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COAL COMBUSTION STUDIES USING THERMOGRAVIMETRIC ANALYSIS

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ABSTRACT

Coal burning profiles can be determined using thermogravimetric analysis. Characteristic temperatures were determined from the burning profiles. Burning profiles could provide a valuable, rapid laboratory method of ranking coals in terms of their burnout performance. In this study, non-isothermal thermogravimetry and derivative thermogravimetry (TG/DTG) experiment were carried out for three types of coal samples, which are Blair Athol (Australian Coal), Merit Pila (Malaysian Coal) and Tanito Harum (Indonesian Coal). Thermogravimetry experiments were performed from ambient to 1000°C in the synthetic air atmosphere. Differential thermogravimetric data were analysed using an Arrhenius type reaction model assuming a first-order reaction. Kinetic parameters of the samples were determined and the results are discussed.

Keywords *: Arrhenius equation, coal, thermogravimetry*

1.0 INTRODUCTION

Coal is a physically heterogeneous and chemically complex mixture of organic and inorganic species which undergoes appreciable physico-chemical changes during heat treatment. The main studies of coal using thermal analysis techniques include characterisation of high pressure application to coal hydrogenation, catalytic effects due to inorganic substances, combustion, pyrolysis and kinetic analysis. In the selection of coals for combustion it is useful to have knowledge of their combustion characteristics.

Thermogravimetry (TG) and differential thermogravimetry (DTG) are the methods widely used in characterisation of fossil fuels undergoing combustion or pyrolysis [1]. Thermogravimetry, TG, is widely used to investigate rate processes. This method involves the continuous measurement of the change in mass or rate of mass loss, DTG, of a sample with temperature (or time). Such data has been used to determine kinetic parameters, such as activation energy and order of reaction.

DTG output from a thermobalance system is plotted against temperature as the sample of fuel is heated at a constant rate in a flowing air stream. A profile is produced, characterized by several features, the most significant of which is the peak temperature, or temperature at which the sample is losing weight at the maximum rate; a high peak temperature is indicative of a less-reactive fuel, and *vice versa* [2]. This test has been established and is now in regular use in assessing the burning characteristics of coals. Minor modifications involve recording four 'datum' temperatures on the burning profile curve; (a) the first initiation temperature where the weight first begins to fall (Volatile Matter Initiation Temperature, ITVM); (b) the second initiation temperature where the rate of weight loss accelerates due to the onset of combustion (Fixed Carbon Initiation Temperature, ITFC); (c) the peak temperature as described (Peak Temperature, PT); and (d) the burnout temperature, where the weight becomes constant at the completion of burning (Burning Temperature, BT). A typical burning profile [3] for a bituminous coal is shown in Figure 1.

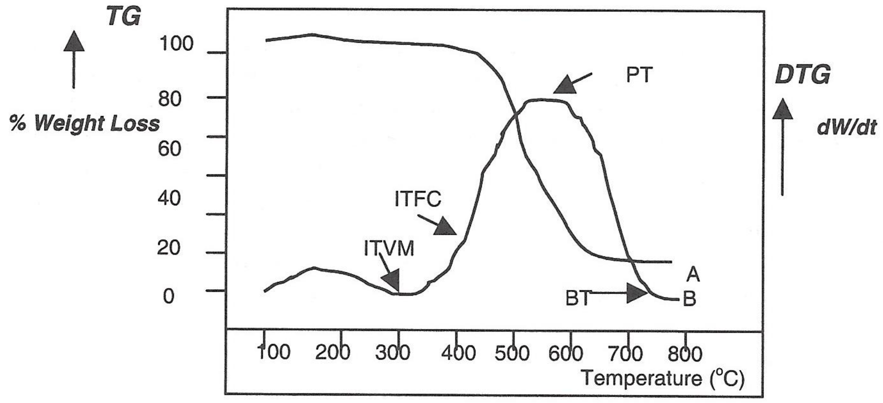

Figure 1 Typical burning profile/TG curves for bituminous coal. (A = TG and B = DTG)

The derivation of activation energy values for the coal combustion process in the burning profile test was reported by Smith [4] and this was used as a basis for the present work. It seemed that a single numerical value to describe the reactivity of a fuel would be much more desirable than using the four datum temperatures, which is rather cumbersome.

Although the use of the Arrhenius equation in homogenous kinetics normally requires no justification and values of the pre-exponential term, or frequency factor, A, and activation energy, E, have been reported for countless chemical reactions of all possible types, serious doubts have been expressed about the theoretical justification for the application of the Arrhenius equation to chemical changes proceeding in the solid state.

1.1 Objectives

From the above introduction, the objectives of this study can be summarized as below:

i. To study the coal reactivity using burning profile (DTG).
ii. To study the kinetic parameters of coal, assuming first-order kinetic for the burning of coals and employing Arrhenius Equation and Activation Energy.

1.2 Kinetic Analysis

The combustion kinetics of coal, as pointed out by Smith [4] are extremely complex, but by making certain broad generalizations, some useful information can be deduced. Most importantly, the assumption is made that the burning process can be described by first order kinetics.

Non-isothermal kinetic study of weight loss under combustion process is extremely complex for coals because of the presence of the numerous complex components and their parallel and consecutive reactions.

For analysing the kinetics of TG/DTG data, the model assumes that the rate of weight loss of the total sample is dependent only on the rate constant, the weight of the remaining sample and the temperature with reaction order of unity. Application of this method to the TG/DTG thermograms are easy and fast. So the equation of Arrhenius-type kinetic model takes the following form,

$$dW/dt = kW^n \qquad (1)$$

$$k = A\exp(-E/RT) \qquad (2)$$

Assuming first-order kinetics,

$$dW/dt = A\exp(-E/RT)W \qquad (3)$$

$$(dW/dt)(1/W) = A\exp(-E/RT) \qquad (4)$$

Taking the logarithm of both sides and assuming $n = 1$ and $(dW/dt)1/W = K$, therefore;

$$\log K = \log A - E/2.303RT \qquad (5)$$

where dW/dt is the rate of weight change of the reacting material, A is the Arrhenius constant, E is the activation energy (KJ/mole), T is the temperature and n is the reaction order. When log K is plotted against 1/T, a straight line is obtained which will have a slope equal to E/2.303R and from the intercept, the Arrhenius constant can be estimated.

In the terminology used for homogenous kinetics, the activation energy (E) is usually identified as the energy barrier (or threshold) that must be surmounted to enable the occurrence of the bond redistribution steps required to convert reactants into products [5]. The pre-exponential term, or frequency factor, A, provides a measure of the frequency of occurrence of the reaction situation, usually invisaged as incorporating the vibration frequency in the reaction to co-ordinate.

Svante Arrhenius (1859-1927) stated that only those molecules which possess energy greater than a certain amount E will react, and these high-energy, active molecules lead to products.

In summary, the activation energy is the energy required for the reaction to occur; that is; it is the energy required to move the reactants over the energy barrier in order for reaction to begin. The activation energy is usually recovered by the heat released by the reaction process.

2. 0 EXPERIMENTAL SET-UP

2.1 Coal Samples

The samples used in this study were Blair Athol, Merit Pila and Tanito Harum coal which were prepared according to ASTM standards. Proximate analysis of the samples were also determined by TG/DTG equipment (Table 1).

Table 1 Proximate Analysis of Blair Athol, Merit Pila and Tanito Harum coals

Coal Name	% Moisture	% Volatile Matter	% Fixed Carbon	% Ash
Blair Athol	4.53	28.18	60.27	7.01
Merit Pila	9.83	43.83	44.06	2.30
Tanito Harum	5.63	44.03	48.13	2.17

Note : M-Moisture (< 100°C), V-Volatile matter (>100°C-550°C), FC – Fixed Carbon (550°C-900°C), A – Ash (>900°C), also depends on the coal types.

2.2 Equipment

The apparatus used in this study was Seiko TG/DTA 220U Thermal Analyser, in the TG-DTG configuration, determine the combustion and kinetic properties of the samples studied.

2.3 Operating Procedure

The TG/DTG experimental procedure involves placing approximately 5 mg of sample, setting the heating and gas-flow rate, then commencing the experiment. All experiments were performed at a heating rate of 50°C/min over a temperature range of ambient to 1000°C with an air flow rate of 200 mL/min. Prior to the experiments, TG/DTG was calibrated for temperature readings using calcium oxalate monohydrate as a reference material. It was essential to calibrate the balance for buoyancy effects to allow quantitative estimation of weight changes.

2.4 Arrhenius Plot

The Arrhenius coordinates used in constructing the log K *versus* 1/T plots from which the activation energies were derived were obtained from the experimental curves (Figure 1) by measuring the TG and DTG values at several intervals throughout the burning range. Rates of weight loss were read off directly from the chart, and weights of unburned material from the TG curve after correction for the ash and moisture contents were determined by a separate proximate analysis. Values of K at each temperature level were calculated and these were then re-plotted in the Arrhenius form, log K *versus* 1/T absolute. From the equation as in Section 1.1, the gradient of this curve is numerically equal to the expression E/2.303 R, and hence E can be calculated [1, 3, 5-8].

3.0 RESULTS AND DISCUSSION

Theoretically, combustion of fuel can be initiated whenever oxygen comes in contact with fuel. However, the temperature and composition of the fuel and oxygen supply dictate the nature of the reaction. In the temperature region of less than 100°C all coals start to loose small amounts of pyrolysis water from decomposing phenolic structures and oxides of carbon from carboxylic and carbonyl groups.

Coal Reactivity

Burning profiles have been determined for coals, covering a range of origin and rank. The main characterisation point in TG/DTG thermogram is the peak temperature where the rate of weight loss is at the maximum (Table 2). A high peak temperature is indicative of a less reactive fuel [8]. Merit Pila coal shows the lowest peak temperature (426°C), followed by Tanito Harum coal (447°C) and the highest peak temperature is Blair Athol coal (514°C) *(Thermogrammes are in the Appendixes Section).*

In the design of the industrial coal-fired boiler furnaces, it is of importance to have an assessment of the reactivity of the intended fuel. The reactivity test of coal can allow the burning characteristics of the candidate fuels to be compared with the original in terms of reactivity or burning rate.

Table 2 Thermal properties (temperature,°C) of Blair Athol, Merit Pila and Tanito Harum coals

Coal Name	Moisture Peak	Ignition Temperature	Peak Temperature	Burnout Temperature
Blair Athol	58	270	514	704
Merit Pila	62	161	426	555
Tanito Harum	61	180	447	631

Coal ranking [2,9] (which is not necessarily regular) also correlates with burnout temperatures value (Table 2). Superior burnout performance is observed with coals having lower burnout temperatures. Merit Pila (local coal) coal showed lowest burnout temperatures, followed with Tanito Harum (Indonesian coal) and the highest burnout temperatures was shown by Blair Athol coal from Australia. PT and BT shall be used as the reactivity data in evaluating the coal burning characteristics.

Reaction kinetics

Linear least square correlation coefficients for the identified rectilinear portions varied from 0.92 to 0.95 and log K vs. 1/T diagrams (Figures 2, 3 and 4) where activation energy and Arrhenius constant were determined are given in Table 3. Activation energy value varies for different types of coal in the range of 5.2-7.3 for Blair Athol, Merit Pila and Tanito Harum Coals. Tanito Harum coal has the highest activation energy, followed with Merit Pila and Blair Athol coal. Tanito Harum coal required more energy which is present in coal in the form of phonons and electronic energy for the reaction or combustion process to occur. However, no correlation can be made between the coal reactivity data and the activation energy in this finding.

Arrhenius equation can fit the rate data in the devolatilization (dW/dT) region (temperature range 250-600°C) for Blair Athol, Merit Pila and Tanito Harum Coals (Figures 2, 3 & 4).

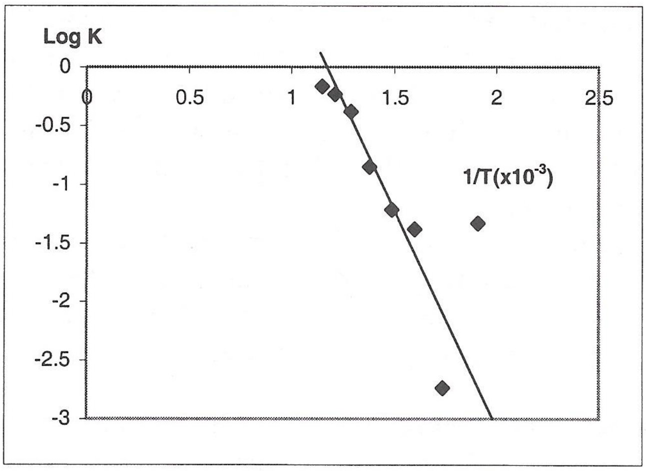

Figure 2 Arrhenius plot for Blair Athol coal

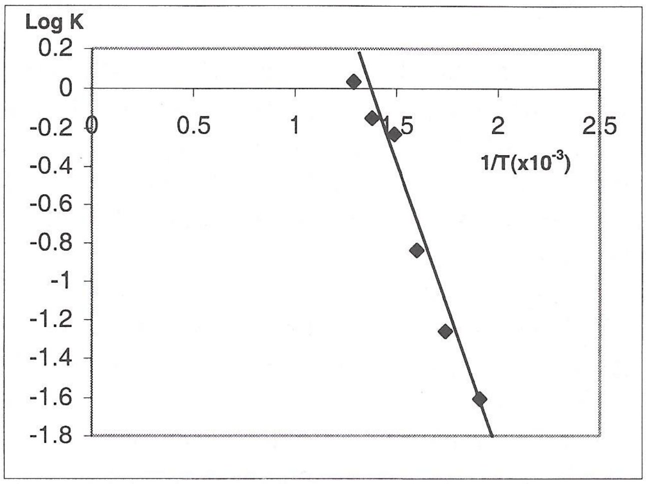

Figure 3 Arrhenius plot for Merit Pila coal

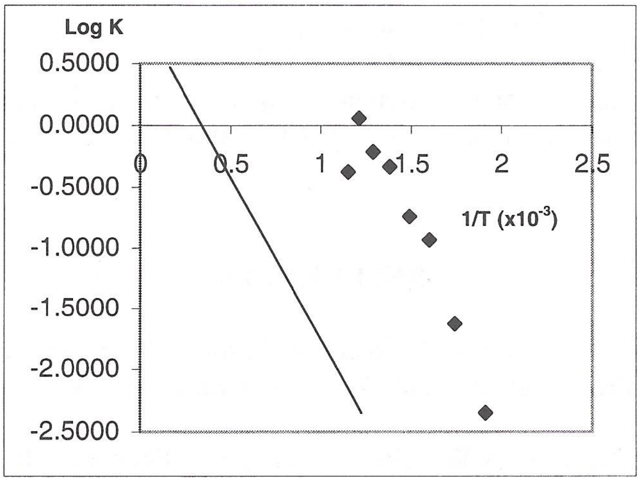

Figure 4 Arrhenius plot for Tanito Harum coal

Table 3 Kinetic Properties of the Coal

Sample Name	Activation Energy, E (KJ/mol)	Arrhenius Constant, A (1/min)
Blair Athol	5.2	11.6
Merit Pila	6.6	3.5
Tanito Harum	7.3	144.7

4.0 CONCLUSIONS

As the rank of coal increased, peak (main) temperatures and burn out temperatures of the samples increased (Blair Athol coal, followed with Tanito Harum and Merit Pila coal). Thus, burning profiles provide a valuable and rapid method of ranking coals in terms of their burnout performance. Derivative thermogravimetric analysis is a novel tool for ranking coals according to the relative ease of combustion.

Coal reactivity also can be promptly, interpreted from the highest and dominant peak (PT) from the DTG plot. From this study, Merit Pila coal is more reactive, which can be seen from its low peak temperature, followed by Tanito Harum and Blair Athol coal.

The rate data shall be interpreted to indicate that during the initial stages of combustion, devolatilization (dW/dT) is important. Calculated activation energies were of the correct orders of magnitude to describe combustion regions. In this study, assumption of the first order reaction of Arrhenius type reaction model shall be applied in the region of the 250°C – 600°C of the burning profiles for the three types of coal with linear least square correlation coefficients for the identified rectilinear portions varied from 0.92 to 0.95

However, application of the Arrhenius equation to the kinetics of solid state reactions has ben criticised in several grounds and still try to be justified by the scientists [5].

REFERENCES

1. Kok, M.V., et al., 1997, "Effect of Particle Size on the Thermal and Combustion Properties of Coal", *Thermochimica Acta*, Vol 302, p 125.

2. Artos, V. and Scaroni, A.W., 1993, "T.G.A. and Drop-tube Reactor Studies of the Combustion of Coal Blends", *Fuel*, Vol. 72, No. 7, p 927.

3. Cumming, J.W., 1984, "Reactivity Assessment of Coals via a Weighted Mean Activation Energy", *Fuel*. Vol. 63, p 1436.

4. Smith, S.E., et al., 1981, "DTGA Combustion of Coals in the Exxon Coal Library", *Fuel*, Vol 60, p 458.

5. Galwey, A.K. and Brown, M.E., 2002, "Application of the Arrhenius Equation to Solid State Kinetics : can this be Justified", *Thermochimica Acta*, Vol. 386, p 91.

6. Conesa, J.A., et al., 2001, "Comments on the Validity and Utility of the Different Methods for Kinetic Analysis of Thermogravimetric Data", *Journal of Analytical and Applied Pyrolysis,* Vol 58-59, p 617.

7. Hart, S., Ward, J. and Biffin, M., 2001, "Development of a Method to Assess the Reactivity of Multi-component Solid Fuel Briquettes", *IFRF Combustion Journal,* p 1.

8. Kneller, W.A., 1986, "Physicochemical Characterization of Coal and Coal Reactivity : A Review", *Thermochimica Acta*, Vol 108, p 357-388.

9. Morgan, P.A., Robertson, S.D. and Unsworth, J.F., 1986, "Combustion Studies by Thermogravimetric Analysis. 1. Coal Oxidation", *Fuel*, Vol. 65, p 1546.

APPENDIXES : DTG, BURNING PROFILES

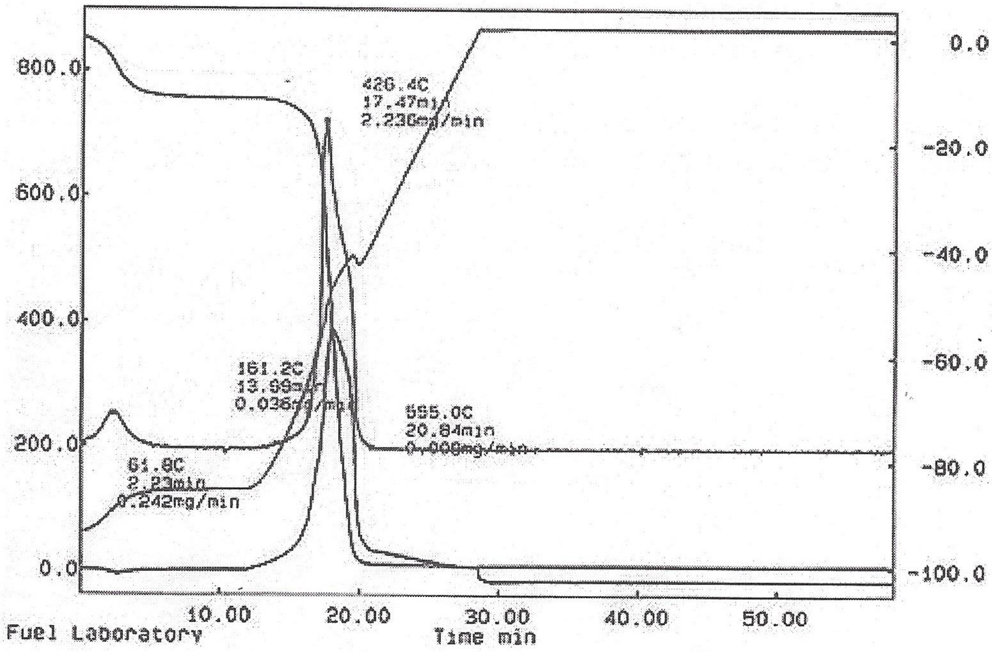

Figure 1 DTG curve for Merit Pila coal, (PT = 426°C).

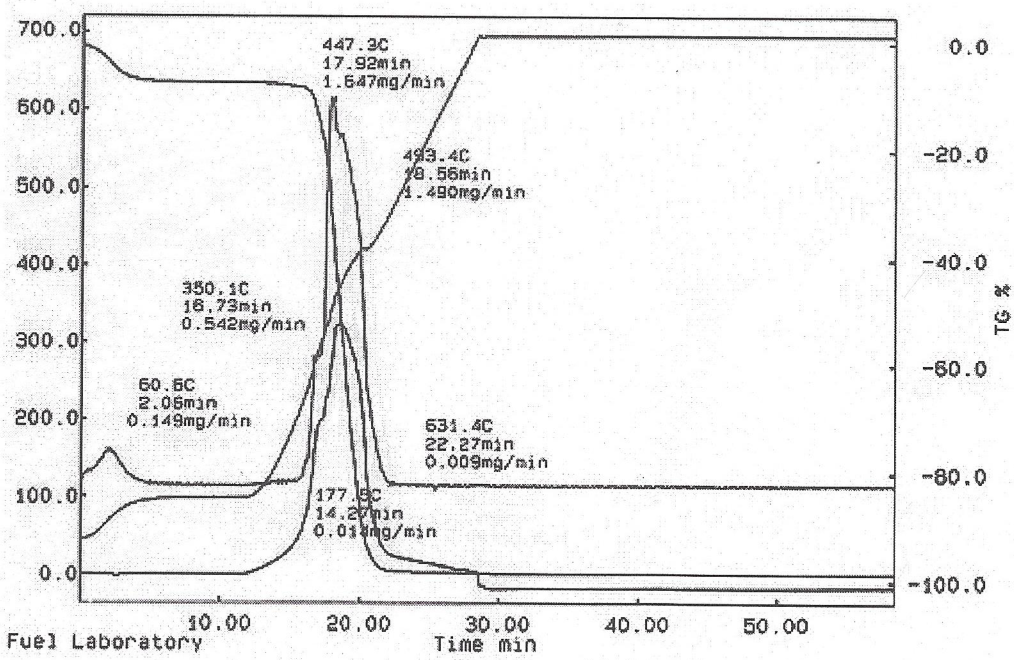

Figure 2 DTG curve for Tanito Harum coal, (PT = 447°C).

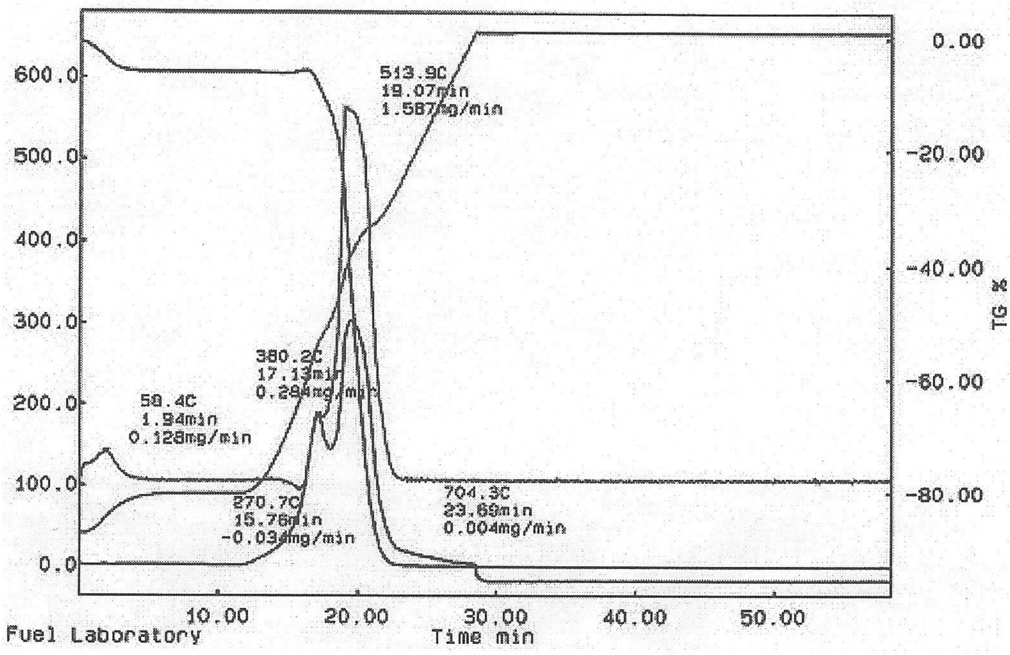

Figure 3 DTG curve for Blair Athol coal, (PT = 514°C).