Properties of pulverized kaolin particles via ball-to-powder weight ratios milling process: XRF and Zetasizer particle size analysis

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Abstract. Kaolin particles were pulverized in order to reduce the size by using high-energy ball milling under various ball-to-powder weight ratios. The elemental composition and particle size analysis of milled kaolin particles were carried out using X-ray fluorescence and Zetasizer particle size analyzer. The increased in ball-to-powder weight ratios have raised the amounts of oxide minerals such as K$_2$O, MgO, Fe$_2$O$_3$, TiO$_2$, CaO, SO$_3$, and LOI in the kaolin particles while reducing the concentration of SiO$_2$, Al$_2$O$_3$, P$_2$O$_5$, and MnO as compared to the control sample. Kaolin particles reached an average of 944nm in size after milling for 4hr under ball-to-powder weight ratio of 4, which is much smaller than unpulverized kaolin particles at the average mean size of 9.985µm. The energy dissipation has produced a very strong energy impacts and fractures in order to produce the number of collisions between balls and container wall in the high-energy ball milling process to allow the reduction of particles size of kaolin. This enables kaolin particles to be reduced in size and produced in the practically simple, effective, and low-cost process using high-energy ball milling. However, the continuous milling has caused the particles to agglomerate as a way to release the excessive specific surface energy and micro strains produced by high-energy ball milling.

1. Introduction

Kaolin particles are traditionally known as hydrated aluminium silicate, which are presents in nature under the form of the layered mineral. This raw kaolin particle underwent a vigorous process such as blunging, centrifuging, chemically treating, classifying, concentrating, drying, grinding, hydro cloning, magnetically treating, slurring, and sieving for it to achieve a specific level of brightness, grade, impurity, particle size, and residue. This procedure is better known as water washed kaolin which converts crude kaolin into refined kaolin particles. Kaolin particles with various sizes have been used extensively in many areas of applications such as ceramics, paints, and construction materials [1-2].

In order to reduce the particle size, the high-energy ball mill technique such as planetary balls mills are commonly used for producing smaller scale particles. This milling process can be regarded as low cost and effective way in reducing particles size and to increase the surface area of solid materials. Modification of structural and textural properties of kaolin particles through high-energy milling process can help to improve kaolin functionalization by the exposure of aluminol groups [3-4]. This
pulverization technique allows changes in the microstructure refinement and micro-deformations in the crystal lattice of the kaolin particles [4-5].

However, the particles are often associated with uneven size, and the quality of milling is relatively depends on the factors such as ball-to-powder weight ratio, rotational speed, diameter and number of balls, the material of grinding tools as well as the duration of milling. Ball mills are commonly known as high-energy mill due to the large energy dissipation during the collision and friction processes between balls and container walls [5]. This energy dissipation appears in the form of ball-wall friction, ball-wall pressure, ball-wall collision, friction between balls, the pressure between balls and clash between the spheres [4]. Besides, the behaviour and variation of particle size subjected to pulverization are largely depending on the physical properties of solid materials such as brittle and ductile attributes [5-6].

The present study involves the production of kaolin particles subjected to high-energy ball milling under different ball-to-powder weight ratios. Kaolin particles obtained after pulverization were examined by X-ray fluorescence (XRF) and Zetasizer particle size analyser to study the effects of various ball-to-powder weights ratios on elementary properties and particles size distribution of kaolin.

2. Experimental procedures
The kaolin particles as process media were purchased from Kaolin (Malaysia) Sdn. Bhd. and commercialized under the label of KM56. Pulverization of kaolin particles was performed by using Planetary Ball Mill (Fritsch Pulverisette 5) at a various ball-to-powder weight ratio of 1, 1.5, 2, 2.5, 3, 3.5, and 4 as shown in Figures 1(a) and b). The rotation speed was fixed at 350 rotations per minute in the duration of 4hr. Ball grinding media and jar materials were made of zirconia oxide. Milling process was carried out in air atmosphere at room temperature. Small amounts of pulverized kaolin particles (Figure 1, (c)) were used for characterization.

![Figure 1](image.png)

**Figure 1.** (a) High energy milling machine, (b) planetary ball milling, and (c) pulverized kaolin particles.
The elementary analysis of kaolin particles was performed by using the XRF (Bruker S1 Titan). The loss on ignition (LOI) was determined in the muffle furnace (Thermo Scientific Thermolyne F6000) at a temperature of 950°C for 2hr in accordance with ASTM D7348-13[7]. The mean size and particle size distribution of kaolin particles were determined with Zetasizer Nano ZS (Malvern Instruments), at a temperature of 25°C with ultrapure water dispersants at a refractive index of 1.33 and viscosity of 0.8872cP. The kaolin particles size was detected using dynamic light scattering at backscatter angle of 173° and refractive index of 1.57. The polydispersity index (PDI) of kaolin particles were examined and classified in order to measure the distribution and heterogeneity of kaolin particles. Table 1 indicates the classification of particles in accordance with the value of PDI.

Table 1. PDI and classification.

| PDI      | Description        |
|----------|--------------------|
| <0.05    | Monodisperse       |
| <0.08    | Nearly monodisperse|
| 0.08 to 0.7 | Mid-range monodisperse |
| >0.7     | Very broad (polydisperse) |

3. Results and discussion

3.1. Elemental properties
Table 2 presents the elemental properties of pulverized kaolin particles under various ball-to-powder weight ratios. The elemental analysis of kaolin particles revealed the significant presence of SiO₂ and Al₂O₃, which are often associated with kaolin structure. Kaolin particles are pozzolanic materials and highly reactive due to high concentrations of SiO₂ and Al₂O₃. However, the increase in ball-to-powder weight ratios during pulverization reduces the concentration of SiO₂, Al₂O₃, P₂O₅, and MnO in the kaolin particles as compared to the control were observed. There were significant differences between means of these properties to the T-test analysis at confidence level of 95% (P value <0.05).

The mechanically activated kaolin particles through high-energy ball milling have caused the fine particles to agglomerate at extremely high surface energy, in order to reduce the surface area of these particles [8]. As for SiO₂, the mechanical milling broke down the Si-O bonds inside the kaolin particles to reduce the particle size of Si-O bonds. The reduction of Al₂O₃ concentrations in the kaolin particles was due to the milling effect of zirconia oxide ball and jar materials which are known to have better mechanical properties than kaolin.

Table 2. Elementary properties of pulverized kaolin particles under different ball-to-powder weight ratios.

| Sample | Ball-to-powder weight ratio | SiO₂ | Al₂O₃ | K₂O | MgO | Fe₂O₃ | TiO₂ | CaO | P₂O₅ | SO₃ | MnO | LOI |
|--------|-----------------------------|------|-------|-----|-----|-------|------|-----|------|-----|-----|-----|
| K0     | 0                           | 64.158 | 28.589 | 2.155 | 1.865 | 1.647 | 0.982 | 0.354 | 0.127 | 0.076 | 0.048 | 16.395 |
| K1     | 1                           | 64.043 | 28.089 | 2.374 | 1.596 | 2.041 | 1.186 | 0.438 | 0.106 | 0.086 | 0.043 | 17.551 |
| K1.5   | 1.5                         | 63.471 | 27.616 | 2.415 | 2.697 | 1.976 | 1.174 | 0.404 | 0.115 | 0.091 | 0.042 | 21.126 |
| K2     | 2                           | 64.021 | 28.048 | 2.381 | 1.523 | 2.095 | 1.211 | 0.469 | 0.128 | 0.086 | 0.040 | 15.605 |
| K2.5   | 2.5                         | 63.420 | 27.711 | 2.373 | 2.651 | 1.995 | 1.155 | 0.456 | 0.107 | 0.087 | 0.046 | 17.777 |
| K3     | 3                           | 63.691 | 27.991 | 2.440 | 1.875 | 2.139 | 1.216 | 0.423 | 0.094 | 0.089 | 0.042 | 16.981 |
| K3.5   | 3.5                         | 63.374 | 27.702 | 2.382 | 2.833 | 1.957 | 1.127 | 0.389 | 0.105 | 0.081 | 0.050 | 16.466 |
| K4     | 4                           | 63.762 | 28.069 | 2.347 | 1.906 | 2.037 | 1.177 | 0.463 | 0.105 | 0.098 | 0.037 | 17.178 |
| P value |                             | 0.006  | 0.001  | 0.001 | 0.213 | 0.001 | 0.001 | 0.002 | 0.006 | 0.002 | 0.021 | 0.136 |

P value <0.05 is significant
Meanwhile, the increased in ball-to-powder weight ratios have increased the oxide minerals of kaolin particles such as K₂O, MgO, Fe₂O₃, TiO₂, CaO, and SO₃. Kaolin particles subjected to high-energy ball milling suffered defects, which are responsible for diffusion length reduction in the microstructure of mechanically activated kaolin particles to enhance the diffusivity of these oxide minerals [9]. Similarly, the LOI properties of kaolin materials were increased at various ball-to-powder weight ratios when subjected to high-energy ball milling as compared to raw kaolin particles. High LOI indicates pre-hydration and carbonation which may be caused by abrasive and fatigue wear through energy dissipation between balls and powders during milling as observed in the sample with lower ball-to-powder weight ratios.

3.2. Particles size analysis

Figure 2 shows the average mean size of kaolin particles produced by high-energy milling at the ball-to-powder weight ratios of 0, 1, 1.5, 2, 2.5, 3, 3.5, and 4 with a constant speed of 350 rpm with the duration of 4 hr. The particle size of kaolin has suddenly decreased at the initial stages of pulverization and gradually decreased at latter stages when subjected to the milling process. Kaolin particles have reached an average of 944 nm in size after milling for 4 hr under ball-to-powder weight ratio of 4, which is much smaller than unpulverized kaolin particles at an average mean size of 9.985 µm. Kaolin particles have undergone a very strong energy impacts and fractures in order to produce a number of collisions between balls and container wall in the high-energy ball milling process. This energy dissipation has produced large amounts of structural and textural defects into the milled powder particles [10]. As a result, the progressive accumulation of defects and interaction between them contribute to crystalline size refinement and expansion of lattice strain [5, 11-12].

Dry milling of kaolin particles also caused the cleavage, broken bonds, and fracturing of kaolin crystals [13]. Another reason for the reduction in the average mean size particles was due to brittle and fragile properties of kaolin as ceramics material [10, 14-15]. The high-energy ball milling also enables kaolin particles of various ball-to-powder weight ratios to be reduced in various stages of formations. The fragmented kaolin particles became ductile and flattened at the early stages, then undergone welding and fragile to form softer particles, began to be a fracture to form more refine particles, and amorphization took place at extreme condition [4].

![Figure 2. Mean size of kaolin particles under various ball-to-powder weight ratio.](image-url)
Figure 3 indicates the particle size distribution of kaolin particles under various ball-to-powder weight ratios when subjected to high-energy ball milling. Under ball-to-powder weight ratios, 100% of kaolin particles passing 6µm sizing as compared to raw kaolin at 10µm sizing. The lowest size reduction was recorded at a ball-to-powder weight ratio of 1 with 10% of sample passing 1.01µm sizing, 50% of sample passing 1.62µm sizing and 90% of sample passing 3.45µm sizing. In contrast, the highest size reduction was achieved at ball-to-powder weight ratio of 4 with 10% of sample passing 300nm, 50% of sample passing 999nm and 90% of sample passing 3.2µm.

The overall particle size analysis of kaolin particles under different ball-to-powder weight ratios is presented in Table 3 including the mean size, particle size distribution, and PDI along with a description. This fragile kaolin broke up the particles by fatigue to decrease the particles size and interlamellar spacing along with material amorphization [4]. Also, the high-energy ball mill has produced rupture to the interatomic bonds of kaolin crystals along with the formation of the supplementary surface due to the cleavage of crystalline grains [13, 16].

Table 3. Particle size analysis of kaolin particles via different ball-to-powder weight ratios.

| Sample | Ball-to-powder weight ratio | Mean size (nm) | Particle size distribution | PDI | Description |
|--------|-----------------------------|----------------|---------------------------|-----|-------------|
|        |                             | D10(nm)        | D50(nm)                   | D90(nm) |             |
| K0     | 0                           | 9985±4735      | >10µm                     | >10µm | 0.954±0.114 | Polydisperse |
| K1     | 1                           | 2314±416       | 1010±229                  | 1620±513 | 0.461±0.259 | Monodisperse |
| K1.5   | 1.5                         | 2362±1338      | 557±187                   | 1210±445 | 0.630±0.192 | Monodisperse |
| K2     | 2                           | 1629±337       | 480±110                   | 1190±258 | 0.643±0.122 | Monodisperse |
| K2.5   | 2.5                         | 2277±1023      | 419±114                   | 1120±736 | 0.821±0.186 | Polydisperse |
| K3     | 3                           | 1212±188       | 325±29                    | 1440±557 | 0.606±0.120 | Monodisperse |
| K3.5   | 3.5                         | 1495±220       | 360±83                    | 1280±448 | 0.851±0.112 | Polydisperse |
| K4     | 4                           | 944±206        | 300±49                    | 999±121 | 0.536±0.168 | Monodisperse |
The PDI values indicate the kaolin particles have appeared in the form of mid-range monodisperse (PDI between 0.08 to 0.7) as compared to a very broad polydisperse range (PDI >0.7) of original kaolin particles. However, the agglomeration of small particles is under formation in sample K2.5 and K3.5. In this ball-to-powder weight ratios, the PDI was observed at greater than 0.7 to present in a very broad polydisperse range. The impact from high-energy ball milling has produced a strong agglomeration due to the smaller size of kaolin and reactive milling reaction. During this process, the collisions between balls and primary kaolin particles have caused fracture and compact clusters to particles [17-18]. Also, higher surface area from the smaller size particles increases stronger agglomeration to the ceramic materials as kaolin. In addition, the increased in specific surface energy and micro strains produced by smaller particles during milling have contributed to kaolin materials instability [19]. Extended milling of kaolin materials has caused the particles to merge to form bigger particles as a way to release excessive energy [16, 19].

4. Conclusion and recommendation

Based on the experiments, kaolin particles were successfully pulverized using the high-energy ball milling process, which is a practically simple, effective, and low-cost process. The ball-to-powder weight ratio of 4 was the optimum case for reducing the size of kaolin particles to an average of 944 nm in size after 4 hr milling from the original size of 9.985μm. The increase in ball-to-powder weight ratios during pulverization reduces the concentration of SiO₂, Al₂O₃, P₂O₅, and MnO in the kaolin particles caused by the reduction of surface area of these particles at high energy milling. However, the oxide minerals of kaolin particles such as K₂O, MgO, Fe₂O₃, TiO₂, CaO, and SO₃ as well as LOI were increased due to abrasive and fatigue wear through energy dissipation between balls and powders during milling. Meanwhile, the PDI values indicate the kaolin particles have appeared in form of mid-range monodisperse (0.08<PDI < 0.7) as compared to a very broad polydisperse range (PDI >0.7) of original kaolin particles with the presence of agglomeration due to high energy milling impacts.

Recommendations are suggested in future studies: (i) pre-treatment methods to improve the particles conditions during high-energy milling and (ii) the pulverized kaolin particles can be incorporated into concrete materials such as ultra-high performance concrete and pervious concrete [20-21] as supplementary cementitious materials for some interesting results.

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