CHAPTER 1

INTRODUCTION

1.1 Rationale/Problem statement

Fossil fuel has been consumed for a long time and most of industrial fuels are fossil fuel such as natural gas, petroleum and coal. Recently, renewable energy has become more important as the fossil fuel reserve gradually been depleted and also because of the concerns over global climate change. Biomass is an important source of renewable energy which is derived from the living mechanism such as the photosynthesis of plants. Due to the lower contents of sulfur and nitrogen in the biomass waste, its energy utilization also emits less environmental pollution and health risk than fossil fuel. Biomass can be used in a variety of ways to provide energy such as providing heat from direct combustion for use in heating and steam production, providing fuel gas from gasification for combustion for heat or it also can be used in engines and turbines for electricity generation, and even provide a liquid fuel that can substitute for fuel oil by pyrolysis [1].

Because the undesirable properties, biomass utilization as a solid fuel still has many drawbacks. In physical terms, biomass is generally bulky and requires a lot of space for storage and transportation which suppresses its energy density. Second, it is hygroscopic which has high moisture content. This property decreases its heating value and drying may be necessary before its utilization. Finally, biomass is difficult to reduce due to its high fibrous composition, that why it is difficult to be reduced into small and homogeneous particles. In chemical terms, biomass has significant lower carbon content compared to coal. Some types also have high ash content which is non-combustible and causes some problem in the boiler.

Pretreatment or upgrading of raw biomass before further utilization is one of the ways to improve their combustion properties. Pyrolysis of raw biomass under inert atmosphere at low temperature is an attractive upgrading technique. This pyrolysis process at low temperature is well known as torrefaction process and the treated solid from torrefaction process is normally called torrefied solid. This torrefaction process removes moisture and causes partial endothermic decomposition of chemical structures of biomass causing biomass to develop more favorable fuel properties; this includes physical, chemical and thermal fuel properties.

There are four types of biomass selected in this study: cassava rhizome, eucalyptus trunk, jatropha trunk, and napier grass. Cassava is a year-round crop particularly grown in poor soils and drought areas in many parts of Thailand. Cassava is one of the most commercial crops in Thailand which widely grown and gives high production yields. In cassava plantation sites, there are plenty of cassava rhizomes which could not be used either for an industry or animal feeding. In practice, planters left cassava rhizomes and parts of cassava lower stem about 30 centimeters long on the ground as an agricultural waste and waited until they became dry enough to be burnt down later. There is one article in the Engineering's Today magazine reported the calorific value of dry cassava rhizome which is about 3,500 - 4,058 kcal/kg (14.7 – 17.0 MJ/kg) which can be compared to the calorific value of charcoal. The calorific value of burnt cassava rhizome in each year is equal to the use of 3,000 million liter of stove oil per year or about 21,000 million baht per year (the calorific value of stove oil is about 39.7 MJ/liter) [2]. Figure 1.1 shows cassava rhizome used in this study.

Figure 1.1 Cassava rhizome

The second studied sample is the eucalyptus trunk. Eucalyptus is widely planted because it is easily grown, has good survival and is tolerant to various climates and soil types. The main propose of eucalyptus plantation is for the pulp industry. The eucalyptus plantations in Thailand already cover around 2.7 million rai (432,000 hectares) in 2000. Eucalyptus has very fast growth rate, most species can be expected to achieve 6 - 12 feet of new growth each year [3]. Figure 1.2 shows eucalyptus trunk used in this study.

Figure 1.2 Eucalyptus trunk

Jatropha trunk is from jatropha plantation. Its main purpose is for biodiesel production. Jatropha tree can grow in dry and marginal lands that is partly the reason why *jatropha curcas Linnaeus* (JCL) oil has been considered as a prospective feedstock for biodiesel production [4]. Thailand has 20,000 acres which are planted with jatropha, mainly in the northeast and north area [5]. Figure 1.3 shows jatropha trunk used in this study.

Figure 1.3 Jatropha trunk

Napier grass is another fast growing plant which is mainly used in animal feeding. It has potential to be an energy crop due to its ability to grow fast. The first cut in napier grass plantation is taken 9 -10 weeks after planting [6]. Many clones of napier grass are now available but the most widely adopted is Bana [7, 8]. This study has used Bana to represent the napier grass and it is shown in Figure 1.4.

Figure 1.4 Napier grass

For this study, eucalyptus trunk and jatropha trunk represent woody biomass while cassava rhizome and napier grass represent herbaceous biomass.

Literature review

Many works have been studied on biomass upgrading techniques such as pyrolysis at low temperature, torrefaction, and pelletization. Pyrolysis in temperature range between 200 - 300°C or torrefaction process has high potential to be used and has been widely studied. Several studies in this field have looked at the effect of experimental parameters on product distribution. The three principal parameters studied are temperature, heating rate, and the nature of biomass. Some studies tried to predict the pyrolysis behaviors of biomass samples from their chemical components such as the work of Couhert *et al.* (2008). This work tried to find out, if it was possible to predict gas yields of any biomass after rapid pyrolysis at high temperature from its compositions which are cellulose, hemicellulose and lignin. The authors have concluded that it is not possible to predict pyrolysis gas yields of any biomass directly from its chemical compositions. These unpredictable behaviors of the biomass samples may be brought about by two main reasons which are (i) components interaction among themselves and the minerals effects during the pyrolysis. However, it does not mean that the information of chemical composition is useless. The trends of pyrolysis gas yields and (ii) the degradation behavior are still relevant to the chemical composition of each biomass even if not in direct proportion [9].

1.2.1 Pyrolysis in temperature range between 200 - 300°C or torrefaction process

Torrefaction was defined in the study of Bridgeman *et al.* (2008) as a thermal treatment that occurs in an inert atmosphere [10]. It removes moisture and low weight organic volatile components and depolymerises the long polysaccharide chains, producing a hydrophobic solid product with an increase in the energy density (on a mass basis) and greatly increased grindability (Bridgeman et al., 2008). Antal *et al.* (1990) called the wood solid residue after pyrolysis above 200 °C that are changed from "toasted" wood to "torrefied" wood. The pyrolysis temperature is increased to higher than 280 °C but not exceeding 350 °C; the solid residue is called "pyrochar". Above 350 °C, the solid residue is called "charcoal" which is generally known as the conventional conditions for charcoal production in several investigations [11].

1.2.2 Effects of elemental and chemical compositions on biomass pyrolysis behaviors

Yang *et al.* (2006) have studied biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin. The pyrolysis characteristics of the three components, palm oil waste, and the synthesized biomass which contains two or three of the biomass components are analyzed. The researchers showed the pyrolysis characteristics from both TG (in weight %) and DTG (in %/°C) curves. The TG and DTG curves of the three components are shown in Figure 1.5. The pyrolysis of hemicellulose started at 220°C, its mass-loss rate (DTG curve) increased greatly with increasing temperature and obtains its maximum value at 260°C. When the temperature is over 315°C, its weight-loss rate is low, < 0.099 wt %/°C, and the amount of solid residue left is high (~20 wt %). On the other hand, the rate of pyrolysis of cellulose has the maximum at the temperature between 315-390°C. The maximum mass-loss rate of cellulose which is about 2.1 wt %/°C was obtained at 355°C. At temperature over 390°C, its mass-loss rate is low, 0.027 wt %/°C and the amount of solid remaining is only about 7 wt %. Compared to the sharper DTG peaks of cellulose and hemicellulose, lignin has a wide and flat DTG peak. From the ambient temperature to 700°C, only ~40 wt % of lignin is lost at a very slow rate (<0.15 wt %/°C). When the temperature is higher than 750°C, its weight-loss rate increases slightly to 0.3 wt %/°C and a total of ~ 67 wt % weight-loss is achieved at 850°C.

The authors also described the behaviors of these main components from their chemical structure as follow: the higher reactivity of hemicelluloses in thermal decomposition might be attributed to its chemical structure. Hemicellulose has a random amorphous structure with little strength, and it is easily hydrolyzed by dilute acid or base. In contrast, the cellulose molecule is a very long polymer of glucose units without any branches, and it is crystalline, strong, and resistant to hydrolysis. On the other hand, the structure of lignin is different from cellulose and hemicellulose. Lignin is composed of three kinds of benzene-propane and is heavily cross-linked. The thermal stability of lignin is thus very high, and it is difficult to be decomposed. In terms of thermal degradation, the order of "difficulty of degrade" of the three components is as follows: hemicelluloses > cellulose > lignin [12].

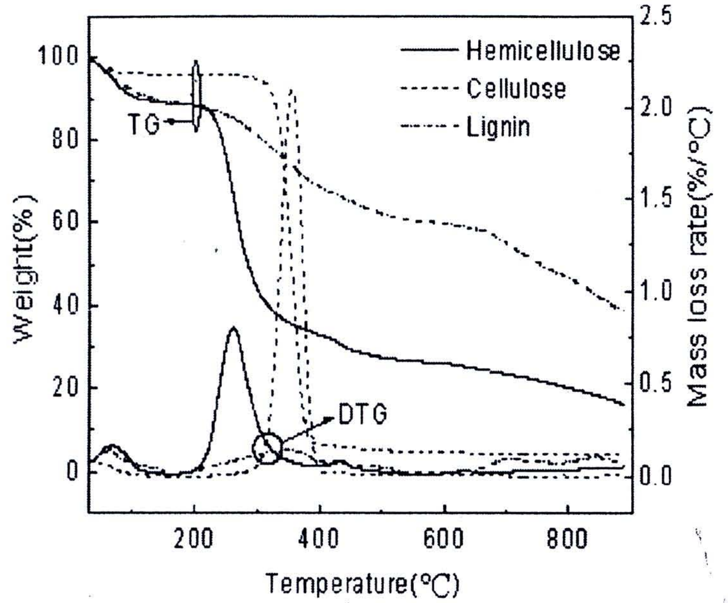

Figure1.5 Pyrolysis curves of three biomass components [12]

Worasuwannarak *et al.* (2007) have studied the changes in weight and gas formation rates during the pyrolysis of rice straw, rice husk and corncob using the TG-MS technique. The authors have studied the relationship between the gas formation rates and the chemical composition of the biomass samples [13]. Table 1.1 shows the results of structural analyses for the biomass samples reported by Xiao et al. (2001). The hemicellulose content of rice straw is higher than the hemicellulose content of corncob, whereas the cellulose content of rice straw is less than that of corncob. At lower temperatures, the evolutions of CO, CO_2, and H_2O are considered due to the degradation of hemicellulose and the initial decomposition of cellulose. Therefore, the early weight loss of rice straw was probably due to the early decomposition of abundant hemicellulose in rice straw to form H_2O.

Table 1.1 The results of structural analyses for biomass samples [14]

Biomass sample	Hemicellulose	Cellulose	Lignin	Extractive matter
Rice straw	35.7	32.0	22.3	10.0
Rice husk	28.6	28.6	24.4	18.4
Corncob	31.0	50.5	15.5	3.5

The yields of products (H_2, CH_4, H_2O, CO, CO_2, and tar) for rice straw, rice husk, corncob, xylan, lignin, and cellulose during the pyrolysis at 600°C are shown in Figure 1.6. Among the biomass samples, rice straw also produced the largest amount of H_2O (0.244 g/g-sample) and the least amount of tar (0.096 g/g-sample).

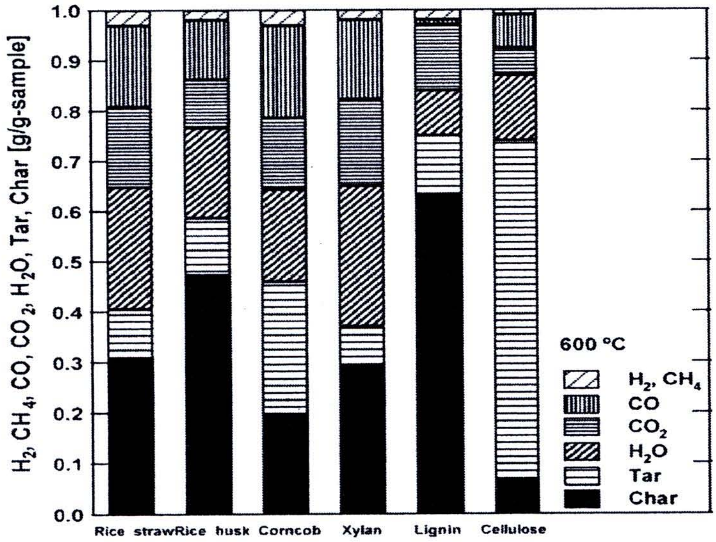

Figure 1.6 Products yields (H_2, CH_4, H_2O, CO, CO_2, and tar) of rice straw, rice husk, corncob, xylan, lignin, and cellulose at 600°C [13]

1.2.3 Effects of pyrolysis temperature and heating rate on biomass pyrolysis behaviors

Prins *et al.* (2006) have examined the product during the torrefaction of wood. The non-condensable volatile product focusing on CO, CO_2 CH_4, and H_2 from varying torrefaction conditions is presented in Figure 1.7. The amount of non-condensable volatile product increased with increasing torrefaction temperature and residence time. Carbon dioxide is the major gaseous product followed by CO through the torrefaction process [10, 15]. Traces of hydrogen and methane were also detected. The formation of carbon dioxide may be explained by decarboxylation of acid groups in the wood [16]. The carbon monoxide is formed by dehydration or decarboxylation reactions [17]. With increase in temperature, the reaction of carbon dioxide and steam with porous char to carbon monoxide is favorable. As increasing of reaction time, the ratio of carbon dioxide to carbon monoxide decreased with time which agreed with the theory that carbon monoxide is formed in a secondary reaction. The difference in the amount of each product among the biomass samples could be explained by the difference in the hemicellulose content.

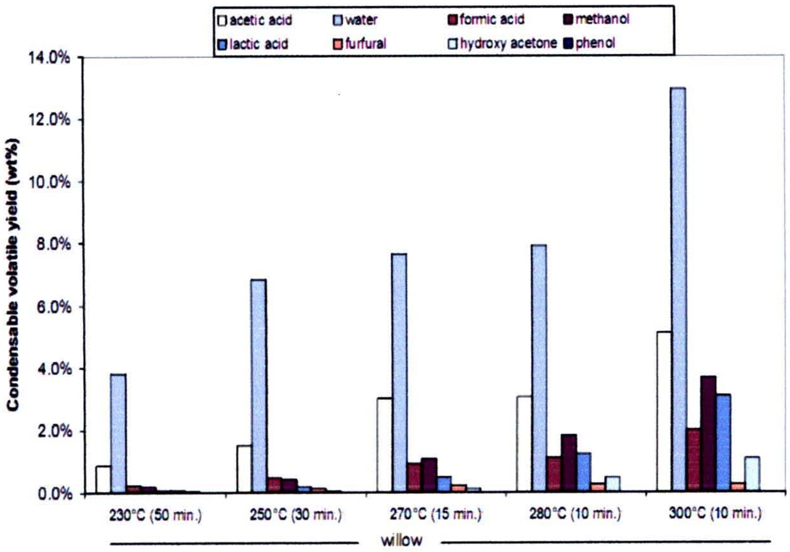

Figure 1.7 Product yield of condensable volatiles formed in torrefaction of willow at different conditions [15]

Strezov *et al.* (2008) have studied the thermal conversion of elephant grass. The authors summarized product yields of elephant grass pyrolysis for the two examined heating rates at the maximum temperature of 500°C in Table 1.2. Higher heating rate was found to decrease, the amount of volatiles and oxides of carbon being the most affected group. The yield of liquid products was found to increase with heating rate while the estimated charcoal yields were little affected. The main reason for the change in pyrolytic product composition is believed to be the reduction of secondary reactions under higher heating rate.

Table 1.2 Comparison of the yields of volatiles, liquid products and charcoal expressed in% of dry biomass for heating rates of 10 and 50°C/min and for the maximum temperature of 500°C [18]

	Yields (%) at 500°C	
	10°C/min	50°C/min
CO_2	18.6	11.0
CO	6.6	3.1
CH_4	0.6	0.39
C_2H_4	0.10	0.07
C_2H_6	0.17	0.12
H_2	0	0
Liquids	44.7	54.37
Charcoal	29.3	31

1.2.4 Energy yield through pyrolysis at low temperature

The calculation of energy yield was suggested by Bergeman *et al.* (2004) in the study of torrefaction for entrained-flow gasification of biomass. This study showed an equation for energy yield calculating which is

$$\text{Energy yield (\%)} = \text{mass yield } (HHV_{product}/HHV_{feed}) \text{ (d.a.f)} \quad (1.1)$$

Where $HHV_{product}$ and HHV_{feed} represent the higher heating values of torrefied biomass and raw biomass, respectively, the results of energy yield and mass yield by using willow as a feedstock are shown in Figure 1.8. From Figure 1.8, for all torrefaction temperatures the energy yield was greater than the mass yield. These trends became more marked for higher temperature treatments [19].

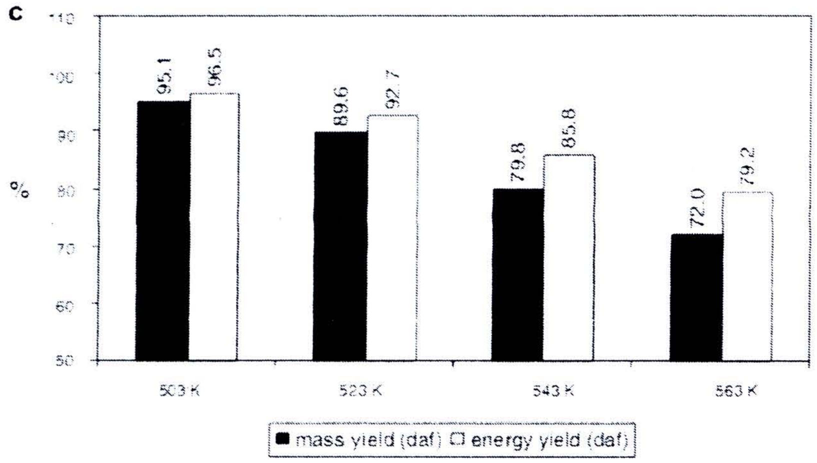

Figure 1.8 Mass and energy yield of willow treated at various temperatures and reaction time of 30 min [20]

1.2.5 Fuel properties of treated biomass by pyrolysis at low temperatures

Bridgeman *et. al.* (2008) have studied the changes in elemental composition during the torrefaction of reed canary grass, wheat straw and willow at temperature 230 – 290°C. Figure 1.9 shows the Van Krevelen diagram of the raw biomass and the torrefied biomass. The Van Krevelen diagram is the plot between atomic ratios of hydrogen to carbon and atomic ratios of oxygen to carbon of the biomass samples. The Van Krevelen diagram of the torrefied biomass shows that the change in elemental compositions of the torrefied biomass moved towards lignite. From the diagram, it can be observed that of the three types of the samples investigated, torrefaction had the biggest effect on wheat straw regarding alterations of its fuel properties [10].

The proximate analyses of raw and torrefied biomass in the study of Bridgeman, (2008) [10] are presented in Table 1.3. The volatile matter, fixed carbon and ash contents are given for the dry sample. The trend is a reduction in moisture content and volatile matter and an increase in fixed carbon and ash content while the calorific values of all torrefied biomass are higher than that of raw biomass.

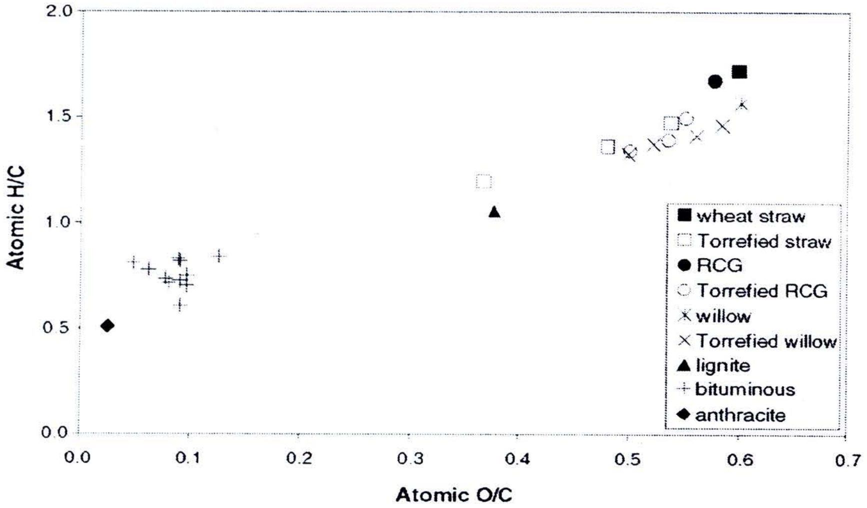

Figure1.9 Van Krevelen diagram for coals, biomass and torrefied biomass [10]

1.2.6 Comparison between combustion behavior of raw and treated biomass

Bridgeman *et. al.* (2008) have studied the burning profile or combustion behavior of raw and torrefied reed canary grass by using DTG curves. The DTG curves of untreated reed canary grass and reed canary grass torrefied at final temperatures of250, 270 and 290°C are shown in Figure 1.10. From this figure, DTG curves of torrefied samples were in narrower range of combustion temperature than raw sample. Among all DTG curves, the curve shape of torrefied reed canary grass at 290°C was in the narrowest temperature range. From this difference, the researchers mentioned that torrefied reed canary grass has faster rate of volatile combustion than raw sample. Apart from the DTG shape, the maximum point of DTG curves of raw and torrefied samples were also different. The researcher found that the maximum point of DTG curves for the torrefied samples had slightly shifted to lower temperature and the maximum rate of reaction of torrefied samples were higher than the maximum rate of raw sample.

Table1.3 Proximate analyses (TGA) of raw and torrefied fuels [10]

	Raw	Torrefaction temperature (K)			
		503	523	543	563
RCG					
Moisture content (%)	4.7	–	1.9	1.3	1.2
Volatile matter[a] (%)	82.5	–	80.3	76.6	70.5
Ash content[a] (%)	5.5	–	6.4	7.3	8.3
Fixed carbon[a] (%)	12.1	–	13.3	16.1	21.3
Wheat straw					
Moisture content (%)	4.1	–	0.9	0.3	0.8
Volatile matter[a] (%)	76.4	–	77.0	65.2	51.8
Ash content[a] (%)	6.3	–	7.4	8.4	10.2
Fixed carbon[a] (%)	17.3	–	15.6	26.5	38.0
Willow					
Moisture content (%)	2.8	0.5	0.1	0.2	0.0
Volatile matter[a] (%)	87.6	82.1	79.8	79.3	77.2
Ash content[a] (%)	1.7	1.8	1.9	2.1	2.3
Fixed carbon[a] (%)	10.7	16.1	18.4	18.6	20.5

[a] Volatile matter, ash content and fixed carbon expressed on a dry basis.

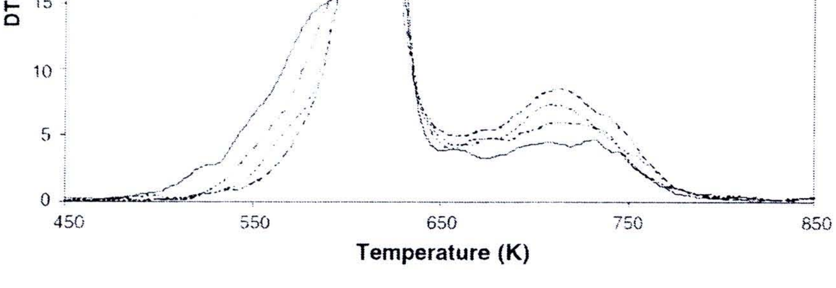

Figure1.10 Burning profiles of untreated reed canary grass and reed canary grass torrefied at final temperatures of 523, 543, and 563 K [10]

1.2.7 Mass and energy balance of pyrolysis process

Prins *et. al.* (2006) have studied the mass and energy balances for torrefaction of willow at temperature of 250 and 300°C. The mass fractions of solid and volatile yields were used for mass balance. The main species of volatile matter released in torrefaction process of this study were steam, acetic acid, carbon dioxide, carbon monoxide, and other organics. The information of mass fraction, heating value and sensible heat of solid and each species of volatile yields were used in the energy balance of this work. From mass balances, solid product was the majority product of torrefaction process from both temperatures. And from energy balances, the researchers concluded that the torrefaction process is an endothermic reaction which requires some amount of energy during the process [21].

1.3 Objectives

1) To upgrade fuel properties of the biomass which are cassava rhizome, eucalyptus trunk, jatropha trunk, and napier grass by pyrolysis at temperature lower than 300°C.

2) To identify the suitable condition of upgrading for each biomass in order to improve their fuel properties.

1.4 Scopes of research work

Upgrading techniques used in this thesis work: slow and fast pyrolysis at low temperature. The pyrolysis at low temperature (200 - 300°C) is well known as torrefaction process, so the treated biomass were called torrefied biomass in this work. There are four types of biomass used in this work. The biomass selected are eucalyptus and jatropha trunk as representatives of woody biomass, cassava rhizome and napier grass as representatives of herbaceous biomass. The chemical properties of raw biomass which are elemental, proximate, and chemical compositions including calorific values and fuel ratios were analyzed. Each biomass sample was treated in both fast and slow pyrolysis at low range of temperature in inert atmosphere. For fast pyrolysis the raw biomass was heated by the heating rate over 200°C/s while the heating rate used for slow pyrolysis was only 10°C/min. In order to study the result of pretreatment or upgrading, the chemical properties, calorific values, fuel ratios and also the combustion behavior of torrefied samples were analyzed.

The detail research work scope cover;

1.4.1 Raw biomass analyses

A. Chemical properties analyses and calorific value calculations

B. Chemical composition analyses

1.4.2 Study the pyrolysis of raw biomass by Thermogravimetric Mass Spectrometer (TG-MS)

1.4.3 Study the slow pyrolysis of raw biomass at low range temperature (200-300°C) by Thermal gravimetric analyzer (TGA)

1.4.4 Study of fast pyrolysis in drop tube reactor at low range temperature (200-300°C)

1.4.5 Study of conventional or slow pyrolysis in fixed bed reactor at low range temperature (200-300°C)

1.4.6 Remaining solid or torrefied biomass analyses
    A. Chemical properties analyses and calorific value calculations
    B. Proximate analyses and fuel ratio calculations
    B. Study of the combustion behaviors
1.4.7 Study of products distribution through the pyrolysis processes
1.4.8 Study of mass and energy balances of pyrolysis processes