Chapter 3
Experimental procedures

3.1 Materials

Twelve coal tar pitch (CTP) samples were obtained from various producers throughout the world, supplying CTPs to Söderberg electrode paste producers. Most of these CTP suppliers requested to remain anonymous; therefore, the CTP samples were only denoted as CTP 1 to CTP 12. Prebaked graphite electrode samples were supplied by GrafTech in Meyerton, South Africa. The toluene, quinoline and acetone (Lindsay Chemical Company) used in the determination of the Toluene Insolubles (TI) and Quinoline Insolubles (QI) of the CTPs were all of analytical grade (AR). The celite powder used as filtering aid was from Parma Technical Centre, Ohio USA. Whatman filter paper was from Merck Chemicals. Nitrogen gas (99.5% purity) used during thermal pre-treatment of the CTP samples was obtained from Afrox Limited.

3.2 Analysis of the fundamental properties of CTP

3.2.1 Softening point (SP)

In order to determine the SP, 5 ± 0.0005 g of CTP was weighed in a clean stainless steel container. The sample was heated to 200 ± 0.3 °C on a hot plate while stirring to obtain a homogeneous solution of melted pitch. The melted hot solution of CTP was poured into an SP measurement ring and the ring was mounted on the SP cartridge. The cartridge was then inserted into a Mettler FP 80 HT central processor analyser, which automatically measured the SP. The SPs of all CTP samples were measured in duplicate and the final result recorded to the nearest 0.1 °C.

3.2.2 Coking value (CV)

CTP was crushed to a powder that passes through 412 μm and retained on a 212 μm sieve. From the crushed sample, 3 ± 0.0005 g was weighed into a pre-weighed ceramic crucible that had been pre-heated to 900 ± 10 °C and cooled in a desiccator prior to being used. The total mass of the sample and the crucible was recorded. The crucible with the CTP was mounted in a fit-for-purpose instrumental setup and heated to 900 ± 10 °C for 30 minutes in an inert environment. After 30 minutes, the crucible with the residue was removed and cooled in a desiccator for 60 minutes. The weight of the crucible and the residue was recorded and the CV calculated from the following equation:

$$\% \, CV = \frac{C - A}{B} \, x \, 100$$

Where:

    A is weight of empty crucible;
    B is weight of sample; and
    C is weight of crucible and residue

3.2.3 Quinoline insoluble content (QI)

CTP samples were crushed and sieved to pass through 412 μm and retained on a 212 μm sieve. From the crushed sample, 1 ± 0.0005 g was weighed into a 250 ml glass beaker. The actual weight of the sample was recorded and the scale was tared. Approximately 0.4g to 0.5 g celite powder (serves as a filtering aid) was added to the beaker with the CTP sample, and the combined weight recorded. 25 ml quinoline was added to the beaker containing the mixture of CTP sample and celite powder. The mixture was placed on a water bath set at a temperature of 75 ± 5 °C and continuously stirred for 30 minutes. In a separate operation, while heating the mixture above, 0.4g to 0.5 g dry celite powder was transferred into a clean stainless steel crucible fitted with a 20 mm diameter filter paper. The weight of the crucible

and the celite powder was recorded and the crucible was mounted on a vacuum filtration setup. The hot solution from the water bath was filtered while hot and washed three times with 65 ml hot (heated at on the water bath to 75 ± 5 °C) quinoline, as well three times with 65 ml acetone. After washing, the crucible was placed in a drying oven at 105 ± 5 °C for 60 minutes. The crucible with the sample was cooled in a desiccator for 60 minutes and weighed. The percentage of QI was calculated from the equation below:

$$\% \text{ QI} = \frac{A - B - C}{D} \times 100$$

Where:

A is the weight of the filtering crucible, celite (added to crucible and sample) and matter insoluble in quinoline;

B is the initial weight of the filtering crucible and dry celite powder;

C is the weight of the celite powder added to the sample; and

D is the weight of the sample taken for the determination of QI.

3.2.4 Toluene insoluble content (TI)

The determination of TI components in CTP involves pitch digestion and extraction with hot toluene in an alundum thimble. To determine the TI, a sample of CTP was crushed and sieved to pass through 412 μm and retained on a 212 μm sieve. From the crushed sample, 1.5 ± 0.0005 g was weighed into a 250 ml beaker and the weight of sample was recorded. 60 ml toluene was added to the beaker with the CTP sample, and stirred continuously to ensure that the sample was evenly spread in the toluene. The beaker with the sample was placed on a water bath set at a temperature of 95 ± 5 °C for 30 minutes with continuous stirring until the sample completely dissolved in toluene. A clean and dry alundum thimble was placed on a filter tube and mounted on an Erlenmeyer flask. After 30 minutes, the insoluble material

remaining in the beaker was transferred into the afore-mentioned alundum thimble (Figure 3.1) and washed with three separate 60 ml aliquots of hot (heated on the water bath at 95 ± 5 °C) toluene. The alundum thimble containing the residue was placed on an extraction apparatus mounted below a heated magnetic stirrer, which was placed on an extraction flask that had boiling stones, as well as fresh toluene. The extraction setup used in determining TI is shown in Figure 3.1.

Figure 3.1 TI extraction apparatus

The extraction was left to run for 18 hours continuously, after which the extraction apparatus was removed and left for 5 minutes to allow all toluene to drain out from the alundum thimble. The alundum thimble with the remaining residue was dried in an oven at 105 ± 5 °C for 60 minutes and cooled in a desiccator for 30 minutes. The mass of the alundum thimble and the residue was weighed and TI was calculated as follows:

$$\% \text{ TI} = \frac{B - A}{C} \times 100$$

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Where:

A is the weight of the alundum thimble;

B is the weight of the alundum thimble and the toluene insoluble material; and

C is the weight of the initial CTP sample.

3.3 Proximate and ultimate analysis

In order to get more information on the composition of the 12 different CTP samples, the proximate and ultimate analyses, as well as the fundamental properties of all 12 samples used in this study were evaluated. In the proximate analysis, the moisture content in the samples was analysed based on the method according to the South African National Standard (SANS) procedure 5925, volatiles were analysed based on the method of International Standards Organization (ISO) 562, and ash and fixed carbon based on the ISO 1171 procedure. In the ultimate analysis, carbon and hydrogen were analysed based on the American Society for Testing Materials (ASTM) method D5373, nitrogen based on the ASTM D3179 method, sulphur based on the method ASTM D 4293 and oxygen was calculated by difference.

3.4 Additional chemical compositional determinations of CTP

The chemical composition of a CTP has an influence on its thermal behaviour and therefore makes it necessary that the chemical composition of the CTP sample is well understood. In order to get an understanding of the chemical composition of the CTP samples, additional chemical composition analyses were carried out using Nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infra-red spectroscopy (FT-IR). The NMR and FT-IR analytical procedures are described in sections 3.4.1 and 3.4.2, respectively.

3.4.1 Nuclear magnetic resonance spectroscopy (NMR)

The structural parameters of different CTP samples were analysed using ^{13}C NMR, which was conducted at Stellenbosch University. The NMR spectra were acquired on a Varian VNMRS 500 MHz two-channel spectrometer using 4 mm zirconia rotors and a 4 mm chematrics T3 HX Magic Angle Spinning (MAS) probe. The cross polarisation (CP) contact time was 2 s. The MAS was performed at a frequency of 12 KHz and Hexamethybenzene (HMB) was used as an external chemical shift standard with the methyl peak referenced at 17.5 ppm. The different measurement parameters are represented in Table 3.1. The different structural parameters (Chapter 4, Table 4.4) obtained from NMR were calculated according to the procedure described by Solum et al. [1989].

Table 3.1 NMR instrument operating parameters

NMR instrument measurement parameters	
MAS frequency (spinning speed)	12000 Hz
Pulse lengths	2.9 us (90° ^{13}C) 3.0 us (90° ^{1}H)
Contact time	2.0 ms
Spin lock field	57 kHz
1H decoupling field	58 kHz
Relaxation delay	5s
Processing parameters	
Line broadening	125 Hz

3.4.2 Fourier Transform Infra-Red Spectroscopy (FT-IR)

FT-IR analysis to determine different functional groups in the 12 CTP samples was performed on a Perkin Elmer Spectrum 400 FT-IR/FT-NIR equipped with a universal Attenuated Total Reflectance (ATR) sampling accessory. The detector on the FT-IR/FT-NIR instrument was made from diamond and no sample preparation was required. During the analysis, ±1 mg of sample was placed in a sample holding hole, after which the sample was pressed down to ensure maximum contact with the detector by means of a gauge force arm mounted on top of the instrument. All FT-IR spectra collected were recorded in the range of 4000 to 650 cm^{-1}.

3.5 Thermal dimensional analysis

3.5.1 Sample preparation

CTP samples on which dimensional analyses were conducted were prepared in three steps. The first was the thermal pre-treatment of raw CTP in a tube furnace (section 3.5.1.1), followed by pulverisation (Section 3.5.1.2) and finally pelletising (section 3.5.1.3).

3.5.1.1 Thermal pre-treatment of CTP samples

The thermal pre-treating of raw CTP samples pitch was undertaken to ensure that the CTP samples analysed in the Thermomechanical analyser (TMA) did not melt in the instrument. When raw CTP is heated to temperatures above its SP, it melts, which will result in the probe of the TMA protruding into the melted CTP. This penetration of the melted CTP will render thermal dimensional measurements useless and could result in damage to the TMA probe.

The thermal pre-treatment of the CTP samples was done on all 12 samples at three different temperatures, i.e. 450, 475 and 500 °C, in a tube furnace. A CoorsTek ceramic crucible

(99.8% pure aluminium oxide) was filled with approximately 25 g raw CTP. The crucible together with the sample was inserted into the middle of an Elite 15 THS tube furnace fitted with a programmable temperature controller. Two ceramic heat shields (CoorsTek AD-998 99.8% pure aluminium oxide) were inserted at both ends of the tube furnace to provide a stable working environment. Before commencement of heating, the tube furnace was flushed for approximately 3 minutes with nitrogen gas flowing at 1 L/minute to prevent sample oxidation, which might influence dimensional changes. The furnace was programmed to heat the CTP samples from room temperature to the required maximum temperature (which was 450, 475 or 500 °C) within 60 minutes and held for 120 minutes, after which the furnace was allowed to cool to below 100 °C under nitrogen. The thermally pre-treated CTP samples were removed from the furnace and stored in sealed plastic bags to avoid sample oxidation and/or contamination. The furnace used in the thermal pre-treatment of all CTP samples is as shown in Figure 3.2.

Figure 3.2 Tube furnace used in the thermal pre-treatment CTP samples

3.5.1.2 Pulverisation of pre-treated CTP

All the thermally pre-treated CTPs were pulverised into fine powders for 20 seconds in a Sibetechnik laboratory disc mill fitted with a tungsten grinding chamber. The resultant powders were compressed into CTP pellets with 10 mm diameter and 8 mm height as discussed in Section 3.5.1.3.

3.5.1.3 Pelletising

An LRX Plus tensile test machine (Ametek Lloyd Instruments), fitted with a 5 kN load cell, was used for pressing pellets usable in the TMA. The procedure involved weighing 0.65 g $\pm$ 0.0005 g finely ground CTP powder, thermally pre-treated at a specific maximum temperature (Section 3.5.1.1), into a Specac PT No.3000 cylindrical 10 mm die set. The powder was then compressed into a small pellet on an LRX Plus tensile test machine. The force applied to press the pellet was 3500 N at a rate of 10 mm/minute and holding for 10 seconds after reaching the maximum force. The tensile test machine used to press CTP pellets is shown Figure 3.3. After each pellet was pressed, the pellet was pushed out of the cylindrical die and stored in a closed container for TMA analysis (Section 3.5.2).

Figure 3.3 Tensile test machine used in pressing CTP pellets

3.5.2 Thermomechanical analysis (TMA)

A single pellet (Section 3.5.1.3) from a specific thermally pre-treated CTP sample (Section 3.5.1.1) was loaded into the TMA SS6100 and heated from room temperature to 800 °C under a constant flow of 1 L/minute of N_2. This was done to determine the lowest pre-treatment temperature that resulted in a solid carbonaceous material remaining after inert high temperature treatment.

After establishing the minimum thermal pre-treatment temperature (3.5.1.1) that did not result in softening of the pellets prepared from the thermally pre-treated CTP, all CTP samples were thermally pre-treated at that specific pre-treatment temperature for the

remaining TMA experiments. The exact value of this pre-treatment temperature and the importance thereof will be discussed in the results section. In these additional thermal dimensional determinations, all CTP pellet samples were thermally treated in the TMA by heating from 30 to 1300 °C and cooling to 30 °C. This TMA thermal cycle was repeated three times per sample. Figure 3.4 below shows the TMA SS6100 instrument used in the measurement of CTP dimensional changes.
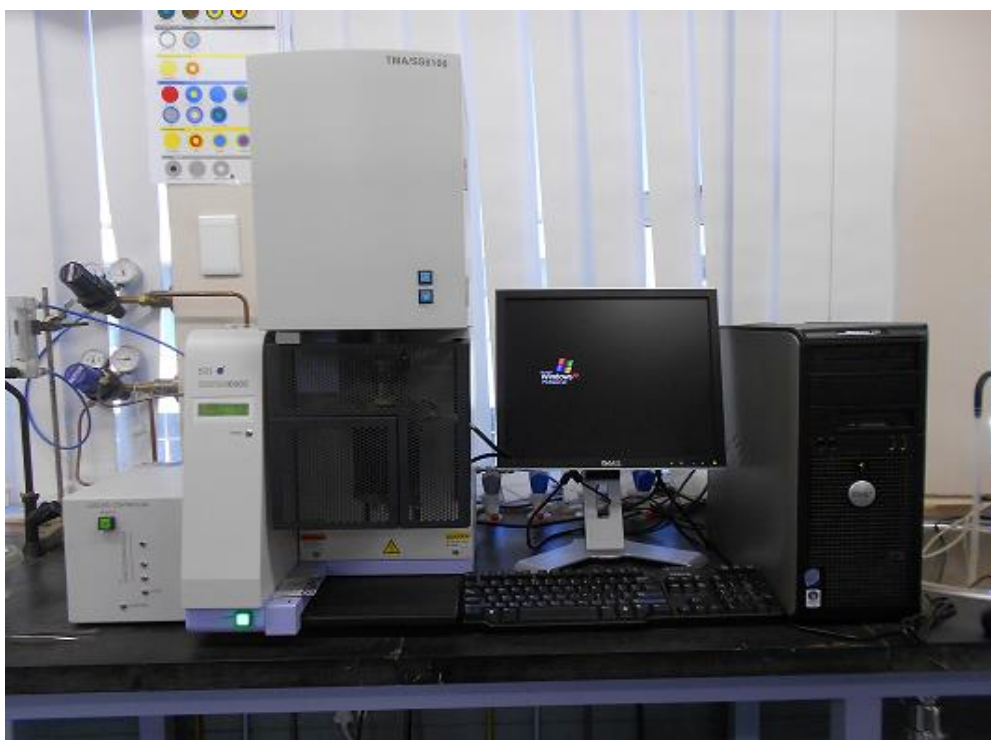

Figure 3.4 TMA used in the measurement of CTP pellets dimensional changes

The heating rate during the above-mentioned TMA dimensional determinations was 10 °C/minute and the holding time for each sample at the maximum temperature was 15 minutes. The total time taken to complete the three heating and cooling cycles per sample was 12.2 hours. A typical example of the heating and cooling cycles, with the associated dimensional changes, measured during the TMA analysis is illustrated in Figure 3.5.
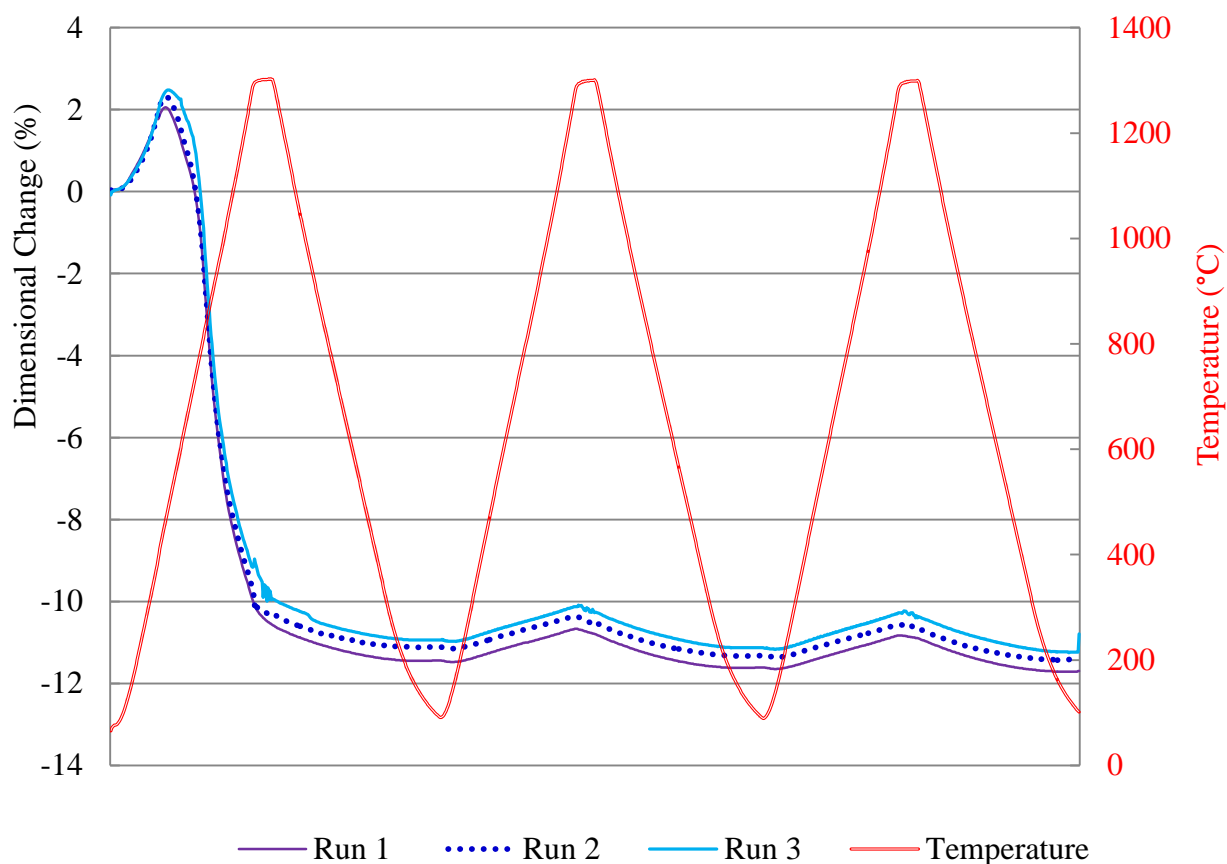
Figure 3.5 Typical heating and cooling cycles, with associated dimensional changes, during TMA analysis of a thermal pre-treated CTP

3.6 Characterisation of graphite intermediates

3.6.1 X-ray diffraction (XRD)

All samples were sent for analysis at XRD Analytical & Consulting in Pretoria. XRD is a technique that is used to analyse, among other properties, the crystallinity of a material. In this study, XRD was used to determine the extent to which the CTP samples that were thermally treated in the TMA have been graphitised. For comparison purposes, raw CTPs, as well as prebaked graphite electrode material, were also characterised with XRD.

3.6.1.1 Sample preparation

All CTP samples for XRD analysis were prepared using a back-loading method. The back-loading method involves clamping the sample holder ring onto the preparation table. 100 g of sample was placed in a sample holder and pressed with a pressing block. Surplus powder remaining on the holder was removed using a sharp-edged blade and soft brush (Fig 3.6).
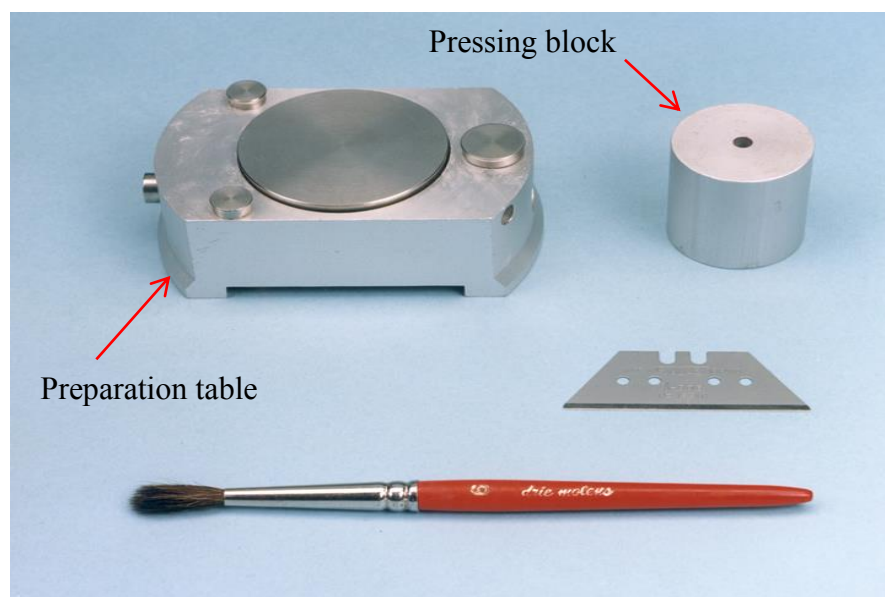
Pressing block

Preparation table

Figure 3.6 XRD sample preparation kit

The bottom plate was clamped onto the sampler holder, after which the sample was considered ready for XRD analysis as shown in Figure 3.7.
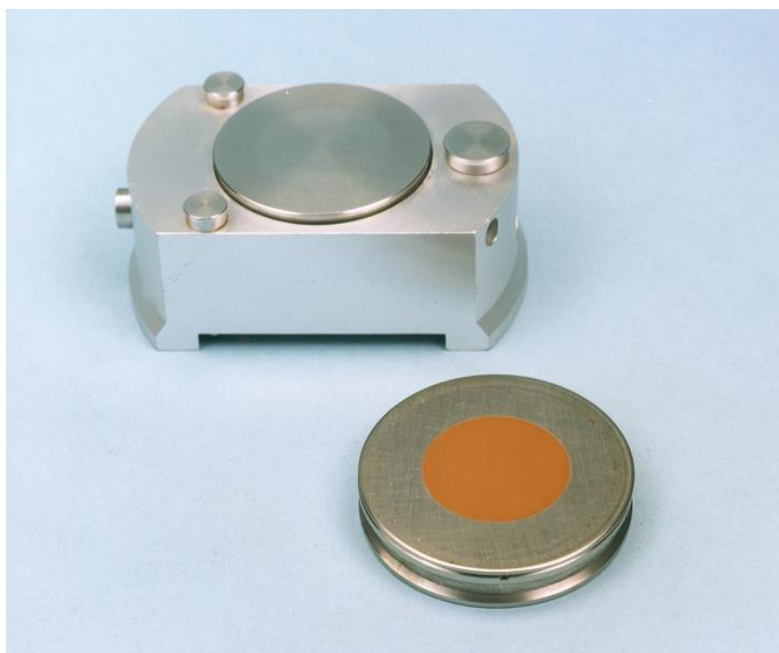
Figure 3.7 XRD samples ready for analysis

The prepared CTP samples were analysed on a PANalytical X'Pert Pro powder diffractometer fitted with an X'Celerator and automatic divergence and fixed receiving slits Fe filtered and Co-Kα radiation. The different XRD instrument parameters are shown in Table 3.2.

Table 3.2 XRD instrument set up parameters

Instrument	CubiX^3 minerals
X-ray tube	Cobalt LFF
Incident beam optics	Fixed divergence slit 1/2°, mask15mm, 0.04rad Soller slit
Sample stage	Spinning sample stage
Diffracted beam optics	Fixed anti-scatter slits 1/2°, 0.04 rad Soller slits, Iron filter
Detector	X'Celerator
Scan time	8 minutes

3.7 Statistical analysis of results

3.7.1 Multi-linear regression analysis

Regression analysis is a statistical method that is normally used to establish relationships among a number of variables. Regression is usually denoted by constants or known parameters β, independent variable X and dependent variable Y [Orlov, 1996]. The technique is normally applied in predicting, forecasting and establishing how dependent variables are related to the independent variable, Y, by fitting a linear equation to the data collected [www.stat.yale.edu/Courses/1997-98/101/linmult.htm]. Regression models can be classified as linear, nonlinear and multi-linear regression (MLR). Linear and nonlinear models are represented by Equations 1 and 2, respectively.

$$Y = \beta_0 + \beta_1 X_1 \text{--------------------- (1)}$$

$$Y = \beta (1 - e^{-bx}) \text{---------------------- (2)}$$

MLR regression models are characterised by more than one independent variable and are evaluated by fitting a linear equation to observed data. In MLR, every value of the independent variable X is associated with a value of the dependent variable Y. The relationship between the dependent variable (Y) and independent variables is denoted by the equations below [Orlov, 1996].

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \text{...................}\beta_P X_P \text{-------------- (3)}$$

$$Y = \beta 0 + \Sigma_i b_i X_i \text{ where } i = 1, 2........p \text{ ------------------------------- (4)}$$

where

β_0 is the intercept;

β_i is the ith coefficient corresponding to X_i where i= 1,2,3……p);

X_i is the ith independent variable from a total set of p variables and i= 1, 2…p; and

Y is the dependent variable.

The correlation line obtained from MLR describes how the response, Y, changes with the independent/explanatory variables. The MLR model can be used to predict the values of the dependent variable (Y). The calculated value should be as close as possible to the experimental value. In this study, a numerical computing environment and fourth-generation programming language known as matrix laboratory (MATLAB) was used for MLR regression statistical computations of the fundamental properties of CTP (SP, CV, QI, and TI), by sing the proximate (moisture, ash, FC and volatiles) and ultimate analysis (C, H, N, O, S) as independent variables. MATLAB is a versatile program that can be used for various applications such as matrix manipulations, plotting of functions and data, implementation of algorithms and creation of user interfaces [www.mathworks.com/products/matlab/]. The MATLAB toolboxes allow for a wide range of applications to be carried out, in addition to numerical computations carried out. In the analysis of CTP, essential parameters such as CV, QI and TI are not always determined by the industries utilising the CTP. In this study, it was therefore attempted to predicted/calculate these parameters with MLR, utilising only the values of the more commonly determined parameters, i.e. SP, as well as proximate and ultimate analyses.