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The Use of Carbon Dioxide Released from Coconut Shell Combustion to Produce Na$_2$CO$_3$

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Abstract

In this investigation, sodium carbonate (Na$_2$CO$_3$) was produced by reacting the CO$_2$ 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 CO$_2$ gas released into the atmosphere by the coconut shell industry. The Na$_2$CO$_3$ powder produced was oven-dried at 110 ^{o}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 CO$_3^{-2}$, confirming the formation of Na$_2$CO$_3$. 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 Na$_2$CO$_3$ is also supported by the presence of C, Na, and O on the EDS results and the presence of the thermonatrite (Na$_2$CO$_3$.H$_2$O) phase, as seen by the XRD. The XRD analysis of the sintered sample at 450 ^{o}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 CO$_2$ gas released by the coconut shell industry.

Abstrak

Pemanfaatan Gas CO$_2$ Hasil Pembakaran Tempurung Kelapa untuk Produksi Natrium Karbonat. Penelitian ini dilakukan untuk mempelajari pemanfaatan gas CO$_2$ hasil pembakaran tempurung kelapa menjadi natrium karbonat (Na$_2$CO$_3$) dengan mereaksikan gas CO$_2$ dengan larutan NaOH dengan konsentrasi 6.5, 7.0, 7.5 dan 8.0 M. Tujuan utama penelitian adalah mengkaji potensi metode diusulkan sebagai cara mitigasi gas CO$_2$ yang dihasilkan dari industri arang tempurung kelapa. Padatan natrium karbonat yang dihasilkan selanjutnya dikeringkan dalam oven pada suhu 110 ^{o}C, lalu dikarakterisasi dengan FTIR, XRD, dan SEM/EDS. Analisis termal menggunakan metode DTA/TGA dilakukan untuk mempelajari karakteristik termal pembentukan Na$_2$CO$_3$. 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 CO$_3^{-2}$. Hasil FTIR juga menunjukkan adanya gugus fungsi C-S, yang kemungkinan besar karena adanya sulfur yang terdapat dalam tempurung kelapa secara alami. Pembentukan Na$_2$CO$_3$ juga didukung hasil karakterisasi dengan EDS yang menunjukkan sampel terdiri dari unsur C, Na, dan O, dan deteksi fase termonatrit (Na$_2$CO$_3$.H$_2$O) dengan XRD. Karakterisasi sampel yang disintering pada suhu 450 ^{o}C dengan XRD menunjukkan perubahan termonatrit menjadi Na$_2$CO$_3$ dan Na$_2$O, 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 CO$_2$ 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 (CO_2) emission, which has been predicted to continuously increase at a rate of more than 3.3% per year [1]. Atmospheric CO_2 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 CO_2, 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 CO_2 into valuable products, one of them Na_2CO_3. In addition to reduction of CO_2 released into the atmosphere, production of Na_2CO_3 offers several advantages simultaneously.

Sodium carbonate/soda ash (Na_2CO_3) 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 main 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 CO_2 gas according to the following equation:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad (1)$$
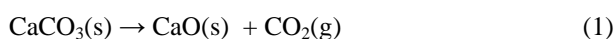
The CO_2 gas is passed through a concentrated aqueous solution of sodium chloride (NaCl) and ammonia (NH_3) to produce sodium bicarbonate ($NaHCO_3$), according to the following equation:

$$NaCl + CO_2 + NH_3 + H_2O \rightarrow NaHCO_3(s) + NH_4Cl \qquad (2)$$
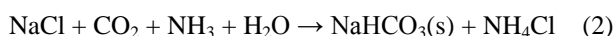
The sodium bicarbonate ($NaHCO_3$) precipitate from Reaction (2) is then converted to sodium carbonate as the final product by calcinations at 160–230 °C, producing water and carbon dioxide as by-products:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \qquad (3)$$
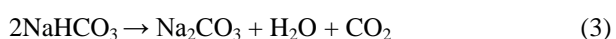
The carbon dioxide from Reaction 3 is recovered and reused in Reaction 2, and ammonium chloride from Reaction 2 is reacted with CaO produced from Reaction 1 to recover the ammonia for reuse, according the following chemical equation:

$$2NH_4Cl + CaO \rightarrow 2NH_3 + CaCl_2 + H_2O \qquad (4)$$
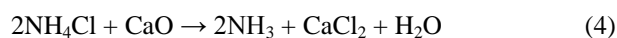
Reaction between CO_2 gas and NaOH solution, as in the Solvay process, has been applied to absorb CO_2 gas, a method known as the wet scrubbing technique. This technique is defined as a method for removal of a gaseous component through contact with a liquid. In this technique, the sorbate is physically dissolved into the sorbent solution, and the reaction between them leads to production of a nongaseous product. Application of this method to CO_2 gas has been reported by several investigators [6-10]. It has also been concluded claimed that the production of Na_2CO_3 could be managed by adjusting the NaOH concentration around 7.2 M [11]. In order to recover the sodium hydroxide, the resultant sodium carbonate (Na_2CO_3) solution could be mixed with calcium hydroxide ($Ca(OH)_2$) to produce sodium hydroxide and calcium carbonate ($CaCO_3$).

With respect to the wet scrubbing process described above, this study was carried out to produce Na_2CO_3 by flowing the CO_2 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 Na_2CO_3 produced. The formation of Na_2CO_3 is based on the following reaction:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad (5)$$
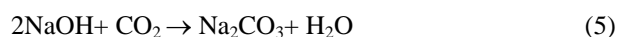
2. Experiment

Raw materials used for the experiments consist of coconut shell and NaOH pellets (Merck, kGaA, Damstadt, Germany) for preparation of the NaOH solution. The CO_2 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 Na_2CO_3 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 $CuK_\alpha(\lambda = 1.5418$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 ℃ to 1000 ℃.

3. Results and Discussion

Typical visuals of raw Na_2CO_3 produced using different concentrations of NaOH solution are presented in Figure 1. As can be seen, the Na_2CO_3 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 Na_2CO_3. 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 ^{o}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 Na_2CO_3 are shown in Figure 2.

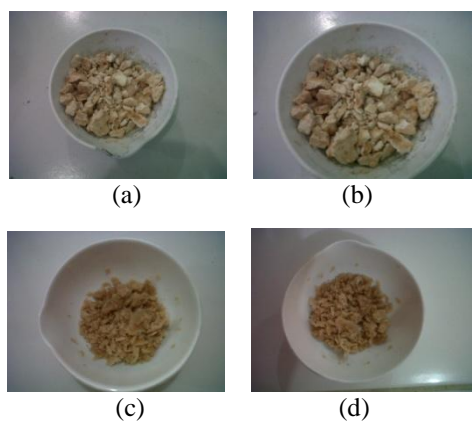**Figure 1. Visual Appearance of Na_2CO_3 Powder Produced at Different Concentrations of NaOH. (a) 6.5 M, (b) 7.0 M, (c) 7.5 M, and (d) 8.0 M**

Table 1. The Yield of Na_2CO_3 Powder Produced Using Different Concentrations of NaOH Solution

NaOH Concentration (M)	Mass of Na_2CO_3 (g)
6.5	105.8
7.0	190.6
7.5	155.2
8.0	55.7

The data presented in Table 1 clearly indicate significant effects of NaOH concentration on the amount of Na_2CO_3 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 Na_2CO_3 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 CO_2 gas into solution. To confirm that the products were Na_2CO_3, the samples were characterized using several techniques.

Figure 3 present the infrared spectra of Na_2CO_3 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 CO_3^{-2}, C-O, and C=O functional groups, confirming the formation of Na_2CO_3 [12-14].

The absorption bands located at 866 and 1446 cm^{-1} are assigned to the stretching vibration of CO_3^{-2}. 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 CO_2 that attached to $NaCO_3$ solid [15] and C=O [12], respectively. The wide

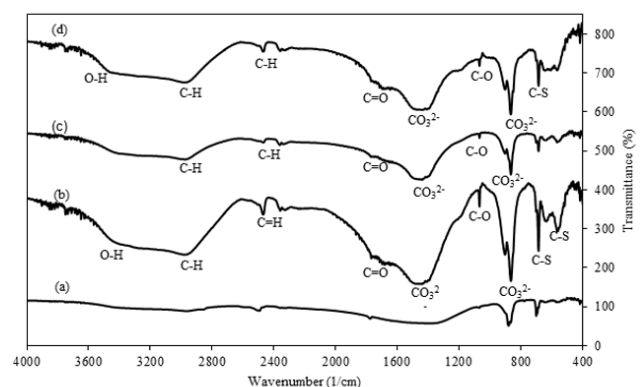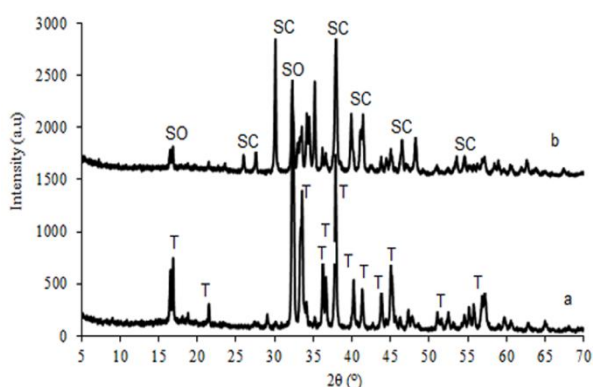**Figure 2. Typical Examples of Sodium Carbonate Pellets after Calcined at 110 ^{o}C**

Figure 3. FTIR Spectra of Na_2CO_3 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_2CO_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_2CO_3, as presented in Figures 4 (a) and (b).

The phases were identified with the PDF diffraction lines using the search-match method [19], showing that the major phases are $Na_2CO_3.H_2O$/thermonatrite (PDF-080448), Na_2CO_3/sodium carbonate (PDF-18-1208), and Na_2O/sodium oxide (PDF-06-0500). The thermonatrite phase confirms the formation of Na_2CO_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_2CO_3 and Na_2O were calculated from the high peaks for each phase, using the Scherrer equation [22]:

$$L = k\lambda/\beta\cos\theta \qquad (6)$$

Where k is the shape factor (0.94), λ is the x-ray wavelength, β is the line broadening at full width at half maximum (FWHM) in radians, and θ is the Bragg angle. The corresponding crystallite sizes calculated from the Scherrer equation are 5 μm for Na_2CO_3 and 7 μm for Na_2O in the sample sintered at 450 °C.

The scanning electron microscopy micrographs of the Na_2CO_3 samples are presented in Figure 5, and the corresponding EDS spectra are presented in Figure 6.

(a)   (b)
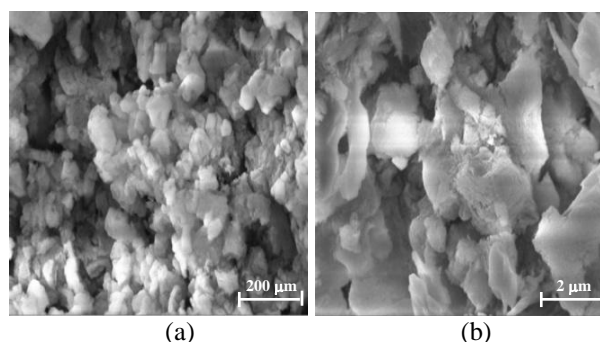
Figure 5. **The Scanning Electron Microscopy (SEM) Images of Na_2CO_3 Sample Prepared at Different Concentrations of NaOH Solution (a) 7.0 M, and (b) 7.5 M**

(a)

(b)
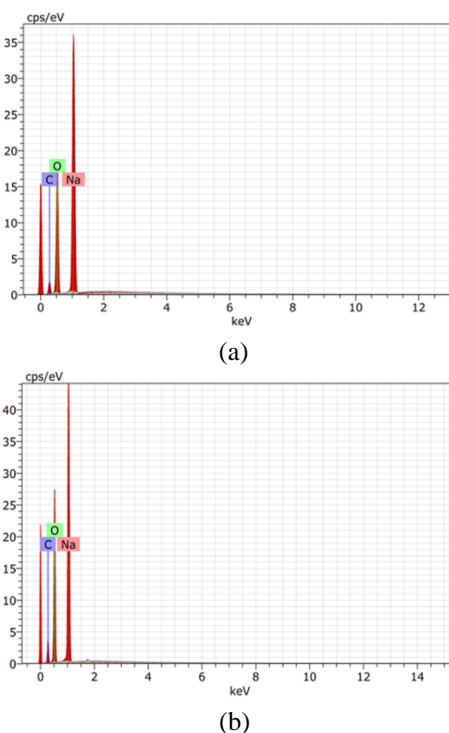
Figure 6. **The EDS Spectra of Na_2CO_3 Prepared at Different Concentrations of NaOH (a) 7.0 M and (b) 7.5 M**

Figure 4. **The x-ray Diffraction Patterns of the Original Sample (a) and the Sintered Sample (b) T= Thermonatrite ($Na_2CO_3.H_2O$), SC= Sodium Carbonate (Na_2CO_3), and SO= Sodium Oxide (Na_2O)**

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_2CO_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_2CO_3 produced to those in Na_2CO_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_2O, 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_2CO_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_2CO_3 particles. At temperatures ranging from 870 to 980 °C, the weight loss is 29.5%. This part of the thermogram

Table 2. Composition of Samples According to EDS Spectra

NaOH (M)	O (wt%)	C (wt%)	Na (wt%)
7.0	47.99	18.33	33.68
7.5	48.96	22.38	28.66
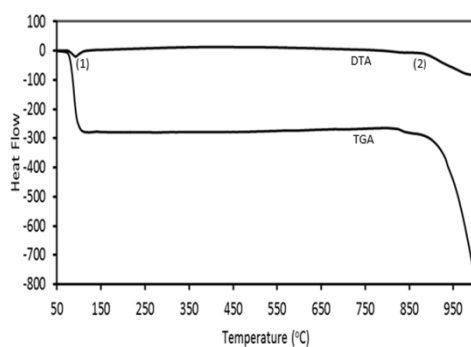
Figure 7. Analysis Thermal of Na_2CO_3

indicates very evident decomposition and crystallization of Na_2CO_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_2CO_3 into sodium oxide (Na_2O), which is in agreement with results of the thermal treatment of Na_2CO_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_2CO_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.

Acknowledgements

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