Reuse of Carbon Paste from Used Zinc-Carbon Battery for Biogas Desulfurizer with Clay as a Binder

Tjokorda Gde Tirta Nindhia, I. Wayan Surata, I. Dewa Gede Putra Swastika, and I. Made Wahyudi

Abstract—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 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 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 mixture of carbon powder, ammonium chloride, and MnO₂ as electrolyte. Hydrogen sulfide (H₂S) is impurities found in the biogas and should be purified before further application as fuel for engine. Hydrogen Sulfide (H₂S) is rising problem for the engine since will caused acidity to lubricant and corrosive to metal part of the engine. In this research the carbon powder of electrolyte part of the used zinc-carbon battery is re-used as desulfurizer. Clay is added as a binder to make possible to create a pellet. It is found that the carbon powder from used zinc carbon battery is excellent as desulfurizer by adding clay as binder.

Index Terms—Battery, zinc-carbon, carbon paste, desulfurizer, biogas.

I. INTRODUCTION

The zinc-carbon battery is widely used due to low price and available everywhere. The zinc-carbon battery consist of zinc case as a container and negative terminal, carbon rod as positive terminal and mixture of MnO₂, graphite powder and ammonium chloride (NH₄Cl) as electrolyte [1] as can be seen in Fig. 1. After used or spent, the used battery still contains ammonium chloride which is mildly acidic that can be disturb the balance of the nature if the used battery is discarded carelessly. Manganese dioxide (MnO₂) is known as hazards material that can stain the human skin.

The zinc-carbon battery is popular energy source for portable electrical energy. 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. Basic 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, it is found that it is necessary and useful to recycle zinc batteries [2].

The recycle of certain part of the zinc-carbon battery for desulfurizer has been done intensively with remarkable result [1]. The zinc case of zinc-carbon battery is already successfully utilized as biogas desulfurizer by applying galvanic coupling method [1]. The zinc case was taken out and cut to become small pieces and iron 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 H₂S.

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

Adsorption is a surface based adhesion of molecules, atoms ions or dissolved solid to a surface and create process a film on the surface of the adsorbent. Adsorbents commercially are usually in the form of particulate (spherical, rods, moldings, or monoliths). It is designed having small pore diameters, to yield higher surface area for high surface capacity of adsorption. By using adsorption process, the H₂S contaminant in the biogas can be removed. Activated carbon [4] were recognized as successful desulfurizer for biogas. Beside as desulfurizer, Activated carbons are the adsorbents with the most favorable characteristics for natural gas storage, because have a large microporous volume, are efficiently compacted into a packed [4].

The manufacturing process 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 as nitric acid (HNO₃) oxidation, metal (Zn and Cu) impregnation, and thermal desorption of oxygen functional groups [6].

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

Manuscript received January 31, 2015; revised June 1, 2015. This work was supported financially by the Ministry of Education Culture, The Republic of Indonesia through second phase scheme of competitive research grant (skim penelitianhibahbersaing) for the year of 2015 granted through Udayana University, Jimbaran, Bali, Indonesia.

The authors are with the Department of Mechanical Engineering, Engineering Faculty, Udayana University Jimbaran, Bali, Indonesia (e-mail: nindhia@yahoo.com).

DOI: 10.7763/IJESD.2016.V7.768
Anaerobic digestion is a series of metabolic interactions of microorganisms. The process is carried out in digesters at temperatures ranging from 30 to 65°C [8]. Anaerobic digesters are designed to operate in the mesophilic (20–40°C) or thermophilic (above 40°C) temperature zones. Sludge produced from the anaerobic digestion is often used as a fertilizer. Biogas recovery 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 robustness, functionality, ease of construction, operation and maintenance would aid the market penetration of biogas plan [8].

There is greater potential for biogas as a transport vehicle fuel. For this purpose, biogas is be compressed in gas cylinders. This is possible only after removing hydrogen sulfide (H\textsubscript{2}S) [7]. Hydrogen sulfide (H\textsubscript{2}S) 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. The H\textsubscript{2}S 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. It is essential to remove before any further utilization of biogas [7]-[10].

Hydrogen sulfide is a pollutant that is regarded as toxic. Inhalation of high concentrations of hydrogen sulfide can be lethal. Hydrogen sulfide mainly attacks the neural system and important organs, like the liver and the kidney [11]. Together with CH\textsubscript{4}, the biogas, H\textsubscript{2}S burns in engines, and it exhausts in the form of SO\textsubscript{2} which is more dangerous than H\textsubscript{2}S as it is hazardous for health and environment such as smog and acid rain. Several small scale plants and projects using biogas have ended because of the corrosion problem of H\textsubscript{2}S. Owing to the potential problems that H\textsubscript{2}S can cause, it is necessary to remove it prior to its use as stable product, at least as a solid residue that can be disposed off easily and safely [12].

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

As presented in Fig. 2, the separation process of used zinc-carbon battery yield 4 main items namely carbon rod, steel case, zinc case, and carbon paste. This work introduce successful work on the effort of reuse carbon paste from used zinc-carbon battery as desulfurizer for biogas purification. Clay is utilized in this research as a binder. The simultaneous solving problems of battery waste and harmful gas of H\textsubscript{2}S in the biogas can be solved by technique that is explained in this article.

II. EXPERIMENTAL

The carbon paste from the used zinc-carbon battery was taken out from the body of the battery and mixed homogeneously with clay. It was prepared four variation of compositions (mass fraction) namely: 0% carbon + 100% clay, 25% carbon + 75% clay, 50% carbon + 50% clay, and 75% carbon + 25% clay. The mixtures are added with water and extruded, continued with drying. A cut of small rods from dry mixture was easy obtained (Fig. 3). About 100 g of mixture of each variation is taken as desulfurizer and installed as can be seen in Fig. 4.
The performance of each four variations of desulfurizers then was investigated by following schematic that is presented in Fig. 4. This schematic was from our previous publication [3].

The flow rate of biogas was arranged about 3 liters/minute. The performance of desulfurizer was evaluated by measuring the H$_2$S contents in the biogas before and after passing the desulfurizer as can be seen in Fig. 4. The biogas was let flow from gas container 1 with flow rate was controlled by using valve 2. The flow rate was checked by using flow rate indicator 3.

![Fig. 4. Schematic of experiment for desulfurizer test performance: 1. Biogas container, 2. Valve, 3. Flow rate indicator, 4. Valve, 5. valve, 6. H$_2$S gas sensor, 7. Desulfurizer, 8. Valve, 9. valve, 10. H$_2$S gas sensor [3].](image)

To measure the H$_2$S 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$_2$S gas sensor 6. If the desulfurizer working well, then the H$_2$S 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$_2$S gas sensor 10. The performance of desulfurizer then can be calculated by using Equation 1. The performance of desulfurizer was measured after passing 50 liters of biogas through desulfurizer.

\[
\frac{\text{H}_2\text{S before desulfurizer} - \text{H}_2\text{S after desulfurizer}}{\text{H}_2\text{S before desulfurizer}} \times 100
\]

III. RESULT AND DISCUSSION

The result of investigation is presented in TABLE I. Clay is found possible to be used as desulfurizer but the performance is found not sufficient (the performance only 27.78%) that can be seen in Fig. 5. Clay can act as desulfurizer due to chemisorption mechanism [14]. By addition just only 25% carbon paste, the performance of desulfurizer increase significantly and reach optimum performance. It can be understood that if activated carbon containing metal is added in to the clay, the performance as desulfurizer will be increase [15]. The carbon paste containing MnO$_2$ in which the manganese is a metal that can increase the performance as desulfurizer.

![Fig. 5. Effect of mass fraction of carbon paste in clay on performance of biogas desulfurizer](image)

| Mass fraction of carbon paste in clay (%) | Performance of desulfurizer (%) |
|----------------------------------------|-------------------------------|
| 0%                                      | 100.00                        |
| 25%                                     | 100.00                        |
| 50%                                     | 100.00                        |

![Fig. 5. Effect of mass fraction of carbon paste in clay on performance of biogas desulfurizer](image)

Addition of carbon paste in to the clay for mass fraction more than 25% until reach 74% are found not reduce the performance of desulfurizer. After passing of about 50 liter biogas, the performance of the desulfurizer still in optimum performance.

With the idea introduce in this article in which desulfurizer of biogas is made from reused carbon paste of waste zinc-carbon battery, two problem can solve simultaneously. The first problem is management of waste zinc-carbon battery can be solved and also the harmful gas of H$_2$S can be eliminated from the biogas.

IV. CONCLUSION

The carbon paste from waste of zinc-carbon battery is potential to be reused as biogas desulfurizer by using clay as a binder. With addition of about 25% carbon paste in clay, the mixture can be used as a good desulfurizer in which best performance is achieved. Addition more that 25% until reach 75% carbon paste is found not reduce the performance of desulfurizer.

ACKNOWLEDGMENT

The authors wish to thanks the Ministry of National and Culture of The Republic of Indonesia for financial support under third phase scheme of competitive research grant (skim penelitian hibah bersaing) for the year of 2015 granted through Udayana University, Jimbaran, Bali, Indonesia

REFERENCES

[1] T. G. T. Nindhia, I. W. Surata, I. K. A. Atmika, D. N. K. P. Negara, and I. W. P. Adnyana, “To recycle zinc (Zn) from used zinc-carbon battery
as biogas desulfurizer,” International Journal of Materials Science and Engineering, vol. 2, no. 1, pp. 39-42, June 2014.
[2] J. P. Viaux and J. P. Waefler, “Recycling zinc batteries: An economical challenge in consumer waste,” Journal of Power Source, vol. 57, pp. 61-65, 1995.
[3] T. G. T. Nindhia, I. W. Surata, I. K. A. Atmika, D. N. K. P. Negara, and I. P. G. Artana, “Processing carbon rod from waste of zinc-carbon battery for biogas desulfurizer,” Journal of Clean Energy Technologies, vol. 3, no. 2, pp. 119-122, March 2015.
[4] I. A. A. C. Esteves, M. S. S. Lopes, P. M. C. Nunes, and J. P. B. Mota, “Adsorption of natural gas and biogas components on activated carbon,” Separation and Purification Technology, vol. 62, pp. 281-296, January 2008.
[5] D. Mescia, S. P. Hernandez, A. Conoci, and N. Russo, “MSW landfill biogas desulfurization,” International Journal of Hydrogen Energy, vol. 36, pp. 7884-7890, February 2011.
[6] M. P. Cal, B. W. Strickler, A. A. Lizzio, and S. K. Gangwal, “High temperature hydrogen sulfide adsorption on activated Carbon. I. Effects of gas temperature, gas pressure and sorbent regeneration,” Carbon, vol. 38, pp. 1767-1774, 2000.
[7] N. Tippayawong and P. Thanompongchart, “Biogas quality upgrade by simultaneous removal of CO₂ and H₂S in a packed column reactor,” Energy, vol. 35, pp. 4531-4535, May 2010.
[8] T. Bond and M. R. Templeton, “History and future of domestic biogas plants in the developing world,” Energy for Sustainable Development, vol. 15, pp. 347-354, 2011.
[9] L. V. A. Truong and N. Abatzoglou, “A H₂S reactive adsorption process for the purification of biogas prior to its use as a bioenergy vector,” Biomass and Bioenergy, vol. 29, pp. 142–151, 2005.
[10] A. B. Baspinar, M. Turker, A. Hocalar, and I. Ozturk, “Biogas desulfurization at technical scale by lithotrophid denitrification: Integration of sulphide and nitrogen removal,” Process Biochemistry, vol. 46, pp. 916–922, January, 2011.
[11] W. Feng, S. Kwon, E. Borguet, and R. Vidic, “Adsorption of hydrogen sulfide onto activated carbon fibers: Effect of pore structure and surface chemistry,” Environ. Sci. Technol, vol. 39, pp. 9744-9749, November 2005.
[12] J. S. Lar and L. Xiujin, “Removal of H₂S during anaerobic coconversion of dairy manure,” Biotechnology and Bioengineering, vol. 17, pp. 273-277, 2009.
[13] M. R. Drouillon and H. Vervaeren, “Techniques for transformation of biogas to biomethane,” Biomass and Bioenergy, vol. 35 pp. 1633-1645, March 2011.
[14] R. K. Tabase, D. Liu, and A. Feilberg, “Chemisorption of hydrogen sulphide and methanethiol by light expanded clay aggregates (Leca),” Chemosphere, vol. 93, pp. 1345–1351, August 2014.
[15] D. Nguyen-Thanh and T. J. Bandoz, “Activated carbons with metal containing bentonite binders as adsorbents of hydrogen sulfide,” Carbon, vol. 43, pp. 359–367, 2005.

**Tjokorda Gde Tirta Nindhia**

Tjokorda Gde Tirta Nindhia was born in Denpasar, Bali, Indonesia on January 16th, 1972. He received the doctor degree in mechanical engineering from Gadjah Mada University (UGM) Yogyakarta, Indonesia in August 2003, with major field of material engineering.

He participated in various international research collaboration such as with Muroran Institute of Technology Japan (2004), Toyohashi University of Technology Japan (2006), Leoben Mining University Austria (2008-2009), Technical University of Vienna Austria (2010) and Recently with Institute Chemical Technology of Prague Czech Republic (2012-now). His current job is as a full professor in the field of material engineering at the Department of Mechanical Engineering, Engineering Faculty, Udayana University, Jimbaran, Bali, Indonesia. His research interests include biomaterial, waste recycle, failure analyses, ceramic, metallurgy, composite, renewable energy, and environmental friendly manufacturing.

Prof. Nindhia is a member of JICA Alumni, ASEA-UNINET alumni, International Association of Computer Science and Information Technology (IACSIT), Asia-Pacific Chemical, Biological & Environmental Engineering Society (APCBEES) and also one member of Association of Indonesian Nanotechnology. Prof Nindhia received the best researcher award in 1997 and in 2013 from Udayana University the place where he is working and again in 2012 received both Best Lecturer Award from Engineering Faculty of Udayana University. In the same years 2012, the research center of Udayana university awarded Prof Nindhia as the best senior researcher. In 2013, Prof. Nindhia was awarded as 15 best performance Indonesian lecturers from Ministry of Education and Culture the Republic of Indonesia. Prof Nindhia received the best paper award during International Conference on Environmental Engineering and Development (ICEED) 2014 in Sydney, Australia.

**I. Wayan Surata**

I. Wayan Surata was born in Nusa Penida, Bali, Indonesia on July 5, 1958. He received the doctor degree in the field of ergonomic from Udayana University in 2011. His research interest very much related in process of manufacture. His current job is a researcher and lecturer at the Department of Mechanical Engineering, Engineering Faculty, Udayana University, Jimbaran, Bali, Indonesia.

**I. Dewa Gede Putra Swastika**

I. Dewa Gede Putra Swastika was born in Bali, Indonesia on November 22, 1955. His current job is a researcher and lecturer at the Department of Mechanical Engineering, Engineering Faculty, Udayana University, Jimbaran, Bali, Indonesia.

**I. Made Wahyudi**

I. Made Wahyudi was an undergraduate student at Mechanical Engineering, Udayana University, Jimbaran, Bali, Indonesia and graduated during 2014.