integrated of pyrolysis and gasification through methanol process. In this study, after bio-methanol production from chicken manure scheme was successfully modeled and simulated, results and details related to the technical and economic aspect of bio-methanol production were obtained.

Furthermore, it's can be conclude integrated pyrolysis and gasification process was the most suitable process for chicken manure with the higher annual saving per year. Even if the annual production was higher, the overall total installed capital still economical. The lowest production was gasification process because it's can only produce syngas but it's still economical, while pyrolysis was almost catch up to the integrated process which is only 5% different from the annual saving per year.

Lastly, the approach was based upon a superstructure that had all the desired alternatives embedded. The structural alternatives include options for different types of reactors and separation tasks and consider all the potential interconnections among the reactor and separation units. The equations involved had been simplified into matrix forms and solved using Aspen Plus® Simulation. Based on the results obtained, alternative gives the optimal solution for integrated pyrolysis and gasification, and the following conclusion for the base case can be drawn:

- A purity of 70.42% is obtained, comparable to other studies.
- The total capital investment was found to be USD$6,012,000 million year-1.
- The manufacturing cost was found to be USD$ 312,000 million year-1.
- The total production cost was found to be USD$ 890,178 million year-1.
- The cost estimated was found to be a rate of USD$0.76 kg-1.

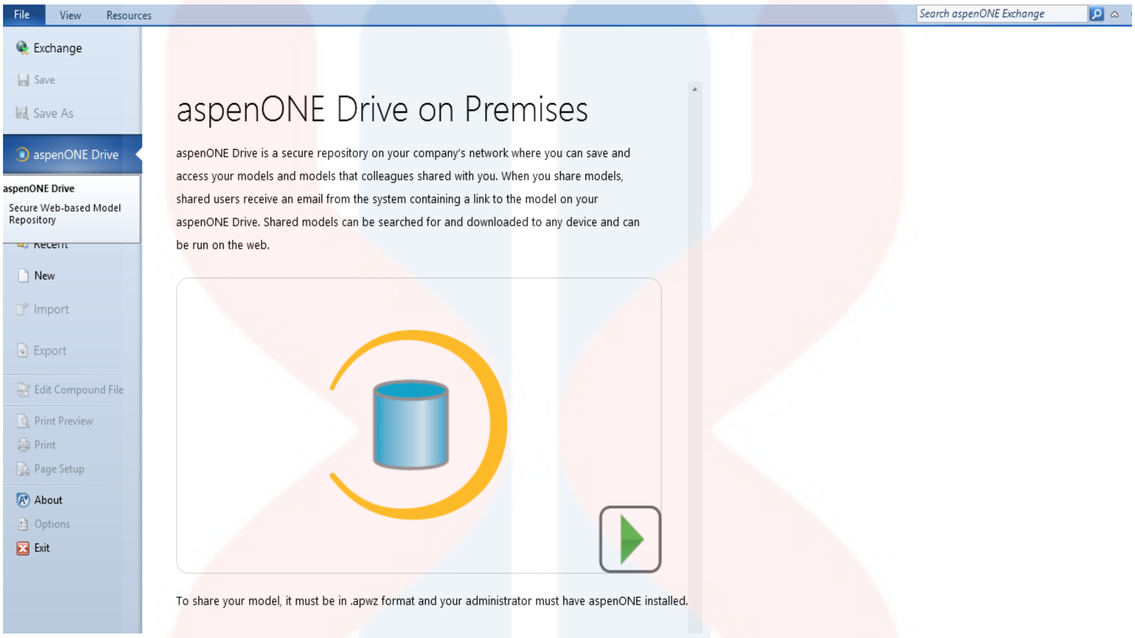
5.2 Recommendations

More research should be carried out through computing software in order to increase exposure, improve skills and related knowledge of students. New modifications on unit procedures and operating conditions involved in bio-methanol production might be done to increase more profitable per year by shorten the bio-methanol production duration by using other types of computing software such as Aspen HYSYS. In Aspen HYSYS, its more efficiency, accuracy and flexibility among different software.

Other than that, the utilities per year can be reduce if we can decrease the operation process and the unit procedure. We just use the process that was most important part and the process that can operate in multi way. Lastly, the labor cost was higher. Then in order to decrease the cost, main control need to be build. Presence of control room may reduce the number of manpower and workers needed to monitor the proper functioning of machines and equipment during production. Therefore, when limited workers are allowed to enter the production site, biological, physical and chemical hazards can eventually be reduced.

The design and heat integration of the system are essential. Therefore, more studies in process systems engineering, including heat integration, are needed to develop a more efficient integrated system that can reduce the exergy efficiency and improve the techno-economics associated with the production of methanol. A scale-up of the process design is also important, particularly for the new advanced processes that have recently been introduced for the production of bio-methanol; in these cases, although the lab-scale methanol production has exhibited a high efficiency, it is necessary to ensure that this efficiency is feasible in a large-scale production. An improvement in the electrolysis process and the renewable electricity efficiency, as well as the cost-effective availability of hydrogen at USD 1–2 kg , would lead to improvements in methanol synthesis.

APPENDIX A



aspenONE Drive on Premises

aspenONE Drive is a secure repository on your company's network where you can save and access your models and models that colleagues shared with you. When you share models, shared users receive an email from the system containing a link to the model on your aspenONE Drive. Shared models can be searched for and downloaded to any device and can be run on the web.

To share your model, it must be in .apwz format and your administrator must have aspenONE installed.

Figure A 1: Aspen Plus Software

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