CHAPTER 3

METHODOLOGY

3.1 Methodology

3.1.1 Biomass preparation

Four types of biomass were used in this study: cassava rhizome, eucalyptus trunk, jatropha trunk, and napier grass. The raw biomass was cut and milled into the particle size less than 75μm for all experiments apart from chemical compositions analyses. The chemical compositions analysis used samples with particle size between 75-150 μm. The size selected biomass sample was dried in a vacuum oven at 70°C for 24 hours before the experiment. The prepared cassava rhizome, eucalyptus trunk, jatropha trunk, and napier grass are shown in Figures 3.1 - 3.4, respectively.

Figure 3.1 Prepared cassava rhizome

Figure 3.2 Prepared eucalyptus

Figure 3.3 Prepared jatropha trunk

Figure 3.4 Prepared napier grass

3.1.2 Raw biomass analysis

A. Chemical properties analysis of raw biomass

1) Ultimate analysis and calorific value calculation

The ultimate analysis gives the composition of the biomass in percentage by weight (wt %) of carbon (C), hydrogen (H), oxygen (O), sulfur (S), and nitrogen (N). Dried and ground biomass was analyzed in the CHONS analyzer. In this technique, a sample was burned in an excess of oxygen, and various traps collect the combustion products. The Automatic Organic Elemental Analyzer used in this study was Thermo Finnigan, Flash EA1112 Series which is shown in Figure 3.5.

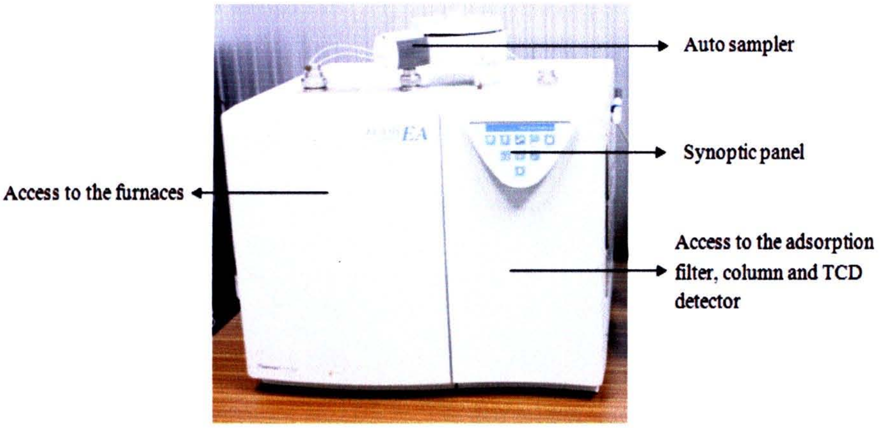

Figure 3.5 A CHONS analyzer used in this study (Thermo Finnigan, Flash EA1112)

The percentages (wt%, dry basis) of carbon (C), hydrogen (H), oxygen (O), sulfur (S), and nitrogen (N) were used in the calorific value calculation. An ordinary least squares regression (OLS) (Eq. (1)) and a partial least squares regression (PLS) (Eq. (2)) which were normally used for biomass heating value calculation were used in this study.

$$\text{HHV (OLS)} = 1.87C^2 - 144C - 2802H + 63.8CH + 129N + 20147 \quad (1)$$

$$\text{HHV (PLS)} = 5.22C^2 - 319C - 1647H + 38.6CH + 133N + 21028 \quad (2)$$

Where C = carbon, H = hydrogen, N = nitrogen content was expressed on a dry mass percentage basis. The reported calorific values were calculated using an average of the results from both two methods [10].

2) Proximate analysis

Proximate analysis gives moisture, volatile matter, fixed carbon and ash content of biomass. The apparatus used in proximate analysis is Thermal Gravimetric Analyzer (TGA). The oven dried samples with particle size less than 75 μm about 5mg was heated in nitrogen stream from room temperature to 900°C in order to quantify moisture and volatile matter. At 900°C, the condition was changed into oxygen or air atmosphere in order to quantify fixed carbon from loss weight in oxygen atmosphere and ash from the remaining solid. The TGA apparatus used in this study is Perkin-Elmer, Pyris1 TGA.

B. Chemical compositions or structural analysis

1) Analysis of extractive in biomass [34]

Sample preparation

For extraction process, the sample must be dried and has particle size between 75-150 μm.

Apparatus

Analytical balance, accurate to 0.1 mg

Medium to large capacity oven set to 105 ± 5°C for glassware drying

Vacuum oven

Desiccators with silica gel

Apparatus for Soxhlet extraction

Glass soxhlet extraction tubes of suitable size (capacity 85 ml)

Heating mantle, suitable for 500 ml boiling flasks

Condensers with appropriate fitting for soxhlet tubes and a source of chilled water or other cooling system

Single thickness cotton cellulose thimbles, 94 mm external length by 33 mm internal diameter (Alundum thimbles, medium porosity, of appropriate size for Soxhlet tube may also be used)

250 ml glass rotary evaporator trap

Reagents

Ethanol (Ethyl alcohol), reagent grade

Procedure

- Boiling flasks and other relevant glassware were dried in a 105 ± 5°C drying oven for a minimum of 12 hours. Then they were removed and allowed to come to room temperature in desiccators. The oven dry weight (ODW) of the glassware used was recorded to the nearest 0.1 mg.

- 2-10 g of sample was added to a tarred extraction thimble. The amount of sample necessary will depend on the bulk density of the biomass. If the height of sample exceeds the siphon height, incomplete extraction will occur.

- Soxhlet apparatus were set. The sample loaded thimble was inserted into the soxhlet tube.

- 190 ± 5 ml proof ethyl alcohol was added to the tarred ethanol receiving flask. Then, the receiving flask was placed on the soxhlet apparatus. The heating mantle was adjusted to provide a minimum of 6-10 siphon cycles per hours.

-The reflux time necessary depended on the removal rate of components of interest, the temperature of the condensers, and the siphon rate. The reflux time is normally between 16-24 hours.

- The heating mantle was turned off and the glassware was allowed to cool to room temperature when reflux time is complete.

- The thimble was removed and the solid was washed with approximately 100 ml of fresh ethanol. The solid was allowed to dry in vacuum oven at 40 ± 2°C for 24 hours.

- The solvent was removed from extractive fraction by using a rotary evaporator.

- The flask was placed in a vacuum oven at 40 ± 2°C for 24 hours and cooled to room temperature in desiccators. The flask was weighed and the weight was recorded.

- The extractive - free cassava rhizome, eucalyptus trunk, jatropha trunk, and napier grass are shown in Figures 3.6 - 3.9, respectively.

Figure 3.6 Extractive - free cassava rhizome

Figure 3.7 Extractive - free eucalyptus trunk

Figure 3.8 Extractive - free jatropha trunk

Figure 3.9 Extractive - free napier grass

Calculations

- The oven dry weight (ODW) of the sample was calculated, using the average total solids content as determined by the LAP "Standard Method for the Determination of Total Solids in Biomass"

$$ODW = \frac{(Weight_{thimble\ plus\ sample} - Weight_{thimble}) \times \%\ Total\ solids}{100}$$

- The amount of extractive in the sample was calculated, on a percentage of dry weight basis.

$$\%Extractives = \frac{Weight_{flask\ plus\ extractives} - Weight_{flask}}{ODW_{sample}} \times 100$$

2) Analysis of Holocellulose (Chlorite Holocellulose) in biomass [35]

Sample preparation

The sample used was extractive and moisture free, but the weight of the extractives was accounted for in the calculation of holocellulose. In this case, the holocellulose must be used for alpha cellulose preparation, the prepared holocellulose must be more than 2 g. And in order to prepare more than 2 g of holocellulose, the raw sample should be about 5 mg.

Apparatus

Analytical balance, accurate to 0.1 mg

Vacuum oven

Desiccators with silica gel

Chemical fume hood
Water bath
250 ml Erlenmeyer flasks
Watch glass
Spatula
1 ml glass pipet
Glass rod
Filter paper with medium porosity
Buchner funnel
1000 ml suction flask
Suction pump
Forceps

Reagents

Acetic acid, reagent grade
Sodium chlorite, $NClO_2$, technical grade, 80%

Procedure

- 80 ml of hot distilled water, 0.5 ml acetic acid, and 1 g of sodium chlorite was added to 2.5 g of sample in a 250-ml Erlenmeyer flask.

- Top of the flask was covered with watch glass while, the mixture was heated in a water bath at 70°C. After 60 minutes of heating, 0.5 ml of acetic acid and 1 g of sodium chlorite was added with shaking.

- Addition of 0.5 ml acetic acid and 1 g of sodium chlorite was repeated until the wood sample was completely separated from lignin. It usually takes 6 to 8 hours of chloriting.

- The sample was cooled and filtered on filter paper using a Buchner funnel until the yellow color (the color of holocellulose is white) and the odor of chlorine dioxide is removed.

- The solid was washed on filter paper with acetone and vacuum oven dried at 105°C for 24 hours. The dry sample was placed in desiccators for an hour before weighting. The holocellulose should not contain any lignin.

- The prepared holocellulose of cassava rhizome, eucalyptus trunk, jatropha trunk, and napier grass are shown in Figures 3.9 - 3.12, respectively.

Figure 3.10 The prepared holocellulose of cassava rhizome

Figure 3.11 The prepared holocellulose of eucalyptus trunk

Figure 3.12 The prepared holocellulose of jatropha trunk

Figure 3.13 The prepared holocellulose of napier grass

Calculation and Report

Calculation of the percentage of holocellulose on the basis of the oven-dried and extractive –free sample, as follows:

$$\%\ \textbf{holocellulose (dry and extractive} - \textbf{free basis)} = \left(\frac{\textbf{weight of filtered solid}}{\textbf{weight of initial dry extractive} - \textbf{free sample}}\right) \times 100$$

3) Analysis of alpha-cellulose (determination of hemicelluloses) in biomass [34]

Sample preparation

Holocellulose prepared from step 2) is used for alpha-cellulose preparation.

Apparatus

Analytical balance, accurate to 0.1 mg
Vacuum oven
Desiccators with silica gel
Chemical fume hood
250 ml Erlenmeyer flasks
Watch glass
Spatula
25 ml glass pipet
Glass rod
Filter paper with medium porosity
Buchner funnel

1000 ml suction flask

Suction pump

Forceps

A thermostat or other constant-temperature device that can maintain a temperature of 20 ± 0.1°C in a container large enough to hold a row of at least three 250-ml Erlenmeyer flasks

Reagents

Sodium hydroxide (NaOH) solution, 17.5% and 8.3%

Acetic acid, 10% solution

Procedure

- About 2 g of vacuum-oven dried holocellulose was weighed and placed into a 250-ml Erlenmeyer flask.
- 10 ml of 17.5% NaOH solution was added to the holocellulose in a 250-ml flask and the holocellulose was lightly manipulated with a glass rod until the entire specimen became soaked with the NaOH solution.
- The reaction flask was covered with a watch glass and maintained in water bath at 20 °C for 5 minutes.
- 5 ml more of the NaOH was added after the addition of the first portion of 17.5% NaOH solution to the specimen. The mixture was allowed to stand at 20°C for 30 minutes making the total time for NaOH treatment 45 minutes.
- 33 ml of distilled water at 20°C was added to the mixture. The contents of the flask was thoroughly mixed and allowed to stand at 20°C for 1 hour before filtering.
- The cellulose was filtered with the aid of suction into the medium pore size filter paper. All of the NaOH wash solution passed through the filter paper and the washing continue at 20°C with distilled water. Washing the sample was facilitated by releasing the suction, filling the Buchner funnel with water, carefully breaking up the cellulose mat with a glass rod. The suction was applied to the solution again and this step was repeated twice.
- 15 ml of 10% acetic acid was poured at room temperature into the Buchner funnel, the cellulose was drawn in acid by suction. However, while the cellulose was still covered with acid, the suction had to be released. The cellulose was subjected to the acid treatment for

3 minutes from the time the suction was released then applied suction to draw off the acetic acid.

- The Buchner funnel was filled almost to the top with distilled water at 20°C and allowed to drain completely without releasing the suction.
- The washing was repeated until the cellulose residue was free of acid as indicated by litmus paper.
- The cellulose was finally washed by drawing, by suction, an additional 250 ml of distilled water through the cellulose in the funnel. Then, the filter paper was dried with cellulose overnight in vacuum oven at 105°C.
- The sample was cooled and kept in desiccators for 1 hour before weighting.
- The prepared alpha-cellulose of cassava rhizome, eucalyptus trunk, jatropha trunk, and napier grass are shown in Figures 3.14 - 3.17, respectively.

Figure 3.14 The prepared alpha-cellulose of cassava rhizome

Figure 3.15 The prepared alpha-cellulose of eucalyptus trunk

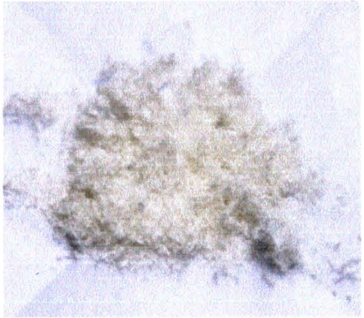

Figure 3.16 The prepared alpha-cellulose of jatropha trunk

Figure 3.17 The prepared alpha-cellulose of napier grass

Calculation and Report

Calculation of the percentage of α-cellulose on the basis of the oven-dried holocellulose sample is as follows:

$$\%\ cellulose\ in\ holocellulose\ (dry\ basis) = \frac{(weight\ of\ initial\ dry\ holocellulose - weight\ of\ filtered\ solid)}{weight\ of\ initial\ dry\ holocellulose} \times 100$$

4) Analysis of of Klason lignin in biomass [35]

Apparatus

Analytical balance, accurate to 0.1 mg

Vacuum oven
Desiccators with silica gel
Chemical fume hood

Water bath
Hot oil bath
500 ml Erlenmeyer flasks
Watch glass
Spatula
25 ml glass pipette
Glass rod
Glass fiber filter with medium porosity
Buchner funnel
1000 ml suction flask
Suction pump
Forceps

Reagent

Sulfuric acid (H_2SO_4), 72%

Procedure

- Approximately 1 g of ground vacuum-dried sample was weighed and placed into a 500 ml Erlenmeyer flask.

- 15 ml of 72% (w/w) H_2SO_4 was added for each 1 g of sample. The mixture was thoroughly stirred and dispersed with a glass rod twice, and then the tubes were incubated in a water bath at 30°C for 60 minutes.

- 280 ml of hot distilled water was added and the reaction flask was kept in hot oil bath for 4 hours.

- The lignin was filtered off with glass fiber filters in Buchner funnel using suction and keeping the solution hot.

- The residue was thoroughly washed with hot water and dried at 105°C overnight in vacuum oven. The dried residue was moved to desiccators and left inside for an hour before weighing.

- Klason lignin content was calculated from the weight of black solid residue.

- The prepared Klason lignin of cassava rhizome, eucalyptus trunk, jatropha trunk, and napier grass are shown in Figures 3.18 - 3.2, respectively.

Figure 3.18 The prepared Klason lignin of cassava rhizome

Figure 3.19 The prepared Klason lignin of eucalyptus trunk

Figure 3.20 The prepared Klason lignin of jatropha trunk

Figure 3.21 The prepared Klason lignin of napier grass

Calculation and Report

Calculation the percentage of lignin on the basis of the oven-dried sample, as follows;

$$\% \text{ lignin } (dry\ basis) = \left(\frac{weight\ of\ filtered\ solid}{weight\ of\ initial\ dry\ sample}\right) \times 100$$

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

In this study, the pyrolysis behaviors which include the weight loss curve and the evolving rate of each pyrolysis product were studied by using of TG-MS technique. The TG-MS technique is the combination between Thermogravimetric analysis and Mass spectrometry technique. The experiment was performed in a closed system where the changing of sample weight was measured by Thermal gravimetric analyzer and the species of gas yield components were identified and quantified from their molecular weight by Mass spectrometry technique. In the experiment, about 5 mg of biomass sample with particle size less than 75 µm was heated in helium atmosphere with heating rate 10°C/min. The sample was heated from room temperature to 800°C, in order to identify the volatile product species and their evolving behaviors during the pyrolysis process. Figure 3.22 shows the TG-MS apparatus used in this study which is Perkin Elmer Clarus 500.

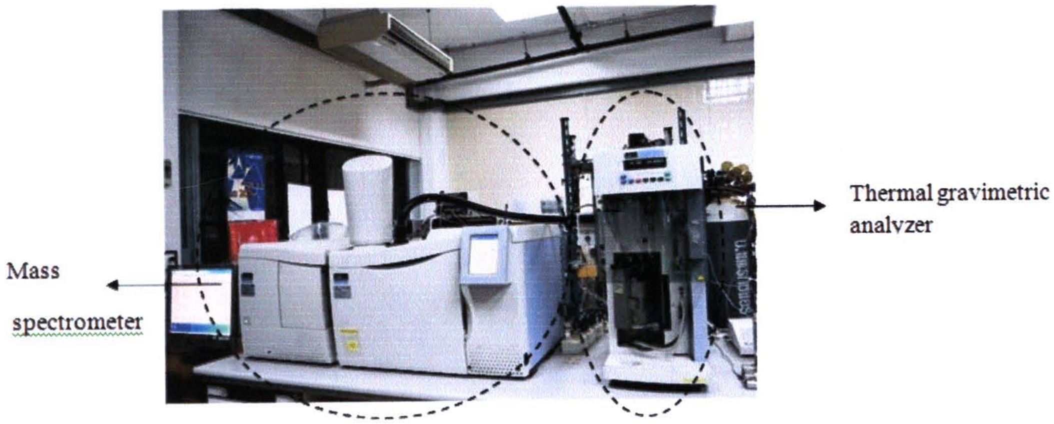

Figure 3.22 A TG-MS apparatus used in this study (TG-MS, Perkin Elmer Clarus 500)

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

Thermal gravimetric analyzer was used to study the pyrolysis behavior of the biomass at low temperature. TGA can be used to analyze the pyrolysis behavior at various ranges of pyrolysis conditions. Pyrolysis behavior of each biomass is significantly different. The differences are according to their chemical compositions: cellulose, hemicelluloses, lignin, extractive, and mineral matter. Apart from their chemical compositions, the chemical bonds have also played an important role. In the experiment, about 5 mg of each raw biomass sample was heated to the various desired pyrolysis temperatures in inert atmosphere by 10°C/min heating rate. At the desired pyrolysis temperature, the sample was held for 1 hour. The temperature holding was performed in order to study the difference of mass yield at different temperature and holding time. This study used Perkin-Elmer, Pyris1 TGA which is shown in Figure 3.23.

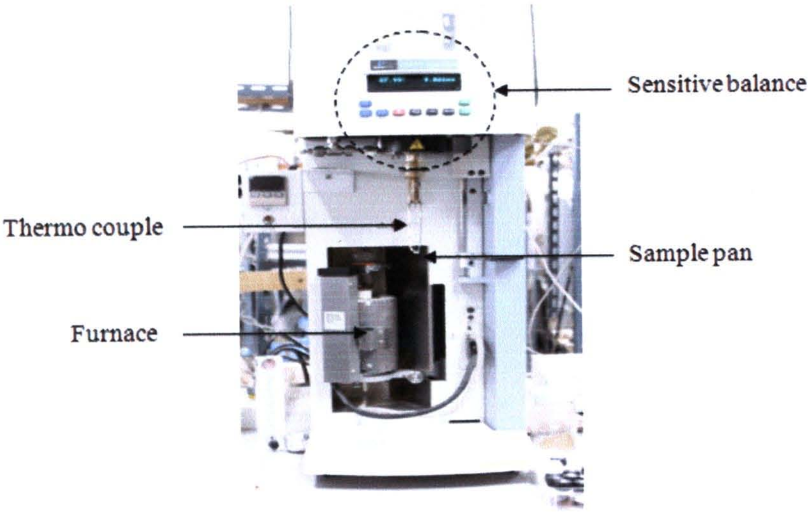

Figure 3.23 A TGA apparatus used in this study (Perkin-Elmer, Pyris1 TGA)

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

The fast pyrolysis of biomass at low temperature was conducted by the use of a drop tube reactor. The drop tube reactor used in this study is shown in Figure 3.24. This reactor consists of an inner quartz tube with inside diameter of ½ in. and outer quartz tube with inside diameter of ¾ in. The lower end of the inner tube was fitted with perforated plate which quartz wool was placed. The temperature of the reactor was controlled by a temperature controller which was linked to the thermocouple that was inserted from the bottom of the reactor. The thermocouple tip was at the same position with the quartz wool that the torrefied sample was dropped on. Before the experiment, the reactor was heated to the desired temperature. When the temperature of the reactor reached the desired temperature, about 50 mg of biomass sample was dropped into the reactor. The heating rates for fast pyrolysis studies were higher than 200°C/min. The gas formed from the pyrolysis was directly injected to the mass spectrometer in order to analyze the gas components. The solid remaining in the reactor was weighed after cooling down to the room temperature in order to measure the solid yield.

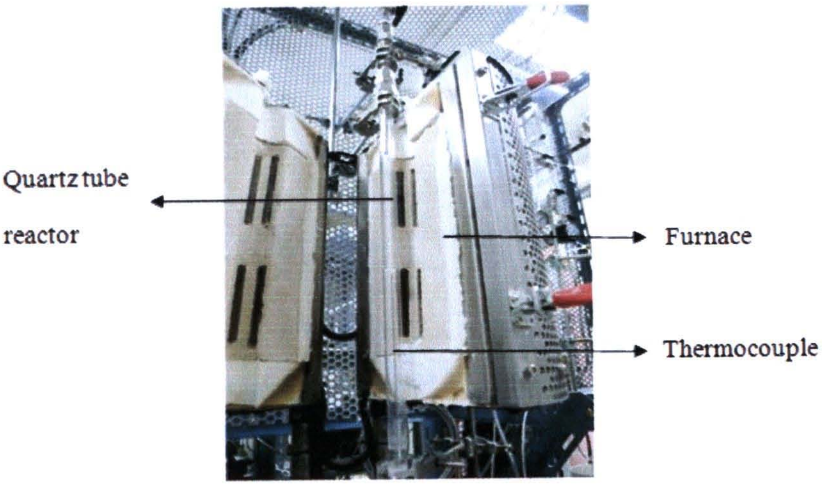

Figure 3.24 Drop tube reactor

3.1.6 Study of slow pyrolysis in fixed bed reactor at low range temperatures (200-300°C)

In order to identify the differences between fast pyrolysis and slow pyrolysis behaviors, the experiments of slow pyrolysis in fixed bed reactor (Figure 3.25) of each biomass samples are necessary. The schematic diagram of experimental set-up of torrefaction process is shown in Figure 3.26. The temperature of the reactor was controlled by a temperature controller which was linked to the thermocouple that was inserted from the top of the reactor and the thermocouple tip was at the same position with the sample bed. In an experiment, about 300 mg of oven dried samples with particle size less than 75 μm was packed on weighed quartz wool in the middle of quartz tube. The sample was heated inside the tube in helium atmosphere by 10°C/min heating rate. Purged and reaction gas were trapped in a gas bag and then quantified by gas chromatography technique (GC). Remaining solid was collected and weighed after it cooled down to room temperature. The collected gas product in the gas bag was immediately injected into GC after the complete experimental condition was reached by 2 ml syringe. The gas product was analyzed trough TCD and FID detectors respectively by using the molecular sieve (MS-5A) column for carbon monoxide analysis and the porapak Q (PQ) column for methane, carbon dioxide and water analysis. The GC apparatus used in this study was Shimadzu, GC-14B which is shown in Figure 3.27.

Figure 3.25 Fixed bed reactor

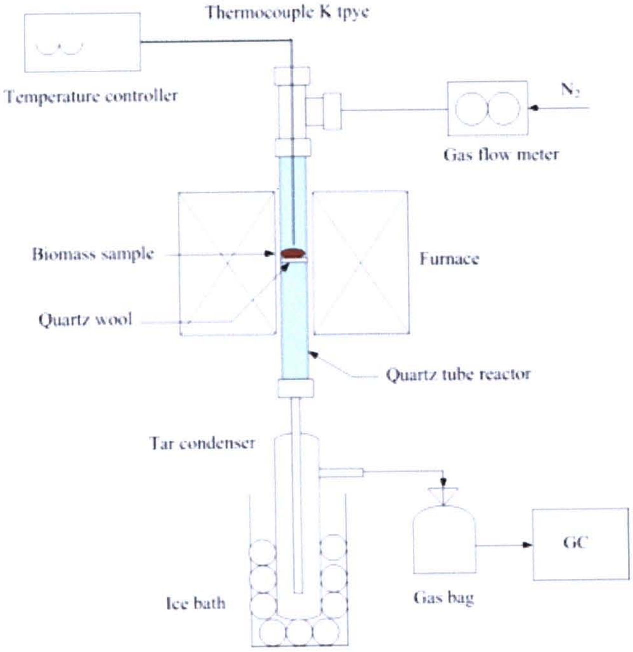

Figure 3.26 Schematic diagram of experimental set-up for pyrolysis in fixed bed

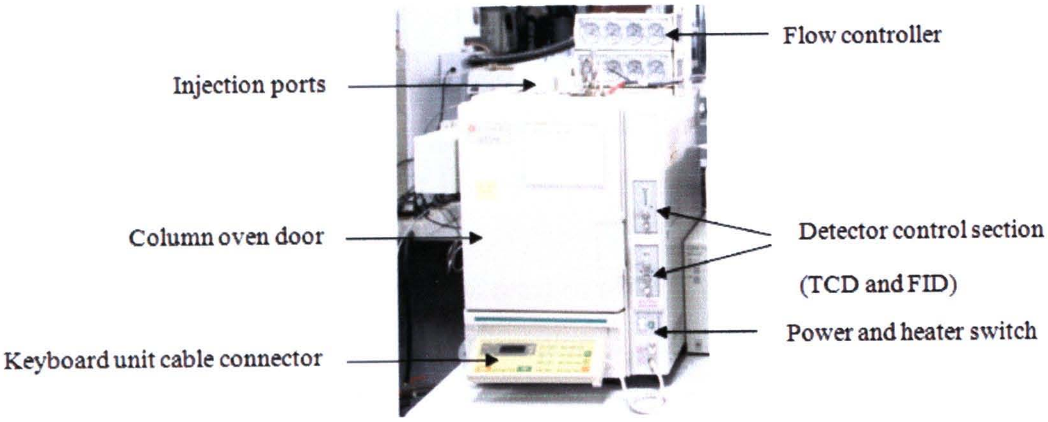

Figure 3.27 A GC apparatus used in this study (Shimadzu, GC-14B)

3.1.7 Analysis of torrefied biomass

In order to examine the fuel properties of biomass, the analyses were performed as follows:

A. Ultimate analyses
B. Calorific value calculations
C. Proximate analyses and fuel ratio calculations

3.1.8 Study of mass and energy balances of pyrolysis process

The overall pyrolysis process can be better understood by study of mass and energy balances. The information needed for mass and energy balances are as follow:

A. The species and mass fraction of each pyrolysis product which are solid and volatile yields.
B. The heating or calorific values of raw sample and each product
C. The sensible heat needed for raw sample and each product at the pyrolysis temperature.

3.1.9 Study of combustion behaviors of raw and torrefied biomass

The combustion behaviors such as weight loss profile and the combustion rate of raw and torrefied biomass were studied by the use of TGA. About 5 mg of sample was heated from room temperature to 600°C in air atmosphere to perform the complete combustion. The grey solid left in sample pan after reaction reached 600 °C was sample ash. The derivative thermogravimetric curve or DTG curves were plotted in order to compare the combustion rate between raw and torrefied samples at different combustion temperatures.