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Study of Physicochemical Properties of Palm Oil Decanter Cake for Potential Syngas Generation

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Biomass waste are attractive energy source that can combat the rising energy challenge facing the world when utilized appropriately and accordingly. Unfortunately, the knowledge of the potential of some biomass waste are still missing and this has affected their maximum utilization as energy source in thermal processes like gasification. In this study, the potential of palm oil decanter cake (PODC) for syngas production through thermal processes was determined by bomb calorimeter, CHNS analyzer, Thermogravimetric analysis (TGA), Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS) and X-ray Fluorescence (XRF). Bomb calorimeter revealed the energy value as 17.40 MJ/Kg. CHNS revealed the amount of C, H, N, S and O as 41.41 %, 5.92 %, 5.31 %, 0.30 % and 47.06 % respectively. TGA revealed the presence of volatile matter, fixed carbon and ash content as 58.38 %, 4.91 % and 31.16 % respectively. SEM-EDS revealed the dominant presence of carbon (74.80 %). XRF revealed SiO₂ (28.60 %) and CaO (22.70 %) as the dominant oxides and the presence of bed materials like Al₂O₃ (6.54 %), MgO (2.76 %), CaO (22.70 %) and Fe₂O₃ (7.49 %) which serve as resistance to ash deposition problems during thermal processes. Overall, PODC show likely potential of being used as fuel for syngas production through thermal processes.

1. Introduction

In recent decades, world energy consumption keeps increasing mainly as a result of economic and population growth. Besides, the depletion of fossil fuel resources and oil price uncertainty have put both developed and developing countries on their toes in search for biomass based renewable energy source. Biomass waste are attractive energy source due to their local availability, sustainability and ability to deliver significant reduction in net carbon emission (Dewayanto et al., 2014; Ishola et al., 2021). Oil palm industry can be considered as potential resources for generation of renewable energy as majority of its waste have been found suitable for heat and power generation. Malaysia is the second largest producer of palm oil and currently strengthening her palm oil production rate due to increase in the global demand (Ramli et al., 2016). The oil palm industry continually expands since planted over 100 years ago and as it expands, more wastes are generated by palm oil mills. The pace of oil palm growth has led to unintended social, economic and environmental consequences as deformation and land conservation for oil palm development contributes to carbon emission increase. (Osman et al., 2019) stated that approximately 416 palm oil mills are operating in Malaysia. From the mill, an estimated waste generation from 1 tonne of fresh fruit bunch (FFB) is 0.6 - 0.8 m³ of palm oil mill effluent (POME), 3.5 % of palm oil decanter cake (PODC), 22 - 23 % of empty fruit bunch (EFB) and 13.5 % palm mesocarp fibre (PMF) (Osman et al., 2019; Rongwang et al., 2017). PODC is produced when crude palm oil is centrifuged for purification process. Installation of more decanter machine across mills to recover remaining oil from the underflow sludge tank have resulted in huge PODC production in recent years (Ramli et al., 2016). According to (Man et al., 2021), an average palm oil mill processing 90 tonnes of FFB per hour produces approximately 160-200 tonnes of PODC in a month, PODC are dumped and left to degrade naturally in dumping ponds (Opobiyi et al., 2019; Osman et al., 2019) while in some mills, they are disposed close to oil palm plantations where they accumulate and pollute the environment (Duaja et al., 2021; Jagaba et al., 2022). PODC has high biodegradable organic content and is an ideal feedstock for the production of methane via fermentation (Man et al., 2021). In few studies, PODC has been used biologically for energy production. (Kaosol & Sohgrathok, 2013) co-digested PODC with different wastewaters and stated that co-digestion of PODC with rubber block wastewater produced high biogas yield of 3,809 mL CH₄/g COD removal and methane gas of 66.7 %. (Tepsour et al., 2019) also co-digested oil palm EFB and PODC. They obtained positive result on the production of methane gas at different organic loading rate and substrate to inoculum ratio. Utilization of PODC has been proven through biological biomass conversion means, however, there is no report on thermal conversion of PODC like gasification. This could be due to lack of information on the potentials of PODC for thermal processes. With a calorific value of 17.4 MJ/Kg which falls within the biomass energy range (15 MJ/Kg – 20 MJ/Kg), PODC looks promising as bioenergy source. There is therefore need to undertake more physicochemical analysis to examine its potential for thermal processes. Therefore, the aim of this study is to conduct physicochemical study on PODC in order to determine its potentials for use as fuel for syngas production.

2. Materials and method

Freshly produced PODC was collected from an oil palm processing factory in Perak, Malaysia and dried immediately with an oven at 110 $^{\circ}$ C for 24 hours to remove moisture. Dried sample was further grinded mechanically with a grinder and sieve to a particle size of 250 μ m for experimental purpose. Each experiment was replicated three times.

2.1 Calorific value

The calorific value of PODC was determined using bomb calorimeter (Brand: Ika, Model: C5003) in accordance with ASTM D240-02 standard (Peres et al., 2019). PODC of 1 g placed in a crucible was used for this experiment.

2.2 CHNS analysis

The basic composition of PODC in respect of the proportion of Carbon, Hydrogen, Nitrogen and Sulphur was determined using CHNS analyser [Brand: Elementar, Model: Micro] in accordance with ASTM D3176-15 standard. 1 g of PODC was weighed in a silver vessel and loaded in the analyzer. The Oxygen proportion was determined by difference (Umar et al., 2020).

2.3 Thermogravimetric analysis

PODC thermal degradation behavior was examined using Thermogravimetric analysis [Brand: Perkin Elmer, Model: STA6000] in accordance with ASTM E1131-98 standard. 5.0 mg of PODC was paved uniformly in a platinum crucible and heated from ambient temperature to 800 °C under ambient atmosphere at a heating rate of 25 °C/min. The value of volatile matter, fixed carbon and ash content were obtained from the process.

2.4 Scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS)

The microstructure of PODC was determined using scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) detector [Brand: Zeiss, Model: Evo LS15 VPSEM] (George et al., 2019). Samples were prepared on circular supports of 12.5 mm diameter over carbon stickers. The working distance (WD) was approximately 10 mm and the dead time (DT%) was kept at less than 30 % for the experiment. The percentage weight of each elements present was determined.

2.5 X-Ray fluorescent (XRF) analysis

10 g of PODC was pressed into a pellet for the analysis. The auto-calibrated XRF analyzer [Brand: Rigaku, Model: Primus IV] spectrometer operating at 55 V and 40 mA was used to determine the elemental composition of PODC (Umar et al., 2020).

3. Results and discussion

3.1 Calorific value

The calorific value (CV), also known as the energy value is of great importance when selecting a desirable fuel (biomass and coal) for energy generation purpose. The higher the heating value, the more the energy dissipated during combustion. The energy value of PODC obtained was 17.40 MJ/Kg which is similar to 17.00 MJ/Kg obtained by (Shrivastava et al., 2021). PODC CV is lower when compare to coal gangue (24.70 MJ/Kg) (Zhou et al., 2014), bitumen (23.25 MJ/Kg) (Guangul, 2013) and olive kernel (20.54 MJ/Kg) (Boumanchar et al., 2017), however, it is higher when compare to oil palm fond (17.2 MJ/Kg) (Umar et al., 2020), lignite coal (16.30 MJ/Kg) (Guangul, 2013), wheat straw (16.00 MJ/Kg) (Zhou et al., 2014) and rice husk (RH) (14.79 MJ/Kg) (Sadig et al., 2017). The difference could be attributed to difference in chemical compositions each possessed. The within

biomass energy range of PODC and higher energy value possession when compare to other biomass and coal proves PODC potential for use as domestic and industrial fuel.

3.2 CHNS analysis

Table 1 depicts the CHNS elemental analysis of PODC and some selected biomass and coal. The values of C, H, N, S and O present in PODC were found to be 41.41 %, 5.92 %, 5.31 %, 0.30 % and 47.06 % respectively, which is similar to (Shrivastava et al., 2021) PODC report. Though less carbon (C) value was found present in comparison with coal, the value was higher than that of Empty fruit bunch (40.73 %), date palm fond (40.48 %), RH (38.74 %) making it suitable for energy generation. Sulphur (S) value shows the environmental suitability of a feedstock and this was found lower in PODC than coal: bitumen (0.90 %), Coal gangue (0.55 %) and lignite (0.90 %) but similar to most biomass.

Table 1: CHNSO elemental analysis of PODC and some selected biomass and coal

Biomass/Coal	C (%)	H (%)	N (%)	S (%)	O (%)	Reference
Bitumen	68	4.00	3.00	0.90	24.1	(Sadig et al., 2017)
Coal Gangue	57.5	2.63	0.54	0.55	9.88	(Zhou et al., 2014)
Lignite	50	4.00	2.00	0.90	43.10	(Sadig et al., 2017)
PODC	45.6	6.41	2.38	0.24	36.4	(Shrivastava et al., 2021)
Oil Palm Fond	45.42	6.35	0.47	0.13	47.63	(Umar et al., 2020)
Sugarcane Bagasse	42.93	5.82	0.68	0.06	54.82	(Sharifah & Yusup, 2010)
PODC	41.41	5.92	5.31	0.30	47.06	This study
Empty Fruit Bunch	40.73	5.75	1.40	0.22	51.90	(Sharifah & Yusup, 2010)
Date Palm Fond	40.48	5.63	0.28	0.00	53.61	(Nasser et al., 2016)
RH	38.74	5.83	0.55	0.06	54.82	(Sharifah & Yusup, 2010)

3.3 Thermogravimetric analysis (TGA)

Table 2 depicts the proximate analysis result of PODC and some selected coal and biomass. Volatile matter (VM), fixed carbon (FC) and ash content (AC) of PODC were found to be 58.38 %, 4.91 % and 31.16 % respectively, however, (Yusoff et al., 2019) reported a higher VM, higher FC and lower AC of 63.92 %, 11.15 % and 20.81 % respectively for PODC which could be as a result of difference in production source, environmental conditions and location. PODC considered in this study has a moisture content of 5.55 % with VM, FC and AC total sum of 94.45 %. The higher the VM, the lesser the minimum ignition temperature required and the easier it burns. PODC has a considerable amount of VM (58.38 %) which is greater than that of RH (48.94 %), municipal sewage sludge (36.71 %), lignite (34.41 %), bitumen (18.69 %), coal gangue (18.40 %) and paper making sludge (17.24 %). The FC of PODC (4.91 %) is relatively low compare to 11.15 % reported by (Yusoff et al., 2019) for PODC and a difference of 4.55 % and 4.65 % from that of RH and municipal sewage sludge respectively. The higher the AC present in feedstock, the more liable the occurrence of ash deposition during thermal processes. There was no significant difference between PODC AC (31.16 %) and RH AC (33.67 %), however, municipal sewage sludge AC (38.27 %) was quite different. As stated by (Umar et al., 2020), less ash content is required as a prerequisite to slagging and agglomeration free gasification process. During biomass gasification, ash deposition is generally experienced at different degree, however, PODC has a moderate ash content and the use of additives or co-combustion with other feedstocks is a good means to combating ash related problems (Abioye, Harun, & Saeed, 2023; Abioye, Harun, Sufian, et al., 2023), thereby making it more suitable for power and energy generation.

Table 2: Thermogravimetric analysis of PODC and some selected coal and biomass

Biomass/Coal	VM (%)	FC (%)	AC (%)	Reference
Wheat Straw	66.40	18.10	13.20	(Zhou et al., 2014)
PODC	63.92	11.15	20.81	(Yusoff et al., 2019)
PODC	58.38	4.91	31.16	This study
RH	48.94	9.46	33.67	(Liu et al., 2020)
Municipal Sewage Sludge	36.71	9.56	38.27	(Li et al., 2021)
Lignite	34.41	48.39	17.20	(Demirel, 2012)
Bitumen	18.69	61.86	19.63	(Demirel, 2012)
Coal Gangue	15.00	16.3	67.9	(Yang et al., 2016)

3.4 Scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS)

The microstructure of PODC is shown in Figure 1. SEM revealed that PODC has a fairly smooth irregular surface with few cracks due to the presence of cellulose, hemicellulose and lignin (Yusoff et al., 2019). Table 3 shows the weight percentage of elements present in PODC and RH. The weight of carbon obtained in EDX for PODC was higher than that of the ultimate analysis. EDX revealed 74.80 % of carbon while ultimate analysis predicted 41.41 %. The difference could be as a result of untraced hydrogen and nitrogen in EDX analysis (Guangul et al., 2012). PODC possess more than twice the amount of carbon present in RH indicating that PODC is a good energy source. The presence of inorganic elements like Al, Na, Mg, K, Si, Ca and Cl in biomass samples are of paramount importance as they are considered in the design of thermochemical conversion systems. 1.19 % and 0.77 % of K were found present in PODC and RH respectively. During gasification, K react with different elements like Cl to form salt which eventually cause ash deposition problems like slagging. Ca was found present in PODC alone with 2.16 %. The Si content in PODC (1.41 %) was relatively negligible compare to 21.62 % of RH. However, silicon content as low as 1 % may lead to problems during biomass combustion as slagging in form of silicates takes place (Akhtar et al., 2019). A low amount of Si present in PODC suggest that ash handling and syngas cleaning during gasification will be minimal.

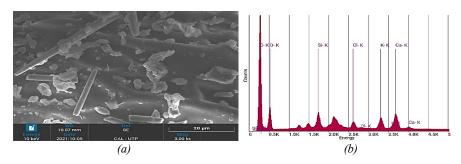


Figure 1: (a) SEM image (b) EDX spectrum of raw PODC

Table 3: EDX result for PODC and Rice Husk

Elements	P	ODC	RH (Guangul et al., 2012)					
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)				
С	74.80	85.63	32.21	42.51				
0	16.22	12.23	45.40	49.98				
CI	0.67	0.26	-	-				
K	1.19	0.47	0.77	0.31				
Ca	2.16	0.65	-	-				
Si	1.41	0.76	21.62	12.20				

3.5 X-Ray fluorescent (XRF) analysis

Table 4 shows the elemental oxide of PODC, RH and oil palm fonds (OPF). In PODC, SiO $_2$ (28.60 %) and CaO (22.70 %) were the major oxides while RH has only SiO $_2$ (73.20 %) as the major oxide. As for OPF, CaO (36.50 %) and K $_2$ O (32.10 %) were the major oxides present. The highest proportion of both K $_2$ O and Cl were found in OPF (32.10 %, 15.20 %), followed by PODC (14.70 %, 4.13 %) and RH (8.78 %, 2.38 %) respectively. RH has high SiO $_2$ (73.20 %) when compare with PODC (28.60 %) and OPF (4.33 %). The higher the presence of K $_2$ O, SiO $_2$ and Cl in a feedstock, the likely the formation of K-species which causes ash deposition problems during gasification. However, the presence of bed materials like Al $_2$ O $_3$, MgO, CaO and Fe $_2$ O $_3$ reduces such problem by promoting the formation of high melting temperature compounds during combustion. The summation of bed materials present in PODC, RH and OPF are 39.45 %, 4.37 % and 40.33 % respectively. Therefore, the high presence of bed materials in PODC and OPF makes them more preferrable for gasification process than RH.

Table 4: XRF analysis of PODC, RH and OPF

D:	Oxides (%)								Reference			
Biomass	CaO	K₂O CI	P ₂ O ₅ SiO ₂	SO ₃	MgO	Fe ₂ O ₃	MnO	Al ₂ O ₃	CuO	ZnO	TiO ₂	2
PODC	22.7	14.7 4.13	3.86 28.60	6.18	2.76	7.49	0.25	6.54	0.26	0.16	2.01	This Study
RH	3.14	8.78 2.38	7.55 73.20	3.35	0.91	0.32	0.31	-	0.04	0.05	-	(Guangul et al., 2012)
OPF	36.5	32.1 15.2	4.45 4.33	1.95	1.93	1.90	1.23	-	0.11	0.11	-	(Umar et al., 2020)

4. Conclusions

In this study, PODC was characterized for possible use as fuel in thermochemical processes like gasification using bomb calorimeter, CHNS analyzer, TGA, SEM-EDS and XRF. The energy value of PODC was 17.40 MJ/Kg which falls within biomass energy range and also higher than lignite coal (16.3 MJ/Kg) and RH (14.79 MJ/Kg). CHNS analysis revealed the amount of C, H, N, S and O present as 41.41 %, 5.92 %, 5.31 %, 0.30 % and 47.06 % respectively. TGA revealed the composition of VM, FC and AC present as 58.38 %, 4.91 % and 31.16 % respectively while the dominant present of carbon (74.80 %) was revealed by SEM-EDS. XRF showed that SiO₂ (28.60 %) and CaO (22.70 %) were the dominant oxides and also revealed the presence of bed materials like Al₂O₃ (6.54 %), MgO (2.76 %), CaO (22.70 %) and Fe₂O₃ (7.49 %). In all, PODC showed positive signal towards being used as fuel for syngas production with high energy value, high Carbon content, high volatile matter, less Sulphur content and presence of ash deposition resistance bed materials. Gasification of PODC should therefore be considered in future works to affirm its suitability.

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