The Utilization Silica from Oil Fly Ash as a Raw material for Paper Filler

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Abstract. Palm Oil Fly Ash (POFA) has been considered as a potential source of silica for paper filler. The objective of this work is to prepare a filler from the Palm Oil Fly Ash (POFA) to reduce disposal and waste problem. The extraction of silica from POFA can be carried out using solution of 5 M NaOH with ratio 1:5 (w/w, with respect to POFA), stirring speed of 600 rpm for 4 hours, resulting the 0.8770 M silica in Na2SiO3. The product is then reacted with Ca(OH)2 to produce paper filler (CaSiO3). The filler was characterized with Fourier Transform Infrared (FTIR), Scanning Electron Microscope-Energy Disperse X-Ray (SEM-EDX), X-ray Diffractometer (XRD) and Particle Size Analyzer (PSA). FTIR spectrum showed the formation of OH, C = O, Si-O-Ca and Si-O-Si functional groups, whereas the SEM-EDX analysis revealed the porous surface with the aggregation of needle-like morphology and contained five elements such as O (45,14%), Mg (0,85%), Si (15,65%), Ca (36,77%) and Al (1,59%). Meanwhile, XRD spectroscopy showed the presence of calcium silicate, calcite, vaterite, calcium hydroxide and quartz. Data from PSA analysis indicated that the filler has narrow particle size distribution compared with commercial fillers (GCC & PCC) and has small average particle size compared with PCC. The filler and the commercial counterparts were then applied as a paper simulation (hand sheet). Analysis of hand sheet showed that the presence of the synthetic filler in the hand sheet can improve brightness, opacity and bulk values, but slightly reduced in tensile and tearing index compared to that of PCC & GCC.

1. Introduction

Palm oil fly ash (POFA) is a solid waste derived from the combustion process of shell and palm fiber in the boiler [1]. The ash is considered as a waste and has not been converted into value-added materials, thus it is mostly discarded in a landfill. The previous reported [2] indicated that POFA has a high silica content (64.34% (w/w) and was considered as a useful silica source for various purposes. For example, the silica is utilized as additive to strengthen mortar [3], as precursor for the synthesis of ZSM-5 [4] and as precipitation silica [5].

Silica in POFA can be extracted through alkali extraction methods, which is based on high amorphous silica solubility in alkaline solution such as NaOH. The resulting silica could be utilized as paper filler. Other materials also could be used as paper filler such as TiO2, clay, precipitated calcium carbonate (PCC), and ground calcium carbonate (GCC) with their inherent advantages and disadvantages. Clay is reported to be useful to increase brightness, opacity, bulk, smoothness, and printability, but has drawbacks such as low brightness. PCC and GCC, on the other hand, provides a...
lower brightness and opacity [6] than TiO₂. Although TiO₂ is regarded as better paper filler than others, it is very expensive and is used only when high an optical property of the final product is required. Thus, paper industries are still focusing alternative paper filler with better properties such as new functions, and environmental friendliness [7] with acceptable price.

Filler-based silica is considered as a promising candidate, especially when is obtained from reaction of Na₂SiO₃ solution with CaCO₃ [8]. It is reported that the filler can improve the optical properties of paper compared to that of PCC. Other report [9] revealed that the paper filler produced from the reaction between calcium carbonate and silica from a coal fly ash resulted in the production of a filler with better grade of brightness, opacity and bulk than GCC [9].

The objective of this work is to prepare fillers from POFA to reduce disposal for the sustainable development. The silica from POFA was extracted with difference of NaOH concentration, ratio of fly ash to NaOH solution (w/w), stirring rate and reaction. The as-prepared fillers were characterized with several analytical techniques, and applied for the production of hand sheet properties. The hand sheet properties from the silica were compared with those obtained using GCC & PCC as the filler.

2. Experiment section

2.1. Material. The POFA was obtained form powder boiler in Perawang, Riau Province, whereas CaO was supplied from Pentawira supplier. Other chemicals include dispersant sinarpers p.a, NaOH, aquadest, sulforic acid, ammonium heptamolydate, oksalat acid, FAS + sulforic acid, fiber from hard wood (Leave bleached kraft pulp), cationic starch, anionic and cationic retention.

2.2. POFA preparation. Preparation of POFA was adapted from the method [5]. POFA was calcined at 600 °C for 2 hours, and then sieved using a mesh sieve. Prior to the extraction process, the POFA was soaked with hot water for 2 hours, then dried for 4 hours using oven at 105 °C.

2.3. Extraction silica from POFA. Silica extraction process was adapted from Zhang et al., (2008) method. In this method, silica in form of Na₂SiO₃ solution was formed from POFA by using alkali leaching process.

2.3.1. Experiment I. To determine the effect of NaOH concentration on the extraction of silica from POFA, the following experimental procedure was conducted. Briefly, 20 g of POFA was added gradually with NaOH solution ratio 1:6 (w/w) then is heated at 130 °C with stirring speed of 500 rpm for 2 hours. After filtration with whatman no. 41 of filter paper, the silica content was determined with Spectrophotometer UV DR 5000. The same procedure was also conducted with the NaOH concentration (1M, 2M, 3M, 4M, and 5M) to study the effect of NaOH concentration on the silica extraction.

2.3.2. Experiment II. To determine the influence ratio (w/w) of POFA and NaOH solution in silica extraction process, the variation of the ratio (w/w) of the POFA over the NaOH solution (1:4, 1:5, 1:6, and 1:7) was conducted. 20 g of POFA was added with 80 g, 100 g, 120 g, 140 g of NaOH 5M solution (optimum NaOH concentration in experiment I), then heated at 130 °C with 500 rpm stirring speed for 2 hours. After that the mixture is filtered with Whatman no 41, the silica content was analyzed using Spectrophotometer UV DR 5000.

2.3.3. Experiment III. The effect of stirring speed in silica extraction was investigated by following protocols. Briefly, 20 g POFA was added with NaOH 5M solution with ratio 1:5 (ratio w/w, the optimum condition in experiment II), then heated at 130 °C with different stirring speed 300, 400, 500 and 600 rpm for 2 hours. The mixture is filtered with Whatman no 41. The silica content in the different speed was analyzed using Spectrophotometer UV DR 5000.
2.3.4. Experiment IV. The effect of reaction time in silica extraction was investigated by following protocols. Briefly, 20 g POFA was added with NaOH 5M solution (ratio 1:5), then heated at 130 °C with 600 rpm with optimum stirring rate (optimum stirring rate obtained from the experiment III) for 60, 120, 180 & 240 minutes. The mixture is filtered with Whatman no 41. The silica content in the different speed was analyzed using Spectrophotometer UV DR 5000.

2.4. Synthesis and characterization of the paper filler. The synthesis of the filler was adopted from previous report [7,10]. Briefly, The CaO and H₂O were mixed with ratio (w/w) 1:4, then the product was stirred to form Ca(OH)₂. The resulting solution Na₂SiO₃ was added to Ca(OH)₂ with molar ratio 1:1, and stirred for 1.5 hours at 100 °C with additional ten small balls mill (Ø10 mm). The resulting solid product was filtered and dried at 350 °C for 2 hours. The as-synthesized filler was then characterized using X-ray diffractometer (XRD) Rigaku SmartLab 3 kW, Microscopy-Energy Dispersive X-ray (SEM-EDX) JEOL JSM-6360 LA, Fourier Transform Infrared (FT-IR) Excalibur and Particle Size Analyzer Malvern Mastersizer 2000.

2.5. Paper Properties Testing. Test method for paper properties testing was adopted from TAPPI T410 om-08 for grammage, TAPPI T 411 om-10 for paper thickness, TAPPI T 494 om-06 for tensile strength and stretch, TAPPI T 414 om-04 for tearing strength, TAPPI 452 om-02 for brightness and TAPPI T 220sp-01 for opacity.

3. Results and Discussion

3.1. POFA preparation. In the POFA pre-treatment, it is calcined at 600 °C to remove residual carbon in the ash. Carbon was known to have an adverse effect since it can form colloidal mixture which is difficult to remove in NaOH solution. Following the calcinations process, the POFA was changed in colour from blackish to gray, which was then sieved using mesh sieve 100 to generate a more uniform particle diameter. This process resulted in the increase in the ash surface, thus providing the effective washing and extraction processes. The POFA was then immersed in hot water for 2 hours, which facilitated the reduction of water soluble compounds such as potassium and sodium [5].

3.2. Extraction silica from POFA. The silica extraction process was adopted from previous report [10]. The extraction process revealed that the optimum condition for silica removal was achieved using 5 M NaOH with the ratio of the POFA to the NaOH solution of 1:5 (w/w), stirring speed of 600 rpm at temperature of 130°C. Silica can react with strong base such as NaOH [12] as shown in the following reaction below:

\[ \text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \] (1)

In SiO₂, the high electronegativity of the oxygen atom attracts electron from Si atom, giving rise to the formation of unstable [SiO₂OH] intermediate. The dehydrogenation process will occur and the second hydroxyl ions will bind to the hydrogen to form water molecules. The two Na⁺ ions will balance the negative charge formed and interact with the SiO₃⁻² ions, thus forming sodium silicate (Na₂SiO₃). The sodium silicate (Na₂SiO₃) formed is dissolved in water to produce a sodium silicate solution [13].

3.3. Extraction silica with the different NaOH concentration. In the previous report, the extraction of POFA was carried out using 2.5 M NaOH. The different NaOH concentrations: 1, 2, 3, 4, 5 M were applied to investigate the effect of NaOH concentration on silica extraction, which is below and above the reported NaOH concentrations reported in the previous studies [1,5].
Figure 1. Effect of NaOH concentration on silica extraction

From the graph in Fig. 1, it is obvious that the increase in NaOH concentration gives rise to an increase in the extraction of the silica. The maximum extraction of silica is achieved using 5 M NaOH concentration.

3.4. Extraction silica with variation ratio (w/w) of POFA: NaOH Solution.

Figure 2. Effect of ratio (w/w) of POFA : NaOH solution to silica extraction

Stirring speed plays a key role in the extraction of silica since it facilitates the transfer and collision of solute among solute particles. The effect of POFA to NaOH solution was shown in Figure 2, which revealed that there is an optimum of the ratio [11]. As shown in Figure 2, the extraction with the ratio 1:4 (w/w) is the least effective for the extraction of silica, while the ratio 1:5 is the most effective ratio for the extraction of silica has highest concentration. The results indicated that the lowest extraction of silica could be due to the lack of solvent to dissolve the POFA. Further increase in the ratio after the optimum condition achieved resulted in the decrease in the extraction of silica, which is believed to be due to the dilution of solution. Thus the ratio 1:5 (POFA: NaOH solution) is the optimum ratio for the maximum extraction of silica.
3.5. Extraction silica with the different stirring speed.

Stirring rate plays a key role for the extraction of silica since it facilitates the transfer and collision between solvent and solute molecule [12]. In the previous report, silica extraction from POFA was carried out at 300 rpm of stirring speed [14], another report used the speed of 500 rpm [4]. In this study, different stirring speeds of 300, 400, 500, 600 rpm were used to study the effect of stirring rate on silica extraction. The chosen speeds was based on the below and above of the stirring rate used in the previous study. The result from Figure 3 revealed that the increase in the stirring speed resulted in the increase in the extraction of SiO2 concentration.

3.6. Extraction silica with reaction time variation

The reaction time for the extraction of silica was also studied and the results are shown in Figure 4. It is obvious that the reaction time plays a decisive role for the extraction of silica. The longer reaction time means that more time provided for the reaction to occur. Figure 4 showed an increase in silica extraction for longer reaction time. The reaction time of 1, 2, 3 hours resulted in the increase in the silica extraction, and the concentrations of SiO2 obtained were 0.5212, 0.6123 and 0.8770 M, respectively. Previous report [5] also showed a similar result.
3.7. Characterization using FT-IR spectrum.

FT-IR is used to determine the functional group in the as-synthesized filler (Figure 5). The FTIR spectrum showed several absorption bands (peaks) on wave numbers 3426 cm\(^{-1}\), 1642 cm\(^{-1}\), 1426 cm\(^{-1}\), 1471 cm\(^{-1}\), 969 cm\(^{-1}\), 668 cm\(^{-1}\), 455 cm\(^{-1}\). The broad peak at 3426 cm\(^{-1}\) is the typical peak for the OH group \[8\]. The peak at wave number 1640 cm\(^{-1}\) is bending vibration of absorption molecular water. The peak at the 1428 cm\(^{-1}\), 1485 cm\(^{-1}\) indicated the asymmetric stretching of C = O bond. The formation of C = O groups occurred is due to the interaction between the product with carbon dioxide during the reaction process which resulted in the formation of bond between the sample with carbon dioxide \[15\]. Peak with a strong intensity at 969 cm\(^{-1}\) is a symmetrical stretching vibration of Si-O-Ca and the band with a wavelength of 455 cm\(^{-1}\) is the bending vibration of the Si-O-Si bond \[16\] The high intensity of the silica peaks indicates the presence of a considerable element of silica in the sample.

3.8. Characterization using SEM-EDX.

Figure 6. SEM analysis results of synthesis filler with magnification, (a) 5000 x (b) 10,000 x and EDX analysis of synthesis fillers

The result of SEM analysis at 5000 x and 10,000 x magnification can be seen in Figure 6. The morphology can be divided into two types: discrete and aggregate \[7\]. The synthesized filler has a morphology similar to calcium silicate from coal fly ash as reported previously \[7,17\]. The filler
surface is aggregation of needle-like particles with a porous surface. Such filler morphology can cause a free space for air [17]. EDX analysis showed that synthesized filler have 5 elements in the form of O (oxygen), magnesium (Mg), silicon (Si), calcium (Ca) and aluminum (Al). Table 1 revealed that the main components in the synthesized filler are element O (oxygen), silicon (Si) and calcium (Ca). The minor elements included 0.85% Mg and 1.85% Al, probably derived from the dissolution of MgO and Al₂O₃ species during the extraction process as reported previously [18].

| No | Element | Weight (%) |
|----|---------|------------|
| 1  | O       | 45.14      |
| 2  | Mg      | 0.85       |
| 3  | Al      | 1.59       |
| 4  | Si      | 15.65      |
| 5  | Ca      | 36.77      |

3.9. Characterization using XRD.

Figure displayed X-ray diffraction patterns of the as-synthesized filler, which is similar to the diffraction peaks of calcium silicate at 2θ = 18.1; 23.1; 25.0; 26.3; 29.5, 31.7; 32.8; 34.1; 36.0 & 39.5 (JCPDS: 01-073-1110). The XRD analysis supported the results obtained from FT-IR and SEM-EDX, where FTIR spectrum indicated the presence of symmetrical stretching vibration of Si-O-Ca at 969 cm⁻¹. In addition, the as-synthesized filler has morphology similar to calcium silicate from coal fly ash reported previously [7,6] with the chemical below:

\[
\text{Na}_2\text{SiO}_3 + \text{Ca(OH)}_2 \rightarrow \text{CaSiO}_3 \downarrow + \text{NaOH} \quad (2)
\]

Other phases also found in the filler, which are calcite and vaterite (CaCO₃), calcium hydroxide (Ca(OH)₂) and quartz (SiO₂) [15].
3.10. Brightness & Opacity of hand sheets.

Table 2. Paper Properties of Handsheet

| No | Handsheet Loaded | Bulk cm$^3$/g | Tensile Index (N.m/g) | Tearing Index (mN.m$^2$/g) | Opacity | Brightness |
|----|-----------------|---------------|----------------------|-----------------------------|---------|------------|
| 1  | Filler synthesis| 1.85          | 34.52                | 7.72                        | 89.40   | 87.90      |
| 2  | GCC             | 1.57          | 46.00                | 7.95                        | 86.35   | 87.00      |
| 3  | PCC             | 1.83          | 35.03                | 8.41                        | 87.36   | 87.50      |
| 4  | Blanko          | 1.56          | 50.45                | 10.09                       | 84.38   | 86.10      |

Table 2 showed the properties of as-synthesized filler, along with other fillers such as GCC and PCC. The as-synthesized filler has higher brightness and opacity compared with unloaded filler (blanko) and handsheets loaded with filler PCC & GCC. The handsheet loaded with the synthesized filler also has better opacity than GCC & PCC. The synthesized filler increases opacity by 5.02% compared to unloaded handsheet, better than PCC (2.98%) & GCC (1.97%). The as-synthesized filler has a smaller particle size than PCC and narrow (uniform) distribution of particles than PCC and GCC. A small particle size with a narrow particle size distribution will cause more light to be reflected and increase opacity and brightness [19]. The as-synthesis filler also has a porous surface morphology. According to previous [7] the porous morphology can have a large surface, thus increasing light scattering. This is a responsible for an increase in the brightness and opacity of paper.

3.11. Bulk and Handsheet. Bulk is one of the most important parameters for a paper. The cost of paper making will decrease if the bulk of paper increases due to the reduction of the percentage of fiber consumption. Data from Table 3. Showed that the addition of the synthesized filler increases the bulk of paper (0.298 cm$^3$/g) compared with unloaded handsheet (0.277 cm$^3$/g) and 0.03 cm$^3$/g when compared to handsheet loaded with PCC. The increasing of bulk associated with an increase in the particle size of the filler [20].

3.12. Tensile and Tearing Index of Handsheet. A filler has negative effect to mechanical strength of paper as it reduces tensile and tearing of paper [19]. Data from Table 3 showed that the handsheet without filler has the highest tensile and tearing index values, followed by GCC, PCC and the as-synthesized fillers. Common inorganic fillers produce fiber–air–filler interfaces, which result in the decrease in hydrogen bonds. Hydrogen bonds in the fiber network are critical for paper tensile and tearing strength. Thus, the tensile and tearing index of paper decrease with the increase in filler content. Fillers can be located either on the free fiber surfaces or in the pores formed by the surrounding fibers without any significant effect on the structure of the fibrous network itself. Fillers can also be located at the crossings of adjacent fibers, which cause no-bonding and significantly reduce the tensile and tearing strength.

4. Conclusion
The paper filler has been successfully synthesized using the silica extracted from POFA and Ca(OH)$_2$. The optimum condition of the extraction of silica from POFA was achieved using 5 M NaOH solution, ratio (w/w) POFA : NaOH solution (1: 5), 600 rpm stirring speed for 4 hours of extraction time. The maximum of the extraction of silica in form of Na$_2$SiO$_3$ is 0.8770 M. The characterization using FTIR, XRD and SEM-EDX indicated that as-synthesized filler confirmed the presence of calcium silicate phase with needle-like morphology on the aggregation of particles with a porous surface. PSA analysis results showed that the synthesis filler have narrow PSD compared with GCC and PCC filler. The as-synthesized filler also has smaller APS compared with PCC and larger APS.
compared with GCC. The handsheet loaded with as-synthesized filler can improved bulk, brightness and opacity values better than hansheets loaded with GCC and PCC. However, the as-synthesized filler also has slightly reduced tensile and tearing index when compared to commercial filler PCC and GCC.

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