International Journal of GEOMATE, March, 2019 Vol.16, Issue 55, pp. 80 - 85
ISSN: 2186-2982 (P), 2186-2990 (O), Japan, DOI: https://doi.org/10.21660/2019.55.4715
Special Issue on Science, Engineering & Environment

# HEATING VALUE ENHANCEMENT BY BIOGAS PURIFICATION USING NATURAL ZEOLITE AND RICE STRAW-BASED BIOCHAR

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**ABSTRACT:** Biogas has many incentives to replace firewood and crop straw for cooking in rural area. However, to access sustained adoption of clean, carbon neutral and eco-friendly household fuels, raw biogas needs to be purified before used. Beside methane ($CH_4$), raw biogas contains trace components adversely affecting appliances or end-user. For example, carbon dioxide ($CO_2$), the greatest impurities in biogas, affect the decrease of heating value. In some literature, the adsorption for $CO_2$ was claimed to be cheap, simple and adoptable for $CO_2$ removal. Carbon dioxide removal using rice straw-based biochar combined with natural zeolite (Z-RB) at room temperature and gas pressure range of 5-7 bar. Carbon dioxide removal using Z-RB increased the theoretical and empirical heating value of biogas from 1214.48 to 1766.34 kJ and from 276 to 288.55 kJ respectively. From this observation, the blue flame that appeared from the combustion of purified biogas using Z-RB went out for longer than using natural zeolite only (Z-Z).

*Keywords: Heating value, Biogas purification, $CO_2$ removal, Rice straw-based biochar, Methane*

## 1. INTRODUCTION

In Indonesia, 96% of national energy needs are supplied from fossil fuels based energy such as petroleum, natural gas and coal [1]. The constantly increasing demand for energy led to a long-term dependency on coal and other fossil fuels [2]. Nevertheless, the traditional biomass energy such as crop straw and firewood are still dominant in rural area [3]. The traditional biomass energy is burnt directly for domestic utilization such as cooking, heating and lighting. Unfortunately, combustion of these fuels leads to high level of health damaging air pollution from particulate matter (PM), carbon monoxide (CO), nitrous oxide ($NO_2$) and poly aromatic hydrocarbons (PAHs) [4]. People in rural areas waste too much of their time to collect crop straw or firewood for cooking, moreover, they breath polluted air from the traditional biomass energy combustion that can threatens their life.

Whereas the availability of clean, low cost and high efficient fuel could significantly improve the living quality, economic sector [5] and public health in rural area. Biogas is a clean and smokeless fuel, which can be an excellent substitute for these traditional biomass energies. H Pathak [6] and Amanda [7] claimed that biogas technology is an attempt of greenhouse gases (GHGs) mitigation. The multiple benefits of biogas technology should encourage government to promote biogas technology as a way to combat global warming and health hazards from the traditional biomass energy combustion. In some developing countries, biogas dissemination has some obstacle, such as Indonesian's policy, public lack of skill and lack of biogas related research [8]. On the other hand, in Indonesia the existence of raw material of biogas, the natural resources of biomass-based livestock and agriculture sector, is abundant [9]. Conversion biomass into biogas through anaerobic digestion which are divided to hydrolysis, acetogenesis and methanogenesis. Conversion of biomass to biogas is shown in Fig. 1.

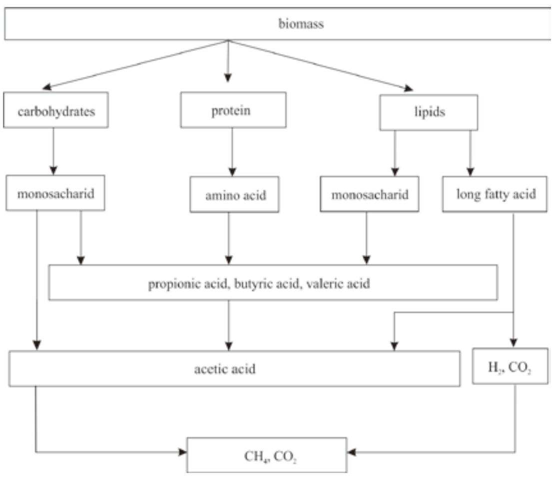


Fig. 1 Conversion pathway in biogas production [10]

Gas that generated in biogas production

mentioned in Table 1. Primarly, biogas contains dominant methane ($CH_4$), a flammable gas with a heating value of 21-24 MJ/m$^3$ [11-12]. Beside it, biogas also contains carbon dioxide gas.

Table 1. Composition of biogas [13]

| Gases | Composition (%) |
|---|---|
| Methane | 55-70 |
| Carbon dioxide | 30-45 |
| Hydrogen sulfide | 1-2 |
| Nitrogen | Small amount |
| Oxygen | Small amount |

The presence of carbon dioxide ($CO_2$) makes biogas having a lower heating value (Table 2), so to increase the biogas heating value the removal of carbon dioxide ($CO_2$) by biogas purification technology is required [10-11, 14-15].

Table 2. Effects of impurities in biogas [16]

| Gases | Effect |
|---|---|
| Carbon dioxide | Non flammable, reducing heating value, corrosion |
| Hydrogen sulfide | Non flammable, corrosion and toxic |
| Water vapour | Corrosion |
| Nitrogen | Reducing heating value |

According to some references, adsorption is a cheap, simple and adoptable method for $CO_2$ removal [17-18]. Carbon dioxide removal using the biomass waste-based adsorbent, such as biochar and activated carbon, has been developed [17,19-21]. However, the application of rice straw based biochar for $CO_2$ removal in biogas purification is rare. This study aims to investigate the influence of rice straw-based biochar application as a natural zeolite partial substitute as adsorbent in biogas purification system. Because it is known that natural zeolite has the best ability to eliminate $CO_2$ [18].

## 2. METHODOLOGY

### 2.1 Materials

Rice straws were prepared to produce biochar as partial substitute of natural zeolite for $CO_2$ removal. Agrotechnology Innovation Center of Universitas Gadjah Mada provided the biogas that will be purified. Biogas was generated from anaerobic digestion of cow manure. Aquadest, thermometer and biogas stove were prepared to calculate the heating value needed for boiling water.

### 2.1 Experimental

*2.1.1 Rice straw based-biochar production*

Rice straws were collected from rice fields and chopped into 10-15 cm size. Rice straw-based biochar was produced through pyrolysis process. Before converted to biochar, rice straws were dried under direct sunlight to evaporate the water content. Pyrolysis was carried out at 500$^o$C and was then held for 4 hours straight when a temperature was reached. The biochar-based rice straw was then characterized using infrared (IR) spectroscopy instruments to identify the surface functional groups.

*2.1.2 Biogas purification through removing $CO_2$*

Carbon dioxide removal in biogas purification aims was to increase the biogas heating value. Stainless steel was used to make the adsorption column with 40 mm diameter and 200 mm length. The detailed scheme of biogas purification unit was illustrated in Fig. 2 and the adsorbents formulations were formulated in Table 3. $CO_2$ adsorption was carried out at room temperature and gas pressure ranged between 5-7 bar. The $CH_4$ contents of before and after adsorption biogas samples then analyzed with gas chromatography (GC) instrument.

*2.1.3Calculation the heating value of biogas*

The heating value of the purified biogas samples was then calculated. Amanda stated that the heating value of biogas is correlated linearly with the content of $CH_4$ dissolved therein [7]. The calculation of the biogas heating value was derived from the percentage of $CH_4$ content, so theoretically heating value calculation can be written as follows:

$$E_{biogas} = LHV x\, {}_{n}CH_4 \quad (1)$$

Equation (1), $E_{biogas}$ shows the heating value in biogas tank (kJ). $LHV$ represents the lower heating value of $CH_4$ (kJ/mol) and ${}_{n}CH_4$ represent the $CH_4$ content in biogas (mol). The heating value of raw biogas and purified biogas were then compared to investigate the $CO_2$ removal effect on the heating value enhancement.

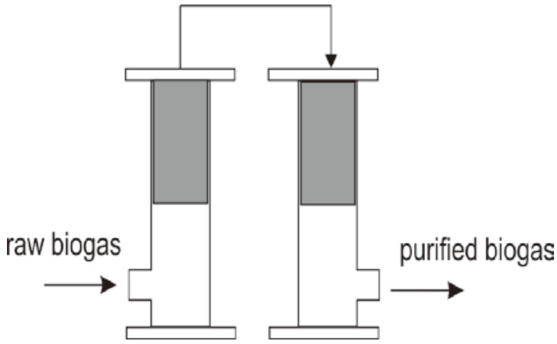


Fig. 2 Details scheme of $CO_2$ adsorption unit

Table 3. Adsorbents for $CO_2$ adsorption in biogas

| Code | Column 1 (40:40 grams) | Column 2 (40:40 grams) |
|---|---|---|
| Z-Z | Natural zeolite : natural zeolite | Natural zeolite : natural zeolite |
| Z-RB | Natural zeolite : rice straw-based biochar | Natural zeolite : rice straw-basesd biochar |

*2.1.4Calculation the heating value needed to boil water*

The purified biogas then packed into a four bar pressure tank. In this study, the purified biogas then used to boiling water using a biogas stove. Each 1000 ml is prepared and boiled with a biogas stove. The temperature rises and boiling time were recorded every 30 seconds until the water boiled. The needed heating value for boiling water was calculated with the formulation in Eq. (2):

$$Q = mxcx\Delta T \quad (2)$$

$Q$ represents the needed heating value for boiling water (kJ), $m$ is mass of water (kg), $c$ is specific heat of water (kJ/kg K) and $\Delta T$ is the difference between initial and final water temperature (K).

## 3. RESULTS AND DISCUSSION

### 3.1 Characteristic functional groups of rice straw-based biochar

Rice straw-based biochar characterized using IR spectroscopy to determine functional group on biochar surface. IR spectroscopy sample was prepared using KBr pellets and analyzed with wave number ranges in between 400-4000 $cm^{-1}$. The result of IR spectroscopy analysis showed in Fig. 3. The IR spectra in Fig. 3 confirmed the typical bands of biochar's functional groups were similar to the previous studies. The bands at 3503 $cm^{-1}$ corresponds to the hydroxyl groups vibration of the biochar [20-21]. The absorption at 1110 $cm^{-1}$ also confirmed the C-O bonds vibration of phenol, alcohol or carboxylic group on biochar's surface [20,22]. The C=C aromatic carbons was confirmed from the absorption at 1609 $cm^{-1}$ [20-22].

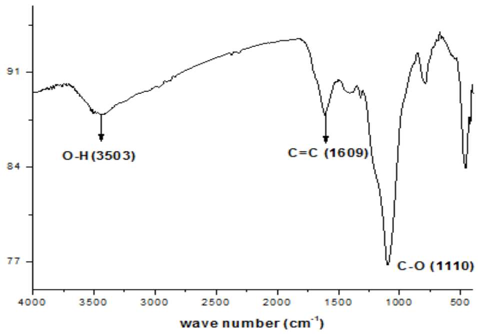


Fig. 3 IR spectra of rice straw-based biochar

### 3.2 The biogas heating value enhancement after $CO_2$ removal

Carbon dioxide removal process using adsorbents aims to enhance the biogas heating value through the increase in $CH_4$ content. Methane played an important role in generating energy by biogas combustion [11-12]. The linear relationship between $CH_4$ content and the biogas heating value was investigated in this paper. The comparison of $CH_4$ content in raw and purified biogas after $CO_2$ removal using adsorbents according to Table 3. is shown in Fig. 4. Fig. 4 showed that raw biogas (biogas before the $CO_2$ removal) has a lower $CH_4$ content compared with purified biogas. This means the biogas purification using $CO_2$ removal has been done successfully. Natural zeolite and rice straw-based biochar are able to capture and trap $CO_2$ molecules on their cavities [18-19].

The greatest increase of CH4 content is shown by purified biogas with Z-RB adsorbent of 44.85% compared to Z-Z adsorbent of only 1.4%. It can be concluded that CO2 adsorption by rice-based biochar is greater than natural zeolite. Yu-Fong et al. [20] reported that the higher specific surface area of rice straw-based biochar play an important role in capturing $CO_2$ molecules, well compared to Z-Z. Ambar *et al.* [21] and Margaretha *et al.* [22] also reported that the higher $CO_2$ removal performed by combination of natural zeolite and livestock waste based-biochar compared to natural zeolite only. Natural zeolite used in this study is similar to natural zeolite used by Margaretha *et al.* [22] with specific surface area of 27.9 $m^2/g$. And biochar, according to , has specific surface area about 200-300 $m^2/g$ [23]. It means that biochar has better capability of $CO_2$ removal than natural zeolite.

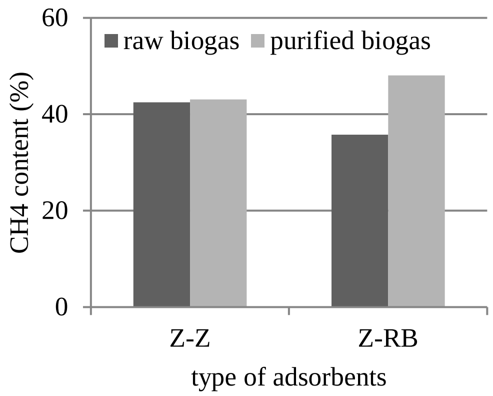


Fig. 4 Methane content of raw and purified biogas

The linear relationship between $CH_4$ content and the biogas heating value was also shown in this Fig.5. The increase of biogas $CH_4$ content was represented by the increase of the heating value. Before the $CO_2$ removal using Z-Z, raw biogas had 1513.65 kJ heating value per tank. There was an increase of 1534.31 kJ per tank in heating value after the $CO_2$ removal. The higher increase in $CH_4$ content was performed by Z-RB from 1214.48 to 1766.34 kJ per tank. The results support that the higher heating value depend on the CH4 content in the biogas. The same phenomenon of the heating value increased after biogas purification has also been reported by previous researcher [11-12,14-15]. Adalberto [11] reported that the raw biogas heating value is 50 MJ/kg has increased to 45 MJ/kg (90% $CH_4$ content) after purifying.

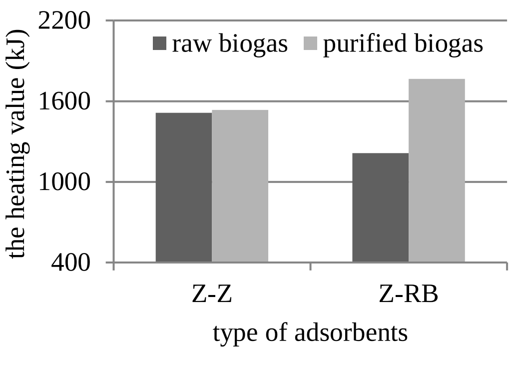


Fig. 5 The heating value of raw and purified biogas

Since purified biogas were prepared for domestic utilization as combustion energy for cooking, combustion test are also necessary. Biogas combustion test was conducted by observation of boiling water with biogas. The biogas heating value was calculated from the energy it needed to boiled water. The empirical biogas heating value was then compared with the theoretical biogas heating value. The results of the needed energy to boiled water showed in Table 4. It was concluded that biogas purification using Z-RB were greater compared to Z-Z. From the observation, the blue flame rose from the purified biogas combustion using Z-RB arise longer than the purified biogas combustion using Z-Z. This is because the purified biogas using Z-RB adsorbent has a greater CH4 content that act as a fuel. The difference between empirical and theoretical heating values on the results of this study is due to the correction energy factors lost due to the use of biogas stoves (biogas stoves have an efficiency of 15-25%).

Table 4. The empirical heating value of raw and purified biogas

| Code | Raw biogas (kJ) | end-point time of blue flame (seconds) | Purified biogas (kJ) | end-point time of blue flame (seconds) |
|---|---|---|---|---|
| Z-Z | 239.44 | 140 | 249.44 | 270 |
| Z-RB | 276 | 540 | 288.55 | 600 |

From the findings showed that there was association between $CO_2$ removal for enhancing heating value of biogas. The increase in heating value after biogas purification through $CO_2$ removal using natural zeolite and biochar would encourage rural communities to use biogas energy for cooking. The higher efficiency energy of biogas has impact on the increasing types of cooking fuel that would be selected by rural communities. Although the use of biogas not fully replaces other fuels for cooking, it can be used as an environmentally friendly and clean alternative fuel for cooking in rural area. Cahyono *et al*. [24] also claimed that biogas purification is a good approach to sustainable bio-energy.

## 4. CONCLUSION

From this study result, concluded that rice straw-based biochar can be used as alternative adsorbent for $CO_2$ removal in biogas purification process. In addition, the use of natural zeolite combined with rice straw-based biochar gave greatest impact of increasing the biogas heating value. The theoretical and empirical biogas heating value after $CO_2$ removal increased from 1214.48 to 1766.34 kJ and from 276 to 288.55 kJ respectively. In other words, the $CO_2$ removal in biogas could enhance the biogas heating value. Based on results in this study, the effort on quality upgrading by biogas purification through $CO_2$ removal would encourage biogas technology adoption in rural areas.

## 5. ACKNOWLEDGMENTS

This research was supported by Grant Program from Universitas Gadjah Mada, Indonesia (Number 1849/UN1/DITLIT/DIT-LIT/LT/2018). The authors also would like to thank Universitas Gadjah Mada through Agrotechnology Innovation Center (Pusat Inovasi Agroteknologi – PIAT) and USAID through Sustainable Higher Education Research Alliances (SHERA) program for helpful.

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