The Use of Carbon Dioxide Released from Coconut Shell Combustion to Produce Na₂CO₃

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Abstract

In this investigation, sodium carbonate (Na₂CO₃) was produced by reacting the CO₂ released from coconut shell combustion with NaOH solution with molar concentrations of 6.5, 7.0, 7.5, and 8.0 M. The main purpose of the study was to assess the potential of the proposed method for mitigation of the CO₂ gas released into the atmosphere by the coconut shell industry. The Na₂CO₃ powder produced was oven-dried at 110 °C and subsequently characterized using FTIR, XRD, and SEM/EDS techniques. Thermal analysis was also carried out using DTA/TGA to investigate the thermal mechanisms of sodium carbonate formation. The experimental results show that the concentration of NaOH influences the mass of sodium carbonate produced, with the highest mass of 190.6 g obtained using 7.0 M NaOH solution. The FTIR analyses show the existence of O-H, C-O, C=O, and CO₃²⁻, confirming the formation of Na₂CO₃. The C-S functional group was also detected most likely due to the presence of the sulfur that naturally exists in the coconut shell. The formation of Na₂CO₃ is also supported by the presence of C, Na, and O on the EDS results and the presence of the thermonatrite (Na₂CO₃·H₂O) phase, as seen by the XRD. The XRD analysis of the sintered sample at 450 °C indicates the transformation of thermonatrite into sodium carbonate and sodium oxide, which is in accordance with the results of DTA/TGA analysis. Based on the results obtained, it is concluded that the proposed method can be applied to mitigation of CO₂ gas released by the coconut shell industry.

Keywords: carbon dioxide, coconut shell, sodium carbonate, sodium hydroxide

Abstrak

Pemanfaatan Gas CO₂ Hasil Pembakaran Tempurung Kelapa untuk Produksi Natrium Karbonat. Penelitian dilakukan untuk mempelajari pemanfaatan gas CO₂ hasil pembakaran tempurung kelapa menjadi natrium karbonat (Na₂CO₃) dengan mereaksikan gas CO₂ dengan larutan NaOH dengan konsentrasi 6,5, 7,0, 7,5, dan 8,0 M. Tujuan utama penelitian adalah mengkaji potensi metode yang diusulkan sebagai cara mitigasi gas CO₂ yang dihasilkan dari industri arang tempurung kelapa. Padatan natrium karbonat yang dihasilkan selanjutnya dikeringkan dalam oven pada suhu 110 °C, lalu dikarakterisasi dengan FTIR, XRD, dan SEM/EDS. Analisis termal menggunakan metode DTA/TGA dilakukan untuk mempelajari karakteristik termal pembentukan Na₂CO₃. Hasil penelitian menunjukkan bahwa konsentrasi NaOH mempengaruhi massa natrium karbonat yang dihasilkan, hasil tertinggi sebesar 190,6 g diperoleh dari penggunaan NaOH dengan konsentrasi 7,0 M. Karakterisasi dengan FTIR menunjukkan dengan jelas pembentukan natrium karbonat, yang ditandai dengan pita serapan gugus fungsi yang berkaitan dengan natrium karbonat, yakni gugus O-H, C-O, C=O, dan CO₃²⁻. Hasil FTIR juga menunjukkan adanya gugus fungsi C-S, yang kemungkinan besar karena adanya sulfur yang terdapat dalam tempurung kelapa secara alami. Pembentukan Na₂CO₃ juga didukung hasil karakterisasi dengan EDS yang menunjukkan sampel terdiri dari unsur C, Na, dan O, dan deteksi fase termonatrit (Na₂CO₃·H₂O) dengan XRD. Karakterisasi sampel yang disintering pada suhu 450 °C dengan XRD menunjukkan perubahan ke Na₂CO₃ dan Na₂O, yang juga didukung oleh hasil karakterisasi dengan DTA/TGA. Berdasarkan hasil yang diperoleh disimpulkan bahwa metode yang diusulkan pada penelitian ini berpotensi untuk diaplikasikan sebagai metode mitigasi gas CO₂ yang dihasilkan oleh industri arang tempurung kelapa.

Keywords: carbon dioxide, coconut shell, sodium carbonate, sodium hydroxide
1. Introduction

Currently, one of the most alarming global environmental problems is the increase of the greenhouse effect resulting from increased production of greenhouse gases. One of these is carbon dioxide (CO₂) emission, which has been predicted to continuously increase at a rate of more than 3.3% per year [1]. Atmospheric CO₂ levels can be largely attributed to the combustion of fossil fuels, cement production, the coconut shell charcoal industry, and land use changes. In Indonesia, the coconut shell charcoal industry is considered one of the main contributors to atmospheric CO₂, since this type of industry is mainly run by farmers using a traditional method of open burning. The ideal solution to the problem is conversion of CO₂ into valuable products, one of them Na₂CO₃. In addition to reduction of CO₂ released into the atmosphere, production of Na₂CO₃ offers several advantages simultaneously.

Sodium carbonate/soda ash (Na₂CO₃) is one of the most important raw materials used in vast arrays of chemical industries such as detergent, glass, soap, fertilizers, and pulp and paper industries. In large-scale industry, production of soda ash was carried out using Le Blanc and Solvay processes [2], although some other methods have been developed such as a carbonation process [3], sesquicarbonate process [4], and monohydrate process [5]. However, the Solvay process remains the most common production method. In the Solvay process, the raw materials used are brine as a source of sodium chloride, limestone as a source of calcium carbonate, and ammonia. The process involves a series of steps and reactions as presented below.

In the first step, limestone is heated at temperatures of 950–1100 °C to produce CO₂ gas according to the following equation:

\[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]  

(1)

The CO₂ gas is passed through a concentrated aqueous solution of sodium chloride (NaCl) and ammonia (NH₃) to produce sodium bicarbonate (NaHCO₃), according to the following equation:

\[ \text{NaCl} + \text{CO}_2 + \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3(s) + \text{NH}_4\text{Cl} \]  

(2)

The sodium bicarbonate (NaHCO₃) precipitate from Reaction (2) is then converted to sodium carbonate as the final product by calcinations at 160–230 °C, producing water and carbon dioxide as by-products:

\[ 2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \]  

(3)

The carbon dioxide from Reaction 3 is recovered and reused in Reaction 2, and ammonium chloride from Reaction 2 is reacted with CaO produced from Reaction 1 to recover the ammonia for reuse, according the following chemical equation:

\[ 2\text{NH}_3\text{Cl} + \text{CaO} \rightarrow 2\text{NH}_3 + \text{CaCl}_2 + \text{H}_2\text{O} \]  

(4)

Reaction between CO₂ gas and NaOH solution, as in the Solvay process, has been applied to absorb CO₂ gas, a method known as the wet scrubbing technique. This technique is defined as a method for removal of a gaseous component through contact with a liquid. In this technique, the sorbate is physically dissolved into the sorbent solution, and the reaction between them leads to production of a nongaseous product. Application of this method to CO₂ gas has been reported by several investigators [6-10]. It has also been concluded claimed that the production of Na₂CO₃ could be managed by adjusting the NaOH concentration around 7.2 M [11]. In order to recover the sodium hydroxide, the resultant sodium carbonate (Na₂CO₃) solution could be mixed with calcium hydroxide (Ca(OH)₂) to produce sodium hydroxide and calcium carbonate (CaCO₃).

With respect to the wet scrubbing process described above, this study was carried out to produce Na₂CO₃ by flowing the CO₂ gas produced from coconut shell combustion into NaOH solution, with the main purposes of investigating the effect of NaOH concentrations on the yield of the process and the characteristics of the Na₂CO₃ produced. The formation of Na₂CO₃ is based on the following reaction:

\[ 2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \]  

(5)

2. Experiment

Raw materials used for the experiments consist of coconut shell and NaOH pellets (Merck, kGaA, Damstadt, Germany) for preparation of the NaOH solution. The CO₂ gas was produced from coconut shell by burning it in a specially designed reactor of 20 L capacity, which allowed the gas to flow into the NaOH solution. Typically, 2 kg of dried coconut shell were placed into the reactor, and the shell was lit to commence combustion. Produced smoke was passed into a chamber filled with NaOH solution of concentrations of 6.5, 7.0, 7.5, and 8.0 M. Each experiment was conducted for two hours, during which the Na₂CO₃ was produced as precipitate. The solid was soaked with ethanol to wash out organic impurities and was then subjected to calcination at 110 °C for six h and ground with a mortar and pestle to obtain powder with the size of 250 mesh.

The functionality of the sample was characterized using Perkin Elmer FTIR spectroscopy. The sample was ground with KBr of analytical grade and scanned over the wave number of 4000–400/cm. Microstructural and elemental composition analyses were conducted using
scanning electron microscopy (SEM) (Philips-XL) coupled with energy dispersive spectrometry (EDS). The x-ray diffraction pattern was recorded with an automated Shimadzu XD-610 X-ray diffractometer equipped with a scintillation counter. The conditions for XRD analysis are as follows: source CuKα (λ = 1.5418 Å), 40 kV and 30 mA. Patterns were recorded over goniometer (2θ) from 5–70° with a step size of 0.02° and counting time per step of 1 s. Thermal analysis was carried out using Differential Thermal Analysis (DTA/TGA Merk Seiko Instrument Inc.). The thermogram was produced by scanning the sample at a temperature range of 50 °C to 1000 °C.

3. Results and Discussion

Typical visuals of raw Na₂CO₃ produced using different concentrations of NaOH solution are presented in Figure 1. As can be seen, the Na₂CO₃ powder is marked by a brownish color, indicating that the products are contaminated by some organics produced during the combustion process and trapped by the Na₂CO₃. For this reason, the raw products were purified by washing with ethanol until the white solid was obtained. The purified samples were then oven-dried at 110 °C for eight hours to remove the absorbed water. The dried sample was then weighed to determine the yield, and the results are presented in Table 1. The typical results of purified Na₂CO₃ are shown in Figure 2.

The data presented in Table 1 clearly indicate significant effects of NaOH concentration on the amount of Na₂CO₃ produced, with the optimum yield obtained using the 7.0 M NaOH solution. The experimental result using 6.5 M NaOH suggests that this solution is not concentrated enough to overcome the dissolution of formed Na₂CO₃ produced, due to its relatively high solubility in water. On the other hand, less product was obtained using the NaOH solution of 7.5 and 8.0 M, most likely due to oversaturated NaOH that hindered the penetration of CO₂ gas into solution. To confirm that the products were Na₂CO₃, the samples were characterized using several techniques.

Figure 3 presents the infrared spectra of Na₂CO₃ produced at different concentrations of NaOH. As can be seen, the spectra are practically similar in terms of the absorption bands detected and are marked by the existence of various absorption bands associated with CO₃²⁻, C-O, and C=O functional groups, confirming the formation of Na₂CO₃ [12-14].

The absorption bands located at 866 and 1446/cm are assigned to the stretching vibration of CO₃²⁻. The presence of this functional group is further supported by the detection of weak peaks located at 1069 and 1684/cm, attributed to deformed gaseous CO₂ that attached to NaCO₃ solid [15] and C=O [12], respectively. The wide

<table>
<thead>
<tr>
<th>NaOH Concentration (M)</th>
<th>Mass of Na₂CO₃ (g)</th>
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<tbody>
<tr>
<td>6.5</td>
<td>105.8</td>
</tr>
<tr>
<td>7.0</td>
<td>190.6</td>
</tr>
<tr>
<td>7.5</td>
<td>155.2</td>
</tr>
<tr>
<td>8.0</td>
<td>55.7</td>
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Figure 1. Visual Appearance of Na₂CO₃ Powder Produced at Different Concentrations of NaOH. (a) 6.5 M, (b) 7.0 M, (c) 7.5 M, and (d) 8.0 M

Figure 2. Typical Examples of Sodium Carbonate Pellets After Calcined at 110 °C

Figure 3. FTIR Spectra of Na₂CO₃ Sample Prepared At Different Concentrations of NaOH, (a) 6.5 M, (b) 7.0 M, (c) 7.5 M and (d) 8.0 M
peaks located at 2987 and 3273/cm are commonly assigned to the stretching vibrations of C-H and O-H. The presence of the O-H vibration shows the contribution of water [16-17]. The peaks at around 540 and 725/cm are assigned to the vibration band of C-S, probably originating from the combustion process and adsorbed by Na$_2$CO$_3$ [18].

The overall results obtained show that the highest yield was obtained using 7 M NaOH solution. This particular sample was subjected to sintering treatment at 450 °C for further characterization. Characterization of the original sample and the sample after being sintered at 450 °C using XRD produced the patterns of Na$_2$CO$_3$, as presented in Figs. 4a and 4b.

The phases were identified with the PDF diffraction lines using the search-match method [19], showing that the major phases are Na$_2$CO$_3$.H$_2$O/thermonatrite (PDF-080448), Na$_2$CO$_3$/sodium carbonate (PDF-18-1208), and Na$_2$O/sodium oxide (PDF-06-0500). The thermonatrite phase confirms the formation of Na$_2$CO$_3$ as a result of reaction of NaOH with CO$_2$ produced from the combustion process, while the sodium carbonate and sodium oxide phases most likely originated from thermonatrite crystallization during the thermal treatment. As can be seen, the sample without sintering (Figure 4a) is practically composed of thermonatrite. On the other hand, the sample sintered at a temperature of 450 °C (Figure 4b) is marked by the existence of sodium carbonate as the prominent phase, together with a small amount of sodium oxide. This finding suggests that at the applied sintering temperature, thermonatrite decomposed to sodium carbonate, followed by decomposition of some of the sodium carbonate into sodium oxide, which is in agreement with observations by others [20, 21]. The mean crystallite sizes ($L$) of Na$_2$CO$_3$ and Na$_2$O were calculated from the high peaks for each phase, using the Scherrer equation [22]:

$$L = \frac{k\lambda}{\beta\cos \theta}$$  \hspace{1cm} (6)

Where $k$ is the shape factor (0.94), $\lambda$ is the x-ray wavelength, $\beta$ is the line broadening at full width at half maximum (FWHM) in radians, and $\theta$ is the Bragg angle. The corresponding crystallite sizes calculated from the Scherrer equation are 5 µm for Na$_2$CO$_3$ and 7 µm for Na$_2$O in the sample sintered at 450 °C.

The scanning electron microscopy micrographs of the Na$_2$CO$_3$ samples are presented in Figure 5, and the corresponding EDS spectra are presented in Figure 6.
The micrograph of the sample produced at 7.0 M of NaOH is characterized by larger grains compared to the sample produced using 7.5 M of NaOH (Figure 5). This difference is most likely due to a higher quantity of the Na$_2$CO$_3$ produced, which resulted in more intensive aggregation. Despite this difference in the crystallinity of the samples, the EDS patterns of both samples are practically similar, marked by the presence of Na, C, and O (Figure 6), suggesting that the samples are of similar compounds. The percent weights of each element composition of the samples as seen by the EDS are compiled in Table 2. By comparing the percent weights of the elements in the Na$_2$CO$_3$ produced to those in Na$_2$CO$_3$, according to the stoichiometric values of Na (43.4%), C (11.3%), and O (45.3%), it can be seen that some difference should be acknowledged. This difference is most likely due to the formation of Na$_2$O, as observed using the XRD method and as previously discussed in the XRD results (Figure 4), and to the possibility of impurities undetected by the EDS. The presence of impurities is indicated by the FTIR results previously presented (Figure 3).

In this study, thermal characteristics of the sample were determined by analyzing with DTA/TGA. The DTA/TGA thermograms of the Na$_2$CO$_3$ sample produced at 7.0 M NaOH solution are shown in Figure 7. The TGA result (Figure 7) indicates the existence of two temperature zones, indicating the pattern of weight loss of the sample. At a temperature range from 50 to 110 °C, the weight loss is 10.2%, corresponding to the endothermic peak at 110 °C (sign 1). This peak is attributed to the removal of physically absorbed water and organic components adsorbed by the Na$_2$CO$_3$ particles. At temperatures ranging from 870 to 980 °C, the weight loss is 29.5%. This part of the thermogram indicates very evident decomposition and crystallization of Na$_2$CO$_3$, which is shown by the existence of an endothermic peak at 980 °C (sign 2). This endothermic peak is associated with the transformation of Na$_2$CO$_3$ into sodium oxide (Na$_2$O), which is in agreement with results of the thermal treatment of Na$_2$CO$_3$ at around 950 °C reported by others [23].

4. Conclusions

This study demonstrates that it is possible to produce sodium carbonate from the reaction of CO$_2$ released from coconut shell combustion with NaOH solution. The formation of Na$_2$CO$_3$ was confirmed by the results of several characterization techniques applied, particularly FTIR, EDS, and XRD. This finding demonstrated that CO$_2$ from coconut shell combustion could be used as a potential alternative raw material for the production of sodium carbonate and a reduction of CO$_2$ released into the atmosphere.

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