

CO-PYROLYSIS AND CHARACTERISTICS OF MALAYSIAN SUB-BITUMINOUS COAL AND WASTE HDPE BLENDS VIA TGA

Article history

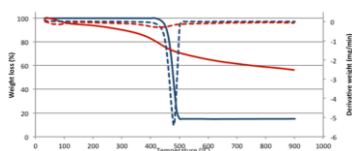
Received
29 November 2014
Received in revised form
30 April 2015
Accepted
31 May 2015

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Graphical abstract



Abstract

Waste polymers co-conversion is an attractive way to dispose of and convert polymer into high value fuel apart from having environmental-friendly advantages. Preliminary studies during pyrolysis and co-pyrolysis of Malaysian sub-bituminous coal, waste High Density Polyethylene (HDPE) and coal/waste HDPE blends have been performed via Thermogravimetry Analysis (TGA apparatus). The tests were carried out in nitrogen atmosphere, under dynamic conditions at a heating rate of 10°C/min. The coal/waste HDPE blends were prepared in the weight ratios of 80:20, 60:40, 40:60 and 20:80. The results showed that the thermal decomposition of the materials can be characterized by single reaction stage both for single and blended fuels between a temperature range of 300-530°C. Overlapping DTG curves, the comparison between experimental and theoretical devolatilization rate and deviation in char yield, suggests that the existence of possible synergistic effect for blended fuels are caused by chemical interactions. An increase in reactivity is observed with increasing HDPE blend ratio which is primarily due to the release of high amount of volatiles in the waste polymer. It was suggested that the degradation of polymer waste in the blends form radicals that abstracted hydrogen from coal and resulted in less char being produced.

Keywords: Pyrolysis, thermogravimetric analysis (TGA), coal, waste HDPE

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1.0 INTRODUCTION

Plastic wastes in Malaysia contribute approximately 18wt% of municipal solid waste (MSW) and the amount is increasing annually due to the demand both from domestic and industrial consumers. While mechanical recycling of plastic wastes is ideally the best option, segregation of post-consumer wastes, improper disposal and occupying the already limited landfill areas are some of the problems that Malaysia need to address. To avoid these situations from worsening, one of the viable and economical ways is

the chemical recycling of plastics waste for energy recovery. Although incineration is the fastest and simplest way to recover heat energy, this method will raise environmental concerns, particularly the possibility of dioxins formation and release of heavy metals [1].

In Malaysia, most of polymer wastes are abandoned and not recycled [2]. Among the common plastic waste disposed of is High Density Polyethylene (HDPE) in which the production of energy from this type of polyethylene waste has been anticipated to be an effective solution for disposal [3,4,5]. Polymers being a petrochemical

origin have intrinsically high calorific value, thus they can be converted back to useful energy and play an active role during coal liquefaction [5,6]. In the present work, co-pyrolytic behaviours of polymer waste/coal mixtures were investigated under inert atmosphere using a thermogravimetric analyzer to obtain an overall understanding of the interaction of both materials.

2.0 MATERIALS AND METHOD

2.1 Coal and Waste HDPE Preparation

Sub-bituminous coal sample of Mukah Balingian (MB) originated from Sarawak, East Malaysia and discarded waste of high density polyethylene (HDPE) from local plastics industry were selected in this study. To eliminate the effect of excessive moisture and to soften the coal samples, both samples were open air dried for minimum of 2 days. Coal samples were then grinded using mortar and both coal and waste HDPE were sieved using Endecotts Shaker Model EFL2 MK3 for 30 minutes to desired particle size of less than 212 μ m. Finally all samples were dried in a vacuum oven set at 80°C for 24 hours and kept in a tightly screw cap bottle. Coal is principally considered as the parent fuel in this co-pyrolysis method and blends of coal to waste HDPE were prepared in four different weight ratios i.e. 80:20, 60:40 40:60 and 20:80.

2.2 Equipment and Procedures

TG/DTG analyses of the coal, waste plastics and their blends were carried out using a thermogravimetric analyser Mettler Toledo/TGA/SDRA51e under dynamic conditions at ambient pressure with inert nitrogen gas atmosphere at constant flow-rate of 50 ml/min and at moderate heating rate of 10°C/min.

20mg of each sample was weighed directly into a 150 μ l alumina crucible and the temperature was kept isothermal for one minute before ramping to the desired temperature from 25°C to 900°C. The calorific values and elemental analyses of the coal and waste HDPE were performed using Ika-works C5000 bomb calorimeter and Thermo Finnigan Flashed 1112 analyzer, respectively. All experiments were replicated at least twice to obtain reproducibility.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Single Fuel

Table 1 shows the proximate and ultimate analyses as well as high heating values (HHV) for both materials. Plastic waste is characterised by its high amount of volatiles of nearly 90wt% which may positively affect the reactivity of the blended samples and considered desirable for subsequent gasification or combustion processes [7]. Waste HDPE exhibits the highest percentage of volatile matter, no fixed carbon and high calorific value which agrees with previous findings [8]. Waste HDPE also contains significantly much less nitrogen and sulphur elements which implies practically no emission of toxics NO_x and SO_x predicted. Thus, the possibility of adding/replacing this polymer waste type to coal is deemed to be suitable in power generation co-utilization [8,9]. The amount of volatile matter indicates the suitability of waste as the feedstock for pyrolysis conversion to liquid or gaseous product where high volatile content is desirable [3]. High fixed carbon gives indication on the char formation during pyrolysis and most significantly, the heating value of the substance.

Table 1 Catalytic alkylation of resorcinol to 4-*tert*-butyl resorcinol and 4,6-di *tert*-butyl resorcinol

Analysis	MB Coal	Plastic Waste (HDPE)
Proximate (db)(wt %)		
Volatile Matter	22.2	87.5
Fixed Carbon	67.3	0
Ash	10.5	12.5
Ultimate (daf)(wt %)		
Carbon	72.8	80.6
Hydrogen	4.6	14.0
Nitrogen	1.9	0.6
Sulphur	0.4	0.1
Oxygen	20.3	5.2
High Heating Value (HHV) (MJ/kg)	24.6	45.1

db – dry basis; daf – dry ash free basis; *calculated by difference

3.2 Thermal Degradation of Single and Blended Fuels

During pyrolysis, the weight loss percentages of the samples were continuously recorded as a function of temperature and time. The thermal evolution profiles (TEP) of single fuels at heating rate of 10oCmin⁻¹ are represented in Figure 1. Based on the method described by Kastanaki et al. (2002), it was deduced that the DTG peak height, R, and maximum peak temperature, Tmax is directly and inversely proportional to the reactivity, respectively and DTG curves of individual samples are displayed as a function of temperature and on a dry and ash-free (d.a.f) basis [10]. The earliest sample to decompose is MB coal followed by waste HDPE. Although polymer waste has the highest volatile matter, it is more stable to high temperature due to its macromolecular structure and stronger bonds compared to coal's. The plastic waste sample thermally degrades via radical depolymerisation whereby the chain backbone of the polymer is split by a radical reaction mechanism [11]. Both fuels display single DTG curves with coal having broader peak with maximum temperature of 431°C. Waste HDPE DTG curve is

almost totally one-step process and considerably steep due to its high volatile matter content with peak temperature of 481oC, which is agreeable with previous researches [5,6].

As for TG and DTG profiles of blended samples, thermal degradation characteristics such as peak temperature (Tmax), reactivity (R) and volatile matter loss (VM%) are as shown in Figures 2(a), Figure 2(b) and Table 2, respectively. Coal-waste HDPE blends (abbreviated as MB:WP ratio) also exhibit single DTG curves which is somewhat similar to that of waste HDPE DTG curve. Both profiles of coal and waste HDPE in the blends overlapped in the temperature region between 440°C to 510°C and as percentage of waste HDPE is increased, the peaks are observed to become steeper. According to Cai et. al (2008), this overlapping is due to free radicals transfer from coal pyrolysis in which these radicals participate in HDPE decomposition reactions [4]. This suggests possible chemical interaction of coal with HDPE during coal fluidicity stage in coke formation and also further degradation of HDPE into its monomer i.e. PE (polyethylene) which finally will evolve into gas form [12].

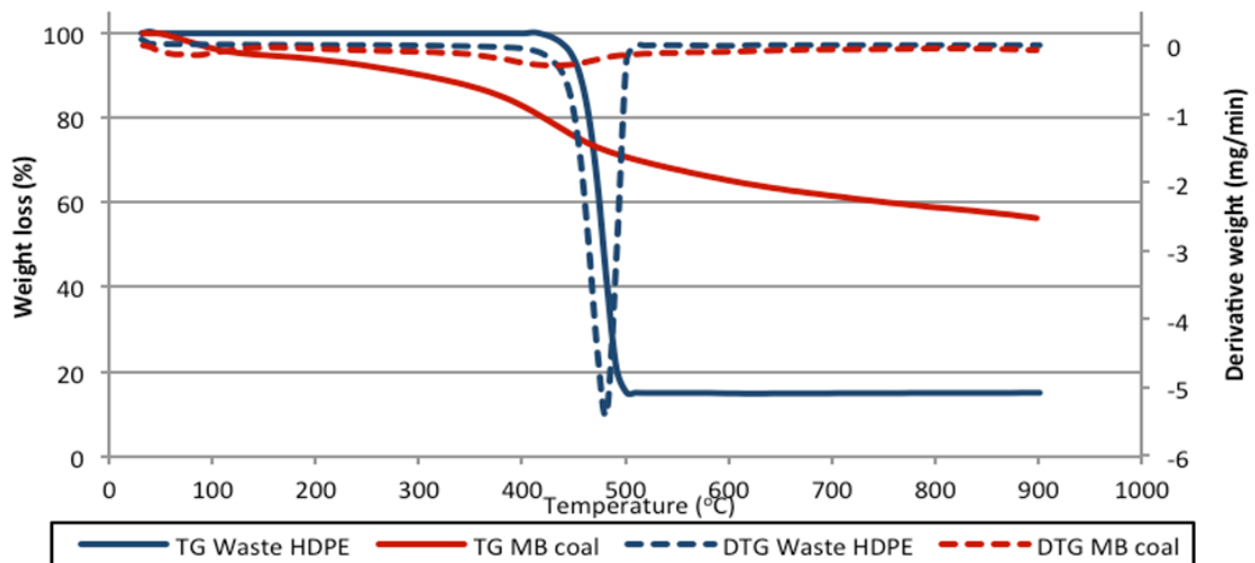


Figure 1 TG and DTG pyrolysis profiles at heating rate of 10oC/min

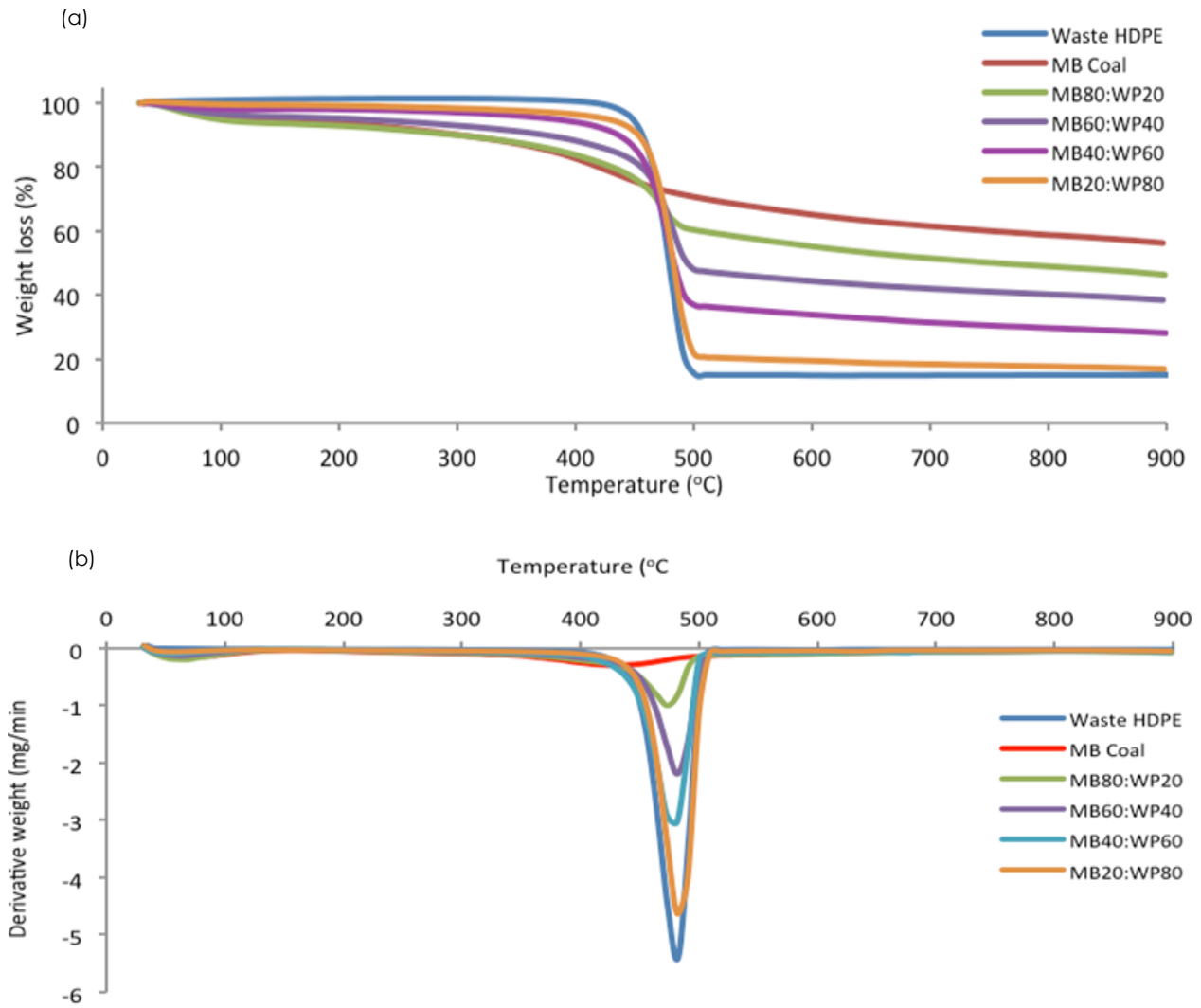


Figure 2 (a) TG and (b) DTG pyrolysis profiles of MB coal /waste HDPE (WP) blends at heating rate of 10°C/min

Table 2 The peak temperature (T_{max}), reactivity of MB coal, waste HDPE and their blends at heating rate 10°C/min

Blend Ratio MB:WP	TEP 1		TEP 2		VM (%)
	T_{max}	R ₁	T_{max}	R ₂	
100:0	431.02	0.25	-	-	33.11
80:20	-	-	475.23	0.90	35.46
60:40	-	-	482.71	2.13	49.76
40:60	-	-	478.88	3.05	61.86
20:80	-	-	484.37	4.71	79.11
0:100	-	-	481.30	5.37	0.00

HR = heating rate (°C/min); SC = Silantek coal; WP = waste hdpe; TEP = thermal evolution profile
 T_{max} = temperature of maximum weight loss (°C); R = peak height (mg/min); VM % = Volatile matter loss

3.3 Study of Synergistic Effect and Char Deviation

The experimental data of the blends were compared with the calculated data based on the weight percentage of each individual fuel in the blends. The existence of synergistic effect between samples were investigated and became more apparent at higher temperature region above 400°C, as observed in TG curves in Figure 3. During major mass loss decomposition stage, a large gap was observed with

deviation up to 28% with increasing weight ratio of waste HDPE in the blends. This difference can be explained on the basis of the distinctly different degradation behaviour of the individual components. Coal degrades earlier and has wider peak while HDPE with higher volatile matter content degrades rapidly where the degradation was assisted by the hydrogen donored during coal's plastic stage [13].

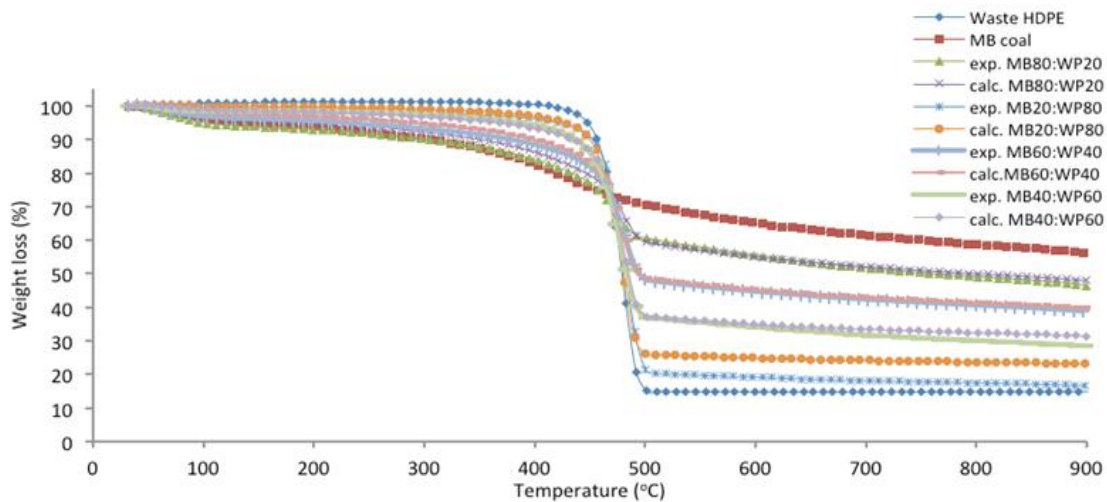


Figure 3 Comparison between experimental and calculated weight loss (%) in TG curves of MB/Waste HDPE (WP) blends

In this study, the possibility of chemical interaction existence was further proven by analysis of char yield deviation. The amount of the solid product remaining after reaching 900 °C was assumed as an indicator of the char yield [14]. Calculated char yield was done according to the assumption of additivity law employed by previous researchers [3,6,13]. Experimental and calculated char yield % in the coal/waste HDPE blends is as represented in Figure 4

with an average deviation of 27.5%. According to Haykiri-Acma and Yaman (2010), medium-low rank coal tends to have greater deviation as compared to higher coal rank [14]. Hydrocarbon species resulted from breakage of bonds during polymer degradation might have taken part in the coal radicals recapping before reaching stabilization.

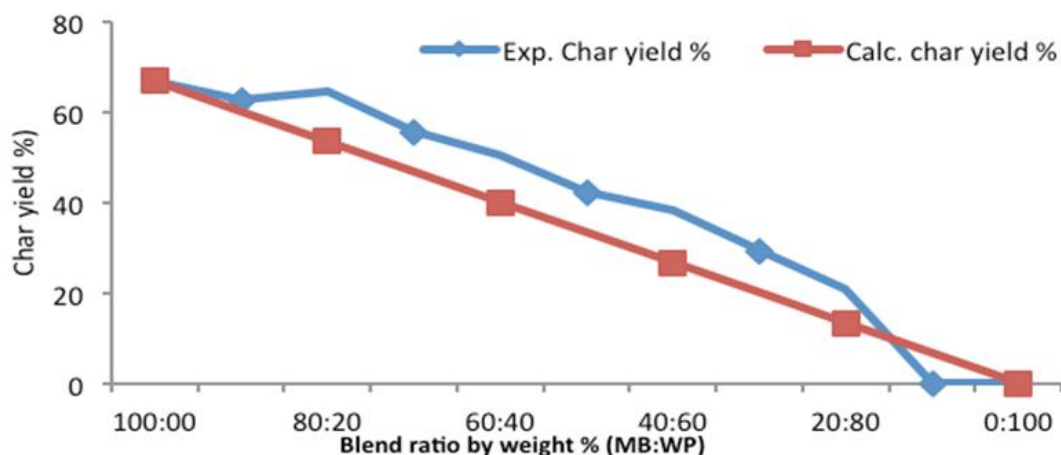


Figure 4 Char yield deviation between experimental and calculated values

4.0 SUMMARY

From this study via thermogravimetric analysis, it can be concluded that waste HDPE showed comparable pyrolysis behaviour during dynamic heating in inert nitrogen atmosphere. The addition of highly volatile HDPE greatly affected the degradation profiles and possible chemical interactions (due to hydrogen and radicals transfer) were evident based on the weight loss analysis of experimental and calculated values and the significant reduction in solid char yield. Although the maximum pyrolysis temperatures (T_{max}) are shifted to higher temperatures, the reactivity of the blends was increased in higher HDPE blend ratio.

Acknowledgement

The authors gratefully acknowledge the financial support received from Education Ministry of Malaysia through Fundamental Research Grant Scheme (FRGS) (600-RMI/FRGS 5/3 (98/2014)), Research Management Institute (RMI) and Faculty of Chemical Engineering, Universiti Teknologi MARA, Malaysia.

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