Characterization of Calcium Oxide Catalyst from Eggshell Waste

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ABSTRACT

Abundance of eggshell waste leads to high generation of solid waste as it is difficult to decompose. Besides, eggshell waste has no economic value and most of the waste is dumped in landfills without any pretreatment. Thus, an efficient method has been conducted to study the chemical characterization of eggshell waste. Eggshells contain potential useful minerals such as calcium oxide (CaO) that can be derived from calcium carbonate (CaCO₃) in the eggshells. The objective of this study is to synthesize and characterize CaO from eggshells. Raw eggshells are analyzed by thermal gravimetric analyzer (TGA). Then, they are calcined at the temperature of 900°C for 1 hour with nitrogen gas. Raw and calcined eggshell are characterized by x-ray fluorescence (XRF) and Fourier transform infrared (FTIR) spectroscopy to obtain elemental composition and functional group of eggshell. TGA showed that the suitable temperature for calcination was 900°C. XRF results showed that CaO in raw eggshell was 98.50% and increased to 98.56% in calcined eggshell. FTIR analysis of eggshell showed the Ca – O band formed around 670 cm⁻¹. CaO from eggshell is expected to act as a catalyst for bio-oil production.

INTRODUCTION

Eggs are a major ingredient in a variety of products such as cakes, fast food, and also in our daily meal. The production of chicken eggs in the industry leads to the generation of eggshells, which are considered as waste. Apart from that, eggshell waste has no economic value and most of it has to be discarded to the landfills without any processing. Consequently, this can cause high risk to public health and pollution to the environment. High generation of eggshell waste may increase the production of solid waste in landfills as eggshells are part of the solid waste. About 642 600 tonnes of egg was produced in Malaysia in the year of 2012 [1]. 11% of the total weight is denoted by the shell which can be estimated at 70 686 tonnes of waste generated per year [2]. The percentage of eggshell waste generation is expected to increase year by year and this will cause an environmental issue.

Eggshells contain calcium carbonate (CaCO₃) which is a main element of the eggshell. An eggshell consists of about 94% of CaCO₃, 1% of magnesium carbonate, 1% of calcium phosphate, and 4% of organic matter [3]. CaCO₃ can be converted into calcium oxide (CaO) via the calcination process. CaO was the active phase in the eggshells and the suitable temperature for calcination process must be above 800°C [4]. CaO is a raw material for producing lime in the industry [5]. Using CaO from lime stone may contribute to environmental problem as the source of this commercial CaO is a non-renewable resource.

Large usage of non-renewable CaO causes rapid depletion of those resources. This has led to many researches being made in order to find alternative ways to replace commercial CaO. Eggshell waste is expected to be a source of this substance as it is non-corrosive, environmentally friendly and economical. CaO from eggshell waste is expected to replace other commercial calcium oxide which is more expensive and high cost of production.

To address these issues, an alternative way had been studied to characterize potential mineral such as CaO from eggshells. The objective of this research is to synthesize and characterize CaO from waste eggshells. CaO from eggshell is expected to be a catalyst for bio-oil production as it can reduce oxygen content, which is an unnecessary compound in the production of bio-oil via catalytic pyrolysis. The presence of oxygen in the bio-oil has a negative effect such as further increasing the corrosion due to its low pH. Lu et al. [6] reported that CaO...
reduced heavy products such as phenol and increased formation of hydrocarbons and light product such as acetaldehyde, 2-butanone, and methanol. CaO can also reduce acidity level. Other catalyst including MgO and TiO$_2$ were not effective as CaO. Hence, CaO is a suitable catalyst for enhancing the quality of bio-oil.

Meanwhile, eggshell containing most of CaO composition after the calcination process is a suitable material to be used as a catalyst. CaO from eggshell waste not only can be used as a catalyst, but also adds value to the waste generated. In this research, CaO derived from eggshell waste was thoroughly investigated by using thermal gravimetric analysis (TGA), X-ray fluorescence (XRF) and Fourier transform infrared spectroscopy (FTIR).

Methodology:

Material:

Eggsheells were collected from local industries and rinsed several times with water to remove impurity and interference materials. Then, they were dried in the oven at a temperature of 100°C for 24 hours. The eggshells were ground with Fritsch Pulverisette 6 Planetary Mono Mill to achieve homogeneous size. Next, they were sieved by Fritsch siever to obtain a desired particle size of 40µm.

Methods:

Eggshells were analyzed by TGA/DSC 1 model Mettler Toledo. Raw eggshells were placed in a cylinder crucible inside an analyzer. Analysis of raw eggshells started at a temperature of 25°C until a temperature of 850°C. The heating rate was 10°C/min with nitrogen flow rate of 20 ml/min. Raw eggshells were calcined with nitrogen gas at a temperature of 900°C for 1 hour in the tube furnace. The temperature of 900°C was determined by using TGA analysis. Calcination process was used for converting calcium carbonate (CaCO$_3$) to CaO, producing grey powder. The sample was kept in an air-tight container to avoid reaction from humidity in air and carbon dioxide (CO$_2$).

Raw and calcined eggshells were analyzed by XRF model PANalyticalminiPAL 4 in order to get the percentage of CaO in the sample. Particle size <40 µm for both eggshells were analyzed. IR spectra of raw and calcined eggshells were then recorded by FTIR model Perkin Elmer in the range of 500-4000 cm$^{-1}$. FTIR was analyzed to determine the functional group of eggshell. Sample preparation consisted of fine powder of each sample raw and calcined eggshell.

RESULT AND DISCUSSIONS

Calcination temperature:

The suitable calcination temperature was analyzed by TGA-DTG. Figure 1 showed that there were two distinct stages of weight losses. The first stage showed the temperature at below 640°C and the second stage was between 640°C and 840°C. A minor weight loss in the first stage can be attributed to a loss of organic compound and adsorption of water molecules to the surface of the material by hydrogen bonds [4, 7]. A major weight loss which occurred in the second stage contributing to 42.2%, occurred at a temperature of 840°C. Carbon dioxides loss at this stage was due to the conversion of CaCO$_3$ phase to CaO phase [8], which can be confirmed by XRF and FTIR results as shown in Table 1 and Figure 2. As the weight of eggshell remains constant at the temperature above 840°C, the temperature of 900°C was chosen to be used as the calcination temperature to ensure complete conversion of CaCO$_3$ to CaO [9]. The DTG peak also showed that a major weight loss occurred at temperature of 840°C and remained constant at a temperature above 840°C.

Calcium Oxide (CaO) content:

Based on the XRF analysis, CaO content increased from 98.50% in raw eggshell to 98.56% in calcined eggshell. From this result, it shows the CaCO$_3$ had approximately converted to CaO. Besides that, other chemical compositions contained in the calcined eggshell were MgO (0.69%), Al$_2$O$_3$ (0.1%), CuO (0.027%), SrO (0.051%). CaO was the most abundant element in the eggshell as CaCO$_3$ was mainly present in the eggshell. The percentage of CaO in calcined eggshell from this study was higher than the percentage of calcined eggshell in a previous research. Witoon [9] reported that the percentage of CaO in calcined eggshell was 97.4%, while the percentage of other chemical compositions was 1.63% for MgO, 0.52% for P$_2$O$_5$, 0.26% for SO$_3$, 0.08% for K$_2$O, 0.05% for SrO, 0.02% for Cl, 0.01% for Fe$_2$O$_3$, and 0.01% for CuO. Thus, it showed that the eggshell was approximately converted to CaO. Small amounts of other composition in the eggshell considered that the eggshell could be a natural carbonate-based material [10].
Fig. 1: TGA and DTG pattern for raw eggshell.

Table 1: Chemical compositions of raw and calcined eggshell.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Raw eggshell</th>
<th>Calcined eggshell</th>
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<tbody>
<tr>
<td>MgO [%]</td>
<td>0.500</td>
<td>0.690</td>
</tr>
<tr>
<td>CaO [%]</td>
<td>98.500</td>
<td>98.560</td>
</tr>
<tr>
<td>Al₂O₃ [%]</td>
<td>0.100</td>
<td>0.100</td>
</tr>
<tr>
<td>CuO [%]</td>
<td>0.045</td>
<td>0.027</td>
</tr>
<tr>
<td>SrO [%]</td>
<td>0.062</td>
<td>0.051</td>
</tr>
</tbody>
</table>

Fourier transform infrared (FTIR) analysis:

Functional group analysis of both raw and calcined eggshell were determined by Fourier transform infrared (FTIR) spectrometry. Based on the results from figure 2, it shows the IR spectra of both raw and calcined eggshell. IR spectra before calcination, which represent raw eggshell shows that the broad transmission band at around 2863 cm⁻¹ can be attributed to OH stretching vibration from waste of residual [11]. The weak band at 2360 cm⁻¹ is attributed to C=O bonds from carbonate [9]. Infrared bands at 1398 cm⁻¹ and 872 cm⁻¹ shows the C – O stretching and bending of CaCO₃, meanwhile the sharp band at 710 cm⁻¹ represents a Ca – O bond [12]. Boro et al. [11] and Witoon[9] had also observed similar band ranges for calcium carbonate study in the eggshell.

IR spectra after calcination, which represents calcined eggshell shows the existence of OH in Ca(OH)₂ in the peak of around 3600 cm⁻¹ and 2360 cm⁻¹. It was formed during adsorption of water by CaO[9]. Another band existence at 670 cm⁻¹ can be attributed to Ca – O band[9]. The functional group of 1981 cm⁻¹, 1414 cm⁻¹, 1398 cm⁻¹, 1063 cm⁻¹, and 710 cm⁻¹ represent the stretching vibration of the CO₃²⁻ group present in the eggshell [7, 13]. Infrared results show that CaCO₃ had completely converted to CaO as Ca – O bond existed in the calcined eggshell.

Conclusion:

The conversion of eggshell waste from CaCO₃ to CaO was analyzed by TGA, XRF, and FTIR analysis. The suitable temperature for the calcination process for eggshell was 900°C which was performed by TGA analysis. After the calcination process, most of the composition of the eggshell was transformed to CaO which was 98.56%. It was found that CaO was the major element in the eggshell. The functional group of eggshell shows that Ca – O bond had existed at 670 cm⁻¹, which proves that CaO had completely converted from CaCO₃. CaO from eggshell is expected to be a catalyst for bio-oil production as the eggshells are eco-friendly and cheaper, which could reduce production cost.
Fig. 2: FTIR spectra of raw and calcined eggshell.

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REFERENCES