Preparation of Synthetic Calcium Carbonate by Continuous Method

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Abstract. The production of precipitated calcium carbonate (PCC) was performed by a continuous method with additional mechanical stirring and retardant agent after the carbonation process. The PCC was produced at four different conditions i.e. without stirring and retardant agent (XSR), PCC with stirring only (S0), PCC with stirring, and 4g of a retardant agent (S4), and PCC with stirring and 20g of a retardant agent (S20). The continuous method 1 L of PCC slurry was consistently achieved at 7 minutes of the carbonation time that was controlled for all samples. The PCC yield was generally consistent with a slight reduction with increasing the retardant agent weight. Laser Particle Size Analyzer (LPSA) showed the finest PCC, which is 5.093 µm was produced without any additional mechanism (XSR) after the carbonation process. FESEM micrographs showed there were two types of PCC structure particles; fine hollow shape and coarse irregular shape. The result of Zeta potential portrayed the negative Zeta values for all samples with the highest values of -2.9 mV for S0 sample. The high purity of high-grade calcium carbonate for all samples was determined using X-ray Fluorescence (XRF). In general, there was no significant change occurred in the morphology of the PCC but offered a larger effect on particle refinement. Meanwhile, mechanical stirring resulted in an increment of the PCC particle size, but the retardant agent provided a particle refinement effect.

1. Introduction
Calcium carbonate (CaCO₃) is commonly found in almost all living creatures, as well as in some human tissues. As for the applications, CaCO₃ is the most extensively used as a filler material in medicine, paint, food, cosmetics, ceramic, plastic, paper, and other industries. But, compared with other inorganic materials, over the year, CaCO₃ has shown promising potential for the development of smart carriers for various anti-malignant neoplastic drugs. It is biodegradable, biocompatible, and a good pH-sensitive material. These properties make CaCO₃ suitable for controlled degradability both in vitro and in vivo [1]. There are anhydrous phases of aragonite, vaterite, calcite, and hydrated phases of monohydrocalcite and hexahydrocalcite [2]. The anhydrous CaCO₃ can be classified as rhombic calcite, needle-like aragonite, or spherical vaterite.

Among them, to be the most stable phase under ambient atmospheric conditions was known as calcite [3]. The crystalline polymorphs (vaterite, aragonite, and calcite) are highly reliant on the precipitation conditions such as temperature, supersaturation, and the existence of polymeric additives. Vaterite is the first phase formed in the CaCO₃ precipitation medium, but it is also unstable and converts rapidly into calcite. Though, the vaterite phase may be stabilized for an extended period or transformed to calcite [4] in the presence of some polymeric additives. Aragonite is metastable at room temperature, and it is easily converted to calcite by changes occurring in the crystallization medium. But, this phase can be
prepared in water at temperatures approaching the boiling point of the solvent and stabilized by polymeric additives [5]. It should be emphasized that vaterite CaCO$_3$ particles have large specific surface areas with porous structures and are more hydrophilic than aragonite dan calcite. These surface properties of vaterite are promising for its uses as pigments in coating colors for high-grade ink-jet papers [6], and as a starting material of hydroxyapatite formation to prepare artificial bones or tooth [7-8].

Precipitated calcium carbonate (PCC) can be accessibly and entirely produced by the carbonation process, which is the precipitation reaction by reacting aqueous produced calcium hydroxide, Ca(OH)$_2$ recognized as milk of lime (MOL) with carbon dioxide (CO$_2$) [9]. In this paper, the quicklime and retardant agent was used to produce PCC by continuous carbonation process. A comparison of several parameters was reported in this paper to study the effect of mechanical stirring and retardant agent that was added after the carbonation process on the PCC formation.

2. Research Methodology

2.1 Materials

Quicklime and promoter agent were purchased from a local company, and purified CO$_2$ gas of 99% purity was supplied by Linde Malaysia Sdn. Bhd.

2.2 Methodology

1 L of an ionic solution containing calcium ions (Ca$^{2+}$) was prepared using quicklime as a starting material with the addition of a promoter agent. The ionic solution and CO$_2$ gas were continuously supplied into a carbonation reactor to promote the high-rate chemical reaction. CO$_2$ gas pressure, liquid air pressure, and cylinder air pressure were kept constant at 30 psi, 30 psi, and 45 psi, respectively. PCC slurry was collected, and during the collection, the slurry was mechanically stirred at 1000 rpm until the volume of slurry reached 1 L. In addition to the stirring, a few grams of the retardant agent (i.e., 4 g and 20 g) were added to study its effect on the formation of PCC. The synthesized PCC was filtered and washed using warm water to remove excess promoter agent. The filtrate was dried in an oven at 60 °C for 24 hours. Table 1 shows the list of parameters that were applied for synthesizing PCC by the continuous method.

| Sample | Stirring Rate (rpm) | Weight of Retardant Agent (g) |
|--------|---------------------|-------------------------------|
| XSR    | 0                   | 0                             |
| S0     | 1000                | 0                             |
| S4     | 1000                | 4                             |
| S20    | 1000                | 20                            |

The morphology of the synthesized PCC was evaluated using Field Emission Scanning Electron Microscope (FESEM) Supra 40V Zeiss, Germany. Analysis of the oxide element in PCC was using X-Ray Fluorescence Spectrometer, XRF-1700, Shimadzu, Japan.

3. Result and Discussion

3.1 Carbonation Process

Table 2 shows the carbonation time and produced a PCC yield. As can be seen, the carbonation process was completed within 7 minutes for the four experimental controlled parameters. This condition indicated the continuous method for producing 1 L PCC slurry was achieved continuously at a considerably high rate of carbonation produced. The produced PCC yield was almost consistent with a slight reduction with increasing the retardant agent weight, which was between 20.463 g to 21.687 g.
This finding suggested that the addition retardant agent offered no significant effect on the amount of produced PCC.

**Table 2.** Carbonation time and PCC yield produced through continuous method at the different weight of the retardant agent

| Sample | Carbonation Time (minutes) | PCC Yield (g) |
|--------|-----------------------------|---------------|
| XSR    | 7.43                        | 21.361        |
| S0     | 7.44                        | 21.687        |
| S4     | 7.50                        | 21.327        |
| S20    | 7.54                        | 20.463        |

3.2 Particle Size

Figure 1 shows the particle size of the produced PCC yield. The mechanical stirring resulted in an increment of the particle size of the PCC. As can be seen, the finest PCC particles (5.093 µm) with no additional mechanical stirring were obtained. At a stirring rate of 1000 rpm, the coarsest particle size (17.527 µm) of the produced PCC was attained with no addition of the retardant agent. The particle size was reduced to 10.258 µm by increasing the retardant agent up to 20 g. This scenario signified that the mechanical stirring resulted in an increment of the PCC particle size, but the retardant agent provided a particle refinement effect.

![Figure 1. The particle size of produced PCC at the different weight of the retardant agent](image)

3.3 Morphology

Figure 2 shows FESEM micrographs of the produced PCC under 1000 rpm without and with 4 g of the retardant agent. As can be seen, there were two apparent structures of PCC particles, i.e., fine hollow shape and coarse, irregular shape for both samples. Also, there was the presence of agglomerated particles, which was attributed to the intergrowth of PCC during its formation, thus resulted in particle enlargement. The micrographs show finer PCC particle distribution was attained with the presence of 4 g of the retardant agent. This situation explained that the retardant agent had no significant effect on the morphology of the PCC but offered a larger effect on particle refinement.
Figure 2. PCC produced under 1000 rpm of mechanical stirring; (a) without a retardant agent and (b) with 4 g of retardant agent

3.4 Zeta ($\zeta$) potential

Figure 3 shows the Zeta values for PCC with and without stirrer and retardant agent. From the graph, it is demonstrated the fluctuating value between PCC without any additional mechanism (XSR) after the carbonation process and PCC produced with an additional mechanism after the carbonation process (S0, S4 & S20). Commonly, for precipitation of CaCO$_3$ (calcite), the principal potential determining ions in solution are: Ca$^{2+}$, CO$_3^{2-}$, HCO$_3^-$ and the secondary ones are H$^+$ and OH$^-$. The neutral sites on the CaCO$_3$ surface may also be represented as -CaOH$^-$ and -CO$_2$H$. Apparently, without any mechanical disturbance (no stirring and no addition of retardant agent), the zeta potential was the most negative (-10.67 mV) among the other produced PCC. This finding suggested at this condition, the precipitation of CaCO$_3$ was dominated by negative species of HCO$_3^-$ and CO$_3^{2-}$, thus resulted in a net negative charge of calcite via hydrolysis reaction [10]. Under mechanical stirring, the Zeta potential increased (more positive), which was fluctuating between -5.66 (S4) mV to -2.9 mV (S0). The more positive Zeta potential indicated that right after the precipitation, there was a small positive net charge on the CaCO$_3$ surface, possibly originating from the surface -Ca$^{2+}$ sites [11].

Particularly, the higher the Zeta potential, the more stable it's ionic kinetic. XSR showed the highest Zeta potential meanwhile S0 gave the lowest Zeta potential. This finding can be supported by the particle size distribution (as reported in Figure 1), where the finer the particles the higher the motion. XSR with 5.093 $\mu$m particle size offered the highest kinetic stability of -10.67 mV, meanwhile, the coarsest particles (17.527 $\mu$m) of S0 gave the lowest kinetic stability with only -2.90 mV. This scenario was also supported by the FESEM micrographs as there were numerous distributions of agglomerated particles under the mechanical disturbance, thus reducing its mobility [12].
Figure 3. Zeta potential of PCC with and without stirrer and retardant agent

3.5 X-ray Fluorescence

Table 3 shows the percentage of elemental oxide in PCC samples produced in this experiment. The high content of calcium oxide above 55% indicates that the samples were provided are of high-grade calcium carbonate. The percentage of calcium carbonate can be calculated based on the calcium oxide percentage obtained from the X-ray Fluorescence result by using Equation 1. To be added to the equation, the molar mass of calcium carbonate is 56[9].

\[
\frac{\%\text{CaO} \times 100}{56} = \%\text{CaCO}_3
\]  

(1)

Table 3. Percentage of elemental oxide in PCC samples

| Type of Sample | CaO  | Fe₂O₃ | MnO  | TiO₂ | K₂O | P₂O₅ | SiO₂ | Al₂O₃ | MgO  | Na₂O | LOI  |
|----------------|------|-------|------|------|-----|------|------|-------|------|------|------|
| XSR            | 55.82| 0.16  | 0.04 | 0.03 | 0.02| 0.05 | 0.06 | 0.05  | 0.24 | 0.03 | 43.50|
| S0             | 56.90| 0.14  | 0.03 | 0.03 | 0.01| 0.02 | 0.05 | 0.03  | 0.26 | 0.03 | 42.50|
| S4             | 56.30| 0.15  | 0.04 | 0.03 | 0.02| 0.04 | 0.07 | 0.04  | 0.27 | 0.03 | 43.01|
| S20            | 57.84| 0.15  | 0.04 | 0.03 | 0.01| 0.04 | 0.06 | 0.03  | 0.27 | 0.03 | 41.50|

Table 4 shows the percentage of calcium carbonate after conversion from the percentage of calcium oxide. The result shows that all the samples produce high-grade calcium carbonate and still have the potential to go through commercialization in mass production.

Table 4. The purity of calcium carbonate produced

| Type of Sample | XSR | S0 | S4 | S20 |
|----------------|-----|----|----|-----|
| CaO (%)        | 55.82| 56.9| 56.3| 57.84|
| CaCO₃ (%)      | 99.6 | 100| 100| 100 |

4. Conclusion

Generally, the addition of mechanical stirring and retardant agents after the carbonation process of PCC did not provide a substantial significant effect on the structure and properties of PCC. The continuous method 1 L of PCC slurry was consistently achieved within 7 minutes of carbonation time that was controlled for all samples. The 7 minutes of carbonation times that was constrained for all sample did not produce a significant effect on the amount of PCC when mechanical stirring and the retardant agent
was added. The PCC yield was generally consistent with a slight reduction with increasing the retardant agent weight, which was 20.463 g (S20) and 21.687 g (S0). Also, from the results, the mechanical stirring resulted in an increment of the PCC particle size, but the retardant agent provided a particle refinement effect. The retardant agent had no significant impact on the morphology of the PCC, but it offered substantial effects on the particle refinement. It was confirmed when a PCC produced under 1000 rpm with 4g of the retardant agent (S4), it has produced particle refinement of PCC structure as compared to the PCC without the retardant agent. The purity of high-grade PCC was achieved, and all of them have the potential to be commercialized.

5. References

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