Article

Carbon Dioxide Adsorption using Activated Carbon via Chemical Vapor Deposition Process

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Abstract. This research aims to study the physical-chemical characteristics and carbon dioxide adsorption using commercial activated carbon (GAC) by comparing with commercial activated carbon. Chemical vapor deposition (CVD) of carbon molecular sieve prepared from activated carbon (CMS$_{GAC}$) was prepared using acetylene at various conditions, such as temperature, time and acetylene flow rate. The results indicated that CMS$_{GAC}$ had high adsorption capacity and high selectivity for the adsorption ratio between carbon dioxide and methane. The experiments were carried out by using the samples of GAC, CMS$_{GAC}$, and commercial carbon molecular sieve (CMS$_{COM}$) for adsorption of mixed gas of 30% CO_2, 20% N_2, and 50% CH_4, respectively. The results showed that the adsorption efficiency at 50% of inlet carbon dioxide concentration of GAC, CMS$_{GAC}$, and CMS$_{COM}$ was at 85, 114, and 140 min, respectively. The purity of methane was 81.53, 93.16, and 98.26%, respectively. The selectivity for the adsorption ratio between carbon dioxide and methane was 1.32, 16.52, and 24.89, respectively. The cycle time of the samples was 3, 7, and 8 cycles, respectively. Finally, the maximum adsorption capacity of the samples was 1.74, 3.26, and 4.06 mole CO_2/kg absorbent, respectively.

Keywords: Carbon molecular sieve, chemical vapor deposition, adsorption, carbon dioxide.

1. Introduction

The greenhouse effect is attributed to increase in the emission of the greenhouse gases, such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), chlorofluorocarbons (CFC), and sulfur hexafluoride (SF_6). Among them, CO_2 is the main greenhouse gas that causes global warming [1] because CO_2 mostly increases among other greenhouse gas which increase from 280 ppm to 387 ppm between 1850 and 2010 [2].

The most important sources of CO_2 emission is human activities, including burning fossil fuels (coal, oil, natural gases) and various industrial processes, such as distillation of petroleum, initial chemical production, manufacturing cement, and metal smelting. Several post-combustion gas separation and capture technologies are being investigated, such as amine scrubber, thermal separation, membrane separation, biofixation, and column adsorption [3].

At present, the preferred technology for the separation of CO_2 in post-combustion applications is amine scrubbing. However, this technology presents several disadvantages because amine scrubbing process requires high energy to operate and to regenerate solvent. Moreover, amine scrubbing process requires also special management from specialists. Other technologies developing aims to reduce the cost in the capture steps, including adsorption with activated carbon which is absorbent that has high adsorption capacity at ambient pressure, insensitiveness to moisture, easy regeneration, and low cost [4].

However, there were various methodologies to improve the CO_2 adsorption efficiency, such as impregnation and chemical vapor deposition process. The chemical vapor deposition (CVD) process would develop activated carbon to be carbon molecular sieve (CMS) prepared from activated carbon which has narrower pore size distribution, higher adsorption efficiency, and higher selectivity for gas adsorption than activated carbon.

In this work, CMS would be prepared from commercial activated carbon by the chemical vapor deposition process to improve physical and chemical characteristics. Finally, CMS prepared form commercial activated carbon would be carried out in CO_2 adsorption with mixed gas for the results of the CO_2 removal efficiency, purity of methane, selectivity, and maximum adsorption capacity.

2. Experimental

2.1. Preparation for Carbon Molecular Sieve

Commercial granular activated carbon (GAC) purchased from METRA Co. Ltd. of 10 g was deposited with acetylene by chemical vapor deposition process under 5, 10, 15, and 20 ml/min of acetylene and 50 ml/min of nitrogen flow for 15, 30, 45, and 60 min at 600, 700, 800, and 900 °C [5]. Afterwards, carbon molecular sieve produced from GAC (CMS_{GAC}) was analyzed for BET specific surface area and iodine number in order to find out the optimum condition as shown in Table 1. The CMS_{GAC} from each condition was designated as $CMS_{f, t, T}$ where f, t, and T were acetylene flow, time, and temperature, respectively. The commercial carbon molecular sieve (CMS_{COM}) used in this study was Shirasagi MSC-3K-172 which was purchased from Shirasagi Co. Ltd.

2.2. Characterization of Samples

The chemical and physical characteristics of GAC, CMS_{GAC}, and CMS_{COM} were analyzed as following:

- The analysis of specific surface area, pore volume, and pore size were determined by nitrogen adsorption-desorption isotherms at 77 K [6] with discontinuous volumetric apparatus (Quantachrome AUTOSORB 1). The measurement of iodine number corresponding to procedure established by the standard method ASTM D4607-94 (2011) [7].
- Analysis of the surface functional group by using Fourier transforms infrared spectroscopy (FTIR) of the GAC, CMS_{GAC}, and CMS_{COM}.
- Analysis of morphology of the GAC, CMS_{GAC}, and CMS_{COM} in order to study the morphological surface of the samples. Morphological analysis was carried out by scanning electron microscope (SEM) by using JSM-6400 scanning microscope model JEOL.

2.3. Adsorption Experiments

The GAC, CMS_{GAC}, and CMS_{COM} were analyzed for CO_2 adsorption in a single column as shown in Fig. 1. The initial chemical compositions of the mixed gas were 30% CO_2, 50% CH_4, and 20% N_2. The mixed gas was fed at controlled pressure of 3 bars with the ratio of flow rate (inlet/outlet) of 1 at 25 °C.
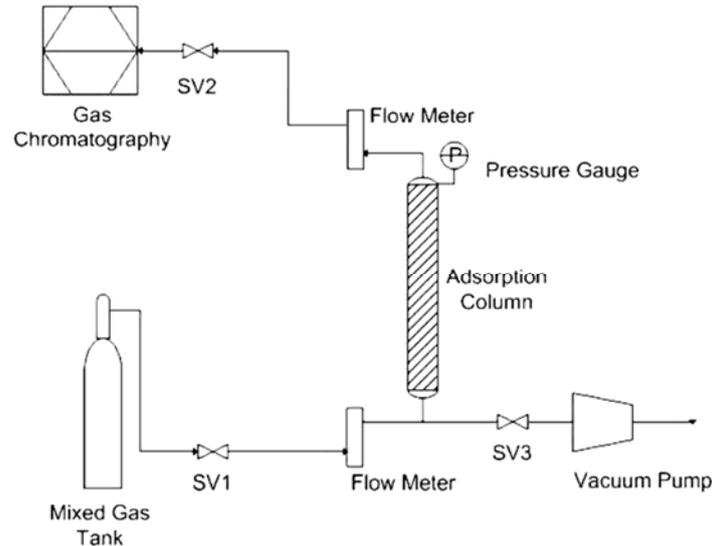

Fig. 1. Diagram of the single column system.

2.3.1. CO_2 removal efficeincy experiment was carried out by collecting outlet gas at 5-150 min to analyze the gas composition by gas chromatograph (Shimadzu model GC2014). The removal efficiency could be calculated by using the Eq. (1).

$$CO_2 \text{ Removal Efficeincy } (\%) = \left(\frac{C_0 - C_1}{C_0}\right) \times 100$$

(1)

where C_0 and C_1 are the initial and the final CO_2 concentration (%), respectively.

2.3.2. The purity of the outlet CH_4 (%) was carried out by collecting outlet gas at 10 minutes to analyze the CH_4 concentration by gas chromatograph. The CH_4 purity could be calculated by using the Eq. (2).

$$CH_4 \text{ purity } (\%) = \left(\frac{C_1}{C_0}\right) \times 100$$

(2)

where C_0 and C_1 are the initial and the final CH_4 concentration (%), respectively.

2.3.3. The selectivity of CO_2:CH_4 ratio (mol/mol) was carried out by collecting the outlet gas at the first cycle time to analyze the gas concentration of CO_2 and CH_4 in order to calculate the ratio of gas concentration which was adsorbed in adsorbent between CO_2 and CH_4 (Selectivity) by Eqs. (3)-(5).

$$n_{ads} = n_{feed} - n_e \tag{3}$$

$$n_{feed} = \frac{P_{ads} \int V_t d_t}{RT} \tag{4}$$

$$n_e = \frac{P_e V_{out}}{RT} \tag{5}$$

where n_{ads} : the concentration of gas adsorbed in adsorbent (mol).

n_{feed} : the concentration of gas fed in adsorption column (mol).

n_e : the concentration of gas in the outlet gas (mol).

T : operating temperature (K).

R : the gas constant 0.08206 (L.bar/mol/K).

P_{ads} : initial pressure (bar).

P_e : post pressure at equilibrium (bar). T is operating temperatre (K).

V_t : inlet gas volume (L).

2.3.4. Maximum adsorption capacity was estimated form Eq. 4 by collecting the outlet gas cumulatively to analyze the CO_2 concentration utill inlet CO_2 concentration equaled outlet CO_2 concentration. Then, Carrying out to calculate the maximum adsorption capacity by the summary of CO_2 which was totally adsorbed.

3.   Result and Discussion

3.1. Specific Surface Area Studies

Analytical by adsorption and desorption technique with nitrogen gas in GAC, CMS_{GAC}, and CMS_{COM} in Table 1; show that specific surface area were a 301.9, 604.0, and 558.6 m^2/g, respectively while the total pore volume were 0.1648, 0.3848, and 0.2529 cm^3/g and the mean pore diameter were 2.183, 2.186, and 2.360 nm, respectively. The optimum condition in chemical vapor deposition process including acetylene flow, time, and temperature were 15 ml/min, 30 min, and 800 °C, respectively.

The results in Table 1 suggested that the chemical vapor deposition by acetylene at optimum condition would increase the specific surface area and the pore volume because macropore and mesopore in CMS_{GAC} was developed as micropore which improve the specific surface area and the pore volume [8].

When diffusion of acetylene through the pores is faster than reaction (low temperatures), there are no diffusion limitations and carbon will deposit uniformly over the entire pore surface. If reaction is faster than diffusion (high temperatures), there will be strong pore diffusion limitations, the reactant will not reach the interior pore surface and carbon deposition will occur mainly at the pore entrance [9].

In case of operation on long time and too fast flow of acetylene, the excess reactant will block the entrance of pore surface, so specific surface area and pore volume will clearly decease [10].

3.2. Iodine Number Studies

The iodine number of GAC, CMS_{GAC}, and CMS_{COM}, listed in Table 1, were 137.2, 325.3, and 295.4 mg/g, respectively. The results showed that the chemical vapor deposition process could improve iodine number due to the increase of surface area after chemical vapor deposition process.

Table 1. The results of BET specific surface area and iodine number.

Materials	Surface Area (m²/g)	Pore Volume (cm³/g)	Diameter (nm)	Iodine number (mg/g)
*GAC	301.9	0.1648	2.183	137.2
$CMS_{5, 30, 800}$	471.8	0.3532	2.182	243.7
$CMS_{10, 30, 800}$	529.3	0.3586	2.184	263.5
$CMS_{15, 30, 800}$	601.2	0.3698	2.185	322.5
$CMS_{20, 30, 800}$	586.6	0.3614	2.219	301.3
$CMS_{15, 15, 800}$	577.3	0.3633	2.179	293.0
$CMS_{15, 30, 800}$	597.8	0.3702	2.182	318.2
$CMS_{15, 45, 800}$	539.8	0.3578	2.197	287.1
$CMS_{15, 60, 800}$	510.7	0.3539	2.221	279.4
$CMS_{15, 30, 600}$	532.6	0.3692	2.178	267.7
$CMS_{15, 30, 700}$	579.7	0.3714	2.177	279.4
*$CMS_{15, 30, 800}$	604.0	0.3848	2.186	325.3
$CMS_{15, 30, 900}$	489.2	0.2954	2.237	251.2
*CMS_{COM}	588.6	0.2529	2.360	295.4

* Samples which were selected to carry out in adsorption experiments

3.3. Fourier Transform Infrared Spectroscopy Studies

Fourier transform infrared spectroscopy (FTIR) spectrums of GAC, CMS_{GAC}, and CMS_{COM} are shown in Fig. 2. Both GAC and CMS_{GAC} had the same functional groups, such as aromatic (-CC stretch) and carboxyl (-OH stretch). In operation of chemical vapor deposition, functional groups of alcohol-phenol in GAC disappeared while new group such as alkane was found. CMS_{COM} possessed several functional groups such as alcohol-phenol (-OH stretch), $1°, 2°$ amide (-NH stretch), alkyl halide (-CH₂X stretch), and aliphatic amine. In brief, certain functional groups disappear in chemical vapor deposition process because the surface area of GAC was coated with reactant.
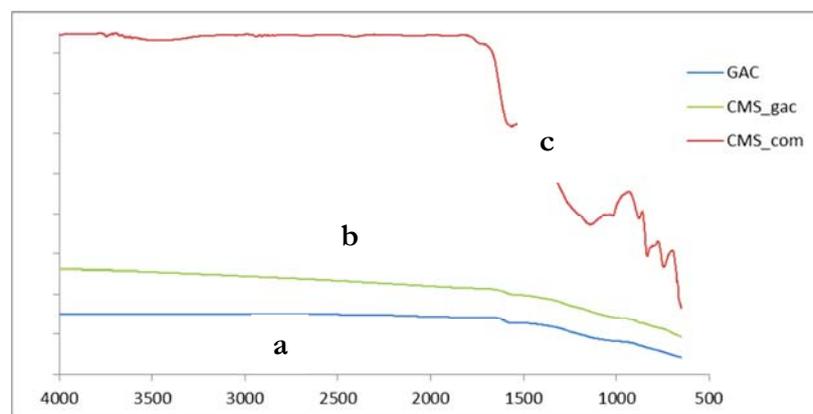

Fig. 2. FTIR spectrums of (a) GAC, (b) CMS_{GAC}, and (c) CMS_{COM}.

3.4. Microscopic Studies

SEM technique was applied in order to study surface morphology of adsorbents, such as GAC, CMS_{GAC}, and CMS_{COM}. The Fig. 3 shows that the porous surface of CMS_{GAC} has more micropore than GAC.
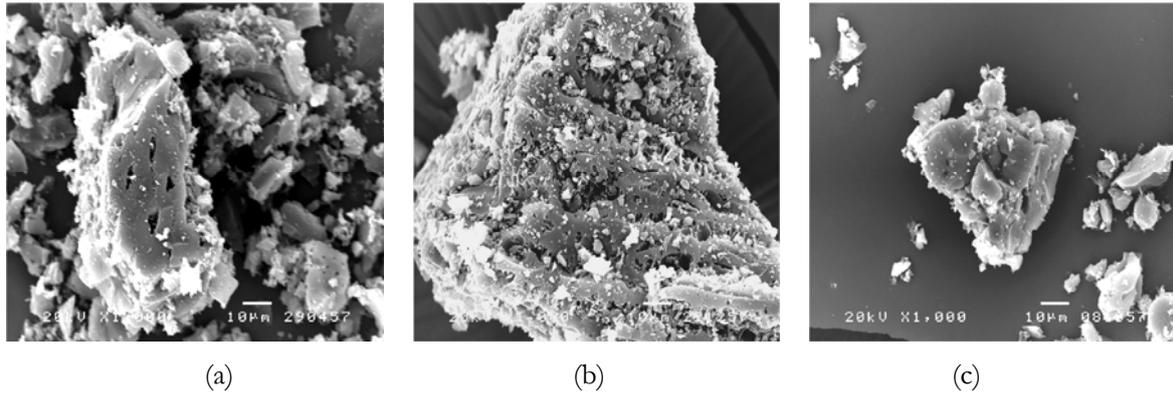
(a)	(b)	(c)

Fig. 3. SEM images of (a) GAC, (b) CMS_{GAC}, and (c) CMS_{COM}.

3.5. CO_2 Removal Efficiency Studies

Analytical results of CO_2 removal efficiency at 50% of initial CO_2 concentration in GAC, CMS_{GAC}, and CMS_{COM} were 27, 38, and 57 min, respectively. The degeneration of adsorption in samples was at 90, 120, and 140 min, respectively, as shown Fig. 4.
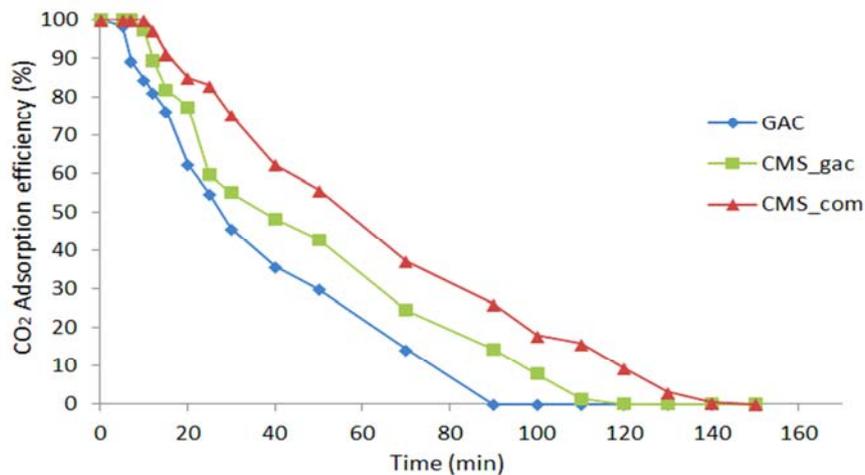

Fig. 4. CO_2 adsorption efficiency of GAC, CMS_{GAC}, and CMS_{COM}.

3.6. Purity of Methane

The analytical result of the purity of methane (CH_4) in synthesis mixed gas for GAC, CMS_{GAC}, and CMS_{COM} was 81.53, 93.16, and 98.26 %, respectively. The outlet CH_4 concentration results were shown in Fig 5.

When the adsorption process in column was carry out continually, the outlet CO_2 concentration would increase and the outlet CH_4 concentration would decrease until breakthrough point of adsorbent (50% of initial CO_2 concentration). At the breakthrough point, the adsorption column would be regenerated before carrying out the adsorption processes again.
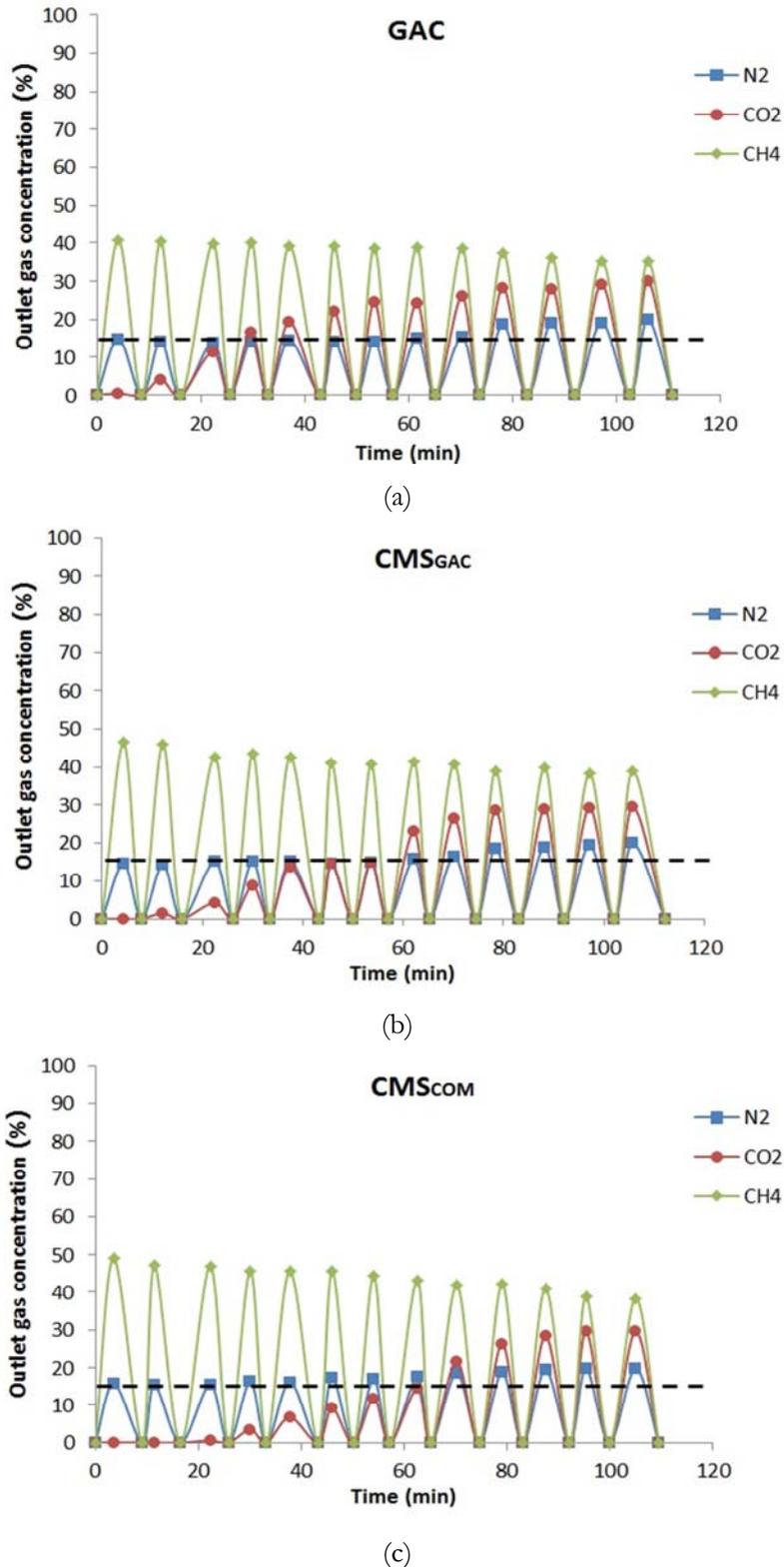
(a)

(b)

(c)

Fig. 5. The outlet gas concentration of (a) GAC, (b) CMS$_{GAC}$, and (c) CMS$_{COM}$.

3.7. Selectivity Studies

Selectivity results of the ratios between CO_2 and CH_4 in GAC, CMS$_{GAC}$, and CMS$_{COM}$ were shown in Table 2. The selectivity of GAC, CMS$_{GAC}$, and CMS$_{COM}$ were 1.32, 16.52 and 24.89, respectively.

Table 2. Comparison of selectivity of various absorbents.

Materials	Pore modification	Selectivity (CO_2/CH_4)	Reference
Palm shell	CVD of benzene (30 %vol in N_2), 800 °C, 30 min	16.0	[11]
Eucalyptus wood	Controlled Pyrolysis by CO_2, 600 °C, 30 min	20.0	[12]
Peach stone	Pyrolysis by O_2, 850 °C, 20 min, 50 ml/min	30.1	[13]
Peach stone	Pyrolysis by char impregnated in HNO_3 (5N) at 625 °C	127.9	[13]
Coffee grounds	CVD of acetylene 10 ml/min in N_2, 800 °C, 30 min	19.41	[14]
Activated carbon	CVD of acetylene 15 ml/min in N_2, 800 °C, 30 min	16.52	This work
MSC-3K-172	-	24.89	This work
Activated carbon	-	1.32	This work
Activated carbon (AC)	Impregnation with chitosan 0.1% in 100 ml of acetic acid	1.94	[15]
AC	-	1.27	[15]

The results in the Table 2 indicate that the chemical vapor deposition process can improve selectivity of adsorbents because of the narrow pore size distribution and selective adsorption capacity of certain components of a mixture. They can discriminate molecules on the basis of size and shape. Therefore, CMS with micropore require the presence of a specific porous network containing pore mouths of molecular sieve dimensions, together with a relatively high micropore volume. These features will confer them with a high adsorption capacity and selectivity [4].

3.8. Selectivity Studies

Figure 6 shows the adsorption capacity profiles of GAC, CMS_{GAC}, and CMS_{COM} were 1.74, 3.26 and 4.06 mol CO_2/kg absorbent, respectively. The profile result showed that a sample which had high cycle time would have also high adsorption capacity.
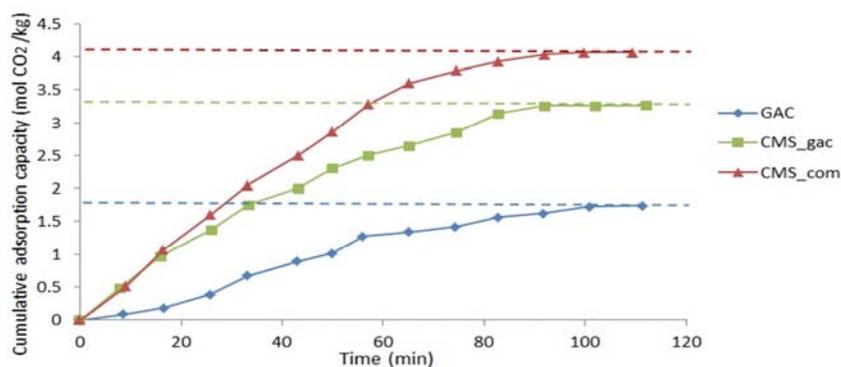

Fig. 6. CO_2 adsorption capacity of GAC, CMS_{GAC}, and CMS_{COM}.

Table 3. Comparison of CO_2 adsorption capacity of various absorbents in other research.

Sorbent	Operating Temperature (°C)	Operating Pressure (kPa)	CO_2 Capture Capacity (mol CO_2/kg sorbent)	Reference
Molecular basket	75	100	2.95	17
Activated carbon	30	30	0.35	17
Activated carbon	30	110	1.58	18
Activated carbon	25	300	1.74	This work
Lithium zirconate	400	100	5.00	19
Lithium orthosilicate	600	100	6.13	19
PE-MCM-41 (TRI)	25	100	2.85	20
PE-MCM-41 (TRI)	75	100	1.80	20
MCM-41	25	100	0.62	20
CGAC	25	300	0.25	21
CMS_{GAC}	25	300	3.26	This work
CMS_{CF}	25	300	3.42	14
MSC-3K-172	25	300	4.06	This work

The previous studies from Table 3 indicate that increasing temperature could decreases CO_2 adsorption capacity because the adsorption process is an exothermic reaction. When the temperature is higher, exothermic reaction will occur slowly. Increasing the operating pressure of the adsorption process would raise the CO_2 adsorption capacity because when the operating pressure was higher, the contacting surface area in adsorption would also be raised [16].

4. Conclusion

The chemical vapor from CVD at the optimum condition could improve the physical characteristics. Including specific surface area, iodine number, and pore volume. Moreover, the chemical vapor deposition with acetylene also improves and develops the CO_2 removal efficiency, purity of methane, selectivity, and maximum adsorption capacity.

Acknowledgements

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