The Waste Recycling of Sugarcane Bagasse-Based Biochar for Biogas Purification

M A Wuri\textsuperscript{1}, A Pertiwiningrum\textsuperscript{2*}, R Budiarto\textsuperscript{3}, M Gozan\textsuperscript{4} and A W Harto\textsuperscript{5}

\textsuperscript{1} Center for Energy Studies, Universitas Gadjah Mada, Yogyakarta, 55281, Indonesia
\textsuperscript{2} Department of Animal Products Technology, Faculty of Animal Science, Universitas Gadjah Mada, Yogyakarta, 55281, Indonesia
\textsuperscript{3,5} Department of Nuclear and Physics Engineering, Faculty of Engineering, Universitas Gadjah Mada, Yogyakarta, 55281, Indonesia
\textsuperscript{4} Bioprocess Engineering Program, Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Depok, 16424, Indonesia

Abstract. The utilization of the recycling of biomass waste for carbon dioxide (CO\textsubscript{2}) adsorption in biogas is still rare. Even though the experiments on the biogas purification still using synthetic biogas. This paper investigated the recycling of biomass waste, sugarcane bagasse for biogas purification. The conversion of biomass into biochar was claimed to expand the surface area of its pores for capturing CO\textsubscript{2} in biogas. Five treatments of adsorbents used in this study, 100\% volume of zeolite or biochar, 75\% volume of zeolite and 25\% biochar, 50\% volume of zeolite and biochar, 25\% volume of zeolite and 25\% volume of zeolite, and 25\% volume of biochar. The difference of volume treatment in adsorbents affected methane (CH\textsubscript{4}) and CO\textsubscript{2} composition of biogas. Biogas purification by adsorption was conducted at 5-7 bar pressure range and room temperature. Biogas before and after purification were tested of CH\textsubscript{4} and CO\textsubscript{2} composition by gas chromatography. A significant reduction in CO\textsubscript{2} was shown when 50\% volume of zeolite was replaced by biochar. The highest in CO\textsubscript{2} reduction showed by the composition of 50\% sugarcane bagasse-based biochar and 50\% natural zeolite. The CO\textsubscript{2} decreases did not accompany by the CH\textsubscript{4} increases because mesopore-sized still dominated the adsorbents’ pore size.

1. Introduction

Liquefied petroleum gas (LPG) in Indonesia is still be subsidized by the government for the poor segments and the vulnerable group of society. Indonesia’s liquefied petroleum gas (LPG) subsidies are not only an increasing drain on the country’s budget, but they are also inefficient from a social equity perspective, as most of the subsidies go to the wealthier segment of the society [1]. Until finally, the Covid-19 pandemic hits Indonesia. The number of positive confirmed cases increased and spread to all regions of Indonesia. The Covid-19 responses has begun to be implemented the social activities restriction or Pemberlakuan Pembatasan Kegiatan Masyarakat (PPKM). The implementation of PPKM has an impact on almost all sectors of socio-economic life. The energy sector is significantly affected by the PPKM implementation. During PPKM, more people stay at home, so that the demand for household energy demand increased. For example, the availability of LPG is one of the challenges during the pandemic. Daily subsidized and non-subsidized LPG demand increased by 1\% to 22.117
million tons from the basic level of 21.927 million tons and 9%, respectively [2]. The increase in LPG demand will increase drain off on the country's budget. Ministry of Energy and Mineral Resources (MEMR) reported that the volume of subsidized LPG sold has continuously risen since the subsidy’s inception in 2009, and LPG subsidies translated into public spending of IDR 54 trillion (USD 3.8 billion) in 2019 [3]. It is predicted to increase with the increasing demand for LPG during the pandemic. In addition, LPG needs or demand in Indonesia are still partially fulfilled by import. In the pessimistic scenario (PES), around 70% of the national LPG supply will be imported [4].

The growth of LPG imports can be suppressed by substituting LPG with massive electricity or natural gas. An alternative solution is starting to use renewable energy resources like biogas technology. Biogas as alternative bioenergy is produced by anaerobic activity or fermentation of organic matter in a digester or reactor. Biogas is flammable and can therefore be used both in energy production and transport. The gas composition produced from the organic fermentation consists of methane and carbon dioxide approximately 55-70% and 30-45%, respectively, and a small amount of nitrogen, hydrogen, hydrogen sulfide, water, and other gases. Biogas is environmentally friendly energy because it uses organic waste as raw material in energy source production [5]. Biomass waste like agricultural and livestock waste is the common raw material in biogas production.

In developed countries, the upgrading of biogas for use as a fuel for vehicular or other applications is more being promoted. The biogas purified and increased the energy density by removing major non-combustible gas, carbon dioxide, from biogas mixtures [6]. Biogas purification by removing carbon dioxide affected the higher calorific value of biogas, making biogas more competitive than LPG [7]. There are many technologies for biogas purification, ranging from absorption, adsorption, and membrane-based gas permeation or separation. For household and communal scales of biogas, purification technology is not yet economically efficient, so that the development of purification technology is still a challenge in biogas technology. One of the ways to reduce the purification cost is to use cheap material, for example, by recycling organic waste. One of the enormous potentials of biomass in Indonesia is waste from sugarcane industries. It was reported that 63 sugar mills in Indonesia could utilize 245,900 tons per cane per day, and in 2019, a total running capacity in sugarcane industries in Indonesia of 278,411 tons per cane per day [8]. It means that more sugarcane bagasse will be produced.

Bagasse is a solid residue produced when sugarcane juice is extracted. Every 1000 tons of sugarcane can generate about 270 tons of bagasse. Sugarcane bagasse is rich in cellulose, hemicellulose, lignin, fat, and wax. It is economically viable for many raw materials in many industries, for example, bioethanol, biomethane, paper making, and bioenergy [9]. There is no option for using sugarcane bagasse, and production biochar is one such possibility as biochar for biogas purification. Biochar as an absorbent in biogas purification from waste is economical, environmentally friendly for biogas purification. The utilization of sugarcane bagasse-based biochar for energy production and absorbent for wastewater, air separation, biogas separation simulation may be standard.

However, the utilization of sugarcane bagasse-based biochar for biogas purification is still rare. Many studies used sugarcane bagasse-activated carbon for carbon dioxide adsorption. Compared to rice husk-activated carbon, sugarcane bagasse-activated carbon showed a higher carbon dioxide adsorption capacity [10]. In another report, Creamer et al. [11], also showed that sugarcane bagasse-biochar resulted in higher carbon dioxide adsorption than hickory wood-biochar. For biogas purification, some reports using synthetic biogas or simulation biogas composition to investigate the carbon dioxide adsorption performance [12][13]. The utilization of commercial biogas to investigate carbon dioxide adsorption or biogas purification performance is rare. This study investigated the utilization of sugarcane bagasse-based biochar combined with natural zeolite in biogas purification performance using commercial biogas. Biogas used in this study is from cattle manure fermentation, not from the synthetic or simulation biogas composition. This approach is expected to be close to the actual condition in biogas purification. These five compositions of sugarcane bagasse-based biochar were conducted in this study to find the best performance in carbon dioxide adsorption or biogas purification.
2. Method
The study was conducted in March 2020 at The Agrotechnology Innovation Center of Universitas Gadjah Mada, involving students of Faculty of Animal Science, Universitas Gadjah Mada. Biogas composition used to investigate carbon dioxide adsorption is biogas derived from cattle manure fermentation at The Agrotechnology Innovation Center. For analyzing biogas composition, primarily methane and carbon dioxide content, gas chromatography was used in this study.

2.1. Biochar production
Sugarcane bagasse collected from sugarcane ice sellers were still wet, so it must be dried under sunlight until getting dried sugarcane bagasse (approximately two days of drying time). Then dried sugarcane bagasse was pyrolyzed at a temperature of 255°C for 3 hours. The characteristics of the adsorbent were analyzed by a surface area analyzer (SAA). The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation, while the pore size and volume were calculated using the Barret-Joyner-Halenda (BJH) equation.

2.2. Biogas purification
Biogas purification was conducted by the adsorption method at room temperature and 5-7 bar pressure range. The adsorption column type used in this study is a packed second-level bed column with a column length of 20 cm and a diameter of 3 cm. Every column filled adsorbent with pure natural zeolite; some compositions of biochar and natural zeolite; and pure of natural zeolite with the formulation in Table 1. The column directly connected with biodigester and biogas holder. Biogas mixture will be passed through the column for carbon dioxide adsorption process for 10 minutes for every sample or treatment (Table 1). The adsorbent was called 100% volume of adsorbent if each adsorption column was filled with full adsorbent.

Biogas samples before and after biogas purification were collected and tested by gas chromatography to analyze methane and carbon dioxide composition. The methane or carbon dioxide composition change after biogas purification was calculated to use the following formula:

\[
\% \Delta \text{CH}_4 \text{ or CO}_2 = \frac{\text{CH}_4 \text{ or CO}_2 \text{ after purification} - \text{CH}_4 \text{ or CO}_2 \text{ before purification}}{\text{CH}_4 \text{ or CO}_2 \text{ before purification}} \times 100\% \quad (1)
\]

Table 1. Composition adsorbent in biogas purification (% volume per each adsorption column).

| Sample | Sugarcane bagasse-based biochar (% volume) | Natural zeolite (% volume) |
|--------|------------------------------------------|-----------------------------|
| ZZ     | 0                                        | 100                         |
| ZB1    | 25                                       | 75                          |
| ZB2    | 50                                       | 50                          |
| ZB3    | 75                                       | 25                          |
| ZB4    | 100                                      | 0                           |

3. Results and discussion
Biogas purification was performed by carbon dioxide adsorption in column adsorption for ten minutes. The difference in carbon dioxide and methane composition was presented in Figures 1 and 2, respectively.

Figure 1 shows that carbon dioxide decreased after biogas purification. It means biogas purification using sugarcane bagasse-based biochar and natural zeolite removed carbon dioxide in the biogas. The same phenomenon was also reported by previous studies [11]. The carbon dioxide decreasing is due to the presence of a porous adsorbent that adsorbed carbon dioxide molecules. The carbon dioxide adsorption in biogas can be explained if the cohesive forces tend to be greater than the adhesion forces.
[12]. From the data in Figure 1, the highest carbon dioxide reduction is performed by ZB2 with the composition of 50% sugarcane bagasse-based biochar and 50% natural zeolite. With the increase in the volume of biochar in the adsorption column, the decrease in carbon dioxide is greater, but the increase in the volume of biochar above 50% showed a decrease in carbon dioxide. So, we concluded that biogas purification using sugarcane bagasse-based biochar and natural zeolite is maximum at the composition of 50% sugarcane bagasse-based biochar and 50% natural zeolite.

Figure 1. Carbon dioxide composition in biogas

Figure 2 shows the methane composition change after biogas purification. The result showed that the same phenomenon with the carbon dioxide decreasing occurred. Methane was decreased after biogas purification at all samples. The opposite of this result, we hypothesized that biogas purification could reduce carbon dioxide and increase methane composition in biogas simultaneously.

If we overlapped the two graphs, the difference of the carbon dioxide and methane composition, it would be seen that the pattern of the methane decreasing is the same as the carbon dioxide. Those can
be explained due to the effect of the physical characteristic of the adsorbent, especially the pore surface [14]. The ability of adsorbents to adsorb carbon dioxide molecules in biogas is practical at micropore-sized pore volume, while methane adsorption is at mesopore-sized pore volume [15].

Table 2 shows the adsorbent’s surface area characteristics analyzed by surface area analyzer (SAA). Either natural zeolite or sugarcane bagasse-based biochar was dominant in mesopore-sized. According to the International Union of Pure and Applied Chemistry (IUPAC), mesopores have a size range of 2-50 nm. The presence of mesopore-sized on the adsorbent’s surface area made carbon dioxide and methane molecules trapped on the pores of adsorbents. The larger pore size of adsorbents (> 2 nm) caused methane molecules to be adsorbed too. However, carbon dioxide adsorption is still more significant than methane adsorption. For selective adsorbents to only adsorb carbon dioxide molecules, it is necessary to make an effort to make adsorbents micropore-sized so that methane molecules are not adsorbed.

Table 2. The specific surface area and pore size of natural zeolite and sugarcane bagasse-based biochar.

| Adsorbent                | Specific surface area (m²/g) | Pore radius (nm) | Total volume pore (cc/g) | Micropore-sized volume (cc/g) | Mesopore-sized volume (cc/g) |
|--------------------------|-------------------------------|------------------|--------------------------|-------------------------------|-----------------------------|
| Natural zeolite          | 47.66                         | 4.74             | 0.11                     | 0.017                         | 0.093                        |
| Sugarcane bagasse-based biochar | 35.45                       | 2.80             | 0.04                     | 0.013                         | 0.027                        |

4. Conclusion
These results concluded that sugarcane bagasse-based biochar could be used as an alternative in carbon dioxide adsorbent combined with natural zeolite. The best performance in carbon dioxide adsorption showed by the composition of 50% sugarcane bagasse-based biochar and 50% natural zeolite. The carbon dioxide decreased after biogas purification and did not accompany with methane increasing because the adsorbents’ pore size was still dominated by mesopore-sized, which at the mesopore-sized methane molecules were also adsorbed. Further research is required to improve carbon dioxide adsorption and enrich methane composition by improving pore size-specific in micropore-sized. The modification on the surface area of adsorbents into micropore-sized makes adsorbents more selective adsorbing only carbon dioxide molecules. Many methods can be offered to improve the pore size into micropore-sized are physical or chemical activation. Several activating agents have been reported to be effective in the biochar activation, for example, base and acid solution.

Improving of adsorbents to adsorb carbon dioxide in biogas purification will encourage an increase in biogas adoption. The Utilization of adsorbents-based agroindustry waste is also expected to reduce the biogas purification cost so that it encourages biogas adoption either at household or community scale and replaces the consumption of LPG that is still dominated by import.

Acknowledgements
We gratefully acknowledge the support from the Center of Agro-Technology Innovation for contribution in this research. We also thank college students of Faculty of Animal Science Universitas Gadjah Mada for helping in collecting the data.

References
[1] Kuehl J, Bajaj M and Boelts S 2021 Global Subsidies Initiative Report; LPG Subsidy Reform in Indonesia: Lessons Learned from International Experience Manitoba Canada
[2] Nugraha A and Yep E 2020 Indonesia’s Fuel Demand Drops Amid Concern of Tighter Pandemic https://www.spglobal.com/platts/en/market-insights/latest-news/oil/040920-indonesias-fuel-demand-drops-amid-concerns-of-tighter-pandemic-measures
[3] Ministry of Energy and Mineral Resources (MEMR) 2020 Handbook of energy and economic statistics of Indonesia 2019 Indonesia

[4] Center for the Study of Process Industry and Energy (PPIPE) 2020 Outlook Energy of Indonesia 2020 Special Edition the Covid-19 Pandemic Effect on Energy Sector in Indonesia Center for the Study of Process Industry and Energy (PPIPE) The Agency of the Assessment and Application Technology

[5] Jorgensen P J 2009 Biogas - Green Energy Digisource Danmark A/S,

[6] Sahota S, Shah G, Ghosh P, Kapoor R, Sengupta S, Singh P and Thakur I 2018 Review of Trends in Biogas Upgradation Technologies and Future Perspectives Bioresour. Technol. Rep. 1 79-88

[7] Sun Q, Li H, Yan J, Liu L, Yu Z and Yu X 2015 Selection of Appropriate Biogas Upgrading Technology - A Review of Biogas Cleaning, Upgrading, and Utilisation Renew. Sust. Energ. Rev. 51, 521-532

[8] Toharisman A and Triantarti 2016 An Overview of the Sugar Sector in Indonesia Sugar Technology 18 636-641

[9] Bhatnagar A, Kesari K and Shurpali N 2016 Multidisciplinary Approaches to Handling Wastes in Sugar Water Air Soil Pollut. 227

[10] Boonpoke A, Chiarakorn S, Lao Siri Pojana N, Towprayoon S and Chidthaisong A 2011 Synthesis of Activated Carbon and MCM-41 from Bagasse and Rice Husk and Their Carbon Dioxide Adsorption Capacity J. Sust. Energ. Enviro. 2 77-81

[11] Creamer A, Gao B and Zhang M 2014 Carbon Dioxide Capture Using Biochar Produced from Sugarcane Bagasse and Hickory Wood Chem. Eng. J. 249 174-179

[12] Huang Y F, Chiueh P T, Shih C H, Lo S L, Sun L, Zhong Y and Qiu C 2015 Microwave Pyrolysis of Rice Straw to Produce Biochar as An Adsorbent for CO2 Capture Energy 84 75-82

[13] Ferella F, Puca A, Teglieri G, Rossi L and Gallucci K 2017 Separation of Carbon Dioxide for Biogas Upgrading to Biomethane J. Clean. Prod. 164 1205-1218

[14] Xu X, Kan Y, Zhao L and Cao X 2016 Chemical Transformation of CO2 during Its Capture by Waste Biomass Derived Biochars Enviro. Pollut. 213 522-540

[15] Peredo-Mancilla D, Ghouma I, Hort C, Ghimbeu C, Jeguirim M and Bessieres D 2018 CO2 and CH4 Adsorption Behavior of Biomass-Based Activated Carbons Energies 11 1-10