Prediction of size reduction by batch ball milling process for crab shell powder prior hydroxyapatite conversion

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Abstract. The crab (Portunus pelagicus) shell is a marine biowaste produced by seafood industries. Traditionally, crab shells were collected to be converted into animal feed, however many of them are disposed of as industrial waste. A conversion of crab shells into hydroxyapatite is a better option for producing high-value biomaterial. Hydroxyapatite materials can be used as slow-release fertilizer while combining them with traditional fertilizer or as a stand-alone green fertilizer with high phosphatic content. Prior to hydroxyapatite conversion, the size reduction of crab shells is required. In this study, crab shell powder is derived from dried crab shell with the water content is approximately 10% wb. The size reduction is processed by using a customized batch type ball mill. This study is aiming at determining the kinetic model of milling parameters for crab shell milling by using the ball mills. An amount of 1.5 kg of dried crabs shell was milled by using 3-size mixed metal balls. The powder was then analyzed its particle size, and the particle size is used as an input in the mathematical model. The computational study focused on the calculation of optimal rotational velocity and kinetic model during the milling process. The kinetic model was based on Population Balance Equation of the mass balance principle, and the results are compared with experimented data characterized by particle size analyzer. It is observed that there are discrepancies between the model and experimental data due to the characteristic of raw materials; however the kinetic model can be used as a prediction of particle size reduction using the ball mill without conducting the real experiment.

1. Introduction

Hydroxyapatite is potentially used as a crop fertilizer due to a high amount of phosphorus substance. A powder form of hydroxyapatite materials can be utilized as stand-alone fertilizer or acts as an absorber and releaser for conventional liquid fertilizer [1]. Hydroxyapatite can be derived from any calcium-rich materials, including marine biowaste [2]. The crab shell is excess materials collected from the seafood industry, which is usually disposed of in the environment without further treatment. The calcium compounds found in the crab shell and potentially used for many applications. In this study, crab shells were reduced its particle size by using a pilot-scale customized ball mill, prior to a conversion process into...
hydroxyapatite materials. A comparison study was conducted to evaluate the performance of the ball milling process for dry crab shell, between experimental and computational methods. The computation method was intended to define important parameters for crab shell ball milling, without spending resources via experimental works, which will help in designing the optimum operational condition.

2. Material and Method

Raw material used in this study was 1.5 kg dried crab (*Portunus pelagicus*) shell with 9.5 ± 0.12 % wet based water content. The crab shell was a marine biowaste produced by seafood industries in Pasuruan, East Java, Indonesia. The crab shell was collected from the factory, then washed and dried under the sun for 12 hours, continued by 4 hours of the electric oven. A customized-made batch type ball mill was used to mill the dried crab shell. The details specification of the ball mills can be found elsewhere [3]. The ball mill was utilized stainless steel balls with different sizes, i.e., 4.5 cm, 3.6 cm, and 2.4 cm diameter, with a mass ratio of 1:2:4, respectively. The mass ratio between the crab shell and the balls was 1:10, the combination of crab shell and the ball's volume is no more than 25% of the total volume of the ball mills. A particle size analyzer (CILAS 1090-DRY) was used to measure crab shell particles after the ball milling process, and the particle size diameter was observed between 0.1-500 μm. The mathematical model used in this study is based on the back-calculation algorithm developed previously, in which the model accumulatively measures the particle distribution from the finest to rough particles [4]. Differential equations were resolved based on Runge-Kutta formulation with the Dorman-Prince method by using MATLAB [3]. The estimated parameters were conducted by using the sum of squared error optimization between the model and experimental data by using the *Isqnonline* function in MATLAB.

The initial parameter guess was obtained from a manual simulation by learning each characteristic on the curve model fitted with experimental data. The milling parameters were \( \alpha; \); \( \alpha; \); \( \delta; \); \( \gamma; \), and \( /{\gamma}; \). These parameters represent the effect of balls quantity, the balls ratio, the rotational velocity of the ball mill, the mass ratio of crab shell powder to the balls, and the milling chamber's effective volume for particle breakage mechanism [3].

Parameter \( a \) and \( \alpha; \) were parameters related to selection function to choose and arrange a certain particle size fraction. Parameter \( a \) affects the milling rate, in which the higher \( a \) value, the faster the finest particles obtained. Parameter \( \alpha; \) affects the subsequent milling rate, in which the higher \( \alpha; \) value, the imminent particle size distribution between adjacent time.

Parameters \( \delta, \gamma, \) and \( /{\gamma}; \) related with the size reduction parameters, from initial particle size into smaller particle fraction. Parameter \( \delta \) affects the size reduction rate at the beginning of particle distribution, in which the higher of \( \delta \) value, the slower the reduction rate for the finest particles. Parameter \( \gamma \) affects the size reduction rate, in which the higher the \( \gamma \) value, the slower the reduction rate for intermediate particle fraction. Parameter \( /{\gamma}; \) affects the size reduction rate at the end of particle distribution, in which the higher of \( /{\gamma}; \) value, the slower reduction rate, or even reach a steady state for rough particle fraction.

3. Result and Discussion

The crab shell milling result was measured every hour up to 4 hours of milling process by using particle size analyzer. The particle size was observed between 0.1-500 μm and examined in contrast with a computational study using five milling parameters. From initial simulation, the prediction parameters were
α; α; δ; γ; \( \phi = 1.1096; 0.2412; 1000; 0.8109; 0.5210 \), respectively. The computational measurements were shown in Figure 1.

![Figure 1. Size distribution of crab shell powder, experimentally and computationally, from 1-4 hours of milling time.](image)

In figure 1, both experimental and computational measurements of the crab shell milling process were shown both in the logarithmic and regular scale axis. The former is able to describe the powder size from fine to rough particles, while the latter is only appropriate for rough particles.

As shown in figure 1, the logarithmic scales were able to describe a quite good fitting between the mathematical model and experimental data. The fit of fine particles was affected by the use of mixture balls with different ball diameters, i.e., 24, 36, and 45 mm. Each ball size contributed to a specific range of particle fractions. The 45 mm balls contributed mainly to a 260 μm - 280 μm particle size diameter, the 36 mm balls contributed on mainly 120 μm - 150 μm particle size diameter, and the 24 mm balls contributed on mainly 30 μm – 40 μm particle size diameter. The fitting between the model curve and experiment data were closer when the particle size below 50 μm and the discrepancies increased when the particle size was increasing. Five estimated parameters and individual confidential intervals were presented in table 1 below.
The mean diameter of crab shell powders experiment data compared to the computational model is shown in figure 2.

![Graph showing comparison between computational and experimental mean diameter of crab shell powders](image.png)

**Figure 2.** Computational and experimental of crab shell powders mean diameter.

As shown in Figure 2, the error percentage at 1 hour, 2 hours, 3 hours, 4 hours of milling were 64.61%, 90.3%, 87.33%, and 140.46%, respectively. All error percentages were above 60%, and even above 100% during the last hour. The results were different from previous measurements for porang chips [4], and it is expected that the characteristic of materials affects the accuracy of the model.

Furthermore, a significant difference between the results of the modeling and the calculation that the data used in the modeling is due to the average particle size obtained from particle size analyzer might be influenced by an interaction between particle morphology and the laser diffraction beam from the device. The laser diffraction occurred along the direction of the x-axis and not for the y-axis [5]. Larger particles have a more irregular shape (as observed by SEM and shown in Figure 3) than the finer ones for all samples. The irregular spherical shape was assumed to contribute to another source of error of laser diffraction measurements. It means that laser diffraction size results were more uniform for the different finer particle populations [6].

### Table 1. Estimated parameters value

| Parameters | Estimated Values | Confidential Intervals (x 10^9) |
|------------|------------------|---------------------------------|
| α          | 1.1096           | -0.0004                         |
| α          | 0.2412           | 0.0000                          |
| δ          | 100              | -5.8902                         |
| γ          | 0.8109           | 0.0000                          |
| φ          | 0.5210           | -0.0002                         |

The mean diameter of crab shell powders experiment data compared to the computational model is shown in figure 2.
By using the existing parameters, we can simulate the milling process for the next few hours. From the simulation results in Figure 4, it can be seen the longer the milling process, the higher the number of fine particles. However, at the last hours of milling, there are no significant differences between 8 hours to 10 hours of processing. This shows that the milling process with the most changes in particle size occurred until the 7 hours.

Figure 4. Simulation of crab shell powder size up to 10 hours of milling.

4. Conclusions
Prediction of particle size reduction of crab shells was successfully simulated by using a back-calculation algorithm model. The size reduction were $a; \alpha; \delta; \gamma; \phi = 1.1096 ; 0.2412; 1000; 0.8109; 0.5210,$
respectively. The irregular morphological shape of crab shell powder might affect the particle size measurement using a laser beam and promotes significantly high diffraction, contributed to an unbalanced result between experimental and computational crab shell powder size. The longer milling process was predicted to produce more homogenous fine particles up to 7 hours of the milling process. Beyond that time, there was no significant particle distribution obtained.

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