

Thermal-gravimetric, calorimetric and chemical analytical characterisation of coal

Misael Silas Nadiye-Tabbiruka^{1,*}, Wilfred Ddamba¹, Kifilwe Tsheko¹, Zakarea Kenewang¹, Estella Judith Salamula²

¹Chemistry Department, University of Botswana, Private Bag 00704, Gaborone

²Chemistry Department, Makerere University, P. O. Box 7062, Kampala, Uganda

Email address:

nadiyem@mopipi.ub.bw (M. S. Nadiye-Tabbiruka), ddambawa@mopipi.ub.bw (W. Ddamba), keftshe@yahoo.com (K. Tsheko), skenewang@yahoo.com (Z. Kenewang), salamula@yahoo.co.uk (E. J. Salamula), matsciejs@yahoo.co.uk (E. J. Salamula)

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Abstract: Coal samples from Morupule colliery in Botswana were characterized by bomb calorimetry, thermal-gravimetric analysis, atomic absorption spectrometry and flame photometry. The average heat of combustion of the coal was found to be 27.3 kJ g⁻¹; with a substantial amount of ashes left behind. Thermo-gravimetric analysis showed peaks at 59.40 °C corresponding to loss of surface water, an exothermic peak at 448.54 °C associated with primary devolatilization in which compounds containing carbon, hydrogen and oxygen are released and finally a second exothermic peak at 682.58 °C associated with the secondary degasification in which methane and hydrogen are released. 70.4% of the coal was left after heating to 1000 °C indicating that in its present form, Morupule coal is of low quality but releases plenty of heat on combustion. The determination of the percentage weights of Calcium, Chromium, Copper, Lead, Iron using Atomic Absorption Spectrometry (AAS) and that of Potassium and Sodium using flame photometry showed that Iron (21.0956%) is the dominant inorganic element. The percentage weights of the other elements varied between zero and 7.4301%.

Keywords: Coal Characterization, Morupule Coal, Coal Chemical Analysis

1. Introduction

The properties and content of coal, depends on its origin, the environment and the processes that lead to its formation. This fossil fuel is formed by the decomposition of land plant remains that have accumulated in swampy areas. In these water logged environments, plants and tree debris accumulated. As the layers of debris increased in thickness,

the floor of these vast swamps subsided slowly in the “coalification” process and is characterized by extensive biochemical reactions. During degradation of dead plant material, proteins, starches and cellulose undergo more rapid decomposition than the woody material (lignin) and the waxy parts of the plants.(the leaf cuticles and the spore and pollen walls).

Table 1. Coalification Sequence [2].

	Peat	Brown coal	Sub-bituminous coal	Bituminous coal	Anthracite
% Water	75-80	50-70	25-30	5-10	2-5
% C	50-60	60-75	75-80	80-90	90-95
% H	5-6	5-6	5-6	4-5	2-3
% O	35-40	20-30	15-20	10-15	2-3
% Volatile matter	60-65	45-55	40-45	20-40	5-7
(i) Specific Energy KJg ⁻¹ Dry Basis	25	25-30	28-32	30-35	35-38
(ii) Wet Net Basis	5	5-15	20-27	24-33	35-38

During humification in the formation of peat, plant constituents are decomposed under aerobic conditions to carbon dioxide, water and ammonia to varying degrees, depending upon climatic conditions. This peat becomes covered with layers of sediment, which excludes air. Hence the second stage of coalification occurs under anaerobic conditions. In this second stage of the process the combined effects of time, temperature and pressure convert the peat firstly into brown coal (lignite) then into the sub-bituminous coal and finally to anthracite.

Consequently, coal is an extremely complex material containing both organic and inorganic materials. The organic materials are the combustible portions. The inorganic material (minerals) is the non-combustible portion. Coal is classified into four categories by using carbon content; lignite; sub-bituminous; bituminous and anthracite. Lignite has the lowest ranking and anthracite the highest [1]. Table 1 shows the coalification sequence together with the properties of the resulting coal type.

In commercial industries, coal is named according to its end use. Any coal used in the production of steam is called steam coal while that used in the production of coke is called coking or metallurgical coal.

Coal properties depend mainly on its composition. Unlike many rocks, some coals weather or break apart as they dry out. They will slowly combine with oxygen in the air and begin to self-heat. This reaction creates an insufficient amount of oxygen in enclosed areas and can lead to spontaneous combustion. In coal and gob waste piles containing large amounts of fine coal, this reaction can create an insufficient amount of oxygen. Generally, coal is composed of five elements; carbon, hydrogen, oxygen, nitrogen and sulphur, as well as traces of almost every element found in nature.

The applications of carbon (coal) are innumerable ranging from simple tablets to sort out a rumbling stomach to jewelry worn by celebrities and the very rich.

The coal used in this work is mined by Morupule Colliery Limited mainly in Morupule coalfield located about 12 kilometers west of Palapye village in the eastern part of Botswana. Carbon dating on the coal shows that it is about 250 million years old. The Morupule coalfield extends to Radisele on the south and Moiyabana on the north. Number 1 and 2 seams underlie the mining lease area. Currently only the number one seam, which is un-weathered, is mined. The number two seam is extensively weathered and contains inter-bedded shale, which renders mining uneconomic. The major consumers of the Morupule coal include; Botswana Power Cooperation which uses it to generate electricity throughout the country, Selibe-Phikwe mines which uses the coal for smelting the copper and nickel and the locals who use small quantities of the coal for cooking.

Little study has been done on Morupule coal no wonder its applications have been limited to power generation, mineral smelting and local consumption as a source of fuel. In this project, coal will be characterized by bomb calorimetric and thermo-gravimetric techniques. Furthermore, the presence of

a selected number of inorganic elements will also be investigated using Atomic Absorption Spectrometry and flame photometry. It is hoped that more applications may consequently result.

1.1. Thermo gravimetric and Differential Thermal Analysis

The rate of coal thermal decomposition reactions is studied by means of a thermo-balance, an apparatus for continuously measuring the weight of the material heated at an adjustable rate. The weight curves thus obtained make it possible to derive the rate of loss in weight as a function of temperature and time (devolatilization curves). Van Krevelen [2] and Boyer [3] used this technique on a low rank coal and coking coal and found that they exhibited two peaks: one in the temperature range of 350 – 550 °C and the other near 700 °C. The initial peak was associated with the primary devolatilization in which compounds containing carbon, hydrogen and oxygen are released. The second peak is caused by the secondary degasification in which methane and hydrogen are released. Thermo gravimetric investigations are normally carried out in two different ways which are by determining: (a).the (rate of) loss in weight as a function of time, at constant temperature (with temperature as the secondary variable parameter); (b).the (rate of) loss in weight as a function of temperature at constant heating rate (with heating rate as the secondary variable parameter). The latter technique was used in this project. In both methods the rank of coal and its petrographic composition are independent variables.

1.2. Differential Thermal Analysis

In this technique, the heat effects produced by these reactions are registered by plotting the temperature difference between the samples and an inert medium – both being heated at constant rate as a function of the temperature prevailing in the inert medium. The thermogram thus obtained is characteristics of the sample examined. The areas under the peaks are proportional to the amount of active materials present. Several methods of analysis have been developed. Berger, A.I. and Whitehead [1] employed vacuum differential thermal analysis and their studies indicated that the various coal types give exothermic peaks that move towards higher temperatures with increasing coal ranks [4, 5] confirmed the predominant character of the thermal effects to be mainly endothermic. His thermograms show that heating of bituminous coal produces three successive endothermic reactions in coal mass. Peak one is caused by the removal of water and lies in the vicinity of 150 °C. Peak two is related to the chemical decomposition of the coal and occurs in the range 350 -550 °C, which is the range of primary devolatilization. Peak three is the measure of the secondary degasification, which is highly endothermic, is between 600- 700 °C [6] found that when cellulose, lignin, peat, xylite and coals of various ranks were carbonized, the release of moisture (90 -120 °C), the softening and release of volatile matter (320-460 °C) and

the shrinkage with release of hydrogen (670-720 °C) were all endothermic, whereas the solidification of plastic mass (480–540 °C) was the only exothermic process.

The differences between these researchers may partly be due to the differences between the types of thermo gravimetric techniques used (vacuum and conventional DTA) or differences due to the origin of the coal samples.

Three methods have been used to liquidize coal; Pyrolysis –the destructive distillation of coal in the absence of oxygen at temperature between 400-500°C, indirect liquefaction – which involves the partial combustion of coal in oxygen and either hydrogen or steam and direct liquefaction – a thermally induced decomposition of coal in the presence of a solvent that serves to transfer hydrogen. The interest in coal conversion technologies has always been to complement supplies in petroleum. For details of these processes see [7].

2. Experimental

2.1. Thermal and Gravimetric Investigation

2.1.1. Determination of Calorific Value

Apparatus and Materials

Oxygen Bomb Calorimeter was used. Coal samples were taken from various parts of the mine, crushed and mixed to give a representative sample. This mixture was used to make pellets for combustion, and powder for TGA-DTA analysis.

2.2. Procedure

A coal sample pellet of known weight, containing an embedded igniting platinum wire to facilitate easier handling and slower burning than with loose samples, made by using a Parr 2811 pellet press was placed in the inner compartment of the calorimeter surrounded with 2000ml of distilled water in its outer jacket. The pellet was burnt in plentiful oxygen by using the platinum wire connected to an external circuit. The temperature of the surrounding water was measured as a function of time until a substantial steady temperature decrease was observed. The remaining ash was weighed to determine the amount of combustible portion. This procedure was repeated for several coal samples and for benzoic acid to calibrate the calorimeter, changing water for every sample.

2.3. Thermo-gravimetric and Differential Thermal Analysis

2.3.1. Apparatus and Procedure

Thermo gravimetric Analysis (TGA) – Differential Thermal Analysis (DTA) machine Universal 2.5H TA Instruments was used. A coal sample of known weight (11.5600mg) was put in the sample cell in the TGA –DTA machine which was then operated and the thermo gram was obtained.

2.4. Inorganic Element Investigation

2.4.1. Coal Sample Preparation

Coal from Morupule was ground in a mortar and sieved to a particle size of $53\mu\text{m}$. The powdered coal was then stored in

a tightly covered polythene container and stored in a desiccator. A coal sample (0.5006g) was digested by adding 20 ml nitric acid in a 250 conical flask. The mixture was heated at 80°C for 20 minutes, after which 10ml of per chloric acid were added and the temperature was raised to 200°C. The heating was continued until the mixture neared incipient dryness (indicated by highly white fumes of per chloric acid). 10ml of concentrated hydrochloric acid were added and the mixture left to cool to room temperature. This was followed by filtration using a 45µm nitrate cellulose filter. The digested sample was transferred into a 100ml volumetric flask and made to the mark with ultra pure water. The solution was then transferred into a polythene bottle and stored in a coal room (4°C) for about 12 hours to reach equilibrium.

2.4.2. Flame Atomic Absorption Spectrometry (AAS)

Measurements were made using an AA-10 spectrometer (Varian Spectra) by using the Air-acetylene flame together with the appropriate bulb for each metal on the prepared samples solutions. The spectrometer was calibrated using a blank (ultra pure water for zero concentration) and concentrated standard solutions in the general range 1ppm to 20 ppm with the specific range depending on the metal in question. Concentrations of the unknown were obtained by interpolation using the calibration graph obtained from the standards.

2.4.3. Flame Emission Spectrometer

For the analysis of sodium and potassium, a corning flame photometer 410 was used. The oxidant (air) and fuel (propane) were allowed to flow through the reaction chamber for a few seconds prior to ignition. The flame was adjusted to suit the required intensity. Calibration of the instrument was done using the highest concentrated standard followed by the one with the lowest concentration. The highest was set to 100 and the lowest (pure water) to 0.

3. Results and Discussion

3.1. Determination of Calorific Value

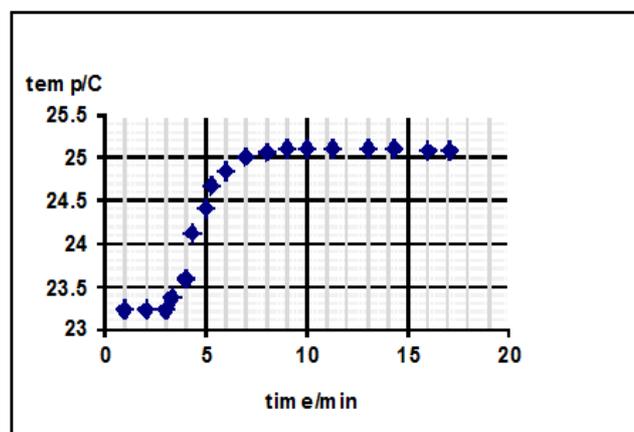


Fig 1. Shows the bomb calorimeter cooling curve after the combustion of Morupule coal sample.

The heat capacity of the bomb calorimeter was determined using benzoic acid and found to be 10.212 kJ K^{-1}

Average heat released = $27.3 \pm 2.0 \text{ kJ g}^{-1}$. The theoretical enthalpy of combustion of carbon based on graphite is 32.83 kJ g^{-1}

3.1.1. Heats of Combustion

In the determination of calorific value or heats of combustion of Morupule coal, pellets were used because they are easier to handle than the powder. The heat capacity of coal was obtained using a bomb calorimeter whose heat capacity had been determined by measuring the heat released by the combustion of benzoic acid whose enthalpy of combustion is accurately known. Ashes were left after the combustion of the coal indicating the presence of impurities in the coal. These may include clays, silt and sandstones, which could not burn to gases completely, together with metal oxides from some trace metals. Despite the large quantity of ashes, the heat released, is substantial and places Morupule coal between brown coal and sub-bituminous coal (see table 1). It must be remembered that the coal sample was used as obtained from the fields hence the heat released would be decreased by endothermic processes such as the release of adsorbed water. Furthermore, coal contains many trace elemental metals such as Cu, Fe, Al, Ni, to mention a few and metals in compounds such as CuSO_4 , Fe_2S_3 together with numerous adsorbed

organic materials. On burning coal in plentiful oxygen, these would undergo exothermic oxidation processes and thus contribute to the heat measured by calorimetry. Since the trace metals are in small quantities, it is assumed that their contribution to the observed heat release is negligible. The bomb calorimeter used was a thick heavy walled oxygen type, surrounded by a large quantity of water to minimize loss of heat to the environment. Fig 1 shows that the loss of heat to the environment after the combustion of the coal was both small and very slow and therefore the corresponding error is negligible.

3.2. Thermal-gravimetric Analysis Results

Figure 2. Shows the results of Thermal-gravimetric Analysis of Morupule Coal *Mass of coal used = 11.5600 mg*

70.41% of the sample was left un-decomposed at around 1000°C . The graph of loss of % weight against temperature shows a fall between 26.88°C and 156.73°C , a constant weight between 156.73°C and 430°C and a fall up to around 1000°C .

Loss of surface water and other volatiles were experienced at 59.34°C . Two decomposition peaks were observed at temperatures around 448.54°C and 682.58°C , there is a broad upwards peak between them showing that the decomposition is exothermic [8, 9].

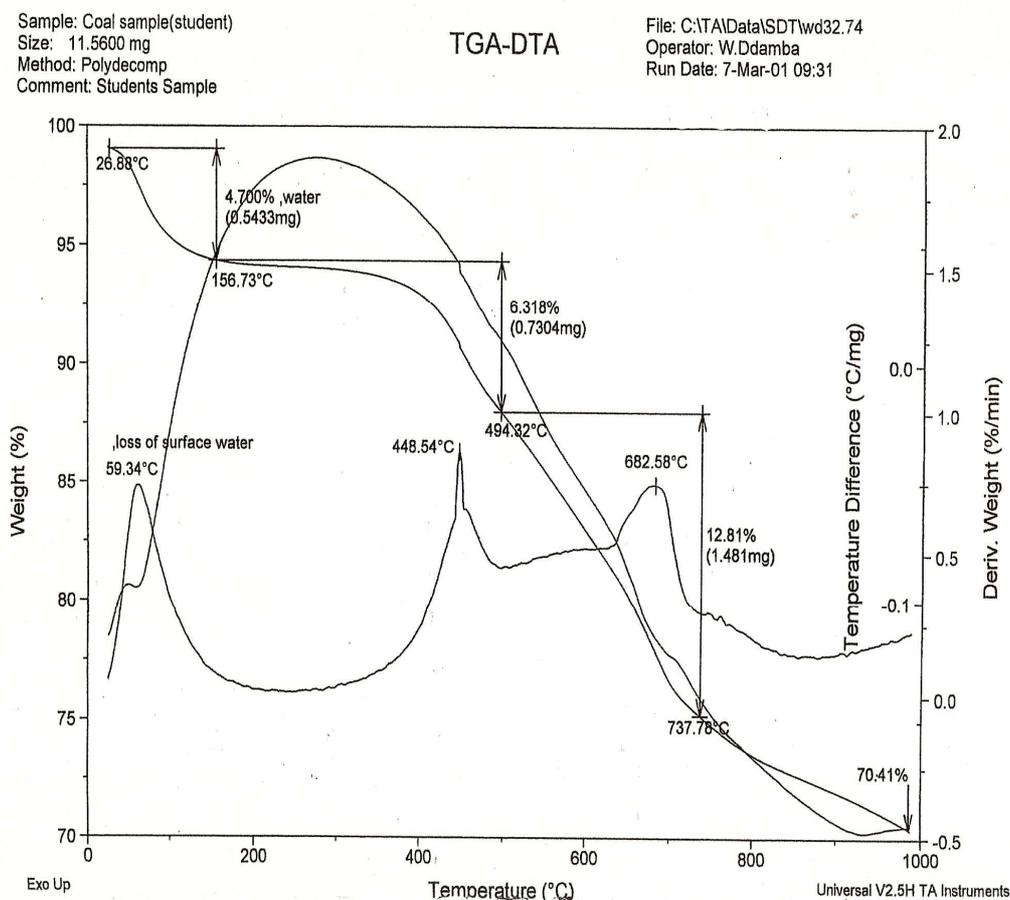


Fig 2. Thermal-gram from analysis of Morupule Coal.

3.2.1. Differential Thermal Analysis

The thermographs in Fig 2 show three different graphs. The graph which shows the loss of percentage weight against temperature shows a decrease in percentage, a constant percentage weight with increasing temperature and a further decrease in the percentage weight of the sample. These decreases in % weight at temperatures between 26.88-156.73 °C are due to losses from the coal. The first decrease in the % weight corresponding to the first peak is believed to be due to the loss of surface water. This is an endothermic process. The constant region is probably because nothing is released. The further decrease in % weight corresponding to the second peak is believed to be due to the primary exothermic devolatilisation process in which compounds containing carbon, hydrogen and oxygen are released. Peak three indicates the secondary endothermic degasification process in which methane and hydrogen are released [8].

Since coal consists of sulphur in three forms i.e pyritic organic and sulphates the release of compounds containing sulphur could be in the second peak especially for the organic sulphur which is chemically bonded to the coal matrix [10]. Breaking of the chemical bonds is usually an exothermic process.

About 70% by weight of the coal sample did not decompose indicating that only about 30% of the coal is decomposable. The rest consists of non decomposable materials, probably clays silt and sand stones. Only one thirds of the coal is combustible confirming that Morupule coal is of low quality.

3.3. Chemical Analysis - Abundance of Elements

Table 2. % weight of elements in Morupule coal.

Element		% Weight	S.D.%
Calcium	Ca	4.9165	1.3
Chromium	Cr	0.6451	4.45
Copper	Cu	0.4572	5.45
Lead	Pb	0.0000	
Iron	Fe	21.0956	2.75
Potassium	K	2.8220	4.45
Sodium	Na	7.4301	1.1

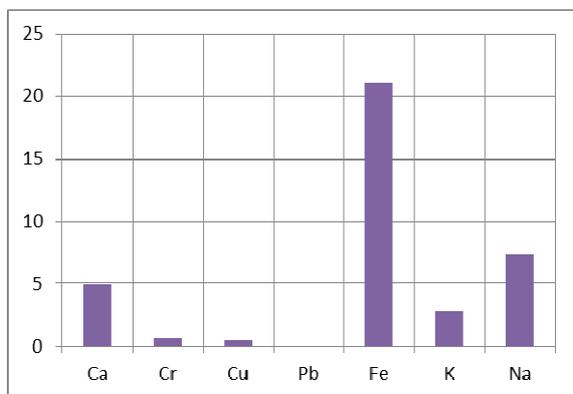


Fig 3. Percentage weight distribution of trace inorganic elements in Morupule coal.

The abundance for trace elements (in order of increasing

weight percentages Fig 3) is: lead (nil %), copper (0.4572%), chromium (0.6451%), potassium (2.8220%), Calcium (4.9165%), sodium (7.4301%) and iron (21.0956%) basing on the calculated percentage weights. Consequently Morupule coal is rich in iron, sodium and calcium.

The zero percentage value for lead might be due to a number of factors including the limitation of the Atomic Absorption Spectrometry since it can only detect up to 0.01ppm in the mode used. If Graphite Flame Atomic Absorption Spectrometry (G-FAAS) was used there might have been a significant detection since it can detect up to 0.01ppb. Also according to the (U.S. Geological Survey Bulletin 1823), as the concentration of the iron increases from 0 to 1,000mg/mL, the lead atomic absorption signal is sharply suppressed. A further increment in iron concentration up to 4,000 or to 5,000 mg/mL produces little further suppression of lead absorption. So it would be necessary to remove the iron from solution by extraction with concentrated hydrochloric acid into methyl isobutyl ketone before measuring lead absorption signal. This could not be done in this work.

The sodium value of 7.403%, closely agrees with that in the literature (seven percent in the U.S Geological Survey Bulletin 1823 [11]).

Mining coal weakens the crust of the earth, burning coal produces unwanted green house gases and pollutants including CO₂, NO₂, SO₂, in addition to traces of radioactive elements and their compounds. All these together with those not mentioned here make coal much less desirable as an energy source than is generally accepted. However, the alternative, nuclear energy, has shown to be a more dangerous prospect in view of the uncontrollable and unpredictable volcanoes and their associated tsunamis in the recent times. Furthermore, the increasing number of applications including pollution control such as the removal of mercury vapour in industry [9], purification of water [12] and improvement of the thermal conductivity and rheological properties of graphite/oil nano-fluids [13] makes more research on coal absolutely necessary.

4. Conclusions and Suggestion for Further Work

The average heat of combustion for crude Morupule coal was found to be 27.3 kJg⁻¹, a very high value, probably because of the oxidation of trace metals and adsorbed matter. It is slightly lower than the theoretical value of 32.83 kJg⁻¹ for graphite indicating that it is of low quality, but a good source of heat even in its original state.

Thermo-gravimetric analysis yielded two graphs. The endothermic peak at 59°C on the differential thermal analysis curve is attributed to loss of surface water. An exothermic peak at 448°C is attributed to devolatilisation of compounds containing carbon hydrogen and oxygen. The third exothermic peak at 682°C is attributed to secondary degasification in which methane and hydrogen are released. Atomic Absorption

and Flame Emission Spectrometry results suggest that Morupule coal contains the following analyzed trace elements: Iron 21.0956%, Sodium 7.4301%, Calcium 4.9165%, Potassium 2.8220%, Chromium 0.6451%, copper 0.4572% and zero Lead.

Further work should include determination of specific surface area and porosity using known methods [14], to see if it has enough space for removing pollutants, adsorption of pollutants from gas and aqueous media [15], and finally attempts to modify it to enable its use for these applications and many more. The presence of radioactive isotopes should also be investigated. The percentage carbon content should also be found using an elemental analyzer. Attempts should be made to produce Morupule coal composites for a variety of uses including hydrogen storage [15]

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