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Mineralogical Component of Palm Oil Fuel Ash With or Without Unburned Carbon

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Abstract**—**The purpose of this paper is to investigate the mineralogical components of palm oil fuel ash (POFA) with or without unburned carbon by using semi-quantitative X-ray diffraction (XRD). Original POFA taken from palm oil mill was ground in ball mill, producing ground POFA (GPOFA). Unburned carbon was removed by heating the GPOFA at 500 °C for 1 h, producing treated POFA (TPOFA). Neither glassy phase crystallization nor agglomeration of GPOFA particles occurred during the heat treatment. The content of crystalline phase and glassy phase in GPOFA or TPOFA was determined using semi-quantitative XRD analysis internal standard method. The results showed that GPOFA and TPOFA contained 67.22% and 73.89% of glassy phase, respectively, which could be used as pozzolanic materials. The presence of P_2O_5, K_2O and Na_2O in POFA was the reason of reducing the melting point of POFA in boiler.

Keywords**:** Palm oil fuel ash, glassy content, unburned carbon, XRD

I. INTRODUCTION

Agricultural waste ashes such as rice husk ash, sawdust ash and bagasse ash are getting more attention recently since they can be used as mineral admixtures to improve the properties of blended cement and reduce the environment problems [1], [2]. At room temperature, SiO_2 and Al_2O_3 in glassy phase containing in these ashes can react with $Ca(OH)_2$ as pozzolanic materials to form calcium silicate hydrate or calcium aluminates hydrate. Palm oil fuel ash also has high content of SiO_2. In palm oil mill, solid waste by-products in the form of fibers and nutshells from fresh fruit bunch are used extensively as biomass fuel for electricity generation in steam boiler. Combustion produces approximately 5% of palm oil fuel ash (POFA). In 2007, the Malaysian Palm Oil Board estimated the amount of POFA produced in Malaysia to be approximately 3 million tons [3]. Because of the limited uses for POFA, it is currently disposed of as landfill; this could lead to environmental problems in the future [4].

To solve this potential environmental problem, many researchers have studied the use of POFA in concrete admixtures. Tay [5] reported that POFA has low pozzolanic properties and should not be used as a cement replacement in quantities greater than 10% by mass of binder. On the other hand, ground POFA (GPOFA), however, is a good pozzolanic material and can be used as a replacement in Portland cement up to levels of 20% ~ 30% [6]. GPOFA also has good potential for preventing the expansion caused by alkali—silica reactions [7]. In addition, the sulfate resistance of concrete can be improved by adding GPOFA [8]. By adding of GPOFA having irregular shape and many pores, the unit weight of waste in concrete or dosage of SP is increased at the same fluidity of concrete without GPOFA [9], [10]. In addition, unburned carbon in POFA absorbs a lot of SP and reduces the fluidity of cement paste, but it can be removed by treatment at temperature of 500 °C for 1 h which neither glassy phase crystallization nor particle agglomeration occurs [11]. Since pozzolanic activity is happened due to the presence of SiO_2 and Al_2O_3 in the glassy phase, it is necessary to determine the content of crystalline phase and glassy phase in POFA. But all of this information is not yet studied. Semi-quantitative X-ray diffraction (XRD) analysis has been applied to quantify the mineral components in fly ashes by using CaF_2 as internal standard [12]. Therefore, the purpose of this paper is to investigate the mineralogical components of GPOFA and TPOFA by using Semi-quantitative XRD.

II. METHODS AND MATERIALS

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1. MATERIALS

POFA was collected from a palm oil mill in Penang, Malaysia. It was sieved using a 300 µm sieve to remove fibers and nutshells which were incompletely combusted. The POFA was then ground in a ball mill to obtain GPOFA. To remove unburned carbon and to prevent glassy phase crystallization and particle agglomeration, all of which affect the pozzolanic properties, GPOFA was heated at 500 °C for 1 h in an electric furnace. This produced treated palm oil fuel ash (TPOFA).

2. CHARACTERIZATION OF GPOFA AND TPOFA

Chemical composition was tested by method for chemical analysis of cements (JIS R 5202). The amount of unburned carbon was determined using a Total Carbon Analyzer (SHIMADZU, SSM-5000A). The crystalline phase was analyzed by X-ray diffraction (XRD) (BRUKER, MXP3 II). A laser diffraction particle size analyzer was used to measure particle size distribution and mean particle size (MICROTRAC HRA, 9320-X1000). The BET specific surface area (S_{BET}) was measured by nitrogen gas absorption (SHIMADZU, MICROMERITICS GEMINI V).

2.3 SEMI-QUANTITATIVE X-RAY DIFFRACTION ANALYSIS

2.3.1 Internal standard method

The content of crystalline phases in GPOFA or TPOFA can be determined using semi-quantitative XRD analysis internal standard method. The ratio between diffraction intensities of crystalline phase A in the powder mixture and internal standard S is linearly proportional to the ratio between mass fraction of crystalline A and internal standard S. Thus, the standard curve can be prepared based on the equation below:

$$I_A/I_S = K.\ W_P/W_S$$

Where, I_A and I_S are diffraction intensity of crystalline phase A in the powder mixture and internal standard S respectively. W_P and W_S are mass fraction of powder mixture and internal standard S respectively. K is a constant.

2.3.2 Sample preparation for standard curves

In preparation standard curve, silica glass was used as matrix and Al_2O_3 was used as an internal standard. The reason of using Al_2O_3 as internal standard because its diffraction peaks do not overlap the diffraction lines of crystalline phases in GPOFA and TPOFA. The XRD patterns of GPOFA and TPOFA in Figure 1 showed that the major crystalline phases was α-quartz (SiO_2) and minor crystalline phases were cristobalite (SiO_2) and potassium aluminum phosphate ($K_3Al_2(PO_4)_3$). A halo is observed in the XRD profiles from 20° to 30°; this represents an amorphous phase. Based on this result, the standard curves for the corresponding peaks were prepared. Sintered cristobalite was produced by heating SiO_2 amorphous at 1500 °C for 10 h, and then its purity was determined using differential scanning calorimetry (DSC 3300S, BRUKER) (ΔH of cristobalite = 1.34 kJ.mol-1) [13]. Sintered $K_3Al_2(PO_4)_3$ single crystals was formed by heating the mixture of KPO_3 with $Al(OH)_2$, in open air, at initial low temperature of 400 °C for 12h to prompt the decomposition of the phosphates and then finally for 24 h at maximum temperature of 900 °C with heating rate of 100 °C per 12 h [14]. The fraction of samples in the mixture for preparing the standard curves were 10—70 mass% for α-quartz, 0.5—1.5 mass% for cristobalite and 2—6 mass% for $K_3Al_2(PO_4)_3$. 20 mass% of Al_2O_3 was added to these mixtures and the remaining mass% was silica glass.

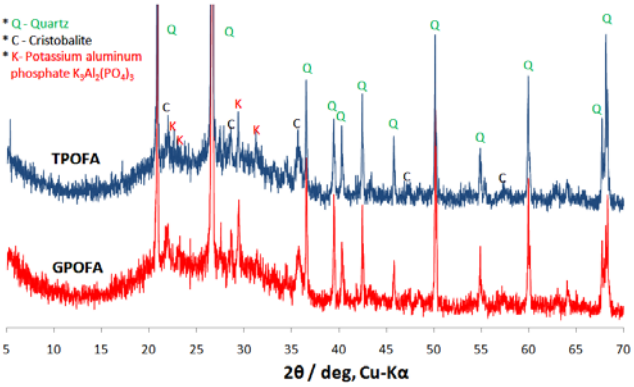


Figure 1: X-ray diffraction patterns of GPOFA and TPOFA.

2.3.3Condition of XRD analysis and quantitative determination

An XRD with Cu target, operated at 40 kV and 30 mA was used. The step scanning was performed with 0.02° with scanning speed of 0.12° per min. The scanning range was 1.64° (2θ). The peaks used for the quantitative analysis is shown in Table 1. Three measurements per each sample were performed to obtain an average value. The amount of crystalline phase of α-quartz, cristobalite and $K_3Al_2(PO_4)_3$ were determined from their standard curves. The amount of glassy phase was obtained by subtracting the amount of crystalline phases and loss on ignition (LOI) from 100 mass%.

Table 1: XRD peaks scanned for quantitative analysis

Phases	**2θ**	**2θ range scanned**
Al_2O_3	52.5	51.67 - 53.33
α-quartz	20.8	20.00 - 21.66
Cristobalite	21.98	21.15 - 22.81
$K_3Al_2(PO_4)_3$	29.54	28.71 - 30.37

III. Results and Discussions

3.1 PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION OF GPOFA AND TPOFA

Table 2 shows the physical properties of GPOFA and TPOFA. The S_{BET} value of TPOFA was lower than those of GPOFA. This shows that unburned carbon, which has a high specific surface area of around 57.3 m^2/g, was removed from GPOFA, resulting in lower S_{BET} values. The density of GPOFA was lower than that of TPOFA because the amount of unburned carbon, which has a low density (around 2.0 g/cm^3), was reduced by the heat treatment. The mean particle sizes of GPOFA and TPOFA were 22.52 µm and 22.53 µm, respectively, showing that there was no significant change in the mean particle sizes of GPOFA and TPOFA; S_{BET} values for both GPOFA and TPOFA particles were very large. Therefore, GPOFA and TPOFA have inner particle surfaces and these particles maybe porous.

Table 2: Physical properties of GPOFA and TPOFA

Materials	**Density (g/cm^3)**	**S_{BET} (m^2/g)**	**Mean particle size (µm)**
GPOFA	2.42	8.96	22.52
TPOFA	2.56	5.56	22.53

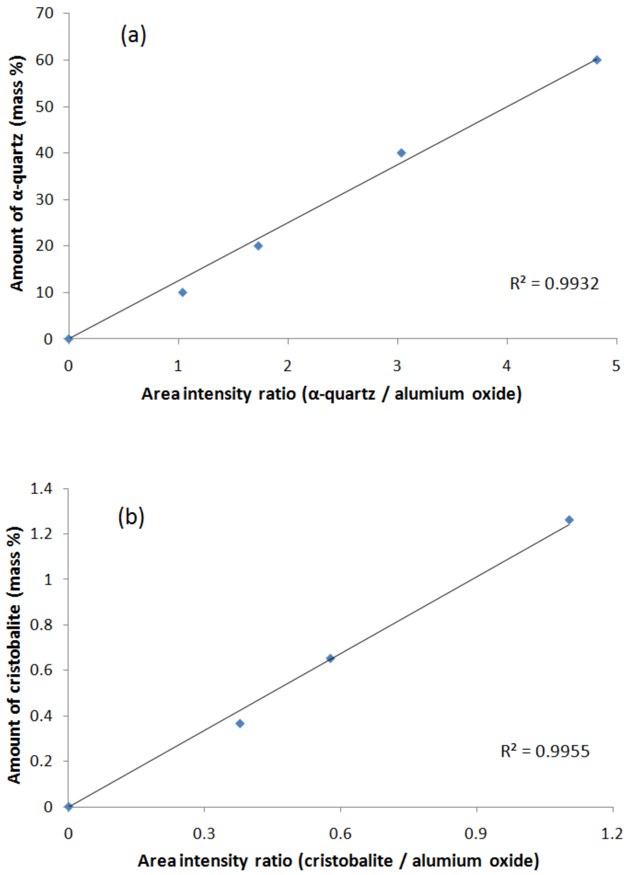
The unburned carbon contents for GPOFA and TPOFA were 6.01% and 0.07%, respectively (Table 3). The unburned carbon content and LOI for TPOFA were significantly lower than those for GPOFA. This shows that unburned carbon can be removed by treatment at 500 °C for 1 h. The main component of both GPOFA and TPOFA was SiO_2. The combined total amounts of SiO_2 and Al_2O_3 were 67.5% and 73.2% for GPOFA and TPOFA, respectively. SiO_2 and Al_2O_3 of TPOFA were higher than GPOFA because of its ignited base increased. The total amounts of P_2O_5, K_2O and Na_2O, which lowered the melting point of POFA, were 8.51% and 9.18% for GPOFA and TPOFA.

Table 3: Chemical composition of GPOFA and TPOFA

Component	**Chemical composition (mass %)**	
	GPOFA	**TPOFA**
SiO_2	61.85	67.09
Al_2O_3	5.65	6.12
Fe_2O_3	5.45	5.92
CaO	5.09	5.58
MgO	2.79	3.06
SO_3	0.28	0.32
Na_2O	0.10	0.11
K_2O	5.09	5.45
Ti_2O	0.32	0.35
MnO	0.11	0.12
P_2O_5	3.32	3.62
LOI	9.88	2.20
(Unburned Carbon)	(6.01)	(0.07)

3.2 MINERAL COMPOSITION OF GPOFA AND TPOFA

The amount of crystalline phase of α-quartz, cristobalite and $K_3Al_2(PO_4)_3$ were determined using standard curve in Figure 2. The content of α-quartz in GPOFA and TPOFA were 17.35% and 18.62%, respectively (Table 4). The amounts of cristobalite were 0.42% and 0.43% for GPOFA and TPOFA, respectively. Also, the content of $K_3Al_2(PO_4)_3$ in GPOFA and TOPFA were 5.13% and 4.86%, respectively. It showed that mineral composition of GPOFA and TPOFA had minor difference. The contents of glassy phase were 67.22% and 73.89% for GPOFA and TPOFA, respectively. However, POFA was heated at maximum temperature of 800 °C in the boiler, but there was much glassy phase can be formed due to the presence of P_2O_5, K_2O and Na_2O which reduced the melting point of POFA [15].



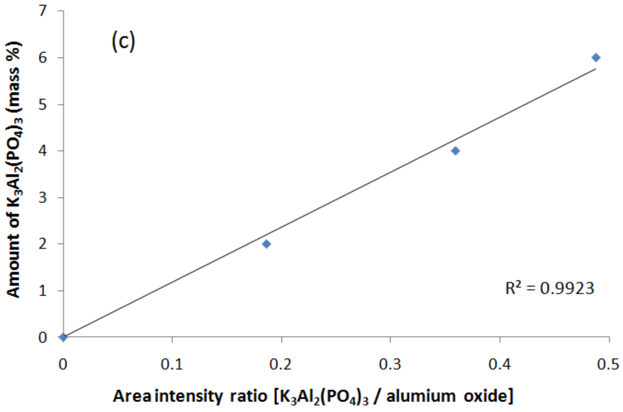


Figure 2: Standard curve of α-quartz (a), cristobalite (b) and $K_3Al_2(PO_4)_3$ (c).

Table 4: Mineral composition of GPOFA and TPOFA

Component	**Mineral composition (mass %)**	
	GPOFA	**TPOFA**
α-quarzt	17.35	18.62
Cristobalite	0.42	0.43
$K_3Al_2(PO_4)_3$	5.13	4.86
Glassy	67.22	73.89
LOI	9.88	2.2

IV. CONCLUSION

The mineralogical component of GPOFA and TPOFA can be determined by using semi-quantitative XRD internal standard method. GPOFA and TPOFA contained large amount of glassy phases and can be used as pozzolanic materials to replace cement. However POFA was heated in boiler at maximum temperature 800 °C, but there was much glassy phase can be formed due to the presence of P_2O_5, K_2O and Na_2O which reduced the melting point of POFA.

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