Nanoporous carbon based palm kernel shell and its characteristics of methane and carbon dioxide adsorption

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Abstract. Biogas is typically composed of 55% methane, 45% carbon dioxide, and small amount of impurities. For high quality of fuel, it is necessary to increase percentage of methane by removing carbon dioxide. This can be performed by molecular sieve utilizing different diffusivity of methane and carbon dioxide passing through pores. This work presents a study of adsorption properties (isotherm and kinetics) of carbon dioxide and methane on porous carbon from palm kernel shell. The biochar of palm kernel shell was activated at high temperature of 800 °C with steam. The carbon produced was then characterized by N2-sorption analysis, and ultimate analysis. The usability of material for CO2 and CH4 adsorption was tested using a static volumetric method. The results showed that steam-activated porous carbon features a higher surface area (650 m² g⁻¹) and more mesoporous structures with respect to the carbon produced without steam activation. In the adsorption study, the results showed that the carbon exhibited a higher adsorption to CO2 (2.0 mmol g⁻¹) than CH4 (1.1 mmol g⁻¹) at 1 atm and 30 °C. In the adsorption kinetics test, results displayed that the adsorption of CO2 on carbon is slower than methane, which is good for separation purposes.

1. Introduction

Depletion of fossil fuel requires a creativity of human to provide alternative fuels by utilizing renewable resources. In this sense, production of biogas from manure and organic waste is promising as the substitute [1–3]. Biogas composition depends on the organic feed, but it is typically composed of 55% methane, 45% carbon dioxide, and small amount of impurities [3]. A high content of CO2 limits the use of biogas. For high quality of fuel, however, biogas needs to be upgraded, hence obtaining a higher methane content by removing carbon dioxide and other impurities from gas body. A possible approach to separate CO2/CH4 is using carbon material-based molecular sieve. This can be performed by molecular sieve due to different diffusivity of methane and carbon dioxide in pores and also the different affinity of gases in pore surface [4].

Porous carbon is a versatile material used widely in gas phase separation [5–7]. The carbon can be produced by pyrolysis of natural and synthetic polymer. But the use of natural resources is beneficial from the availability and cost point of view. One possible precursor which need to be explored is palm kernel shell (PKS). PKS is abundantly available as by-product of palm oil industry. Currently, the use
of PKS is still limited for biochar production and it is used directly as fuel [8]. It is necessary to upgrade quality of biochar, for example for porous carbon synthesis. Efforts to produce porous carbon from PKS were performed for example by carbonization process with carbon dioxide [9] or steam activation [10]. But no detailed study yet is available to investigate adsorption characters of isotherm and adsorption kinetic data of CO$_2$ and CH$_4$, which are essential for separation purposes.

This paper presents a study of utilization of biochar of palm kernel shell (PKS) for porous carbon production and its adsorption properties of carbon dioxide and methane. The palm kernel shell was carbonized at high temperature of 800 °C with steam or without steam activation. The carbon produced was then characterized and adsorption parameters of isotherm and kinetics were determined. We demonstrate that activation using steam is remarkably effective to induce nanopores (enhancement of specific surface area up 5.4 times with respect to without steam activation). Also, the nanoporous carbon obtained could adsorb more CO$_2$ than CH$_4$ and showed separation ratio of CO$_2$/CH$_4$ of 10 based on apparent diffusivity.

2. Materials and methods

2.1. Materials
Biochar of palm kernel shell were obtained from PT Jambi Nusantara Energi, Indonesia. Nitrogen (99% purity) was used as inert during carbonization process. Carbon dioxide (99% purity) and methane (99.9% purity) were employed as adsorbents. All gases were purchased from PT Samator Indonesia.

2.2. Carbonization of palm kernel shell-derived biochar
The carbonization of biochar of palm kernel shell was carried out based procedures as described elsewhere [7]. In short, biochar was placed in the furnace (OTF-1200X by MTI, USA). After the system was vacuumed, nitrogen was flowed. The furnace was then heated to 800 °C with ramp rate of 2 °C/minutes and hold at this temperature for 2 h. Steam was injected to the system when the temperature reached to 600 °C. The carbons produced are labeled as PKS Activated Carbon and PKS Carbon, for carbon produced with and without steam activation, respectively.

2.3. Porous carbon characterization
The properties of porous carbon were determined using N$_2$-sorption analysis (Quantrachrome NOVA 2000, USA) and ultimate analysis (Metler Toledo, USA).

2.4. Adsorption test of methane and carbon dioxide
Adsorption isotherm and kinetics of CH$_4$ and CO$_2$ on carbon were measured by using static volume method, as described elsewhere [11]. The isotherms were recorded in the pressure between 0-1 bar. It was performed by dosing adsorbate gradually to porous carbon. The initial and equilibrium pressure were recorded by 910 DualTrans (MKS, Singapore) and were employed to calculate the amount of gases adsorbed in the porous carbon, using mass balance. The temperature was set to 30 °C. For kinetics test, the data of pressure vs. time was obtained from experiment in a batch adsorber. It was simply by dosing an amount of gas into a pre-vacuumed adsorption cell and the pressure of the system was recorded over time. The mathematical model (Equation (1)) was employed to evaluate apparent diffusivity of gas in the spherical adsorbent [4,11].

$$\frac{\partial C}{\partial t} = D_{app} \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial C}{\partial r} \right]$$

(1)

where $D_{app}$ is the apparent diffusivity, $C$ is the gas concentration in the solid phase, $t$ is the time, $r$ is the radius.
3. Results and discussion

3.1. Porous carbon characteristics

Figure 1A and 1B exhibit the results of pore analysis using nitrogen sorption measurements. Figure 1A displays isotherms while Figure 1B shows the quenched solid density functional theory (QSDFT) pore size distribution, for PKS Carbon with steam and without steam activation. PKS Carbon (without activation) possesses lower adsorption of nitrogen indicating low specific surface area (SSA) [12]. The SSA of PKS Carbon and PKS Activated Carbon are 120 and 650 m$^2$/g (shown in inset of Figure 1A and also provided in Table 1). It means that activation with steam effectively creates pores. Regarding the shape of isotherm, PKS Activated Carbon features a combination of Type I and Type IV isotherm according to IUPAC classification [12]. It suggests a presence of micropores and mesopores, which is confirmed by evaluation using $t$-plot method (percent of mesopores by SSA: 25% and mesopores by volume: 56%) and also evaluation of QSDFT pore size distribution (Figure 1B). Average pore diameter of PKS Activated Carbon is ca. 2.1 nm which is smaller than that of carbon without steam activation.

![Graph A](image1.png)

**Figure 1.** a) Nitrogen sorption isotherm. b) Pore size distribution evaluated by QSDFT method using equilibrium mode

| Pore parameters calculated from N$_2$-sorption isotherm |
|--------------------------------------------------------|
| Porous textural parameter                              | PKS Activated Carbon | PKS Carbon (non-activated) |
| Specific surface area $^{a)}$ [m$^2$/g$^{-1}$]          | 120                  | 650                       |
| Percentage of micropore area $^{b)}$ [%]               | 81                   | 75                        |
| Total pore volume $^{(c)}$ [cm$^3$/g$^{-1}$]            | 0.08                 | 0.47                      |
| Percentage of micropore volume $^{(b)}$ [%]            | 57                   | 44                        |
| Average pore diameter $^{(d)}$ [nm]                    | 2.9                  | 2.1                       |

$^{a)}$ Multipoint BET method
$^{b)}$ Determined by $t$-plot method
$^{c)}$ Pore volume at 0.995 $P/P_0$
$^{d)}$ Calculated with $d_v = \frac{4V_T}{area}$

Table 1. Pore parameters calculated from N$_2$-sorption isotherm

For the results of ultimate analysis, PKS Activated and PKS Carbon has ca. 91% C, while the rest is elemental O (6-8%) and H. High content of oxygen is likely correlated with the initially high content oxygen in this lignocellulose material.

3.2. Methane and carbon dioxide adsorption isotherms

PKS Activated Carbon was then tested for CO$_2$ and CH$_4$ adsorption at fixed temperature of 30 °C. Figure 2A compares the isotherms showing that adsorption of CO$_2$ on carbon is higher than CH$_4$. It is in
agreement with literature [13]. It is noted that at pressure of 1.1 bar, uptake capacities of \( \text{CO}_2 \) and \( \text{CH}_4 \) are ca. 2.0 and 1.1 mmol g\(^{-1}\) respectively.

Isotherm data were evaluated the equilibrium parameters using Toth model according to Equation (2).

\[
C_{\mu} = C_{\mu s} \frac{bP}{1 + (bP)^{1/t}}
\]  

(2)

The evaluated Toth parameters for \( \text{CO}_2 \) and \( \text{CH}_4 \) adsorption in PKS Activated Carbon are presented in Table 2. Maximum uptake capacity \( (C_{\mu s}) \) of \( \text{CO}_2 \) (ca. 5.7 mmol g\(^{-1}\)) is higher than \( \text{CH}_4 \) (4.3 mmol g\(^{-1}\)). Moreover, from the \( b \) value (adsorption affinity), it is clear that \( \text{CO}_2 \) is more favorable to be adsorbed in the porous carbon.

Selectivity of \( \text{CO}_2/\text{CH}_4 \) can be evaluated by dividing uptake capacity of \( \text{CO}_2 \) and \( \text{CH}_4 \) along the pressure (see Figure 2B). Selectivity in the range 1.7-2.5 results. Also, the selectivity decreases when the pressure increases, which it likely has a tendency to be a plateau [14].

![Figure 2](https://example.com/figure2.png)

**Figure 2.** A) Adsorption performance of carbon synthesized from palm kernel shell for methane and carbon dioxide adsorption at 30 °C temperature (data fitted with Toth equilibrium model). B) Selectivity of separation of \( \text{CO}_2 \) and \( \text{CH}_4 \) using PKS Activated Carbon

| Adsorbate | \( C_{\mu s} \) (mmol/g) | \( b \) (kPa\(^{-1}\)) | \( t \) |
|-----------|-----------------|----------------|--------|
| \( \text{CO}_2 \) | 5.718           | 0.017          | 0.519  |
| \( \text{CH}_4 \) | 4.256           | 0.006          | 0.653  |

3.3. Methane and carbon dioxide adsorption kinetics

The dynamic adsorption was studied by recording the pressure over time. The data are displayed in Figure 3. Both curves of \( \text{CO}_2 \) and \( \text{CH}_4 \) shows that initially the uptake is very fast, followed by slower adsorption rate. With the same initial pressure, the final equilibrium pressure in fluid phase for \( \text{CO}_2 \) is lower indicating that more \( \text{CO}_2 \) is adsorbed in the carbon.

Apparent diffusivity was then evaluated using Equation (1) and results are tabulated in Table 3. The apparent diffusivity of \( \text{CO}_2 \) and \( \text{CH}_4 \) are \( 1x10^{-11} \) and \( 1x10^{-10} \), respectively. It means that the movement of \( \text{CO}_2 \) is slower. A large different of apparent diffusivity results which is good for separation purposes [7,15].
Figure 3. Dynamic change of pressure over the adsorption time for CO$_2$ and CH$_4$ in PKS Activated Carbon

Table 3. Apparent diffusivity of CO$_2$ and CH$_4$ in PKS activated carbon

| Adsorbate | $D_{app}$ (m$^2$/s) |
|-----------|---------------------|
| CO$_2$    | $1 \times 10^{-11}$ |
| CH$_4$    | $1 \times 10^{-10}$ |

4. Conclusions
An approach to increase utilization of palm kernel shell was studied by converting it to porous carbon. The results showed that steam activation is effective, resulting porous carbon with a high specific surface area of 650 m$^2$ g$^{-1}$. When testing for adsorption study of CO$_2$ and CH$_4$, PKS Activated Carbon (porous carbon produced by steam activation of palm kernel shell) exhibited a higher uptake capacity to CO$_2$ (2.0 mmol g$^{-1}$) than CH$_4$ (1.1 mmol g$^{-1}$) at 1 atm and 30 °C. Furthermore, when evaluating the apparent diffusivity, it is noted that the carbon is suitable for separation purposes with $D_{app}CO_2/D_{app}CH_4$ of 10.

Acknowledgements
This study was supported by Indonesian Fund Management Agency for Oil Palm Estate (BPDP-KS, Grant No. PRJ-65/DPKS/2018).

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