Effect of Liquid Feeding Rate on Carbonation of Precipitated Calcium Carbonate via Continuous Method

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Abstract. Precipitated calcium carbonate (PCC) is an innovative product generated from lime that significantly offers various functional characteristics in fulfilling numerous market demand. PCC is produced by hydrating high-calcium quicklime resulting slurry so-called milk-of-lime and reacting the slurry with carbon dioxide (CO2) via carbonation process. The resulting PCC product is extremely white and typically has a uniform narrow particle size distribution. PCC is available in various crystal morphologies and sizes, which can be tailored to optimize performance in a specific application. The final properties of the PCC can be diversified by controlling processing parameters. In this current work, effect of liquid air pressure corresponding to feeding rate on a formation of PCC was investigated. In enhancing the product yield, the quicklime was initially converted into a solution containing calcium ion (Ca2+) using natural promoter agent. Subsequently, CO2 gas was continuously supplied into the Ca-rich ionic solution, thus inducing carbonation reaction to form PCC. This present work showed the carbonation time of producing PCC was effectively reduced as a function of feeding rate from 15 minutes at 10 psi to only 7 minutes at 50 psi. The PCC yield slightly increased from 19 g to 23 g with increasing the feeding rate from 10 psi to 50 psi, respectively. Morphologically, the PCC particles were dominated by rhombohedral structures at various feeding rates with an indication of intergrowth mechanism. This current finding signified the increasing feeding rate offered a significant reduction of PCC production time that might be efficiently applied by the industrial manufacturers.

1 Introduction

In nature, calcium carbonate (CaCO3) can be found in sedimentary rocks (chalk, limestone), marbles and minerals (dolomite). Several typical properties of CaCO3 are 2.7-2.9 g/cm3 density, pH 11 of water suspension, 0.2-30 μm of particle size distribution, 13–21 g/100 g of oil absorption and 5–24 m2/g specific surface area [1, 2]. Attributable to their origin and path
of formation and their impurities, these carbonates have different properties. Previously, the natural CaCO₃ had been applied as a filler by processing the limestones and other minerals forming ground calcium carbonate (GCC). However, due to its uncontrollable purity and limited particles refinement, the use of GCC has restricted industrial needs.

Therefore, precipitated calcium carbonate (PCC) has been developed to form a synthetic CaCO₃. Over the years, the market demand of PCC has shown an ascending trend. This white filler has been commercially used in numerous industrial applications including in paper making, paint, polymer, and modern use as drug carrier in pharmaceutical field [3, 4]. PCC is one of a versatile classes of additives which can be categorized as multi-functional filler by providing the end user with an outstanding performance opportunity and cost reduction. In addition to its regular and controlled crystalline shape and ultrafine particle size, the hydrophobic surface coating is a good combination to benefit both material processing and subsequent physical properties [5].

In producing PCC, various techniques have been introduced and applied. In fulfilling the industrial requirement, the most economic technique is performed by converting limestone into calcium oxide (quicklime; CaO) and carbon dioxide (CO₂) through calcination at elevated temperature in excess of 900 °C [6]. During the process, natural gas is applied in order to ensure a high level of purity of the produced PCC. Subsequently, the calcined lime is slaked using water, the resulting milk of lime is purified and carbonated using CO₂ gas acquired from the calcination process. The chemical reactions of the production of PCC are as followed:

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\text{Calcination of Limestone} \quad \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad \text{(1)}
\]

\[
\text{Slacking of Quicklime} \quad \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad \text{(2)}
\]

\[
\text{Precipitation of CaCO}_3 \quad \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad \text{(PCC)} \quad \text{(3)}
\]

A complete carbonation results in a suspension of CaCO₃. The suspension is then filtered in order to attain a cake comprising 40% - 60% solid matter (depending on particle diameter). Afterward, the filter cake is dried and ground to deagglomerate the PCC particles. The production of PCC by the reaction of gaseous CO₂ with a colloidal suspension of calcium hydroxide (Ca(OH)₂) is sufficiently adaptable to produce a number of different morphologies. The PCC may present in three common crystal forms i.e. calcite, vaterite and aragonite [7, 8]. The crystal form as well the fineness of the grain can be manipulated by controlling processing factors including temperature, concentration of reactants and time [9, 10, 11]. Distinctive and reliable reaction control criteria for the production of PCC where morphology and crystalline size can be varied in order to meet the requirement [3, 12]. The ability to exert control the processing parameters enables to gain the balance of required properties. Interestingly, depending on the chemical composition of the milk of lime used and on the purifying stages during production, both technical as well as foodstuff and pharmaceutical grades of PCC can be produced and functionally applied [4, 9] in the industries.

In this present work, PCC was produced via continuous carbonation reaction by introducing CO₂ gas and ionic solution containing calcium ions (Ca²⁺) in a close reactor. In order to investigate effects of the liquid feeding rate on yield, particles size and morphology
of the produced PCC, the liquid air pressure was controlled (i.e. 10, 20, 30, 40 and 50 psi). A set of characterization was performed in evaluating properties of the produced PCC.

2 Research Methodology

2.1 Materials

Quicklime (CaO) as a calcium (Ca)-based starting material was supplied from Simpang Pulai quarry in Malaysia. Sucrose that acted as a promoter agent was purchased from a local company and compact CO$_2$ gas of 99% purity was supplied by Linde Malaysia Sdn. Bhd.

2.2 PCC Production via Continuous Precipitation

In this present work, the precipitation of CaCO$_3$ was conducted via carbonation of Ca-rich ionic solution under continuous flow of CO$_2$ gas. Prior to a preparation of Ca-rich ionic solution, disaccharide solution as a promoter agent was prepared as a medium for optimally extracting calcium ions (Ca$^{2+}$) from the Ca-based starting material. About 4 wt.% of quicklime was added into 1 L of disaccharide solution. This Ca-containing solution was mixed homogenously and left overnight in order to allow the optimum extraction the of Ca$^{2+}$ ions into the solution. Afterwards, the Ca-ionic solution was filtered in attaining a clear Ca$^{2+}$-rich ionic solution and removing any residue.

Subsequently, 1 L of Ca$^{2+}$-rich ionic solution and CO$_2$ gas were continuously supplied into a carbonation reactor to promote the high-rate chemical reaction. CO$_2$ gas pressure and cylinder air pressure were kept constant at 30 psi, and 45 psi, respectively. The effect of liquid feeding rate on the carbonation and production of PCC was investigated by varying liquid air pressure i.e. 10, 20, 30, 40 and 50 psi. The carbonation process was monitored by pH value and the process was stop at ±pH 8 where the precipitation of the CaCO$_3$ was considerably completed. The synthesized PCC was then filtered and washed using warm water to remove any excess promoter agent. The filtrate was oven-dried at 60 °C for 24 hours. The time taken for the carbonation process and weight of the PCC yield was measured.

2.3 Characterization of Produced PCC

The morphology of the synthesized PCC was evaluated using Field Emission Scanning Electron Microscope (FESEM) Supra 40V Zeiss, Germany. The particle size distribution of the PCC was measured using Fritsch Laser Particle Size Analyzer (LPSA) Analysette 22-Compact. Analysis of the oxide element in PCC was conducted using X-Ray Fluorescence Spectrometer, XRF-1700, Shimadzu, Japan.

3 Results and Discussion

3.1 Carbonation Time and PCC Yield

Fig. 1 shows carbonation time and weight of produced PCC at various feeding rates of Ca-rich ionic solution. Apparently, the carbonation time significantly reduced from 15 minutes at 10 psi to only 7 minutes at 50 psi. This phenomenon suggested that a complete precipitation mechanism of the PCC was effectively achieved at higher feeding rate. The substantial time reduction of PCC production might offer a significant impact for industry in order to enhance the efficiency and production rate of immense PCC. Meanwhile, the production of PCC yield was slightly increased as a function of the feeding rate from only 19.7 g to 23.4 g at 10 psi and 50 psi, respectively.
3.2 Particle Size Distribution

Fig. 2 shows the particle size distribution of PCC increased from 12.8 μm to 19.5 μm by increasing the feeding rate from 10 psi to 30 psi. The coarsest PCC particles at 30 psi were obtained which might be due to the particle intergrowth mechanism that occurred during the carbonation reaction [10]. This phenomenon suggested that the concentration of Ca\(^{2+}\) ions and CO\(_3^{2-}\) were considerably achieved an equilibrium thus, providing sufficient time for the PCC particles to recrystallize and grow during the carbonation time. However, a further increment of feeding rate over 30 psi resulted in higher ratio of Ca\(^{2+}\) ions to CO\(_3^{2-}\) ions. At this condition, a further growth of nucleated particles was restricted leading to formation of finer PCC particles.

![Graph showing carbonation time and weight of PCC yield at various feeding rate of Ca-rich ionic solution](image1)

**Fig. 1.** Carbonation time and weight of PCC yield at various feeding rate of Ca-rich ionic solution

![Graph showing particle size distribution of produced PCC at various feeding rates](image2)

**Fig. 2.** Particle size distribution of produced PCC at various feeding rates
3.3 Morphological Analysis

Fig. 3 illustrates the morphologies of PCC particles at different feeding rates. According to the micrographs, the PCC particles were dominantly formed in rhombohedral structure with a detection of intergrowth particles. The particle size distribution increased up to certain liquid feeding rates. Apparently, the PCC particles started to attach together with increasing rate up to 20 psi which was known as the intergrowth of particles. According to the micrograph, a further rate increment above 40 psi resulted in a formation of irregular shapes of PCC particles. In addition, there was also a formation of fine spherical particles that dispersed among the large particles. This scenario might be resulted by insufficient internal pressure for the PCC particles to grow into a stable form of rhombohedral calcites. This finding suggested that a control of liquid feeding rate was necessary in order to produce PCC particles with a certain shape or morphology.

Fig. 3. Micrograph of PCC particles at (a) 10 psi, (b) 20 psi, (c) 30 psi and (d) 40 psi

3.4 X-ray Fluorescence

Table 1 shows the contents of PCC samples produced at different feeding rates. As can be observed, the calcium oxide (CaO) content was from 54.97% to 55.30%. This relatively high CaO content approaching 56% signified that the produced PCC possessed high purity. As a confirmation, the content of CaCO₃ was calculated according to Equation 4. Apparently, the attained CaCO₃ content was about 98% which commercially might be categorized as high-
grade PCC. This current finding suggested that this continuous carbonation technique offered high potential for producing high-grade PCC effectively for commercialization in a wide range of industrial applications.

\[
\%\text{CaCO}_3 = \frac{\%\text{CaO}}{5.6} \times 100
\]

(4)

Table 1. XRF analysis of PCC samples at various feeding rates

| Feeding Rate (psi) | Content (%) |  |
|-------------------|-------------|---|
|                   | LOI         | CaO | Mg | Fe_{2}O | SiO | Al_{2}O | Mn | TiO | Na_{2}O | CaCO_{3} |
| 10                | 42.75       | 54.97 | 0.23 | 0.16 | 0.07 | 0.04 | <0.1 | <0.1 | <0.1 | 98.2 |
| 20                | 43.35       | 55.08 | 0.28 | 0.13 | 0.06 | 0.05 | <0.1 | <0.1 | <0.1 | 98.4 |
| 30                | 43.50       | 55.30 | 0.24 | 0.14 | 0.07 | 0.03 | <0.1 | <0.1 | <0.1 | 98.8 |
| 40                | 43.25       | 55.05 | 0.22 | 0.16 | 0.06 | 0.05 | <0.1 | <0.1 | <0.1 | 98.3 |
| 50                | 42.50       | 55.13 | 0.22 | 0.15 | 0.05 | 0.04 | <0.1 | <0.1 | <0.1 | 98.5 |

3.5 Whiteness and Brightness of PCC

As the most commonly used white filler, the whiteness of PCC plays significant effect of the final products. The higher the whiteness index, the higher the improvement of certain final products might be achieved. However, at relatively low whiteness index, the use of PCC might deteriorate its usefulness. According to finding of this current work, the produced PCC showed a range of 80% to 83% of whiteness and 83 to 88% of brightness (Table 2). According to TS 11653/1995 standard, the acceptable whiteness and brightness of the white filler in papermaking was >91% and >96%, respectively [1]. Thus, this condition signified that the PCC produced by this method was not suitable for papermaking but the PCC might be applied for other industrial applications including in sealant and polymer industries.

Table 2. Whiteness and brightness of PCC at various feeding rates

| Feeding Rate (psi) | Whiteness (%) | Brightness (%) |
|-------------------|---------------|----------------|
| 10                | 80.21         | 88.24          |
| 20                | 83.38         | 87.56          |
| 30                | 81.12         | 83.61          |
| 40                | 81.89         | 84.38          |
| 50                | 82.62         | 84.89          |
| TS 11653/1995     | >91%          | >96%           |

4 Conclusions

This current work showed that high-grade PCC with 98% purity was successfully produced via this continuous method. A significant time reduction in producing PCC was attained by increasing the liquid feeding rate from 10 psi to 50 psi with a reduction from 15 minutes to only 7 minutes of carbonation times, respectively. The was no apparent change of PCC yield and particle size distribution as a function of the feeding rate. The PCC morphology was dominated by rhombohedral structure with a formation of spherical particles due to the rate increment above 40 psi. The produced PCC only offered 80% to 83% of whiteness and 83 to 88% of brightness. This index was lower than the filler requirement for papermaking. However, this PCC was considerably relevant for other applications including sealant and polymer industries.
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