### FRI-9.3-1-THPE-08

# A REVIEW OF THE TECHNOLOGIES FOR HYDROGEN SULFIDE REMOVAL AND UTILIZATION FROM BIOGAS INSTALLATIONS

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**Abstract:** Current material presents an overview of the existing hydrogen supfide  $(H_2S)$  removal and utilization technologies and provides discussions about its application to biogas installations. A new 2-steps technology is proposed for separation of  $H_2S$  gas to Sulfur and  $H_2$  on the first step and for  $H_2$  gas utilization on the second step.

Keywords: biogas installation, hydrogen sulphide, H<sub>2</sub>S utilization, H<sub>2</sub>S removal

#### **INTRODUCTION**

Biogas typically refers to a mixture of several gases that are produced by the decomposition of organic matter in the absence of oxygen. Its liquid counterparts include biodiesel and biogasoline. Biogas can be produced from raw materials such as agricultural waste, manure, municipal waste, plant material, sewage, green waste or food waste. Biogas is a renewable energy source and in many cases exerts a very small carbon footprint.

The composition of biogas varies with the type of feed stock and operating condition of the digester. In Table 1 are listed the main components of a biogas.

| Species          | Chemical         | Heating value | Units | Volume fraction |
|------------------|------------------|---------------|-------|-----------------|
|                  | formula          | kJ/kmol       |       |                 |
| Methane          | CH <sub>4</sub>  | 802500        | %     | 50-75           |
| Carbon dioxide   | $CO_2$           | -             | %     | 25-45           |
| Water            | H <sub>2</sub> O | -             | %     | 2-7             |
| Hydrogen sulfide | $H_2S$           | 518150        | ppm   | 20-20000 (<2%)  |
| Nitrogen         | $N_2$            | -             | %     | <2              |
| Oxygen           | $O_2$            | -             | %     | <2              |
| Hydrogen         | H <sub>2</sub>   | 241840        | %     | <1              |

Table 1. Biogas components

Methane is the component of a biogas that contributes the most to its heating value.

Hydrogen sulfide is typically one of the most problematic components of a biogas because it is toxic and corrosive to most equipment. Additionally, combustion of  $H_2S$  leads to sulfur dioxide emissions, which have harmful environmental effects. Removing  $H_2S$  at the earliest possible stage is recommended to protect downstream equipment, increase safety, and enable possible utilization of more efficient technologies such as micro turbines and fuel cells.

The intent of this paper seeks to highlight briefly the present status, challenges, and potential of the main technologies for hydrogen sulfide removal and utilization in biogas installations

#### EXPOSITION

#### Traditional H<sub>2</sub>S gas-phase removal methods

#### Dry H<sub>2</sub>S Removal Processes

The dry  $H_2S$  removal techniques have historically been used at facilities with less than 200 kg of S per day (Lena Neija et al., 2016). All of the dry sorption processes given here is configured with dry media in box or tower type vessels where gas can flow upwards or downwards through the media. Since all of the dry-sorption media to be discussed eventually becomes saturated with contaminant and inactive, it is common to have two vessels operating in parallel. In this way, one of the vessels remains in service while the other one is being offline for media replacement or regeneration.

**Iron Oxides** - As one of the oldest methods still in practice, iron oxides remove sulfur by forming insoluble iron sulfides. It is possible to extend bed life by admitting air, thereby forming elemental sulfur and regenerating the iron oxide, but eventually the media becomes clogged with elemental sulfur and must be replaced. The most well - known iron oxide product is called "iron sponge". Iron-oxide-impregnated wood-chips (generally pine) are used to selectively interact with  $H_2S$  and mercaptans. The primary active ingredients are hydrated iron - oxides (Fe<sub>2</sub>O<sub>3</sub>) of alpha and gamma crystalline structures. Lesser amounts of Fe<sub>3</sub>O<sub>4</sub> (sometimes referred to as  $FeO \cdot Fe_2O_3$ ) also contribute to the activity.

Alkaline Solids - Alkaline substances, such as hydrated lime, will react with acid gases like

 $H_2S$ ,  $SO_2$ ,  $CO_2$ , carbonyl sulfides and mercaptans in neutralization reactions. Usually liquid-based scrubbers are used, but fixed-beds of alkaline granular solid can also be used in a standard dry box arrangement with up-flow of gas.

*Adsorbents* - According to (Cheng Chen et al., 2016) adsorbents rely on physical adsorption of a gas-phase particle onto a solid surface, rather than chemical transformation as discussed with the previously dried sorbents.

*Molecular Sieves* (*Zeolites*) - Zeolites are naturally occurring or synthetic silicates with uniform pore size and dimension and are especially useful for dehydration or purification of gas streams. Polar compounds, such as  $H_2O$ ,  $H_2S$ ,  $SO_2$ ,  $NH_3$ , carbonyl sulfide, and mercaptans, are very strongly adsorbed and can be removed from such non-polar systems as CH<sub>4</sub>.

*Activated Carbon* - Granular activated carbon is a preferred method for removal of volatile organic compounds from industrial gas streams (Yiwen et al., 2016).

#### Liquid H<sub>2</sub>S Removal Processes

The Liquid-based  $H_2S$  removal processes have replaced many dry-based technologies for natural-gas purification due to reduced ground-space requirements, reduced labor costs, and increased potential for elemental-sulfur recovery.

*Iron- and Zinc-Oxide Slurries* - Iron-oxide slurry processes historically mark the transition between dry-box technologies and modern liquid-redox processes. The basic chemistry is similar to that for the dry oxide reactions.

*Chelated-Iron Solutions* - Chelated-iron solutions utilize iron-ions bound to a chelating agent and are gaining popularity for H<sub>2</sub>S removal (Elena Sisani et al., 2014).

Alkaline Salt Solutions - As with alkaline solids, acid gases such as  $H_2S$  and  $CO_2$  react readily with alkaline salts in solution. The regenerative processes employ alkaline salts including sodium and potassium carbonate, phosphate, borate, arsenite, and phenolate, as well as salts of weak organic acids.

*Caustic Scrubbing* - Hydroxide solutions are very effective at removing  $CO_2$  and  $H_2S$ , but are non-regenerative mercaptans (R-SH). Process can be organized so to get less-strongly-bound mercaptides, which are regenerable at high temperatures, and commercial caustic-plants have operated with this specialty (Michel Reinderr et al., 2015).

*Amine Solutions* - The amine processes constitute the largest portion of liquid-based naturalgas purification technologies for removal of acid gases. They are attractive because they can be configured with high removal efficiencies, designed to be selective for  $H_2S$  or both  $CO_2$  and  $H_2S$ , and are regenerable.

*Physical Solvents* – When acid gases make up a large proportion of the total gas stream, the cost of removing them with heat-regenerable processes, such as amines, may be out of line with the value of the treated gas. Physical solvents, where the acid gases are simply dissolved in a liquid and flashed off elsewhere by reducing the pressure, have been employed with limited success. Since these processes depend on partial-pressure driving forces, some product will invariably be lost, especially at higher pressures.

*Water Washing* - Liquids with increased solubility for  $CO_2$  and  $H_2S$  is typically chosen over water, but the principal advantages of water as an absorbent are its availability and low cost.

*Membrane Processes* - Membranes operate based on differing rates of permeation through a thin membrane, as dictated by partial pressure. Because of this, 100% removal efficiency is not possible in one stage, and some product will inevitably be lost (Cheng Chen et al., 2016).

Based on the study of the existing  $H_2S$  removal technologies a new method is proposed for  $H_2S$  removal from biogas installations. This method suggests decomposing hydrogen sulfide to hydrogen and sulfur. The scheme of the idea is shown on Fig. 1.



Fig. 1. Schematic diagram of the proposed H<sub>2</sub>S decomposition technology

The H<sub>2</sub>S decomposition can be done using some of the processes given below.

### **Thermal decomposition**

### Thermodynamic considerations

Hydrogen sulfide breaks down into hydrogen and sulfur on the application of heat. At lower temperatures, molecules of vapor containing one to eight atoms of sulfur and many sulfane species  $(H_2S_2 \text{ to } H_2S_8)$  may be present in the reacting mixture. Equilibrium calculations have been made for the complex equilibrium mixture by free energy minimization techniques and the results have been verified experimentally (J. Zaman et al., 1995). It is observed that in the temperature range 973-1123 K and pressure 101-405 kPa, the diatomic sulfur molecules constitute more than 99.8% of the total sulfur molecules. Experimental conversions obtained at lower pressures also agreed with these results. Overall, since the decomposition reaction requires temperatures in excess of 1000 K for significant conversions, the sulfur produced will be necessarily diatomic. The thermal decomposition reaction can therefore be considered to follow the stoichiometric reaction given by equation 1:

$$2H_2S \Leftrightarrow 2H_2(g) + S_2(g) \tag{1}$$

The process of thermal decoposition can be organised by using different types of reactors, examples of which are given in Table 2.

| Type of reaction | Operating variables                            | Important results                       |
|------------------|--|---|
| system           |  |   |
| Tubular reactor  | 873-1133K, pressure 131-314kPa                 | Kinetic studies were carried out        |
|                  |  | for thermal decomposition               |
| Recirculating    | 773-1073K, pressure 5.3-12kPa,                 | 95% conversation of H <sub>2</sub> S by |
| reactor          | MoS <sub>2</sub> and WS <sub>2</sub> catalysts | continuous removal of S and             |
|                  |  | intermittent removal of H <sub>2</sub>  |
| Membrane reactor | 673-1073K, MoS <sub>2</sub> , catalyst         | Conversion twice the                    |
|                  |  | equilibrium value obtained              |

Table 2. Reactors used for thermal decomposition

| Thermal diffusion | Hot wall at 673-1073 K, Cold wall at   | Equilibrium shift obtained       |
|-------------------|--|----------------------------------|
| reactor           | 353-373 K, Catalysts/sulfides used   | because of separation of         |
|                   | $MoS_2$ , $V_2S_3/FeS$ , $V_2S_3/Cu_9S_5$ ,  | products. The performance        |
|                   | $V_2S_3/ZnS$ , Fe <sub>7</sub> S <sub>8</sub> , Fe <sub>7</sub> S <sub>8</sub> /MoS <sub>2</sub> and | evaluated with different         |
|                   | Fe <sub>7</sub> S <sub>8</sub> /NiSi <sub>2</sub>  | catalysts and reactor variables  |
| Solar reactor     | Temperature 893-1043K, catalysts   | Cobalt – molybdenum catalyst     |
|                   | used: Ni-W,Ni-Mo,Co-Mo and   | has the highest activity. A      |
|                   | alumina  | hydrogen yield of 19% was        |
|                   |  | obtained at 770°C and residence  |
|                   |  | of 0.3 s. Kinetic rate equations |
|                   |  | were developed                   |

Hydrogen sulfide plasma dissociation is a promising method for  $H_2S$  utilization. The conventional method based on multi-stage Claus Process is currently considered the industry standard (Guldal et al, 2015). The Claus process is based on partial oxidation of  $H_2S$ , which results in the production of sulfur and water:

$$2H_2S + O_2 \to S_2 + 2H_2O \tag{2}$$

Plasma dissociation of H<sub>2</sub>S follows the direct dissociation path:

 $2H_2S \rightarrow S_2 + 2H_2$ 

(3)

There are two main benefits of dissociation over the Claus Process. The first one is the production of hydrogen, which is widely used in the oil refining industries and also is considered as "green" fuel. The second one is the high specific productivity of catalyst-free plasma process that can reduce capital cost of  $H_2S$  utilization.

# **APPLICATION OF HYDROGEN AND SULFUR**

Shematic representation of the possible applications of the derived hydrogen and sulfur are given on Fig. 2 and Fig. 3.



Fig. 2- Hydrogen utilisation



Fig. 3. Sulphur utilisation

# CONCLUSION

This paper summarizes some of the exsisting methods for removal of hydrogen sulfide from biogas mixtures of different origin. It was focused on the possible aspects of  $H_2S$  separation, its chemical convertion and products' utilization.

Based on this review a separate study will be conducted. This study aims at investigating a two-stage technology for  $H_2S$  decomposition to  $H_2$  and S. The first stage envisages  $H_2S$  capturing. The second stage aims at deriving elemental sulfur and hydrogen.

# REFERENCES

Cheng Chen, Wenshan Guo, Huu Hao Ngo, Duu-Jong Lee, Kuo-Lun Tung, Pengkang Jin, Jie Wang, Yun Wu, *Challenges in biogas production from anaerobic membrane Bioreactors*, Renewable Energy, v.98, 120-134, 2016

Sisani, E., Cinti, G., Discepoli, G., Penchini, D., Umberto Desideri, U., & Marmottini, F. (1995). Adsorptive removal of  $H_2S$  in biogas conditions for high temperature fuel cell systems, International journal of hydrogen energy, v.39, 1753 - 1766

J. Zaman, A. Chakma, Production of hydrogen and sulfur from hydrogen sulfide, Fuel Processing Technology 41 (1995), 159-198

Neija, L., Heiskanenb, E., & Strupeita, L. (2017). *The deployment of new energy technologies and the need for local learning*, Energy Policy, v.101,274–283

Reinders, M., Beckhaus, P., Illing, F., Misz, U., Riße, H., Schreoder, M., Schulte, P., & Teichgreaber, B. (2015). *Biogas as a source for producing hydrogen at wastewater treatment plants e EuWaK - A pilot project*, International journal of hydrogen energy, v.40, 8601 - 8606

Guldal, N. O., Figen, H. E., & Baykara, S. Z. (2015). *New catalysts for hydrogen production from H*<sub>2</sub>*S: Preliminary results*, International journal of hydrogen energy, v.40, 7452 - 7458

Yiwen Ma, Zezhi Chen, Huijuan Gong, Study on selective hydrogen sulfide removal over carbon dioxide by catalytic oxidative absorption method with chelated iron as the catalyst, Renewable Energy, v.96, 1119-1126, 2016