

CHAPTER 3

Experimentation

The chapter describes methods of coal, ash, and slag measurement. These methods are necessary for analyzing the coal, ash, and slag characteristic. The factors influencing the potential of slag are processed and analyzed in the last part.

3.1 Methodology for Coal, Ash, and Slag Sampling

Lignite coals were collected from the Mae Moh mine. Locations of collected lignites are shown in Figure 3.1. The data about heating value, sulfur, and CaO contents were surveyed by EGAT. The lignites with low CaO (free SO_3) in ash were collected from zone C1 (center 1), and the lignites with high CaO (free SO_3) in ash were collected from zone SE (southeast). The raw materials are shown in Figure 3.2.

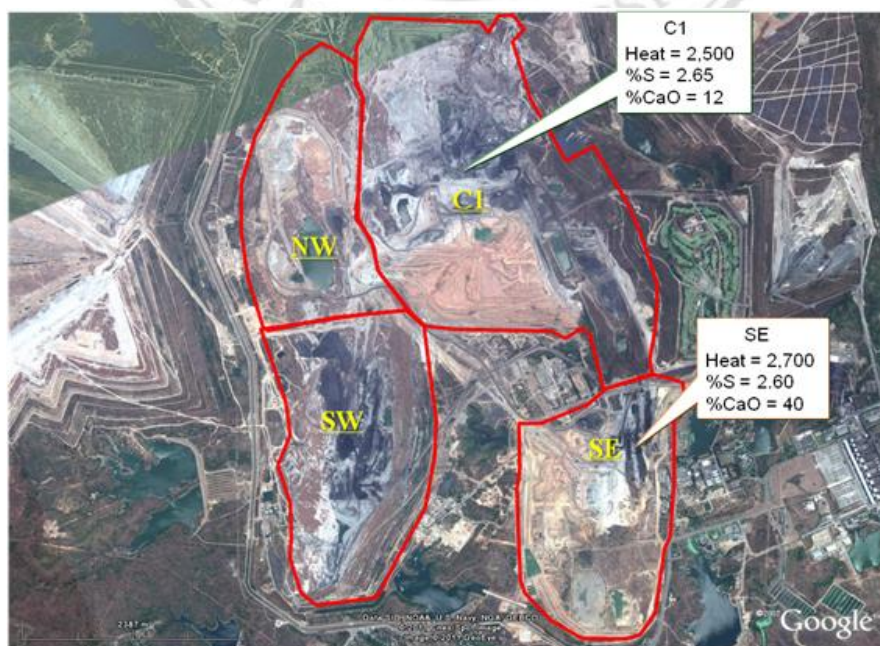


Figure 3.1 The map of Mae Moh mine with zone of collected samples



Figure 3.2 The lignites collected from Mae Moh mine

Before the coal and ash samples were analyzed, the samples were prepared. The flowchart of samples preparation in order to be suitable for testing is shown in Figure 3.3. Firstly, the Mae Moh lignites were reduced to 13 mm (the same size with those fed to the power plant) by jaw crusher for hardgrove grindability test, which is one of the important coal parameters for the power plant. The lignite C1 and SE were investigated by SEM, EDS, and XRD for compare the characterization. The lignites with 13 mm. sizing were subsequently reduced to 8 mesh size (2.38 mm.) by hammer mill. Some of the samples were collected for ash composition test. The ash compositions were tested by XRF. The Cao (free SO₃) in ash was calculated from Eq. (3.1).

$$CaO_{freeSO_3} = CaO \left(\frac{100}{100 - SO_3} \right) \quad (3.1)$$

For the remaining lignites, surface moisture was removed by air dryer at room temperature (25°C) at least 18 hours. Blending of lignite was required to vary CaO (free SO₃) in ash between 20, 25, 30, 35, 40% ±2. They were investigated and checked by ash composition test. The samples were separated into two groups. The first group was burned in air at temperature of 750°C in carbolite furnace (Figure 3.4) to produce the ash and reduced size to 60 mesh (0.25 mm.) by hammer mill again. The samples (Figure 3.5) were used in ash fusion temperature test. The second group of sample was dried in ambient temperature for about 18 hours and reduced size to 60 mesh (0.25 mm.) for proximate, ultimate, heating value, mineral composition, and nonisothermal thermogravimetric analysis.

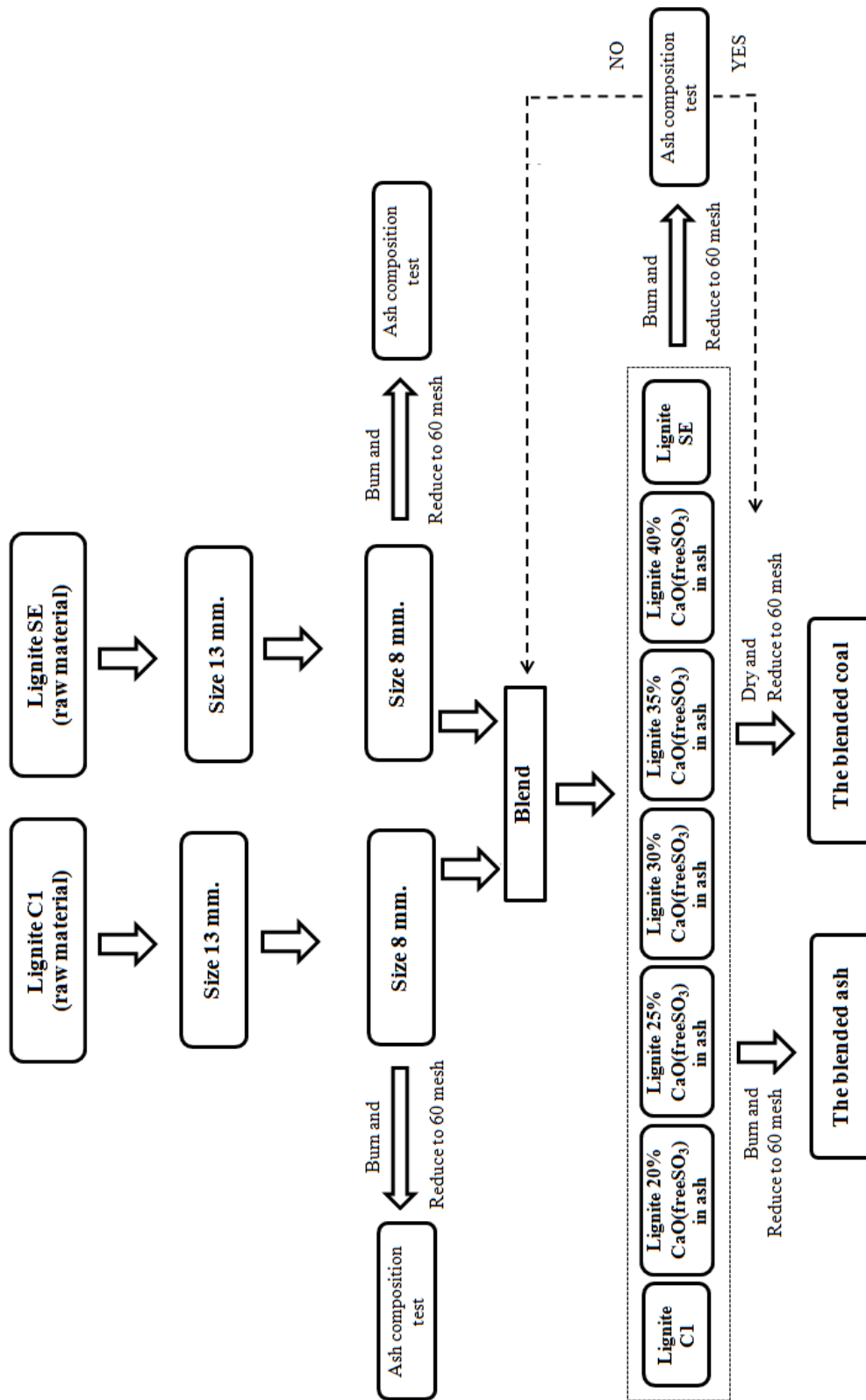


Figure 3.3 Flow chart of sample preparation



Figure 3.4 Carbolite furnace for prepare the ash samples



Figure 3.5 The ash samples for AFT test

Real slag samples with different appearances were randomly collected from a unit of the Mae Moh power plant. For the high Ca content ($>23\%$ CaO free SO_3) test, the operational conditions were combustion temperature of $950\text{-}1000^\circ\text{C}$ and power generated at 87% of full load (about 260 MW). Figure 3.6 showed the representative boiler slag samples. They appeared as: (a) dark brown to black with a shiny surface, riddled with small and large holes (b) brown like cement, large but fragile (c) brown with small holes, hard but brittle (d) brown, like a fusion of lava, full of holes, crystals contain a large amount of sand-like substances.

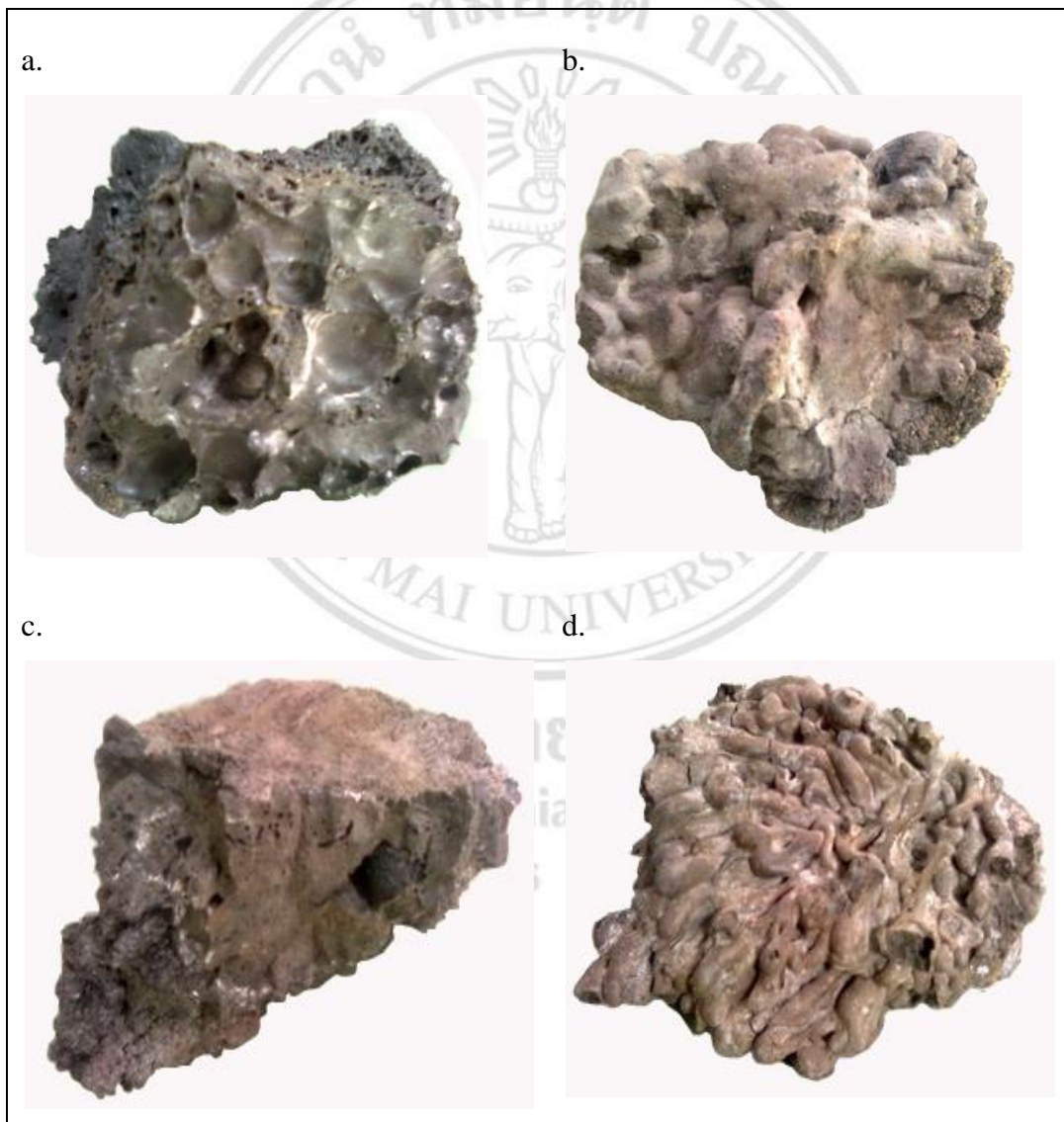


Figure 3.6 Boiler slag sample from the Mae Moh power plant

3.2 Slag Characterization Techniques

3.2.1 Microstructural Feature and Chemical Composition Analysis

The boiler slag samples were analyzed for microstructural and chemical composition by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), respectively (Lopez et al. 2004, Fernandez-Turiel et al. 2004, Van Dyk et al. 2009, Van Dyk 2006).



Figure 3.7 Gold sputter coater for SEM sample



Figure 3.8 The scanning electron microscopy with dispersive x-ray spectroscopy

The samples were prepared, dried, sized to no larger than 3 mm. Their top surfaces were coated with gold to conduct electricity by SPI module sputter coater (Figure 3.7). The analysis was conducted on a low vacuum SEM model JEOL JSM-5910LV (Figure 3.8) at 15 kV and EDS.

3.2.2 Mineral Composition Analysis

X-ray diffraction (XRD) is a very useful technique, and it is one of the most common and widely used methods (together with SEM) for the identification and characterization of mineral matter and, to a lesser extent, inorganic amorphous matter and organic matter (Stanislav and Christina 2005). The samples were analysed by D8 X-ray Diffractometer Bruker AXS GmbH (Figure 3.9) at 40 kV, 40 mA, X-ray tube with Cu anode K-Alpha, step size of 0.04° , step time of 1 s, scanning speed between 2θ 1-140° and temperature 25°C.



Figure 3.9 The X-ray diffraction analyzer

3.3 General Coal and Ash Analysis

3.3.1 Proximate Analysis

The analysis was carried out for determination of moisture, volatile matter, and ash using a LECO TGA701 thermogravimetric analyzer (Figure 3.10), following the standard of ASTM D 3172-07a, D 3173-03, D 3174-04, and D 3175-07. The samples were dried and ground to the 60 mesh of the particle size. Approximately 1 ± 0.0001 g of samples was put to the crucible. The temperature was raised at a heating rate of 15°Cmin^{-1} from ambient to 104°C . For moisture determinations, nitrogen was used as the drying gas in the oven at 104 to 110°C . The samples were weighed automatically. The analysis was completed when the weightings agree with the plateau deviation specified for the instrument. For volatile matter determinations, the temperature was heated at heating rate of 50°Cmin^{-1} to $950 \pm 20^\circ\text{C}$ and held for 7 min. The weight of samples was automatically recorded at the end of 7 min. For the ash determinations, the temperature was cooled to 600°C . The furnace atmosphere was the changed to pure oxygen, and gradually raised to 750°C until the samples reached a constant weight. The samples were automatically weighed at the end. The fractions of moisture, volatile matter, and ash were calculated and shown automatically. The fraction of fixed carbon can be calculated by Eq. 3.1. The result can be used in classification of coal by means of the ratio of the combustible materials to non-combustible materials. This information is used in assessing the quality of coal.

$$\%Fixed\ Carbon = 100 - \%Moisture - \%Volatile\ Matter - \%Ash \quad (3.1)$$

Fixed Carbon is carbon concentration of trace elements in the coal or the remnants of the coal before combustion. Moisture is composite surface moisture, inherent moisture, and water of hydration. Since it replaces combustible matter, it decreases the heat content per kg of coal. Volatile

Matter is volatile, flammable hydrocarbon type, such as methane (CH_4), hydrogen (H_2), carbon dioxide (CO_2) and vapors of tar. Ash is the inorganic salts contained in the coal or ash left from burning. The main compositions of the ash are oxide of silica (SiO_2), Ferric (Fe_2O_3), alumina (Al_2O_3), calcium (CaO), sodium (Na_2O), sulfure (SO_3). In addition, the oxide of magnesia (MgO), potassium (K_2O), phosphorus (P_2O_5), titanium (TiO_2) and manganese (Mn_3O_4) may be included.



Figure 3.10 Thermogravimetric analyzer in Mae Moh power plant laboratory

3.3.2 Ultimate Analysis

It can provide a thorough analysis of the mass percentage of the chemical elements contained in coal. This analysis follows ASTM Standard D 3176 and used VarioMAX CHN elemental (Figure 3.11). The samples were dried and ground into the 60 mesh of the particle size. Approximately 170 milligram of samples was used in the crucible. The test is to determine carbon, hydrogen, and nitrogen. Total sulfur usually appears in the following 3 types. Firstly, Sulfate Ion or Sulfate Sulfur (SO_4) is after being burned. It is still intact. Sulfide Ion or Pyrite Sulfur (FeS_2) is often found in iron. It is sulfides such as Pyrite and Marcasite. And Organic Sulfur is

usually in the form of organic compounds in coal. The sulfur can be determined from LECO S-144DR sulfur analyzer (Figure 3.12).

The results are useful in determining the quantity of air required for combustion and the volume and composition of the combustion gases. This information is required for the calculation of flame temperature and the flue duct design etc.



Figure 3.11 Elemental analyzer for carbon, hydrogen, and nitrogen in coal samples



Figure 3.12 Sulfur analyzer for sulfur in coal samples

3.3.3 Heating Value

LECO AC600 (Figure 3.13) is used to determine heating value of the coal samples according to ASTM D 5865-07 standard. 1 gram of samples was used, dried and pulverized to 60 mesh, into the crucible. The calorimeter heat capacity is determined by burning a specified mass of benzoic acid in oxygen as same the condition for analysis samples. The heating value of the analysis sample is computed by multiplying the corrected temperature rise, adjusted for extraneous heat effects, by heat capacity and dividing by the mass of the sample.



Figure 3.13 Bomb calorimeter for use to determine heating value of coal samples

The heating value is sorted as follows. Lower Heating Value (LHV) is the heat that occurs after the water has completely burned in a gas or vapor. Occur as a byproduct of the process. Higher Heating Value (HHV) is the heat occurs after the complete combustion. The water in gas or vapor, which is byproduct of the process. That is the lower heating value plus the latent heat of condensation of vapor into water. The difference between HHV and LHV is shown in equation (3.2) and (3.3).

$$LHV = HHV - m_w h_{fg} \quad (3.2)$$

$$LHV = HHV - 9m_{H_2} h_{fg} \quad (3.3)$$

where m_w is the mass of water vapor after combustion per unit mass of fuel consumed. h_{fg} is latent heat of vaporization of water at a fraction of the water vapor pressure in the process. m_{H_2} is the mass of H_2 in the fuel per unit mass of fuel used, which are derived from the % H_2 ultimate analysis. The constant mass ratio of H_2O to H_2 is 9.

3.3.4 Nonisothermal Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is the measurement of the sample weight loss versus its temperature for use to define the temperatures of physical and chemical reactions.



Figure 3.14 Thermogravimetric analyzer for nonisothermal isoconversional approach

Thermal analysis of lignite samples was carried out in a computer controlled Perkin Elmer TGA 7 thermal analyzer (Figure 3.14). Prior to the experimental runs, the instrument was calibrated for precise temperature and weight readings. A quantity of 5.2 ± 0.1 mg of coal sample was used for each test. The digital microbalance is sensitive to $0.1 \mu\text{g}$. Nonisothermal experimental runs were performed at three different heating rates of 10, 30, and $50^\circ\text{C min}^{-1}$ under oxygen atmosphere. The flow rate of the carrier gas was maintained at $50 \text{ cm}^3\text{min}^{-1}$. The furnace temperature operated from ambient up to 1300°C . These dynamic runs were carried out on a platinum pan. The continuous records of weight loss and the weight loss rate with temperature were obtained. Thermal degradation behaviors were shown as TG and differential TG (DTG) profiles. They were also used as data for kinetics modeling.

For kinetics modeling, nonisothermal isoconversional approach was adopted in studying the kinetics of the Thai lignite. The approach has been shown to be able to estimate kinetic parameters without modeling assumptions (Khawam and Flanagan, 2005; Otero et al., 2008). The kinetics of the thermal decomposition based on the rate equation for solid state decomposition processes (Gunes and Gunes, 2005) can be written in Eq. (3.4).

$$\frac{dx}{dt} = kf(x) \quad (3.4)$$

where x is the decomposed fraction of solid at time t , $f(x)$ is a function of x depending on the reaction mechanism, and k is the rate constant given by the Arrhenius equation for nonisothermal chemical reaction as show in Eq. (3.5) as the same with Eq. (2.4).

$$k = k_0 \exp(-E/RT) \quad (3.5)$$

where A is the pre-exponential factor, E is the apparent activation energy, R is the universal gas constant, and T is the absolute temperature. Replacing k with the Arrhenius equation gives in Eq. (3.6).

$$dx/dt = A \exp(-E/RT) f(x) \quad (3.6)$$

The decomposed fraction, x , found convenient to express a reaction by using a certain function $f(x)$, is defined in terms of the normalized change in mass of the sample as show in Eq. (3.7)

$$x = (w_0 - w_t)/(w_0 - w_f) \quad (3.7)$$

where w_0 is the initial weight, w_f is the final weight, and w_t is the weight at time t of the sample analyzed by the nonisothermal TG analysis.

The FWO method (Xiao et al., 2009) is this equation below.

$$\ln \beta = \ln \left(\frac{AE_x}{Rg(x)} \right) - 5.331 - \left(\frac{E_x}{RT_x} \right) \quad (3.8)$$

where β is the heating rate and (x) is the integral form of the (x) . At a constant conversion, the plot of $\ln \beta$ versus $1/T$ obtained at several heating rates is approximated to be a straight line whose slope allows evaluation of the activation energy. The intercept can be obtained from the straight line and assumed to be first order of reaction from $f(x) = (1-x)$, and $g(x) = -\ln(1-x)$, and second order of reaction from $f(x) = (1-x)^2$ and $g(x) = (1-x)^{-1} - 1$, and third order of reaction from $f(x) = (1-x)^3$ and $g(x) = 0.5[(1-x)^{-2} - 1]$ (Jankovic et al., 2007; Chen et al., 2013; Naktiyok et al., 2013).

The KAS method (Xiao et al., 2009) is as follows.

$$\ln\left(\frac{\beta}{T_x^2}\right) = \ln\left(\frac{AR}{E_x g(x)}\right) - \left(\frac{E_x}{RT_x}\right) \quad (3.9)$$

The activation energy can be calculated from plotting $\ln\left(\frac{\beta}{T_x^2}\right)$ against $1/T$ and from the preexponential factor from the intercept of the resulting straight line.

3.3.5 Ash Composition

The ash composition can be obtained using X-ray fluorescence (XRF) techniques (ASTM D 4326). Prepared ash of 1.85 g was mixed with 9.25 g of di-Lithium tetraborate (flux), as ratio of 1:5. The mixed samples were put into stainless crucibles and fused at approximately 1000°C in a fusion furnace (Figure 3.15). The fused samples were cooled at the room temperature, forming glass disks. The disks were put in the slot of the BRUKET S4 EXPLORER XRF spectrometer (Figure 3.16).



Figure 3.15 The furnace is used for XRF sample preparing



Figure 3.16 The XRF spectrometer for ash composition analysis

The disks were irradiated by an X-ray beam at 50 kV and 20 mA. The sensitive detectors measured the atom characteristic x-rays at selected wavelengths. The output is oxide components of coal ash, generally expressed as SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , Na_2O , K_2O , TiO_2 , P_2O_5 , and SO_3 . This technique can be used to analyze the chemical composition of slag.

3.3.6 Ash Fusibility Temperature Analysis

ASTM Standards D 1857, Fusibility of Coal Ash, gives the experimental procedure for method of testing. The test is based on the gradual thermal deformation of a pyramid-shaped ash sample, 19.1 mm in height and 6.4 mm in equilateral-triangular base width. The triangular pyramids (cones) are made from brass con mold as shown in Figure 3.17. The sample is mounted on a refractory substrate in the furnace of LECO AF700 ash fusibility determinator (Figure 3.18) at temperature not over 400°C . A controlled condition (oxidizing atmosphere) is maintained inside the furnace. The condition is significant in deposits formation on heating surface (Huggins et al., 1981). The heating rate $8\pm 3^\circ\text{C min}^{-1}$ of temperature is maintained to 1500°C .

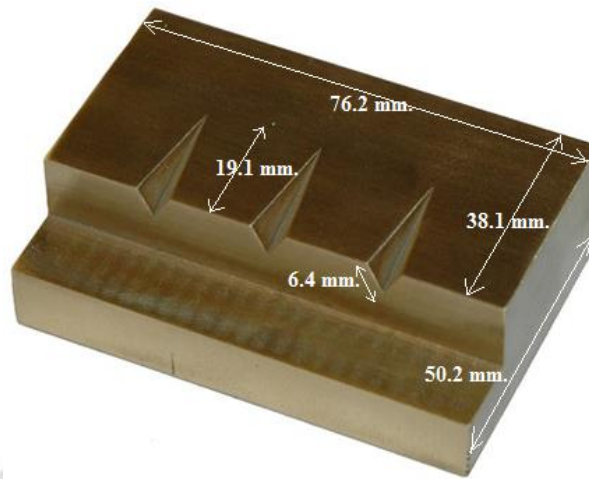


Figure 3.17 Brass cone mold for use in AFT test



Figure 3.18 The ash fusibility determinator for measure the AFT

During the heating process, changes in the shape of the pyramid are observed (Figure 3.19). The following four characteristic deformation temperatures are reported:

- 1) Initial Deformation Temperature (IT) is the temperature at which the tip of the ash pyramid begins to show any evidence of deformation. Shrinkage of the cone is ignored if the tip remains sharp.
- 2) Softening Temperature (ST) is the temperature at which the ash sample has fused into a spherical shape in which the height is equal to the width at the base.
- 3) Hemispherical Temperature (HT) is the temperature at which the ash sample has fused into a hemispherical shape where the height is equal to the half of width at the base.
- 4) Fluid Temperature (FT) is the temperature at which the ash sample has fused down into a nearly flat layer with a maximum height of 1.6 mm.

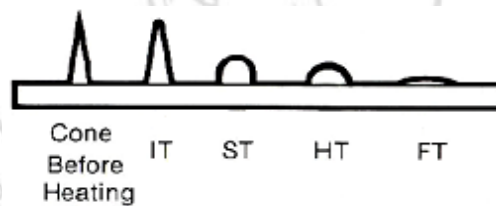


Figure 3.19 Ash fusion temperatures as defined in ASTM Standard D 1857 (Singer, 1981)

The fused ash will be investigated by SEM and EDS, which are slag characterization techniques, because the fused ash was assumed to slag from blended coal combustion.

3.4 Data Processing and Analysis

For the repeated experiments, the statistics methodologies were used to analyze the data. The average (\bar{x}) is chosen to analyze the center tendency of data and the standard deviation (S.D.) is chosen to analyze the dispersion of the data from the average (Delorme, 2014). The calculation is shown in Eq. (3.10) and (3.11) respectively.

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n} \quad (3.10)$$

$$S.D. = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \quad (3.11)$$

where x_i is the data and n is the number of data.

The properties of coal and ash are used as inputs in simulation modelling. The main ash compositions by XRF, were Al_2O_3 , SiO_2 , K_2O , CaO , TiO_2 , Fe_2O_3 , MgO , and Na_2O . They are used in the calculation of base to acid ratio (B/A), silica/alumina ratio, iron/calcium ratio, and iron/dolomite ratio (Eqs. 2.26 to 2.29 respectively). The ash composition and B/A ratio were used as parameters for correlating ash fusibility that are associated with the melting behavior of ash to slag.



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