BIODESULPHURIZATION WITHIN NATURAL GAS IN OIL AND GAS FIELD

Sri Astuti Rahayu, M. Fierdaus, Syafrizal, and M. Udiharto

Research and Development Centre for Oil and Gas Technology, Jakarta, Indonesia

E-mail: sriar@lemigas.esdm.go.id

Abstract

The presence of sulphur compounds in natural gas can interfere to the quality of natural gas. The decline of combustion gas capacity, metal instrument corrosion in gas piping, and the environmental pollution from gas emission can affect by their presence. Bio-filter is one of the methods that selected to reduce sulphur content in natural gas. A lab scale study of hydrogen sulphide reduction in natural gas had conducted in oil and gas field using bio-filter method. The bio-filter system (±1 L volume) contains an active carbon and thiosulphide medium as a substrate, *Thiobacillus thioparus* as a single culture of sulphur bacteria, and *Thiobacillus thioparus* with sludge as a mixed culture of sulphur bacteria. The study of hydrogen sulphide reduction was conducted with continuous flow line process. The gas flow rate approximately 1.5 L/min with a fluctuate presence of Hydrogen sulphide (approximately 40 – 70 mg/L). The bio-filter system contains active carbon, thiosulphide medium, and single culture of *T. thioparus* appear as a good filter for hydrogen sulphide reduction. During 24 hours, the hydrogen sulphide reduction obtains 93% to 16%. When culture media added, the hydrogen sulphide reduction will increase almost 60% and then the reduction decrease to 4% after 20 hours. It is concluded that the bio-filter have potential to develop for sulphur reduction in natural gas.

Keywords: biofilter, hydrogen sulphide reduction

1. Introduction

Presently the natural gas constitute as potential energy source in the world. The availability of natural gas reserve is higher than the reserve of crude oil. The quality of natural gas can interfered with the presence of sulphur compounds. The presence of them in natural gas can make the decline of combustion gas capacity, metal corrosion in gas piping/instrument, and the environmental pollution from gas emission, etc.

The presence of sulphur compounds in natural gas must be reduced to preserve the quality of natural gas. Commonly, sulphur compound in natural gas is removed by chemical treatment, but this method have many disadvantages including the high cost of equipment, toxic chemical usage and secondary contaminations. On the other hand, the biological treatment can be reduced sulphuric compound without high cost equipment.

Various microbes, both aerobic and anaerobic, can be used to remove sulphur compound. The aerobic microbes that are known to oxidize hydrogen sulphide are *Thiobacillus, Pseudomonas, Beggiatoa, Thiotrix. Thiobacillus* species such as *T. thioparus, T. thiooxidans, T. ferooxidans, T. denitrificans, T.* sp. are most widely used in laboratory scale test [1-6].

T. thioparus isolated from soil which taken surrounding of wellhead in an oil field, this bacteria capable to reduced sulphur content in crude oil, the reduction of sulphur compound has reached 26% during 48 hours [7] *T. thiooxidans* can oxidized sulphur to sulphide, with 1 mol of O_2 consumption per mol of sulphur oxidize to sulphide, when the oxidation of sulphide is inhibited with 2-n-heptyl-4-hydroxyquinoline N-oxide [8]. *T. neapolitanus* that isolated from soil of an oil field is capable to reduced sulphur compounds in petroleum, the reduction of sulphur compound has reached 9.5 % during 48 hours incubation [9]. The oxidation reaction by aerobic species in standard conditions are as follows [10]:

$$H_2S + 2O_2 \longrightarrow SO_4^{2-} + 2H^+ \quad (1)$$
$$\Delta G_o = -188.7 \text{ Kcal mol}^{-1}$$

$$S + H_2O + 1.5O_2 \longrightarrow SO_4^{2-} + 2H^+ \quad (2)$$
$$\Delta G_o = -140.6 \text{ Kcal mol}^{-1}$$

$$S_2O_3^- + H_2O + 2O_2 \longrightarrow 2\,SO_4^{2-} + 2H^+ \quad (3)$$
$$\Delta G_o = -97.7 \text{ Kcal mol}^{-1}$$

A bio-filter system immobilized with *Thiobacillus* sp. showed a 95% removal efficiency of hydrogen sulphide at gas flow rate up to 93 litre h^{-1} with an inlet concentration of 60 ppm, but the efficiency was reduced to 78% for gas flow rate of 180 litter h^{-1} and the reduction was attributed to diffusion limitation [11].

Thiobacillus sp. IW showed optimum growth at 30oC, pH 7 and was in the exponential growth period for 9 – 21 hours [12]. The specific growth rate of *Thiobacillus* sp. IW in the exponential growth period was 1.1 h-1 and the cell doubling time was 38 min [13].

2. Objective of the Study

The aim of the biodesulphurization study is to reduce hydrogen sulphide in natural gas by bio-filter system. The study is laboratory scale and it is conducted in an oil and gas field.

3. Material and Methods

Microbial culture
Two type culture microbes that used in the study as hydrogen sulphide reduction are *Thiobacillus thioparus* as single culture and microbial from sludge as mixed culture. *T. thioparus* isolated from the soil which taken from an oil field. Mixed cultures isolated from a sewer. All microbes is grown in thiosulphate medium.

Biofilter
The reduction of hydrogen sulphide in natural gas use bio-filter system. The unit of bio-filter is shown in Figure 1. The tubes of filter are made from glass. It filled with active carbon and thiosulfat medium as substrate, and single or mixed culture microbes as sulphur reduction. Three type filter are used for treatment process. The first type (M-1) using only active carbon and thiosulfat medium as filter. Second type (M-2) using active carbon, thiosulfat medium, and single culture of T. thioparus. The third type (M-3) similary with type M-2 whereas single culture was substituted by mixed cultures.

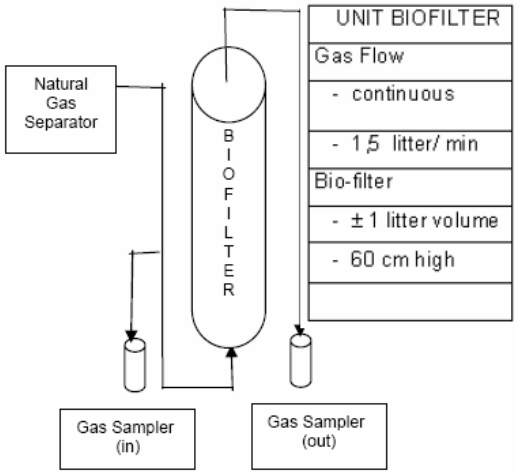

Figure 1. Schematic diagram of bio-filter unit

Analysis
Hydrogen sulphide content, microbial cell population, and pH were investigated to monitor the activities of desulphurization. Hydrogen sulphide content is measured by titrimetric method, cell population is calculated by plate count method, and pH is measured with pH meter.

Calculation of hydrogen sulphide reduction
Hydrogen sulphide reduction is calculated by using Equation as follow:
Hydrogen sulphide reduction =

$$\frac{H_{inlet} - H_{outlet}}{H_{inlet}} \times 100\% \quad (4)$$

Where:
H_{inlet} : the amount of H_2S content in natural gas before came in the biofilter
H_{outlet} : the amount of H_2S content in natural gas after came out the biofilter

4. Results and Discussions

Component of Natural Gas
The application of the desulphurization study had conducted with natural gas in some oil and gas field. This study is still laboratory scale with the feed gas came from separator. During normal operation, the gas pressure on separator is about 220 psi. The natural gas which came out from separator contain very low (nil) water. The component of natural gas (except sulphur content) are showed on Table 1. The content of hydrocarbon compounds are more than 50%, and almost 40% is carbon dioxide.

Table 1. Component of natural gas as feed for desulphurization

No.	Component	% mol
1	O_2	0.00
2	N_2	1.25
3	CO_2	39.36
4	C_1 (methane)	42.57
5	C_2 (ethane)	6.80
6	C_3 (propane)	6.00
7	i-C_4 (iso butane)	1.02
8	n-C_4 (normal butane)	1.47
9	C_6+ (hexane plus)	0.68
		100

Natural gas contains many kind of sulphur compounds which hydrogen sulphide is dominant. During application of the study, the hydrogen sulphide content in natural gas is fluctuate about 40 to 70 mg/L. The result of hydrogen sulphide analysis is showed on Figure 2.

Desulphurization on Natural Gas

Desulphurization of this study base on hydrogen sulphide reduction in natural gas. Reduction of hydrogen sulfite in natural gas treated by bio-filter. The bio-filter contains substrate, additive, and microbial. Active carbon used as substrate and thiosulfat medium used as additive. There is three way of the treating for desulphurization process. Method number one (M-1) is hydrogen sulphide reduction treatment without microbial addition, the second (M-2) is treatment with *Thiobacillus thioparus* culture addition, and the third (M-3) is treatment with additional mixed culture. The capability of three type treating within hydrocarbon sulphide reduction is showed on Figure 3.

During five hours incubation, bio-filter containing active carbon without microbial culture addition (M-1) capable to reduce hydrogen sulphide content in natural gas. The reduction obtained 50% to 70%. When *T. thioparus* culture added (M-2), the reduction will be increase 60% up to more than 90%. The result showed that *T. thioparus* capable to reduce hydrogen sulphide content in natural gas.

T. thioparus, a member of sulphur bacteria, is potential to support desulphurization process. However, the treatment with mixed culture addition showed the opposite. In few minutes during the process, the reduction is decrease. This condition indicated that mixed culture were not dominated with sulphur microbes. It clearly showed in Figure 4. The population of mixed culture is lower than *T. thioparus* population. Thus, mixed culture are not potential to develop for hydrogen sulphide reduction in natural gas.

During hydrogen sulphide reduction acid matter was produced. It showed by decreasing of pH (see Figure 5). However, the ph level is still suitable for bacterial growth condition.

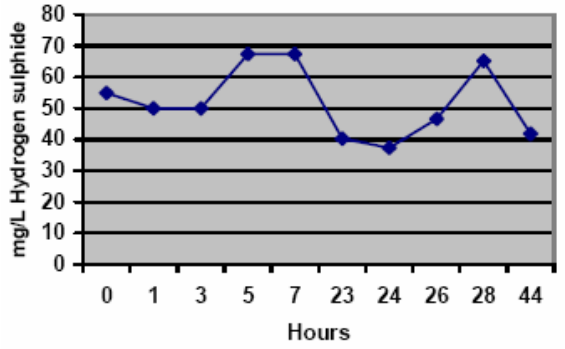

Figure 2. Result analysis of hydrogen sulphide content on natural gas during desulphurization process

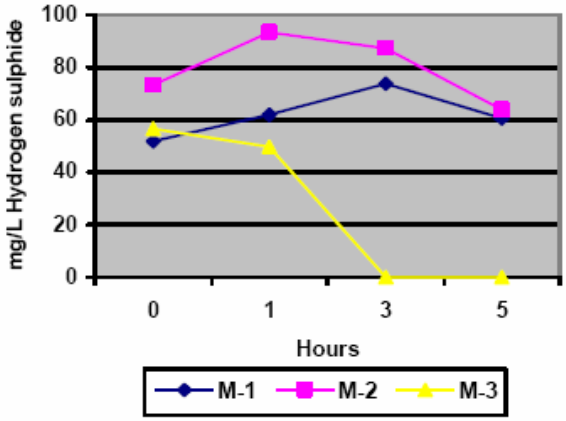

Figure 3. The capability of three type of treatment (M-1; M-2; M-3) within hydrogen sulphide reduction on natural gas

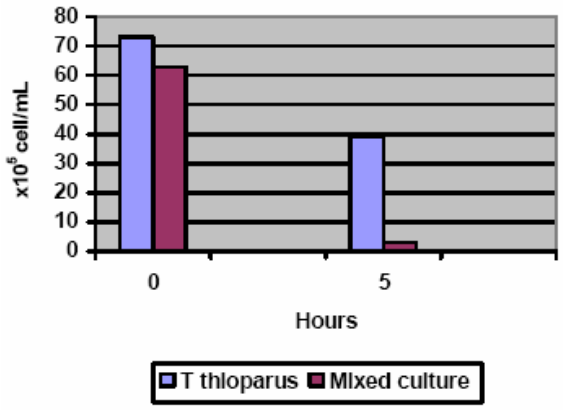

Figure 4. The calculation of microbial population during five hours incubation

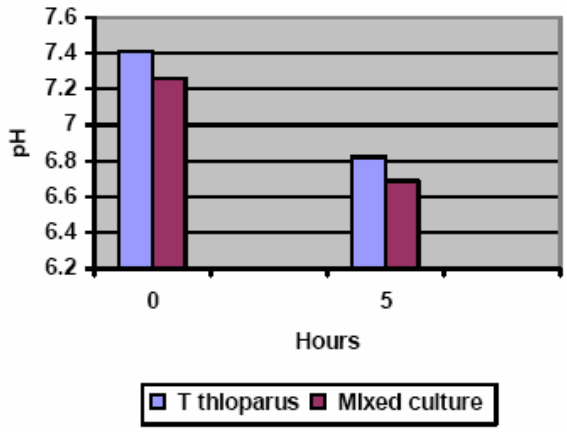

Figure 5. pH level of substrate during five

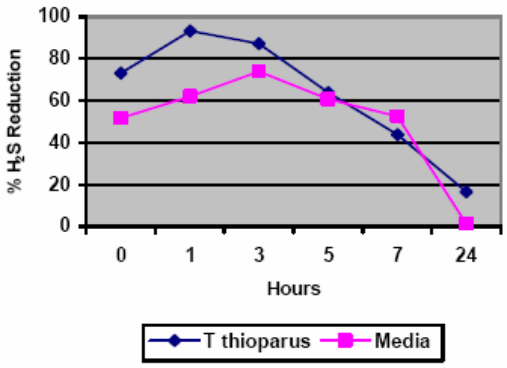

Figure 6. Hydrogen sulphide reduction on bio-filter M-1 and M-2 during 24 hours incubation

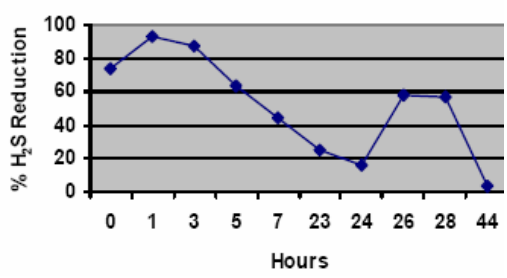

Figure 7. Hydrogen sulphide reduction on bio-filter which contain active carbon as substrate and culture of *T. thioparus* during 44 hours incubation

The data showed the capability of bio-filter M-1 and M-2 for desulphurization process on 5 hours. If Incubation process continued until 24 hours, the result is showed on Figure 6. On the bio-filter M-1 (without microbial addition), the maximum hydrogen sulphide reduction (73%) has reached in 3 hours and after 24 hours there is no more reduction. When the bio-filter is added with *T. thioparus* culture, the maximum reduction (increase to 93%) has obtained in 2 hours and after 24 hours the reduction is still 16%. The reduction is increase significantly by *T. thioparus* culture addition.

Furthermore, the capability of bio-filter M-2 (with *T. thiopharus* culture addition) was observed more longer. The activity bio-filter M-2 as reducer hydrogen sulphide has decrease to 16% after 24 hours incubation. After fresh thiosulphide medium was added, it is obvious that hydrogen sulphide reduction has increase almost to 60%, and reduction will be decrease to 4% after 44 hours incubation. The data of this desulphurization process has showed in Figure 7

5. Conclusion

Bio-filter with active carbon and thiosulphide medium as a substrat has capable to reduce hydrogen sulphide content in natural gas. But the capability of this biofilter as reducer is limited and they can not be activated again. Bio-filter containing active carbon, thiosulphide medium, and *T. thiopharus* is more active to reduce hydrogen sulphide in natural gas. The capability of this bio-filter as reducer is not limited and they can be activated.

References

[1] Cho, K.S., Zang, L., Hirai, M., Shoda, M., 1991. Removal characteristics of hydrogen sulphide and methanethiol by *Thiobacillus* sp. Isolated from peat in biological deodourisation. Journal of Fermentation and Bioengineering 71, 44-49.

[2] Ryu, H.W., 1996. Microbial desulphurization of a bituminous coal by iron-oxidazing bacteria *Thiobacillus ferrooxidans*. Korean Journal of Biotehnology and Bioengineering 11, 238-245.

[3] Chung, Y.C., Huang, C., Tseng, C.P., 1999a. Biodegradation of hydrogen sulphide by a laboratory-scale immobilized *Pseudomonas putida* CH11 Biofilter. Biotechnology Progress 12, 773-778.

[4] Chung, Y.C., Huang, C., Tseng, C.P., 1999b. Kinetics of hydrogen sulphide oxidation by immobilized autotrophic bacteria in bioreactors. Biotechnology Techniques 10, 743-748.

[5] Hallberg, K.B., and Borje, E., 1994. Characterization of *Thiobacillus caldus* sp. Nov., a moderately Thermophilic acidophile, Mycrobiology, vol. 140 part 12.

[6] Oh, K.J., Kim, D., Lee, I.-H., 1998. Development of effective hydrogen sulphide removing equipment using *Thiobacillus* sp. IW. Environmental Pollution 99, 87-92.

[7] Udiharto, M., 1997a. Desulphurization of petroleum using *Thiobacillus neapolitanus*, LEMIGAS Scientific Contributions, 2 / 1997.

[8] Suzuki, I., et al, 1992. Oxidation of elemental sulphur and sulphide by *Thiobacillus thiooxidans*. Cell Applied and Environmental Microbiology, Nov., p 3767-3769.

[9] Udiharto, M., 1997b. Desulfurisasi dalam minyak bumi dan medium oleh *Thiobacillus thioparus*. Proceeding Temu Karya Pengolahan, Jakarta.

[10] Brock, T.D., Madigan, M.T., 1991. Biology of Microorganisms, 6th Edition. Prentice-Hall, Englewood Cliff, NJ.

[11] Huang, C., Chung, Y.C., Hsu, B.M., 1996. Hydrogen sulphide removal by immobilized autotrophic ang heterotrophic bacteria in the bioreactors. Biotechnology Techniques 10, 595-600.

[12] Cha, J.M., Park, Y., Lee, I.W., 1994. Effect of cultivation condition on growth of hydrogen sulphide-degrading *Thiobacillus* sp. IW isolated

from waste coal mine water. Korean Journal of Biotechnology and Bioengineering 9, 287-293.

[13] Kim, S.M., Oh, K.H., Kim, D., 1996. The immobilized characteristics of *Thiobacillus sp*. IW. Korean Journal of Biotechnology and Bioengineering 11, 78-85.