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Producing Precipitated Calcium Carbonate with and without Terpineol

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In this study, six experiments to produce precipitated calcium carbonate were carried out, two experiments without terpineol and four experiments with terpineol. The volumes of terpineol used were 1 mL and 2 mL with 90 % purity. The starting material used was calcium oxide. Terpineol and sucrose were used as additive. The flow rates of carbon dioxide gas used were 0.2 L/min and 2 L/min. Precipitation concept was employed in producing precipitated calcium carbonate (PCC). PCC products produced were analysed using X-ray fluorescence (XRF) and Field Emission Scanning Electron Microscope (FESEM). XRF was used to determine elemental oxides such as calcium oxide, iron oxide, manganese oxide, etc. FESEM was used to determine the morphology of the PCC produced. The highest purity of calcium carbonate obtained was from PCC3 that used 1 mL terpineol with CO_2 gas flow rate 0.2 L/min. The highest amount of PCC product produced was 20.1 g with flow rate of CO_2 gas 0.2 L/min and without terpineol. Grain shape PCC was produced with flow rate of CO_2 gas 0.2 L/min and without terpineol. Cubic shape PCC was produced with flow rate of CO_2 gas 0.2 L/min and with 1 mL terpineol.

1. Introduction

Precipitated calcium carbonate (PCC) is a versatile material that can be used in many industries such as paper making, pharmaceutical, cosmetic, paint, plastic, sealant, etc (Kirboga and Oner, 2013). PCC is also widely used in toothpaste and food industries (Mantilaka et al., 2013). The product quality produced using PCC is better compared to product produced using ground calcium carbonate (GCC). GCC is known as the cheapest inorganic material compared to others (Wang et al., 2007). The market value price of PCC is eight times higher compared to GCC because of the higher purity of PCC (Teir et al., 2005). PCC has certain grades but commonly the purity of calcium carbonate mineral is above 99 % and its density is 2700 kg/m^3 (Teir et al., 2005). Calcium carbonate presents in nature in three different types of minerals; calcite, aroganite and vaterite (Berger et al., 2009). The minerals have same chemical formula but different crystal arrangement known as polymorph. Among them, calcite is the most stable, second is aragonite and third is vaterite. The minerals also can be produced by chemical process; namely lime soda process, calcium chloride process and carbonation process (Teir et al., 2005). Xiang et al. (2004) reported that PCC can be produced by co-precipitation also known as liquid-liquid-solid route and carbonation also known as gas-liquid-solid route. In this study carbonation process was used in producing PCC because it was simple and easy to carry out in laboratory compared to the other two methods; lime soda process and calcium chloride that use more chemicals. In lime soda process, the chemicals need to produce PCC are hydrated lime and sodium carbonate. In this process PCC is the by-product and sodium chloride is the main product. In calcium chloride process, the chemicals used are hydrated lime and ammonium chloride. Both chemicals react to produce calcium chloride solution and ammonia gas. Then calcium chloride reacts with sodium carbonate to produce calcium carbonate and sodium chloride (Teir et al., 2005).PCC for commercialisation should have iron content less than 0.1 % (Teir et al., 2005). The particle shaped and polymorph formed are affected by the condition of process such as reactant concentration, temperature, aging time and additive (Sangwal, 2007). PCC with specific minerals such as calcite, aragonite or vaterite can be synthesised based on the types of additives

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used at room temperature (Kirboga and Oner, 2013). Example of additive is such as polyelectrolites which can affect the growth mechanism, nucleation, shape and sizes of the crystal (Oner and Calvert, 1994). Also reported that the carbonation process can occur at temperature around 41 ºC to 90 ºC to produce PCC products with scalenohedral shape and rhombohedral shape at temperature -1 ºC to 10 ºC. The temperature needs for the formation of aragonite is around 49 ºC (Marthur, 2001). There are many materials that can be used as starting material in producing PCC. The materials are limestones, quick lime, hydrated lime, carbide lime, calcium silicate, dolomite, etc. Zhang et al. (2012) had reported that calcium carbide residue or carbide lime can be used as starting material in producing PCC. The use of hydrated lime as starting material in producing PCC was reported by Othman et al. (2015). Also there are many modifiers or additives that can be used in producing PCC such as terpineol, calcium lignosulphate, Dispex A40V, Dispex A40, polyacrylic acid and octadecyl dihydrogen phosphate (Feng et al., 2007). The aim of using these materials is to modify certain properties of PCC final products (Feng et al., 2007). In this study, terpineol and sucrose were used as additives or modifiers in producing PCC because sucrose can increase or enhance the solubility of calcium ion in solution. Xiang et al. (2004) reported that terpineol is used as vesicant in hyrometallurgy, it can accelerate the absorption of CO_2 in producing PCC to produce nano particle size. The study showed that the increasing of terpineol can produce large and irregular shape of PCC particles because of its ability to reduce surface tension of bubbles effectively (Feng et al., 2007). Mohd Sabri et al. (2016) had reported that sucrose can be used as promoter or additive to increase the solubility of calcium ion in solution. Previous study only used terpineol as additive but in this study both additives sucrose and terpineol were used together. Both additives were used in this study because they have hydroxyl group that has the capability to attract calcium ion in solution. Sucrose has more of hydroxyl group in its chemical structure compared to terpineol. The objective of this study is to investigate the effect of using terpineol in producing the highest purity and on morphology of PCC.

2. Materials and Methods

Materials used in this study are quick lime or calcium oxide (CaO), sucrose, terpineol, carbon dioxide gas and filtered water. Carbonation method is used in this study.

2.1 Materials

Quick lime was obtained from a quarry in Simpang Pulai, Ipoh, sucrose was obtained from local shop, purified terpineol 90 % (Merck, Germany), purified CO_2 gas 99 % was supplied by Linde Malaysia Sdn.Bhd., Selangor.

2.2 Methods

For ionic solution preparation, 100 g of sucrose was dissolved in 1 L of filtered water contained in 3 L beaker. Then, 36 g of quick lime was added and the solution was stirred at 1000 rpm by mechanical stirrer for 15 min. The solution was filtered by using whatman filter paper no.1. The calcium sucrate solution obtained was used for carbonation process in producing PCC. In this study, six experiments were carried out; two experiments without terpineol and four experiments with terpineol. The two experiments without terpineol used sucrose as additive and the flow rate of carbon dioxide gas introduced into the calcium sucrate solutions were 0.2 L/min and 2 L/min. The first and second experiments were named PCC1 and PCC 2. The following four experiments used terpineol, in which third and forth experiments used 1 mL terpineol and the CO_2 flow rates were 0.2 L/min and 2 mL/min whilst fifth and sixth experiments used 2 mL terpineol and the CO_2 flow rates were 0.2 L/min and 2 L/min. The experiments were named PCC3, PCC4, PCC5 and PCC6. Figure 1 shows the carbonation process. Figures 1(a) shows the terpineol was added into ionic solution before the carbonation process. Figures 1(b) and 1(c) show the carbonation process before and after completion. Figure 1(d) shows one of the PCC products produced in the experiments.

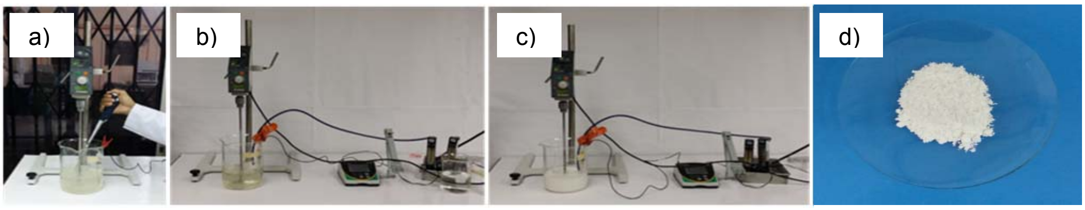

Figure 1 : Carbonation process (a) terpineol was added into ionic solution, (b) before, (c) after completion and (d) PCC product

In carbonation process, carbon dioxide gas was introduced into ionic solution (calcium sucrate) until the pH of the solution reached 8 and then, the flow rate of CO_2 gas was terminated. The mechanical stirring rate used was 1000 rpm and the experiments were carried out at room temperature around 30 °C to 33 °C. The solution that contained PCC was filtered using whatman filter paper no. 1. Then, the residue was rinse by hot water to wash the sucrose. The residue was dried in oven at 60 °C for 6 h.

3. Results and Discussions

Table 1 shows the results of the six experiments that were carried out in the laboratory in producing PCC. The results demonstrate that amongst the six experiments, experiment 1 (PCC1) with flow rate of CO_2 gas 0.2 L/min and without terpineol produced the highest weight, 20.1 g of PCC compared to others especially experiments 3 and 5 that used same flow rate of CO_2 gas but with the presence of 1 mL and 2 mL terpineol.

Table 1: Experimental parameters and results

No. of sample	Volume of Ionic solution (L)	Volume of terpineol (mL)	pH of ionic solution	CO_2 gas flow rate (L/min)	Time for carbonation process completed (min)	Product weight (g)
PCC1	1.0	-	13.0	0.2	30.4	20.1
PCC2	1.0	-	13.0	2.0	9.9	19.2
PCC3	1.0	1.0	13.0	0.2	36.2	17.8
PCC4	1.0	1.0	13.0	2.0	10.7	16.6
PCC5	1.0	2.0	13.0	0.2	33.9	17.0
PCC6	1.0	2.0	13.0	2.0	14.4	18.5

Figure 2 portrays the weights of PCC produced in relation to the flow rate of CO_2 gas. Both experiments without terpineol produced higher products compared to other four PCC products produced with terpineol. In experiments using terpineol with flow rate of CO_2 gas 0.2 L/min, the weight of PCC produced using 1 mL terpineol is higher than PCC produced using 2 mL terpineol. However, in the experiments using terpineol with flow rate CO_2 gas 2 L/min, the weight of PCC produced using 2 mL terpineol is higher than PCC produced using 1 mL terpineol. From the result it can be concluded that the presence of terpineol in calcium sucrate solution does not contribute to the increasing amount of PCC produced. In the experiments with terpineol, the amount of PCC products produced are affected by the volume of terpineol and flow rate of CO_2 gas as shown in PCC6.

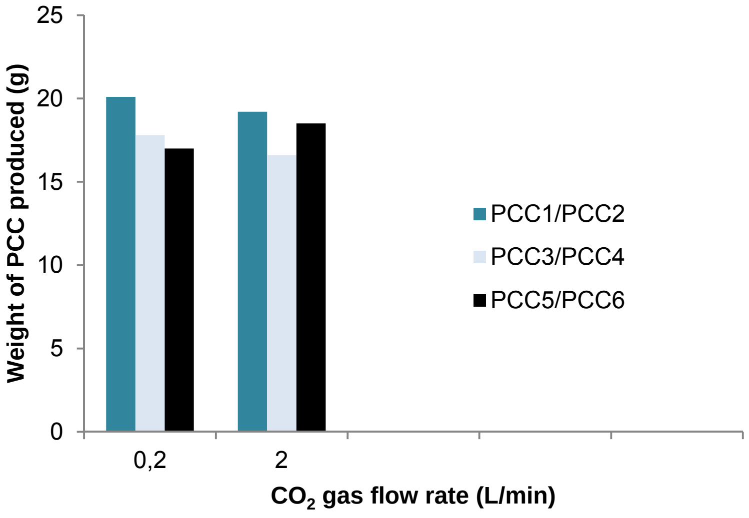

Figure 2: The effect of CO_2 gas flow rate in producing PCC

The completion time for carbonation process shows that experiments without terpineol took shorter time than experiments that used terpineol as portrays in Figure 3. Figure 3 also shows that the time for carbonation process is shorter by using flow rate of CO_2 gas 2 L/min in the experiments with or without terpineol compared to experiments with flow rate 0.2 L/min. Based on the experiments that were carried out, terpineol has retarded the formation of calcite mineral during the carbonation process. Calcite mineral is one of common calcium carbonate minerals besides aragonite and vaterite.

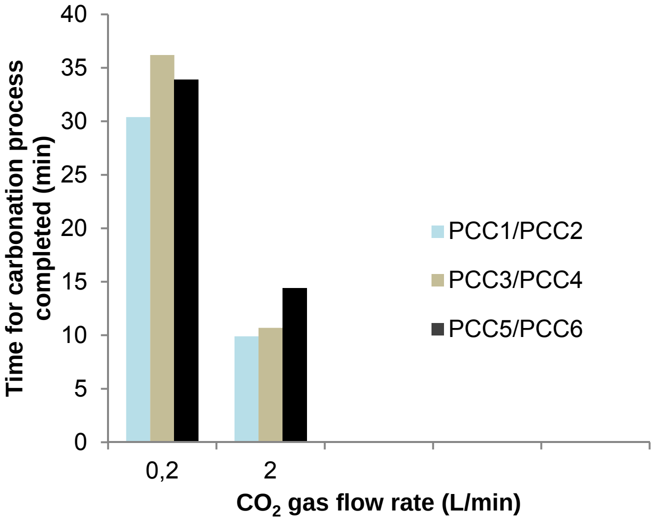

Figure 3: Time for carbonation process to complete

In this study X-ray Fluorescense (XRF – 1700, Shimadzu, Japan) was used to determine the presence of oxide metals in PCC products produced. Nowadays, X-ray Fluorescense is widely used in analysing chemicals content in materials science such as in calcium carbonate, dolomite, clay, etc.

Table 2 shows the percentage of elemental oxide in PCC products produced in the experiments. The high content of calcium oxide above than 55 % indicates that the product produced is of high grade calcium carbonate. Percentage of calcium carbonate can be calculated based on the calcium oxide percentage that obtained from X-ray Fluorescence result by using Eq(1). 56 is molar mass of calcium oxide. Table 3 shows the percentage of calcium carbonate after conversion from percentage of calcium oxide. The result shows that PCC3 recorded 99.8 % of calcium carbonate content which is considered as high grade calcium carbonate (Teir et al., 2005) and other PCC products also attained quite high grade calcium carbonate. All PCC products produced have potential to be commercialised (Teir et al., 2005). Based on the X-ray Fluorescence result, the experiment using 1 mL terpineol with CO_2 gas flow rate 0.2 L/min (PCC3) is the suitable parameter in producing the highest percentage of calcium carbonate compared to others. Terpineol can be used as material to increase the purity of calcium carbonate content in PCC.

$$\frac{\%CaO}{56}x100 = \%CaCO_3 \qquad (1)$$

Table 2: Percentage of elemental oxide in PCC products

No. of sample	Elemental oxide (%) CaO	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	Na_2O	K_2O	LOI
PCC1	55.16	0.23	0.04	0.06	0.02	0.29	0.14	0.02	44.00
PCC2	55.41	0.17	0.05	0.04	0.01	0.16	0.11	0.02	44.00
PCC3	55.87	0.27	0.05	0.06	0.02	0.28	0.12	0.02	43.28
PCC4	55.43	0.30	0.06	0.06	0.01	0.26	0.14	0.02	43.68
PCC5	54.99	0.37	0.04	0.07	0.01	0.31	0.16	0.02	44.00
PCC6	55.22	0.19	0.06	0.06	0.01	0.30	0.09	0.02	44.00

Table 3: Percentage of calcium carbonate produced

No. of sample	PCC1	PCC2	PCC3	PCC4	PCC5	PCC6
CaO (%)	55.16	55.41	55.87	55.43	54.99	55.22
$CaCO_3$ (%)	98.5	99.0	99.8	99.0	98.2	98.6

Field Emission Scanning Electron Microscope (Merlin, Zeiss, Germany) was used to determine the morphology of the PCC produced. Figure 4 shows the FESEM micrographs of PCC1 and PCC3. Based on the FESEM analysis grain shape was produced from PCC1 and cubic shape was produced from PCC3. Both of the PCC products used similar flow rate of CO_2 gas that was 0.2 L/min but PCC1 without terpineol and PCC 3 with 1 mL terpineol. Figure 4 also shows that particle size of PCC1 is more finer compared to particle size of PCC3. It means that by using terpineol the particle size of PCC can be increased.

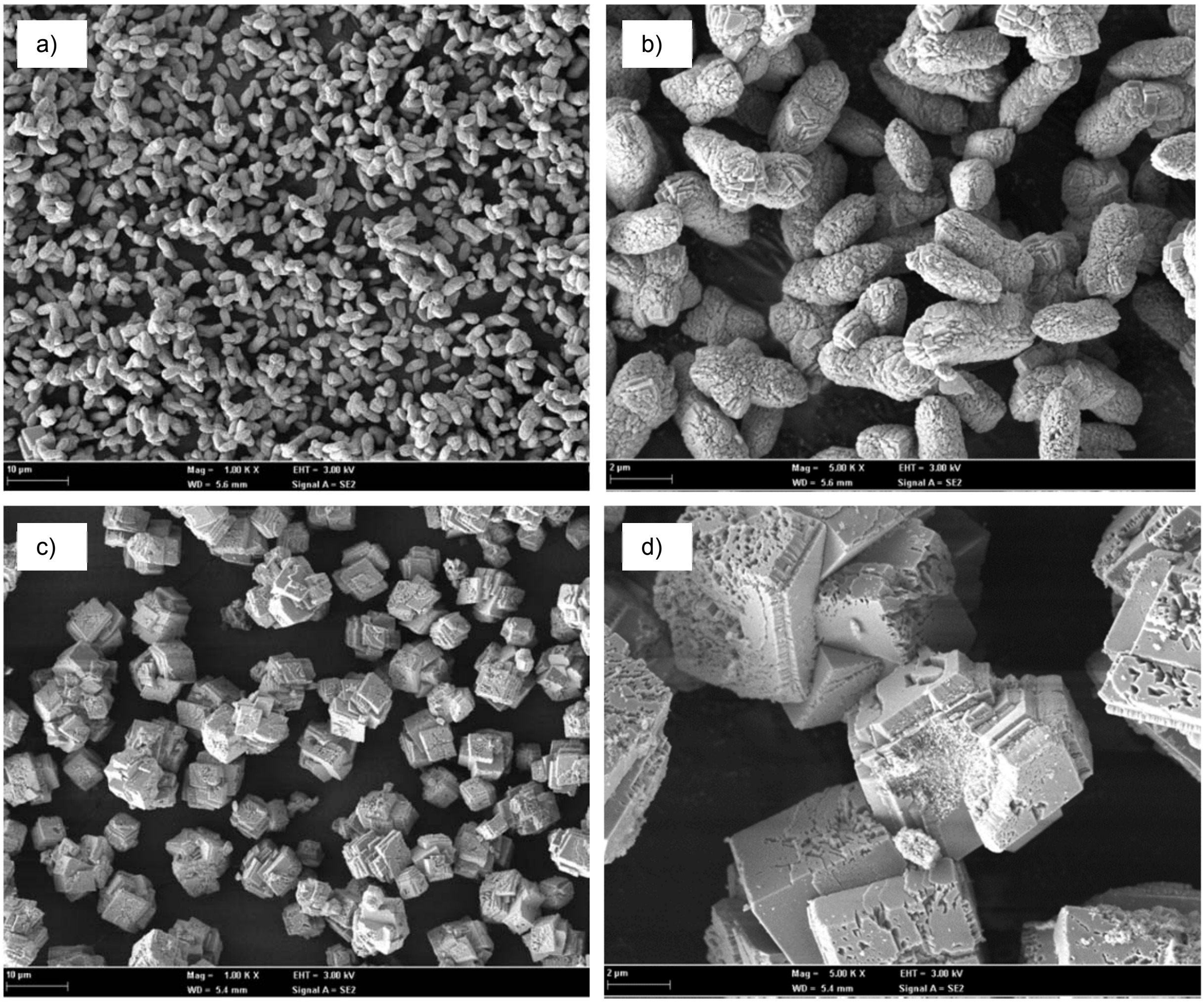

Figure 4: Fesem micrographs of (a) PCC1 with magnification 1000 times, (b) PCC1 with magnification 5000 times, (c) PCC3 with magnification 1000 times and (d) PCC3 with magnification 5000 times

4. Conclusions

From the results, it can be concluded that PCC1 product with flow rate of 0.2 L/min and without terpineol produced the highest weight, 20.1 g of PCC. Time for carbonation process to complete is shorter in the experiments that were carried out without terpineol and with the flow rate of CO_2 gas 2 L/min. XRF result shows that PCC3 product produced from solution with added 1 mL terpineol and flow rate of CO_2 gas 0.2 L/min gives the highest purity of calcium carbonate, 99.8%. The significance of this study is to demonstrate that by using terpineol the purity of calcium carbonate can be enhanced, in this case 99.8 % purity was obtained in PCC3. With flow rate of CO_2 gas 0.2 L/min and without terpineol the grain shape PCC was produced and whilst with 1 mL terpineol cubic shape was produced. Other effect of using terpineol was it also can increase the particle size of PCC.

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