Chemical and Physical Characterization of Boiler Ash from Palm Oil Industry Waste for Geopolymer Composite

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The characterizations of boiler ash waste from waste of palm oil industry were performed. The boiler ash was obtained from the boiler in the palm oil processing factory. The chemical and physical characterization has been analyzed using X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), particle size distribution, Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). From the XRF analysis, the major component of boiler ash is silica oxide (SiO_2), followed by calcium oxide (CaO) and ferum oxide (Fe_2O_3). In order to produce geopolymer, the raw material needs to contain enough SiO_2 and aluminium oxide (Al_2O_3). However, the content of Al_2O_3 is only 3.7% but it contained high amount of SiO_2 (40.60%) and CaO which may influence the strength of the geopolymer. The median particle size of boiler ash was comparable with fly ashes, morphology of boiler ash showed irregular particle size and shape. The surface particle of boiler ash look similar with calcined kaolin but no plate like structure was observed. Hence, we believe that this material has a potential use as raw material for geopolymer production.

Keywords: boiler ash, physical, chemical, characterization, geopolymer

Geopolymers or alkali-activated binder has been considered as one of issue in producing sustainable development due to less emission of carbon dioxide towards environment [1]. The production of geopolymer used industrial by-product rich in aluminium and silica oxide such as blastfurnace slag, fly ash, kaolin and metakaolin [2-13]. Alkaline activator was required in the process of geopolymer where the common materials used as alkaline activator were sodium hydroxide (NaOH), potassium hydroxide, sodium silicate (Na_2SiO_3) and potassium silicate. It was found that the type of alkaline activator plays an important role in the geopolymerization process [14]. Geopolymerization process is the chemical reaction that involves the source of aluminium and silicon oxide where it was synthesized or dissolved by alkaline activator [15]. There are three major steps in geopolymerization process [16-17]; (1) dissolution of Si and Al atoms from the source material through the action of hydroxide ions, (2) transportation or orientation or condensation of precursor ions into monomer and (3) setting or polycondensation/ polymerisation of monomers into polymeric structures. The rate of geopolymerization process is high when the alkaline activator contains soluble silicate (sodium or potassium silicate) compared to the use of alkaline hydroxide. It has been proved that the combination of Na_2SiO_3 with NaOH solution improved the reaction of source materials with alkaline activator [16].

The particles size distribution of fly ash plays an important role in the reactivity of the fly ash [18, 19]. The fly ash with finer particle size resulted in higher surface area and also reactivity, producing geopolymer with higher compressive strength [19]. Other than that, the calcium composition in fly ash also gives significant effect in the strength development of geopolymer [20]. However, for clay type of sources such as kaolin to be successfully used as geopolymer it required calcinations process. The reactivity of kaolin can be improved when it was calcined at temperature between 650 – 850°C with the elimination of OH- group [21]. Liew et al. [7] have produced the cement powder from calcined kaolin using geopolymerization technique with compressive strength 7.4 MPa at 7 days.

The application of geopolymer also has been expand years by years where before this only focus on the production of geopolymer cement and concrete [5, 7, 22, 23] but now its application have covered coating application [24-26] including for fire resistant purpose [27, 28].

Malaysia is one of the largest palm oil productions in the world where it is produced large amount of solid waste such as fibers, nutshells, kernels and empty fruit bunches [29]. The kernels, nutshell and fibers were burnt in the boilers to generate steam to run a turbine to generate electricity as shown in Figure 1. When these wastes were incinerated, the waste from the burning process known as boiler ash was obtained at the lower compartment of the boiler. The production of boiler ash as in Figure 2 was estimated to be over 4 million tones/ year [30]. Usually the boiler ash was used for land application such as roads in the palm oil mill [31]. The boiler ash was seen with more large particles where it consists of clinkers and also ashes. Past research have been done on palm ash for its use as concrete admixtures [19, 32-34], absorbent in wastewater treatment and air purifier in cleaning of atmospheric contaminants [35]. Meanwhile, no research has been

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done on utilization of boiler ash into usable products. This research will study the characterizations of boiler ash as a potential raw material for geopolymer production by comparing to fly ash and calcined kaolin.

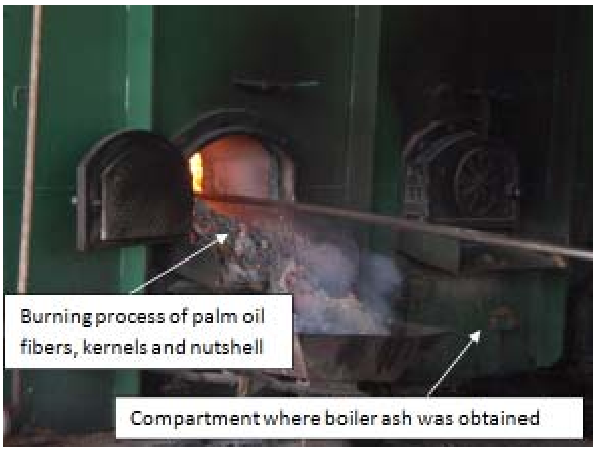

Fig. 1. Palm oil fibers, kernels and nutshell as biomass fuel in boiler

Fig. 2. Raw boiler ash

Experimental part

Materials and methods

The boiler ash was obtained from palm oil mill in Penang, Malaysia. As shown in figure 2, the boiler ash consists of coarse particle of the unburn palm oil nutshells, fibers and kernels; hence it required grinding process to refine the particles sizes. The boiler ash has been grind and was sieved passing through 100μm sieve to remove coarser particles.

The boiler ash samples were prepared in powder form and analyzed using XRD-6000, Shimadzu X-ray diffractometer with Cu Kα radiation. From the analysis, the pattern of crystalline phase was determined. The boiler ash in powder form was analyzed using Mastersizer 2000 to determine the particles sizes.

By using Perkin Elmer FTIR Spectrum RX1 Spectrometer the detecting functional groups and characterization of covalent bonding information were determined. The infrared spectra were scanned from 650 cm^{-1} until 4000 cm^{-1}. Meanwhile the microstructure of boiler ash was observed using JSM-6460LA model scanning electron microscope (JEOL).

Results and discussions

Chemical and Physical Properties of Boiler Ash

Result of XRF analysis as presented in table 1 exhibit that the main chemical composition of boiler ash is silica oxide SiO_2, followed by CaO, Fe_2O_3, and potassium oxide (K_2O). The boiler ash contained the sum of SiO_2 and Al_2O_3 about 44% which is the most required composition to produce geopolymer [14, 36]. Moreover, calcined kaolin, class F and C of fly ash which has been successfully produced geopolymer also contained the sum of SiO_2 and Al_2O_3 about 97.1, 83.7 and 35.7 % [6, 7, 19]. Since the sum of SiO_2 and Al_2O_3 in boiler ash was within this range, hence this material is potentially used as geopolymer. The content of CaO is the second highest where it has been reported to influence the properties of fresh geopolymer mixture and also hardened geopolymer [20, 37].

Besides that, the ratios of Si/Al play an important role to determine the geopolymeric application in the field of industries. Davidovits [17] has classified the application of geopolymer material according to ratio of Si/Al as shown in table 2. The ratio of Si/Al for boiler ash is 14 which is suitable to be used as sealant for industry.

Table 1
CHEMICAL COMPOSITIONS OF BOILER ASH, CALCINED KAOLIN, CLASS F AND CLASS C FLY ASH

Compositions	Boiler ash (%)	Calcined kaolin (%) [38]	Class F fly ash (%) [24]	Class C fly ash (%) [25]
SiO_2	40.60	55.90	55.07	26.40
Al_2O_3	3.71	41.20	28.61	9.30
Fe_2O_3	15.74	0.36	6.22	30.10
CaO	19.60	0.06	1.97	21.60
MgO	1.30	0.04	1.08	-
P_2O_5	2.73	0.24	-	-
K_2O	13.80	0.93	2.63	2.58
SO_3	0.44	-	0.19	1.30
TiO_2	0.35	0.35	-	3.10
MnO	0.28	-	-	0.30
LOI	5.01	-	1.82	-
$SiO_2 + Al_2O_3$	44.31	97.10	83.68	35.70

Table 2
APPLICATIONS OF GEOPOLYMERIC MATERIALS BASED ON SILICA-TO-ALUMINA ATOMIC RATIO [17]

Si/Al ratio	Applications
1	Bricks, ceramics, fire protection
2	Low CO_2 cements, concretes, radioactive and toxic waste encapsulation
3	Heat resistance composites, foundry equipments, fibre glass composites
> 3	Sealants for industry
20-35	Fire resistant and heat resistant fibre composites

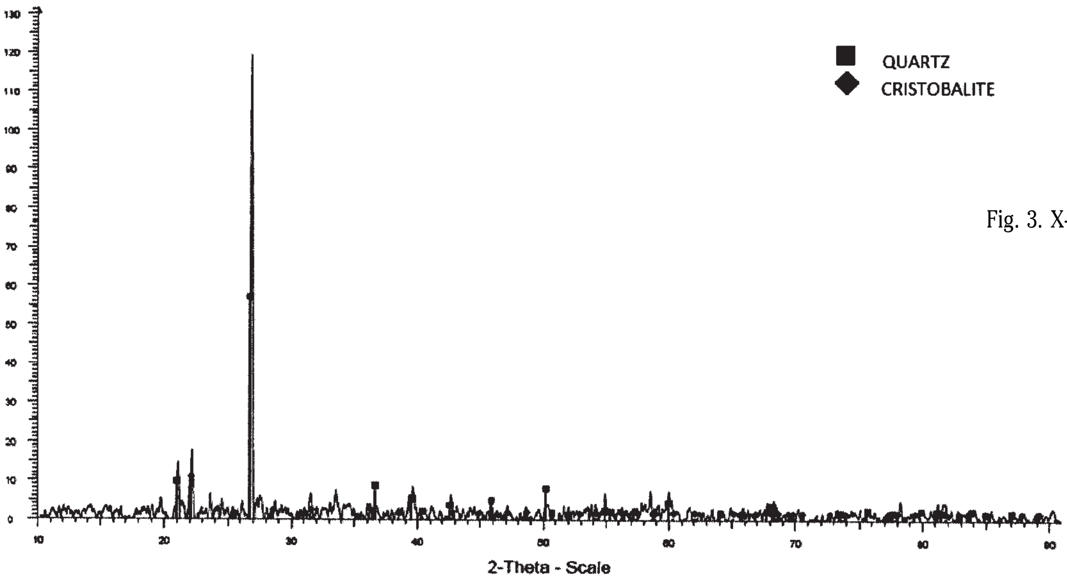

Fig. 3. X-ray pattern of boiler ash

The phase of boiler ash has been examined by XRD, the identified compound was shown in figure 3. From the XRD pattern it indicates that boiler ash consists of quartz (SiO_2) as the major crystalline phase at 2θ = 27°. The high intensity of quartz phase was supported by XRF analysis where 40.60% of SiO_2 was found. Other than that, cristobalite which represents the minor crystalline also was detected. For class C fly ash, it was found that the main mineral components were quartz, mullite, anhydrite and f-CaO, where the maximum peak of quartz was detected at 2θ= 27° [39]. Meanwhile for class F fly ash, it contained major vitreous phase between 2θ = 20° and 2θ = 35° with the existence of minor crystalline phase such as quartz, mullite, hematite, magnetite and some CaO and TiO_2 [18]. As according to previous research, the calcined kaolin produced the maximum quartz peak at 2θ = 27° and showed semi-crystalline to amorphous phase though the kaolinite peaks also exist in less intense peaks [7].

The particles size distribution of grinding boiler ash is shown in figure 4. The grinding boiler ash recorded median particle size (d_{50}) of 46.51μm as shown in table 3 where the median particle size of fly ash and calcined kaolin were compared with the previous research work. There is not much difference between boiler ash and fly ash particle size, although the d_{50} of calcined kaolin is much smaller.

Figure 5 contains FTIR spectra of boiler ash where most of the band contributed by stretching vibration of (-OH) and (HOH) which appears at band between 3600 – 2200 cm^{-1}. Besides that, the (-OH) group also detected at band 1426 cm^{-1} and around region 1009 cm^{-1} the stretching of (Si-O) and also Al-O was detected. At the same time, the (Al-O) or (Si-O-Al) group was found around region 829-791 cm^{-1}.Table 4 shows the summary of chemical bonding between boiler ash, calcined kaolin and fly ash. Following Table 4, it can be seen that there is a certain bonding which does not exist in boiler ash. However, further comparison could be elaborated when boiler ash was used as geopolymer.

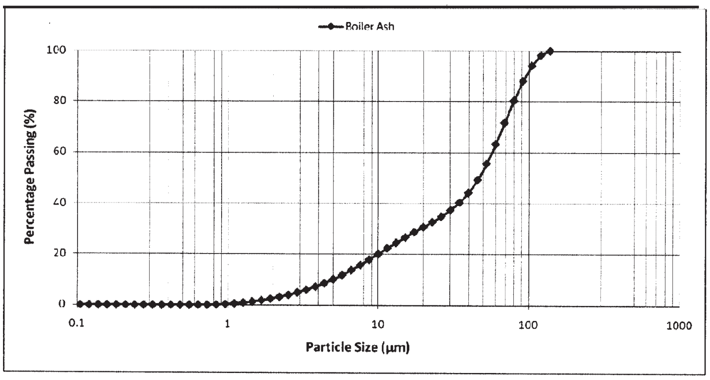

Fig. 4. Particles size distribution of boiler ash

Table 3
MEDIAN PARTICLE SIZES OF BOILER ASH CALCINED KAOLIN AND FLY ASH

Materials	Median particle size, d_{50} (μm)
Boiler ash	46.51
Calcined kaolin [38]	11.65
Class F fly ash [40]	37.73
Class C fly ash [41]	41.00

Table 4
CHARACTERISTIC FTIR BAND OF BOILER CALCINED KAOLIN AND FLY ASH

Bonds	Boiler ash (cm^{-1})	Fly ash (cm^{-1})	Calcined kaolin (cm^{-1}) [7]
Stretching vibration (-OH, HOH)	3600-2200	3500-2300 [42,43]	3422
Stretching vibration (-OH)	1426	-	-
Asymmetric stretching (Si-O-Si, Al-O-Si)	-	1200-950 [44]	-
Stretching vibration (Si-O, Al-O)	1009	1060 [14,45]	1031
Al-O or Si-O-Al	829-791	-	781
Symmetric stretching vibration (Si-O-Si)	-	800-780 [46]	-

Fig. 5. FTIR spectra of boiler ash

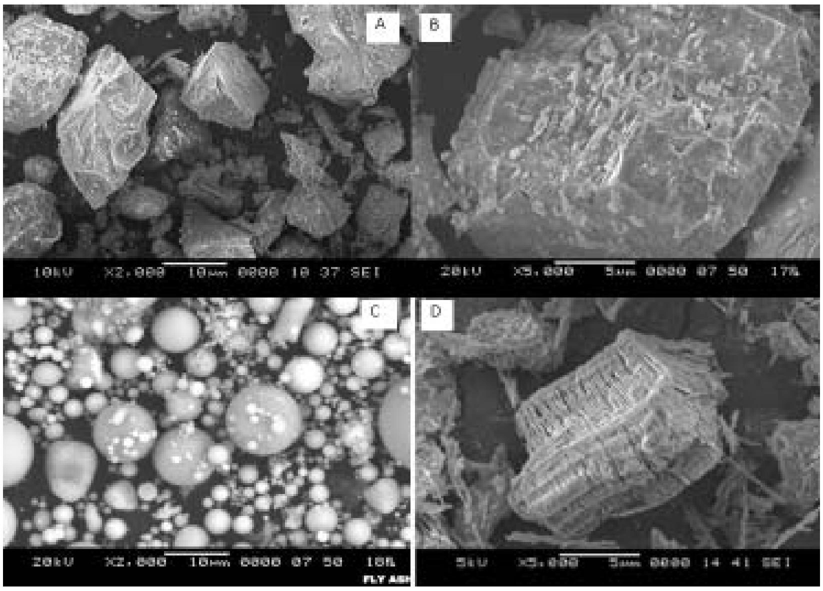

Fig. 6. Morphology studies of (a) boiler ash, (b) higher magnification of boiler ash, (c) fly ash [6], (d) calcined kaolin [7]

Morphology Study

The morphology of boiler ash is in angular, irregular and crushed shape with various sizes of particles as shown in figure 6a. Meanwhile figure 6b shows the closed up of the boiler ash particle, where the irregular and flaky surface is clearly seen. On the other hand, different particles shapes of fly ash were clearly shown in figure 6c, where it consists of spherical particles with different sizes [6]. The fly ash particles are usually hollow with some sphere shape where they may contain smaller particles in their interior [48]. The close up of fly ash surface displayed smooth surface [18] and the unshaped fragment of quartz particles also can be seen [48]. The calcined kaolin showed plate-like with layers structures [7, 49-51] as in Figure 6d. The irregular surface of boiler ash contributed to smaller surface area for geopolymerization process compared to fly ash which has sphere microstructure.

Conclusions

From this study, the below conclusion were drawn:

-the major component of boiler ash is SiO_2, followed by CaO and also Fe_2O_3. The suitability of material to be use in geopolymer is the existence of SiO_2 and Al_2O_3. Since, the boiler ash contained both of these components, thus it has the potential to be used as raw material for geopolymer;

-from the XRD analysis, it was shown that boiler ash contained quartz as major crystalline phase with highest peak at $2\theta = 27^{\circ}$;

- the particle size distribution showed that boiler ash has median particle size of 46.51μm which is in range between fly ash;

-FTIR spectra showed the stretching vibration of Si-O and Al-O at 1009 cm^{-1}, Al-O or Si-O-Al at 829-791 cm^{-1} and stretching vibration of –OH, HOH at 1426, and 3600-2200 cm^{-1};

-the microstructure of boiler ash showed that it consists of irregular surface with different sizes and shapes of particles. It was expected that boiler ash will required less liquid (small S/L ratio) than fly ash due to its microstructure morphology.

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