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Production of biocoke from microalgae powder

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Abstract. Biocoke has been invented to replace commercial coke in order to reduce the consumption of fossil fuels. However, the main target of the feedstock has been limited to plant and wood biomass, while algal biomass is rarely used. This work evaluated four microalgae species: *Chlorella*, *Nannochloropsis*, *Diatoms*, and *Aurantiochytrium* as the feedstocks to produce biocokes. The production of the biocoke was set to 100°C at 20 MPa for 6 mins 20 secs. Based on visual observation, the color of the biocokes produced was darker than the microalgae powder due to the Maillard reaction. This study suggested that the *Chlorella* and *Nannochloropsis* biocoke have the potential to produce the biocoke due to their oleaginous characteristic. *Nannochloropsis* had a higher apparent density than *Chlorella* biocoke. However, the *Chlorella* had a higher compression strength of 37.55MPa, compared to *Nannochloropsis* (27.70MPa). Meanwhile, *Aurantiochythrium* biocoke had an irregular shape and was sticky due to the high lipid content in the species. The *Diatoms* biocoke was hard but chalky due to its silica shell on the microalgae cell. Therefore, the *Aurantiochythrium* and *Diatoms* were not suitable for producing the biocokes.

1. Introduction

Biomass, a traditional energy resource, is readily available in the environment. However, there are issues with employing biomass as a fuel, including the low calorific value per unit volume and the need for particular treatment before transport and storage. Pelletizing and briquetting biomass to increase energy density are well-known densification methods that have been available for a long time. Meanwhile, biocoke has been introduced recently to partially substitute coal coke in the metal casting process [1]. This highly densified biomass is produced from biomass or municipal waste with high temperature and pressure. Biocoke is a carbon-neutral fuel that has the potential to reduce carbon dioxide emissions. According to Fuchigami et al. [2], the application of biocoke could reduce 2.16 tons of carbon dioxide emission compared to coal-coke. Most of the research utilized agricultural biomass to create biocokes, such as rice straw, rice husk, palm oil residues, mushroom spent, orange and banana peel [3] [4] [5]. However, the primary feedstock target has been limited to plant and wood biomass, whereas algal biomass is rarely used.

Algae are photosynthetic organisms that live in both fresh and salt water. They would consume carbon dioxide and produce approximately 50% of the oxygen in the atmosphere. Furthermore, the algae may help reduce contaminants in the water, such as nitrogen, phosphorus, and heavy metals [6]. The algae would intake the contaminants from wastewater quickly, removing the contaminants in the water. Meanwhile, growing lignocellulosic biomass would require more time and land to achieve mass production. Compared to lignocellulosic biomass, algae can capture 50 times more carbon dioxide during photosynthesis [7]. Algae has long been used as a dietary supplement, cosmetic, and energy source [8]. It has the potential to produce biofuel in a carbon-neutral manner. Microalgae have been used as a binder in the production of pellets [9], but no microalgae biocoke has been produced.

This preliminary study aims to investigate the feasibility of microalgae biocoke from various species. Four species of oleaginous microalgae, namely *Chlorella*, *Nannochloropsis*, *Diatoms*, and *Aurantiochytrium,* were utilized as raw materials for biocoke production. These microalgae powders were heated under high pressure and collected for further analysis. The color, apparent density, and maximum compressive strength of microalgae biocokes were determined.

2. Methodology

2.1 Production of biocoke

Four microalgae species were used to produce biocokes: *Chlorella*, *Nannochloropsis*, *Diatoms*, and *Aurantiochytrium.* Biocoke production followed the method described in the Japan patent WO2006077652 [10]. Firstly, 11g of microalgae powder was placed into a 20 mm diameter closed-end cylinder. Then, the cylinder was sealed with a mold and loaded with a pressure of 20 MPa by hydraulic pressure (SMP–3012B, Riken Kiki, Japan). Afterward, the cylinder was heated to 100°C by an electric furnace (ARF-50M, Asahi Rika, Japan) and retained for 6 min 20 s. Lastly, the cylinder was cooled to room temperature, and the biocoke was collected. All samples were prepared in triplicate.

2.2 Apparent density measurement

The collected biocoke was weighed and measured. The apparent density was obtained from the mass and volume of the biocoke, as stated in equation 1 [11]. Since the biocoke's shape is a cylinder, the volume was calculated by equation 2.

$$D = \frac{M}{V} \quad (1)$$

$$V = \pi r^2 h \quad (2)$$

where D is the density (g/cm^3), M is the mass (g), V represents the volume (cm^3), r is the radius (cm), and h represents the height (cm).

2.3 Compressive strength

Compressive strength is defined as the maximum load that samples can withstand. In this analysis, the compressive strength of the biocoke was determined by a universal testing machine (AG-X plus kN20, Shimadzu, Japan). The biocoke sample was placed in the middle of the machine. Then, the load was applied from the top until it cracked. The loading rate was 1.5 mm/min. The experiment was conducted at room temperature [12].

3. Result and discussion

The primary components of the microalgae were protein, carbohydrates, residual sugar, and lipids. Based on Figure 1, the color of the biocokes was darker than the raw microalgae powder due to the heating process, causing the Maillard reaction. This chemical reaction happens between the amino acid and reducing sugar during heat [13]. Firstly, condensation of the reducing sugar with the amino groups leads to the amadori product. During the subsequent reaction stage, the amadori product was disintegrated into multiple fission products of the sugar-amino compound. At the final reaction stage, condensation of amino compounds and sugar fragments into polymerized protein and brown pigments called melanoidins results in the brown compound [14].

Among the four types of biocoke, *Aurantiochythrium* biocoke had an irregular shape and was sticky due to the high lipid content in the species. This biocoke was soft and sticky when freshly removed

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from the cylinder, and this caused the irregular shape of the biocoke. The sticky characteristic generates difficulty in removing the biocoke from the cylinder mold, creating much raw material loss. Meanwhile, the *Diatoms* biocoke was hard but chalky due to its silica shell on the cell of the microalgae species. The biocoke was not formed into a perfect cylinder due to its chalky characteristic. This chalky characteristic may cause ash deposition during combustion in the equipment.

Chlorella and *Nannochloropsis* biocokes were easy to remove from the cylinder resulting in a regular cylinder shape because they were oleaginous microalgae. Since the *Aurantiochythrium* and *Diatoms* biocokes were not in perfect shape and had chalky properties, they were not suitable for producing biocoke. Thus, only *Chlorella* and *Nannochloropsis* biocokes had proceeded for further analyses.

No.	Type of microalgae	Raw microalgae powder	Top view of biocoke	Side view of biocoke
1	*Nannochloropsis*			
2	*Chlorella*			
3	*Aurantiochytrium*			
4	*Diatoms*			

Figure 1. Raw microalgae powder, top and side view of *Nannochloropsis*, *Chlorella*, *Aurantiochytrium*, and *Diatoms* biocokes samples.

Based on Table 1, the apparent densities of the *Nannochloropsis* and *Chlorella* biocokes were 1.22 g/cm^3 and 1.32 g/cm^{3,} respectively. The apparent density of both microalgae biocokes was higher than the lignocellulosic biomass pellet, such as oil palm empty fruit bunch pellet (1.185 g/cm^3) [15]. Those values are comparable to the apparent density of various lignocellulosic biocokes in the range of 1.255 – 1.444 g/cm^3 [15]. The result also shows that *Nannochloropsis* biocoke had a higher apparent density than the *Chlorella* biocoke. High apparent density is vital for the transportation and storage of the biocoke to save space and lower the cost [15].

High compressive strength will reduce the damage or loss during the biocoke's transportation and storage [15]. Both microalgae biocokes show high strength compared to biomass pellets ranging from 5.97 MPa to 11.80 MPa [16]. The *Chlorella* had higher compression strength of 52.70 MPa, compared to the *Nannochloropsis* (26.41 MPa). Therefore, the *Nannochloropsis* and *Chlorella* biocoke could be a candidate for biocoke production in the future.

Table 1. The apparent density and maximum compressive strength of the biocokes.

Type of biocoke	Apparent density (g/cm^3)	Maximum compressive strength (MPa)
Chlorella	1.22 ± 0	52.70 ± 0.60
Nannochloropsis	1.32 ± 0.0015	26.41 ± 11.57

4. Conclusion

In conclusion, four types of microalgae as biocoke feedstock have been evaluated. Two are suitable, while the other two are not. Due to their irregular shape and chalky characteristics, A*urantiochythrium* and *Diatoms* biocokes are unsuitable for biocoke sample production. On the contrary, *Chlorella* and *Nannochloropsis* biocokes had a regular shape, indicating their suitability for biocoke production. In addition, *Nannochloropsis* biocokes had a higher apparent density (1.32 0.0015 g/cm3) than *Chlorella* biocokes. Meanwhile, the *Chlorella* biocoke obtained higher maximum compressive strength (52.70 ± 0.60 MPa) than *Nannochloropsis* biocokes. The high compressive strength and apparent density of the biocoke would facilitate its transportation and storage.

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