Characteristics and Thermal Behaviour of Low Rank Malaysian Coals towards Liquefaction Performance via Thermogravimetric Analysis

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Abstract. In this study, thermal behaviour of two low-rank Malaysian coals namely Mukah Balingian (MB) and Batu Arang (BA) were obtained under pyrolysis conditions via Thermogravimetric analysis (TGA) at a heating rate of 20°C min^{-1}. The thermal characteristics of the coals were investigated prior to direct liquefaction in order to determine the liquefaction performance, i.e. coal conversion and oil yield. The differential weight loss (DTG) results for both coals showed that there are three main stages evolved which consists of moisture, volatile matter and heavier hydrocarbons that correspond to temperature range of 150, 200-500 and 550-800°C, respectively. Apparently, the DTG curves of BA coal reveals a similar pattern of thermal evolution profile in comparison to that of the MB coal. However, the calculated mean reactivity of BA coal is higher than that of MB, which implied that BA would probably enhance coal conversion and oil yield in comparison to MB coal. Interestingly, results showed that under the same liquefaction conditions (i.e. at 4MPa pressure and 420°C), conversion and oil yield of both coals were well correlated with their reactivity and petrofactor value obtained.

Keywords: Coal liquefaction, low rank coal, thermal behavior, TGA

1. Introduction

The incentive to develop coal liquefaction arose mainly from the increasing demand for liquid fuels, particularly for transport applications and also due to the depleting of other fossil fuels such as petroleum and natural gas. Previously, most researchers correlated the liquefaction performance i.e. coal conversion and/or oil yield obtained with parameters based on the chemical structure, reactivity or petrological composition of coals [1, 2]. Several correlations have been proposed for predicting the thermal behaviour of coal during combustion and devolatization. Relationships exist between characteristic temperatures of the thermogram during coal combustion [3]. A number of correlations were established between volatile matter/fixed carbon (VM/FC), carbon/hydrogen (C/H) and (carbon+hydrogen)/oxygen ((C+H)/O) ratios and coal reactivity [4]. The fuel ratio (FC/VM) is used in many commercial specifications for power station contracts. The evaluation of the inverse of fuel

IOP Conf. Series: Materials Science and Engineering **136** (2016) 012089 doi:10.1088/1757-899X/136/1/012089

ratio, i.e. VM/FC with the coal reactivity is an important parameter for the characterization of a particular fuel [5].

Artanto et al. [2] studied the effect of coal rank and H/C atomic ratios towards liquefaction conversion using 35 ml tubular batch-wise reactor at temperatures of 320, 350 and 405°C at 6 MPa under nitrogen and hydrogen gas atmospheres. The comparison was made between a sub-bituminous coal and brown coals originating from Indonesia. They found that the reactivity of the coals generally followed the correlation between total conversion and H/C atomic ratio, with conversion increasing with increasing H/C atomic ratio of the coal. It has been shown that, characterization of the evolved volatile matter can be done by leading the gaseous material into a GC, IR or MS [6]. These methods are usually cumbersome. Furthermore, they have limitations in as far as tar measurements are concerned. It is almost impossible to ensure the complete and quantitative transfer of the condensable tar components to the analytical instrument without loss or change. Thus, in this present study thermogravimetric analyzer (TGA) was used as a tool to obtain thermal evolution profiles of coals, which correspond to characteristics or thermal behaviour of the fuel. The thermal characteristics obtained under pyrolysis mode of two low-rank Malaysian coals namely Mukah Balingian (MB) and Batu Arang (BA) were investigated prior to direct liquefaction at established optimal conditions. The liquefaction results i.e. coal conversion and oil yield will determine the correlation between reactivity and thermal behaviour of coals with liquefaction performance.

2. Methodology

2.1 Coal preparation, coal assays and reactivity analysis

The samples used in this study were low-rank, Mukah Balingian (MB) and Batu Arang (BA) originating from Sarawak and Selangor, Malaysia, respectively. The procedure for coal preparation has been reported earlier [7]. Table 1 shows the ultimate, proximate and petrography analyses of the raw MB and BA coal samples. The procedure of ultimate and proximate analyses has been reported elsewhere [8]. For the reactivity study, pyrolysis mode was applied by heating the sample from ambient temperature to a final temperature of 1000°C under a nitrogen gas stream, with heating rate of 20°C/min. The gas stream flow rates of nitrogen were fixed at a flow rate of 100 ml/min. The mass loss data with temperature were recorded and were then converted into derivative thermal gravimetric (DTG) using the analyzer software provided.

2.2 Coal liquefaction procedure

The detail procedure for coal liquefaction has been reported elsewhere [8]. Briefly, the coal liquefaction experiments were carried out in duplicate (within 2% error) in a 1-litre high-pressure high-temperature batch-wise reactor system. In this study, optimal liquefaction conditions obtained from previous investigation was chosen i.e. 1:10 coal-to-solvent ratio, temperature at 420°C, 4 MPa pressure, 30 min reaction time and with stirring [7]. The results of coal liquefaction were reported as percent conversion and product yield i.e. oil.

3. Results and Discussions

3.1 Characteristics of Mukah Balingian and Batu Arang coals

Table 1 shows the characteristics of Mukah Balingian (MB) and Batu Arang (BA) coals, which include ultimate, proximate and petrographic analyses, respectively.

Table 1: Characteristics of MB and BA coal samples.

Ultimate analysis (wt% daf)			Proximate analysis (wt% db)			Petrographic analysis (vol. %)		
	MB	BA		MB	BA		MB	BA
Carbon	63.9	73.8	Vol. Matter	44.7	44.5	Vitrinite	60	48
Hydrogen	5.1	5.5	Fixed carbon	35.6	49.3	Liptinite	31	44
Nitrogen	1.9	1.0	Ash content	4.2	6.2	Inertnite	8	7
Sulphur	0.5	0.7	Fuel ratio[1]	1.1	1.1	Min. matter	1	1
Oxygen[2]	28.6	19.0						
H/C ratio	1.0	0.9	Cal. Value	24.6	27.1	Vit. Ref.	0.4	0.4

[1] = fixed carbon/volatile matter; [2] = by difference; daf = dry-ash-free; db = dry-basis
Cal. Value = Calorific value (MJ/kg); Vit. Ref. = Vitrinite reflectance

From Table 1, it can be seen that MB and BA coal samples have relatively high oxygen and volatile matter contents. The petrographic analysis of these coals show a vitrinite reflectance value of 0.40% and thus, can be categorised as low rank coal i.e., sub-bituminous C rank [7]. It has been suggested that low rank coals are normally composed of small aromatic clusters and contain many cross-links and functional groups and thus, are very reactive and undergo fast and extensive bond breaking during liquefaction [9]. Interestingly, it shows that most of the analysis parameters of the MB coal were comparable to that of the BA coal, although both coal samples are from different deposition, i.e MB is located in Sarawak and BA is in Selangor. The differences between the two coals can be seen with carbon and distributions in maceral contents (petrographic analysis). BA coal contains ca. 10% higher carbon and ca. 13% higher liptinite content with total reactive macerals of ca. 92%, in comparison to MB coal. It has been established by King et. al. [10] that under a wide range of liquefaction conditions the more reactive maceral is liptinite followed, in decreasing order, by vitrinite and inertinite. Thus, the reactivity of BA coal is expected to be higher than MB coal during the liquefaction process and contribute higher coal conversion and oil yield.

3.2 Thermal behaviour of Mukah Balingian and Batu Arang coals

Figures 1, 2 and 3 show the the thermal behaviour of decomposition of MB and BA coal samples under pyrolysis conditions via thermogravimetric analyser (TGA), respectively.

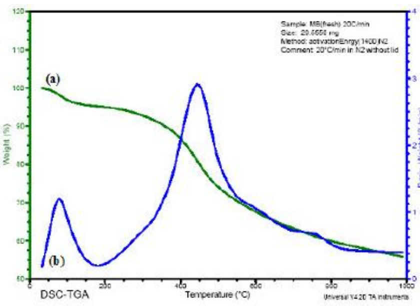

Fig. 1: TG (a) and DTG (b) profiles for the thermal decomposition of pyrolysed MB coal.

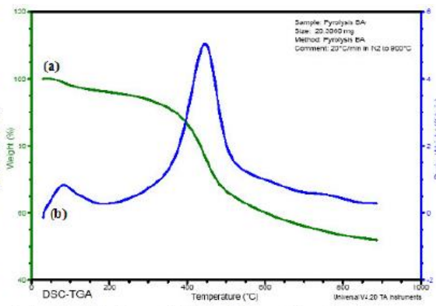

Fig. 2: TG (a) and DTG (b) profiles for the thermal decomposition of pyrolysed BA coal.

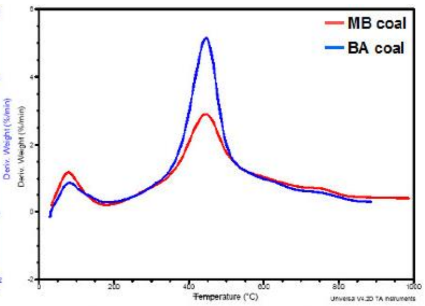

Fig.3: Superimposed DTG profiles for the pyrolysed MB and BA coal samples.

The pyrolysis of MB coal via TGA at a heating rate of 20°C min-1 is shown in Figure 1. The TG curve (Figure 1(a)) of the coal shows the weight loss profile with the weight decreasing as temperature is increased from ambient to 1000°C. The weight loss profile resembles that of a first order reaction. Figure 1(b) shows the differential weight loss (DTG) for MB coal that consists of three main stages. This conforms to previous findings as reported by Probstein and Hicks [11], Kastanaki et. al. [12], Serio et. al. [13] and Radovic et. al. [14]. The first stage pyrolysis, which occurs at temperatures ranging from ambient to 150°C, involves the dehydration of water and releasing of gas composed of oxides of carbon from the coal. The second stage pyrolysis, which occurs at temperatures of 200 – 550°C, however, is due to the release of volatile matter such as hydrocarbon gases, light oils and tars, and is of interest in this study. Finally, the third stage pyrolysis shows the appearance of some minor curves at temperatures ranging from 550 – 650°C and 700 – 800°C, that were attributed to the release of heavier hydrocarbons and non-condensable gases, mainly hydrogen, and from thermal decomposition of carbonates that are abundant in low rank coals. Also from the DTG profile of MB coal, it can be estimated that the softening temperature of this coal is around 350°C. Merrick [15] suggested that with extraction using liquid solvents, the preferred extraction temperatures lie in the range where the coal starts to decompose thermally, and typically the extraction is carried out at about 350 – 450°C. Moreover, Van Krevelen [16] suggested that temperatures around 350°C were found to be an indicative value for softening temperature in order to characterise coal for direct liquefaction. Thus, it can be suggested that MB coal would be a good feedstock and suitable for liquefaction and/or gasification processes and, hence, optimise the utilisation of low rank Malaysian coal. Apparently, the DTG curve of BA coal as shown in Figure 2(b) reveals a similar pattern of evolution profiles in comparison to that of MB coal (Figure 1(b)). However, when the DTG curves of both coal samples are superimposed, as shown in Figure 3, the peak height (R) for the second thermal peak of BA coal is higher than MB coal

Table 2: DTG reactivity of MB and BA coal samples during pyrolysis.

Coal Sample	Peak temperature T_{max} (°C)	Peak height R (mg min^{-1})	Mean reactivity Rm (mg min^{-1} °C^{-1})
MB	446.6; 607.8; 754.2	0.584; 0.211; 0.138	0.184
BA	446.4; 610.4; 751.6	1.085; 0.194; 0.115	0.290

MB = Mukah Balingian coal; BA = Batu Arang coal.

Previously, it has been reported that the DTG peak height (R) and maximum peak temperature (Tmax) is directly and inversely proportional to the reactivity, respectively [17]. The overall reactivity of both MB and BA coal samples was calculated based on the mean reactivity, Rm by using a parameter (R Tmax-1)100 to calculate for each peak, adding the share of any secondary peaks or shoulders present in the thermal profile with the exception of the peak due to released moisture [18]. In this calculation the rate of weight loss (mg min-1) was used, giving the dimensions for the mean reactivity as mg min-1 °C-1. The mean reactivity (Rm) values for both coal samples are displayed in Table 2. Hence, based on the calculated mean reactivity (Rm) value in Table 2, it shows that the reactivity of BA coal is higher than that of MB coal. This indicates that, under the same liquefaction conditions, BA coal would probably enhance coal conversion and oil yield in comparison to the MB coal. Thus, it can be suggested that BA coal would also be a good feedstock and suitable for liquefaction and/or gasification processes.

3.3 Correlation between coal reactivity and thermal behaviour with liquefaction results

Table 3 and Figure 4 show the liquefaction results of MB and BA coal samples, respectively. From Table 3 and Figure 4, it can be seen that the coal conversion of 91.2%, which was obtained for BA coal is comparable with the total amount of its reactive macerals (vitrinite + liptinite), i.e. 92%. The percent of oil yield obtained on the BA coal was ca. 75%. In order to evaluate the effect of intrinsic coal reactivity and contribution of macerals toward coal conversion and oil yield in BA coal, liquefaction results of MB coal at the same conditions were compared. It can be seen that the coal conversion and oil yield obtained for BA coal were higher than those of MB coal, i.e., ca. 7 and 8%, respectively. This observation seems to agree with the higher reactivity of BA coal as revealed from its DTG profile shown in Figure 3. Indeed, the calculated mean reactivity value of BA coal is also higher than that of MB coal (see Table 2). In terms of contribution of macerals; since the inertinite content of both coals is comparable (i.e., 7 and 8%) and less likely to be involved in the conversion processes of coal [19,20], the higher coal conversion and oil yield obtained for BA coal was attributed to liptinite. From Table 3, it shows that liptinite content of BA coal was ca. 13% higher than that of MB coal. Thus, this showed that the liptinite was more significant in determining the formation of oil yield during liquefaction. Furthermore, it has been established that liptinite is more reactive than vitrinite [10]. This showed that the intrinsic coal reactivity and reactive coal macerals especially liptinite were the contributing factors in determining higher coal conversion and oil yield during liquefaction. Hence, these results thus far showed that the use of thermogravimetric analysis (TGA) in determining the sample reactivity under pyrolysis or combustion mode was found to be useful in correlating the coal reactivity with liquefaction performance.

Table 3: Liquefaction[1] results and macerals content of MB and BA coals.

Results	MB coal	BA coal
Coal conversion	84.0%	91.2%
Oil	67.7%	75.3%
Asphaltene	9.7%	2.5%
Preasphaltene	6.7%	13.4%
Vitrinite	60%	48%
Liptinite	31%	44%
Inertinite	8%	7%

[1]conditions: at 420 °C, 4 MPa, 30 min, 1:10 coal-to-solvent ratio and with stirring at 500 rpm.

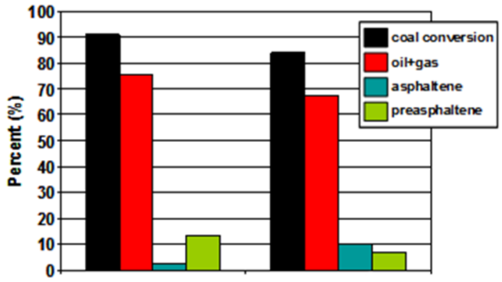

Figure 4: Liquefaction results of MB and BA coal samples.

Conclusion

The thermal characteristics of two low-rank Malaysian coals were investigated prior to direct liquefaction. The differential weight loss (DTG) results for both coals showed that there are three main stages evolved which consists of moisture, volatile matter and heavier hydrocarbons that correspond to temperature range of 150, 200-500 and 550-800°C, respectively. Apparently, the DTG curve of both coals reveals a similar pattern of evolution profiles, however when the curves are superimposed the peak height for the second evolution profile of BA coal is higher than MB coal. The higher coal reactivity of BA is in agreement with liquefaction results obtained on this coal with comparison to MB coal. Thus, the usage of TGA to predict sample reactivity under pyrolysis or combustion mode was found to be useful and the usage of the instrument prior to liquefaction is highly recommended.

Acknowledgment

This research work was funded by the Ministry of Education, Malaysia under the FRGS grant scheme. The authors also thank the management of Universiti Teknologi MARA for supporting the research work.

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