Synthesis and Characterization of Biochar from Crab Shell by Pyrolysis

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Abstract. Carapace, which is part of the crab shell exoskeletons were analysed through structural and chemical methods. This material was compared between grinded and ungrinded process. This two processes resulted product called biochar. SEM-EDS, FT-IR, XRD, TG-DSC, AAS, and PSA were conducted to characterized biochar. The SEM images showed different in biochar particles size. The composition of biochar differ for each pyrolyzed temperature, where Ca was the dominant element and C was the poor element. FT-IR spectra provided different spectra for biochar prepared at 500-600 °C and biochar prepared at 700-900 °C. XRD data showed that calcite and lime-based biochar depend on pyrolyzed temperature. Thermal analysis generated that biochar decomposed into three main stages. Otherwise, biochar through grinded step give resemble result as like biochar without grinded step, but has smaller particle size, which means grinded process did not give significant effect both structural and chemical composition, but give any effect on particle size. Furthermore, these study indicate that biochar potentially can be used as adsorbent.

Keywords: Biochar, crab shell, grinded, lime, pyrolysis

1. Introduction

Every year, around 6 to 8 million tonnes of waste crab, lobster, and shrimp shell are produced globally, where in developing countries, waste shells are often just dumped in landfill or the sea [1]. The abundant source of waste shell should be used, because the shell consist of some material that beneficial for many fields. But unfortunately, the potential value of such shell for chemical industry is being deficieneted. But now, many researcher have great attention on this material. Some material from crustacean like crab, shrimp and wood lice being study now.

Crustacea are one of omnifarious group of aquatic animals, that lives at different places, like in tropical to artic water, extending into freshwater and in some onto land for part of their life history, and the shoreline to the deep ocean [2]. For crustacea, the main important part is exoskeleton. The exoskeleton is the outer part of animal that has function to stabilizes animal body and as protection against predators. The crustaceans exoskeleton consist of biomineralized stucture which construct by organic matrix, along with inorganic mineral, that mostly contain calcium carbonate [3]. Calcium carbonate is widely used as filler [4], extender material in paper [5], cosmetic, medicine, paint, plastic, sealant, food, ceramics, textile, adhesive, etc. In previous paper, calcium carbonate has been produced from waste marble powder (WMP) by calcination-dissolution-precipitation (CDP) method [6]. While...
in animal, calcium carbonate is material that made exoskeleton of animal harder, for example in crab shell exoskeleton.

The exoskeleton of crab shell is a natural composite consist of highly mineralized chitin-protein fibers arranged in a twisted plywood or Bouligand pattern [7], where it was (snow crab) consist of 34.2% dw protein and amino acids, 17.1% dw fat, and 28.5% dw (calcium, phosphorous, and magnesium as major materials), and yother materials 21.2% bw [8]. This exoskeleton divided into three parts: carapace, claw, finger. Here, carapace was used as raw material of the study.

Carapace is the hard upper shell of tortoise, crustacean, or arachnid. In crustaceans, the function of carapace is as protective cover. This part of crab shell can be used as raw materials to produce biochar after pyrolysis applied because that is the most abundant part in crab shell. Combined with its application in soils, the production of biochar have been suggested as promising for mitigating climate change [9, 10], enhancing crop production [11] the waste disposal [12], and as simultaneously amending soil [13, 14]

Previously, researcher have been investigated SEM, X-ray micro diffraction, optical microscopy to decipher the functional role of calcium carbonate in lobster [9-11], identify the composition of the exoskeleton of two crustacea (lobster and crab) [12], investigate calcium rich biochar from the pyrolysis of crab shell for phosphorus removal [13]. But in present study, the as overarching objective was to compare the effect of insertion grinded and ungrinded process of biochar derived from carapace of crab shell. SEM-EDS, FT-Ir, TG-DSC, XRD, AAS, and PSA were conducted to analysed the sample characteristics.

2. Experimental method

2.1. Materials and biochar preparation

Crab shell waste was collected from Grogol Village, Gunung Jati District, Cirebon Regency. The shell was separated based on their parts (Carapace, claw, finger, etc). On this study carapace was used as raw materias. The carapace was washed with clean water, after that dried in the oven at 90 °C for 24 h.

The carapace was placed in mortal and pounded roughly. Then, with ground, finally sieved through 200 meshes (0.74 μm) before use. Carapace powder that passes 200 meshes sieving machine was collected. A crucible with around 6 gram of carapace powder was put in furnace for pyrolysis. Each of carapace powder was pyrolysis at 500 to 900 °C using Nabertherm GmbH Bahnhofstr 20.28865. at at heating rate 10 °C/min and keep for 1.5 h before cooling to room temperature. Further, the sample produced from this step was called biochar. The sample denoted for pyrolysis temperature 500 to 900 as follow: B500 (biochar pyrolysis at 500 °C), B600, B700, B800, B900 respectively with interval temperature 100 °C. Each of biochar produced from pyrolysis was weighed to calculate powder loss when pyrolysis occured.

Another sample was prepared with the same procedure, but between sieving and pyrolysing, carapace was grinded using high energy milling (HEM) for 15 h, then pyrolyzed at 500 °C (BG500). For grinded pros, the apparatus controlled as follow: 1 h grinded (on), 10 minutes rest grinded (off).

2.2. Characterization of biochar

The morphology of carapace powder and biochar were captured using scanning electron microscopy (SEM JEOL JSM IT-300) at 20.0 kV accelerating voltage for scanning the surface, whereas the electron dispersive spectroscopy (EDS) used to monitored the % composition of sample. Thermogravimetric-differential thermal analysis (TG-DTA) is used to quantitatively determine the mineral constituent, and also organic compounds that might be consist in the samples. The sample was measured by using TGA 209 Lybra (Netzsch), where the sample was heated from 40 to 900 °C for 10 °C/min of heating rate under N2 gas. Diffraction peak of biochar and carapace 200 mesh were recorded by x-ray diffraction (XRD) Bruker D8 ADVANCE at ambient temperature. Analysis was performed on peaks from the 2θ range between 10° to 70° with the rotating anode CuKα tube (λ = 1.5418 Å).
Particle size was calculated using particle size analyzer (PSA) Beckman Coulter™ LS I3 320 Laser Diffraction, where the powder were dispersed in DMF. Fourier transform infrared (FT-IR) Thermo Scientific Nicolet iS5 was taken to observe functional group in the sample. Atomic absorpsion spectroscopy (AAS) Agilent Technologies 200 Series AA was conducted to measure calcium and magnesium content. In this processes, wet destruction was applied to sample using HNO$_3$ and H$_2$O$_2$ overnight, continued with digestion using Advanced Microwave Digestion System Ethos at 1800 watt, 200 °C for 15 minutes, where 15 minutes was time to reach that temperature.

3. Results and discussion

3.1. Pyrolysis temperature variation and mineral analysis of biochar

Yield of crab shell pyrolyzed at various temperature were taken. It was shown that the yield was decreased from 66.21% for BG500 and 66.36% for B500 to 43.07% for B900. As temperature pyrolysis increase, % yield of biochar getting lower. It was happened because CaCO$_3$ decomposed to be CaO and CO$_2$, this carbon dioxide was release to the atmospher caused low of % yield. For BG500 dan B500 also showed quite similar data. In which for grinded process the % yield was 66.21%, and for ungrinded % yield 66.36%. The EDS was conducted to measure material composition. While AAS taken to compare composition data with EDS and provided data quantitatively. The detailed yield for each treatment are summarized in Table 1.

| Treatment          | % Yield | Particle Size (μm) | (PSA data) |
|--------------------|---------|--------------------|------------|
| 200 mesh           | -       | Mean 1.01          | Mode 1.75  |
| Grinded 15 h, pyrolysis 500 °C | 66.21   | 23.22              | 18.00      |
| 500 °C             | 66.36   | 9.19               | 5.36       |
| 600 °C             | 64.86   | 155.60             | 153.80     |
| 700 °C             | 45.66   | 17.64              | 19.76      |
| 800 °C             | 45.74   | 12.48              | 13.61      |
| 900 °C             | 43.07   | 90.73              | 168.90     |

Table 2. Summary of EDS and AAS result for elemental analysis.

| Treatment                          | Ca  | C   | O   | Mg  | Other (Na, Cl, Al) (wt.%) | Ca | Mg |
|------------------------------------|-----|-----|-----|-----|--------------------------|----|----|
| Method                             |     |     |     |     |                          |    |    |
| 200 mesh                           | 27.97 | 24.19 | 43.83 | 1.46 | 2.55 | 13.29 | 3.26 |
| Grinded 15 h, pyrolysis 500 °C     | 24.90 | 17.83 | 52.34 | 2.03 | 2.90 | 24.78 | 4.68 |
| 500 °C                             | 27.78 | 15.52 | 48.84 | 1.92 | 5.94 | 24.32 | 4.63 |
| 600 °C                             | 22.16 | 16.58 | 49.88 | 3.23 | 8.15 | 28.96 | 5.11 |
| 700 °C                             | 31.49 | 9.13  | 54.84 | 2.66 | 1.88 | 40.61 | 6.35 |
| 800 °C                             | 41.04 | 6.79  | 48.06 | 1.88 | 2.23 | 38.05 | 6.20 |
| 900 °C                             | 39.20 | 6.46  | 46.83 | 4.12 | 3.39 | 45.14 | 6.49 |

Energy dispersive spectroscopy detected that the mineral content varies for each treatment. Calcium, carbon, oxygen, phosphorus, magnesium present as major components of crab shell and biochar, whereas sodium, aluminium, chloride exist as minor components. This result is in tune that
calcium is the highest percentage of element, followed by magnesium [15]. From this result, as a function of pyrolysis temperature increased, the total calcium tend to increased (27.97 to 41.04 wt.%), except for B600 and B900, where calcium in B600 lower then B500, and B900 lower then B800; oxygen around 50 wt.%; and carbon 24.19 for B500, BG500 to 6.46 wt.% for B900.

Atomic absorption spectroscopy was conducted to measure elemental analysis of magnesium and calcium. The resulted data showed that there was not orderliness for magnesium, while for calcium, as temperature pyrolysis increased, the total calcium in the sample increase, except for calcium prepared at 800 °C. This measurement indicated that there was relationship between EDS and AAS calculation, namely there was not orderness both in EDS and AAS for magnesium as pyrolysis temperature increased, and there was an increasing tendency of calcium as pyrolysis temperature increased. Table 2 summarizes EDS and AAS results.

3.2. Biochar morphology and particle size

The SEM image afforded that there was not significant surface morphology from crab shell, BG500, B500 to B900. From SEM scanning, the all sample seems like powder, layer stacking and still in micrometer size. Crab shell 200 mesh typically has bigger size than grinded crab shell for 15 h. Furthermore, after pyrolysis treatment applied, the size of particle seems like smaller (Figure 1). But, by validating with PSA measurement, actually, after pyrolysis applied, the interval size of particle became wider. The mean, mode, size interval also varied, and there was not any trend. Table 1 presented PSA measurement result.

![Figure 1. SEM analysis of crab shell and biochar, (a) crab shell, (b) crab shell grinded 15 h, (c) BG500, (d) B500, (e) B600, (f) B700, (g) B800, (h) N900.](image)

3.3. TG-DSC analysis

Crab shell and biochar treated at 500 to 900 °C showed a quite different weight loss at some temperature (Figure 2, 3, 4). For crab shell and biochar, the first decomposition occurred at ambient temperature, which was signified to the volatilization such solvent and include endothermic process. The second stage at around 380-475 °C is exothermic process, it resulted two different appearance which attributed to organic matrix. For crab shell, BG500, B500, B600 this decomposition process do not appear, but appear at B700 to B900. On this stage, % mass loss 14.44%, 14.44%, and 14.77% for B700, B800, and B900 respectively. Whereas the mass loss associated to calcite thermal decomposition take placed at around 475-900 °C. At under pyrolysis treatment 600 °C, it involved high % mass loss calcite, from 36.39% to 38.38%, while for higher temperature, its content of calcite decreased slight with
temperature increased. These thermal analysis showed that, the spectra of BG500 is typical to B500. It mean, grinded did not change thermal properties. The thermal decomposition of calcite is endothermic.

![Figure 2](image2.png)

**Figure 2.** TGA of crab shell and biochar at different pyrolysis temperature.

![Figure 3](image3.png)

**Figure 3.** DTG of crab shell and biochar at different pyrolysis temperature.

### 3.4. XRD analysis

Crystalization of crab shell and biochar pyrolysis at temperature under 600 °C mainly constructed with calcite in which evidence with strong peak at 29.6° and slowly decreased at pyrolysis temperature above 700 to 900 °C. 23.2° also assign calcite peak, but in weak peak intensity [16]. Meanwhile, as peak 29.6° decreased, peak at 34.1° increased significantly at B700, B800, B900. The peak suggested that calcite has been undergo thermal decomposition to another crystal form. This crystal form known as lime. The thermal decomposition of calcite shown in Figure 5. The other peak that showed lime were at 50.8°, and 18.0°.
The crystallinity of all sample also determined. The crystallinity from crab shell to B600 gradually increase, and decline for B700, further increase slowly from B700 to B900. The crystallinity of crab shell, BG500, B500, B600, B700, B800, and B900: 65.9%, 79.5%, 79.1%, 80.6%, 74.3%, 77.5%, 78.6% respectively. The reduced % crystallinity from B600 to B700 because the transformation crystallinity form from calcite to lime. This XRD result conclude that biochar prepared at bellow 600 °C was calcite-based biochar, and at above 700 °C resulted lime-based biochar [17].

![Figure 4. DSC of crab shell and biochar at different pyrolysis temperature.](image)

![Figure 5. XRD data of crab shell and biochar at different pyrolysis temperature.](image)

3.5. FT-IR Analysis
The FT-IR analysis of crab shell and biochar with different pyrolysis temperature showed specific band of calcite and lime (Figure 6). The calcite band occurred around 1450 cm\(^{-1}\), 874 cm\(^{-1}\), 712 cm\(^{-1}\) for crab shell, BG500, B500, B600. This peak is in a good agreement with calcite typical absorption peaks around 1433, 874, and 713 cm\(^{-1}\) [16]. The other literature resulted that calcite (CaCO\(_3\)) in crab shell occurred at 1796, 1456, and 874 cm\(^{-1}\) [18].
On the other hand, lime band represented at 2642 cm\(^{-1}\), it was suggested that Ca(OH)\(_2\) formed. This band appeared to crab shell which pyrolyzed at above 700 °C. Together with XRD data, the FT-IR data showed that calcite is the main calcium crystal for biochar prepared under 600 °C, while at pyrolysis temperature above 700 °C, lime is formed and the most abundant calcium crystal form. However, the other band appeared for CH, CH\(_2\), CH\(_3\) at 2925-2850 cm\(^{-1}\).

**Figure 6.** FT-IR of crab shell and biochar at different pyrolysis temperature.

4. **Conclusions**

This study presented that there was not any effect on the insertion grinded proses for 15 h before pyrolysis. Furthermore, from FT-IR and thermal analysis the grinded did not give different significant chemical or physical properties of biochar. XRD analysis showed that at below 600 °C, it produced calcite-based biochar, while at above 700 °C produced lime-based biochar. This data also conclude that as temperature pyrolysis increased, % yield of biochar gradually decrease. From elemental analysis showed that calcium is the major component, and carbon is the minor component, where EDS and AAS calculation give linear trend for magnesium and calcium element.

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**References**

[1] Yan N and Chen X 2015 Don’t waste seafood waste *Nature* **524** 155-157 DOI 10.1038/524155a

[2] Penn J W, Caputi N, Lestang S D, Johnston D, Kangas M, and Bopp J 2018 Crustacean fisheries *Earth Systems and Environmental Sciences* DOI: 10.1016/B978-0-12-409548-9.09577-4

[3] Meldrum F C 2003 Calcium carbonate in biomineralisation and biomimetic chemistry *International Materials Reviews* **48** 187-224 DOI: 10.1179/095066003225005836

[4] Karakas F and Celik M S 2012 Effect of quantity and size distribution of calcite filler on the quality of water borne paints *Progress in Organic Coatings* **74** 555-563 DOI: 0.1016/j.porgcoat.2012.02.002
[5] Lopez-Periago A M, Pacciani R, Garcia-Gonzalez C, Vega L F and Domingo C 2010 A breakthrough technique for the preparation of high-yield precipitated calcium carbonate J. Supercrit. Fluids 52 298–305 DOI: 10.1016/j.supflu.2009.11.014

[6] Erdogan N and Eken H A 2017 Precipitated calcium carbonate production, synthesis and properties, Physiochem. Probl. Miner. Process 53 57-86 DOI: 10.5277/ppmp170105

[7] Chen P-Y, Albert Y-M, Joana M and Marc A M 2008 Structure and mechanical properties of crab exoskeletons Acta Biomaterialia 4 587-596 DOI: 10.1016/j.actbio.2007.12.010

[8] Maria A L Y, Maria V M, Susana A P and Julia L H 2011 Chemical composition of snow crab shells (chionoecetes opilio) CyTA-Journal of Food 9 265-270 DOI: 10.1080/19476337.2011.596285

[9] Cusack D F, Axsen J, Shwom R, Hartzell-Nichols L, White S and Mackey KRM 2014 An interdisciplinary assessment of climate engineering strategies Frontiers in Ecology and the Environment 12 280–287 DOI: 10.1890/130030

[10] Smith P 2016 Soil carbon sequestration and biochar as negative emission technologies Global Change Biology pp. 1-10 DOI: 10.1111/gcb.13178

[11] Dickinson D, Balduccio L, Buyssse J, Ronsses F, van Huylkenbroeck G and Prins W 2015 Cost-benefit analysis of using biochar to improve cereals agriculture Global Change Biology Bioenergy 7 850–864 DOI: 10.1111/gcbb.12180

[12] Jeffery S, Bezemer T M, Cornelissen G, Kuyper T S W, Lehmann J, Mommer L, Sohi S P, Voorde T F J V D, Wardle D A and Groenigen J W V 2015 The way forward in biochar research: targeting trade-offs between the potential wins Global Change Biology Bioenergy 7 1-13 DOI: 10.1111/gcbb.12132

[13] Gul S, Whalen J K, Thomas B W, Sachdeva V, Deng H Y 2015 Physico-chemical properties and microbial responses in biochar-amended soils: mechanisms and future directions Agriculture, Ecosystems and Environment 206 46–59 DOI: 10.1016/j.agee.2015.03.015

[14] Puga A P, Abreu C A, Melo L C A and Beesley L 2015 Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium Journal of Environmental Management 159 86–93 DOI: 10.1016/j.jenvman.2015.05.036

[15] Bobelmann F, Romano P, Fabritius H, Raabee D and Eppele M 2007 The composition of the exoskeleton of two crustacea: the american lobster Homarus americanus and the edible crab Cancer pagarus Thermochemica Acta 463 65-68 DOI: 10.1016/j.tca.2007.07.01

[16] Jimoh O A, Otitoju T A, Hussin H, Arieffin K S and Baharan N 2017 Understanding the precipitated calcium carbonate (PCC) production mechanism and its characteristics in the liquid-gas system using milk of lime (MOL) suspension S. Afr.J.Chem. 70 1-7 DOI: 10.17159/0379-4350/2017/v70a1

[17] Dai L, Tan F, Li H, Zhu N, He M, Zhu Q, Hu G, Wang L, and Zhao J 2017 Calcium-rich biochar from the pyrolysis of crab shell for phosphorus removal Journal of Environmental Management 198 70-74 DOI: 10.1016/j.jenvman.2017.04.057

[18] Gbenor O P, Adeosun S O, Lawal G I and Jun S 2016 Role of CaCO3 in the physicochemical properties of crustacean-sourced structural polysaccharides Materials Chemistry and Physics 184 203-209 DOI: 10.1016/j.matchemphys.2016.09.043