PYROLYSIS CHARACTERISTICS AND KINETICS OF OIL PALM BIOMASS: A PATHWAY TO PRODUCING ENGINEERED BIOCHAR

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ABSTRACT

Biochar produced from oil palm biomass has been demonstrated to be effectively utilized in energy, soil amendment, wastewater treatment, catalyst and composting applications. However, the industrial development of biochar plants for specific biomass requires an adequate description of the pyrolysis process of the feedstock. Knowledge of biomass devolatilization characteristics and kinetics may describe the pyrolysis process adequately, which would be needed for the proper industrial process design and optimization. Therefore, in this review, the thermal degradation characteristics and pyrolysis kinetics of oil palm biomass residues are discussed to reveal important influential factors and pyrolysis reaction mechanisms. The findings from the literature indicate that the main devolatilization temperature range and the overall reactivity are 352 to 380 °C and 0.360 mg min⁻¹ °C⁻¹ for kernel shell, 336 to 360 °C and 0.270 mg min⁻¹ °C⁻¹ for mesocarp fiber, and 329 to 356 °C and 0.530 mg min⁻¹ °C⁻¹ for empty fruit bunch. The kinetic parameters for the consecutive reactions model suggest that the ease to commence pyrolysis reaction was in the following order: frond < kernel shell < mesocarp fiber < empty fruit bunch. The percentage biochar yield for the residues was higher than 23 wt.% under slow pyrolysis conditions and the tendency of obtaining high biochar yield followed this order: kernel shell > mesocarp fiber > empty fruit bunch > trunk > frond. The tendency for high biochar yield could be attributed to the proportion of lignin content which slowly decomposes over a wide temperature range. The treatment temperatures of 400, 500, and 600 °C are adequate to carbonize the oil palm biomass residues for producing biochars suitable for use as biofuels, activated carbon, and reducing agent, respectively.

KEYWORDS: Oil palm biomass, pyrolysis, devolatilization rates, activation energy, reaction mechanism.

1. INTRODUCTION

Carbon-rich materials are among the highly utilized materials in our daily lives owing to their several applications. Coal and petroleum have been the most important resources of carbon-rich materials, however, exploiting them continuously is a matter of concern because of the short depletion time of their reserve and the negative environmental impacts of their by-products (Shafiee and Topal, 2009). To address these concerns, the need to utilize other alternative

resources that are renewable, abundant and friendly to the environment becomes necessary. One of such alternatives is biomass, which has garnered interest in scientific and industrial spheres for several decades (di Blasi, 2008; Diyanilla *et al.*, 2020). During the past few decades, the conversion of biomass using pyrolysis has witnessed significant research efforts as a result of its ability to produce biochar, a carbon-rich material, with diverse properties appropriate for effective use in numerous applications (Nanda *et al.*, 2016), which include, but not limited to, wastewater treatment and water purification (Dawood *et al.*, 2017), composting (Awasthi *et al.*, 2017), gas pollution control (Chen *et al.*, 2017), and remediation and revitalization of soil (Liu *et al.*, 2020).

Taking advantage of its widespread availability and high carbon content, oil palm biomass (OPB) could be an important feedstock for biochar production plants. In the year 2014, about 95.4 million metric tons of OPB residues were generated in Malaysia alone (Onoja et al., 2019). The biomass consists of the trunk (OPT), frond (OPF), empty fruit bunch (EFB), mesocarp fibre (MF) and kernel shell (PKS). Most of these biomass residues are being commercially utilized for several purposes including livestock feed (Sharmila et al., 2014), biocomposite (Yasim-Anuar et al., 2019), raw material for paper and pulp production (Singh et al., 2013), organic fertilizers (Hayawin et al., 2016) and briquettes (Onoja et al., 2019). In addition to these products, biochar can be produced from OPB and used for several applications (Sulaiman et al., 2011). In this respect, several investigations have been carried out and their findings demonstrate the ease of converting OPB to biochar using the pyrolysis technique. Pyrolysis is the thermal decomposition of carbon-bearing material in an oxygen-limited environment. Pyrolysis is the common and easiest technique for producing biochar and the analytical procedure employed by researchers for investigating the chemical and physical properties of biochar and the thermal behaviour of biomass (Bach and Chen, 2017; Chen et al., 2015a; Dawood et al., 2017; Keiluweit et al., 2010; Li et al., 2014).

Despite being an important feedstock for producing biochar, an adequate description of the pyrolysis process of OPB residues is required for successful biochar production on an industrial scale. In addition, the wide compositional variation among OPB residues related to lignocellulosic and mineral contents makes it necessary to obtain sufficient information on their thermal decomposition characteristics and pyrolysis kinetics for optimum production process design and plant development. Therefore, in this review, the thermal degradation characteristics and pyrolysis kinetics of OPB residues are discussed to reveal important influential factors and pyrolysis reaction mechanisms. To achieve this objective, the characteristics of OPB residues were introduced; analysis, evaluation and comparison of thermal degradation parameters, pyrolysis kinetics and mechanism are established by summarizing, synthesizing and evaluating thermogravimetric (TG) data extracted from published studies. TG data analysis is among the common techniques used to characterize the thermal process, describe the decomposition behaviour and determine kinetics parameters.

2. COMPOSITIONAL CHARACTERIZATION OF OIL PALM BIOMASS RESIDUES

Biomass of oil palm origin is typically found in tropical regions as residues generated in oil palm mills and plantations. The estimated global generation of the residues was reported to be around 184.6 Mt/year on dry weight bases (Kelly-Yong *et al.*, 2007), whereas in Malaysia alone the quantity generated increased from 55.7 Mt in 2005 to 82.0 Mt in 2015 and 100 Mt was estimated

by 2020 (Akhlisah *et al.*, 2021; Shuit *et al.*, 2009). The quantities of OPT, OPF, EFB, MF and PKS generated per annum in Malaysia are presented in Figure 1. The cellular structure of these vegetative components differs due to variations in their biological function, which invariably determines the lignocellulosic and mineral content of each residue. For instance, the percentage content of cellulose, hemicellulose, lignin and extractives reported in the literature varies from 20.5 to 49.1%, 9.8 to 36.6%, 18.1 to 51.5%, and 1.7 to 8.6%, respectively (Table 1). Carbohydrates, proteins and lipids are other biochemical components that are also present in trace amounts in the residues. The content of carbon varies between 43 and 51%, and those of hydrogen, oxygen and nitrogen vary between 5 and 7%, 38 and 41%, and 3 and 10%, respectively (Liew *et al.*, 2018). The mineral contents are low compared to many agricultural crop residues and municipal solid wastes (Kong *et al.*, 2014; Ordoñez-Frías *et al.*, 2020).



Figure 1: Availability of Oil Palm Biomass Residues in Malaysia. Source (NBS, 2013; Shuit et al., 2009).

Oil palm	Lignocellulosi	ic composition (%)		Extractives	Ash	Reference
biomass	-			(%)	(%)	
	Cellulose	Hemicellulose	Lignin			
PKS	33.2	18.2	48.7	_	_	(Sabil et al., 2013)
PKS	27.7	21.7	44.0	_	_	(Rugayah et al., 2014)
PKS	20.5	22.3	51.5	4.7	1	(Saka et al., 2008)
MF	25.4	21.2	24.6	_	_	(Zakaria et al., 2015)
MF	44.0	23.0	32.9	_	_	(Sabil et al., 2013)
MF	39.2	9.8	32.9	8.6	9.3	(Saka <i>et al.</i> , 2008)
EFB	48.0	25.1	19.9	_	2.5	(Abdul Rahman et al.,
						2012)
EFB	49.1	24.5	26.5	_	_	(Sabil et al., 2013)
EFB	28.3	36.6	35.1	_	_	(Palamae et al., 2017)
EFB	33.3	23.2	25.8	_	_	(Barlianti et al., 2015)
EFB	37.9	35.0	24.0	2.7	1.5	(Saka et al., 2008)
OPF	48.4	23.1	18.1	_	0.5	(Abdul Rahman et al.,
						2012)
OPF	39.5	29.8	23.3	1.7	5.7	(Saka <i>et al.</i> , 2008)
OPT	44.4	29.3	21.2	_	1.5	(Abdul Rahman et al.,
						2012)
OPT	38.9	23.8	2.4	_	_	(Saka et al., 2008)
OPT	30.6	33.2	28.5	3.6	4.1	(Abdul Rahman <i>et al.</i> , 2012)

Table 1. List of Lignocellulosic Composition, Extractive and Ash of Oil Palm Biomass Residues

3. PYROLYSIS OF OIL PALM BIOMASS RESIDUES

3.1 Production of Biochar

The lignocellulosic components of biomass decompose into char, condensable (bio-oil) and noncondensable gasses in an inert and high-temperature environment, a process referred to as pyrolysis (Wang *et al.*, 2017). Generally, the percentage yield for each product correlates with the pyrolysis conditions and reactor type (Bach and Chen, 2017). Reports in the literature indicate that biochar can be produced from OPB via several pyrolysis modes namely: fast pyrolysis, slow pyrolysis, microwave pyrolysis, catalytic pyrolysis and self-sustained carbonization (Table 2). The classification is based on operating conditions and has been employed in either lab- or pilot-scale reactors. The slow and microwave modes are commonly carried out in a fixed-bed reactor while a fluidized-bed reactor typically handles fast pyrolysis. Both fixed-bed and fluidized-bed reactors are common for catalytic pyrolysis.

Based on the reports of previous studies (Table 2), the yield of biochar from OPB produced using slow pyrolysis mode at 500 °C varies from 26.4 to 40.6 wt.%, where PKS and OPF had the highest and lowest percentage biochar yield, respectively. The range for the biochar yields is observed to be slightly lower (24.5 to 37.8 wt.%) under fast pyrolysis conditions. Under catalytic effect, biochar yield is significantly reduced to 12.4 wt.% for PKS (Kim *et al.*, 2014a). Microwave pyrolysis is capable of yielding a high amount of biochar similar to slow pyrolysis. Overall, biochar yields from OPB are dependent on the mode of pyrolysis: slow pyrolysis and microwave pyrolysis favour high biochar yield, whereas fast pyrolysis and catalytic pyrolysis produce more bio-oil and non-condensable gasses than biochar.

3.2 Thermal Degradation Characteristics

Adequate knowledge of biomass thermal behaviour and pyrolytic kinetics is critical for understanding its thermal stability, conversion and product formation (Bach and Chen, 2017). The thermal degradation characteristics of several biomass materials are typically examined under pyrolytic conditions using TG analysis. The pyrolytic characteristics of OPB have been investigated by examining the critical role played by the thermal degradation of their lignocellulosic components: cellulose, hemicellulose, and lignin. The TG and derivative thermogravimetric (DTG) curves represent the thermal behaviour of biomass during thermal treatment. Several parameters obtained from TG and DTG curves related to temperature, devolatilization rates and mass fractions are used to quantify the thermal degradation characteristics of biomass materials. To find out the degradation parameters of OPB residues, the TG and DTG parameters reported in the literature are summarized in Table 3. Similar to the thermal degradation of most lignocellulosic-based biomass, the pyrolytic thermal degradation of OPB residues could be divided into three sequential reactive zones viz: moisture drying, pyrolysis, and carbonization (Idris *et al.*, 2010; Khor *et al.*, 2010; Lee *et al.*, 2017; Liew *et al.*, 2018).

OPB	Particle	Pyrolysis	Reactor		Operating co	nditions		Yield (wt.	%)	Reference
residue	size (mm)	Mode		Temperature (°C)	Heating rate (°C min ⁻¹)	Residence time (min)	Purge gas flow rate (cm ³ min ⁻¹)	Biochar	Bio- oil	-
PKS	1–2	Slow	Fixed-bed	500	10	60	2000	35.3	47.4	(Abnisa et al., 2013)
PKS	_	Slow	Fixed-bed	500	10	120	150	40.6	_	(Lua et al., 2006)
PKS	1–2	Slow	Fixed-bed	450	10	30	150	38.9	_	(Lua and Guo, 1998)
PKS	0.5–2	Slow	Fixed-bed	500	10	60	50	37.1	_	(Lee et al., 2017)
EFB	0.5–2	Slow	Fixed-bed	500	10	60	50	35.1	_	(Lee et al., 2017)
EFB	2-4	Slow	Fixed-bed	600	30	15	30	35.5	29.6	(Yakub et al., 2015)
EFB	0.106	Slow	fixed bed	400	30	10	1500	25.0	36.0	(Sukiran et al., 2009)
EFB	1–2 0.125–	Slow	Fixed-bed	500	10	60	2000	29.1	45.8	(Abnisa <i>et al.</i> , 2013)
MF	0.25	Slow	Fixed-bed	400	10	15	200	33.0	47.0	(Kabir et al., 2017)
MF	_	Slow	Fixed-bed	500	10	60	_	33.1	38.9	(Hooi et al., 2009)
MF	_ 0.063_	Slow	Fixed-bed	400	10	60	2000	44.8	34.7	(Safana <i>et al.</i> , 2018) (Khanday and
MF	0.5	Slow	Fixed-bed	550	10	10	200	34.0	38.0	Hameed, 2016)
MF	1–2	Slow	Fixed-bed	500	10	60	2000	29.8	43.9	(Abnisa et al., 2013)
OPT	2–4	Slow	Fixed-bed	600	30	15	30	29.7	34.3	(Yakub et al., 2015)
OPT	2	Slow	Fixed-bed	600		120	_	30.0	_	(Deris et al., 2006)
OPT	1–2	Slow	Fixed-bed	500	10	60	2000	33.6	40.9	(Abnisa et al., 2013)
OPF	1–2	Slow	Fixed-bed	500	10	60	2000	30.2	43.5	(Abnisa et al., 2013)
OPF	2–4	Slow	Fixed-bed	600	30	15	30	29.4	34.2	(Yakub et al., 2015)
OPF	0.6 0.125–	Slow	Fixed-bed	500	40	_	50	26.4	21.4	(Isa <i>et al.</i> , 2016)
OPF	0.25	Slow	Fixed-bed Fluidized-	400	10	15	200	27.0	49.0	(Kabir <i>et al.</i> , 2017) (Asadullah <i>et al.</i> .
PKS	1–2	Fast	bed	500	_	_	_	32.0	51.0	2013)

Table 2: List of Literature of Oil Palm Biomass Pyrolysis

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OPB	Particle	Pyrolysis Reac	tor		conditions		Yield (wt.	%)	Reference	
residue	size (mm)	mode		Temperature (°C)	Heating ra (°C min ⁻¹)	te Residence time (min)	Purge gas flow rate (cm ³ min ⁻¹)	Biochar	Bio- oil	_
PKS	0.125–1.4	Fast	Fluidized -bed Fluidized	485	_	3.8 (s)	2950	30.2	32.1	(Kim <i>et al.</i> , 2014b) (Kim <i>et al.</i> ,
PKS	-	Fast	-bed Fluidized	478	_	3.8 (s)	_	23.2	30.3	$\begin{array}{ccc} (1111) & (111) \\ 2013) \\ (Kim & et & al., \end{array}$
EFB	_	Fast	-bed Fluidized	478	_	3.8 (s)	_	28.9	36.6	2013) (Sulaiman and
EFB	0.3–0.355	Fast	-bed Fluidized	500	_	1.32 (s)	3500	25.9	50.2	Abdullah, 2011) (Abdullah <i>et al.</i> ,
EFB	0.355-0.6	Fast	-bed Fluidized	500	_	1.1 (s)	-	24.5	_	2011) (Rinaldi <i>et al.</i> ,
OPF	< 0.07	Fast	-bed Fixed-	500 - 600	_	2 - 5 (s)	_	35.8	35.4	2017) (Liew <i>et al.</i> ,
PKS	1–2	Microwave	bed Fixed-	500 W 405	_	25	_	38.0	_	2018) (Nam <i>et al.,</i>
PKS	_	Microwave	bed Fixed-	(750 W)	_	30	vacuum	28.0	_	2018) (Salema and
PKS	_	Microwave	bed Fixed-	450 W - 500	_	25	20000	47.0	25.0	Ani, 2011) (Abubakar and
PKS	_	Microwave	bed Fixed-	(450 W) 500	_	_	_	34.0	28.0	Ani, 2013)
PKS	_	Microwave	bed Fixed-	(800 W) 500	_	_	_	39.2	38.0	(Ho <i>et al.</i> , 2018)
EFB	_	Microwave	bed Fixed-	(800W) 500	_	_	_	32.0	36.0	(Ho <i>et al.</i> , 2018)
MF	_	Microwave	bed Fixed-	(800 W)	_	_	_	29.0	37.0	(Ho <i>et al.</i> , 2018) (Salema and
MF	0.3–0.6	Microwave	bed Fixed-	450 W 500	_	25	20000	50.0	22.0	Ani, 2011) (Hossain <i>et al.</i> ,
MF	_ 1.18_3	Microwave Catalytic	bed	(500 W)	_	_	-	27.2	17.4	2017)
PKS		(Na ₂ CO ₃) microwave	Fixed- bed	600 W	_	_	4000	30.1	31.0	(Mushtaq <i>et al.</i> , 2014)
PKS	0.125–1.4	Catalytic (zsm- 5) fast	Fluidized -bed	485	_	3.8 (s)	2950	12.4	42.9	$\begin{array}{llllllllllllllllllllllllllllllllllll$

PKS	0.125–1.4	Catalytic (Ecat) fast	Fluidized -bed	485	_	3.8 (s)	2950	30.1	33.5	(Kim <i>et al.</i> , 2014b)
	0.063-0.5	Catalytic	Fixed-							(Khanday and
MF		(OPAZ)	bed	550	10	10	200	35.0	38.0	Hameed, 2016)
EFB	30–99	Self-sustained carbonization	Fixed- bed	417 - 590	_	900–1900	_	16.3	_	(Idris <i>et al.,</i> 2015)

Table 3. Pyrolytic TG and DTG Characteristic Parameters of Oil Palm Biomass

OPB	TGA conditions	Weight	Thermal degradation zones										Reference
residue		Loss (%)	Moi drying	sture				Pyrolysis			ca	rbonization	
			• 0		First	region		Second	l region				
			Temp. range (°C)	T _{peak1} (°C)	Tonset (°C)	T _{peak2} (°C)	Y _{peak2} (mg min ⁻¹)	T _{peak3} (°C)	Y _{peak3} (mg min ⁻¹)	T _{offset} (°C)	T _{peak4} (°C)	Y _{peak4} (mg min ⁻¹)	-
PKS	10 °C min ⁻¹ , 900 °C, 20 mg, <0.212 mm	_	30 – 150	_	200	282	0.390	352	0.760	_	704	0.180	(Idris <i>et al.,</i> 2010)
PKS	10 °C min ⁻¹ , 900 °C, 1–2 mm, 25 mL min ⁻¹	~ 78	90 – 150	110	~ 200	_	-	_	_	430	_	_	(Liew <i>et al.</i> , 2018)
PKS	10 °C min ⁻¹ , 900 °C, 15 mg, 0.5–2 mm, 50 cm ³ min ⁻¹	~ 75	$\begin{array}{c} 30 \\ 200 \end{array} -$	120	_	282	_	356	_	_	_	_	(Lee <i>et al.,</i> 2017)
PKS	15 °C min ⁻¹ , 850 °C, 5 mg, < 0.3 mm, 150 mL min ⁻¹	~ 69	< 150	61	_	300	0.395*	364	0.535*	_	700	0.148*	(Asadieraghi and Wan Daud, 2015)
PKS	20 °C min ⁻¹ , 900 °C, 10 mg, 50 mL min ⁻¹	~ 64	< 170	_	_	274	_	354	_	_	_	_	(Ninduangdee and Kuprianov, 2013)
PKS	10 °C min ⁻¹ , 550 °C, 8 mg, 0.21 mm	~ 68	_	119	_	280	0.362	358	0.470	_	_	_	(Surahmanto et al., 2017)

PKS	20 °C min ⁻¹ , 700 °C 10 mg, 0.3 mm, 100 mL min ⁻¹	~ 70	_	_	_	305	0.995	380	1.449	_	_	_	(Luangkiattikh un <i>et al.</i> , 2008)
MF	10 °C min ⁻¹ , 900 °C, 20 mg, <0.212 mm	_	$\begin{array}{rr} 30 & - \\ 150 \end{array}$	_	180	277	0.250	336	0.600	_	_	-	(Idris <i>et al.</i> , 2010)
MF	10 °C min ⁻¹ , 900 °C, 1–2 mm, 25 mL min ⁻¹	~ 78	90 – 150	110	~ 200	_	_	_	_	420	_	_	(Liew <i>et al.</i> , 2018)
MF	15 °C min ⁻¹ , 850 °C, 5 mg, < 0.3 mm, 150 mL min ⁻¹	~ 77	< 150	61	_	301	0.500*	351	0.700*	_	_	_	(Asadieraghi and Wan Daud, 2015)
MF	10 °C min ⁻¹ , 550 °C, 6–8 mg, 100 mL min ⁻¹	~ 78	_	_	_	300	_	360	_	_	_	_	(Nordin <i>et al.,</i> 2013)
MF	5 °C min ⁻¹ , 900 °C, 0.25– 0.33 mm	~ 80	_	_	_	300	_	350	_	_	_	_	(Safana <i>et al.</i> , 2018)
EFB	10 °C min ⁻¹ , 900 °C, 20 mg, <0.212 mm	_	30 – 150	_	200	_	_	301	1.600	_	_	0.180	(Idris <i>et al.,</i> 2010)
EFB	10 °C min ⁻¹ , 900 °C, 1–2 mm, 25 mL min ⁻¹	~ 79	90 – 150	110	~ 200	_	_	_	_	410	_	_	(Liew <i>et al.</i> , 2018)
EFB	10 °C min ⁻¹ , 900 °C, 15 mg, 0.5–2 mm, 50 cm ³ min ⁻¹	~ 87	30 – 200 –	66	_	295	_	356	_	_	_	_	(Lee <i>et al.,</i> 2017)
EFB	15 °C min ⁻¹ , 850 °C, 5 mg, < 0.3 mm, 150 mL min ⁻¹	~ 87	< 150	60	_	_	_	329	0.900*	_	_	_	(Asadieraghi and Wan Daud, 2015)
EFB	10 °C min ⁻¹ , 600 °C, 100 mL min ⁻¹	~ 70	_	_	_	_	_	355	0.255	_	_	_	(Abdullah and Gerhauser, 2008)

Table 3. (cont.)

OPB	TGA conditions	Weight					The	rmal deg	radation zone	S			Reference
residue		Loss (%)	Moi drying	sture				Pyrolysis			ca	rbonization	-
			• •		First 1	region		Second	l region				
			Temp. range (°C)	T _{peak1} (°C)	Tonset (°C)	T _{peak2} (°C)	Y _{peak2} (mg min ⁻¹)	T _{peak3} (°C)	Y _{peak3} (mg min ⁻¹)	Toffset (°C)	T _{peak4} (°C)	Y _{peak4} (mg min ⁻¹)	-
OPT	10 °C min ⁻¹ , 900 °C, 1–2 mm, 25 mL min ⁻	~ 70	90 – 150	110	~ 200	_	_	_	_	430	_	_	(Liew <i>et al.,</i> 2018)
OPF	10 °C min ⁻¹ , 900 °C, 5 mg, 100 mL min ⁻¹	~ 93	_	_	_	279	0.240	341	0.505	_	_	_	(Soon <i>et al.,</i> 2016)
OPF	10 °C min ⁻¹ , 800 °C, 0.38 mm, 10–15 mg	~ 71	50 – 150 –	_	_	_	_	_	_	_	_	_	(Nordin <i>et al.</i> , 2016)
OPF	10 °C min ⁻¹ , 900 °C, 1–2 mm, 25 mL min ⁻¹	_	90 – 150 –	110	~ 200	_	_	_	_	520	_	_	(Liew <i>et al.,</i> 2018)

 T_{peaki} is the temperature at a maximum weight loss rate, Y_{peaki} is the maximum weight loss rate in a reaction zone, T_{onset} is the temperature at the beginning of the reaction, T_{offset} is the temperature at the end of the reaction and * represent unit reported in wt.% °C⁻¹.

The moisture in all the OPB residues evaporated at a lower temperature range from 30 to 150 °C within which the peak drying rate occurred at approximately 110 °C. After the removal of free moisture, the thermal decomposition of the residues commenced at a temperature of ~ 200 °C, except for MF with a slightly lower onset degradation temperature of 180 °C. The lower temperature for MF degradation could be attributed to the high content of extractives which are less thermally stable than the lignocellulosic components (Grønli *et al.*, 2002). During the second reactive zone, the other residues exhibited two characteristic reaction regions except for EFB (Table 3). The first region recognize as a shoulder is considered the stage for the decomposition of hemicellulose. The decomposition of hemicellulose attained a maximum rate of 0.39 mg min^{-1} at 282 °C for PKS, 0.25 mg min⁻¹ at 277 °C for MF and 0.24 mg min⁻¹ at 279 °C for OPF. The main devolatilization comprised the overlap of the continuous decomposition of hemicellulose and commencement of decomposition of cellulose. The peak temperature of the second region for PKS varied within a higher temperature range from 352 to 380 °C depending on the sample and TGA conditions, while the peak values for MF and EFB occur at slightly lower temperature ranges from 336 to 360 °C, and 329 to 356 °C, respectively. The individual devolatilization rates at the corresponding second peak temperature revealed that OPF decomposing at $0.505 \text{ mg min}^{-1}$ is less reactive compared to MF (0.600 mg min⁻¹), PKS (0.760 mg min⁻¹) and EFB (1.60 mg min⁻¹) ¹). Likewise, the overall reactivity comprising the two regions can be expressed in the decreasing order of EFB (0.530 mg min⁻¹ °C⁻¹), PKS (0.360 mg min⁻¹ °C⁻¹), and MF (0.270 mg min⁻¹ °C⁻¹) (Idris *et al.*, 2010). It is worth noting that a very low overall reactivity value of 0.234 mg min⁻¹ for OPF was calculated from the degradation rate results reported by Soon et al. (2016).

The offset temperatures of 430, 420, 410, 430 and 520 °C mark the end of the second reactive zone and the beginning of the third reactive zone for PKS, MF, EFB, OPT, and OPF, respectively (Liew *et al.*, 2018). Meanwhile, the absence of a peak in the third reactive zone for the residues is due to the low decomposition rate of lignin which started at the initial stage of the second reactive zone and ended at around 700 °C. Although Idris *et al.* (2010) and Asadieraghi and Daud (2015) reported a peak at 700 and 704 °C, respectively for PKS, they indicated that it was not a decomposing activity of a lignocellulosic component but rather a decomposing activity of mineral carbonates. In summary, the thermal decomposition of the OPB residues ends at a temperature below 600 °C and if carbonized at 850 or 900 °C, the approximate weight loss is reported to be around 64 to 92 %. The weight loss reported for PKS reveals that it is relatively the most thermally stable residue. As for both OPT and OPF, there is limited information in the literature to support the quantitative description of their thermal behaviours.

3.3 *Pyrolysis Kinetics*

Pyrolysis kinetics is crucial for describing biomass conversion behaviours and the rate of its thermochemical process. Pyrolysis kinetics is commonly expressed using the Arrhenius law, which comprises the activation energy, frequency factor, and reaction order. Both rate expressions for the isothermal and non-isothermal conditions were mathematically derived and can be found in reputable studies (Bach *et al.*, 2015; Chew *et al.*, 2016; Guo and Lua, 2000, Guo and Lua, 2001; Mohd Din *et al.*, 2005; Plis *et al.*, 2017). During pyrolysis, the lignocellulosic components of biomass decompose into numerous intermediates and final products through thermochemical reactions that occur sequentially and/or simultaneously. Consequently, pyrolysis kinetic models were proposed based on the assumptions and were successfully applied to OPB residues. A list of studies for TG pyrolysis including the types of models and kinetic parameters

are summarized in Table 4. The one-step global model or single reaction model assumes that all lignocellulosic components have similar thermal reactivity, consequently, information about their reaction mechanisms is limited and only approximate values for activation energy and frequency factor can be obtained using the first-order reaction model from DTG data (Bach and Chen, 2017; Guo and Lua, 2001; Hameed *et al.*, 2019). The two-step consecutive reactions model assumes that the main components of biomass transform into biochar and volatile products via intermediates. Based on the assumption of the two-step consecutive reaction model, the collection of the pyrolytic rates of converting the individual lignocellulosic components into intermediate products forms the primary pyrolysis rate, while converting intermediates to char constitutes the secondary pyrolysis rate (Guo and Lua, 2001; Luangkiattikhun *et al.*, 2008). The model for the parallel reaction (Table 4) has been tested on PKS and MF based on the assumption that these residues consist of cellulose and hemicellulose and each decomposed simultaneously at different rates and temperatures (Luangkiattikhun *et al.*, 2008).

From Table 4, it can be seen that the activation energy and frequency factor reported for OPB residues appeared to be significantly influenced by the reaction order. The higher the reaction order, the higher the activation energy and frequency factor. For the one-step global reaction model, the activation energy of PKS ranged from 54.8 to 205 kJ mol⁻¹. Evaluation of the TGA conditions revealed that the activation energy of PKS increased as pyrolysis temperature increased. The activation energy of EFB exhibited a similar trend as pyrolysis temperature increased. MF at a pyrolysis temperature of 700 °C has the highest value of activation energy compared to PKS which could be a result of the higher content of extractives in MF that slowly decomposed at a lower energy level (Luangkiattikhun *et al.*, 2008) . At peak pyrolysis temperature of 900 °C, the activation energy value of PKS was the highest, EFB was the medium and OPF was the lowest. The frequency factor for the OPB residues also exhibited a similar trend. Overall, it can be inferred from the one-step reaction model that OPF requires low activation energy to commence and complete pyrolysis while PKS and MF require relatively higher activation energy.

For the consecutive reactions model, the values of activation energies and frequency factors for OPB residues during the primary pyrolysis are lower than the values for secondary pyrolysis irrespective of reaction order. During the first-order reaction, the magnitude of activation energies for the formation of intermediates from the residues are in the following order EFB > MF > PKS > OPF. A similar trend with little difference can also be observed for the activation energies during char formation. According to the kinetic results presented by Soon et al. (2016) and Asadieraghi and Daud (2015), OPF and PKS have similar activation energies but different frequency factors indicating that pyrolytic reaction would be faster for OPF. Yang et al. (2004) examined almost similar values of activation energies for MF and EFB and it can be observed that their values are relatively higher than those for OPF and PKS. Luangkiattikhun et al. (2008) calculated and compared the kinetic parameters for PKS and MF using three different models; one-step global, consecutive reactions and parallel reactions. They found that the experimental data for PKS and MF were best described by the two-parallel reactions model. In conclusion, the kinetic parameters calculated from the consecutive reactions model suggest that the ease to commence pyrolysis reaction is in the following order: OPF < PKS < MF < EFB. However, as the pyrolytic reaction begins, it was observed that the OPF reaction was the fastest while PKS showed the slowest reaction.

OPB	TGA conditions	Kinetic reacti	on	Kinetic par		Reference					
residue			-	E _{A1} (kJ mol ⁻¹)	E _{A2} (kJ mol ⁻¹)	A ₁ (s ⁻¹)	A ₂ (s ⁻¹)		Ν	R ²	-
PKS	10°C, 600°C, 10 mg, 1–2 mm, 50 cm ³ min ⁻¹	single react model	tion	54.8	_	9.78 x 10 ³	-		1.07	0.991	(Guo and Lua, 2001)
PKS	20°C min ⁻¹ , 700°C 10 mg, 0.3 mm, 100 mL min ⁻¹	single react model	tion	109.1	_	2.05 x 10 ⁷	_		2.65	_	(Luangkiattikhun <i>et al.</i> , 2008)
PKS	10°C, 800°C, 3–6 mg,	single react model	tion	199.0	_	1.1 x 10 ¹⁷	_		5.00	0.998	(Khan <i>et al.,</i> 2011)
PKS	10°C min ⁻¹ , 900°C, 15 mg, 0.5–2 mm, 50 cm ³ min ⁻¹	single react model	tion	205.0	_	_	_		_	_	(Lee et al., 2017)
MF	20°C min ⁻¹ , 700°C 10 mg, 0.3 mm, 100 mL min ⁻¹	single react model	tion	125.9	-	1.96 x 10 ⁹	_		3.32	_	(Luangkiattikhun et al., 2008)
EFB	10°C, 800°C, 3–6 mg,	single react model	tion	151.0	_	1.4 x 10 ¹⁵	-		5.30	0.997	(Khan <i>et al.</i> , 2011)
EFB	10°C min ⁻¹ , 900°C, 15 mg, 0.5–2 mm, 50 cm ³ min ⁻¹	single react model	tion	169.4	_	_	-		_	_	(Lee et al., 2017)
OPF	50°C min ⁻¹ , 900°C, 100 mL min ⁻¹	single react model	tion	59.2	_	_	-		-	-	(Atnaw <i>et al.</i> , 2013)
PKS	10°C, 600°C, 10 mg, 1–2 mm, 50 cm ³ min ⁻¹	consecutive reaction mode	1	110.3	168.4	6.85 x 10 ⁷	9.82 10 ¹²	х	1 & 2/3	0.985 & 0.987	(Guo and Lua, 2001)
PKS	10°C min ⁻¹ , 900°C, 20 mg, <0.212 mm	consecutive reaction mode	1	150.0	192.1	$1.16 x 10^{12}$	$1.12 \\ 10^{14}$	X	_	0.998 & 0.999	(Idris <i>et al.,</i> 2010)
PKS	20°C min ⁻¹ , 700°C 10 mg, 0.3 mm, 100 mL min ⁻¹	consecutive reaction mode	1	82.1	299.3	6.99 x 10 ⁴	3.89 10 ²⁴	X	5.24	_	(Luangkiattikhun <i>et al.</i> , 2008)
PKS	10°C min ⁻¹ , 850°C, 1–2 mm	consecutive reaction mode	1	54.0	33.0	1.53 x 10 ⁴	25.3		1.20 & 0.70	0.99 & 0.99	(Mohd Din <i>et al.</i> , 2005)
PKS	15°C min ⁻¹ , 850°C, 5 mg, < 0.3 mm, 150 mL min ⁻¹	consecutive reaction mode	1	34.1	57.3	8.7 x 10 ⁻¹	$2.5 \\ 10^2$	X	1.00	0.994 & 0.996	(Asadieraghi and Daud, 2015)

Table 4. List of Literature of Pyrolysis Kinetic Parameters of Oil Palm Biomass

PKS	PKS 10°C min ⁻¹ , 550°C, 8 mg, consecutive 0.21 mm reaction model		47.6	22.4	2.389 x 10 ³	5.431	1.00	0.929	(Surahmanto <i>et al.</i> , 2017)
Table <u>4. (cont.)</u>	TCA conditions	Vinatia reaction	Vinctia na	nomotons					Doforonao
Orb	I GA conditions	Kinetic reaction	Kinetic pa	rameters					Kelefence
residue			E _{A1} (kJ mol ⁻¹)	E _{A2} (kJ mol ⁻¹)	A ₁ (s ⁻¹)	A ₂ (s ⁻¹)	N	R ²	-
MF	10°C, 600°C, 10 mg, 0.5– 1 mm, 50 cm ³ min ⁻¹	consecutive reaction model	107.6	166.7	6.85 x 10 ⁷	1.86 x 10 ¹³	_	0.982 & 0.987	(Guo and Lua, 2000)
MF	10°C min ⁻¹ , 900°C, 20 mg, <0.212 mm	consecutive reaction model	166.2	216.1	$\begin{array}{ccc} 6.55 & x \\ 10^{13} & \end{array}$	$\begin{array}{ccc} 3.54 & x \\ 10^{16} & \end{array}$	_	0.998 & 0.988	(Idris <i>et al.,</i> 2010)
MF	20°C min ⁻¹ , 700°C 10 mg, 0.3 mm, 100 mL min ⁻¹	consecutive reaction model	71.4	326.3	9.73 x 10 ³	$7.93 ext{ x} 10^{28}$	5.24	_	(Luangkiattikhun et al., 2008)
MF	10°C, 900°C, 25 mg, 0.125–0.15 mm, 40 mL min ⁻¹	consecutive reaction model	51.8	67.7	1.03 x 10 ¹	3.644 x 10 ²	1.00	0.997 & 0.998	(Yang et al., 2004)
MF	15°C min ⁻¹ , 850°C, 5 mg, <0.3 mm, 150 mL min ⁻¹	consecutive reaction model	26.1	52.7	1.6 x 10 ⁻¹	1.15 x 10 ²	1.00	0.997 & 0.998	(Asadieraghi and Daud, 2015)
EFB	10°C min ⁻¹ , 900°C, 20 mg, <0.212 mm	consecutive reaction model	-	209.7	-	$1.45 ext{ x} 10^{17}$	_	0.999	(Idris <i>et al.</i> , 2010)
EFB	10°C min ⁻¹ , 900°C, 25 mg, <0.125 mm, 40 mL min ⁻¹	consecutive reaction model	59.5	67.6	7.74 x 10 ¹	6.197 x 10 ²	1.00	0.987 & 0.995	(Yang <i>et al.,</i> 2004)
OPF	10°C min ⁻¹ , 900°C, 5 mg, 100 mL min ⁻¹	consecutive reaction model	33.8	56.2	3.3 x 10 ³	5.3 x 10 ⁵	1.00	0.954 & 0.981	(Soon <i>et al.</i> , 2016)
PKS	20°C min ⁻¹ , 700°C 10 mg, 0.3 mm, 100 mL min ⁻¹	parallel reaction model	226.4	173.5	$4.05 ext{ x} ext{ 10}^{16}$	$\begin{array}{ccc} 1.2 & x \\ 10^{14} & \end{array}$	3.88	_	(Luangkiattikhun et al., 2008)
MF	20°C min ⁻¹ , 700°C 10 mg, <1 mm, 100 mL min ⁻¹	parallel reaction model	201.0	156.8	9.04 x 10^{14}	$1.86 ext{ x} ext{ 10}^{13}$	3.69	_	(Luangkiattikhun et al., 2008)

 E_{Ai} is activation energy, A_i is frequency factor, n is reaction order, and R^2 is the quality of fit

4. CONCLUSION

The PKS appeared to be the most relatively thermally stable OBP residue, while OPF is the least stable OPB residue. The kinetic parameters calculated from the consecutive reactions model suggest that the ease to commence pyrolysis reaction is in the following order: OPF < PKS < MF < EFB. As pyrolysis reaction commences, OPF reaction is the fastest while PKS reaction is the slowest. The thermal decomposition of the OPB residues ends at a temperature below 600 °C and is fully carbonized at 850 or 900 °C with an approximate weight loss of around 64 to 92 %. Overall, yields of OPB-derived biochar are highly dependent on the pyrolysis mode: slow pyrolysis and microwave pyrolysis favour higher biochar yield, while fast pyrolysis and catalytic pyrolysis yielded more bio-oil than biochar. The asymptote biochar yield is higher than 23 wt.% under slow pyrolysis conditions and the tendency of obtaining biochar with high asymptotic yield is in the following order: PKS > MF > EFB > OPT > OPF. The order is attributed to the proportion of lignin content which slowly decomposes over a wide temperature range. The treatment temperature of 400, 500, and 600 °C are suitable carbonization temperatures for OPB to respectively produce biochars that can be used as biofuels, feedstocks for activated carbon, and reducing agents in steel manufacturing process.

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