

# EXPERIMENTAL STUDY ON PRESSURIZED ADSORPTION OF CARBON DIOXIDE AND METHANE FROM COMPLEX GAS MIXTURE OF BIOGAS IN ZEOLITE 13X

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## Article history

Received

19 March 2022

Received in revised form

06 July 2022

Accepted

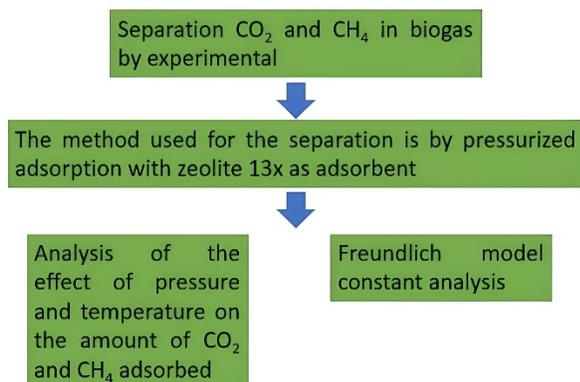
07 July 2022

Published online

28 February 2023

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## Graphical abstract



## Abstract

The majority of research on biogas adsorption does not use biogas gas but by mixing CO<sub>2</sub> and CH<sub>4</sub> gas or (binary gas) or with additional other gases, such as N<sub>2</sub> or H<sub>2</sub>S. In real application, the adsorption method of biogas purification is conducted by using its complex mixture of biogas to obtain the purer methane gas. Accordingly, in case of biogas purification, adsorption capacity of the adsorbent towards both CH<sub>4</sub> and CO<sub>2</sub> gases from a complex gas mixture of biogas is indispensable to be studied thoroughly for improving the existing purification method, such as the pressure swing adsorption (PSA) method. The objective of this experiment is to compare the adsorption of carbon-dioxide and methane from complex mixture of biogas by Zeolite 13X under pressurized condition using experimental data. The experiment was conducted using a specially designed experimental setup, and the data obtained was evaluated and analyzed using the Freundlich Isotherm Model. The results show that experimental study on the adsorption of CO<sub>2</sub> and CH<sub>4</sub> gas from complex mixture of biogas in Zeolite 13X was distinguishable by their values of Freundlich coefficient. CO<sub>2</sub> and CH<sub>4</sub> gas adsorption in zeolite vary directly with pressure raised to the power 1/n, where its value for CH<sub>4</sub> adsorption was higher than CO<sub>2</sub>. However, within the range of applicable pressure, the equilibrium adsorption of CO<sub>2</sub> in Zeolite 13X was still higher than that of CH<sub>4</sub>.

**Keywords:** Adsorption, Carbon dioxide, Biogas, equilibrium adsorption, Freundlich model, zeolite 13X

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## 1.0 INTRODUCTION

Biogas has its own advantage, both economically and environmentally to be considered as a promising alternative of renewable energy. However, the raw biogas, which is a mixture of 45-70% methane, 24-40% CO<sub>2</sub> and a small amount of other gases, such as NH<sub>3</sub> (15-180 ppm), and H<sub>2</sub>S (0.6-1.1 mg/m<sup>3</sup>) [1], needs to be pretreated prior to its utilization as energy. The amount of CO<sub>2</sub> and other impurities gives impact to a lower heating value of the biogas [2], and accordingly has to be removed in order to harvest the CH<sub>4</sub> gas. Moreover, conversion of the biogas to biomethane needs stricter purification process by removing the CO<sub>2</sub> and other impurities.

Adsorption is one among other processes that is widely used for separating gasses. With this process, a certain gas (adsorbate) is adsorbed in a solid adsorbent. Adsorbents that are often used for biogas purification are zeolite and activated carbon. Singh and Kumar [3] conducted a comparative study of the adsorption ability of CO<sub>2</sub> gas between zeolite and activated carbon. They found that zeolite can adsorb CO<sub>2</sub> gas more than activated carbon.

Adsorption a certain gas in a solid occurs by steric mechanism and adsorption equilibrium. Steric mechanism is the binding of gas components to the adsorbent pores due to its size. The gas is bound into the pores of the adsorbent if the gas size is smaller than the pore size of the adsorbent, while the larger one get away from the adsorbent [4]. However, due to inhomogeneity of the adsorbent pores there still a possibility for other gasses to be adsorbed by the adsorbent. This is true for separation of CH<sub>4</sub> and CO<sub>2</sub> since the respective size is only slightly different, i.e. 3.8 Å and 3.3 Å, respectively.

The majority of research on biogas adsorption does not use biogas gas but by mixing CO<sub>2</sub> and CH<sub>4</sub> gas (binary gas). Vicario et al. [5] conducted a study on pressure swing adsorption of biogas made with a mixture of nitrogen gas, Yuan et al. [6] used a mixture of three gases CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub> to model the adsorption equilibrium isotherm. Belmabkhout et al. [7] used a mixture of CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>S gases and stated the presence of H<sub>2</sub>S gas had an effect on the CO<sub>2</sub> adsorption process. The sticky H<sub>2</sub>S and NH<sub>3</sub> gases in biogas will reduce the adsorption capacity of the adsorbent, and the air in the biogas will compete with the gas to be adsorbed on the adsorbent [8].

In real application, the adsorption method of purification is conducted by using the complex mixture of the biogas to obtain the pure methane gas. Accordingly, in case of biogas purification, adsorption capacity of the adsorbent towards both CH<sub>4</sub> and CO<sub>2</sub> gases from a complex gas mixture of biogas is indispensable to be studied thoroughly for improving the existing purification method, such as the pressure swing adsorption (PSA) method [4].

The amount of gas adsorbed on the zeolite will reach equilibrium adsorption when all sites in the zeolite have stored gas. There are many models of adsorption equilibrium such as Langmuir Isotherm, Freundlich Isotherm, Toth Isotherm and other adsorption equilibrium models. The model will get a value of equilibrium adsorption capacity which describes the amount of gas adsorbed at equilibrium [9]. Equilibrium adsorption capacity is affected by pressure and temperature.

It is necessary to study the characteristics of the separation of CO<sub>2</sub> and CH<sub>4</sub> in biogas because most of the previous studies only used a mixture of pure CO<sub>2</sub> and CH<sub>4</sub> gas. Data regarding the difference in the value of the equilibrium adsorption capacity of

CO<sub>2</sub> and CH<sub>4</sub> gas in biogas at a certain temperature and pressure will be useful as a guide during the adsorption process. In this study, the equilibrium adsorption was sought using the Freundlich model. The objective of this experiment is to compare the adsorption of carbon-dioxide and methane from complex mixture of biogas by Zeolite 13X under pressurized condition using experimental data.

## 2.0 METHODOLOGY

Schematic diagram of the experimental set up is shown in Figure 1. The experimental set up is an adsorption column unit equipped with data acquisition system for controlling the pressure and temperature in the column. The adsorption column made of cylindrical steel with 0.3 m heights and 0.03 m diameter. A gas analyzer (portable infrared syngas analyzer gas board-3100P) was used for the gas measurements. The gas cooling unit consists of a pipe coil and a cold fluid. This unit functions to cool the gas coming out of the adsorption column so that the gas content can be directly read by the gas analyzer. The gas cleaner consists of a dust filter that prevents dust or other small particles from entering the gas analyzer.

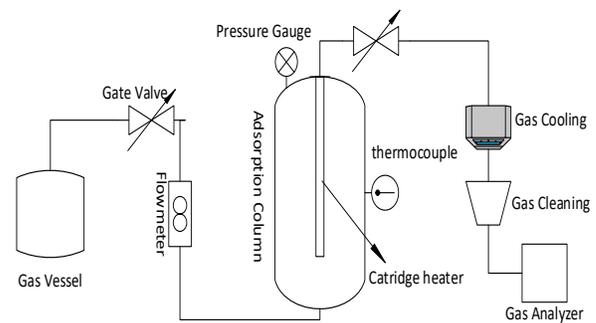


Figure 1 Schematic diagram of experimental biogas adsorption system

Zeolite 13X was used as adsorbent and was replaced with new one for each experimental running. The porosity of the zeolite in the column is about 55%. Zeolite 13X inside adsorption column was heated by a cartridge heater 400 watt and the temperature was kept constant by the PID and SSR control system. Type k thermocouple is used for reading the temperature in the adsorption column. Biogas produced from cow dung digestion was filled into a gas vessel with pressure around 10 bar to be used in the experiment. Biogas from the gas vessel was flowed into the biogas column with a flow rate of 4 L/minute and held by a globe valve until the working pressure was reached. The experiments were conducted with varied working absolute pressure in adsorption column, i.e., 1.8, 2.2, 2.6 and 3 bar, and varied temperature, i.e., 30 °C, 50 °C, and 100 °C. The adsorbed gas (CO<sub>2</sub> and CH<sub>4</sub>) was measured continuously by a gas analyzer.

The amount of gas adsorbed by zeolite at any time ( $q_t$ ) was calculated by using Equation (1) [10]

$$q_t = \frac{C_0 - C_t}{m_s} \quad (1)$$

Where  $q_t$  is the amount of biogas adsorbed by zeolite at any time (g of CO<sub>2</sub>/g of zeolite),  $C_0$  and  $C_t$  (g/L) are concentration of CO<sub>2</sub> at initial and any time  $t$  (s), respectively, while  $m_s$  is the dosage of zeolite in the adsorption column (g/L).

Empirical equations of adsorption equilibrium isotherms model are important for adsorption data interpretation, prediction and evaluation of experimental results [11]. One model that is often used is the Freundlich model, which is applicable for a multilayer adsorption. The model that calculates the amount of CO<sub>2</sub> gas adsorbed onto the adsorbent at constant pressure and temperature is called the isotherm adsorption model [12]. For heterogeneous and multilayer adsorbent surfaces, the Freundlich Isotherm equation is suitable for modeling the adsorption process [9]. Non-linear and linear form of Freundlich Isotherm take the form as shown in Equation (2) [13].

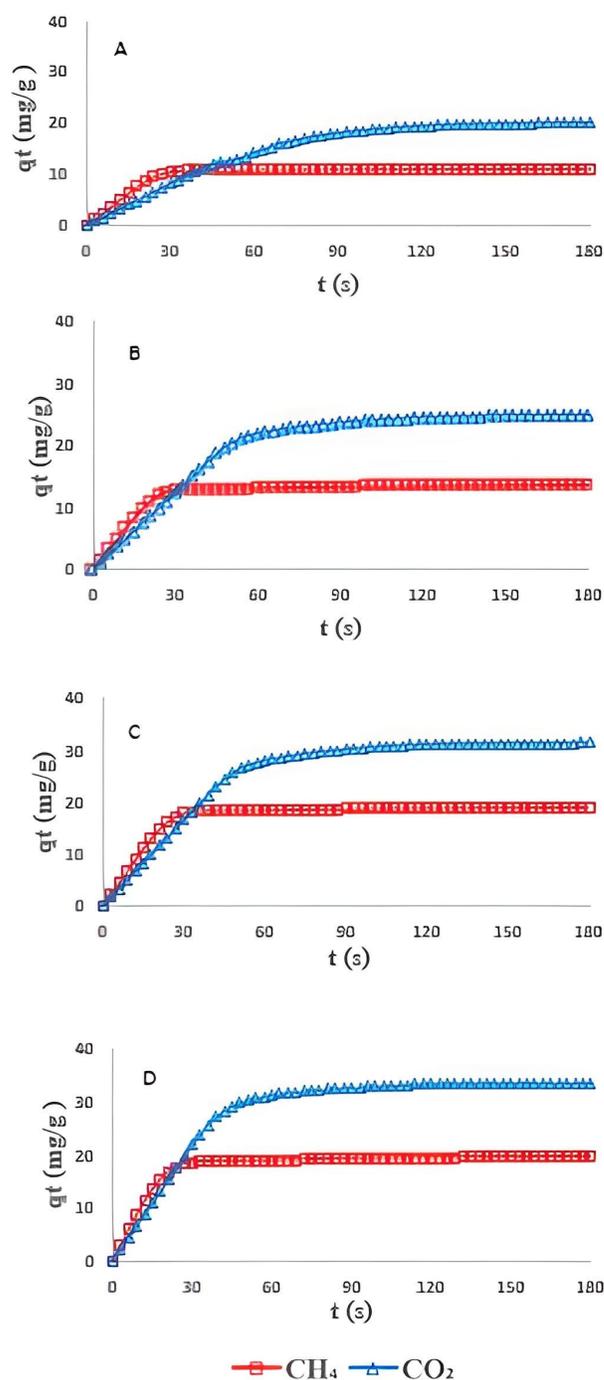
$$q_e = K_F * P^{\frac{1}{n}} \quad (2)$$

Where  $q_e$  is equilibrium adsorption capacity (mg of gas/g of adsorbent),  $P$  is the absolute pressure (bar),  $K_F$  is the Freundlich coefficient (mg of gas/ g of adsorbent), and  $1/n$  is adsorption intensity. Value of  $1/n$  and  $K_F$  can be obtained respectively from the gradient and intercept of the linear plot of  $\log q_e$  vs  $\log P$ . Linear regression analysis has been one of the most applied tools for defining the best fitting adsorption equilibrium isotherms model [9].

### 3.0 RESULTS AND DISCUSSION

Figure 2 shows the amount of adsorbed CH<sub>4</sub> and CO<sub>2</sub> in zeolite 13X as measured during the experiments with constant temperature and varied pressure.

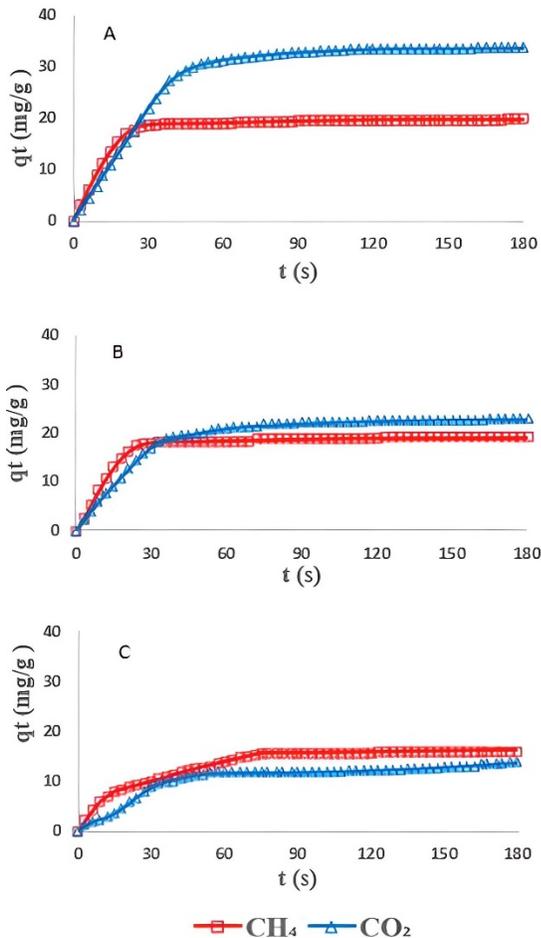
The figure depicts that variation of pressures affect the difference in the gradient of  $q_t$  over time before the onset of equilibrium as indicated by the constant value of the  $q_t$  over time. Lower pressure gives higher gradient of CH<sub>4</sub> compared to CO<sub>2</sub>. Moreover, the figure shows that higher pressure results in higher amount of adsorbed gas for both CH<sub>4</sub> and CO<sub>2</sub>. At 30 °C, the concentration of CO<sub>2</sub> adsorbed by Zeolite 13X after reaching equilibrium was higher with higher pressure. This result is similar to what was done by Wadi et al [14] and Arya et al [15] where the amount of CH<sub>4</sub> and CO<sub>2</sub> adsorbed is directly proportional to the increase in pressure. This is because more CO<sub>2</sub> gas collides with the surface of the zeolite and is adsorbed and has something to do with the size of the gas. Furthermore, Zeolite 13X adsorbed more CO<sub>2</sub> compared CH<sub>4</sub> after the equilibrium was reached at the same pressure. This phenomenon is caused by a more frequent collisions between gases, which gives impact to the higher probability for the gas to be adsorbed by the zeolite, even though the impact is not the same for CO<sub>2</sub> and CH<sub>4</sub>. Further discussion on this phenomenon is given in terms of adsorption equilibrium isotherm.



**Figure 2.** The amount of adsorbed CO<sub>2</sub> and CH<sub>4</sub> at the experiment with constant temperature of 30 °C and various pressure of (A) 1.8 bar, (B) 2.2 bar, (C) 2.6 bar, and (D) 3 bar

On the other hand, adsorbed capacity of CO<sub>2</sub> and CH<sub>4</sub> at constant pressure with varied operational temperature is given in Figure 3. It is well comprehended from the figure that adsorption is an exothermic process, which make the adsorption capacity was lower at higher temperature. However, the decrease in CO<sub>2</sub> adsorption capacity was more than that of CH<sub>4</sub>. Accordingly, the difference between adsorption capacity of CO<sub>2</sub> and CH<sub>4</sub> was decreasing as the operational temperature was

increasing, and finally almost equal at temperature of 100 °C. This phenomenon could be related to a more energetic molecules at higher temperature and the exothermic process of adsorption.



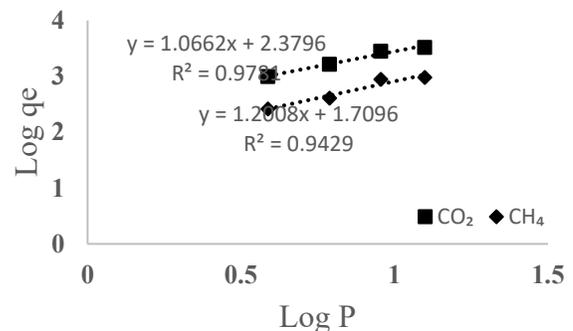
**Figure 3.** The amount of adsorbed CO<sub>2</sub> and CH<sub>4</sub> at the experiment with constant pressure of 3 bar and various temperature of (A) 30°C, (B) 50°C, and (C) 100°C

This study also calculated the enthalpy change, and found the value of -2.654 kJ/mol and -13.36 kJ/mol for CH<sub>4</sub> and CO<sub>2</sub> gas adsorption, respectively. This phenomenon obviously indicates that separation of CO<sub>2</sub> from CH<sub>4</sub> using zeolite 13X can be realized better at higher pressure, but at lower temperature. For clearer comparison, the numerical value of the equilibrium amount of absorbed CO<sub>2</sub> and CH<sub>4</sub> as well as its difference is given in Table 1. The larger difference between adsorption capacity of CO<sub>2</sub> and CH<sub>4</sub> can be obtained at ambient temperature of 30 °C. This result is in line with that of Song et al [16], where the difference in the amount of CO<sub>2</sub> and CH<sub>4</sub> gases adsorbed by carbon molecular sieve is greater when under conditions of high pressure and ambient temperature.

**Table 1.** Equilibrium adsorption capacity at various pressures and temperatures.

Pressure (bar)	Temperature (°C)	q <sub>e</sub> (mg/g)		
		CO <sub>2</sub>	CH <sub>4</sub>	q <sub>e</sub> difference
1.8	30	20.00	11.22	8.78
2.2		24.91	13.61	11.30
2.6		31.42	19.07	12.35
3		33.69	18.92	14.77
3	50	22.92	19.13	3.80
3	100	13.90	13.84	0.06

Further analysis on the experimental data was conducted in terms of adsorption equilibrium isotherm, using the Freundlich model as given in equation 2. The plot of Log q<sub>e</sub> and Log P for a constant temperature of 30 °C, for both CO<sub>2</sub> and CH<sub>4</sub> adsorption in the Zeolite 13X, is shown in Figure 4. Then, its linear regression gives the value of Freundlich coefficient (K<sub>F</sub>) and adsorption intensity (1/n) as in Table 2. It is obvious from the value of K<sub>F</sub>, that the amount of CO<sub>2</sub> adsorbed by Zeolite 13X at equilibrium condition is higher than adsorption of CH<sub>4</sub>. On the other hand, the adsorption intensity (1/n coefficient) was higher for CH<sub>4</sub> than CO<sub>2</sub>, which indicates that at higher pressure the equilibrium adsorption capacity of CH<sub>4</sub> could be higher than CO<sub>2</sub>. The lower value of adsorption intensity for CO<sub>2</sub> than CH<sub>4</sub> at normal temperature was also found by previous researcher [17][18].



**Figure 4** Linear plot of the adsorption equilibrium model for both CO<sub>2</sub> and CH<sub>4</sub> adsorption in Zeolite 13X

**Table 2** Freundlich's constants of CO<sub>2</sub> and CH<sub>4</sub> at a temperature of 30 °C.

Gas	Freundlich constant	
	K <sub>F</sub>	1/n
CO <sub>2</sub>	10.08	1.07
CH <sub>4</sub>	5.53	1.20

Simulation on the effect of pressure to the adsorption equilibrium capacity of both CO<sub>2</sub> and CH<sub>4</sub> gases, at constant temperature of 30 °C, is shown in Figure 5. Experimentally, it was found that CO<sub>2</sub> and CH<sub>4</sub> gas adsorption in zeolite varies directly with pressure raised to the power 1/n. However, at pressure

higher than saturation pressure, the rate of adsorption will also saturate. This is widely recognized as the limitation of Freundlich adsorption isotherm which fails at higher pressure. However, at an applicable pressure range, the phenomenon can be used for purification of CH<sub>4</sub> gas from other gases in a complex gas mixture, such as biogas.

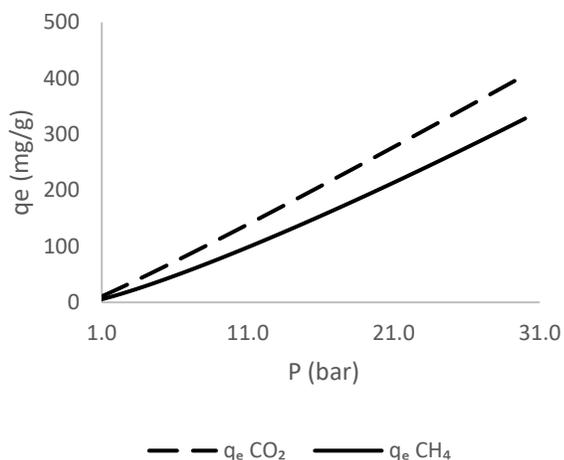


Figure 5 Adsorption equilibrium curves in Freundlich Model

#### 4.0 CONCLUSION

Experimental research on the adsorption of CO<sub>2</sub> and CH<sub>4</sub> gases in biogas at temperatures of 30 °C, 50 °C and 100 °C and at pressures of 1.8 bar, 2.2 bar, 2.6 bar and 3 bar has been carried out and the adsorption capacity values have been obtained. The amount of CO<sub>2</sub> gas adsorbed was more than CH<sub>4</sub> gas at pressure variations and at high pressure, the difference of q<sub>e</sub> was getting bigger. At high temperatures, the amount of CO<sub>2</sub> and CH<sub>4</sub> adsorbed decreases and the difference in q<sub>e</sub> is getting smaller.

Carbon dioxide and methane gas adsorption in zeolite vary directly with pressure raised to the power 1/n, where its value for CH<sub>4</sub> adsorption was higher than CO<sub>2</sub>. However, within the range of applicable pressure 1.8 bar to 3 bar, the equilibrium adsorption of CO<sub>2</sub> in Zeolite 13X was still higher than that of CH<sub>4</sub>.

#### Acknowledgement

Author thanks financial support from the Ministry of Education and Research of Indonesia through the scheme of Doctoral Dissertation Research.

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