



**Biomass (Non-Palm) Characterization in Enriching Hydrogen and Energy  
Production for Gasification Technology**

by

Nursyamimi Yusof

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

JULY 2009

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# CERTIFICATION OF APPROVAL

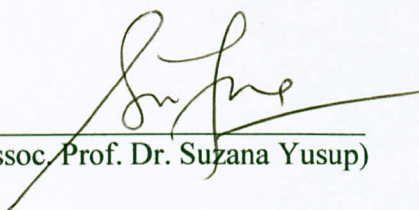
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Approved by,

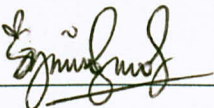


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July 2009

## 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 original work contained herein have not been undertaken or done by unspecified sources or persons.



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NURSYAMIMI YUSOF



## ABSTRACT

Alternative fuels, such as biomass now play an increasingly important role in the energy industry. One biomass energy based technology that has been proven reliable and had been extensively used is biomass gasification. Biomass gasification is defined as incomplete combustion of biomass resulting in production of combustible gases consisting of Carbon monoxide (CO), Hydrogen (H<sub>2</sub>) and traces of Methane (CH<sub>4</sub>). In this project, the feedstock is focusing on the non-palm biomass sources only due to its wide area to be explored compared to palm biomass that had been commonly used in biomass studies. Based on the statistic of United States energy consumption, in 2007, biomass recorded 3.615 quadrillion Btu energy consumed, which is a quite low as compared to other energy sources. This give a signal that there are wide chance to enhance the energy consumption using biomass especially the non-palm biomass resources. The objective of this project is to investigate the biomass characterization in gasification technology in enriching hydrogen production. The biomass samples will be characterized in order to identify their physical and chemical properties. The result will be analyze and relate to hydrogen produced from the gasification of the biomass.

## **ACKNOWLEDGEMENT**

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Sincere appreciation goes to the author's supervising lecturer, Mr. Tazli Azizan and co-supervisor Assoc. Prof. Dr. Suzana Yusup for their guidance and reminders on the project schedule. Thanks are also extended to all of the coordinator of the Final Year Project ( FYP) for giving full commitment and support throughout this project.

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# **CHAPTER 1**

## **INTRODUCTION**

### **1.1 Problem Statement**

#### **1.2.1 Problem Identification**

Renewable biomass could be gasified to produce a hydrogen-rich gas or hydrogen. Among the biomass energy conversion schemes, gasification produces a product gas which based on its properties could be used either to make value-added byproducts or hydrogen.

Biomass may become a significant component in the global sustainable energy as fossil fuel resources begin to deplete. This consideration might include the pollution that caused by fossil fuels as well. Hydrogen or hydrogen-rich gas produced from biomass could be readily used in most of the present natural gas or petroleum derived hydrogen energy conversion devices and also in advanced systems such as fuel cells. However, the new challenge faced in gasification technology nowadays is less hydrogen is being produce. Some factors that affecting this matter are moisture content of the biomass and the oxygen content. There are other factors also that might influence the hydrogen production.

## **1.2.2 Significance of the Project**

Therefore, it is very important to seek for modifications that can be made in gasification technology in order to enhance the hydrogen production. These biomasses should be characterized and further analyzed to investigate their potential in enriching hydrogen, which later could be a valuable source of energy.

## **1.2 Objectives and Scope of Study**

### **1.2.1 Objectives of the Study**

This research is to investigate the feasibility of a few types of biomasses in gasification technology in producing hydrogen. There will be four types of biomasses that will be characterized throughout the project. At the end of the research, it is hope that the best type of biomass among the four could be identified for enriching the hydrogen production. The detailed of the objectives are as follows:

1. To investigate the characteristics of the biomass samples (paddy straw, rice husk and coconut shell).
2. To analyze how the characteristics of the biomass samples could effect hydrogen production.
3. To identify the most favorable biomass samples that will have high H<sub>2</sub> production from gasification process.

### **1.2.2 The Relevancy of the Project**

This study will improve the possibility of using the biomass waste as source of hydrogen production as well as energy production. This will indirectly reduce human dependency on fossil fuels and to cater the possibility of fuel shortage in the future. Other than that, biomass waste also is abundant source and can easily found, therefore, it is very useful if people can make use of the waste to produce energy.



### **1.2.3 Feasibility of the Project within the Scope and Time Frame**

The project had been conducted throughout the year within two semesters. The first semester had been dedicated for literature review phase. Meanwhile, in the second semester (consists of 15 weeks) is when the experimental part of the project was conducted. The period allocation is actually feasible for the project but due to some reason such as unavailability of the equipment had caused the project was not able to be completed within the time frame.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 World Energy

The increase demands of energy from day to day had inflated the burning of fossil fuels, thus, the amount of carbon dioxide in the atmosphere has been increasing globally. Even though carbon dioxide contains a very small part of the atmosphere (0.04%), it plays a significant role in energy balance of the planet. Carbon dioxide in the atmosphere would radiate heat away from the planet.

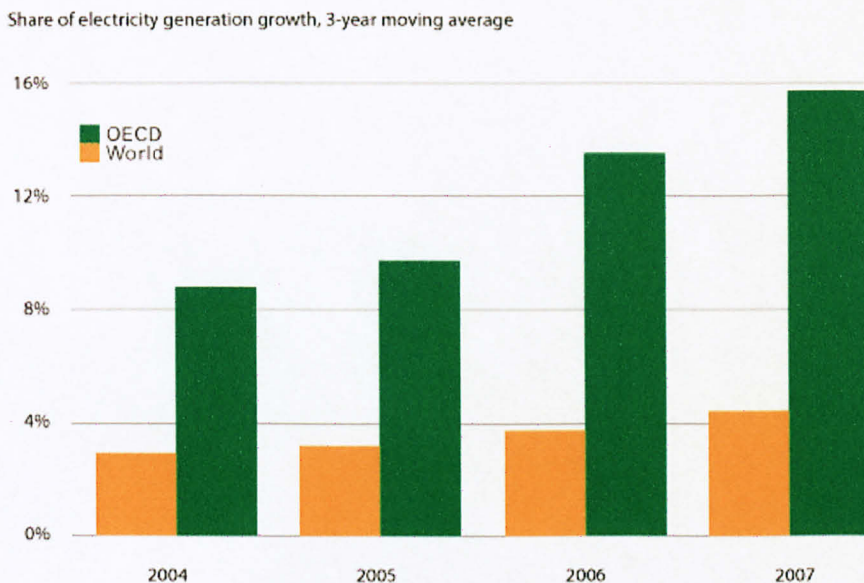


Figure 2.1: Share of electrical generation growth

The mounting growth of electrical generation shows that the importance of energy in recent years. However, to increase the usage of fossil fuels in obtaining the energy will increase the carbon dioxide in atmosphere, thus affecting the environment. Therefore, alternative sources of energy or also known as renewable energy are now to be commercialized to the people in reducing the problem.

Table 2.1: United States Energy Consumption by Energy Source, 2003-2007  
(Quadrillion Btu)

| Energy Source              | 2003          | 2004           | 2005           | 2006          | 2007           |
|----------------------------|---------------|----------------|----------------|---------------|----------------|
| <b>Total</b>               | <b>98.209</b> | <b>100.351</b> | <b>100.503</b> | <b>99.861</b> | <b>101.605</b> |
| Fossil Fuels               | 84.078        | 85.830         | 85.816         | 84.662        | 86.253         |
| Coal                       | 22.321        | 22.466         | 22.795         | 22.452        | 22.786         |
| Coal Coke Net Imports      | 0.051         | 0.138          | 0.044          | 0.061         | 0.025          |
| Natural Gas                | 22.897        | 22.931         | 22.583         | 22.191        | 23.625         |
| Petroleum                  | 38.809        | 40.294         | 40.393         | 39.958        | 39.818         |
| Electricity Net Imports    | 0.022         | 0.039          | 0.084          | 0.063         | 0.106          |
| Nuclear                    | 7.959         | 8.222          | 8.160          | 8.214         | 8.415          |
| Renewable                  | 6.150         | 6.261          | 6.444          | 6.922         | 6.830          |
| Biomass                    | 2.817         | 3.023          | 3.154          | 3.374         | 3.615          |
| Biofuels                   | 0.414         | 0.513          | 0.595          | 0.795         | 1.018          |
| Waste                      | 0.401         | 0.389          | 0.403          | 0.407         | 0.431          |
| Wood Derived Fuels         | 2.002         | 2.121          | 2.156          | 2.172         | 2.165          |
| Geothermal                 | 0.331         | 0.341          | 0.343          | 0.343         | 0.353          |
| Hydroelectric Conventional | 2.825         | 2.690          | 2.703          | 2.869         | 2.463          |
| Solar/PV                   | 0.064         | 0.065          | 0.066          | 0.072         | 0.080          |
| Wind                       | 0.115         | 0.142          | 0.178          | 0.264         | 0.319          |

Sources: Non-renewable energy: Energy Information Administration (EIA), Monthly Energy Review

(MER) March 2008, DOE/EIA-0035 (2008/03) (Washington,DC, March 2008,) Tables 1.3, 1.4a and 1.4b. Renewable Energy: Table 2 of this report.

From Table 2.1, it can be seen that the highest energy source that being consumed in United States is fossil fuels. This will give an alarming signal to the



environment as per discussed earlier. Petroleum is another energy source that highly consumed after fossil fuels. Petroleum is non-renewable source of energy, thus, it is not a reliable energy source of energy in long-term condition. Other than these two main sources of energy, there are also several alternatives source of energy listed in Table 2.1. There are biomass, biofuels, waste, wood derived fuels and many more. It is to be highlighted that energy consumption from biomass is increasing from year to year. This is a good sign shown that biomass is to be accepted by the people as an alternative source of energy and becoming more commercialized.

## **2.2 Biofuels**

Biofuels or biodiesels are fuels that are, in essence, biodegradable and non-toxic. They are manufactured from vegetable oils, waste cooking oils, animal fats or tall oil (a by-product of the pulp and paper industry) (NBEP, 2007). These oils undergo a process called transesterification whereby they are subjected to a reaction with an alcohol (usually methanol or ethanol) using a catalyst such as sodium hydroxide. The resulting chemical reaction produces an ester called biodiesel and a by-product called glycerin (Canada, 2007).

### **2.2.1 First Generation**

This generation is mainly referring to the fuels that derived from sources such as starch, sugar animal fats and vegetable oil. It is obtained by using the conventional techniques of production. A few types of first generation of biofuels are biodiesel, vegetable oil, biogas, bioalcohols and syngas.

A study by Timothy Searchinger et al, “*Use of U.S. Croplands for Biofuels Increases Greenhouse Gases Through Emissions from Land Use Change.*” appeared in 7<sup>th</sup> February 2008 of *Sciencexpress*. It reported that prior studies “have failed to count the carbon emissions that occur as farmers worldwide respond to higher prices and convert forest and grassland to new cropland to replace the grain (or cropland) diverted to biofuels”. The study models an increase in United States corn ethanol of 56 billion



liters above projected 2016 production levels. This would divert 12.8 million hectares of U.S. corn production to ethanol, bringing 10.8 million hectares of new cropland into cultivation, primarily in Brazil, China, India and the U.S. It assumes that land converted to farming will release 25 percent of its soil carbon, an average of 351 metric tones per hectare.

### **2.2.2 Second Generation**

The development of the second generation is due to some limitations of first generation biofuels. This biofuels supply sustainable and larger amount of fuels with greater environment benefits. The aim of this generation is to extent the amount of biofuels that can be produced sustainably by using the biomass residual such as non-food parts (stems, leaves and husks) or other crops that are not for food purposes such as switch grass and jatropha. Besides, the industry wastes such as wood chips, skins and pulp are also some biomass residual that can produce biofuels.

Pulp Mill Engineering Department is working on implementation of the first and second generation biofuel plants and analyzing the opportunities involved in more advanced biofuels. The new biofuel technologies such as production of ligno-cellulosic ethanol and biomass-to-liquid (BTL), it uses a non-food renewable feedstock that is largely based on residues from agriculture and forestry or specific energy wood. Besides, it also offers substantially larger greenhouse gas reductions, up to 90 percent.

### **2.2.3 Third Generation**

The third generation that also known as Oilgae, is having a low cost and high yield production. Based on Zeeshan (2008), this generation has a very high energy production that almost 30 times more energy per acre as compared to the land required by other conventional feedstock to produce biofuels. Currently, researches are being conducted by Alga culture (farming Algae) to produce different fuels like vegetable oils, biodiesel, bioethanol, biomethanol, biobutanol and other biofuels. The approach of using algae to

produce biodiesel is a sustainable method to replace the need of gasoline used for automotive.

A research paper on a new process called Consolidated Bioprocessing (CBP) in which cellulase production, substrate hydrolysis, and fermentation are accomplished in a single process step by cellulolytic microorganisms. Due to simpler feedstock processing with lower energy inputs and higher conversion efficiencies, CBP offers the potential for lower biofuel production costs compared to separate hydrolysis and fermentation processes. It is an economically attractive for short-term goal of third generation biofuels. The production of third generation biofuels from cellulosic feedstocks will be addressed to the metabolism of cellulolytic bacteria and the development of strategies to increase biofuel yields through metabolic engineering.

## **2.3 Hydrogen Fuels**

Hydrogen can be produced using various feedstocks including fossil fuels, such as natural gas and coal; nuclear power; and biomass and other renewable energy technologies, such as wind, solar, geothermal, and hydro-electric power. There are some technologies being introduced in producing hydrogen. Some of the technologies are as follows:

### **2.3.1 Steam Methane Reforming**

In steam methane reforming, methane reacts with steam under 3 to 25 bar pressure in the presence of a catalyst to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide. Heat must be supplied to the process in order for the reaction to proceed because steam reforming is endothermic.

There are two main steps involve in steam methane reforming. The first one is called the "water-gas shift reaction," the carbon monoxide and steam is reacted using a catalyst to produce carbon dioxide and more hydrogen. Secondly, the step is called "pressure-swing adsorption," carbon dioxide and other impurities are removed from the



gas stream, leaving essentially pure hydrogen. Steam reforming can also be used to produce hydrogen from other fuels, such as ethanol, propane, or even gasoline.

**Methane:**



**Propane:**



**Ethanol:**



**Gasoline** (using iso-octane and toluene as example compounds from the hundred or more compounds present in gasoline):



**Water-Gas Shift Reaction**



However, the major drawback with steam methane reforming is the use of a fossil fuel causing a release of carbon dioxide in the air during the process.

### **2.3.2 High-temperature Water Splitting**

High-temperature water splitting is a thermochemical process. It needs a high-temperature heat (500 - 2000°C) to drive a series of chemical reactions that produce hydrogen. According to Cutler J.Cleveland (2008), the chemicals used in the process are reused within each cycle, creating a closed loop that consumes only water and produces hydrogen and oxygen. The high-temperature heat needed can be supplied by next-generation nuclear reactors under development (up to about 1000°C) or by using sunlight with solar concentrators (up to about 2000°C).

### **2.3.3 Electrolytic Processes**

Electrolysis is the process of using electricity to split water into hydrogen and oxygen. This reaction takes place in a unit called an electrolyzer. Hydrogen produced via electrolysis can result in zero greenhouse gas (GHG) emissions, depending on the source of the electricity used.

However, the cost, efficiency and emissions resulting from electricity generation must be considered when evaluating the benefits of hydrogen production via electrolysis. In many regions of the country, it is not ideal for providing the electricity required for electrolysis because of the greenhouse gases released and the amount of energy required to generate electricity. Hydrogen production via electrolysis is being pursued for renewable (wind) and nuclear options. These pathways result in virtually zero GHG emissions and criteria pollutants.

### **2.3.4 Gasification of Coal**

In the presence of steam and limited amount of oxygen, coal can be converted into a gaseous mixture of hydrogen, carbon monoxide, carbon dioxide, and other compounds. A certain amount of heat under pressure must be applied as well in order to achieve that. The coal is chemically broken apart by the gasifier's heat, steam, and oxygen that produce a synthesis gas, or "syngas" which is the mixture of primarily hydrogen, carbon monoxide, and carbon dioxide. The carbon monoxide is reacted (in a separate unit) with water to form carbon dioxide and more hydrogen. Adsorbers or special membranes can separate the hydrogen from this gas stream.

According to Cutler J.Cleveland (2008), an advantage of this technology is that carbon dioxide can be separated more easily from the syngas and captured, instead of being released into the atmosphere. If carbon dioxide can be successfully sequestered, hydrogen can be produced from coal gasification with near-zero greenhouse gas emissions.



Coal gasification can also be used to produce electricity by routing the syngas to a turbine to generate electricity. Coal gasification technology could be used to generate both electricity and hydrogen in one integrated plant operation.

### **2.3.5 Gasification of Biomass**

Biomass is converted into a gaseous mixture of hydrogen, carbon monoxide, carbon dioxide, and other compounds by applying heat under pressure in the presence of steam and a controlled amount of oxygen. The chemical reactions will produce a synthesis gas, or "syngas", which consists a mixture of primarily hydrogen, carbon monoxide, and carbon dioxide. The carbon monoxide is then reacted with water to form carbon dioxide and more hydrogen (water-gas shift reaction). Adsorbers or special membranes can separate the hydrogen from this gas stream.

#### ***Simplified Example Reaction***



Note: The above reaction uses glucose as a substitute for cellulose. Actual biomass has highly variable composition and complexity, with cellulose as one major component.

#### ***Water-Gas Shift Reaction***



Pyrolysis is the gasification of biomass in the absence of oxygen. According to Cutler J.Cleveland (2008), biomass generally does not gasify as easily as coal and it produces other hydrocarbon compounds in the gas mixture exiting the gasifier; this is especially true when no oxygen is used. As a result, typically an extra step must be taken to reform these hydrocarbons with a catalyst to yield a clean syngas mixture of hydrogen, carbon monoxide, and carbon dioxide. Then, just as in the gasification process for hydrogen production, a shift reaction step (with steam) converts the carbon monoxide to carbon dioxide. The hydrogen produced is then separated and purified.

## 2.4 Hydrogen Properties

### 2.4.1 Physical Properties

Hydrogen is colourless. It is highly flammable where explosive mixtures are easily formed if the gas mixes well with air. The gas is light in weight. Hydrogen is diatomic and much lighter than air. The hydrogen density is  $0.0899 \times 10^{-3} \text{ g.cm}^{-3}$  at  $20^{\circ}\text{C}$ . It has a melting point of  $-259.2^{\circ}\text{C}$  and boiling point of  $-252.8^{\circ}\text{C}$ . Pure hydrogen is a gas under normal conditions.

### 2.4.2 Chemical Properties

Hydrogen can easily reacts with other chemical substances. However, it does not react with other chemicals at room temperature. Its electronegativity according to Pauling is 2.1. Hydrogen is slightly more soluble in organic solvents than in water. It has energy of ionization of  $1311 \text{ kJ.mol}^{-1}$ . Combination of two hydrogen molecules ( $\text{H}_2$ ) and one oxygen molecule ( $\text{O}_2$ ) will form two molecules of water ( $\text{H}_2\text{O}$ ). This reaction releases energy and it is extraordinarily slow at ambient temperature.

Hydrogen bonds form covalent bonds with each other and with other atoms. In some molecules containing hydrogen, the covalent bond between one of the hydrogen atoms and another atom is weak and breaks easily. Compounds made of these bonds are called acids. Hydrogen also forms ionic bonds with some metals, creating a compound called a hydride. Hydrogen can also form a unique bond known as a hydrogen bond. Hydrogen bonds only form between hydrogen and the elements oxygen (O), nitrogen (N), or fluorine (F). Water is a good example of hydrogen bonding.

Many metals absorb hydrogen. Hydrogen absorption by steel can result in brittle steel, which leads to fails in the chemical process equipment. At normal temperature hydrogen is a not very reactive substance. Atomic hydrogen reacts with organic compounds to form a complex mixture of products.



Under extreme pressure hydrogen can actually act like a metal. Heating of hydrogen may cause violent combustion or explosion. It reacts violently with air, oxygen, halogens and strong oxidants causing fire and explosion hazard. Hydrogen is also widely used as a reducing agent.

## **2.5 Technology Using Hydrogen**

There are two primary uses for hydrogen today. About half is used to produce ammonia ( $\text{NH}_3$ ) via Haber process, which is then used as fertilizer. The demand for ammonia keeps increasing because of world population and the intensive agriculture used to support it is growing.

The other half of current hydrogen production is used to convert heavy petroleum sources into lighter fractions suitable for use as fuels. This process is known as hydrocracking. Hydrocracking represents an even larger growth area, since rising oil prices encourage oil companies to extract poorer source material, such as tar sands and oil shale.

## **2.6 Hydrogen Economy**

Hydrogen economy is a theoretical economy in which the energy needed for automotive power or electricity is derived from reacting hydrogen ( $\text{H}_2$ ) with oxygen. While the primary purpose is to eliminate the use of carbon-based fossil fuels and reduce carbon dioxide emissions, a secondary goal is to provide a supportive energy to replace declining supplies of petroleum as well as to train energy independence to the countries without oil resources. Hydrogen is energy storage medium and it is not a primary energy source.

According to University of Leeds (2007), hydrogen production is a large and growing industry. In 2004, some 50 million metric tons of hydrogen, equal to about 170 million tons of oil equivalent were produced globally. The growth rate is around 10% per year. Within the United States, 2004 production was about 11 million metric



tons (MMT), an average power flow of 48 gigawatts. As of 2005, the economic value of all hydrogen produced worldwide is about \$135 billion per year.

2.7 Gasification

Gasification is define by Christine & Scott Gable from About.com as a thermo-chemical process in which carbonaceous (carbon-rich) feedstock such as coal, petro-coke or biomass are converted into a gas consisting of hydrogen and carbon monoxide (and lesser amounts of carbon dioxide and other trace gases) under oxygen depleted, high pressure, high-heat and steam conditions. This process produce gaseous compound known as syngas. It is an efficient energy extracting process if conducted under proper conditions.

In the overall process of biomass, gasification is the third stage before the energy is produced. The gasification must be carried out in air sealed, closed chamber, under slight suction or pressure relative to ambient pressure in order to accomplish the gasification process. The general flow of the process is explained in Figure 2.2.

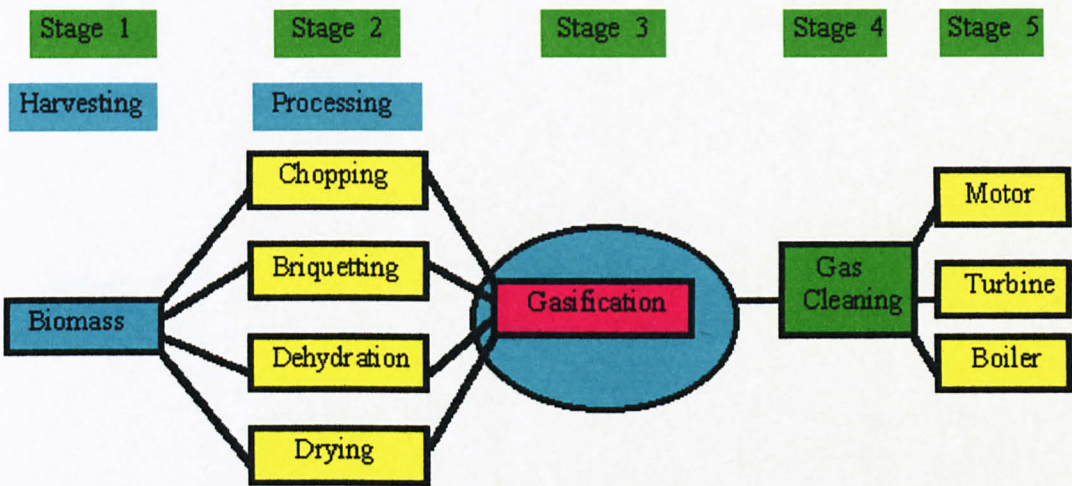


Figure 2.2: Complete gasification process

### 2.7.1 Gasification Process

There are four distinct processes take place in gasifier as the fuel makes its way to gasification according to Anil K.Rajvanshi (1986) and the processes are drying of the fuel, pyrolysis, combustion and reduction. All the processes occur at the same time in different parts of gasifier. Four distinct processes take place in a gasifier as the fuel makes its way to gasification

#### *Drying*

There is no decomposition happen in the drying process. The water in the biomass is removed and converted to steam at temperature above 100°C. Moisture content in biomass fuels is ranging from 5 to 35%.

#### *Pyrolysis*

Based on Chandrakant Turare from University of Flensburg, pyrolysis is the thermal decomposition of biomass fuels in the absence of oxygen. Pyrolysis involves release of three kinds of products: solid, liquid and gases. The ratio of products is influenced by the chemical composition of biomass fuels and the operating conditions. The heating value of gas produced during the pyrolysis process is low.

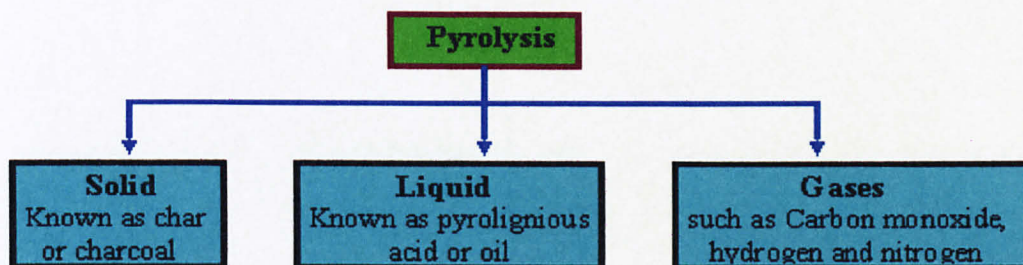
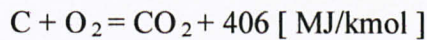


Figure 2.3: Pyrolysis products

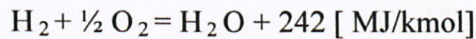
## ***Oxidation***

In this process, air, oxygen, water vapors and inert gas are being introduced in the oxidation zone according to Chandrakant Turare from University of Flensburg. These inert gases such as nitrogen and argon are considered to be non-reactive with fuel constituents. The oxidation takes place at the temperature of 700°C to 2000°C.

Oxygen in the air reacts with solid carbonized fuel to produce carbon monoxide. Plus and minus sign indicate the release and supply of heat energy during the process respectively.



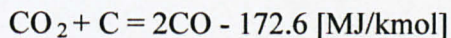
Meanwhile, hydrogen in fuel reacts with oxygen to produce steam.



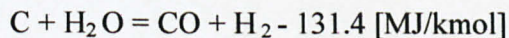
## ***Reduction***

According to Chandrakant Turare from University of Flensburg, in reduction zone, a number of high temperature chemical reactions take place in the absence of oxygen. The principal reactions that take place in reduction are mentioned below.

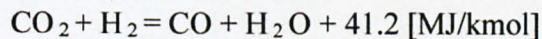
Boudouard reaction:



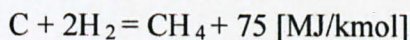
Water-gas reaction:



Water shift reaction:



Methane production reaction:





If complete gasification takes place, all the carbon is burned or reduced to carbon monoxide, a combustible gas and some other mineral matter is vaporized. The remains are ash and some char (unburned carbon)

### **2.7.2 Types of Gasifier**

#### ***Updraft or Counter Current Gasifier***

The air intake is at the bottom and the gas leaves at the top. Near the grate at the bottom the combustion reactions occur, which are followed by reduction reactions somewhat higher up in the gasifier. In the upper part of the gasifier, heating and pyrolysis of the feedstock occur as a result of heat transfer by forced convection and radiation from the lower zones. The tars and volatiles produced during this process will be carried in the gas stream. Ashes are removed from the bottom of the gasifier.

The major advantages of this type of gasifier are its simplicity, high charcoal burn-out and internal heat exchange leading to low gas exit temperatures and high equipment efficiency, as well as the possibility of operation with many types of feedstock (sawdust, cereal hulls, etc.).

Major drawbacks result from the possibility of "channeling" in the equipment, which can lead to oxygen break-through and dangerous, explosive situations and the necessity to install automatic moving grates, as well as from the problems associated with disposal of the tar-containing condensates that result from the gas cleaning operations. The latter is of minor importance if the gas is used for direct heat applications, in which case the tars are simply burnt.

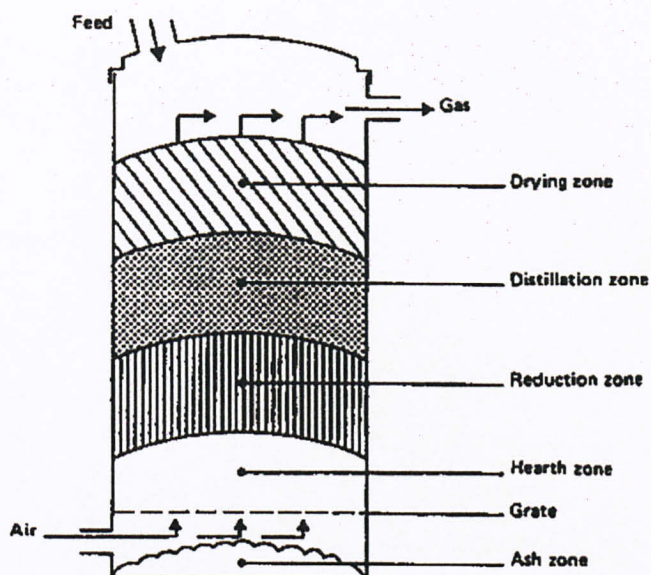


Figure 2.4: Updraft or counter current gasifier

### *Downdraft or Co-Current Gasifier*

In downdraft gasifier, primary gasification air is introduced above the reduction zone in the gasifier. The producer gas is removed at the bottom of the apparatus, so that fuel and gas move in the same direction, as schematically shown in Figure 2.5.

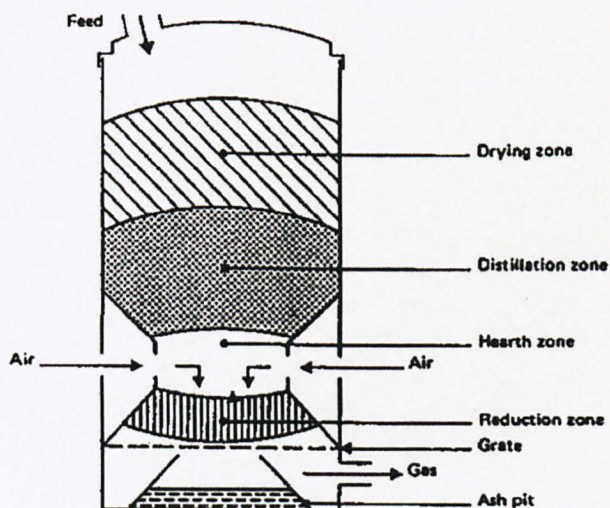


Figure 2.5: Downdraft or co-current gasifier

On their way down the acid and tarry distillation products from the fuel must pass through a glowing bed of charcoal and therefore are converted into permanent gases hydrogen, carbon dioxide, carbon monoxide and methane.

The main advantage of downdraught gasifiers lies in the possibility of producing a tar-free gas suitable for engine applications. Because of the lower level of organic components in the condensate, downdraft gasifiers suffer less from environmental objections than updraft gasifiers.

A major drawback of downdraught equipment lies in its inability to operate on a number of unprocessed fuels. In particular, fluffy, low density materials give rise to flow problems and excessive pressure drop, and the solid fuel must be pelletized or briquetted before use. Downdraught gasifiers also suffer from the problems associated with high ash content fuels (slagging) to a larger extent than updraft gasifiers. Minor drawbacks of the downdraft system, it is somewhat lower efficiency resulting from the lack of internal heat exchange as well as the lower heating value of the gas.

### ***Cross-draft Gasifier***

Cross-draught gasifiers, schematically illustrated in Figure 2.6 are for the use of charcoal. Charcoal gasification results in very high temperatures (1500 °C and above) in the oxidation zone which can lead to material problems. In cross draft gasifiers insulation against these high temperatures is provided by the fuel (charcoal) itself.



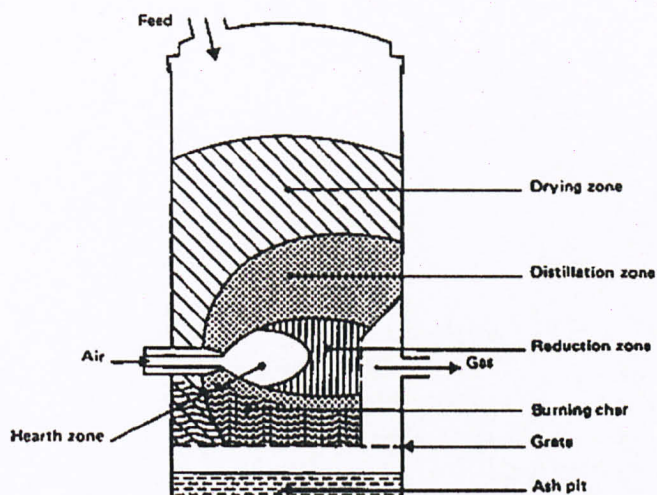


Figure 2.6: Cross-draft gasifier

An advantage of the system is when it operated in very small scale. Installations below 10 kW (shaft power) can be economically feasible under certain conditions. The reason is because it needed a simple gas-cleaning train consists of a cyclone and a hot filter which can be employed when using this type of gasifier in conjunction with small engines. The disadvantage of cross-draught gasifiers is their minimal tar-converting capabilities and the consequent need for high quality (low volatile content) charcoal.

All the advantages and disadvantages of each type of gasifier are being summarized in Table 2.2.

Table 2.2: Advantages and disadvantages of gasifiers

| Gasifier Type | Advantages                                                                                                                                                                                                                                                     | Disadvantages                                                                                                                                                                                                                                                        |
|---------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Updraft       | <ul style="list-style-type: none"> <li>• Simplicity</li> <li>• Low gas exit temperatures</li> <li>• High equipment efficiency</li> <li>• Able to operate with many types of feedstock (sawdust, cereal hulls, etc.).</li> <li>• Small pressure drop</li> </ul> | <ul style="list-style-type: none"> <li>• Possibility of "channeling" in the equipment, which can lead to oxygen break-through</li> <li>• Disposal of the tar-containing condensates</li> <li>• Great sensitivity to tar and moisture and moisture content</li> </ul> |

|            |                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                                                                                                                   |
|------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|            | <ul style="list-style-type: none"> <li>• Good thermal efficiency</li> <li>• Little tendency towards slag formation</li> </ul>                                                                                                          | <ul style="list-style-type: none"> <li>• of fuel</li> <li>• Poor reaction capability with heavy gas load</li> </ul>                                                                                                                                                                                                               |
| Downdraft  | <ul style="list-style-type: none"> <li>• Produce a tar-free gas suitable for engine applications</li> <li>• Flexible adaption of gas production to load</li> <li>• Low sensitivity to charcoal dust and tar content of fuel</li> </ul> | <ul style="list-style-type: none"> <li>• Unable to operate on a number of unprocessed fuels</li> <li>• Low density materials give rise to flow problems and excessive pressure drop</li> <li>• Not feasible for very small particle size of fuel</li> <li>• Lower efficiency</li> <li>• Lower heating value of the gas</li> </ul> |
| Crossdraft | <ul style="list-style-type: none"> <li>• Economically feasible because it needed a simple gas-cleaning train</li> <li>• Very fast response time to load</li> <li>• Flexible gas production</li> </ul>                                  | <ul style="list-style-type: none"> <li>• Minimal tar-converting capabilities</li> <li>• Consequent need for high quality (low volatile content) charcoal</li> <li>• Very high sensitivity to slag formation</li> <li>• High pressure drop</li> </ul>                                                                              |

## 2.8 Biomass

Biomass is a renewable fuel and the fourth largest following coal, oil and natural gas according to Colomba Di Blasi (2008). Some examples of biomass are wood, agricultural residues, forestry residues, energy crops, etc. The advantage of it is being neutral in regard to the emissions of the green-house gas carbon dioxide compared to fossil fuels. Carbon dioxide participates in biomass growth through the photosynthesis reactions, and reducing pollutant species generation, besides of low sulfur and nitrogen contents.

In recent years, renewable biomass resources such as agricultural residues have received increasing attention as an interesting renewable energy source. As a source of renewable energy, biomass energy has significant environmental benefits. One of the attractive ways to utilize biomass energy is hydrogen production. According to Ningbo Gao et al. hydrogen has good properties as a fuel for internal combustion engines in automobiles. It is used as a clean power source for fuel cells. Also, its use could be advantageous as a clean energy carrier for heat supply and transportation purposes.

Table 2.3 is showing about biomass energy consumption and electricity net generation in year 2006. From the table, the highest biomass energy consumption and electricity net generation is coming from manufacturing industry with total about 1,868 trillion Btus energy consumption and 28,716 million kilowatthours for the net electricity generation. Based on this information, it is understand that most of the biomass energy resources are from manufacturing industry. From Table 2.3, it is also observed that agricultural industry contributes about 13 trillion Btus energy consumption and a net electricity generation of 181 million kilowatthours. This indicates that agricultural industry also plays important role as biomass resources as its rank the second highest after the manufacturing industry. The rank then is followed by food and kindred products industry and lastly chemicals and allied products industry.



Table 2.3: Industrial Biomass Energy Consumption and Electricity Net Generation by  
Industry and Energy Sources, 2006

| Industry                                     | Energy Source                     | Biomass Energy Consumption<br>(trillion Btus) |                                    |          | Net Generation<br>(million<br>kilowatthours) |
|----------------------------------------------|-----------------------------------|-----------------------------------------------|------------------------------------|----------|----------------------------------------------|
|                                              |                                   | For<br>Electricity                            | For<br>Useful<br>Thermal<br>Output | Total    |                                              |
| <b>Agricultural</b>                          | Agricultural<br>Byproducts/Crops  | 2.888                                         | 10.31                              | 13.198   | 181                                          |
| <b>Manufacturing</b>                         |                                   | 354.767                                       | 1513.389                           | 1868.156 | 28,716                                       |
| <b>Food and<br/>Kindred<br/>Products</b>     | Agricultural<br>Byproducts/Crops  | 0.937                                         | 33.75                              | 34.687   | 29                                           |
|                                              | Other Biomass<br>Gases            | 0.042                                         | 0.568                              | 0.61     | 8                                            |
|                                              | Other Biomass<br>Liquids          | 0.069                                         | 0                                  | 0.069    | 6                                            |
|                                              | Wood/Wood<br>Waste Solids         | 0.278                                         | 2.39                               | 2.668    | 56                                           |
| <b>Chemicals and<br/>Allied<br/>Products</b> | Landfill Gas                      | 0.078                                         | 0.082                              | 0.16     | 4                                            |
|                                              | Municipal Solid<br>Waste Biogenic | 0.079                                         | 0.711                              | 0.79     | 10                                           |
|                                              | Other Biomass<br>Liquids          | 0.014                                         | 0.146                              | 0.16     | 3                                            |
|                                              | Other Biomass<br>Solids           | 0                                             | 0.005                              | 0.005    | 0                                            |
|                                              | Sludge Waste                      | 0                                             | 0.389                              | 0.389    | 0                                            |
|                                              | Wood/Wood<br>Waste Solids         | 0.689                                         | 2.328                              | 3.017    | 17                                           |

Source: <http://www.eia.doe.gov/cneaf/solar.renewables/page/wood/wood.html>

The selection of biomasses for this project is focusing on agricultural and food products industries is because there are demands for biomass energy from these industries. Besides, there is possibility for resources from these industries to be commercialized and be the same level with manufacturing industry. Therefore, types of biomasses chosen for this project are coconut shell, sugarcane, tea waste and saw dust.

## **2.9 Characterization**

Biomass from different sources presents very variable compositions. Consequently, there is a wide variation in the nature and quantities of gaseous products obtained after thermal treatment of biomasses.

The aim of characterization of the biomass is to establish a link between the composition of a biomass and its pyrolysis gas yields. This will lead to determination of most suitable biomass that can be further used in gasification technology in producing enriched hydrogen. There are four conditions that to be determined and they are moisture content, oxygen content, the heating value and the chemical structure of the biomass. The chemical structure is referring to cellulose, hemicellulose and lignin.

### **2.9.1 Effect of moisture content**

According to Sheth and Babu (2008), it is found that with an increase in the moisture content, the biomass consumption rate decreases. It is because a higher energy requirement is needed for drying the higher moisture content of biomass and thus reduces the biomass pyrolysis. The biomass moisture content greatly effects both the operation of the gasifier and the quality of the product gas. The constraint of moisture content for gasifier fuels are dependent on type of gasifier used. Higher values of moisture content could be used in updraft systems but the upper limit acceptable for a downdraft reactor is generally considered to be around 40% on dry basis based as reported by Dogru et al (2002).

In the meantime, A. Demirbas (2007) investigate the effects of moisture and hydrogen contents on lower heating value (LHV) of fuels. The LHV at constant pressure measures the enthalpy change of combustion with and without water condensed, respectively. Moisture in biomass generally decreases its heating value. Moisture in biomass is stored in spaces within the dead cells and within the cell walls. Higher heating value (HHV) of a fuel decreases with increasing of its moisture content. The



LHV of a fuel increases with increasing of its hydrogen content. The LHV of a fuel depends on its oxygen content and the LHV of a fuel decreases with increasing of its oxygen content. The LHV of a fuel increases with increasing the hydrogen content due to cause combustion water. Moisture in a fuel generally decreases its HHV. The LHV of a fuel increases with increasing the sulfur content due to cause  $\text{SO}_x$  gases absorbed by water.

### 2.9.2 The influence of the oxygen

Understanding of the effect oxygen content on major design parameters is crucial in designing of a biomass gasifier. According to B.V. Babu and Pratik N. Sheth (2004), the calorific values of the producer gas increase as the oxygen fraction increases and also as the steam to air ratio increases.

Figure 2.7 shows how the composition of gas changes with oxygen fraction in the air. Most of the variations of the line are more or less linear. However, the mole fraction of  $\text{N}_2$  decreases with increasing oxygen fraction.

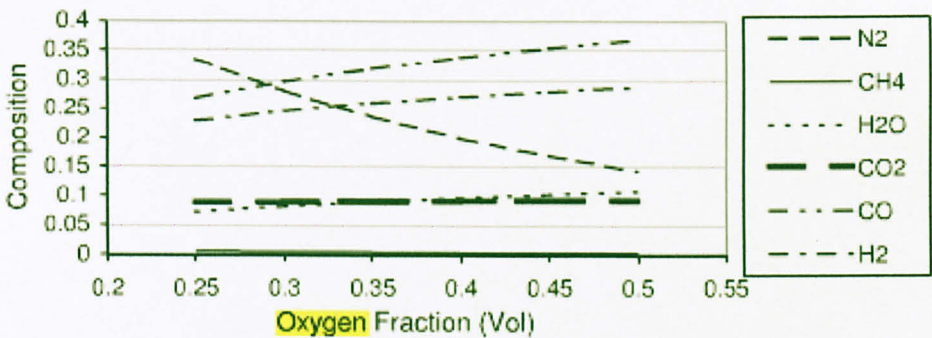


Figure 2.7: Effect of oxygen enrichment on the composition

A significant increase in the calorific values of fuel gas at higher oxygen fraction as can be seen in Figure 2.8. Calorific value increment is due to increase in the amount of  $\text{CO}$  and of  $\text{H}_2$ .



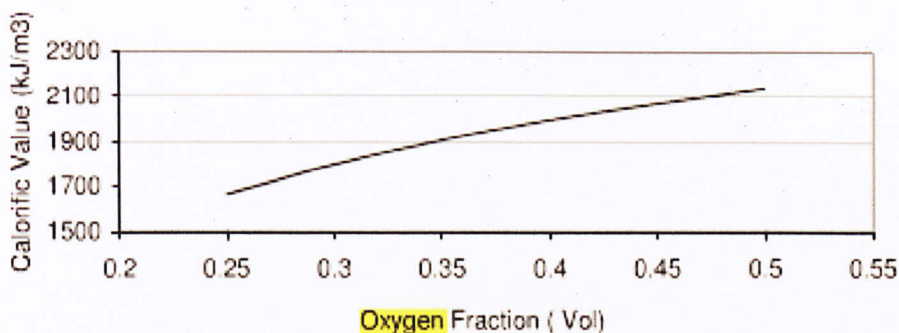


Figure 2.8: Effect of oxygen enrichment on calorific value

### 2.9.3 The effect of the chemical structure

The ultimate analysis is done on the biomass samples to know the component content within the biomass sample in term of percentage. Through this analysis, the composition of the component within the material can be obtained. Table 2.4 is showing the ultimate analysis of coconut shell and paddy straw obtained from literature review.

Table 2.4: Ultimate analysis of biomass samples

| Biomass                        | Coconut Shell | Paddy Straw |
|--------------------------------|---------------|-------------|
| <b>C (wt. %)</b>               | 52.3          | 39.1        |
| <b>H (wt. %)</b>               | 6.57          | 5.08        |
| <b>N (wt. %)</b>               | 0.3           | 1.91        |
| <b>S (wt. %)</b>               | 0.8           | 0.2         |
| <b>O (wt. %)</b>               | 39.5          | 44.1        |
| <b>Ash (wt. %)</b>             | 0.5           | 9.6         |
| <b>Volatile matter (wt. %)</b> | 76.1          | 88.8        |
| <b>Calorific Value (kJ/kg)</b> | 21,799        | 14,416      |

Meanwhile, Figure 2.9 is showing the theoretical value for mass fraction of cellulose, hemicellulose and lignin in coconut shell, rice husk and paddy straw. From the graph, coconut shell has the highest composition of hemicellulose and lignin compared to rice husk and paddy straw. Meanwhile, paddy straw has the highest composition of cellulose compared to other two biomasses.

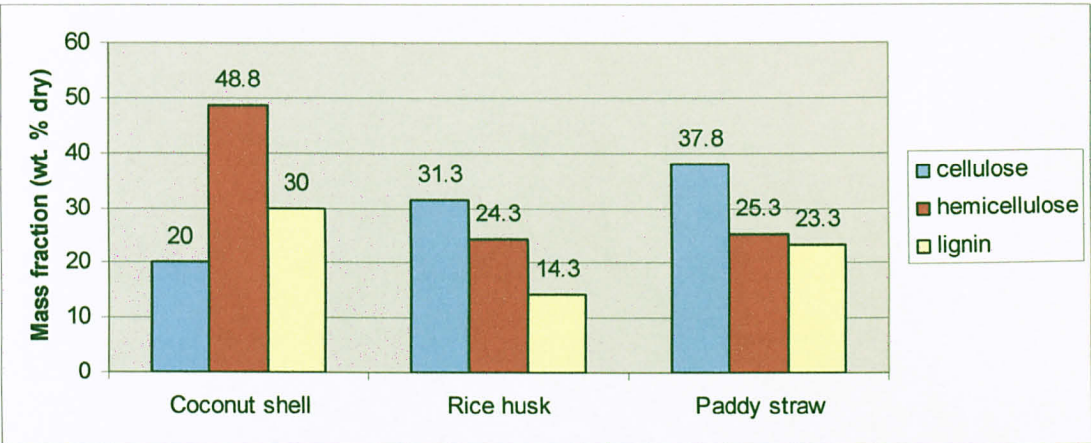


Figure 2.9: Mass fractions of cellulose, hemicellulose and lignin in each biomass

Based on Carole Couhert et al (2008), the higher the concentration of minerals in biomass, the higher the total gas yield will be.  $H_2$  and  $CO_2$  yields increase and  $CH_4$  and CO yields decrease.

Table 2.5 shows the amounts of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) that were obtained by ultimate analysis according to types of minerals in the biomass. There are also stated the amounts of ash, volatile matter and fixed carbon that were attained by proximate analysis. The amount of oxygen (O) was obtained as the complement to 100% of C, H, N, S and ash.

Table 2.5: Ultimate analysis and proximate analysis of components

| Components                            | Ultimate analysis<br>(mass% daf) |     |      |     |      | Proximate analysis<br>(dry mass%) |                  |              |
|---------------------------------------|----------------------------------|-----|------|-----|------|-----------------------------------|------------------|--------------|
|                                       | C                                | H   | N    | S   | O    | Ash                               | Volatile matters | Fixed carbon |
| Microcrystalline cellulose            | 44.4                             | 5.8 | 0.3  | 0.1 | 49.3 | 0                                 | 94.8             | 5.2          |
| Sigmacell microcrystalline cellulose  | 44.5                             | 5.6 | 0.3  | 0.1 | 49.5 | 0                                 | 94.1             | 5.9          |
| Xylan from birchwood (hemicellulose)  | 46.7                             | 5.7 | 0.2  | 0   | 47.4 | 4.1                               | 73.3             | 22.6         |
| Xylan from beechwood (hemicellulose)  | 44.3                             | 5.4 | 0.3  | 0   | 49.9 | 4.8                               | 75.3             | 19.9         |
| Xylan from oat spelts (hemicellulose) | 44.8                             | 5.6 | 0.04 | 0   | 49.5 | 10.1                              | 71.1             | 18.8         |
| Alkali lignin                         | 56.6                             | 4.2 | 0.5  | 1.6 | 37.1 | 10                                | 49.9             | 40.1         |
| Lignin from Borregaard                | 65                               | 4.9 | 0.6  | 0.8 | 28.7 | 13.5                              | 45               | 41.5         |
| Lignin from Meadwestvaco              | 66.7                             | 5.6 | 1.1  | 0.5 | 26.1 | 2.4                               | 58.9             | 38.7         |

Source: Journal entitled "*Is it possible to predict gas yields of any biomass after rapid pyrolysis at high temperature from its composition in cellulose, hemicellulose and lignin?*", Carole Couhert, Jean-Michel Commandre and Sylvain Salvador (2008)

Celluloses contain a large quantity of oxygen in comparison with lignins. On the other hand, lignins hold more hydrogen compared to celluloses. Meanwhile, the amount of each element in hemicelluloses is quite similar with amount in celluloses.



## **CHAPTER 3**

### **METHODOLOGY**

#### **3.1 Equipment/ Tools Identification**

Some equipment that involved in this project are:

- Oven
- Grinder
- Sieve
- Halogen Moisture Analyzer (HMA)
- Bomb Calorimeter
- Carbon Hydrogen Nitrogen Sulphur (CHNS) Analyzer
- BET Analyzer

#### **3.2 Preparation of Raw Material**

Three different types of biomass were chosen as the raw materials for this project and they are coconut shell, rice husk and paddy straw. Only a small amount of these materials are needed for each experiment approach.

At first stage of the experiment, all these raw materials need to be dried at a temperature of 100°C in order to remove the moisture content. All the samples were placed into the oven for about one whole day to make sure that most of the moisture had been removed. After finished the drying process, the dried samples were grinded into

small particles with different sizes by using grinder. The grinded samples were then sieved into particle sizes of 500  $\mu\text{m}$ .

### 3.3 Halogen Moisture Analyzer (HMA)

The function of this equipment is to analyze the moisture content of the sample and on the same time to remove the moisture. The procedure took place in handling HMA are as follows:

1. The sample that has been grinded and sieved is weighted out before it is placed within this analyzer.
2. The temperature is set at 100°C. Even though drying has been done previously, this process is taken because there might still have an amount of moisture in the sample that being introduced during the grinding process.
3. The samples weight is observed until a constant percentage weight is obtained. The moisture content of the of the samples are calculated by using the following formula:

$$\text{Moisture content, } X_e = \frac{\text{Initial weight of sample} - \text{Final weight of sample}}{\text{Initial weight of sample}} \times 100\%$$

### 3.4 Calorific Value Analysis

The bomb calorimeter is the most common device for measuring the heat of combustion or calorific value of a material. With this apparatus the sample of specified mass is burned under standardized conditions. The heat of combustion determined under these conditions is calculated on the basis of the observed temperature rise while taking account of heat released during the process. It can be measured in units of energy per amount of the material. Following are the bomb calorimeter's manual experiment:

1. Oxygen gas regulator is turned on (Pressure: 20 – 30 kg/cm<sup>2</sup>)
2. The bomb calorimeter unit and refrigerator batch switch are turned on. It is waited for 20 minutes for waiting stable.
3. The sample is prepared (weighing below 1.0 gram) and placed into crucible. A cotton thread with a loop in it is secured on the middle of the ignition wire. Then, it is placed into the decomposition vessel.
4. The sample dialog window is opened to key-in the weight of sample.
5. The decomposition vessel is suspended into the filling head of the measurement cell cover.
6. Start is activated. The measurement cell cover closes the decomposition vessel is filled with oxygen. Next, the inner vessel is filled with water.
7. A graph display of the change over time in temperature of the inner vessel is shown.

### **3.5 Carbon Hydrogen Nitrogen Sulphur Analyzer (CHNS)**

The main purpose of this equipment is to identify the percentage of carbon, hydrogen, nitrogen and sulphur of the biomass samples. The sample tested should be taken directly from HMA in order that the moisture content of the sample is at optimum level. The summary of the operating procedure are as the following:

1. A small amount (approximately 2 miligram) of each sample are weighted and put in two separate tin capsules.
2. The analyzer is set to operate at the following temperature and pressure:  
Oxidation Furnace Temperature: 1000°C  
Reduction Furnace Temperature: 650 °C  
Helium, oxygen and compressed air are set to 40 psi
3. All samples (in capsule) are placed in the slot inside the analyzer. The weight of each samples are recorded into the analyzer
4. Each run is completed about threee minutes. The composition of carbon, hydrogen, nitrogen and sulphur are obtained from the printed result.



### **3.6 Thermogravimetric Analyzer (TGA)**

Thermogravimetric analyzer is interfaced to a microcomputer for data acquisition. It consists of a sample that is suspended from the weighing mechanism with wire. In thermal gravimetric analysis, the duration of the process is shorter which about 30 minutes. The percentage of fixed carbon can be obtained directly by measuring the plotted graph of weight loss versus time that is referred as thermograms (refers to Figure 4.6).

TGA analyzes the results based on weight loss of samples as a function of temperature. In the process, a known sample is placed in a furnace in a controlled gaseous atmosphere at a desired temperature.

### **3.7 Determination of Lignin in Biomass**

This procedure uses a spectrophotometric method that has been developed for rapid pulp kappa number measurements under strongly acidic reaction conditions. Pulp kappa number is derived from the ratio of the absorption spectral intensities at a specific wavelength measured at the beginning and end of the reaction of the pulp with permanganate. The kappa number of pulp is one of the important parameters in pulp manufacturing because it relates to the degree of delignification of the pulp. It is defined as the volume of 0.02 mol/L potassium permanganate solution consumed by one gram of moisture free pulp in an acidic medium. The procedure uses 5mL of standardized 0.02mol/L potassium permanganate solution to react with pulp/ biomass samples under acidic condition by adding 20mL standard 2.0mol/L sulfuric acid.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Moisture Content

Based on Figure 4.1, the results show that coconut shell has the lowest moisture content that is 5.12% at particle size of 500  $\mu\text{m}$ . This is followed by paddy straw 7.72% and the highest moisture content is rice husk 8.87%.

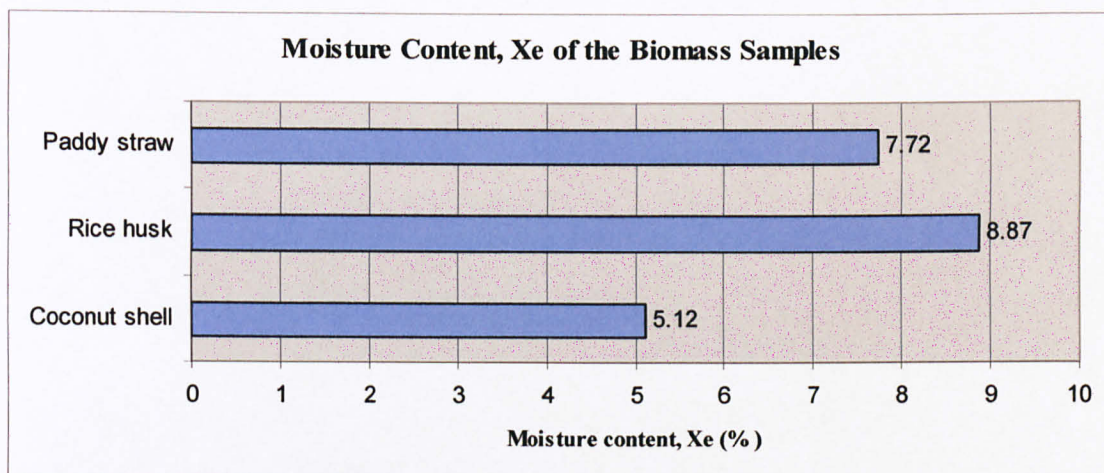


Figure 4.1: Graph of Moisture Content,  $X_e$  of the Biomass Sample

It is understand that the moisture content of the samples will influence the net calorific value. This is because vaporizing the water will require energy and thus this will reduce the energy content of the samples. The higher the mount of water in the sample, the more energy required to vaporize it, thus, the lower the heating value will be. Therefore, from the result, it is understand that the rice husk should have lowest

heating value, followed by paddy straw and the highest heating value will be coconut shell.

4.2 Elemental Composition Analysis

The elementary analysis or known as ultimate analysis is concern with the composition of carbon, hydrogen, nitrogen and sulphur inside the biomass samples. This analysis was carried out by using CHNS Analyzer and the result such in Figure 4.2 and Figure 4.3 are obtained.

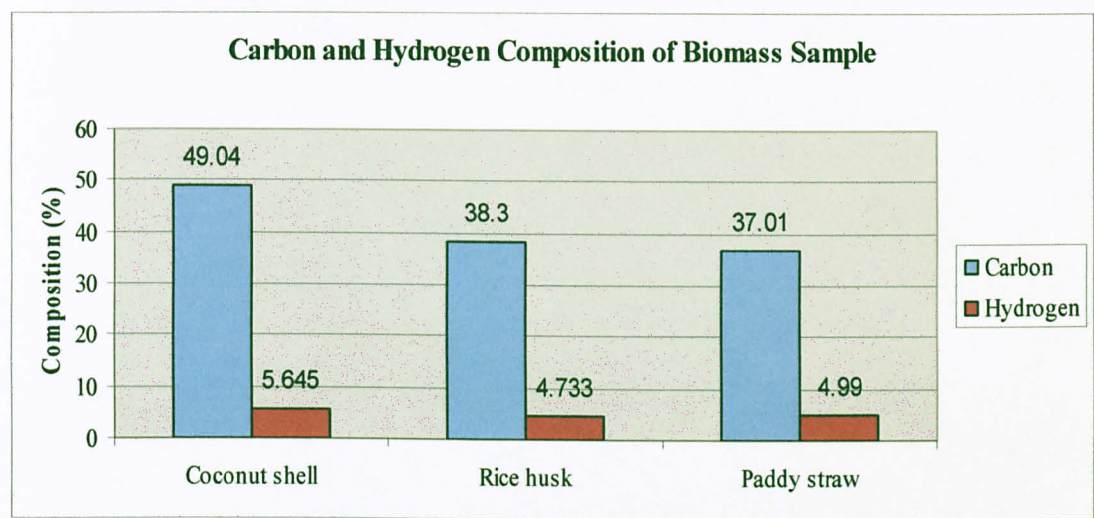


Figure 4.2: Graph of Carbon and Hydrogen Composition of the Biomass Sample

Based on the graph in Figure 4.2, it is observed that all samples have a high composition of carbon ranges from 37 mol % to 49 mol % approximately. Sample that has the highest amount of carbon is coconut shell which is about 49.04 mol%. It is followed by rice husk 38.30 mol% and the lowest carbon content is paddy straw 37.01 mol %.



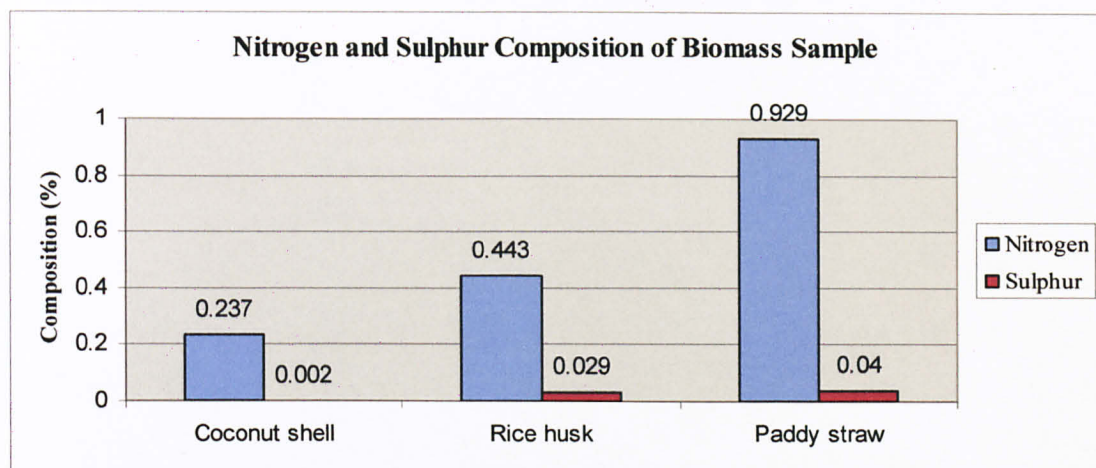


Figure 4.3: Graph of Nitrogen and Sulphur Composition of the Biomass Sample

Meanwhile, Figure 4.3 is showing the percentage of nitrogen and sulphur content in each biomass samples. The results obtained showed that all of the samples had the percentage of nitrogen content within the range of the reference value. The amount of sulphur of each samples also were very low mostly less than 0.2 mol%.

### 4.3 Calorific Value Analysis

This analysis was done using bomb calorimeter. The results had been calculated and summarized in Table 4.1.

Table 4.1: The result of calorific value

| BIOMASS SAMPLE | CALORIFIC VALUE (kJ/kg) |
|----------------|-------------------------|
| Coconut shell  | 19,663                  |
| Rice husk      | 15,761                  |
| Paddy straw    | 14,352                  |

From Table 4.1, the calorific value obtained for coconut shell is 19,663 kJ/kg which is the highest calorific value obtained among three. Then, it is followed by rice husk with 15,761 kJ/kg and the lowest calorific value is paddy straw with 14,352 kJ/kg.

The results shown that paddy straw have the lowest calorific value compared the other two biomass samples. This is inconsistent with the prediction that has been made during the moisture content analysis that is rice husk should have lowest heating value. This error might be due to the effect of physical structure of the samples. Rice husk has a fine particle structure compared to paddy straw. A fine particle will have a larger surface area and give more chance for the moisture to evaporate. Since both biomass samples have a small difference of moisture content, there might be a possibility that the moisture content in rice husk had been released throughout the experiment. Thus, this has affected the calorific value or the heating value of the rice husk to be higher than paddy straw.

#### 4.4 Determination of Lignin Composition

Based on Figure 4.5, the graph displays the lignin composition of biomass samples that had been determined by using UV visible spectrophotometer and analyze by Kappa number method. The results show that coconut shell has the lowest composition of lignin that is 32.18%. The value is nearing to the theoretical value of lignin content in the coconut shell that is 30%. On the other hand, the results show that the paddy straw has the highest lignin composition among the three with 33.57% lignin composition.

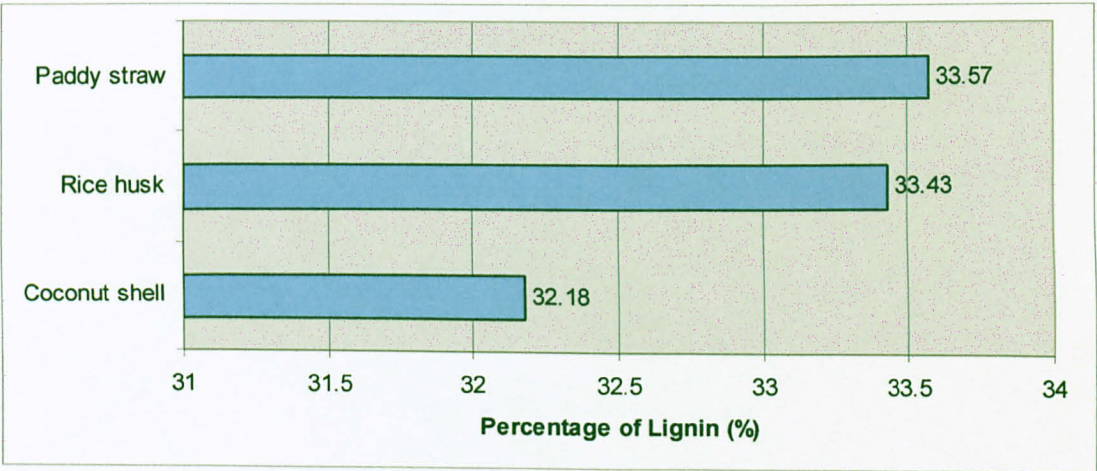


Figure 4.5: Graph of Lignin Composition of the Biomass Sample



The actual lignin composition obtained from the results for rice husk and paddy straw are 33.43% (rice husk) and 33.57 (paddy straw). It is observed that these two values are actually not nearing to the theoretical value of lignin content gain from the literature review. This is due to some error that might occurs during the experiment was conducted. There are possibility of potassium permanganate that had been used in this experiment as the oxidizing agent were not totally consumed by the lignin in the biomass sample, but also been oxidized and decomposed by other organic materials exist in the biomass. Besides, the error might be due to the assumption of rapid oxidation is completed by 10 minutes is not accurate. The actual oxidation time is much shorter than 10 minutes, as per mentioned by Li and Gellerstedt (1998).

### 4.5 Determination of Fixed Carbon and Ash Content Using TGA

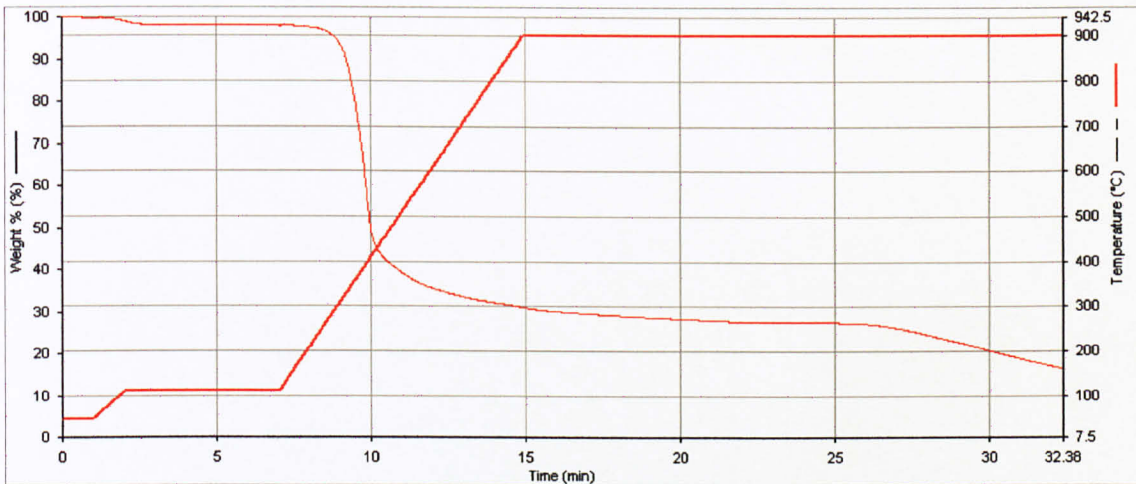


Figure 4.6: Thermogram for Paddy Straw Proximate Analysis

Figure 4.6 illustrates the TGA experimental profile that was obtained for proximate analysis of paddy straw. From the profile, it can be seen that there is a slight decrease in the weight of sample while the temperature is held at 110°C from the initial temperature 50°C. The slight decrease is due to removal of moisture content in the sample. Although the sample has been dried until the mass is constant during the initial part of the experiment, it has to be noted that exposure to ambient may contribute to the moisture accumulation in the sample.



As the experiment proceeds by increasing the heating from 110°C to 900°C, a significant drop of weight percentage is observed indicating a increase in the sample weight loss. This due to the expelled of the volatile matters contained in the sample that lead to the reduction in weight percentage.

The experiment was continued by letting the temperature of the TGA constant at 900°C for seven minutes before oxygen is introduced into the system where combustion of the sample took place. This process caused the fixed carbon to be combusted, thus, further weight loss of the sample and leaving ash as residue. After five minutes the oxygen is introduced into the system, sample weight stays constant indicates that the fixed carbon has completely combusted.

K.G. Mansaray and A.E. Ghaly (1998) reported that there is a correlation between fixed carbon content to the cellulose and hemicellulose content of biomass. It was reported that a high content of fixed carbon reflects a high content of cellulose and hemicellulose. These two components of biomass are known to have higher decomposition rate than lignin according to A.S. Bining and B.M. Jenkins (1992).

Table 4.2: The result extracted from TGA analysis

|                                | <b>Paddy Straw</b> | <b>Rice Husk</b> | <b>Coconut Shell</b> |
|--------------------------------|--------------------|------------------|----------------------|
| <b>Volatile matter (wt. %)</b> | 70.28              | 67.81            | 72.02                |
| <b>Fixed carbon (wt. %)</b>    | 6.714              | 7.192            | 5.927                |
| <b>Ash content (wt. %)</b>     | 3.73               | 1.275            | 1.103                |

Table 4.2 displays the results extracted from the thermogram obtained from TGA analysis which are the volatile matter, fixed carbon and ash content. From the results, it is observed that coconut shell has 72.02 wt.% of volatile matter which is the highest among the other two samples. Meanwhile, rice husk has the lowest volatile matter with 67.81 wt.%. On the other way, the results for fixed carbon shown that the highest is rice husk with 7.192 wt.% while coconut shell is the sample that has the lowest fixed carbon that is 5.927. Other than that, the ash content results obtained from the experiment

shown that paddy straw has the highest ash content 3.73 wt.%. The lowest ash content is coconut shell.

4.6 Overall Analysis

The results for all analysis that have been conducted had been summarized in Table 4.2. The completed analyses are the moisture content determination, elemental composition analysis, calorific value analysis and determination of lignin content.

Table 4.3: The comparison results between the biomass samples

| Characteristics          | Paddy Straw | Rice Husk | Coconut Shell |
|--------------------------|-------------|-----------|---------------|
| Moisture content (%)     | 7.72        | 8.87      | 5.12          |
| Carbon composition (%)   | 37.01       | 38.30     | 49.04         |
| Hydrogen composition (%) | 4.99        | 4.73      | 5.65          |
| Calorific value (kJ/kg)  | 14,352      | 15,761    | 19,663        |
| Lignin content (%)       | 33.57       | 33.43     | 32.18         |
| Volatile matter (wt. %)  | 70.28       | 67.81     | 72.02         |
| Ash content (wt. %)      | 3.73        | 1.275     | 1.103         |

From all the analysis performed, there are five characteristics that are in concern in this experiment. The first characteristic is the moisture content. From Table 4.3, it is observed that rice husk has the highest moisture content while coconut shell has the lowest moisture content. Low moisture content is most desired because it will produce a higher calorific value.

The second characteristic is the carbon composition. From Table 4.3, it displayed that the paddy straw has the lowest carbon composition while coconut shell has the highest carbon composition. The preferable characteristic is a high carbon composition because the more carbon exists in sugar chain in a biomass indicates more hydrogen are connected to the carbon that can be extracted.



The third characteristic is the hydrogen composition. From Table 4.3, it shown that rice husk has the lowest hydrogen composition while coconut shell has the highest hydrogen composition. The aim for this project is enriching hydrogen. Therefore, the high hydrogen composition is most favorable.

The fourth characteristic is the calorific value. From Table 4.3, the highest calorific value is coconut shell while the lowest calorific value is paddy straw. It is desired for high calorific value because high calorific value indicates a high energy will be produced from the biomass.

The fifth characteristic is the lignin content. Among the three biomass samples, paddy straw has the highest lignin content and coconut shell has the lowest lignin content. The most preferable will be the lowest lignin content because lignin exists in the cell's wall of the biomass. With large amount of lignin indicates the difficulty for the cell's wall to decompose. The cellulose and hemicellulose that contain inside the cell will be blocked inside, thus, the cellulose will not be able to release to further process producing energy.

Next characteristic is the volatile matter of every sample. Coconut shell has the highest volatile matter compared to the other two samples. It is appropriate to have a certain level of volatile matter in order the biomass can easily gasified.

The last characteristic is the ash content. It is preferred to have low ash content in every sample. From Table 4.3, sample with lowest ash content is coconut shell while sample with the highest ash content is paddy straw.

Therefore, it can be concluded that coconut shell is the most favorable compared to paddy straw and rice husk. It is because coconut shell has low moisture content, high carbon, hydrogen and oxygen composition, high calorific value, low lignin content, high volatile matter and low ash content.



## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATIONS**

#### **5.1 Conclusion**

The characterization of all three biomass samples; coconut shell, rice husk and paddy straw have completed several analysis such as the moisture content determination, elemental composition analysis, calorific value analysis, lignin composition determination and the proximate analysis.

Some characteristics that have been characterized in this experiment are the moisture content, carbon composition, hydrogen composition, oxygen composition, calorific value, lignin content, volatile matter and also the ash content. For the moisture content determination, biomass sample that has the lowest moisture content after drying is coconut shell which contains 5.12 % moisture.

Meanwhile, the composition of the three biomass samples; carbon, hydrogen and oxygen were determined by the elemental analysis. Based on the analysis, coconut shell has the highest amount of all carbon and hydrogen composition. For the calorific value analysis, the paddy straw obtained the lowest calorific value that is 14,352kJ/kg, rice husk with 15,761 kJ/kg and the highest calorific value obtained by the coconut shell with 19,663 kJ/kg.

Meanwhile, the determination of lignin content had given a result of paddy straw as the highest lignin content with 33.57%, followed by rice husk with 33.43% and the

lowest lignin content is coconut shell with 32.18%. Other than that, the proximate analysis result shown that coconut shell has the highest volatile matter with 72.02 wt.% and the lowest ash content with 1.103 wt.%. From all the characterization's results, it can be concluded that the best biomass sample that would have high hydrogen production and produce high energy among the three biomass samples is the coconut shell.

## **5.2 Recommendations**

For this study, there are errors in the analysis that could be minimized in the future in order to obtain better results. Besides, there some suggested future work of the project for further expansion.

### **5.2.1 Error in performing the proximate analysis**

TGA is used in performing this analysis. There are some flaws happened relating to the equipment even though the equipment had been calibrated before the experiment is conducted. The sample temperature is usually deviates quite far from the program temperature and caused the curve formed does not represent the real characteristic of the samples. The solution for this is by constantly calibrate the TGA to ensure a more accurate results can be obtained.

Besides, the inaccuracy of the results also was due to the analysis was not been repeated. This is due to time constraint to use TGA because there are number of students to use the equipment but there is only one TGA available. Therefore, the solution to this problem is to add more equipment in the lab. However, this is costly solution. Another better solution is to properly schedule at early semester. This will need cooperation from the technician and lecturer to arrange the schedule in order to avoid congestion and queue up of students to use the equipment towards the end of semester.

### **5.2.1 Suggested future work for expansion and continuation**

Further improvement can be done for purpose of continuation of the project. The suggested for future works are as follow:

- Performed gasification process of all the biomass samples in order a better conclusion can be made to the analysis conducted.
- To further analyze the correlation between cellulose and hemicellulose content with the hydrogen production of each sample.



## REFERENCES

1. A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, and D. Crocker, "*Determination of Structural Carbohydrates and Lignin in Biomass*", technical report National Renewable Energy Laboratory, Colorado, pgs. 4-15, 2008.
2. A. Sluiter, R. Ruiz, C. Scarlata, J. Sluiter, and D. Templeton, "*Determination of Extractives in Biomass*", technical report National Renewable Energy Laboratory, Colorado, pgs. 4-10, 2005.
3. Carole Couhert, "*Is it possible to predict gas yields of any biomass after rapid pyrolysis at high temperature from its composition in cellulose, hemicellulose and lignin*", Fuel, Volume 88, Issue 3, France, pgs. 408-417, 2009.
4. Colomba Di Blasi, "*Combustion and gasification rates of lignocellulosic chars*", Progress in Energy and Combustion Science, Volume 35, Issue 2, Italy, pgs. 121-140, 2009.
5. Jeffrey Phillips, "*Different Types of Gasifiers and Their Integration with Gas Turbines*", Advanced Coal Generation, Charlotte, pgs. 2-4.
6. Ningbo Gao, Aimin Li, Cui Quan and Fan Gao, "*Hydrogen-rich gas production from biomass steam gasification in an updraft fixed-bed gasifier combined with a porous ceramic reformer*", International Journal of Hydrogen Energy Volume 33, Issue 20, China, pgs. 5430-5438, 2008.
7. Pratik N. Sheth and B.V. Babu, "*Experimental studies on producer gas generation from wood waste in a downdraft biomass gasifier*", Bioresource Technology, Volume 100, Issue 12, India, pgs. 3127-3133, 2009.
8. P. Grammelis, P. Basinas, A. Malliopoulou and G. Sakellaropoulos, "*Pyrolysis kinetics and combustion characteristics of waste recovered fuels*", Fuel, Volume 88, Issue 1, Greece, pgs. 195-205, 2009.
9. Rajvanshi, A.K., "*Biomass Gasification*", Published as a chapter in book Alternative Energy in Agriculture, Vol. II (Ed. D.Yogi Goswami), CRC Press, 1986, pgs. 83-102.

10. Siyi Luo, Bo Xiao, Zhiquan Hu, Shiming Liu, Xianjun Guo and Maoyun He, *"Hydrogen-rich gas from catalytic steam gasification of biomass in a fixed bed reactor: Influence of temperature and steam on gasification performance"*, International Journal of Hydrogen Energy, Volume 34, Issue 5, China, pgs. 2191-2194, 2009.
11. Suresh P. Babu, *"Biomass Gasification for Hydrogen Production – Process Description and Research Needs"*, Gas Technology Institute, U.S.A.
12. William G. Rosenberg, Michael R. Walker and Dwight C. Alpern, *"National Gasification Strategy: Gasification of Coal & Biomass as a Domestic Gas Supply Option"*, 2005.
13. BP (1999-2009), <http://www.bp.com/sectiongenericarticle>, Retrieved on 15<sup>th</sup> February 2009.
14. Energy Information Administration, *Official Energy Statistics from the U.S Government*, <http://www.eia.doe.gov/fuelrenewable.html>, Retrieved on 16<sup>th</sup> February 2009.
15. Energy Research Centre of the Netherlands, <http://www.ecn.nl/phyllis/single.html>, Retrieved on 10<sup>th</sup> March 2009.
16. Operating Instructions for the Bomb Calorimeter, [faculty.northseattle.edu/tfurutani/chem121\\_04/calorimeter.pdf](http://faculty.northseattle.edu/tfurutani/chem121_04/calorimeter.pdf), Retrieved on 10<sup>th</sup> March 2009.
17. The Encyclopedia of Earth (2008), [http://www.eoearth.org/article/Hydrogen\\_production\\_technology](http://www.eoearth.org/article/Hydrogen_production_technology), Retrieved on 15<sup>th</sup> February 2009.
18. WorldChanging, <http://www.worldchanging.com/archives/007868.html>, Retrieved on 19<sup>th</sup> April 2009.