Gasification and Characterization of Refinery Sludge Using Aspen Plus Simulation

By

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Dissertation submitted in partial fulfillment of
The requirements for the Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

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TRONOH, PERAK
AUGUST 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SATYASHEELAN VASUDEVAN

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ABSTRACT

Gasification is a process of converting organic or fossil based carbonaceous materials into carbon monoxide & hydrogen known as syngas and carbon dioxide. This is achieved by reacting carbonaceous feedstock at high temperature with a controlled amount of air/oxygen often in combination with steam. Simulation of this process is conducted to study the effect of different operating parameters on gasification of dried refinery sludge (DRS) using a countercurrent gasifier. The composition of by-products in refinery sludge is also analyzed and studied to determine its characteristics so as to determine the behavior of the by-products. From our results, it can be concluded that the optimum operating condition is obtained by gasifying refinery sludge at a temperature of 1200 to 1400°F with a flow rate of 10,000 lb/hr at ambient pressure.

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CHAPTER 1: INTRODUCTION

1.1 Background of Study

In this modern era of globalization, the traditional fossil fuels continues to be the major source of energy in the world but the known fact is that the increasing energy demand will speed up the exhaustion of fossil fuel and result in depletion in the years to come. An alternative source of energy which has gained popularity recently is biomass. Biomass is one of the largest sources of energy in the world, third only to coal, oil and natural gas (Thompson, 2008). Biomass energy is a type of energy that is derived from things that are considered as organic such as plants. As a readily renewable energy, biomass has become one of the significant components in the global sustainable and environmentally friendly energy.

Biomass absorbs CO_2 from the atmosphere during photosynthesis, and the CO_2 is the returned to the environment through combustion. Because of this cycle, CO_2 is neutral, making it an advantage and a dominant choice for replacement of fossil fuel (How Biomass Energy Works, 2010). Today, with a global climate crisis looming on the horizon and power-hungry nations on the hunt for alternative energy sources, gasification is making a comeback (Harris, 2009). Gasification of biomass is a process used to produce gas from solid biomass. It is a process that converts organic or fossil based carbonaceous material into a combustible gas by reacting the material at high temperature with a controlled amount of air/oxygen commonly in combination with steam. This resulting gas mixture is called syngas or producer gas which is composed of hydrogen and carbon monoxide and is itself a fuel (Painter). Biomass gasification coupled with other renewable energy options would cut the dependency on fossil fuels and would help to ensure energy security.

1.2 Problem Statement

One of the main factors influencing gasification is the operating conditions of the gasification system as it has the ability to affect the product formed and one of the major issues in refinery sludge gasification is dealing with the tar and particulate which are the by-products that are formed during the process.

1.3 Objectives

The main objective that needs to be achieved when completing this project is to develop an Aspen Plus simulation based gasification model to predict product composition for dried refinery sludge characteristics and operating conditions using textural analysis (proximate and ultimate analysis).

1.4 Scope of study

The scope of the study will be on investigating the process variable and its effects on gasification conditions (limited to temperature and flow rate). This research will also use results from textural experimental data to simulate and validate the gasification model using Aspen Plus software. Finally, the Aspen Plus model developed will be utilized to suggest the optimum operating condition for refinery sludge gasification process.

1.4.1 Relevance of the study

This project will focus on the topic of simulation/modeling using Aspen Plus and characterization and analysis of materials. These topics are much related to Material and Energy Balance, Thermodynamics, Separation Process, Process Plant Design and Organic Chemistry. Knowledge on these subjects is needed to perform research for this project.

1.4.2 Feasibility of the project within the time scope and time frame

The project is definitely within the scope since Material Energy Balance and Organic Chemistry are core subjects. This helps since the author already have a basic idea about the project. The project is divided into two sections. The first section will basically be on finding, collecting, and reading of journals, technical papers, and books of the research topic. After the literature review part, the author will then start with the planning of the simulation as well as the laboratory experiment. The second section of the project will be mainly on carrying out the simulation and simultaneously the experiment in the laboratory to determine the characteristics and chemistry of the by-products formed during gasification. The author was given roughly around nine months to complete this project which is considered adequate to conduct the laboratory work, data gathering, and analysis of result using Aspen Plus software.

CHAPTER 2: LITERATURE REVIEW

This following chapter will describe the fundamental of gasification. Several research papers and journals have been reviewed in order to understand the process. Biomass in general refers to wood, woody products, grasses, crop residue, construction and demolition waste, and post-consumer recycled paper products (R3 Sciences). In this research however, the biomass which is used will be dried refinery sludge (DRS).

2.1 Gasification

Gasification is a process that uses heat, pressure, and steam to convert biomass directly into a gas comprising primarily of carbon monoxide (CO) and hydrogen (H_2). Gasification is a thermochemical process unlike an incineration or combustion process. Gasification is a conversion process intended to produce more valuable and useful products from carbon containing materials. Gasification operates with limited amount of oxygen, while combustion processes operates with excess oxygen (R3 Sciences). Gasification includes both bio-chemical and thermo-chemical process gasification. Biochemical gasification means gasification by microorganism at normal room temperature and pressure while thermo-chemical gasification means using either air, oxygen or steam at temperature more than $800^{o}C$ (Chiew, 2010). Since there is limited information of gasification of refinery sludge in open literature, the literature review on gasification will be discussed with biomass as feedstock

2.2 Theory of Gasification

In typical gasifiers, the following physiochemical processes take place at temperatures indicated:

1. Drying	($>150^{o}C$)
2. Pyrolysis	($150-700^{o}C$)
3. Combustion	($700-1500^{o}C$)

4. Reduction (800-1100^{o}C)

Process 1, 2 and 4 absorb heat provided by the exothermic combustion process 3. In the drying process, the moisture in the solid fuel evaporates. The pyrolysis process separates the water vapor, organic liquids and non-condensable gases from the char or solid carbon of the fuel. The combustion process oxidizes fuel constituents in an exothermic reaction, while the gasification process reduces them to combustible gases in an endothermic reaction (Basu, 2006). Though there is a considerable overlap of the processes, each can be assumed to occupy a separate zone where fundamentally different chemical and thermal reactions take place. The following are the reaction chemistry that takes place in combustion and reduction zone.

2.2.1 Drying Zone

In the drying zone, the main process is of drying the biomass. Biomass entering the gasifier has moisture content of 10-30%. Various experiments on different gasifiers in different conditions have shown that on average the condensate formed is 6-10% of the weight of gasified biomass.

2.2.2 Pyrolysis Zone

Biomass pyrolysis is an intricate process that is still not completely understood. The products depend upon temperature, pressure, residence time and heat losses. Up to the temperature of 200^{o}C only water is driven off. Between 200^{o}C to 280^{o}C carbon dioxide, acetic acid and water are given off. The real pyrolysis takes place between 280-500^{o}C produce large quantities of tar and gases that contain carbon dioxide. Besides light tars, some methyl alcohol is also formed. Between 500-700^{o}C the gas production is small and contains hydrogen. Thus it is easy to see that the updraft gasifier will produce much more tar than the downdraft one. In downdraft gasifier the tars have to go through combustion and reduction zone and are partially broken.

2.2.3 Reduction Zone

The products of partial combustion (water, carbon dioxide, and uncombusted partially cracked pyrolysis products) now pass through a red hot bed where the following reduction reactions take place.

Boudouard rxn	$C + CO_2$	=	$2CO$	+172 MJ/kg mole
Water gas rxn	$C + H_2O$	=	$CO + H_2$	+131 MJ/kg mole
CO shift rxn	$CO + H_20$	=	$CO + H_2$	- 41 MJ/kg mole
Methanation rxn	$C + 2H_2$	=	CH_4	- 75 MJ/kg mole

Reaction 1 and 2 are main reduction reactions and being endothermic have the capability of reducing gas temperature. Consequently the temperature in the reduction zone is normally 800-1000^{o}C. Lower the reduction zone temperature (700-800^{o}C), lower is the calorific value of gas.

2.2.4 Combustion Zone

The combustible substance of solid fuel is usually composed of elements carbon, hydrogen and oxygen. In complete combustion, carbon dioxide is obtained from carbon in fuel and water is obtained from the hydrogen, usually as steam. The combustion reaction is exothermic and yields a theoretical oxidation temperature of 1450^{o}C. The main reactions therefore are:

$C + ½ O_2$ = CO_2 (-111 MJ/kg mole)

$H_2 + ½ O_2$ = $2H_2O$ (-242 MJ/kg mole)

$CO + ½ O_2$ = CO (-283 MJ/kg mole)

2.3 Type of Gasifier

A gasifier is an equipment to convert solid fuel into the syngas/producer gas through a thermo-chemical process. Depending upon how the gas and fuel contact each other, gasifiers can further be divided into four types which are entrained bed, fluidized bed (bubbling or circulating), spouted bed and fixed or moving bed (Basu, 2006). In fixed or moving bed, there are four main types of gasifier available for commercial uses which are the updraft, downdraft, and cross draft (Ahmad, 2010). Gasifier equipments are generally classified based on the direction of air/oxygen flow in the equipment (Enggcyclopedia). In this project, updraft gasifier will be the main concern to be considered into the situation.

2.3.1 Fixed Bed Gasifiers

Fixed bed reactors are those in which solids move either countercurrent or concurrent to the flow of gas as reaction takes place, and the solids are converted to gases (Sadaka). In fixed bed gasifiers, large coal particles move slowly downward through a bed while reacting with gases moving in the opposite direction going upward through the bed. Coarse particles are used in fixed bed gasifier to ensure good bed permeability and help to avoid excess pressure drop and chemical burning (Gasifipedia). Fixed beds are particularly suited to solid fuel contacting operations that require close temperature control, carryover of particles away from the reaction zone, simple operation and minimum erosion of the body of the reactor (Sadaka).

2.3.1.1 Updraft Gasifier

The oldest and simplest gasifier among all the other types of gasifier is the updraft gasifier (Jared P. Ciferno, 2002). The material will be fed at the top of the gasifier and will move down due to gasification and ash removal process. The air will be supplied from the bottom and the syngas will leave at the top. That is the reason why it is called an updraft gasifier (Enggcyclopedia). In the updraft or counter current, gasifier air is injected from the bottom and biomass enters at the top and moves down under the force of gravity as it is gasified. The principle of operation of this type of gasifier is that the biomass material first goes through the drying phase, followed by the distillation (pyrolysis) and reduction phase and finally the combustion of the un-gasified solid fraction. The relatively high energy efficiency of this type of gasifier is due to the efficient counter current heat exchange between the rising gases and descending biomass. The main problem of the updraft gasifier is the high concentration of tars and oils in the producer gas, which must go through intense filtering and cleaning if it is to be utilized for generating electricity or mechanical power with a steam turbine or engine (IEA Bioenergy). The major advantages of this type of gasifier is its simplicity, high charcoal burn out and internal heat exchange leading to low temperature of exit gas and high equipment efficiency. This gasifier can work with several kind of feedstock ranging from coal to biomass (Enggcyclopedia).

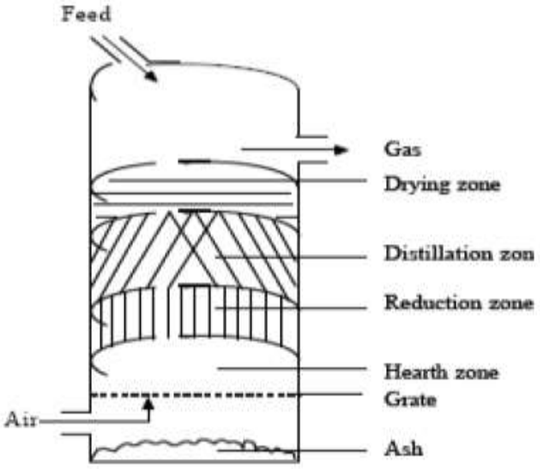


Figure 1 : Sketch of Typical Updraft Gasifier

The biomass gasification process can be used for “green” power or fuel production. It is a relatively mature technology compared to other thermochemical and biochemical processes (Gopal Gautam, 2011). However, experimental study of biomass gasification can be costly and dangerous to human being. Simulation and modeling approach is expected to be more cost saving, safe and easy to scale up in order to study the biomass gasification process (Tamidi, 2011).

2.3.1.2 Downdraft Gasifier

In updraft gasifier, there is a problem of tar entrainment in the product gas leaving stream. A solution is to have primary gasification air introduced at or above the oxidation zone in the gasifier. The produced gas in then taken from the bottom resulting in the fuel and gas to move in the same direction (Enggcyclopedia). This gasifier is applicable for medium and large scale of power generation ranging from 80 kW up to 500 kW or more. Some lab scale gasifiers are available in 5 kW (Rajvanshi, 1986). The zones are slightly different from the updraft gasifier as the reduction zone occurs at the bottom of the gasifier.

The main advantage of a downdraft gasifier lies in the possibility of producing tar free gas for engine operation. However in practice, the probability of tar free gas produced is very rare but the percentage of tar leaving from the product stream is considerably lower than that leaving through the updraft gasifier (Enggcyclopedia). Low moisture biomass (<20%) and air or oxygen are ignited in the reaction zone at the top of the reactor. The flame generates pyrolysis gas/vapor, which burns intensely leaving 5 to 15% char and hot combustion gas. These gases flow downward and react with char at 800 – 1200^{o}C, generating more CO and H_2 while being cooled to below 800^{o}C. Finally, unconverted char and ash pass through the bottom of the grate and are sent to disposal (Jared P. Ciferno, 2002). The residence time is the important factor to consider to ensure the tar is combusted through the hottest zone. Main disadvantage is that the downdraft gasifier cannot be operated with range of different feedstock. Low density feedstock gives rise to flow problems and excessive pressure drop. High ash content and coal also gives more problems with this kind of gasifier than updraft gasifier.

2.3.1.3 Crossdraft Gasifier

The gasification process in crossdraft gasifier results in very high temperature which is nearly 1500^{o}C and even higher in the hearth zone which can lead to material problems. The disadvantages such as high exit gas temperature, poor CO_2 reduction and high gas velocity are the consequences of the design and the reason why there are not ideal despite having certain advantages over updraft and downdraft gasifiers. Unlike updraft and downdraft gasifiers, fire and reduction zones in crossdraft gasifiers are separate. These design characteristics limit the type of fuel usage restricted to only low ash fuels such as wood, charcoal, and coke. The load following ability to crossdraft gasifier is quite good due to concentrated zones which operate at temperature up to 1200°C. (Enggcyclopedia).

2.4 Gasification simulation with Aspen Plus software

Numerical simulation is an effective technology to study and to optimize the performance of gasifier (P. Ji, 2009). It is also considered as the best method for scale-up investigations. The successful design and operation of H_2 production from biomass gasification depends on the ability to predict the behavior of hydrodynamics, mixing of individual phases, mass transfer and multiple chemical reactions. An experimental approach to directly measure all these behavior is quite difficult and it involves high cost of operation (B. Dou, 2008). In this work, a simulation model is developed in Aspen Plus process simulator and is used to investigate the technical feasibility of refinery sludge gasification and the effects of the operating conditions on the quality of products. Aspen Plus is a commercial process simulator and has been used by different investigators to simulate coal conversion. It is used to investigate the effect of various operating parameters on various reactions. Previous reports that simulated coal conversion include integrated coal gasification combined cycle (IGCC) power plants (J. N. Philips, 1986) and coal gasification simulation (H. G. Lee, 1992). Although the simulation work done on biomass gasification is limited, (K. G. Mansaray, 2000) in the article stated that the high amount of volatile material in biomass and the complexity of biomass reaction rate kinetics in fluidized beds, resulted in them ignoring the char gasification and the simulation of the gasification process was done by the assumption that biomass gasification follows Gibbs equilibrium.

2.5 Tar Formation in Gasification

Although biomass has been said to be the next big thing after fossil fuel in power generation and having the potential in replacing fossil fuel as an alternative energy, the gasification process by itself has its disadvantages. High contents of tar, fly ash and other pollutant gases accompanying with producer gases are the most crucial technical obstacles in application. Tar is undesirable because it can cause blocking and fouling problems in engines and turbines due to condensation and polymerization (Hongfang Chen, 2011).

Tar is one of the most unpleasant constituents of the gas as it tends to deposit in the carburetor and intake valves causing sticking and troublesome operations (Skov, 1974). It is a product of highly irreversible process taking place in the pyrolysis zone. The physical property of tar depends upon temperature and heat rate and the appearance ranges from brown and watery (60% water) to black and highly viscous (7% water) (Kaupp, 1982). There are approximately 200 chemical constituents that have been identified in tar so far. Gas cleaning and tar reduction have been the subject of research on thermochemical conversion of biomass for the production of energy and chemicals.

Very little research work has been done in the area of removing or burning tar in the gasifier so that relatively tar free gas comes out. Thus the major effort has been devoted to cleaning this tar by filters and coolers (Rajvanshi, 1986). Gas cleaning systems is one of the methods to reduce the tar produced in gasification process and Vidian (2012) in his journal succeeded in reducing the tar content by using a ventury scrubber. Zwart (2009) in their research summarized the information on the reactivity of tars during the pyrolysis and gasification and discussed the mechanism of the reactions involved. In the present research, the study is intended to understand further on the chemistry of the tar generated. Gasification in general has its drawbacks and trade-offs just like any other complex endeavor, and whether it is ultimately fruitful and sustainable remains to be seen. Looking at the big picture though, gasification, and its resulting syngas, with its potential to create all types of useful chemicals and synthetic fuels, certainly deserves a spot at the table with other alternatives.

CHAPTER 3: METHODOLOGY

3.1 Research Methodology

Different findings and methodologies are gathered from the research work of other researchers and to be incorporated in this project. First and foremost, various journals and technical papers were read through the get the general understanding on the project. It is also needed to identify the objective of this project and to come up with a proven method to run the experiment later.

Next would be the commencing of simulation work. Prior to that, all calculation regarding the composition percentage and content of all components as well as the operating parameters will be finalized. Biomass characterization will include proximate analysis, ultimate analysis, energy content and particle size distribution. While the operating conditions of the gasification system includes fuel flowrate, steam to fuel ratio, air to fuel ratio, temperatures of air and steam of the gasifier, together with training and practice of the simulation software, Aspen Plus. This is first done as the knowledge and information about the software will be trustworthy. Once finalized, the simulation work will begin with the assistance and guidance from a senior person. Meanwhile, as the simulation work goes on, concurrently, the further study and research on the characteristics of tar as well as the by-products formed during gasification will be ongoing. Each of the samples will be tested and analyzed with laboratory equipment such as CHNS Analyser, Atomic Absorption Spectrophotometer, Calorimeter, and many more. Once the laboratory test is done, the results will be analyzed, evaluated and discussed with the supervisor. Microsoft Excel will be used to ease data representation.

3.1.1 General Steps to work on Aspen Plus

The software that is being used, Aspen Plus, uses unit operation blocks, which are models of specific process operations. These blocks are placed on a flow sheet specifying material and energy streams. An extensive built in physical properties is used for the simulation calculations. Aspen Plus has the capability to incorporate gasification thermodynamic model into the model. The development of a model in Aspen Plus involves the following steps:

1. Stream class specification and property method selection
2. System component specification from previous data
3. Defining the process flow sheet (unit operation blocks, connecting material and energy streams)
4. Specifying feed streams (flow rate, composition and thermodynamic condition)
5. Specifying unit operation blocks (thermodynamic condition and chemical reactions)

3.2 Project Activities

Meeting with supervisor will be conducted whenever necessary to report on the progress of the project as well as to clarify doubts related to the project.

In order to achieve the objectives of the project, several key factors have to be taken into account so that research and execution is done in a systematic manner.

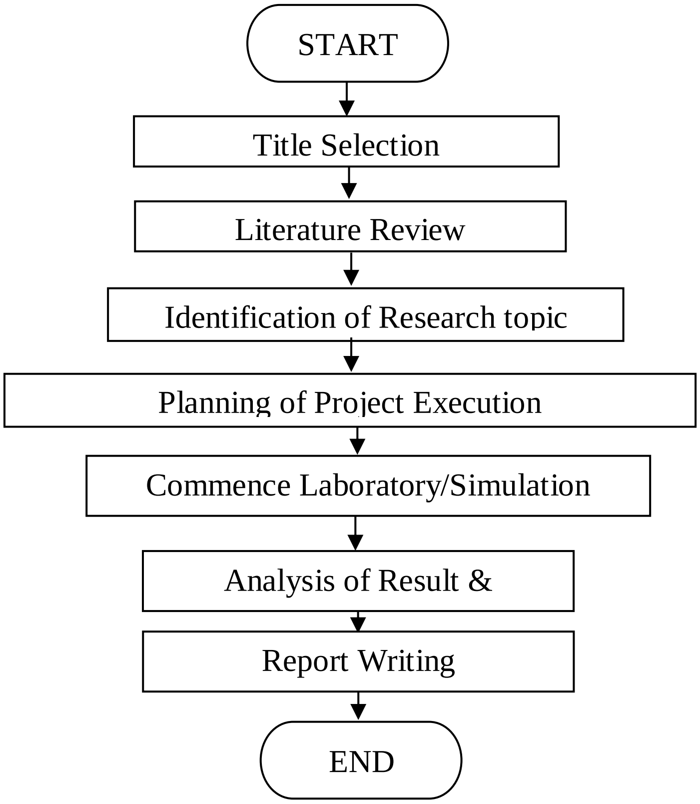


Figure 2 : Project Activities Flow

The methodology created, describes three main phases in the execution of the project.

❖ **Phase 1** : Research & Planning

- Background Study
- Materials to be considered
- Planning simulation work
- Testing method

❖ **Phase 2** : Simulation/Laboratory Work

- Collection of data and parameters
- Materials preparation for laboratory test

❖ **Phase 3** : Analysis & Conclusion

- Tabulation of results
- Analysis of data
- Conclusion & recommendation

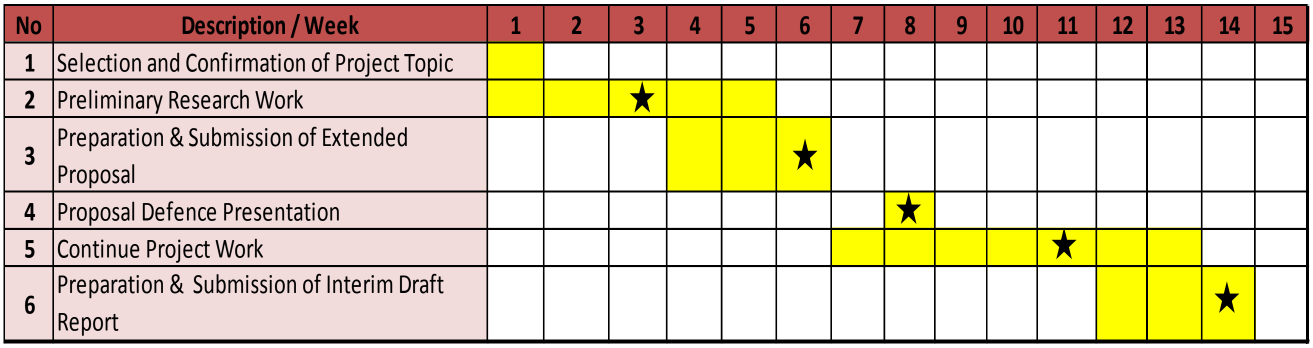
Figure 3 : Breakdown of detailed activities

Phase	Start Date	End Date
Phase 1	Jan 2013	February 2013
Phase 2	February 2013	June 2013
Phase 3	July 2013	September 2013

Table 1 : Timeline of each phase

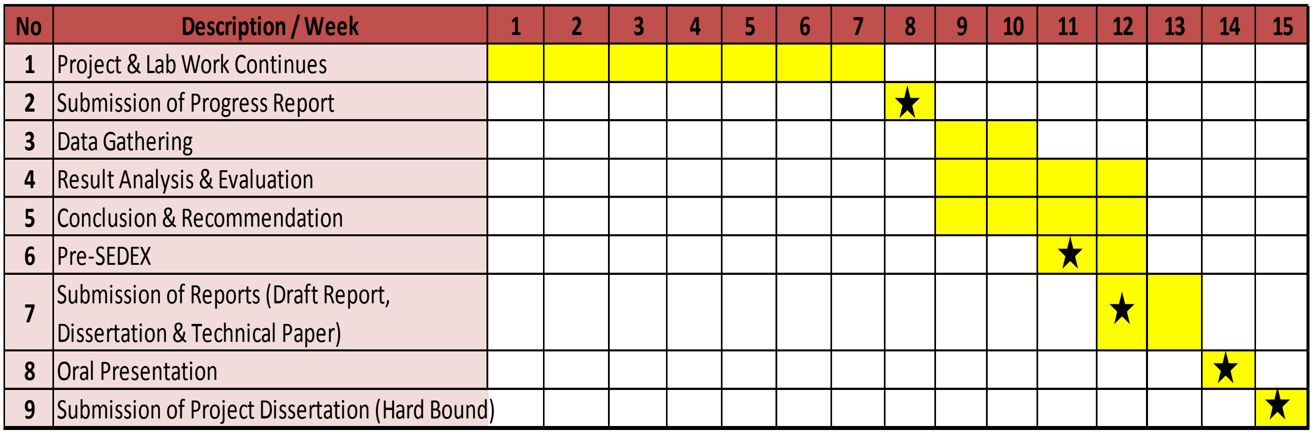
3.3 Gantt Chart & Key Milestones

Final Year Project 1



No	Description / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Selection and Confirmation of Project Topic	🟨														
2	Preliminary Research Work	🟨	🟨	★	🟨	🟨										
3	Preparation & Submission of Extended Proposal				🟨	🟨	★									
4	Proposal Defence Presentation								★							
5	Continue Project Work							🟨	🟨	🟨	🟨	★	🟨	🟨		
6	Preparation & Submission of Interim Draft Report												🟨	🟨	★	

Final Year Project 2



No	Description / Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project & Lab Work Continues	🟨	🟨	🟨	🟨	🟨	🟨	🟨								
2	Submission of Progress Report								★							
3	Data Gathering									🟨	🟨					
4	Result Analysis & Evaluation									🟨	🟨	🟨	🟨			
5	Conclusion & Recommendation									🟨	🟨	🟨	🟨			
6	Pre-SEDEX											★	🟨			
7	Submission of Reports (Draft Report, Dissertation & Technical Paper)												★	🟨		
8	Oral Presentation														★	
9	Submission of Project Dissertation (Hard Bound)															★

★ Key Milestones

3.4 Tools Required

3.4.1 Software

- **Aspen Plus 2006.5** – to simulate the gasification process and perform material energy balance
- **Microsoft Excel 2010 –** performance analysis purpose (e.g. graph, charts etc.)

3.4.2 Hardware/Equipment (available at the laboratory)

All the equipment necessary to conduct the experiment are available at the UTP laboratory. Most of it is in the Chemical Laboratory and approval from the supervisor as well as laboratory executive is needed to use any equipment.

- CHNS Analyzer
  An elemental analyzer dedicated to the simultaneous determination of the amount of (%) of Carbon, Hydrogen, Nitrogen, Sulphur and Oxygen contained in organic, inorganic and polymeric materials and in substances of different nature and origin i.e. solid, liquid and gaseous samples. ASTM methods D 5373 was used for this analysis.
- Thermal Gravimetric Analysis (TGA)
  A method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature with constant heating rate, or as a function of time (with constant temperature and/or constant mass loss). For this analysis, a Perkin Elmer Pyris 1 was used.

3.5 Reactor Specifications and Characteristics

In carrying out the simulation, some assumptions are made. The following are the assumptions made to draw the model:

1. The process is in steady state and ideal condition
2. This process is to occur instantaneously at equilibrium with volatile products limited to CO, CO_2, H_2, CH_4 and H_2O.
3. Tars are assumed to be negligible in the syngas composition
4. Do not consider chemical kinetics limitations of various chemical processes.
5. Ash will not participate in the reaction.

Since the ASPEN Plus process simulator do not have a built in gasifier model, a number of reactors types defined in ASPEN are used to model each zone of gasification. DECOMP or Yield reactor model is used to analyze the pyrolysis process. This model calculates the yield distribution of the product without need to specify reaction stoichiometric and reaction kinetics. It makes use of the ultimate and proximate analysis of the sludge for computation. BURN or Gibbs reactor model is selected for reduction and combustion zones under the assumption that the reaction is in equilibrium.

Yield Reactor

RYield reactor is used to represent the pyrolysis region. RYield reactor can be used to quickly calculate reaction products. It is used to simulate the decomposition of feed. By specifying the reaction yields of each component, the RYIELD models a reactor. When reaction stoichiometry and kinetics are unknown but the yield distribution or correlations are available, this model is very useful. Refinery sludge is converted into its components such as carbon, hydrogen, nitrogen, sulfur and ash by specifying the composition to the ultimate analysis

Gibbs Reactor

The Gibbs reactor is used to represent the combustion region. The Gibbs reactor does not require stoichiometric equations. Equilibrium is determined from the free energy and the heat of reaction is calculated automatically. When the pressure and temperature is known but the reaction stoichiometry is unknown, this model is used. The method is completely general and predictive. Processes that are in equilibrium or close to equilibrium can be modeled with this reactor.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Simulation Diagram (Gibbs Reactor with Separator Model)

In this simulation diagram, the feed that is refinery sludge will be supplied to the Conversion reactor. In this reactor, the sludge is converted into its constituting components including carbon, hydrogen, oxygen, sulfur, nitrogen and ash by specifying the yield distribution based on the ultimate and proximate analysis done in the lab and is specified in Table 2 below.

Table 2 : Ultimate and Proximate Analysis Results

Components	Dried Refinery Sludge
	Ultimate Analysis
Carbon	59.66
Hydrogen	2.10
Nitrogen	4.88
Sulfur	0.81
Total	100.00
	Proximate Analysis
Moisture	7.876
Volatile Matter	45.331
Fixed Carbon	30.884
Ash	15.697
Total	99.788

The results are analyzed using sensitivity analysis. The derivation from this analysis can be seen in Table 4 for pressure, air flow rate and temperature variation respectively. In the present study the fuel flow rate was kept constant at 10,000 lb/h for all 3 process variables (pressure, air flow rate and temperature)

Table 3 : Sensitivity Analysis

Parameter	**Sensitivity**
	Pressure
Minimum Pressure	14.7 psia
Maximum Pressure	99.7 psia
Increment	5.0 psia
Output	Mole Composition of syngas and CH_4
	Air Flow Rate
Minimum Pressure	10,000 lb/hr
Maximum Pressure	30,000 lb/hr
Increment	2,000 lb/hr
Output	Mole Composition of syngas and CH_4
	Temperature
Minimum Pressure	900 F
Maximum Pressure	2000 F
Increment	100 F
Output	Mole Composition of syngas and CH_4

Figure 4 shows the simulation diagram for gasification of refinery sludge. The product from the RYield Reactor that is symbolized by stream S1 will flow to the separator reactor. The separator functions as to separate the syngas and other impurities such as ash and sulfur. The resulting product stream, S2 travels to a mixer where it combines with air and enters the RGibbs reactor. At the RGibbs reactor, combustion and reduction process occurs which finally produces syngas as a product. Several simulation models had been developed for dried refinery sludge gasification process and improved as time progressed to obtain the most accurate simulation model. Temperature, pressure and air flow rate are the varied operating parameters and their effect on syngas composition are presented. The results are shown in Figure 5 to Figure 7.

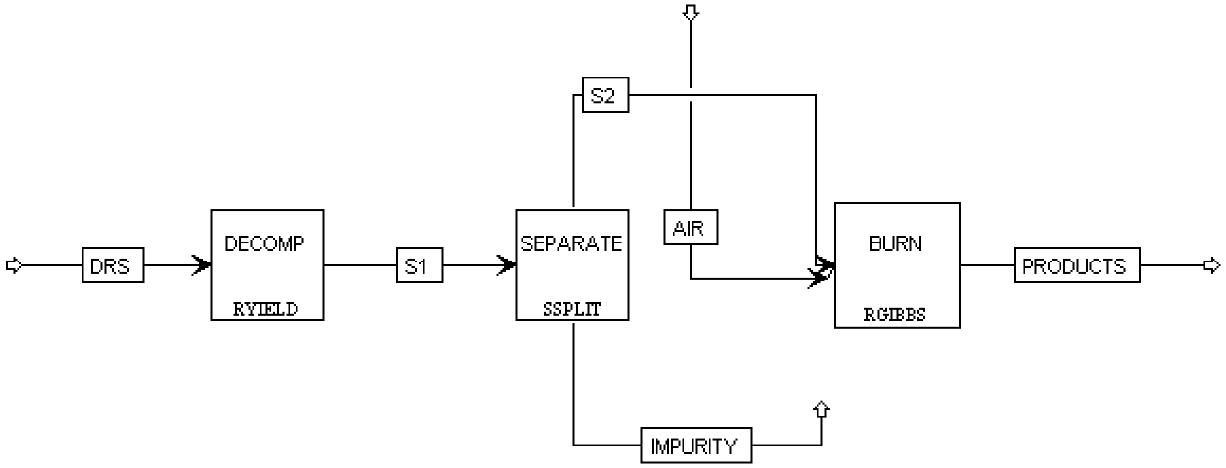


Figure 4 : Simulation Diagram

4.2 Effect of pressure to mole composition syngas and methane

In order to simulate the effect of pressure, the air flow rate and temperature was fixed at 10,000 lb/hr and 1500°F respectively. Figure 5 shows the simulation results with pressure variation with fixed air flow rate and temperature. From the simulation, it can be seen that the mole composition of carbon monoxide and hydrogen was found to be decreasing with increase in pressure but the decrease was small about 0.03 and 0.06 mole for CO and H_2 respectively.

Methane on the other hand shows an increase in the mole composition by about 0.04 moles. Although the increase is marginal, in industrial application, the usage of high pressure is not practical due to the high fabrication and operational cost. The result obtained is compared with (Ahmad, 2010) paper, Figure 6 and the result shows that the syngas composition remains almost constant throughout and CH_4 increases by 0.05 moles. It has to be taken into account that the biomass used by him was oil palm fronds instead of dried refinery sludge and thus the difference in the results obtained. Therefore based on the results obtained, it can be assumed that high pressure is not justified for industrial application. From the simulation the recommended pressure for gasification of refinery can be limited to 14.7 psia to 24.77 psia for optimum composition of syngas.

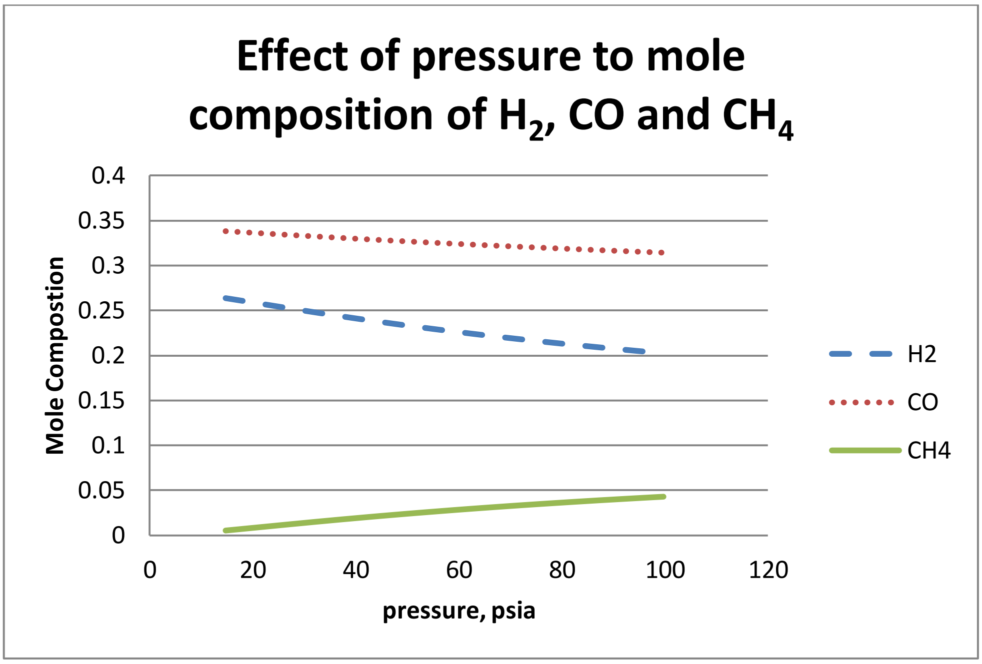


Figure 5 : Effect of pressure to mole composition of syngas and methane

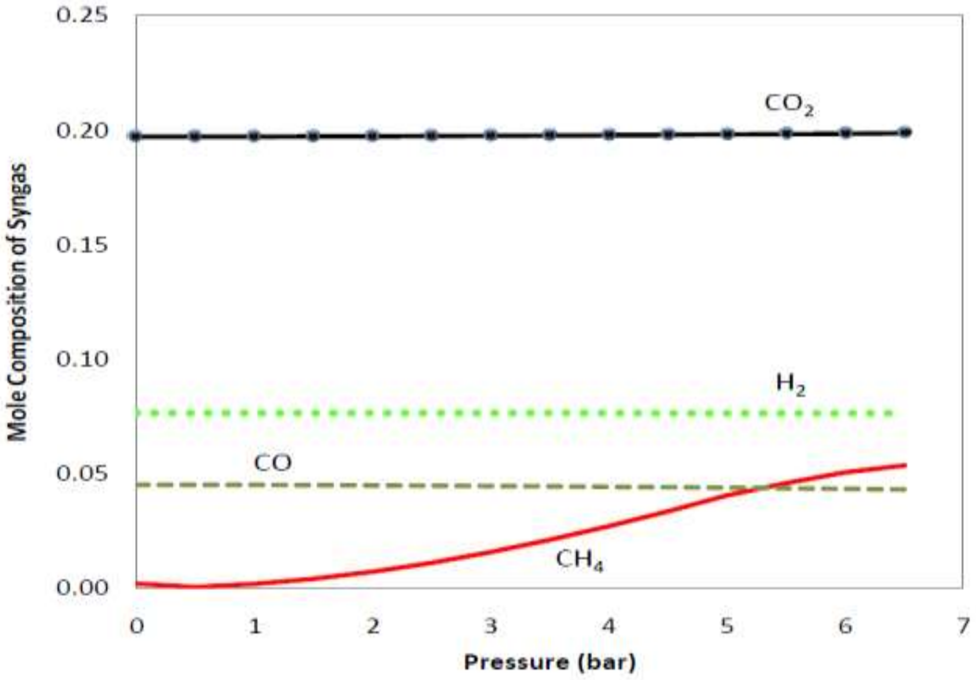


Figure 6 : Effect of pressure to mole composition of syngas and methane (Ahmad, 2010)

4.3 Effect of air flow rate to mole composition of syngas and methane

Gasification products can be influenced in many ways by the air flow rate. Air, the source of oxygen for combustion is of great importance as it influences the reaction toward the direction of gasification or combustion. By increasing the amount of air supply, oxygen content in the fuel to air flow rate ratio will increase leading or favoring combustion reaction instead of the favorable gasification reaction. An excess of combustion, results in the decreased energy content of the gas due to increase formation of CO_2 and water (combustion reaction) at the expense of CO and H_2 (Fuel). Thus, keeping the oxygen supply minimum will be ideal in the reduction zone. Figure 6 represent the effect of the air flow rate against the fixed values for pressure and temperature set at 14.7psia and 1500°F respectively.

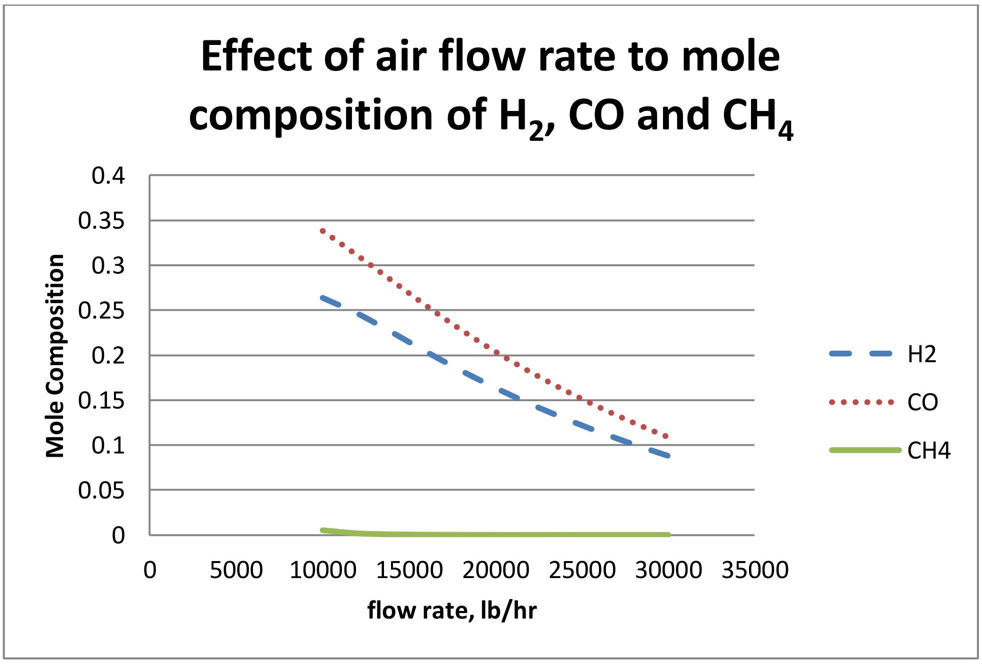


Figure 7: Effect of air flow rate to mole composition of syngas and methane

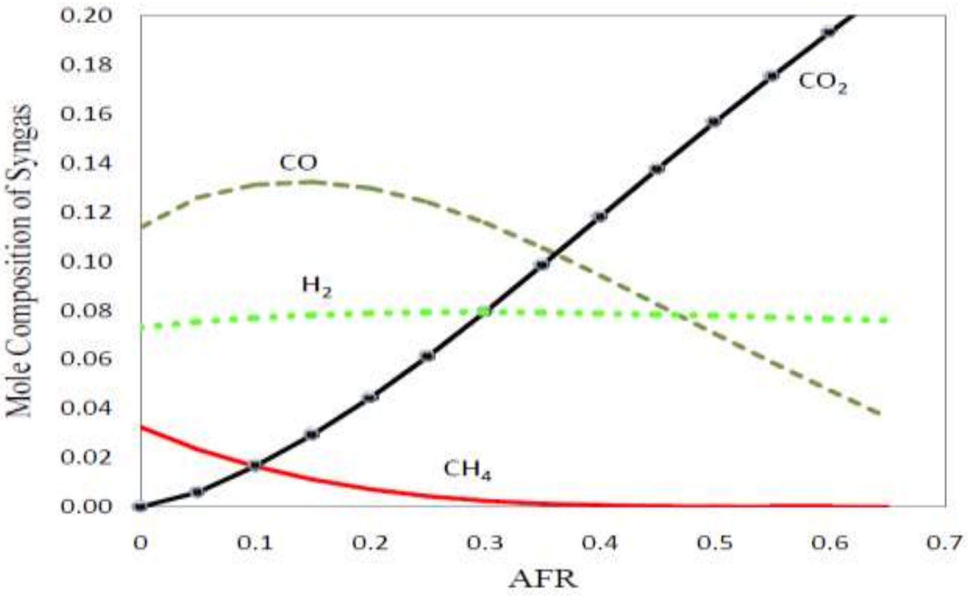


Figure 8 : Effects of air fuel ratio to mole composition of syngas and methane (Ahmad, 2010)

Figure 7 shows the plot of syngas and methane obtained by simulation using ASPEN Plus version 2006.5 for the effect of air flow rate while keeping the other 3 parameters constant. From the same figure it can be observed that the hydrogen as well as carbon monoxide reduces as the air flow rate increases, while methane is noticed to be unaffected by the change. In the case of CO and H_2 a decrease of 0.23 and 0.17 mole respectively is observed. With increase in air flow rate, combustion reaction is favored. The CO and H_2 produced are consumed to increase the combustion reaction. This results in loss of both CO and H_2. On the other hand methane is less affected due to its very low conversion.

This indicates that by increasing the air flow rate, gasification reaction is reduced, resulting in less favorable product of CO_2 and H_2O at the expense of favorable CO and H_2. This result is compared with (Ahmad, 2010) paper, Figure 8 but as it can be seen in his paper Ahmad did the simulation based on air fuel ratio instead of air flow rate. Although the method used is different but the basis of calculation for both is the same that is increasing the air flow rate. When compared, a similar trend is observed for CO and CH_4. Based on the result obtained, the optimum air flow rate is 10,000 lb/hr.

4.4 Effect of temperature to mole composition of syngas and methane

The next simulation is done to investigate the influence of temperature while keeping the air flow rate and pressure fixed at 10,000 lb/hr and 14.7 psia respectively. As it can be seen from Figure 9, the effect of temperature on syngas and methane produced is observed. From the figure, it can be seen that the mole composition of hydrogen and carbon monoxide increases sharply from 1000 to 1500°F thereafter it is constant. The reason for the increase in hydrogen and carbon monoxide is because at high temperature the char decomposes/cracks to produce the syngas. The Boudouard and water gas shift reaction is favored over combustion. Both the Boudouard and water gas shift reaction is endothermic which is favored by increase in temperature. Above 1500°F, the production of syngas is constant. This may be due to side reactions taking place, for example the production of higher hydrocarbon.

In the case of methane, we notice that methane is consumed with increase in temperature. We suspect that methane is used as fuel to maintain the high temperature and cracked to produce CO and H_2. This increase in temperature is favored for gasification reaction because more syngas is produced. The drawback of this reaction is the consumption of methane, a high caloric value gas. Due to the endothermic reaction that occurs in gasification, the syngas composition is sensitive towards temperature changes. Methane on the other hand decreases due to the high temperature which favors cracking of methane. When compared with (Ahmad, 2010) paper, a nearly similar trend is observed for CO and CH_4.

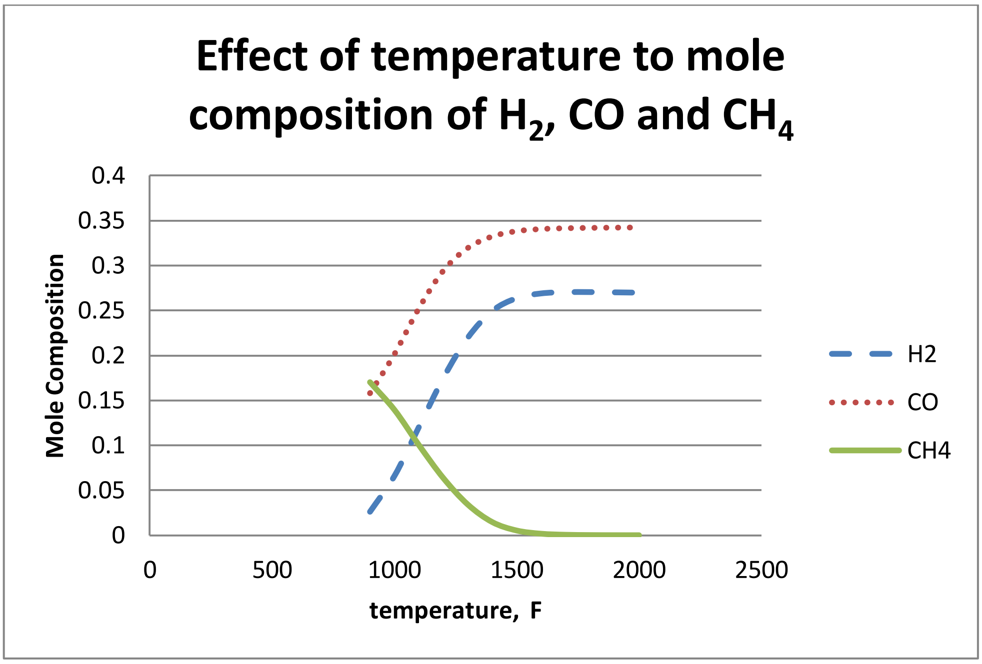


Figure 9: Effect of temperature to mole composition of syngas and methane

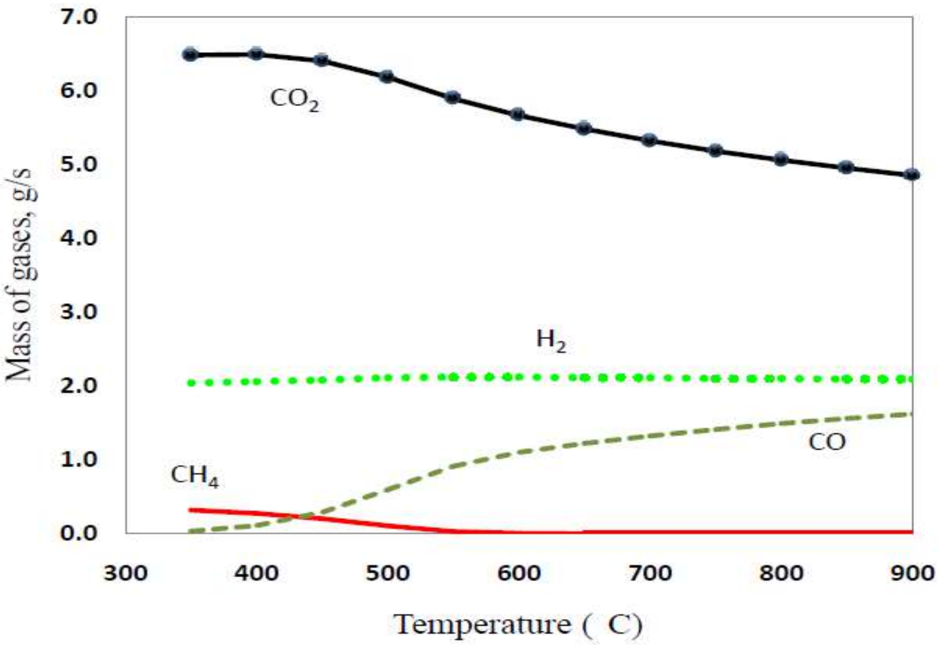


Figure 10 : Effects of temperature to mass of gases (Ahmad, 2010)

Based on the result obtained, the optimum temperature is taken to be between 1200 to 1400°F.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

The project has successfully met all its predetermined objectives with the main objective of determining the optimum operating conditions that would result in the best composition of syngas by using the Aspen Plus software. Based on the simulation results from the author’s work and previous reports, it can be concluded that Aspen Plus can be a suitable simulation software to develop a gasification process model. The simulation results for the mole composition of hydrogen, carbon monoxide and methane was successfully obtained by varying the pressure, air flow rate and temperature. Based on the result, it can be concluded that the optimum operating condition is obtained by gasifying refinery sludge at a temperature of 1200 to 1400°F with a flow rate of 10,000 lb/hr at ambient pressure.

In the future, to improve the accuracy of the results obtained, chemical kinetics should be considered. Also, the comparison made from the present simulation was with a past work which used Oil Palm Fronds which may not be accurate. Therefore, future work can be done using this present work as a platform. Besides that, to further justify the simulation result, an experiment that uses dried refinery sludge as feedstock should be conducted and the results compared with the present simulation.

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APPENDICES

```
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IN-UNITS ENG

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DESCRIPTION "
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Started -
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    "

DATABANKS PURE20   / AQUEOUS   / SOLIDS   / INORGANIC   /   &
        NOASPENPCD

PROP-SOURCES PURE20   / AQUEOUS   / SOLIDS   / INORGANIC

COMPONENTS
    H2O H2O /
    N2 N2 /
    O2 O2 /
    COAL /
    NO2 NO2 /
    NO NO /
    S S /
    SO2 O2S /
    SO3 O3S /
    H2 H2 /
    CL2 CL2 /
    HCL HCL /
    C C /
    CO CO /
    CO2 CO2 /
    ASH /
    CH4 CH4

FLOWSHEET
    BLOCK DECOMP IN=DRS OUT=S1
    BLOCK BURN IN=S2 AIR OUT=PRODUCTS
    BLOCK SEPARATE IN=S1 OUT=S2 IMPURITY

PROPERTIES IDEAL
```

```
NC-COMPS COAL PROXANAL ULTANAL SULFANAL

NC-PROPS COAL ENTHALPY HCOALGEN 6 / DENSITY DCOALIGT

NC-COMPS ASH PROXANAL ULTANAL SULFANAL

NC-PROPS ASH ENTHALPY HCOALGEN / DENSITY DCOALIGT

PROP-DATA HEAT
    IN-UNITS ENG
    PROP-LIST HCOMB
    PVAL COAL 11700

PROP-SET ALL-SUBS VOLFLMX MASSVFRA MASSSFRA RHOMX MASSFLOW  &
        TEMP PRES UNITS='lb/cuft' SUBSTREAM=ALL
;  "Entire Stream Flows, Density, Phase Frac, T, P"


STREAM AIR
    SUBSTREAM MIXED TEMP=77.0 PRES=14.7 MASS-FLOW=10000.
    MOLE-FRAC N2 0.79 / O2 0.21

STREAM DRS
    SUBSTREAM NCPSD TEMP=77. PRES=14.7
    MASS-FLOW COAL 10000.
    COMP-ATTR COAL PROXANAL ( 7.876 30.884 45.331 15.697 )
    COMP-ATTR COAL ULTANAL ( 15.7 59.66 2.1 4.88 * 0.81  &
        16.85 )
    COMP-ATTR COAL SULFANAL ( 0.2 0.41 0.2 )
    SUBS-ATTR PSD ( 0 0 0 0 0 0 0.1 0.2 0.3 0.4 )

BLOCK DECOMP RYIELD
    PARAM TEMP=77.0 PRES=14.7
    MASS-YIELD MIXED H2O 0.2 / NCPSD ASH 0.1 / CIPSD C  &
        0.37 / MIXED H2 0.03 / N2 0.05 / CL2 0.1 / S  &
        0.05 / O2 0.1
    COMP-ATTR NCPSD ASH PROXANAL ( 0 0 0 100 )
    COMP-ATTR NCPSD ASH ULTANAL ( 100 0 0 0 0 0 0 )
    COMP-ATTR NCPSD ASH SULFANAL ( 0 0 0 )
    SUBS-ATTR 1 CIPSD PSD ( 0 0 0 0 0 0 0.1 0.2 0.3  &
        0.4 )
    SUBS-ATTR 2 NCPSD PSD ( 0 0 0 0 0 0 0.1 0.2 0.3  &
        0.4 )

BLOCK BURN RGIBBS
    PARAM TEMP=1500. PRES=14.7

BLOCK SEPARATE SSPLIT
    FRAC MIXED S2 1.0
    FRAC CIPSD S2 1.
    FRAC NCPSD S2 0.0

EO-CONV-OPTI

CALCULATOR COMBUST
```

```
    VECTOR-DEF ULT COMP-ATTR STREAM=DRS SUBSTREAM=NCPSD  &
        COMPONENT=COAL ATTRIBUTE=ULTANAL
    DEFINE WATER COMP-ATTR-VAR STREAM=DRS SUBSTREAM=NCPSD  &
        COMPONENT=COAL ATTRIBUTE=PROXANAL ELEMENT=1
    DEFINE H2O BLOCK-VAR BLOCK=DECOMP VARIABLE=YIELD  &
        SENTENCE=MASS-YIELD ID1=MIXED ID2=H2O
    DEFINE ASH BLOCK-VAR BLOCK=DECOMP VARIABLE=YIELD  &
        SENTENCE=MASS-YIELD ID1=NCPSD ID2=ASH
    DEFINE CARB BLOCK-VAR BLOCK=DECOMP VARIABLE=YIELD  &
        SENTENCE=MASS-YIELD ID1=CIPSD ID2=C
    DEFINE H2 BLOCK-VAR BLOCK=DECOMP VARIABLE=YIELD  &
        SENTENCE=MASS-YIELD ID1=MIXED ID2=H2
    DEFINE N2 BLOCK-VAR BLOCK=DECOMP VARIABLE=YIELD  &
        SENTENCE=MASS-YIELD ID1=MIXED ID2=N2
    DEFINE CL2 BLOCK-VAR BLOCK=DECOMP VARIABLE=YIELD  &
        SENTENCE=MASS-YIELD ID1=MIXED ID2=CL2
    DEFINE SULF BLOCK-VAR BLOCK=DECOMP VARIABLE=YIELD  &
        SENTENCE=MASS-YIELD ID1=MIXED ID2=S
    DEFINE O2 BLOCK-VAR BLOCK=DECOMP VARIABLE=YIELD  &
        SENTENCE=MASS-YIELD ID1=MIXED ID2=O2
C      FACT IS THE FACTOR TO CONVERT THE ULTIMATE ANALYSIS TO
C      A WET BASIS.
F      FACT = (100 - WATER) / 100
F      H2O  = WATER / 100
F      ASH  = ULT(1) / 100 * FACT
F      CARB = ULT(2) / 100 * FACT
F      H2   = ULT(3) / 100 * FACT
F      N2   = ULT(4) / 100 * FACT
F      CL2  = ULT(5) / 100 * FACT
F      SULF = ULT(6) / 100 * FACT
F      O2   = ULT(7) / 100 * FACT
    EXECUTE BEFORE BLOCK DECOMP

SENSITIVITY S-1
    DEFINE H2 MOLE-FRAC STREAM=PRODUCTS SUBSTREAM=MIXED  &
        COMPONENT=H2
    DEFINE CO MOLE-FRAC STREAM=PRODUCTS SUBSTREAM=MIXED  &
        COMPONENT=CO
    DEFINE CH4 MOLE-FRAC STREAM=PRODUCTS SUBSTREAM=MIXED  &
        COMPONENT=CH4
    TABULATE 1 "H2" COL-LABEL="H2"
    TABULATE 2 "CO" COL-LABEL="CO"
    TABULATE 3 "CH4" COL-LABEL="CH4"
    VARY STREAM-VAR STREAM=AIR SUBSTREAM=MIXED  &
        VARIABLE=MASS-FLOW LABEL="AIR" "FLOW" "     " "RATE"
    RANGE LOWER="10000" UPPER="30000" INCR="2000"

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Thermo gravimetric analysis performed to determine the proximate analysis.

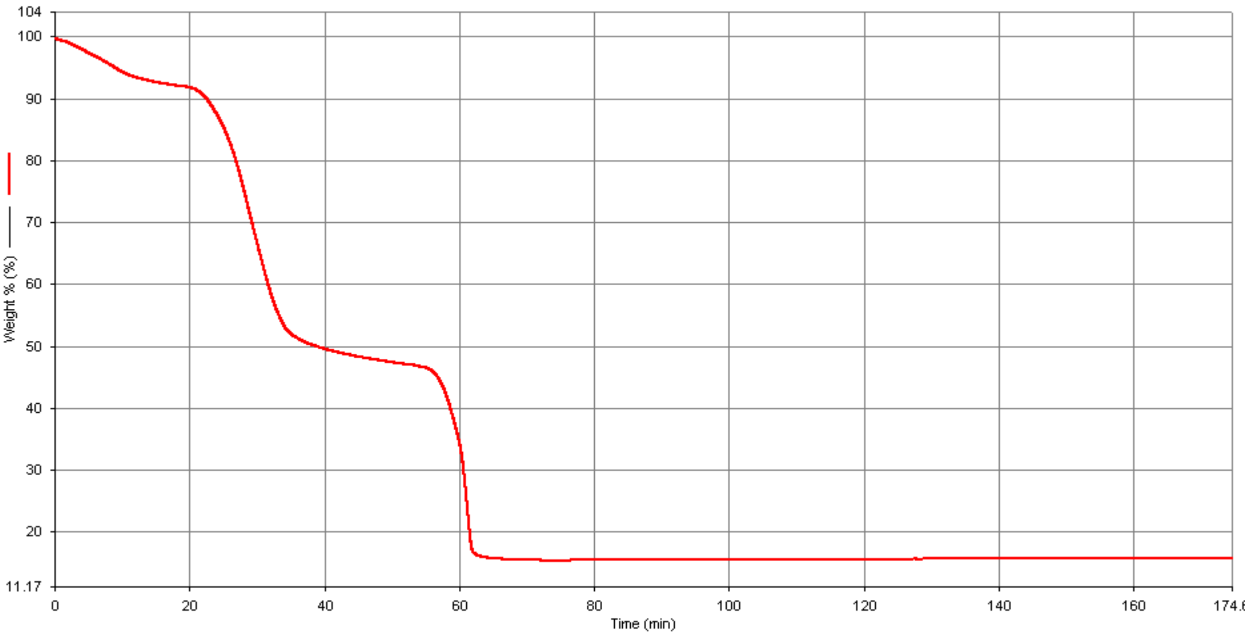

Figure 11 : Weight vs time graph for Thermo gravimetric analysis

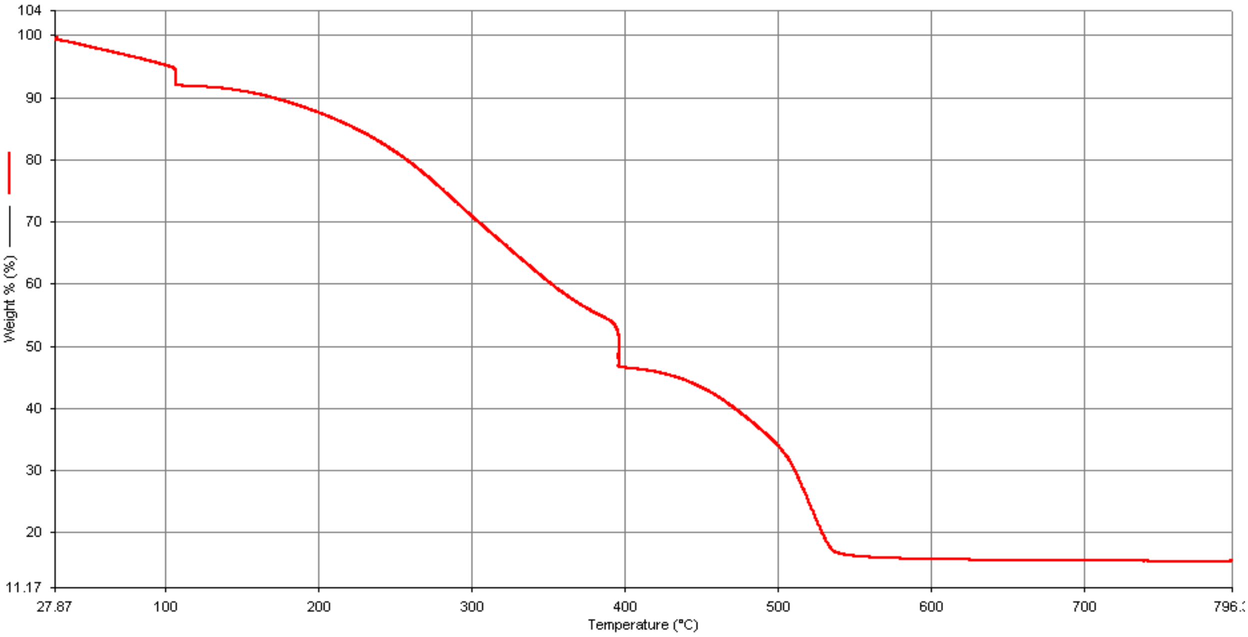

Figure 12: Weight vs temperature graph for Thermo gravimetric analysis