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Calcination of Various Eggshell Wastes into CaO Heterogeneous Catalysts

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ABSTRACT. The high food industry waste can cause pollution, including a pungent odor and the emergence of bacteria that cause disease. Egg shells are confectionery waste that is commonly found in household waste and the food industry. The accumulation of eggshell waste can cause various conditions such as abdominal pain, diarrhea, fever, and cramps in the stomach caused by Salmonella bacteria. Thus, further processing of eggshells is required. In this study, eggshell waste was processed into heterogeneous catalysts of CaO. This heterogeneous CaO catalyst can be used as a catalyst in the manufacture of biodiesel. In this process, egg shells are processed by the calcination method. The variables used are shell type and calcination temperature. The shell variables used were chicken egg shells, duck egg shells, and quail egg shells. At the same time, the temperature variables used are 600 ºC and 800 ºC. To determine the quality of heterogeneous CaO catalysts, characteristic tests were varied in the form of SEM-EDX and FTIR. Based on the EDX and FTIR data, the samples calcined at 800 ºC showed a complete decomposition and CaO formation. The compostion, morphology, and spectroscopy analysis confirmed that CaO derived from chicken eggshells exhibited the best characteristic and promising to be applied for biodiesel production.

1. INTRODUCTION

Eggs are one of the foods widely consumed by the people of Indonesia, so a lot of eggshell waste is obtained. Eggshells often contain poultry feces which are the habitat of fecal coliform bacteria. Species of fecal coliform bacteria can enter the shell by osmosis diffusion. Some species of fecal coliform bacteria, for example, *Escherichia coli* and *Salmonella typhimurium,* are pathogenic microbes that cause many health problems in humans.[1]. Therefore, the utilization of eggshell waste needs to be done to reduce the risks posed. Eggshells are one of the wastes that contain various kinds of minerals. Eggshells are composed of 94% $CaCO_3$, 1% $MgCO_3$, 1% $(Ca_3PO_4)_2$, and the remaining 4% is organic matter [2]. $CaCO_3$ can be converted into CaO through the calcination process, which can be used as a catalyst with high purity. In the eggshell calcination process, the thermal decomposition reaction of $CaCO_3$ occurs to form CaO heterogeneous catalysts. The CaCO3 decomposition reaction in the calcination process can be seen according to equation (1).

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \quad (1)$$

Catalysts are compounds that can accelerate reactions. The use of homogenous or heterogenous catalysts in chemical product manufacturing is a usual thing. One of the advantages of a heterogeneous catalyst is that it is solid so that it is easily separated at the end of a reaction; however, with improper handling, the catalyst suffers from reduced activity due to its sensitivity to the atmospheric condition. In addition, homogeneous catalysts cannot be reused and will become a hazardous waste if disposed of directly [3]. Calcium Oxide (CaO) is a heterogeneous catalyst with high basicity[4]. CaO heterogeneous catalyst to biodiesel production by a calcination process of eggshell is commonly used during the transesterification of fatty acid methyl esters (FAME) [5]. In this study, we prepared CaO powders via thermal decomposition or calcination of eggshells: chicken eggshells, quail eggshells, and duck eggshells. The as-prepared powders' functional groups, morphology, and composition are investigated. The result of the study is beneficial for developing the biodiesel manufacturing process.

2. MATERIALS AND METHODS

2.1 Materials and Tools

The raw materials for production are chicken eggshell waste, duck eggshells, and quail eggshells obtained from local food stalls. At the same time, the chemicals used are sodium hypochlorite solution (NaClO). The tools used in this experiment are the washing tub, measuring cup, mortar and pestle, oven, furnace, porcelain crucibles,

2.2 *CaO Synthesis*

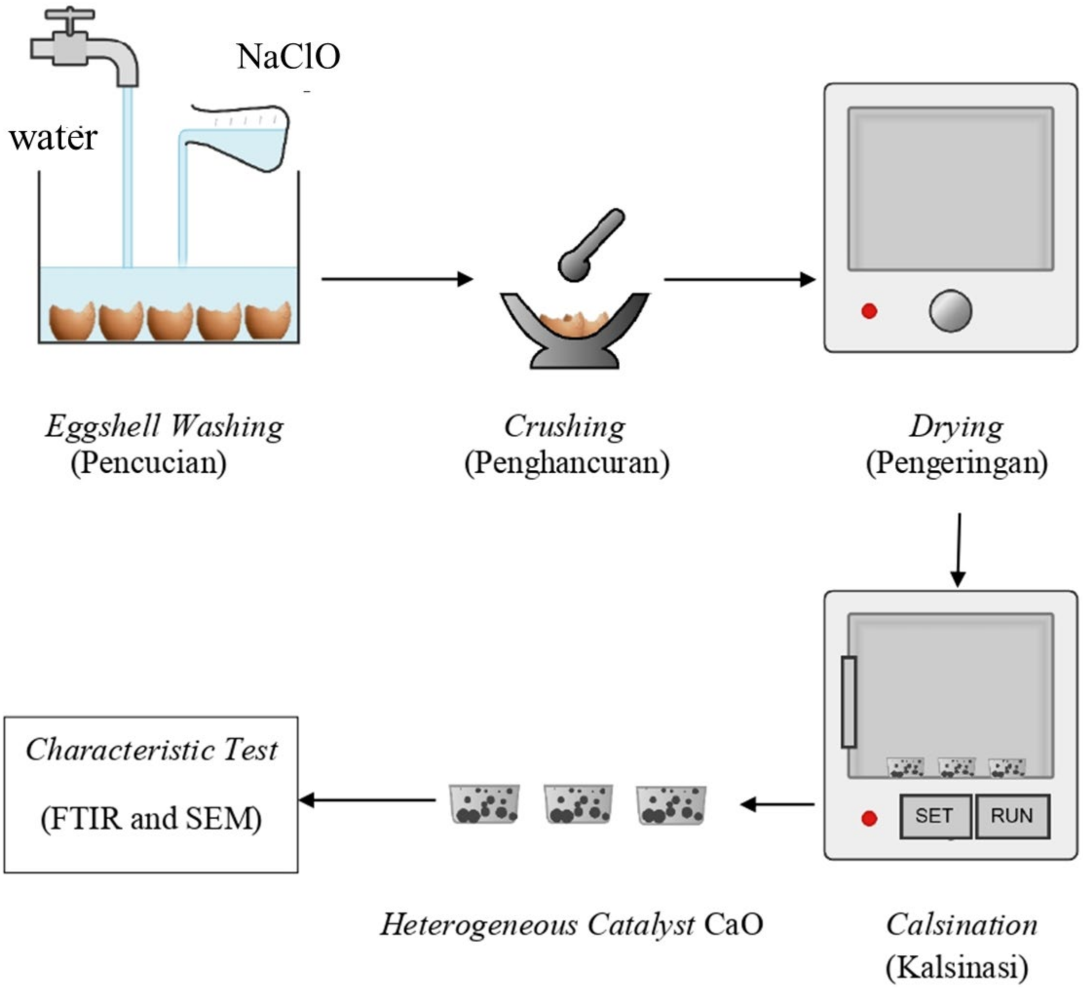


Figure 1. Eggshell Calcination Process into CaO Heterogeneous Catalysts

The process of making CaO heterogeneous catalysts from eggshell waste can be seen in Figure 1. The process of making CaO heterogeneous catalysts is generally divided into several stages: washing, drying, crushing, calcination, and characteristic tests. In the washing process, the eggshell waste was washed with a 10% Sodium Hypochlorite (NaClO) solution. This washing process aims to kill bacteria on eggshell waste. After washing, the shells are dried using an oven at 100 °C for 2 hours. After drying, the eggshells were pulverized using a mortar and pestle and then calcined for 2 hours at variable temperatures of 600 °C and 800 °C. In this calcination process, a heterogeneous CaO catalyst is formed.

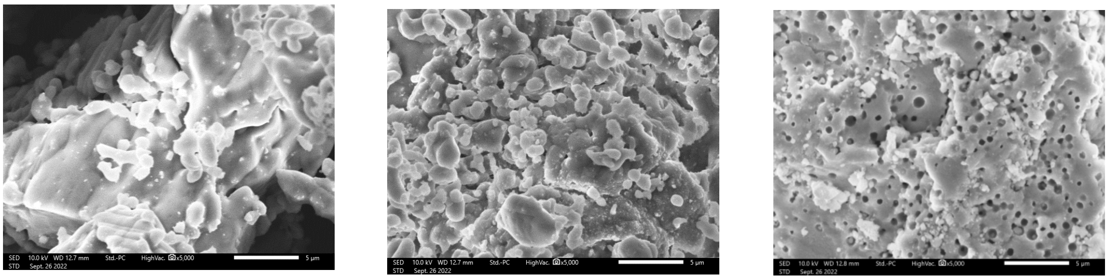
2.3. CaO characterization

To determine the quality of the catalyst, characterization and analysis are carried out. SEM-EDX and FTIR tests. The morphology of the samples is investigated using Scanning Electron Microscope (SEM) by JCM7000 (JEOL, Japan). The composition of the samples is analyzed using EDX (JEOL, JAPAN). The functional group of the samples is investigated using Fourier transformed infra-red spectroscope (FTIR) by Shimadzu (Japan).

3. RESULTS AND DISCUSSION

3.1 SEM-EDX Analysis

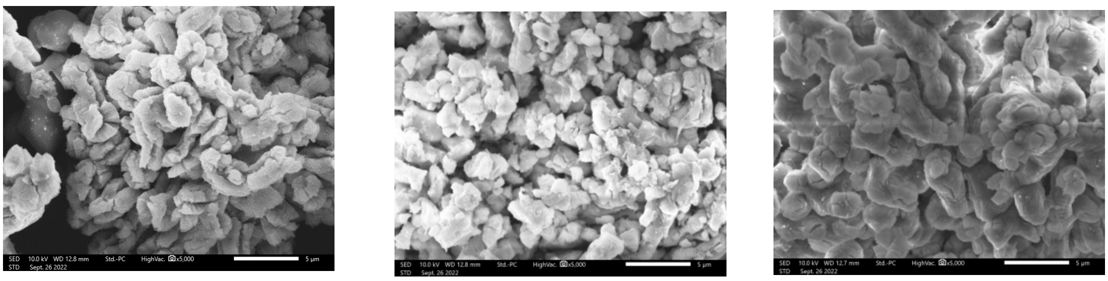
Scanning Electron Microscopy (SEM) analysis was conducted by comparing data from calcination temperature variations of the three samples: chicken eggshell, duck eggshell, and quail eggshell. This analysis aims to determine the structure and surface morphology of the resulting eggshell catalyst. The SEM Images at 5000x magnification of CaO from various sources are displayed in Figures 2 and 3.



(a) (b) (c)

Figure 2. SEM of 600°C CaO Heterogeneous Catalyst ((a) chicken eggshell 5000x, (b) duck eggshell 5000x, (c) quail eggshell 5000x)

Based on the direct observation or physical appearance, ts the CaO heterogeneous catalysts was obtained in dark gray. The dark gray color is caused by the formation of metal oxides in the calcination process is not optimal. The dark gray powder indicates the presence of a carbonaceous compound as a result of an incomplete calcination process [4].



(a) (b) (c)

Figure 3. SEM of 800°C CaO Heterogeneous Catalyst ((a) chicken eggshell 5000x, (b) duck eggshell 5000x, (c) quail eggshell 5000x)

In the calcination process with a temperature of 800 °C, the results of CaO heterogeneous catalyst powders were obtained to have pale gray and slightly white color. The pale gray-white color of the powder indicates the successful formation of metal oxides. The higher the calcination temperature, the more metal oxides are formed, which is characterized by the change in color of ground eggshells to bright-white[6]. The morphological study of each CaO sample is listed in Table 1. The shape of the particles prepared at 600 °C is irregular, which is the result of the partial decomposition and dehydration reaction of eggshells, mainly from the egg membranes. The rough surface of the particles is an indication of CO_2 generation during the calcination process. In contrast, the CaO particles prepared at 800°C show an agglomeration of oval-shaped particles with good homogenous morphology. This indicates that at 800°C, the carbonate group decomposed into CO_2, thus leaving, more significant gaps between particles [7]. The decrease in particle size is also the result of this phenomenon.

Table 1. Surface Characteristics of CaO Heterogeneous Catalysts

Characteristics	Temperature					
	600 °C			800 °C		
	Chicken Egg Shell	Duck Egg Shell	Quail Egg Shell	Chicken Egg Shell	Duck Egg Shell	Quail Egg Shell
Shape	Irregular	Irregular	Irregular	Oval	Oval	Oval
Size average (μm)	174.612	148.286	158.298	169.419	111.010	137.770
Maximum (μm)	226	226	246	225	162	182
Minimal (μm)	49	74	95	103	65	95
Length (μm)	48.042	183.521	170	30	100.439	60.033

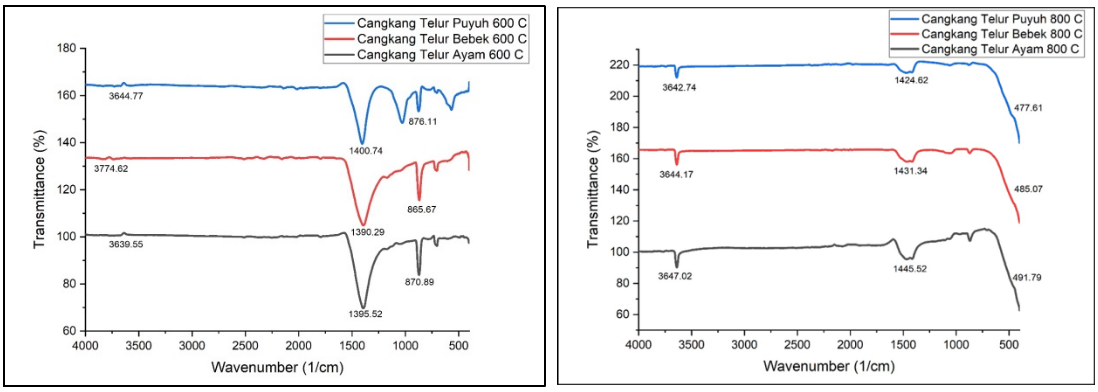
Table 2. EDX Analysis Result Data

Material Type	Temperature (°C)	Elements								
		Ca	Atom %	O	Atom%	C	Atom%	Mg	Atom%	Total
CA	600 °C	√	26.60±1.49	√	62.37±3.41	√	11.03±0.64	x	-	100%
CB	600 °C	√	25.14±0.95	√	62.75±2.22	√	11.42±0.43	√	0.69±0.13	100%
CP	600 °C	√	26.47±1.19	√	62.62±2.73	√	10.20±0.50	√	0.71±0.17	100%
CA	800 °C	√	38.03±2.07	√	58.08±4.13	√	3.89±0.45	x	-	100%
CB	800 °C	√	35.57±2.21	√	59.79±4.55	√	4.64±0.54	x	-	100%
CP	800 °C	√	38.91±1.67	√	61.09±3.35	x	-	x	-	100%

Description:
CA: Eggshell; CB: Duck Shell; CP: Quail Shell

In the EDX analysis presented in Table 2, the composition of eggshells after calcination shows the highest mass percentage in the elements Ca and O, which are the main constituents of CaO. The decomposition of $CaCO_3$ compounds causes the formation of CaO compounds due to the heating process. The composition of Ca and O elements as the dominant elements accompanied by a decrease in the carbon composition of the calcined eggshell results indicates the formation of CaO compounds as a product of $CaCO_3$ (Magnesium Carbonate) decomposition [8]. ased on qualitative EDX analysis, the best of the six samples is the variable type of quail eggshell at 800 °C. This is indicated by the highest Ca content after calcination of 38.91 ± 1.67, O content of 61.09 ± 3.35, and no C and Mg content.

3.2 FTIR Analysis



(a) (b)

Figure 4. FTIR of CaO Heterogeneous Catalyst ((a) heterogeneous catalyst prepared at 600°C, (b) heterogeneous catalyst prepared at 800°C (black: Chicken Eggshell, Red: Duck Eggshell, Blue: Quail Eggshell)

The FTIR spectra of all samples are presented in Figure 4. FTIR analysis was performed by comparing calcination temperatures of 600 ℃ and 800 ℃ with variations in eggshell type. Data analysis of CaO catalysts from chicken eggshells, duck eggshells, and quail eggshells was carried out at a wavenumber of 4000 $cm-1$ to 400 $cm-1$, as shown in the figure above. In Figure 4(a), firm peaks at 1400/cm-600/cm indicate the presence of the carbonate group due to the incomplete decomposition of $CaCO_3$ to CaO. In Figure 4(b), the OH band's appearance is considered a characteristic peak match between the three samples. However, the formation of the OH group cannot be used absolutely to justify that the analyzed sample is CaO because the presence of Ca(OH) also causes the formation of a dip or decrease in the area around the peak. The peak occurrence is likely due to the presence of water adsorbed on the surface of CaO because of its nature as a water absorber from the air. Based on the graph, it shows that at a temperature of 600 ℃, no OH group appears by the three samples. While at a temperature of 800 ℃, all samples have OH group. In the 800 ℃ samples, the OH band appears in the chicken eggshell sample at wavenumber 3647.02 cm^{-1}; duck eggshell catalyst sample at wavenumber 3644.17 cm^{-1}; quail eggshell catalyst sample at wavenumber 3642.74. cm^{-1}. CaO was detected referring to the wavenumber of the region around 400 $cm-1$ in the samples. Referring to the spectra of CaO, $CaCO_3$, and standard Ca(OH), the spectrum of CaO appears broadened at these wavenumbers.[9]. In the graph, the decrease occurs in the area around 400 $cm-1$ to 600 $cm-1$ associated with the strain of the Ca-O bond. The sample with a calcination temperature of 800 ℃ showed more CaO formation due to the widening of the peak at the wavenumber of the three samples. Overall, the FTIR analysis shows consistency with the SEM analysis.

Based on the SEM-EDX and FTIR results, CaO is successfully obtained from three eggshells (Chicken, duck, and quail) as long as the calcination temperature is higher than 600 ℃ to assure the complete decomposition of $CaCO_3$ to CaO. The samples calcined at 800 ℃ have good morphology and characteristic based on FTIR spectra. The presence of hydroxyl function on the sample indicates that the samples should be stored in dryer conditions to avoid water vapor adsorption to the surface of the CaO. For future research, it is essential to confirm the purity of the CaO by XRD and XPS analysis [10,11]. Furthermore, the TG/DTA analysis should also be performed to ensure the precise temperature for the complete decomposition of various eggshells.

4. CONCLUSIONS

Based on the research conducted, it can be concluded as follows.

1. The calcination method can process Chicken eggshells, duck eggshells, and quail eggshells into CaO heterogeneous catalysts.
2. The optimal CaO heterogeneous catalyst content is obtained from calcination with a temperature of 800°C. ℃
3. The CaO obtained from chicken, duck, and quail eggshells is highly potential to be used as catalysts for biodiesel production.

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