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Methane enrichment on biogas generated from anaerobic digester using coconut shell-based activated carbon

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Abstract. This study evaluates methane enrichment on biogas generated from Anaerobic Digester (AD) through CO_2 adsorption process so that biogas can be used as fuel for vehicle engines, power plants, and natural gas substitutes. The experiment was observed by passing biogas synthesis (45% CH_4 + 55% CO_2) and biogas from cattle manure ±59.7% CH_4, ± 37.1% CO_2 and ±3.2% other gases) in spontaneously pressurized adsorption column. In addition, observation of CO_2 adsorption capacity at various pressure and fixed temperature (27°C) was performed using pure CO_2 (±98%). Methane in biogas has been successfully purified to 92% at 0.5 L/min flowrate and 79.6 seconds retention time. The adsorbent will be saturated after gas flowing for 60 and 80 minutes for synthesis biogas and biogas from AD on the amount of adsorbent of 266 grams. A change of surface area of activated carbon (AC) after thermal regeneration at 160°C for 2 hours was 7.51% and regeneration efficiency was 67%. The adsorption process followed Freundlich isothermal. This process can be feasible alternative technology to meet the need for biogas with high levels of methane in small-scale AD.

1 Introduction

Energy content of biogas is directly proportional to the levels of methane in biogas. Biogas typical composition is 50-80% methane, 15-50% CO_2, N_2 0-5%, 0-1% O_2 and 0-1% other gases [1]. A process of reducing CO_2 levels (upgrading) is required in biogas to obtain methane with a high enough purity. The CO_2 content in biogas can significantly reduce the calorific value of biogas because CO_2 is an inert compound. Biogas upgrading process is highly dependent on the utilization of biogas that will be done. Some applications of biogas utilization require biogas to have a high enough methane content that can meet the burning energy required. For example, application of biogas in Europe for injection in domestic gas pipelines and motor vehicle fuels or generators requires a minimal concentration of methane in biogas is 93% [2] and 95% [3], [4]. In most developing countries, biogas production facilities are still on a small scale, less than 10 m^3 [5]. Small-scale biogas purification technology is required to encourage the use of biogas as a renewable energy source. Therefore, the development of a simple and efficient biogas purification technology becomes

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a thing to be developed nowadays. The adsorption technology can be applied to small-scale digester because it is relatively cheaper in operation and can be operated easily [6]. AC has been widely adopted for gas separation processes including biogas upgrading [7].
This study analyzed CO_2 removal efficiency, CO_2 adsorption isotherms, regeneration efficiency, and the characteristics of the solid granular AC made from coconut shell as an adsorbent of methane enrichment process using synthetic biogas and cattle manure biogas. The efficiency of the removal and characteristics of the AC was revealed at before and after the regeneration of AC. Thus, this research got design criteria of methane enrichment technology on biogas by adsorption method using coconut shell based active carbon adsorbent.

2 Experimental setup

2.1 Gas separation kinetics

The adsorption column is 25.4 mm in diameter or 1 inch maximum height of 150 cm and the sampling port is every 25cm. With variation of gas flow rate from 0.5 to 1.5 L / min will get variation of resistance time 15.19–91.16 second. Adsorbate in this research is biogas synthesis in laboratory scale and biogas result of Anaerobic Digester in pilot scale. The synthesis biogas used is a gas mixture with a composition of 45% CH_4 and 55% CO_2.

The gas retention time variation is 15.19, 30.39, 45.58, 60.77, 75.97 and 91.16 for 0.5 L/min flow rate. At a flow rate of 1 L / m the retention time variation is 7.60, 15.19, 22.79, 30.39, 37.98 and 45.58 seconds. At a flow rate of 1.5 L / the retention time variation is 5.06, 10.13, 15.19, 20.26, 25.32 and 30.39 seconds. Methane concentration data at difference retention time matched with first, second, and third order kinetics plots [8].

2.2 Adsorption isotherm

The isothermal adsorption test was performed at 0-2 bar pressure range and temperature 27°C. The pure carbon dioxide gas from pressurized gas cylinders flows into the Dozing Cylinder which will regulate and measure the amount of gas to be injected into the Sampling Cylinder. Cylindrical sampling is an alloy metal cylinder with a diameter of 0.25 inches and a length of 20cm containing 3.48 grams adsorbent.

2.3 Regeneration efficiency

Regeneration of the activated carbon is performed when adsorbent is saturated. The regeneration efficiency was obtained by comparing the breakthrough time of activated carbon before (Tb_o) and after regeneration (Tb_r). Breakthrough time was obtained by flowing gas up to 100 minutes with a flowrate of 0.5L / min and 79 seconds retention time. Thermal regeneration is done by heating at a temperature of 160°C for 2 hours [9] with an ambient atmosphere.

$$\text{Regeneration Efficiency (RE)} = (Tb_o / Tb_r) \times 100\% \quad (1)$$

2.4 Pilot scale experimental

Biogas used is obtained from 7 m^3 Anaerobic Digester with cattle manure substrate at PT SWEN Inovasi Transfer, Bogor. The biogas composition is ±59.7% CH_4, ±37.1% CO_2 and

±3.2% other gas. Breakthrough time in the pilot scale test was obtained by flowing gas up to 100 minutes with a flowrate of 0.5 L/min and 79 seconds retention time.

2.5 Surface characteristics of activated carbon

Adsorbent is granular coconut shell based activated carbon on size 12–20 mesh. Changes in the characteristics and surface area due to regeneration were carried out with SEM JOEL JSM-6390A and Surface Area Analyzer Quantachrome Nova e1200.

3 Results and Discussion

3.1 Gas Separation Kinetics

Data of methane concentration at different retention time have been obtained. Figure 1 is a comparison of the retention times (Tr) versus methane content in the first, second, and third order kinetics plots.

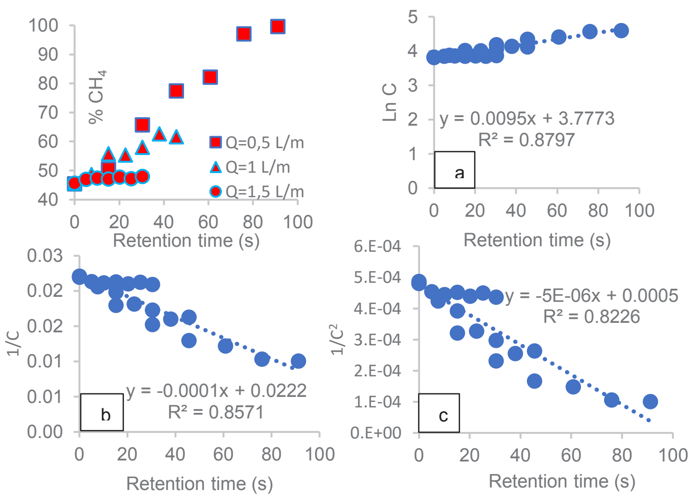

Fig 1. The first, second, and third kinetical adaption plots are (a), (b) and (c), respectively

The determination coefficient value (R^2) for the first, second and third order kinetics plots is 0.8797, 0.8571 and 0.8226 respectively. Based on these values, it can be concluded that the gas separation process that runs with first-order kinetics. Equation 2 is the kinetic equation of adsorption rate applicable for increasing methane content in biogas using coconut shell activated carbon adsorbent with C and Co is purified and raw methane concentration on biogas.

$$\text{Ln } C = 0{,}0095\ Tr + \text{Ln } Co \quad (2)$$

3.2 Adsorption Isotherm

Adsorption capacity at various pressures matched with the isothermal plots Langmuir, Freundlich and BET by regression of the straight-line equation of the three types of

$$\text{Ln } q = 0{,}7558 \text{ Ln } (P/Po) - 1{,}3681 \quad (3)$$

adsorption isothermal [10]. Figure 2 shows that the isothermal plots of Langmuir, BET and Freundlich have determination coefficient of 0.9605, 0.8771, and 0.9957 respectively. CO_2 adsorption with coconut shell AC follows Freundlich isothermal with the following equation: where q and P/Po is amount of adsorbate per unit adsorbent (mmol/gr) and relative pressure to atmospheric pressure. Similar results were obtained by rashidi et al. [11] using Norit® AC.

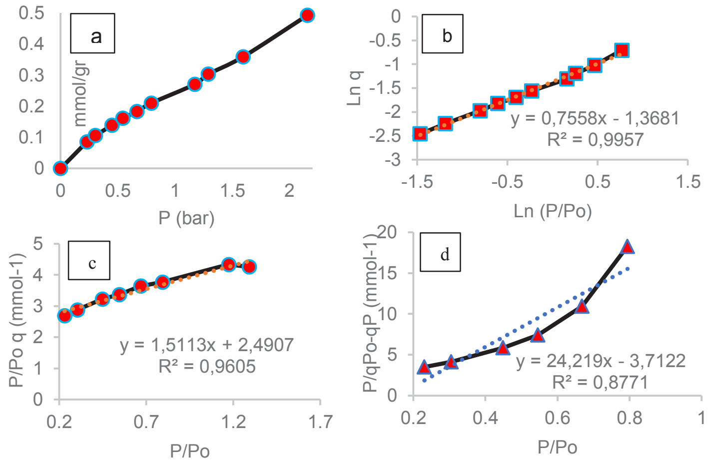

Fig 2. (a) Adsorption of CO_2 at 27°C; (b) Isotherm Freundlich;(c) Langmuir;(d) BET

3.3 Regeneration Efficiency

Figure 3 shows that the breakthrough time of fresh and regenerated activated carbon is 60 minutes and 40 minutes, respectively. Regeneration efficiency of activated carbon is 67% based on Equation 1. The low value of regeneration efficiency indicates that there has been an incomplete regeneration process.

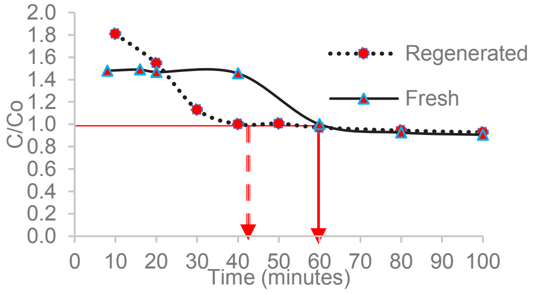

Fig 3. Comparison of fresh and regenerated activated carbon breakthrough time

3.4 Pilot Scale Experimental

This pilot scale analysis use of the same conditions as laboratory scale aims to enable pilot-scale results to be compared with laboratory-scale. The pilot scale breakthrough time in Figure 4 shows that the breakthrough time of CO_2 adsorption process with biogas from AD and biogas synthesis shows slightly different result. In pilot scale, breakthrough time occurred at 80 minutes, whereas on laboratory scale breakthrough time occurred in 60 minutes, this is due to the raw gas methane concentrations in the AD biogas much higher than in the synthesis biogas. The concentration of methane on the AD biogas is ± 60%, while the concentration of methane in the synthesis biogas is 45%, there is a difference of about

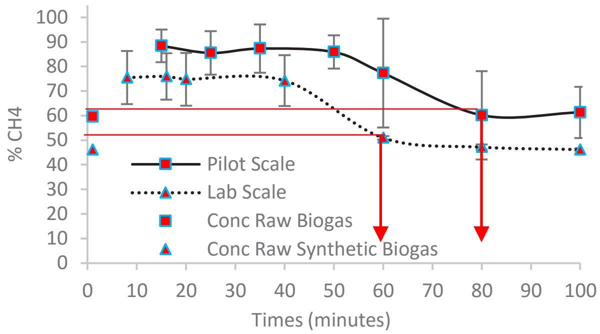

Fig 4. Breakthrough time curve of pilot and lab scale adsorption

15% methane levels at the initial state of adsorption. Higher levels of methane in the initial state make the amount of CO_2 that must be adsorbed by activated carbon to reach pure methane becomes reduced, so that with the same amount of activated carbon produces a longer breakthrough time.

Based on Figure 4, the concentration of methane in column outlets can be maintained at ±89% in pilot-scale and ±74% in laboratory scale until breakthrough time reached. There is an increase in methane content (C-Co) in pilot-scale of ±28.8% and ±29.2% on laboratory scale. Methane content increasing that occurs at laboratory and pilot scale adsorption do not show any significant difference. This further reinforces that a similar process occurs in adsorption with biogas synthesis and AD biogas, so the design criteria obtained on laboratory scale testing can be applied well on a pilot scale.

3.5 Surface Characteristics of Activated Carbon

The results of SEM characterization that can be seen in Figure 5 show the difference of average pore diameter and degree of surface roughness between fresh and regenerated activated carbon. In the regenerated activated carbon (Figure 5b and 5d) have a rougher

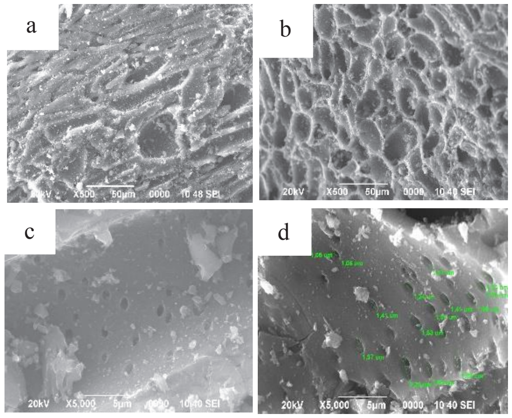

Fig 5. Results of SEM Characterization of Active Carbon Surfaces. (a) and (c) are activated carbon before regeneration 500× and 5,000×, respectively. (b) and (d) are activated carbon after regeneration (500× and 5,000×)

surface and higher macro pore number than fresh activated carbon (Figures 5a and 5c). In addition, the regenerated also has a larger mean macro-pore diameter (±1.3 μm) compared with the fresh one (±0.7 μm). This shows the change of surface characteristics due to thermal regeneration.

BET surface area of fresh activated and regenerated carbon is 916.78 m^2/gram and 847.96 m^2/gram. The changes in mesopores and micropores are not significant, this is indicated by a decrease in surface area of only 68.8 m^2/ gram or 7.51%. The decrease in surface area will directly affect the regeneration efficiency, because will also decreases the space for adsorbate molecule on the surface.

The fact that regeneration efficiency is only 67% indicates that the main cause of low regeneration efficiency is not due to changes in the surface structure (7.51%). The main factor of low regeneration efficiency is probably caused by uncompleted regeneration process with uncontrolled heating atmosphere.

4 Conclusion

Based on the research can be concluded that the adsorption column with coconut shell-based activated carbon adsorbent can increase the methane level by 28.8% for 80 minutes on the AD biogas with 79 seconds retention time. The adsorption process of CO_2 follows Freundlich adsorption isothermal. Thermal regeneration with heating for 2 hours at 160°C in an uncontrolled atmosphere provides poor regeneration results.

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