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Characterization of Coal Fly Ash Based Adsorbent for CO₂ Removal

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Abstract. The study of CO₂ removal from air-CO₂ mixture using coal fly ash (CFA) based adsorbent has been conducted. The sieved CFA was calcined at various temperature (200, 300 and 400 °C) for 4 hours. The calcined adsorbent pellets were characterized before utilizing in CO₂ removal. Result suggested that calcination temperature slightly affected the yield of adsorbents. Increasing calcination temperature decreased the density and bulk density; but increased the percentage of adsorbed moisture of the adsorbents. SEM micrograph revealed various shape and size of the adsorbent and matched the result of XRD pattern and EDS analysis. The characterized adsorbents then were utilized to remove CO₂ in an adsorption column. The inlet mixture contained 35%-vol of CO₂ with flow rate of mixed gas of 200 ml/min. The highest removal was accomplished by using CFA based adsorbent pellet with particle size of 140 mesh, calcination temperature 300 °C for 4 hours. The CO₂ removal efficiency was 71.43% with adsorbent capacity of 8.027 mg CO₂/g adsorbent.

1. Introduction
Coal fly ash (CFA) is a coal power plant by-product that mostly comprises of SiO₂, Al₂O₃ and Fe₂O₃. However, CFA also contains poisonous elements such as heavy metals from coal and polyaromatic hydrocarbons that condense from the flue gas [1]. With the highly demand of energy worldwide, the discharge of CFA also increases. From the total production of CFA, only 20% is used as an additive for cement and concrete-related applications [2] while the remaining is disposed in landfill and lagoon. The large quantities of CFA disposal and storage are potential sources for air, soil and water contamination [1, 2].

Many researchers have taken intensive study on the utilization of CFA to overcome industrial problems. They have developed low cost CFA adsorbent for the removal of phenolic compound, heavy toxic metals, dyes, organic pollutants and organic acids from industrial flue gases and effluents [3]. Some studies also utilized CFA in zeolite synthesis due to the high content of SiO₂ and Al₂O₃ in CFA. Zeolite is microporous crystalline aluminosilicates that have molecular shape selective properties [4]. The synthesized zeolite can be utilized as ion-exchanger, adsorbent, catalyst, detergent builder, mine-water treatment, and oil spill treatment [2].

In this paper, we studied the utilization of waste CFA from coal power plant of paper industry in Medan for CO₂ removal from air-CO₂ mixture as the preliminary study to increase the quality of biogas. Biogas is a promising renewable energy that is produced from the decomposition of organic waste. Biogas generally contains 55-70% CH₄, 30-45% CO₂ and other trace components such as H₂S

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(1000-3000 ppm), NH$_3$ (80-100 ppm) and hydrocarbon (<100 ppm). The presence of CO$_2$ in 25-50% by volume in biogas can lower the calorific value, increase the methane number and the anti-knock properties of engines, cause corrosion (low concentrated carbon acid) if the gas is wet and damages alkali fuel cells [5]. Therefore, the reduction of CO$_2$ content in biogas is crucial step.

Previous works performed absorption/scrubbing and adsorption to remove CO$_2$ for biogas purification [6-9]. Water scrubbing in [6] showed low efficiency since the process could only reduce 21.2% of CO$_2$ with the initial CO$_2$ concentration of 15%. In [7], they used Lewatit and PEI/SiO$_2$ (polyethyleneimines on a silicon oxide support) as adsorbents. The result demonstrated that PEI/SiO$_2$ adsorbent had breakthrough capacity of 1.36 mol/kg of ternary mixtures CH$_4$/CO$_2$/H$_2$O at 40°C, while Lewatit of 0.95. Further simulation using Aspen Plus exhibited that adsorption system with both adsorbents could produce clean gas containing 9.8% CO$_2$ from the initial CO$_2$ concentration of 41.5% [7]. The utilization of natural zeolite could remove as high 92.5% CO$_2$ [8]. Whereas results of [9] indicated complete removal of CO$_2$ when they apply 1 M NaOH and ethanolamine solution as absorbent. However, the utilization of bog iron ore and activated carbon in adsorption showed poor performance since they did not change the CO$_2$ concentration.

The aim of this study was to reduce the CO$_2$ concentration so that the purified gas contained maximum 10%. This target was in accordance to the requirement of natural gas grid [7]. The utilization of CFA was chosen due to it exist abundantly as industrial waste in Medan. The preparation was quite simple and need no chemical addition.

2. Experimental Procedure
2.1. Adsorbent Preparation

The CFA in this study was collected from the power plant unit in a paper industry in Medan. The raw material was sieved to 140 meshes for the adsorbent manufacture. The sieved CFA was weighed and mixed with water at certain ratio. The mixture was then molded so that it formed pellet with size of 1 cm in diameter and 2 cm in length. The pellets were dried in an oven at 120°C for 2 hours and then calcined at various temperatures (200, 300 and 400°C) for 4 hours. The calcined adsorbent was labelled as CFA1, CFA2 and CFA3 respectively referring to the variation of calcination temperature. Adsorbent preparation was conducted in triplicate. Figure 1 depicts the physical form of raw CFA and the CFA-based adsorbent after calcination.

The yield of each adsorbent was calculated by dividing the mass of the calcined adsorbent by the initial mass of the raw CFA used. The density, bulk density and percentage of adsorbed moisture of each adsorbent was also analysed. One of the adsorbents was then characterized using XRD (X-Ray Diffraction) to obtain the type of minerals, SEM-EDX (Scanning Electron Microscopy - Energy Dispersive X-Ray Analysis) to obtain the surface morphology image and elemental/oxides composition and BET (Brunauer-Emmett-Teller) to obtain the surface area.

2.2. CO$_2$ Removal

The CO$_2$ removal was conducted using a set of adsorption column as previously described in [8]. The adsorbent was placed in the adsorption column. Air and CO$_2$ were mixed into the air chamber until a constant concentration of CO$_2$ of 35% (v/v) was achieved. Then, mixed gas was fed into an inline mixer at a total flow rate of 200 ml/min. The adsorption was conducted at atmospheric pressure for 30 min. The purified gas was stored in the gas collector. The outlet CO$_2$ concentration in the purified gas mixture was analyzed using SAZQ biogas analyzer to determine CO$_2$ removal efficiency. The procedure was performed in triplicate.
3. Result and Discussion

3.1. Yield of the CFA-Based Adsorbent

Figure 2 presents the average yield of the CFA-based adsorbents. In this study, the increased calcination temperature didn’t have any substantial influence on the yield of adsorbents. The yield was in the range of 89.38 – 90.34%. Thus, the calcination decreased about 9.66 – 10.63% of the initial mass of raw CFA. The decrease of mass was due to the loss of moisture content during the calcination.

3.2. Characteristics of the CFA-Based Adsorbent

The density, bulk density and percentage of adsorbed moisture of each adsorbent is shown in Figure 3. The increase of calcination temperature decreased the density and bulk density of the adsorbent. At higher calcination temperature, higher heat was transferred to the sample thus decreased the moisture content and organic content in the sample. Hence, more pores were formed [10] and pellet mass decreased. Bulk density affects the cost of transportation and storage. Bulk density also influences the system of material handling and material behavior on the further thermochemical process or biological treatment [11]. The density of the adsorbents under this study was in the range of 1.296 – 1.381 g/cm³; whereas the bulk density was in the range of 0.985 – 1.500 g/cm³. The bulk density was close to fly ash with close packed storage or vibration with bulk density was in the range of 1120 – 1500 kg/m³ (1.120 – 1.500 g/cm³) [12]. Whilst another literature informed that it is in the rage of 0.6 – 0.9 g/cm³ [3].

Figure 1. Physical form of (a) raw CFA and (b) CFA-based adsorbent after calcination

Figure 2. The yield of CFA-based adsorbent at various calcination temperatures.
The measurement of the adsorbed moisture of the adsorbents was conducted by placing the adsorbents in a porcelain container and let it came into contact with the environment for 24 hours at ambient temperature. The adsorbed moisture was calculated based on the recorded mass increase. The ability of the adsorbents in adsorbing moisture increased with the increase of calcination temperature. More pores that were formed due to the rise of temperature lead to more surface area and volume of pore [10]. This phenomenon was in contrary to the bulk density of the adsorbents. The percentage of the adsorbed moisture was in the range of 0.850 – 0.979%.

Further analysis was carried out for adsorbent CFA3 due to its better yield and other physical properties. Analysis results of XRD, SEM-EDX and BET were presented below.

3.3. XRD Analysis
The XRD patterns of the CFA3 is presented in Figure 4. The diffraction pattern referenced with JCPDS (Joint Committee on Powder Diffraction Standard) was also included for comparison. According to the XRD patterns, the major crystalline phase in the sample was quartz (Q, SiO$_2$), followed by mullite (M, Al$_6$Si$_2$O$_{13}$), magnetite (G, Fe$_3$O$_4$) and hematite (H, Fe$_2$O$_3$). The sample had the highest peak at 26.56° with intensity of 1128. This result is consistent with that of reported in [4, 13].

3.4. SEM-EDX Analysis
The surface structure of CFA3 was in line with the XRD result. The major mineral constituents of the adsorbent could be observed in Figure 5. It could be observed that adsorbent was made of particles with different shapes and sizes. This might derive from different mineral phases as shown in Figure 4. Quartz has sharp edged, elongated, oval and spherical form; mullite has shapes of pillar like, single form with cleavage and colorless; magnetite has spherical form and hematite has spheroidal aggregates. Spherical forms of magnetite and hematite have smaller size than that of quartz [11].

Figure 3. Physical properties of CFA-based adsorbents: (a) density, (b) bulk density and (c) percentage of adsorbed moisture at various calcination temperatures.
The EDX analysis (Table 1) demonstrated that Si was the dominant metal in the adsorbent, followed by Fe, Ca and Al. Based on the elemental composition, the ratio of Si/Al in the adsorbent was 3.12. Meanwhile, based on the CaO content that higher than 10%, the adsorbent belonged to class C fly ash or high-calcium fly ash. It means that the sample has self-cementing behavior, i.e. able to form cementitious product upon contact to water with no activator addition. This character makes the class C fly ash a very effective and economic stabilization agent for use in variety of construction applications [14].

3.5. BET Analysis
Results of BET analysis revealed that the surface area, total pore volume and average pore diameter of CFA3 was 8.045 m$^2$/g, 0.0429 cm$^3$/g and 0.204 nm respectively. These results were relatively low compared to [3] that stated CFA has surface area in the range of 25 – 70 m$^2$/g. However, the surface area of the CFA3 adsorbent was higher than that of the solid residue of acid treated fly ash originated from a coal power plant in South Africa Province i.e. 3 m$^2$/g [13]. Another study reported that CFA from Brazilian thermal power plant had surface area of 3.4 m$^2$/g [4]. Both results agreed with [12] stated that CFA can have surface area as low as 0.2 m$^2$/g and as high as 0.7 m$^2$/g.

**Figure 4.** XRD pattern of CFA-based adsorbent at calcination temperature of 400 °C (CFA3).
Figure 5. SEM photograph of CFA-based adsorbent at calcination temperature of 400 °C (CFA3).

Table 1. Chemical composition of CFA3 based on EDX result analysis

<table>
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<th>Element</th>
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<th>O</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>Ca</th>
<th>Ti</th>
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<td>10.52</td>
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<td>0.52</td>
<td>0.82</td>
<td>15.49</td>
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3.6. Performance of CO₂ Removal

The initial concentration of CO₂ in the mixture was 35%. The performance of the adsorbents in removing the CO₂ is shown in Figure 6. It depicted from Figure 6 that CFA2 gave the best result. The outlet concentration after contact time of 30 minutes was 10% with CO₂ removal efficiency was 71.43% with adsorption capacity of 8.027 mg CO₂/g adsorbent or 0.211 mmol CO₂/g adsorbent. This result showed equivalent performance as of natural zeolite utilization in CO₂ removal published in [8]. The previous research [7-8] aimed to obtain adsorbent pellets that can reduce CO₂ content to ± 10%. This value meets the requirement of natural gas grid [7].

Figure 6. (a) CO₂ removal efficiency and (b) adsorption capacity of CFA-based adsorbents at various calcination temperatures.

Furthermore, the performance of the adsorbent in this study should be improved to achieve better removal efficiency. This is due to several countries have defined standards for grid injection of upgraded biogas or for utilization as vehicle fuel. The standard requirement of CO₂ content in purified
biogas should be lower than 6%-vol in Germany and Switzerland and lower than 2%-vol in France. Meanwhile, in Sweden, the total content of CO$_2$, O$_2$ and N$_2$ in biogas should be below 5%-vol [15].

4. Conclusion
The coal fly ash based adsorbent pellet has been successfully manufactured by simple calcination process. The highest yield of 90.34% was achieved at calcination temperature of 400 °C for 4 hours with particle size of 140 mesh (CFA3). The increasing calcination temperature decreased the density and bulk density; but increased the percentage of adsorbed moisture of the adsorbents. For CFA3, the density was 1.296 g/cm$^3$, the bulk density was 0.985 g/cm$^3$ and the ability in adsorbing moisture in overnight was 0.979%. Based on the results of XRD and EDX analysis, the major constituent in the adsorbent was SiO$_2$. The highest CO$_2$ removal by adsorption was attained by utilization of CFA2 adsorbent, i.e. adsorbent produced at calcination temperature of 300 °C. The result implied that the efficiency of CO$_2$ removal was 71.43% with adsorbent capacity of 8.027 mg CO$_2$/g adsorbent or 0.211 mmol CO$_2$/g adsorbent. With this result, the residual CO$_2$ content was 10%-vol and meet the requirement of natural gas grid. Further research will conduct to improve the removal efficiency for better quality and performance of biogas.

References

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