Processing of Steel Chips Waste for Regenerative Type of Biogas Desulfurizer


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Received: 09.11.2012 Accepted: 31.01.2012

Abstract-In this research regenerative type of biogas desulfurizer by utilizing waste steel chips is introduced. The waste of steel chips was obtained form metal forming process of turning. The annealing process was conducted on steel chips prior compacting to yield a billet. The purpose of annealing was to eliminate the residual stress as well as to let the oxidation to occur in order to obtain iron oxide. As residual stress eliminated, the steel chips was possible for compacting as a billet. The annealing process was carried out by burning the steel chip at 900°C. During the annealing process the steel will react with oxygen to form iron oxide (Fe₂O₃) and if during oxidation there is water vapor in the air then the iron bog ore (Fe(OH)₃) will be formed. Both Fe₂O₃ and Fe(OH)₃ are reactive to H₂S and therefore able to eliminate the H₂S contaminant inside the biogas. The result from the process of desulfurization was precipitation of sulfur (S) in the form of Fe₂S₃ in the surface of steel chips which will reduce the performance of desulfurizer. The effectivity of desulfurizer then is recovered by reacting the Fe₂S₃ in the same time with O₂ and H₂O, therefore the desulfurizer can be used again (regenerative used).

Keywords-hydrogen sulfide, desulfurizer, regenerative, waste, steel chips, biogas.

1. Introduction

This work is continuation of our initial work [1]. As an alternative for the renewable energy, the utilization of biogas should be promoted especially for the developing countries due to simplicity and low cost of installation. An improvement for better process should always introduce for the optimum result.

In Asian emerging Countries such as China [2] the rapid economic development has also seen a development in the scales of biogas plants constructed. Although the technology has been improved, it has identified problems in the construction and operation of biogas plants. In South Korea [3] it was found that there are several lacks of conceptual design of biogas technology. Designs which deliver lower cost, improved robustness, functionality, ease of construction, operation and maintenance would aid the market penetration of biogas plants for future of domestic biogas plants in the developing world [4].

As well known that hydrogen sulfide (H₂S) always found in the biogas and generally in the developing country, the biogas digesters are not completed with component to reduce or eliminated the H₂S contaminant. Some of the desulfurizer for filtering the H₂S contaminant are available in the market but the process quite complicated and difficult to be implemented in developing country. Hydrogen sulfide is a harmful gas and very corrosive to metal that corrode the stove. Another serious problem due to existence of the H₂S in the Biogas is: If the biogas is used as a fuel for the internal combustion engine for electrical generator for instance. The combustion chamber will hardly corrode and the function of lubricant of the engine will fail to operate.

The hydrogen Sulfide (H₂S) is a pollutant gas that can be found as contaminant in the commercial gas. The hydrogen Sulfide (H₂S) is a smelly and deadly gas and very corrosive for certain type of metals. The disadvantages of H₂S contaminant is limited the application for a fuel of internal combustion engine [1,5,6,7]. It should be criticized that the recently life cycle assessment of biogas upgrading
technologies [8] is ignoring the existence of the \( \text{H}_2\text{S} \) as impurities in the biogas and only focusing in removing its CO\(_2\) content.

The result of combustion of the gas that contains \( \text{H}_2\text{S} \) is a sulfur and sulfuric acid that is very corrosive to metals. The \( \text{H}_2\text{S} \) content that reach 200 ppm can cause death in 30 minutes. The safety and healthy standard give maximum content of \( \text{H}_2\text{S} \) in the level of 20 ppm [5]. Other sources also informs that the \( \text{H}_2\text{S} \) contaminant will reduce the life time of the plumbing system in the installation in which the biogas is used [1, 9].

The result form the combustion in which the \( \text{H}_2\text{S} \) involved will yield sulfur oxide that will corrode the metal component and cause the lubricant oil become acid. If it is used in the combines heat and power generation (CHP). Therefore to avoid the damage caused by \( \text{H}_2\text{S} \), then this gas should be eliminated or at least have to reduce in the system [1, 9].

As proposed by Deublein, and Steinhauser [9], \( \text{H}_2\text{S} \) is possible to reduce by consider to the reaction with iron. The \( \text{H}_2\text{S} \) will react to the bog steel ore (\( \text{Fe(OH)}_3 \)) or iron oxide of Fe2O3. Both of this reaction is similar and recognize as the way to eliminate \( \text{H}_2\text{S} \) by dry desulfurization processes as written in the Equation (1) and (2).

\[
\begin{align*}
2\text{Fe(OH)}_3 + 3\text{H}_2\text{S} & \rightarrow \text{Fe}_2\text{S}_3 + 6\text{H}_2\text{O} \quad (1) \\
\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{S} & \rightarrow \text{Fe}_2\text{S}_3 + 3\text{H}_2\text{O} \quad (2)
\end{align*}
\]

The result from the process of desulfurization in equation (1) and (2) is precipitation of sulfur (\( \text{S} \)) in the form of \( \text{Fe}_2\text{S}_3 \) in the surface of ironoxide that is used, which will reduce the performance of desulfurization. To recover the affectivity of desulfurization process, the process in equation (3) was introduced. It is by reacting The \( \text{Fe}_2\text{S}_3 \) in the same time with \( \text{O}_2 \) and \( \text{H}_2\text{O} \) which is yield \( \text{Fe(OH)}_3 \) and element of sulfur [9].

\[
\text{Fe}_2\text{S}_3 + 3\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + 6\text{S} \quad (3)
\]

The element of sulfur then was cleaned by flowing water in to the desulfurizer.

It is an urgent to eliminate the \( \text{H}_2\text{S} \) contaminant in the biogas for better quality of combustion and lubrication process in the combustion chamber. Another important reason is \( \text{H}_2\text{S} \) is harmful and poison gas that should be minimize its existence in the biogas. The principal goal of this research is to develop regenerative purification component in the biogas digester system from impurity of \( \text{H}_2\text{S} \) which is can be used repetitively (not only one time use). The material that will be utilized is steel waste chips from the turning process. Effort should be done to recycle this steel chips waste to become biogas purifier from the \( \text{H}_2\text{S} \) impurity.

2. Experimental

The experimental was started by selecting the waste of steel chips. Fig. 1 is the waste of the steel chips (low carbon steel) obtained from the turning process. Effort should be done to recycle this steel chips waste to become biogas purifier from the \( \text{H}_2\text{S} \) impurity.

Fig. 1. The waste of steel chips.

Only spiral and long types of chips were selected. The annealing process was conducted in the furnace by burning the chips at 900°C with slowly cooling. The oxidation process was also happen during process of annealing to yield \( \text{Fe}_2\text{O}_3 \) and also \( \text{Fe(OH)}_3 \). Fig. 2 is the appearance of the chips after annealing and oxidation process. The result from process of annealing is the steel chips free from residual stress due to turning process, therefore it is possible to be compacted as a billet. The size of each billet was 1 cm of thickness, with 6 cm of diameter, and the weight was 50 gram as shown in Fig. 2.

Fig. 2. The appearance of the steel chips after annealing and oxidation process.

The compacting process was conducted by using cylindrical die and was compacted by using hydraulic pressing machine. There were 10 billet was provided in this research with total weight of 500 gram. Afterward the billets were set in the pipe of biogas line. The biogas was obtained directly from the fixed dome digester [4]. The advantage of this type of digester is the application without bag of gas holder or without storing the biogas. The flow of Biogas is caused by high pressure that is yield by the dome. The biogas then was flowed to pass the billet with the rate about 4 liter/minute. This flow rate is an average of the flow rate in the biogas system for the household during cooking. The \( \text{H}_2\text{S} \) concentration before and after passing the billet then was detected and measured by using gas analyzer as described in Fig. 3. The appearance of the billet.

Fig. 3. The appearance of the billet.
Fig. 4.(a). The measurement in this research was done up to volume of 300 liters of biogas that flow through the billet. The volume measurement of the gas was conducted by using gas volume meter as shown at Fig 4(b).

![Portable H₂S gas analyzer](image1)
![Gas volume meter](image2)

Fig. 4. (a) Portable H₂S gas analyzer, (b) Gas volume meter

After 300 liters of biogas passed the desulfurizer, the process of 1<sup>st</sup> recovery was conducted by putting the desulfurizer into the water with bubbling air in order reaction in Equation (3) to occur. The performance of desulfurization after 1<sup>st</sup> recovery then was evaluated by measuring the H₂S concentration before and after passing the desulfurizer. To ensure that the desulfurizer can be used repeatedly, 2<sup>nd</sup> recovery was conducted again after passing 300 liter of biogas and tested again its performance after used as desulfurizer for the next 300 liter of biogas. The result is presented in the graph for analyze. The laser induced breakdown spectroscopy (LIBs) was used to proof that there is a residue of sulfur in the desulfurizer.

3. Result and Discussion

A positive result is obtained in this research that make possible for the waste of steel chips to be used as a desulfurization of biogas repetitively. Fig. 5 is the graph of ability of the desulfurizer at initial performance after passing 300 liter of biogas. Initially the desulfurizer is able to reduce H₂S contends up to around 80% and then decrease gradually until reach around 30% after use to purify about 300 liter of biogas. In this process the Equation 1 and 2 as proposed by Deublein, and Steinhauser [9] is found to occur.

The performance of desulfurizer after 1<sup>st</sup> recovery is presented in Fig 6. The performance increase significantly to reach around 90% and just a little decrease until reach 85% after passing 300 liter of biogas. Finally the result from 2<sup>nd</sup> recovery is depicted in Figure 7. The performance of desulfurizer again increases to reach 90% and gradually decrease again to reach around 30%. The Equation 3 that is suggested by Deublein and Steinhauser [9] is occurred during recovery process. It can be proofed that the desulfurizer that is developed in this research work successfully and can be used repetitively. Previously, for the purpose of using biogas as an engine fuel, the existence of H₂S in the biogas was overcome by increasing frequency of engine oil change which is will increase the operating cost [10]. By using the technology in this invention, a frequency oil change can be avoided. In comparison with recently publication related with desulfurization of the biogas [11], the invention in this report still have advantage which is can be used repetitively so that designs which deliver lower cost, improved robustness, functionality, ease of construction, operation and maintenance [4] can be realized.
It should be noted here that water is used in the process of recovery in this research together with bubbling air. In order there is no condensate of water after recovery process, a hot air (simply by using hair drier) was blowed in to the desulurizer. Water condensat was recognized can reduce the sensitivity of Fe$_2$O$_3$ or Fe(OH)$_3$ as desulurizer [12].

The laser induced breakdown spectroscopy (LIBs) was used to detect the existence of sulfur in the slurry precipitate during recovery process as depicted in Fig 8. At the wave length around 550 nm is found the peak for sulfur (S). The recovery process that is conducted by putting the desulurizer in to the water with bubbling air which is yield a waste of brown slurry with contain sulfur (S) in the water and can easily taken out by let it precipitate at the bottom of the recovery batch.

In this research only 500 gram of the desulfurizer billet was installed with specific flow rate of biogas (4 liters/minute). For the application in the final product the mass of the billet should determined by direct measurement of the H$_2$S impurity that is detected after passing the desulfurizer. If the biogas still contains H$_2$S impurities, then the mass of the billet should be added until reach zero level of H$_2$S impurities.

4. Conclusion

It can be concluded that the desulfurizer that is developed in this research is proofed successfully to reduce H$_2$S impurity in the biogas repetitively. This is meant that the desulfurizer can be use not only one time as desulfurizer that available in the market by today but can be used repetitively. The material uses for desulfurizer is obtained from the waste of steel chips which is yield in low cost for commercialization for the mass scale.

Acknowledgements

This research was supported financially by the Ministry of Education Culture The Republic of Indonesia through Scheme National Strategic Research under contract number: 30.7/UN.14/LPPM/2012.

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