Figure 3.2 Corncob in original shape.

Rice straw, the dry stalk of the plant, is an agricultural residue after the rice grain has been harvested on fields, and it was selected in this work for bed agglomeration study. In Thailand, rice is a domestic cereal staple and an important export product. It had been evaluated that about 25.6 million tons of straw, or 6,217 ktoe equivalent, is produced as the available potential in 2009 [152]. The use of straw in commercial-scale biomass power plants becomes a mainstream in the European Union [12] but in Thailand straw is mainly used as roughage animal feed, mainly for the cattle, and in agricultural sector as the culture media for mushrooms and mulch. Due to its relatively low bulk density, the densification of straw is needed for effective handlings and transportation, as shown in Figure 3.3.

Figure 3.3 Cubic bale of rice straw.

3.1.2 Bed particle

In this work only quartz sand, four different size ranges, was used as the bed particle to study their agglomeration by burning with the above mentioned biomass at given experimental conditions in fluidized bed reactors.

3.2 Material characterizations and instruments

Biomass is a very heterogeneous and physically/chemically complex renewable resource. Understanding this natural variability and range of properties is essential for conducting research and developing energy technologies using biomass resources. Physical property of biomass plays an important role particularly in sizing of the reactor/fuel handling equipments, such as conveyor, hopper or shredder, and in extent of co-firing [12], while chemical property describes its potential to undergo some chemical change or reaction by virtue of its composition. The former includes the material strength, particle and bulk densities and size, while the later is importantly the organic and ash compositions, and the energy value.

Basically, biomass fuels are characterized chemically by the standard methods of Proximate and Ultimate analyses, heating value determination and the ash composition analyses. The proximate analysis is a technique that separates and identifies categories of compounds in a sample and reports the contents of moisture, volatile, fixed carbon and ash in the sample. The ultimate analysis is also similar technique giving the contents of carbon, oxygen, hydrogen, sulfur, and nitrogen elements. The energy value of fuel substances analyzed in laboratory is reported generally in term of the high heating value (HHV) based on the complete combustion of the sample to carbon dioxide and liquid water (The low heating value, LHV, gives the heat released when the hydrogen is burned to gaseous water). The analysis of fuel ashes gives the composition of inorganic elements in the ash. The results of these analyses are so important for fuel handling, combustion/gasification system design, operation, and emission control [12].

Comparison of fresh and used bed materials based on their chemical and morphological characteristic are also necessarily.

The standard analytical methods used in this study were mainly based on ASTM (American Standard of Testing Materials). The analysis items, ASTM codes and the further advance analyses including laboratory instruments, used in this study, were listed in Table 3.1.

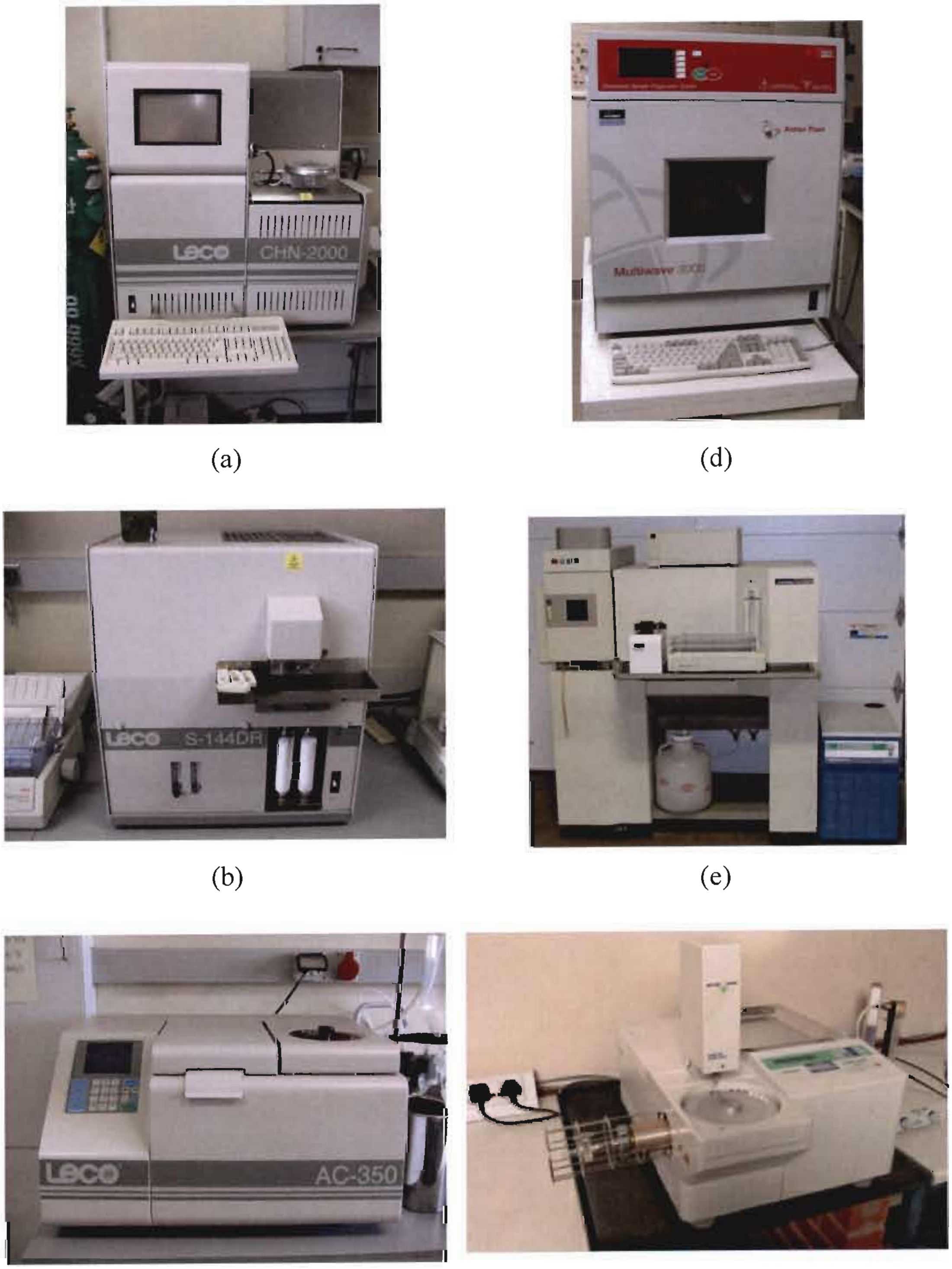
Table 3.1 Methods and instruments for characterization

Item	Code/Analysis	Instrument	Note/Description
Biomass			
Bulk density	E873-82 (1998)		- As fired basis
Size distribution	E828-81 (2004)		- As fired basis
Char particle density	D167-93 (2004)e1		
Fuel preparation	D2013-11		- As received and fired basis - Treating biomass before intensive characterization
Proximate analysis - Moisture - Volatile - Ash - Fixed carbon	E870-82 (2006) - E871 - E872 - D1102		- As received and fired basis - Fixed carbon is determined by difference
Ultimate analysis - C, H - N - S - O	E870-82 (2006) - E777 - E788 - E775	- CHN elementary Analyzer (Fig. 3.4a, **LECO; CHN-2000**) - S Analyzer (Fig. 3.4b, **LECO; S-144DR**)	- As dry basis - Oxygen is determined by difference
Chlorine	E776-87 (2004)		- As dry basis
Heat calorific value	E711-87 (2004)	- Bomb Calorimeter (Fig. 3.4c, **LECO; AC-350**)	- As dry basis
Ash composition (Si, Al, Ca, Mg, Na, K, Fe, P, Cl, S)	- D1102-84 (2007) - a digestion method [153]	- Microwave oven (Fig. 3.4d, **Anton Paar; Multiwave 3000**) - Inductively Coupled Plasma Atomic Emission Spectrometry (*ICP-AES*, Fig. 3.4e, **Perkin Elmer; OPTIMA 3000**)	- Dry ash - Ash sample is prepared according to ASTM and then digested into solution state in the microwave oven.
Thermal behavior		- Thermal Gravimetric Analysis (*TGA*, Fig. 3.4f, **Mettler Toledo; TGA/SDTA 851e**)	- Pulverized biomass as fired basis - Tested environment is air - Amount and rate of weight loss is determined as function of temperature

Table 3.1 Methods and instruments for characterization (Continue)

Item	Code/Analysis	Instrument	Description
Quartz sand (fresh and spent)			
Size distribution	sieve analysis (gradation test)	- A set of standard sieves - A mechanical shaker	
Chemical composition		- X-Ray Fluorescent (*XRF*, Fig. 3.5a, **Philips; PW2400**)	
Crystalline structure		- X-Ray Diffraction (*XRD*, Fig. 3.5b, **Bruker AXS; D8 DISCOVER**)	
Agglomerate sample			
Structure and composition of coating and neck		- Scanning Electron Microscope with Energy Dispersive X-ray Spectrometer (*SEM-EDS*, Fig. 3.5c, **JEOL; JSM-6400**) - X-Ray Diffraction	- Specimen preparation of agglomerate sample is needed, prior to SEM analysis.

The brand and model of instruments in bold are referred

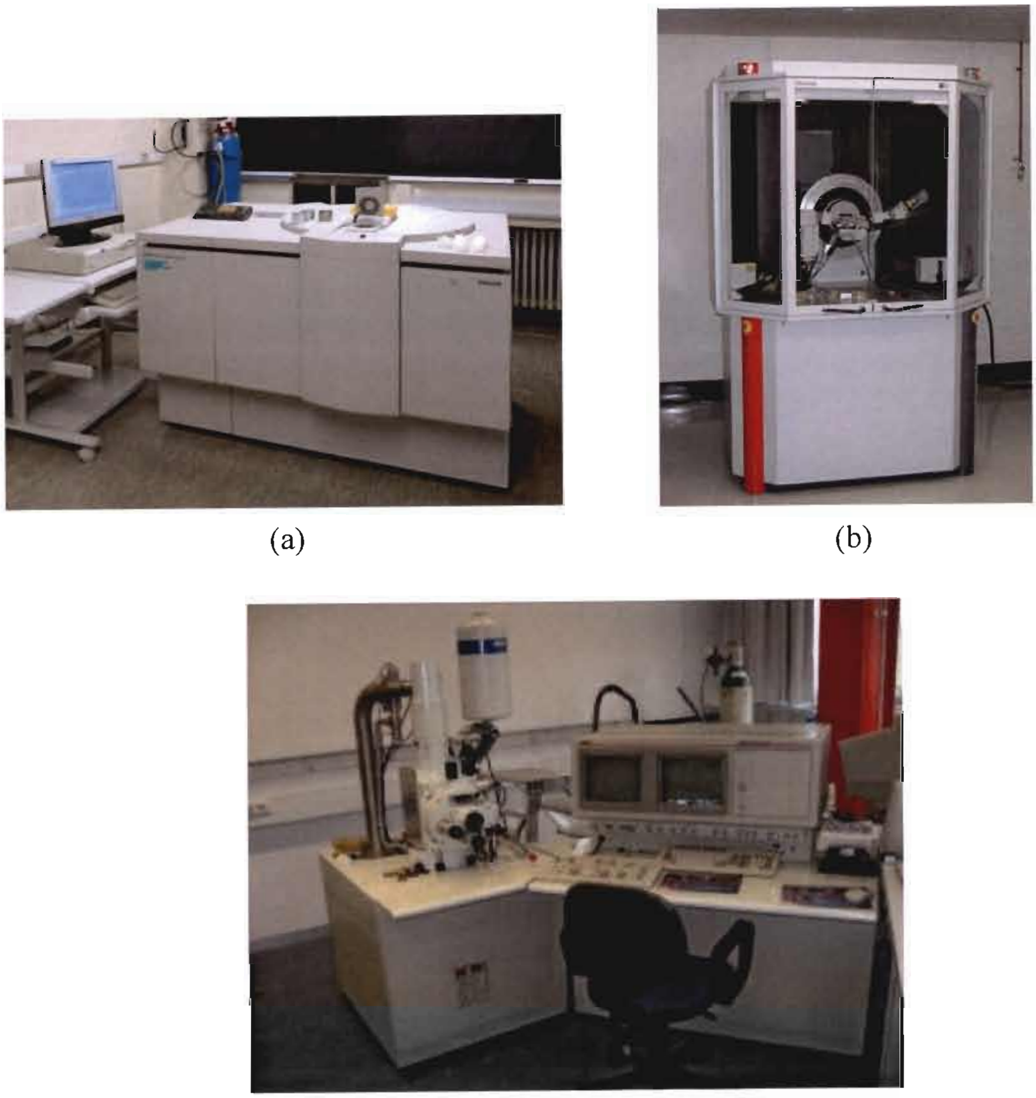


(a) (d)

(b) (e)

(c) (f)

Figure 3.4 Biomass characterization instruments, (a) CHN elementary analyzer; (b) S analyzer; (c) Bomb calorimeter; (d) Microwave oven; (e) Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES); (f) Thermal Gravimetric Analyzer (TGA).



(a) (b)

(c)

Figure 3.5 Characterization instruments for bed material, (a) X-Ray Fluorescent (XRF); (b) X-Ray Diffraction (XRD); (c) Scanning Electron Microscope equipped with Energy Dispersive X-ray Spectrometer (SEM-EDS).

3.2.1 Biomass

Prior to intensive chemical characterization, a number of samples of each biomass were taken and then pulverized separately to be in powder form of up to 250 µm grain size, according to ASTM D2013-11. The analyses of proximate and ultimate, heating value and chlorine content of these samples were then carried out. Additionally the amount and rate of mass loss of biomass samples during combustion in air ambient were also measured via TGA.

The quantitative analysis of the inorganic elements in biomass ash samples was carried out by using ICP-AES. As this technique requires the liquid form of the sample, the ash samples of biomass prepared according to ASTM D1102-84 (2007) were digested with the mixture of concentrated acids ($HF+HNO_3+H_2O_2$) in a microwave oven into solution state, according to the methods in a literature [153]. These ash solutions were then introduced to ICP to measure the concentrations of the required ash forming elements.

3.2.2 Bed material

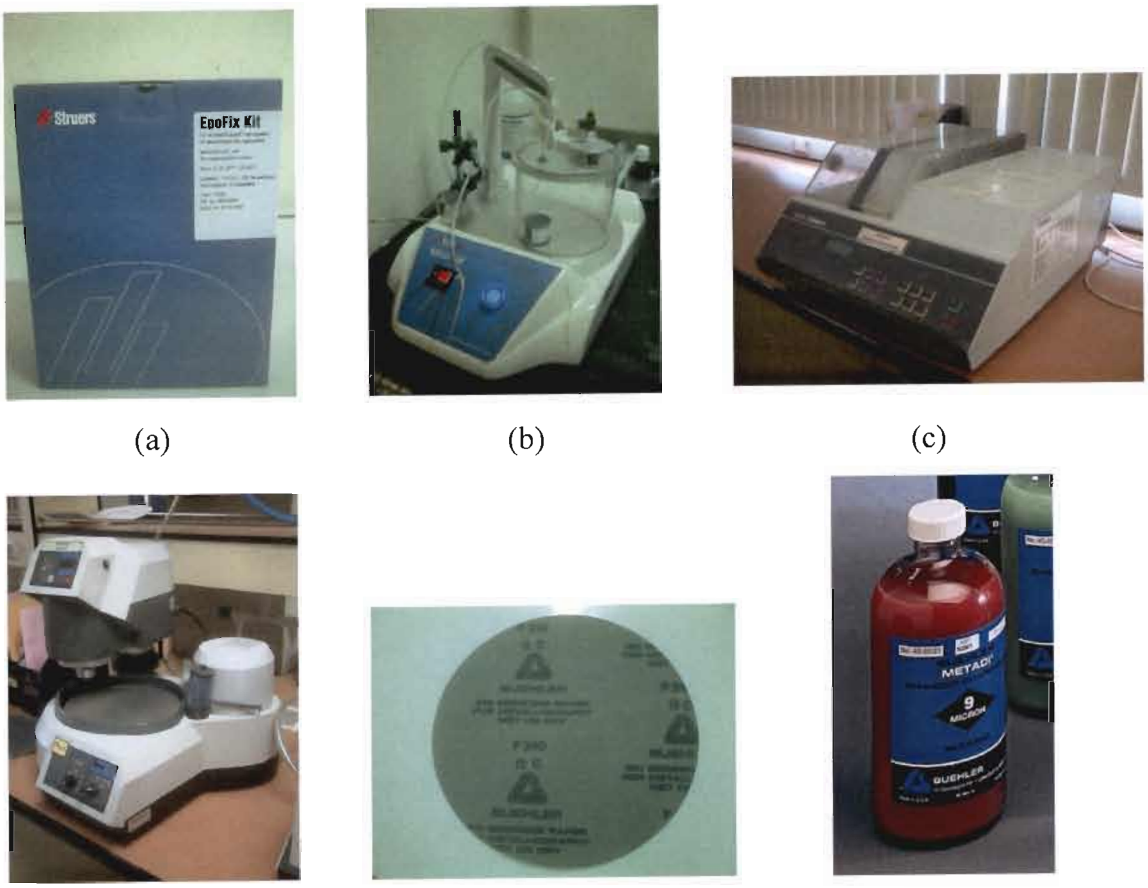
Firstly, fresh quartz sand obtained was analyzed for the size distribution and then sorted out the size range for lab and pilot scale experiments. The ranges of 300-355 μm ($d_{p,av}$:323 μm) and 425-500 μm (459 μm) of sand sizes were used for lab scale experiments, as the controlled conditions, while 150-600 μm (354 μm) and 150-1180 μm (573 μm) in the original size ranges were tested in pilot scale, for verification. Secondly, the chemical properties of this sand were analyzed by using XRF and XRD to determine the composition and identify the crystalline structure, respectively.

3.2.3 Spent bed and agglomerate samples

The exhausted bed samples from FBC experiments were sized by a set of standard sieves to analyze their size distributions, and to separate the agglomerates. Prior to SEM-EDS analysis, the agglomerates samples had been prepared to be the specific specimen as follows:

- embedding by the slow curing epoxy resin (Fig. 3.6a, Struers; EpoFix) in a vacuum chamber (Fig. 3.6b, Mega advance; VEGA 5).
- cross-sectional cutting by the diamond saw of a precious cutting machine (Fig. 3.6c, Struers; Accutom-5).
- grinding (Fig. 3.6d, Buehler; Phoenix Beta) the prepared surface with the silicon carbide abrasive paper No.240 (Fig. 3.6e, Buehler).
- polishing with the 9 μm diamond suspension (Fig. 3.6f, Buehler; MetaDi).
- finishing the surface of agglomerate specimen by carbon sputtering to make specimen electrically conductive during SEM examination.

The SEM analysis was operated at the backscatter mode to characterize the appearance and EDS analysis was performed to determine the elemental distribution of the coating and neck in agglomerates.


(a) (b) (c)

(d) (e) (f)

Figure 3.6 Materials and instruments of SEM specimen preparation, (a) epoxy resin; (b) vacuum chamber; (c) precious cutting machine; (d) grinder; (e) Si-C abrasive paper; (f) diamond suspension.

3.3 Fuel preparation for FBC experiments

Fuel preparation was required to treat the variable particle size and inappropriate properties of the fresh biomass samples, in order to feed uninterruptedly by existing fuel feeders and be efficiently the combustion process. The preparation was biomass specifics and described in details below. The controlled size range of biomass fuels in the present laboratory scale experiments was 0.8-1.0 cm.

3.3.1 Palm shell and fruit bunch

The mature fruit bunches cropped are steamed for a certain time, as the initial step of kernel separation process. They are then threshed to separate palm seeds by gravity. Only palm seeds are steamed once again to make the fiber to be easily peeled, while sodden empty bunches are sent off. The peeled palm seed are cracked by mechanical press to separate their kernels, as the final step. As a result, palm shell and empty bunch have substantially high moisture contents. They lead to poor combustion and subsequent increased stack emissions, and maintenance and operational problems [12]. Reducing these excessive moistures was necessary, as a fuel preparation.

The size range of 0.3-1.3 cm of actual shell as received from the mill was suitable to the present combustion experiments, and sufficiently amount was separated for lab scale tests (Fig. 3.7).

Figure 3.7 Size of palm shell particles for lab scale experiments.

Palm fruit bunch is the drop-like shaped bundle of natural long thread-like fibers (Fig. 3.1b), and the more steps in preparation were required. Initially, sodden bunches were ripped away and then introduced into a small agricultural shredder. Subsequently, the intermediate (Fig. 3.8a), which was still too large to be fed, were cut into the adopted size (Fig. 3.8b), and was employed in both lab and pilot scale tests.

Finally, both palm residues fuels were dried in the open air to remove the excess water.

(a) (b)

Figure 3.8 Treated palm bunch; (a) shredded by an agricultural shredder and (b) cut to end-used sample.

3.3.2 Corncob

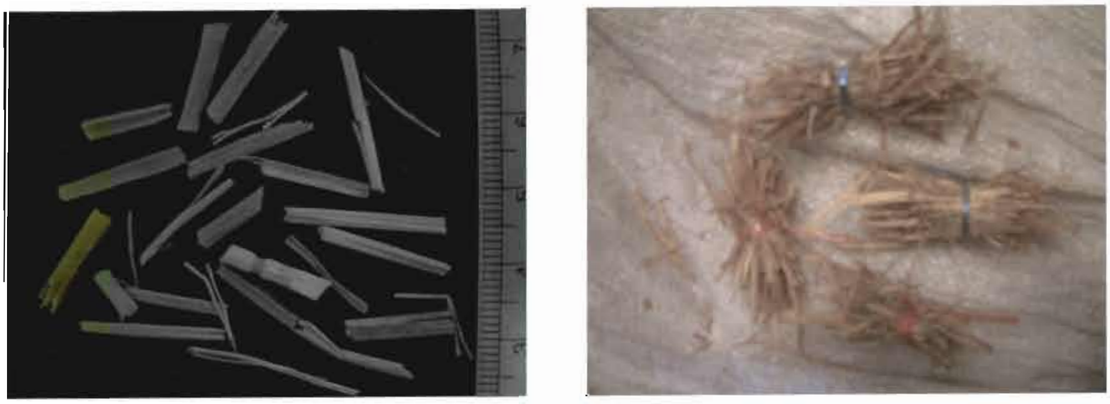
Corncob from silo of the mill which had been dried naturally during storage was smashed by a laboratory hammer crusher generating the corncob flakes for the pilot scale experiments (Fig. 3.9a). The adopted size of lab scale tests was then separated out (Fig. 3.9b).

(a) (b)

Figure 3.9 Corncob samples; (a) crushed by a hammer mill and (b) end-used sample of lab scale test.

3.3.3 Rice straw

The bales of rice straw that had been dried by exposing to the sun at field for a certain time, after the grains were harvested, were unfolded and fed into a small shredder. The straw was then taken to further cut into internodes within the sizes for lab scale tests. For pilot scale tests, these internodes were bunched to form the cylindrical bale. The two treated straw samples were shown in Figures 3.10a and 3.10b, respectively.



(a) (b)

Figure 3.10 Straw samples; (a) for lab scale test and (b) for pilot scale test.

3.4 Bubbling fluidized bed facilities

The bed agglomeration behaviors were investigated in the laboratory and pilot scales of bubbling fluidized bed apparatuses. The schematics and details of both facilities were illustrated in Figures 3.11-3.13.

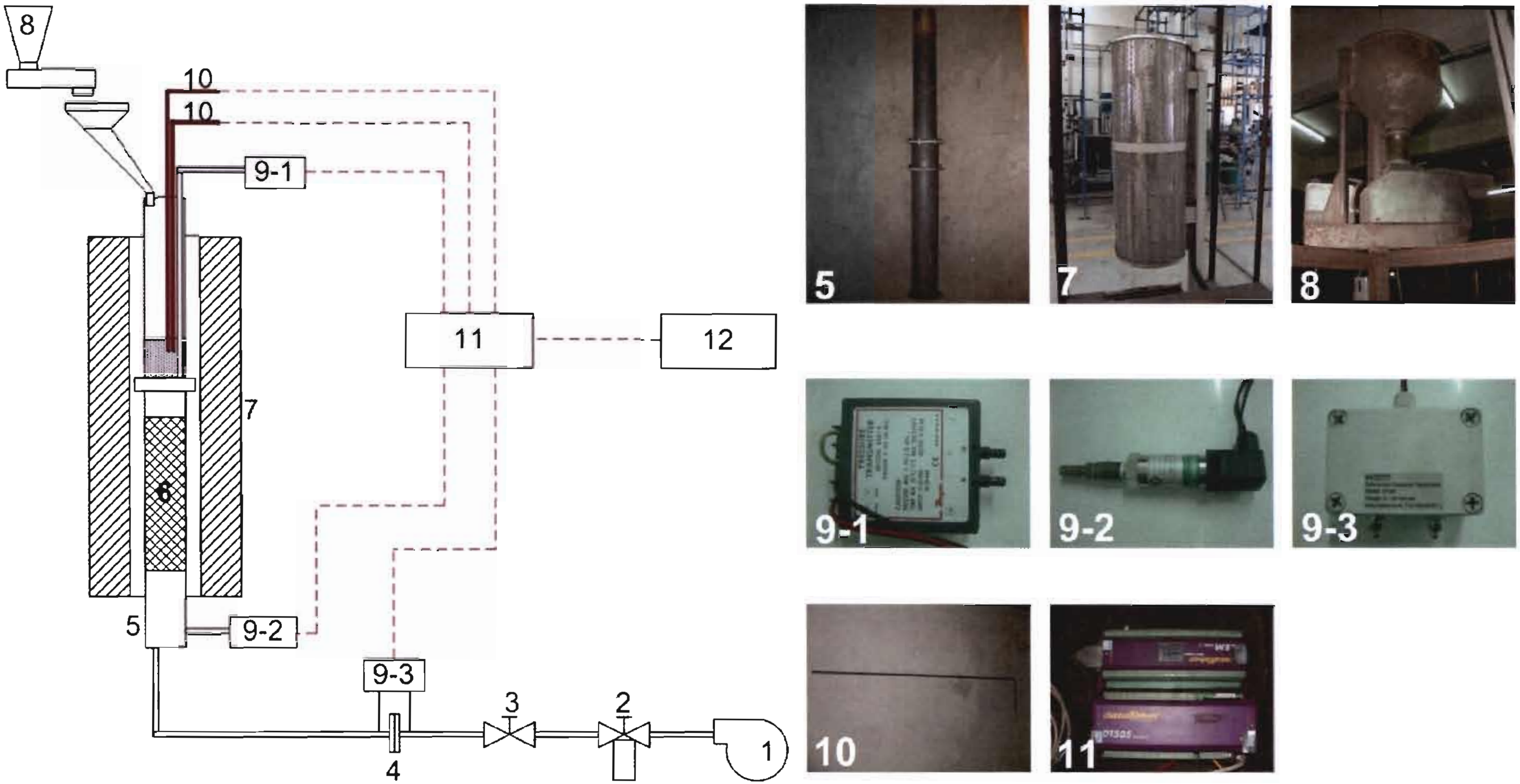


Figure 3.11 Laboratory scale fluidized bed apparatus: (1) air compressor; (2) pressure regulator with water/oil trap; (3) air control valve; (4) calibrated orifice; (5) a fluidized bed reactor; (6) air pre-heater; (7) electrical furnace; (8) fuel feeding device; (9) pressure transmitters; (10) K-type thermocouple; (11) data logger; (12) computer (PC).

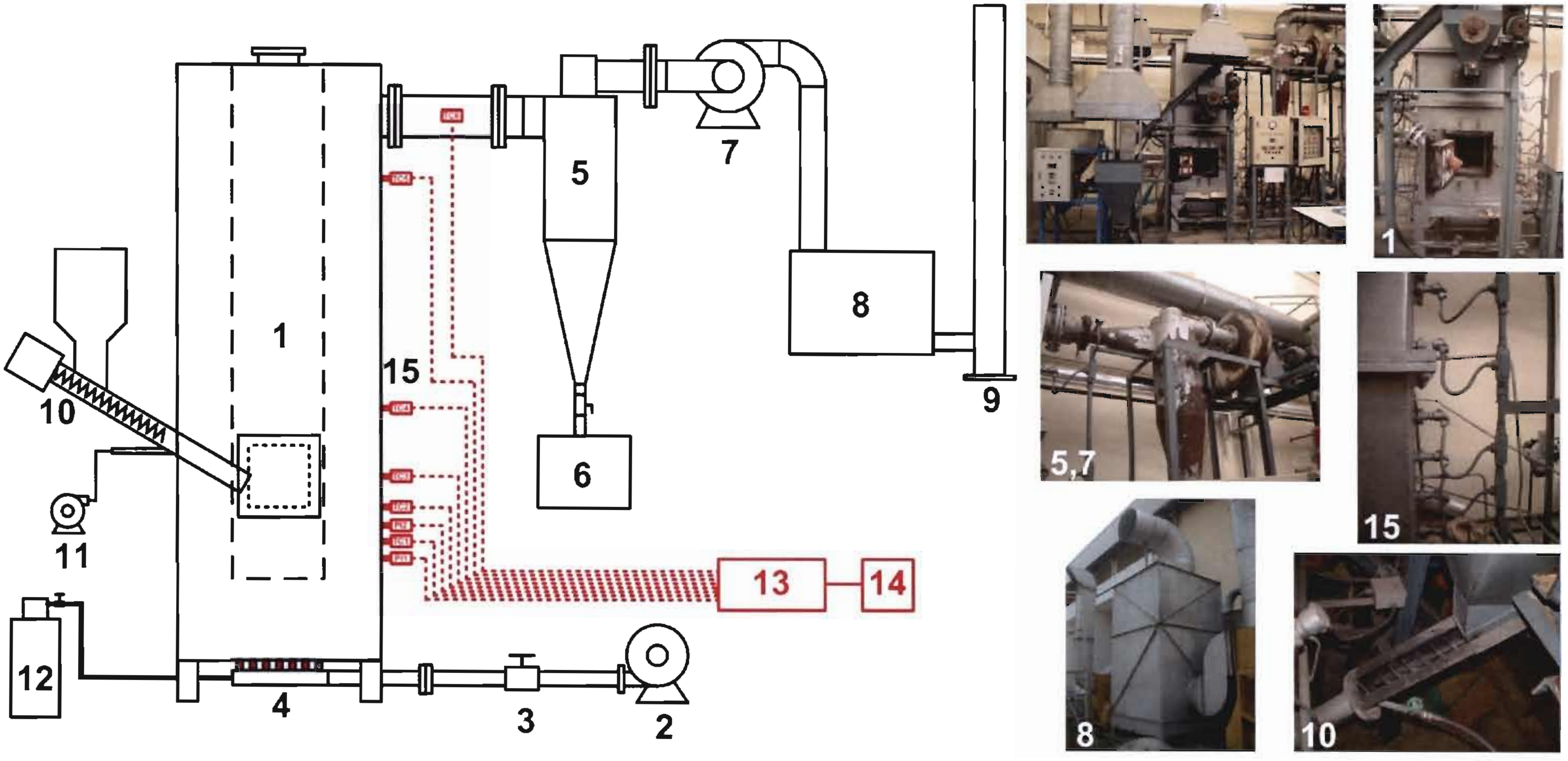


Figure 3.12 Pilot scale fluidized bed apparatus: (1) chamber; (2) force draft centrifugal fan; (3) air flow control valve; (4) air box with tuyeres; (5) cyclone separator; (6) fly ash receiver; (7) induced draft centrifugal fan; (8) wet scrubber; (9) chimney; (10) screw feeder with hopper; (11) air compressor; (12) LPG tank; (13) data logger;(14) computer (PC); (15) measuring devices.

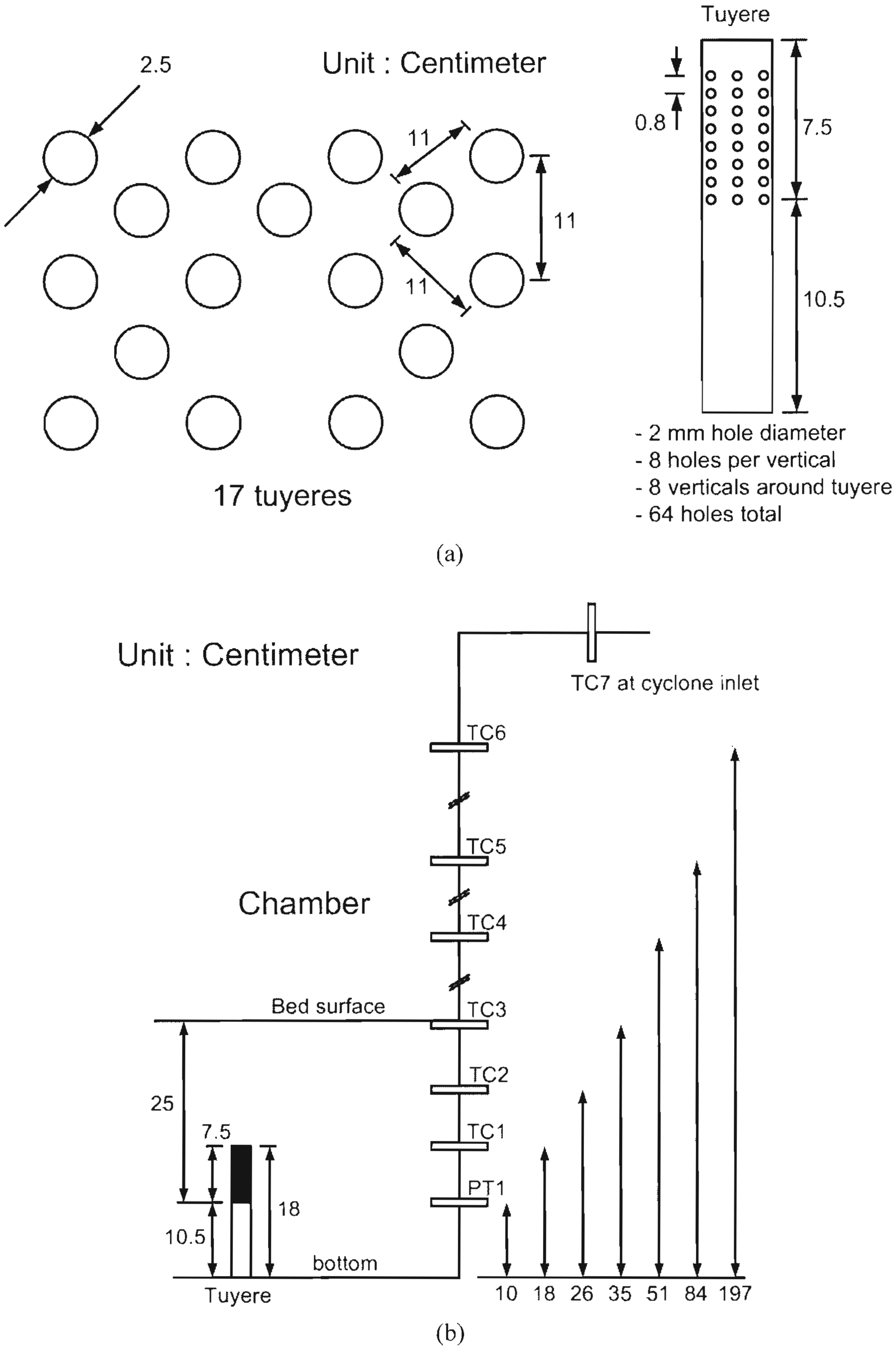


Figure 3.13 Layouts/Specifications of (a) tuyeres and (b) measuring devices (TC=thermocouple, PT=pressure transmitter).

3.4.1 Laboratory scale facilities

A laboratory scale unit sketched in Figure 3.11 consisted mainly of a cylindrical fluidized bed reactor, a fuel feeding unit, a set of devices and a data acquisition system. The reactor was made of a 316L-cylindrical stainless steel tube with 1.8 m-length, 9 cm-ID and 4 mm-thickness. A stainless perforated air distributor plate with 85 holes of 0.6 mm. diameter in equilateral triangular array was fitted to the chamber, approximately 1% opening area. The start up was accomplished electrically by a cylindrical tube furnace (Carbolite; STF), preheating the bed and fluidizing air. In a wind-box, the twisted stainless steel strips were packed to serve as an air pre-heater. The fluidized bed section was located near the middle of the furnace. An over bed fuel feeding unit was a frequency adjustable shaker mounted with a fuel hopper. The volumetric flow rate of fluidizing air supplied from an air compressor was measured by a calibrated orifice.

Three pressure transmitters were fitted at a calibrated orifice, an air-box and above an air distributor to measure the air flow rate, the air-box pressure and the whole bed pressure drop, respectively. Two K-type thermocouples for the bed temperature measurements were located along the vertical axis at 2 and 6 cm-heights above an air distributor. All devices were connected to a data acquisition instrument (data logger) to online record and display via PC in order to observe the bed pressure and temperature profiles.

3.4.2 Pilot scale facilities

A schematic diagram of a pilot scale unit was shown in Figure 3.12. A cubic and tall furnace chamber with the inner lining of refractory bricks had 45 x 45 cm^2 of bed cross-sectional area and 2.5 m of height. The plenum air box was connected with 17 tuyeres serving as the air distributor, which was detailed in Figure 3.13a, and to an access port of liquefied petroleum gas (LPG) tank for preheating. Biomass fuel was fed over the bed by a speed adjustable screw feeder mounted with a fuel hopper, and was spread onto the bed surface by the air jet produced by an air compressor. Dusty flue gas was treated in 2 sequential steps of a hot gas cyclone and then a water wet scrubber before emission. Several ports were fitted along the hot path for the pressure transmitters and K-type thermocouples, positioning in Figure 3.13b. Similarly the bed pressure and temperature profiles were monitored and logged on a PC via a data acquisition unit (data logger).

The bed pressure and temperature profiles were observed in both facilities in order to observe the changes in bed hydrodynamics and mark the onset and completion of bed defludization.

3.5 Experimental procedures

The bed agglomeration experiments were carried out under the atmospheric condition and steady state combustion at constant bed temperature and fluidizing air velocity. The influences of bed temperature (T_b), superficial air velocity (U), bed particle size (d_p) and static bed height (as H_b/D_b) on the bed agglomeration tendency was investigated.

3.5.1 Pre test

Prior to the bed agglomeration testes, these experiments were formerly carried out only in the lab scale unit to determine the significant characteristics of bed, viz;

1. Minimum fluidization velocity

In order to transition from a packed bed to a fluidized condition, the velocity of gas that passes over it is continually raised. A free-standing bed will reach to an incipient fluidization point, whereby the bed mass is suspended directly by the flow of gas stream. The corresponding gas velocity is termed the minimum fluidization velocity (U_{mf}). The transition boundaries between various fluidization regimes (i.e., bubbling to turbulent, and turbulent to fast fluidization) are affected by gas and solid properties and gas superficial velocity [148]. The regime of bubbling bed for the particle in Geldart group B, such as sand, is generally 3-5 of U/U_{mf}.

To investigate U_{mf}, a certain amount of quartz sand at given sizes (in section 3.2.2) in the lab scale reactor was heated up electrically to a given bed temperature without fluidizing air flow. Until reach, the gas flow was raised gradually and simultaneously the bed pressure and temperatures were recorded, until obtained the complete fluidization.

2. Reference profiles

As mentioned, the changes in bed hydrodynamics by bed defluidization were observed by monitoring the bed pressure and temperature. Their reference profiles would be formerly done by fluidizing the given sand at high temperature, derived from the electrical furnace, without fuel feeding. During a trial, the ongoing fluidized bed initially set at 0.5 of static bed height to bed diameter ratio (H_b/D_b) was doubled by immediately adding an identical amount and size of sand particle. The used bed samples would be sieved to find the abnormal sized particles at the end of tests, after cooling.

3.5.2 Agglomeration test

To start up, the bed was heated up by the external heat sources (the electrical furnace and burning LPG) from ambient to a certain temperature and then fluidized at a required air velocity. A required bed temperature was reached by subsequent combustion with biomass, and the external heat sources were then shut off. The recorded time started as the fuel feeding began. In the course of lab scale trials, regularly sampling the bed particles in reactor and visual observing (recorded by digital VDO camera) the fluidization were carried out. The trial completed when the bed was completely defluidized. The fuel consumption of each trial was estimated from the measured initial and final weights of biomass. The bed samples taken during the trial and discharged after defluidization were further characterized, as mentioned in section 3.2.3. All conditions were repeated twice to establish reproducibility.

In the next chapter, additional literature reviews on the theoretical prediction of bed agglomeration and the development of the present mathematical models will be mentioned and discussed in details.