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Immobilization of Carbon Paste from Waste of Zinc-Carbon Battery by Using Portland Cement (PC) for Biogas Desulfurizer in Livestock Waste Management

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Abstract. Livestock waste usually treated in the digester to avoid odor problem and produce biogas. The slurry that is yield from digester is useful for fertilizer. Hydrogen sulfide (H_2S) is impurities found in the biogas and should be eliminated before further application for the reason of health and safety. Hydrogen Sulfide (H_2S) is rising problem for the engine since will caused acidity to lubricant and corrosive to metal part of the engine. The waste of used battery should be well manage or even reused again for other useful purpose to reduce dangerous risk for heal and environment. The batteries containing materials which are dangerous for health and safety of environment. In some type of battery, its application should be replaced when the power get lost. The zinc-carbon battery is a type of battery that can be used only one time, consist of carbon rod as positive terminal, zinc case as negative terminal, and carbon paste as mixture of carbon powder, ammonium chloride, and MnO_2 as electrolyte. In this research the carbon powder of electrolyte part of the used zinc-carbon battery is reused as desulfurizer. Portland cement (PC) is added for immobilization of the carbon paste waste to create a pellet. It is found that the carbon paste from used zinc carbon battery is excellent as desulfurizer by adding Portland cement as binder

Keywords: Portland cement, battery, zinc-carbon, carbon paste, desulfurizer, biogas

1. Introduction

The zinc-carbon battery is widely used due to its available everywhere with reasonable price . The zinc-carbon battery consist of zinc case as a container and negative terminal, carbon road as positive terminal and mixture of MnO_2, graphite powder and ammonium chloride (NH_4Cl)as electrolyte as can be seen in Fig. 1 [1]. After used or spent, the used battery still contains ammonium chloride which is mildly acidic that can be disturbing the balance of the nature if the used battery is discarded carelessly. Manganese dioxide (MnO_2) is known as hazards material that can stain the human skin.

The zinc-carbon battery is popular source of energy for portable electrical appliances. It is a challenge to achieve the recycling of consumer-type batteries. Individuals should cooperate in such a program in order to ensure its success. it is found that it is necessary and useful to recycle the used zinc-carbon batteries base on energy balance of the chemical active part of the battery, the value and supply of the material and finally the steps and alternative route to the recycling of zinc-carbon batteries[2].

The recycle of certain part of the zinc-carbon battery for desulfurizer has been done intensively with remarkable result. The zinc case of zinc-carbon battery is already successfully utilized as biogas desulfurizer by applying galvanic coupling method. The zinc case was taken out and cut to become small pieces and iron

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chips is prepared for galvanic coupling. The composition was immersed in to the salt water solution in order corrosion to occur and resulting corrosion product that reactive to H_2S [1].

Other part from waste of zinc-carbon battery that already investigated for biogas desulfurizer is the carbon rod. The carbon rod from waste of zinc-carbon battery is potential to be recycled as desulfurizer of biogas more even the carbon rod can be directly used as desulfurizer. The carbon rod can be processed by putting in the solution of KMnO4 with concentration minimum 20gram $KMnO_4$ in 1 liter water to increase the performance of the desulfurizer,. Low level of flow rate of the biogas (around 1-3 liters/minute) is suggested to achieve best performance of desulfurizer during application [3].

Adsorbents commercially are usually in the form of particulate (spherical, rods, moldings, or monoliths). Adsorption is a surface based adhesion of atoms, molecules, ions or dissolved solid to a surface and create a film on the surface of the adsorbent. It is designed to have small pore diameters to yield higher surface area for high surface capacity of adsorption [4].

Activated carbons were recognized as successful desulfurizer for biogas. By using adsorption process, the H_2S contaminant in the biogas can be removed. Beside as desulfurizer, Activated carbons are the adsorbents with the most favorable characteristics for natural gas storage, because efficiently compacted into a packed and have large microporous volume [4]. The manufacturing process of activated carbon consists of two steps which are carbonization and activation. The carbonization process includes drying and then heating to separate with tars and other hydrocarbons of any gases generated. The next step is carbonized particles by exposing them to an oxidizing agent such a steam at high temperature. This agent eliminated pore blocking structures created during the carbonization phase and develop a porous structure [5]. Carbon active was found success to be used as desulfurizer by using various chemical treatments, such as nitric acid (HNO_3) oxidation, metal (Zn and Cu) impregnation, and thermal desorption of oxygen functional groups [6]

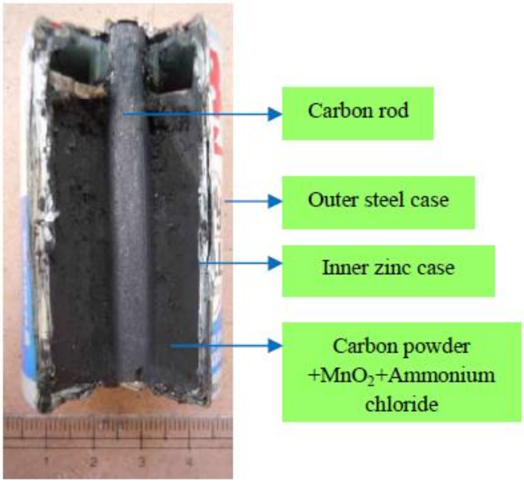

Fig. 1: Inner side of zinc-carbon battery

Biogas is source of renewable methane which is deriving from biomass sources and has great potential for growth to meet future energy demands. Biogas is obtained from anaerobic biodegradation of biomass in the absence of oxygen and the presence of anaerobic microorganisms [7].

Anaerobic digestion is a series of metabolic interactions of microorganisms. Sludge produced from the anaerobic digestion is often used as a fertilizer. The process is carried out in digesters at temperatures ranging from 30 to 65^{o}C. Anaerobic digesters are designed to operate in the mesophilic (20–40 ℃) or thermophilic (above 40 ℃) temperature zones. Biogas technologies have been failures in many developing countries, with low rates of technology transfer and longevity and a reputation for being difficult to operate and maintain. Designs which deliver lower cost, improved functionality, robustness, ease of construction, maintenance and operation would aid the market penetration of biogas plan [8].

There is greater potential for biogas as a fuel for transport vehicle. The biogas need to be compressed in gas cylinders for this purpose. This is possible only after removing hydrogen sulfide (H_2S). The H_2S content in biogas vary from 100 to 10.000 ppm. This contaminant is undesirable in combustion systems due to its conversion to highly corrosive and environmentally hazardous compounds [7]. It is essential to remove of H_2S before any further utilization of biogas. Hydrogen sulfide (H_2S) is contaminant in biogas and other S-containing compounds that come from S-bearing organic matters which is depending on the composition of the organic matter [7] - [10].

Hydrogen sulfide mainly attacks the neural system and important organs, like the liver and the kidney Hydrogen sulfide is a pollutant that is regarded as toxic. Inhalation of high concentrations of hydrogen sulfide can be lethal [11].

Together with CH_4 in the biogas, H_2S burns in engines, and it exhausts in the form of SO_2 which is more dangerous than H_2S as it is hazardous for health and environment such as smog and acid rain. Owing to the potential problems that H_2S can cause, it is necessary to remove it prior to its use at least as a solid residue that can be disposed off safely and easily. Several small scale plants and projects using biogas have ended because of the corrosion problem of H_2S [12].

During digestion, removal of H_2S can be done by dosing air of oxygen in to digester of by adding iron chloride into the digester. Mean while H_2S can be removed after digestion by using several techniques such as biological filter, adsorption, or membrane separation. Adsorption can be carried out by using liquid, iron oxide, or activated carbon. Hydrogen sulfide can cause damage motors and in piping, it is removed in an early state of the biogas upgrading process. Several techniques are applied: (1) removal of H_2S during digestion and (2) removal of H_2S after digestion [13].

Path of the zinc from used zinc-carbon battery is already established [1] by using galvanic coupling method. Galvanic coupling is a potential difference that usually exists between two dissimilar metals when they are immersed in conductive solution. The technique involved galvanic coupling between zinc and iron that can release ion Zn^{2+} which is reactive to H_2S. The potential difference produce electron flow and metal ion will be released from one of the coupling. The metal react with H_2S so that process of desulfurization to occur [1]. A best performance is obtained for mixture of 75% Zn +25% Fe as desulfurizer. This result is due to three reactions with H_2S to occur: reaction beween ZnO and H_2S and small amount reaction between $Fe(OH)_3$ with H_2S . Since galvanic coupling between Zn and Fe, the coupling will release ion Zn^{2+} that will react with H_2S. The amount of Zn mass is smaller that Fe in the mixture then the galvanic coupling is not so active in releasing Zn^{2+} [1].

The separation process of used zinc- carbon battery yield 4 main items namely carbon paste, carbon rod, steel case, zinc case. These works introduce successful work on the effort of reuse carbon paste from used zinc-carbon battery as desulfurizer for biogas purification. Portland cement (PC) is utilized in this research as a binder. The simultaneous solving problems of battery waste and harmful gas of H_2S in the biogas can be solved by technique that is introduced in this article.

2. Experimental

The carbon paste from used zinc-carbon battery was separated from the body of the battery and mixed homogenously with Portland cement (PC). The mixtures were added with water and extruded, continued with drying. It was prepared four variations of compositions in mass fraction namely: 0% carbon + 100% PC, 25% carbon + 75% PC, 50% carbon + 50% PC, and 75% carbon + 25% PC.

A dry mixture was easy obtained (Fig. 2). The performance of each four variations of desulfurizers then was investigated by following schematic that is presented in Fig. 3. This schematic was from our previous publication [3]. About 100 g of mixture of each variation is taken as desulfurizer and installed as can be seen in Fig.3. The performance of desulfurizer then can be calculated by using Equation 1.

The flow rate of biogas was arranged about 3 liters/minute. The performance of desulfurizer was evaluated by measuring the H_2S contents in the biogas before and after passing the desulfurizer as can be seen in Fig. 3. The biogas was let flow from gas container 1 with valve 2 was used to control the. The flow rate was checked by using flow rate indicator 3. The performance of desulfurizer was measured after passing

50 liters of biogas through desulfurizer. To measure the H_2S contents in the biogas before entering the desulfurizer, the valve 4 was closed and the valve 5 was opened and let the biogas flow to the H_2S gas sensor 6. If the desulfurizer working well, then the H_2S contents in the biogas will decrease and can be measured by closing valve 8 and open the valve 9 and let the biogas flow to the H_2S gas sensor 10.

$$\frac{H_2S\ \text{before desulfurizer} - H_2S\ \text{after desulfurizer}}{H_2S\ \text{before desulfurizer}} \times 100\% \quad (1)$$

Fig. 2: Dry mixture pellets of carbon paste from used zinc-carbon battery mixed with Portland cement (PC). (a). 0% carbon + 100% PC, (b) 25% carbon + 75% PC, (c) 50% carbon + 50% PC, and (d) 75% carbon + 25% PC.

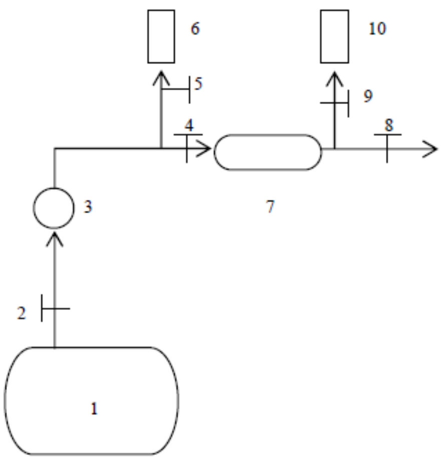

Fig. 3: Schematic of desulfurizer performance testing:
1. Biogas container, 2.Valve, 3.Flow rate indicator, 4. Valve, 5. valve, 6. H_2S gas sensor, 7. Desulfurizer, 8. Valve, 9.valve, 10. H_2S gas sensor .

3. Result and Disscusion

Table 1 is the result of investigation. Pure portland cement (PC) without addition of carbon paste is possible to use as desulfurizer but the performance is found not sufficient (the performance only 15.00 %) that can be seen in Fig. 4.

Portland cement can act as desulfurizer due to reaction of H_2S with lime ($Ca(OH)_2$) in the PC as reaction in the Equation 2 [14]. The main composition of PC is calcite ($CaCO_3$) (Fig. 5) and due the existence of H_2O in the biogas the lime ($Ca(OH)_2$ then is formed and react with H_2S following Equation 2.

$$Ca(OH)_2 + 2H_2S \rightarrow Ca(HS)_2 + 2H_2O \quad (2)$$

Table 1: Averages desulfuizer performance after filtered 50 liters biogas

Averages desulfurizer performance (%)			
0%C+100%PC	25%C+75%PC	50%C+50%PC	75%C+25%PC
15.00	91.62	97.75	99.53

By addition just only 25% carbon paste, the performance of desulfurizer increase significantly and reach 91.62%. The performance increase approaching 97.75 with addition of 75% carbon paste and about reach its maximum value of 99.53%. The activated carbon in the carbon paste increases the performance as desulfurizer [15]. This is due to reaction between carbon (C) and H_2S that occurring base on Equation 3.

$$C + H_2S \rightarrow C\text{-}S + H_2 \quad (3)$$

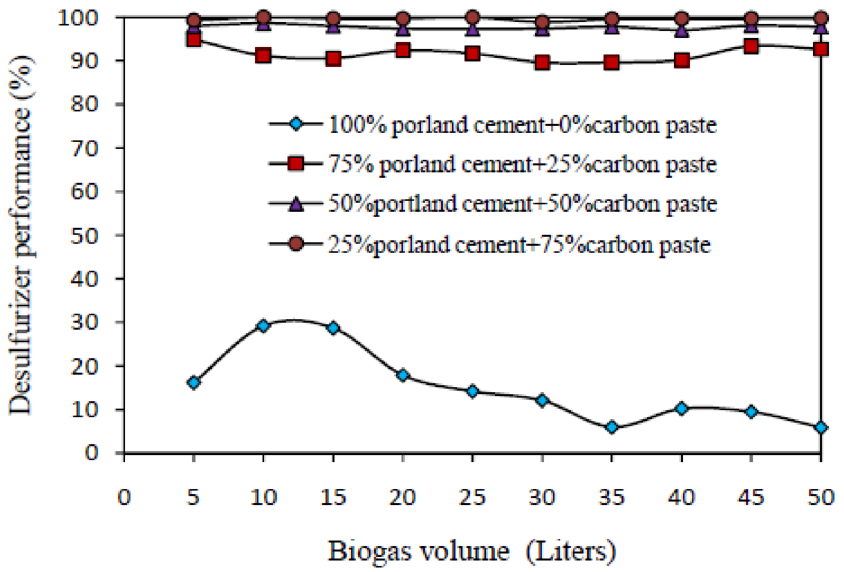

Fig. 4: Effect of mass fraction of carbon paste in Portland cement (PC) on performance of biogas desulfurizer

That is not only reaction in Equation 3 that occur but also involving reaction of carbon (C) and oxygen (O) from MnO_2 as reaction in the Equation 4 bellow:

$$C\text{-}O + H_2S \rightarrow C\text{-}S + H_2 \quad (4)$$

The carbon paste containing manganese (MnO_2). Manganese is a metal that can increase the performance as desulfurizer [15].

The result from this research can be use to complete our previous research [16] which is the carbon paste can also be immobilized d by using clay. Clay is found possible to be used as desulfurizer but the performance is found not sufficient. Clay can act as desulfurizer due to chemisorptions mechanism. The carbon paste from the used zinc-carbon battery was mixed homogenously with clay. The mixtures are added with water, extruded ,and continued with drying. A cut of small rods from dry mixture was easy obtained [16].

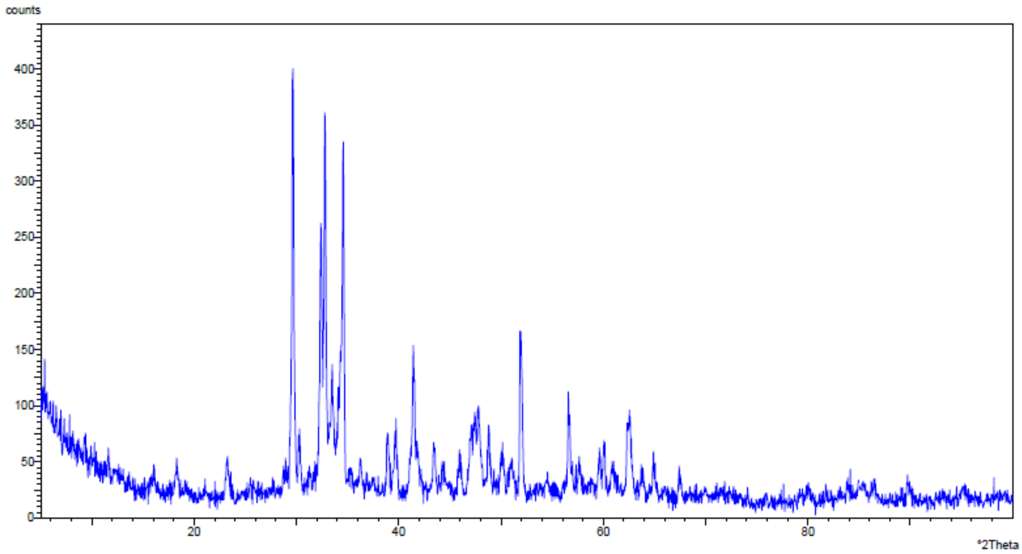

Fig. 5: Result of X ray difractometer (XRD) on Portland cement. The composition mainly (65%) is calcite ($CaCO_3$)

Two problems can solve simultaneously with the idea that is introduced in this article in which desulfurizer of biogas is made from reused carbon paste of waste zinc-carbon battery. The first problem is the management of waste zinc-carbon battery can be solved and also the harmful gas of H_2S can be eliminated from the biogas with simply method by using Cement as a binder for immobilization of carbon paste.

4. Conclusion

The carbon paste from waste of zinc-carbon battery is potential to be reused as biogas desulfurizer by using porland cement (PC) as a binder. With addition of about 25% -75% carbon paste, the mixture can be used as a good desulfurizer in which best performance is achieved with Addition about 5% carbon paste. In this studies, attention just addressed to reducing of the H_2S impurities that contained in the biogas. For further study the effect to other gas impurities such as CO_2, NH_3, and H_2O will also be studied.

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