To Recycle Zinc (Zn) from Used Zinc-Carbon Battery as Biogas Desulfurizer

Tjokorda Gde Tirta Nindhia, I Wayan Surata, I Ketut Adi Atmika, Dewa Ngakan Ketut Putra Negara, and I Wayan Putra Adnyana
Department of Mechanical Engineering, Engineering faculty, Udayana University, Jimbaran, Bali, Indonesia, 80361
E-mail: nindhia@yahoo.com

Abstract—Biogas should be purified before further application as a fuel for engine. Hydrogen Sulfide (H$_2$S) is one of the gas impurities that rising problem for the engine since will caused acidity to lubricant and corrosive to metal part of the engine. In this research, zinc obtained from used battery is utilized as desulfurizer. Two methods are introduced in this article for processing zinc as desulfurizer. First by immersing in the salt water to produce zinc oxide (ZnO) and secondly by galvanic coupling with iron in order to obtain ion Zn$^{2+}$. It is found that both processing techniques having optimum result in reducing H$_2$S impurity in the biogas.

Index Terms—zc, used battery, recycle, desulfurizer, hydrogen sulfide, biogas

I. INTRODUCTION

In developed country such as Japan [1] and Switzerland [2], the battery waste is well managed. The Japanese government takes care of establishing a system to transport and treat them. Similarly in Switzerland there is an action to treatment of the unrecoverable waste in an environmentally safe manner.

Zinc is in a limited amount on the earth. The world resource of zinc is in the range 20-40 year [3]. Therefore recycle of the zinc should be promoted.

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 as electrolyte as can be seen in Fig. 1. After used or spent, the used battery still contains zinc case that possible to be recycled again.

In order to use biogas as fuel of the engine, the removal of hydrogen sulfide (H$_2$S) is particularly crucial because it can cause corrosion to metal parts of the engine [4]. Several techniques of H$_2$S removal from biogas are available in several publications. In situ removal of H$_2$S from biogas during anaerobic digestion process [5] for example, this technique using FeCl$_3$ dosing which is quite problem for local farmer in developing country to obtain it.

The next generation of desulfurizer was introduced by Tippayawong and Thanompongchart [6] which involved column reactor. This technique using external energy for circulating aqueous solution countercurrent flow so that not appropriate for small portable or mobile type of biogas system because consume quite large space. By using just activate carbon (AC) as demonstrated by Mescia et al. [7] resulting in low selectivity of activated carbon towards the adsorption of only sulfur species. Finally it was informed recently [8] that ZnO is powerful for desulfurization of biogas.

II. EXPERIMENTAL

The zinc case from the used battery was taken out and cut to become small pieces as depicted in Fig. 2 and iron...
chips as can be seen in Fig. 3 was prepared for galvanic coupling. The iron chips were come from waste of metal manufacturing process. Five compositions were prepared namely: 100% Zn, 75% Zn + 25% Fe, 50% Zn + 50% Fe, and 25% Zn + 75% Fe and 100% Fe. The total mass of each composition were 100 gram.

Each composition was immersed in to the salt water solution (2500 grams salt + 20 liters water) for 2 days in order corrosion to occur and resulting corrosion product that could be reactive to H\textsubscript{2}S.

The desulfurizer then was installed in the biogas pipe line system. The system was arranged with flow rate about 3 liters/minute. The performance of desulfurizer was evaluated by measuring the H\textsubscript{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. To measure the H\textsubscript{2}S contents in the biogas before entering desulfurizer, the valve 4 was closed and the valve 5 was opened and let the biogas flowed to the H\textsubscript{2}S gas sensor 6. If the desulfurizer working well, then the H\textsubscript{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\textsubscript{2}S gas sensor 10. The performance of desulfurizer then can be calculated by using equation (1). The performance of desulfurizer was measured for every 5 liters of biogas that passed the desulfurizer and was stopped until reach 50 liters. The averages of desulfurizer performance for total 50 liters then will be calculated and presented in form of graph for analyzed.

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

(1)

III. RESULT AND DISCUSSION

Positive result is obtained from the composition of 100% zinc as can be seen in Fig. 5. The performance of desulfurizer is found optimal to reach 100%. This is caused by during immersion in the salt water, the zinc is corroded and form product of corrosion of ZnO [10]. The ZnO is very reactive to H\textsubscript{2}S according chemical reaction as written in the equation (2) [11].

\[
\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}
\]  

(2)

As can be seen in Fig. 5. The performance of desulfurizer made from 100% Zn is much better that desulfurizer made from 100% Fe. The iron (Fe) also reactive to H\textsubscript{2}S because during immersion in to the salt water will yield the iron oxide (Fe(OH)\textsubscript{3}). This type of iron oxide is reactive to H\textsubscript{2}S according reaction from the equation (3) [12], [13].

\[
2\text{Fe(OH)}_3 + 3\text{H}_2\text{S} \rightarrow \text{Fe}_2\text{S}_3 + 6 \text{H}_2\text{O}
\]  

(3)

An interesting result is obtained for mixture of 75% Zn + 25% Fe as desulfurizer which is resulting also optimum performance. This result is appear due to three reactions with H\textsubscript{2}S to occur: primarily is reaction between ZnO and H\textsubscript{2}S (equation (2)) and small amount reaction between Fe(OH)\textsubscript{3} with H\textsubscript{2}S (equation (3)). Since galvanic coupling between Zn and Fe, the coupling will release ion Zn\textsuperscript{2+}. The desulfurizer was prepared for galvanic coupling.
that will react with H$_2$S as can be explained in Fig 6. Since the number of Zn mass is smaller that Fe in the mixture then the galvanic coupling is not so active in releasing Zn$^{2+}$.

![Schematic of galvanic coupling between Zn and Fe which can yield ion Zn$^{2+}$ that will react with H$_2$S](image)

Figure 6. Schematic of galvanic coupling between Zn and Fe which can yield ion Zn$^{2+}$ that will react with H$_2$S

In contrary, if the contains of Zn and Iron in the mixture is equal as in the mixture of 50% Zn+50% Fe, the performance of desulfurizer become decrease to the level of 83.894% as depicted in Fig. 5. The galvanic coupling is not effective to release Zn$^{2+}$ since the coupling is in the same quantity and further more the fraction of ZnO that more reactive then Fe(OH)$_3$ is reduced make composition of 50% Zn+50% Fe is not appropriate as desulfurizer.

It is important to note that the mixture with composition 25% Zn +75% Fe also resulting an optimum performance as desulfurizer which is reach 100%. Even though contains small amount of Zn that make reaction of ZnO and H$_2$S not as main part of desulfurization process but reaction of Zn$^{2+}$ with H$_2$S become main reaction of desulfurization since quantity of Zn is lower than Fe in the mixture that make galvanic coupling effective to release Zn$^{2+}$ and react with H$_2$S impurity in the biogas.

IV. CONCLUSIONS

The used zinc-carbon type of battery contains Zn case that can be recycled as desulfurizer. By process of immersing in the salt water, the zinc is ready to be used as desulfurizer. Other technique is by mixing with Fe with not in equal quantity for examples 75% Zn+25% Fe or 25% Zn+75% Fe respectively and immersing it in the salt water.

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I Wayan Surata was born in Nusa Penida, Bali, Indonesia on July 5, 1958. He received 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 researcher and lecturer at Department of Mechanical Engineering, Engineering Faculty, Udayana University, Jimbaran, Bali, Indonesia.

I Ketut Adi Atmika was born in Negara, Bali, Indonesia on May 18, 1969. Received Master degree in mechanical engineering From Institute Technology of Sepuluh November, Surabaya, Indonesia. His current job is researcher and lecturer at Department of Mechanical Engineering, Engineering Faculty, Udayana University, Jimbaran, Bali, Indonesia.

Dewa Ngakan Ketut Putra Negara was born in Payangan, Bali, Indonesia on June 13, 1971. He received M.Sc from University of Bradford, UK in 2001 in Manufacturing Systems Engineering and Management. His Current job is researcher and lecturer at Department of Mechanical Engineering, Engineering Faculty, Udayana University, Jimbaran, Bali, Indonesia.

I Wayan Putra Adnyana was undergraduate student at Mechanical Engineering, Udayana University, Jimbaran, Bali, Indonesia and graduated during 2012.