Rice husk-based biochar for carbon dioxide adsorption in biogas

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Abstract. Rice husk-based biochar has been prepared by pyrolysis process for carbon dioxide adsorption in biogas. Biochar is considered as porous material for carbon dioxide adsorption. In this study, the adsorption of carbon dioxide, the largest impurity in biogas, was evaluated. The adsorptions were conducted in five treatments (mass variation): 80 grams of biochar (RB1), 60 grams of biochar and 20 grams of zeolite (RB2), 40 grams of biochar and 40 grams of zeolite (RB3), 20 grams of biochar and 60 grams of zeolite (RB4), 80 grams of zeolite (RB5). The best performance of carbon dioxide adsorption showed by RB1 with the decrease in carbon dioxide up to 31.59%. Characterization of adsorbents were also investigated by surface area analyzer to know relation between surface area and adsorption capability. It was found that the larger surface areas are favorable to adsorb carbon dioxide.

1. Introduction
Bio-methane in biogas brings a new alternative energy for cooking or lighting [1],[2]. Bio-methane is produced from anaerobic digestion of biomass such as livestock manure or organic waste in biodigester. The largest raw material resources for biogas production comes from agriculture and livestock waste. But many people in rural areas of Indonesia still use firewood for cooking where causing respiratory problem [3]. Since development of biogas technology, it’s considered as alternative clean energy for cooking in developing countries. Biogas reduces global warming emissions by trapping bio-methane that produced from anaerobic digestion of biomass [4]. Moreover, infection agents such as bacteria, viruses, and parasites from organic waste can be minimized through biogas technology [5]. It works by converting biomass to bio-methane and isolating bio-methane as fuels for cooking or lighting. Bio-methane makes up combustible part of biogas, a colourless and odourless gas and has calorific value of 39.8 MJ/m3 [6]. Besides bio-methane, carbon dioxide and a smaller hydrogen sulfide are also produced in biogas. Carbon dioxide in biogas causes calorific value reduction so that it must to be removed from biogas.

There are many ways to reduce carbon dioxide contents and increase bio-methane in biogas. They fall on three categories: physical, chemical and biological methods. Adsorption becomes one of physical method that low energy and capital cost compared to the other methods [7]. The adsorption principal is how to separate certain gases from gas mixtures based on the affinity to solid adsorbent
Many researchers have evaluated utilization of biomass-based biochar to adsorb carbon dioxide such as based on chicken manure [9-10], rice straw [11], sawdust [12] and the others. Biochar is carbon-based material with carbon content range of 50-93%. Benefit from utilizing biochar compared to activated carbon is more environmentally friendly because of low energy and chemical consumption [13],[14]. In this study we investigated rice husk-based biochar. Rice plants is the biggest crops commodity in Indonesia. Statistics Indonesia [15] reported that estimation of total rice production in 2018 amount to 56.54 million ton of dry gain. It means that rice husk, which is a major by-product from rice milling industries, is abundant. Like other biomass waste, rice husk contains carbon material from cellulose and hemicellulose. Therefore, it could be recognized as potential valuable carbon-based material. Besides, giving waste management solution [16], rice husk-based biochar production is the key for enhancing the performance of bio-methane for cooking or lighting. Rice husk-based biochar has been prepared in this work to adsorb carbon dioxide in biogas. The adsorption of carbon dioxide aims to enhance bio-methane content in biogas. Carbon dioxide adsorption was conducted in adsorption column. The different focus study from other studies is carbon dioxide adsorption implementation directly using pure biogas, not synthetic biogas or pure carbon dioxide.

2. Methodology

2.1. Adsorbents preparation
Rice husk were collected from farmers in Bantul, near Center of Agrotechnology Innovation, Universitas Gadjah Mada. Rice husk were pyrolyzed in a pyrolysis column with oxygen free condition and temperature at 225°C condition. Prior to pyrolysis, rice husk was dried under sunlight for one day. After 3 hours pyrolysis, the column pyrolysis was cooled down over night.

Natural zeolite was also prepared in this work. Natural zeolite crushed to 1-3 mm and then used as combination adsorbent in this work. Rice husk-based biochar and natural zeolite samples were prepared for carbon dioxide adsorption and characterization. Surface area analysis of biochar and natural zeolite were examined by nitrogen adsorption using surface area analyzer.

![Scheme of adsorption column for carbon dioxide reduction in biogas.](image)

2.2. Carbon dioxide adsorption
Carbon dioxide adsorption was performed at room temperature and gas pressure range of 5-7 bar. The combination of adsorbents, rice husk-based biochar and zeolite were inserted into adsorption column (see figure 1). Design of adsorption column was adopted from Lalhmingsanga [17] with modification. Biogas was passed in adsorption column containing adsorbents with formula in table 1. After 10 minutes contact with adsorbents, biogas were analyzed using gas chromatography.
Table 1. Adsorbent formulations.

| Samples | $1^{st}$ column (gr) | $2^{nd}$ column (gr) |
|---------|----------------------|----------------------|
|         | biochar  | zeolite | biochar  | zeolite |
| RB1     | 80       | 0       | 80       | 0       |
| RB2     | 60       | 20      | 60       | 20      |
| RB3     | 40       | 40      | 40       | 40      |
| RB4     | 20       | 60      | 20       | 60      |
| RB5     | 0        | 80      | 0        | 80      |

3. Results and discussion

Carbon dioxide adsorption aimed to enhance biogas performance for cooking or lighting by methane enrichment. Carbon dioxide content in raw biogas (biogas before passing in adsorption column) and purified biogas (biogas after passing in adsorption column) were analyzed by gas chromatography. Carbon dioxide adsorption after biogas purification indicated the enhancement biogas performance. The schematic of adsorption column is showed in Fig. 1. Natural zeolite was placed at the bottom of the column while biochar was above natural zeolite. The carbon dioxide adsorption contact time followed others researches that based on carbon dioxide breakthrough curve for activated carbon [17]-[19]. The carbon dioxide content in raw and purified biogas are showed in Table 2.

Table 2. The carbon dioxide content in biogas

| Samples | Raw biogas (ppm) | Purified biogas (ppm) | The decrease of carbon dioxide (%) |
|---------|------------------|-----------------------|-----------------------------------|
| RB1     | 223086           | 152607                | 31.59                             |
| RB2     | 244708           | 199795                | 18.35                             |
| RB3     | 228307           | 207409                | 9.15                              |
| RB4     | 225230           | 196016                | 12.97                             |
| RB5     | 228307           | 202401                | 11.35                             |

The study showed that after purification, carbon dioxide content in biogas decreased. It means that biochar and natural zeolite were capable to capture carbon dioxide in biogas. The decrease in carbon dioxide increased when the mass of biochar was heavier than zeolite. The best performance in carbon dioxide adsorption was performed by RB1 with the decrease in carbon dioxide of 31.59%. By adding mass of biochar in adsorption column, carbon dioxide concentration decreased.

The carbon dioxide adsorption can relate to pore size of adsorbent [20]. Specific surface area of biochar and zeolite are showed in Table 3. Either biochar or natural zeolite has pores on its surface. Pores on surface of them have important role to adsorb carbon dioxide [19]. The capability of carbon dioxide has an implication on the increase in methane composition and calorific value of biogas. Ambar [11] and Margaretha [21] were also reported that the use of biochar enriched methane composition and calorific value of biogas. These results also showed that the greater amount mass of biochar in adsorption column impacted on the greater carbon dioxide reduction.
Table 3. The result of surface area from biochar and natural zeolite based on this study and other references

| Adsorbent                  | Specific surface area (m²/g) | Specific surface area (m²/g) |
|----------------------------|------------------------------|------------------------------|
| Natural zeolite            | 27.90                        | 38.6 [22]                    |
| Rice husk-based biochar    | 33.04                        | 33.5 [23]                    |

Based on Table 3, we concluded that the carbon dioxide adsorption capacity related to specific surface area of adsorbent. The larger specific surface area lead to higher capacity to adsorb carbon dioxide. In this study, biochar has larger specific surface area compared to natural zeolite. Many hollow aromatic carbons of biochar formed many pores and made larger specific surface area. Rice husk-based biochar could be proposed as a substitute for natural zeolite in carbon dioxide adsorption. Although the increase in adsorbing carbon dioxide has not been significant, it could be a good start in alternative material for biogas purification implementation with further innovation.

4. Conclusion
From this study, we concluded that rice husk-based biochar could be an alternative porous material that adsorb carbon dioxide in biogas. Formulation of 100% biochar or without combination gave the best performance in carbon dioxide adsorption although not significantly. Rice husk-based biochar was considered as an adsorbent in biogas purification. Further research relating to optimal condition in the carbon dioxide adsorption needs to be developed in future work.

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