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Precipitated calcium oxide nanosize from limestone and blood clam shells

Caecilia Pujiastuti[1]*, Srie Muljani[1], Ketut Sumada[1]
[1] Chemical Engineering Study Program, Faculty of Engineering, Universitas Pembangunan Nasional Veteran Jawa Timur, Indonesia

* Corresponding author's e-mail: caecilia.tk@upnjatim.ac.id

ABSTRACT
Calcium oxide (CaO) is a product that is needed by various industries, such as the pharmaceutical, chemical, agricultural and health industries. CaO is generally produced by the calcination method of CaCO3 materials such as calcium carbonate rocks or from various types of shells. The calcination method requires a large amount of energy because the operating temperature is above 1000 C and the resulting calcium oxide product is still micrometer size. This study developed nanosized precipitated CaO from two calcium sources: blood clam shells and limestone. For clam shells use hydrochloric acid as a solvent, sodium hydroxide as a precipitating agent, while for limestone using phosphoric acid as a solvent and potassium hydroxide as a precipitating agent. The effect of acidity (pH) and calcination temperature on the characteristics of the precipitated CaO was observed. The blood-clam shell produces precipitated CaO 85-92 % with a particle size of 200-250 Nm and the limestone produces precipitated CaO 42-66% with a particle size of 250-300 Nm.

Keywords:
calcium oxide; calcium carbonate; calcination; precipitation; blood clam shell

Introduction

Calcium oxide (CaO) is a product that is needed by various industries, such as the pharmaceutical, chemical, agricultural and health industries (Buasri et al., 2013; Lesbani et al, 2016; Widiarrti et. al, 2017). CaO is generally produced by the calcination method of calcium carbonate ($CaCO_3$) materials such as calcium carbonate rocks (Lailayah et al, 2012) or from various types of shells, from eggs shell (Nuryantini et al, 2019; Murakami et al, 2007), from blood clam shells (Yahya et al., 2016; Walendraet al., 2020) also from chicken bones (Mohadi et al., 2013). The calcination method requires a large amount of energy because the operating temperature is above 1000 °C and the resulting calcium oxide product is still micrometer (μm) in size. The method used to produce calcium oxide from limestone is by evaporating CO_2 gas at 700 °C and obtaining CaO nanoparticles (Munawaroh et al., 2018; Itodo et al., 2017; Ives et al., 2015). Calcium oxide size 26 nm can also be made from chicken eggshells by physical method Ashok et al., (2014). Calcium oxide can be produced from dragon fruit peel extract reacted with $CaCl_2$ $2H_2O$ as a precursor of calcium metal in the system (Ramli et al., 2019).

Referring to the problem of energy use and the size of the calcium oxide product, a research was carried out using the precipitation method. The reaction mechanism for calcination is as follows (Ramli, et al. 2019; Mutamah, 2011):

$$CaCO_{3\,(s)} \longrightarrow CaO_{\,(s)} + CO_{2\,(g)} \qquad (1)$$

The reaction mechanism (1) requires a high temperature above 1000 °C. The reaction mechanism for the precipitation method is as follows (Khaira, 2011; Ramli, 2019):

$$CaCO_{3\,(s)} + 2\,HCL_{\,(l)} \longrightarrow CaCl2_{\,(l)} + H_2O_{\,(l)} + CO_{2\,(g)} \qquad (2)$$

$$CaCl_{2\,(l)} + H_2O_{\,(l)} + 2NaOH_{\,(l)} \longrightarrow Ca(OH)_{2\,(s)} + 2\,NaCl_{\,(l)} + H_2O_{\,(l)} \quad (3)$$

$$Ca(OH)_{2\,(s)} \longrightarrow CaO_{\,(s)} + H_2O_{\,(g)} \quad (4)$$

The reaction mechanism (2) and (3) take place at room temperature, and the reaction mechanism (3) take place at a temperature 500 – 600 °C.

Methods

Research materials

The source of carbonate is Calcium carbonate rock ($CaCO_3$) obtained from Bandung and blood clam shells obtained from the fish market in Bandar Kediri. Hydrochloric acid (HCl) 5N as a solvent for blood clam shells and phosphoric acid (H_3PO_4) 10N as a solvent for calcium carbonate rock. The sodium hydroxide (NaOH) solution is used for precipitation blood clam shells and potassium oxide (KOH) solution for precipitation of calcium carbonate rock.

Research methods

This research, aim to study the effect of raw material and solvent types on the characteristic of calcium oxide precipitated (Itodo et al., 2017). The blood clam shells are milled until 100 mesh, dissolved with 5 N of HCl, filtration to get filtrate. The filtrate was added to NaOH solution until the acidity degree (pH) of 7, 9, 11, and 13 were reached and produced solids precipitated. The precipitate is filtered, washed until neutral pH and dried in an oven at 100 °C. The solid product of drying is $Ca(OH)_2$. The $Ca(OH)_2$ was calcined at temperatures of 300, 400, 500, 600 and 700 °C for 3 h. For limestone, dissolved with 5 N of H_3PO_4 solution, then the filtrate was added with the KOH solution until the pH of 5, 7, 9 and 11 were reached and produced solid (precipitate). The precipitate is filtered and dried in an oven at 100 °C. The precipitated product is $Ca(OH)_2$. The $Ca(OH)_2$ was calcined at temperatures of 300, 400, 500, 600 and 700 °C for 3 h. The precipitated CaO was characterised using SEM-EDX and X-ray Fluorescence.

Results and Discussions

The characteristic of the blood clam shell and calcium carbonate material is shown in table 1. The source of calcium from blood clam shells and limestone contains CaO 97.49% and 98.75%, respectively.

Table 1. The Characteristic of blood clam shell and calcium carbonate rock material

No	Parameter	Materials (%)	
		Blood clam shell	**Calcium carnonate rock**
1	CaO	97.490	98.750
2	Fe2O3	0.949	0.715
3	CuO	0.031	0.031
4	MnO	0.097	0.340
5	Yb2O3	0.420	----
6	Lu2O3	0.100	0.170

Figure 1 shows the effect of the acidity degree (pH) and the temperature of calcination on the CaO content in the precipitated CaO. The concentration of calcium in the precipitated CaO prepared from clam blood shells increased with increasing pH and calcination temperature. It can be explained that the evaporating crystal water will increase at higher calcination temperature.

With an increase in temperature, the energy to evaporate the crystal water contained in calcium oxide becomes greater. Thus the evaporation of crystal water contained in calcium oxide becomes more.

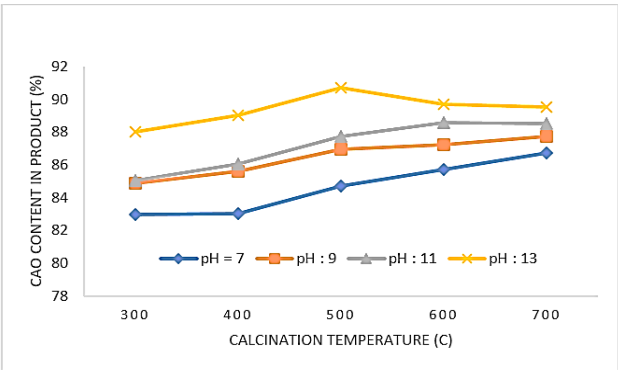

Figure 1. The effect of pH and the temperature of calcination on the CaO content in the precipitated CaO prepared by clam blood shells

The CaO content in the precipitated calcium oxide product ranges from 85 – 92%. The product still contains impurities such as sodium chloride (NaCl); this is shown in the reaction (3).

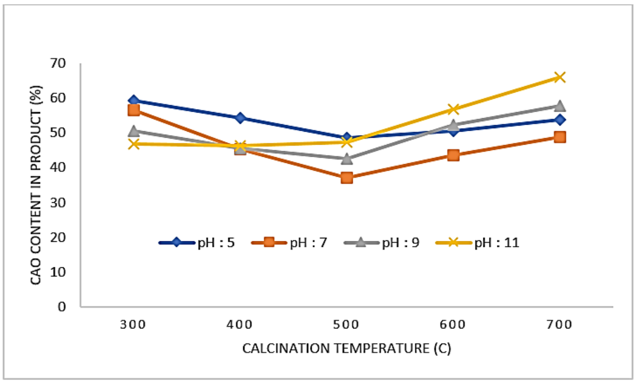

Figure 2. The effect of pH and the temperature of calcination on the CaO content in the precipitated CaO prepared by limestone

The calcium concentration in the precipitated CaO prepared from limestone decreases from 300 to 500, then increases with the calcination temperature up to 700 °C. The best calcination temperature condition is at 300 C and 700 °C. Calcium oxide content in calcium oxide products ranged from 35 – 66 %. The calcination temperature of Calcium carbonate at 700 ^{o}C for 7 hours (Lesbani, 2016) and at 900 ^{o}C for 3 hours of clam blood shells (Mohadi et al., 2013; Yahya et al. 2016) will produce high concentrations of calcium oxide.

The product still contains impurities such as potassium oxide (K_2O) and phosphorus pentoxide (P_2O_5), ranged 35 – 65%. The high level of impurities, as shown in figure 3 is due to the use of phosphoric acid as a solvent and potassium hydroxide as a precipitation agent. The precipitated CaO crystal size prepared by blood clam shells and limestone is shown in Table 2.

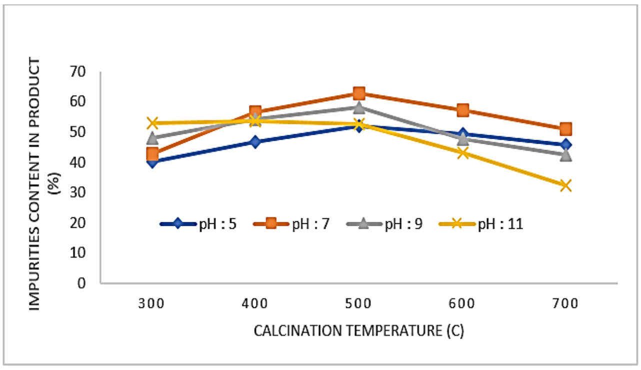

Figure 3. Impurities content in product with calcium carbonate rock material

Table 2. The precipitated CaO crystal size at temperature calcination of 500 °C

No	Acidity degree (pH)	CaO Crystal Size (Nm)	
		Blood clam shell	**Calcium carnonate rock**
1	7	202	250
2	9	215	260
3	11	240	255

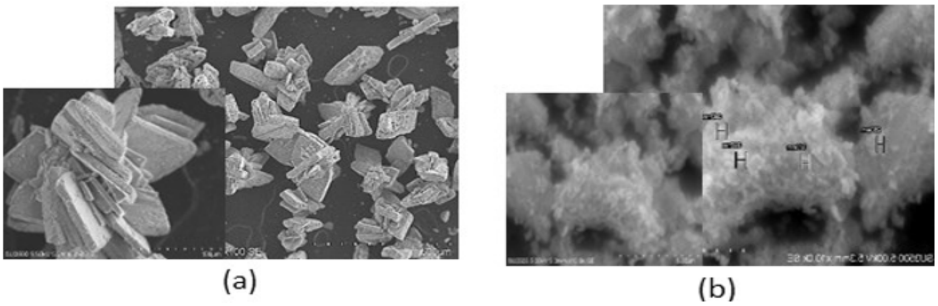

Figure 4. SEM Image of precipitated CaO prepared by blood clam shells at (a) pH 7 and (b) pH 11

The morphology of CaO measured by scanning electron microscopy (SEM) is presented in Figures 4 and 5. Visual SEM data of precipitate CaO prepared from blood clam shells showed a different morphology than precipitated CaO from carbonate rock (limestone). The surface structure of the CaO agglomerates changes with changes from pH 7 to pH 11.

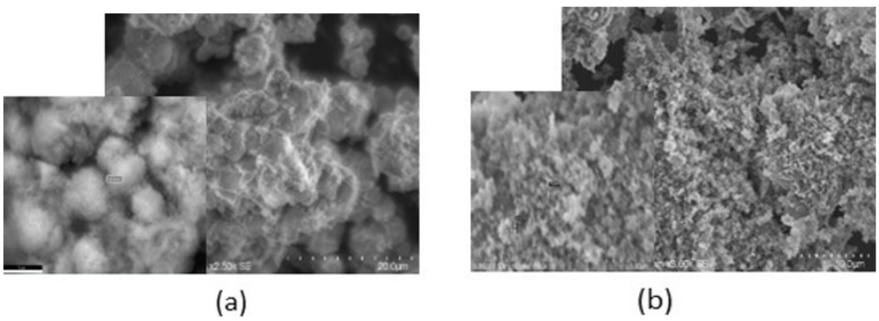

Figure 5. SEM Image of precipitated CaO prepared by carbonate rock material at (a) pH 7 and (b) pH 11

Observation at the SEM EDX analysis found that precipitated CaO prepared by blood clam shells has a slightly smaller crystal size than precipitated CaO prepared by limestones. The CaO precipitated from blood clam shells contains small impurities. The difference in solvent (HCl and

H_3PO4) may influence purity level due to the presence of elements or compounds trapped in the precipitated product. If used phosphoric acid as a solvent, the particle size is still larger than used chloric acid (HCl) because the product still contains more impurities, namely phosphor (P) and sodium (Na). If used a chloric acid, the impurities are sodium chloride (NaCl). The reactions that occur when using phosphoric acid as a solvent (Hussain, 2015) and (Habraken, 2016):

$$CaCO_{3\,(s)} + H_3PO_{4\,(l)} \longrightarrow CaHPO_{4\,(l)} + H_2O_{(l)} + CO_{2\,(g)} \tag{5}$$

$$CaHPO_{4\,(l)} + H_2O_{\,(l)} + NaOH_{\,(l)} \longrightarrow Ca(OH)_{2\,(s)} + NaHPO_{4\,(l)} \tag{6}$$

$$Ca(OH)_{2\,(s)} \longrightarrow CaO_{\,(s)} + H_2O_{\,(g)} \tag{7}$$

Conclusion

The effect of acidity (pH) and calcination temperature on the characteristics of the precipitated CaO was observed. The blood-clam shell produces precipitated CaO 85-92 % with a particle size of 200-250 Nm and the limestone produces precipitated CaO 42-66% with a particle size of 250-300 Nm.

Acknowledgments

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Conflicts of interest

The authors declare that there are no conflicts of interest.

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