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Pyrolysis Study of Sarawak Coal Using Thermogravimetric Analysis

Nor Fadzilah Othman*[1] and Mohd Hariffin Boosroh[+]

Abstract – *Pyrolysis of Sarawak coal was conducted using thermogravimetric (TG) study. Two coal samples, sub-bituminuous (Merit Pila coal) and bituminous (Silantek coal) were investigated within the temperature range of 300 900 ºC at different heating rates of 10, 20, 30 and 40 ºC min^{-1}, under inert nitrogen gas atmosphere. Differential thermogravimetric (DTG) data were analyzed using an Arrhenius type reaction model assuming a first-order reaction. Kinetic parameters, such as reactivity value, R_T and activation energy, E_a for the coals, were determined at different heating rates. Maximum rate temperatures and reactivity values for the coals were increased as the heating rates increased. The temperature at which maximum rate of decomposition occurred was found to be higher for bituminous coal than for lower rank coal. The activation energy E_a for the coal is 37.40-38.92 kJ mol^{-1}, with sub-bituminous coal showing slightly higher E_a than bituminous coal.*

Keywords – Activation energy, pyrolysis, reactivity, Sarawak coal, thermogravimetric (TG) analysis.

1. INTRODUCTION

Coal reserve in Malaysia currently stands at about 1712 million tones of various coals ranging from lignite to anthracite and about 69% of the reserves are in Sarawak while 29% are found in Sabah and the remaining 2% are found in Peninsular Malaysia [1]. Generally, the coal reserves in Malaysia have calorific values ranging between 21,000 and 30,000 kJ/kg with low levels of ash and sulphur contents. This shows that Malaysian coals are good quality coals and have high potential to be utilized in coal conversion processes.

Pyrolysis is the initial step in most coal conversion processes, such as combustion, gasification and liquefaction, and has a significant influence on the subsequent stages. Accurate descriptions of coal pyrolysis are helpful in the effective utilization of coal. The heterogeneous nature of coal and the complexity of the process have made it very difficult to perform unambiguous experiments on pyrolysis [2]. Thermogravimetric analysis (TG) is widely used to determine the rate of composition reaction occurring in solid fuels under the action of heat. Most of the works in the field of coal study have used TG related to the kinetics of the thermal decomposition on conversion of coal.

In general, gasification process can be broadly separated into two main reaction stages: pyrolysis and char gasification [3]. Pyrolysis studies can be performed in various devices, such as the pyroprobe, the Curie-point reactor, fixed bed reactor, thermal analysis, etc. TG is among the most widely used method as it enables the determination of apparent kinetic parameters of heterogeneous reactions, such as the reaction order, n, the apparent activation energy, E_a and the frequency factor, A. The present calculation methods are based on several TG and DTG curves measured at various heating rates.

In the present study, the initial stage of the gasification processes, which is the pyrolysis processes have been investigated, using a TG apparatus under non-isothermal conditions. The aim of this investigation is to study the pyrolysis behaviour of the Malaysian Sarawak coals in inert atmosphere, N_2. This study will provide preliminary information on the kinetic characteristics of Sarawak coals. The outcome of this study will be useful in identifying its potential utilization in the gasification system, such as in Integrated Gasification Combined Cycle (IGCC) power plants.

2. METHODOLOGY

Types of Coals Used

Two coals from Sarawak coal fields, which are Merit Pila and Silantek coals were selected for this study. Merit Pila is from sub-bituminous coal rank, while Silantek is from bituminous rank. The calorific value and proximate analysis of the coal samples are shown in Table 1. The analysis was conducted at the Fuel Testing Laboratory, TNB Research Sdn. Bhd.

Table 1. Properties of Sarawak coal.

Parameters	Coal Types	
	Merit Pila	Silantek
Calorific Value (kJ/kg)	24,200	31,400
Proximate Analysis (%)		
- Moisture	14.6	1.2
- Volatile Matter	41.4	24.2
- Fixed Carbon	39.6	61.5
- Ash	4.4	13.1

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Thermogravimetric Analysis

The tests were performed in a Seiko TG/DTA 220U Thermogravimetry system (Figure 1) with the temperature programming software of the furnace. The purge gas was N_2, for pyrolysis, supplied at a constant rate of 400 mL min^{-1}. The sample weight loss (TG signal) and rate of weight loss (DTG signal) as functions of time or temperature were recorded continuously under dynamic conditions (constant heating rates) in the range 30-900 ºC. In this investigation, TG data were used to determine the effect of different coal samples on the constant heating rate.

Pyrolysis was carried out non-isothermally using a coal sample, about 10 mg, place in the platinum crucible, under the inert environment of N_2 gas. The pre-programmed control-unit regulates all the automatic functions of the recorder (*e.g.* the continuous change in the mass of the sample is measured), as well as the temperature programming of the furnace. Finally, and after the furnace temperature had achieved its set value, the sample was allowed to cool to normal room-temperature.

3. RESULTS AND DISCUSSION

Weight Loss Profile for Different Types of Coals in N_2

Figures 2(a) and (b) show the graphs of weight loss graph for Merit Pila, and Silantek coals at different heating rates of 10, 20, 30 and 40 ºC min^{-1}. The results indicate that the weight loss is related to temperature; since the higher the temperature, the larger the weight loss. The results also show that sub-bituminous coal (Merit Pila coal) has higher weight loss during the pyrolysis process, compared to bituminous coal (Silantek coal). This is because sub-bituminous coal contains higher volatiles content, and these volatiles are expected to be easily released during the pyrolysis process.

The weight loss of the sample still continued, as the temperature was increased beyond ~600 ºC, which could be attributed to the possibility of continued pyrolysis, as well as the presence of CO_2 (which evolved as a result of carbonate decomposition) and which reacts with the residual char, as described by the Boudouard reaction (*i.e.* $C + CO_2 \rightarrow 2CO$), forming carbon monoxide. The finding also shows that the rate of decomposition during the loss of hydrocarbon material during the pyrolysis phase is almost invariant irrespective of the heating rate applied. As the heating rates increased, the maximum rate of decomposition occurs at higher temperatures. Similar behavior of the weight loss of coal at different heating rates was reported by [4].

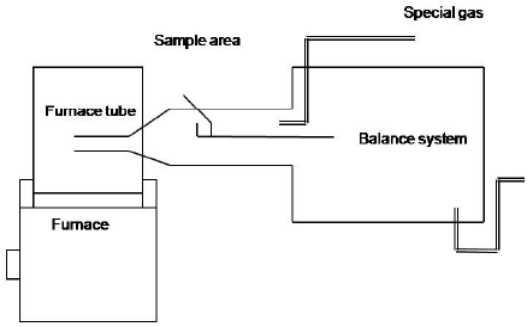

Fig. 1. Schematic of the Seiko TG/DTA 220U thermogravimetry system.

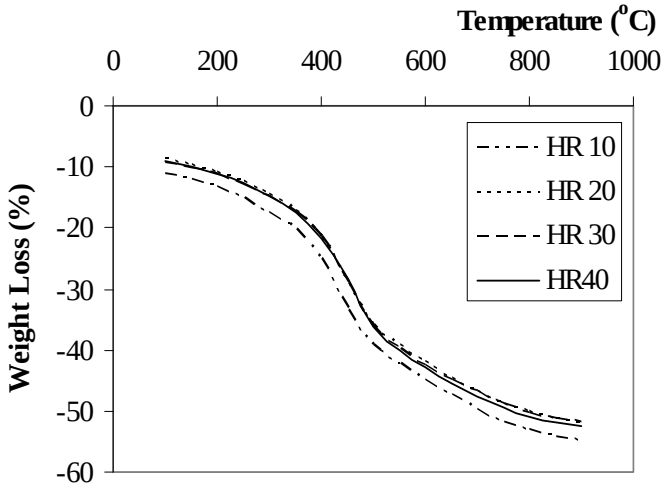

Fig. 2(a). Weight loss of Merit Pila coal.

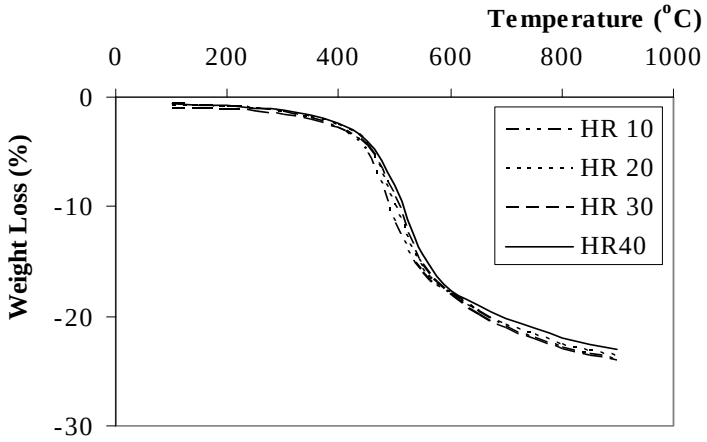

Fig. 2(b). Weight loss of Silantek coal.

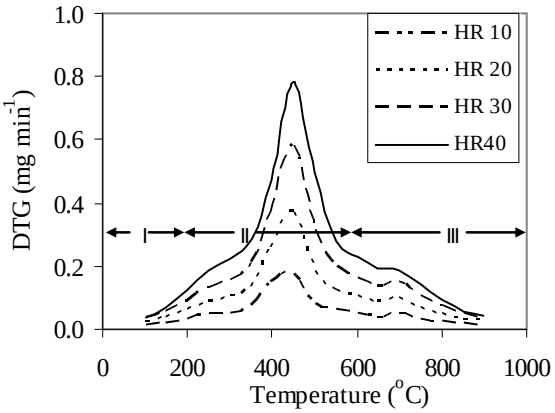

Fig. 3(a). DTG curve of Merit Pila coal.

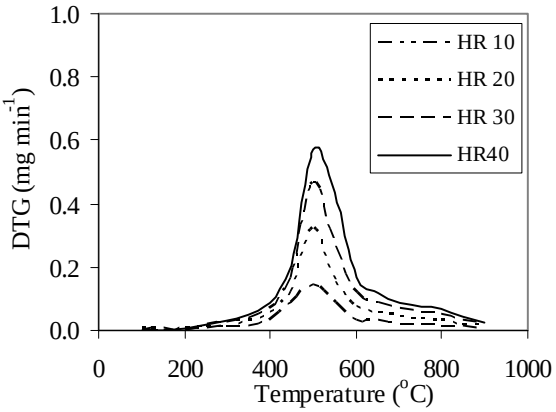

Fig. 3(b). DTG curve of Silantek coal.

DTG Curves for Different Types of Coals in N_2

Figures 3(a) and (b) show the DTG curves for the Merit Pila and Silantek coals. The DTG curves can be divided into three zones. According to Serageldin and Pan [5], Zone I represents the evolution of water and occurs below 250 ºC. Zone II covers the temperature range of 250-665 ºC, in which compounds containing carbon, hydrogen and oxygen were released as a result of reactions of the functional groups. Zone III contains the second decomposition range in which mostly methane and hydrogen evolved.

In this study the three zones can be divided into different temperature range as shown in Figure 3(a) for Merit Pila coal. Zone I represent the evolution of water and occur below 200 ºC. Zone II covers the temperature range 200-650 ºC and Zone III contains the second decomposition range of 600-900 ºC. However, Zone III was almost negligible for bituminous coal (Silantek) as shown in Figure 3(b). The occurrence of this pattern is probably due to the stronger chemical bonding of C-H in higher rank coals which is difficult to break.

Table 2 shows the temperature at which maximum rate of decomposition is higher for bituminous coal (Silantek) than sub-bituminous coal (Merit Pila). Similar trend was reported in [6] that also found that maximum rate of weight loss for sub-bituminous coal occurred below 490 º C. Thus, it is apparent that with a decrease in rank there is a corresponding shift towards a lower temperature range of the region of maximum rate of weight loss. This is possibly due to the fact that as a coal matures, unstable components of the coal matrix are driven off, by the action of heat and pressure and this leads to a more heat stable coal structure with lower volatile matter content, which decomposes at higher temperatures [6].

Table 2. Maximum rate temperature for the coals at different heating rates.

Coal Types	Heating Rate (ºC min^{-1})	Maximum Rate Temperature (ºC)
Merit Pila	10	442.3
	20	444.5
	30	452.2
	40	456.3
Silantek	10	481.1
	20	501.3
	30	511.8
	40	517.4

Reactivity and Activation Energy

Yun *et al.* [7] reported that more detailed method to determine coal reactivity is by TGA. TGA has already been extensively used in comparing the char combustion reactivity [8]. The shift in the DTG main peak in Figures 3(a) and (d) are relatively the measure of reactivity value. Equation 1 is used to evaluate reactivity, R_T as reported by [9]-[11].

$$R_T = \frac{1}{W_o} \cdot \frac{dW}{dt} \quad (1)$$

where W_o is the initial weight of the coal for pyrolysis period and $\frac{dW}{dt}$ is the instantaneous weight loss rate of the DTG curve (as illustrated in Figures 3(a) and (b). The maximum reactivity values for the pyrolysis were determined from each TGA profile. The maximum reactivity values, R_{max} for pyrolysis at different heating rates of Merit Pila and Silantek coals are shown in Table 3.

Table 3. Maximum reactivity values, R_{max} of the coals at different heating rates.

Coal Types	Heating Rate (^oC min^{-1})	R_{max} (mg mg^{-1} h^{-1})
Merit Pila	10	1.07
	20	2.21
	30	3.43
	40	4.69
Silantek	10	0.91
	20	1.86
	30	2.84
	40	3.73

The activation energies, E_a, of the coals were obtained using the Arrhenius relation given by Equation 2:

$$R_{max} = A\exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

where, R_{max} is the maximum reactivity

$$\ln R_{max} = \ln R_o - \frac{E_a}{RT_{max}} \quad (3)$$

By plotting $\ln R_{max}$ against $\frac{1}{T_{max}}$ at different heating rates (Equation (3)), a straight line was obtained. The activation energy and pre-exponential factor, $\ln R_o$ are determined from the slope and intercept, respectively. These plots are shown in Figures 4(a) and (b).

The linear graphs were fitted very well with the Arrhenius equation at correlation coefficient, r^2 = 0.9. According to [9], a linear Arrhenius plot indicates all reactions were in the chemical reaction control region. The activation energies of the coals found from the Arrhenius plots are presented in Table 4. It is observed that activation energies are 16.24 and 16.90 kJ mol^{-1} for the studied coals.

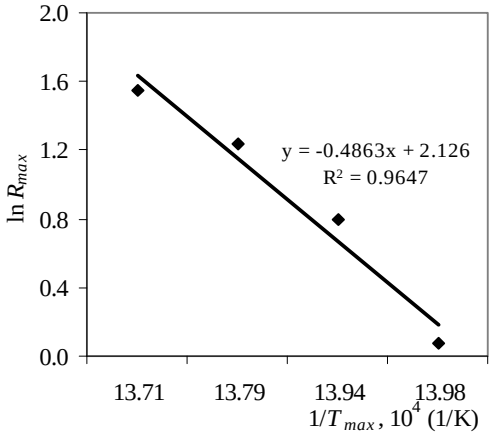

Fig. 4(a). A plot of ln (R_{max}) against 1/T_{max} of Merit Pila coal at heating rates of 10, 20, 30 and 40 ^oC min^{-1} in N_2.

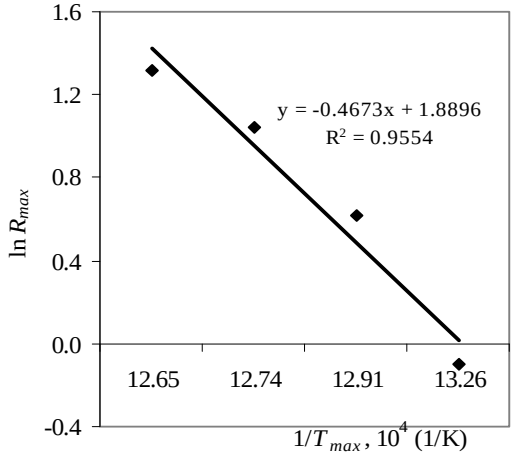

Fig. 4(b). A plot of ln (R_{max}) against 1/T_{max} of Silantek coal at heating rates of 10, 20, 30 and 40^{o}C min^{-1} in N_2.

From this study, the determination of reactivity values using the DTG maximum peak temperature has shown significant contribution of the heating rates towards the reactivity values. Overall, the reactivity values for all the coals were increased as the heating rates increased in the pyrolysis process.

Previous study has shown that higher reactivity coals will show lower activation energy from single heating rate DTG curve [8]. However, in this study the activation energy for sub-bituminous (Merit Pila) is slightly higher than bituminous coals (Silantek). This indicates that different heating rates had shown significant contribution towards the determination of activation energy using maximum reactivity values calculated from maximum rate temperatures. Slightly higher energy is required for lower rank coal to start the chemical reactions and break the chemical bondings of the coal structure compared to the higher rank coal [11]. In relation to this observation, a study [12] also reported that reaction with high activation energy needs higher temperature or a longer reaction time.

Table 4. Activation energies of Merit Pila and Silantek coals in N_2 at different heating rates.

Coal Types	E_a (kJ mol^{-1})	ln R_o
Merit Pila	16.90	2.13
Silantek	16.24	1.89

4. CONCLUSION

The study shows that maximum rate temperatures and reactivity values for the coals were increased as the heating rates increased. The temperature at which maximum rate of decomposition occurs is higher for bituminous coal than for sub-bituminous coal.

The kinetics parameters such as maximum reactivity value, R_{max} and activation energy, E_a from different heating rates for the studied coals are well-fitted with the Arrhenius equation (r^2 =0.9). The activation energy E_a for Silantek and Merit Pila coals are 16.24 and 16.90 kJ mol^{-1}, with sub-bituminous coal showing a slightly higher E_a than bituminous coal. Higher reactivity coal has shown slightly higher activation energy.

This work, therefore, will serve as a preliminary study for more extensive research in this area. Further studies can be done using other methods of kinetic parameters determination.

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