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Production of Precipitated Calcium Carbonate (PCC) using Continuous Stirred Bubble Reactor (CSBR)

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ABSTRACT

Precipitated calcium carbonate ($CaCO_3$) has advantages such as small white and fine particle size, high homogeneity, and uniformity of particle shape. Hence, it is a product that is much sought after by various industries. PCC synthesis must be accompanied by using an efficient reactor for the reaction. PCC can be synthesized via a carbonation method that utilizes CO_2 gas. This research aims to optimize all processes in the PCC production circuit using a CSBR reactor in the form of a tank reactor to optimize the PCC synthesis process from the previous reactor and accommodate the number of tools to be economical. Based on the research results, the PCC synthesis process is influenced by the type of solvent, temperature, CO_2 gas flow rate, reaction time, and reactor type. The performance of the CSBR reactor was carried out using variations of R1, R2, R3, and R4 using the carbonation method, resulting in the highest purity and yield of 94.6% and 92.08%.

1. Introduction

Precipitated Calcium Carbonate (PCC) is a natural substance that results from the refining and synthesis of limestone. This process involves carbonation and produces a product with the chemical formula $CaCO_3$. PCC is valued for its outstanding properties, including small white color, particle size, high homogeneity, and uniform particle shape. As a result, PCC is increasingly used as fillers or additives in various industries, such as paper, ink, food, ceramics, and pharmaceutical industries. Precipitated calcium carbonate crystals (PCC) have a different shape from other types of calcium carbonate, as well as different physical properties such as density, surface area, and adsorption ability, making PCC a highly sought product in various industries. Commercially available PCC is synthesized through a carbonation process where hydrated lime is reacted with CO_2 gas using a reactor. The carbonation method using CO_2 gas in PCC synthesis is one of the efforts to utilize CO_2 exhaust gas, which is the result of industrial activities. The level of CO_2 gas emissions in Indonesia in 2021 will reach 41.4 million tonnes [1], this gas is known as a greenhouse gas emission which causes global warming. These high CO_2 emissions have various impacts, one of which is on human health [13].

The PCC synthesis process using the carbonation method involves several factors that influence the PCC formation reaction, such as the type of solvent, temperature, CO_2 gas flow rate, reaction time, and reactor type. This research focuses on the type of reactor used for PCC synthesis, which generally uses two types of reactors: CSTR and PFBR. However, it is difficult to precisely control the crystals' phase, shape, and aspect ratio [2]. The hydrodynamic conditions resulting from the reactor used influence the production process, and the characteristics of the particles produced [3]. Many studies have performed PCC synthesis using the carbonation method in various types of reactors. However, the efficiency of the reactor equipment used needs to be further innovated in order to produce PCC products that have quality in terms of the yield produced and quality in terms of crystal shape and particle uniformity. In research [4], the synthesis of PCC was done using a tubular column reactor with the carbonation method. In research [5], PCC synthesis was carried out using CSTR and PFBR reactors. Research [6] claims the synthesis of PCC using a CSTR reactor equipped with a paddle stirrer with the aim of obtaining 0.1 micrometer PCC particles. Another study used a bubble column reactor with external circulation with the column equipped with a glass microporous gas distributor and gas flow regulated by a rotameter. The intensity of the gas flow allows the formation of microbubbles that ensure a high gas-liquid contact surface [7]. Research by Hansen et al. contacts Calcium hydroxide with CO_2 gas using a reactor system consisting of two reactors, where the first and second reactors are interconnected through a recirculation loop [8].

The deposition of gas-liquid-solid systems requires the establishment of gas-liquid contacts to allow good mass transfer from the gas to the liquid phase and sufficient circulation to avoid precipitation of the resulting calcium carbonate particles. Efficient conditions for chemical reactions to occur can be created by increasing the surface contact area between the reactants and the reactor, which can be controlled by choosing a design and type of reactor that is in accordance with the fluidization concept that occurs in the reactor. The contribution of this research is to optimize the PCC product synthesis process using a different type of reactor, namely a CSBR reactor (Continuous Stirred Bubble Reactor) in the form of a tank reactor, in order to minimize the number of tools used from previous research, and it is hoped that this will maximize the yield and quality of the product produced.

2. Research Methodology

2.1. Materials

In this research, the equipment used consisted of a CSBR reactor, CO_2 gas cylinder, 1000 mL beaker glass, pH meter, oven, desiccator, analytical balance, filter paper, and 325 and 60 mesh filtering. The PCC product analysis tool uses X-ray fluorescence (XRF) analysis. The materials used are CaO Padang Panjang, water (H_2O), Carbon dioxide (CO_2), Aloe vera extract, Ammonium chloride (NH_4Cl), and Stearic acid ($C_{18}H_{36}O_2$).

2.2. Procedures

1) Synthesis of Precipitated Calcium Carbonate (PCC)

The steps of PCC synthesis using a CSBR reactor are shown in Fig. 1.

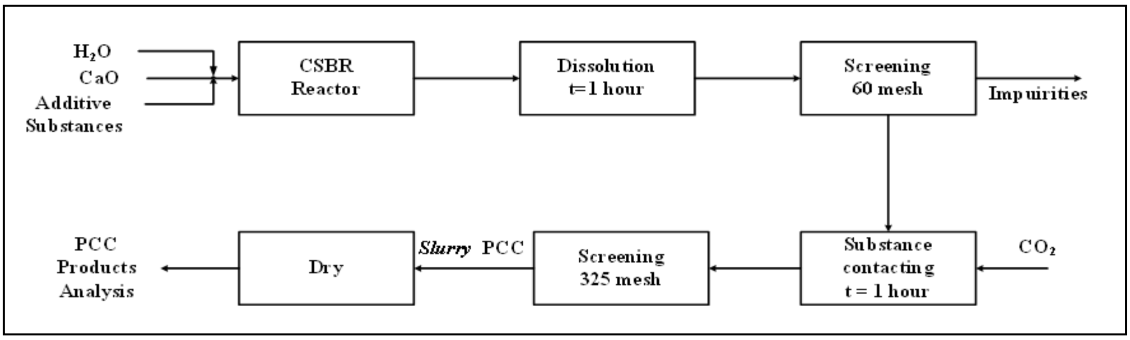

Fig. 1. PCC Synthesis uses a CSBR Reactor

The CaO raw material, additives, and solvent used enter the reactor for dissolution for 1 hour. Next, the dissolution is filtered using a 60-mesh sieve. The filtered impurities are removed and the solution is put back into the CSBR reactor and a second reaction is carried out, namely being contacted with CO_2 for 1 hour. PCC products are filtered with a 325-mesh sieve.

2) Sample Variations for Tool Performance

Variation of test samples for tool performance are listed in Table 1.

Table 1. Reactor Working Experimental Sample Variables

Running Tool	Variable Sample					
	H_2O (L)	*CaO (kg)*	*NH_4Cl (kg)*	*Aloe vera extract (L)*	*$C_{18}H_{36}O_2$ (kg)*	*CO_2 (L/min)*
R1 (CaO + Aloevera exctract)	50	1.5	-	1.44	-	7.5
R2 (CaO + NH_4Cl + Aloevera extract)	50	1.5	0.57	1.44	-	7.5
R3 (CaO + $C_{18}H_{36}O_{2)}$	50	1.5	-	-	1.1762	7.5
R4 (CaO +NH_4Cl)	50	1.5	0.625	-	-	7.5

The PCC synthesis process is carried out in the CSBR reactor. The illustration of the CSBR reactor using Microsoft Visio software is presented in Fig. 2.

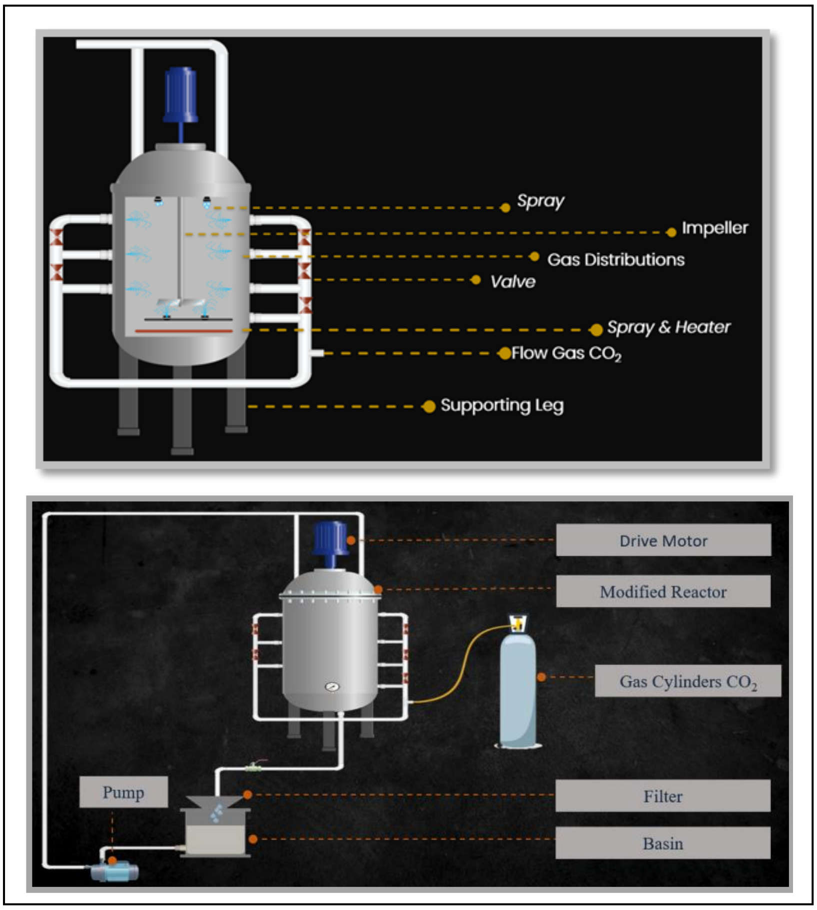

Fig. 2. Continuous Stirred Bubble Reactor Illustration

3) Analysis of Results Data

The PCC product synthesized using a CSBR reactor was analyzed using an X-ray fluorescence (XRF) tool to determine the elements contained in the resulting product. The yield calculation is carried out using the following equation:

$$Yield = \frac{product\ weight}{sample\ weight} \times 100\% \quad (1)$$

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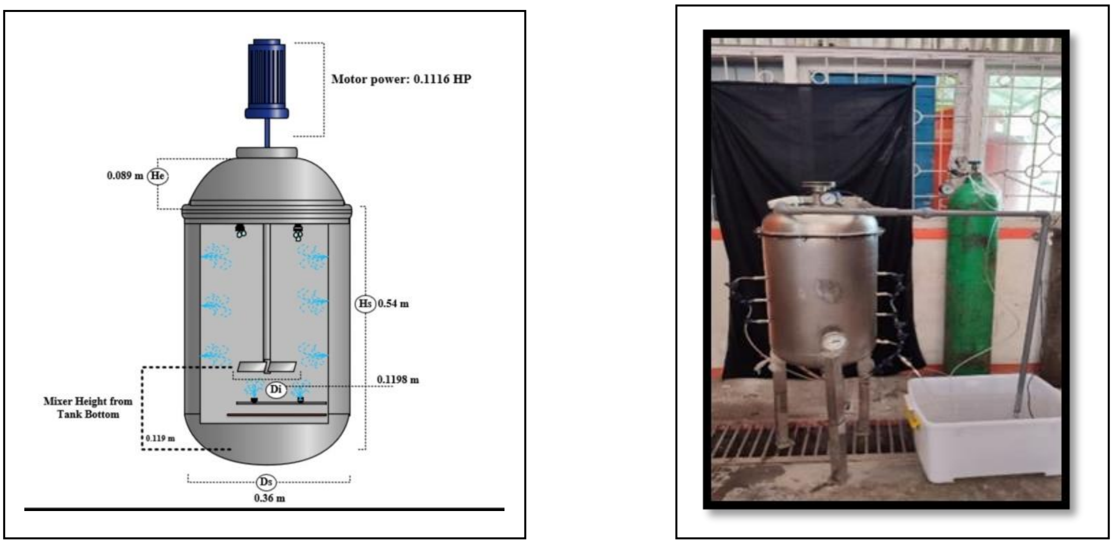
3. Results and Discussion

3.1. PCC Synthesis using the Continuous Stirred Bubble Reactor (CSBR)

The following is a real view of the CSBR reactor used for PCC synthesis, shown in Fig. 3.



(a) (b)

Fig. 3. (a) Design of CSBR Reactor (b)PCC Synthesis uses the CSBR Reactor

The specifications and dimensions of the CSBR reactor are described using Microsoft Visio software as shown in Table 2.

Table 2. Specifications of CSBR Reactor

SPESIFICATIONS		
Name	Continuous Stirred Bubble Reactor (CSBR)	
Amount	1 Unit	
Function	Reacting CaO with water and where the carbonation process occurs	
Contructions materials	Plate Stainless Steel 304	
Component	***Unit***	***Value***
Reactor capacity (Vt)	M3	0.06
Reactor diameter (Dt)	M	0.36
Reactor height (Hs)	M	0.54
Ellipsoidal height (He)	M	0.089
Liquid height (Hc)	M	0.359
Design pressure (Pd)	Atm	1.36
Component	***Unit***	***Value***
Thickness of reactor wall (td)	Mm	0.734
Thickness of ellipsoidal cap (te)	Mm	0.7347
Impeller diameter (Da)	M	0.111
Width of impeller (W)	M	0.022
Length of impeller leaf (L)	M	0.028
Motor power	hP	0.11

3.2. PCC Product Analysis Using CSBR Reactor

The performance of the continuous stirred bubble reactor in PCC synthesis is reviewed based on the yield and purity of the PCC product produced. The yield and purity of the resulting PCC products are shown in Fig. 4.

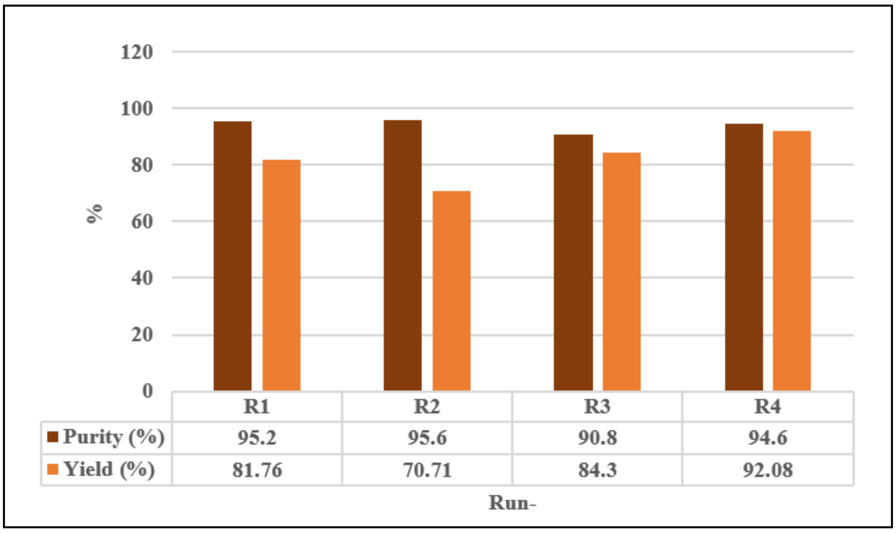


Fig. 4. Yield and Purity of PCC Products using a CSBR Reactor

Fig. 4 shows a comparison of the yield and purity of PCC products produced using the CSBR reactor. Based on the research results, the yield and purity values are influenced by the type of solvent or additive used and the flow rate of CO_2 gas in the CSBR reactor Fig. 4 shows the highest yield and purity values found in the R4 treatment, namely 94.6% and 92.08%. Based on research [9], this occurs because the adding of NH_4Cl increases the solubility of CaO in water. Apart from that, it is also influenced by the increased flow rate of CO_2 gas, so that more PCC is formed. The type of reactor will influence the hydrodynamic conditions which will affect the process. The process of dissolving CaO and contacting CO_2 gas is carried out in the same reactor, which is a tank reactor equipped with a stirrer and gas distribution channels distributed on the reactors left-right sides and bottom side walls so that the process dissolution and CO_2 exposure become more effective. The general PCC synthesis reaction as follows;

2) *CaO reacts with H_2O to form $Ca(OH)_2$:*

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2\,(l)}$$

3) *Contacting CO_2 with $Ca(OH)_2$ and forming $CaCO_3$:*

$$Ca(OH)_{2\,(l)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(l)}$$

For the reaction to form PVC with the addition of additives as follows:

a) NH_4Cl

Following is the reaction with the addition of NH_4Cl:

$$CaO_s + 2\,NH_4Cl_{(s)} + H_2O_{(l)} \rightarrow CaCl_{(s)} + 2NH_4OH_{(aq)}$$

$$2NH_4OH_{(aq)} + CO_{2(g)} \rightarrow (NH_4)CO_{3(aq)} + H_2O_{(l)}$$

$$(NH_4)CO_{3(aq)} + CaCl_{(aq)} \rightarrow CaCO_{3(s)} + 2NH_4Cl_{l(aq)}$$

b) Aloevera exctract

Following is the reaction with the addition of aloevera extract:

$$CaO_{(s)} + H_2O_{(l)} \xrightarrow{\text{Aloevera extract}} Ca(OH)_{2\,(l)}$$

$$Ca(OH)_{2\,(l)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(l)}$$

XRF analysis of PCC products was carried out to determine the constituent elements contained in PCC. The results of the XRF analysis are presented in the Table 3.

Table 3. Result of XRF Analysis of PCC Products

Component	Experiment To -			
	R1* *(CaO+ Aloe vera extract)	***R2* *(CaO + NH4Cl + Aloe vera extract)***	***R3* *(CaO + C18H36O2)***	***R4* *(CaO + NH4Cl)***
Al_2O_3 (%)	0.814	0	3.257	0.88
SiO_2 (%)	0.687	0	1.97	1.51
MnO (%)	0.011	0.015	0.034	0.013
Fe_2O_3 (%)	0.923	0.932	0.731	0.901
SrO (%)	0.086	0.084	0.071	0.079
Cl (%)	0.007	0.0841	0.031	0.356

Table 3 shows the highest impurity elements contained in each PCC product. These elements from raw materials, and solvents for the PCC synthesis process. This element can affect the color, smoothness, morphology, and level of toxicity for use in food products. Adding NH_4Cl additives can increase the solubility of CaO to water so that more PCC is formed. But the addition of NH_4Cl makes the Cl content in PCC products high, causing toxic effects in pharmaceutical and medical applications. Therefore, aloe vera extract is used to minimize the Cl content in the PCC products produced [5]. Aloe vera contains soluble proteins, such as glycine, aspartic acid, and glutamic acid, that can form calcium-protein complexes in situ when the protein binds to Ca_2^+ [10].

The use of additional ingredients from plant extracts (such as artificial aloe vera extract) which contain proteins and biopolymers can control morphology because plant extracts act as additional ingredients in modifying crystal morphology due to their polarity and solubility [11].

3.3. Comparison of Reactor Types in PCC Synthesis

A comparison of the use of reactor types in PCC synthesis in previous research reviewed based on yield quantity and purity is presented in Table 4.

Table 4. Result of XRF Analysis of PCC Products

Research	Reactor Type	Method	Raw Materials	Additivies	Yield (%)	Purity (%)
This research (2023)	*CSBR*	Carbonation	CaO	Aloevera extract	81.76	95.2
Sari, E., *et.al*, (2022) (lab.scale)	*CSTR & PFBR*	Carbonation	CaO	Aloevera extract	81.62	91.78
Jimoh, *et.al,* (2017) (lab.scale)	*Tubular column*	Carbonation	Marble stone	Aloevera extract	99.8	99.5

Table 4 shows a comparison of the results of PCC products with CaO and aloe vera extract using several types of reactors in terms of yield values and product purity. The PCC product in research [4] was found to be higher than in this research, this is because the raw material for this research used marble stone which has a calcium content of 99% higher than the CaO raw material in Padang Panjang. The high yield is due to the contacting process of CO_2 gas which is evenly distributed in the slurry in the reactor so that more $Ca(OH)_2$ comes into contact or reacts with CO_2 gas to form PCC.

The use of CSTR and PFR reactors in PCC synthesis in [5]-[12] already has quite high conversion advantages, but this process requires a large series of tools. Research [4] on column tubular reactors, liquid-solid mass transfer processes between CaO raw materials and solvents needs to be considered. Therefore, this research tries to develop the use of CSBR reactor types in PCC synthesis.

4. Conclusion

Based on the results of the research that has been carried out, it can be concluded that the shape of the reactor will influence the solid-liquid-gas deposition system and the fluidization concept that occurs in the reactor, thus affecting the product produced. This research seeks to produce a better PCC product than before by using a reactor that is more economical than the CSTR and PFR reactors, namely the CSBR reactor. The results of this research have shown the results, purity and constituent elements of PCC using XRF analysis, to confirm the chemical content of the PCC R1-R4 samples. The highest yield and purity from synthesis using the CSBR reactor was produced in R4 with the addition of NH_4Cl with a yield of 92.08% and a purity of 94.6%. However, some of the limitations of this research are the use of CSBR reactors to produce PCC products with better quality and quantity, seem to be a barrier to obtaining further information related to the use of CSTR and PFR reactors in innovation in the type of reactor used. Further information on PCC synthesis reactors, and the effect of additives on the products produced are needed to improve the efficiency of reactors used in PCC synthesis.

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