Coal Bottom Ash as a Potential Adsorbent for CO₂ Capture

N H A Rani¹, N F Mohamad¹, M Onn², M J Jalil³ and N Muda⁴

¹Faculty of Chemical Engineering, Universiti Teknologi MARA, Pasir Gudang Campus, Jalan Purnama, Bandar Seri Alam, 81750 Masai, Johor, Malaysia
²Faculty of Applied Science, Universiti Teknologi MARA, Pasir Gudang Campus, Jalan Purnama, Bandar Seri Alam, 81750 Masai, Johor, Malaysia
³Faculty of Chemical Engineering, Universiti Teknologi MARA, Penang Campus, 13500 Pematang Pauh, Pulau Pinang, Malaysia
⁴Low Carbon Power Generation Research Group, TNB Research Sdn Bhd, No.1 Lorong Ayer Itam, Kawasan Institusi Penyelidikan,43000, Kajang, Selangor, Malaysia

*Corresponding author: hidayurani@uitm.edu.my

Abstract. Coal bottom ash (CBA) is the solid residue produced from coal-fired power plant. It is classified as hazardous material, which can cause adverse effect to the environment and public health. In view of the situation, exploring and discovering possible utilization of these coal residues into value-added products has to be performed. Hence, the aim of this paper is to investigate the potential of raw CBA as an adsorbent for carbon dioxide (CO₂) gas adsorption. The physicochemical characteristics of CBA were determined using ultimate and proximate analysis, nitrogen adsorption-desorption isotherm, scanning electron microscopy (SEM), and elemental diffraction x-ray (EDX) analysis. CO₂ adsorption study was conducted using simulated flue gas by pressure swing adsorption process in a fixed-bed reactor to evaluate the suitability of CBA as an adsorbent material. High carbon content in CBA makes it’s become a good precursor for production of carbonaceous adsorbent. Trace elements like calcium, silica and alumina, indicating that the material had a good adsorption capacity. The result indicated that CBA was able to adsorb CO₂ with the adsorption capacity of 0.000276 mol CO₂/g CBA. As a conclusion, CBA has the potential to be an adsorbent for its application in gas phase especially in CO₂ adsorption.

1. Introduction

Presently and in more years to come, the power generation in Malaysia will continue to rely heavily on gas and coal as the source of fuel. In 2016, gas usage has declined due to the to the retirement of several gas plants. The consumption of gas is also expected to further decrease in 2019 to 32% as coal usage increases and make up 64 % of the overall mix and overtake gas as dominant fuel [1]. This have resulted in the increase of carbon dioxide (CO₂) concentration in the atmosphere that causes a significant environmental problem such as global warming [2]. Therefore, the national and international regulation for power plant regarding CO₂ emission became more stringent. Carbon Capture and Storage (CCS) is considered as one of the most suitable method to reduce the GHG emission to an acceptable range in order to avoid any permanent and irreversible damage of climate change [3]. Based on the report from the International Energy Agency (IEA), approximately 19% of energy related CO₂ emissions can be mitigated by CCS method by 2050 [4]. One of the most established technologies CO₂ capture is through
sorbent adsorption. However, the commercial adsorbent is quite expensive. Therefore, the alternative ways to reduce the cost is utilizing a solid waste residue.

Coal fired-power plant not only as a major contributor to CO$_2$ emission problem but also further increased by coal ash (fly ash and bottom ash) generated in these plants as a solid waste residue which creates not only a solid waste disposal problem but also a dusting problem in the atmosphere and in the surrounding land area [5]. In 2010, 29 million of coal ash are produced where 15-20 % is coal bottom ash (CBA) and 75-80% is coal fly ash (CFA) [6]. Due to this, huge amount of coal ash is expected to form and thus, leads to storage and disposal issues as it requires large space. It is also feared that with the presence of heavy metals, coal ash will cause ground and surface water contaminations that can pose a threat to the environment [7]. Therefore, recycling and reuse of the coal ash can help mitigate the issues that may be encountered by the industry and at the same time improve the quality of the environment.

At present, the reutilization of coal bottom ash (CBA) as adsorbent materials have gained favorable interest in diverse research field due to its nature as low cost waste material and abundant availability which can easily be obtained from coal combustion processes. Moreover, the chemical composition of CBA which was reported to consist a high content of silica and alumina, contributed to an excellent adsorbent property [8]. However, CBA has a limited application and previous study found only 21% of the waste was recycled in the industries [9]. For example, a study done by Ishaq et.al., (2014) used coal ash adsorbent to remove xylenol orange from aqueous solution and revealed that the coal ash removed about 80% of xylenol orange from the aqueous solution within 40 min [10]. This is due to the availability of many active sites on the coal ash surface to react with dye molecules and give high adsorption capacity. Meanwhile, CBA that was activated at high temperature was able to adsorb acid red 114 until 91.2% at 80 min contact time [11]. However, most of the previous work on the utilization of CBA focuses on aqueous phase adsorption for instance dyes removal in textile industry wastewater and limited study was found on the usage of CBA as natural adsorbent in the gas phase.

The present study aims to explore the potential of CBA as adsorbent in a gas phase application for the adsorption of CO$_2$. The percentage of reduction of CO$_2$ in a pressure swing adsorption was determined for gas phase adsorption study. The properties of the CBA were analyzed using ultimate and proximate analysis, nitrogen adsorption-desorption isotherm based on Brunauer-Emmett-Teller (BET), scanning electron microscopy (SEM) and elemental diffraction x-ray (EDX) analysis for a better understanding of this industrial waste, prior to reuse. The results of this research are presented herein.

2. Materials and Methods

2.1. Sample Preparation
Coal bottom ash (CBA) was obtained from TNB Janamanjung Kapar (sub-bituminous coal). The CBA was dried in the oven at 110°C for 24 h to remove moisture. The dried CBA was sieved using sieve shaker machine (Thermo Fisher Scientific) to get 1-2 mm particle size.

2.2 Characterization
CBA was characterized by different techniques to determine structural properties of porous carbon. Proximate analysis was performed using thermogravimetric analyzer, TGA/DSC (Mettler Toledo, United States) according to the ASTM D7582-10 and the results are shown in terms of moisture, volatile content, fixed carbon and ash contents. Elemental analysis was carried out using CHNS-O Analyzer (FlashEA,1112 Series) to determine carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) (by difference) of the sample. The pore architecture particularly specific surface area, pore diameter, total pore volume and pore size distribution were determined by nitrogen adsorption-desorption isotherm operating at 77K using gas sorption analyzer (AUTOSORB-iQ/MP-XR). Meanwhile, the microstructure, organic and inorganic compounds and weight percentage of sample was characterized by the scanning electron microscopy (SEM) and elemental diffraction x-ray (EDX) analyses.
2.3 Adsorption Study
For these experiments, 16% CO\textsubscript{2} and 84% N\textsubscript{2} gas mixture were used and was carried out in a pressure swing adsorption column (figure 1). In each experiment, 290 g of CBA was used in the adsorption column. The gas flow rate was 2 L/min under 4 bar pressure was passed until the saturation was reached, i.e., until the point at which the outlet CO\textsubscript{2} concentration equals that of the inlet stream, in order to assess the maximum dynamic adsorption capacity of adsorbent. The effluent gas from the outlet of the column was monitored and recorded at an online portable gas analyzer (MRU Model OPTIMA 7, Germany).

3. Results and Discussion

3.1 Characterization of Coal Bottom Ash

3.1.1 Proximate and Ultimate Analysis. The ultimate and proximate analyses were summarized in table 1. For ultimate analysis, it showed that CBA consists of carbon content is 18.10%, whereas 10.5% represents its fixed carbon. The element of carbon in CBA can be increase by physical separation. However, steam activation is not suitable for enrichment in carbon because the ash content in the sample is too high (82.7%) and it will lead to more ash content since the degree of burn-off is achieved. According to Rubio et al., (2007), chemical demineralization process is capable in reducing the ash content and simultaneously increases the carbon content [12]. With high carbon content in CBA, this makes the material a good precursor for production of carbonaceous adsorbent.

| Sample | Moisture | Volatile | Fixed carbon | Ash | Bulk density (kg/m\textsuperscript{3}) | Ultimate analysis (wt%) |
|--------|----------|----------|--------------|-----|----------------------------------------|------------------------|
| CBA    | 0.3      | 6.5      | 10.50        | 82.7| 1020                                   | 18.10 1.36 0.29 80.25 |

3.1.2 BET Surface Area. The CBA was characterized by N\textsubscript{2} adsorption/desorption, BET surface and pore size distribution analysis. Table 2 shows the comparison of CBA in present study and previous researches in terms of surface area, pore volume and pore size. In this study, the surface area of CBA is 20.80 m\textsuperscript{2}/g and the pore size is 35.69Å, which falls under mesoporous group. Mesoporous particle
mainly contributes around 2-50 nm (20-500Å). Meanwhile, for pore volume, CBA consists of 0.019 cm³/g. A study conducted by Herman et al., (2016) obtained the surface area is 58.01 m²/g and pore volume is 0.040 cm³/g. This is due to the particle size, which plays an important role to enhance the CBA’s surface area. From the point of view of adsorption process, low surface area of granular CBA is unfavorable, as it indicates lower adsorbate uptake during the adsorption process [13]. Thus, to enhance the absorptivity of the CBA material, crushing, grinding and sieving steps are crucial in order to obtain smaller particle size as well as improving surface area [14]. As a conclusion, with high pore volume and high surface area, it is expected that more molecules will be penetrated and retained in the pores, which can contribute to an increase in adsorption capacity. Therefore, a large surface area is favorable for an efficient CO₂ adsorption [15,16].

| Sample          | BET surface area (m²/g) | Size particle (nm) | Pore volume (cm³/g) | Pore size (Å) | Reference               |
|-----------------|-------------------------|--------------------|---------------------|---------------|-------------------------|
| CBA (Manjung)   | 20.80                   | 1-2                | 0.019               | 35.69         | Present study           |
| CBA (Perak)     | 58.01                   | 0.25               | 0.04                | 30.10         | Herman et al., 2016 [8] |
| CBA (Korea)     | 1.41-8.47               | 1.19-4.75          | -                   | -             | Gorme et al., 2010 [9]  |

3.1.3. SEM and EDX Analysis. Figure 2 represent the SEM images at 1500 times magnification of CBA morphology and surface texture. It shows that the CBA consists of mixture of coarse and fine grains particles with no particular pattern. With this an irregular structure of the CBA’s surface, indicates the presence of cavities and pores on the exterior side of the CBA [17]. Besides, Bumanis et al, (2013) stated that the bottom ash that has rough, gritty and angular structure is owed to the metallic compounds that deposit onto the surface [18]. After adsorption process, the pores probability filled with CO₂. Meanwhile, table 3 shows the EDX analysis of CBA, which presented the wt% of different elements in the CBA sample. The major constituent of the CBA are silica, SiO₂ (18.29 wt%) followed by alumina, Al₂O₃ (8.63 wt%) and iron, Fe₂O₃ (5.81 wt%). Other constituents included calcium, CaO (9.95 wt%), magnesium, MgO (1.28 wt%), potassium, K₂O (0.93 wt%) and sodium, Na₂O (2.29 wt%). Asokbunyarat et al, (2015) reported that high alumina and silica compositions in bottom ash make the material a very good adsorbent because both of elements are the best support matrix in order to capture CO₂ [8]. When the molecule of silica and CO₂ comes closer, it can promote the initial chemical interaction between of them and the reaction will be occurred only on the channel surfaces, forming unidentate, bidentate, and bridged carbonates [19]. Meanwhile, a high content of CaO is accountable for the alkaline characteristics and this help to increase CO₂ adsorption capacity via carbonation reaction which is denoted by Equation (1) [20, 21].

\[
\text{CaO (s) + CO}_2 \text{(g)} \rightarrow \text{CaCO}_3
\]
Figure 2. SEM of the CBA sample

Table 3. Composition of element in CBA from EDX analysis

| Element | Wt% |
|---------|-----|
| Si      | 18.29 |
| Al      | 8.63 |
| Fe      | 5.81 |
| Ca      | 9.95 |
| Mg      | 1.28 |
| K       | 0.93 |
| Na      | 2.29 |

3.2. \( \text{CO}_2 \) Adsorption Study

Figure 3 exhibit the adsorption curve for raw coal bottom ash. \( \text{C/Co} \) represents the concentration of \( \text{CO}_2 \) adsorb by the adsorbent, and the \( \text{Co} \) represent the initial concentration of \( \text{CO}_2 \). It can be seen that the adsorption of \( \text{CO}_2 \) on raw bottom ash is inadequate. Initially, the \( \text{CO}_2 \) concentration in the exit gas is around 5% and within 100 seconds it reached to the inlet gas concentration 16% (Co). At 100 seconds the maximum value of \( \text{C/Co} \) is 80%. The adsorption capacity of the sample until saturation point was obtained at 0.000176 mol \( \text{CO}_2/g \) or 7.76 mg \( \text{CO}_2/g \) CBA which was much lower than the typically 0.001 mol/g for Norit activated carbon as reported by Hosseini et al., (2015) [22]. Although the adsorption capacity is low, CBA is able to adsorb \( \text{CO}_2 \) probably due to its physicochemical properties such as BET surface area. \( \text{CO}_2 \) molecules diffused into pores of CBA and were adsorbed onto the surface of pores of CBA by weak forces of intermolecular cohesion (physisorption) rather than a chemical interaction [23]. In addition, calcium oxide (CaO) found in CBA sample may also assist in the adsorption of \( \text{CO}_2 \). However, treatment of the ash samples with amines, acids or steam can significantly improve the adsorption capacity of coal ash because amine impregnation was found to help increase the selectivity of CBA towards non-polar molecules. For example, a study conducted by researchers in [24], where the fly ash was activated with steam and impregnated with amine gave adsorption capacity of 68.6 mg \( \text{CO}_2/g \) and Yahia et al., (2015) prepared activated carbon from fly ash using chemical activation achieve an adsorption capacity of 26 mg \( \text{CO}_2/g \) [24,25]. For those reasons, it is expected that by converting CBA to adsorbent i.e., activated carbon, the adsorption capacity of \( \text{CO}_2 \) will significantly increase.
4. Conclusion
Coal bottom ash is a waste product from the coal power plant and based on the characterization studies, it is evident that CBA has good potential to be used as adsorbent for CO₂ capture. With high carbon content confirms that CBA can be an effective adsorbent since its can make the material a good precursor for production of carbonaceous adsorbent. In addition, these elements such as Si, Ca and Al confirm its potential to be used as helper to enhance CO₂ adsorption capacity. Through adsorption testing, CBA is able to adsorb CO₂ with the adsorption capacity of 0.000176 mol CO₂/g CBA or 7.76 mg/g CBA. Even though the adsorption capacity is relatively low, the transformation of CBA into value-added products such as zeolites, activated carbon and mesoporous silica will increase the adsorption capacity. Therefore, the physiochemical properties of the CBA have been well-explained in order to have better understanding of these products prior to their utilization. As a conclusion, CBA has a potential to be an adsorbent for its application for CO₂ capture.

Acknowledgement
The authors gratefully acknowledge the financial support by Universiti Teknologi MARA Johor under grant Bestari 600-UitMJC (PJIA.5/2). In addition, we thank the Management of TNB Research Sdn Bhd for providing the coal bottom ash samples for this research work.

References
[1] Peninsular Malaysia Electricity Supply Industry Outlook 2013 Suruhanjaya Tenaga (Energy Commission) http://www.st.gov.my
[2] Shariff A M, Murshid G, Keong L K, Bustam M A, Ahmad F 2014 Solubility of carbon dioxide in aqueous solutions of piperazine (PZ) at elevated pressure Adv. Mat. Res. 917 144-150.
[3] Parshetti G K, Shamik C, Balasubramanian R 2015 Biomass derived low-cost microporous adsorbents for efficient CO₂ capture Fuel 148 246-254.
[4] Energy and Climate Change 2015 World Energy Outlook Special Report International Energy Agency (EIA).
[5] Rashidi N A, Yusup S 2016 Overview on the Potential of Coal-Based Bottom Ash as Low-Cost Adsorbents ACS Sustain. Chem. Eng. 4 1870-1884.
[6] Ramzi N I R, Shahidan S, Maarof M Z, Ali N 2016 Physical and Chemical Properties of Coal Bottom Ash (CBA) from Tanjung Bin Power Plant *JOP Conf. Ser. Mater. Sci. Eng.* **160** 1-10.

[7] Abubakar A U, Baharudin K S 2012 Potential use of Malaysian thermal power plants coal bottom ash in construction. *Int. J. Sustain. Constr. Eng.* **3** 25-37.

[8] Asokunyarat V, Van Hullebusch E D, Lens P N L, Annachhatre A P 2015 Coal bottom ash as sorbing material for Fe (II), Cu (II), Mn (II), and Zn (II) removal from aqueous solutions. *Water, Air, Soil Pollut.* **226** 1-17.

[9] Mohamed M, Yusup S, Bustam M A, Azmi N 2017 Effect of coal bottom ash and binder addition into CaO-based sorbent on CO₂ capture performance *Chem. Eng. Trans.* **56** 325-330.

[10] Mohammad I, Khalid S, Imitiaz A, Sirraj S 2014 Coal Ash as a Low Cost Adsorbent for the Removal of Xylenol Orange from Aqueous Solution *Iran. J. Chem. Chem. Eng.* **33** 53-58.

[11] Kuntaria, Apriliatib NH, Suherman 2017 Utilization of Coal Bottom Ash a Low-Cost Adsorbent for the Removal Acid Red 114 Dye *Eksakta: Jurnal Imu-Ilmu MIPA* **17** 11-19.

[12] Rubio B N, Izquierdo M T, Mayoral M C, Bona M T, Andres J M 2007 Unburnt carbon from coal fly ashes as a precursor of activated carbon for nitric oxide removal *J. Hazard. Mater.* **143** 561-566.

[13] Ding X Li Y, Guo L, Liao Q, Zhu X and Wang H 2019 Non-aqueous energy-efficient absorbents for CO₂ capture based on porous silica nanospheres impregnated with amine *Energy* **171** 109–119.

[14] Thaarrini J, Venkatasubramani R 2015 Feasibility studies on compressive strength of ground coal ash geopolymer mortar *Period. Polytech. Civ. Eng.* **59** 373–379.

[15] Herman A P, Yusup S, Shahbaz M, Patrick D O 2016 Bottom ash characterization and its catalytic potential in biomass gasification *Procedia Engineering* **148** 432-436.

[16] Choi W, Park J, Kim C and Choi M 2020 Structural effects of amine polymers on stability and energy efficiency of adsorbents in post-combustion CO₂ capture *Chem. Eng. J.* **408** 127289.

[17] Gorme J B, Maniquiz M C, Kim S S, Son Y G, Kim Y T, Kim L H 2010 Characterization of bottom ash as an adsorbent of lead from aqueous solutions. *Env. Eng. Res.* **15** 207-213.

[18] Bumanis G, Bajare, D, Korjakins A 2013 The economic and environmental benefits from incorporation of coal bottom ash in concrete. *4th Int. Scient. Conf. Civil Eng.* **142-152**.

[19] Yong X, Tse J S, Chen J 2018 Mechanism of Chemical Reactions between SiO₂ and CO₂ under mantle conditions *ACS Earth Space Chem.* **2(6)** 548-555.

[20] Zhang L, Zhang B, Yang Z, Guo M 2015 The role of water on the performance of calcium oxide-based sorbents for CO₂ capture: a review. *Energy Techn.* **3** 10-19.

[21] Khan Z, Yusup S, Ahmad M M, Rashidi N A 2014 Integrated catalytic adsorption (ICA) steam gasification system for enhanced hydrogen production using palm kernel shell *Int. J. Hydrog. Energy* **39** 3286-3293.

[22] Hosseini S, Marahel E, Bayesti I, Abbasi A, Abdullah L C, Choong T S Y 2015 CO₂ adsorption on modified carbon coated monolith: effect of surface modification by using alkaline solutions. *Appl. Surf. Sci.* **324** 569-575.

[23] Hidayu A R 2017 *Chapter 6-The preparation and application of activated carbon for gas adsorption* Nova Science Publisher p 165-184.

[24] Maroto-Valer M, Lu Z, Zhang Y, Tang Z 2008 Sorbents for CO₂ capture from high carbon fly ashes. *J. Waste Manag.* **28** 2320-2328.

[25] Alhamed Y A, Rather S U, El-Shazly A H, Zaman S F, Daous M A, Al-Zahrani A A 2015 Preparation of activated carbon from fly ash and its application for CO₂ capture. *Korean J. Chem. Eng.* **32** 723-730.