CHAPTER 1

INTRODUCTION

1.1 Project Background

The project entitled as “Torrefaction of coconut shell, rice husk, and paddy straw to improve its properties for enhancing gasification efficiency” will study on how to conduct torrefaction or mild pyrolisis process on these biomass to become torrefied material that will be better fuel (feed) for gasification application. This process would change the biomass’s properties that would make the material to be a much better fuel quality for gasification applications. It would cause the biomass become completely dried, increasing the calorific energy value in the material, and loose it tenacious and fibrous structure. According to past research, these properties would reduce the gasification problem such as tar formation which leads to increasing the gasification efficiency. Higher efficiency of gasification should increase the hydrogen production rate. Moreover, the amount of biomass like rice husk, rice (paddy) straw and coconut shell are available in Malaysia in large quantity. Therefore, it is a good opportunity to conduct a details research and development on the product which has high potential benefit to the country.

1.2 Problem Statement

1.2.1 Shortage of fossil fuels

Dependence on fossil fuels as the main energy sources has led to serious energy crisis (fossil fuel depletion) and environmental problems (pollutant emission). United Arab Emirates, one of the major oil export countries, would fail to meet the share in the oil and natural gas demands by 2015 and 2042, respectively. The fossil fuel resources in Egypt would be exhausted within one to two decades. China claimed that the imported oil amounted to 31% to meet the energy demand in 2000 will be increased into 45–55% in 2010. Obviously, the increasing energy demands will speed up the exhaustion of the finite fossil fuel. Moreover, combustion of fossil fuel produces substantial greenhouse and toxic gases, such as CO_2, SO_2, and other pollutants, causing global warming and acid rain.

It is now essential to improve the efficiency with the usage of natural resources, and develop renewable alternatives wherever possible to protect the resources on which the current and future generations depend. Renewable resources including fish stocks, water and timber should be consumed only at rates at which they can be naturally replaced. Alternative sources of energy and raw materials need to be developed.

1.2.2 Gasification Process as Alternative Energy Producer

In order to meet the alternative energy demand which is increasing nowadays, research had been done to find out suitable process to produce type of energy and gasification is one of the processes. This process is used to produce hydrogen gas and others from biomass like sugarcane baggage which can be used as alternative energy for the fossil fuel energy. However, researches found that production rate of gas are not sufficient when using untreated biomass as the feed. The problems may occur are like unwanted tar and ash formation in gasifier.

A research had been done by Mark J. Prins et al (2005) where they found that even though wood is a clean fuel with low nitrogen, sulphur and ash content, it is thermally unstable, which may lead to formation of condensable tars in gasifiers, thus giving problems in down-stream equipment such as choking and blockage of piping. Other disadvantages are the low energy density of wood, typically 18 MJ/kg, in combination with its high moisture content due to its hygroscopic character, typically around 10 wt%, even after drying. These problems would reduce the gasification efficiency.

1.3 Objectives

- To investigate the properties of rice husk, coconut shell and paddy straw which are available in large amount in this country especially at northern and east-coast states like Kedah and also Terengganu
- To investigate the properties of selected biomasses either being improved or not after the torrefaction process

1.4 Scope of Studies

- Study on the concept of biomass as alternative energy resources and its importance to people today.
- Study on the concept and experimental procedure of torrefaction process.
- Study on rice husk, paddy straw and coconut shell as potential materials to be developed for gasification technology.
- Study on the concept, principle and parameters of torrefaction process and possibility of applying the process to improve the biomass properties
- To conduct torrefaction experiments on rice husk, paddy straw, and coconut shell, as well as investigating their properties before and after experiment

CHAPTER 2

LITERATURE VIEW

2.1 Energy & Environment Issues

Fossil fuels provide around 66% of the world's electrical power, and 95% of the world's total energy demands (including heating, transport, electricity generation and other uses). Coal provides around 28% of energy, oil provides 40% and natural gases provide about 20%. A concern is that the fossil fuels are being used up at an increasing rate, and that they will soon run out. If these fossil fuels were to run out now there would not be a suitable replacement for them that is equally as efficient at producing the same amount of energy.

The basic element of fossil fuels is carbon and carbon dioxide can be formed by the burning of carbon containing materials.Carbon dioxide is part of the greenhouse effect, which prevents the heat of the sun from leaving the atmosphere. The consumption of coal, oil and natural gases has some terrible effects on the environment. Gradually the world’s temperature is heating up due to the greenhouse effect. In addition, research done by National Oceanic & Atmospheric Administration (NOAA) under United States of Commerce also found that the concentration of CO_2 and CH_4 have been increasing in the atmosphere since 1850 and are now become higher as a result of human use of fossil fuels and land clearing. They claimed half of total carbon emitted to atmosphere is taken up by the oceans (and land) in form of these gases. According to Pidwirny (2008), the emissions from fossil fuel combustion account for about 65% of the additional carbon dioxide currently found in the Earth's atmosphere. The other 35% is derived from deforestation and the conversion of natural ecosystems into agricultural systems

The continuous emission of carbon dioxide to the atmosphere will affect climate and ocean chemistry, subsequently influencing both marine and terrestrial ecosystems. The warming effects of increasing CO2 and other greenhouse gases impinge on agriculture, natural systems, and a host of environmental variables. Increasing CO2 in the atmosphere also directly translates to increasing acidity of the oceans. Carbon dioxide dissolves in water to form carbonic acid, which is corrosive to the shells and skeletal material of many marine organisms.

One way the world is trying to reduce greenhouse gas emissions is by a treaty, called the Kyoto agreement (http://unfccc.int/kyoto_protocol/items/2830.php). This agreement requires those countries that have signed, to reduce the emissions to an acceptable level, sustainable forms of agriculture and to promote and provide research on the increased use of renewable forms of energy. It is an international agreement linked to the United Nations Framework Convention on Climate Change. The major feature of the Kyoto Protocol is that it sets binding targets for 37 industrialized countries and the European community for reducing greenhouse gas (GHG) emissions.

Under the treaty, countries must meet their targets primarily through national measures. However, the Kyoto Protocol offers them an additional means of meeting their targets by way of three market-based mechanisms which purposely to stimulate green investment and help parties meet their emission targets in a cost-effective way:

- Emissions trading – known as “the carbon market"
- Clean development mechanism (CDM)
- Joint implementation (JI).

The Kyoto Protocol is generally seen as an important first step towards a truly global emission reduction regime that will stabilize GHG emissions, and provides the essential architecture for any future international agreement on climate change.

2.2 Biofuel

Biofuel are looked as one of the best way to reduce the greenhouse effect. Besides that, it can be an alternative of fossil fuels which are limited nowadays. Many countries from Asia, Europe and America has started look into this alternative. These fuels are derived from biomass or bio waste like sugarcane bagasse and rubber seed kernel. It was mainly used in trasnsportation sector as engine oil. It can be easily pumped and easy to handle it. There are many types of biofuel which may reduce the fossil fuel usage as cited in the next paragraph.

2.2.1 Biodiesel

This is a famous biofuel in Europe. Its composition is just like mineral diesel. When biodiesel is mixed with mineral diesel, the mixture can be used in any diesel engine. It is observed that in several nations, the diesel engines under warranty are converted to 100% biodiesel use. It has also been proved that most people can run their vehicles on biodiesel without any problem. A large number of vehicle manufacturers recommend the use of 15% biodiesel mixed with mineral diesel. In Europe, a 5% biodiesel blend is generally used at gas stations.

A study had been done Hanbey Hazar (2008) from Firat University, Turkey entitled as "effect of biodiesel on a low heat diesel engine". The objective of this study is to examine the effect of using biodiesel in a diesel engine that has had its combustion chamber elements coated with ceramic, in order to determine any significant effects on performance and exhaust gas emissions. In this study, diesel oil named as 2D and biodiesel which is Canola methyl ester (CME) are tested in a single cylinder direct injection of a diesel engine. The piston surface, cylinder head, and valves were coated with ceramic materials. The result showed that ceramic coating in cylinder engine with using mixture of diesel and biodiesel oil could be applied succesfully without any significant modifications to the structural characteristics of the internal combustion engine as well as reducing harmful emission (carbon monoxide gas).

2.2.2 Bioalcohols

It biologically produced alcohols. Common among these are ethanol and rare among these are propanol and butanol. Biobutanol can be used directly in a gasoline engine and hence is considered a direct replacement for gasoline. The butanol can be burned straight in the existing gasoline engines without any alteration to the engine or car. It is also claimed that this butanol produces more energy. Also, butanol has a less corrosive effect and is less soluble in water than ethanol. Other bioalcohol, Ethanol most commonly used biofuel in the world and particularly in Brazil.

Ethanol can be put to use in petrol engines as a substitute for gasoline. Also, it can be mixed with gasoline in any ratio. The contemporary automobile petrol engines can work on mixtures of gasoline and ethanol that have 15% bioethanol. This mixture of gasoline and ethanol has more quantity of octane. This indicates that the engine would burn hotter and more efficiently. In high altitude spots, the mixture of gasoline and ethanol is used as a winter oxidizer and thereby atmospheric pollution is decreased.

Hsieh et al (2001) investigated the engine performance and pollutant emission of a commercial SI engine by using ethanol-gasoline blended fuels. From the investigations, it was showed that with increasing of ethanol content, the heating value of the blended fuel increases. Beside that, the torque output and fuel consumption of the engine was slightly increased and carbon monoxide (CO) emissions decreased dramatically (10 – 90%) as a result of the leaning effect cause by ethanol addition while CO2 emission is slightly increased in range 5 – 25% depending on engine condition.

2.2.3 Syngas

The combined processes of gasification, combustion and pyrolyis gives rise to syngas which is a biofuel. This syngas can be directly burned in internal combustion engines. Syngas can be used to produce hydrogen and methanol. By using the Fischer-Tropsch process, it can be transformed to a synthetic petroleum substitute.

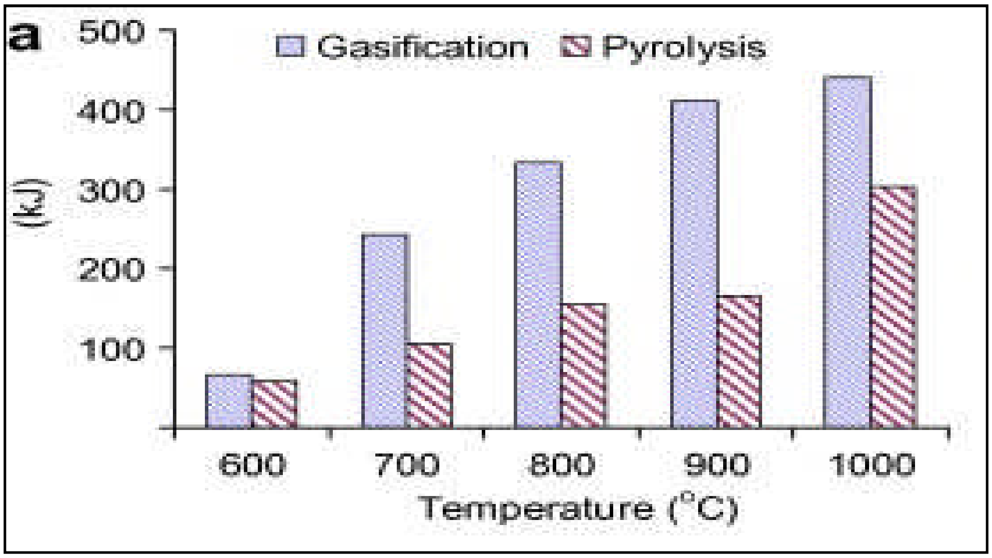


Figure 2.1: Comparison Energy Yield beween Gasification and Pyrolisis of Paper (Ahmed et al, 2008)

An experiment had been done by Ahmed et al (2008) which investigated the syngas yield from gasification and pyrolisis of paper. The experiment had been carried out at several different temperature and resulting to the gasification may contributed better results in terms of increasing material destruction, and increasing yields of hydrogen and chemical energy. The result showed that gasification of 35 g of white paper yielded 250 – 440 kJ as compared to 50 – 300 kJ in case of pyrolisis at range temperature from 700 to 1000 °C (Figure 3.1). For reactor at temperature of 600 °C, both processes yielded almost the same amount of energy and hydrogen. This project will do further study on mild-pyrolisis or torrefaction process of other rice husks, coconut shell, and paddy straw in order to study its capability (product from torrefaction process) to increase the gasification efficiency to produce more amount of syngas especially hydrogen.

2.3 Hydrogen production

One of the methods to produce hydrogen is by doing conversion from biomass, which is abundant, clean and renewable. Alternative thermochemical (pyrolysis and gasification) and biological (biophotolysis, water–gas shift reaction and fermentation) processes can be practically applied to produce hydrogen.

The available energy production processes from biomass can be divided into two general categories: thermochemical and biological processes. Combustion, pyrolysis, liquefaction and gasification are the four thermochemical processes.

2.3.1 Hydrogen from biomass pyrolysis

Pyrolysis is the heating of biomass at a temperature of 650–800 K at 0.1–0.5 MPa in the absence of air to convert biomass into liquid oils, solid charcoal and gaseous compounds. Pyrolysis can be further classified into slow pyrolysis and fast pyrolysis. As the products are mainly charcoal, slow pyrolysis is normally not considered for hydrogen production. Fast pyrolysis is a high temperature process, in which the biomass feedstock is heated rapidly in the absence of air, to form vapor and subsequently condensed to a dark brown mobile bio-liquid. The products of fast pyrolysis can be found in all gas, liquid and solid phases as shown below:

- Gaseous products include H_2, CH_4, CO, CO_2 and other gases depending on the organic nature of the biomass for pyrolysis.
- Liquid products include tar and oils that remain in liquid form at room temperature like acetone, acetic acid, etc.
- Solid products are mainly composed of char and almost pure carbon plus other inert materials.

2.4 Concept of Gasification

As stated in problem statement, gasification is one of effective process to produce hydrogen. However, the problem during the process like tar formation which resulting on blockage at downstream piping had made this process less efficient.

Gasification is the process which converting a substance into a gas. The substances like coal, petroleum or biomass will converted into a gas mixture containing carbon dioxide, carbon monoxide and hydrogen in the presence of oxygen. The gas mixture produced (syngas) can then be treated with steam to produce more hydrogen. Gasification occurs through chemical reactions at high temperature and often at high pressure.

Many studies have been done on various type of biomass material on this process like sawdust, cotton stem, wood, bagasse and others which show gasification process can be used for various types of biomass sources. The biomass particle will undergo partial oxidation resulting in gas and charcoal production. The charcoal is finally reduced to form H_2, CO, CO_2, and CH_4. The conversion can be expressed as:

$$\text{Biomass + heat (presence of } O_2) \rightarrow H_2 + CO + CO_2 + CH_4 + \text{light and heavy hydrocarbon + char}$$

Hydrogen production from biomass gasification

Gasification mainly producing gaseous product compared to pyrolysis. The main product of pyrolysis is solid fuel and liquid (bio fuel). In order to increase the hydrogen production, the gaseous product can be steam reformed where CH_4 will react with steam (H_2O) to produce other amount of hydrogen as expressed in reaction below:

$$CH_4 + \text{Steam } (H_2O) \rightarrow CO + 3H_2$$

Moreover, this process also can be further improved by using water – gas shift reaction:

$$CO + H_2O \rightarrow H_2 + CO_2$$

From the reaction and conversion stated, it shows that the amount of hydrogen can be efficiently increased when gasification process is further improved by steam reformed and water-gas shift reaction process.

Besides looking at process on hydrogen production, there are other factors which also affect the amount of hydrogen produced from biomass like:

i) Type of feedstock
ii) Type of reactor used
iii) Type of catalyst used
iv) Operation parameter like temperature, residence time etc.

Many studies have been done by scientists to investigate the factor affect the amount of hydrogen production from biomass gasification. Table 2.1 shows some studies and results found by them

Meng Ni et al (2005)

Table 2.1: Investigation on factors affecting the gasification process

Feedstock	**Reactor type**	**Catalyst used**	**Hydrogen production (vol.%)**
Sawdust	Not Known	Na_2CO_3	48.31 at 700 °C
			55.4 at 800 °C
			59.8 at 900 °C
Sawdust	Circulating fluidized bed	Not used	10.5 at 810 °C
Wood	Fixed bed	Not used	7.7 at 550 °C
Sawdust	Fluidized bed	Not known	57.4 at 800 °C
Sawdust	Fluidized bed	K_2CO_3	11.27 at 964 °C
		CaO	13.32 at 1008 °C
		Na_2CO_3	14.77 at 1012 °C
Pine sawdust	Fluidized bed	Not known	26–42 at 700–800 °C
Bagasse			29–38 at 700–800 °C
Cotton stem			27–38 at 700–800 °C
Eucalyptus gobulus			35–37 at 700–800 °C
Pinus radiata			27–35 at 700–800 °C
Sewage sludge	Downdraft	Not known	10–11
Almond shell	Fluidized bed	La–Ni–Fe	62.8 at 800 °C
		Perovskite	63.7 at 900 °C
Switchgrass	Moving bed	Cu–Zn–Al	27.1

From Table 2.1, operating temperature also play its role in producing hydrogen from biomass. According to the first three row of the table, saw dust feedstock has been heated in difference level of temperature (same reactor and catalyst used for each level). As expected, difference amount of hydrogen has been produced at each level where 900°C (highest temperature level) producing highest amount of gas than others.

Beside that, scientists also found that the amount of hydrogen would be difference when using various type of biomass feedstock. According to the table, an experiment had been done by using same type of reactor (fluidized bed reactor) with constant range of temperature (70 - 800 °C). Highest amount of hydrogen has been produced from pine sawdust (26 – 42 vol%) feedstock compared to Pinus radiata feedstock which just produce hydrogen in range 27 – 35 vol% at constant range temperature. This experiment shows type of biomass become an important factor to produce efficient amount of hydrogen too.

Issues in biomass gasification

Tar formation in biomass gasifier becomes one of major issues in gasification process. The unwanted tar may cause formation of tar aerosols and polymerisation to a more complex structure. When the complex structure substance formed in gasifier, steam reforming cannot be done hence no more hydrogen can be further produced. Figure 2.2 shows clearly the location of tar formation. Increasing of this structure may block the downstream pipe. Hence, the process like biomass drying will be interrupted. This problem would make the feed cannot be dried efficiently hence reducing the production. Besides that, Meng Ni et al (2004) claimed that, this process is applicable for biomass that having moisture content less than 35%. Hence, biomass without pre-treatment (to reduce the moisture content) before undergo gasification process will make the process unefficient.

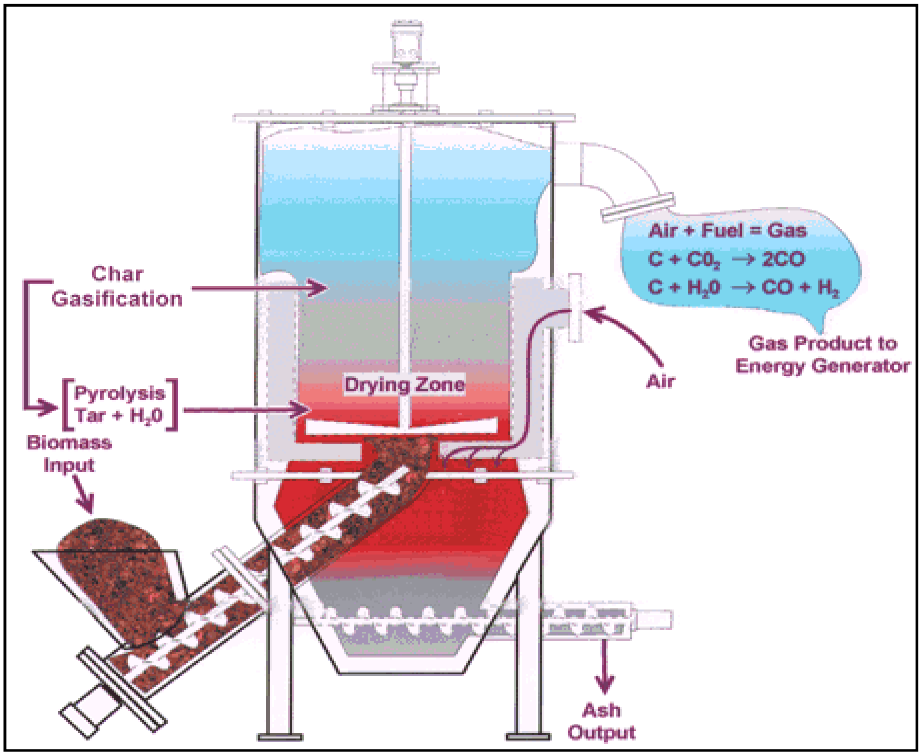


Figure 2.2: Gasification Process
(http://www.thermogenics.com/gasification.html)

Scientists currently found three methods which are available to minimize tar formation during gasification process:

i) Proper design of gasifier
ii) Proper control and operation
iii) Using additives/catalysts

Proper control and operation

Operation parameters like temperature, gasifying agent, and residence time affect the formation/decompostion of tar in gasifier. When the operating temperature is exceeding 1273 Kelvin, tar will thermally crack. Beside that, ordinary gasification process can be modified like doing two-stage gasification and secondary air injection process which may reduce tar formation in gasifier.

Using Additives/catalyst

Using additives/catalyst can eliminate tar and also improving gas product quality and conversion efficiency. For example, by using dolomite, 100% of tar in gasifier can be eliminated. Other catalysts like olivine and char can be used to reduce the amount of tar in gasifier. Other catalysts like Ni-based catalyst, alkaline metal oxides as well as dolomite are widely used in gasification process to improve the product quality and conversion efficiency.

Another issue in gasification process is formation of ash in gasifier. Formation of this substance in reactor (gasifier) can cause deposition, sintering, slagging, fouling, and also agglomeration.

Scientists have found some methods to reduce ash formation in reactor which are:

i) Fractionation
ii) Leaching

Both methods have their own advantages and distadvantages on the process/products when be used. For example, fractionation is the effective method for ash removal while the disadvantage is it may deteriorate the quality of remaining ash. Leaching method is good for removing inorganic biomass fraction which also contributes to improve the quality of remaining ash. A study have been done regarding to leaching method by P. Garcia I-banez et al (2004) entitled as Gasification of Leached Olive Oil Waste in Circulating Fluidized Bed Reactor

Combination of Torrefaction and Gasification (Wood)

Mark J. Prins et al (2005) had come out an idea to investigate the efficiency of biomass gasification via torrefaction. The main idea behind combining biomass torrefaction and gasification is in gasifiers, biomass such as wood is converted into combustible product gas and heat. This heat is normally recovered in the form of medium or high pressure steam.The steam can be used to supply the heat for the torrefaction process.

Bone-dry torrefied wood with increased heating value is formed, which is subsequently gasified. The design of a torrefaction reactor, which is placed in front of the gasifier, is similar to a drier. In this case, indirect heat transfer based on heat conduction is selected, which allows precise temperature control. A steam tube drier, possibly with rotation to promote contact between the solid particles and hot steam tubes, may be used. The concept of torrefaction aided gasification is similar to two-stage pyrolysis–gasification, but differs in two aspects which are:

- The temperature of the torrefaction stage is carefully controlled at or below 300 °C in order to minimize pyrolysis of cellulose and avoid tar formation.
- The heat requirements for torrefaction are smaller than those for pyrolysis at higher temperatures. Therefore, instead of taking heat from the gasifier itself (like by recirculation of hot sand), sufficient heat can be taken from the gasifier product gas.

2.5 Concept of Torrefaction

Torrefaction is a mild pre-treatment of biomass at a temperature between 200-300 °C. During torrefaction of biomass its properties are changed to obtain a much better fuel quality for combustion and gasification applications. Torrefaction of biomass is an effective method to improve the grindability of biomass to enable more efficient co-firing in existing power stations or entrained-flow gasification for the production of chemicals and transportation fuels

Patric et al (2005) said biomass torrefaction is a pre-treatment method carried out at 200-300 °C in absence of oxygen. The occurring decomposition reactions at this temperature level cause the biomass to become completely dried and to loose its tenacious and fibrous structure. Therewith the grindability of the subjected biomass is improved significantly. In addition, torrefaction increases the calorific value and the biomass its hygroscopic nature can be destructed to yield a hydrophobic material. Depending on the applied torrefaction conditions, torrefied biomass is coloured brown to dark-brown and approaches the properties of coal.

These changes make torrefied biomass very attractive for combustion and gasification applications. Moreover, besides the thermal conversion of biomass also logistic properties can be improved through torrefaction when torrefaction is combined with densification (pelletisation). By this combination very energy dense fuel pellets are produced.

The amount of mass and energy yield from torrefaction process are strongly depending on:

- Torrefaction temperature
- Reaction time
- Type of biomass

From experiment done by researchers, more energy is yield compared to amount of mass after torrefaction process has been done. The loss mass is transformed into gass phase during the proces. Basically, the amount of energy and mass yields can be 0.9 and 0.45 respectively.

There are several polymers in biomass material which influencing the torrefaction process like cellulose, hemicellulose and lignin. The combination of these three polymers is called as lignocellulose. Studies showed that in general they cover 20 – 40 wt% (Hemicellulose), 40-60 wt% (cellulose), and 10 – 25 wt.% (lignin) of lignocellulose biomass. Furthermore, research had found that biomass pyrolisis (like torrefaction) was divided into four individual stages:

1. Moisture evolution
2. Hemicellulose Decomposition
3. Cellulose decomposition
4. Lignin decomposition

These polymers will affect the rate of devolatilisation and carbonisation.

Hemicellulose is the most reactive polymer. At the temperature below 250 degree, only limited devolatilisation and carbonisation will occur. However, when the temperature exceeds 250 degree, extensive devolatilisation and carbonisation will occur. At this level, cellulose and lignin is only subjected to limited devolatilisation and carbonisation only. Table below shows clearly the process of treatment:

Table 2.2: Process occurred on biomass within temperature range
(Torrefaction for Biomass Upgrading, Patrick C.A Bergman)

Temperature Range	Process Occurred
Below 250 degree	• Biomass dried • Soften Lignin
Over 250 degree	• Hemicellulose decomposes into volatiles and char • Limited devolatilisation and carbonisation of lignin and cellulose

Cellulose is the most abundant organic molecule on the earth. Its structure is composed of a long, linear polymer of glucose units that is found in the plant cell wall. Cellulose is water-insoluble, although it can be modified chemically to be more soluble and used as an additive in foods. Some examples of foods high in cellulose relative to other fibers include bran, legumes, peas, root vegetables, vegetables of the cabbage family, outer covering of seeds, and apples.

Hemicellulose, like cellulose, is found in the plant cell wall. It consists of sugar units containing 5 or 6 carbons. Hemicellulose is insoluble in water, but soluble in alkali. Lignin is the most common bio energy source available. Since lignin consists more than 60 wt% of carbon and only about 25 -28 wt% of oxygen, it is the biomass component with highest energy content which approximately 9,000 – 11,000 Btu/lb while cellulose is around 7,300 – 7,500 Btu/lb only. It means that 15-30 wt% of lignin present in lignocellulosic biomass corresponds to 30-45 wt% of its total energy content.

During the pre treatment process, biomass wills loss its tenacious features due to depolymerisation of cellulose which also decreases the length of fibres. Torrefaction also will make more oxygen and hydrogen losses to surrounding compared to carbon component. Water is the best proof of oxygen and hydrogen loss because it will dehydrate during the process. Since more loss on oxygen and hydrogen, high calorific value (energy) will be obtained which may increase from 17 – 19 MJ/kg to 19 – 23 MJ/kg.

Biomass is expected to be completely dried after torrefaction process. When it happens, the hydrosgopic natures of it will partly loss which imparts the destruction of OH groups. It also will prevent any hydrogen bonding to be occurred anymore.

Beside that, complete drying has make biomass to shrink. The mass loss during torrefaction makes biomass becomes porous hence reducing its volumetric density.

2.5.1 Torrefaction Technology

2.5.1.1 Old Technology

During eighties, a torrefaction process had been developed which named as Pechiney process. This process had capacity up to 12,000 ton for one production. Diagram below shows clearly the process:

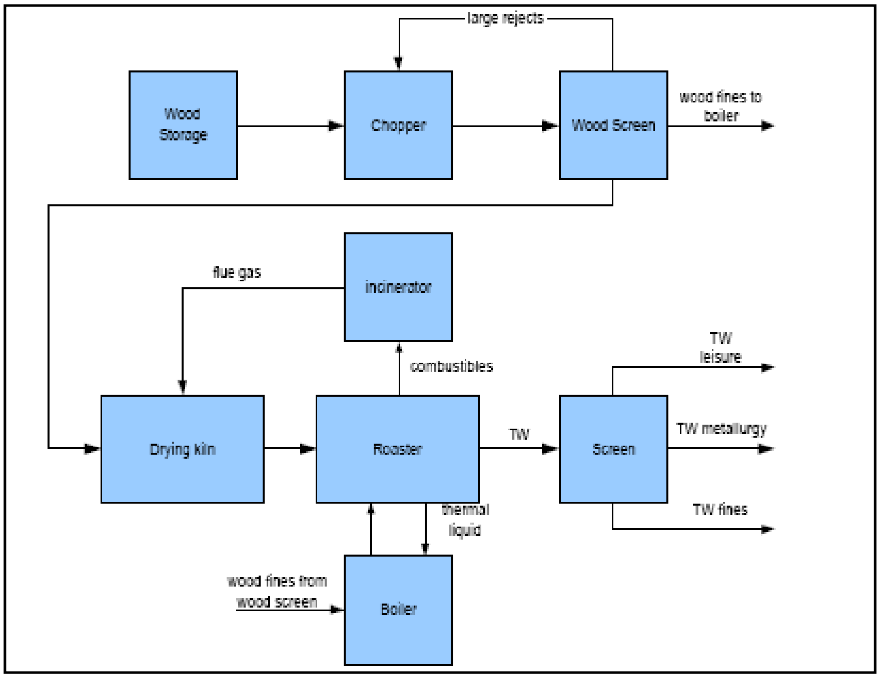


Figure 2.3: Pechiney Process

(www.techtp.com/recent%20papers/ECN- ***Torrefaction****%20for%20biomas%20***upgrading***%20-2005.pdf, 2005)*

(TW: Torrefied Wood)

The process is started with chopping process where the feed will be chopped into small sizes. The main process consisted of biomass drying, torrefaction (roaster) including product cooling, and combustion of the torrefaction gas (combustibles) to generate heat for drying. The residence time of the reactor was 60-90 min. Although this technology proofed to be technically feasible for torrefaction, it suffered from a low energy efficiency (60- 80%) and the screw reactor has poor scaleup characteristics.

2.5.1.2 New Technology

New torrefaction project has been carried out at Energy research Centre of Netherlands (ECN) in order to improve energy efficiency with low production and logistical costs. This project/process was named as Torrefaction and Pelletisation (TOP) technology as shown in the figure below:

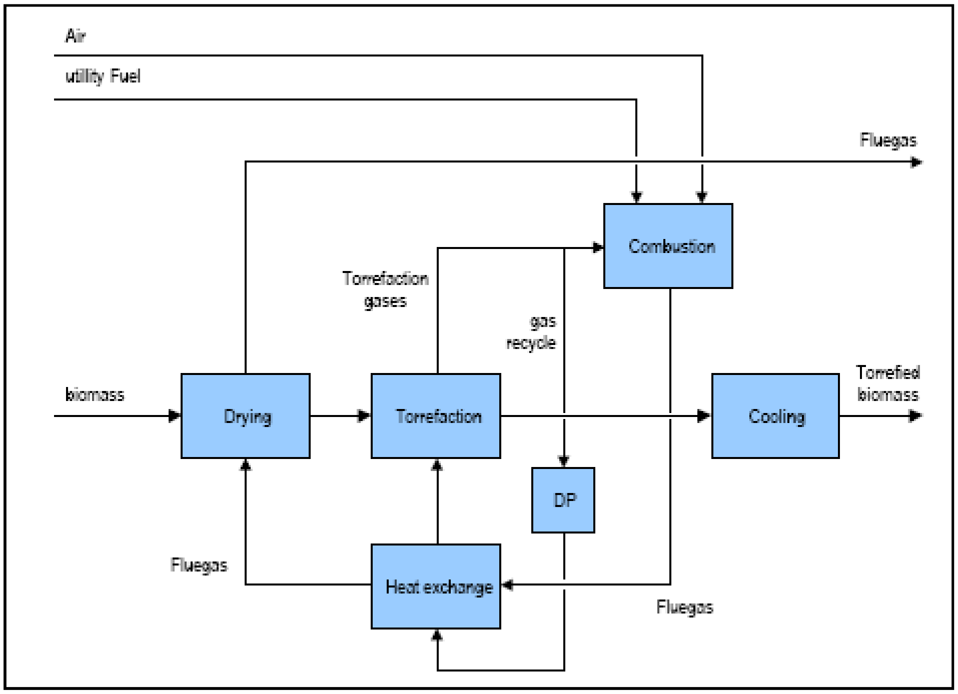


Figure 2.4: TOP Process

(www.techtp.com/recent%20papers/ECN-Torrefaction%20for%20biomas%20upgrading%20-2005.pdf, 2005)

This process is based on direct heating during torrefaction which is different with Pechiney Process. In older process, heat is supplied indirectly using circulating thermal oil which heated in an individual boiler. In contrast, the direct heating process will be done by hot gas that continuously recycled within the process. The hot gas will transfer heat when it flows into the reactor (where torrefaction process is occurred).Hot gas is consists of torrefaction gas itself which will be repressurized and recycled after each cycle has done. However, there will be possibility for the gas does not have sufficient heat to do its duty. Hence, utility fuel will be used in order to overcome that problem. In this technology, the expected production is approximately around 60 – 100 kton per annum.

The thermal efficiency from this process is estimated to be 96% on lower heating value (LHV) basis. This value is quite higher compared to Pechiney process where the themal efficiency is around 60 – 80%. However, sometimes the efficiency can be lower due to devolatilisaton of biomass torrefaction which sometime is too severe.

2.5.2 Wood Torrefaction

Mark J.Prins et al (2005) have been carried out laboratory experiments in a small-scale (5–10 g sample) fixed-bed torrefaction reactor placed inside an oven as shown in figure 2.5. The experiments were aimed at recovering and identifying all reaction products, which are present in three phases: a solid product (which retains at least 80% of the energy content of the wood feedstock), condensable gases (such as moisture, acetic acid and other oxygenates) and non-condensable gases (mainly carbon dioxide, carbon monoxide and small amounts of hydrogen and methane). By determining the amount and composition of each phase, it was possible to obtain good quantitative closure of the elemental carbon, hydrogen and oxygen balances.

Figure 2.5: Bench-scale experimental set-up for wood torrefaction.

Table 2.3 presents the composition of wood and torrefied wood, obtained by two experiments: at a reaction temperature of 250 °C and reaction time of 30 min, and 300 °C and 10 min, respectively. Reaction times exclude a heating time (from 200 °C to the reaction temperature) of 8.5 min and 17 min, respectively. As a result of the torrefaction process, the lower heating value (LHV) of the wood increases from 17.6 to 19.4 and 21.0 MJ/kg, respectively.

Table 2.3:Composition of wood and torrefied wood

	Wood	**Torrefied wood (250 °C, 30 min)**	**Torrefied wood (300 °C, 10 min)**
Carbon	47.2%	51.3%	55.8%
Hydrogen	6.1%	5.9%	5.6%
Oxygen	45.1%	40.9%	36.2%
Nitrogen	0.3%	0.4%	0.5%
Ash	1.3%	1.5%	1.9%
LHV(MJ/kg)	17.6	19.4	21.0

2.6 Raw Material (Biomass)

2.6.1 Concept of Biomass:

Biomass is one of renewable energy source. It can be referred as living and recently dead biological material that can be used as fuel or for industrial production. In other words, it is a form of chemical energy, which is energy stored in the bonds of atoms and molecules. This chemical energy in biomass is converted into other forms of energy to be used by mankind.

According to Abdullah (2008), the energy source that induces the renewability of biomass is the sun in the form of photosynthesis from the photoactive properties of radiation, sustaining the growth of plants with subsequent release in the biosphere. The term “biomass” was introduced by Eugene Adam and relates to the quantity of all living matter from the five kingdoms in biology which are plants, animals, fungi, protists, and monerans. As with all living system, biomass is a highly diverse and complex resource, and has to be studied in a holistic in the overall system of land, water, people, nutrients and all the five kingdom of live.

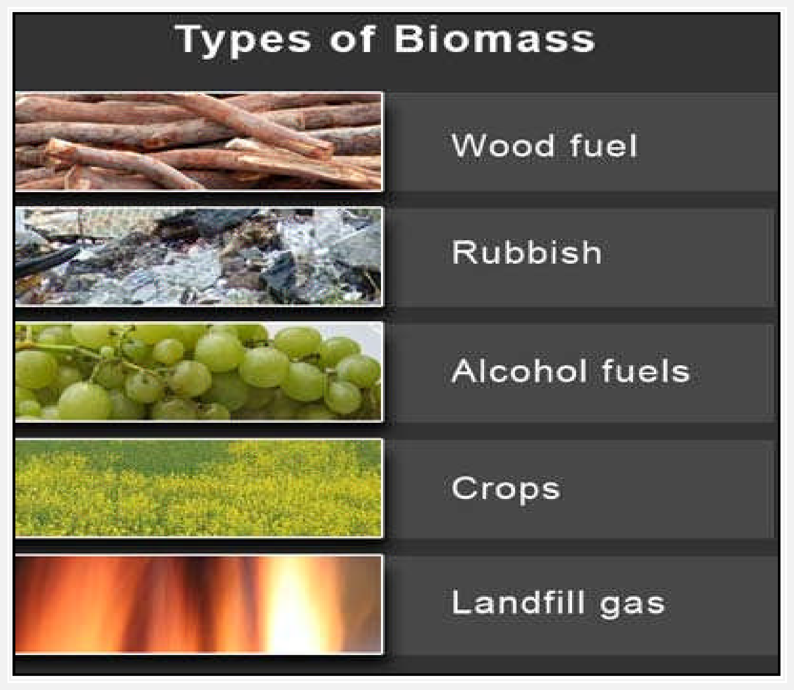


Figure 2.6: Type of Biomass

Bioenergy comes from biomass. Bioenergy is the conversion of chemical energy – which is stored in the biomass - into an industrially useful form, such as heat or electricity. Through bioenergy, we can produce electricity from biomass materials such as trees, grass cuttings, sugars and vegetables. However, the practical development of bioenergy is still relatively costly.

2.6.2 Advantages of biomass:

- The conversion of plant and animal materials (biomass) into electricity does not contribute to global warming, or the greenhouse effect. This is because the amount of carbon dioxide released by the biomass (when it is converted into energy) is the same as the amount of carbon dioxide absorbed by the biomass material during its growth.
- Biomass fuels have negligible sulphur content and therefore do not contribute to sulphur dioxide emissions which cause acid rain.

- The combustion of biomass generally produces less ash than coal combustion. Unlike coal ash, the "biomass ash" can be used as a soil additive on farm land to recycle material such as phosphorous and potassium.

- The use of agricultural and forestry residues and other waste materials for energy production is helping to reduce the significant problem of waste disposal.

- Biomass is a domestic resource which is not subject to world price fluctuations. In developing countries, the use of liquid biofuels, such as ethanol, reduces the economic pressures of importing petroleum products.

- The growth of perennial "energy crops" (such as grasses and trees that are processed for energy use) has a lower environmental impact than conventional agricultural crops.

2.6.3 Disadvantages of biomass:

- After the biomass conversion process, transportation and handling can be very difficult and costly. The solution has been to move the "process" closer to the biomass source and this has resulted in sawmills, sugar mills and pulp mills being built near plantations.

- On a large scale, biomass can lead to the widespread use of natural forests in developing countries. In many Asian countries, much of the wood fuel used for energy purposes comes from indigenous forest areas. This has ecological and social ramifications.

- On a smaller scale, some biomass applications are not fully competitive at this stage. In electricity production for example, there is strong competition from new, highly efficient natural gas-fired combined-cycle plants.

- There are often political constraints to biomass use. For example, government energy policies, taxes and subsidies may encourage the use of coal to support local employment in coal mining towns.

2.6.4 Rice Husk

Rice milling generates a by product know as husk. During milling of paddy about 78 % of weight is received as rice, broken rice and bran. Rest 22 % of the weight of paddy is received as husk. This husk is used as fuel in the rice mills to generate steam for the parboiling process. This husk contains about 75 % organic volatile matter and the balance 25 % of the weight of this husk is converted into ash during the firing process, is known as rice husk ash (RHA). This RHA in turn contains around 85 % - 90 % amorphous silica.

About 220kg (22 %) of rice husk is produced for every 1000 kg of paddy milled, and when this husk is burnt in the boilers, about 55 kg (25 %) of RHA is generated. India is a major rice producing country, and the husk generated during milling is mostly used as a fuel in the boilers for processing paddy, producing energy through direct combustion and / or by gasification. About 20 million tones of RHA is produced annually. This RHA is a great environment threat causing damage to the land and the surrounding area in which it is dumped. Lots of ways are being thought of for disposing them by making commercial use of this RHA.

2.6.4.1 Rice Husk Properties

The treatment of rice husk as a ‘resource’ for energy production has denied the perception that husks present disposal problems. The concept of generating energy from rice husk has great potential, particularly in those countries that are primarily dependant on imported oil for their energy needs. Rice husks are one of the largest readily available but most under-utilized biomass resources, being an ideal fuel for electricity generation.

Rice husk ash (RHA) is a general term describing all types of ash produced from burning rice husks. In practice, the type of ash varies considerably according to theburning technique. The silica in the ash undergoes structural transformations depending on the conditions (time, temperature etc) of combustion. At 550°C – 800°C amorphous ash is formed and at temperatures greater than this, crystalline ash is formed. These types of silica have different properties and it is important to produce ash of the correct specification for the particular end use.

If a long-term sustainable market and price for rice husk ash (RHA) can be established, then the viability of rice husk power or co-generation plants are substantially improved.

2.6.4.2 Potential and current uses of RHA

- Insulator in the steel industry and as a pozzolan in the cement industry.
- RHA can also replace silica fume in high strength concrete. Silica fume or micro silica is the most commonly used mineral admixture in high strength concrete.
- RHA is used by the steel industry in the production of high quality flat steel. Flat steel is a plate product or a hot rolled strip product, typically used for automotive body panels and domestic 'white goods' products.
- RHA is used, in the manufacture of low cost building blocks and in the production of high quality cement.

2.6.5 Paddy Straw

Rice/paddy straw is referred as leaves and stalks of paddy plant after the grains have been harvested. It is commonly used in Malaysia as feed cattle. Rice straw is straw material as well as rice husk. Lage quantity of rice straw can be found in nothern and eastern states of Malaysia like Perlis, Kedah, and Kelantan since these states are the rice producer for this country.

Figure 2.7: Paddy Straw

Table 2.4: Residue Product Ratio and Potential Power Generation from Paddy Residues Year 2000 (Pusat Tenaga Malaysia, PtM, 2000)

Type of Industry	Production Year 2000 (Thousand Tonne)	Residue	Residue product Ratio (%)	Residue Generated (Thousand Tonne)	Potential Energy (PJ)	Potential Power (MW)
Rice	2,140	Rice Husk	22	471	7.536	72.07
		Paddy Straw	40	856	8.769	83.86
TOTAL	2,140			1327	16.305	155.93

From Table 2.4, in year 2000, 856 000 tonnes of paddy straw has been produced which cover 40% of rice production (2 140 000 tonnes). This indicates our country has large amount potential sources of paddy straw which can be further developed to be energy sources.

More over, Pusat Tenaga Malaysia (PtM) had classified this biomass has high potetial to produce energy and power for daily uses. According to figure 2.8, by year 2010 paddy straw could be used to generate electricity power approximately 100 MW. In year 2000, where the amount paddy straw generated was 856 000 tonne, the total power can be generated from that amount was around 70 MW. The increment of power generation from year 2000 to 2010 is estimated around 43% and it is believed will be continuously increased because the demand of rice will always be consistent. Hence, this biomass has high potential to be developed for energy production through gasification process.

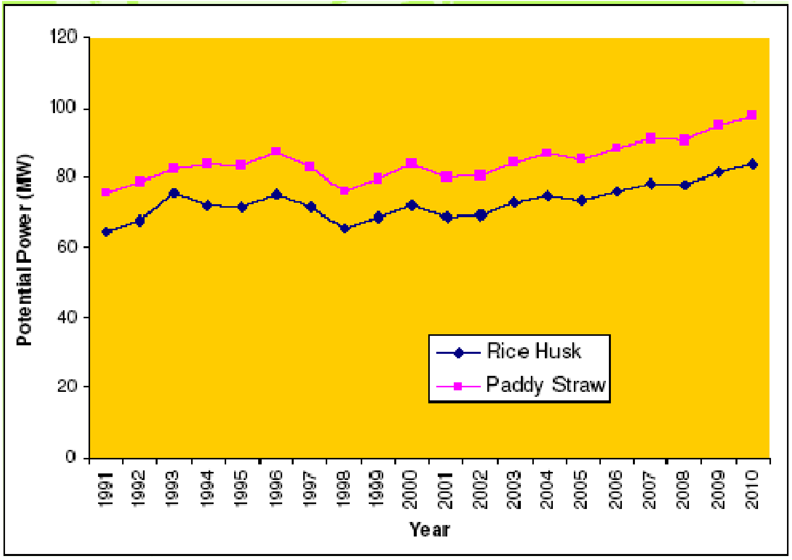


Figure 2.8: Potential Power generated by Paddy Straw and Rice Husk
(Pusat Tenaga Malaysia, PtM, 2000)

CHAPTER 3

METHODOLOGY

The objective of this project is to prepare torrefied material for gasification process. It is believed that using torrefied material in gasification to produce hydrogen is more efficient than using biomass without any pre treatment like torrefaction.

3.1 Tool and Equipment

The experiment need laboratory furnace named as Fixed Bed Activation Unit (FBAU) to heat the biomass. However, before it can be conducted, the raw material (biomass) needs to be prepared first. For this purpose, tools like grinders, ceramic beaker, dryer, and sieve are needed. After experiment has been done, the results need to be analyzed to check wheter the result meet the objective or not. Some analyzers like CHNS (Carbon, Hydrogen, Oxygen, Nitrogen, and Sulfur) need to be used. The summary of tools and equipment are as follows:

Table 3.1: Lists of experiment and analyzing part

EXPERIMENT PART	ANALYZING PART
Fixed Bed Activation Unit (FBAU)	Thermal Gravimetric Analyzer (TGA)
Molecular Seive	CHNS Analyzer
Dryer	Bomb Calorimeter
Grinder	Halogen Moisture Analyzer
Ceramic Beaker	

3.2 Methodology

3.2.1 Sample Pretreatment

1. Coconut shells (read: sample) obtained from local supply were cleaned to remove physical impurities.
2. The sample was dried in oven at 100 - 110 °C for 24 hours to remove water content inside it. The temperature range must be controlled in that range to avoid damaging the molecul structure.
3. Step 2 is repeated until the sample's weight is constant. This is done in order to make sure all the moisture content is removed.
4. Then, it will be ground into smaller particle size and sieved into two mesh sizes:
   i. 250 μm
   ii. 500 μm
5. The samples then stored in air tight plastic to maintain low moisture content of the samples.
6. Steps 1 to 5 were repeated for paddy straw and rice husk.

After completing pretreatment, the treated samples after this will be used for two purposes:

- Analyzing sample before undergo torrefaction process
- Torrefaction experiment by using Fixed Bed Activation Unit (FBAU)

3.2.2 Torrefaction experiment by using Fixed Bed Activation Unit (FBAU)

Methodologies for torrefaction experiment are as followed:

1. Three samples coconut shell with different particular size are weighted and put in a crucibles
2. The reactor outlet is untied to locate in the sample from the bottom.
3. The samples are positioned in the middle of the tube where the heated coil is located to ensure a complete burning.
4. The reactor outlet opening is closed tightly to ensure no gas or liquid will be released from the reactor.
5. The FBAU power supply is switch on.
6. Nitrogen gas cylinder is connected to the nitrogen gas inlet of Fixed Bed Activation Unit (FBAU).
7. Valve 1 and valve 5 green buttons were switched on to open the valves. Valve 2, 3 and 4 remain closed.
8. Nitrogen gas flow is controlled by approximately at 0.3 ml/min by using flow meter controller attached to the panels.
9. After the nitrogen flow is stable, the temperature is set to 200°C
10. The reaction will be done at 1.5 hours.
11. Once the reaction has reached the reaction time, the sample will be cooled down to room temperature which takes about 4 to 5 hours.
12. After the temperature has decreased, the reactor outlet tube is untied and the product from the reactor is collected.
13. The product is weighted to determine the weight loss of the sample.
14. Step 1 – 13 is repeated for temperature 250°C and reaction time 3 hours.
15. Step 1 – 14 is repeated for rice husk and paddy straw.

3.3 Type of Analysis

3.3.1 Proximate analysis

Proximate analysis is carried out in this study to determine properties of torrefaction and pyrolysis products. The specified equipment to achieve this purpose is by Thermal Gravitational analyzer (TGA). The outcome of the analysis will be displayed in term of graph part where then further analysis will be done. TGA is used to determine the elements of:

i. Volatile fraction
ii. Fixed carbon content
iii. Ash content

TGA Methodology

1. Initial weight of TGA is noted before experiment started. The weight is denoted as W_1
2. Aprroximately 10 gram of coconut shell is placed into the sample pan.
3. The sample will be heated in temperature range 50°C - 800°C under sweeping gas at rate of $40cm^3$/min
4. The aqueous and oil phases is separated and weighted while the released gas is calculated from material balance
5. Percentage of torrefaction yield, oil yield, gas yield, and collected water is determined
6. Torrified solid formed is collected and locating it on stell wool. At the moment, the torrefacation temperature still being maintained until there is no more gas released from the sample.
7. The reactor is weighted again after cooling down. The weight is denoted as W_2
8. Char yield now can be calculated by using $W_1 – W_2$
9. Step 1 – 9 is repeated with paddy straw and rice husk.

3.3.2 Ultimate Analysis

The ultimate analysis is done on the torrified and pyrolysed material to know the component content within the biomass sample in term of percentage. The analysis is done using Carbon Hydrogen Nitrogen Sulphur (CHNS) Analyzer. Through this analysis, the composition of the component within the material can be obtained.

Samples Preparation

1. Weigh a CHNS tin capsule
2. Approx. 2.0mg of standard sample is put into the capsule
3. The capsule is closed properly before weighing the weight
4. Repeat the procedure for all other samples
5. Placed those samples into the slot inside the analyzer
6. The weight of the samples is input into the analyzer
7. Each run complete in 3 minutes

Standard Operating Procedure (SOP)

1. Make sure Helium, O2 and compressed air are set to 40 psi
2. Checked the ambient monitor for proper values
3. Monitor the CO2, H2 and sulfur IR Cells between ‘7.5-9.2’ volts
4. Set the Oxidation Furnace Temperature to 1000oc
5. Set the Reduction Furnace Temperature to 650oc
6. Run leak check if necessary
7. Set ‘Auto/Manual’ switch to Auto when using carousel / to manual when loading samples individually
8. Set the gas switch to analyze position
9. Wait until furnace Temperature is stable
10. Run blank analysis and standard samples
11. Run the experiment samples.

3.3.3 Halogen Moisture Analysis (HMA) Analysis

The main purpose of this analysis is to determine the moisture content in the sample. The best equipment to give the results is by HMA where it analyzes the amount of moisture in the biomass sample. Good product is determined by having low moisture content.

3.3.4 Calorific Value Analysis

The heating value of biomass is determined by analyzing through bomb calorimeter. Using this equipment, calorific value of biomass material heated at different parameters can be obtained accurately. Higher calorific value determines better quality of products obtained.

Bomb calorimeter's standard operating procedure:

1. Turn on oxygen gas regulator (Pressure: 20 – 30 kg/cm2)
2. Turn on bomb calorimeter unit and refrigerator batch switch, wait 20 minutes for waiting stable
3. Prepare sample (weighing below 1.0 gram)
4. Place sample into crucible, secure a cotton thread with a loop in it on the middle of the ignition wire. Place into the decomposition vessel.
5. Open the sample dialog window to key-in wieght of sample.
6. Suspending the decomposition vessel into the filling head of the measurement cell cover
7. Activate Start. The measurement cell cover closes the decomposition vessel is the filled with oxygen. Next, the inner vessel is filled with water. As soon as the system begins with the experiment, the display shows a graph temperature vs residence time of the inner vessel.
8. When the measurement is complete, remove the decomposition vessel, clean and prepare for the next experiment.

CHAPTER 4

RESULTS AND DISCUSSION

Experimental study has been started approximately early of this semester with obtaining the biomass from local supply. After that, the biomass would be drying, grinding and sieving. The purpose of drying step is to make sure all moisture content being removed from the raw material. According to Ariff Syah (2009), this step is very important before going further to another step in order to make the torrefaction process (main process) will be reliable and efficient. He claimed that excess moisture content in the sample will evaporate during pyrolysis (torrefaction) hence the vapor released will be flowing into the condenser. The warm vapor will intact with cold water which makes it condensed. This will reduce the efficiency of cooling and condensing of torrefied material. Hence, after removing all physical impurities, the biomass has been dried at 110 degree for 24 hours. After drying, the sample has been kept in air-tight wrapper to maintain low moisture content.

Two particular sizes will be studied in these experiments which are 500 and 250 μm. Torrefaction will be done on both sizes (for each sample) at temperature 240 and 280 degree Celcius. During the experiment, nitrogen gas will be flowed continiously in the reactor bed at rate 0.2 L/min to bring out air (oxygen) from the reactor. Existence of oxygen during the reaction may burn out the sample into gaseous and liquid products. This process is not classified as torrefaction since the objective of this process to produce mainly solid fuels which have improvement in its properties. According to Patric et al (2005), the occuring decomposition reactions at these temperatures level cause the biomass to become completely dried and to loose its tenacious and fibrous structure. He added, the grindability of the samples also will be improved significantly. In addition, the torrefaction increases the calorific value and the hygroscopic nature of the samples will be destructed to yield a hydrophobic products. The torrefied biomass colour also will be changed from coloured brown to dark-brown and approaches the properties of coal.

4.1 Mass Loss after Torrefaction

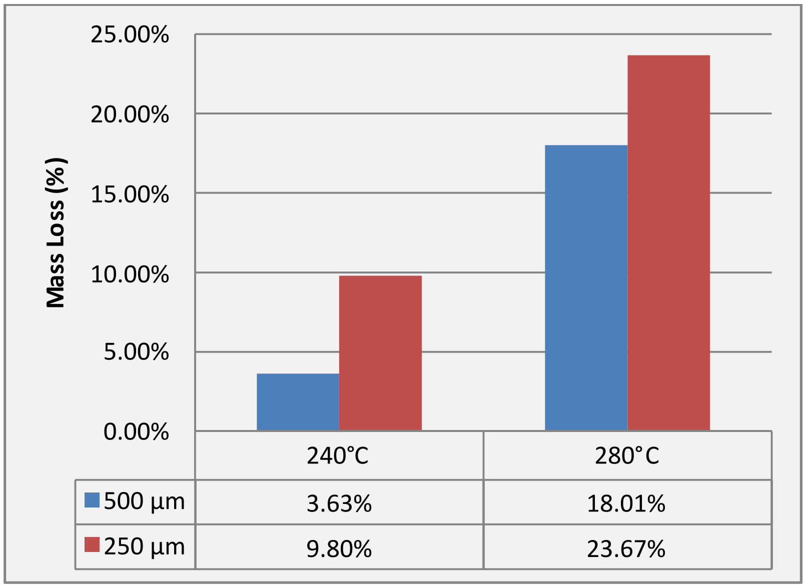


Figure 4.1: Mass Loss (%) after Torrefaction vs Temperature Reaction (°C) for coconut shell at each particle size (µm)

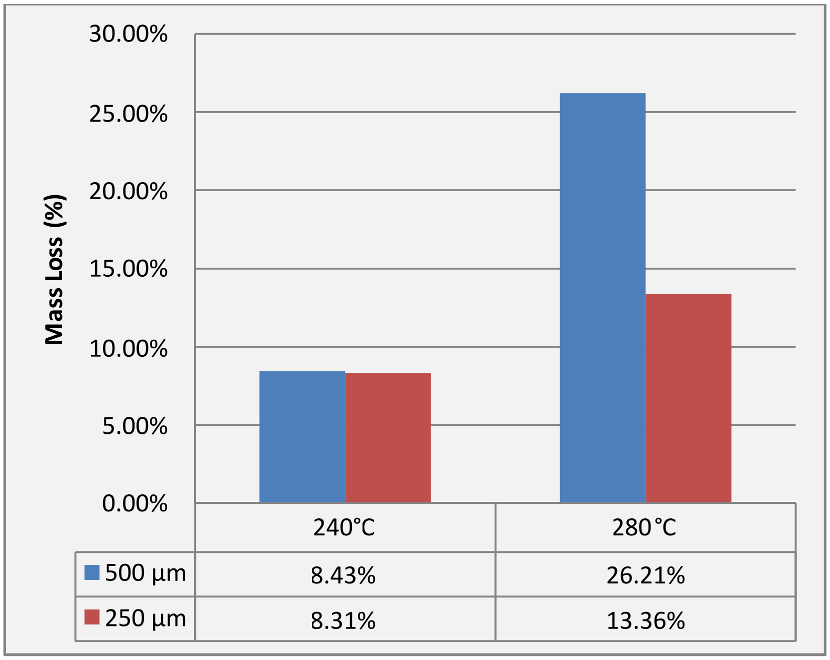


Figure 4.2: Mass Loss (%) after Torrefaction vs Temperature Reaction (°C) for paddy straw at each particle size (µm)

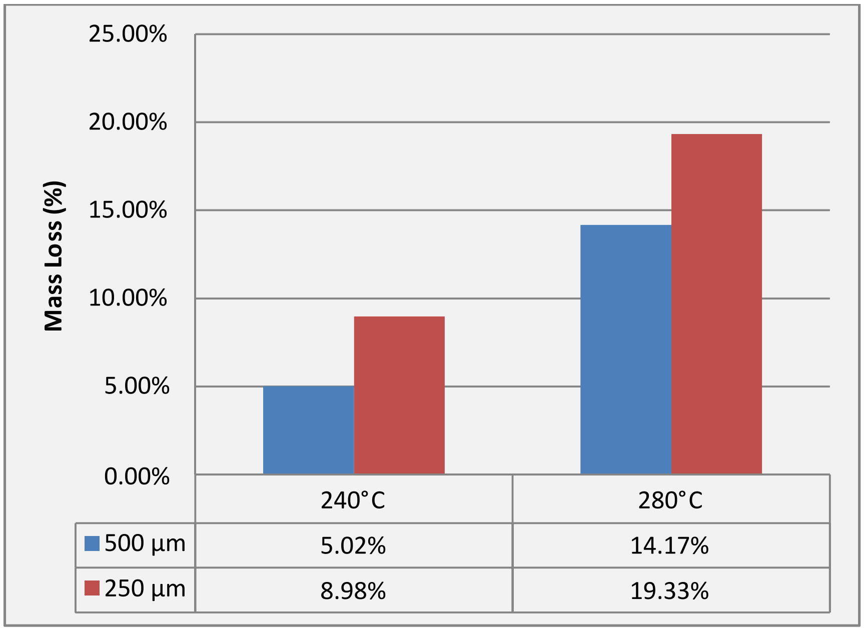


Figure 4.3: Mass Loss (%) after Torrefaction vs Teamperature Reaction (°C) for rice husk at each particle size (µm)

4.2 Moisture Content before & after Torrefaction

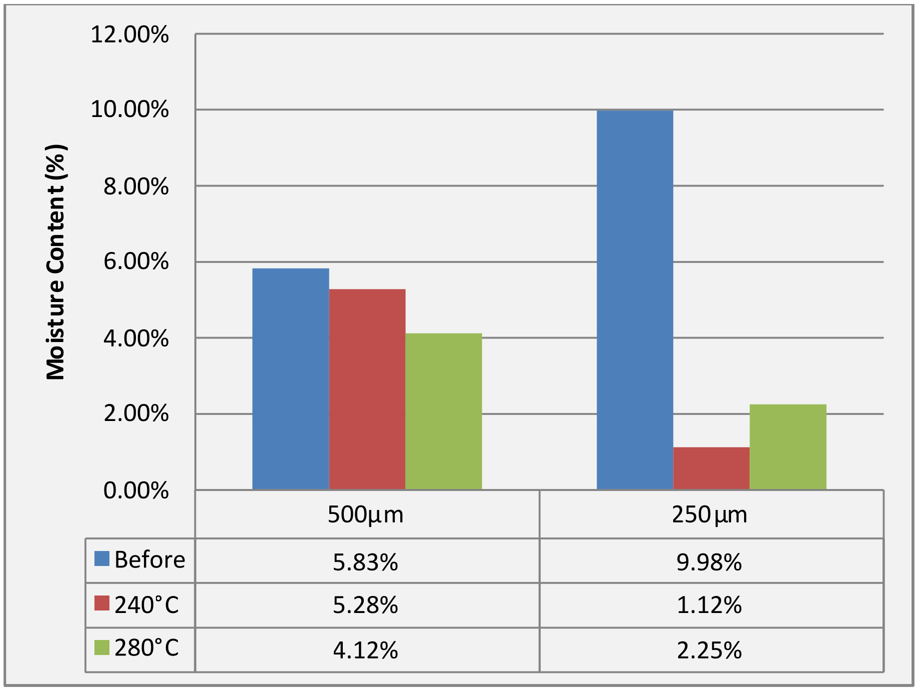


Figure 4.4: Moisture content (%) vs Particle size (µm) for coconut shell before and after each temperature reaction (°C)

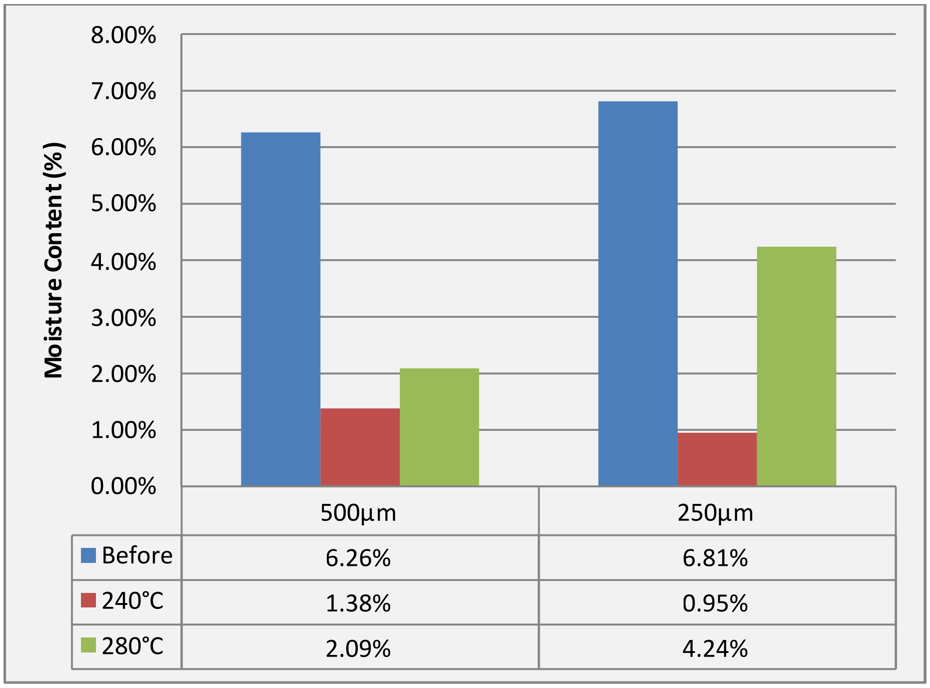
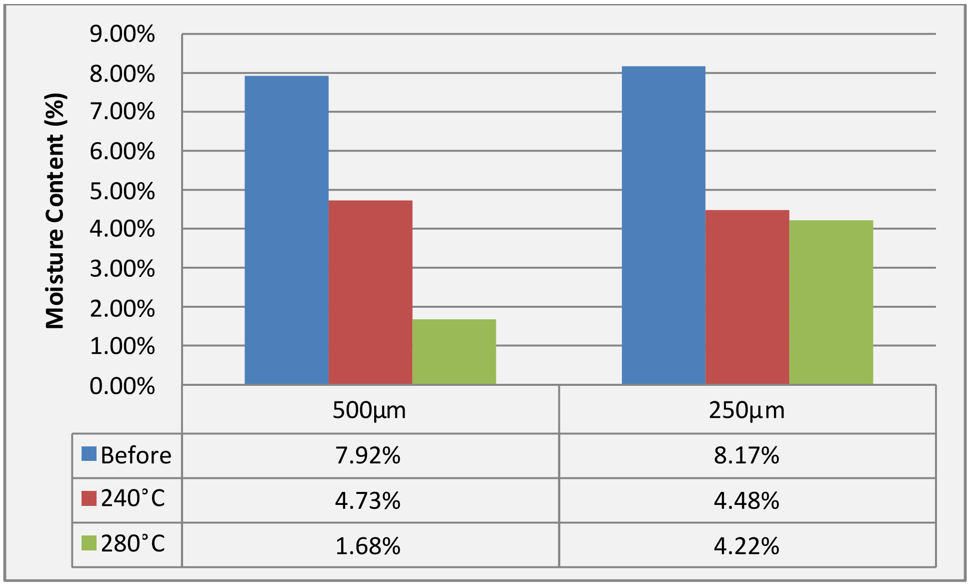


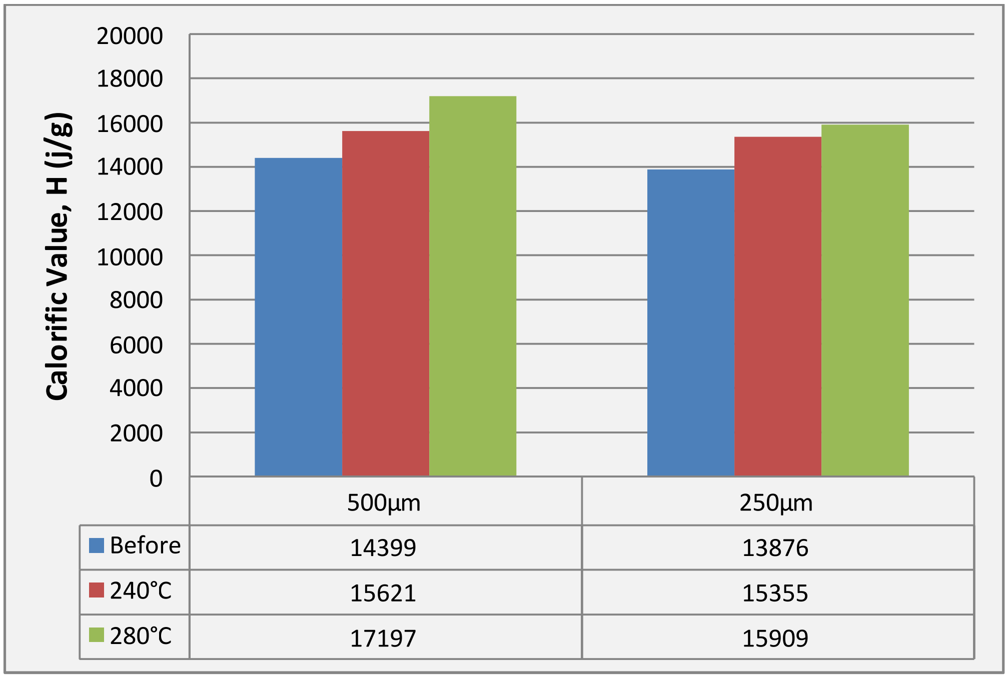
Figure 4.5: Moisture content (%) vs Particle size (µm) for rice husk before and after each temperature reaction (°C)



	500µm	250µm
🟦 Before	7.92%	8.17%
🟥 240˚C	4.73%	4.48%
🟩 280˚C	1.68%	4.22%

Figure 4.6: Moisture content (%) vs Particle size (µm) for paddy straw before and after each temperature reaction (°C)

4.3 Calorific Value before and after Torrefaction



	500µm	250µm
🟦 Before	14399	13876
🟥 240°C	15621	15355
🟩 280°C	17197	15909

Figure 4.7: Calorific value (j/g) vs particle size (µm) for paddy straw before and after each temperature reaction (°C)

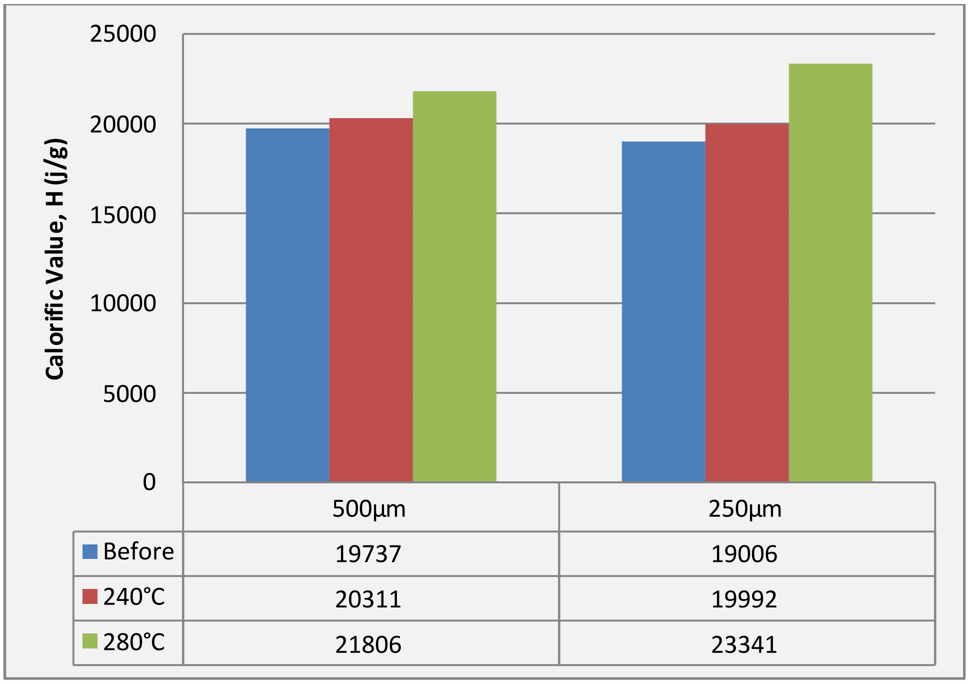


Figure 4.8: Calorific value (j/g) vs particle size (µm) for coconut shell before and after each temperature reaction (°C)

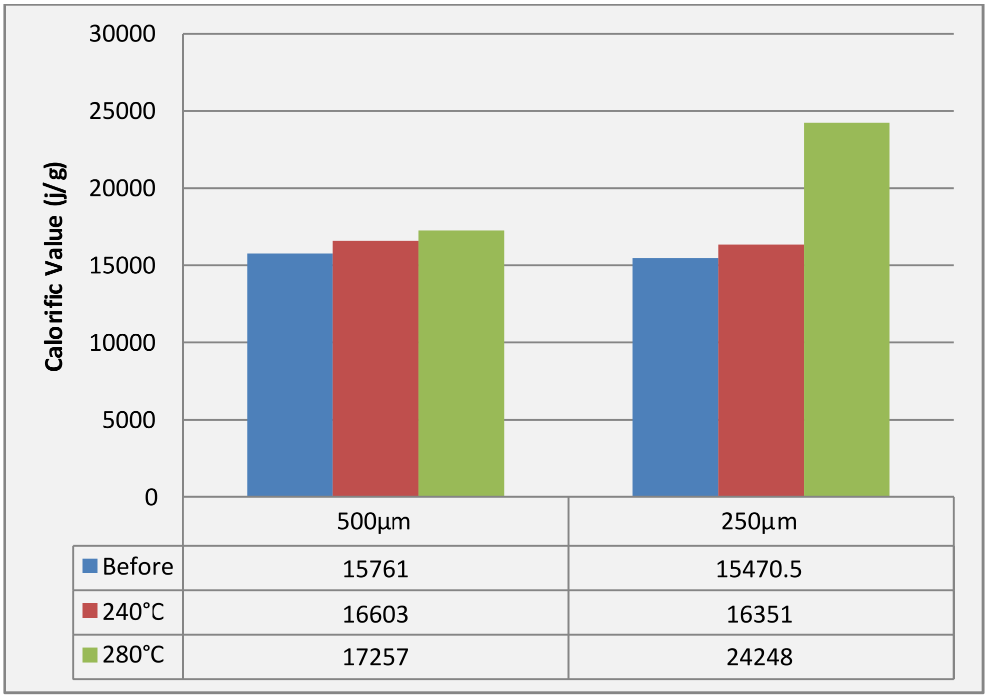
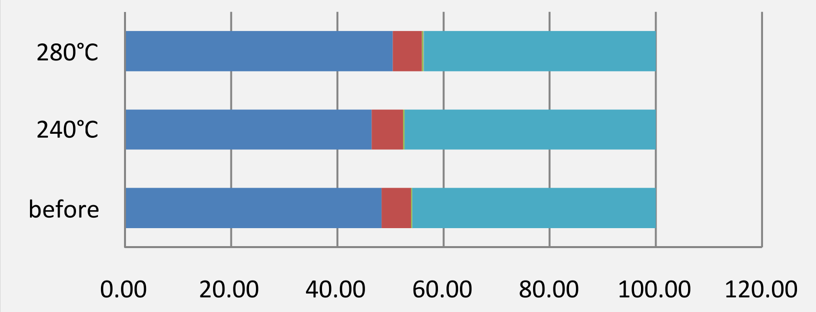


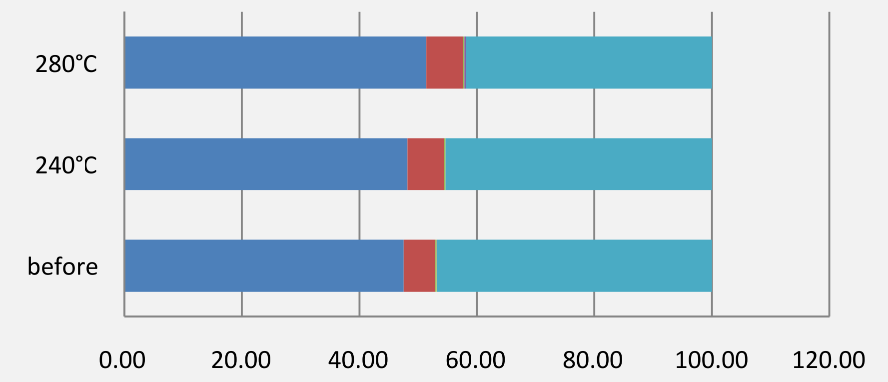
Figure 4.9: Calorific value (j/g) vs particle size (µm) for rice husk before and after each temperature reaction (°C)

4.4 Ultimate Analysis before and after Torrefaction



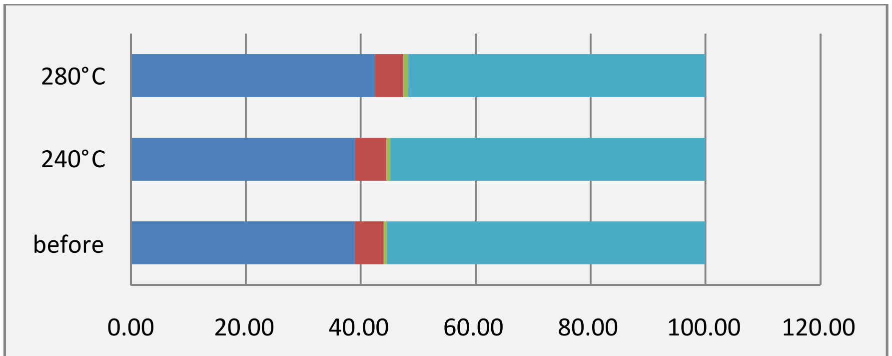
	before	240°C	280°C
🟦 C (%)	48.32	46.46	50.46
🟥 H (%)	5.56	5.93	5.48
🟩 N (%)	0.25	0.26	0.30
🟪 S (%)	0.01	0.01	0.03
🟦 O (%)	45.86	47.34	43.73

Figure 4.10: Ultimate analysis (%) for Coconut Shell (250μm) before and after each temperature reaction (°C)



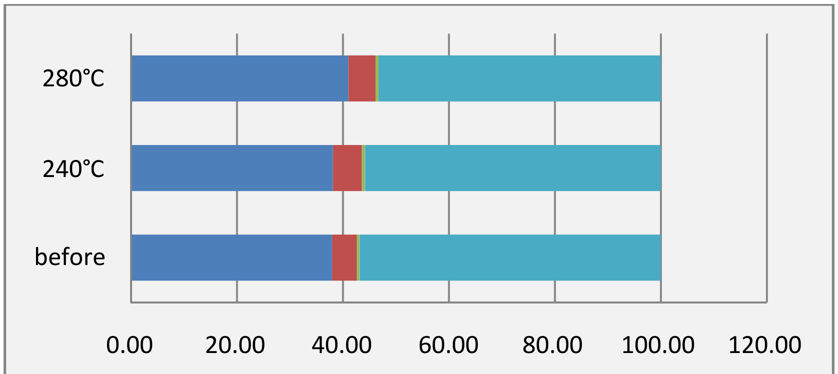
	before	240°C	280°C
🟦 C (%)	47.54	48.17	51.41
🟥 H (%)	5.38	6.22	6.23
🟩 N (%)	0.24	0.25	0.25
🟪 S (%)	0.02	0.00	0.23
🟦 O (%)	46.82	45.35	41.87

Figure 4.11: Ultimate analysis (%) for Coconut Shell (500μm) before and after each temperature reaction (°C)



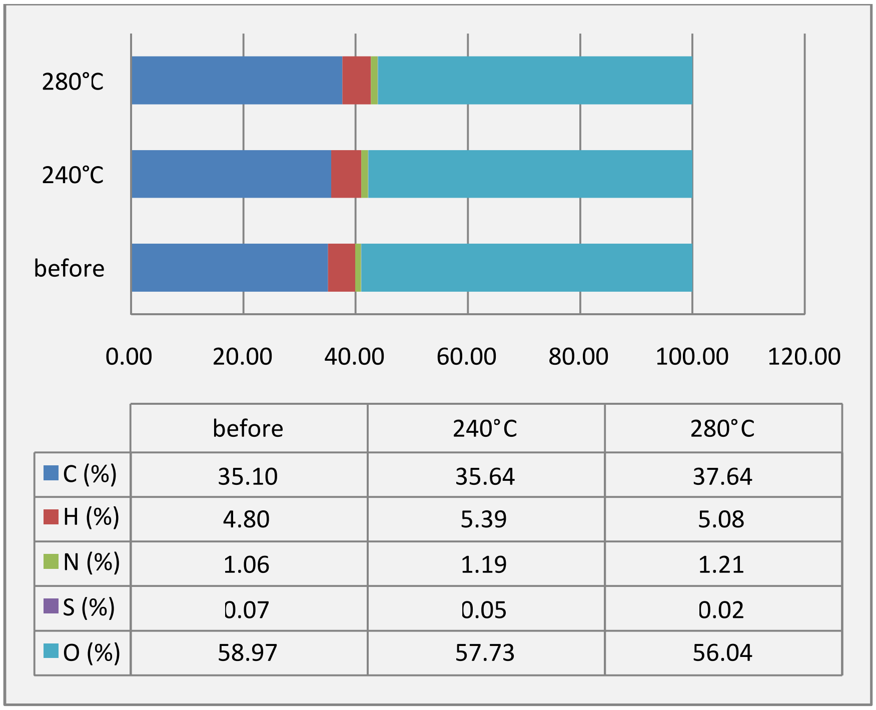
	before	240°C	280°C
🟦 C (%)	39.03	39.03	42.48
🟥 H (%)	4.97	5.49	4.95
🟩 N (%)	0.58	0.63	0.83
🟪 S (%)	0.04	0.03	0.01
🟦 O (%)	55.39	54.81	51.73

Figure 4.12: Ultimate analysis (%) for rice husk (250 µm) before and after each temperature reaction (°C)



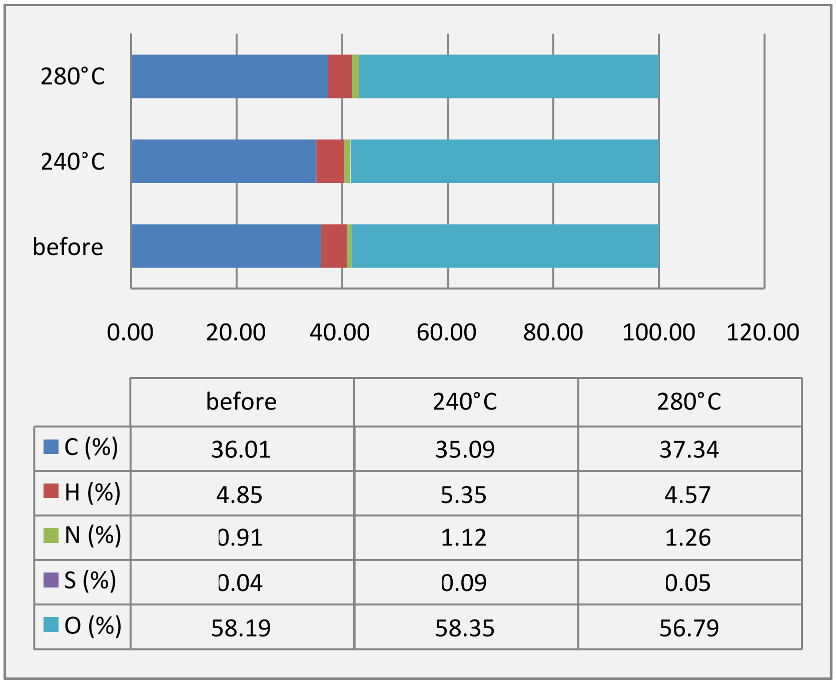
	before	240°C	280°C
🟦 C (%)	37.93	38.12	41.02
🟥 H (%)	4.69	5.45	5.14
🟩 N (%)	0.47	0.54	0.54
🟪 S (%)	0.03	0.03	0.00
🟦 O (%)	56.89	55.86	53.30

Figure 4.13: Ultimate analysis (%) for rice husk (500 µm) before and after each temperature reaction (°C)



	before	240°C	280°C
■ C (%)	35.10	35.64	37.64
■ H (%)	4.80	5.39	5.08
■ N (%)	1.06	1.19	1.21
■ S (%)	0.07	0.05	0.02
■ O (%)	58.97	57.73	56.04

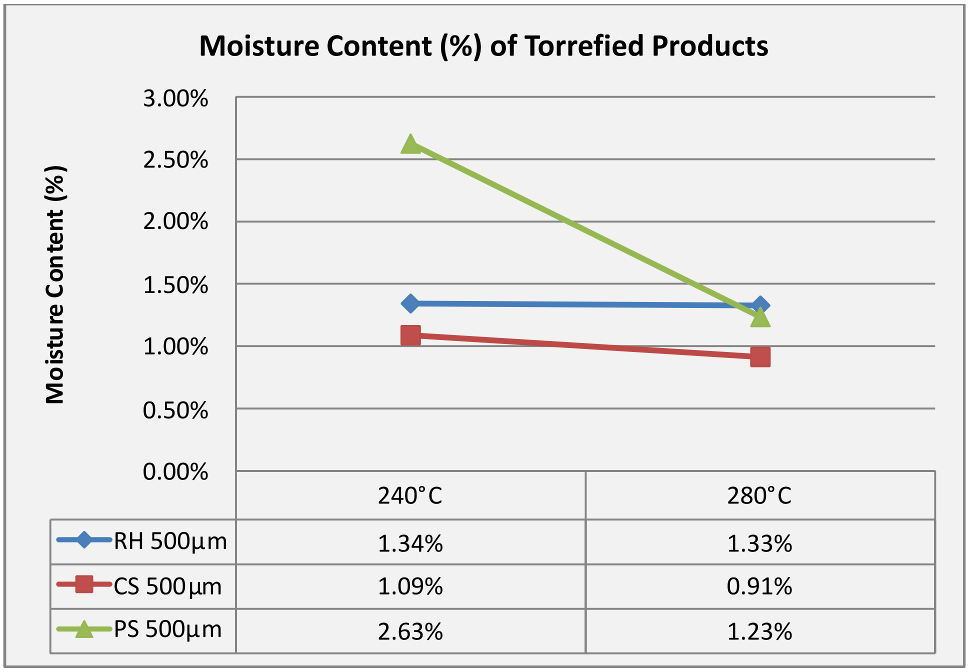
Figure 4.14: Ultimate analysis (%) for paddy straw (250 μm) before and after each temperature reaction (°C)



	before	240°C	280°C
■ C (%)	36.01	35.09	37.34
■ H (%)	4.85	5.35	4.57
■ N (%)	0.91	1.12	1.26
■ S (%)	0.04	0.09	0.05
■ O (%)	58.19	58.35	56.79

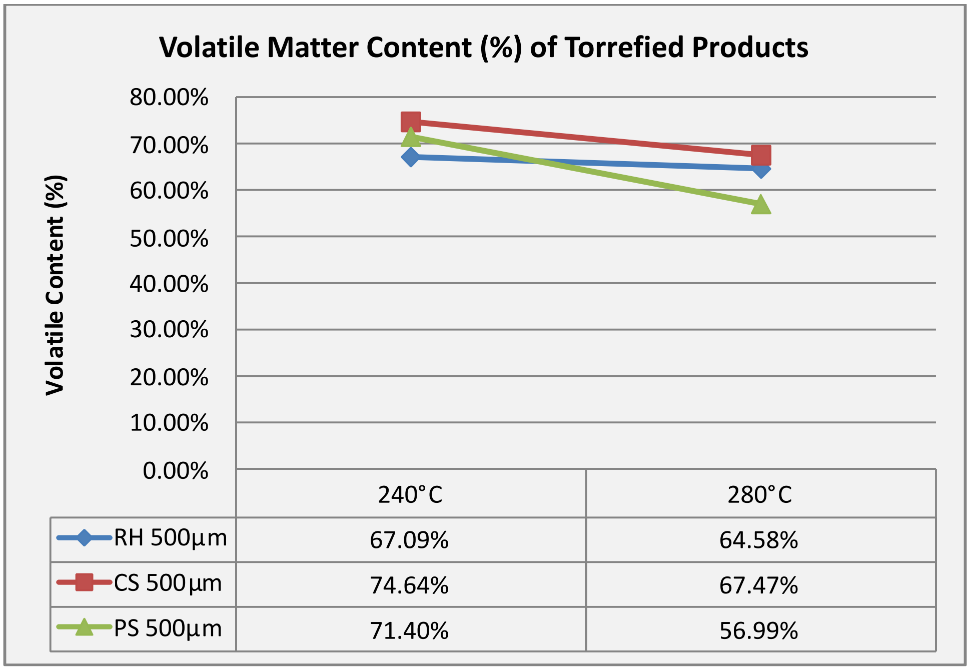
Figure 4.15: Ultimate analysis (%) for paddy straw (500 μm) before and after each temperature reaction (°C)

4.5 Proximate Analysis



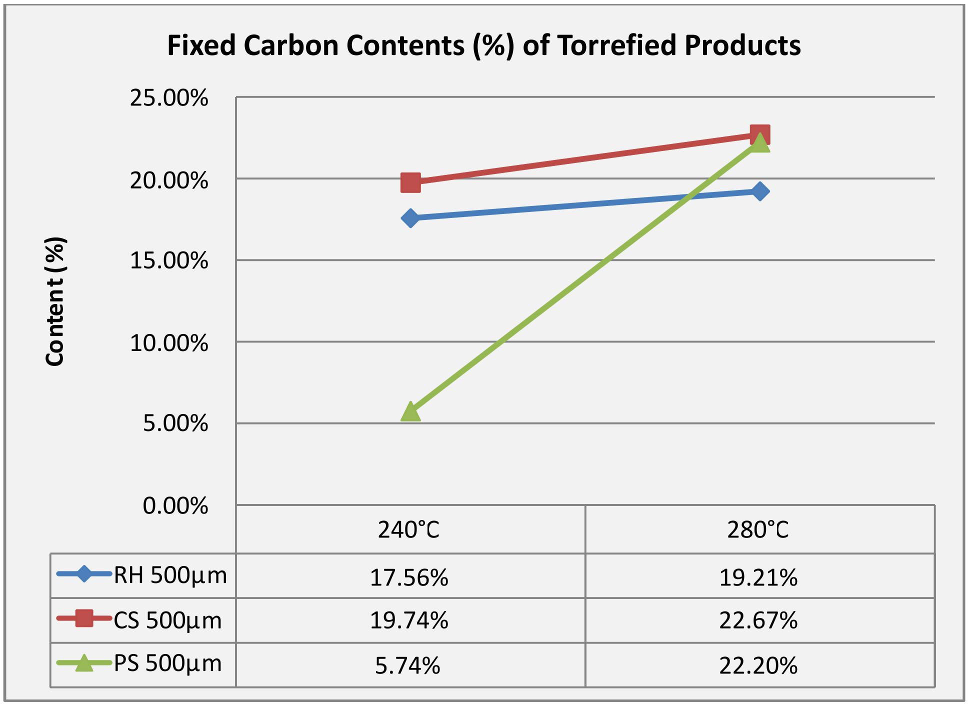
	240°C	280°C
RH 500µm	1.34%	1.33%
CS 500µm	1.09%	0.91%
PS 500µm	2.63%	1.23%

Figure 4.16: Moisture content (%) from TGA each reaction temperature (°C) for particle size 500 µm



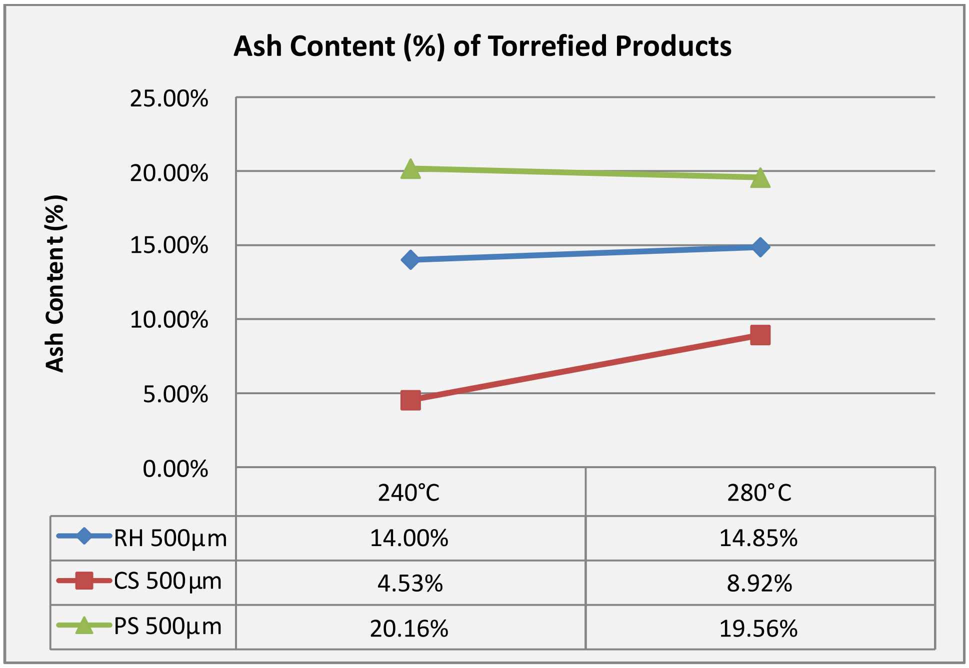
	240°C	280°C
RH 500µm	67.09%	64.58%
CS 500µm	74.64%	67.47%
PS 500µm	71.40%	56.99%

Figure 4.17: Volatile matter (%) from TGA after each reaction temperature (°C) for particle size 500 µm



	240°C	280°C
RH 500µm	17.56%	19.21%
CS 500µm	19.74%	22.67%
PS 500µm	5.74%	22.20%

Figure 4.18: Fixed Carbon content (%) from TGA each reaction temperature (°C) for particle size 500 µm



	240°C	280°C
RH 500µm	14.00%	14.85%
CS 500µm	4.53%	8.92%
PS 500µm	20.16%	19.56%

Figure 4.19: Ash content (%) from TGA each reaction temperature (°C) for particle size 500 µm

4.6 Mass Loss Analysis after Torrefaction

From figure 4.1, coconut shell at size 250 µm underwent greater mass loss (23.67%) at temperature 280 degree Celcius. This loss is quite significant at temperature 280 degree Celcius compare with at temperature 240 where it just having smaller (9.80%) loss. For coconut shell at size 500, it also underwent greater mass loss at temperature 280 compared at temperature 240 degree. Paddy straw and rice husk samples for both sizes also underwent same trend like coconut shell (figure 4.2 and 4.3 respectively).These results showed torrefaction temperature have great influence to the torrefaction process where it will release more amount of mass at higher temperature.

It happens because higher temperature will promote faster water evaporation rate as well as devolatilation rate. In term of particular sizes, by having smaller size, it will lead to more surface area available for reaction process at spesific time. Higher surface area will provide more heat transfer into the molecules which increase the molecules release. Within one hour and 30 minutes reaction time, coconut shell and rice husk at size 250 has greater mass loss compared with sample 500 under same torrefaction temperature (280 degree Celcius). The torrefied products also transformed into dark brown solid after undergo 280 degree torrefaction.

Referring to figure 4.10 till 4.15, before undergo torrefaction reaction, each sample has lower percentage of carbon content but higher percentage amount of hydrogen. However, the percentage of carbon becomes higher after reaction while the percentage of oxygen has been reduced. The mass loses will be in form of lipids, organics, gases and water (Bergman et al). These products indicate biomass loses relatively more oxygen compared to carbon. The increasing percentage amounts of carbon happen because the torrefied product is mainly consist of fix carbon with little propotion of ash content. This component supposedly cannot be released to the air at torrefaction temperature. Higher temperature (more than 300 degree Celcius) needed to break the molecule bond to release the carbon. As result, only low volatility matters like moisture and lipid as well as gases being released to the air during the torrefaction process.

4.7 Moisture Content & Calorif Value Analysis

Each sample contains difference moisture content readily before torrefaction. It is because, those samples have difference polymeric structure which influce the moisture content before and after reaction. Some samples may have high hemicellulose while others just having low content of it. Having high hemicellulose will contribute more moisture contain in the samples. Commonly, these kind of biomass initially will behave as hygroscopic (like-water) in nature before undergo torrefaction process.
The torrefaction process will decompose most of hemicellulose to release more moisture to the air. It will change the sample nature to be hydrophobic (water-hatred).

According to figure 4.4 till 4.6, all samples for both sizes losing the moisture after undergo torrefaction process. Coconut shell at size 250 μm showed the lowest moisture content compared to sample at size 500 μm for both temperatures. Result from rice husk also showed the same trend where the lowest particular size sample losing most moisture compared to bigger size (500 μm). These results have proved that the smaller particle size, the higher possibility of moisture loss. Smaller particle size will increase the surface area which promoting higher evaporation rate. However, results obtained from paddy straw sample showed the highest particle size had lowest moisture content while the lowest partcle size gained the highest moisture content. This may be happened due to unefficient heat distribution into the samples during torrefaction (a thermo-chemical reaction) which lead to little decomposition of hemicellulose in the samples. Hence, it is believed that the samples still have high hemicellulose which contains moisture.

Having low moisture content will contribute to the improvement of energy content in the samples. Figure 4.7, 4.8 and 4.9 showed the calorific value before and after torrefaction for each type of biomass. Based on those figures, commonly each biomass got increament of the calorific value after torrefaction. The increament can be also due to the higher percentage amount of carbon content in the solid products and also the losses of other component which mostly oxygen. Having high moisture content in biomass will make some energy is needed to vaporise the water before undergo other reaction. R. Zanzi et al also stressed the higher amount of oxygen in biomass can reduce the calorific value through component calculation as shown below:

Calorific Value (MJ/kg),

$$CV = 0.34\%C + 1.40\%H - 0.16\%O$$

Coconut shell gained higher energy content after the torrefaction. The amount of calorific value is higher at temperature 280 degree than at 240 degree Celcius. Moreover, the calorific value at size 250 is higher than at size 500. Higher temperature with assistance of smaller size will contribute to greater loss of oxygen from the sample. It is believed also the amount of carbon component has increased after the torrefacation which also contribute to the increament of calorific value. According to figure 4.10 till 4.15, the ultimate analysis done proved that there is increament percentage amount of carbon and hydrogen and reduction of oxygen in the samples after reaction.

4.8 Proximate Analysis using Thermogravimetric Analyser (TGA)

The purpose of using this analyzer is to analyze the decomposition regime of the torrefied products in term of the moisture content, volatile matters and fixed carbon content. Ash content also can be determined from this analyzer. The temperature ranging used for thie pupose is from 50 to 900 degree Celcius. The results obtained from this analysis can be viewed at Figure 4.16, 4.17, 4.18 and 4.19.

According to Figure 4.16, it is proved that torrefaction at higher temperature are able to reduce the moisture content as low as possible. This can be explained with hemicellulosic compound in the products which has been decomposed and therefore unable to contain the moisture anymore. The moisture is released to the air during the process.

Figure 4.17 shows the volatile matter content has decreased after undergo torrefaction 280 degree Celcius compared at temperature 240 degree Celcius. These results demonstrate more volatile matter had been released during the torrefaction process at 280 degree Celcius. Because of that, the torrefied products at this temperature only retain smaller percentage amount of these matters as measured by TGA. As stated before, more volatile matter released will give more improvement to the quality of fuel since the volatile matter has brought out the oxygen molecules in form of lipids and gas like CO and $CO_{2.}$ Paddy straw obtains lowest volatile matters after undergo 280 degree Celcius torrefaction compared to other samples.

As the result of the decreasing percentage amount of volatile matter in the torrefied products, the percentage amount of fix carbon content had increased at temperature 280 degree Celcius compared to at temperature 240 degree Celcius. The fix carbon content is believed mainly consist of lignin and cellulose which can be decomposed at temperature more 300 degree Celcius. Paddy straw shows great increament percentage of fix carbon content which indicate that it has high content of lignin.

Ash content mainly consists of metal oxide which cannot be decomposed at torrefaction temperature. Higher temperature is needed to break the bond of molecules before released to the air. Hence, having high percentage amount of ash content in the retained product is not good where it can cause problems like blockage in the downstream piping system of gasification. According to figure 4.19, paddy straw contains high percentage amount of ash even though it undergo reduction at temperature 280 degree Celcius. Rice husk and coconut shell exhibit smaller percentage amount of ash content (compared to paddy straw) even though both of samples had higher percentage amount of ash content after 280 degree Celcius torrefaction.

4.9 Selection of the most suitable sample as Gasification's feed

Properties like low moisture content, high calorific value and low ash content are used to determine the best sample to be used as solid fuel/feed for gasification. Table 4.1, 4.2 and 4.3 show how the measurement being done to select the most suitable samples as the feed for gasification.

Table 4.1: Coconut shell assesment

	CS 500µm		CS 250µm	
	240°C	280°C	240°C	280°C
Low Moisture Content	1	2	4	3
High Calorific Value	2	3	1	4
TOTAL	3	5	5	7
Low Ash Content*	5	6		
TOTAL (+ ash content)	8	11		

Table 4.2: Rice husk assesment

	RH 500µm		RH 250µm	
	240°C	280°C	240°C	280°C
Low Moisture Content	3	2	4	1
High Calorific Value	2	3	1	4
TOTAL	5	5	5	5
Low Ash Content*	4	3		
TOTAL (+ ash content)	9	8		

Table 4.3: Paddy straw asesssment

	PS 500μm		PS 250μm	
	240°C	280°C	240°C	280°C
Low Moisture Content	1	4	2	3
High Calorific Value	2	4	1	3
TOTAL	3	8	3	6
Low Ash Content*	1	2		
TOTAL (+ ash content)	4	10		

Marking scheme:
Low moisture content and high calorific value: 1 – 4 (4 is the best)
Low ash content: 1 – 6 (6 is the best). This property only available for sample at size 500μm

Without considering the ash content measurement, paddy straw 500 μm at temperature 280 degree Celcius and coconut shell 250 μm at temperature 280 degree Celcius become the best samples as feed for gasification process. After requirement of low ash content included, coconut shell with size 500 μm at torrefaction temperature 280 degree Celcius become the most suitable sample as feed for gasification process.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

Results obtained after the experiment show that properties of all samples can be improved by torrefaction process. Hence, it has proved that torrefaction can be used as pre treatment method to biomass before it being feed in to gasification. Particular sizes and torrefaction temperatures also can influence the properties of biomass after undergoing torrefaction process. Only some of the samples do not affected by particular sizes and torrefaction temperature where the results are not as expected. It may be due to other factors which need to be analysed further. Properties like low moisture content, high calorific value and low ash content are used to determine the best sample to be used as solid fuel/feed for gasification. After doing the comparison, coconut shell at size 500 μm (with exception of samples at particular size 250 since no proximate analysis on this size) is looked as the best sample which meets desired properties.

5.2 Recommendation

More time and facilities is needed to analyse the torrefation products since some results obtained do not meet the expectation results as done by past research. Difficulty to do second experiment and analysis due to limited equipment had made some unexpected result cannot be analysed again. Hence, it is suggested to management to provide more equipment like reactor and TGA hence repeating analysis can be done to get expected results.

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