Research Article

The Effect of Amine Types on Breakthrough Separation of Methane on Biogas

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ABSTRACT. Methane (CH_4) and carbon dioxide (CO_2) are the main components of a renewable energy source of biogas. Separation of CO_2 from biogas is significantly important to improve biogas performance, due to heating value in biogas depends on the concentration of methane. One of the gas separation technologies that has been widely used in chemical industries is carbon molecular sieve (CMS). This research explores the potential of CMS for biogas purification. CMS was prepared by modification of palm kernel shell-derived porous carbon using amine groups such as monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), and diethanolamine (DEA). The effect of amine types on the separation parameters was studied by using a breakthrough experiment to obtain the most potential CMS materials. The methods of this research include the process of carbon oxidation using hydrogen peroxide, impregnation with an amine group, characterization of the CMS material obtained, CO_2 and CH_4 gas separation testing with a breakthrough system. The CMS was characterized by using N_2 sorption analysis, fourier transform infrared spectroscopy, and scanning electron microscopy. The breakthrough experiment showed that CMS-MEA had the highest performance for separating CO_2 and CH_4 gases. In addition, the results also showed that loading of amine groups on carbon caused an increase in the uptake capacity of CO_2, and the highest capacity was achieved by CMS-MEA of 13.2 mg/g.

Keywords: amine groups, biogas, breakthrough time, carbon molecular sieve, CO_2 gas separation

1. Introduction

Renewable energy sources are used as an alternative to minimize the use and dependence of fossil fuels. Research and development of renewable energy have been widely studied. Biogas is a renewable energy source that can be an alternative solution to supply energy demand with advantages such as low environmental impact and high energy efficiency (Appels *et al.*, 2008; Ariyanto *et al.*, 2017; Poletti *et al.*, 2011). Biogas has the potential as a substitute for fossil fuels in several applications, such as for heating, electricity generation, and vehicle fuel when upgraded to bio-methane (Rasi *et al.*, 2011). Therefore, biogas can contribute to reducing greenhouse gas emissions.

The composition of biogas consists of methane (CH_4) and carbon dioxide (CO_2) and other impurities in very small amounts such as water (H_2O), hydrogen (H_2), nitrogen (N_2), hydrogen sulfide (H_2S), oxygen (O_2), and ammonia (NH_3). Biogas components are divided into two categories, namely combustible and non-combustible components. The detailed composition of biogas is presented in Table 1.

Compared with natural gas which has a heating value of 36 MJ/Nm³, biogas containing 60% CH_4 has a lower heating value, namely 21.5 MJ/Nm³ (Hosseini & Wahid, 2014). The purity of the biogas is a very important consideration because it affects the calorific value

produced. The energy in biogas depends on the concentration of methane so that the biogas produced needs to be purified against other impurities.

The carbon dioxide content can limit the use of biogas as renewable energy. The high percentage of CO_2 in biogas causes the calorific value of the biogas to decrease, corrodes equipment, and increases emissions (Akkarawatkhoosith *et al.*, 2019; Ricaurte *et al.*, 2012). Removal of CO_2 content can convert the concentration of methane to a higher level, which is commonly referred to as biomethane (>95% methane) so that the calorific value of biogas can be increased as contained in natural gas.

Table 1
Composition of biogas(Mursec *et al.*, 2009; Surendra *et al.*, 2014)

Component	Concentration	Category
Methane (CH_4)	50-75%	Combustible
Carbon dioxide (CO_2)	25-50%	Non-combustible
Water (H_2O)	1-5%	Non-combustible
Hydrogen (H_2)	<1%	Combustible
Nitrogen (N_2)	0-5%	Non-combustible
Hydrogen sulfide (H_2S)	0-5000 ppm	Combustible
Oxygen (O_2)	<1%	Non-combustible
Ammonia (NH_3)	0-500 ppm	Non-combustible

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The method that can be used to separate CO_2 and CH_4 in biogas is a molecular sieve. One of the effective potential molecular sieves for CO_2 gas separation is the carbon molecular sieve (CMS). CMS is a porous carbon material with most of the pores scattered in micropore size, which are able to distinguish molecules based on differences in diffusion rate, size, and shape (Mohamed *et al.*, 2010; Prasetyo *et al.*, 2020; Silvestre-Albero *et al.*, 2009; Wahby *et al.*, 2012). The separation of gas mixtures at CMS is determined by several parameters such as pore structure, affinity, and interaction of gas molecules with the carbon surface (Prasetyo *et al.*, 2017). Due to the CMS has large micropores and excellent molecular sieving properties so that CMS plays an important role in gas separation (Tae-Hwan *et al.*, 2003). One of the materials that have the potential to be used as CMS is biomass from palm kernel shells because it has a high carbon (C) content of around 50% (Rashidi & Yusup, 2017).

Several studies related to the separation of CO_2 gas using carbon molecular sieve have been studied. Palm shell was used to prepare CMS and the results showed high selectivity for the separation of O_2/N_2 and CO_2/CH_4 (Ahmad *et al.*, 2008). The working capacity and the selectivity of the separation of CO_2 and CH_4 using commercial carbon molecular sieve have been studied, the results show that the adsorption capacity of CO_2 is greater than that of CH_4 (Song *et al.*, 2017). Separation of CO_2/CH_4 using CMS prepared from coal tar pitch which presents molecular sieving properties to separate CO_2 from CH_4 results comparable to the yield of commercial molecular sieves (Alcañiz-Monge *et al.,* 2011).

The performance of porous carbon such as CMS for binary gas separation can be improved by several treatments such as oxidation, heat treatment, and chemical impregnation with acid or alkaline solutions on the carbon surface (Lee *et al.*, 2013). In previous research, hydrogen peroxide has been applied for the oxidation of carbon molecular sieve to enhance the separation of CH_4/CO_2 mixed gas (Cho *et al.*, 2015). Other research has been reported to identify the effect of impregnation CMS using ammonium hydroxide (Bai *et al.*, 2013). Both kinds of research show the improvement of the breakthrough separation process of CO_2 and CH_4 gases. Based on this literature, the presence of chemical species on the carbon surface greatly affects the performance of carbon materials.

Research related to CMS modification on the performance of breakthrough separation is still being developed. Porous carbon impregnated with alkaline groups such as amines have the potential to capture CO_2 in biogas due to the primary and secondary amines can react with CO_2 to form stable compounds and can be regenerated to release adsorbed CO_2 (Das & Meikap, 2020). However, CMS is less hydrophilic than other similar porous materials (Tae-Hwan *et al.,* 2003). In this study, a combination of several treatments was used to improve the performance of CMS. CMS was prepared by modification of palm kernel shell-derived porous carbon using two treatments including oxidation and impregnation of amine groups. The oxidation treatment using hydrogen peroxide was previous carried out during the impregnation process. Oxidation is a pre-treatment that can change the nature of CMS from hydrophobic to hydrophilic so that the impregnation process of amines becomes easier. Then the types of amines used for the impregnation process include monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), and diethanolamine (DEA). The three types of amines were studied to determine their effect on breakthrough time so that the material with the best performance for CO_2 separation was obtained.

2. Materials and Methods

2.1 Materials

The materials used in this study were palm kernel shell-based carbon molecular sieve (CMS) provided by PT Home System, Indonesia, hydrogen peroxide (H_2O_2) 50% and monoethanolamine (MEA) 99.5% supplied by Merck,2-amino-2-methyl-1-propanol (AMP) 90%, and diethanolamine (DEA) 98% obtained from Sigma Aldrich. Then, the gases used for separation testing such as nitrogen (N_2) gas 100% and a gas mixture of methane (CH_4) 55% and carbon dioxide (CO_2) 45% which represents the composition of the biogas were imported from PT Samator Gas.
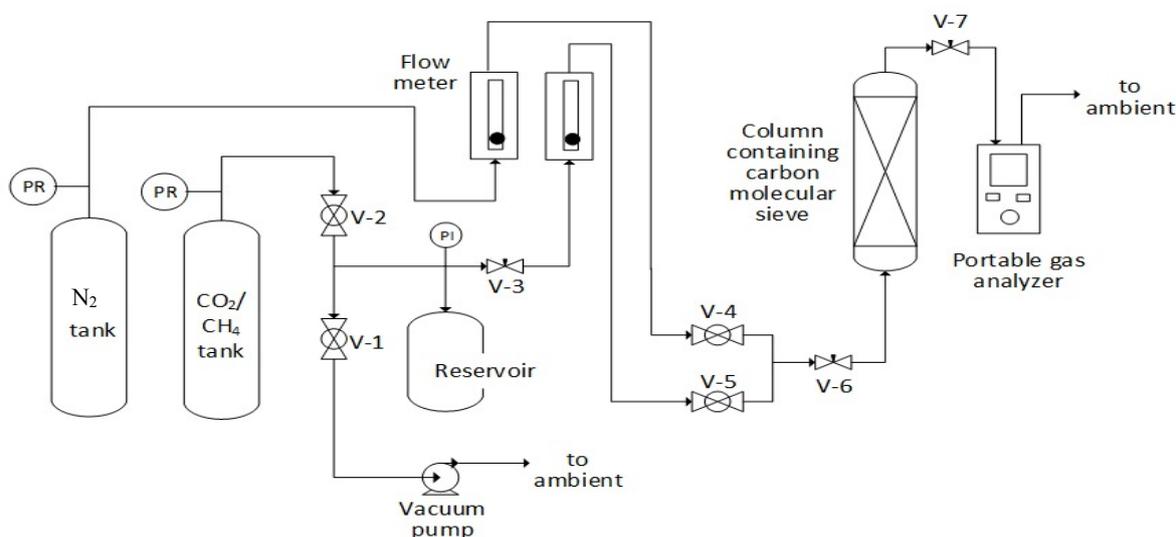
Fig. 1. Scheme of separation testing with a breakthrough system. The scheme taken from (Prasetyo *et al.*, 2020).

2.2 Oxidation Process

The CMS was crushed and sieved with a size of around 20-25 mesh and then oxidized using a 10% H_2O_2 solution. The oxidation process begins by diluting the 50% H_2O_2 solution to 10%. Oxidation was carried out in a three-neck flask by mixing 25 grams of CMS with 250 ml of 10% H_2O_2 solution at room temperature for 2 h. After that, the oxidized carbon was separated with H_2O_2 solution and dried in an oven at 70 ºC for 24 h.

2.3 Impregnation Process

In this method, amines were mixed with the CMS with the help of a solvent. The solvent was then removed by evaporation. The impregnation process was prepared by mixing 25 grams of oxidized CMS, 1.3 grams of amines such as MEA, AMP, and DEA (5% w/w) in the beaker, and adding distilled water until form slurry. The slurry was stirred using a magnetic stirrer at 300 rpm for 1 h at room temperature. The mixture of CMS and amines was allowed to stand for 24 h at room temperature until the distilled water evaporated and then dried in an oven at 70ºC for 24 h. The materials impregnated were labeled as CMS-MEA, CMS-AMP, and CMS-DEA.

2.4 Characterization

Total surface area, pore-volume, and pore size of the CMS materials were characterized by the N_2 sorption method using the NOVA 2000 analyzer (Quantachrome) at 77 K. Identification of the functional groups in the wavenumber range 400-4000 cm^{-1} was carried out by Fourier transform infrared spectroscopy (FTIR) using 8201 PC FTIR, Shimadzu. Then, the morphology of the materials was characterized using scanning electron microscopy (SEM) with the JEOL JSM-6510LA instrument at a voltage of 15 kV.

2.5 Separation testing

The separation process of CO_2 and CH_4 was carried out using a breakthrough system whose equipment scheme is shown in Fig.1. Inside the bed was filled with 14 grams of CMS material. CMS was first flushed by nitrogen gas with a flow rate of 200 ml/min until the gas detector showed no detected CH_4, CO_2, and O_2 gas content. After that, the gas mixture of CH_4 and CO_2 flowed into the system with a flow rate of 100 ml/min at ambient temperature and pressure of 1.2 bar. The composition of methane and carbon dioxide was detected by a portable gas analyzer (Biogas Analyzer Gas board 3200plus, Hubei Cubic-Ruiyi Instrument Co. Ltd). The separation process was stopped when the concentrations of CO_2 and CH_4 gases detected by the portable gas analyzer were 35.5% and 54.5% respectively. After the separation process, CMS was flushed by passing nitrogen gas to the separator column at a flow rate of 200 ml/min.

Table 2
Physical properties from N_2 sorption at 77 K

Materials	Total surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size(nm)
CMS	708	0.33	1.87
CMS-MEA	164	0.10	2.40
CMS-AMP	228	0.14	2.39
CMS-DEA	211	0.13	2.40
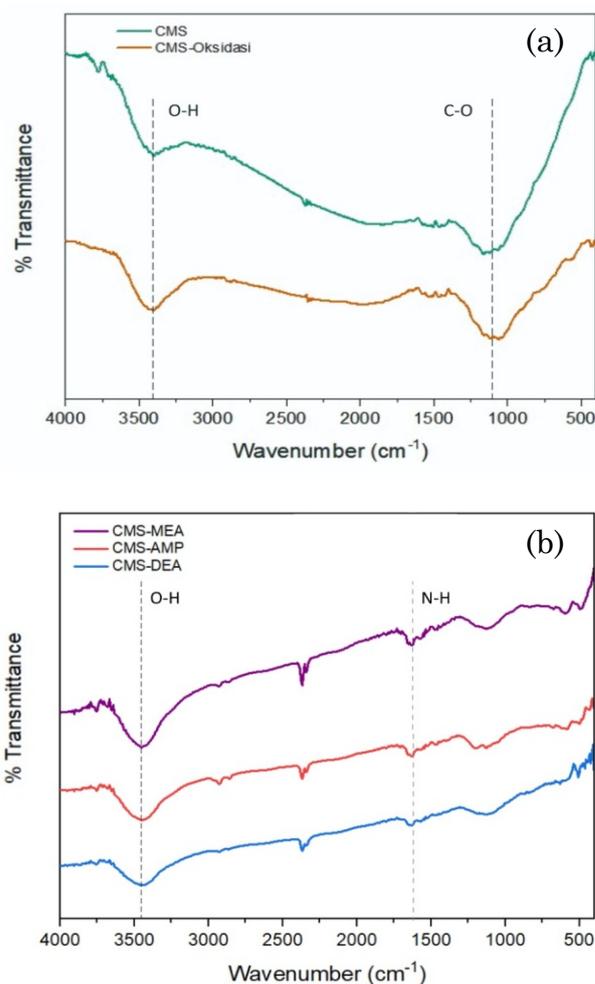
Fig. 2. FTIR spectra of the CMS and CMS-Oxidation (a), CMS-MEA, CMS-AMP, and CMS-DEA (b)

3. Results and Discussion

3.1 Characterization Results

3.1.1 N_2 Sorption Analysis

Table 2 shows the total surface area, pore-volume, and average pore size of the unmodified and modified CMSs. The results of the N_2 sorption analysis showed that the modified CMS experienced a significant reduction in surface area and pore volume. The decrease in pores indicates that the impregnation process has been successful. The total surface area of the CMS is 708 m^2/g, after impregnation, the surface area drops to 164 m^2 / g (CMS-MEA), 228 m^2/g (CMS-AMP), and 221 m^2/g (CMS-DEA). The total pore volume respectively decreases to 0.10 cm^3/g (CMS-MEA), 0.14 cm^3/g (CMS-AMP), and 0.13 cm^3/g (CMS-DEA). This decrease is caused by amine groups that have filled the pores of the carbon and blocked most of the pore structures. Although they clog pores, amines provide an active site that can increase the interaction between CO_2 and carbon. The specific surface area and pore volume are considered very important parameters during physisorption. However, in this study, the pores have a role to increase the number of amines that enter the carbon through the impregnation process.
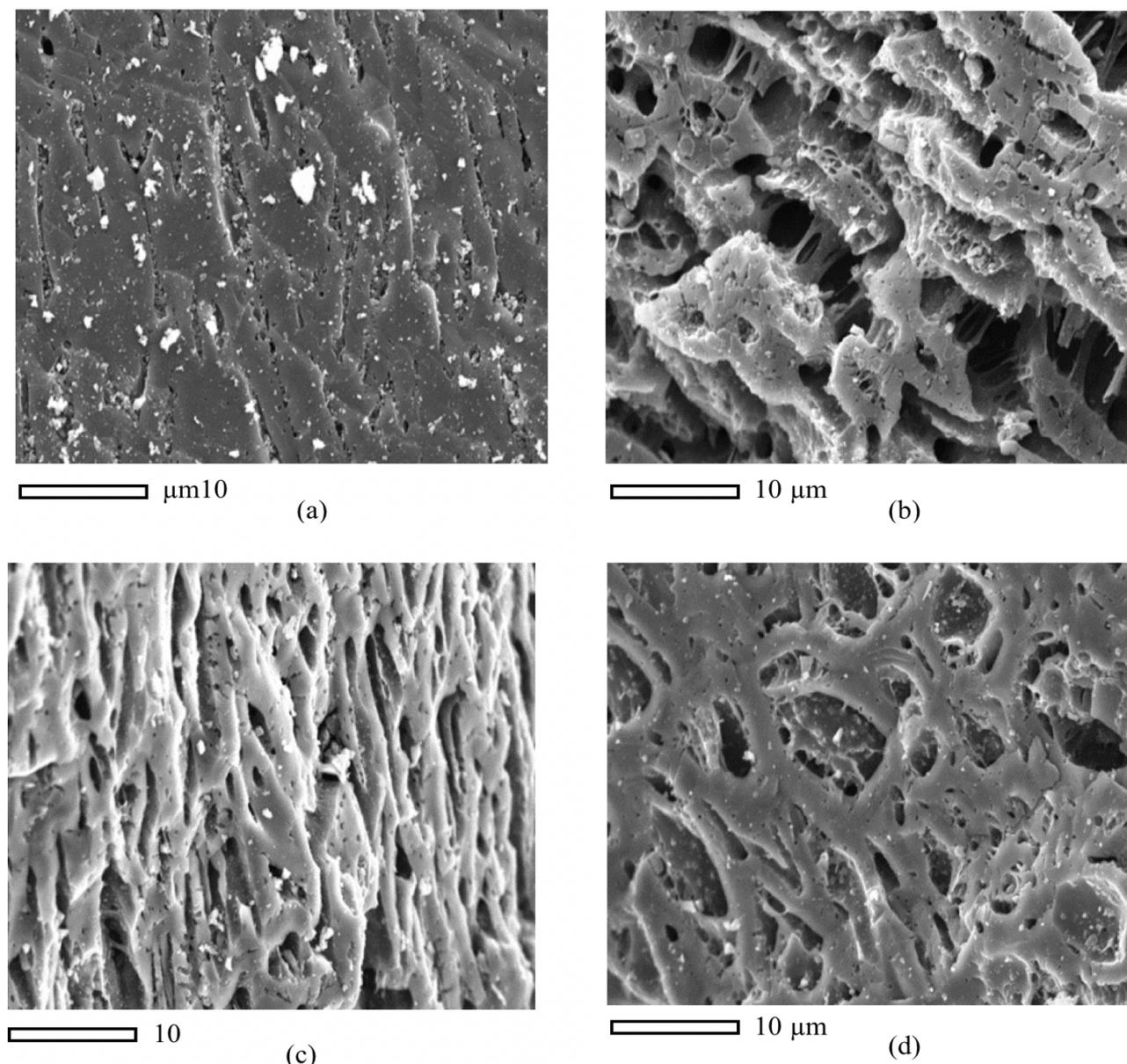
Fig. 3. SEM image of (a) CMS, (b) CMS-MEA, (c) CMS-AMP, and (d) CMS-DEA magnified 1.000 time

3.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fig. 2(a) shows the FTIR spectrum of unmodified CMS and oxidized CMS using hydrogen peroxide. A strong peak at 3400 cm^{-1} indicates O-H stretching, while the strong spectra at 1085cm^{-1} show the presence of C-O stretching of alcohol groups. In the FTIR spectra, it was shown that oxidized CMS had a sharper peak. This indicates that oxidation using hydrogen peroxide produces an OH group. The pre-oxidation helps to increase the N loading during the impregnation process, due to the presence of the O functional on the surface plays an important role in determining the amount of N loading to the carbon surface.

FTIR spectrum of the amine impregnated CMS is shown in Fig. 2(b) the success of the amine impregnation process into the carbon structure can be seen from the presence of the N-H bending vibration of amines groups at the spectra of 1655-1641 cm^{-1} (Kongnoo et al., 2016). In this study, FTIR results on CMS-MEA, CMS-AMP, and CMS-DEA materials showed that the N-H bending was indicated at the peaks of 1650 cm^{-1}. In addition, it is seen that the C-O stretching peak of the carbon-bound alcohol group is not as sharp as in Fig. 2(a), due to the C-O has reacted with an amine. The wavenumber 3400 cm^{-1} associated with the N-H stretching where shows that CMS-MEA has a sharper peak than other materials. This allows that the loading amount of amines is greater.

3.1.3 Scanning Electron Microscopy (SEM)

SEM analysis results showed a significant difference in morphological structure between carbon without impregnation and carbon loaded with amines. The carbon

surface before impregnation is presented in Fig. 3(a), while the carbon surface after impregnation with amines is presented in Figs. 3(b-d). Fig. 3(a) shows that carbon without impregnation has a denser morphology. Meanwhile, the amine impregnated carbon has a more hollow morphology as shown in Figs. 3(b), 3(c), and 3(d). CMS-MEA shows a large cavity compared to CMS-AMP and CMS-DEA. SEM images only show the surface morphology of the carbon, not showing a micro or meso-sized pore.

3.2 Breakthrough time result

The breakthrough time was studied to measure the performance of CO_2 and CH_4 gas separation. Fig. 4(a) shows the breakthrough curves of CO_2, while the breakthrough curve of CH_4 can be seen in Fig. 4(b). In the beginning, CH_4 and CO_2 gas detected by the portable gas analyzer showed the same concentration of 0%. However, the difference in the diffusion rate of gas molecules causes the CH_4 molecule to pass through the pores faster than the CO_2 molecule which allows the two gases to separate. The diffusivity of CH_4 and CO_2 was 1×10^{-10} m²/s and 1×10^{-11} m²/s respectively (Prasetyo *et al.*, 2020). In addition, carbon is more selective towards CO_2 than CH_4 because of its higher affinity for carbon. Due to the diffusion rate of the CO_2 molecule is slower, it allows this molecule to be trapped on the carbon. The CO_2 gas started to breakthrough out from the carbon when carbon is in the saturation stage. Thus, the CO_2 concentration displayed increases to its initial concentration and the methane gas concentration decreases again.

Modification of CMS by impregnated amine is the method mostly used to enhance the interaction between the carbon surface and acid molecules, such as CO_2, H_2S, and SO_2 (Sevilla *et al.*, 2012). The results showed that CMS-MEA, CMS-AMP, and CMS-DEA take a longer time to reach saturation point compared to non-impregnated CMS. The amine group provides the active site on the carbon surface which can increase the capture of CO_2 molecules

due to the chemisorption effect. The active site from the N functional group will cause increasing the polarity and basicity properties of the carbon surface (Sevilla *et al.*, 2012). The interaction between CO_2 and amines occurs based on the Lewis acid-base principle. Amine acts as Lewis's base inducing electron-donor, while CO_2 acts as an electron-accepting Lewis acid. its properties provide a high affinity for a stronger interaction between CO_2 and carbon (Chiang & Juang, 2017).

On the breakthrough curve seen that CMS-DEA is the first to reach the saturation point of the three types of amines. It may be related to DEA which is a group of secondary amines and has a larger molecular weight (105 g/mol). Secondary amines were less reactive than primary amines (Zelenak *et al.*, 2008). MEA and AMP were included as primary amines. However, for the same amine groups, the structure of the smaller amine and have fewer branches will provide more active sites (Khalil *et al.*, 2012). AMP has a larger molecular weight (89 g/mol) and more branched which makes it difficult for the amines molecule to occupy the pores. Therefore, this experiment shows that CMS-MEA has a longer breakthrough time than CMS-AMP and CMS-DEA.

The CO_2 sorption capacity can be determined when CO_2 first interacts with carbon until the CO2 molecules started to breakthrough out from the column. The uptake capacity of CO_2 for impregnated and non-impregnated CMS is presented in Table 3. Based on Table 3 the loading of amines on carbon shows a better CO_2 sorption performance. The sorption capacity of CO_2 increased to 13.2 mg/g for CMS-MEA, 11.8 mg/g for CMS-AMP, and 9.9 mg/g for CMS-DEA, respectively. Thus, the active site on the carbon surface has stronger properties so that in this study the process is more likely to be chemisorption. In previous studies, CMS impregnated with ammonium hydroxide had increased CO_2 sorption capacity by 24 % (1.61 mmol/g to 2.0 mmol/g at 298K) as an effect of the introduced nitrogen function (Bai *et al.*, 2013). Other materials such as fly ash carbon-impregnated by MEA can increase the CO_2 uptake up to 64% (41.8 mg/g to 68.6 mg/g at 30ºC) (Mercedes Maroto-Valer *et al.*, 2008).
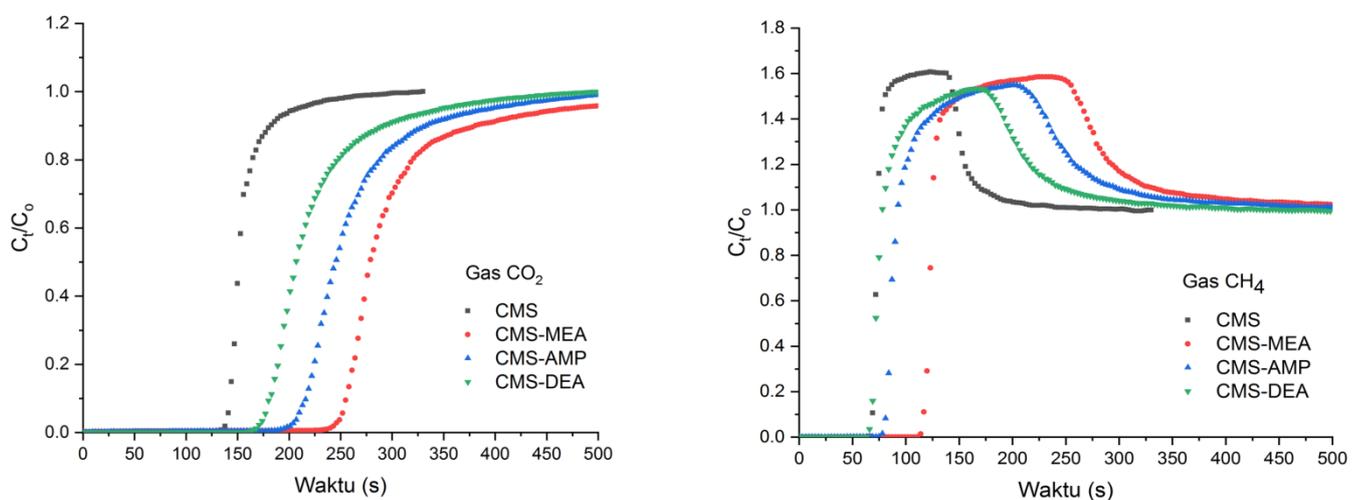
Fig. 4 Breakthrough curve of a) CO_2 and (b) CH_4

Table 3
Uptake capacity of CO_2

Materials	CO_2 uptake (mg/g)	Enhancement (%)
CMS	7.9	-
CMS-MEA	13.2	67
CMS-AMP	11.8	49
CMS-DEA	9.9	25

6. Conclusion

CMS was prepared by modification of palm kernel shell-derived porous carbon using amine groups that have the potential for biogas purification. The introduction of amine groups into the carbon structure causes the pore structure to become clogged so that the surface area is reduced as shown in the BET results. However, impregnation of carbon with base groups has increased the chemical surface for carbon capture. The presence of N functional groups can increase the acid-base interaction between CO_2 and the carbon surface due to the chemisorption effect. The oxidation treatment before the impregnation process gives the functional group O on the carbon surface as seen in the FTIR results, where the O functional group has an important role in increasing the N loading on the carbon. Loading of amines on CMS showed better breakthrough separation performance compared to CMS without amine impregnated. CMS impregnated with MEA showed a longer breakthrough time and higher CO_2 sorption capacity.

Acknowledgments

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