Characterization of Different Biomass for Biohydrogen Production

by

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A project dissertation submitted to the Chemical Engineering Programme Universiti Teknologi PETRONAS in partial fulfilment of the requirement for the BACHELOR OF ENGINEERING (Hons) (CHEMICAL ENGINEERING)

Approved by,

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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.

Jul

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ABSTRACT

The aim of this project is to study the potential of biomass resource available in the country for use in biohydrogen production. The objectives of the research project are to characterize different biomass sources based on biomass properties. The biomass properties being studied are moisture content, calorific value, elemental composition, ash content, volatile matter content and fixed carbon content. In general, two main analyses are conducted: Ultimate and Proximate analysis. The main equipments to be used are CHNS Analyzer, Moisture Analyzer, Bomb Calorimeter and Thermal Gravimetric Analyzer. The study consists of a series of experiments and analysis relating to the properties of the biomass samples to look into the prospect for biohydrogen production. Biomass means any plant-derived organic matter available on a renewable basis. Biomass is basically organic material cultivated energy crops derived from agriculture or woodbased operations to produce solid, liquid or gaseous fuels. Biohydrogen is the process of producing hydrogen from biological processes or biomass. Biohydrogen production has become an important study since it is known that fossil fuels resources in the world is depleting at a high rate. The analysis would help characterize different biomass samples for the purpose of biohydrogen production and help realize the potential of biohydrogen production in the country.

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Hydrogen is widely known to be an attractive energy source to replace fossil fuel in terms of social, environmental and economic perspective (Nath and Das, 2003). Conventional method to produce hydrogen is by steam reforming of natural gas or naphtha. Other than that, hydrogen is produced from coal gasification and water electrolysis. However, these methods use non-renewable energy sources and are not sustainable (Manish and Banerjee, 2008). Therefore, hydrogen production from renewable sources is necessary.

Petroleum and fertilizer industry are the largest users of hydrogen with 50% and 37% respectively (Nath and Das, 2003). The demand for hydrogen is expected to increase by 5% annually mainly due to the increase use of hydrogen in refineries as a result of stricter fuel quality standards (Nath and Das, 2003). Hydrogen is applied in various chemical process industries. It is used in hydrogenation process to produce lower molecular compounds. It is also used to saturate compounds, crack hydrocarbons and remove sulfur or nitrogen compounds. Besides that, hydrogen is used in the manufacturing of ammonia, methanol and synthesis gas. The future use of hydrogen includes fuel for automobiles; distributed and central electricity; and thermal energy generation (Nath and Das, 2003).

Renewable biomass is also an attractive alternative to fossil feedstock because of the essentially zero net Carbon Dioxide impact. Carbon-negative Biohydrogen is a fully

decarbonised energy carrier as it contains no carbon. This implies that the Carbon Dioxide released during its production can be captured and sequestered. When such carbon capture and storage (CCS) technologies are coupled to biohydrogen production, a carbon-negative fuel is obtained. This is why biomass feedstock for hydrogen production is very interesting. It points to a possible future in which biomass plantations would generate "negative emissions" (Kelly-Yong, 2007).

Biomass has the potential to become a significant source for renewable hydrogen. In addition the processes for producing hydrogen from biomass are complementary to those that produce biomaterials. Countries with huge resource of agricultural economies have great potential to have significant economic growth through implementation of the biohydrogen sector.

1.2 Problem Statement

Fossil fuels reserves of the world are depleting at an alarming rate. Most of the current hydrogen production technique is through steam reforming of natural gas or naphtha. However, these conventional methods are less environmental friendly, not sustainable and require high production cost. Biohydrogen has great prospects as hydrogen is produced from renewable energy sources such as biomass. Biomass resources available in the country are still in abundance and not fully utilized. Current implementation of biomass has only been focused on bio-fuels. Therefore it is important to explore the potential of hydrogen production from these biomass resources.

1.3 Objectives

The objectives of the research project are:

- To characterize different biomass resources using the CHNS analyzer to perform an Ultimate Analysis
- To conduct a Combustion analysis of different biomass in order to obtain the Calorific Values
- To conduct a Moisture content analysis of different biomass resources
- To perform a Proximate Analysis of the various biomass samples using the Thermal Gravimetric Analysis
- To characterize and study the potential of different biomass for biohydrogen production based on the analysis conducted

1.4 Scope of Study

The project will be divided into several steps which will be further discussed. In order to achieve the objective, the project will be completed based on the planned schedule and within the time frame. The scope of study will focus on:

- Identifying and selecting the biomass sources for the research project
- Characterizing of various biomass resources by Ultimate analysis method using the LECO 932 CHNS Analyzer to determine the Carbon, Hydrogen, Nitrogen and Sulfur compositions
- Characterizing of various biomass resources by Combustion analysis of the samples using the IKA C5000 Bomb Calorimeter to determine its Calorific Value
- Identifying the moisture content of various biomass resources
- Characterizing of various biomass by Proximate analysis using the Thermal Gravimetric Analysis method
- Identifying biomass resources with high potential for biohydrogen production

CHAPTER 2

LITERATURE REVIEW

2.1 Biomass as renewable source

The term "biomass" means any plant-derived organic matter available on a renewable basis. Biomass is basically organic material cultivated energy crops derived from agriculture or wood-based operations to produce solid, liquid or gaseous fuels. Biomass is the plant material derived from the reaction between CO_2 in the air, water ad sunlight, via the photosynthesis process, to produce carbohydrates that form the building block of biomass. The biomass resources can be considered as organic matter, in which the energy of sunlight is stored in chemical bonds. The chemical energy is released when the bonds between adjacent carbon, hydrogen and oxygen molecules are broken either by digestion, combustion or decomposition.

There are a variety of biomass resources that can be used to convert to energy. They are generally divided into four main categories:

- i. Energy crops: industrial crops, woody energy crops, herbaceous crops, agricultural crops and aquatic crops.
- ii. Agricultural residues: crop waste and animal waste.
- iii. Forestry waste and residues: mill wood waste, logging residues, trees and shrub residues.
- iv. Industrial and municipal wastes: municipal solid waste, sewage sludge and industry waste

The potential of biomass energy resources in the country includes:

- Oil Palm Residues Empty Fruit Bunches (EFB), Fibres, Palm Kernel and Palm Oil Mill Effluent (POME)
- ii. Paddy Residues Rice Husk and Paddy Straw
- iii. Sugar cane Residues
- iv. Wood Residues

Malaysia is also the world's largest producer of palm oil, supplying about 59 percent of the world's needs or 4,530,000 Mg of palm oil per year. Furthermore, the oil palm industry generates more than 184.6 million tones of residues worldwide (Kelly-Yong, 2007). The production of 4.53 million Mg of crude palm oil generates about 13.5 million Mg of effluent. Empty fruit bunch of oil palm (EFB) comprises about 22 percent of fresh fruit bunch, and it is estimated that 5 Mg of EFB are produced per hectare per year (Chan, 1980). With a total of 1.6 Mha now planted to oil palm, about 8.0 million Mg of EFB are produced every year (Sharifuddin and Zaharah, 2005).

Malaysia's national policies stresses on the importance of developing renewable energy. These also include the target of 350 MW of green electricity to the national grid as stated in the Ninth Malaysia Plan. As biomass resources in the country are still in abundance and not yet fully utilized, the target is expected to be mostly contributed from the oil palm industry. The Malaysian Government implemented the Small Renewable Energy Power (SREP) program in 2002 with the purpose of intensifying and encouraging of palm biomass for power generation and link to the power grid. This program together with the incentives offered by the Clean Development Mechanism (CDM) and Kyoto Protocol will definitely boost the number of biomass energy projects implemented n the country. Malaysia currently has 12 registered CDM projects which utilizes palm biomass as fuel feedstock (Chin, Wahid and Weng, 2008)

2.2 Biohydrogen

Biohydrogen is the process of producing hydrogen from biological processes or biomass. The importance of biohydrogen production began when it was known that fossil fuels resources in the world is depleting at a high rate. Further more, hydrogen production from fossil fuels causes atmospheric pollution and also significant climate changes globally. Biohydrogen production is slowly growing interest among agricultural economic nations as the there are many advantages. If practical processes for biohydrogen production can be implemented, the results will be a sustainable and renewable energy source without greenhouse emissions and environmental pollution.

Oil palm biomass has been described as having the greatest prospect as feedstock for biohydrogen purpose. The transforming of this residue into a more-valuable end product can be met by converting it into biohydrogen by means of gasification process using supercritical water reaction (SWR) technology (Kelly-Yong, 2007). The biomass feedstock has a high energy and moisture content which is an important requirement for the SCW reactions.

2.3 Biohydrogen Processes

Hydrogen can be produced from biomass using various process routes. The available energy production processed can be divided into two general categories: thermochemical and biological processes. The thermochemical conversion consists of combustion, Pyrolysis, liquefaction and gasification. The biological method consists of Biophotolysis, biological water-gas shift reaction, photo-fermentation and dark-fermentation. The different process routes for biohydrogen production can be classified as follows:

- 1. Thermochemical gasification coupled with water gas shift
- 2. Fast Pyrolysis followed by reforming of carbohydrate fractions of bio-oil
- 3. Direct solar gasification
- 4. Miscellaneous novel gasification process

- 5. Biomass-derived syn-gas conversion
- 6. Supercritical conversion of biomass
- 7. Microbial conversion of biomass

(Nath and Das, 2003)

Combustion is the direct burning of biomass in air to convert the biomass chemical energy into heat, mechanical power or electricity using equipment such as stoves, furnaces, boilers and steam turbines. Combustion is not a suitable hydrogen production for sustainable development as the energy efficiency is low (10-30%) and the by-products releases pollutant emissions (Ni, Leung, Leung and Sumathy, 2006)

Biomass liquefaction is the process where biomass is heated to 552-600 K in water under pressure of 5-20 MPa in the absence of air. Solvent and catalyst are normally added in the process. Liquefaction is also not a suitable as a sustainable energy production process because the process has low production of hydrogen and operating conditions are difficult to achieve. The other thermochemical and biological processes are feasible and have been receiving much attention in hydrogen production.

2.3.1 Biomass pyrolysis

Pyrolysis is the process where biomass is heated at a temperature of 650-800 K and pressure of 0.1-0.5 MPa in the absence of air to convert biomass into liquid oils, solid charcoal and gaseous compounds. There are two types of pyrolysis: slow pyrolysis and fast pyrolysis. Slow pyrolysis is not considered for hydrogen production since the products are mainly charcoal. Fast pyrolysis occurs at high temperature in which the biomass feedstock is heated rapidly in the absence of air forming vapour and further condensed to a dark brown liquid called bio-oil. Most pyrolysis processes are designed for production of bio-fuel. However, hydrogen can be formed directly through fast pyrolysis if high temperature and volatile phase residence time are available.

Fast pyrolysis produces a liquid product called bio-oil which is used in several processes for the development of fuel chemicals and materials. The process is as follows:

$$Biomass + Energy \longrightarrow Bio-oil + Char + Gas$$
(1)

Bio-oil is then converted to hydrogen using the catalytic steam reforming with the reaction as follows:

$$Bio-oil + H_2O \longrightarrow CO + H_2$$
(2)

Water-gas shift reaction is applied to further increase hydrogen production as follows:

$$CO + H_2O \longrightarrow CO_2 + H_2$$
 (3)

In the fast pyrolysis process, temperature, heating rate, residence time and type of catalyst used are important process control parameters. High temperature, high heating rate and long volatile phase residence time are required to form gaseous products such as hydrogen (Demibras, 2002). These parameters can be regulated by selecting among different reactor types and heat transfer modes, such as gas-solid convective heat transfer and solid-solid conductive heat transfer. The process flow of the fast pyrolysis process is shown in Figure 1.



Figure 1: Process flow of fast pyrolysis

2.3.2 Biomass gasification

Gasification is normally performed at high temperatures (above 1000 K). Biomass will undergo partial oxidation forming gas and charcoal. Charcoal is then reduced to form H_2 , CO, CO₂ and CH₄. The process can be shown as follows:

Biomass + heat + steam
$$\longrightarrow$$
 H₂ + CO + CO₂ + CH4 (4)

+ light and heavy hydrocarbons + char

Water-gas shift reaction is carried out to further increase hydrogen production as follows:

$$CO + H_2O \longrightarrow CO_2 + H_2 \tag{5}$$

Gasification is conducted in the presence of oxygen. The difference between gasification and pyrolysis is that gasification aims to produce gaseous products whereas pyrolysis aims to produce bio-oils and charcoal. Hydrogen produced from the gasification products is similar as the procedure of steam reforming and water-gas shift reactions as in the pyrolysis process. The gasification process is more preferable for hydrogen production since the products are mainly in gas.

The major issue in selecting this process is to overcome the tar formation that occurs during the process. Unwanted tar may cause formation of tat aerosols and polymerization to a more complex structure which is not desirable in hydrogen production. Another issues is formation of ash that causes deposition, sintering, slagging, fouling and agglomeration (Arvelakis and Koukios, 2002).

2.3.3 Biological processes

There are five different classification of biological hydrogen production: (i) direct photolysis, (ii) indirect Biophotolysis, (iii) biological water-gas shift reaction, (iv) photo-fermentation and (v) dark-fermentation. Biological means of hydrogen production are controlled by hydrogen-producing enzymes such as hydrogenase and nitrogenase. Hydrogenase enzymes are divided into two categories: (i) uptake hydrogenase and (ii) reversible hydrogenase. Uptake hydrogenase acts as important catalyst for hydrogen consumption as follows:

$$H_2 \longrightarrow 2e^2 + 2H^+$$
 (6)

Reversible hydrogenase produces hydrogen as well as consumes hydrogen depending on the reaction condition as follows:

$$H_2 \leftrightarrow 2e^2 + 2H^4$$
 (7)

Direct photolysis process of hydrogen production is actually a biological process using microalgae photosynthetic systems to produce hydrogen by converting solar energy into chemical energy.

$$2 H_2 O \xrightarrow{\text{Solar energy}} O_2 + 2H_2$$
(8)

Indirect photolysis is a four steps process: (i) biomass production by photosynthesis, (ii) biomass concentration, (iii) aerobic dark fermentation yielding 4 mol hydrogen/ mol glucose in the algae cell, along with 2mol of acetates and (iv) conversion of 2 moles of acetates into hydrogen (Gaudernack B., 1998).

Photo-fermentation is the process where photosynthetic bacteria produce hydrogen through the action of their nitrogenase using solar energy and organic acids of biomass. Examples of biomass waste which produces hydrogen from photo-fermentation are Lactic acid (Rhodobacter spharoides immobilized bacteria), wastewater (Rhodobacter spharoides immobilized bacteria) and Lactate feedstock (Rhodobacter capsulatus bacteria).

Dark fermentation is the process of fermentation of anaerobic bacteria and microalgaes on carbohydrate-rich substrates which produces hydrogen at 30° C in a dark condition. Dark fermentation produces H₂ and CO₂ together with other gases such as CH₄ and H₂S.

2.4 Properties of Biomass

1. Moisture Content

Moisture content is the quantity of water contained in a material on a volumetric or gravimetric basis. It can either be calculated based on Moisture Content Wet Basis (MCWB) or Moisture Content Dry Basis (MCDB). This method is normally done with the aid of an oven and a top pan balance.

MCWB = 100 X (Initial Wt - Dry weight)/ (Initial Weight) MCDB = 100 X (Initial Wt - Dry weight)/ (Dry Weight)

An alternative method is by using the Moisture Content Analyzer.

2. Elemental Analysis

Elemental analysis is a process where a biomass sample is analyzed for its elemental composition. Elemental analysis can be qualitative (determining what elements are present), and it can be quantitative (determining how much of each are present). Elemental analysis falls within the field of analytical chemistry.

3. Ultimate Analysis

The ultimate analysis gives the composition of the biomass in weight percentage of carbon, hydrogen, oxygen, sulfur and nitrogen and the gross calorific values.

4. Proximate Analysis

The proximate analysis gives moisture content, volatile content (when heated to 950 °C), fixed carbon content and ash content in the sample.

Table 1: Ultimate analysis of solid biomass waste

			Ultimate A	nalysis (%)		
Solid waste	С	Н	N	0	S	GCV/ MJ/kg
Palm shell	47.62	6.2	0.7	43.38	-	19.1
Rice Husks	38.2- 55.2	0.2-0.31	1.7-1.9	29.9-31.7	0.07-0.12	12.12- 19.0

Table 2: Proximate analysis of solid waste

		Proximate	Analysis (%)	
Solid waste	Moisture	Volatile	Fixed Carbon	Ash
Palm shell	9.7	67	21.2	2.1
Rice Husks	12.0	52.4	17.1	18.5

(Ahmad H., Farid N. A., Amer N. D. & Zainal A., 2006)

5. Lower Heating Value

Lower heating value (LHV) (also known as net calorific value or net CV) is defined as the amount of heat released by combusting a specified quantity (initially at 25 °C or another reference state) and returning the temperature of the combustion products to 150 °C.

6. Higher Heating Value

Higher heating value (HHV) (gross calorific value or gross CV) includes the heat of condensation of water in the combustion products.

The HHV can also be calculated from the following equation:

HHV (in MJ/kg) = 0.3491C + 1.1783 H - 0.1034 O - 0.0211 A + 0.1005 S -0.0151 N

(Where C is the weight fraction of carbon; H of hydrogen; O of oxygen; A of ash; S of sulfur and N of nitrogen appearing in the ultimate analysis)

(Channiwala, 1992)

7. Ash Content

Ash content is the nonvolatile inorganic matter of a compound which remains after subjecting it to a high decomposition temperature.

8. Volatile Matter

Volatile matter in biomass refers to the components, except for moisture, which are liberated at high temperature in the absence of air.

9. Fixed Carbon

The fixed carbon content of the biomass the carbon found in the material which is left after volatile materials are driven off.

10. Alkali metal content

The alkali metal contents of biomass are Na, K, Mg, P and Ca. Theses alkali metal are important for any thermo-chemical conversion processes. Reaction of alkali metals with silica which are present in the ash will produce a sticky, mobile liquid phase which causes blockages of airway in furnace and boiler plants.

11. Cellulose/ lignin ratio

Cellulose and lignin proportions are important in biochemical conversion processes. Cellulose has a higher biodegradability compared to lignin. When selecting a biomass resource for biochemical processing, it is better to select biomass with higher overall conversion of cellulose proportions. Table 3 shows the proportions of cellulose/hemicelluloses/ lignin for different biomass.

Biomass	Lignin (%)	Cellulose (%)	Hemi-cellulose (%)
Softwood	27-30	35-40	25-30
Hardwood	20-25	45-50	20-25
Wheat Straw	15-20	33-40	20-25
Switchgrass	5-20	30-50	10-40

Table 3: Lignin/cellulose/hemi-cellulose content of biomass

12. Bulk density

Bulk density is an important characteristic of biomass resources. Bulk density is helpful when considering the transportation and storage costs of the biomass resources.

2.5 Van Krevelen Diagram

The Van Krevelen diagram is a useful means of comparing biomass and fossil fuels in terms of their O:C and H:C ratios as shown in Figure 2. The lower the respective ratios the greater the energy content of the material.



Figure 2: Van Krevelen Diagram

CHAPTER 3

METHODOLOGY

3.1 Biomass Identification

The biomasses used in the study were selected by identifying the resources available, value and prospects for biohydrogen production in the country. This process screening was conducted mainly through data and information gathered through researches from past papers.

The biomass samples as of current selected for the project are:

- Coconut fibre
 Coconut husk
 Coconut husk
 Palm oil frond
 Palm oil kernel
 Woodchips
 Residues of
 Banana Stem
 Sawdust
 Plywood
 Sugarcane residue
 Empty Fruit Bunch (EFB)
 Rice husks
- 7. Palm oil trunk

3.2 Sample Preparation

The first step in the characterization process of biomass is the pre-treatment of the raw material. Pre-treatment is where the biomass materials are dried and grinded. The sample must be homogeneous because of the small weighed quantity. Therefore all the granular samples are finely grinded and dried.



Figure 3: (a) Empty fruit bunches; (b) Palm oil kernels; (c) Wood Residues; (d) Sugar Cane Residues; (e) Rice Husk; (f) Paddy straw







(a)

(b)

(c)



(c)



(e)



(f)

Figure 4: (a) Empty Fruit Bunch; (b) Unripe Fruit Bunch; (c) (From L-R) Unripe Fruit Bunch, Fresh Fruit Bunch, Empty Fruit Bunch; (c) Coconut Husk; (d) Banana Stem; (e) Sawdust & Woodchips; (f) Various biomass samples

3.3 Moisture Content Analysis

The moisture content of the biomass samples is obtained using the Mettler Toledo HR73 Halogen Moisture Analyzer. This instrument operates on the thermogravimetric principle. A halogen radiator dries the sample under investigation while the precision balance integrated in the instrument continuously measures the sample weights. The total weight loss is interpreted as moisture content.

This instrument involves a short measurement time. The ring shape of the halogen radiator and its position above the sample results in an even heating of the sample. The basis of the calculation of the moisture content is the weight loss of the sample at the end of drying.



Figure 5: Halogen Moisture Analyzer

A different method for obtaining the moisture content will be using the oven where samples are dried in the oven and weighed simultaneously. The moisture content is obtained when there is no more change in the sample's weight.

3.4 Multi-element Analysis using the CHNS analyzer

The instrument used for the purpose is the LECO 932 CHNS analyzer. This instrument is based on a vertical furnace system and permits a nominal 2mg sample size. A single weighed sample is used to determine the four elements simultaneously. The instrument involved the qualitative conversion of the four elements into carbon dioxide, water vapour, nitrogen gas and sulfur dioxide respectively:

CHNS compound $\overrightarrow{\text{Oxidation}}$ CO_2 ; H_2O , NO_X ; SO_2 Reduction CO_2 ; H_2O , N_2 ; SO_2

After separation of the gases, each component is measured by infrared absorption.

The operating procedures for the system are as the following:

- 1. The samples are burned at 1000°C in flowing Oxygen.
- 2. CO_2 , H_2O , NO_x and SO_2 combustion gases are passed through a reduction tube (helium as carrier gas) for converting the NO_x nitrogen oxides into N_2 .
- 3. CO₂, H₂O and SO₂ combustion gases are measured by selective IR detectors.
- 4. The content of the remaining nitrogen are determined by thermal conductivity detection.



Figure 6: LECO 932 CHNS Analyzer



Figure 7: CHNS Analyzer side view



Figure 8: (a) Sample weighed; (b) Samples inserted in cell; (c) Weight of sample entered; (d) System allowed to run; (e) CHNS results obtained

3.5 Combustion Analysis

The combustion analysis is actually determining the calorific value (CV) or Higher heating Value (HHV) of different solid biomass feedstock. This can be conducted using the IKA C5000 Bomb Calorimeter.

The instrument consists of the Oxygen gas regulator, Bomb Calorimeter, Refrigerator bath system and control system. The Oxygen gas regulator is first turned on to enable oxygen supply to the system. After the Bomb Calorimeter and refrigerator bath system is stabled, the biomass sample weighing below 5.0 gram is prepared. The system is able to produce a graph of the change over time in temperature of the inner vessel and the Calorific Value (J/g).

The procedures for operating the system are as the following:

- 1. The system is switched on and left for 30 minutes until the stable temperature conditions are relevant in the measurement cell.
- 2. The sample is weighed in a pan balance and inserted into a crucible.
- 3. The *System* menu is opened and *sample* is selected. The weight of the sample is entered.
- 4. The decomposition vessel is prepared by cleaning and drying it entirely.
- 5. A cotton thread with a loop is secured in the middle of the ignition wire before being placed in the decomposition vessel.
- 6. The Start option is selected. The decomposition vessel is then filled with oxygen followed by water.
- 7. After 15-20 minutes the system will display the result of the experiment.
- 8. The decomposition vessel is vented and the measurement cell cover opens.
- 9. The decomposition vessel is removed and opened when the *Bomb* + appears.
- 10. The crucible is checked for combustion residue. Both the cotton thread and the fuel sample must have been burned completely. If there any signs of incomplete combustion, the experiment must be repeated.
- 11. The System menu is opened and Exit is selected to turn off the calorimeter system.



(a)

(b)





(c)

Figure 9: (a) Sample weighed; (b) Sample inserted into crucible with string attached to ignition wire; (c) Decomposition vessel tightened; (d) Decomposition vessel placed in the measurement cell (e) Results obtained from display screen.

3.6 Proximate Analysis

The proximate analysis is carried out using the Perkin Elmer Pyris 1 Thermal Gravimetric Analysis (TGA). The analysis will provide the values of the moisture content, fixed carbon content, volatile matter content and ash content of the samples.

The operating procedure of the equipment is as follows:

- 1. Platinum sample pan is removed from hanger using tweezers.
- 2. The sample pan is cleaned using the cotton bud with acetone.
- 3. The sample pan is placed into the hanger.
- 4. The furnace is raised up by pressing 'raising furnace' and 'zero weight' was selected.
- 5. The sample pan is removed again to insert the samples. 'Lower furnace' is selected.
- The sample pan is placed back into the hanger using the provided tweezers. The weight is monitored around 10-20 mg.
- 7. At the Pyris 1 DSC program, 'Method Editor' is selected and the required parameters are inserted.
- 8. The initial temperature is set and wait till initial temperature is reached.
- 9. The "Start/Stop" was selected to run the analysis.











Figure 10: (a) TGA balance; (b) Perkin Elmer Pyris 1 TGA; (c) Overall system of Perkin Elmer Pyris 1 TGA

The outcome of the analysis will be displayed in terms of a decomposition regime graph. From the curve, the moisture content, volatile matter, fixed carbon and ash content are obtained as shown in the curve below:



Figure 10.1: TGA profile

CHAPTER 4

RESULTS & DISCUSSION

4.1 Moisture Content Analysis

The moisture content analysis was conducted for the biomass samples currently available. Moisture content is defined as the quantity of water contained in a material on a volumetric or gravimetric basis. It is calculated based on Moisture Content Wet Basis (MCWB). The MCWB is defined as:

MCWB = 100 X (Initial Wt - Dry weight)/ (Initial Weight)

Table 4: Initial and dry weight of th	e biomass samples
---------------------------------------	-------------------

Biomass Sample	Initial Weight (g)	Dry Weight (g)
Coconut Fibre	0.968	0.888
Woodchips	3.948	3.524
Sawdust	4.159	3.627
Empty Fruit Bunch (EFB)	5.314	2,499
Unripe Fruit Bunch	5.305	2.066
Palm Oil Stem	11.407	2.528
Banana Stem	15.63	0.888
Sugarcane residue	16.928	8.174

 Table 5: MCWB of the biomass samples

Biomass Sample	MCWB (%)	
Coconut Fibre	8.27	
Woodchips	10.76	
Sawdust	12.78	
Empty Fruit Bunch (EFB)	52.98	
Unripe Fruit Bunch	61.06	
Palm Oil Stem	77.40	
Banana Stem	94.32	
Sugarcane residue	51.7	

From the results obtained, Banana stem has the moisture content with 94.32 % while coconut fibre shows the lowest 8.27%. EFB has a moisture content of 52.98%. In general, the relationship between moisture content and the appropriate conversion technology is straight forward. Thermal conversion requires a low moisture content biomass feedstock (<50%) whereas bio-conversion technology requires a high value of moisture content. Thermal conversion can also operate at high biomass moisture content but this will affect the overall energy balance of the conversion process. On this basis, woody biomass feedstock (woodchips and sawdust) are the most efficient for thermal conversion. Lower moisture content will result in a higher energy value.

The moisture content analysis results attained using the does not reflect the exact values. The moisture content analysis conducted from the Proximate Analysis using the Perkin Elmer Pyris 1 TGA will be obtained and compared with this analysis results.

4.2 Combustion Analysis

The gross calorific value of the biomass samples available were determined accordingly two runs each using the IKA C5000 Bomb Calorimeter. GCV experimental indicates the calorific values from the IKA C5000 Bomb Calorimeter whereas the GCV calculated is obtained using the equation below.

GCV (in kJ/g) = 0.3491C + 1.1783 H - 0.1034 O - 0.0211 A + 0.1005 S - 0.0151 N

Where C is the weight fraction of carbon; H of hydrogen; O of oxygen; A of ash; S of sulfur and N of nitrogen appearing in the ultimate analysis)

From the GCV experimental analysis, woody biomass resources which are the woodchips and sawdust show the highest values of GCV while Paddy straw has the lowest value of GCV. As for GCV calculated from the equation, woodchips has the highest GCV and Paddy straw the lowest. In general all the biomass materials indicate a GCV of between 13-18 %.

Both values obtained were compared and the percentage difference shown in Table 3. The percentage difference for both Empty Fruit Bunch and Banana fibre are below 9% and the rest of the samples are below 3%.

GCV is actually an indication of the maximum amount of energy potentially recoverable from a given biomass source. However, the actual amount of energy recovered will vary with the conversion technology used and also the form of the energy (combustible gas).

Biomass	GCV experimental	GCV calculated	Percentage Difference
	(MJ/kg)	(MJ/kg)	%
Coconut Fibre	18.02	17.66	2.02
Empty Fruit Bunch	16.96	15.54	8.33
Unripe Fruit Bunch	17.61	16.69	5.24
Palm Oil Trunk	15.16	15.39	1.53
Saw dust	18.22	17.93	1.60
Wood chips	18.22	18.48	1.39
Banana Fibre (Stem)	14.45	13.28	8.08
Sugarcane Residue (Bagasse)	17.00	16.53	2.76
Paddy Straw	12.97	12.61	2.75
Rice Husks	14.76	14.50	1.73

Table 6: Gross Calorific Values of the biomass samples

4.3 Ultimate Analysis

The ultimate analysis shows the percentage of carbon, hydrogen, nitrogen and sulfur. The percentage of oxygen was obtained by subtracting the overall CHNS percentage from 100. From the analysis, all biomass samples shows carbon percentage of 33-45%. The hydrogen percentage of the samples is 5-6%. Sulfur and Nitrogen content in the biomass is the lowest >0.2% while Oxygen's percentage is 45-60%.

Comparisons were conducted with respect to the composition of each element. For carbon content percentage, woodchips is the highest followed by coconut fibre while the biomass source with the lowest carbon content is paddy straw. As for hydrogen content, sawdust is the highest while unripe fruit bunches indicates the lowest. Sawdust has the lowest nitrogen content amongst the biomass samples while unripe fruit bunches shows the highest. EFB shows the highest content for sulfur while sawdust shows the lowest sulfur content. Paddy straw indicates the highest oxygen content with woodchips the lowest. From the percentage of the composition, the C:H, H:C and O:C ratios were determined.

Biomass	Ultimate Analysis				
	C(%)	H(%)	N(%)	S(%)	O(%)
Coconut Fibre	45.78	6.38	0.72	0.07	47.05
	45.16	5.87	0.84	0.12	48.02
	44.13	5.54	0.86	0.11	49.37
	45.58	5.80	0.79	0.07	47.77
Average	45.16	5.90	0.80	0.09	48.05
Empty Fruit Bunch	41.28	6.26	1.31	0.23	50.93
	40.33	5.63	1.40	0.21	52.43
	40.57	5.40	1.50	0.21	52.32
Average	40.73	5.76	1.40	0.22	51.89
Unripe Fruit Bunch	43.52	5.61	2.37	0.17	48.33
	43.16	5.72	1.87	0.20	49.05
	43.00	5.81	2.26	0.21	48.72
Average	43.23	5.71	2.17	0.20	48.70
Palm Oil Trunk	39.84	5.76	0.49	0.08	53.84
	39.10	5.73	0.53	0.06	54.58
	40.71	6.50	0.78	0.09	51.92
Average	39.88	6.00	0.60	0.08	53.44
Saw dust	43.90	6.78	0.21	0.05	49.06
	42.90	6.55	0.29	0.03	50.23
	44.25	6.61	0.20	0.04	48.90
Average	43.68	6.65	0.23	0.04	49.40

Table 7: Ultimate analysis of different biomass sources

TTT 1 1 1					
Wood chips	45.73	6.43	0.23	0.04	47.57
	45.58	6.32	0.35	0.04	47.71
	46.37	6.03	0.38	0.06	47.16
Average	45.89	6.26	0.32	0.04	47.48
Banana Fibre (Stem)	35.19	6.02	0.47	0.07	58.25
	36.95	5.83	0.50	0.04	56.68
	37.28	5.72	0.50	0.06	56.44
Average	36.47	5.86	0.49	0.06	57.12
Sugarcane Residue (Bagasse)	43.64	5.70	0.68	0.05	49.93
	42.41	5.85	0.64	0.07	51.04
	42.75	5.91	0.72	0.07	50.55
Average	42.93	5,82	0.68	0.06	50.51
Paddy Straw	33.67	6.09	1.38	0.16	58.70
	32.50	5.75	1.38	0.14	60.23
	36.28	6.19	1.62	0.14	55.77
Average	34.15	6.01	1.46	0.15	58.23
Rice Husks	38.48	5.78	0.53	0.05	55.16
	39.39	5.81	0.50	0.08	54.22
	38.34	6.19	1.62	0,14	53.71
Average	38,74	5.93	0.88	0.09	54.36

Legend:

CF= Coconut Fibre; EFB= Empty Fruit Bunch; UFB= Unripe Fruit Bunch; POT= Palm Oil Trunk; SD= Sawdust; WC= Woodchips;

BF= Banana Fibre; BGS= Bagasse; PS= Paddy straw; RH= Rice Husks

Biomass	Ra	tio
	H:C	0: C
CF	1.57	0.80
EFB	1.70	0.96
UFB	1.59	0.84
РОТ	1.80	1.01
SD	1.83	0.85
WC	1.64	0.78
BF	1.93	1.17
BGS	1.63	0.88
PS	2.11	1.28
RH	1.84	1.05

Table 8: The H:C and O:C ratios of biomass samples

The Van Krevelen diagram in Figure 11 shows the position of biomass as compared to coal. Coal was selected as fossil fuel to be compared with the biomass sources. The H:C and O:C ratios of coal are 0.59 and 0.11 respectively obtained from reference journals.

The lower the respective ratios, the greater will be energy content of the material. The higher the proportion of oxygen and hydrogen, compared with carbon will reduce the energy value of the biomass. This is mainly due to the lower energy contained in carbon-oxygen and carbon-hydrogen bonds, than in carbon-carbon bonds.

From the Van Krevelen diagram, coconut fibre, woodchips and unripe fruit bunches have the lowest ratios thus having the highest energy content.



Figure 11: Van Krevelen Diagram from analysis



Figure 12: Carbon content in biomass



Figure 13: Hydrogen content in biomass

Figure 14: Oxygen content in biomass

Figure 16: Sulfur content in biomass

4.4 Proximate Analysis

Proximate analysis includes moisture content, ash content, free carbon content and the volatile content. The proximate analysis was conducted using the Perkin Elmer Pyris 1 Thermal Gravimetric Analysis (TGA). Proximate analysis was conducted on five samples which are EFB, paddy straw, rice husks, sawdust and woodchips.

Biomass generally has higher volatile matter content and lower fixed carbon and ash content compared to fossil fuels. Volatile matter and fixed carbon contents provide measure of ease which biomass can be ignited and subsequently gasified or oxidized (conversion). Ash content affects handling and processing cost of overall biomass energy conversion cost.

Biomass	Proximate Analysis					
	Moisture Content	HHV	Fixed Carbon content	Volatile Matter content	Ash content	
	(% H2O)	(MJ/kg)	(%)	(%)	(%)	
EFB	6.5	16.96	18.6	86.8	5.1	
PS	7	12.97	7.5	64.5	21	
RH	8.5	14.76	5.5	71.4	14.6	
SD	6	18.22	17.9	76	0.1	
WC	4.5	18.22	14.6	80.5	0.4	

Lable 9: Proximate Analysis of biomass samples	Table 9:	Proximate	Analysis	of biomass	samples
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Figure 18: Fixed Carbon content in biomass

Figure 19: Volatile Matter content in biomass

Figure 20: Ash content in biomass

CHAPTER 5 CONCLUSION & RECOMMENDATION

This project is mainly a research on the prospect of biomass resource in the country for biohydrogen production. The research project was conducted on biomass resources that are available in the country. The research covered investigating the elemental and combustion analysis of different types of biomass to characterize them based on biohydrogen production potentials. Ultimate analysis which studies the elemental composition of the biomass and its Gross Calorific Value (GCV) was conducted. Proximate analysis which includes moisture content, ash content, free carbon content and the volatile content will be carried out depending on the availability of the equipment. The main equipments be used were CHNS Analyzer, Moisture Analyzer, Bomb Calorimeter and Thermal Gravimetric Analyzer. The laboratory equipments were ensured to be in perfect condition to obtain accurate data for the project. This is vital to accomplish all the objectives that have been listed. There are also other analyses that need to be conducted such as the determination of the Cellulose/ lignin proportions and the alkali metal content of the biomass. Further more, further research on the conversion and technology strategies for biohydrogen production will have to be studied. The analyses that have been conducted based on the biomass properties would be of great use for future studies on biohydrogen production. Within the timeframe that is given for the research project, the project has been successful in realizing the potential of the country's wide biomass resource to produce hydrogen commercially.

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APPENDICES

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Figure 22: World annual oil palm biomass generation from 1980 to 2005

		Cellulose (%)	Hemi-cellulose (%)	Lignin (%)
Biomass Feedstocks	corn	35	28	16-21
recusiocas	sweet	27	25	11
	sorghum	**	**	**
	sugarcane	32-48	19-24	23-32
	bagasse	**	**	**
	sugarcane	**	**	**
	leaves	**	**	**
	hardwood	45	30	20
	softwood	42	21	26
	hybrid	42-56	18-25	21-23
	poplar	**	**	**
	bamboo	41-49	24-28	24-26
	switchgrass	44-51	42-50?	13-20
	miscanthus	44	24	17
	Arundo donax	31	30	21
		·		

 Table 10: Composition of selected biomass feedstock

(Scurlock, 2002)

CHNS Elemental Analysis

Sample	N%	С%	H%	S%
1	0.0649	45.7746	6.1044	0.0288
	0.0677	45.8869	6.2031	0.0274
	0.0666	46.1076	6.1345	0.0285
	0.0651	45.7568	6.1504	0.0275
	0.0664	45.8578	6.0941	0.0279
Avg %	0.0661	45.8767	6.1373	0.0280
2	0.0882	47.1092	6.1197	0.0312
	0.0910	47.0881	6.1050	0.0324
	0.0895	47.1071	6.1088	0.0315
	0.0902	47.0995	6.1115	0.0331
	0.0890	47.1042	6.1065	0.0319
Avg %	0.0896	47.1016	6.1103	0.0320

Table 11: CHNS analysis of wood residue samples

(Krotz and Giazzi, 2003)

Moisture content and Combustion Analysis

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Moisture Content (%)	Calorific Value (MJ/kg)	
50	9.2	
agasse pith 40		
Spent bagasse 40		
35	11.3	
10-15	12.6-13.8	
6	14.4	
16	11.3	
11-14	15-17.5	
10	16.75	
10	18.8	
8	16.75	
7	18.4	
7-8	15.5-15.9	
	Moisture Content (%) 50 40 40 35 10-15 6 16 11-14 10 8 7 7-8	

Table 12: Moisture and gross calorific value of different biomass feedstock

(Nath K. & Das D., 2003)

Figure 25: CHNS composition of different biomass

Figure 27: TGA profile for paddy straw

Figure 28: TGA profile for rice husks

Figure 29: TGA profile for sawdust

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Figure 30: TGA profile for woodchips