METHANE ENRICHMENT OF BIOGAS BY CARBON DIOXIDE ADSORPTION ON NATURAL ZEOLITE AND BIOCHAR DERIVED FROM CHICKEN MANURE

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ABSTRACT

Although biogas is claimed clean and environmental friendly, its existence is often unsustainable especially in rural area. Consumption energy still dominated by energy from fossil fuel because it's cheaper, higher in energy efficiency and more ready to use than biogas. The efforts to make biogas can compete with fossil fuel energy had been done by increasing calorific value. The lower calorific value is due to the presence of carbon dioxide (CO2) in biogas. Reduction of CO2 by adsorption is able to enhance calorific value that evidenced by methane (CH4) enrichment. In this report, we investigated the effect of zeolite (Z-Z) and combination of zeolite-biochar from chicken manure without or with modification (Z-A1U dan Z-A1N) on CO2 and CH4 contents. These adsorbents were characterized by infrared spectrophotometer (FTIR) and surface area analyzer (SAA). FTIR spectra showed that functional groups of zeolite were represented by Si-O or Al-O bands at 1050, 796, 466 cm-1. Zeolite's spesific surface area was 27,9 m2/g and pores width were dominated at 2,67 nm. The other hand, modified biochar showed the typical bands of nitorgenous group at 1039, 1047 and 1079 cm-1 that confirmed vibration of C-N streching. A board peak at 3393 and 1799 cm-1 corresponded to N-H and C=O band respectively. The result indicated that there was interaction between biochar and ammonia. Adsorption was carried out at room temperature with gas pressure ranging from 2 to 7 kg/cm2. Before and after adsorption, biogas were analyzed by gas chromatography (GC) to determine the effect adsorbent against CO2 and CH4 contents.

K E Y W O R D S : biogas, purification, methane enrichment, adsorption and carbon dioxide

INTRODUCTION

Background

Global warming that is happening in recent years caused by increasing of green house gases (GHG) emissions. The continuous increase the major contributor of global warming, carbon dioxide (CO2), have been reported by National Oceanic and Atmospheric Administration (NOAA). The increase in CO2 has been occured since 1958 and the peak at 2016 [1]. The same phenomenon was also occured to non CO2 GHG such as methane (CH4) and dinitrogen oxide (N2O) [2]. More attention, CH4 and N2O have the potential 21 times and 300 times greater than CO2 to cause global warming. Emissions of CH4 dan N2O in the atmospheric were 10-12% of total GHG emissions and dominated by agriculture and livestock sectors [3-5]. The benefical mitigation of GHG emissions from these sectors has been developed through biogas technology. Biogas technology has benefits to isolate GHG emissions from agriculture and livestock waste and convert it directly into energy [6].

Although biogas has benefits in mitigating and overcoming waste issue, implementation of biogas technology is often unsustainable. Lower energy eficiency of biogas becomes one of barriers in biogas technology development. The presence of non CH4 gases esspecially CO2 have significant negative impact to decrease calorific value [7-8]. An innovation to improve calorific value of biogas is through biogas purification. Biogas purification is a method to enrich CH4 by separation of CH4 from gases that can decrease calorific value [9]. Various biogas purification technologies have been developed and evaluated, such as water scrubbing, cryogenic, membrane separation, chemical absorption and adsorption [7-8]. A cheap, simple and viable technology becomes an attractive method to purify biogas in rural area [9]. From all the mentioned methods, adsorption is the most potential option to be selected to purify biogas because adoptable and inexpensive [10].

In this study our focus on the CO2 adsorption because CO2 is the largest amount contaminant in biogas [9,11]. Many researchers had studied and reviewed CO2 adsorption on different comercial adsorbents such as zeolite [12], activated carbon [13] and biochar [14]. The best adsorption capacity was performed by zeolite, with adsorption capacity about 3,9 – 6,8 mmol/g [13,15]. Although having good performance, zeolite has disadvantages which material is not always available in rural area. The fact has implication on high cost of adsorbent. Moreover, zeolite exploitation causes environmental degradation. To overcome these drawbacks, the low cost, effective for CO2 capture and easily synthesized adsorbents must be developed for rural communities. Today, biochar (carbon based material) becomes interesting option as alternative adsorbent. However the ability to adsorb CO_2 is lower than zeolite and activated carbon, it's more inexpensive and environmental friendly [16-17]. Production of biochar can utilized existing biomass in rural area for example around the site of biogas installations or agriculture and livestock area.

The aim of this study is to investigate the effect types of adsorbent for capturing CO_2 againts CO_2 and CH_4 levels in biogas. Surface modification of biochar was also carried out in this study. Many reported studies said that surface modification on adsorbent using nitrogenous compounds can improve its ability to capture CO_2 [17-19].

Methodology

Materials. Natural zeolite that were used in this study was commercial zeolite. Zeolite was pretreated by calcination at 255oC for 3 hours [20]. Chicken manure that was collected from PT. Charoend Phokpand prepared for biochar production. Ammonia solution that was purchased from Bratachem used as modification agent.

Biochar production. The raw materials were dried by aeration a full day and then converted into biochar through pyrolisis at 500oC for 4 hours under N_2 atmosphere [21]. Surface modification on biochar followed the previous procedure [22]. Biochar was immersed in ammonia solution 10% at a 1:10 solid/liquid ratio for 24 hours. After this time was reached, the mixture was separated by filtration then oven dried at 105oC for 4 hours. Biochar derived from chicken manure (A1U) and the modified biochar (A1N) were stored in a desiccator room.

Characterization of adsorbents. The spesific surface area, total pores volume and pores size of adsorbents were measured with Quantachrome Instruments analyzer. Samples were pretreated by degassing at 110oC for 3 hours under vacuum. The spesific surface area were calculated by BET method form N_2 adsorption data. Samples were also analyzed with Fourier Transform Infrared Spectrophotometer (FTIR) to investigate surface functional groups on adsorbents.

Biogas purification. The aim of biogas purification by CO_2 adsorption is to enrich CH_4 conten in biogas. The adsorption used two interconnected columns that each column filled 40 grams adsorbent with zeolite-biochar ratio at 1:1. These columns were connected to the suction hose on the compressor which directly related to the biogas holder and the other end were connected to the tapping biogas holder. Adsorption was carried out at room temperature and gas pressure ranging from 2 to 7 kg/cm2. To determine the effect of adsorbents against CO_2 and CH_4 contents, biogas was analyzed with gas chromatography (GC).

RESULT AND DISCUSSION

Zeolite is the common adsorbent that applied to separate CO2/CH4 in biogas [12,15]. In this study, the physical characteristic of natural zeolite were presented in Table 1. Spesific surface area was calculated by BET method. Table 1. showed that zeolite had spesific surface area at 27 m2/g. This value was close to the result that reported by previous researcher at 29 m2/g [23]. Pores width are dominated at 2,67 nm, included in mesopore region according to Internationl Union of Pure and Applied Chemistry (IUPAC) classification.

Table 1. Characteristics of natural zeolite

Sample	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	D (nm)
Natural zeolite	27,9	0,1105	0,0131	0,0974	2,67

SBET, spesific surface area; Vtotal, total pore volume; Vmicro, micropore volume; Vmeso, mesopore volume, D, pore width

N2 adsorption-desorption on zeolite was demonstrated by Fig.1. The graph showed that the volume of adsorbed or desorped N2 on zeolite are almost same in the same range of relative pressure P/Po. It indicated that adsorption by zeolite can occur reversible [20]. In other words, zeolite had the potential to be used as CO2 adsorbent for several cycles.

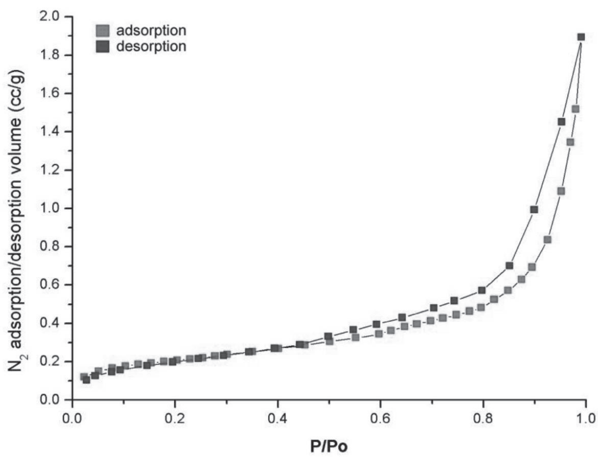

Fig 1. N2 adsorption and desorption isotherms

The functional group on surface of adsorbents was exhibited by FTIR spectra at Fig 2. Typical functional groups of zeolite at 1050, 796, 466 cm-1 corresponded to vibration of Si-O or Al-O [23]. The FTIR spectra of biochar and modified biochar presented some similarities but several new bands appeared on modified biochar. The board peak at 3393 cm-1 that overlapped

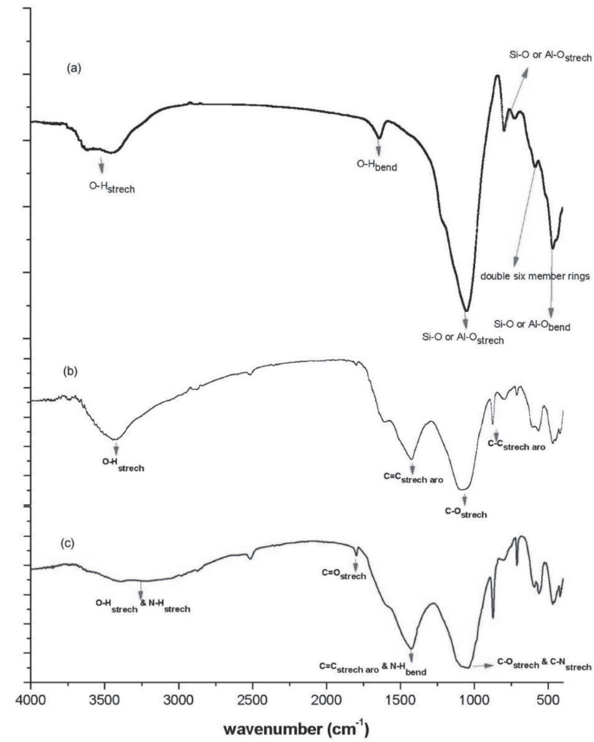

Fig 2. FTIR spectra of adsorbents (a) natural zeolite; (b) A1U, biochar from chicken manure; (c) A1N, modified biochar from chicken manure

with vibration of O-H confirmed vibration of N-H [17]. The band at 1799 cm-1 attributed to C=O in the carbonyl group. The band that confirmed vibration of N-H bending appeared at 1426 cm-1 and overlapped with C-OH band [24]. The band of C-N streching was also appeared at 1085 cm-1[25]. The appearance of new bands related to nitrogenous groups that doped on biochar. The other words, surface modification had been generated succesfully. The nitrogen doping on adsorbent can improve alkalinity of biochar and enhance CO2 capture capability.

CONCLUSION

Characterization of adsorbents had been done. Natural zeolite was reported having spesific surface area at 27 m2/g and capable used for CO2 adsorption at several cycles. The success of surface modification on biochar that was evidenced by the presence of nitrogenous group bands may improve of CO2 adsorption capacity.

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