

# **ECONOMICAL AND EFFECTIVE BIOGAS PROCESS TO PURIFY ALTERNATIVE FUELS FOR POWER GENERATION**

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## **ABSTRACT**

Energy recovery from biogas is becoming more common, but the processes are hampered with the presence of hydrogen sulfide (H<sub>2</sub>S). Biogas is a mixture of methane and carbon dioxide (CO<sub>2</sub>) and is often contaminated with toxic quantities of H<sub>2</sub>S. Sources of biogas are: municipal landfills that produce landfill gas (LFG); wastewater treatment plants; industrial plants; and large scale livestock farms. The H<sub>2</sub>S levels can range between 200-5000 ppmv from municipal facilities to over 30,000 ppmv from industrial facilities.

H<sub>2</sub>S has an offensive “rotten egg” odor at concentrations as low as 5 ppbv, and is an acute toxic hazard at concentrations above 100 ppmv. H<sub>2</sub>S is a health, safety, and environmental hazard, and when combined with CO<sub>2</sub> and water vapor, it can corrode boilers, piping, and other equipment. Reducing H<sub>2</sub>S in biogas reduces sulfur dioxide emissions, equipment corrosion, and fouling. H<sub>2</sub>S reduction also offers cost savings through lower maintenance requirements, and results in greater energy recovery for increased power generation.

This paper describes a biogas scrubbing process for the removal of H<sub>2</sub>S and particulate matter from biogas as it is produced. Using a patented, high efficiency gas-liquid contacting process, H<sub>2</sub>S is absorbed and the gas is purified for use in power generation facilities, cogeneration facilities, boiler units, and other heating applications. A case history of the scrubbing technology will be presented.

## Introduction

The future of power generation from alternative fuels rests on advancing technology to address the removal of contaminants, increase efficiencies in processing, and present means to effectively utilize the fuels. Biogas, also known as “swamp gas”, “marsh gas”, “landfill gas”, and “digester gas”, is the product of the anaerobic digestion by bacteria of biodegradable materials, including human and animal feces, agricultural and industrial wastes, and some components of municipal garbage. It can be produced in complex digesters, designed and manufactured by specialist companies, or generated naturally, as in landfill sites. Typical compositions and properties are tabulated below:

**Table 1: Typical Composition and Properties of Biogas**

<b>Component/Property</b>	<b>Mesophilic Process</b>	<b>Thermophilic Process</b>
Methane (CH <sub>4</sub> )	50-70%	60-80%
Carbon Dioxide (CO <sub>2</sub> )	30-50%	20-40%
Hydrogen Sulfide (H <sub>2</sub> S)	Municipal: 50-5000 ppmv Industrial: 50-35,000 ppmv	Industrial: 50-50,000 ppmv Agricultural: 100-3000ppmv
Ammonia (NH <sub>3</sub> )	10-350 ppmv (Est'd)	10-300 ppmv (Est'd)
Oxygen (O <sub>2</sub> )	0-2%	0-1%
Water Vapor	Saturated	Saturated
Particulates	NA	NA
Silanes and Siloxanes	Land-fill: 0.5 – 50 ppmv Digester: 0.5-140 ppmv	Digester: 0.5-140 ppmv
Temperature	30-40°C	55-70°C
Pressure	-500 to + 2000 Pa	-500 to + 2000 Pa

Under normal conditions, 250 – 300 scfm, of biogas may be used directly to generate 1 MW of electric power, and with cogeneration systems, an accompanying amount of heat. Gas availability depends on the amount and type of bio-waste available:

- Greater than 90% of municipal waste water systems produce between 100 to 1000 scfm.
- Large cities tend to have plants that produce more than 1000 scfm.
- Landfill gases are usually harvested at between 1000 to 6000 scfm.
- Industrial food processing plants can produce from <500 scfm up to several thousand scfm.
- Sugar, cellulose and corn-ethanol plant now projected or under construction will produce up to 6000 scfm.

However, before most of the biogases described above can be used economically, hydrogen sulfide concentrations must be reduced:

- Typically to <200-400 ppmv in reciprocating engines.
- If the gas is to be used in boilers, H<sub>2</sub>S must be <500 ppmv.
- To bring the gas to pipeline quality, CO<sub>2</sub> must be <2%, and H<sub>2</sub>S <4 ppmv. The treated gas must then be compressed, de-watered and cooled to be successfully injected into a pipeline

Additionally, in reciprocating engines, particulates, condensate should be removed and especially silanes and siloxanes should be reduced to <1 ppmv to prevent excessive formation of sand from the silicon content. In gas turbine engines, silanes and siloxanes can deposit on turbine blades.

### Properties of Hydrogen Sulfide

Hydrogen sulfide is a flammable, explosive, toxic, highly odorous gas, with an odor threshold of as low as about 5 ppb for most people. Odor cannot be relied on as a means of detecting safe concentrations of the gas, because it anesthetizes the biosensors in our noses at concentrations that can be fatal. The ACGIH<sup>®</sup> has recently reduced its recommended concentrations which are deemed not to be injurious to health over a working lifetime of exposure (8 hours/day, 5 days/week). These are now:

Threshold Limit Value (TLV) <sup>®</sup>	5 ppmv
Short Term Exposure Limit (STEL) <sup>®</sup>	10 ppmv

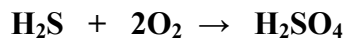
Other important safety data:

IDLH (Immediately Dangerous to Life and Health):	100 ppmv
Fatality Limit at 30 minutes exposure (literature):	600 ppmv
Lower Explosive Limit:	4%

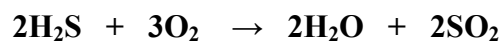
### Impact of Hydrogen Sulfide on Operability and the Environment

Operational difficulties with the utilization of biogas arise mainly from relatively high hydrogen sulfide concentrations. These difficulties include<sup>1</sup>:

- Corrosion in engines, including the combustion chamber exhaust system, bearings, etc. due to the reaction of H<sub>2</sub>S, CO<sub>2</sub> and water with engine materials.
- Elemental hydrogen can form during the combustion process due to decomposition of H<sub>2</sub>S at high temperature, causing cracking and blistering of metal parts.
- Oxidation of H<sub>2</sub>S to sulfuric acid in combination with water vapor, increasing the risk of corrosion



- The partial oxidation of H<sub>2</sub>S to sulfur dioxide in the engine or boiler exhaust can also lead to complaints about odor and citations from EPA. In addition, combinations of sulfur dioxide and water are particularly corrosive to mild steel.



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<sup>1</sup> EMG International, "Biogas Clean-Up Technologies" Innovations in Agriculture, New York State ERDA, Presented in Syracuse, New York, April 17, 2007.

Biogas delivery is usually not steady, with frequent and significant changes in both flow rate and hydrogen sulfide concentration. These can result in short running times, low temperature during start-ups and thermal stresses on the equipment. If silanes and siloxanes are present, requirements for more frequent oil changes in engine oil can exacerbate the problem with frequent start-ups.

## **Hydrogen Sulfide Control Strategies**

The necessity and desirability of managing hydrogen sulfide concentrations in biogas before its energy value can be captured as electrical energy and/or heat has been established. Means for the economic control of hydrogen sulfide will now be evaluated. Briefly, these include:

- Addition of iron salts in the anaerobic digester
- Solid state scavenging systems
- Non-regenerable liquid scavenging systems
- Alkaline scrubbing with bacterial regeneration of reagent
- Full-scale amine-Claus process technology
- Regenerable redox reagent systems
- Modified Claus absorption technology

### *Iron Salts*

Iron salts,  $\text{FeCl}_3$  or  $\text{Fe}_2(\text{SO}_4)_3$ , are often added to municipal waste digesters to enhance flocculation of bio-solids and incidentally remove hydrogen sulfide as iron sulfide. This approach is normally used in smaller systems, and is usually followed by aerobic treatment to oxidize hazardous iron sulfide to iron sulfite and sulfate. Main concerns are cost of the salts and enhanced corrosion problems due to the presence of chloride ions.

### *Scavenger Systems*

Solid state scavengers are very effective at removing hydrogen sulfide, but are normally cost-effective only at relatively low sulfur loading, typically <50-100 lbs/day. The scavenger system involves two packed beds, used alternately. One bed is active while the other is cleaned, or in some systems, partially regenerated with air. Disposal of spent media is an additional cost.

Non-regenerable liquid scavenging systems are not widely used, and have cost limitations like those of solid-state systems. Most liquids are hazardous, and disposal or return to manufacturers can be costly.

### *Alkaline Scrubbing*

A number of commercial systems have been developed which utilize alkaline scrubbing. Without regeneration of the scrubbing solution, this system is low in capital cost, but extremely expensive to operate on higher sulfur loadings (e.g., >100 lb S/day). For this reason, regeneration technologies have been developed, utilizing bacteria, which can selectively oxidize bisulfide ion, regenerating the alkaline solution and producing elemental sulfur. Like all biologically based systems, the bacteria require careful maintenance of temperature and addition of nutrients, and the vessel has a fairly high footprint. The produced sulfur must then be separated from the bacteria, which are returned to the regeneration vessel.

### *Claus Technology*

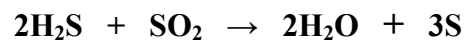
Full-scale amine-Claus technology relies on an amine scrubber to recover hydrogen sulfide and carbon dioxide, followed by combustion of part of the hydrogen sulfide to elemental liquid sulfur and sulfur dioxide. The sulfur dioxide is then catalytically reacted with the remainder of the hydrogen sulfide rich gas, producing liquid sulfur. The process has a very high capital cost, moderate operating cost, and is normally considered uneconomic at sulfur loading less than 15 tons S/day.

### *Regenerable Oxidation-Reduction Reagent Systems*

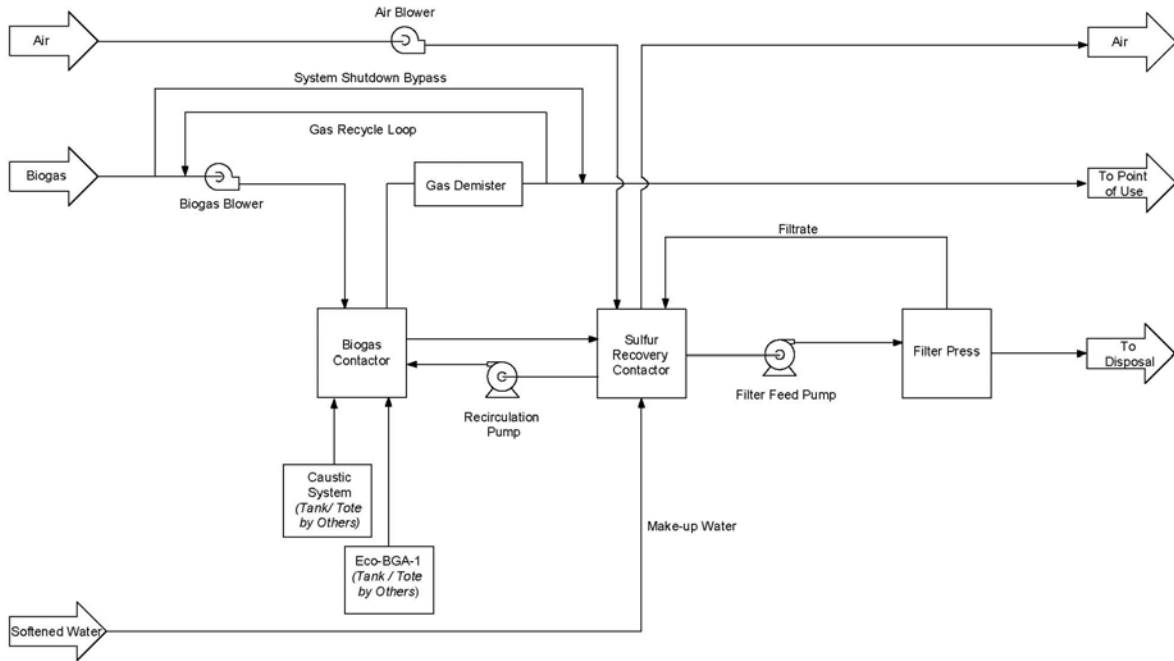
The Stretford Process was among the first regenerable technologies developed initially for town- and coke oven gas purification. It relies on an anthraquinone-Vanadium oxidation reagent to produce elemental sulfur by partial oxidation of hydrogen sulfide. It is not commonly used for treating biogas.

An advanced, proprietary regenerable oxidation-reduction reagents system is illustrated in Figure 1 below. This system removes hydrogen sulfide, at very high mass transfer rates, from biogas in an absorption vessel, normally with >99% removal efficiency. The process utilizes a non-toxic agriculturally acceptable reagent, producing a sulfur product that is acceptable as a fertilizer. The scrubbing medium is then regenerated with air in a separate vessel, producing micro-crystalline elemental sulfur which is concentrated by flotation and thickened to about 85% solids in a washing type concentrator. The system has a small footprint, is skid-mounted, and economical to install and operate.

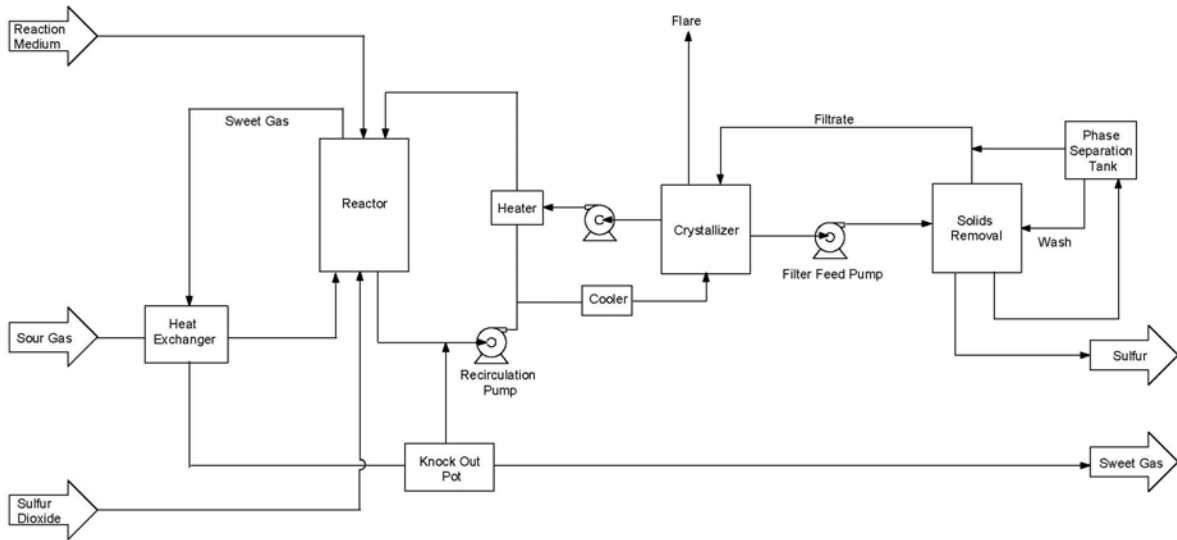
Relatively high biogas flow and hydrogen sulfide concentration are being increasingly associated with corn- and sugar- ethanol production. Proprietary technology (See Figure 2 below) is based on the direct oxidation of biogas hydrogen sulfide with sulfur dioxide.



This reaction is effected in a conventional packed bed, commonly used for gas- liquid contacting. The proprietary reagent catalyzes the reaction, and acts as a solvent for sulfur. Sulfur is recovered from a slip-stream by chilling the reagent-sulfur mixture. The sulfur produced in the process is crystalline, pure and free-flowing.



**Figure 1: Schematic of Biogas Purification System**



**Figure 2: Schematic of Sour Gas Purification System**

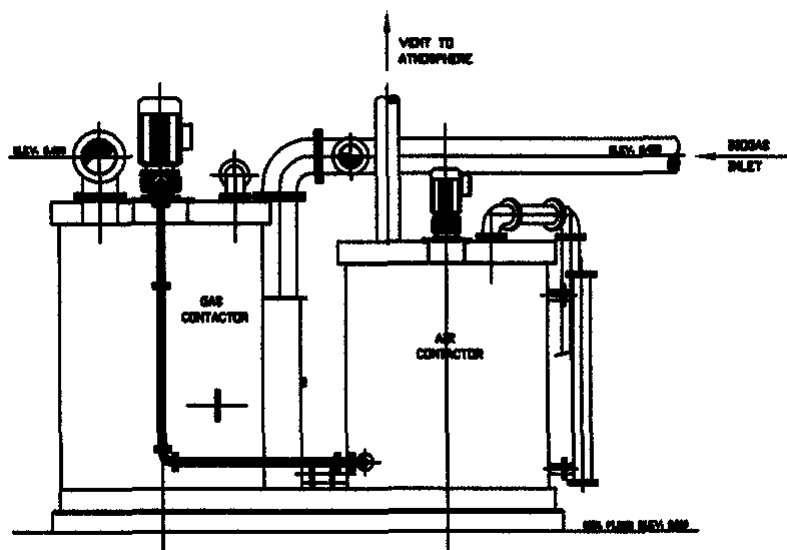
## Regenerable Oxidation-Reduction Reagents Applied: A Case History

### *Eastern Creek Processing Plant, Sydney Australia*

A municipal garbage processing plant, the Eastern Creek Processing Plant required a biogas purification system as part of a full solution for the fermentation of biodegradable organic material separated from municipal garbage. The metals and plastics are separated and recycled while the non-biodegradable organic biosolids are recycled as compost. The produced biogas from the waste contains H<sub>2</sub>S with levels ranging from 4000 to 5000 ppmv. Following the purification, the biogas is fed into two 1.2 MW reciprocating engines.



**Figure 3: Biogas Purification System at Eastern Creek Processing Plant, Sydney Australia**

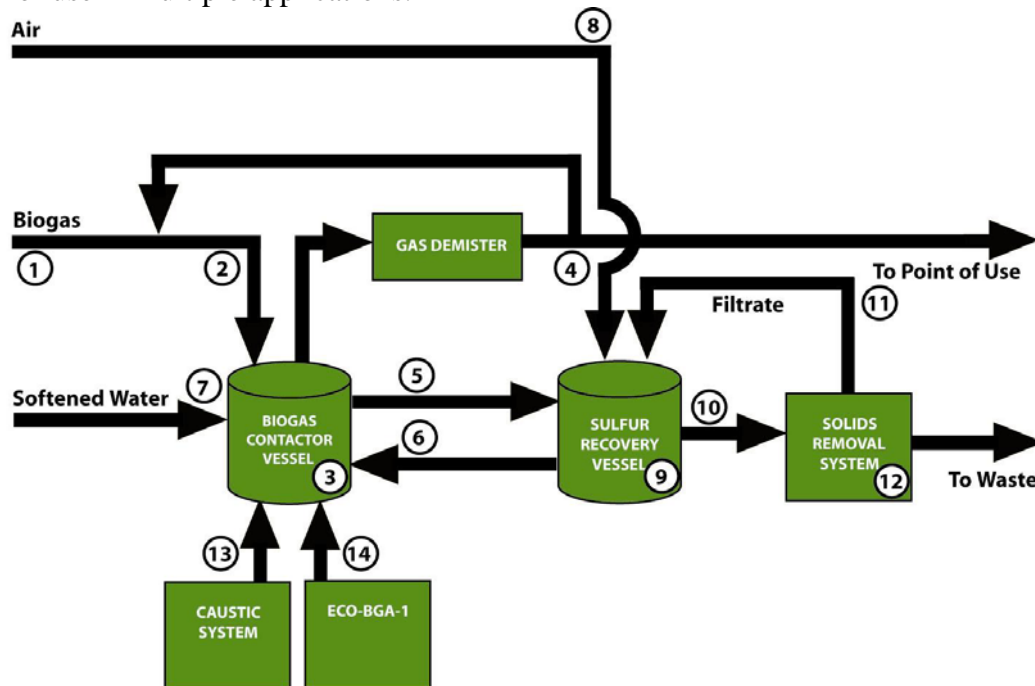


**Figure 4: Line Art rendition of the BgPur™**

The biogas purification system was designed to process the H<sub>2</sub>S at flows of 1080 Nm<sup>3</sup>/hour followed by an ammonia scrubber, a gas chiller to remove water and siloxanes, and a compressor to feed the reciprocating engines. Gas tube measurements and laser spectroscopy of the exit gas indicated less than 2 ppmv of H<sub>2</sub>S. The overall system resulted in over 70% of the municipal garbage being recycled, with the engines utilizing the purified biogas to produce up to 2.4MW of power.

### *Biogas Purification System Description*

The system is designed to reduce sulfur dioxide emissions, equipment corrosion, and fouling by removing the H<sub>2</sub>S from biogas. This proprietary system offers cost savings and greater energy recovery for use in multiple applications.



**Figure 5: Schematic of Biogas Purification System**

### *Biogas Contactor Vessel and System:*

1. Biogas enters the unit boundary or it can be by-passed to a storage/flare system.
2. Biogas and recycled biogas are fed to a blower that operates at a flow rate at least 10% greater than the maximum actual flow rate, and at a pressure high enough to meet hydrostatic head and pressure losses, ensuring that no untreated gas can enter the discharge line.
3. In the biogas contactor vessel, biogas is intimately contacted with the proprietary absorption solution at a pH of about 7.9 to 8.1, which absorbs greater than 99% of the H<sub>2</sub>S and almost all carry-over particulates. A pH meter is installed in the biogas contactor vessel that alerts the system when make-up chemicals should be added.
4. Treated biogas exits this biogas contactor vessel through a mist eliminator. A portion is returned to the blower as recycle gas, the remainder being made available for utilization at essentially the same pressure and flow rate as the supply gas. No pressure control system is required on the gas side with only a pressure gauge used to assist in monitoring the performance of the contactor.

#### *Absorption Solution Circuit*

5. The H<sub>2</sub>S rich absorption solution discharges from the vessel over a weir and is fed to the bottom of the sulfur recovery vessel through a water column gas seal.
6. The regenerated solution discharges from the bottom of the sulfur recovery vessel and is pumped into the biogas contactor vessel for recontact with the biogas.
7. Make-up water is added into the biogas contactor vessel based on level control in a still well in the sulfur recovery vessel, which is equipped with a level transmitter and controller.

#### *Sulfur Recovery Contactor*

8. Air is added through a blower impeller-shroud system to regenerate the solution. By contacting the spent absorption solution with air, the solution is regenerated and producing elemental sulfur.
9. The sulfur recovery vessel, in addition to regenerating spent absorption solution, also acts as a floatation cell where the microcrystalline sulfur slurry froth floats over an adjustable discharge weir into a slurry chamber.

#### *Sulfur Slurry Chamber*

10. Dilute sulfur slurry (about 5% solids) is discharged into the Sulfur Slurry Chamber, from which it is pumped to the solids removal system. Slurry level is monitored in the slurry chamber and when it is within the desired level, pumps sulfur slurry to the solids removal system.
11. Filtrate solution from the solids removal system is returned back into the sulfur slurry tank where it is used to break up the sulfur slurry froth.

#### *Solids Removal System*

12. The solids removal system is designed for either continuous sulfur removal or in the case of filter presses, to be typically opened every 24 hours.

#### *Make-Up Chemicals*

13. Caustic Soda
14. Proprietary chemical additive solution. The chemicals are fed into the standpipe of the biogas contactor vessel using metering type drum pumps based on pH in the vessel. Residual H<sub>2</sub>S measurements downstream from the unit are made periodically to evaluate system performance.

This system can be configured for various applications such as municipal wastewater treatment, industrial wastewater treatment, industrial processing, pulp and paper mills, food and beverage processing, meat rendering plants, landfill gas, and agriculture.

## **Conclusion**

Utilization of biogas for energy production has been growing exponentially as a result of high natural gas and electrical energy prices and government emphasis on sustainable use of renewable resources. Hydrogen sulfide is one of the main contaminants that can adversely affect performance in engines and boilers, and its concentration must be maintained below levels frequently encountered in biogas. Means for controlling hydrogen sulfide levels have been reviewed in this paper. Such means must be both performance and cost effective.