A Retrospection of Hydrogen Sulphide Removal Technologies in Biogas Purification

Srinivas Kasulla¹, S J Malik², Salman Zafar³, Aparna Saraf⁴

¹Waste to Energy Expert, Hyderabad, Telangana, India ²Biogas Expert, Pune, Maharashtra, India ³Bioenergy Consult, Uttar Pradesh, India ⁴The Institute of Science, Mumbai, Dr Homi Bhabha State University, India

ABSTRACT

Biogas is a valuable renewable energy source and a secondary energy carrier provided by anaerobic digestion of biodegradable organic materials. It can be used as a fuel in a number of ways. Methane (CH₄) and carbon dioxide (CO₂) are the main components of biogas, with other pollutants such as ammonia (NH₃), water vapour (H₂O), hydrogen sulphide (H₂S), methyl siloxanes, nitrogen (N₂), oxygen (O₂), halogenated volatile organic compounds (VOCs), carbon monoxide (CO), and hydrocarbons present in varying amounts. H₂S is a toxic and odorous compound formed by the anaerobic digestion of bio-solids and other organic materials, and it is also one of the pollutants in biogas. Hydrogen sulphide must be eliminated because it is toxic to human health, poisonous to process catalysts, and corrosive to machinery. Desulfurization, or the removal of hydrogen sulphide, is an integral part of biogas utilization efficiency. The conventional desulfurization technologies for biogas that are currently available were reviewed in this paper.

KEYWORD: Biogas, Methane, Carbon dioxide, Hydrogen sulphide, Carbon monoxide, Hydrocarbons, Ammonia

of Trend in Scientific Research and Development

SSN: 2456-6470

How to cite this paper: Srinivas Kasulla | S J Malik | Salman Zafar | Aparna Saraf "A Retrospection of Hydrogen Sulphide Removal Technologies in Biogas

Purification"PublishedinInternational Journalof Trend in ScientificResearchandDevelopment (ijtsrd),ISSN:2456-6470,Volume-5| Issue-3,



April 2021, pp.857-863, URL: www.ijtsrd.com/papers/ijtsrd39996.pdf

Copyright © 2021 by author (s) and International Journal of Trend in Scientific Research and Development Journal. This

(CC

(http://creativecommons.org/licenses/by/4.0)

is an Open Access article distributed under the terms of the Creative Commons

License



BY

Attribution

4.0)

INTRODUCTION

Waste management has become a critical issue for everyone, particularly in urban India. When the world's population grows, so does the amount of waste generated and proper waste management has become a necessity. Biogas accounts for just 1.5 percent of total global renewable energy, but it has grown at a rate of 15% per year since 1990. When it comes to crude oil, the price is rising while the supply is declining, placing economic pressure on developing countries. Furthermore, the demand for energy in all industries has risen significantly, resulting in increased waste production and the use of renewable resources. To meet these demands, more renewable energy options must be explored. The growing energy crisis is posing a serious threat to humanity's long-term development, and the need for renewable energy is becoming increasingly urgent. As a new green energy source, biogas has gradually grown in popularity. In order to ease the energy crisis and protect the environment, biogas will become more and more feasible in practical application as the target product of the anaerobic fermentation process. It's a gas mixture that usually includes 55-80% methane, 20-45% carbon dioxide, 0-10% nitrogen, and trace amounts of H₂S and other impurities. Hydrogen sulphide (H₂S) is a poisonous and dangerous gas that not only endangers human health but also induces corrosion of metal pipes and machinery in hot and humid environments. H₂S, in both gaseous and solution form, is highly corrosive to piping and manufacturing facilities (Garcia-Arriaga et al. 2010). When sulphur is oxidized to sulphur oxide (SO_2) during combustion and released into the atmosphere, acid rain will result. H₂S has a significant poisoning effect on noble metal catalysts in many industrial processes such as hydrogenation, ammonia synthesis, and fuel cells, also in trace quantities. As a result, it is critical to extract the gas from the manufacturing plant. Chemical industries such as natural gas refining and utilization, crude oil hydro desulfurization, and coal chemistry all emit significant amounts of H₂S. Carbon steel, which is widely used as a pipeline material in the oil and gas industry, is also highly corrosive to H₂S. Environmental issues on a global scale As H₂S is burned, it is oxidized to SO₂, which is a significant pollutant in the atmosphere. Furthermore, in some applications, such as waste water treatment plants, animal processing plants, and food processing plants, H₂S produces an unusual odour. The H₂S in biogas must not exceed 20 mg/m³ in order to avoid the aforementioned problems associated with the use of biogas energy. However, the concentration of H₂S in biogas is usually 200-18000 mg/m³ (sometimes 30000-50000 ppm in the case of spent wash), far beyond the provisions of environmental regulations. As a consequence, the H₂S removal of biogas is a necessary

process in order to achieve biogas environmental security, high value, and productive use. This paper looked at and reviewed traditional biogas desulfurization technologies.

Hydrogen Sulphide removal unit/ Desulphurization

Hydrogen sulphide (H₂S) can occur, depending on the origin of the biogas, in concentration ranges from \sim 70 mg/nm³ up to (in some cases) over 30,000 mg/mn3(ppm). In combination with water, sulphuric acid can be formed. In order to avoid corrosion of the parts of the production installation and to comply with the quality requirements in force for feeding the BioCNG into natural gas grids (the same applies for its direct use as a fuel), the biogas needs to be desulphurised. The processes of coarse and fine desulphurization are distinguished. Biological desulphurization is normally carried out in the fermenter by inserting doses of air in traditional agricultural biogas plants directly using gas in CHP units for coarse desulphurization. Since the effect is a thinning of the biogas with atmospheric nitrogen, this method is only applicable to a limited extent and is subject to strict preconditions in biogas plants including biogas upgrading. Practically none of the biogas upgrading technologies will separate this any longer.

H₂S Removal Technologies: Introduction:

Hydrogen sulfide (H₂S) is always present in biogas, normally at concentrations between 80 – 50,000 ppm depending on the feedstock, here in this case when we consider spent wash then generally the H₂S concentrations ranges from 20,000 – 30,000 ppm. H₂S can be removed from gas streams using a variety of technologies. These methods can be tested to see if they work well with biogas systems. The best choice is determined by the gas's final usage, the structure, variability, and volume of the gas to be processed, the H_2S concentration, and the absolute amount of H₂S to be extracted. Each technology has advantages and disadvantages. In addition, two or more processes may be combined to remove more H₂S. Hydrogen sulphide may be extracted from the digester, the crude biogas, or the upgrading process. In general, H₂S removal methods can be divided into two categories based on their principles: physical-chemical methods, which are the most common and still dominate the market, and biotechnological methods.

	Addition of iron salts/oxides to the digester slurry		
Physical & Chemical	Adsorption	> Activated carbon	
		> Molecular sieve	
		Iron oxides (iron sponge, SulfaTreat®, Sulphur-Rite®)	
		Zinc oxides	
		Alkaline solids	
	Absorption/Scrubbing	> Water	
		No-water physical solvents (Selexol®)	
		Alkaline solutions	
		Zinc oxide slurries	
		Firon oxide slurries	
		Iron salts, chelated and no chelated (Lo-Cat®, SulFerox®,	
		> Sulfothane®)	
		Quinone and vanadium salts (Stretford)	
		Chemical oxidants: hypochlorite,	
		> H ₂ O ₂ , KMnO ₄	
		> Amines	
	Membrane purification		
	Claus process (+ SCOT / + Superclaus)		
	Incineration		
	Air/Oxygen dosing digester slurry		
Biotechnological	Bio filter/Bio trickling filter (BiogasCleaner®, Biopuric®, DMT filter®)		
	Bio scrubber (ThiopaqTM)		
Combined physical- chemical/biotechnological	Chemical absorption with iron salts and microbial regeneration of the solution.		

H₂S Removal Technologies – Table 1

Digester - sulfide abatement by addition of iron salts/oxides to the digester slurry:

In a pre-storage tank, iron chlorides, phosphates, or oxides are directly applied to the digester slurry or the feed substrate. The most widely used approach is to add FeCl₂, which is a liquid. Ferrous chloride (FeCl₃) and iron hydroxide {Fe(OH)₃ or Fe(OH)₂} in solid form may also be used. They then react with the hydrogen sulphide formed to form insoluble iron sulphide salts. The removal of H₂S from the biogas is prevented as a result of this precipitation. This approach is very effective at reducing high H₂S levels, but it is less effective at achieving a low and stable H₂S level in the range of vehicle and gas grid injection demands. H₂S concentrations in biogas have been reduced to between 200 and 100 parts per million. A large excess of iron ions was needed for removal to lower concentrations.

Biological H₂S reduction by air/oxygen dosing to digester slurry:

The simplest method of desulfurization for biogas produced by anaerobic digestion is to introduce oxygen or air directly into the digester or into a storage tank that also serves as a gas holder. Thiobacillus bacteria conduct biological aerobic oxidation of H_2S to elemental sulphur and sulphates in this manner. They thrive on the surface of the digestate, which provides the necessary micro-aerophilic surface as well as the required nutrients. The small amount of oxygen needed in this process (3–6% air to biogas) is injected into the biogas system through an air pump, for example. Full-scale digesters have estimated 80–99 percent H_2S reduction, down to 20–100 ppm H_2S , depending on temperature, reaction time, and the volume and position of air (McKinsey, 2003). After desulfurization, the oxygen content of biogas would be between 0.5 and 1.8 percent per volume. Sulphur concentrations are tracked in a limited number of slurry digesters, and most of the applications are unsuccessful in practice.

When no further upgrading of biogas is needed, i.e. when the biogas is cleaned only to avoid corrosion and odour problems, this is likely the least costly and easiest to maintain method of scrubbing for on-farm use. The coupling to the anaerobic degradation process, as well as the need to supply oxygen to the anaerobic fermentation process, are two major disadvantages of desulfurization in the digester. As a result, the fermentation process is interrupted, and methane formation is hindered. As a result, the biogas yield falls. Furthermore, residual sulphur or sulphates in the system may lead to the re-formation of H_2S and the deposition of yellow sulphur clusters on surfaces, raising the risk of corrosion.

Adsorption

Pollutants are stuck on a solid with a wide surface area. The solid is usually activated carbon or a crystalline material with high internal porosity (silica gel, zeolites, activated alumina, etc.) that traps the pollutant on its surface using intermolecular forces. Physical adsorption, in which the pollutant molecules are kept in place in the pores by relatively weak physical attraction forces, and chemical adsorption, in which much stronger chemical bonding forces are also present, are the two forms of adsorption. When the solid becomes saturated, it can either be discarded or returned to the producer for washing, or it can be are regenerated in place. Heat or lower pressure is used in the regeneration process to reverse the adsorption process and volatilize the absorbed compounds. The most popular method of supplying heat for regeneration is direct steam injection.

Adsorption on impregnated activated carbon

If low concentrations of H₂S are needed, activated carbon is the most widely used adsorbent among the available options. In addition to physical adsorption, activated carbon provides a catalytic surface for oxidation of H₂S to elemental sulphur and sulphates, greatly enhancing the H₂S removal ability. The elementary sulphur is adsorbing to the activated carbon's internal surface. The activated carbon must have a moisture content of 20-30% and the necessary amount of oxygen. Air is pumped into the gas stream in massive biogas plants, but on a small scale, routine removal of AC and exposure to ambient air suffices. Pressures of 7 to 8 bar and temperatures of 50 to 70 °C are suitable for the reaction. The temperature of the gas is easily achieved thanks to the heat produced during compression. Typically, the carbon filling is set for a 4,000 to 8,000-hour operating period. Regeneration is needed if the gas contains high levels of H_2S (> 3,000 ppm).

Adsorption on molecular sieve

Molecular sieves (zeolites) are excellent products to separate different compounds in gas streams. The selectivity of adsorption is achieved by different mesh sizes and/or application of different gas pressures. Polar compounds, such as water, H_2S , SO_2 , NH_3 , carbonyl sulfide, and mercaptans, are very strongly adsorbed and can be removed from such non-polar systems as methane. Both activated

carbons and hydrophobic molecular sieves present advantages and drawbacks. The former are rather cheap materials, readily available from many companies. Moreover, they have high initial adsorption capacities. On the other hand, the latter, despite their limited initial capacity, are thermally and chemically very stable products and generally do not lead to side reactions. Their relatively high cost prevents their extensive use for the moment.

Molecular sieves (zeolites) are useful for separating various compounds from gas streams. Adsorption selectivity is accomplished by using different mesh sizes and/or applying different gas pressures. Water, H_2S , SO_2 , NH_3 , carbonyl sulphide, and mercaptans are very easily adsorbed and can be removed from non-polar systems like methane. Enabled carbons and hydrophobic molecular sieves each have their own set of benefits and disadvantages. The former are relatively inexpensive materials that are readily available from a variety of sources. They also have a high initial adsorption power. On the other hand, despite their low initial capacity, the latter are thermally and chemically very stable products that rarely cause side reactions. For the time being, their relatively high cost prevents them from being widely used.

Adsorption using iron oxides

As one of the oldest methods still in practice, iron oxides remove hydrogen sulfide by forming insoluble iron sulfides. It is possible to extend bed life by admitting air, thereby forming elemental sulfur and regenerating the iron oxide. This regeneration process is highly exothermic. Regeneration is possible for a limited number of times (until the surface is covered with natural sulfur), after which the tower filling has to be renewed. If using one column systems the regeneration can be applied by injecting 1 - 5% air into the reaction column but loading is limited when compared to a two-column system. In a two-stage system the raw biogas streams through the first column and iron sulfide is generated. In parallel in the second column air is injected and the regeneration takes place.

Iron Sponge

Iron oxides eliminate hydrogen sulphide by creating insoluble iron sulphide, which is one of the oldest methods still in use. By allowing air into the bed, elemental sulphur is formed, and the iron oxide is regenerated, the bed's existence can be extended. This regeneration process generates a lot of heat. The tower filling can be regenerated for a limited amount of times (until the surface is covered with natural sulphur), after which it must be replaced. When using a one-column system, regeneration can be accomplished by injecting 1-5% air into the reaction column, but loading is constrained in comparison to a two-column system. In a two-stage method, raw biogas passes through the first column, which produces iron sulphide. In the second column, air is injected and regeneration occurs simultaneously.

SulfaTreat®

SulfaTreat® is a sulphur scavenger developed by M-I SWACO that consists primarily of Fe_2O_3 or Fe_3O_4 compounds coated onto a proprietary granulated support. SulfaTreat® is compatible with partially or completely hydrated gas streams and is used in a low-pressure vessel with down-flow of gas, similar to iron sponge. Commercial conversion efficiency is in the range of 0.55 - 0.72 kg H₂S/kg iron oxide, which is equivalent to, or slightly higher than, batch iron

sponge conversion efficiency. SulfaTreat® is non-regenerable, and, like iron sponge, properly disposing of the spent product can be difficult or costly. The manufacturer suggests that spent product be used as a soil amendment or as a raw material in the construction of roads and bricks, but they also state that each consumer must develop a spentproduct disposal plan that complies with local and state regulations.

Sulphur-Rite®

GTP-Merichem sells Sulphur-Rite®, an iron-oxide commodity. Sulphur-Rite® is unusual in that it states that the end product is insoluble iron pyrite. Sulphur-Rite® systems come in pre-engineered cylindrical units that handle gas flow rates up to 4,300 m3/h (i.e. H_2S gas concentrations 1,765 mg/m³) and are recommended for installations with less than 180 kg/d. Sulphur-Rite® is around the same price as SulfaTreat®. 1 kg of H_2S is extracted by 8.5 kg of SulfaTreat® or Sulphur-Rite®. According to company literature, spent product is non-pyrophoric, land fillable, and 3–5 times more effective than iron sponge.

SOXSIA®

Gastreatment Services B.V. developed SOXSIA® (Sulfur Oxidation and Siloxanes Adsorption), a catalyst that absorbs siloxanes and extracts H_2S from raw gas. At 40 °C, ambient pressure, and 1,000 nm³ raw gas/h, up to 2,000 ppm of H_2S can be separated from the gas.

Absorption/Scrubbing

H₂S is dissolved by physical absorption in water or other solvents such as methanol and polyethylene glycol ethers. The water solubility of H₂S is increased in chemical absorption by rendering the water alkaline or oxidising it to more water-soluble compounds. If liquid regeneration is possible, regeneration columns are typically used in tandem with the absorber to allow for continuous processing. If the displaced H₂S has not been transformed to elemental sulphur, it is contained in the regeneration unit's stripper steam. The main drawback of absorption is that it normally solves an issue with a polluted gas stream by producing a contaminated liquid stream or a more concentrated gas liquid stream (if regeneration is used) that must be treated again. Other drawbacks include high initial investment costs and high water and/or chemical consumption. High removal efficiency (up to 99 percent), a small footprint, and the ability to manage a large variety of pollutant concentrations are all advantages. Absorption systems can handle flow rates ranging from 100 to 10,000 m3/h and pollutant concentrations of 8 to 30 g/m^3 .

Water scrubbing

High-pressure scrubbing of biogas with pressurized water is the foundation of these processes. This eliminates a large portion of the acid gas pollutants (including carbon dioxide) that can be emitted from wash water in an air or steam stripping tower. The resulting 'regenerated' water may either be re-circulated or used only once. Since they have access to a wide supply of water and wastewater treatment capability on site, non-regenerative water wash is mainly used with biogas from WWTPs. However, due to bacterial growth, using WWTP water can cause problems in pipes and vessels. Cleaning is needed in these situations. Cleaning the column with detergent or removing the media and cleaning it externally might be necessary many times a year. It can be done without interrupting the biogas flow by using a nonregenerative process. Water consumption is about 150 l/nm³ raw biogas in non-regenerating processes. Plants that reuse water use a hundred times less water than those that do not. Before being discharged into the atmosphere, used water would need to be properly handled.

Physical Absorption

Physical absorption using organic solvents is essentially equivalent to water scrubber technology. Chemical solvents with high H_2S selectivity, such as methanol, propylene carbonate, and ethers of polyethylene glycol, are used instead of water. Genosorb® 1753, which is primarily composed of polyglycol dimethyl ethers and is used in the Selexol® process, is a well-known industrial solvent. The cost of selective H_2S removal has not yet proven to be competitive, and this method will most likely be considered only for applications where upgrading to relatively pure methane is needed, similar to water scrubbing. Furthermore, using Selexol for H_2S removal can only be cost-effective if very large gas flows are being handled.

Chemical absorption by catalytic oxidation with chelated-iron salt solutions

Iron ions are bound to organic chelating agents in chelatediron solutions. The reduction of a soluble ferric chelated iron $[Fe_3+]$ into a ferrous chelated iron $[Fe_2+]$ is used to turn hydrogen sulphide into elemental sulphur. The chelating agents prevent the formation of iron sulphide or iron hydroxide, allowing the reduced (ferrous) iron to be reoxidized to ferric iron by air stripping. Chelated iron $[Fe_3+]$ acts as a catalyst in the absorption process; in reality, without catalysts, the chemical oxidation of aqueous H₂S by dissolved oxygen occurs at a very slow rate. With this technology, sulphur removal efficiencies of 99.99 percent or higher can be achieved. Many of the units based on this technology, however, have plugging and foaming issues.

Membrane separation

It involves using semi permeable membranes to separate H₂S from a pollutant gas stream by generating a partial pressure gradient through the membrane's semi permeable glassy or rubbery surface. The membrane is built to allow gas or pollutant molecules to pass through it preferentially, resulting in a more concentrated pollutant stream on one side. High-pressure membrane systems with gas phase on both sides and low-pressure membrane systems with a liquid adsorbent on one side exist. A single-stage separation unit is unable to achieve complete separation, necessitating multistage separation. Membranes can eliminate CO₂ and other impurities at the same time, but today, H_2S is separated before high-pressure membranes to prolong membrane life. Membranes are not yet competitive for selective H₂S removal due to their high cost. The use of lowpressure gas-liquid membrane processes to remove H₂S is a promising technology.

Bio-filters and bio-trickling filters

Biogas is forced into a moist, packed bed containing microorganisms in these processes. Microbes form a biofilm on the surface and crevices of the support. The H_2S in the biogas is moved from the gas phase to the biofilm, where it is used as an energy source by the microorganisms, which generate mostly sulphur or sulphates depending on whether the oxidation is partial or complete. The bed medium, moisture content, temperature, pH, contact time, nutrient, and oxygen levels are all factors that influence the process. Since the bacteria commonly used to remove H_2S are aerobic, they require oxygen. Injecting directly air (4–10

percent) into the gas stream is the traditional method of supplying oxygen to a bio-filter/bio-trickling filter.

Bio-filters and bio-trickling filters vary mostly in the form of the carrier content, which is organic in bio-filters and inert in bio-trickling filters. As nutrients are not available in the carrier material of the bio-trickling filters, they are supplied to the microorganisms by recirculating a liquid phase through the reactor in a counter-current or co-current to the gas flow. This liquid phase provides moisture as well as a way to regulate the pH and other operating parameters. The acidification of the media caused by the formation of sulfuric acid from the oxidation of H₂S is a major issue in bio- filters. Special steps are typically taken to mitigate the pH decrease. The general approach is to improve the media's buffering potential by adding alkaline compounds, using a carrier base with some alkaline properties, and/or cleaning the filter media with water on a regular basis. Since the acid reaction products are constantly washed out of the media in biotrickling filters, this issue is avoided.

The Dutch company DMT Environmental Technology has commercialized the BioSulfurex[@] which claims a reduction of more than 95% in H₂S for incoming biogas with up to 1% vol. Colsen B.V., a Dutch corporation, has created the Bidox system, which claims to reduce H₂S levels from over 10,000 ppm to 50 ppm with a power consumption of 0.21 kWh/kg H₂S removed and combined operating and maintenance costs of 0.10 – 0.25 €/kg H₂S removed. EnviTec biogas has also developed a biological trickling filter for desulphurizing biogas. This process produces elementary sulphur as an oxidation product, which settles to the bottom of the filter and is then discharged. On average, EnviTec claims a desulphurization efficiency of more than 94 percent.

More than 100 BiogasCleaner® desulfurization plants have been supplied by the Danish company BioGasclean. They are made up of a bio-trickling filter that operates at a low pH in one or more fiberglass or steel tanks with acid-proof liners. The main product is sulphate, which is injected directly into the system. In the event of a clog, BioGasclean's gas cleaners are designed to be cleaned in less than one working day, without removing the filter material from the tank manually, using the QSR[®] method (Quick Sludge Remover). This method has been used in biogas plants with H₂S concentrations as high as 5% and sulphur loads as high as 5,500 kg/d. BioGasclean can guarantee a clean gas with as little as 10 ppm H₂S and can upgrade projects with pure oxygen rather than ambient air.

Bio-scrubber

Two reactors make up a bio-scrubber. The first component is an absorption tower, which absorbs contaminants in a liquid phase. This liquid phase is directed to a second reactor, which works similarly to an active sludge unit. Microorganisms develop in suspended flocks in the water, degrading contaminants in the process. This unit's effluent is re-circulated through the absorption tower. To sustain microbial growth and activity, nutrient addition, oxygen, and pH are all constantly monitored. The device is actively purged of surplus biomass and by-products.

The THIOPAQTM Process, which is licensed by Paques, is the most well-known scrubber method for extracting H_2S from biogas. The THIOPAQTM device acts as a caustic scrubber, with naturally occurring microorganisms continually regenerating the spent caustic solution in a bioreactor. The scrubber combines the H_2S -containing biogas with the

alkaline liquid of the bioreactor (pH varying from 8.2 to 9) in a counter-current mode, allowing the H₂S in the biogas to be absorbed into the liquid phase. The solution (NaHS + H_2O) that exits the scrubber is directed to the bioreactor. The bioreactor is aerated (constant mix) with a regulated inflow of ambient air and operates at near atmospheric pressure. The spent scrubber solution reacts with colorless sulphur bacteria, converting the dissolved sulphide to solid elemental sulphur (NaHS + $0.5O_2 \rightarrow S^0$ + NaOH). Just about 5% of the dissolved sulphide is fully converted to sulphate $(2NaHS + 4O_2 \rightarrow NaHSO_4 \rightarrow Na_2SO_4 + H_2SO_4)$. In contrast to a traditional chemical caustic scrubber, the solution alkalinity is partially regenerated during the processing of elemental sulphur, and less than 5% of NaOH is needed to sustain pH above 8.2. To avoid sulphate accumulation, a continuous bleed stream is required, and the produced elemental sulphur is removed from the system. It can either be used as a raw material in sulfuric acid manufacturing plants or discarded. For properly controlled systems, H₂S removal efficiency is claimed to be about 99 percent.

This method has the advantage of not adding oxygen or nitrogen into the biogas source, which is a benefit of bio filters/bio trickling filters. The disadvantage is that the basic cost is higher. In general, the H₂S content of the biogas is reduced from about 2% to 10 to 100 ppm, while amounts as low as a few ppm can be achieved. Normally, gas flows range from 200 to 2,500 m³. As in the THIOPAQTM process, H₂S is absorbed in a caustic solution that is regenerated in a bioreactor where colorless sulphur bacteria turn the H₂S into elemental sulphur. Innovative Environmental Technologies Pvt Ltd. is an Indian company that has also developed a biological scrubber called BioskubberTM. The company claims to have removal efficiencies of more than 99 percent, which it has demonstrated in more than 30 installations across India.

Chemical absorption with $Fe_2(SO_4)_3$ and microbial regeneration

A combined method for the removal of H₂S from waste gas has been identified, in which H₂S is oxidized to elemental sulphur in an absorber with ferric ion in the first step, and the ferric ion is regenerated in the second step. One benefit of this approach is that the first reaction is so quick and complete that there is no chance of hazardous waste gas being released. Sulphur may also be removed from the medium. Several types of absorbers, such as jet scrubbers, bubble-cap towers, and packed towers, are suitable depending on the gas flow rate and the efficiency needed. In a separator, elemental sulphur is isolated and extracted from a reduced solution of ferrous sulphate. Depending on the quality of elemental sulphur available, sulphur separators may include settlers, filter presses, and sulphur melters. Following the recovery of elemental sulphur, the ferrous sulphate solution is passed into an aerated bioreactor, where T. ferroxidans converts the ferrous ion to ferric.

Cost analysis of H₂S technologies:

It is difficult to find costs estimations in literature for different systems in a uniform way. Different cost for several systems with different gas capacities and H_2S removal amounts are given here. Although comparisons are difficult to make, these costs gives an overall impression. An overview of three different H_2S removal technologies costs is given in Table 2. Since we are dealing with spent wash there are certain technologies which may not be suitable to treat the biogas generated from spent wash. As mentioned earlier

spent wash based biogas generally has 20,000 - 30,000 ppm of H₂S. According to calculations bio chemical and biological scrubbing was the most economical, both in regards to investment and operation costs. Assuming estimated range

of the capital costs and the range of annual operating costs for $1000 \text{ m}^3/\text{hr}$ biogas systems the details can be summarized as below:

Table 2				
Technologies	Capital Cost (Rs in INR – Lacs)	Annual Operating Cost		
Biological – Biogas Clean	200.00 - 225.00	30.00 - 40.00		
Biological H ₂ S Cleaning System	210.00 - 235.00	35.00 - 45.00		
Biological H ₂ S – BioSulfurex	300.00 - 320.00	50.00 - 60.00		
Caustic Desulphurization - Sulfurex	250.00 - 275.00	150.00 - 170.00		
Sulfatreat	170.00 - 190.00	200.00 - 210.00		
Thiopaq**	450.00 - 475.00	220.00 - 230.00		

Annual costs calculated above covers only electricity and normal utility expenses

** Thiopaq systems are working and are in good shape and particularly from Spent wash which has more H₂S content and the systems are actually working on spent wash based biogas, rest most of the technologies mentioned above are installed and are either not working, or facing operational problems & design issues. The other technologies work well when the

** H₂S content ranges from 200-10000 ppm.

Conclusion:

At present, the traditional desulfurization technologies including the ones mentioned in this paper are more frequently used, but there are some problems such as high desulfurization costs and easy to produce two pollution problems. The government is coming up with more stringent environmental laws and regulations, the development of efficient, low input, recycling and no two pollution technology has become the mainstream of desulfurization technology development. Infact, people are looking out for the technologies which claim to be zero discharge solutions. As a new desulfurization technology, biological desulfurization has attracted more and more attention because of its advantages of low energy consumption and no to the pollution. From the desulfurization equipment and arc technology, the bio desulfurization still remained in the stage of laboratory research. In order to obtain large-scale applications, it is necessary to make efforts in the fields of desulfurization bacteria, bioreactor and desulfurization process. When it comes to treating the high levels of H₂S like we gave an example of biogas generated from spent wash then in this case the only viable option will be Bio Chemical scrubber from CAPEX, OPEX and reliability point of view. Though every technology has some merits and demerits it is always suggested to select a right type of technology based on the amount of gas to be scrubbed along with the raw gas parameters. Sometimes if the gas is only to be used in the biogas generators perhaps only iron filing technology will work to the best if the raw biogas has very low levels of H₂S and vice versa.

References:

- [1] J. Lasocki, K. Kolodziejczyk, A. Matuszewska, Polish Journal of Environmental Studies, 2015, 24(3), 1427.
- [2] Malik, S J & Gunjal, B.B. & Kasulla, Srinivas & Gunjal, Aparna. (2019). Spentwash and Pressmud to BIOCNG - An Overview.
- [3] Malik, S J & Gunjal, B.B. & Kasulla, Srinivas & Gunjal, Aparna. (2019). Techno Commercial Aspects of bio-CNG from 100 TPD Press mud Plant..
- [4] Pourzolfaghar H, Mohd Halim S I, Izhar S, et al. Review of H2S sorbents at low-temperature desulfurization of biogas [J]. International Journal of Chemical & Environmental Engineering, 2014.

- [5] Beil M. and Hoffsted U. (2010). Guidelines for the implementation and operation of biogas upgrading systems, Biogasmax. Project supported by the EU under RTC contract: 019795
- [6] Malik, S J & Gunjal, B.B. & Kasulla, Srinivas. (2018). Study of Upgradation Technologies to Treat Biogas from Spentwash to BioCNG.
- [7] https://www.bioenergyconsult.com/hydrogensulphide-removal-from-biogas/
- [8] Kasulla, Srinivas & Malik, S J. (2020). Enhancement in Biogas Production from Press Mud. International Journal of Engineering Applied Sciences and Technology. 5. 10.33564/IJEAST.2020.v05i05.036.
- [9] Malik, S J & Kasulla, Srinivas. (2020). Biogas Production from Sugar Cane Press Mud and Sugar Cane Bagasse by Anaerobic Co-Digestion. 10.33564/IJEAST.2020.v05i07.030.
 - [10] L. Dubois, D. Thomas, Chemical Engineering Technology, 2010, 33(10), 1601.
 - [11] Boudou J P, Chehimi M, Broniek E, et al. Adsorption of H2S or SO2 on an activated carbon cloth modified by ammonia treatment [J]. Carbon, 2003, 41(10): 1999-2007.
 - [12] Malik, S J & Saraf, Aparna & Kasulla, Srinivas. (2020).
 Biogas Production from Decanter Cake of Palm Oil Mill from South India. 10.5281/zenodo.4409642.
 - [13] Kasulla, Srinivas & Malik, S J & Siddiqui, Ahmad.(2021). Optimisation of Biogas Production using Nanotechnology. 10.5281/zenodo.4656046.
 - [14] McKinsey, S. Z. (2003). Removal of Hydrogen Sulfide from Biogas using cow-manure compost. A Thesis Faculty of the Graduate School of Cornell University
 - [15] D. Panza, V. Belgiorno, Process Safety and Environmental Protection, 2010. 88, 420.
 - [16] Carnell P J H, Joslin K W, Woodham P R. Fixed-bed processes provide flexibility for COS, H2S removal [J]. Oil & Gas Journal, 1995, 93 p.
 - [17] Garcia C L, Lercher J A. Adsorption of H₂S on ZSM₅ zeolites [J]. Cheminform, 1992, 96(5): 2230-2235.

International Journal of Trend in Scientific Research and Development (IJTSRD) @ www.ijtsrd.com eISSN: 2456-6470

- [19] Nishimura S, Yoda M. Removal of hydrogen sulfide from an anaerobic biogas using a bio-scrubber [J]. Water Science and Technology, 1997, 36(6–7): 349-356
- [20] Soreanu G, B Land M, Falletta P, et al. Investigation on the use of nitrified wastewater for the steady-state operation of a bio-trickling filter for the removal of hydrogen sulphide in biogas [J]. Journal of Environmental Engineering & Science, 2008, 7(5): 543-552
- [21] Nagl G. (1997). Controlling H2S emission. Chemical Engineering Journal 104 (March): 125 – 128
- [22] Chaiprapat S, Mardthing R, Kantachote D, et al. Removal of hydrogen sulfide by complete aerobic oxidation in acidic bio filtration [J]. Process Biochemistry, 2011, 46(1): 344-352.
- [23] Montebello A M, Baeza M, Lafuente J, et al. Monitoring and performance of a desulphurizing bio trickling filter with an integrated continuous gas/liquid flow analyser [J]. Chemical Engineering Journal, 2010, 165(2): 500-507.
- [24] Kang J W, Jeong C M, Kim N J, et al. On-site removal of H₂S from biogas produced by food waste using an aerobic sludge bio filter for steam reforming processing [J]. Biotechnology and Bioprocess Engineering, 2010, 15(3): 505-511.
- [25] An S, Tang K, Nemati M. Simultaneous biodesulphurization and de-nitrification using an oil reservoir microbial culture: Effects of sulphide loading rate and sulphide to nitrate loading ratio [J]. Water Research, 2010, 44(5): 1531-1541.
- [26] Cline, C., Hoksberg, A., et al. (2002). Biological process for H_2S removal from gas streams: The Shell-

Paques/Thiopaq[™] gas desulfurization process. Paper for the LRGCC, 23 – 26 February 2003, Norman (Oklahoma)

- [27] Pulsa, M. 2008. Injection of biogas into the natural gas grid. Master's thesis. Lappeenranta University of Technology. In Finnish. 145 p.
- [28] Graubard, G., Bogner, J. & Rouleau, W. 2007. Costeffective tools for removing H2S from landfill gas. Proceedings of 11th International Waste Management and Landfill Symposium, 1–6.10.2007.Cagliari, Italy.
- [29] Pagella, C, Silvestri, P., et al. (1996). "H₂S treatment with Thiobacillus ferroxidans: overall process performance and chemical step." Chemical Engineering Technology 19(1): 79-88.
- [30] Petersson A, and Wellinger A. (2009). Biogas upgrading technologies-developments and innovations. IEA Bioenergy. Task 37
- [31] HORIKAWA, M.; ROSSI, F.; GIMENES, M.L.; COSTA, C.M.M.; DA SILVA, M.G.C. Chemical absorption of H2S for biogas purification. Braz. J. Chem. Eng., v.21, n.3. 2004.
- [32] Lee, E. Y., Lee, N. Y., Cho, K. S. & Ryu, H. W. Removal of hydrogen sulfde by sulfate-resistant Acidithiobacillus thiooxidans AZ11. J Biosci Bioeng 101, 309–314 (2006).
- [33] Vannini, C., Munz, G., Mori, G., Lubello, C., Verni, F., Petroni, G., 2008. Sulphide oxidation to elemental sulphur in a membrane bioreactor: Performance and characterization of the selected microbial sulphuroxidizing community. Systematic and Applied Microbiology, 31, 461-473.
- [34] Wubs, H.J. and Beenackers, A.A.C.M., Kinetics of H₂S
 6-647 Absorption into Aqueous Ferric Solutions of EDTA and HEDTA, AICHE Journal, vol. 40 no. 3, pp. 433 444 (1994).