Comparison study between POFA and POCP in terms of chemical composition and physical properties- Review paper

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Abstract. High volume waste from agriculture industry can be utilized in concrete production instead of causing environmental problems. Palm oil fuel ash POFA and palm oil clinker powder POCP are two agricultural wastes resulted from palm oil industry. The high content of silica oxide SiO2 in the POFA and POCP are responsible for pozzolanic reaction required to improve the hydration products in the concrete mixture. However, both of POFA and POCP can be used as greener cement due to the small particle size and high surface area required to improve the mechanical properties of concrete. In addition to reduce the environmental problems due to accumulate the agriculture waste in landfills and open area.

1. Introduction
Consumption huge amount of cement led to generate CO2 and other harmful gases into the atmosphere and causing the environmental pollution [1, 2]. In 2005, the Intergovernmental Panel on Climate Change (IPCC) stated that, approximately 7% out of the total CO2 emission was resulted from manufacturing of cement [3]. Along with the rapid development, the cement manufacturing within period (2005 to 2030) will increase yearly, that will be resulted to emission high CO2 gas to reach around two times when it was in 2005 [4, 5]. Therefore, the carbon dioxide that generated from the cement manufacturing will be increasing with time and contribute in the global warming if not treatment this issue [6-8]. To maintain on the sustainable environment and renewable materials in the concrete industry, use the pozzolanic materials in concrete and cement have become popular. Hence, utilization the waste materials such as palm oil fuel ash POFA [9-11] and palm oil clinker powder POCP [12-15] are necessary to get the clean and sustainable construction materials with no problem environment.

POFA is a waste material resulted from biomass thermal power plants, it has been generated from oil palm residues which burned to generate electricity [16]. POCP is a supplementary cementitious material resulted from treatment the palm oil clinker by the grinding and heating, it has a pozzolanic reaction made it a suitable material to be as cement replacement [17, 18]. Many studies have been done by researchers on the replacement of partial weight of cement by POFA [19, 20] and POCP [12, 17] but there still remains high amount of ash abundantly available in the landfill which lead to environmental problems [17, 21]. It is reported that the maximum strength gain occurred at the cement replacement level of 30% POFA with the size of 45 μm [22]. Further increment in the ash content would reduce the strength of mortar gradually [11]. Tangchirapat and Jaturapitakkul [23] reported that increasing the fineness of POFA has positive effect on the reduction of drying shrinkage and permeability of concrete. However, few researchers have studied the effect of POFA in nano size.
The short term performances of nano palm oil fuel ash NPOFA have been studied as cementitious materials in terms of chemical and physical properties [24]. Therefore, in this paper, the comparison study of NPOFA and NPOCP as cement replacement in terms of physical properties and chemical composition and effect on the sustainable environmental will be conducted.

2. Properties of POFA and POCP

The chemical composition of POFA and POCP are shown in Tables 1 and 2, respectively. The high content of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ in POFA and POCP made it a suitable material to improve the hydration products. The sum of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ in POFA or POCP are more than 70% in many samples which meet the standards of pozzolanic reactivity [29]. The difference of the chemical composition in POCP caused by the burning conditions of boiler, feeding ratio, and the geological conditions of the palm oil trees area [15]. While, the notable differences in the chemical composition and physical properties of POFA are due to many factors also such as the burning temperature, quantity of palm oil waste in the boiler, and grinding time [25].

2.1. Physical properties of POFA and POCP

The physical properties of POFA and POCP are very important factors should be examined before chose the materials. Many physical properties such as specific gravity, particle size, colour, specific surface area, and water absorption of materials can be determined before the concrete casting. From the last studies, it illustrates that the POFA and POCP have somehow similar physical properties such as particle size and specific surface area.

2.1.1. Specific gravity. The specific gravity of unground POFA around 40% lower than that corresponding in the OPC which ranging from 1.78 to 1.97 as reported by Tay in 1990 [26]. Sata et al., [27] stated that the specific gravity of POFA increase when exposed to more grinding to get fine particle size. The specific gravity of POFA is ranging between 1.81 [28] and 2.6 [29]. While, the specific gravity of POCP is lighter than cement, it is around 2.53, while the specific gravity of cement is 3.14 and the specific surface area is about 379 m$^2$/kg [12]. Overall, as compared with POFA, the specific gravity of POCP is higher.

2.1.2. Colour. The colour of ground POFA is dark gray [30]. In general, colour of POFA is gray and becomes dark when increase quantity of unburned carbon [31]. While, the colour of POCP is blackish, the shape is irregular and porous. The organic carbon is responsible for the colour and porosity of POCP.

2.1.3. Size and shape. Generally, the particle size of POFA ranging between 1.06 and 82 µm, while POCP as cement replacement used by the few researchers such as Alnahhal et al. [12] who examined the particle size of POCP which was 37.97 µm. In terms of the shape of POFA, it is an irregular and angular shape because of its consist of crushed particles [32]. While, the shape and particle size of POCP depend mainly on the burning temperature in the boiler [13]. Figure 1 show the particle shape and size of POFA.
While, the particle shape and size of POCP can be seen in figure 2, it has an irregular shape and small size made it a suitable binding material with other concrete materials.

While, the irregular shape and porous of POCP is due to unburned carbon [36]. The unburned carbon in the POCP lead to decrease the mechanical and durability properties of concrete.

2.2. Chemical components of POFA and POCP

POFA sample has silica content more than that corresponding in POCP, this will be resulted to improve the pozzolanic activity of POFA more than that in the POCP. The high percentages of SiO$_2$, Fe$_2$O$_3$, and Al$_2$O$_3$ made it as Class F pozzolanic material [37]. The chemical compositions of POFA have been examined by many researchers as shown in table 1 below. They had various results in their experimental works, the notable variations due to various conditions such as burning temperature, quantities of palm oil to produce POFA from different factories and other factors.
Table 1. Chemical compositions of POFA by the previous studies

| Ref. | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | Na$_2$O | K$_2$O | SO$_3$ | LOI |
|------|---------|-------------|-------------|-----|-----|---------|--------|--------|-----|
| [38] | 54.0    | 0.9         | 2.0         | 12.9| 4.9 | 1.0     | 13.5   | 4.0    | 3.7 |
| [39] | 64.2    | 3.7         | 6.3         | 5.8 | 4.8 | 0.18    | 5.18   | 0.72   | 16.3|
| [40] | 65.01   | 4.68        | 3.2         | 8.19| 4.58| 0.07    | 6.48   | 0.33   | 2.53|
| [41] | 53.5    | 1.9         | 1.1         | 8.3 | 4.1 | 1.3     | 6.5    | ---    | 18.0|
| [42] | 43.6    | 11.4        | 4.7         | 8.4 | 4.8 | 0.39    | 3.5    | 2.8    | 18.0|
| [31] | 59.62   | 2.54        | 5.02        | 4.92| 4.52| 0.76    | 7.52   | 1.28   | 8.25|
| [43] | 65.3    | 2.5         | 1.9         | 6.4 | 3.0 | 0.3     | 5.7    | 0.4    | 10.0|
| [27] | 65.2    | 2.6         | 2.0         | 6.4 | 3.1 | 0.3     | 5.7    | 0.5    | 10.1|
| [23] | 65.3    | 2.5         | 1.9         | 6.4 | 3.0 | 0.3     | 5.7    | 0.4    | 10.0|
| [32] | 57.8    | 4.6         | 3.3         | 6.6 | 4.2 | 0.5     | 8.3    | 0.3    | 10.1|
| [44] | 60.42   | 4.26        | 3.34        | 11  | 5.31| 0.18    | 5.03   | 0.45   | 2.55|
| [45] | 64.17   | 3.73        | 6.3         | 5.8 | 4.87| 0.18    | 8.25   | 0.72   | 16.3|
| [46] | 69.3    | 5.30        | 5.1         | 9.15| 4.1 | --      | 11.1   | 1.59   | 1.3 |
| [47] | 51.55   | 4.64        | 8.64        | 5.91| 2.44| 0.07    | 5.50   | 0.61   | 5.00|
| [48] | 43.60   | 11.40       | 4.70        | 8.40| 4.80| 0.39    | 3.50   | 2.80   | 18.0|

Table 2 illustrated the chemical composition of POCP which investigated by the previous researches. The POCP composed different proportions of silica, potassium, alumina, and calcium oxides. The chemical composition results are different among the researchers which depend on the materials sources and treatment methods as in Table 2. The differences in the chemical composition in POCP caused by the variation in the burning temperature, the feeding ratio and operating conditions of boiler, as well as the geological conditions of the planted area [49]. The pozzolanic activity will be achieve when the total oxides of Fe$_2$O$_3$, Al$_2$O$_3$, and SiO$_2$ more than 70% of total weight.

Table 2. Chemical composition of POCP by the various studies

| Ref. | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | P$_2$O$_5$ | Fe$_2$O$_3$ | SO$_3$ | TiO$_2$ | LOI |
|------|---------|-------------|-------------|-----|-----|-----------|-----------|--------|---------|-----|
| [50] | 59.90   | 3.89        | 6.93        | 6.37| 3.30| 3.47      | 15.10     | 0.39   | 0.29   | 1.89 |
| [13] | 63.90   | 3.89        | 3.30        | 6.93| 3.37| 2.12      | 10.20     |        |        |      |
| [14] | 60.0    | 4.0         | 4.0         | 8.0 | 5.0 |           | 12.0      |        |        |      |
| [35] | 59.63   | 3.7         | 4.62        | 8.16| 5.01| 0.32      | 11.66     | 0.73   | 0.22   | 67.95|
| [17] | 62.78   | 3.41        | 6.49        | 6.89| 3.52| 0.39      | 10.54     | 0.08   | 0.21   | 3.67 |
| [17] | 64.91   | 3.53        | 6.71        | 7.12| 3.64| 0.47      | 10.91     | 0.11   | 0.22   | 0.12 |
| [51] | 59.63   | 3.7         | 4.62        | 8.16| 5.01| 0.32      | 11.66     | 0.73   | 0.22   | 1.89 |
| [52] | 59.90   | 3.89        | 6.93        | 6.37| 3.30| 3.47      | 15.1       | 0.39   | 0.29   | 70.72|
| [53] | 59.9    | 5.37        | 6.93        | 6.37| 3.13| 0.24      | 11.56     |        |        | 72.2 |
| [54] | 59.63   | 3.7         | 4.62        | 8.16| 5.01|           |           |        |        |      |
| [55] | 59.90   | 3.89        | 6.93        | 6.37| 3.30| 0.29      | 15.10     | 0.39   | 0.29   | 1.89 |
| [15] | 60.29   | 5.83        | 4.71        | 3.27| 3.76| 3.10      | 7.79      | 0.11   | 0.13   | 70.83|
| [49] | 62.52   | 0.82        | 1.10        | 16.74| 3.43|           | 8.44      |        |        | 64.4 |
| [56] | 59.9    | 3.89        | 6.93        | 6.37| 3.30| 0.32      | 15.10     | 0.39   | 0.29   | 1.89 |
| [57] | 59.9    | 3.89        | 6.93        | 6.37| 3.30| 3.47      | 15.10     | 0.39   | 0.29   | 1.89 |
| [58] | 59.90   | 3.89        | 6.93        | 6.37| 3.30| 3.47      | 15.10     | 0.39   | 0.29   | 1.89 |
| [59] | 59.63   | 3.7         | 4.62        | 8.16| 5.01| 0.32      | 11.66     | 0.73   | 0.22   | 67.95|
The main oxide in the POCP is the silica oxide SiO$_2$ which ranging between 59.63 as examined by [59] and 64.91 as examined by [17]. Karim et al. [15] studied the behaviour of POC powder as one of the cementitious materials. Many researchers investigated the pozzolanic activity of POCP by the modern techniques such as thermogravimetric analysis (TGA), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). The field emission scanning electron microscopy (FESEM) technique has been used to find out the microstructure properties of the hydrated cement paste. The SiO$_2$ and Fe$_2$O$_3$ required for the pozzolanic activity in POFA more than that in POCP, while the Al$_2$O$_3$ content in POFA less than that in POCP [12].

3. Conclusions

The POFA and POCP particles have physical properties and chemical composition made it a suitable material as cementitious material due to their specific gravity, small particle size and high specific surface area. On the other hand, the high content of SiO$_2$ in their particles led to be a pozzolanic material and produce of C-S-H gels needed for pozzolanic reactions with free lime. However, there is some different between the POFA and POCP in terms of colour, silica content, calcium oxide, whereas the calcium content in the POCP higher than that in the POFA. Overall, both the POFA and POCP have somehow similar chemical and physical characteristics and can be used as cement replacement due to similar to the cement properties.

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