

**PHYSICOCHEMICAL PROPERTIES CHANGES  
ON WOODY BIOMASS TORREFACTION:  
EFFECT OF TEMPERATURE AND  
RESIDENCE TIME**

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ON WOODY BIOMASS TORREFACTION:  
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RESIDENCE TIME**

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Thesis submitted in partial fulfilment of the requirements  
for the award of the degree of  
Bachelor of Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering  
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JANUARY 2017

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## **DEDICATION**

This thesis is dedicated to my supervisor, my friends and my family who taught me that the best kind of knowledge to have is that which is learned for its own sake. Special appreciation to my supervisor Dr.Suriyati Binti Saleh, who taught me that even the largest task can be accomplished if it is done one step at a time.

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## ABSTRACT

Biomass can be used as a source of energy and it most often refers to plants or plant-based materials such as woody sawdust or oil palm residues. Wood waste was the one important biomass energy source to convert to value added product which was carbon particles. The best option to overcome the issues face with biomass was to carry out a pre-treatment process called torrefaction. Torrefaction is a pre-thermal treatment that has the potential to improve these characteristics. This thesis covers three areas of investigation work. The first area investigated the influence of fundamental parameters (temperature, residence time) on the behaviour of woody biomass when treated with torrefaction. The woody biomass used in this study were Meranti and Seraya, had been torrefied in furnace at temperatures of 240 °C, 270 °C, 300 °C and 330 °C with inert nitrogen gas for the residence time 30 min and 60min. As a whole, the torrefaction temperature was increased, the mass of the torrefied wood was decreased. Moreover, higher the torrefaction temperature caused the energy loss decreased in shorter duration. The second area that covered how torrefaction has improved the physical and chemical properties of biomass. Torrefied fuels contained higher energy yields behaviours between both sawdust used which were Meranti and Seraya sawdust. Furthermore, SEM studies were carried out to gain a better insight into any changes in morphology and chemical composition of torrefied biomass. The overall results indicated that careful optimization was required to maximize the benefits of torrefaction whilst maintaining a good energy yield. The third area examined the nature of products of torrefaction in terms of composition, proximate and ultimate analysis to provide comparisons between the products obtained from torrefaction and when the woody biomass were untreated. The presence of mass and heat transfer limitations was suggested to explain the observed significant changes.



## ABSTRAK

Biojisim boleh digunakan sebagai sumber tenaga dan ia juga merujuk kepada tumbuh-tumbuhan atau bahan-bahan berasaskan tumbuh-tumbuhan seperti sisa kayu habuk gergaji atau kelapa sawit. Sisa kayu adalah satu sumber tenaga biomass penting untuk menukar ke produk tambah nilai yang zarah-zarah karbon. Pilihan terbaik untuk mengatasi isu-isu terhadap dengan biojisim adalah untuk menjalankan proses rawatan pra yang dipanggil 'Torrefaction'. Torrefaction adalah rawatan pra haba yang mempunyai potensi untuk meningkatkan ciri-ciri ini. Tesis ini merangkumi tiga bidang kerja-kerja penyiasatan. Kawasan pertama disiasat pengaruh parameter asas (suhu, masa tinggal) pada tingkah laku biojisim kayu apabila dirawat dengan torrefaction. Torrefied kayu biojisim di Relau pada suhu 240 °C, 270 °C, 300 °C and 330 °C dengan gas lengai nitrogen bagi kediaman masa 30 minit dan 60 minit. Secara keseluruhannya, suhu torrefaction meningkat, jisim kayu torrefied dikurangkan. Selain itu, lebih tinggi suhu torrefaction yang disebabkan kehilangan tenaga yang menurun dalam tempoh yang lebih pendek. Kawasan kedua yang meliputi bagaimana torrefaction bertambah sifat-sifat fizikal dan kimia biojisim. Torrefied pembakar yang mengandungi tinggi tenaga hasil tingkah laku antara habuk gergaji yang digunakan iaitu Meranti dan Seraya habuk kayu. Selain itu, SEM pengajian telah dijalankan mendapat pemahaman lebih baik sebarang perubahan morfologi dan komposisi kimia torrefied biojisim. Keputusan keseluruhan menunjukkan pengoptimuman yang berhati-hati adalah diperlukan untuk memaksimumkan faedah torrefaction sambil mengekalkan hasil tenaga yang baik. Torrefaction adalah masih di peringkat pembangunan dan matlamat ilmu pengetahuan dan Sains adalah masih diperlukan. Bahagian ketiga mengkaji jenis produk torrefaction dari segi komposisi, analisis proksimat dan mutlak dan tindak balas mereka terhadap pembakaran memberi perbandingan antara produk-produk yang diperolehi dari torrefaction dan apabila jisim kayu yang tidak dirawat. Kewujudan had pemindahan jisim dan haba adalah dicadangkan untuk Bincangkan perubahan-perubahan penting yang diperhatikan. Akhirnya, beberapa cadangan untuk kerja-kerja masa depan dibincangkan pada akhir tesis.

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**LIST OF ABBREVIATIONS**

C	Carbon
CV	Calorific Value
DTA	Differential Thermal Analysis
DTG	Differential Thermalgravimetric
EU	European Union
FC	Fixed Carbon
GC	Gas Chromatography
GCV	Gross Calorific Value
H	Hydrogen
H/C	Hydrogen-to-Carbon
HHV	Higher Heating Value
IEA	International Energy Agency
LHV	Lower Heating Value
MC	Moisture Content
O	Oxygen
O/C	Oxygen-to-Carbon
NCV	Net Calorific Value
NO	Nitrogen Oxide
RCG	Reed Canary Grass
SEM	Scanning Electron Microscopy
SO <sub>2</sub>	Sulphur Dioxide
TGA	Thermogravimetric analysis
UK	United Kingdom
US	United States
VM	Volatile Matters
wt	Weight Basis



# 1 INTRODUCTION

## 1.1 Background of the study

Biomass energy is currently sought as a major source of alternative energy. It is a renewable, potentially sustainable and environmentally benign source of energy. Biomass contribute about 12% of today's world primary energy supply, while in many developing countries, its contribution range from 40% to 50% (Tye et al., 2011). World production of biomass is estimated at 146 billion metric tons a year (Balat and Ayar, 2005). Biomass is still the world's second largest source of renewable energy. Although the applications of renewable energy grow lately, the limitation of application is due to the high cost and poor technology reliability. Under the development and evolution, the latest technology was biomass torrefaction for commercialization. Commercial development of torrefaction is currently in early phase. Several of the companies are moving toward commercial market introduction. Furthermore, the woody biomass is more light compare to the other heavy products. woody biomass ease to bring everywhere, even carry in the flight cabin.

Biomass can be used in virtually any energy application where fossil fuel is used. Biomass and its utilization have been intimately associated to renewable energy in the recent years (Chew and Doshi et al., 2011). However, the properties of biomass is not desirable such as high moisture content low energy density, tenacious and fibrous in nature, become a barrier to its competitiveness in the energy generation market. Therefore, one of the viable option to overcome the issues associated with biomass feedstock is to carry out a pre-treatment process is called torrefaction. Torrefaction is the slow heating of biomass in an inert or reduced environment to a maximum temperature of approximately 300 °C (Tumuluru et al., 2011). Torrefaction also can be defined as thermal process applied to the wood to obtain the reaction to convert them into high quality of solid biofuel that is more suitable to combustion pyrolysis or gasification in the range of temperature 200°C to 300°C. The progress is eliminate the water content portion from the organic sample which is complete the calibration process. The mass of sample is loss and the structure is broken by depolymerisation process. Therefore, this produces a solid fuel which is called biocoal.

### **1.1.2 Biomass as a potential renewable source of energy**

The versatility of biomass as a source of energy for heat, power and transport has been viewed as a source of energy that has the potential to offset fossil fuel use and continues to attract worldwide attention (McKay, 2006; Nowakowski *et al.*, 2007). The IEA Bioenergy Task 40 reported that most of the biomass use globally is accounted for inefficient residential use (66%) that is mainly in developing countries for cooking and heating. Industry is the second largest, followed by electricity and transportation (IEA, 2013).

Table 1.1 presents a list of countries that uses biomass in the industrial sector, where Brazil, India and the United States present the top three who use the largest amount of biomass (IEA, 2013). With regards to UK, Ares (2013) mentioned that in 2011, 0.6% of its generation of energy comes from dedicated biomass. These fuels include straw and short rotation energy crops and the rest was animal biomass. The author also reported that half of the biomass was imported while the animal biomass is usually home produced. The use of dedicated plant biomass has reached more than double over the past four years (Ares, 2013). On the other hand, UK often uses wood for heating in homes and industry rather than for electricity generation. Therefore, Ares (2013) stated that UK is a net exporter of wood and wood waste for energy.

In the transportation sector, ethanol is the major transport biofuel in the US and Brazil while biodiesel is widely used in EU area (IEA, 2013a). Almost half of the global liquid biofuels production are consumed by the US (43%) as recorded in 2011 and interestingly, 87% of the ethanol produced in Brazil is used as fuel (IEA, 2013).

**Table 1.1** Countries that use biomass in the industrial sector (IEA, 2013a)

<b>No.</b>	<b>Country</b>	<b>Share of global use (%)</b>
1	Brazil	18
2	India	16
3	United States	16
4	Nigeria	5
5	Canada	4
6	Thailand	4
7	Indonesia	4
8	Democratic Republic of Congo	3
9	Sweden	2
10	Pakistan	2
11	Finland	2
12	Australia	1
13	Germany	1
14	France	1
15	Japan	1
Other Countries		20
World		100

## **1.2 Motivation**

Wood waste is reused to create new technologies to convert biomass waste nowadays. It contributes to reduce the greenhouse gas effect. However, high cost of particle synthesis production and conversion technologies is the disadvantages of the biomass. Woody biomass like energy source has its advantages and disadvantages after processing of torrefaction. Therefore, this proposed study can reduce the amount of abundant wood waste from the industries by adding the value of the solid material and avoid pollution to the environment.

The torrefaction technology is the latest technology brings attractive financial returns to many investors. Hence, they are poised to pour millions of dollars into building new plants especially in European Union. The European Union (EU) aims to achieve

an ambitious 10% share of biofuels by 2020 (European Commission. Green Paper, 2006). While the market is ready and eager to accept torrefied products, technology is not yet ready due to a lack of in-depth and objective research in this field. For example, some partially-ready technology used for a scale-up faced major setbacks. This underscores the dire need for systematic research in the general field of torrefaction, which this present research proposes that to do.

### **1.2.2 Biomass pre-treatment technologies**

Biomass fuels are usually prepared in some way prior to being used in energy conversion processes (Murphy et al., 1996). There is no specific technology that can serve all production plants. In other words, the effectiveness of a pre-treatment depends on the type of feedstock (hardwoods, softwoods, herbaceous crops, agricultural residues) being processed (NNFCC, 2009). A number of pre-treatment methods that aim to reduce the problems associated with biomass have been developed to improve the energy conversion efficiency. Pre-treatment of biomass refers to a number of technologies, which can modify the biomass either by changing the content of hemicellulose, cellulose and lignin or the characteristics of the biomass to improve its efficiency (NNFCC, 2009).

According to NNFCC (2009) and Harmsen et al (2011), some of the pre-treatment technologies comprise of:

- a) Mechanical pre-treatment, which aims to reduce the particle size of biomass and such treatments include milling, chipping and grinding. This type of approach is often required to make the handling easier and to increase the surface: volume ratio. Densification is the other pre-treatment to overcome problems like high transportation cost. This process can reduce storage problem, improve transportation and energy efficiency,
- b) Thermal pre-treatment, for example, drying that are used in gasifiers and combustion equipment (Murphy et al., 1996). Drying produces a more homogeneous fuel and this aids in controlling the process (Murphy et al., 1996),

c) Chemical pre-treatment involves destruction of the biomass that is initiated by chemical reactions. Such treatments are acid-based to allow the breakdown of lignin and hemicellulose to access the cellulose using mineral acids and alkali-based to induce the breakdown of bonds, which link hemicellulose to lignin using calcium hydroxide, and

d) Biological pre-treatment that make use of enzymes from bacteria, fungi and other microorganisms to break down the hemicellulose and lignin fraction of the biomass. This treatment requires low energy and mild conditions but the progression is usually very slow.

### **1.3 Problem Statement**

Torrefaction is a relatively new area in scientific research. The torrefaction of biomass may be explained by the degradation of its polymeric constituent (hemicelluloses, cellulose, lignin, xylan and dextran). This is because woody biomass consists of hemicelluloses, cellulose, lignins, and extractives. Traditionally, biomass has been utilized through direct combustion. Burning biomass produces some pollutants, including dust and the acid rain gases sulphur dioxide ( $\text{SO}_2$ ) and nitrogen oxides (NO). Burning wood produces 90% less sulphur than coal. Therefore, these can all be reduced before releasing the fuel gases into the atmosphere (Lipinski et al, 2002). To date, wood fuels represent by far the most common sources of bioenergy and not only for less developed regions. Wood fuels provide energy security service for large segments of society and wood fuels technology is developing and expanding rapidly. If the world use the fossil fuels continuously, environmental degradation is gradually increased. Substitution of fossil fuels for energy production with biomass will result in a net reduction in greenhouse gas emissions and the replacement of a non-renewable energy source. Therefore, some challenge need to overcome in order to utilize the woody biomass efficiently. Biomass has relatively low energy density and high moisture content in its untreated form compared to fossil fuel. Due to this issue faced with biomass, torrefaction is the pre-treatment biomass that can be used to overcome this problem.

### **1.3.2 Economic value of Torrefaction**

The economic assessment of torrefaction is based on a case study that was conducted by the Topell Energy (IEA, 2012a). They compared the financial perspectives between torrefied wood pellets and wood pellets and consider all process steps from the biomass resource to the pellet production. All in all, it shows that the production costs for torrefied pellets are higher than those for wood pellets (IEA, 2012a). However, great savings can be achieved in transportation and end use. With that, it was concluded that there could be a business case for torrefaction. Because torrefied pellets have similar characteristics to those of low rank coals, this enables higher co-firing percentages to power plants for torrefied pellets than woodpellets (IEA, 2012a). Basu (2013) stated that the commercial use of torrefaction is relatively new, therefore, there is only a limited data available on its capital cost.

### **1.3.3 Current challenges for market implementations of torrefaction technologies**

The information in this section is mainly based on the report obtained from the IEA Bioenergy Task 32 that describes the status of torrefaction technologies (IEA, 2012a).

### **1.3.4 Technical challenges**

#### **a) Flexibility of feedstock**

Particle size and moisture content of feedstock are the two main criteria that seemed to limit the flexibility to be used in current developing torrefaction technologies. The accepted particle size is 5-20 mm and the moisture content not to exceed 15% in order to avoid incomplete combustion of wet torrefaction gases and minimise the process residence time. Agricultural residues such as straw have low bulk density and need large reactors, which leads to high capital costs and more difficult to operate. That is why most torrefaction projects use woody biomass instead of those residues.

#### **b) Treatment of torrefaction gases**

Torrefaction evolves volatiles such as carbon dioxide, carbon monoxide and other condensable organics such as acetic acid and formic acid. These gases are usually de-

dusted using a cyclone before they are released as fuels to dry incoming biomass. Any presence of heavy tars in the gases may condense in the pipework, leading to operational problems. Therefore, insulation of pipework is necessary. Biomass fuels that have high contents of fluorine, chlorine and sulphur, the burner flue gases has to be treated using an activated coal filter or wet precipitator. Clean biomass fuels will have to use dust filters instead.

### **c) Process control and the quality and consistency of torrefied products**

A well-controlled temperature profile and residence time in a torrefier is important to achieve an efficient process and optimal product quality. If the torrefaction process is based on an indirect heating, it will be more difficult to control, resulting heterogeneity in the products.

## **1.4 Objectives**

The objectives of this research are:

- To investigate the influence of fundamental parameters (temperature, residence time) on the behaviour of woody biomass when treated with torrefaction.
- To examine relationship between the elemental composition of biomass fuels and energy yields with increase severity of torrefaction.
- To examine the nature of products of torrefaction in terms of composition, physical and chemical characteristics as well as to provide comparisons between the products obtained from torrefaction and when the woody biomass are untreated.

## **1.5 Scopes of study**

- Using two different types of wood (Seraya and Meranti) for torrefaction in the torrefaction reactor.
- Torrefaction of woody biomass in torrefaction reactor at different temperatures (240°C, 270°C, 300°C, 330°C) with different time which are 30min and 60min.
- The standard fuel characterization of torrefied woody biomass in terms of proximate and ultimate analysis, mass and energy yields and physical appearance.

## 2 LITERATURE REVIEW

### 2.1 Torrefaction Process

Torrefaction is one of the thermal processes usually applied to the wood to obtain the reaction to convert them into high quality of solid biofuel that is more suitable to combustion pyrolysis or gasification. Nitrogen is the commonly used carrier gas to provide a non-oxidizing atmosphere in most laboratory tests. Since torrefaction is conducted at conditions similar to those of torrefaction which usually takes place between 200 and 300°C. When biomass is torrefied, the pre-treatment can be further classified into light, mild and severe torrefaction processes, corresponding to the temperatures of approximately 240–270, 270–300 and 300–330 °C respectively. After the biomass has been torrefied it can be densified by using conventional densification equipment, to further increase the density of the material. In addition, the biomass exchanges its hydrophilic properties to hydrophobicity, which allows an not effort storage that goes to face with a greater resistance against biological degradation, self-ignition and physical decomposition in general.

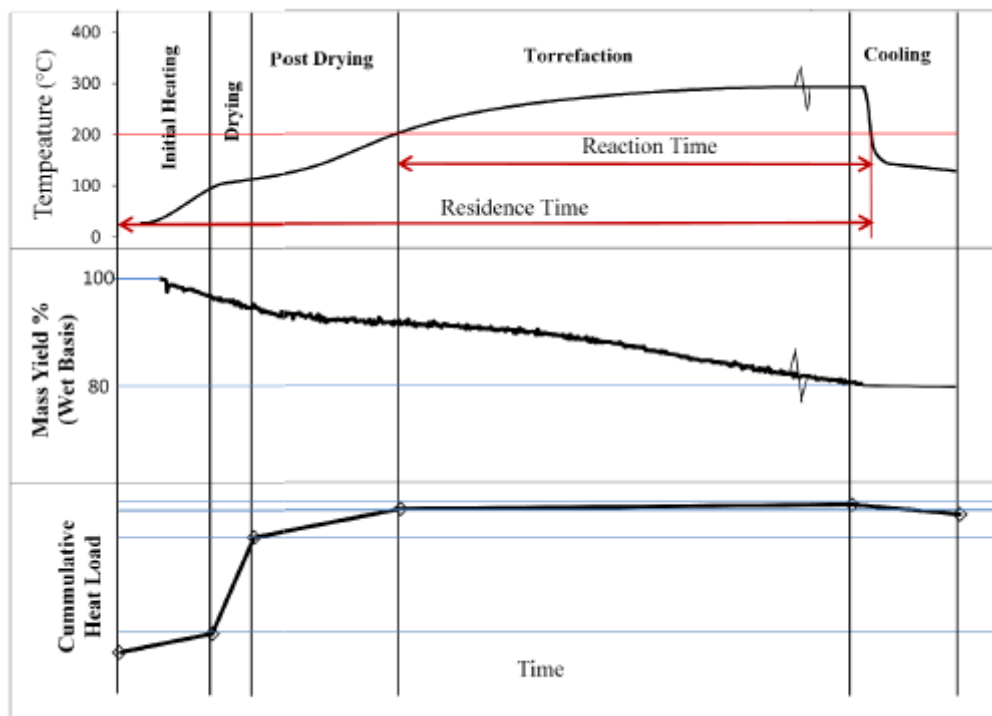
To improve for better mass yield, heating should occur slowly (below 50 °C/min). Faster heating will increase the liquid yield at the expense of solid char. Thus, biomass temperature is raised slowly from room temperature to the torrefaction temperature (Figure 2.1) and left there for sufficiently long time to ensure the reaction. Depending on the temperature effect on biomass, the temperature curve is divided into different zones (Bergman et al., 2005a). This assists in many ways in designing a torrefaction setup, because an ideal torrefaction reactor should provide the required amount of heat efficiently during the process. Figure 2.1 demonstrates 5 temperature zones, which are explained below:

**- Initial Heating:** At first, the biomass is heated from room temperature to the drying temperature at 100 °C. Here, the reactor should provide a small fraction of heat for a sensible rise in temperature. This is be accompanied by a steady drop in mass (wet mass) due to moisture loss. Since the temperature is measured at the core of the biomass, the outer layer heats faster and starts to get dried.



- **Pre-Drying (Drying):** As biomass starts to lose moisture, the temperature profile flattens and an almost a horizontal line is observed until all the surface moisture or free water is driven off. When the critical moisture constant is reached, the rate of evaporation starts to decrease and the temperature starts to climb. Depending on the moisture of the biomass, this stage requires the largest fraction of the total heat load. As can be seen in Figure 2.1, there is a sharp increase in cumulative heat demand.

- **Post-Drying:** This stage again involves raising the sensible temperature of the biomass until the torrefaction process starts at 200 °C. In this stage, all physically bound moisture is released along with some light organic compounds such as terpenes (Bergman et al., 2005). As seen in Figure 2.1, the energy demands of this stage are not a large fraction of the total heat energy demand.



**Figure 2.1:** Stages in the heating of a moist biomass (50% moisture) particle from ambient temperature to the desired torrefaction temperature (280 °C) and subsequent cooling of the torrefied product projected in the temperature, mass yield (experimental) and cumulative heat load (theoretical) profile. (Assuming 140 °C as drying temperature and 20% moisture remains after drying). (Bergman et al., 2005)

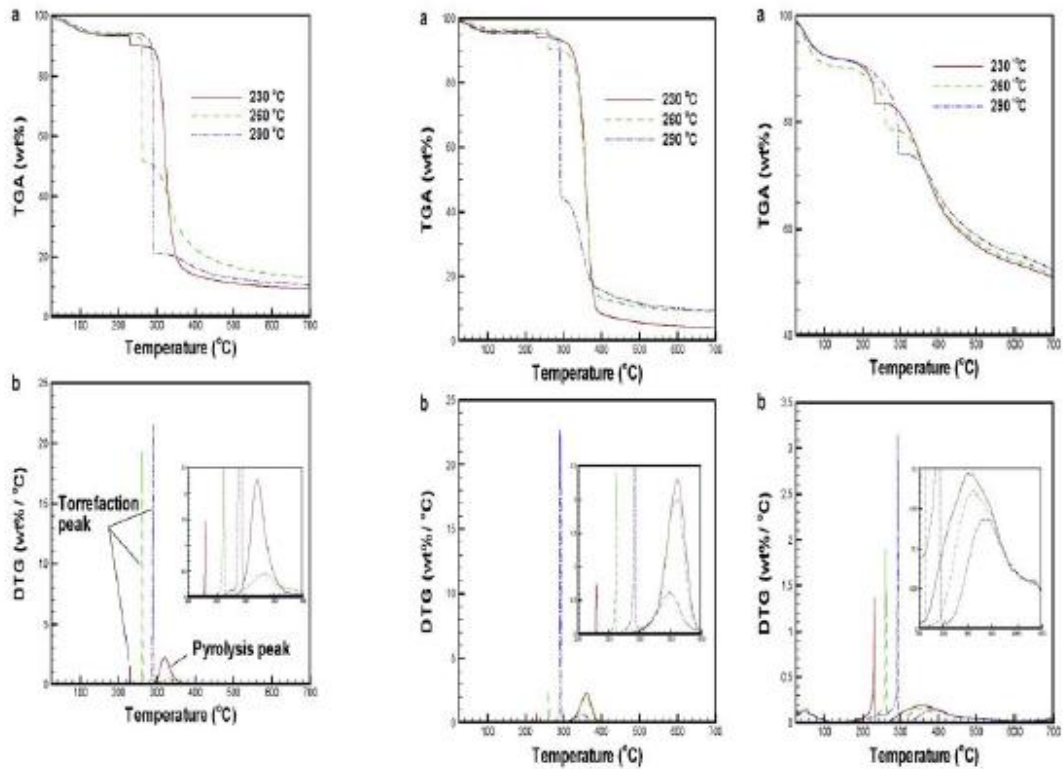
- **Torrefaction:** The torrefaction process occurs in this stage. Here, the biomass still requires sensible heat to raise it to the specified torrefaction temperature. A gestation period is needed to allow the depolymerisation reactions to continue until the desired severity of torrefaction is achieved. This stage requires very little amount of energy (Figure 2.1), but this does not imply that torrefaction is an endothermic process, as it still needs a sensible heat. Prins (2005) concluded that torrefaction is mildly endothermic within the range of 250 to 300 °C. On the contrary, Knezevic et al. (2009), Felfli et al.(2004), Chen and Kuo (2011) and Englisch (2011) have suggested that torrefaction is endothermic at lower temperature and exothermic at higher temperature (greater than 230 - 250 °C). Turner et al. (2010) proved that the exothermic reaction is not dependent only on temperature but on the size of the biomass as well. However, this represents a very small fraction of energy compared to the amount of energy being supplied for the entire process. Nevertheless, in situations involving large-sized biomasses or in a fixed bed torrefier of a large cross-section, this exothermic heat can build up and cause temperature run-off. Another important parameter in torrefaction is residence time. With increasing residence time the biomass mass continues to fall. Not apparent in Figure 2.1, after a long time its mass starts to level. Figure 2.1 clearly defines the residence time and reaction time which are used often in this thesis. Residence time is the total time the biomass resides in the torrefier, while reaction time is defined as the time the biomass is above 200 °C (Figure 2.1).

- **Solid Cooling:** Biomass is then cooled down from the torrefaction zone to the desired final temperature for further processing or storage. This process releases heat and can be recycled back to the torrefaction process. Figure 2.1 is much useful in the design of the torrefaction unit. The heat load for drying is much higher than that for torrefaction, and drying can be performed at lower temperatures; any innovative ideas of utilization of low-grade waste heat could make the system more efficient. For the torrefaction process, energy demand can be met by combusting the volatiles generated during the torrefaction process.

## 2.2 Mechanisms of torrefaction

Torrefaction takes place at a low pyrolysis temperature range (200-300 °C). Exploratory studies have shown that this thermal treatment has a great impact on the behavior of the cell wall in the biomass particularly hemicellulose (Prins et al., 2006).

Chen et al (2011) carried out torrefaction processes that focussed on these lignocellulosic materials using thermogravimetry with increasing temperatures (230, 260, 290 °C), followed by pyrolysis until the temperature reached 800 °C. The results were analysed by means of thermogravimetric analysis (TGA), derivative thermogravimetric (DTG) and differential thermal analysis (DTA). As in agreement with Yang et al (2007), the TGA shown in Figure 3.2 a) indicates that the hemicellulose starts to degrade slightly during torrefaction even at a temperature as low as 230 °C (Chen et al., 2011). The DTG peak observed in Figure 3.2 b) for hemicellulose at 230 °C was the least intense, which also indicates it has the slowest rate of mass loss in comparison to the other peaks upon torrefaction at 260 and 290 °C. The other peaks showed that the increased in intensity were of ten-folds (20-22 wt%/°C). A significant rate of degradation due to cellulose occurred at the highest torrefaction temperature (23 wt%/°C), while only to a less extent for that of lignin (about 3 wt%/°C). Cellulose would take more energy for it to degrade and often responds at higher temperatures (Yang et al., 2007). Even though, lignin did not seem to show any significant change, its decomposition did take place yet gradually over a wide range of temperature and at a very low mass loss rate during pyrolysis heading towards 800 °C (Chen et al., 2011).



**Figure 2.2:** a) Thermogravimetric analysis and b) derivative thermogravimetric of hemicellulose (left), cellulose (middle) and lignin (right) at three torrefaction temperatures (230, 260 and 290 °C with a residence time of 1 hour) (Chen et al., 2011).

### 2.3 Differences between carbonization, pyrolysis and torrefaction

Carbonization, pyrolysis and torrefaction are the three processes that involved thermal degradation of biomass and sometimes can be confusing. Their main difference is the product of interest. Basu (2013) mentioned that the objective of pyrolysis is to maximize the liquid production and minimize the char yield. Carbonization is aimed to maximize fixed carbon and minimize hydrocarbon content of the solid product, while torrefaction is aimed to maximize energy and mass yields of the solid product that also contains low O:C and H:C ratios (Basu, 2013). Moreover, even though carbonization is similar to torrefaction for example in terms of heating rates, there are some important differences between the two. Carbonization involves high temperature ( $> 300$  °C) and drives away most of the volatiles, while torrefaction retains them and only drives away the low energy

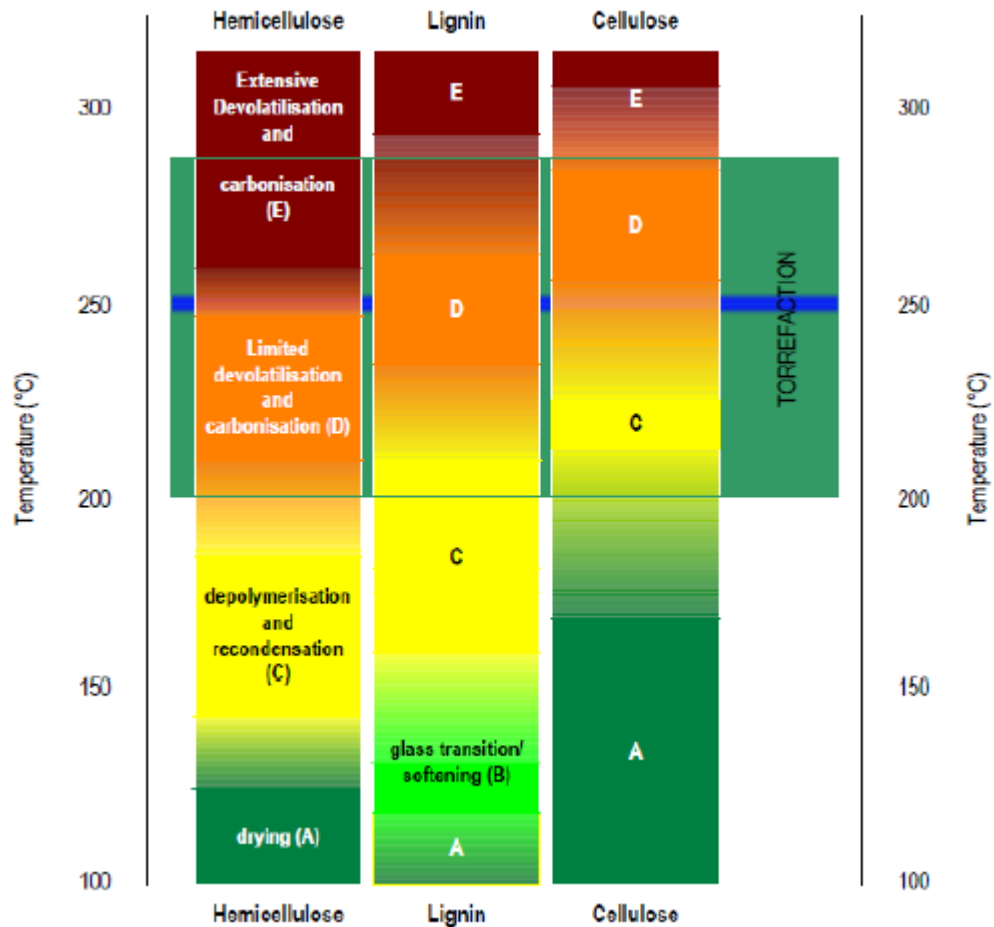
density volatiles (Basu, 2013). In addition to that, carbonization requires a certain amount of oxygen that allows sufficient combustion for heat supply and torrefaction would prefer to take place in an inert environment.

## **2.4 Mass and Energy Yield**

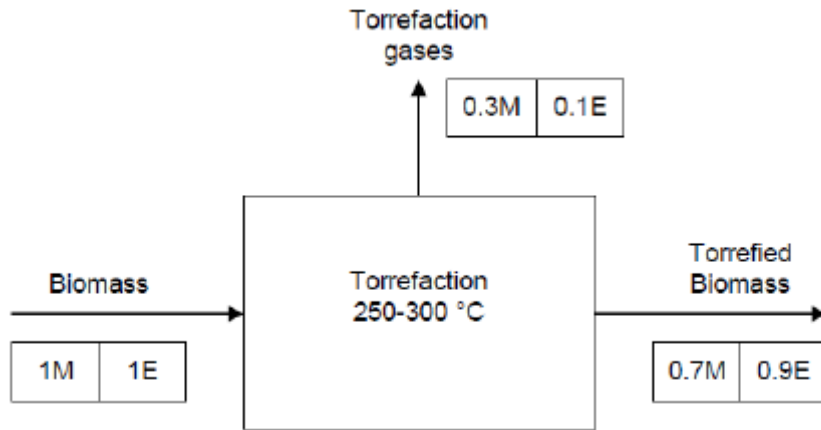
Mass yield is defined as the percentage of the mass of the coal relative to the mass of wood used in its torrefaction process. In the torrefaction process, mass loss is dominated by dehydration and devolatilization in the reaction regime of hemicelluloses component. The significant mass loss at the preliminary stage of torrefaction shows reduction in the moisture of the treated biomass (J.J. Chew et al., 2011). Energy yield is defined by the energy content ratio between torrefied biomass and its raw biomass, which is equivalent to the multiplication of the solid yield and the enhancement factor of HHV (Park SW et al., 2012, Chen WH et al., 2012). The calorific value of a material decreased almost linearly with increasing torrefaction mass loss (Almeida et al., 2012, Peng et al., 2012). Mass yield and energy yield of different biomass subjected to torrefaction process. Conversion rate of agricultural residues is comparatively higher than woody biomass due to its higher hemicelluloses content, thus resulting in lower mass yield. Higher content of xylan, the main fraction in hemicelluloses fraction, will increase the rate of reaction. The effect of torrefaction duration is reported to be less significant compared to temperature and the ideal operating condition is either at a lower temperature regime or higher torrefaction temperature coupled with shorter duration to minimize energy loss (Bergman et al., 2005).

Figure 2.4 illustrates the typical mass and energy balances of torrefaction of biomass as presented in (Bergman et al., 2005a). A considerable energy densification can be achieved via torrefaction when 70% of the mass yield and about 80-90% of energy yield can be retained (Bergman et al., 2005a). 30% of the mass is removed in the form of volatiles (torrefaction gases, where some would call it 'torgas'), which contain 10-20% of the energy content of the biomass. According to IEA (2012a) stated that the energy contained in the torgas can be used to drive off moisture in the dryer. According to Prins et al (2006a), provided a mass and energy balances for

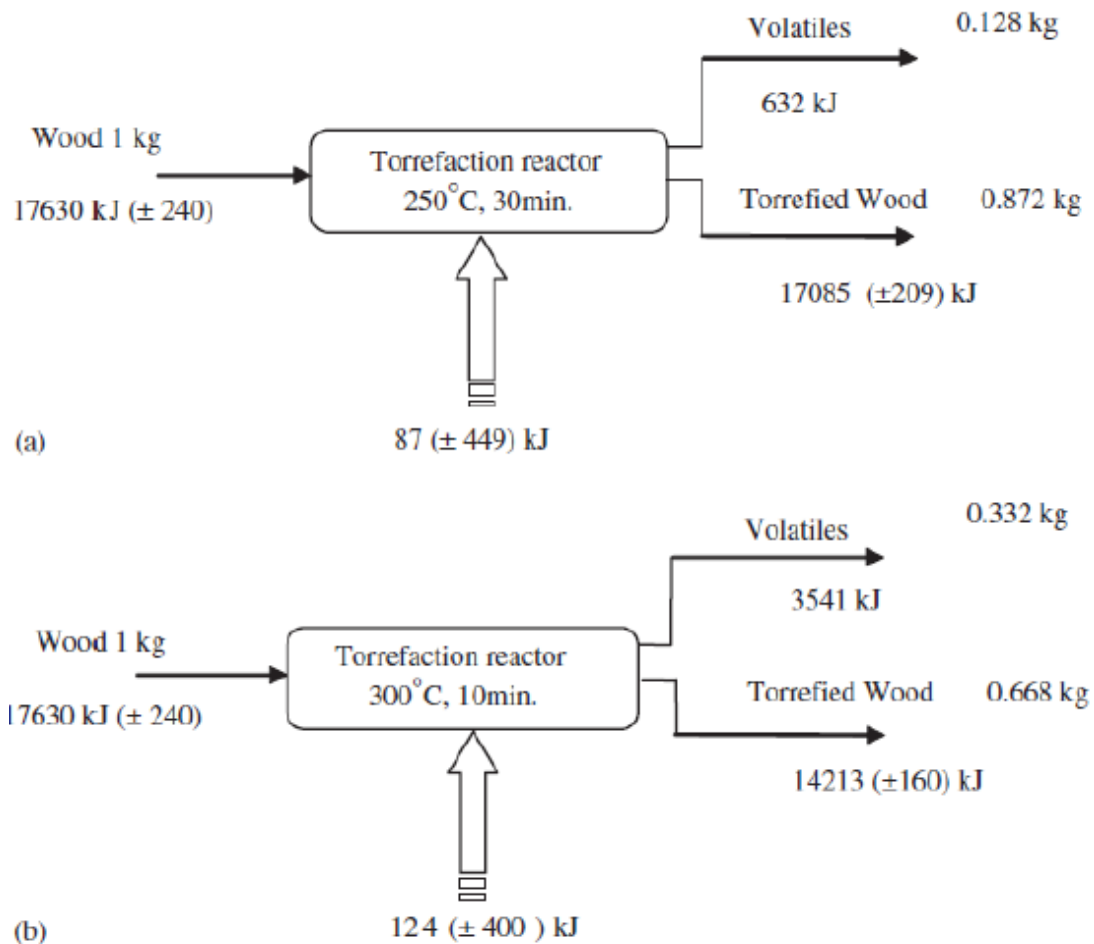
torrefaction of willow as shown in Figure 2.5. Temperature plays a more of a significant role in torrefaction than residence time. The figure shows that even though the residence time is set longer in Figure 2.5 a), increasing the temperature still produces a lower mass yield of biomass (67%) as seen in 2.5 b). Moreover, increasing the temperature releases more volatiles. This results in a lower energy balance, where 95% and 79% of the respective energy input is retained in the torrefied biomass.



**Figure 2.3:** Main physico-chemical reactions during the heating of lignocellulosic components at torrefaction (Bergman et al., 2005a).



**Figure 2.4:** Mass and energy balance of the torrefaction process, where E and M represent the energy and mass units (Bergman et al., 2005a).

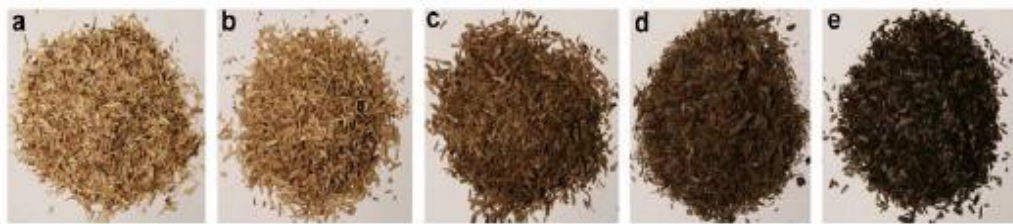


**Figure 2.5:** Example of overall mass and energy balances of torrefaction of at temperature and residence time of a) 250 °C and 30 min and b) 300 °C and 10 min (Prins et al., 2006a).

## 2.5 Physical and chemical changes of biomass fuels upon torrefaction

### 2.5.2 Colour

One apparent change in a torrefied biomass is the colour. Studies have shown that the colour changed to a more intense brown with increased torrefaction condition whether it is increase in temperature and longer residence time (Bridgeman et al, 2010; Phanphanich and Mani, 2011). Figure 2.9 illustrates the changes in colour for woody biomass fuels at various conditions.

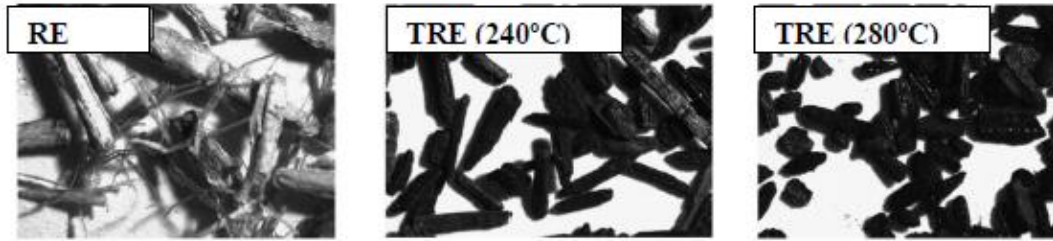


**Figure 2.6:** Images of willow: a) untreated; b) low temperature, short residence time; c) low temperature, long residence time; d) high temperature; short residence time; e) high temperature, long residence time (Bridgeman et al., 2010).

### 2.5.3 Particle size and shape

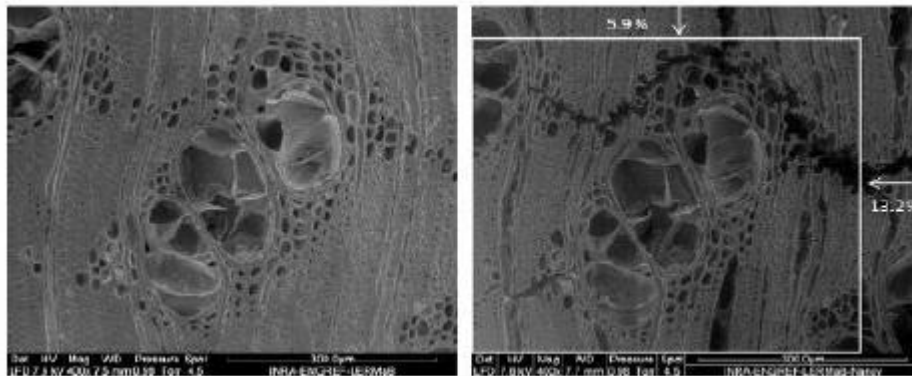
The other observable transformation is the difference in particle size and shape. Arias et al (2008) looked into these changes using an optical microscope to get a deeper insight of the structural modification of eucalyptus that was subjected to torrefaction (at 240 °C and 280 °C with a residence time of 3 hour). Figure 2.10 shows that the raw biomass fuel started off as being highly fibrous in nature and it became more spherical and less fibrous when torrefied. Particle sizes also decreased with increased conditions (temperature and residence time). When a sieving process was conducted, a large number of small particles were able to pass through the sieves, which indicate the reduction in size for torrefied biomass and was assumed to have become more spherical.





**Figure 2.7:** Images of raw eucalyptus (RE), torrefied eucalyptus (TRE) at 240 °C and 280 °C respectively (Arias et al., 2008).

These changes can be explained by the transformation in the structure of hemicellulose. Repellin et al (2010) stated that torrefaction leads to the shrinkage of the lignocellulosic material, thus, creates stress in the wood fibres and favours cracks. Almeida et al (2010) examined raw and torrefied Eucalyptus Saligna (E.Saligna) via Scanning Electron Microscopy (SEM) and the results can be observed in Figure 2.11. Here, damage to the structure with several fractures appeared in the most fragile tissues, while the raw E.Saligna was seen to be strong and intact.

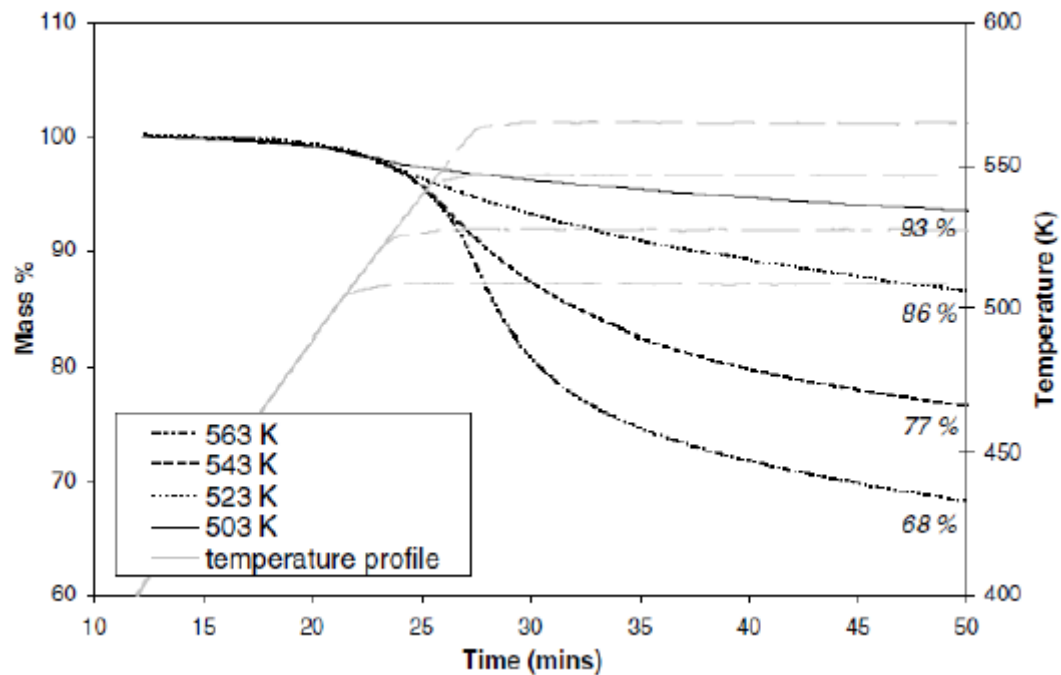


**Figure 2.8:** SEM images of raw (left) and torrefied (right) E.Saligna at 280 °C with a residence time of 5 hours (Almeida et al., 2010).

Particle size is rarely uniform in a commercial plant. Thus, to ensure a proper design, it is necessary to know the effect of particle size. With current information being limited and conflicting, there is an urgent need to explore the effects of particle size on biomass torrefaction.

#### 2.5.4 Mass loss

Figure 2.12 illustrates the reduction of the percentage mass of reed canary grass (RCG) with increasing temperature, from 230 to 290 °C (Bridgeman et al., 2008). This change was not only primarily due to the loss of moisture via evaporation during the drying stage but also because of the further release of reaction water vapour and the production of volatiles from the degradation of hemicellulose and minor decomposition of cellulose throughout the treatment process.



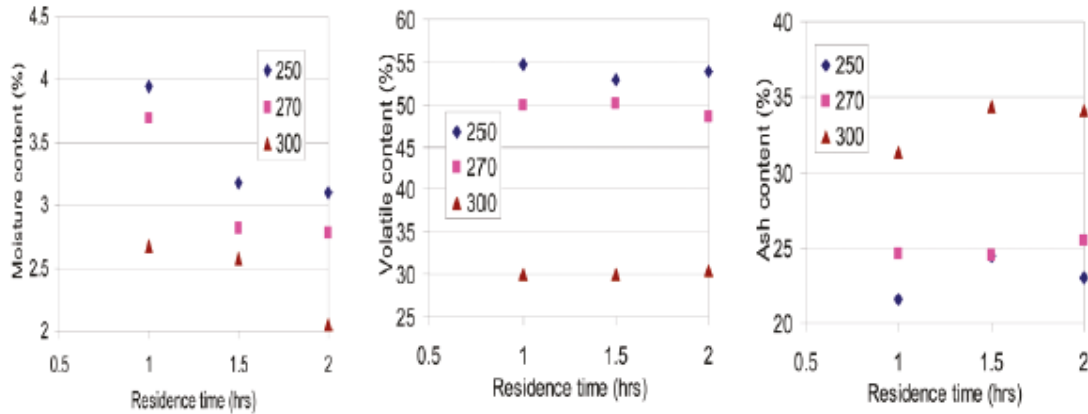
**Figure 2.9:** Mass loss during torrefaction of reed canary grass at different temperatures (Bridgeman et al., 2008).

#### 2.5.5 Moisture, ash, volatile and fixed carbon content

Apart from the colour, particle size and shape, physicochemical properties of interest in a biomass also include the contents of moisture, ash, volatile matter and fixed carbon. This can be determined from proximate analysis. It is one of the two fundamental standard fuel analysis that provides an indication for the suitability of a biomass fuel to be utilised for energy purposes. The moisture content (MC) of wood is tied directly to the relative humidity of the surrounding air, the higher the relative humidity, the higher the MC of the wood. Moisture content is an important property of biomass fuels, because a high moisture level in a fuel leads to a high energy loss in the course of burning. As a feedstock, it is desirable to lower the moisture content

of biomass. For example, the biomass feedstock must be dried to moisture content below 30wt% in the synthesis gas production process, preferably to about 15wt%, and to below 10wt% in the pyrolysis process (Fagernas L et al., 2010). To increase the energy efficiency, improve the energy product quality and reduce the emissions in the thermochemical energy conversion process, the reduction of biomass moisture content plays a vital role (Pang S, Mujumdar AS., 2010). In addition, biomass with less moisture can be stored stably over extended period of time, with a low risk of biological deterioration. Also, the transportation of hydrophobic solids is less expensive, as consequence of less moisture to be delivered along with the biomass. The lower saturated moisture content in torrefied biomass could also result from tar condensation inside the pores, obstructing the passage of moist air through the solid, and then a voiding the condensation of water vapour. The apolar character of condensed tar on the solid also prevents the condensation of water vapour inside the pores (Felfli FF et al., 2005).

The changes obtained from proximate analysis of torrefied biomass fuels have been widely studied in Bourgois and Guyonnet (1988), Pentananunt et al (1990), Felfli et al (2005); Blagini et al (2006), Bridgeman et al (2008; 2010), Sadaka and Negi (2009), Yan et al (2009), Almeida et al (2010), Pimchuai et al (2010), Wannapeera et al (2011), Medic et al (2012) and Pirraglia et al (2012). In general, with increased severity of torrefaction condition, the moisture content and volatiles are reduced, while those of ash and fixed carbon increased. Figure 2.13 illustrates the changes in these contents for torrefied rice husks, where the moisture content and volatiles have reduced from 4.0 to 2.5% and 55 to 30% respectively, while the ash content has increased from 20 to 32% when the temperature increased from 250 to 300 °C with a residence time of an hour. In this experiment, temperature is seen to have a more significant influence to the results than residence time. With a longer residence time, the moisture content continued to decrease, but minor changes were observed in volatile and ash contents.



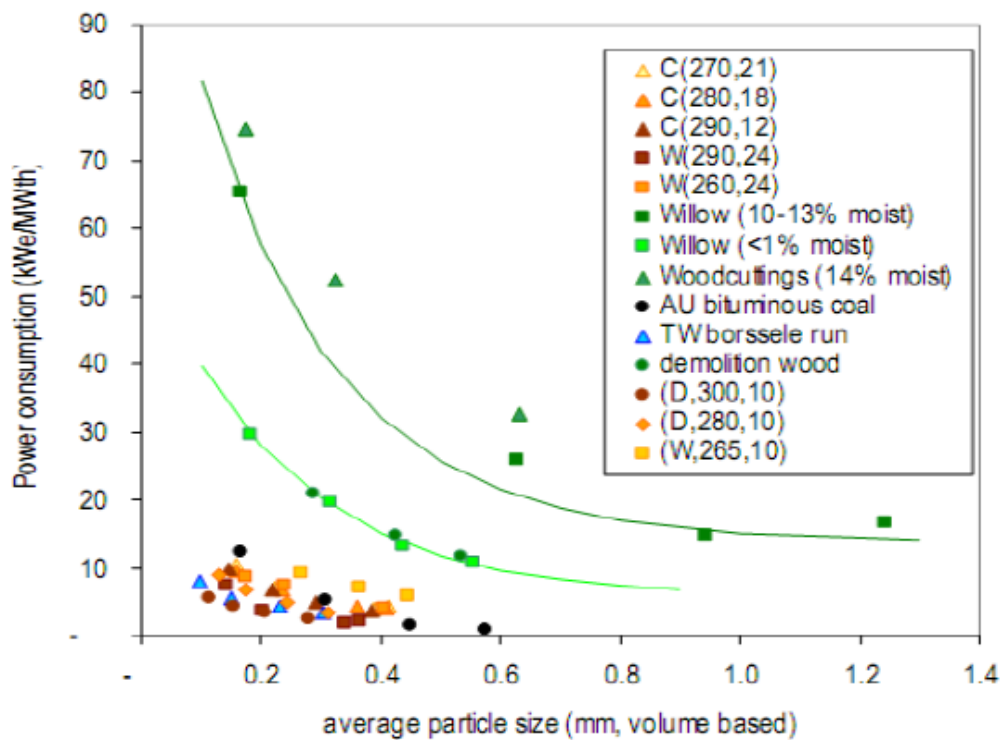
**Figure 2.10:** The change in the moisture, volatile and ash contents of torrefied rice husks (Pimchuai et al., 2010).

### 2.5.6 Grindability

Grindability test is a measure for the grindability of coal or wood. Grindability tests were carried out in a lab scale planetary type ball-mill. The grindability of the biomass is enhanced by torrefaction due to the modification of its molecular structure, so that existing problems arising from untreated biomass in the milling component of a coal power plant are overcome. In lignocellulosic biomass, cellulose microfibrils are embedded in a matrix of hemicelluloses, with hemicellulose and cellulose being densely packed by layers of lignin (Hu ZH, Wen ZY et al., 2008). The grindability of torrefied fuels has been studied and compared to corresponding properties of coals and untreated biomasses. Usually a significant improvement in grindability requires quite high torrefaction temperatures in the range of 290–300 °C. A reduction of grinding energy consumption by ten times for torrefied pine chips compared to untreated biomass has been reported at a torrefaction temperature of 300 °C (Phanphanich et al., 2011).

Many utility companies are considering using torrefied biomass as a substitute for coal in existing power plants. One of the major challenges of introducing biomass for direct cofiring is matching the power demand on the existing milling machine. Being less brittle and fibrous, biomass requires considerably greater efforts to be ground to an appropriate fineness. Therefore, energy density and grindability of the biomass must be close to that of coal (Bergman et al., 2005a). Figure 2.14 shows that power consumption of a mill for torrefied biomass reduces significantly around 70-90%

compared to that for raw biomass, depending upon the biomass and torrefaction condition.



Net power consumption curves

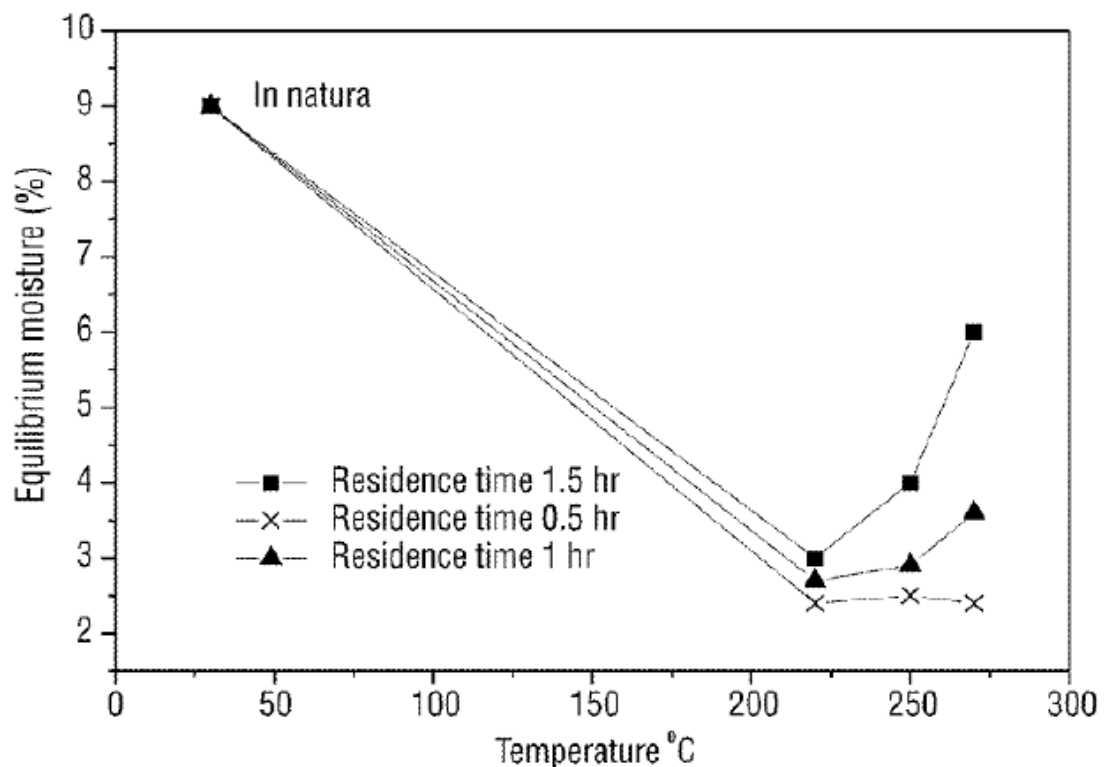
**Figure 2.11:** Size reduction results of coal, biomass feedstock, and various torrefied biomasses. Example of (C- Coal,W- Wood, D- Demolition wood for temperature of 270 °C and residence time of 21 minutes (270,21)) (Bergman, 2005)

While the potential exists for minimizing operational and investments costs for the production of torrefied biomass pellets, very little research has yet examined potential equipment or process modifications to suit torrefied biomass.

### 2.5.7 Hydrophobicity

Hydrophobicity is the physical property of a molecule (known as a hydrophobe) that is seemingly repelled from a mass of water. Biomass absorbs moisture due to the presence of the OH (hydroxyl) group in biomass (Tumuluru et al., 2010). The torrefaction process removes this group in hemicellulose, and newly-formed molecules are also hydrophobic (Sadaka and Negi, 2009; Ciolkosz and Wallace,

2011). These new molecules and condensed tar might block the pores so as not to allow capillary uptake of water vapour and subsequent condensation (Felfli, 2005). According to Bergman (2005) performed a qualitative assessment of the hydrophobic nature by immersing raw and torrefied biomass pellets in water for 15 hours. It was found that raw biomass pellet quickly disintegrated into original particles while torrefied biomass only took around 7-20% moisture by its weight. Felfli et al. (2005) quantified this property by calculating the equilibrium moisture of biomass at different torrefaction times.



**Figure 2.12:** Equilibrium moisture content of raw biomass and torrefied biomass briquette at different temperature and residence time (Felfli et al. 2005).

Figure 2.15 shows that, with increased torrefaction temperatures, the equilibrium moisture of the biomass decreased drastically from 9 to 3-4%. However, with further increase in torrefaction temperature, equilibrium moisture started to increase. This was predicted due to increase in porosity. However, the process of calculating the equilibrium moisture is not presented by Felfli et al. (2005). Moreover, there seems to be a lack of a standard methodology in calculating the hydrophobicity of torrefied biomass.

Biomass with no moisture will not support any biological organism. Hence, unlike raw biomass, it will not degrade when stored for an extended period. This is because of this property of biomass. For example coal can be stored in an open ground for avoiding the cost of an indoor storage facility.

## **2.6 Thermogravimetric analysis (TGA)**

Thermogravimetric analysis (TGA) is a method of thermal analysis to measure the amount of weight change of a material. The measurements in TGA can be performed during a rising in temperature, in static rate (isotherm) or under a temperature program. Its primary use is in the characterisation of phase transformations while a solid sample is being heated at a constant rate in the presence of a gas. Typically, a TGA consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust. The reaction between gas and solid may lead to either an increase or a decrease in the sample weight. Any reduction in the sample mass is usually due to the release of by-products from the reaction. Usually biomass devolatilization is referred to in terms of its three main components namely lignin, cellulose and hemicelluloses (Katarzyna Slopiecka et al., 2011).

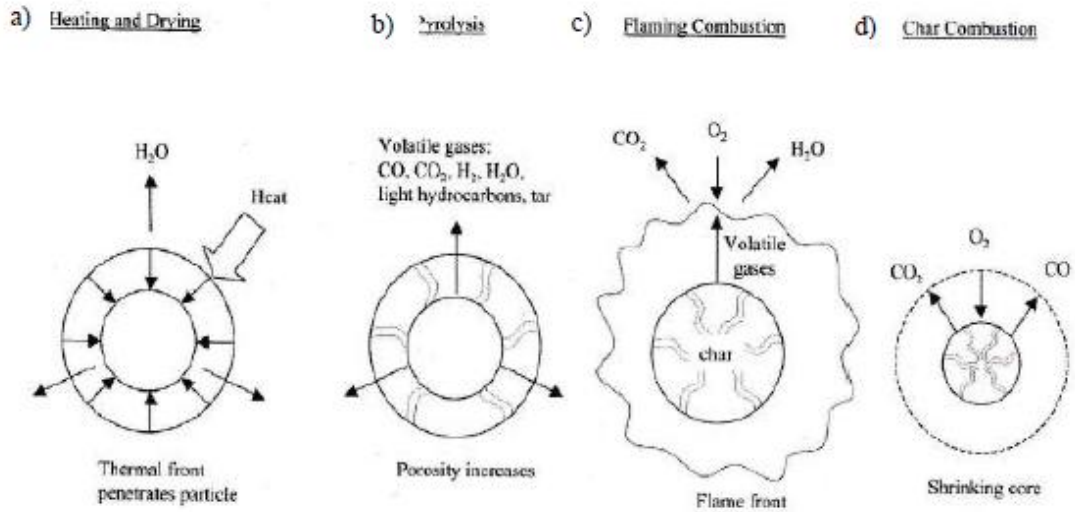
## **2.7 Biomass characterization**

Proximate and ultimate analyses are two standard analyses that are used to provide information about the fuel's characteristics as to whether the biomass would be ideal to be used as a fuel for energy and also, when it comes to designing a proper biomass utilization system such as a gasifier and combustor.

### **2.7.1 Fuel characteristics: Proximate analysis**

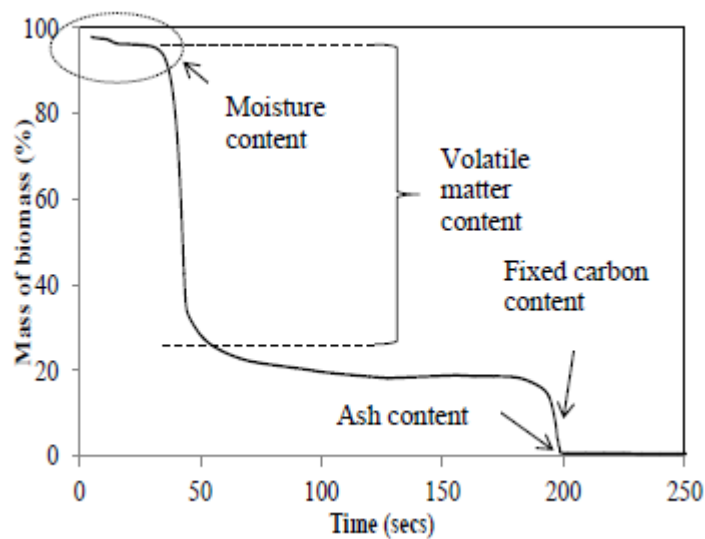
Proximate analysis measures the physical and chemical parameters of a biomass, which can be obtained by means of heating a weighted sample in an oven/furnace under a controlled temperature or in a thermogravimetric analysis (TGA). TGA involves the combustion of a biomass that is comprised of four stages: drying, pyrolysis, volatile combustion and char combustion, as shown in Figure 2.13

(Brown, 2003). What happens to the biomass at each stage determines the characteristics of the fuel and this type of analysis provides the information about the moisture, volatile matter, fixed carbon and ash contents of the fuel. Upon analysis, the results can be corrected to a dry or dry ash free basis except moisture content.



**Figure 2.13** Stages involved in the solid fuel combustion (Brown, 2003).

Figure 2.14 is an example of a result from the TGA, which represents the change in mass against time that takes place throughout each stage. In general, it can be seen that the biggest change in mass takes place during the devolatilisation stage, which will be explained in more detail shortly.



**Figure 2.14** A typical diagram of a thermogravimetric analysis of a biomass.



Figure 2.13 a) illustrates the drying stage, after the heat was introduced and the temperature has reached the boiling point of water. Drying stage determines the moisture content of the biomass because it only involves the removal of moisture. The loss of water led to a slight mass loss as shown in Figure 2.14. In terms of biomass as a feedstock for combustion, gasification or other thermochemical processing, moisture content is a very crucial parameter (Murphy *et al.*, 1996). Dealing with biomass can be difficult because it readily absorbs moisture when it is exposed to air and degrades gradually upon long storage. The moisture content depends on the type of biomass, location as to where it is planted, when it was harvested, the storage conditions and the duration of storage (Murphy *et al.*, 1996). The moisture content of a biomass fuel can go as high as 90% (Basu, 2013). If the moisture content is high, a great amount of heat energy is required for evaporation during biomass thermal processes and Basu (2013) stated that the energy used for evaporation is non-recoverable. Drying is an energy intensive process. This parameter is also important in milling for pelletisation and co-firing purposes.

Volatile matter studies the amount of components in the biomass that are converted and liberated as volatiles at high temperatures (Montross and Czarena in Crocker, 2010). Volatile matter content is important in designing burners and gasifiers for biomass (Brown, 2003). The second stage shown in Figure 2.13 b) represents pyrolysis and it involves a series of thermally driven chemical reactions. This is when lignocellulose materials start to degrade at above 200 °C. Decomposition of organic molecules takes place, producing a large variety of volatile compounds, such as carbon dioxide, carbon monoxide, water, methane and high molecular weight compounds (Brown, 2003). Pyrolysis follows the thermal front through the particle and allows the release of volatile compounds, creating pores that penetrate through to the surface of the particle. The content of the volatile matter depends on the heating rate and temperature it is heated (Basu, 2013).

Figure 2.13 c) shows that in the presence of oxygen and sufficient temperature flame, the volatile or flame combustion takes place, in which carbon dioxide and water are the final products (Brown, 2003). At the end of pyrolysis, a porous carbonaceous residue, char remains and again, in the presence of oxygen, char combustion takes

over (Figure 2.13 d)). Brown (2003) stated that the char oxidation is governed by mass transfer of oxygen instead of chemical kinetics. Oxygen may react with the char in two ways at the surface of the particle and results in a shrinking core reaction or it may penetrate into the pores and increase the porosity of the char while the diameter remains constant (Brown, 2003). Char is a carbon residue of pyrolysis (devolatilisation). It is not a pure carbon, nor a fixed carbon of the biomass. It contains the remaining volatiles, ash and the fixed carbon. The fixed carbon content is the amount of carbon contained in the char that is left after volatile materials are driven off. Moreover, it includes “the elemental carbon in the original fuel plus any carbonaceous residue formed while heating, in the determination of volatile matter” (Basu, 2013). An increase in the fixed carbon content indicates that the biomass is suitable for energy production (Pierre et al., 2011; Basu, 2013).

### **2.7.2 Fuel Characteristics: Ultimate analysis**

Ultimate analysis studies the elemental composition that makes up a biomass. The contents of carbon, hydrogen, oxygen, nitrogen and sulphur are usually analyzed as they are the five most abundant elements present in solid fuels. The percentages of each element are usually presented on a dry, ash free basis. Chemical properties are important for the energy efficiency, environmental concerns and ash related operating problems (Murphy et al., 1996).

According to Friedl et al (2005), the study of the correlation between C, H and O contents and the calorific values of fuels were carried out. Calorific value (CV), which is also known as the heating value is described as “an expression of the energy content evolved when burnt in air” (McKendry, 2002). Friedl et al (2005) stated that the determination of heating values is important for the design and control of power plants. The CV can be expressed in two forms: the higher heating value (HHV) or gross calorific value (GCV) and the lower heating value (LHV) or net calorific value (NCV). The HHV includes the total energy released when a fuel is burnt in air and therefore includes the latent heat from water vapour. The LHV is defined as “the amount of heat released by fully combusting a specified quantity less the heat of vapourisation of the water in the combustion product” (Basu, 2013). As most energy conversion technologies do not recover the latent heat, the LHV is the appropriate value to use for energy (McKendry, 2002).

A Van Krevelen diagram is a plot that is often used to classify coals. The lower the O:C or H:C ratio that is present in the fuel, the higher the heating value, then the better is the fuel. For example, Figure 2.15 shows that anthracite has a high carbon content than lignite, therefore, it can be said that the anthracite is of higher rank than lignite. However, it is important to note that in a formal system, the ranking is not based on the C content or where the fuel is positioned in the Van Krevelen diagram, but rather on how it behaves as a fuel such as during combustion or how much heat is released when it is burned (Schobert, 1990).

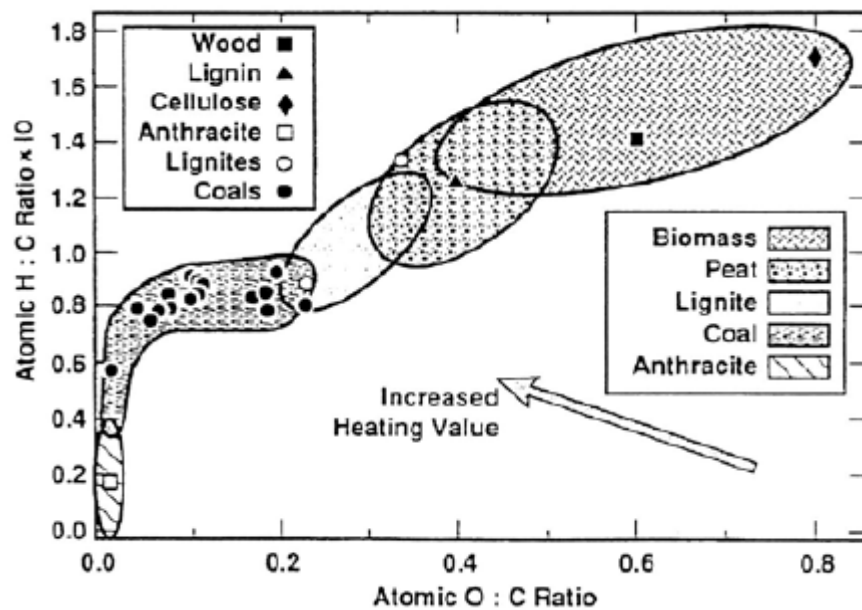


Figure 2.15 Van Krevelen diagram of solid fuels (McKendry, 2002).

### 3 MATERIALS AND METHODS

#### 3.1 Samples

The raw biomass used in this study is waste wood from Sawmill factory in Kuantan, Pahang. Woody biomasses were Seraya and Meranti sawdust.



Seraya sawdust



Meranti sawdust

**Figure 3.1:** Woody biomass samples used in this study.

#### 3.2 Apparatus

The apparatus that used were Bomb calorimeter, gas catalytic reactor, grinder, sieve and furnace.

#### 3.3 Methods

##### 3.3.2 Preparation of Biomass Sample

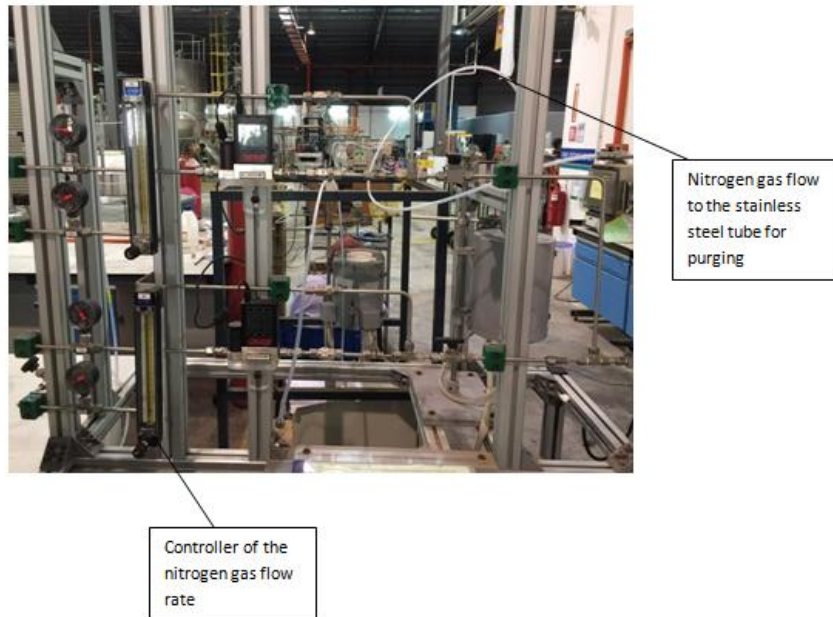
The raw biomass were grounded and sieved in order to obtain a sample with diameter of 0.5 – 1.0 mm. The samples were dried in the oven for 4-8 hours approximately at 60 °C until it consists about 10% of moisture content. The samples were stored in a sampling bag with desiccators for further usage.

### 3.3.3 Torrefaction Experiment

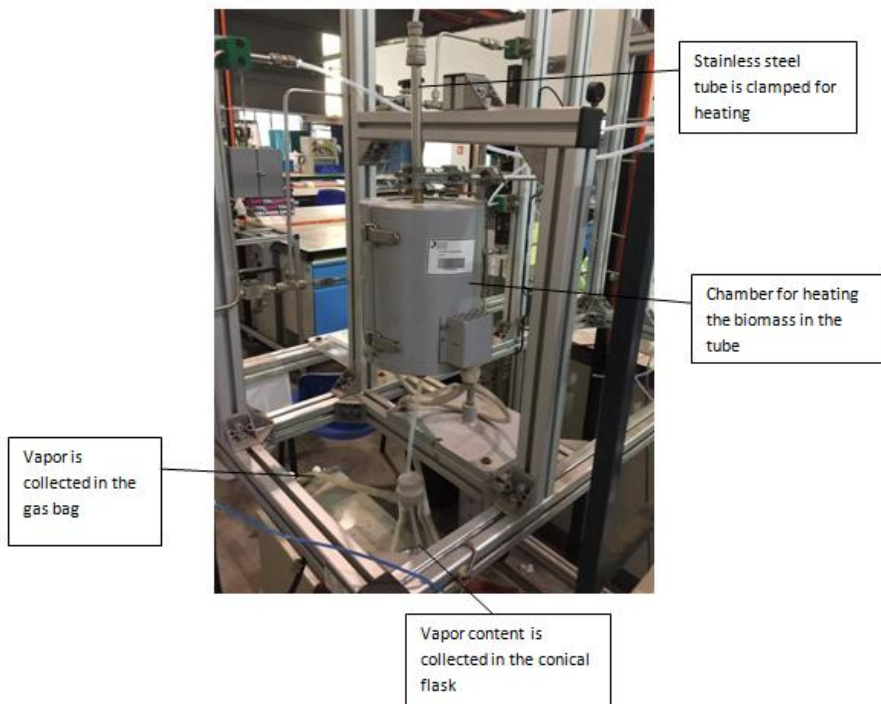
A stainless steel tube with an internal diameter of 12.4 mm and a length of 500 mm of vertical reactor was used for the torrefaction process. In each experiment, about 2 grams of biomass was placed on the sieve plate of the reactor and then the reactor was put manually in the reactor. Each case a small amount of glass wool was placed above the plate to prevent biomass sample from leaking during the torrefaction process. The torrefaction temperature was kept constant within a range of  $\pm 3$  °C in different final temperature (240 °C, 270 °C, 300 °C and 330 °C) during the whole process. Finally, the reactor was pulled out and cooled with a nitrogen flow rate 10mL/min purge to prevent further reaction with the surrounding air. A plate with a hole was originally fixed and located 200 mm above the bottom of the tube. After 30 minutes, the heater was turned off and the reactor was left to cool down to ambient temperature. The experiment was repeated with different woody biomass. Samples were initially dried at 240 °C for 30 min and 60 min. The final temperatures and residence times used were listed in Table 3.1. Here, the residence time was taken as the time at which the treatment dwells at the maximum reaction temperature, after which the samples were rapidly quenched under nitrogen flow to prevent further reaction. However, it was noted that the cooling stage exhibited a sample dependency, and cooling to below 200 °C could be of significant duration. Therefore, strictly speaking the residence times were between 10-20 min longer than intended. The final temperature in the centre of the bed was also noted to be higher than the set point (up to 20 °C higher), indicating the torrefaction process can be exothermic. The resulted torrefied product was weighed and the mass yield was calculated as percentage of the original mass sample.

**Table 3.1:** Conditions used in this study.

Species	Temperature/°C	Residence Time/min
Seraya	240,270,300,330	30 and 60
Meranti	240,270,300,330	30 and 60



**Figure 3.2:** Apparatus for purging the biomass by nitrogen gas.



**Figure 3.3:** Apparatus used for the torrefaction biomass and collection of the gas and liquid product.

In this research, the torrefaction of the investigation biomass fuels were investigated. The gas bag used to collect the gas from torrefaction was connected to a gas chromatography (Gas Chromatography GC 6890 Series) as shown in Figure 3.4, where methane, carbon dioxide and carbon monoxide were detected. Gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of torrefied sample pass in a gas stream at different rates depending on their various chemical and physical properties and their interaction with a specific column filling which is called the stationary phase. The chemicals exit the end of the column, they were detected and identified electronically. The graph result of the different samples was obtained within 20 minutes.



**Figure 3.4:** Gas chromatograph 6890 Series that was used to detect the permanent gases (CH<sub>4</sub>, CO<sub>2</sub> and CO)

### 3.3.4 Torrefaction of biomass in Furnace

The torrefaction experiment was performed using a furnace and the mass loss rate with temperature was recorded under inert gas atmosphere. In the case, the biomass was heated by furnace for proximate analysis after preheated. The analysis will be conducted at three different temperatures which are 240 °C, 270 °C, 300 °C and 330 °C, and will be held for 30 min. The experiment was repeated with different woody biomass.

## 3.4 Measurements

### 3.4.1 Fuel characterization

#### 3.4.1.1 Proximate analysis using ASTM Standard methods

Determination of moisture, ash and volatile matter content were carried out based on the methods laid out in the ASTM standards D-1762-84 (ASTM International. 2007) and E-1755-01 (ASTM International. 2015) respectively. These determinations were carried out in duplicates and the mean values were taken for further analysis. These determinations were done for samples studied in Chapter 4 result and discussion.

#### 3.4.1.2 Moisture content, $M_{ad}$

A minimum of 1 g of the ground sample was added into a flat dish in an even layer and this was weighed together with its lid on to the nearest 0.0001 g. The uncovered dish and lid was heated separately in the oven at 105 °C for two to three hours. After drying, the lid was replaced while the dish was still in the oven. They were allowed to cool at the room temperature in desiccators and reweighed. Only the raw materials of Seraya and Meranti sawdust were calculated.

$M_{ad}$  is expressed as percentage by mass and calculated using the formula equated below:

$$M_{ad}(\%) = \left( \frac{m_A - m_B}{m_A} \right) \times 100$$

where,

$m_A$  is the grams of air-dry sample used, and

$m_B$  is the grams after drying at 105 °C

#### 3.4.1.3 Ash content, $A_d$

A minimum of 1 g of Seraya sawdust for the residence time 30 min was added into a crucible in an even layer and this was weighed to the nearest 0.0001 g. The crucible was then heated into a furnace at 250 °C for 60 min and raised to (550±10) °C for another two to three hours. In the end, the crucible was allowed to cool and then weighed. The process repeated for Meranti sawdust.



$A_d$  is expressed as percentage by mass on a dry basis and calculated using the formula equated below:

$$Ash (\%) = \left( \frac{m_{ash} - m_{Cont}}{m_s} \right) \times 100$$

where,

$m_{ash}$  is the mass of ash and container, and

$m_{Cont}$  is the tare mass of container, and

$m_s$  is the mass of moisture free solids in the prepared biomass sample

#### **3.4.1.4 Volatile matter content, $V_d$**

A minimum of 1 g of Seraya sawdust for the residence time 30 min was added into a crucible in an even layer and this was weighed together with its lid to the nearest 0.0001 g. The covered crucible was preheated in the furnace at  $(900 \pm 10)$  °C for seven minutes. Then the furnace door opened for 2 min on the outer edge of the furnace (300 °C) and then for 3 min on the edge of furnace 500 °C. Then the crucible was left to cool to room temperature for 1 hour and reweighed. The process repeated for Meranti sawdust.

$V_d$  is expressed as percentage by mass on a dry basis and calculated using the formula equated below:

$$Vd (\%) = \left( \frac{m_B - m_C}{m_B} \right) \times 100$$

where,

$m_B$  is the grams after drying at 105 °C, and

$m_A$  is the grams of sample after drying at 950 °C

#### **3.4.1.5 Fixed carbon content, $FC$**

Fixed carbon content (dry basis) can be determined using the following equation by difference:

$$FC = 100 - \% Mad - \% Ad - \% Vd$$

### 3.4.2 Ultimate analysis

The elemental composition, C, H, N and S contents were measured using ELEMENTAR Vario Macro Cube analyser as pictured in Figure 3.5. Samples were ground and sieved to particle sizes of less than 1 mm in accordance with the requirements to do an ultimate analysis. Each was then weighed to 3-4 mg, wrapped in tin capsules and dropped into the chamber inside the analyser. Each sample was carried out in duplicates.

Carbon dioxide, water vapour and nitrogen dioxide were produced and separated into a chromatography column. Each quantity was detected using a thermal conductivity detector and compared with standards to determine the percentage of carbon, hydrogen and nitrogen. All instrument functions including gas flows and pressures are under digital control allowing computer diagnosis or even trouble shooting via internet. Advanced micro-electronics and Windows® software with integrated database are in full compliance with 21 CFR Part 11 for the most stringent requirements.



**Figure 3.5:** ELEMENTAR Vario Macro Cube analyser analyser.

### 3.4.3 Calorific Value Determination

According to Friedl et al., 2005, the author selected a data of 154 biomass samples (a subset of 122 samples) to investigate the correlation between heating values of biomass and elemental composition. Samples were grouped according to the type of biomass. The determination of C, H, N, S, and high heating values (HHV) were carried out as detailed in Friedl et al (2005).

In this research, the method using bomb calorimeter to compare the before and after of the torrefaction process which used to calculate HHV as pictured in Figure 3.6. The crucible of the calorimeter was filled with the sample mass of 0.5 g of woody, and then it was ignited. This heats the surrounding water, and the initial and final temperatures were recorded using a thermometer. The calorific value was determined using the heat balance. Heat given by the fuel was equal to the heat gained by the water. In the experiment, the torrefaction gas that was produced at high energy yields had the lowest calorific value and it can be problematic to combust. The Calorific Value, CV(MJ/kg) of raw and torrefied product was calculated as percentage of the original mass sample, as follows

$$CV \left( \frac{MJ}{Kg} \right) = \left[ \frac{(T \times W) - (2.3 \times B)}{M} \right] \times (4.18 \times 10^3)$$

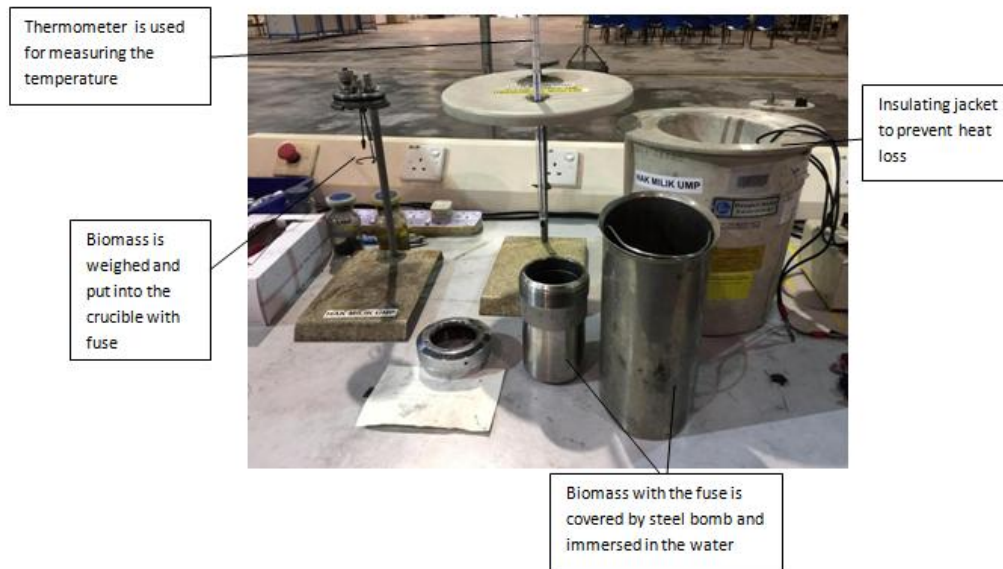
where

T = Temperature Different, °C

W = Weight of water, g

B = Length of unburned fuse, cm

M = Mass of biomass, g



**Figure 3.6:** Bomb calorimeter that was used to measure the HHV of biomass.

### 3.4.4 Mass and Energy Yield Analysis

The biomass subjected to change in mass and energy yield during the process. The energy yield of the torrefied biomass was less compared to higher heating value of the original biomass, as some of the volatile matter which contributed to the energy content leaves the solid torrefied product. Mass and energy yield were calculated using the equations below (Bergman et al., 2005).

$$\text{Mass Yield (\%)} = \frac{\text{Mass torrefied solid product} \left[ \frac{\text{kg}}{\text{kg}} \right]}{\text{Mass organitng biomass} \left[ \frac{\text{kg}}{\text{kg}} \right]} \times 100$$

$$\text{Energy Yield (\%)} = \text{Mass yield} \times \frac{\text{HHV of torrefied solid product}}{\text{HHV of organitng biomass}} \times 100$$

Where HHV is the higher heating value

### 3.5 Morphology of Raw and Torrefied Biomass

#### 3.5.1 Carl Zeiss Scanning Electron Microscope

Scanning Electron Microscopy (SEM) EVO-50 analysis was carried out to study the changes in structure and chemical composition of the samples due to the treatments respectively. Samples were sieved between 500 $\mu\text{m}$  to 1mm to this experiment. Samples were then stuck onto a carbon coated and placed inside the analyser for analysis. Figure 3.7 presents the instruments used were EVO-50 SEM with the magnificant of 1000%.



**Figure 3.7:** Scanning Electron Microscopy (SEM) EVO-50 that was used to take SEM images

## 4 RESULT AND DISCUSSION

### 4.1 Introduction

Problems associated with the properties and characterization of torrefied biomass have long been identified ever since they are put into energy use. There is no doubt that the biomass as a renewable source of energy can provide positive contributions to reach the EU target. However, high maintenance costs, loss of financial support and loss of jobs can be part of the reasons for its decline in the future if the issues continue. Several pre-treatments have been practiced and they are previously discussed in Chapter 1. One of the pre-treatments of biomass that now has increasing interest is torrefaction. This thermo-chemical treatment has been studied for its ability to upgrade the chemical and physical properties of a biomass.

Several studies, as thoroughly described in Chapter 3, have been conducted using different final temperatures within the range of 240-330 °C and residence times, that is mainly 30-60 min (Prins et al., 2006b; Rodrigues and Rousset, 2009; Bridgeman et al., 2008; 2010; Chen et al., 2011; Phanphanich and Mani, 2011; Medic et al., 2012). A few studies extended the residence time to three to five hours (Arias et al., 2008; van der Stelt et al., 2011). In general, all results showed that the more severe the torrefaction conditions are improved the solid end-product is such as the ease of grinding and the greater amount of milling energy that can be saved (Melkior et al., 2012). However, the mass loss of the solid torrefied product must be kept as low as possible to attain a reasonably high energy yield (Melkior et al., 2012).

With regards to the solid torrefied biomass, there has been a great deal of research considering the standard fuel analysis, mass yield and energy yield (Chen et al., 2011; Bridgeman et al., 2008; Prins et al., 2006; van der Stelt et al., 2011; Pentananunt et al., 1990; Pimchuai et al., 2010; Rousset et al., 2011). While a few studies have reported the improvement of their grindability properties (Chen et al., 2011; Arias et al., 2008). However, very little research has given a thorough look into the structure and physicochemical properties of the solid product (Chen et al., 2011). This chapter focuses on the investigation of not only the morphology and composition of the solid torrefied biomass but also, their physical and chemical characteristics. Furthermore,

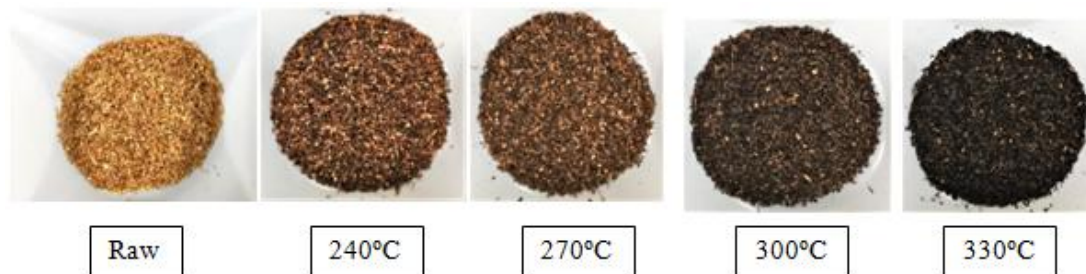
the chemical composition of the torrefied products were also studied. All these methods are described in Section 3.4.2.

## 4.2 Visual Observation

The change in colour was recorded for all torrefied samples compared with the raw biomass. The originally pale brown Seraya sawdust turned dark black-brown from raw material to 330 °C, and the mostly grey wood Meranti turned black in Figure 4.1 to Figure 4.4. The harsher the torrefaction conditions for example increased temperature and residence time, the darker the product colour.

From manipulation of samples after torrefaction, the originally dense, high strength woods seemed more brittle. No change in particle size and shape was recorded and is attributed to the stationary nature of reaction within the furnace and the raw biomass used being pre-processed.

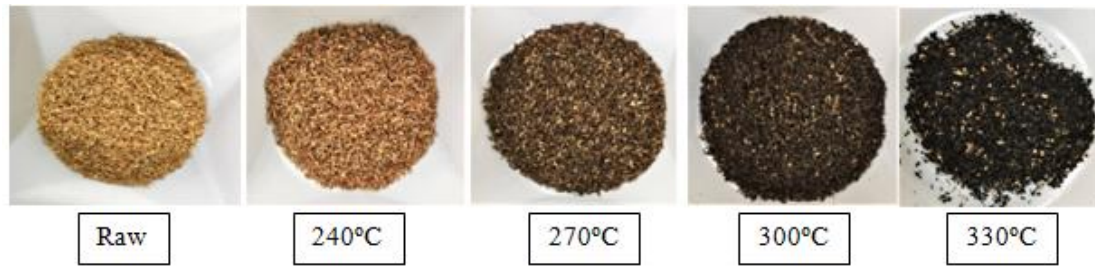
### 4.2.1 Visual appearance of the raw and torrefied Seraya sawdust for the residence time 30 minutes



**Figure 4.1:** Visual appearance of the raw and torrefied Seraya at different temperature (240 °C, 270 °C, 300 °C and 330 °C) for the residence time 30 minutes

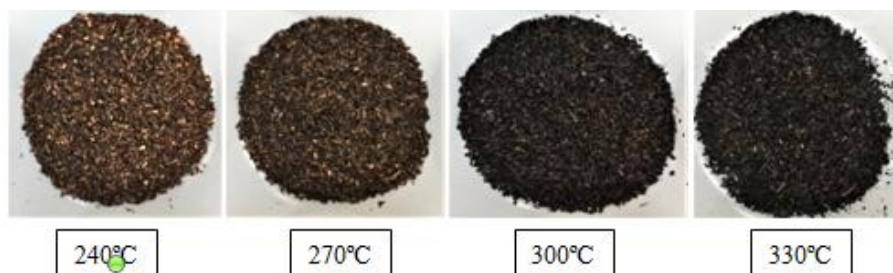


**4.2.2 Visual appearance of the raw and torrefied Meranti sawdust for the residence time 30 minutes**



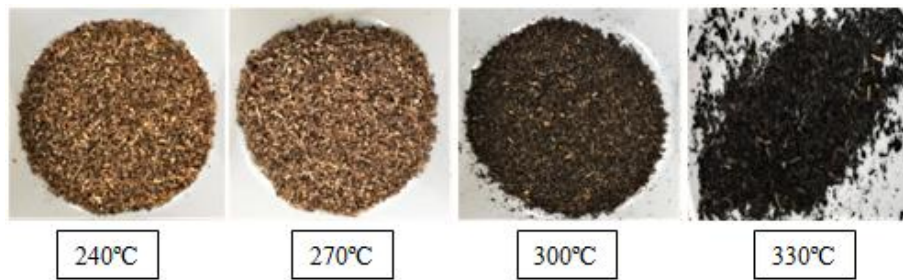
**Figure 4.2:** Visual appearance of the raw and torrefied Meranti at different temperature (240 °C, 270 °C, 300 °C and 330 °C) for the residence time 30 minutes

**4.2.3 Visual appearance of the raw and torrefied Seraya sawdust for the residence time 60 minutes**



**Figure 4.3:** Visual appearance of the raw and torrefied Seraya at different temperature (240 °C, 270 °C, 300 °C and 330 °C) for the residence time 60 minutes

#### 4.2.4 Visual appearance of the raw and torrefied Meranti sawdust for the residence time 60 minutes



**Figure 4.4:** Visual appearance of the raw and torrefied Meranti at different temperature (240 °C, 270 °C, 300 °C and 330 °C) for the residence time 60 minutes

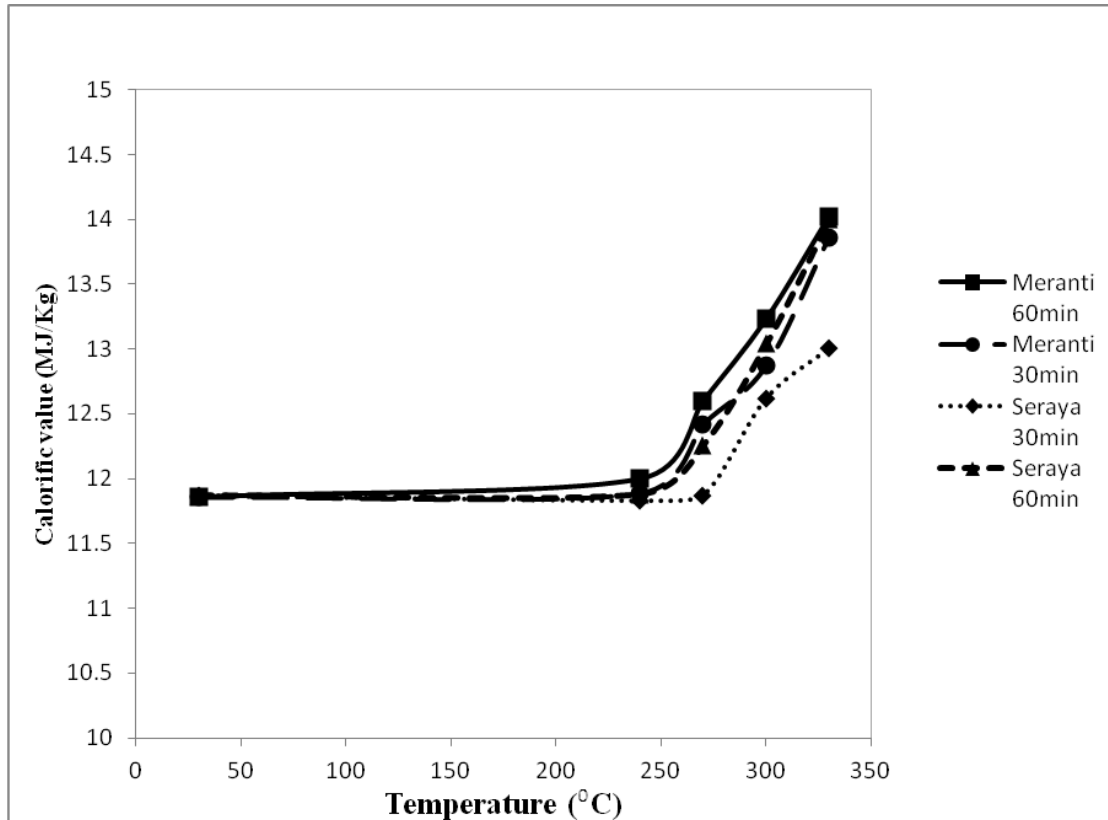


### 4.3 Calorific Value Determination

Analysis of the calorific value for the torrefied woods were performed in order to evaluate the effect of this treatment in the heating value delivered per unit mass. Table 4.1 shows the average heating value obtained for the torrefied wood of two species in different residence time, in MJ/Kg.

**Table 4.1:** Calorific Value of raw and torrefied of wood biomass that were treated at different temperature (°C) and residence time (min)

Biomass	Time(min)	Temperature (°C)	Calorific Value (MJ/Kg)
<b>Raw Seraya</b>			11.87
<b>Seraya</b>	30	240	11.83
		270	11.87
		300	12.62
		330	13.01
	60	240	11.88
		270	12.26
		300	13.04
		330	14.00
<b>Raw Meranti</b>			11.86
<b>Meranti</b>	30	240	11.89
		270	12.42
		300	12.87
		330	13.86
	60	240	12.00
		270	12.61
		300	13.23
		330	14.02



**Figure 4.5:** The raw and torrefied Seraya and Meranti sawdust for the residence time 30 minutes 60 minutes in different temperature.

Results from the net calorific value tests of the torrefied wood in Figure 4.5 indicated a high increased in energy that was obtained from the torrefied samples. The highest calorific value obtained is 14.02 MJ/Kg for the sample Wood Meranti with the residence time 60 minutes. After wood torrefaction, oxygen with negative contribution to the heating value were removed from the biofuel, reacting with hydrogen to form mainly H<sub>2</sub>O and volatile carbon to form mainly CO<sub>2</sub>. This results in an energy dense hydrochar with increased heating value compared with raw biomass. The improvement in HHV of various biomass fuels after wood torrefaction was demonstrated in Figure 4.5. Therefore, this enhanced heating value was related to the low moisture content of the product and partial elimination of volatiles content from the wood and leaving more carbon (as a percentage weight) for use as burning fuel (Pirraglia et al., 2012).

According to Uslu et al., 2008, the authors report an estimated torrefied wood production cost of around 58€ per ton at the present time, without considering feedstock costs and in a small- scale factory. Further analysis is needed to assess

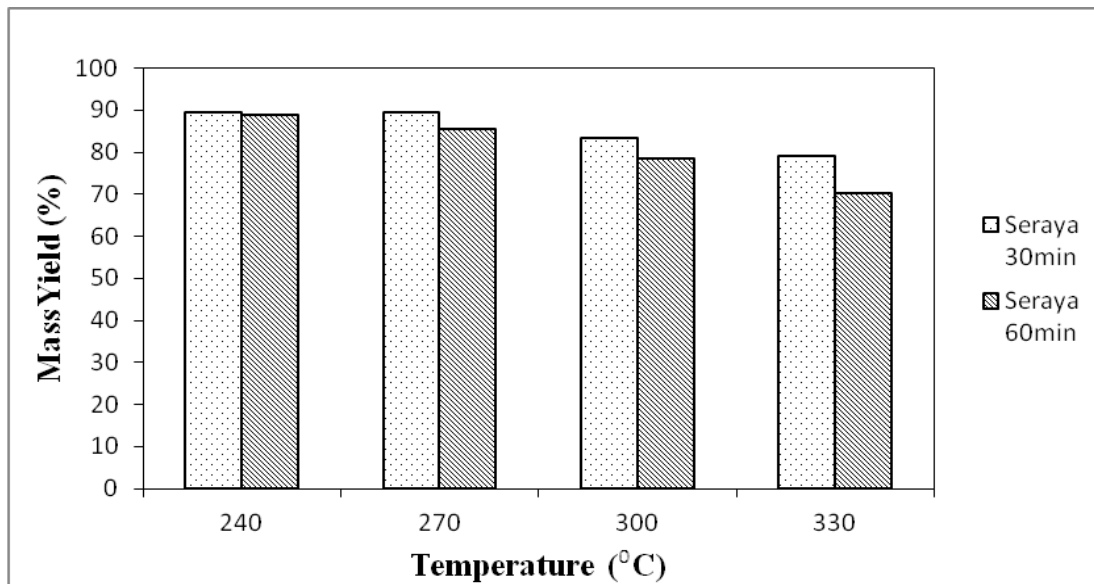
production costs of torrefied wood considering economy of scale and Malaysia market conditions.

#### 4.4 Mass Yield

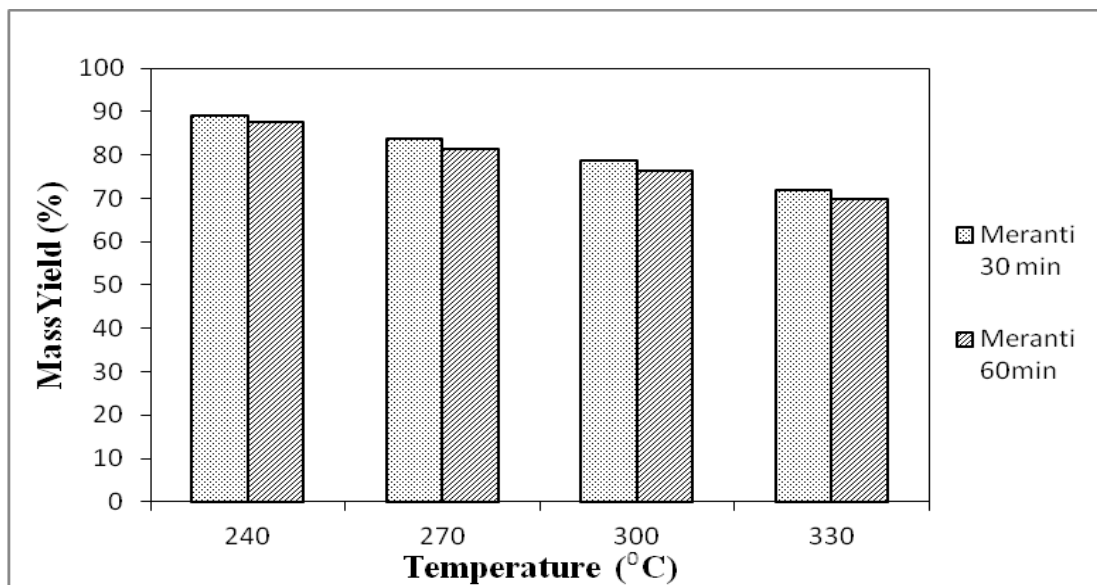
The resultant mass yields of biomass fuels and the changes in mass yields with response to temperature, T and residence time, t are listed in Table 4.2. In general, the results showed that temperature plays a more important role in torrefaction than the residence time. For example, the change in mass yield received a greater impact with a change in T than t, which was about 20-30% mass loss extra. According Bridgeman et al., 2010, the process variables with a factorial method using a three-factor methodology (temperature, residence time and particle size). They concluded that temperature had the greatest influence on the change in both mass yields of willow and Miscanthus, followed by residence time (Bridgeman et al., 2010). With regards to Meranti, the changes of mass yields due to both changes seem to show a bigger impact in comparison to the other biomass fuels such as Seraya.

**Table 4.2:** Mass yields of wood biomass that were treated at different temperature (°C) and residence time (min)

<b>Biomass</b>	<b>Time(min)</b>	<b>Temperature (°C)</b>	<b>Mass Yield (%)</b>
<b>Seraya</b>	30	240	89.7
		270	89.7
		300	83.55
		330	79.1
	60	240	89
		270	85.5
		300	78.5
		330	70.3
<b>Meranti</b>	30	240	89
		270	83.7
		300	78.8
		330	71.8
	60	240	87.7
		270	81.3
		300	76.2
		330	69.8



**Figure 4.6:** Effect of time on mass yields of Seraya sawdust with different residence time



**Figure 4.7:** Effect of time on mass yields of Meranti sawdust with different residence time

Raw biomass was deliberately subjected to limited conversion in the torrefaction process. According to Juniper, the valuable intermediates synthesized in the process are used for energy recovery at a later stage. In the torrefaction temperature range of 240–330 °C, mass loss was dominated by dehydration and devolatilization in the reaction regime of hemicelluloses component (Arias et al., 2008). In Section 2.4, analysis indicates that weight loss was accompanied by reduction in the hemicelluloses and primary lignin sections (Nimlos et al., 2003). The significant mass

loss at the preliminary stage of torrefaction showed reduction in the moisture of the treated biomass (Sadaka S. et al., 2009). Mass yield of different biomass subjected to torrefaction process is illustrated in Table 4.2. The mass yield of torrefied biomass can vary from 10% to 30% of its original weight. Conversion rate of agricultural residues is comparatively higher than woody biomass due to its higher hemicelluloses content, thus resulting in lower mass yield (Bridgeman et al., 2008).

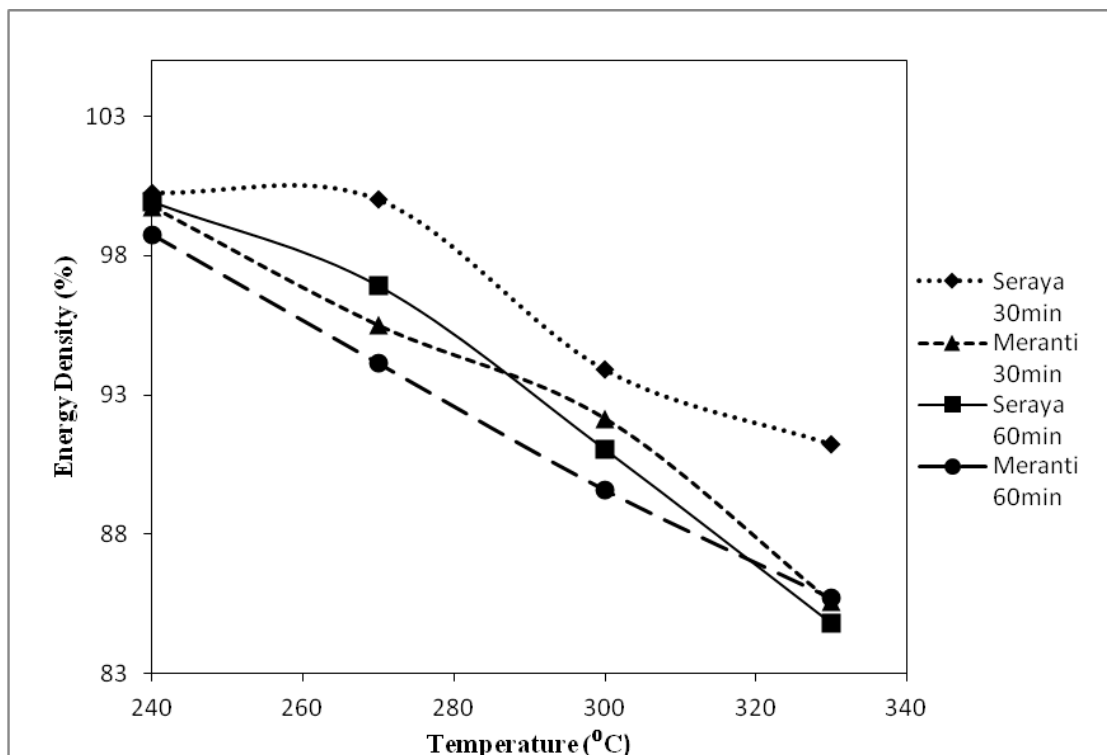
Figure 4.6 and 4.7 shows the effect of torrefaction temperature on the mass yield of torrefied Seraya and Meranti sawdust. The mass loss of woody attributed to the release of moisture and volatile matter. During the torrefaction, moisture content was released following two different mechanisms. The first mechanism was the evaporation of moisture content in biomass, and the second one was the dehydration reaction of organic components of biomass.

Torrefaction temperature greatly influenced the mass yield. When the torrefaction temperature was 240 °C, the mass loss was not obvious and the mass yield of Seraya sawdust were 89.7% and 89% for the residence time 30 and 60 minutes respectively. Whereas the mass yield of Meranti sawdust were 89% and 87.7% for the residence time 30 and 60 minutes respectively. The mass loss was caused by the evaporation of moisture content and only a slight decomposition of sample. At 330 °C, the mass yield of Seraya sawdust decreased to 79.1% and 70.3% for the residence time 30 and 60 minutes respectively. Whereas the mass yield of Meranti sawdust decreased to 71.8% and 69.8% for the residence time 30 and 60 minutes respectively. The mass loss in this stage was caused by the dehydration reaction of the components biomass. Therefore, the wood Meranti had the lowest the mass yield for the residence time 60 minutes at 330 °C.

#### 4.5 Energy Yield and Energy Density

Energy density is the amount of energy stored in a given system or region of space per unit volume or mass, though the latter is more accurately termed specific energy. Often only the useful or extractable energy is measured, which is chemically inaccessible energy such as rest mass energy is ignored. The important characteristic of torrefied wood biomass was its decreased in energy density when compared to raw biomass. This was the result of decreased in mass of torrefied wood through the release of compounds rich in carbon (Dorde, 2012). It can be seen in Figure 4.8 that temperature had strongest impact on energy density of torrefied biomass, while the effect of time and moisture is much less expressed. At 240 °C, the highest energy density was 100.30% of Seraya sawdust with the residence time 30 minutes. The trend of energy density was decreased to 91.24% at 330 °C. The lowest energy density was 98.75% of Meranti sawdust with the residence time 30 minutes at 240 °C. However, the lowest energy density was 84.75% of Seraya sawdust with the residence time 60 minutes at 330 °C. The energy density formula is given as below,

Energy Density,  $U = \text{Energy yield} / \text{Mass yield} * 100\%$



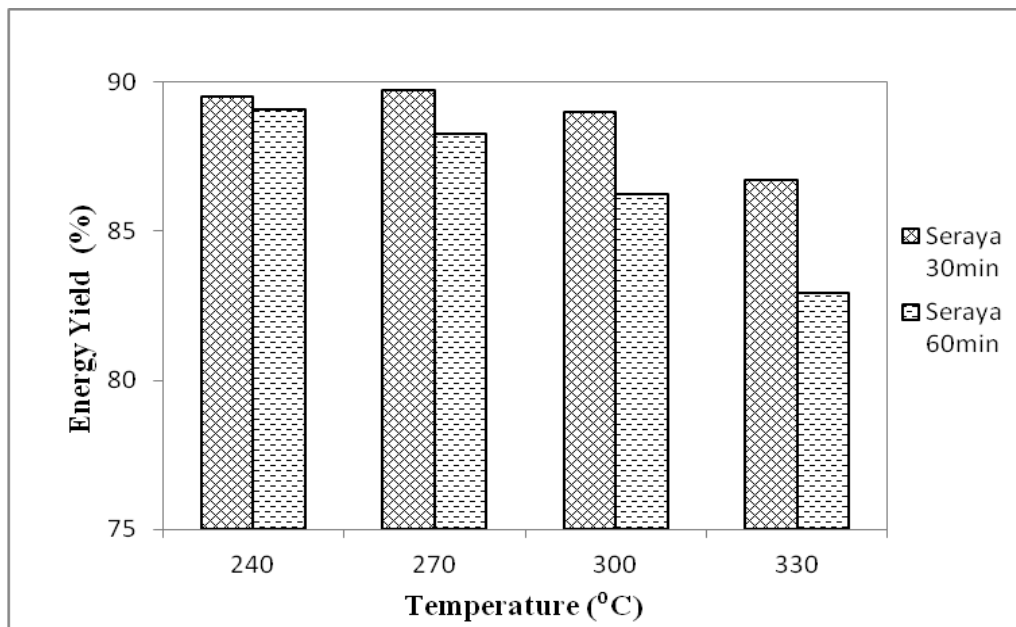
**Figure 4.8:** Energy density of wood biomass that were treated at different temperature (°C) and residence time (min)

Energy yield based upon the mass yield and calorific value was viewed as an indicator of the amount of energy lost during torrefaction. It was computed from mass yield and calorific values using Equation below and expressed as a percentage of energy content of untreated dry biomass.

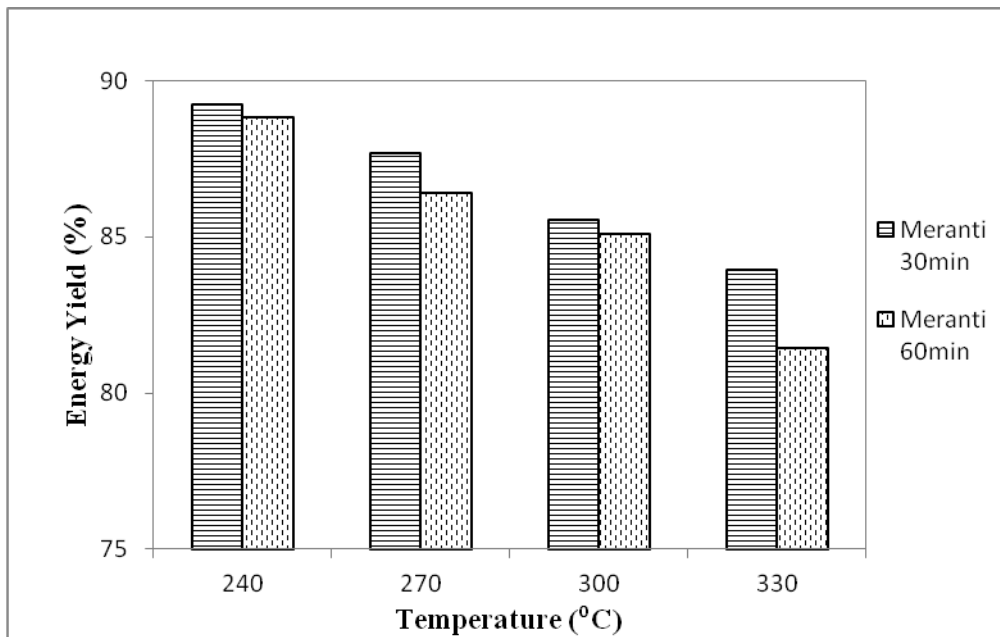
$$\text{Energy Yield (\%)} = \text{Mass yield} \times \frac{\text{HHV of torrefied solid product}}{\text{HHV of organititing biomass}} \times 100$$

Where HHV is the heating value

Energy yields computed using Equation 3 are shown in Figure 4.9 and 4.10.



**Figure 4.9:** Effect of time on energy yields of Seraya sawdust with the different residence time



**Figure 4.10:** Effect of time on energy yields of Meranti sawdust with the different residence time

Figure 4.9 and 4.10 showed the effect of torrefaction temperature on the energy yield of torrefied wood in the residence time 30 minutes and 60 minutes respectively. The mass losses of woods were attributed to the release of moisture and volatile matter. During the torrefaction, hydrogen content is reduced but increased the carbon content of wood with increasing the temperature.

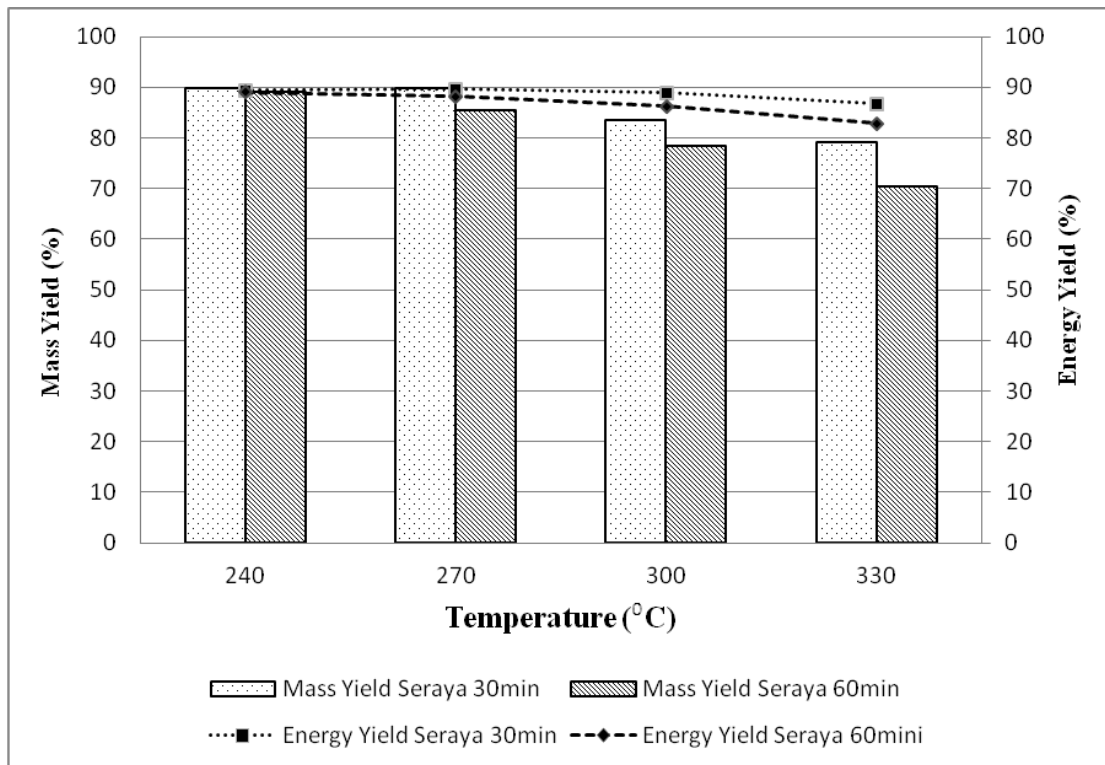
In the Table 4.3, comparison of the energy yield of torrefied wood in difference residence time, wood Meranti for the residence time 60 min had a more noticeable impact on the energy yield. When the torrefaction temperature was at 240 °C, the energy yield of Seraya sawdust at residence time 30 and 60 min were 89.47% and 89.07% respectively while the energy yield of Meranti sawdust was less than 0.25% of energy yield compared with wood Seraya at 89.23% and 88.81% respectively. When temperature was increased at 330 °C, the energy yield decreased quickly due to the most of the carbon content increased and the cellulose started to decompose. The energy yield of Seraya sawdust at residence time 30 and 60 min, were 86.7% and 82.91% respectively compared to torrefied Meranti sawdust had a large difference. The value of energy yield of the wood Meranti were 83.91% and 81.44% respectively. However the energy yield at 60 min, wood Meranti is more than 1.4% of energy yield compared with wood Seraya at 82.91% and 81.44%. Therefore the torrefied wood



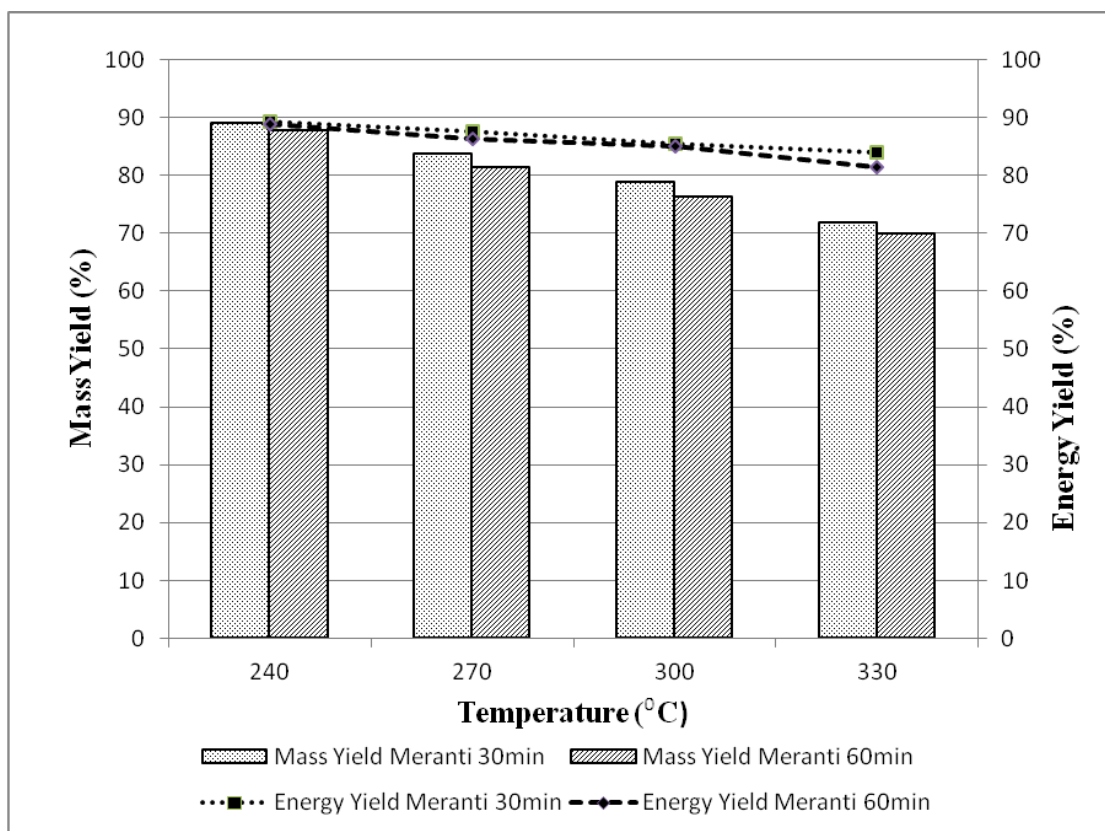
Meranti had lowest energy yield compared with wood Seraya when the temperature increased.

**Table 4.3:** Energy yields of wood biomass that were treated at different temperature (°C) and residence time (min)

<b>Biomass</b>	<b>Time(min)</b>	<b>Temperature (°C)</b>	<b>Energy Yield (%)</b>
<b>Seraya</b>	30	240	89.47
		270	89.7
		300	88.97
		330	86.7
	60	240	89.07
		270	88.24
		300	86.24
		330	82.91
<b>Meranti</b>	30	240	89.23
		270	87.65
		300	85.51
		330	83.91
	60	240	88.81
		270	86.37
		300	85.06
		330	81.44



**Figure 4.11:** Effect of temperature on mass and energy yields of Seraya sawdust with different residence time



**Figure 4.12:** Effect of temperature on mass and energy yields of Meranti sawdust with different residence time

The results were shown in Figure 4.11 and 4.12 was the comparison of the mass and energy yield for the torrefied wood biomass in residence time 30 minute and 60 minutes. The losses in the quantitative measure (mass yield) did not show any importance while selecting an operating condition of the torrefaction process. The higher mass loss could be desirable if the qualitative measure (energy yield) was within an acceptable range (Bridgeman et al., 2008). Therefore, the quality of the sawdust which was measured in term of the energy density of torrefied biomass that was a greater importance.

Mass yield and energy yield were remained mass, in solid phase, and energy content of torrefied biomass compared to raw biomass (Nithitron, 2011). The results of the energy and mass yield of different torrefied biomass at torrefaction temperatures of 270 °C are shown in Figure 4.11 and 4.12. It can be seen that, for all products of torrefied biomass, the energy yield was greater than the mass yield and becomes more marked for higher torrefied temperature, as shown in Figure 4.11 and 4.12. This phenomenon affected to increase in calorific value of torrefied biomass as mentioned above. At torrefaction temperature higher than 270 °C, the mass lost was more pronounced than energy lost. This was believed to result in markedly increasing of calorific value of torrefied biomass at torrefaction temperature greater than 270 °C in Figure 4.5.

The heating value of the torrefied biomass increases because it has more C-C and C-H bonds with the aromatic molecules (Ben and Ragauskas, 2012) with an ability to release more energy than O-H and C-H bonds in the raw biomass. The reduction in the hydrogen reduces the O/C and H/C ratios of biomass. This moves the torrefied biomass towards the coal side. The higher torrefaction temperature and residence time decrease O/C and H/C ratios and move the torrefied product close to that of the coal. Thus the mass yield and energy yield of torrefied wood decreased when the temperature raised up. At temperature 330 °C, the mass yield of wood Seraya and Meranti were 79.1% and 71.8% for residence time 60 minutes is lower than the residence time 30 minutes that mass yields were 70.3% and 69.8% respectively. On the other hand, the energy yield of wood Seraya and Meranti were 82.91% and 81.44% for residence time 60 minutes is lower than the residence time 30 minutes that

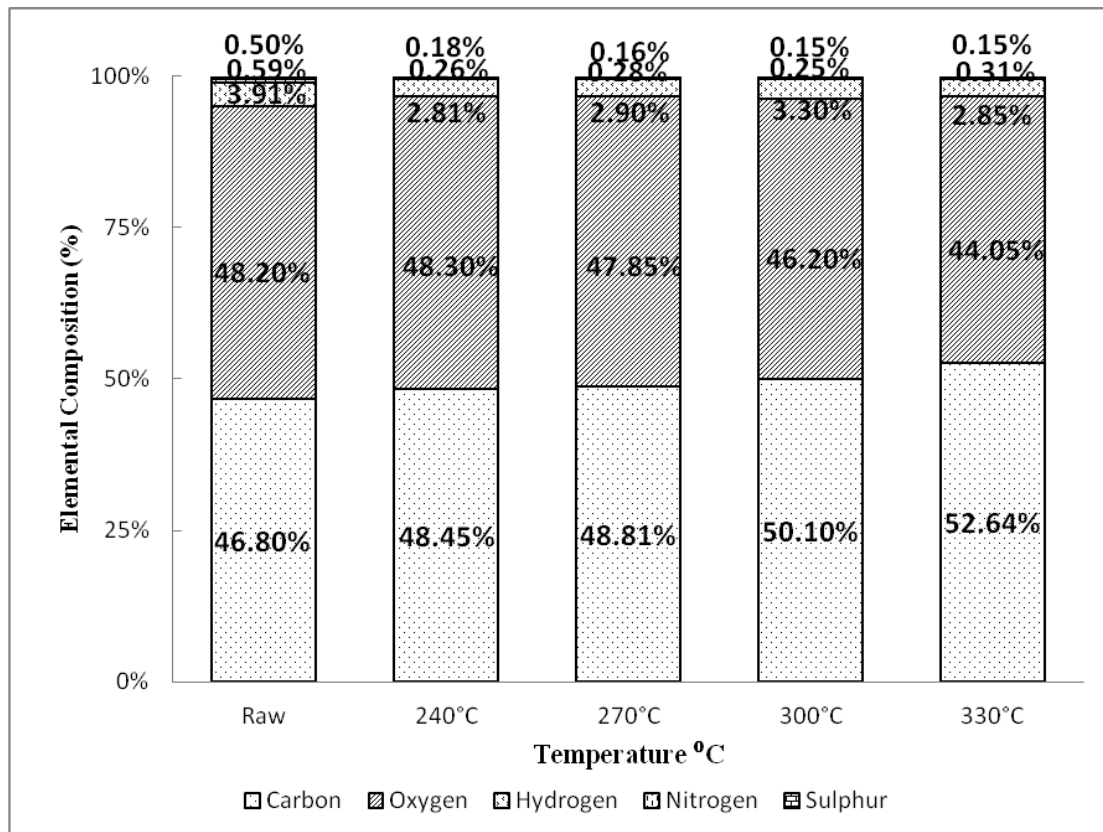
energy yields were 86.7% and 83.91% respectively. The torrefied wood Meranti had the lowest of the mass yield and the highest of energy yield for the residence time 60 minutes compare to torrefied wood Seraya for the residence time 30 minutes and 60 minutes. As a result, torrefied wood Meranti can be provided a high heating energy as a fuel.

## **4.6 Fuel characterization**

### **4.6.2 Ultimate analysis**

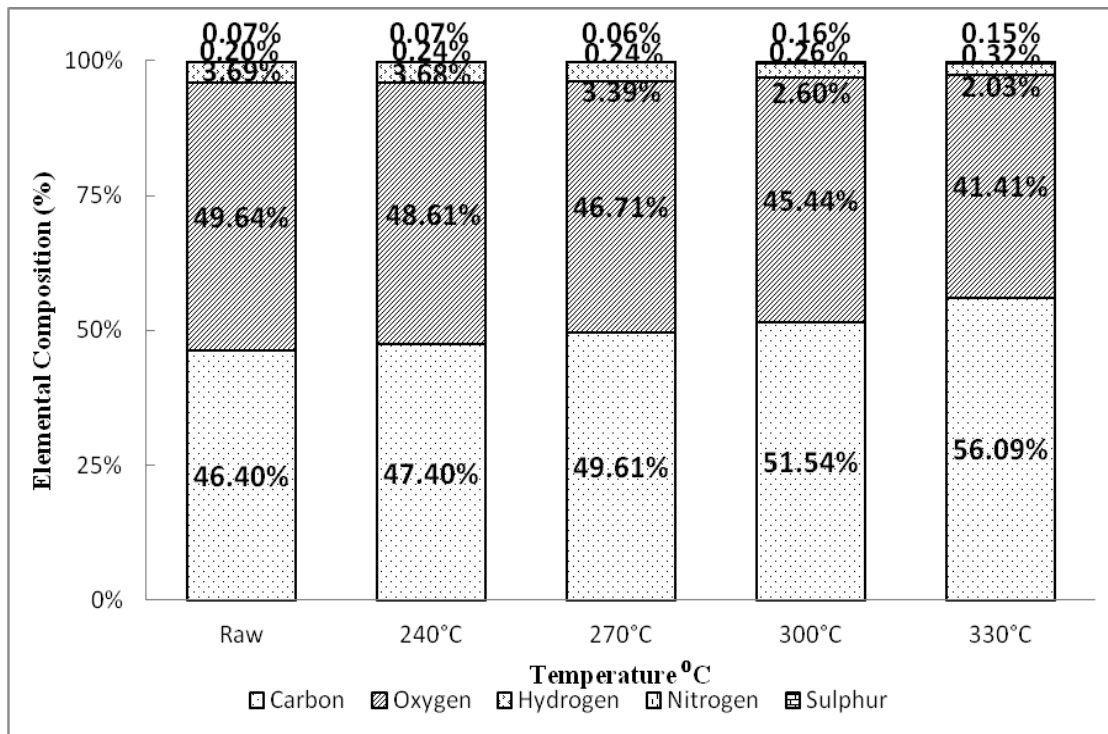
The determination of carbon, hydrogen, oxygen, and nitrogen composition for each torrefied wood sample was determined assuming the composition of the torrefied wood is based on these four elements. Figure 4.13 and 4.14 showed the average of C, H, O, N, and S, based on the average of raw and torrefied wood Seraya and wood Meranti with the residence time 30 minute in different temperature.

The ultimate analysis of the torrefied wood Seraya showed lower hydrogen content in the samples (3.91% for raw and 2.85% for torrefied wood at 330 °C), decreased 1.06% compared to the raw material in Figure 4.13. The nitrogen and sulphur contents did not show a difference as substantial as the one found for oxygen (0.59% and 0.31% for raw respectively, and 0.50% and 0.15% for torrefied wood at 330 °C), while the samples also displayed a high increase in the elemental carbon content (46.80% for raw material, and 52.64% for torrefied wood at 330 °C), increased 5.84% compared to the raw material due to the displacement of oxygen out of the torrefied sawdust in Figure 4.13. The increasing elemental carbon content was an indication of an enhanced heating value of the material being torrefied (Uslu et al. 2008), as it was demonstrated the HHV tests of the samples in section 4.3.



**Figure 4.13:** Ultimate analysis for the torrefied Seraya sawdust compared to the temperature

The ultimate analysis of the torrefied wood Meranti showed lower hydrogen content in the samples (3.69% for raw and 2.03% for torrefied wood at 330 °C), decreased 1.63% compared to the raw material in Figure 4.14. The nitrogen and sulphur contents did not show a difference as substantial as the one found for oxygen (0.20% and 0.32% for raw respectively, and 0.07% and 0.15% for torrefied wood at 330 °C), while the samples also displayed a high increased in the elemental carbon content (46.40% for raw material, and 56.09% for torrefied wood at 330 °C), increased 9.69% compared to the raw material due to the displacement of oxygen out of the torrefied sawdust in Figure 4.14. The increasing elemental carbon content was an indication of an enhanced heating value of the material being torrefied (Uslu et al. 2008), as it was demonstrated the HHV tests of the samples in section 4.3.



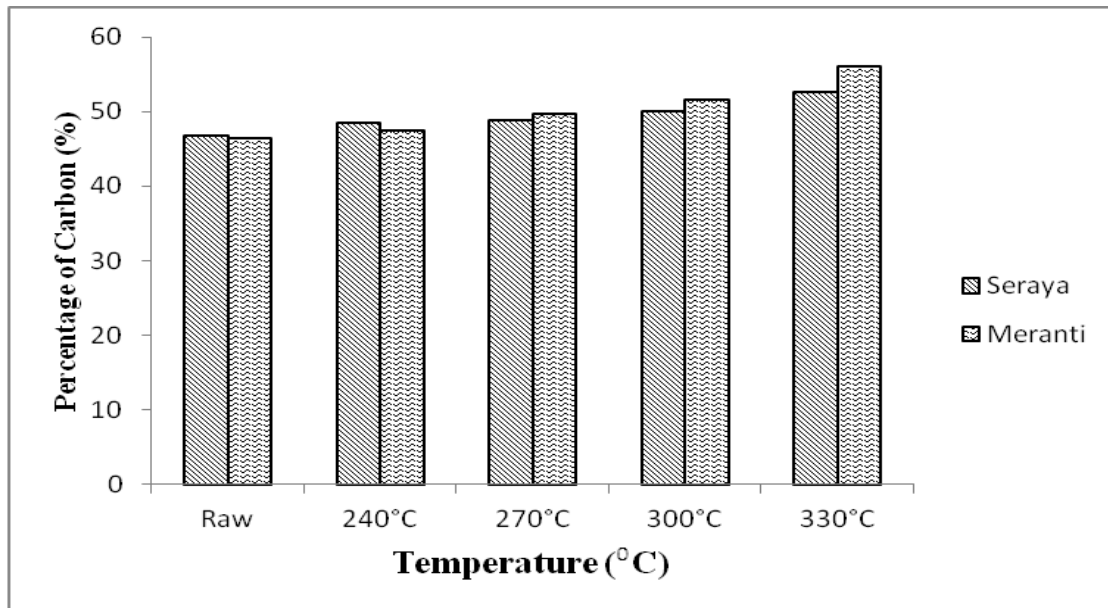
**Figure 4.14:** Ultimate analysis for the torrefied Meranti sawdust compared to the temperature

**Table 4.4:** The ultimate analysis of the biomass Seraya and Meranti sawdust for the residence time 30 minutes

Biomass	Condition	C (%)	H (%)	N (%)	O (%)	S (%)
MERANTI	Raw	46.40	3.69	0.2	49.64	0.07
	240	47.40	3.68	0.24	48.61	0.07
	270	49.61	3.39	0.24	46.71	0.06
	300	51.54	2.60	0.26	45.44	0.07
	330	56.09	2.03	0.32	41.41	0.15
SERAYA	Raw	46.80	3.91	0.59	48.20	0.50
	240	48.45	2.81	0.26	48.30	0.18
	270	48.81	2.90	0.28	47.85	0.16
	300	50.10	3.30	0.25	46.20	0.15
	330	52.64	2.85	0.31	44.05	0.15

Results from the carbon content of the torrefied wood between two species of wood in Figure 4.15 indicated a high content of carbon that was obtained from the wood Meranti. The highest percentage of carbon obtained is 56.09% for the sample Meranti sawdust with the residence time 30 minutes. Therefore, this enhanced heating value is

related to the high carbon content of the product for use as burning fuel (Pirraglia et al., 2012).



**Figure 4.15:** Graph of percentage carbon for raw and torrefied wood on different temperature

### 4.6.3 Proximate analysis

#### 4.6.3.1 Moisture content

The moisture content for the raw wood of Meranti and Seraya was calculated by cooling vs. the weight after drying the raw materials in an oven at  $103 \pm 2^\circ$ , being the moisture content reported in a dry-basis.

No technical published data were available describing moisture content of torrefied for the Seraya and Meranti sawdust species evaluated in this research. The original material moisture content Seraya and Meranti around 10.30% and 9.33% in an oven-dry basis respectively.

#### **4.6.3.2 Volatile matter, ash content, and fixed carbon content**

Experiments for the determination of volatile matter, ash content, and fixed carbon content were performed for each torrefied wood species in Table 4.3. These experiments were performed using the ASTM standard for the analysis of wood samples from Seraya to Meranti (Standards ASTM D-1762 and ASTM E-1755-01). Torrefied wood species were performed, and the results) are presented in Figure 4.16 and 4.17.

Biomass fuel compared to coal was its higher volatile matter (VM) and lower fixed carbon content (FC). Wood torrefaction helped to overcome these issues by reducing the VM and increasing the FC of the hydrochar, making the fuel more coal-like. Fig 4.16 and 4.17 showed graph of VM, FC and ash of hydrochars obtained from wood torrefaction of several biomasses including Seraya and Meranti (Bach et al., 2013).

Results of the proximate analysis for the torrefied material Table 4.3 indicated a higher content of ash is 2.71% and fixed carbon 31.51% for Meranti and Seraya at temperature 330 °C respectively as compared to the original material. This characteristic is due to the displacement of volatile matter (65.89% for Meranti, and 66.48% for Seraya) from the samples, caused by the heat treatment at the temperature 330 °C. Figure 4.16 and 4.17 demonstrated the change in Volatiles Matters, Fixed Carbon, and Ash content from the original material to the torrefied one. In this sense, the ash content obtained from Meranti torrefied (2.71%) was notably higher than the one obtained from Seraya (2.02%). Furthermore, the fixed carbon content of Seraya torrefied (31.51%) was considerably higher than that obtained with Meranti torrefied (31.43%). These results indicate that Seraya provided better fixed carbon content with lower ash content as compared to Meranti, when exposed to the torrefaction process. However, both species showed an increase in their fixed carbon content in weight percentage.

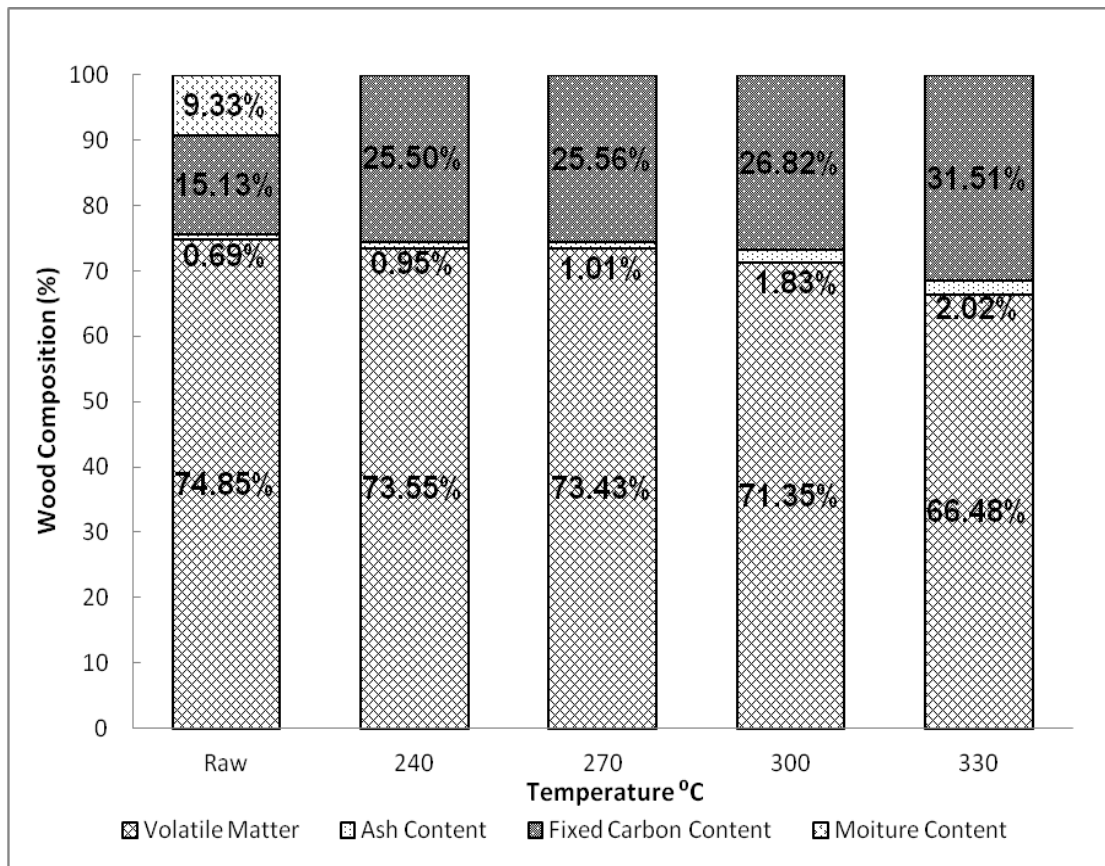
Table 4.5 showed that fixed carbon content increased while volatile content decreased as torrefaction temperature and residence time intensifies across different biomass. The disintegration of oxygen functional group had been accounted for the change of the proximate analysis compounds (Wannapeera et al., 2011). Volatile loss for Seraya and Meranti sawdust were around 12% which was relatively higher compared to the



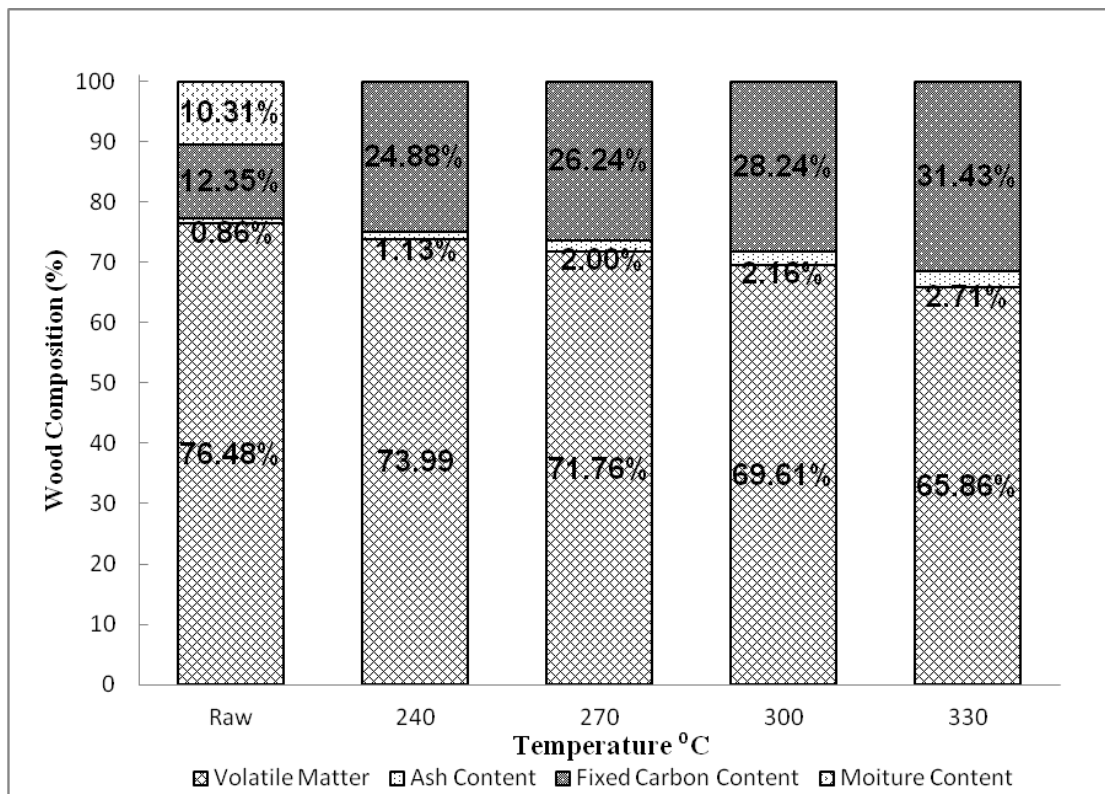
remaining biomass. Catalytic effect of inorganic mineral matter in the biomass has been accredited for the higher loss in volatile matter (Sadaka et al., 2009). Ash content generally increases from 0.69 to 2.71% after torrefaction, though comparatively lower compared to the change in fixed carbon content (12.35–31.51%). As the ash content is inherent to the sawdust chosen for torrefaction, the initial ash content of feed has relative impact on the resulting torrefied product (Bridgeman et al., 2010).

**Table 4.5:** Properties of proximate analysis for the wood Meranti and Seraya with the residence time 30 min

Biomass	Condition (°C)	Moisture Content (%)	Volatile Matter (%)	Ash Content (%)	Fixed Carbon Content (%)
MERANTI	Raw	10.31	76.48	0.86	12.35
	240		73.99	1.13	24.88
	270		71.76	2.00	26.24
	300		69.61	2.16	28.24
	330		65.86	2.71	31.43
SERAYA	Raw	9.33	74.85	0.69	15.13
	240		73.55	0.95	25.50
	270		73.43	1.01	25.56
	300		71.35	1.83	26.82
	330		66.48	2.02	31.51



**Figure 4.16:** Proximate analysis of the Seraya sawdust



**Figure 4.17:** Proximate analysis of the Meranti sawdust

The main elements in biomass include carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulphur (S). Carbon in a fuel was the major source of heat released from combustion. Hydrogen was also an important source of heat in combustion. However, more hydrogen contained in a biomass was usually accompanied by a lower content of carbon. Oxygen contained in biomass was conducive to fuel burning, but it reduced the calorific value of biomass. The higher the oxygen and ash contents in a fuel, the lower the heating value. Moreover, the moisture content in raw biomass was usually higher than that in torrefied biomass. As a result, the calorific value of biomass is lower than torrefied biomass.

In general, the atomic oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios in raw biomass were in the ranges of 1.03-1.07 and 0.01, respectively. After undergoing torrefaction, moisture and light volatiles, which contain more hydrogen and oxygen, are removed from biomass, whereas relatively more carbon is retained. This results in the slight or mild carbonization of biomass. As a consequence, the atomic O/C and H/C ratios are decreased to 0.74-0.84 and 0-0.001, respectively. The atomic H/C ratio and the atomic O/C ratio follow approximately linear relationship. Compared to torrefied, the sulphur content in biomass was much lower. Therefore, much less sulphur oxides were emitted into the atmosphere when biomass was burned. In recent studies it was found that sulphur contained in biomass was also reduced after torrefaction (Chen et al., 2012). The results demonstrated the suitability of both the torrefaction process and the utilization of its product as a biofuel, either as raw material for further processing, or for direct burning and co-firing, since the fixed carbon content is directly related to the heating value of a given biomass (Demirbas 1997; Parikh et al. 2005).

**Table 4.6:** The ratio O/C and H/C for the wood Meranti and Seraya with the residence time 30 min

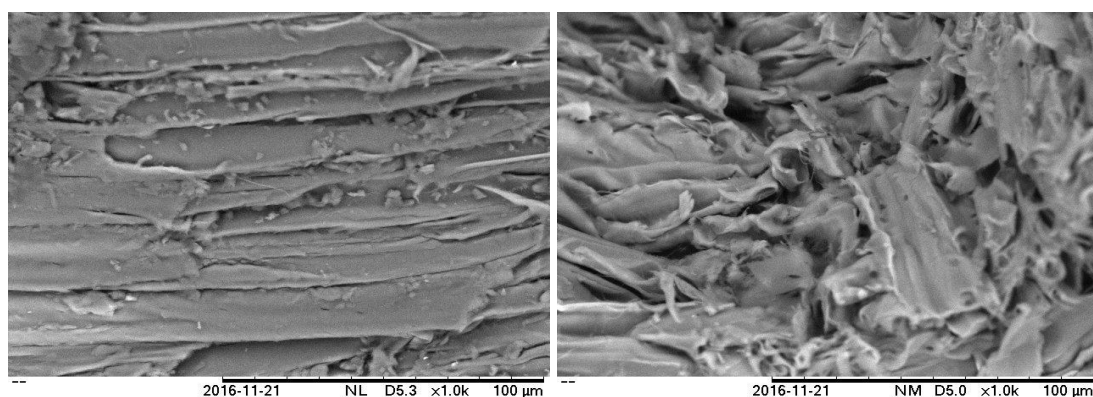
Biomass	Condition	Ratio	
		O/C	H/C
Seraya	Raw	1.030	0.001
	240 °C - 30 min	0.997	0.001
	270 °C - 30 min	0.980	0.001

	300 °C - 30min	0.922	0.001
	330 °C - 30 min	0.837	0.001
Meranti	Raw	1.070	0.001
	240 °C - 30 min	1.026	0.001
	270 °C - 30 min	0.941	0.001
	300 °C - 30min	0.882	0.001
	330 °C - 30 min	0.738	0.000

#### 4.7 Electron microscopy

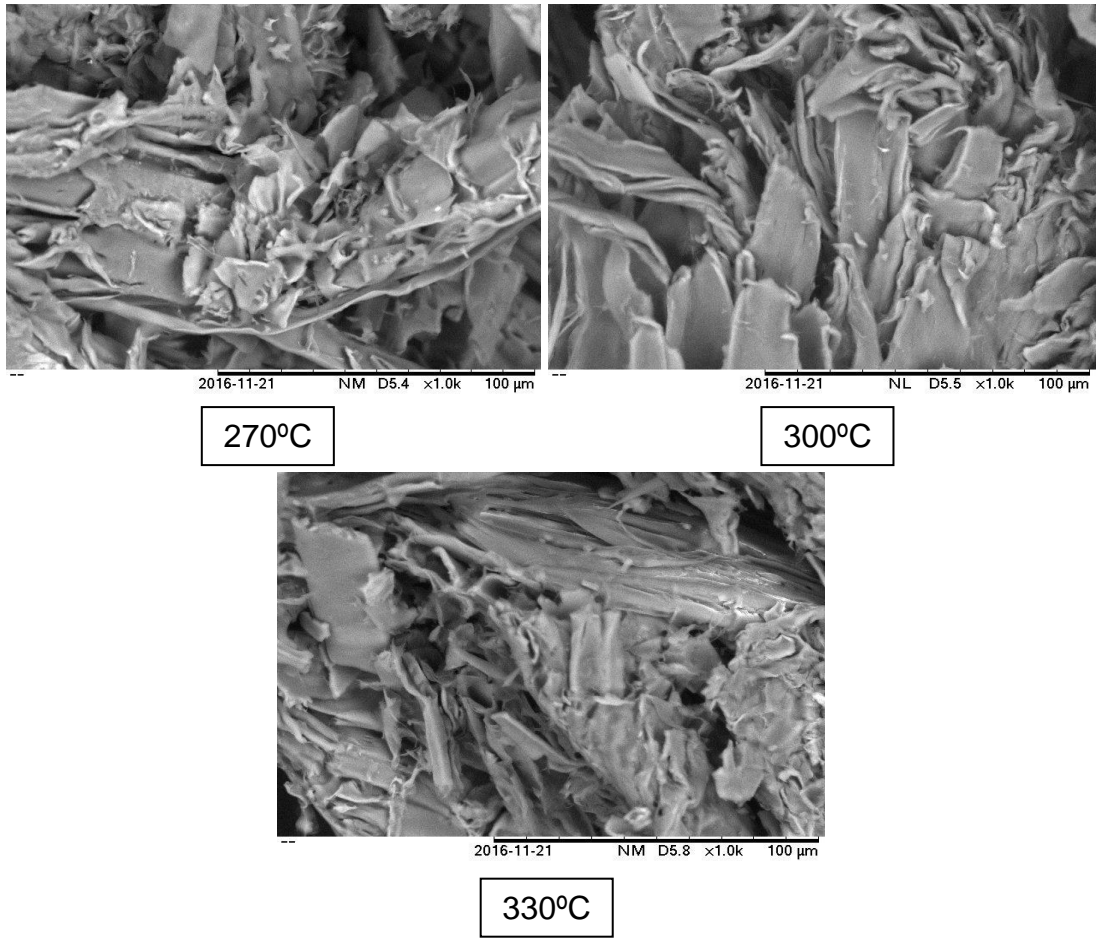
Figure 4.18 and Figure 4.19 showed the SEM images of raw and torrefied wood Seraya and wood Meranti at increasing treatment temperatures (240 °C, 270 °C, 300 °C, 330 °C and both treated with a residence time of 30 min). The SEM images was magnificent 1000%. It can be seen that the raw biomass looked compact, hard and contains very strong, bulky xylem tissues. Upon torrefaction, the biomass began to lose its bound fibrous structure and cracks and fissures became more obvious in the particles. This is particularly evident in the samples torrefied at 330 °C. These images are in agreement with Arias et al (2008), who torrefied eucalyptus at increased temperatures and observed similar structural changes as displayed in Figure 2.10 and discussed in Section 2.6.2. Torrefied wood Meranti in the study became more spherical in shape and less fibrous. This section provides a better insight for the improved grindability behaviour of biomass fuels after torrefaction.

##### 4.7.2 Wood Meranti with residence time 30 minutes



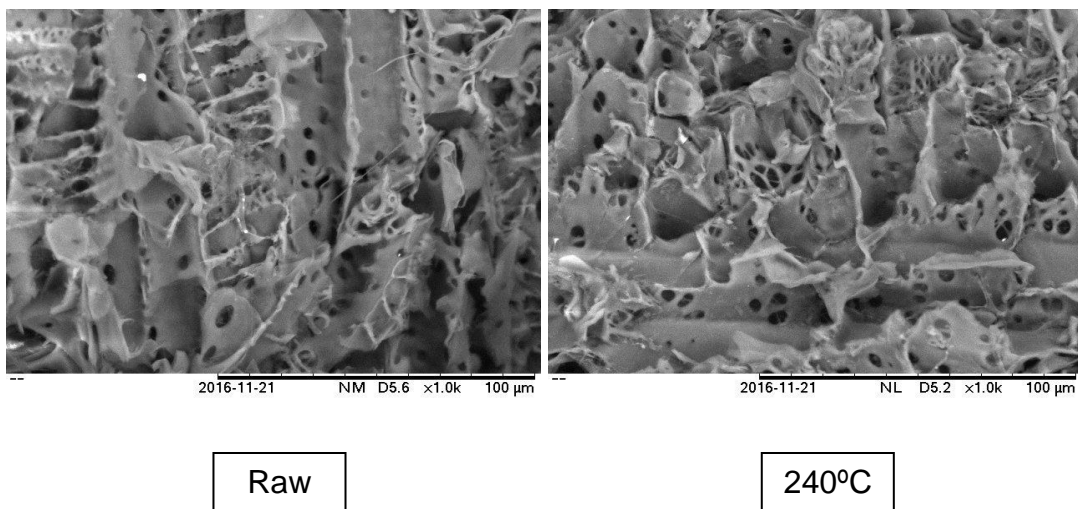
Raw

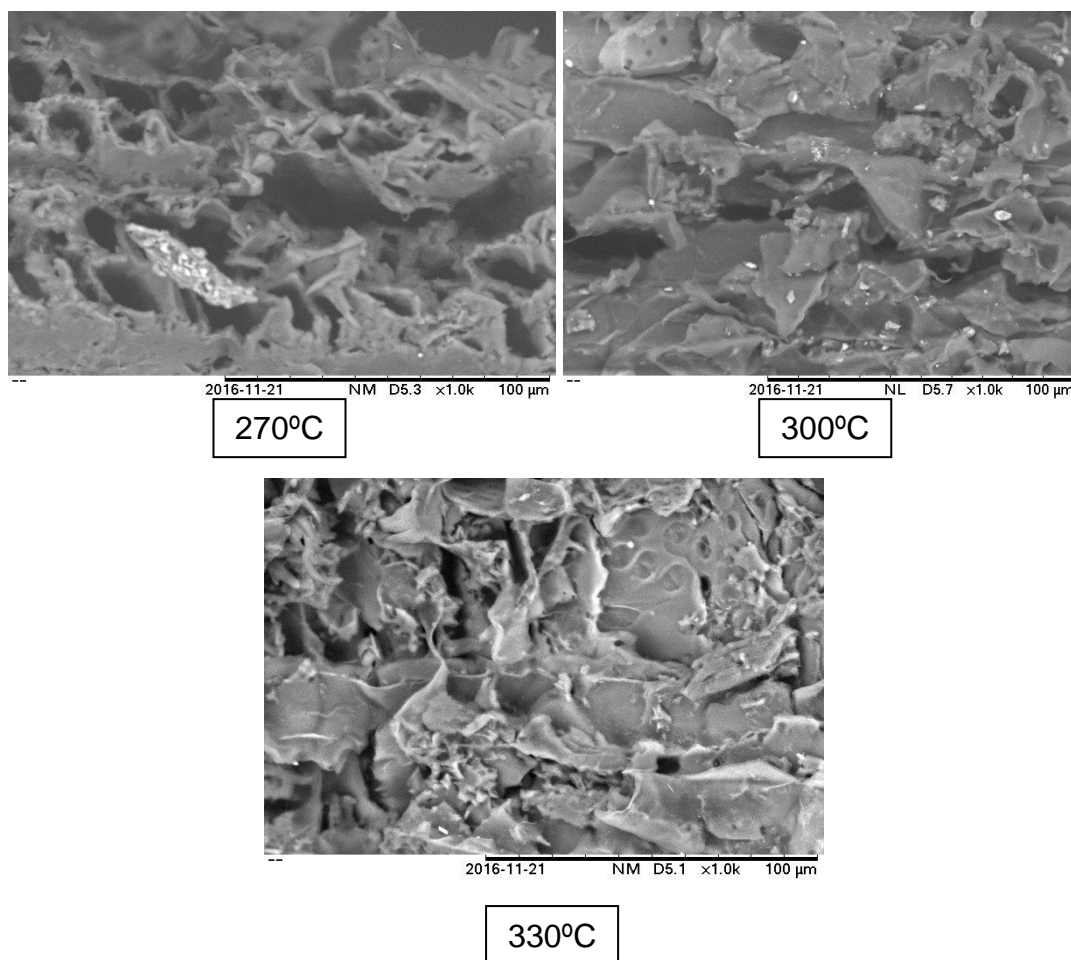
240°C



**Figure 4.18:** SEM image of magnificent 1000% of the raw and torrefied Meranti sawdust in different temperature

#### 4.7.3 Wood Seraya with residence time 30 minutes





**Figure 4.19:** SEM image of magnificent 1000% of the raw and torrefied Seraya sawdust in different temperature

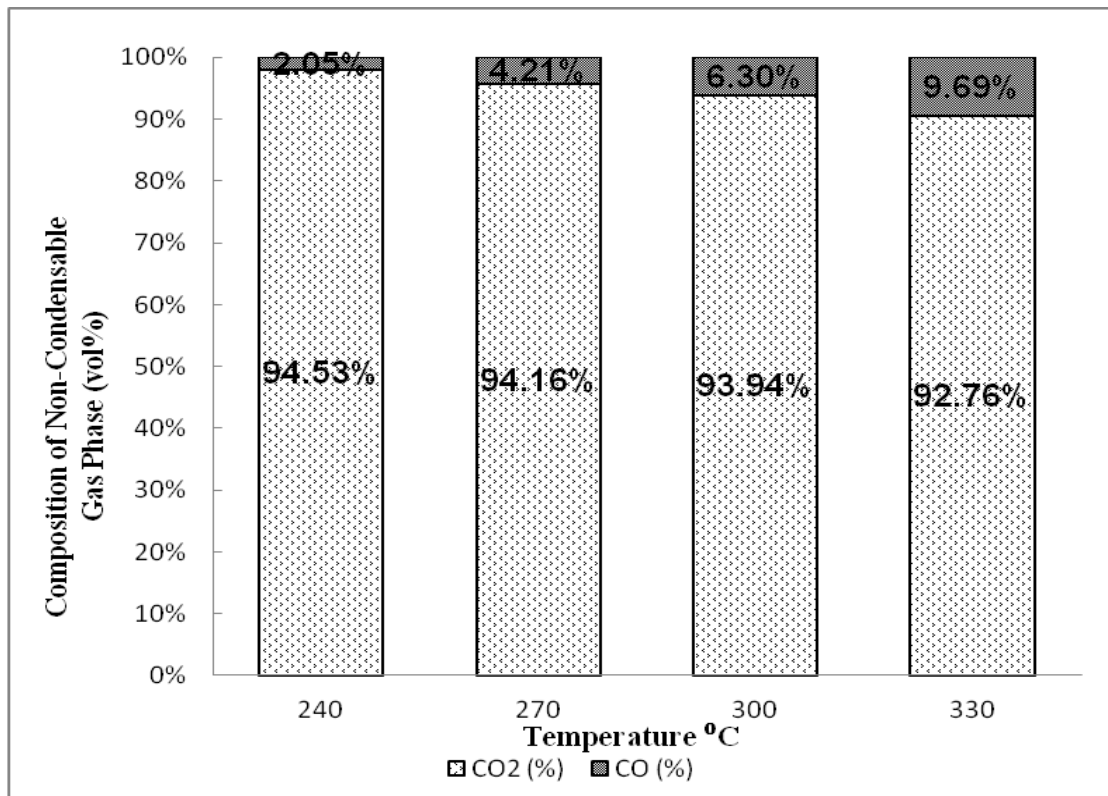
#### 4.8 Non-Condensable Volatile

The major gases formed in torrefaction are carbon dioxide and carbon monoxide, with only traces of other gases (Bergman et al., 2005). Carbon monoxide (CO) is the main source of calorific value of the non-condensable torrefaction products. The formation of CO<sub>2</sub> may be explained by decarboxylation of acid groups in the wood. The formation of CO cannot be explained by dehydration or decarboxylation reactions. The increased CO formation is reported in literature (White and Diertenberger, 2001) as the reaction of carbon dioxide and steam with porous char. This reaction produces CO. Traces of hydrogen and methane are also detected in non-condensable products. A gas composition comparison between wood and agricultural residues indicates that the latter is characterized by a higher CO<sub>2</sub> production (Bergman et al., 2005; Prins et al., 2006; Deng et al., 2009). In addition, a kinetic study on the generation of main

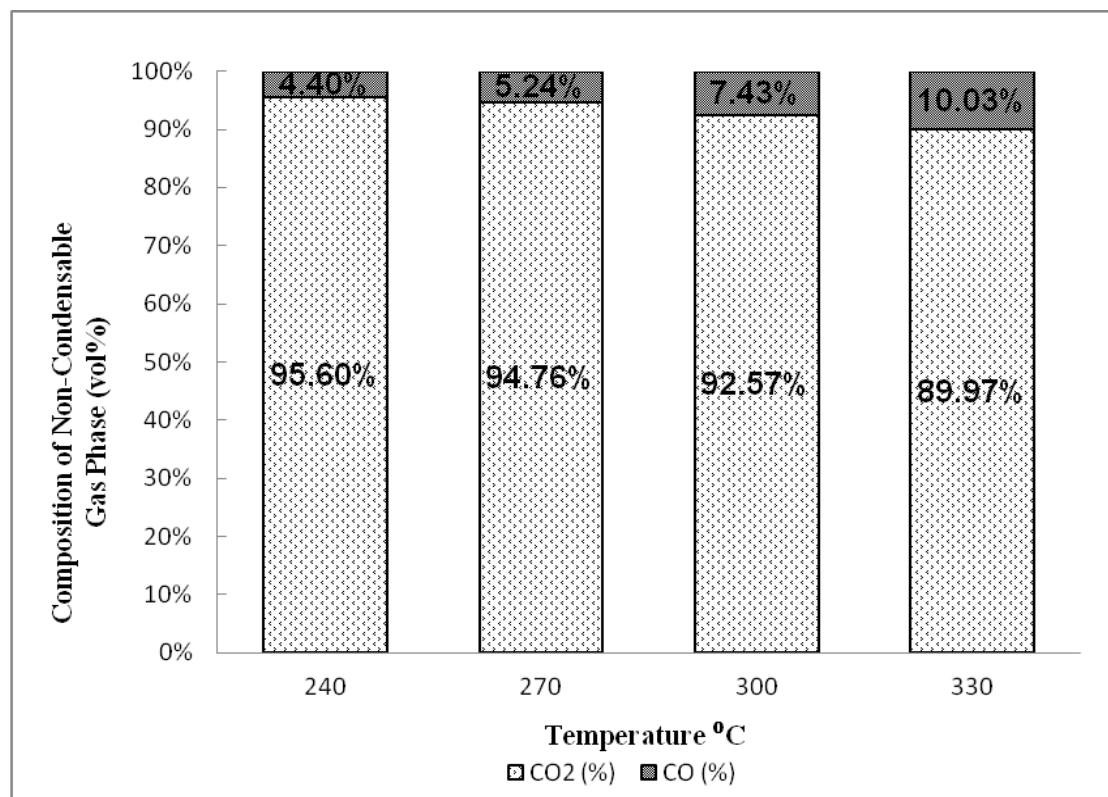
non-condensable gases shows that the gases are formed through parallel independent first-order reactions (Prins et al., 2006). The composition of the non-condensable volatile product obtained from torrefaction at different conditions with more CO<sub>2</sub> than CO. The ratio of CO to CO<sub>2</sub> increased with temperature because cellulose and lignin decompose at higher temperatures (Prins et al., 2006). Figure 4.20 to 4.23 shows the gas composition of the non-condensable products over time ( not totalling exactly to 100% because only the main components, CO<sub>2</sub> and CO, are shown) (Prins et al., 2006). These results were obtained by torrefaction of larch and willow at 250 °C and analysis of non-condensable gases after 30 and 60 minutes. It was found that the ratio of CO<sub>2</sub> to CO decreases with time, in line with the theory that CO is formed in a secondary reaction. Tables 4.4 showed the gas composition of the off-gases during torrefaction of wood Seraya and Meranti.

**Table 4.7:** Gaseous products composition during torrefaction (nitrogen and water free basis)

Biomass	Time(min)	Temperature (°C)	Gaseous Product Composition	
			CO <sub>2</sub> (%)	CO (%)
Seraya	30	240	94.53	2.05
		270	94.16	4.21
		300	93.94	6.30
		330	92.76	9.69
	60	240	96.52	3.48
		270	95.93	4.07
		300	93.70	6.30
		330	90.48	9.52
Meranti	30	240	95.60	4.40
		270	94.76	5.24
		300	92.57	7.43
		330	89.97	10.03
	60	240	96.20	3.80
		270	95.93	4.07
		300	93.04	6.96
		330	88.85	11.15

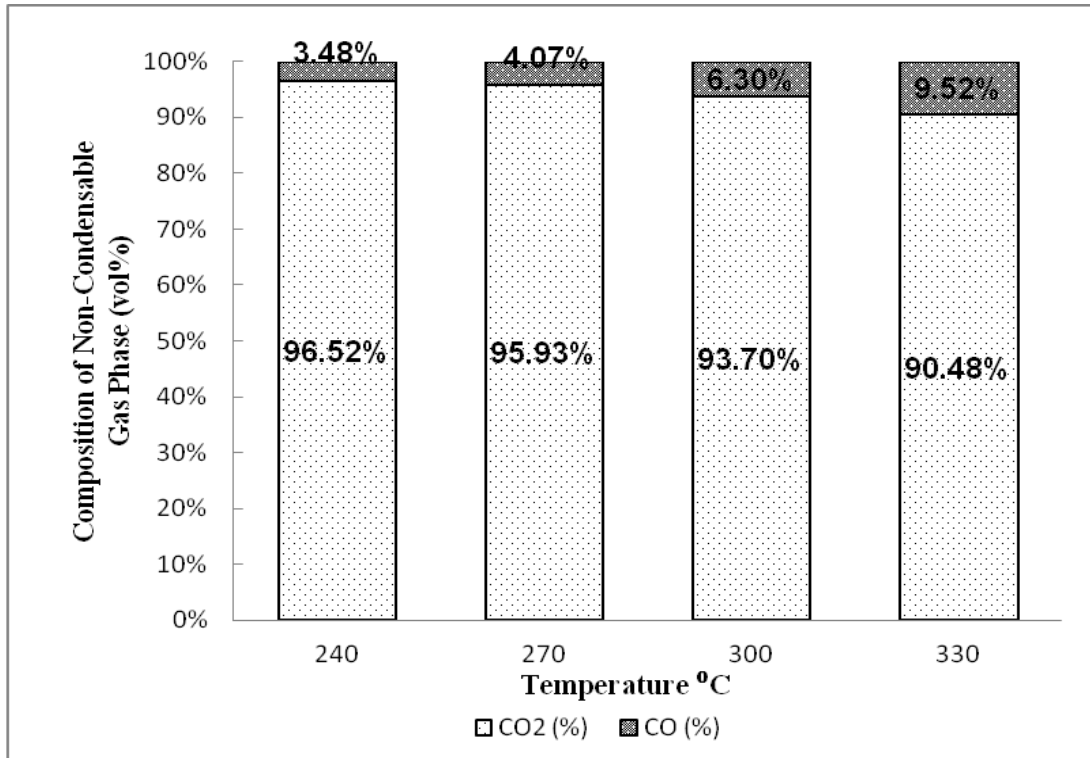


**Figure 4.20:** Changes in gas composition over temperature for Seraya sawdust with the residence time 30 min

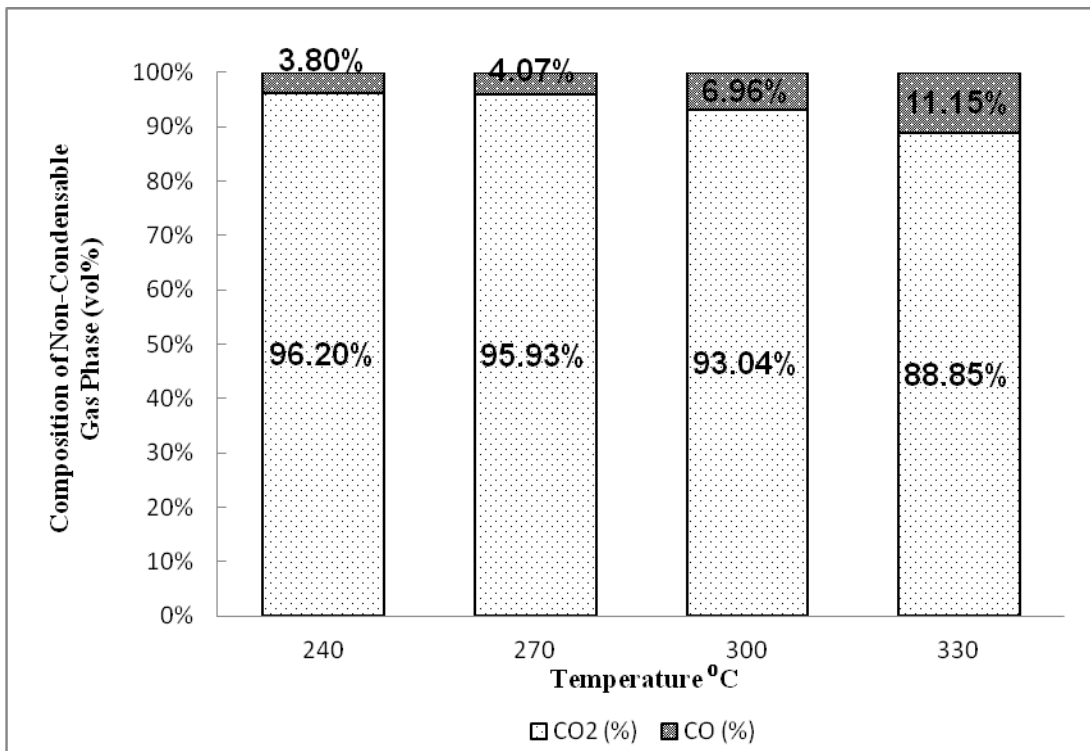


**Figure 4.21:** Changes in gas composition over temperature for Meranti sawdust with the residence time 30 min





**Figure 4.22:** Change in gas composition over temperature for Seraya sawdust with the residence time 60 min



**Figure 4.23:** Change in gas composition over temperature for Meranti sawdust with the residence time 60 min

## 5 CONCLUSION

The physical and chemical characteristics of some torrefied woods have been investigated. Overall mass balances of torrefaction of wood Seraya and Meranti were the only ones that were carried out in this study. In this study, the temperature of torrefaction of wood Seraya and Meranti (240 °C, 270 °C, 300 °C and 330 °C) were compared by increasing the temperature of heating with the different residence time 30 min and 60 min and the outcomes upon torrefaction treatment showed that this parameter plays an important role in the process. The torrefaction temperature was increased, the mass of the torrefied wood was decreased. Moreover, higher the torrefaction temperature caused the energy loss decreased in shorter duration. Apart from this, SEM studies were carried out to gain a better insight into any changes in morphology and chemical composition of torrefied biomass. The overall results indicated that careful optimization was required to maximize the benefits of torrefaction whilst maintaining a good energy yield. Proximate and ultimate analyses and their response to combustion to provide comparisons between the products obtained from torrefaction and when the woody biomass were untreated. The presence of mass and heat transfer limitations was suggested to explain the observed significant changes. Carbon contents is higher in composition compare to the other contents, therefore the heating value is increased when the carbon contents increased. Furthermore, more characterization for all of the biomass fuels could have been made apart from just Meranti and Seraya. Gases were detected using the GC-MS chromatography but the some gas phase data (CH<sub>4</sub>) were not available. Careful collection of permanent gases using the chromatography needs to be re-visited for future work. Comparison between two woody biomasses, wood Meranti contained high carbon content and high heating value and loss mass yield from wood Seraya. This result showed the wood Meranti was more feasible to be a biofuels. Wood torrefaction has a high potential to become an efficient route to produce cleaner biomass fuels from cheap and low quality biomass resources. However, some engineering issues of wood torrefaction need to be solved in order to achieve a successful process commercialization.

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