

PYROLYSIS OF SARAWAK COALS- MERIT PILA AND MUKAH BALINGIAN

Nor Fadzilah Othman*, Mohd Hariffin Bosrooh

College of Graduate Studies,
Universiti Tenaga Nasional (UNITEN), KM 7, Jalan Kajang-Puchong,
43009 Kajang, Selangor

ABSTRACT

Thermogravimetry (TG) analysis has been applied for the pyrolysis of two low rank Sarawak coals Merit Pila (MP) and Mukah Balingian (MB). The coal samples, about 10 mg were investigated within the temperature range 30-900°C at different heating rate of 10, 20 and 30°C min⁻¹, under nitrogen atmosphere for the pyrolysis study. Differential thermogravimetric (DTG) data were analysed using an Arrhenius type reaction model assuming a first-order reaction. Kinetic parameters, which are reactivity value, R_T and activation energy, E_a for MP and MB coals were determined at different heating rates. The R_T values for MP were 0.02, 0.04 and 0.06 mg mg⁻¹ min⁻¹ and for MB coal were 0.02, 0.03 and 0.05 mg mg⁻¹ min⁻¹. While, the E_a for MP coal were 5.49, 5.52 and 5.72 kJ mol⁻¹ and for MB coal were 4.96, 5.48 and 5.78 kJ mol⁻¹. The kinetic parameters for MP and MB coals had shown almost similar pattern, and the R_T and E_a were increasing as the heating rates increased.

Keywords: *Pyrolysis, Sarawak coals, thermogravimetric, arrhenius, reactivity value, activation energy.*

1.0 INTRODUCTION

Coal remains the most important source of primary energy for the generation of electricity power. Coal is also, however, the source of the greatest amounts of CO₂ emissions caused by the combustion of fossil fuels to electricity. IGCC (integrated gasification combined-cycle) is one of the most promising processes for the conversion of coal to electrical energy, due to its higher efficiencies and lower CO₂ released and ash production.

Since, Malaysia also have own coal reserves, mainly in Sarawak, the feasibility study of the utilisation of the coal in the gasification system should be done.

Gasification, which is a means to convert fossil fuels, biomass and wastes into either a combustible gas or a synthesis gas for subsequent utilisation, offers the potential both for clean power and chemicals production. In general, a total gasification process can be broadly separated into two main reaction stages: pyrolysis and char gasification [1]. In view of the industrial importance of coal gasification, fundamental studies of the nature and course of the reactions involved have been carried out in the past by numerous workers. Among the

* Corresponding author: E-mail: norfadzilahohtman@yahoo.com

different aspects investigated, kinetics plays as very important role since it provides useful data for the correct understanding of the chemical reactions and energy involved in the gasifiers. In typical gasifiers, the physicochemical processes, including pyrolysis take place at temperature of 150-700°C. The pyrolysis process separates the water vapor, organic liquids and noncondensable gases from the char or solid carbon of the fuel [2].

Thermogravimetry (TG) is widely applied to determine the reaction rate processes of coals [3]. This method involves a continuous measurement of the change in mass or rate of mass loss (differential thermogravimetric, DTG) of a sample with temperature or time. Kinetic parameters, such as activation energy and order of reaction, can be derived from these types of data.

Many experimental techniques have been employed in the studies of reaction mechanism and kinetics for carbon gasification reaction such as temperature-programmed desorption (TPD), thermogravimetric analysis (TG), transient kinetics (TK), transmission electron microscopy (TEM) and scanning tunneling microscopy (SEM) [4]. Among them, TG is the most popular and widely used method. The non-isothermal TG with a linear temperature growth is a method frequently used to characterize materials from their thermal behavior standpoint. In addition, 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 either based on several TG curves measured at various heating rates (HR).

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, for Merit Pila, MP and Mukah Balingian, MB coals in relation to the final temperature. The aim of this investigation is to study the pyrolysis behaviour of the Malaysian coals in inert atmosphere, N_2 . Prior to these reactions, the coals were characterized according to the Reactivity value, R_1 and the Apparent Activation Energy, E_a . This paper will discuss the pyrolysis study of Sarawak coals using TG and DTG data, as well as the kinetic parameters.

2.0 MATERIALS AND EXPERIMENTAL METHOD

2.1 Types of Coals Used

Two types of coals have been chosen from the Sarawak coalfield, which are Merit Pila (MP) and Mukah Balingian (MB) coals. The calorific value and proximate analysis of the coal samples, which were conducted at Fuel Testing Laboratory, TNB Research Sdn Bhd, are shown in Table 1.

Table 1: Properties of two Sarawak coals

Coals	Calorific Value (Kcal/kg, HHV)	Proximate Analysis (%)			
		Moisture	Volatile Matter	Fixed Carbon	Ash
MP	5800	15	43	36	6
MB	5030	15	38	39	8

2.2 Thermogravimetric Analysis

The tests were performed in a Seiko TG/DTA 220U Thermogravimetry system with the temperature programming software of the furnace. The purge gas was N₂, 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°C. 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 N₂ 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.

3.0 RESULTS AND DISCUSSION

Figures 1 and 2 show the weight loss and DTG curves for the MP and MB coals respectively, at different heating rates (HR) of 10, 20 and 30°C min⁻¹. The rate of weight loss is related to the temperature: the higher the temperature, the larger the weight loss. This is because, at low temperatures, pyrolysis proceeds slowly. The important features of such the DTG curves are that the major pyrolysis peak is a singular one. The DTG curve exhibits three zones which can be seen in the MP coal curve. Zone I represents the evolution of water and occurs below 200°C. Zone II covers the temperature range 200-600°C. Compounds containing carbon, hydrogen and oxygen are released as the result of reactions of the functional groups. This is termed the primary devolatilization range. Zone III contains the second decomposition range (600-900°C) in which mostly methane and hydrogen are evolved. As shown in Figure 2, most of the CH₄ appeared in zone II rather than in zone III, which agrees with the work of Serageldin [5].

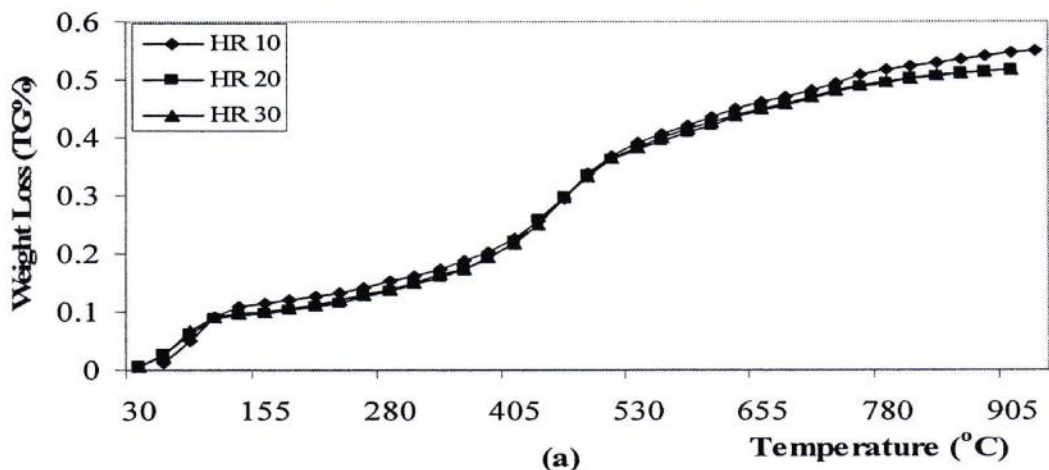


Figure 1: Pyrolysis behaviour of coals at different heating rates (HR):
(a)MP, (b)MB

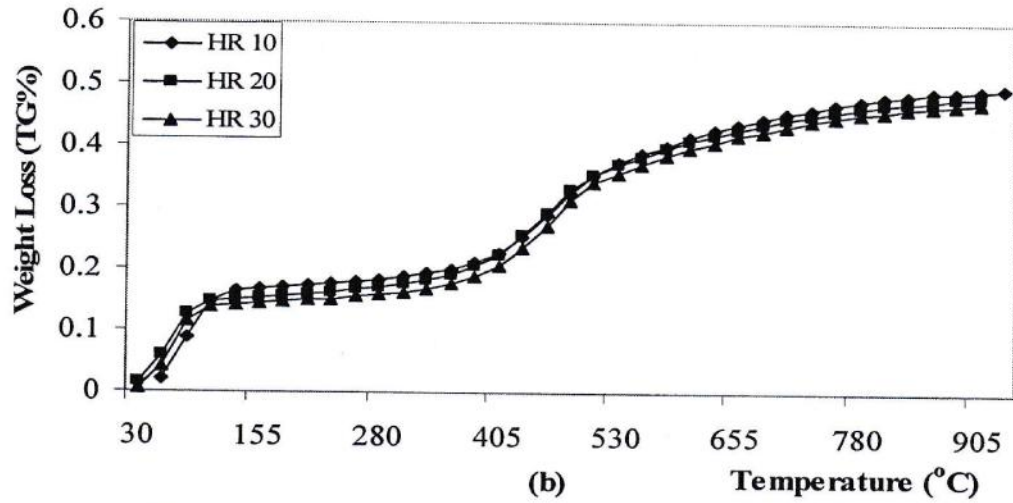


Figure 1: Pyrolysis behaviour of coals at different heating rates (HR): (a)MP, (b)MB (continued)

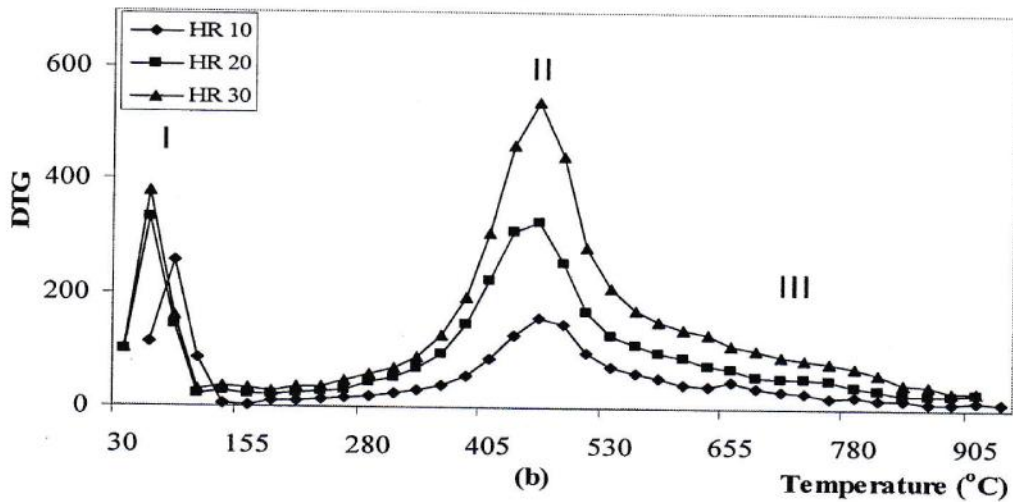
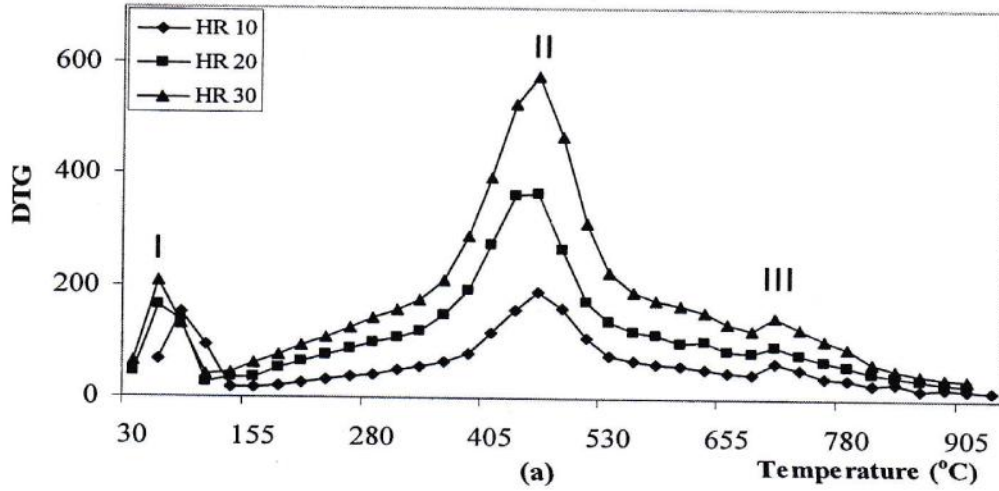


Figure 2: DTG of coals at different heating rates (HR), in relation to the pyrolysis temperature: (a)MP, (b)MB

The sample's continued loss of weight, as the temperature was increased beyond ~600°C, could be attributed to the possibility of continued pyrolysis, as well as the presence of CO₂ (which evolved as a result of carbonate decomposition) and which reacts with the residual char, described by the Boudouard reaction (i.e. C + CO₂ → 2CO), forming carbon monoxide. The increase in the amount of coal decomposed with increasing temperature is greater in the range of 200-500°C than for temperatures exceeding 550°C.

The two coals exhibit qualitatively the same patterns of thermal degradation when the pyrolysis temperature was raised over the studied range. During the pyrolysis phase (i.e. within temperature range below 550°C), MP coal exhibits 42, 39 and 40% of its total weight loss compared with the MB coal (i.e. more than MB coal by about 2, 1 and 3% at heating rates of 10, 20 and 3°C min⁻¹), which exhibits the total weight loss of 40, 38 and 37% at heating rates of 10, 20 and 30°C min⁻¹.

The weight losses during the pyrolysis of both coal samples, with regard to heating rate and the temperature at which the maximum rate of decomposition occurred, are presented in Table 2. Examination of these values confirms the conclusions reached from Figure 1, that the rate decomposition during the loss of hydrocarbon material during the pyrolysis phase is almost invariant irrespective of the heating rate applied. As the heating rate is increased, the maximum rate of decomposition occurs at higher temperatures. The shift in the DTG peak, which is a measure of relative reactivity (i.e. defined as either the ratio of the rate of weight loss per unit time or the rate of weight loss relative to the initial weight of the sample), is illustrated in Figure 2. This can be attributed to the variations in the rate of heat transfer with the change in the heating rate and the short exposure time to a particular temperature at the higher heating rates, as well as the effect of kinetic decomposition. Almost complete decomposition of the coal occurred at the lower heating rates, whereas, for high heating rates (e.g. 50°C min⁻¹), complete decomposition would occur at a higher pyrolysis temperature than the original of about 550°C.

The temperature at which the maximum rate of decomposition occurred for MP and MB coals are almost the same as presented in Table 2. The examination of these values confirms the conclusions reached from Figure 1, that both the rate of decomposition during the pre-heating stage and the loss of hydrocarbon material during the pyrolysis phase are almost the same for MP and MB coals. The shift in the DTG peak is a measure of reactivity value. The reactivity values [6] were calculated according to the relationship

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

where W_o is the starting weight of the coal char on a *daf* basis and dw/dt is the maximum from the DTG curve (are illustrated in Figure 3 and 4). The reactivity values for pyrolysis of MP and MB in N₂ are shown in Table 2. The apparent activation energies, E_a obtained by applying the Arrhenius equation (Equation 2), to the R_T values in the range 703-803 K for MP and MB at heating rate of 10°C min⁻¹ and 728-828 K for MP and MB at heating rates of 20 and 30°C min⁻¹. Arrhenius plots are shown in Figures 3 and 4.

$$\ln R_T = \ln R_o - E_a/2.303RT \quad (2)$$

Table 2: Reactivities of MP and MB coals in N₂

Coal Type	Heating Rate (°C min ⁻¹)	Maximum Rate Temperature (°C)	R _T (mg mg ⁻¹ h ⁻¹)	E _a (kJ mol ⁻¹)
MP	10	430	1.24	5.50
	20	455	2.37	5.52
	30	455	3.72	5.67
MB	10	430	1.13	4.96
	20	444	2.34	4.97
	30	456	3.71	5.79

A close look at the DTG curves shows that the maximum decomposition rate is almost identical for both the MP and MB samples at different heating rates. This suggests that approximately equal values occurred for the reactivities of both coals and it was approved with the calculated R_T for MP and MB coals as shown in Table 2.

Similar trends, were observed for the Arrhenius plots of MP and MB coals as shown in Figures 3 and 4 and it is clear that the R_T data are fitted very well by the Arrhenius equation ($r^2 = 0.93-0.98$). The slope of these straight lines are related to the apparent activation energy. The values obtained are given in Table 2. The R_T and E_a values in the pyrolysis process can be linearly correlated with the increasing heating rates, as shown in Table 2. The influence of heating rate on the activation energy (which is directly related to the heating rate) is clear: there is an increase in the apparent activation energy upon increasing of the heating rate. However, the increasing of R_T and E_a values are small.

The E_a values for MP coal and MB coal in pyrolysis process are much more lower compared with the E_a value from previous studies using different types of coal, with E_a values between 100-300 kJ mol⁻¹ [6-8].

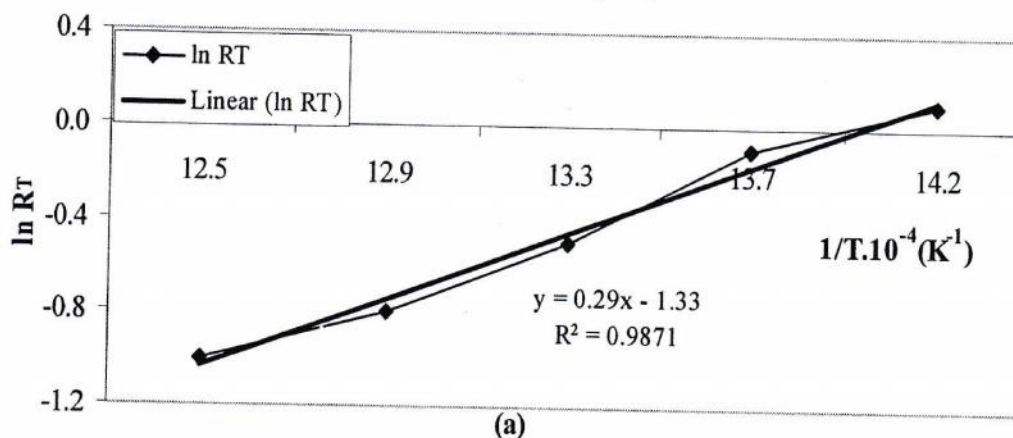
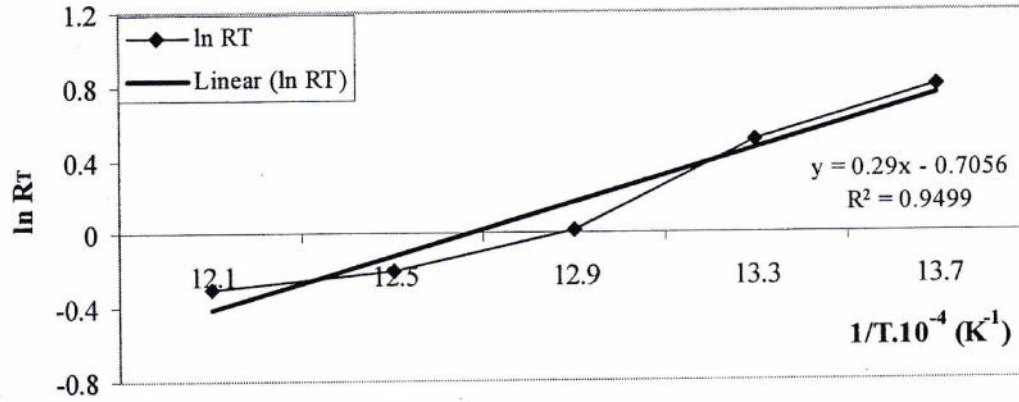
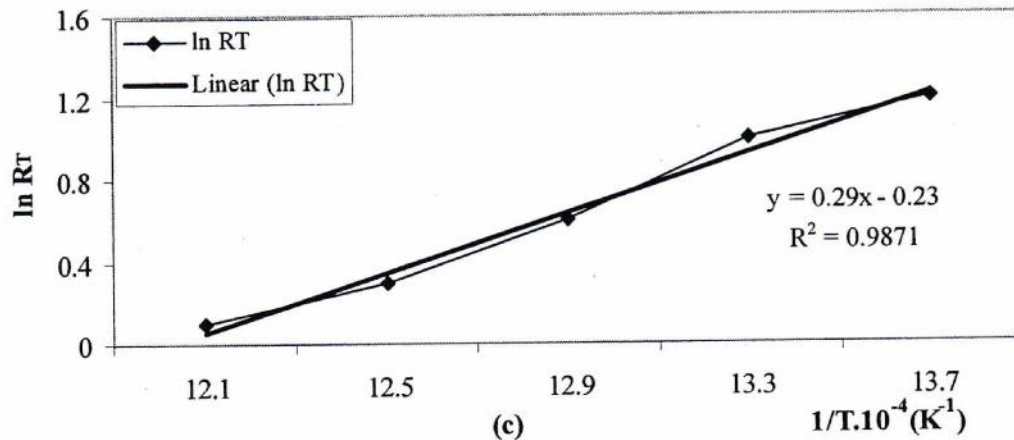


Figure 3: Arrhenius plots for pyrolysis of MP coal at heating rates of (a)10, (b) 20 and (c) 30°C min⁻¹ in N₂

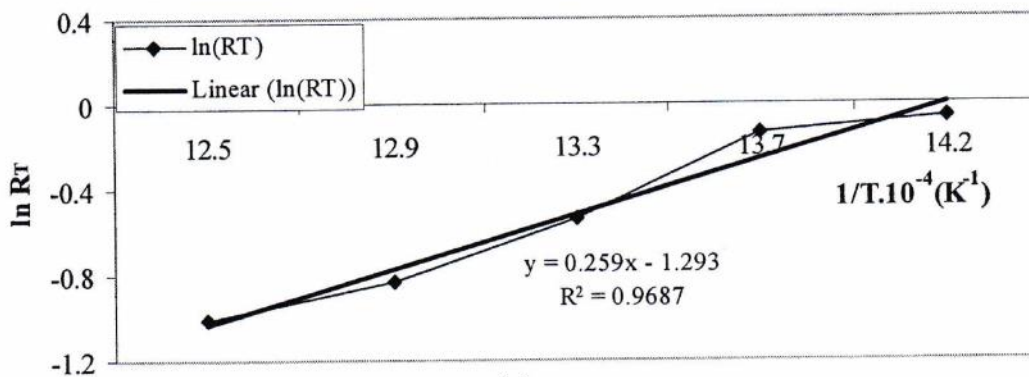


(b)



(c)

Figure 3: Arrhenius plots for pyrolysis of MP coal at heating rates of (a) 10, (b) 20 and (c) 30°C min⁻¹ in N₂ (continued)



(a)

Figure 4: Arrhenius plots for pyrolysis of MB coal at heating rates of (a) 10, (b) 20 and (c) 30°C min⁻¹ in N₂

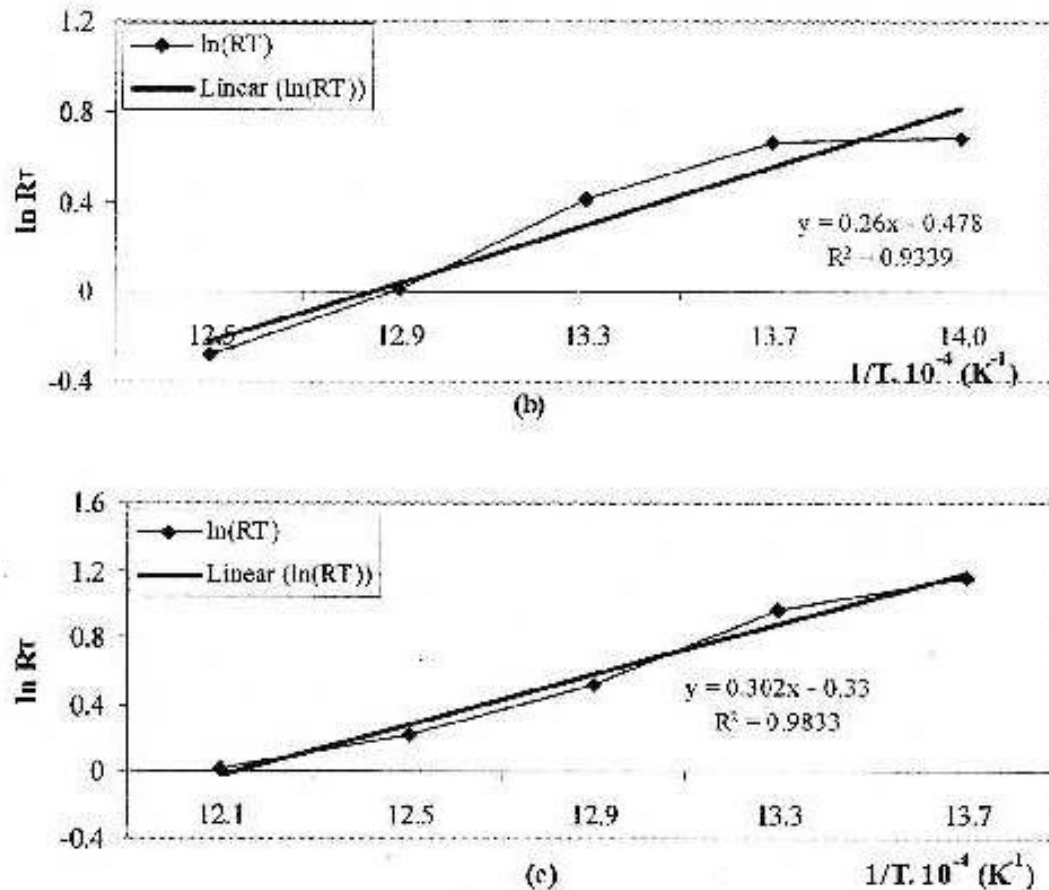


Figure 4: Arrhenius plots for pyrolysis of MB coal at heating rates of (a)10, (b)20 and (c)30°C min⁻¹ in N₂ (continued)

4.0 CONCLUSIONS

Similar weight loss (TG) and DTG curves pattern were seen in the pyrolysis of MP and MB coals at different heating rates. The kinetics parameters such as R_T and E_a are well-fitted with the Arrhenius equation ($r^2 = 0.9$) and also gave approximately, the equal values, which indicate the similar behaviour of MP and MB in the pyrolysis process.

There has been very little study on the kinetics of Malaysian Coals reported in the literature. This work, therefore, will serve as a preliminary study for more extensive research in this area. Further studies can be done using other types of Malaysian coals and other methods of kinetic parameters determination.

ACKNOWLEDGEMENT

Authors acknowledge the financial support from Seeding Fund, TNB Research Sdn. Bhd.

REFERENCES

1. Pan, Y.G., Velo, E., Puigjaner, L., 1996. Pyrolysis of blends of biomass with poor coals, *Fuel*, 75(4), 412-418.
2. Basu, P., 2006. *Combustion and gasification in fluidized beds*, CRC Press, Taylor & Francis Group, USA, 63.
3. Kneller, W.A., 1986. Physicochemical characterization of coal and coal reactivity, A review, *Thermochimica Acta*, 108, 357-388.
4. Wang, S., Slovak, V., Haynes, B.S., 2005. Kinetic studies of graphon and coal-char reaction with NO and O₂: direct non-linear regression from TG curves, *Fuel Processing Technology*, 86, 651-660.
5. Serageldin, M.A., Pan, W.P., 1984. Coal analysis using thermogravimetry, *Thermochimica Acta*, 76, 146-160.
6. Fernandez-Morales, I., López-Garzon, F.J., López-Peinado, A., Moreno-Castilla, C., José Rivera-Utrilla, J., 1985. Study of heat-treated Spanish lignites, Characteristics and behaviour in CO₂ and O₂ gasification reactions, *Fuel*, 64, 666-673.
7. Liu, X., Li, B., Miura, K., 2001. Analysis of pyrolysis and gasification reactions of hydrothermally and supercritically upgraded low-rank coal by using a new distributed activation energy model, *Fuel Processing Technology*, 69, 1-12.
8. Ye, D.P., Agnew, J.B., Zhang, D.K., 1998. Gasification of a South Australian low-rank coal with carbon dioxide and steam: kinetics and reactivity studies, *Fuel*, 77, 1209-1219.