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Potential of Palm Oil Fuel Ash (POFA) Layers as Secondary Raw Material in Porcelain Stoneware Application

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ABSTRACT

Porcelain stoneware is a product produced from kaolinite clay, quartz, and feldspar. This paper studies the potential of POFA layers as a secondary raw material in the porcelain stoneware application. POFA was separated to four layers. Each layer was investigated by using scanning electron microscopy (SEM) and energy dispersive X-Ray spectroscopy (EDX) in order to analyse the microstructure images and elemental analysis of POFA layers. The result was compared to all basic raw materials of porcelain stoneware for a benchmark. The result shows that the fourth layer has the largest silica content. It is the layer that has a characteristic close to the real porcelain stoneware. The microstructure and elemental analysis of POFA layers are compared with previous finding of POFA. There is little published information on POFA layers but certain POFA layers have approached the result of published POFA.

Keywords: *POFA Layer, Porcelain Stoneware, Microstructure, Element Analysis*

Introduction

The world's production of building and tiling ceramics requires huge amounts of natural raw materials, which until now mainly belong to the

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system clay–quartz–feldspar [1]. Clay provides plasticity and green strength to the body and acts as a binder. Feldspar acts as a fluxing material which generates low melting phase and helps vitrification. Quartz is a filler material which remains stable in the normal firing range and reduces distortions and shrinkage [2]. Many works demonstrate the use of waste material as a replacement material in ceramic application. Blast furnace slag [1], [3]–[5] and fly ash [3], [6]–[10] are the familiar waste materials used either as secondary flux or filler materials.

Parallel to the infrastructure boom, Malaysia's agricultural sector has also been developing over time. Palm oil is a popular vegetable oil for cooking and food processing [11]. Currently, Malaysia is the second largest global palm oil producer and exporter after Indonesia [12]. Palm oil industry had daily wastage during burning of empty fruit bunch, fiber and palm oil shell in the boiler. This wastage is called POFA. Currently, POFA usage is very limited and unmanageable, and most of it was disposed of in landfills. Figure 1 shows the summary of palm oil processing and production process of POFA. Consequently, it has caused numerous environmental problems [13]. Previous researchers claim that utilizing the waste from the palm oil industry for producing composite materials will solve the global waste issues. Usually, POFA was dried and sieved to remove coarser particles. Then, it was grounded to become ground POFA (GPOFA). It was grounded up until 90% passing 45 µm sieves [14]. More broadly, POFA could be studied in the form of treated POFA (TPOFA) where it was heated to 500 °C for 1 hour in a furnace to remove the excessive unburned carbon [14]. Advanced study of POFA is in the form of ultrafine POFA (UPOFA) by further grinding using ball mill until it reaches the meridian size of less than 1 µm [14].

Many researchers carried out studies using this POFA in concrete mixture. They found that POFA can be used as filler to increase the strength of concrete. Lightweight foamed concretes with certain percentage of POFA replacement filler obtained better strengths performance compared to the controlled specimens with solely sand filler [15]. POFA can also be potentially utilized as an effective polymer concrete filler [12].

The researchers also found that POFA can be used as a pozzolanic material in which it can improve the durability of the concrete. POFA with high fineness is a good pozzolanic material and it can be used to replace Portland cement [16]. Ground POFA and treated ground POFA are also good pozzolanic materials which can be used in massive concrete for preventing volume change and micro-cracks which are caused by thermal stresses [17].

Previously, POFA can also control the heat of hydration for a concrete. Concrete with POFA reduced the total temperature rise and it delayed the time at which the peak temperature occurred [18]. POFA can reduce the total temperature rise compared to the normal ordinary Portland cement (OPC) mortar regardless the size of POFA [14]. POFA based Self

Compacting Concrete (SCC) was more reliable as a ternary blended mix in terms of workability and heat of hydration [19]. Total heat of hydration of OPC pastes is higher than that of all other blended cement pastes containing ground POFA and treated ground POFA [17]. The POFA can also improve strength, surface resistance and water permeability of concrete containing high amount of recycled concrete aggregates [20].

Limited number of researchers use this POFA in porcelain application. Hence, the aim of this study is to introduce the potential of POFA as the secondary raw material in porcelain stoneware application. POFA was produced in terms of several layers. Previous study involving variety of waste materials in porcelain stoneware application is also reviewed as benchmark.

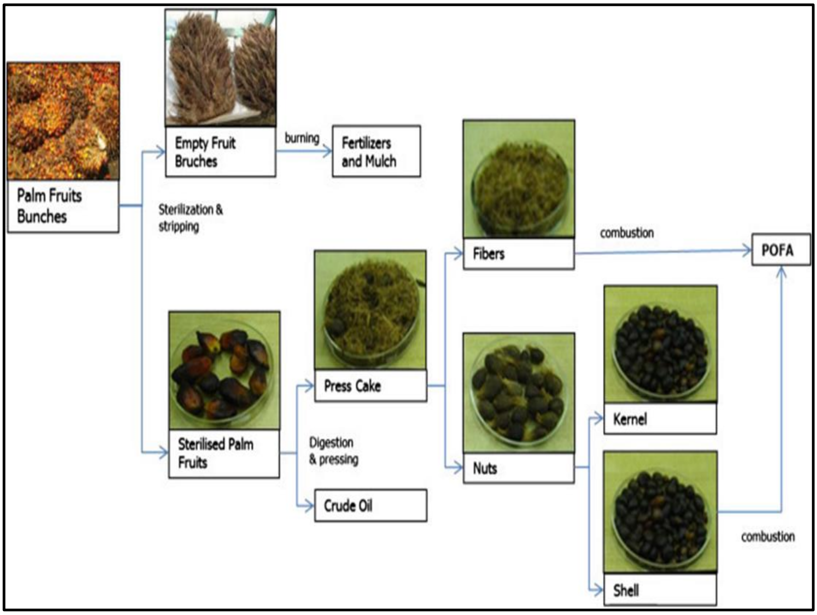


Figure 1: The schematic diagram for palm oil processing and POFA production [19]

Experimental Procedure

Main material used in this study is POFA which was collected from Genting Ayer Hitam Oil Mill, Johor, Malaysia. It includes large particles and impurities. The 500g POFA was measured for the layers formation. POFA was added with approximately 50% (volume) of water in measuring cylinder and stirred manually for 10 minutes. The mixture was left for 48 hours. The rough image of layer formation of the measuring cylinder was captured. The number of layers was determined.

In order to eliminate all moisture content, all layers were manually separated and placed in an oven at 100°C for 24 hours. Dried layers were weighted separately and milled by using ball mill (250 RPM, 30 minutes, 100 g) to achieve the desired size. The fine particle of POFA layers was characterized in terms of microstructure and elemental analysis by using the SEM-EDX analysis. The result was compared with certain studies as the benchmark.

Result and Discussion

The result shows that POFA produced four main layers based on different colors and particle sizes as presented in Figure 2. From the observation, all layers floated in the water were named as Layer 1. For all sank particles, the layer boundary between them was determined based on particle size and colors. The top layer for all sank particles is in the form of large particle of dark colors. This layer was named as Layer 2 in this study. Then, the other two layers were separated based on the saturation of colors due to almost the same particle size. The bottom layer of these two layers was named as Layer 4 while the upper layer was named as Layer 3. The arrangement of all layers was shown in Figure 2.

The image of dried POFA layers was displayed in Figure 2. From the displayed images, almost the same particle size was observed between Layer 1 and Layer 2. The difference between these two layers is that Layer 1 floated in the water. Layer 3 and Layer 4 also had almost the same of particle size. These two layers were distinguished based on the color of particles. The Layer 3 is darker than Layer 4 particles. Moreover Layer 3 had the potential to float like Layer 1 if it contains larger particle sizes.

Based on Figure 3, three points were identified and denoted as point 001, 002, and 003 for each layer. All POFA layers consisted irregular shaped particles of porous cellular surfaces. Microstructure of Layer 1 as shown in Figure 3(a) had the largest porous with cellular surfaces which push up these particles to float in water. Meanwhile, microstructure of Layer 2 as shown in Figure 3(b) had smaller porous surface compared to Layer 1 due to certain parts which have burnt incompletely. Smaller porous surface with similar particle sized caused the particle denser and sink in the water. Then, microstructure of Layer 3 as shown in Figure 3(c) showed a compact structure compared to Layer 1 and Layer 2. But the microstructure of Layer 3 showed almost a similar layer with Layer 1 but smaller in particle size. It makes Layer 3 denser than Layer 1. Lastly, microstructure of Layer 4 as shown in Figure 3(d) was compact in particle size. The smallest porous surface was presented by this Layer 4. Furthermore, this layer consisted of smaller particle size which raised its density to sink in water during layer formation process.

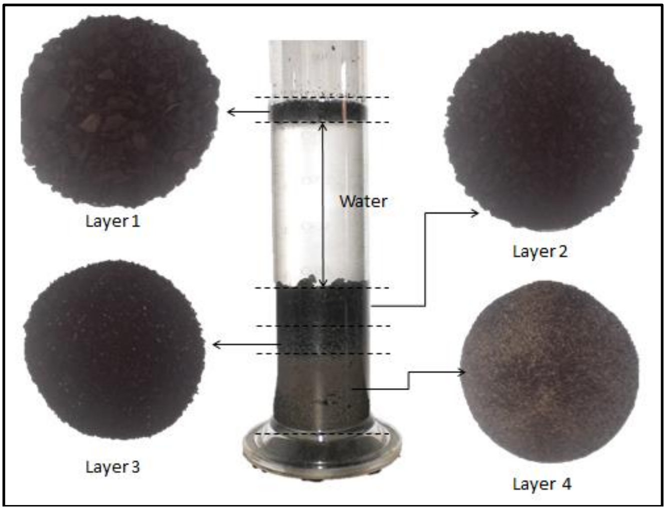
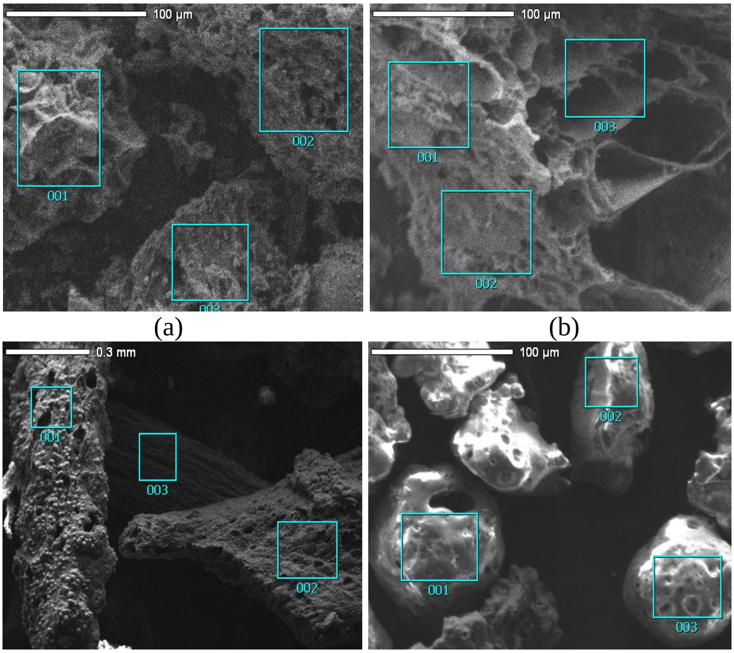


Figure 2: Layer of POFA



(a) (b)

(c) (d)

Figure 3: SEM images of POFA a) Layer 1; b) Layer 2; c) Layer 3; and d) Layer 4

Table 1 shows the chemical composition of all POFA layers from EDX analysis. Three points were denoted for each layer. The elemental analysis for each point was different from each layer. In this study, oxide of carbon and silica content was focused due to its high influence on the porcelain stoneware properties. Based on the carbon content, Layer 1 had the highest content as much as 85.16 wt %. The highest content of carbon in Layer 1 was due to 100 wt % carbon contents of the point 003 in Figure 3(a). Meanwhile, carbon contents of point 001 and 002 were 80.86 wt % and 74.61 wt % respectively. The smaller carbon content of Layer 2 compared to Layer 3 was caused by both points 001 and 002 which are around 60 wt % but exceeding 90 wt % for point 003. The Layer 4 showed the smallest carbon content that was caused by the larger silica content.

In terms of silica contents, Layer 4 had the highest percentage followed by Layer 3, Layer 1 and Layer 2. The highest silica contents of Layer 4 are point 003(67.68 wt %) followed by 002(47.39 wt %) and 001 (46.27 wt %).

Table 1: Chemical composition of the POFA layers

Oxide	**Chemical composition (%)**			
	Layer 1	**Layer 2**	**Layer 3**	**Layer 4**
C	85.16	70.88	79.68	15.55
MgO	3.28	1.66	2.25	3.99
Al2O3	-	2.20	1.40	6.85
SiO2	7.99	5.11	12.76	53.78
P2O5	4.67	-	-	3.49
K2O	4.64	6.84	1.42	6.75
CaO	5.67	13.32	2.49	3.23
FeO	-	-	-	9.55

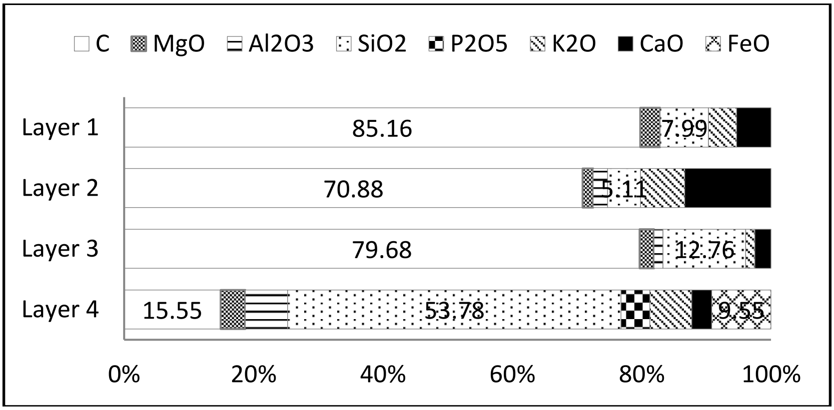


Figure 1: Trend of chemical composition of the POFA layers

Based on the result of EDX analysis, Layer 4 approached the result of previous POFA studied by certain researchers. Table 2 shows the review for chemical composition of POFA. The POFA can be in various names like ground POFA (GPOFA), treated POFA (TPOFA) and ultrafine POFA (UPOFA). Previous findings show silica as the major oxide existed. It matched the result of Layer 4 from this study. Layer 4 can be named as unground POFA if it matches with previous studies.

Table 2: Review for chemical composition of POFA

Location	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**Fe_2O_3**	**Na_2O**	**C**		**Ref**
Johor, Malaysia	4.10	1.90	53.30	6.10	9.20	1.90	1.30	-		[12]
Sarawak, Malaysia	1.46	8.99	56.23	3.13	3.21	1.06	0.56	-		[19]
Selangor, Malaysia	4.87	3.73	64.17	8.25	5.80	6.33	0.18	-		[21]
Penang, Malaysia	4.69	7.02	61.33	6.50	8.20	5.11	0.12	-	T	[22]
Penang, Malaysia	4.10	1.90	53.50	6.50	8.30	1.10	-	0.30	G	[14]
	4.10	5.30	69.30	11.10	9.15	5.10	-	0.10	U	

G: Ground POFA; T: Treated POFA; U: Ultrafine POFA

Table 3 presents the review for chemical composition of porcelain raw materials. From the review, silica is the highest oxide. The silica content usually exceeds 60 wt % except clay which is around 40-60 wt %. Based on the result of EDX of this study, only Layer 4 achieves these findings. The 53.78 wt % content of silica in Layer 4 approached the result of feldspar and quartz. Layer 4 is not suitable for clay replacement since it has low content of alumina. In terms of ferric oxide content, Layer 4 does not match the requirement of all basic raw materials. Most studies had a low content of ferric oxide of around below 2 wt % while the EDX result showed ferric oxide content was 9.55 wt %. The higher content of ferric oxide in Layer 4 must be caused by the formation of POFA layers. Usually, the POFA was sieved directly to remove all large particles. Only the remaining particles were applied for the study.

Table 3: Review for chemical composition of porcelain raw materials

	MgO	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**Fe_2O_3**	**Na_2O**	**TiO_2**	**Ref**
F	0.07	19.11	65.35	11.64	0.21	0.04	3.33	0.01	[23]
	0.03	17.29	66.48	11.95	0.31	0.14	2.94	0.02	[3]
	0.12	18.22	66.91	11.75	0.27	0.13	2.55	0.02	[24]
K-F	0.17	13.5	72.35	6.58	2.53	1.02	0.21	0	[25]
	0.17	13.5	72.35	6.58	2.53	1.02	0.21	0	[26]

	0.14	10.6	79.85	4.38	0.41	0.45	3.64	0.03	[27]
Na-F	0.19	17.82	70.11	0.59	1.32	0.3	8.97	0.06	[25]
	0.2	18.8	68.2	0.3	1.1	0.1	10.6	0.3	[28]
	0.1	18.27	70.48	0.57	0.74	0.13	0.07	0.24	[27]
Q	Trace	0.41	98.11	0.07	0.68	0.22	0.15	Trace	[29]
	0.01	0.39	98.66	0.12	0.1	0.07	0.09	0.01	[3]
	0.22	0.41	98.11	0.07	0.68	0.22	0.15	Trace	[30]
C	0.76	34.39	45.41	0.42	1.07	1.13	0.87	0.89	[3]
	0.3	36.86	47.83	1.65	0.07	0.67	0.1	0.02	[24]
	0.41	31.49	64.01	1.86	0.25	1.18	0.29	0.5	[31]

F: Feldspar; K-F: Potash Feldspar; Na-F: Soda Feldspar; Q: Quartz; C: Clay

Conclusion

In this investigation, POFA was characterized in terms of layers. The layers were determined according to particle size and colors of POFA particles. Four layers were investigated. Starting from the top layer, it was assigned as Layer 1, Layer 2, Layer 3 and Layer 4. The results on particle morphology images from SEM analysis showed that porous surface was found in all layers except in Layer 4. This explains that Layer 4 has a compact structure and a larger amount of silica compared to other layers. The result of EDX showed that POFA has a large amount of carbon. In terms of layers, only Layer 4 had a little amount of carbon content. The result of EDX was compared to the previous study. Layer 4 is the highest potential as a secondary raw material on porcelain stoneware. Layer 4 of POFA definitely had the potential to replace either feldspar or quartz.

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