

Thermogravimetric Investigation of The Behaviour of Malaysian Oil Palm Biomass, Sub-Bituminous Coal And Their Blends During Pyrolysis

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ABSTRACT: An experimental study on co-pyrolysis of Malaysian palm biomass (mesocarp fibre and empty fruit bunches (EFB)) and Senakin bituminous coal was performed in a Thermogravimetry Analyser. All the tests were carried out in nitrogen atmosphere under dynamic conditions at heating rates of 20, 40, and 60°C/min. The operation temperature was in a range of 25 – 900 °C, and the biomass to coal blend was in a weight ratios of 80:20 and 50:50. The thermal events of EFB and mesocarp fibre show one thermal event only. The thermal events correspond to the disintegration of hemicellulose. Pyrolysis of coal/EFB and coal/palm fibre blends generates a bimodal derivative thermogravimetry (TG) curve. The thermal events of coal/palm fibre and coal/EFB blends during pyrolysis, however, showed the domination of the biomass pyrolysis at lower temperature, with the coal pyrolysis (i.e. volatile matter released) occurred at much higher temperature. Apparently, no interactions were seen between the coal and biomass indicating a general lack of synergistic effects. As such, the yield of the major pyrolysis products is linearly proportional to the weight ratio of biomass and coal in the blend mixture in an additive manner at a constant heating rate. Likewise, an increased in the coal reactivity was observed with increasing heating rates as the coal ratio increases in the blends. First order equations were used to determine the biomass and coal component thermal decomposition kinetics. The results showed that for 50:50 wt% blends, with respect to the coal volatile matter released, revealed the lowest activation energies of 118.6 and 112.6 kJ/mol for coal/EFB and coal/mesocarp fibre blends, respectively. These findings will provide useful data for power generation industries for the development of co-firing.

Keywords: pyrolysis, TGA, oil palm biomass, coal, coal blend

NOMENCLATURE

T _{max}	Maximum peak temperature (°C)
R	Peak height (mg/min)
R _m	Mean reactivity (mg/min°C)
VM	Volatile matter released(%)
H _r	Heating rate at the peak(°C/min)
T	Temperature at the peak (K)
Z	Pre-exponential factor (sec ⁻¹)
E _a	Activation energy (J/mole)
R	Gas constant (8.314 J/mole K)
n	Reaction order (dimensionless)
α	Fraction of decomposition

1. INTRODUCTION

The term biomass energy or bio-energy is referred to the energy produced from the biomass or organic matter such as wood, agriculture waste, animal wastes and etc. The fact that biomass is renewable and could be sustainably developed in the future are amongst the attractive reasons of employing biomass as the major source for renewable energy[1]. Furthermore, it appears to have soundly positive environmental properties resulting in net zero releases of carbon dioxides and very low sulfur content.

In practice, about half of the agricultural residues are utilized for energy generation which contributes 20% of the primary energy demand industries. The role of biomass is presently limited in power development, but opportunities exist for increasing its share. It is estimated that by 2050 biomass could provide nearly 38% of the world's direct fuel use and 17% of the world's electricity [2].

Malaysia is blessed with favourable climate conditions which prevail throughout the year are advantageous for palm oil cultivation. Evidently, it is the world's largest producer and exporter of palm oil, replacing Nigeria as the chief producer since 1971 [3]. Presently, there are more than 2.8 million hectares of land under oil palm cultivation and it is the main contributor to

biomass resources in Malaysia. As of today, approximately 368 palm oil mills operated in the country produced substantial amount of lignocellulosic biomass in the form of mesocarp fibre, empty fruit bunches (EFB) and palm kernel shell. It was estimated that the amount of solid wastes produced could reach 39 million tons by the year 2020.

Even though, there are various researches investigating on the ways of utilising these wastes, there are still a large fraction of the residues abundantly unattended [3].

Combustion of fossil fuels such as coal contributes to CO₂ emission that can cause global warming effect to the environment. Coal-biomass co-combustion is one of the promising short term alternatives for the use of renewable fuels. Besides the advantage of net zero release of CO₂ to the atmosphere, the use of biomass may represent an alternative to the disposal of waste and its exploitation as energy source.

Pyrolysis of coal, biomass and coal/biomass blends are relatively new area of research and several researchers have investigated their pyrolysis and combustion behaviour [4,5,6,7]. Recently, Vamvuka *et al.*, [8] developed a kinetic modelling for the volatile matter released during the pyrolysis of several biomass (i.e. olive kernel, forest and cotton residues) blends with lignite using thermogravimetry (TG). Their findings revealed that the biomass possess higher thermochemical reactivity with shorter devolatilisation times in comparison to the lignite. In another work, Moghtaderi *et al.*, [9] investigated the pyrolytic behaviour of coal/woody biomass (i.e. pine dust) blends over a wide range of heating rates and temperatures using tubular reactors in an attempt to simulate the pulverized fuel boilers [9]. Importantly, they found that the total yield of the major pyrolysis products were linearly proportional to the blending ratio, indicating no synergistic effect between coal and biomass. Likewise, Vuthaluru [10] also reported the same observation during the investigation on the

thermal behaviour during co-pyrolysis of coal/biomass (i.e. wood waste and wheat straw) using thermogravimetry.

The aims of this work were to investigate the thermal behaviour of coal, mesocarp fibre, EFB, coal/mesocarp fibre and coal/EFB blends during pyrolysis process using thermogravimetry. The thermogravimetric technique was chosen to identify the thermal events occurred during pyrolysis and to obtain the kinetic data during the process. The effect of varying heating rates on the reactivity of coal, mesocarp fibre, EFB and their blends will be reported.

2. MATERIALS AND METHODS

2.4 Coal, palm mesocarp fibre and EFB preparation

Senakin sub-bituminous coal and Malaysian oil palm waste (i.e. palm mesocarp fibre and EFB) originated from Kalimantan, Indonesia and Selangor, Malaysia, respectively, were selected in this study. The mesocarp fibre and EFB were open air dried for 2 to 3 days to remove moisture and to ease crushing. Both of these samples were pulverized into powder and were sieved into specific particle size of less than 212 μm . Sieving was accomplished by shaking the ground coal, mesocarp fibre and EFB in a Endecotts Shaker Model EFL2 MK3 for 30 minutes and dried in a vacuum oven set at 80°C overnight and were kept in a tightly screw cap bottle.

2.2 Instrumental Analysis

The elemental analyses and calorific values of the coal, mesocarp fibre and EFB were performed using a Thermo Finnigan Flashed 1112 analyzer and Ika-works C5000 calorimeter, respectively. The ultimate and proximate analyses of the coal, mesocarp fibre and EFB were presented in Table 1. The pyrolysis on the coal, mesocarp fibre, EFB and their blends were performed using

thermogravimetric analyser Metler Toledo/TGA/SDRA51e. The tests were carried out in nitrogen atmosphere, under dynamic conditions at heating rates of 20, 40 and 60°C/min to raise the temperature from room temperature to 900°C. The biomass was added to coal at weight ratios of 0:100, 20:80, 50:50 and 100:0. The sample (20 mg) was weighed directly into ceramic crucible and the temperature was kept isothermal for one minute until steady condition was obtained before ramping to the desired temperature. The experiments were replicated twice to obtain reproducibility.

Table 1: Ultimate and Proximate Analyses of coal, palm mesocarp fibre and EFB

	Coal	Biomass	
	Senakin	EFB	Fibre
Proximate Analysis (wt %)			
Moisture	2	7.4	1
Volatile Matter	29.2	68.7	73.7
Fixed Carbon	54	21.2	22.5
Ash	14.8	2.7	2.8
Ultimate Analysis (daf) (wt%)			
Carbon	70	27.2	33.4
Hydrogen	8.5	4.1	4.2
Nitrogen	2.2	3.8	1.5
Sulphur	0.8	0	0
Oxygen ^a	18.5	64.9	60.9
Calorific Value (MJ/kg)	29.4	9.8	13.9

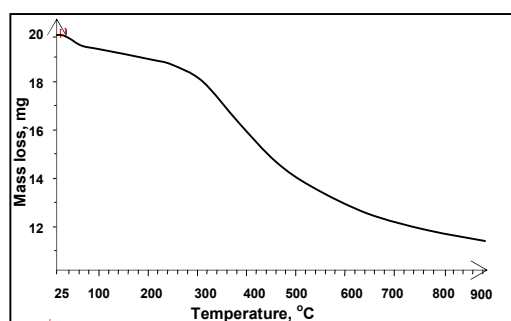
^a calculated by difference
daf – dry ash free basis

3. RESULTS AND DISCUSSION

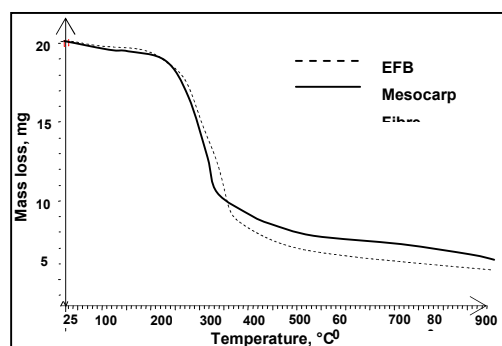
3.1 Thermal Decomposition of Pure Samples.

The TG and DTG curves for the thermal decomposition of mesocarp fibre, EFB and coal during pyrolysis at heating rate of 20°C/min are shown in Figures 1 and 2, respectively. Apparently, in Figure 1, the TG curves for mesocarp fibre, EFB and coal showed an initial decrease in weight at

temperature below 200°C that was due to the release of moisture remaining in the samples. This initial decrease in weight loss corresponds to the first curve in the differential weight loss (DTG) profiles for mesocarp fibre, EFB and coal shown in Figures 2. In this study, this curve was not taken into consideration for the determination of thermal events of mesocarp fibre, EFB and coal. According to Ismail et al.,[4], the thermal events for the decomposition of these materials were defined as the region where the slope of TG curve is constant. Apparently, both oil palm biomass samples start to degrade at temperature $\sim 255^\circ\text{C}$ and the weight loss starts promptly after that temperature. No obvious weight loss is observed beyond temperature of 385°C and 405°C for mesocarp fibre and EFB respectively. The main difference between the two biomass fuels is that DTG curve of fibre produce a single peak with a shoulder located on the left unlike EFB with only one peak appears. The lower temperature shoulder in represents the disintegration of hemicellulose present in the fibre and the higher temperature peak corresponds to decomposition of cellulose [11, 5,18]. Likewise, single peak appear in DTG curve of coal also revealed one major thermal event but at a higher temperature range of 380 – 580°C compared to biomass which was attributed to the released of coal volatile matter [4].

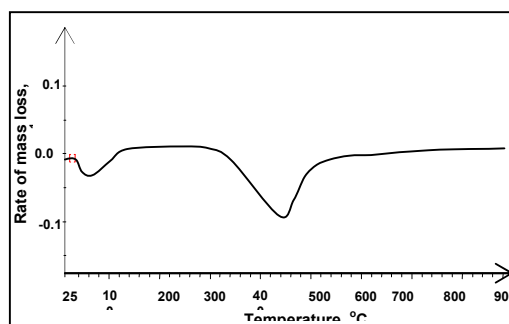


(a)

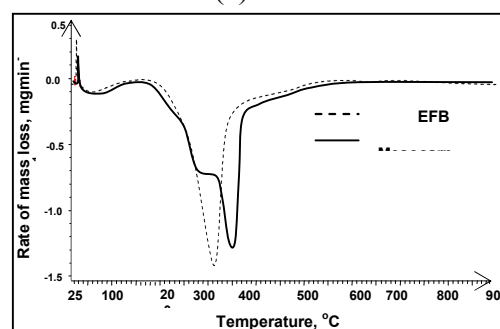


(b)

Figure 1: TG curves of (a) coal, (b) oil palm biomass.



(a)



(b)

Figure 2: DTG curves of (a) coal, (b) oil palm biomass.

Based on the method described previously [12], it was deduced that the DTG peak height, R and maximum peak temperature, $T_{\max}$ is directly and inversely proportional to the reactivity, respectively. Hence, from the DTG profiles of mesocarp fibre, EFB and coal decompositions, it appears that the volatile matter released of the former occurred at lower peak

temperature with higher peak height indicating the high reactivity of the biomass materials in comparison to coal during pyrolysis condition.

3.2 Thermal Decomposition of Coal/Mesocarp Fibre and Coal/EFB Blends.

Figure 3 shows the typical DTG profiles for the thermal decomposition of 50:50 coal/mesocarp fibre and coal/EFB blends during co-pyrolysis condition at 20°C/min heating rate. The DTG profiles revealed two thermal events. The first thermal event correspond to the volatile matter released from degradation of hemicellulose and cellulose in the mesocarp fibre and EFB, with the second event being assigned to the volatile matter released from decomposition of coal that occurred at higher temperature regime. Table 2 shows the reactivity of coal, mesocarp fibre, EFB and their blends. From Table 2, it was observed that the DTG peak height (R) for the first thermal event decreased with increasing in the percentage of the coal in the blends. These observations indicated that the reactivity for the volatile matter released from degradation of cellulosic materials of the blends was slightly reduced by the presence of coal. Similarly, the second thermal event for the volatile matter released from coal decomposition in the blends showed a slight decreased in peak height with increasing in the percent of coal in the blends. Thus, it seems that the amount of volatile matter released from the mesocarp fibre, EFB and coal is directly proportional to the percent of respective fuels that presence in the blends, indicating lack of interaction between the three fuels during pyrolysis. The results agree reasonably well with those of slightly similar studies [4].

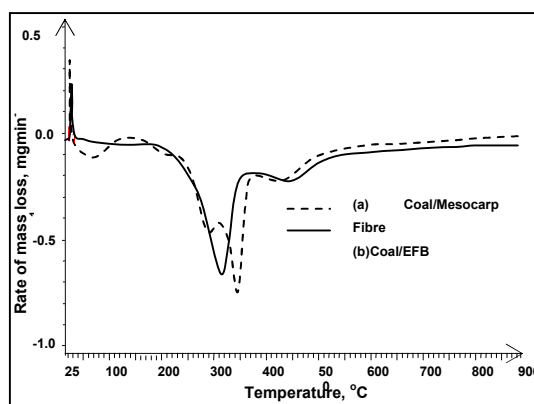


Figure 3: Thermal events for 50:50 wt% of (a) coal and mesocarp fibre and (b) coal and EFB blends at 20°C/min.

Table 2: The reactivity of coal, palm mesocarp fibre, EFB and their blends

Hr	Blend Bio:SC	EFB					
		Event 1		Event 2		Rm	VM
		Tmax	R	Tmax	R		
20	0:100			319.6	0.6	0.2	29.0
	20:80	319.9	0.8	354.4	0.8	0.5	41.1
	50:50	320.6	1.3	361.1	1.3	0.8	56.1
	100:0	380.2	5.2			1.4	68.7
40	0:100			342.0	0.8	0.2	26.3
	20:80	331.5	1.5	367.5	0.9	0.7	40.8
	50:50	334.6	2.0	368.2	1.5	1.0	55.3
	100:0	388.0	6.6			1.7	63.3
60	0:100			363.1	1.1	0.3	22.9
	20:80	337.6	2.3	378.6	1.4	1.1	36.7
	50:50	339.8	2.3	381.2	2.5	1.3	49.5
	100:0	402.5	8.2			2.0	62.6

Hr	Blend Bio:SC	Palm Mesocarp Firbe					
		Event 1		Event 2		Rm	VM
		Tmax	R	Tmax	R		
20	0:100			319.6	0.6	0.2	29.0
	20:80	332.8	1.3	357.3	0.9	0.6	58.2
	50:50	336.6	1.9	383.1	1.4	0.9	63.8
	100:0	397.5	6.3			1.6	73.7
40	0:100			342.0	0.8	0.2	26.3
	20:80	347.0	1.5	365.3	1.2	0.8	57.3
	50:50	350.4	2.6	370.5	1.6	1.2	60.2
	100:0	408.4	7.6			1.9	71.2
60	0:100			363.1	1.1	0.3	22.9
	20:80	329.6	1.8	380.3	1.8	1.0	56.2
	50:50	358.2	2.8	381.8	2.1	1.3	58.5
	100:0	420.6	8.7			2.1	71.0

SC Senakin coal;
Bio Biomass materials

Evidently, T_{max} , R and R_m for the first and second thermal events increased with increasing heating rates (i.e. 20, 40 and 60°C/min) during pyrolysis of coal, mesocarp fibre, EFB and its blend, indicating an increased reactivity with increasing heating rates. However, the amount of percent volatile matter released (VM) differs between the three fuels. Mesocarp fibre generates the highest volatile yields in comparison to that of EFB and coal regardless of heating rates and followed those of the parent fuels in an additive behaviour. Further, as the heating rate increased from 20 to 60°C/min, T_{max} and R of the thermal events gradually increased and approached to a similar value to that of pure samples. Again, this indicates that the pyrolytic behaviour of the blends followed those of the parent fuels in an additive behaviour. On the other hand, the total volatile matter released presents a decreasing trend as the heating rate increases and T_{max} shifts toward higher temperature at a higher heating rate. This behaviour can be explained on the basis of heat transfer and medium diffusion. Since the pyrolysis experiment at higher heating rate has a shorter reaction time (in the same temperature region), the evolution is shifted toward higher temperature. The same observation was also been reported by Zhang *et. al.* on pyrolysis of pulverized China coal [14]. Thus, under pyrolysis condition, the three fuels seem to undergo independent thermal degradation process without any chemical interaction in the solid phase.

3.3 Blending Effect on Activation Energy

The kinetics of thermal decomposition reactions of carbonaceous materials is complex involving a large number of reactions in parallel and in series. The data obtained from TGA besides providing general information on the overall reaction kinetics, could also be used as a tool for providing comparison of kinetic data of

various reaction parameters such as temperature and heating rate. Moreover, only a single sample and considerably fewer data are needed to obtain kinetics behaviour over entire temperature range in a continuous manner. In this work, temperatures at different heating rates were used to obtain the kinetic parameters of coal, mesocarp fibre, EFB and their blends during pyrolysis and co-pyrolysis conditions. The dynamic heating rate from TGA provides one of the high-resolution approach by which both the heating rate and rate of weight loss continuously vary during decomposition. The decomposition kinetics obtained from dynamic heating rate TGA experiments using a derivation of the Arrhenius equation first published by Seferis and Salin [17] and the equation is as follows.

$$\left(\frac{d\alpha}{dt}\right) = Z \exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \dots\dots(1)$$

By applying a second derivative and natural log to the Arrhenius equation against temperature produced equation (2):

$$\ln\left(\frac{H_r}{T^2}\right) = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln\left(\frac{ZR}{E_a} n(1-\alpha)^{n-1}\right) \dots\dots(2)$$

Assuming:

α is constant

dH_r/dT is zero at the peak maximum

$d(d\alpha/dT) / dT$ is zero.

Hence, the activation energy can be determined directly by plotting in $\ln(H_r/T^2)$ versus $1/T$ provides a straight line with an intercept of $\ln(ZR/E_a)$ and slope of (E_a/R) , thus enabling determination of activation energy (E_a).

The kinetic parameters obtained from the pyrolysis and co-pyrolysis of mesocarp fibre, EFB, coal and its blend are summarised in Table 3. Obviously, the activation energies decreased with increasing percentage of biomass in the blends for the first thermal event (i.e. degradation of hemicellulose and

cellulose) with minimum values of 109.6 and 96 kJ/mol of coal/EFB and coal/mesocarp fibre, respectively, being achieved with 50 wt% of mesocarp fibre and EFB. Similarly, the activation energy of the reaction for the second thermal event (i.e. decomposition of coal) in the blend is at minimum value of 112.6 and 118.6 kJ/mol, respectively, being achieved with 50 wt% of coal. The activation energy for the pyrolysis of coal alone was higher by 120 kJ/mol of energy with comparison to the 50 wt% coal/mesocarp fibre and coal/EFB blend. This implies that to ensure less energy required for decomposition of coal during co-pyrolysis condition, a 50 wt% of coal/mesocarp fibre and coal/EFB content are recommended in the blend.

Table 3: The activation energy, E_a of coal, palm mesocarp fibre, EFB and their blends.

Feeds	Blend ratios	E_a (kJ/mol)	
		Event 1	Event 2
Senakin Coal	100	-	231.8
EFB	100	158.2	-
Palm Mesocarp Fibre	100	140.1	-
Coal/EFB	80:20	115.9	144.9
	50:50	109.6	118.6
Coal/Mesocarp Fibre	80:20	124.1	124.7
	50:50	96	112.6

4. CONCLUSIONS

Thermogravimetric studies showed that the thermal degradation of the mesocarp fibre and EFB occurred at lower temperature as comparison to the coal sample. Shorter devolatilisation time is needed for the mesocarp fibre and EFB to decompose during pyrolysis. Obviously, lacks of interaction were seen between coal, mesocarp fibre and EFB in solid phase. The mesocarp fibre and EFB are more reactive than coal in most cases. The presence of the mesocarp fibre and EFB in the blends enhanced the reactivity of the coal. Two thermal events were observed in the blended

fuels, whereby first thermal event was dominated by the decomposition of hemicellulose and cellulose materials and second thermal event was contributed by decomposition of coal. The 50:50 blend, with respect to the coal volatile matter released showed the lowest activation energy for both coal/mesocarp fibre and coal/EFB blend and again revealed that the presence of the mesocarp fibre and EFB conducive to the reduction of activation energy of coal.

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