The Effects of Zn/Natural Zeolite Ratio and Adsorbent Calcination on H$_2$S Adsorption in Biogas on the Processing of Palm Oil Mill Effluent (Pome)

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Abstract. Biogas is a renewable energy source derived from organic material that is anaerobically degraded by bacteria in an oxygen-free environment. The main components of biogas are methane (CH$_4$) and carbon dioxide (CO$_2$). In addition, there are other relatively small amounts of gas, namely nitrogen (N$_2$), hydrogen sulfide (H$_2$S) and hydrogen (H$_2$). The quality of biogas that is non-optimal can be improved by separating or eliminating impurity gases, one of which is hydrogen sulfide (H$_2$S). Hydrogen sulfide (H$_2$S) is a poisonous and odorous gas that causes corrosion, so it needs to be reduced in biogas. Hydrogen sulfide (H$_2$S) in biogas can be reduced by adsorption methods using modified natural zeolites. The purpose of this study is to determine the effect of the natural Zn/zeolite impregnation ratio and the effect of the adsorbent calcination temperature on biogas purification and determine the concentration of hydrogen sulfide (H$_2$S) from biogas purification. The adsorbent is synthesized with variation: natural Zn/zeolite ratio of 10%, 20%, 30% w/w and calcination temperature of 200°C, 300°C, 400°C. Adsorbents are characterized using X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The result of this research show that the optimum adsorption capacity of hydrogen sulfide (H$_2$S) in biogas is obtained at a variable ratio of Zn/zeolite natural 20% and calcination temperature of 300°C is 6.36 mg S g adsorbent and H$_2$S can be purified or adsorbed up to 99%.

Keywords. Adsorption, Adsorption Capacity, Biogas, Hydrogen Sulfide (H$_2$S), Natural zeolites.

1. Introduction

Biogas, an alternative renewable and is green energy, produced from wastewater treatment, plants, landfills, municipal and agricultural waste. Biogas contains 50-65% methane (CH$_4$), 30–45% carbon dioxide (CO$_2$), moisture and traces of hydrogen sulfide (H$_2$S). Biogas without a complete purification process contains a small percent of impurities such as hydrogen sulfide (H$_2$S), ammonia (NH$_3$) and siloxanes. The existence of these components in biogas affects the biogas quality and limits the biogas application. This drawback results in decreased biogas utilization and thereby its economic benefit and also generates harmful environmental emissions. The hydrogen sulfide contaminants present in biogas result in complex sequences of purification processes based on conventional physical/chemical and biological technologies capable of producing biogas with CH$_4$ purities of 88–98% and H$_2$S removals of >99%. Currently, adsorption processes have attracted much attention and are used widely in many important applications due to their advantages of low initial capital cost, simplicity of design, ease of
operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions [1].

Currently, activated carbon, metal oxide, and zeolite are the most studied adsorbents by many researchers. Activated carbon has been reported as an effective adsorbent, however, activated carbon also have disadvantages such as being non-selective to H$_2$S, sensitive to dust and an expensive adsorbent. Metal oxide also has been widely used for contaminant removal from the waste stream. Even though metal oxide adsorbents have been used widely for H$_2$S removal from the gas stream but they are not suitable for the low-temperature regime. Meanwhile, zeolite is a low-cost adsorbent that has been used for H$_2$S removal but its H$_2$S adsorption capacity is low compared with activated carbon and metal oxide [1]. Long et al. [2] have conducted research on H$_2$S gas adsorption at room temperature by modifying zeolite X adsorbents. Zeolite X is synthesized through the hydrothermal method and exchanged ions with six different metal ions namely Co$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Ca$^{2+}$ and Zn$^{2+}$. They have found that the Zn component in zeolites was confirmed to be the most influential factor in H$_2$S adsorption.

Binh and Long [3] have conducted biogas purification research using Zn-exchanged zeolites. The material was synthesized using the microwave-assisted method to reduce crystallization time. Zeolite treated with three different microwave heating times is 0.5, 1.0, and 1.5 h. H$_2$S gas mixed with CO$_2$ with two different concentrations is 0, and 40000 ppm. They have found that the longer microwave heating time made increasing adsorption capacity and the presence of CO$_2$ can be decreasing adsorption capacity but zeolite still can selectively adsorb H$_2$S.

All of the findings of the above-mentioned studies were reported in relatively quick succession. However, the effect of interaction between variables has not been explored yet. If those variables like as Zn/natural zeolite ratio and calcination temperature is investigated its effect on adsorption capacity. In this paper, adsorption has carried out in a fixed bed vertical reactor in ambient temperature condition. The effects of Zn/natural zeolite ratio and calcination temperature were investigated using SEM and XRD.

2. Materials and Methods

2.1 Material Preparation

Natural zeolites are crushed to size 100 mesh and then an alkaline hydrothermal reaction was carried out on the treated zeolite. Sodium hydroxide, 2.75 M, was added to the metakaolin in the ratio of 5 mL NaOH/g zeolite. The mixture was mixed thoroughly by mechanical stirring (200 rpm) at 70°C for 2 h. The mixture was left at 105°C in the oven for 12 h for crystallization. Then, the crystallized zeolite was separated by vacuum filtration and dried at 105°C for 24 h in an oven. The dispersion of zinc oxide into the microporous channels of zeolite by the incipient wetness impregnation method was carried out at room temperature. The samples were prepared by impregnating zeolite with different amounts of zinc oxide (10, 20 and 30 wt/v%). For this purpose, 1 mL of aqueous solutions of zinc nitrate (Zn(NO$_3$)$_2$.6H$_2$O) for each gram of zeolite has been used to prepare the 10, 20 and 30 wt/v% ZnO impregnated zeolite, respectively. The wet impregnated samples were left at room temperature overnight and then dried in an oven at 105 °C for 8 h. The adsorbents were activated by varied calcination at 200°C, 300°C and 400°C for 3 h for the formation of zinc oxide

2.2 Purification Process

The biogas used comes from biogas power plant of PTPN V Tandun, Rokan Hulu. The samples (157 g) was placed in a reactor with dimension 1 1/2” ID, 12 cm height and made from PVC. Purification was performed in a fixed bed vertical reactor in which is shown in Figure 1. The flow rate of biogas is 0.025 L/s and continuously flowing into the reactor. The purification process is stopped when the outlet concentration equals the input. The concentration of H$_2$S detected by H$_2$S detector in ppm unit.
2.3 Result Analysis

2.3.1 Adsorption Capacity
A breakthrough curve is made to see how long the adsorbent adsorbs the adsorbate and is used to calculate the adsorption capacity. Adsorption capacity is calculated from the following equation [4]:

$$SC = \frac{v \times t \times (C_{in} - C_{out}) \times M \times 10^{-3}}{V_{mol} \times m_s}$$

Where $SC$ is the breakthrough sulfur capacity (mg-S/g-adsorbent), $v$ is the inlet gas flow rate (L/min), $t$ is the breakthrough time (min), $C_{in}$ and $C_{out}$ are the inlet and outlet concentrations of H$_2$S (ppmv) respectively, $M$ is the molar mass of S (32 g/mol), $V_{mol}$ is the molar volume (24.45 L/mol at 25°C, 1 atm), $m_s$ is the weight of adsorbent (g), $10^{-4}$ is the normalizing coefficient adjusting the units.

2.3.2 X-Ray Diffraction (XRD) Analysis
The structural properties before and after modification were characterized using XRD. One sample to be analyzed for XRD was selected based on optimum adsorption capacity.

2.3.3 Scanning Electron Microscope (SEM) Analysis
Morphology of zeolite before and after modification were identification using an SEM with the magnifications of 3000x. One sample to be analyzed for SEM was selected based on optimum adsorption capacity.

3. Result and Discussion

3.1 Adsorbent Capacity
Figure 2 shows the breakthrough curve for various adsorbent in this research.

Figure 1. Series of Tool for Purification Proses
From Figure 2 shown that addition zinc on natural zeolite prolongs the use of adsorbent. Increasing the calcination also prolong the use of adsorbent. The performance of each adsorbent in term of concentration before and after purification. The adsorbent performance will decrease when the concentration outlet increasing and saturated if the concentration outlet equals to concentration inlet. The result shows that Zn-20%-300°C adsorbent has the longest purification time.

From the blank natural zeolite (ZA) breakthrough curve, the calculated H$_2$S adsorption saturated capacity was only 0.94 mg-S/g-adsorbent, it shown in Figure 3. The adsorption performance of adsorbent was increased to 1.43 mg-S/g-adsorbent after natural zeolite was modified with 10 wt% zinc and calcination in 200°C. Addition of 20 wt% and 30 wt% zinc increased the H$_2$S adsorption capacity to 1.90 and 2.47 mg-S/g-adsorbent respectively in 200°C calcination temperature. Performance In 300°C calcination temperature also can significantly increase adsorption capacity in addition of 10 wt%, 20 wt% and 30 wt% to 5.46, 6.36 and 5.85 mg-S/g-adsorbent. Performance In 300°C calcination temperature also can significantly increase adsorption capacity in addition of 10 wt%, 20 wt% and 30 wt% to 4.19, 4.02 and 3.31 mg-S/g-adsorbent. Based on this adsorption experiment, the 20 wt% zinc-modified natural zeolite and 300°C were selected to be the optimum loading and optimum calcination temperature.

From the H$_2$S adsorption experiment, it can be concluded that the addition of zinc to natural zeolite and increasing calcination temperature brings several significant impacts on the adsorbent performance. The time before the adsorbent was saturated becomes longer with zinc-modified natural zeolite then unmodified natural zeolite and before adsorbent is saturated, the adsorbent can reduce H$_2$S up to 99%.

The result also showed that decreased adsorbent capacity when 30 wt% loading in 300°C. Decreasing adsorbent capacity caused by several factors such as the pore is blocked due to excess zinc loading so contact with adsorbate is getting smaller. When exceeding the support critical dispersion capacity, a comparatively less reactive aggregate of active zinc site formed. The result shows a good agreement with other published studies. Li et al. [4] published the performance of H$_2$S removal for ZnO supported on three different 3-D mesoporous molecular structures (SBA-16, MCM-48, and KIT-6) at room temperature. From that work, they found that for all types of 3-D mesoporous molecular structures H$_2$S adsorption capacity was increased by the addition of zinc oxide. Adsorbent capacity of various adsorbent in this research can be seen in Figure 3.
Figure 3. Sulfur Capacity of Adsorbent at different Zn loading (m = 157 g, C_o = 800 ppm, F = 0.025 mL/s).

From Figure 3 shown that calcination in 300°C is the optimum temperature to increase adsorbent capacity and when calcination in 400°C the adsorbent capacity decreased. Elevated temperature can cause zinc oxide crystals damage on the surface of zeolite so that the adsorption of hydrogen sulfide decreases. Zhu et al. [5] proved that when calcination temperature is too high, the desulfurization performance is seriously reduced. This is because the crystal structure of modified zeolite is subjected to high-temperature destruction, and the modified zeolite pore collapses. Moreover, if the temperature is too high, the metal ion salt will be sintered and inactivated, causing the surface of zeolite to be covered by metal, thereby seriously affecting the adsorption and adsorption performance. Other researchers have also conducted H2S purification, Table 1 shows some results for the H2S adsorption capacity of the modified adsorbent.

Table 1. Comparison of 20Zn/Natural Zeolite Adsorbent Adsorption Capacity with Other Published Literature

| Adsorbent               | H2S Inlet Concentration (ppmv) | Inlet Gas     | Adsorbent Capacity (mg-S/g-adsorbent) | Reference |
|-------------------------|---------------------------------|---------------|---------------------------------------|-----------|
| 20ZnO/Na-A Zeolite      | 200                             | H2S           | 15.75                                 | [1]       |
| Zn^{2+}-Zeolite X      | 100                             | H2S & N2      | 23.5                                  | [3]       |
| Zn^{2+}-Zeolite X      | 1000                            | H2S           | 13                                    | [2]       |
| Zn^{2+}-Zeolite X      | 1000                            | H2S & CO2     | 10.2                                  | [2]       |
| 20Zn/Natural Zeolite   | 800                             | Biogas        | 6.36                                  | This work|

Table 1 shows that this research has the lowest adsorbent capacity due to the direct use of biogas, not using one or two biogas component like other published this data that the presence of other gas beside H2S can reduce adsorbent capability to adsorb H2S. Long et al [3] did research H2S adsorption in the presence of CO2, the result shows that adsorbent adsorption capacity reduces when CO2 mixed with H2S.
3.2 X-Ray Diffraction (XRD) Analysis

Figure 4 is XRD pattern on unmodified and modified zeolite. In this pattern, the ZnO crystal phase can be seen from several peaks.

![XRD Pattern of ZnO on unmodified and Modified Zeolite](image)

**Figure 4. XRD Pattern of ZnO on unmodified and Modified Zeolite**

(Zn20%/Natural Zeolite, T = 300°C)

From Figure 4, different pattern between unmodified and modified zeolite seen in the value of relative intensity ($I_{rel}$) and the location of some of the highest peak. $I_{rel}$ value in unmodified zeolite is greater than modified zeolite, which is in agreement with previous reports [6]. Some of the new highest peaks occur on modified zeolite and location of some peaks change after modification of zeolite. The crystalline phase of zinc oxide can be observed at $2\theta$ values of 32.10, 34.98, 36.71, 48.17, 63.53, 68.81, and 78.06, compared to JCPDS No. 36-1451 data for ZnO with $2\theta$ values of 31.798, 34.444, 36.326, 47.588, 56.560, 62.852 dan 67.967. $2\theta$ values from this research are close to the standart value, so that the zinc oxide crystal successfully grows on the surface of the zeolite. The average size of the ZnO crystal diameter on modified zeolite calculated by the Scherrer equation is 54.584 nm, the average size of crystal diameter on modified zeolite is 124.275 nm and the average size of crystal diameter on unmodified zeolite is 50.96 nm. It is shown that diameter changed after modification. The addition of diameter is caused by the formation of a thin layer on the surface of zeolite crystals. This confirms that zinc oxide successfully added to the zeolite. Besides characterization using XRD, SEM characterization was also carried out to see the zeolite surface morphology before and after modification shown in Figure 5.
Figure 5. SEM Image of (a) Natural Zeolite and (b) ZnO/Natural Zeolite

From Figure 5, shown adsorbent morphology of natural and ZnO/Natural Zeolite surface. In Figure 5 can be seen that the addition of crystal diameter in the modified zeolite. This is due to the formation of a thin layer of ZnO on the surface of the zeolite crystals which causes the crystals to enlarge. ZnO particles on zeolite surface gathered and generated pores leading to mass transfer improvement during the adsorption process [3]. The appearance of white mass indicates the presence of metal on the surface of the zeolite. The appearance of white mass on the modified zeolite more than the unmodified zeolite. The white dispersed mass of zinc adheres to the zeolite surface, which is in agreement with previous reports [7]. This shows that the addition of zinc as a metal modification has been successful.

4. Conclusion
In this study shows that the optimum adsorption capacity occurs at a ratio of 20% natural Zn / Zeolite at a calcination temperature of 300°C. Excessive zinc oxide buildup in the zeolite pore and too high calcination temperature can reduce the adsorption capacity. Adsorbents can reduce H₂S concentrations up to 0 ppm or 99% from the inlet, but when the adsorbents begin to saturate, the H₂S concentrations that are adsorbed become less. The characterization of XRD and SEM shows the success of adding zinc oxide to the surface of the zeolite.

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