CHAPTER III
EXPERIMENTAL

3.1 Sample Collection and Preparation

Sewage sludge samples used in this study were collected from 20 different wastewater treatment plants (WWTPs) in Bangkok and vicinity in accordance with the standard method, ASTM D346-90, 1999. The sample sources include municipal, hospital and industrial WWTPs. The sample collection was carried out monthly over throughout a year. The total number of collected samples exceeded 219 samples. The detail on samples and their source are available in Appendix B. Even though the samples may come from the same source, once the sample was collected, it was thought to be different from others and analyzed individually. The benefit on this distinguishing is to observe the difference between samples or seasonal process operations which might be possible.

The samples were naturally dried for 1–2 days minimizing the moisture in samples. The samples were then ground by using a ball mill. The fraction of 150–250 μm in particle size was selected for further study. This step was not only for preparation of a suitable sample size for experiments but also providing better homogeneity of samples.

3.2 Equipment and Method

The research was carried out mainly at PPC laboratory. However, part of research activities, especially in the Chapter VI, was done at UNSW campus. Different equipment models and conditions were used. Some information might be partly described through Chapter VI in the corresponding section. Indeed, the results were analyzed separately in order to avoid the equipment errors.

3.2.1 Characterization

The characterization of sewage sludge was directed toward their thermal properties. All samples were analyzed according to the following standards:

1) Proximate analysis, the method to find proximate compositions of materials namely moisture, volatile matters, fixed carbon and ash (ASTM D-3172)
2) Ultimate analysis, which provides major elemental compositions of materials such as Carbon, Hydrogen, Nitrogen, Sulfur and Oxygen (by subtraction) (ASTM D-3176)
3) Heating value, using bomb calorimeter (ASTM D-2015).

3.2.2 Composition Analysis

3.2.2.1 Analysis Scheme

The composition analysis corresponds to Chapter VI, at which the main compositions of sewage sludge were proposed in accordance with biomass species. The analysis was done in accordance with the ASTM standard, D-1106 and D-1107.

The first standard is to extract the ethanol-toluene soluble contents. The analysis was performed by following procedures below:

1) The solvent was prepared by mixing 1000 ml absolute ethanol with 427 ml toluene (or the same ratio)
2) Approx. 5 g of specimen was placed into a cellulose thimble in the Soxhlet extraction apparatus while 250 ml of solvent was used for each experiment.
3) The extraction was performed for at least 8 hours at which the solvent was kept briskly boiling that provides with 4-6 siphoning per hour. The cooling water was set at 15 °C.
4) After evaporating the solvent from the extraction flask, the residue was dried overnight and kept in a dessicator.

The latter analysis is the determination of acid insoluble lignin in samples. The soluble substance was considered cellulose. The analysis was performed by the following procedures:

1) The extracted residue of 2-3 g was initially digested in 400 ml of hot water (approx. 100 °C) for three hours. Some of water-digested residue was separated, dried and kept for pyrolysis experiment in order to observe the difference if there is any.
2) The sample was next digested in 15 ml of 72 wt% sulfuric acid for two hours using a glass-stoppered weighting bottle. The solution was stirred thoroughly and oftenly.
3) Consequently, the solution was diluted to 3% concentration by adding 560 ml of water and boiled for four hours.
4) The solution was finally filtered rinsed by water. The acid-digested residue was dried overnight and kept in dessicator.

Overall analysis scheme was given in Figure 3.1. Abbreviations namely RS, ES, WDS and ADS referred as raw, extracted, water-digested and acid-digested sludge, are used throughout this book.

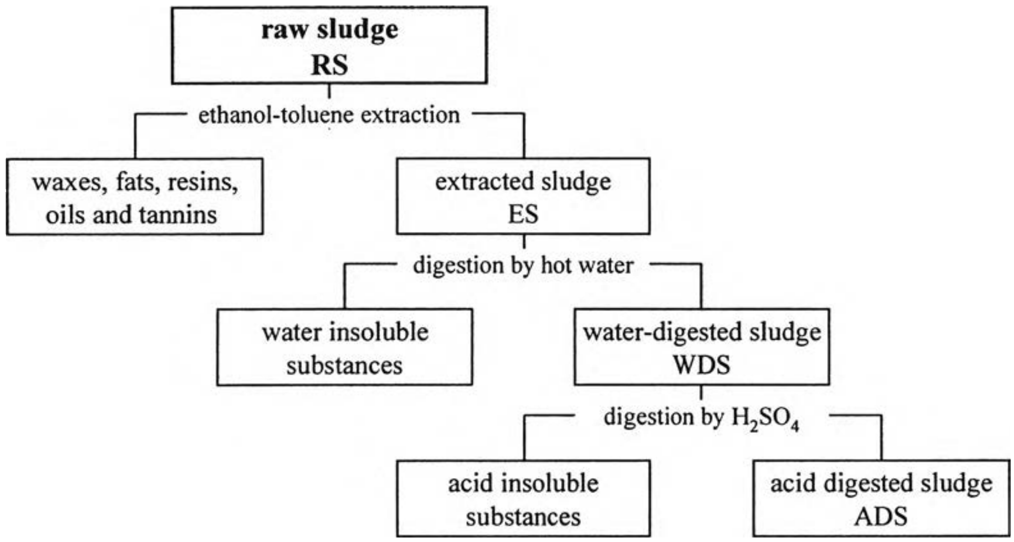

Figure 3.1 Sewage sludge analysis scheme according with the biomass analysis.

3.2.2.2 Fourier Transform Spectroscopy

Original sludge and extracted/digested residues were characterized by Fourier Transform Infrared (FTIR) Spectroscopy in order to observe their functionalities. The equipment and condition used is in Table 3.1.

3.2.3 Pyrolysis Experiment

3.2.3.1 Thermogravimetric Analysis

The pyrolysis behaviour of all samples were studied by Thermogravimetric Analysis (TGA). The schematic diagram of TGA apparatus is shown in Figure 3.2. The samples were pyrolized in temperature-controlled environment up to 800 °C under the flow of nitrogen. Mass loss data will be collected during pyrolized by computer acquisition and controlled modules. The detail on equipment and condition use is in Table 3.2.

With the compact equipment described in Table 3.2, the sample was placed in a platinum pan hanged down from a microbalance at the top. The cylindrical furnace was place in a vertical direction. The temperature probe located right under the sample pan was used to detect the actual temperature as well as to provide a signal for temperature control program.

Table 3.1 FTIR equipment and condition used

Equipment	
- Model:	NEXUS 670 ThermoNicolet
Condition used	
- number of scan:	32 (estimated 68s)
- sample gain:	1
- mirror velocity:	0.6329
- spectral resolution:	4 cm^{-1}
- standard background:	dried KBr pellet measured daily

The equipment was calibrated several times especially after cleaning up and maintenances. Both weight and temperature calibrations were done by using small pieces of metals and alloys namely Ni, Perkalloy, Alumel, Fe and Hisat-50. The transition temperatures where they defeat the magnetic property were used in setting up the control program.

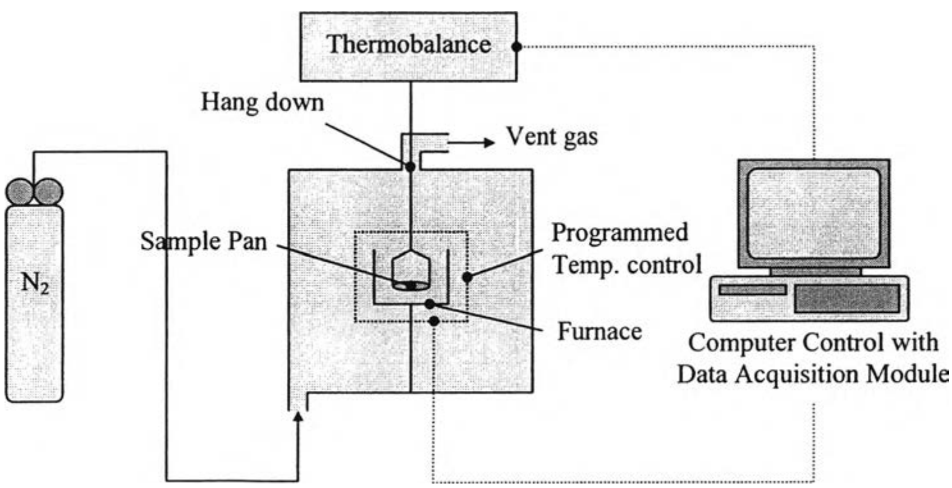

Figure 3.2 Schematic of the employed thermogravimetric apparatus.

Table 3.2 TGA equipment and condition used

Equipment	
- Model:	TG7 Perkin-Elmer
Parameters	
- Sample weight:	controlled at approx. 10 mg for each run
- Temperature program:	Three heating steps
	1) heating from ambient temperature to 105 °C
	2) hold until weight constant (approx. 15 min)
	3) heating from 105 to 800 °C
- Heating rate:	20 °C/min
- Carrier gas:	Nitrogen
- Carrier gas flow :	20 ml/min

All samples were subjected to the TGA experiment while some samples (approx. 10% of total sample number) were randomly selected for repeating the experiment to ensure the reproducibility. The results were found to be very consistent for individual sample. The effect of heating rate was also studied by varying at 5, 10 and 20 °C/min. The thermogravimetric and differential thermogravimetric (TG–DTG) data were used to characterize the pyrolysis behavior of the sludge samples as well as to provide estimates of their kinetic parameters.

3.2.3.2 Temperature-programmed Pyrolysis/Mass Spectroscopy

Gas fraction produced from pyrolysis was also be studied by coupled Temperature Programmed Pyrolysis/Mass Spectroscopy (TPP/MS). Pyrolysis reaction was carried out in a compact pyrolyzer. In this equipment, the samples were pyrolized in vertical quartz tube reactor, sandwiched by grass wool and under nitrogen flow. As the temperature increase, the evolved gas was detected by directly-equipped mass spectrometer. The equipment and operating conditions used were listed in Table 3.3.

Table 3.3 TPP/MS equipment and condition used

Equipment	
- TPP:	TPDRO 1100, ThermoFinnigan
- MS:	Blazers OmnistarTM
Parameter	
- Sample size:	control at 5 mg (±0.1 mg)
- Carrier gas:	Nitrogen
- Temperature program:	10 °C/min
- Signal preparation:	The ion intensities were normalized to the sample mass as well as the intensity of the $^{28}N_2$ isotope of the carrier gas, in order to minimize errors caused by a shift in the mass spectrometer sensitivity.