Improving the Separation of CO_2/CH_4 Using Impregnation of Deep Eutectic Solvents on Porous Carbon

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ABSTRACT: The separation of CO_2/CH_4 using porous carbon can be increased by the presence of a functional group of nitrogen on the carbon surface. This study explores the potential of porous carbon derived from the palm kernel shell (C-PKS) impregnated with a deep eutectic solvent (DES), which is one of the chemicals containing a nitrogen element. The DES was composed of a quaternary ammonium salt of choline chloride (ChCl) and a hydrogen bond donor of alcohol. Three alcohols of 1-butanol (-ol), ethylene glycol (-diol), and glycerol (-triol) were employed to study the effects of a number of hydroxyl groups in the separation performance. The research steps included (i) the preparation of DES-impregnated porous carbon synthesized from the palm kernel shell (DES/C-PKS), (ii) characterization of the material, and (ii) a separation test of CO_2/CH_4 with a breakthrough system. Materials were characterized using scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX), N_2-sorption analysis, and Fourier transform infrared (FTIR) spectroscopy. SEM images showed a significant morphological difference of pristine carbon and DES/C-PKS. There was a significant decrease in the range of 67−73% of a specific surface area with respect to pristine carbon, having initially 800 m^2/g. However, the N element on the carbon surface increased after impregnation treatment, which was shown from the intensity of the FTIR graphs and EDX analysis. Adsorption isotherm revealed that DES/C-PKS could enhance up to 1.6 times the adsorption capacity of CO_2 at 1 atm and 30 °C while increasing the selectivity of CO_2/CH_4 up to 125%. The breakthrough experiment showed that all DES/C-PKS materials displayed a better performance for the separation of CO_2/CH_4, indicated by a longer breakthrough time and enhancement of CO_2 uptake. The best separation performance was achieved by DES/C-PKS using glycerol as a hydrogen bond donor with 15.4 mg/g of CO_2 uptake or equivalent to 95% enhancement of the uptake capacity compared to pristine porous carbon. Also, the cycling test revealed that DES/C-PKS can be used repetitively, which further highlights the efficiency of the material for the separation of CO_2/CH_4.
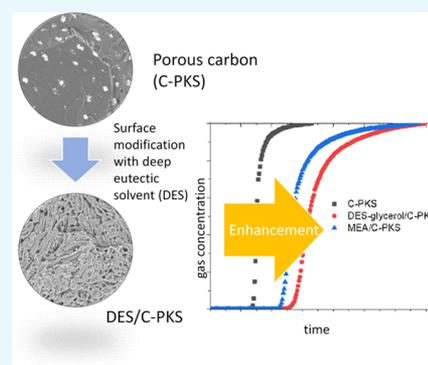
1. INTRODUCTION

Methane is an important substance utilized as raw material and fuel in chemical industries. The demand for sustainability pushes to produce methane (CH_4) from renewable resources, for instance, from agricultural waste,[1] fruit waste,[2] sludge,[3] and palm oil effluent.[4] If using a bioprocess method, the production can be divided into two main steps, i.e., (i) anaerobic digestion to produce biogas (50−75% CH_4, 25−50% CO_2, and relatively small impurities (water, H_2S, and NH_3)) and (ii) biogas upgrading to obtain biomethane (>95% CH_4). The second step is required, hence producing high purity methane, which is beneficial in increasing gas quality. Typically, small impurities are captured at first and then CH_4 is separated from CO_2. Indeed, a high effort is required to separate CO_2 due to a large quantity in the biogas stream.

Technologies to separate CO_2/CH_4 include absorption, molecular sieves, membrane separation, and cryogenic separation. Among them, molecular sieves are of high interest, which work based on the differences in the molecular size,

diffusion, and affinity of CH_4 and CO_2.[5] The key for molecular sieve separation is the nanoporous solid with special pore structures and/or chemical properties to selectively inhibit the movement of carbon dioxide and/or to adsorb carbon dioxide in the material surface. Nanoporous solids for this purpose include carbon materials, zeolites, metal−organic frameworks, etc. Porous carbon has been employed as a molecular sieve (called a carbon molecular sieve (CMS)), and it can be produced from various precursors like coal,[6,7] carbide,[8,9] biomass,[10−12] and synthetic polymers.[9,13] Indeed, the utilization of biomass has advantages in terms of availability, renewability, and cost.

Table 1. Quaternary Ammonium Salt, e.g., Choline Chloride and Hydrogen Bond Donors of Three Types of Alcohols as Components of DES

Quaternary ammonium	hydrogen bond donor		
choline chloride (ChCl)	1-butanol	ethylene glycol (EG)	glycerol
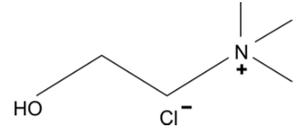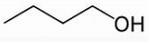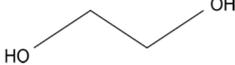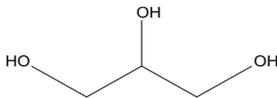
Porous carbon synthesized from the palm kernel shell (PKS) was explored as the CMS material for CO_2/CH_4 separation. Our previous study concluded that the separation ratio of ca. 2 was obtained, and the material had a good cyclability.[5] However, the capacity of adsorption of CO_2 in this CMS is quite low, and hence an enhancement is required. To improve the uptake capacity of CO_2, the modification of porous carbon using amines like monoethanolamine (MEA) and 2-amino-2-methyl-1-propanol (AMP) can be performed. Amine-modified porous carbon showed high CO_2 uptake and could enhance the separation time between CO_2 and CH_4.[14] It seems that a strong primary amine can enhance more CO_2 adsorption. However, in the reusability experiment, the amine-modified material exhibited a strong decrease in the separation performance. Strong chemisorption likely causes a strong binding of CO_2 and amine, and hence it is difficult to be removed during a regeneration step. Therefore, finding a chemical substance that can enhance the sorption capacity of CO_2 but has a low interaction is necessary.

Deep eutectic solvents (DESs) are green designer solvents that have recently drawn attention and tested for numerous applications in chemical synthesis. DESs are easy to synthesize, relatively low cost, nonvolatile, and nontoxic, hence providing an alternative for highly expensive ionic liquids. One of the DES types is composed of a quaternary ammonium salt, e.g., choline chloride (ChCl), and hydrogen bond donors, e.g., amide, carboxylic acid, and alcohol.[15] Due to the N content in the DES, it is expected that the DES can help to increase the affinity of CO_2 adsorption, and hence could provide a positive effect on the purification process of CH_4. However, to the best of our knowledge, the use of the DES impregnated on porous carbon for separation purposes is still limited, including the data of isotherm and a breakthrough study.

In this work, DES-impregnated porous carbon was synthesized as a molecular sieve for the separation of CO_2/CH_4. Porous carbon was synthesized from an abundant biomass source of the palm kernel shell. Choline chloride (ChCl) was used as a hydrogen acceptor and three alcohols of 1-butanol (-ol), ethylene glycol (-diol), and glycerol (-triol) were employed as hydrogen bond donors. Three different types of alcohols were used to study the effect of the amount of hydroxyl functional group on the performance of a material for CO_2/CH_4 separation, which is not reported previously. The representative schemes of ChCl and alcohols are shown in Table 1. The study includes the characterization of a material to investigate the success of impregnation, adsorption isotherm, breakthrough separation, and repeatability test of separation to investigate the potential of the material for separation purposes.

2. RESULTS AND DISCUSSION

2.1. Characteristics of Materials. *2.1.1. Surface Morphologies and Elemental Content.* To investigate the surface morphologies of pristine carbon materials and carbon after pretreatment and loading of deep eutectic solvents, SEM images were taken. Figure 1a displays the reference material of
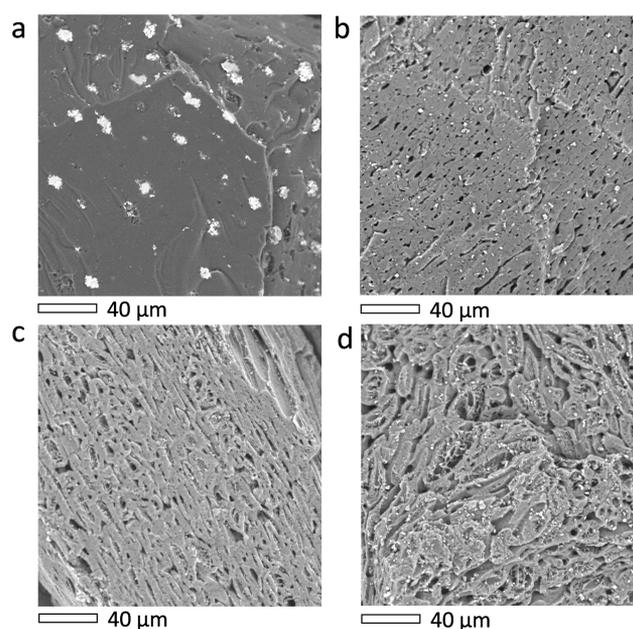
Figure 1. SEM images of C-PKS (a), DES-(1)-butanol/C-PKS (b), DES-EG/C-PKS (c), and DES-glycerol/C-PKS (d).

C-PKS, which has a smooth surface. White spots are seen, which are likely correlated to the oxide compound in carbon, as reported in the literature.[5] Figure 1b−d shows SEM images of C-PKS after pretreatment with peroxide and modification by DES-(1)-butanol, DES-ethylene glycol, and DES-glycerol, respectively. All DES/C-PKS materials exhibit a similar appearance, that is, a brighter surface and more cavities. According to the literature, the bright surface corresponds to a conductive material in the surface, which is DES,[16] and voids are developed during surface oxidation using hydrogen peroxide.[17]

Combined with SEM, energy-dispersive X-ray spectroscopy (EDX) analysis was performed to account for elemental C, O, and N in the material. These elemental contents are essential since they are present in DESs. Table 2 exhibits the elemental composition of all DES/C-PKS and C-PKS reference materials. C-PKS features the composition of a high content of C (ca. 92%). The oxygen content of ca. 6% is present, which is likely

Table 2. Elemental Composition of Material Analyzed by EDX

material	element (wt %)		
	C	O	N
C-PKS	93.37	6.32	0.31
DES-(1)-butanol/C-PKS	82.22	10.08	7.71
DES-EG/C-PKS	82.99	11.37	5.64
DES-glycerol/C-PKS	80.48	13.27	6.25

caused by the lignocellulosic precursor. While the N content in C-PKS is very small, DES/C-PKS materials possess a high N content in the range of 5.6−7.2%. Theoretically, the N content in all DES/C-PKS is equal since the content of DES is similar. The variation is likely due to equipment accuracy. In the DES/PKS material, C contents decrease while O contents increased when a higher number of hydroxyl groups are used.

2.1.2. Pore Structures. The pore structures are important factors for carbon as a molecular sieve, and hence the pore textural properties of all DES/C-PKS and the reference material were evaluated. This was conducted by performing N_2-sorption analysis. Figure 2a shows N_2 isotherm of the materials. From the isotherm, it can be seen that the C-PKS reference material has a type I isotherm according to the IUPAC classification.[18] While C-PKS shows a high nitrogen absorbed volume (ca. 200 cm^3/g STP at 0.1 P/Po), DES/C-PKS materials display a high decrease of the adsorbed volume of nitrogen by ca. 80%. The reduction is likely due to the occupation of the pore by impregnated materials.[19] Interestingly, adsorption/desorption isotherms for DES/C-PKS were unclosed, which was most likely due to the strong interaction of an adsorbate and an adsorbent and the existence of ink bottle shape pores after the impregnation process.[20] Pore size distribution was evaluated by the QSDFT model using only adsorption data, and the results are shown in Figure 2b. C-PKS reference material features ca. 85 vol % in a micropore region (<2 nm) with small tails of volume in a 4−5 nm region. For the DES/C-PKS material, a decrease in the pore volume in the micropore region is seen and there is a shift of small tails to the 2−3 nm region. It seems that the small pore is occupied by DES materials, resulting in a block of some portion of accessible pores.

Pore textural parameters of the specific surface area (S), total pore volume (V), micropore specific surface area (S_{mic}), micropore pore volume (V_{mic}), and mean pore diameter (d_m) were calculated from the N_2-isotherm data and are tabulated in Table 3. The C-PKS reference material possesses a high

Table 3. Pore Textural Parameters Evaluated from N_2-Sorption Isotherm[a]

material	S (m^2/g)	S_{mic} (m^2/g)	V (cm^3/g)	V_{mic} (cm^3/g)	d_m (nm)
C-PKS	800	762	0.34	0.29	1.67
DES-(1)-butanol/C-PKS	244	210	0.13	0.09	2.36
DES-EG/C-PKS	218	169	0.10	0.07	2.29
DES-glycerol/C-PKS	260	224	0.13	0.09	2.33

[a]S = specific surface area; S_{mic} = specific surface area of micropore; V = total pore volume at 0.99; V_{mic} = pore volume of micropore; and d_m = mean pore diameter assumed a cylindrical pore.

specific surface area of 800 m^2/g, while the DES/C-PKS material displays a lower specific surface area in the range of 210−260 m^2/g. As discussed previously, a high decrease is caused by the loading of DES materials. C-PKS materials feature a dominantly microporous content both for the surface area and pore volume. The mean diameter of this material is 1.67 nm. For DES/C-PKS materials, after loading DESs, the content of the micropore is reduced up to 75% and the mean pore diameter is larger than ca. 2.3 nm.

2.1.3. FTIR Spectra. FTIR spectra were recorded to investigate the success of DES loading on the carbon surface. Figure 3 shows the FTIR curves of DES/C-PKS materials and the reference of C-PKS. C-PKS shows a peak of −OH stretching (3500−3250 cm^{-1}) and C−O stretching (1085−1050 cm^{-1}). For DES materials, all display peaks of −OH (3500−3250 cm^{-1}), peaks of N−H bending (1650−1580 cm^{-1}), and C−O stretching (1085−1050 cm^{-1}).[21] Compared to the material before modification of DES, it is notable that there is an increase of intensity in the −OH stretching and addition of N−H bending. To strengthen the analysis, thermogravimetric analysis (TGA) of C-PKS and DES-glycerol/C-PKS was performed in a nitrogen atmosphere from room temperature to 700 °C, indicating the degradation curves of the DES component in the DES-glycerol/C-PKS
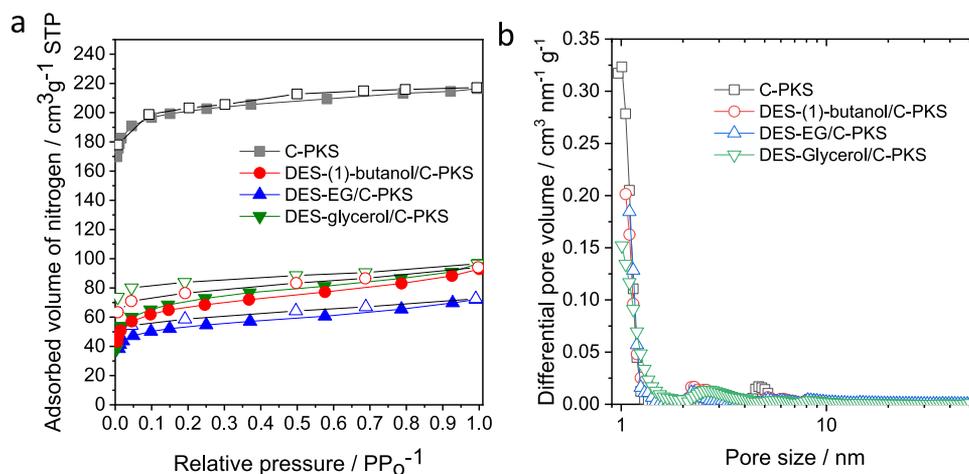
Figure 2. N_2 adsorption (closed symbols)−desorption (open symbols) isotherm data (a) and pore size distribution (b) of DES/C-PKS and the reference of C-PKS.
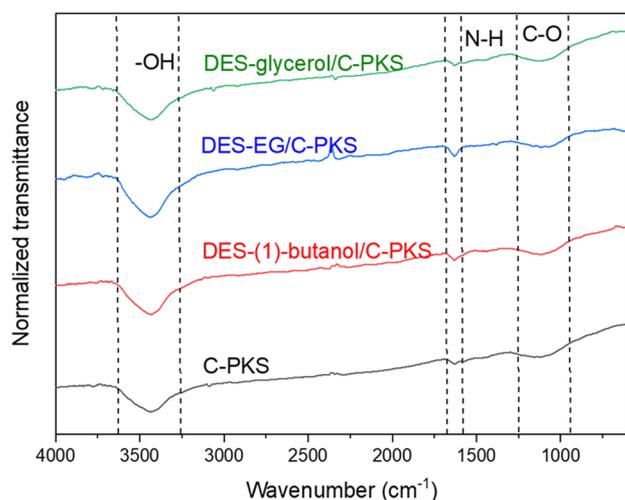
Figure 3. FTIR spectra of DES/C-PKS and the reference of C-PKS.

material (Figure S1 in the Supporting Information). Therefore, combined with EDX analysis, nitrogen sorption, FTIR data, and TGA, it can be concluded that the loading of DES materials in C-PKS is successful.

2.2. Adsorption Isotherms. Figure 4a shows isotherm curves of CO_2 and CH_4 gas adsorption, measured at a temperature of 30°C and a pressure of up to 1 atm. Based on the data, the amount of CO_2 adsorbed was much larger than the amount of CH_4 adsorbed, which is in accordance with literature studies.[5,22] In addition, the curve shows that the modification of the carbon surface with DES can increase the CO_2 adsorption uptake. At 1 atm, pristine carbon (C-PKS) has a CO_2 adsorption capacity of ca. 1.70 mmol/g, while DES-glycerol/C-PKS, DES-EG/C-PKS, and DES-(1)-butanol/C-PKS had adsorption capacities of ca. 2.75, 2.60, and 2.40 mmol/g, respectively. DES-impregnated carbon will provide an active site on the activated carbon surface so that the interaction between the carbon surface and CO_2 molecules increases.[23] This phenomenon will cause CO_2 to be more easily adsorbed, resulting in an increase in the adsorption uptake. The obtained adsorption capacity of CO_2 at 1 atm and

room temperature is in the range of 2.0−4.5 mmol/g, which is in accordance with the recent studies of nitrogen-doped porous carbon.[24−27] However, DES impregnation on carbon caused a decrease in the CH_4 adsorption capacity, which is good for the separation purpose of CO_2/CH_4. Furthermore, it is noticed that the adsorption uptake of CH_4 on the modified carbon is smaller than that of pristine carbon. The order of CH_4 adsorption capacity at 1 atm was C-PKS (ca. 1.1 mmol/g) > DES-(1)-butanol/C-PKS (ca. 0.85 mmol/g) > DES-EG/C-PKS (ca. 0.82 mmol/g), and > DES-glycerol/C-PKS (ca. 0.63 mmol/g).

Figure 4b displays the ratio of the adsorbed amount of CO_2/CH_4 in the range of 0−1 atm, defined as the selectivity of CO_2/CH_4. The selectivity value decreases by increasing pressure and has the tendency to be a plateau, which is in agreement with literature studies.[28,29] DES/C-PKS materials exhibit a batter selectivity with respect to the C-PKS reference material. It can be seen that DES-glycerol/C-PKS is superior with the selectivity in the range of 4.5−5.5, and it is comparable to the previously reported literature.[22] Adsorption isotherm and selectivity can be an indication that DES prepared by more hydroxyl groups of alcohol has a stronger interaction with carbon dioxide. It can be correlated to the strength of hydrogen donors, which is in the order of glycerol, ethylene glycol, and 1-butanol.[30] A stronger hydrogen donor can make nitrogen in deep eutectic solvent more positive, and it is better for the adsorption of CO_2.[23,31] Indeed, this phenomenon needs a further detailed study.

2.3. Performance of Materials. The efficacy of DES/C-PKS materials for methane purification was tested using a breakthrough experiment. A mixed gas of CH_4/CO_2 of 55:45% was flowed in a packed bed containing the carbon material, and the gas composition in the outlet was recorded over time. Figure 5 displays the results of the breakthrough experiment showing the outlet concentration of gas species at a certain time (C_t)/initial concentration in the inlet (C_0) vs time. From Figure 5a, we can see that initially, no gas of CH_4 and CO_2 is present until 60 s, CH_4 then appears with a purity of >98% until 130 s, and finally, CO_2 emerges until the final concentration in the outlet is equal to the inlet. For all
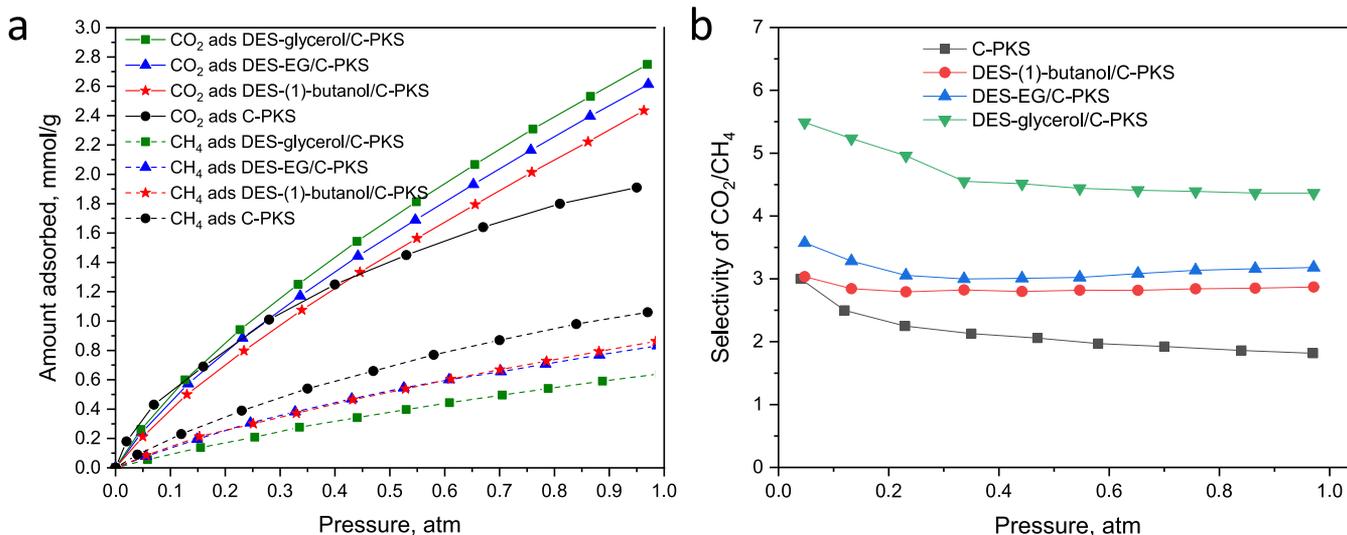
Figure 4. Adsorption isotherm of CO_2 and CH_4 using DES/C-PKS and the reference of C-PKS (a) and selectivity of CO_2/CH_4 based on the ratio of adsorption uptake (b).
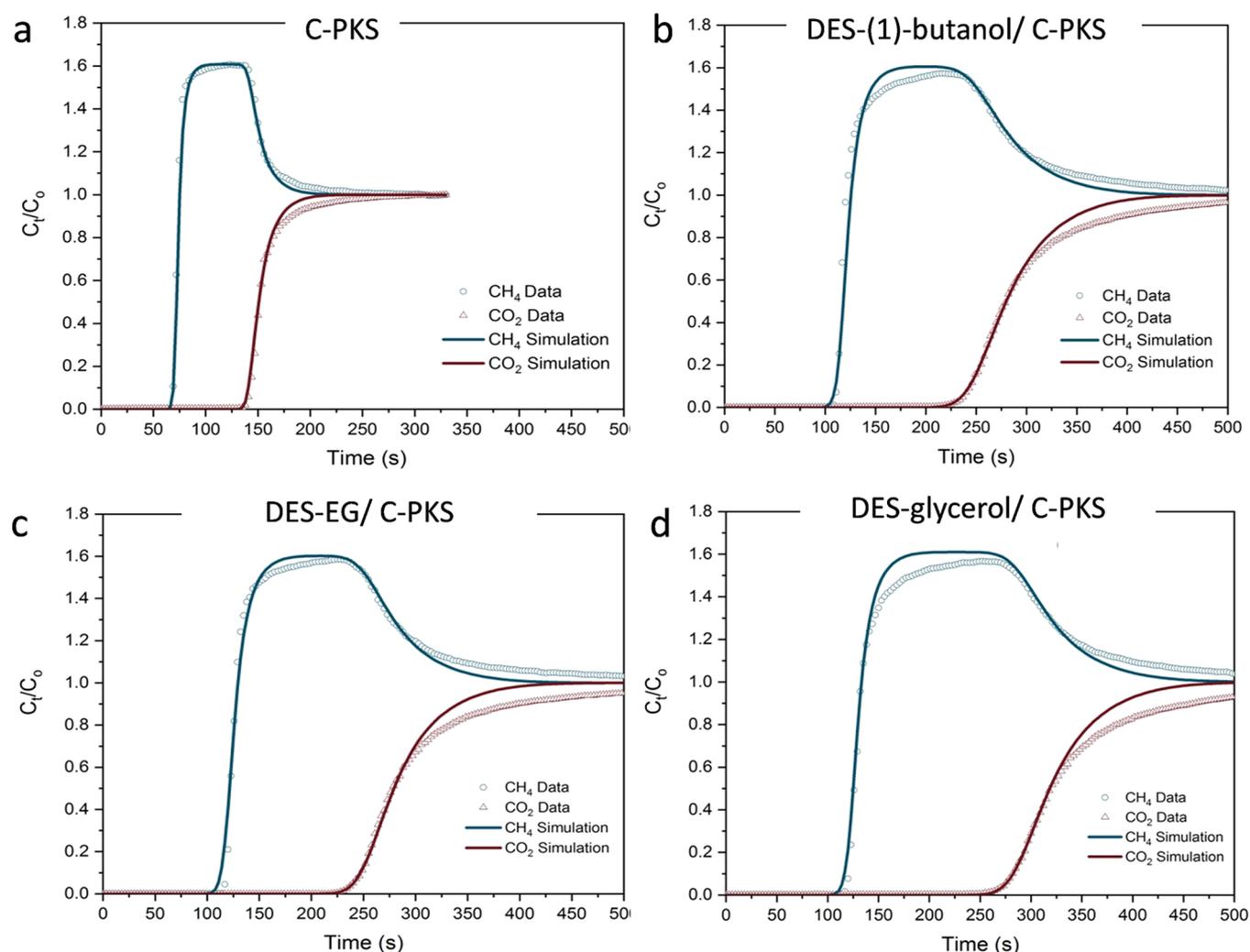
Figure 5. Breakthrough curves of a flowing mixed gas of CO_2/CH_4 of 55:45% through a packed bed of carbon material for (a) C-PKS, (b) DES-(1)-butanol/C-PKS, (c) DES-EG/C-PKS, and (d) DES-glycerol/C-PKS. Conditions: 30 °C temperature, atmospheric pressure, bed diameter of 1 cm, length of 20 cm, and 14 g of material.

Table 4. Capacity of CO_2 Uptake during Breakthrough Experiment[a]

material	uptake capacity of CO_2 (mg/g adsorbent)	uptake enhancement (%)	refs
C-PKS	7.9		this work
DES-butanol/C-PKS	13.3	68	this work
DES-EG/C-PKS	13.5	71	this work
DES-glycerol/C-PKS	15.4	95	this work
sea mango-based AC with CO_2 activation	8.4		23
DES-glycerol/sea mango-based AC with CO_2 activation	9.9	18	23
AC-based palm kernel shell	18		14
MEA/palm kernel shell-based AC	49	172	14
AMP/palm kernel shell-based AC	34	89	14

[a]AC: activated carbon.

DES/C-PKS materials (see Figure 5b−d), a similar curve is obtained but with a delay of the CH_4 outlet time with respect to C-PKS (ca. 105 s). A delayed flow of CH_4 in the outlet could represent a slower diffusion of gas through the bed,[32] which is caused by the interaction between the DES in the carbon surface and gas species. Furthermore, a larger curve between CH_4 and CO_2 signals indicates a better separation performance of CH_4 and CO_2. The uptake capacity of CO_2 was then evaluated by integrating the area between the two

curves, and the results are summarized in Table 4. For a reference material of C-PKS, the uptake capacity of 7.9 mg/g adsorbent is seen and the DES/C-PKS has a significantly higher value of the uptake capacity in the range of 13−16 mg/g adsorbent. The results showed that DES-glycerol/C-PKS is superior with a 15.4 mg/g adsorbent uptake capacity or equivalent to 95% enhancement with respect to C-PKS. Comparing with other literature studies (Table 4), the breakthrough uptake capacity of CO_2 of DES-glycerol is
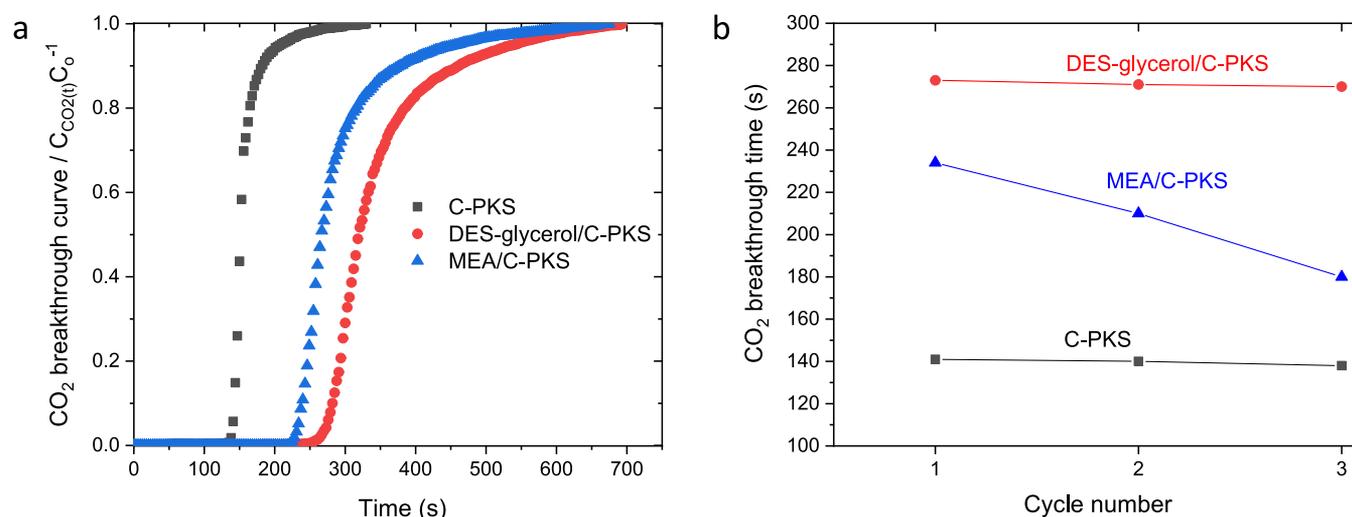
Figure 6. (a) Carbon dioxide-breakthrough curves of a flowing mixed gas of CO_2/CH_4 of 55:45% through a packed bed of carbon material. (b) Repeatability of CO_2/CH_4 separation using different types of CMS. Conditions: 30 °C temperature, atmospheric pressure, bed diameter of 1 cm, length of 20 cm, and 14 g of material.

attractive and can compete with other nitrogen group-impregnated porous material.

2.4. Performance Comparison of Different CMS. DES-glycerol/C-PKS, which shows high CO_2/CH_4 separation performance, was tested in more detail and compared with surface-modified C-PKS with MEA (MEA/C-PKS) and reference of pristine C-PKS. MEA/C-PKS was selected as representative of amine-loaded carbon since MEA could show a high affinity of CO_2 and a good quality for separation CO_2/CH_4.[14,33] Figure 6a depicts a breakthrough of CO_2 for the three materials. For C-PKS, an ideal breakthrough curve is seen, indicating that there is an instantaneous mass transfer.[34] As amine and DES loaded in C-PKS, it increases the affinity of CO_2 to the carbon surface, and hence the breakthrough curve is distorted. The breakthrough time for CO_2 was defined as the time when the concentration of CO_2 is 5%, as the requirement for biomethane is a minimum of 95%. The order of breakthrough time is C-PKS (140 s) < MEA/C-PKS (235 s) < DES-glycerol/C-PKS (270 s).

A repeatability study was performed by cycling the sequence of separation of CO_2/CH_4 and regeneration of the bed after full of CO_2. The CO_2 breakthrough time was then recorded, as shown in Figure 6b. Among the three materials, DES-glycerol/C-PKS exhibits the longest CO_2-breakthrough time, suggesting a better separation for CO_2/CH_4. Interestingly, for three sequences, DES-glycerol/C-PKS can maintain the breakthrough time. The performance is like the C-PKS reference material but a better uptake capacity. In contrast, MEA/C-PKS displays a significant decrease for the second and the third cycle, indicating that MEA/C-PKS is losing performance, which was also observed in the reference material.[35] The cycling test shows that separation using DES-glycerol/C-PKS is repetitive. Therefore, it can be concluded that DES-glycerol/C-PKS can be effectively employed as a molecular sieve for the separation of CO_2/CH_4.

3. CONCLUSIONS

The potential of deep eutectic solvents impregnated in porous carbon for the separation of CO_2/CH_4 was evaluated. Three types of alcohol of 1-butanol (-ol), ethylene glycol (-diol), and glycerol (-triol) were employed and combined with choline

chloride to produce DES as a modifier of the carbon surface. Characterization of SEM-EDX, FTIR, and N_2-sorption analysis proved the success of the impregnation of DES on porous carbon. The adsorption isotherm and separation test of CO_2/CH_4 showed that all DES/porous carbons displayed a better performance with respect to pristine carbon, but DES with a component of triol of glycerol showed superiority. The DES/porous carbon material could provide an enhancement up to 95% of the CO_2 uptake capacity and can be used repetitively without losing separation performance.

4. EXPERIMENTAL SECTION

4.1. Materials. The main materials include porous carbon synthesized from the palm kernel shell, labeled as C-PKS (PT Home System Indonesia), hydrogen peroxide (50% purity, PT Indonesia Inti Pratama), ethylene glycol (99.5% purity, Sigma Aldrich), glycerol (99% purity, Sigma Aldrich), 1-butanol (99.8% purity, Sigma Aldrich), and choline chloride (98% purity, Sigma Aldrich). A mixed gas of 55% CH_4/45% CO_2 (PT Samator Gas, Indonesia) was employed as a biogas representative.

C-PKS with a size of 20−25 mesh was pretreated using 10% H_2O_2 to increase the surface wettability of porous carbon.[17] DES solutions of 5 wt % were prepared by mixing choline chloride and 1-butanol/ethylene glycol/glycerol in a mol ratio of 0.5:0.5 in an aquadest solvent, according to ref 36.[36]

4.2. Preparation of DES/C-PKS. Pretreated C-PKS was degassed and heated up to 120 °C temperature to remove residual water and pore contaminants. After cooling to room temperature, C-PKS was impregnated using the DES solution with a ratio of 1:1 wt/vol using a vacuum impregnation method at a pressure of −0.5 bar; hence, obtaining 5% DES on porous carbon. The slurry obtained was dried using an oven at 105 °C for 20 h. The selection of 5% DES/C-PKS was in accordance with a preliminary study of the effect of the amount of DES in the performance for the separation of CO_2/CH_4 as provided in the Supporting Information (Figure S2).

4.3. Material Characterization. The pore textural parameters of the total specific surface area, pore volume, and pore size of the carbon material were analyzed by N_2 sorption analysis using the NOVA 2000 by Quantachrome Inc.

Functional groups of the material were characterized by Fourier transform infrared (FTIR) with the FTIR instrument of Thermo Nicolet Avatar 360. In this study, FTIR spectra were recorded at a wavelength of 500−4000 cm^{-1}. Meanwhile, the morphology of the carbon surface impregnated with DES was characterized using SEM-EDX with the Phenom Desktop ProXL at a voltage of 15 kV. Thermogravimetric analysis was conducted using Linseis STA PT1000, Germany, in the range of 30−700 °C in a nitrogen atmosphere and 5 °C/min ramp rate.

4.4. Adsorption Isotherm Measurement. Adsorption measurement of CH_4 and CO_2 on DES-impregnated porous carbon and the reference of C-PKS was conducted using a static volume method at 30 °C temperature. The scheme adsorption rig and detailed procedures are described in the literature.[37,38] Adsorbate of CH_4 and CO_2 was dosed individually step-by-step from 0 to 1 atm to sample a cell containing an adsorbent. The adsorption capacity was determined by balancing mol in the system before and after the adsorption using the initial and equilibrium pressure (monitored by 910 DualTrans (MKS, Singapore)).

4.5. Separation Test with a Breakthrough System. A schematic of equipment for the separation test of CO_2/CH_4 using a breakthrough system was presented in Figure 7.
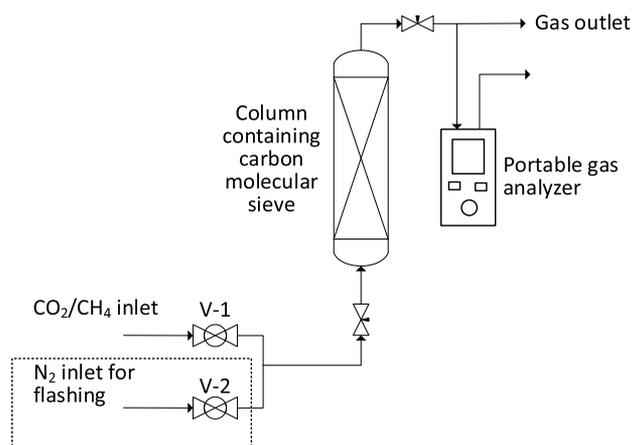
Figure 7. Scheme of breakthrough measurement set-up for the separation of CO_2/CH_4.

Fourteen grams of material were placed in the fixed bed column. Then, the bed was flushed using nitrogen gas with a flow rate of 200 mL/min until the gas content of CH_4, CO_2, and O_2 was not detected on the gas detector. After that, the CH_4 and CO_2 gas mixture was flowed into the system with a flow rate of 100 mL/min at room temperature and 1.2 bar pressure. The composition of CH_4 and CO_2 was monitored using a portable gas analyzer (Biogas Analyzer Gas board 3200plus, Hubei Cubic-Ruiyi Instrument Co., Ltd.). The separation process was continued until the gas composition is returned to initial gas inlet concentrations. For a regeneration process, the fixed bed was flushed by flowing nitrogen at a flow rate of 200 mL/min.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02545.

Results in thermogravimetric analysis (TGA) (Figure S1) and performance comparison of the breakthrough experiment using various concentrations of DES (Figure S2) (PDF)

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■ REFERENCES

(1) Paudel, S. R.; Banjara, S. P.; Choi, O. K.; Park, K. Y.; Kim, Y. M.; Lee, J. W. Pretreatment of Agricultural Biomass for Anaerobic Digestion: Current State and Challenges. *Bioresour. Technol.* **2017**, *245*, 1194−1205.

(2) Ariyanto, T.; Cahyono, R. B.; Vente, A.; Mattheij, S.; Millati, R.; Sarto; Taherzadeh, M. J.; Syamsiah, S. Utilization of Fruit Waste as Biogas Plant Feed and Its Superiority Compared to Landfill. *Int. J. Technol.* **2017**, *8*, 1385−1392.

(3) Kor-Bicakci, G.; Eskicioglu, C. Recent Developments on Thermal Municipal Sludge Pretreatment Technologies for Enhanced Anaerobic Digestion. *Renewable Sustainable Energy Rev.* **2019**, *110*, 423−443.

(4) A Aziz, M. M.; Kassim, K. A.; ElSergany, M.; Anuar, S.; Jorat, M. E.; Yaacob, H.; Ahsan, A.; Imteaz, M. A.; Arifuzzaman. Recent Advances on Palm Oil Mill Effluent (POME) Pretreatment and Anaerobic Reactor for Sustainable Biogas Production. *Renewable Sustainable Energy Rev.* **2020**, *119*, No. 109603.

(5) Prasetyo, I.; Mukti, N. I. F.; Cahyono, R. B.; Prasetya, A.; Ariyanto, T. Nanoporous Carbon Prepared from Palm Kernel Shell for CO_2/CH_4 Separation. *Waste Biomass Valorization* **2020**, *11*, 5599−5606.

(6) Alcañiz-Monge, J.; Marco-Lozar, J. P.; Lozano-Castelló, D. Monolithic Carbon Molecular Sieves from Activated Bituminous Coal Impregnated with a Slurry of Coal Tar Pitch. *Fuel Process. Technol.* **2012**, *95*, 67−72.

(7) Yang, Z.; Wang, D.; Meng, Z.; Li, Y. Adsorption Separation of CH4/N2 on Modified Coal-Based Carbon Molecular Sieve. *Sep. Purif. Technol.* **2019**, *218*, 130−137.

(8) Silvestre-Albero, A.; Rico-Frances, S.; Rodriguez-Reinoso, F.; Kern, A. M.; Klumpp, M.; Etzold, B. J. M.; Silvestre-Albero, J. High Selectivity of TiC-CDC for CO_2/N_2 Separation. *Carbon* **2013**, *59*, 221−228.

(9) Duan, L.; Ma, Q.; Chen, Z. Fabrication and CO_2 Capture Performance of Silicon Carbide Derived Carbons from Polysiloxane. *Microporous Mesoporous Mater.* **2015**, *203*, 24−31.

(10) Heidari, A.; Younesi, H.; Rashidi, A.; Ghoreyshi, A. A. Evaluation of CO_2 adsorption with Eucalyptus Wood Based Activated Carbon Modified by Ammonia Solution through Heat Treatment. *Chem. Eng. J.* **2014**, *254*, 503−513.

(11) Ahmad, M. A.; Wan Daud, W. M. A.; Aroua, M. K. Adsorption Kinetics of Various Gases in Carbon Molecular Sieves (CMS) Produced from Palm Shell. *Colloids Surf., A* **2008**, *312*, 131−135.

(12) Son, S. J.; Choi, J. S.; Choo, K. Y.; Song, S. D.; Vijayalakshmi, S.; Kim, T. H. Development of Carbon Dioxide Adsorbents Using Carbon Materials Prepared from Coconut Shell. *Korean J. Chem. Eng.* **2005**, *22*, 291−297.

(13) Prasetyo, I.; Rochmadi; Wahyono, E.; Ariyanto, T. Controlling Synthesis of Polymer-Derived Carbon Molecular Sieve and Its Performance for CO_2/CH_4 Separation. *Eng. J.* **2017**, *21* (4), 83−94.

(14) Khalil, S. H.; Aroua, M. K.; Daud, W. M. A. W. Study on the Improvement of the Capacity of Amine-Impregnated Commercial Activated Carbon Beds for CO_2 Adsorbing. *Chem. Eng. J.* **2012**, *183*, 15−20.

(15) Smith, E. L.; Abbott, A. P.; Ryder, K. S. Deep Eutectic Solvents (DESs) and Their Applications. *Chem. Rev.* **2014**, *114*, 11060−11082.

(16) Wang, M.; Li, R.; Chen, G.; Zhou, S.; Feng, X.; Chen, Y.; He, M.; Liu, D.; Song, T.; Qi, H. Highly Stretchable, Transparent, and Conductive Wood Fabricated by in Situ Photopolymerization with Polymerizable Deep Eutectic Solvents. *ACS Appl. Mater. Interfaces* **2019**, *11*, 14313−14321.

(17) Ariyanto, T.; Sarwendah, R. A. G. R. A. G.; Amimmal, Y. M. N. Y. M. N.; Laksmana, W. T. W. T.; Prasetyo, I. Modifying Nanoporous Carbon through Hydrogen Peroxide Oxidation for Removal of Metronidazole Antibiotics from Simulated Wastewater. *Processes* **2019**, *7*, No. 835.

(18) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051−1069.

(19) Zhang, G. R.; Munoz, M.; Etzold, B. J. M. Boosting Performance of Low Temperature Fuel Cell Catalysts by Subtle Ionic Liquid Modification. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3562−3570.

(20) Chen, H.; Chen, X.; Qin, Y.; Wei, J.; Liu, H. Effect of Torrefaction on the Properties of Rice Straw High Temperature Pyrolysis Char: Pore Structure, Aromaticity and Gasification Activity. *Bioresour. Technol.* **2017**, *228*, 241−249.

(21) Sigma Aldrich IR Spectrum Table & Chart, https://www.sigmaaldrich.com/technical-documents/articles/biology/ir-spectrum-table.html#ir-table-by-compound (accessed April 24, 2021).

(22) Yi, H.; Li, F.; Ning, P.; Tang, X.; Peng, J.; Li, Y.; Deng, H. Adsorption Separation of CO_2, CH_4, and N_2 on Microwave Activated Carbon. *Chem. Eng. J.* **2013**, *215−216*, 635−642.

(23) Zulkurnai, N. Z.; Md Ali, U. F.; Ibrahim, N.; Abdul Manan, N. S. Carbon Dioxide (CO_2) Adsorption by Activated Carbon Functionalized with Deep Eutectic Solvent (DES). *IOP Conf. Ser.: Mater. Sci. Eng.* **2017**, *206*, No. 012001.

(24) Li, Q.; Liu, S.; Wang, L.; Chen, F.; Shao, J.; Hu, X. Efficient Nitrogen Doped Porous Carbonaceous CO2 Adsorbents Based on Lotus Leaf. *J. Environ. Sci.* **2021**, *103*, 268−278.

(25) An, L.; Liu, S.; Wang, L.; Wu, J.; Wu, Z.; Ma, C.; Yu, Q.; Hu, X. Novel Nitrogen-Doped Porous Carbons Derived from Graphene for Effective CO_2 Capture. *Ind. Eng. Chem. Res.* **2019**, *58*, 3349−3358.

(26) Pang, R.; Lu, T.; Shao, J.; Wang, L.; Wu, X.; Qian, X.; Hu, X. Highly Efficient Nitrogen-Doped Porous Carbonaceous CO2 Adsorbents Derived from Biomass. *Energy Fuels* **2021**, *35*, 1620−1628.

(27) Liu, S.; Rao, L.; Yang, P.; Wang, X.; Wang, L.; Ma, R.; Yue, L.; Hu, X. Superior CO_2 Uptake on Nitrogen Doped Carbonaceous Adsorbents from Commercial Phenolic Resin. *J. Environ. Sci.* **2020**, *93*, 109−116.

(28) Ariyanto, T.; Prasetyo, I.; Mukti, N. F.; Cahyono, R. B.; Prasetya, A. Nanoporous Carbon Based Palm Kernel Shell and Its Characteristics of Methane and Carbon Dioxide Adsorption. *IOP Conf. Ser.: Mater. Sci. Eng.* **2020**, *736*, No. 022057.

(29) Kenarsari, S. D.; Yang, D.; Jiang, G.; Zhang, S.; Wang, J.; Russell, A. G.; Wei, Q.; Fan, M. Review of Recent Advances in Carbon Dioxide Separation and Capture. *RSC Adv.* **2013**, *3*, 22739−22773.

(30) National Center for Biotechnology Information. National Library of Medicine National Center for Biotechnology Information, https://pubchem.ncbi.nlm.nih.gov/. (accessed June 14, 2021).

(31) Zohdi, S.; Anbia, M.; Salehi, S. Improved CO2 Adsorption Capacity and CO_2/CH_4 and CO_2/N_2 Selectivity in Novel Hollow Silica Particles by Modification with Multi-Walled Carbon Nanotubes Containing Amine Groups. *Polyhedron* **2019**, *166*, 175−185.

(32) Prasetyo, I. *Kinetics Characterization of Hydrocarbons on Activated Carbon with New Constant Molar Flow and Differential Permeation Techniques*, Doctoral dissertation; University of Queensland, 2000.

(33) Masruroh, K.; Cahyono, R. B.; Prasetyo, I.; Ariyanto, T. The Effect of Amine Types on Breakthrough Separation of Methane on Biogas. *Int. J. Renewable Energy Dev.* **2021**, *10*, 249−255.

(34) Gabelman, A. Adsorption Basics: Part 1. *Chem. Eng. Prog.* **2017**, *113*, 1−6.

(35) Lee, C. S.; Ong, Y. L.; Aroua, M. K.; Daud, W. M. A. W. Impregnation of Palm Shell-Based Activated Carbon with Sterically Hindered Amines for CO_2 Adsorption. *Chem. Eng. J.* **2013**, *219*, 558−564.

(36) Masruroh, K. Seleksi Material Carbon Molecular Sieve (CMS) Berbasis Cangkang KelapaSawit Termodifikasi Untuk Separasi Gas CO_2 dan CH_4, Master Thesis, Universitas Gadjah Mada, 2021.

(37) Pambayun, G. Y. S. Modifikasi Permukaan Karbon Aktif Berbasis Cangkang KelapaSawit Dengan Impregnasi Deep Eutectic Solvent (DES) untuk Adsorpsi CO_2, Master Thesis, Universitas Gadjah Mada: Yogyakarta, 2021.

(38) Prasetyo, I.; Mukti, N. I. F.; Fahrurrozi, M.; Ariyanto, T. Removing Ethylene by Adsorption Using Cobalt Oxide-Loaded Nanoporous Carbon. *ASEAN J. Chem. Eng.* **2018**, *18*, 9−16.