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## Optimizing Hydrogen Sulfide Removal and Biogas Production Using the Water Wash Method

Brian Leightner  
*University of Wisconsin-Milwaukee*

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OPTIMIZING HYDROGEN SULFIDE REMOVAL AND BIOGAS PRODUCTION  
USING THE WATER WASH METHOD

by

Brian G. Leightner

A Thesis Submitted in

Partial Fulfillment of the

Requirements for the Degree of

Master of Science

in Engineering

at

The University of Wisconsin – Milwaukee

December 2019

## ABSTRACT

# OPTIMIZING HYDROGEN SULFIDE REMOVAL DURING BIOGAS UPGRADING AND MINIMIZING ITS ENVIRONMENTAL IMPACTS

by

Brian G. Leightner

The University of Wisconsin – Milwaukee, 2019  
Under the Supervision of Professor Jin Li

Biogas forms from decomposing organic material in agricultural digesters, landfills, and wastewater treatment plant digesters. Biogas is mostly composed of methane, and can be used as a carbon-based fuel. Microorganisms that consume organics in these waste streams also produce hydrogen sulfide (H<sub>2</sub>S) as part of the biogas, in varying trace amounts. H<sub>2</sub>S is corrosive to engines and pipes for machinery, a human health hazard when inhaled, and an aquatic hazard when dissolved in water. Water washing is an absorption process that dissolves hydrogen sulfide and other water soluble compounds in this process and carries it away from the gas, thereby purifying it. A water wash absorption column process at Jones Island in Milwaukee is being tested to purify landfill biogas by varying gas and water flowrates, as well as the gas pressure, resulting in an observed 90-99% removal of hydrogen sulfide from biogas was observed.

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## LIST OF ABBREVIATIONS

BTU/lb	British thermal units (of energy) per mass pound
CO <sub>2</sub>	Carbon dioxide
CHP	Combined heat and power
DIC	Dissolved inorganic carbon
ETI	Energy Tech Innovations, LLC
Gpm	Gallons per minute
GJ	Gigajoule (of energy)
H <sub>2</sub> S	Hydrogen sulfide
H <sup>+</sup>	Hydronium, expressed as hydrogen ions
OH <sup>-</sup>	Hydroxide ion
kWh	Kilowatt-hours (of energy)
Lpm	Liters per minute
LEL	Lower explosive limit
MJ/kg	Megajoules (of energy) per kilogram
CH <sub>4</sub>	Methane
MMSD	Milwaukee Metropolitan Sewerage District
MMBTU	Million British thermal units
N <sub>2</sub>	Nitrogen gas
n.d.	No date available
O <sub>2</sub>	Oxygen gas
Ppm	Parts per million
RNG	Renewable natural gas
WWTP	Wastewater treatment plant
WHO	World Health Organization
USEPA	United States Environmental Protection Agency

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## Introduction

When microorganisms are exposed to quantities of organic wastes, they are able to aid in the decomposition of these wastes by consuming a portion of the organics. A byproduct of this continuous decomposition is biogas. The chemical composition of this gas can vary based on the waste inputs. The average gas produced by microorganisms in these waste streams is 50-70% methane and 30-50% carbon dioxide, with a few trace contaminants that include H<sub>2</sub>S (Kennedy, Zhao, Ma, Chen, & Frear, 2015; Environmental Research & Education Foundation, 2019). Methane combustion is a highly exothermic reaction and therefore a valuable energy source. Methane is the main constituent in natural gas, a known and reliable fossil fuel resource. There are several advantages of gas fuel. Both biogas and natural gas have fewer impurities than coal, diesel, and gasoline. Gas fuels will vaporize into the atmosphere when leaking from a storage container, whereas liquid fuels will collect or leave a trail back to the reservoir of fuel. Biogas also requires a higher ignition temperature than liquid fuels, which is an advantageous feature to avoid accidents (Rasi, 2009). From an environmental perspective, it is better to convert methane to carbon dioxide than to emit methane, due to a difference in global warming potentials. Global warming potential (GWP) is a method of measuring the environmental impacts of a ton of one particular greenhouse gas. As a reference, carbon dioxide has a GWP of 1, while methane has a GWP of 28-36, depending on the year and other gases emitted into the atmosphere. This is due to greater amount of the sun's energy able to be absorbed by methane, which raises the temperature in the atmosphere (United States Environmental Protection Agency, 2017).

Although the average biogas produced at these waste sites has a lower methane concentration than natural gas, the biogas can be utilized as a fuel for boiler or a combined heat and power (CHP) unit. While this option requires minimal additional gas processing after production, biogas can become a supplement or even alternative to natural gas if it can be purified by removing the carbon dioxide and other impurities (Nock, Walker, Kapoor, & Heaven, n.d.; Wheeler, et al.).

### **Composition from different sources**

Biogas can come from any collection of organic waste by anthropogenic activities that are decomposed by microorganisms. The organic waste streams of interest for biogas production are agricultural digesters, landfills, and wastewater treatment plant (WWTP) digesters. As an example, Table 1 shows the biogas production variation from a few sites based on differing waste streams (Rasi, 2009).

**Table 1 - Biogas Composition**

Plant	Designation	Methane (CH <sub>4</sub> ) [%]	Carbon Dioxide (CO <sub>2</sub> ) [%]	Oxygen (O <sub>2</sub> ) [%]	Nitrogen (N <sub>2</sub> ) [%]	Hydrogen Sulfide (H <sub>2</sub> S) [ppm]
<b>Landfills:</b>						
Mustankorkea	W1	47-57	37-43	<1	<1-17	36-230
Koukujärvi	W2	47-62	37-41	NA	NA	27-32
Tarastenjärvi 1	W3	49-57	32-35	NA	NA	108-125
Tarastenjärvi 2	W4	51-61	35-37	NA	NA	53-84
Ämmässuo	W5	50-52	36-38	NA	NA	300-500
<b>WWTP digesters:</b>						
Jyväskylä	S1	60-65	34-38	<1	<2	<1-4
Tampere	S2	61-67	33-38	NA	NA	2-4
Tampere	S3	61-66	35-36	NA	NA	2-4
Espoo	S4	64-66	34-36	NA	NA	<1-2
<b>Livestock Biogas plants:</b>						
Kupferzell	B1	56	NA	NA	NA	300
Remlingen	B2	55	44	NA	NA	300
Vaasa	B3	56-65	38-40	NA	NA	500-1000
Ilmajoki	B4	65-70	29	NA	NA	3-5
Laukaa	B5	55-58	37-38	<1	<1-2	32-169

Digesters from livestock and WWTPs tend to have higher methane content than landfills due to fewer types of materials and a higher organic content in materials received (Cebula, 2009). Landfills accept more sources of waste that are not organic materials, and these wastes do not deteriorate as quickly. The USEPA conducted a twenty year study and found that the organic content of landfills has been decreasing. The USEPA largely attributes this change to a decline in the paper and yard waste sent to landfills. Both of these organic materials represent a large portion of the organic carbon attributing to biogas production. Paper recycling and a cultural shift away from print media, along with composting yard waste, have led to alternate

disposal methods of these carbon-based materials (Environmental Research & Education Foundation, 2019).

Additionally, digesters are in a completely anaerobic water treatment environment whereas landfills are vulnerable to air intrusion from the atmosphere and results in a microbiome that metabolizes a portion of this oxygen to biodegrade the organic wastes into methane, carbon dioxide and lesser amounts of hydrogen sulfide (Cebula, 2009). While this reduces the amount of oxygen that enters the biogas stream, nitrogen also passes through the waste and it is collected but nitrogen is not metabolized by these microorganisms, however this decreases the caloric value of the raw landfill gas.

### **Energy Value**

As stated earlier, methane is primary molecule in both biogas from organic waste streams and natural gas. While there is no methane content regulation or requirement for natural gas, a common assumption for modeling purposes is that natural gas is at least 86% methane and 14% nitrogen (Rasi, 2009). Since methane produces 55.5 MJ/kg (23,800 BTU/lb), which is more than the 46.4 MJ/kg (19,900 BTU/lb) produced by gasoline, upgrading the biogas to higher methane content increases its value (Bashar, 2018) such that it can be competitively priced in the market place. Natural gas is priced around \$8.29/GJ (\$8.75/MMBTU), and the biomethane upgraded from biogas would be priced slightly higher, but expected carbon taxes would keep it a competitive option (Electrigaz Technologies Inc, 2008).

## **Uses and Requirements**

The minimum methane content required in gas varies based on the use. In studies in the United States involving the use of upgraded biogas demanded different degrees of purity. Upgraded biogas for vehicle fuel required minimum methane content between 90-96%, while grid injection is typically set at 97-98%. These minimum requirements varied between studies (Electrigaz Technologies Inc, 2008).

## **Impurities in Biogas**

Methane is the only molecule in biogas produced by microorganisms that can be used as an energy source. These microorganisms produce other molecules that are in the biogas. Some molecules, such as carbon dioxide, merely bring down the caloric value of the gas on a volumetric basis. Other molecules, including hydrogen sulfide, are a hazard to equipment and the environment, so special consideration is needed when utilizing this gas.

## **Carbon Dioxide**

Carbon dioxide is classified as inorganic carbon, which is a carbon substance that is found in the atmosphere, ores, and minerals rather than in living creatures. It possesses minimal energy potential, so its presence in the gas reduces the caloric value of the gas (Gltenboth & Lehmusluoto, 2006).

## **Hydrogen Sulfide**

Hydrogen sulfide is a colorless and flammable gas that originates in organic waste streams and other natural sources when microorganisms reduce elemental sulfur found in waste (Zytner). Hydrogen sulfide causes a host of issues in the environment.

### ***Effect of Hydrogen Sulfide in Engines and Pipes***

Hydrogen sulfide itself is corrosive in gaseous form. It leads to deterioration in engines and steel pipes that transport and use the upgraded biogas. Some equipment can tolerate a higher hydrogen sulfide concentration than others. Additionally, stricter H<sub>2</sub>S limits are imposed when the upgraded biogas is used in commercial and residential appliances than when it is used in industrial equipment. Table 2 lists accepted maximum concentrations of hydrogen sulfide allowed in gas supplied for various intentions (Wheeler, et al.; Electrigas Technologies Inc, 2008).

**Table 2 - Hydrogen Sulfide Requirements**

<b>Task</b>	<b>Maximum [H<sub>2</sub>S] (ppm)</b>
<b>Boiler</b>	1000
<b>Electric generator/CHP</b>	500
<b>Vehicle fuel</b>	23
<b>Natural gas grid injection</b>	4
<b>Fuel cell</b>	1

### ***Human Hazards of Hydrogen Sulfide***

There is little difference between the concentration that hydrogen sulfide that can be detected in air and the concentration that it becomes a human health hazard. It produces an odor described as a “rotten egg smell.” The human health hazards of hydrogen sulfide and the levels at which they are experienced are given in Table 3 with the detection limit coming from the USEPA (Zytner; McVay, n.d.; United States Environmental Protection Agency, 1986).

**Table 3 - Hazards of Gaseous Hydrogen Sulfide**

<b>[H<sub>2</sub>S] (ppm)</b>	<b>Human Effect</b>
<b>0.002</b>	Detected
<b>10</b>	Eye irritation
<b>100</b>	Coughing/loss of smell
<b>200-300</b>	Reddening eyes
<b>300-700</b>	Unconsciousness/death within an hour
<b>1000-2000</b>	Rapid unconsciousness/imminent death
<b>4300</b>	Lower explosive limit (LEL)

### ***Hydrogen Sulfide in Water***

Pollutants in wastewater effluent are regulated differently than they are in drinking water effluent. While the USEPA has no H<sub>2</sub>S standard in its drinking water standards, the World Health Organization (WHO) has set a guideline of 0.05 ppm for hydrogen sulfide in drinking water to preserve its aesthetic taste and smell quality (Sawyer, McCarty, & Parkin, 2003). In contrast, wastewater discharges have few actual H<sub>2</sub>S requirements, though there are recommendations. As part of the Clean Water Act, the United States Environmental Protection Agency (USEPA) recommended a chronic maximum hydrogen sulfide concentration 2 ppb when discharging wastewater into an aquatic environment. This recommendation is set low due to the observed increase in fish mortality and reduced hatch rate from Walleye eggs when hydrogen sulfide was present at 25 ppb. When the concentration was increased 47 ppb, none of the eggs were able to hatch. The highest concentration hydrogen sulfide was able to reach before adverse were observed on fish populations was 14 ppb for eggs and 4 ppb for fish (United States Environmental Protection Agency, 1986). The recommendation for the maximum concentration of hydrogen sulfide at 2 ppb introduces a factor of safety. The USEPA report acknowledges that concentrations vary within these aquatic environments. Additionally,

fish are able to detect the hydrogen sulfide in water and avoid it when possible. This mirrors the ability of humans to detect hydrogen sulfide in air at very low levels. It is also important to note that this recommendation only applies to the hydrogen sulfide species. When hydrogen sulfide dissociates into bisulfide and again into sulfide ions, its hazardous effects are negated (United States Environmental Protection Agency, 1986).

### **Methods of Upgrading Biogas**

There are various methods of purifying biogas. A common requirement is to constantly remove stated impurities from the gas as it flows through a system.

#### **Pressure Swing Adsorption**

An adsorbing material, such as activated carbon or zeolites, can get impurities in biogas to stick to it under high pressures. The materials are later depressurized, allowing the impurities to vaporize into the off-gas. This regenerates the material's adsorption capacity to purify more biogas (Chen, Vinh-Thang, Ramirez, Rodrique, & Kaliaguine, n.d.). However, hydrogen sulfide is more reluctant to desorb from materials once attached, which decreases the future adsorption capacity (Peterson & Wellinger, 2009). To avoid this situation, adsorption processes require pre-treatment to remove the hydrogen sulfide. As hydrogen sulfide removal is a focus of this paper, this method is not explored.

#### **Membrane Separation**

Permeable materials selective to impurities of biogas can be used to increase the methane content of the gas. These membranes filter out larger molecules like carbon dioxide and hydrogen sulfide while letting smaller ones such as methane and nitrogen pass through the

filter (Peterson & Wellinger, 2009). A major disadvantage of this process is the highest potential for methane slip into the off-gas of explored methods (Bortoluzzi, Gatti, Sogni, & Consonni, 2014).

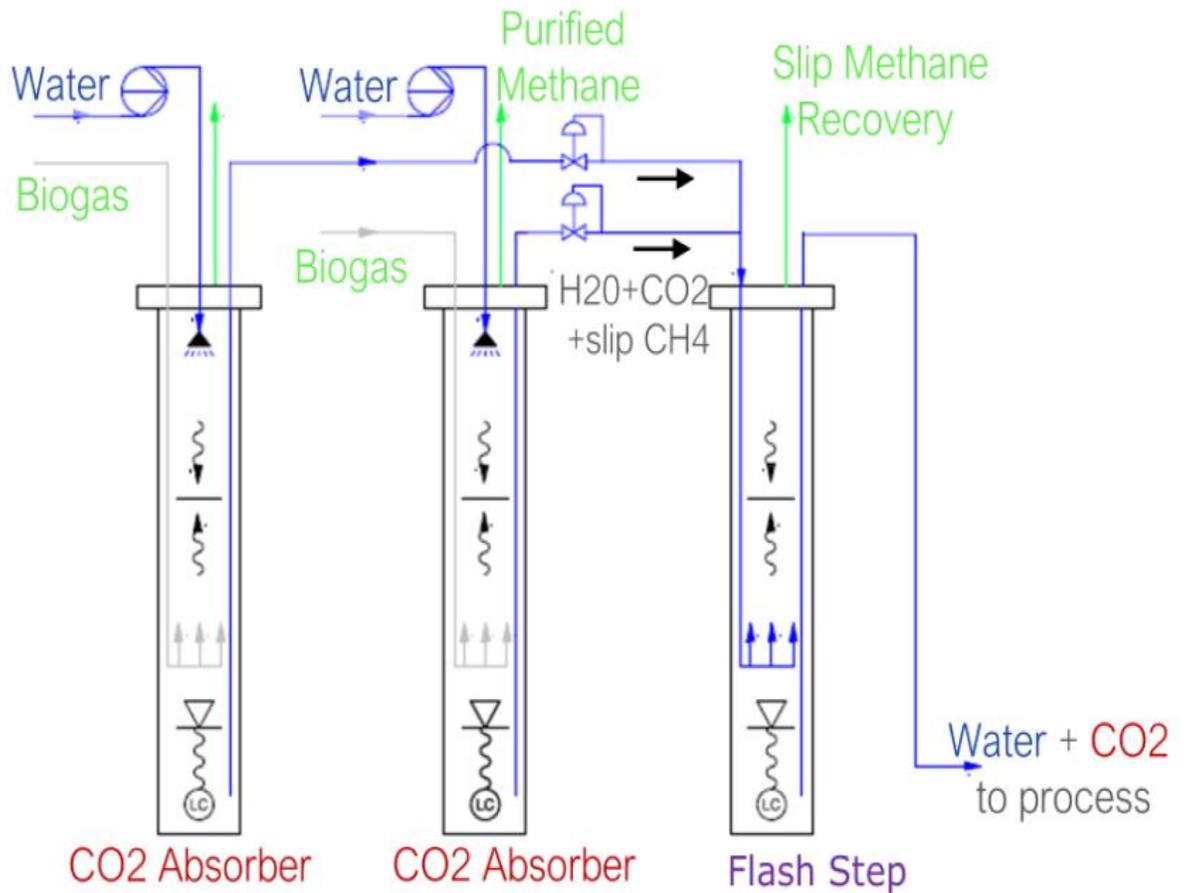
### **Cryogenic Separation**

A method distinct from others explored in this paper relies on the variance of boiling points of gases composing the biogas. By cooling the gas to below the boiling of carbon dioxide while remaining above that of methane, the carbon dioxide can be removed from the biogas when separating purified gas from liquefied impurities (Chen, Vinh-Thang, Ramirez, Rodrique, & Kaliaguine, n.d.). However, this requires extra equipment and energy input, increasing the energy costs to purify the biogas.

### **Water Wash**

A primary method of removing impurities, such as carbon dioxide and hydrogen sulfide, from the raw biogas is to expose the gas to water acting as a solvent so that the impurities are absorbed into the solvent as the gas comes into contact counter-current with the solvent. Gas is fed from the bottom of a column filled with packed media while the solvent is sprayed from the top and becomes evenly distributed across the column as the gas flows upward. The solvent then carries the impurities away via an outlet at the base and as a result, the biogas has been upgraded to a higher methane content. Often, the solvent is regenerated using an air stripping column to remove the CO<sub>2</sub> and H<sub>2</sub>S if present. The flash column, where the solvent is exposed to a lower pressure and any product loss in the form of “slip” methane can be

collected to recycle back into the process in some cases as shown in Figure 1 that depicts the overall pilot water wash process (Energy Tech Innovations, LLC).



**Figure 1 - Diagram of typical overall water wash process (Energy Tech Innovations, LLC)**

Water is typically used as a solvent for being inexpensive and readily available. This method is effective since water solubilizes carbon dioxide and hydrogen sulfide at a higher rate than methane (Cozma, Wukovits, Mămăligă, Friedl, & Gavrilesu, 2014; Lien, Lin, & Ting, 2014). Organic solvents, mainly polyethylene glycol or alkanol amine solutions, can be used as alternatives to water in this method of upgrading biogas. These organic solutions are more effective at absorbing carbon dioxide than water. However, organic solvents are more

expensive to procure, meaning that the wash method will produce organic waste that must be replaced or the solvents will have to be regenerated to release the carbon dioxide back into gaseous form and removing it through an exhaust (Kennedy, Zhao, Ma, Chen, & Frear, 2015; Schruender, 2019).

## Solubility

The solubility of carbon dioxide and hydrogen sulfide in water are affected by various physical factors. Under standard conditions, the solubility of a gas in water can be modeled using Henry's Law (Rasi, 2009; Sawyer, McCarty, & Parkin, 2003):

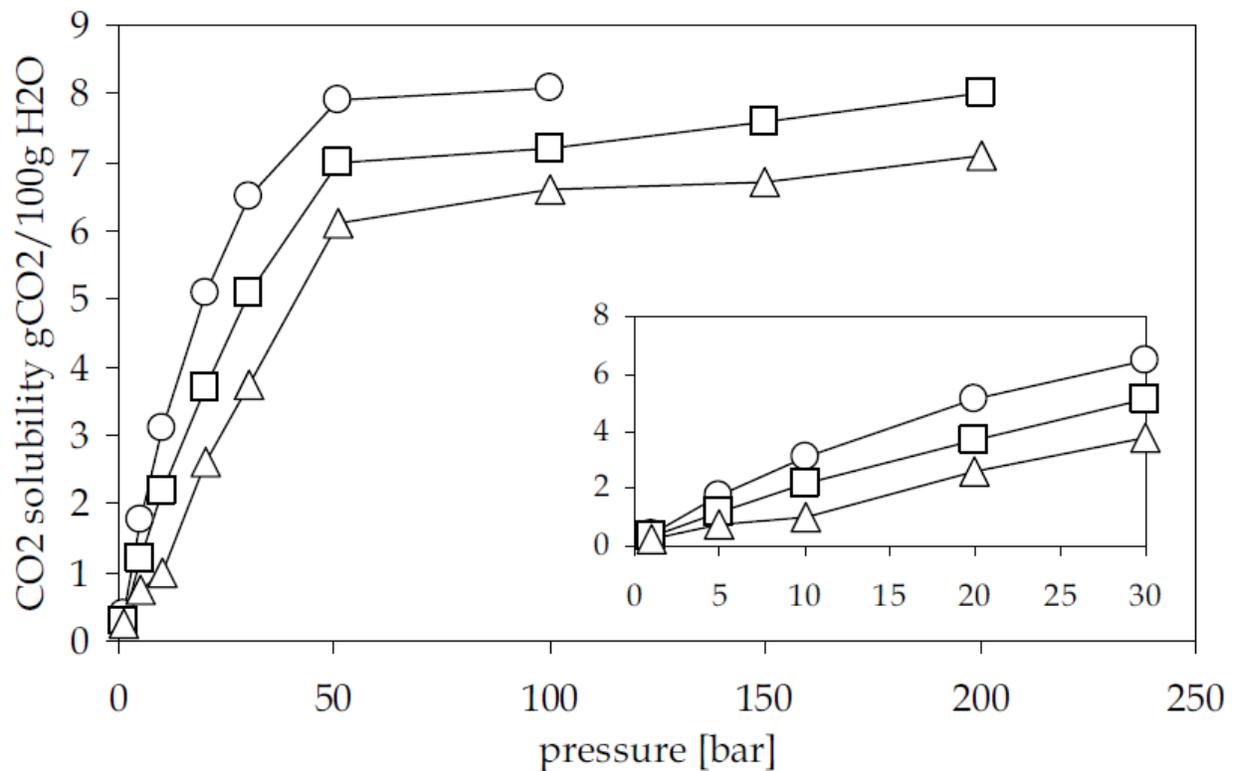
$$(Equation 1) \quad P_A = H_A \times C_A$$

Where  $P_A$  is the partial pressure due to gas A, expressed in atmosphere unites (atm)

$C_A$  is the mole fraction of gas A dissolved in a liquid, expressed as M, the molarity

$H_A$  is the Henry's constant for gas A, expressed as atm/M

This equation is simple to use, however it is not accurate in all situations. Gas solubility is not a completely linear relationship with pressure. As pressure increases beyond 50 bar, temperature becomes the determining factor. Figure 2 plots the plateau of solubility of carbon dioxide as dependent on pressure (Rasi, 2009). A collection of research papers converges on a Henry' constant for hydrogen sulfide of  $1 \cdot 10^{-1}$  atm/M in water (Bashar, 2018).



**Figure 2 - Solubility of CO<sub>2</sub> (Rasi, 2009)**

When carbon dioxide and hydrogen sulfide dissolve in water, they behave as acids.

Carbon dioxide in this process reacts with water to form carbonic acid and then bicarbonate (National Oceanic and Atmospheric Administration). Similarly, hydrogen sulfide will dissociate into bisulfide. Figures 3 and 4 are the pC-pH diagrams for carbon dioxide and hydrogen sulfide in water (Lower, 1996; McVay, n.d.).

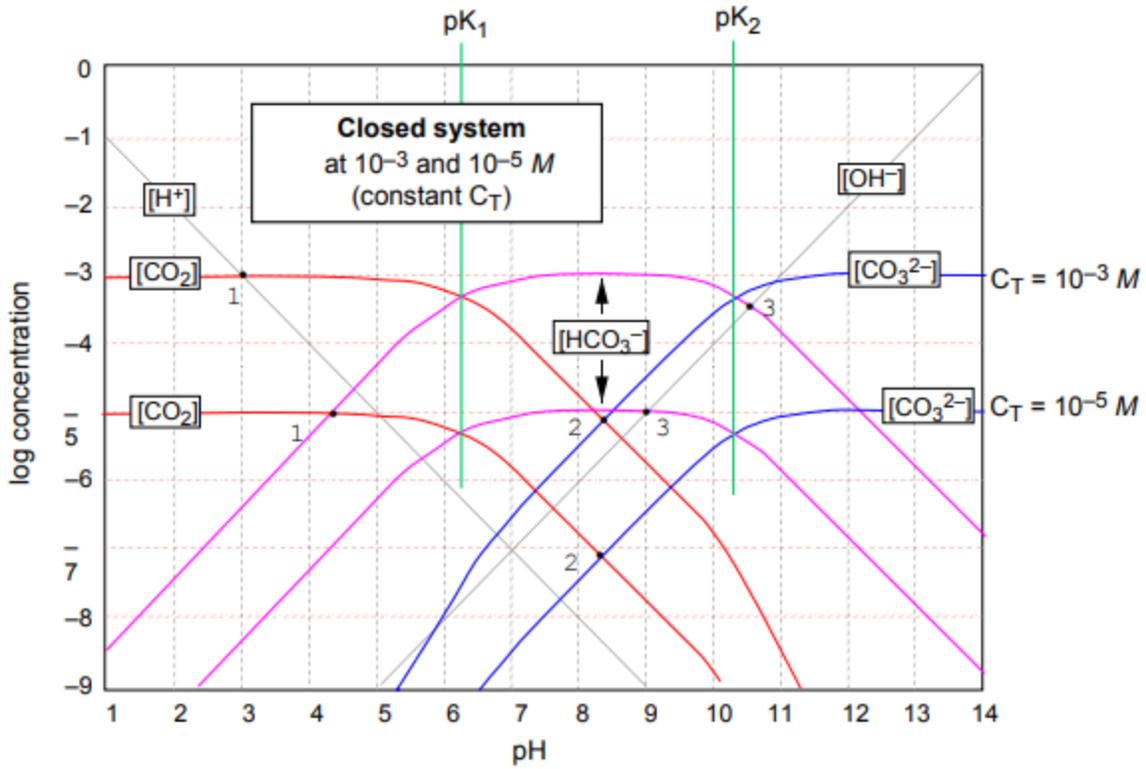


Figure 3 - pC-pH diagram of CO<sub>2</sub> in water (Lower, 1996)

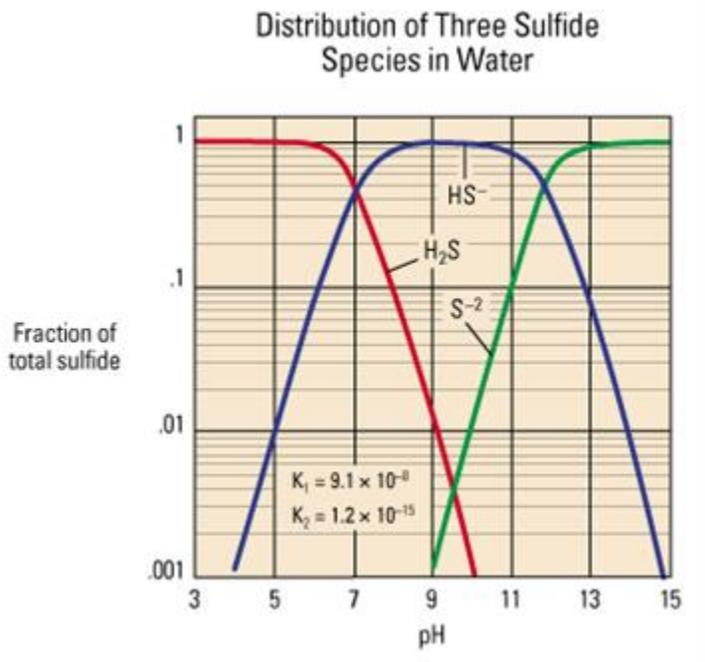


Figure 4 - pC-pH diagram of H<sub>2</sub>S in water (McVay, n.d.)

## Materials and Methods

The water wash method was utilized to study the removal of hydrogen sulfide under various conditions of pressures and gas-to-liquid flowrates. It was also of interest to compare carbon dioxide removal from the biogas and solubility in the wash water to that of hydrogen sulfide under the same conditions. With collected data and estimating the fraction of hydrogen sulfide dissolved in the wash water that would not dissociate into bisulfide, it can be predicted whether this process wash water discharge would pose a hazard when discharged into an aquatic environment.

These tests were conducted by Energy Tech Innovations (ETI) with support from the Milwaukee Metropolitan Sewage District (MMSD) in Milwaukee, Wisconsin. Biogas collected at Veolia Environmental Services' Emerald Park Landfill was pretreated of hydrogen sulfide and other impurities and then transported via piping to Jones Island Water Reclamation Facility, as mapped in Figure 5. The figure notes the use of repurposed pipe from petroleum product conveyance with the dashed line. The solid gold line denotes new pipeline installed for landfill gas flow. The pipe can pressurize the pre-treated landfill gas to a maximum of 100 psig (MMSD, 2019). ETI had setup a pilot technology demonstration station of water wash absorber system near the landfill gas distribution and monitoring building at the water reclamation facility. The pilot featured two absorption columns with two smaller flash columns. However, tests conducted in this part of the study only used the absorption column in the front of the figure, and did not use either of the flash columns. Freshwater was used as a solvent along with gas pass through the either of the absorbers counter-concurrent flow direction. The absorbing column is packed with open structure plastic media that creates a lot of void space that is

supported by a horizontal mesh support grid that drains to a sump. The upgraded biogas was discharged to a small flare while the used wash water was not recycled but rather released to an onsite manhole sewer connection for treatment (Energy Tech Innovations, LLC).

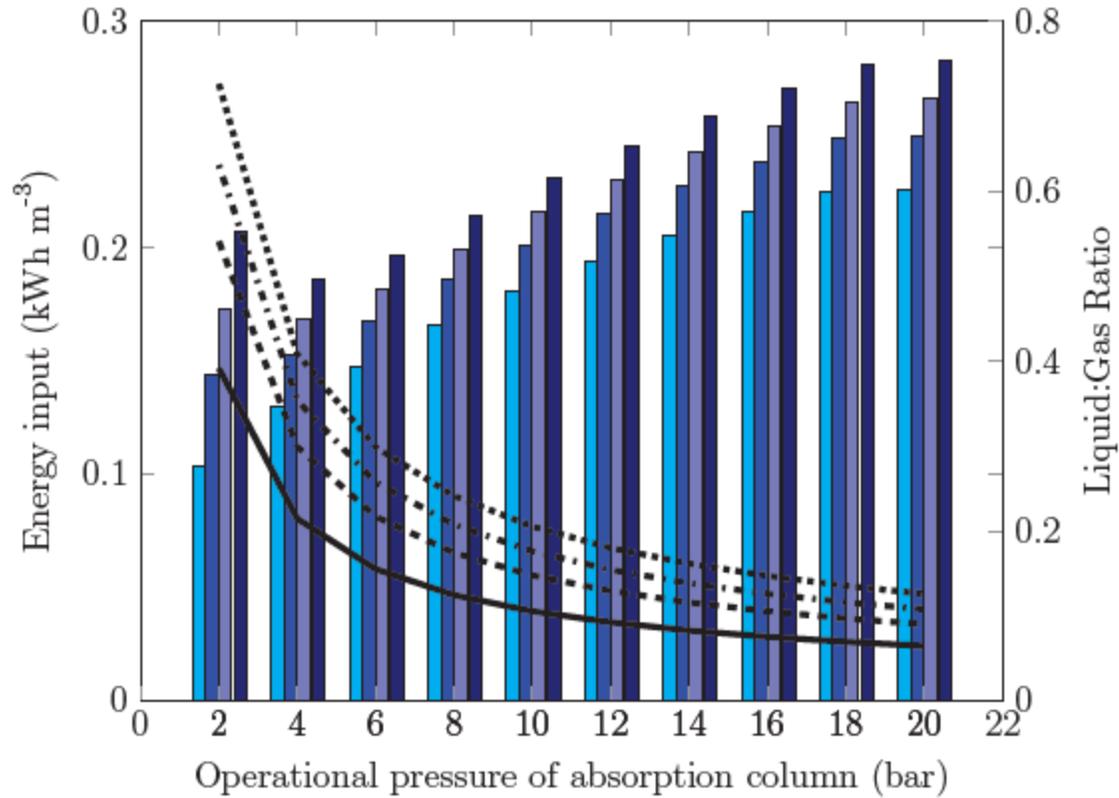
In the thesis paper by Schruender in 2019, she noted the limited range of gas and water flowrates to test carbon dioxide removal during the water wash process. With the same pilot test at Jones Island in her paper, the last round of 2019 tests studied the removal rates at an expanded range of gas and water flowrate ratios between them. Additionally, carbon dioxide removal has now been compared to hydrogen sulfide removal for a number of the test runs.



Figure 5 - Map of biogas pipeline from Emerald Park to Jones Island (MMSD, 2019)

## Parameters set

Some of the physical pilot operating parameters were based on correlations to of Nock et al. to verify the requirements to achieve stated degrees of methane purity once the biogas had been upgraded. Figure 7 plots the necessary input energy to achieve a certain level of methane purity at a specified gas to liquid ratio and gauge pressure. Different levels of methane purity are denoted with different colored bars for energy input and dash type lines for liquid to gas ratios (Nock, Walker, Kapoor, & Heaven, n.d.).



<i>CH<sub>4</sub> Conc.</i>	80 %	90 %	95 %	98 %
Energy Input <i>kWh m<sup>-3</sup> (input)</i>				
Liquid: Gas Ratio	—	---	---	.....

Figure 6 - Requirements to obtain specified methane concentrations (Nock, Walker, Kapoor, & Heaven, n.d.)

**Gas quality measurements**

Incoming gas quality from the landfill was monitored and recorded using the display console for a gas chromatography spectrophotometer at the landfill gas distribution and monitoring building. This console provided measurements of biogas composition by percent mass and hydrogen sulfide volumetric concentrations. A Landtec GEM 2000 LFG portable meter

measured upgraded biogas composition and a RAE System MultiRAE Pro portable meter measured hydrogen sulfide concentration of the upgraded gas from the discharge pilot piping after the absorption column. The GEM 2000 meter was also used to verify the pre-treated biogas composition a manifold preceding the absorption column. The MultiRAE Pro meter could not verify the hydrogen sulfide concentration pre-treated biogas since the meter sensor could not measure concentrations exceeding 100 ppm (v).

### **Physical measurements**

Gas flow was measured with rotameter type air flowmeters, which pushes a weight upwards in a tube and can be interpreted as a flowrate based on the scaled markings. Water flow was measured with multiple flowmeters, one being a Pitot tube insertion meter and the other a rotameter, though they both operated by visual observation of scaled readout markings. These flowmeters were verified by measuring the discharge from the wash water by a stopwatch via recording the time taken to fill a 5.7 gallon bucket.

Both gas and water pressures were recorded using pressure gauges. Temperature was recorded using temperature gages. These gauges for gas were mounted to the same manifolds where gas quality was sampled. Gauges for water were mounted to a pipe preceding the column.

### **Data analysis**

The landfill gas composition was measured by percent mass of carbon dioxide, methane, nitrogen, and oxygen. As the gas flowrate of the pre-treated and upgraded flows were measured using air flowmeters, conversions were necessary to accurately interpret data. Molar

mass of the biogas was determined for pre-treated and upgraded flows of each trial by finding the quotient of the percent mass of a molecule in the biogas flow by that molecule's molar mass, then taking the inverse of the sum of those quotients, as done in Equation 2. The biogas' molar mass can be used to find its specific gravity by dividing the molar mass into that of air, which is approximately 28.96 based on its composition (Helmenstine, 2019).

These flowmeters were meant for air, so the measurements had to be adjusted by accounting for the difference in molar mass between the raw biogas and air, and then product biogas and air. The molar mass of the biogas flows was found using equation 2:

$$\text{(Equation 2)} \quad MM_{biogas} = \sum_{i=1}^4 \frac{MM_i}{\%_i}$$

Where i is one of the 4 main molecules in biogas, being carbon dioxide, methane, oxygen, and nitrogen

$MM_{biogas}$  is the molar mass of the biogas

$MM_i$  is the molar mass of the ith molecule

$\%_i$  is the percent mass of the ith molecule in the biogas

The specific gravity is used to adjust the flow detected on the air meter to reflect the actual flow of the biogas, which is lighter than air. Equation 3 below is a gas control valve sizing formula.

$$\text{(Equation 3)} \quad Q_{s-gas} = C_V \times \sqrt{\frac{P_a \Delta P}{T_a G_{gas} Z_{gas}}}$$

Where:  $Q_{s-gas}$  is the flowrate of the gas

$C_v$  is a valve constant, expressed as flowrate over pressure multiplied by the square root of temperature

$P_a$  is the actual pressure

$\Delta P$  is the differential pressure

$T_a$  is the actual temperature

$G_a$  is the dimensionless specific gravity of the gas relative to air

$Z_{gas}$  is the dimensionless compressibility factor

When taking the ratio between the gas and air, equation 3 can be simplified to equation 4 which can be done in the relatively low pressure range conducted in this study (engineering.com, Inc., 2007). The compressibility factor in the pressure range was found to be consistently between 0.99 and 1 and was assumed to be negligible in these experiment analyses (Natural Gas Compressibility Factor, 2015).

$$\text{(Equation 4)} \quad Q_{s-gas} = Q_{s-air} \times \sqrt{\frac{1}{G_{gas}}}$$

Where  $Q_{s-gas}$  is the flowrate of the gas

$Q_{s-air}$  is the flowrate of air under these parameters

$G_{gas}$  is the specific gravity of the gas relative to air

With the corrected air flow, the ideal gas law, stated in Equation 5, was used to determine the total moles of gas flowing into and out from the absorber.

$$\text{(Equation 5)} \quad \dot{n} = \frac{P \times V}{R \times T}$$

Where  $\dot{n}$  is the molar gas flowrate

P is the gas pressure

V̇ is the gas volumetric flowrate

R is a gas constant

T is the gas temperature

Along with the molar mass of the biogas previously determined, the mass flowrate of gas in moles was converted to an overall mass, which then could be apportioned to each molecule based on the percent weight detected with the gas meter. With individual molecule mass flowrates, the mass flowrate of carbon dioxide absorbed into the wash water and the waste dissolved inorganic carbon (DIC) concentrations were found for each trial.

Hydrogen sulfide results were reported by a different flowmeter as a volumetric concentration with units of ppm (v), as it is a trace contaminant and not as present in biogas as carbon dioxide. To convert the concentration expressed as a volume to a mass, the Centers for Disease Control and Prevention has posted an online calculator to determine the concentration in mg/m<sup>3</sup> (The National Institute for Occupational Safety and Health, 2014). However, the conversion assumed standard pressure and temperature. The equation was adjusted and reformatted below as Equation 6.

(Equation 6) 
$$Y = \frac{X \times MM_X}{\frac{RT}{P}}$$

Where Y is the mass based concentration in mg/m<sup>3</sup>

X is the volume based concentration in ppm (v)

MM<sub>x</sub> is the molar mass of the X molecule

R is the gas constant

T is the gas temperature

P is the gas pressure

Both of these concentrations were then multiplied by the gas flowrate to determine mass flowrates through the absorption column. The mass flowrate absorbed into the wash water was divided by the water flowrate to determine the hydrogen sulfide concentration in the waste wash water stream.

## Results

### Biogas quality

Because the tests were conducted with landfill gas that contains measurable concentrations of oxygen and nitrogen gas, product gas quality is impacted by how much of these gases are present in the pre-treated gas, as they are harder to remove than carbon dioxide and hydrogen sulfide. The amount of these gases in the biogas fluctuates by the day, so this interferes with data analysis. To remove this interference, methane content in the upgraded gas will be stated as “methane equivalent.” This is the percent by mass in the gas that methane would have if the mass of oxygen and nitrogen gas in the biogas is ignored. Only methane and carbon dioxide were considered for biogas composition by percent mass, with hydrogen sulfide was considered the only trace compound in the gas. This reduced the number of variables impacting measured gas quality.

As carbon dioxide and hydrogen sulfide were washed from the biogas into the water, the biogas composition changed as the carbon dioxide percentage decreased, thereby increasing the methane percentage. Nock, et al. use a performance index,  $\xi$ , to represent the percent molar change in carbon dioxide and hydrogen sulfide from the pre-treated biogas to the upgraded biogas, as in equation 7.

$$\text{(Equation 7)} \quad \xi = \frac{1 - \frac{y_u}{100}}{1 - \frac{y_r}{100}}$$

Where  $\xi$  is the performance index for the molecule in question

$y_u$  is the mole fraction of the gas in the upgraded biogas

$y_r$  is the mole fraction of the gas in the raw biogas

The performance index was then used to determine if different independent variables had an impact on the performance index of the water wash process. Figures 8 through 10 are the impacts of gas pressure, water flowrate, and gas flowrate on the performance index, respectively. The performance indices of both carbon dioxide and hydrogen sulfide are plotted.

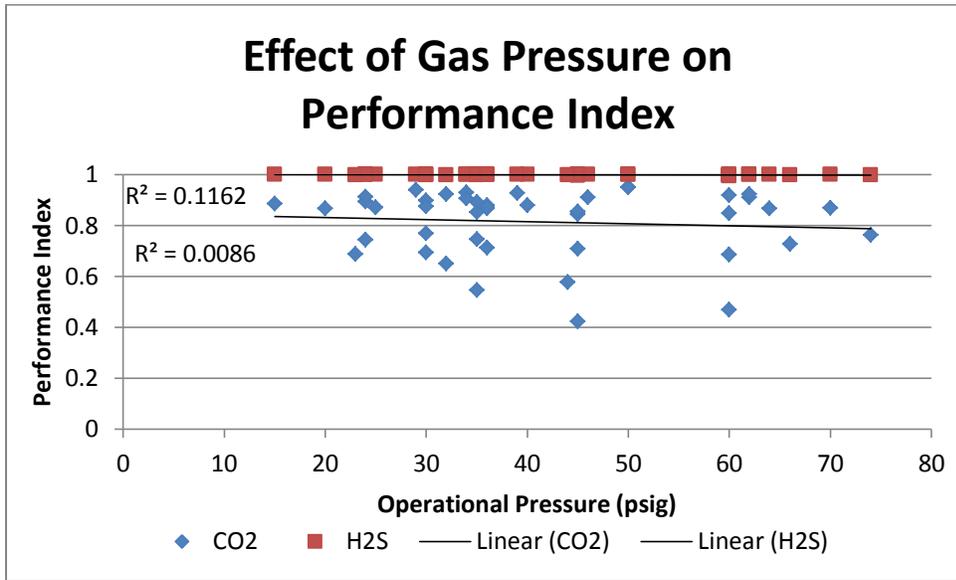


Figure 7 - Gas Pressure and Performance Index

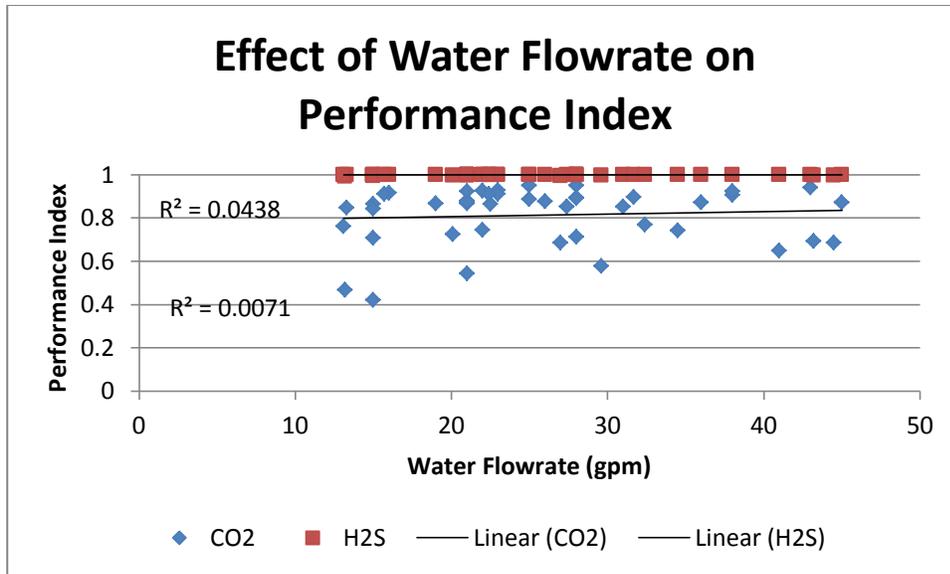


Figure 8 - Water flowrate and performance index

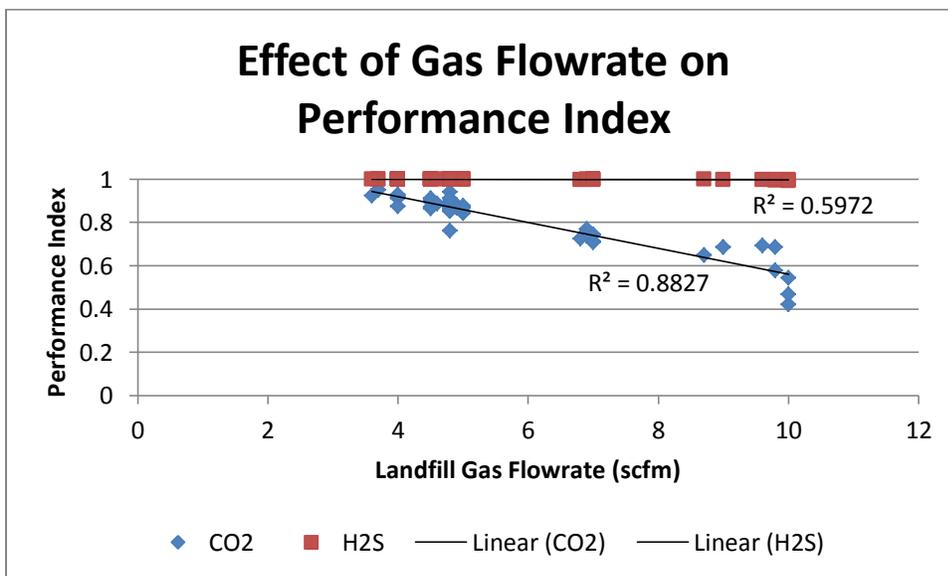


Figure 9 - Gas flowrate and performance index

Based on the above figures, gas pressure and water flowrate did not have any impact on the performance of the absorber. The gas flowrate of the pre-treated biogas demonstrated a general downward trend in performance when gas flow increased, though this is not a conclusive correlation.

## Hydrogen sulfide

The absorber reduced hydrogen sulfide concentrations in the upgraded biogas to below 10 ppm(v) for all but one tests conducted. Figures 11 and 12 plot the hydrogen sulfide concentrations in the upgraded biogas as a function of gas-liquid ratio and gas pressure, respectively. On both figures, the accepted requirement for maximum hydrogen sulfide in natural gas supplies is also plotted for reference.

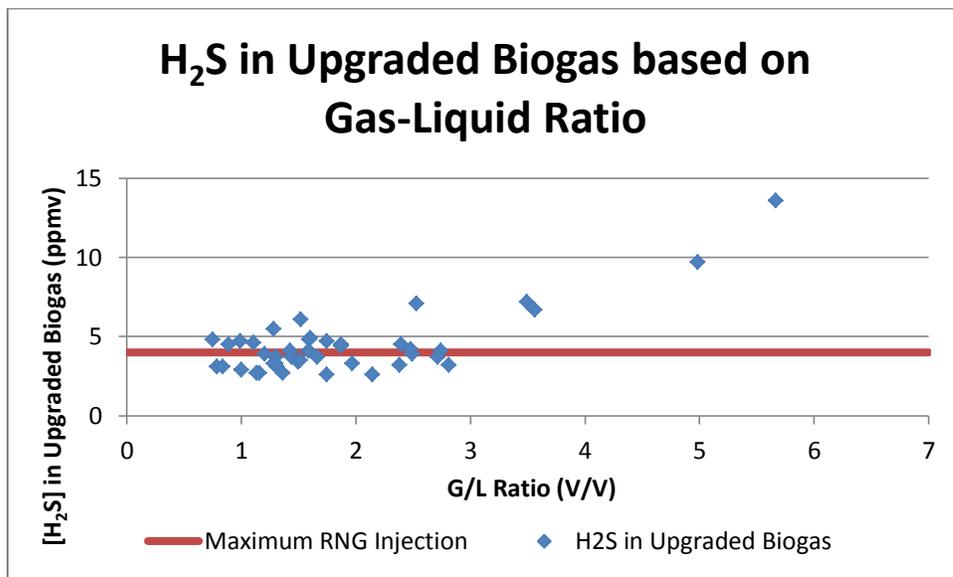
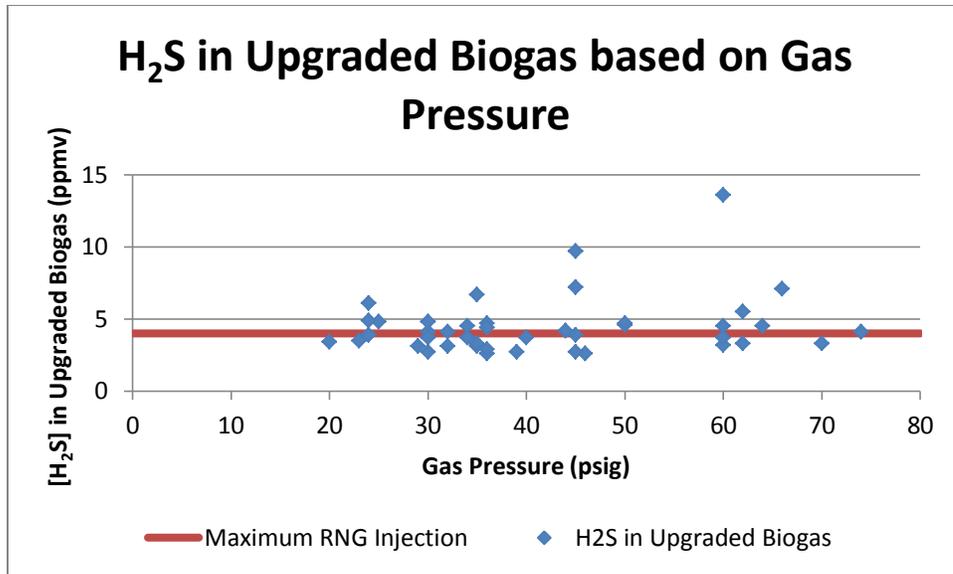


Figure 10 - Hydrogen sulfide concentration in product gas as a function of gas-liquid ratio



**Figure 11 - Hydrogen sulfide concentration in product gas as a function of gas pressure**

While the exiting hydrogen sulfide concentration is shown to have little correlation to gas pressure in Figure 12, there is a possible second-order relationship between gas-liquid ratio and exiting H<sub>2</sub>S. This inference is based on the curvilinear upward trend of H<sub>2</sub>S in the product gas at higher ratios. All of the tests show low enough hydrogen sulfide concentrations that the produced gas is safe to use as vehicle fuel, but only some tests were able to treat the gas to a level of safety for injecting the upgraded biogas into a natural gas grid.

Figure 13 below plots the removal rate as a function of the gas-liquid volumetric ratio. This is part of a trend seen in Kennedy, et al. 2015’s study in Figure 14, though this study conducted absorption tests until the hydrogen sulfide was not removed from the biogas.

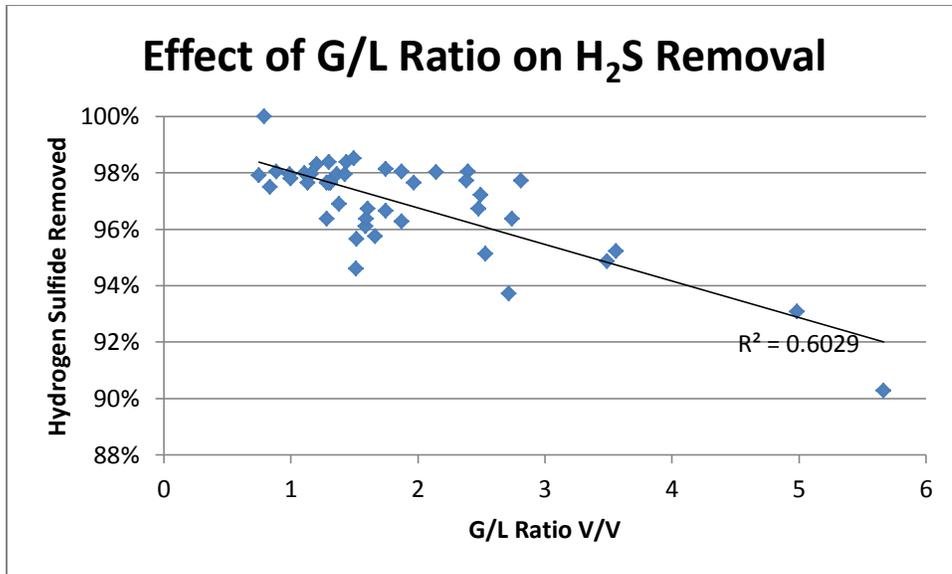


Figure 12 - Hydrogen sulfide removal rates at various G/L ratios

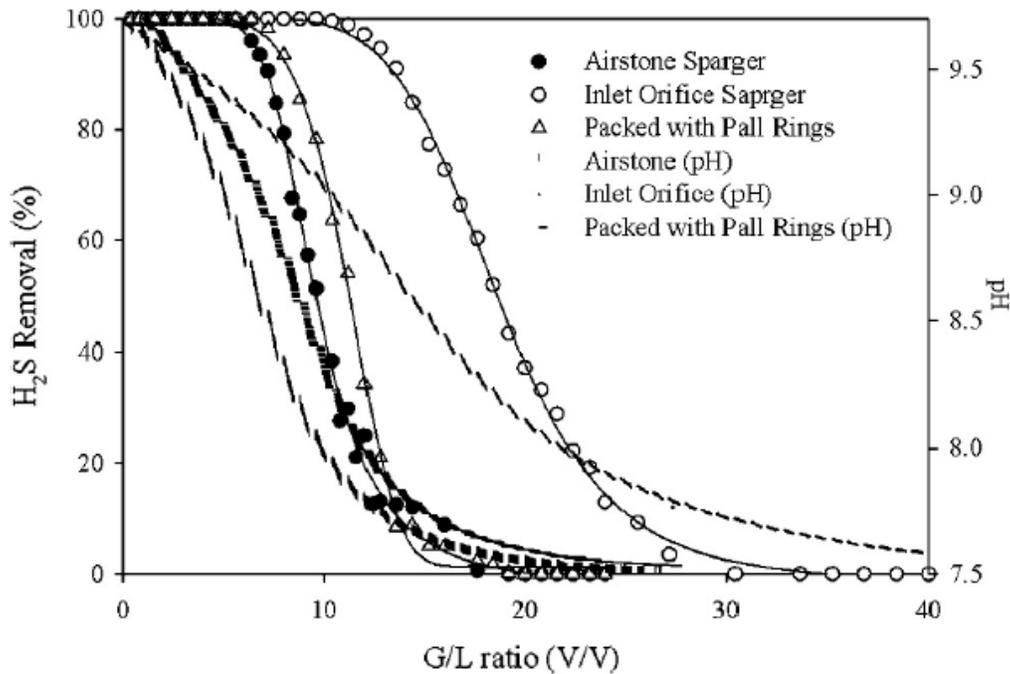


Figure 13 - Hydrogen sulfide removal rates at various G/L ratios and their pH values (Kennedy, Zhao, Ma, Chen, & Frear, 2015)

Kennedy, et al. also suggested the use of a selectivity factor,  $S$ , to determine if the water wash absorber process is selective towards removing hydrogen sulfide over carbon dioxide. This selectivity index is the ratio of the absorption rate of hydrogen sulfide over that of carbon dioxide. A simplified computation of the selectivity factor is in the following equation 8.

$$(Equation\ 8) \quad S = \frac{\left(\frac{M_{H_2S}}{M_{CO_2}}\right)_{liquid\ phase}}{\left(\frac{M_{H_2S}}{M_{CO_2}}\right)_{gas\ phase}}$$

Where  $S$  is the selectivity factor

$M_{H_2S}$  is the hydrogen sulfide molarity

$M_{CO_2}$  is the carbon dioxide molarity

The selectiveness of the absorber can be determined to be in favor of hydrogen sulfide if the selectivity factor is greater than the ratio of the partial pressures (Kennedy, Zhao, Ma, Chen, & Frear, 2015). In all tests, the selectivity index was approximately equal to the ratio of partial pressures. However, the greater solubility of hydrogen sulfide to carbon dioxide allows for greater absorption capacity of hydrogen sulfide. This bias towards hydrogen sulfide can be seen in the Figure 15 comparing the two absorption rates.

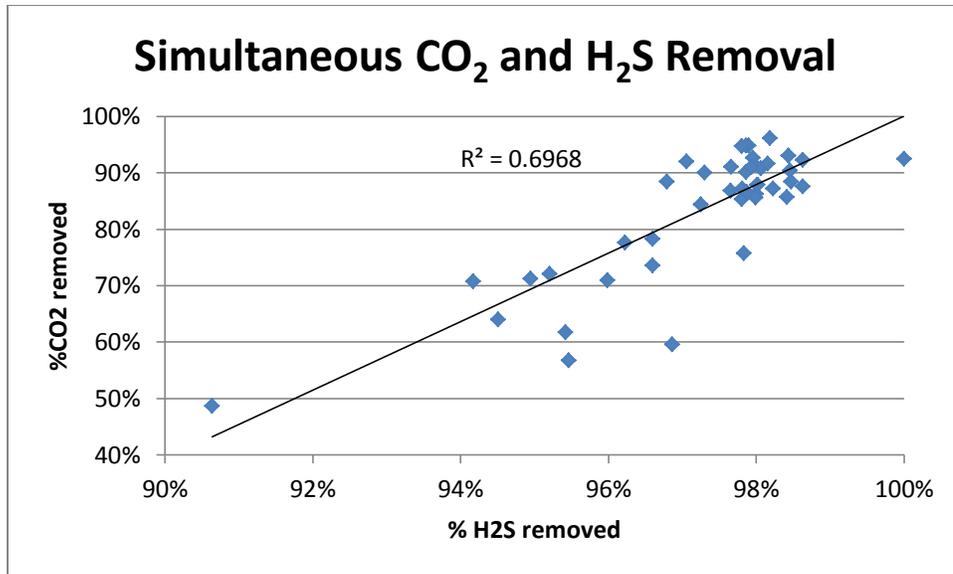


Figure 14 - Comparison of carbon dioxide and hydrogen sulfide removal rates

### Energy Required

Though no electrical equipment was used in the water wash absorber itself, existing pumps at the water reclamation facility and compressors were used to provide the fluid flows for these tests. These energy inputs will vary based on the amount of gas and water used to upgrade the biogas. Energy required to run each test was determined by equation 9 and using 83% motor efficiency. The constants listed are for unit conversions.

$$(Equation 9) \quad IE_{required} = \frac{Q_{water}}{Q_{gas}} \times \frac{P}{1714} \times \frac{0.7457kW}{1 hp} \times \frac{1 hr}{60 min} \times \frac{1}{\eta}$$

Where  $IE_{required}$  is the input energy required to run the water wash absorption column,

expressed as kWh/ft<sup>3</sup>

$Q_{water}$  is the water flowrate in gpm

$Q_{gas}$  is the gas flowrate in scfm

P is the water pressure in psig

$\eta$  is the pump and motor efficiency

Figures 16 through 18 correlate the removal of hydrogen sulfide and carbon dioxide, as well as upgraded methane content to the input energy required to complete the process at specific flow rates and pressures.

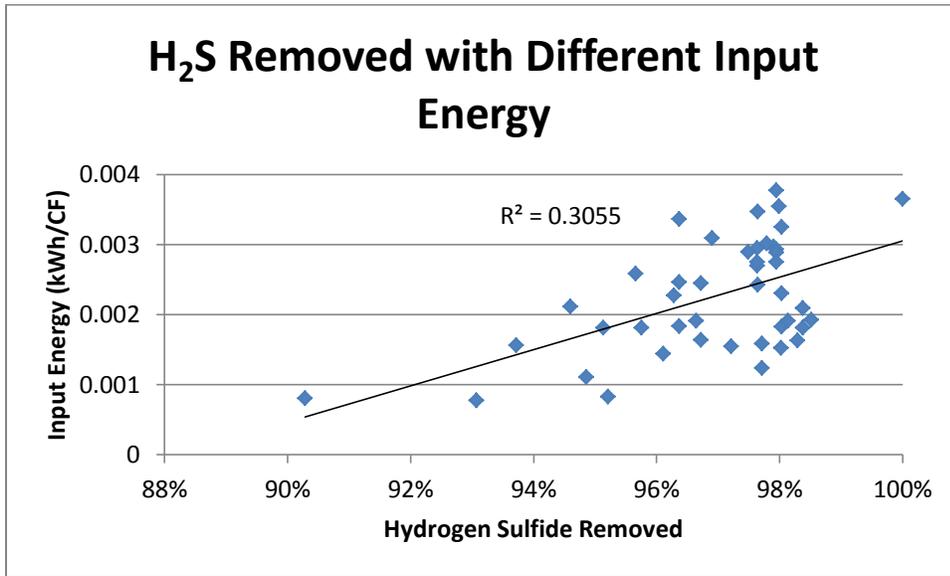


Figure 15 - Input required at various hydrogen sulfide removal rates

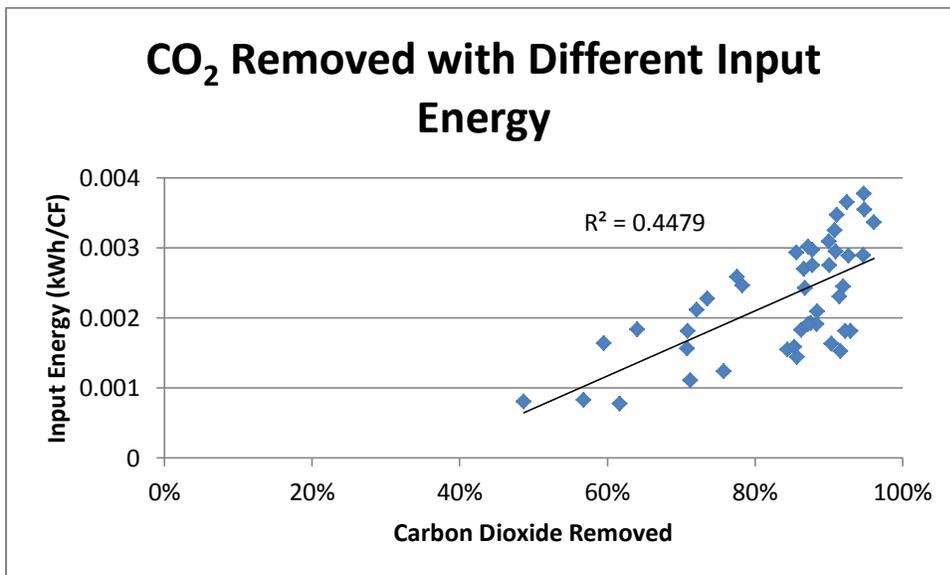
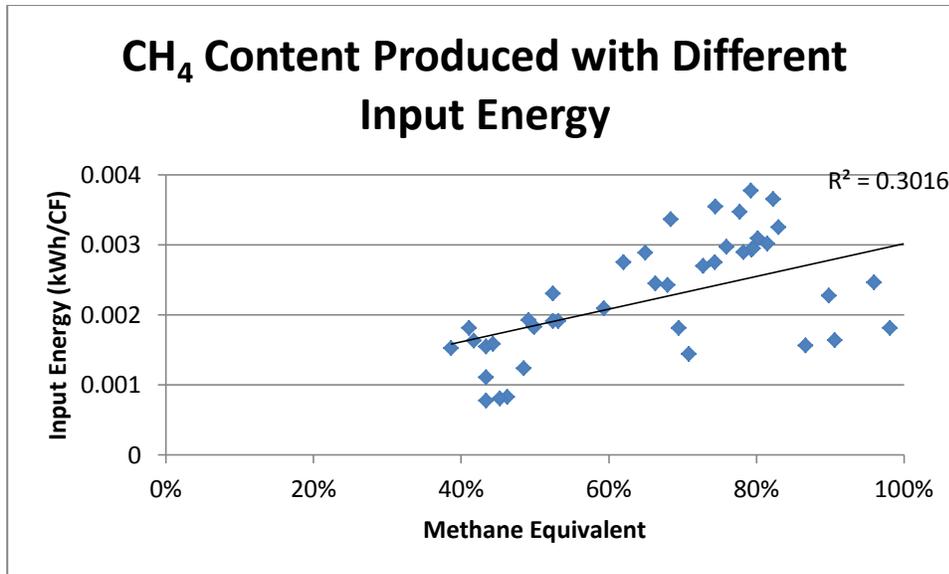


Figure 16 - Input required at various carbon dioxide removal rates



**Figure 17 - Input required at various methane content upgrades**

The daily output chemical energy from the upgraded biogas can be calculated using the following equations 2-5 after acquiring data then following Equation 10, and that methane has a caloric value of 55.5 MJ/kg (Bashar, 2018).

$$\text{(Equation 10)} OE = \frac{\dot{n}}{MM_{\text{upgraded biogas}}} \times \%_{\text{methane}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{55.5 \text{ MJ}}{\text{kg}_{\text{methane}}} \times \frac{0.27778 \text{ kWh}}{1 \text{ MJ}} \times \frac{1440 \text{ min}}{1 \text{ day}}$$

Where OE is the daily output chemical energy in kWh/day

$\dot{n}$  is the mass flowrate in moles/min

$MM_{\text{upgraded biogas}}$  is the molar mass of the upgraded biogas

This equation assumes the pilot absorber at Jones Island would be used constantly.

With the required input energy and expected output energy determined, net energy outputs across all tests can be compared to find the optimal setup for the water wash absorption

process. The figures below compares all net energy outputs as a function of the gas-liquid volumetric ratio and gas pressure.

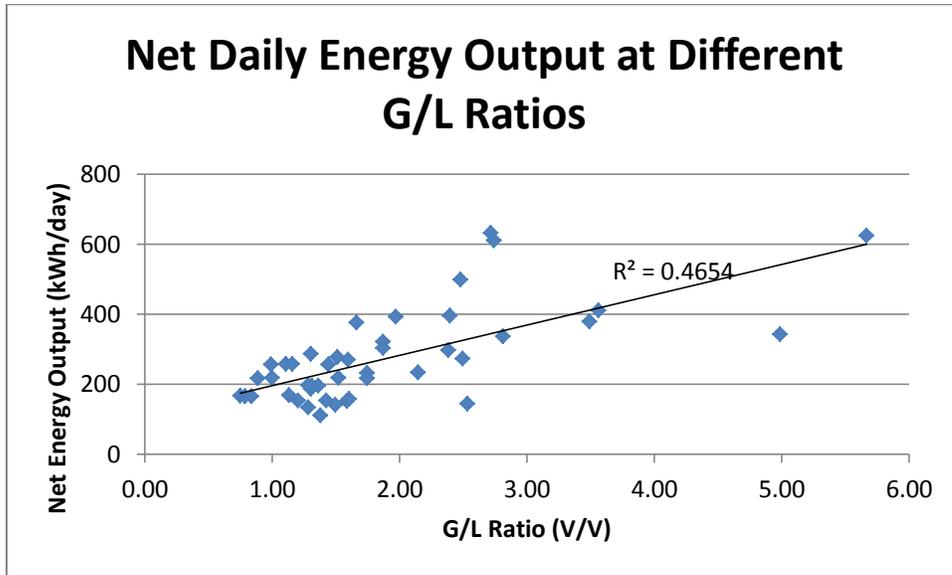


Figure 18 - Impact of G/L ratios on net energy output

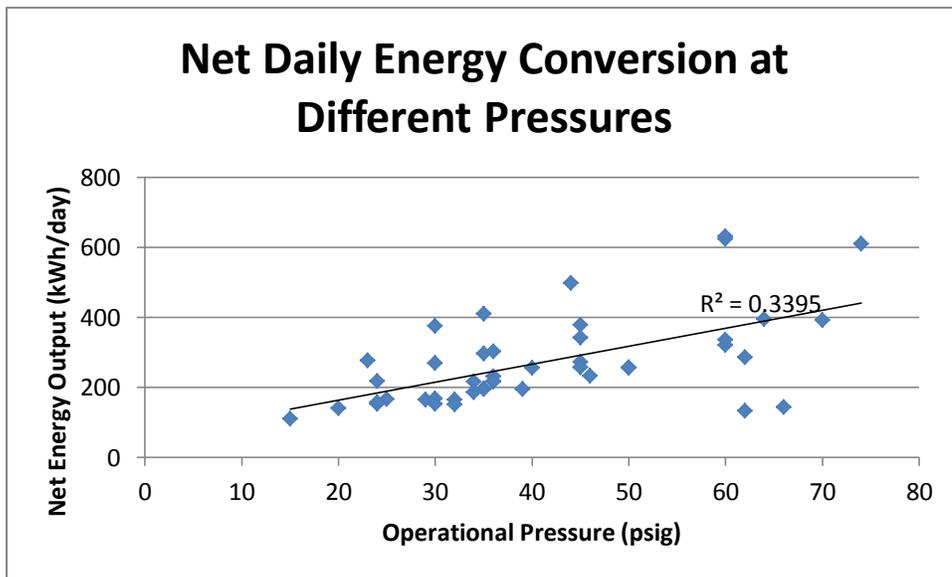
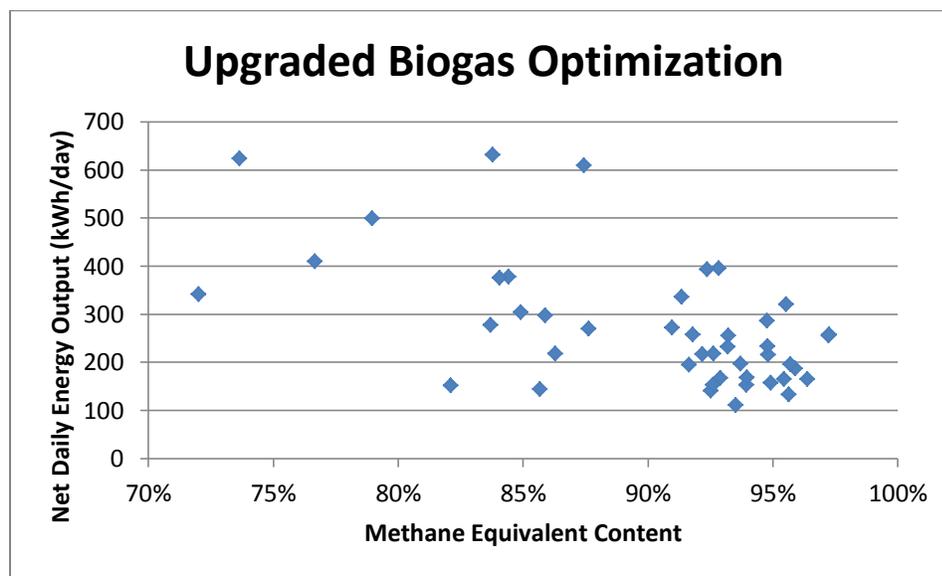


Figure 19 - Impact of gas pressures on net energy output

As seen above, the optimal daily net energy output is 623 kWh/day by setting the gas pressure to 60 psig and the gas-liquid volumetric ratio to 2.74.

### Optimizing Biogas

It was important to determine the parameters to achieve the highest upgraded biogas production rate, as well as the highest methane equivalent. The former is important from an energy standpoint, while the latter ensures good quality and thereby lower concentrations of impurities. Figure 21 plots the biogas quality as methane equivalent against the estimated energy output for continuously running the absorbing column.



**Figure 20 - Comparison of Biogas Qualities and Energy Outputs**

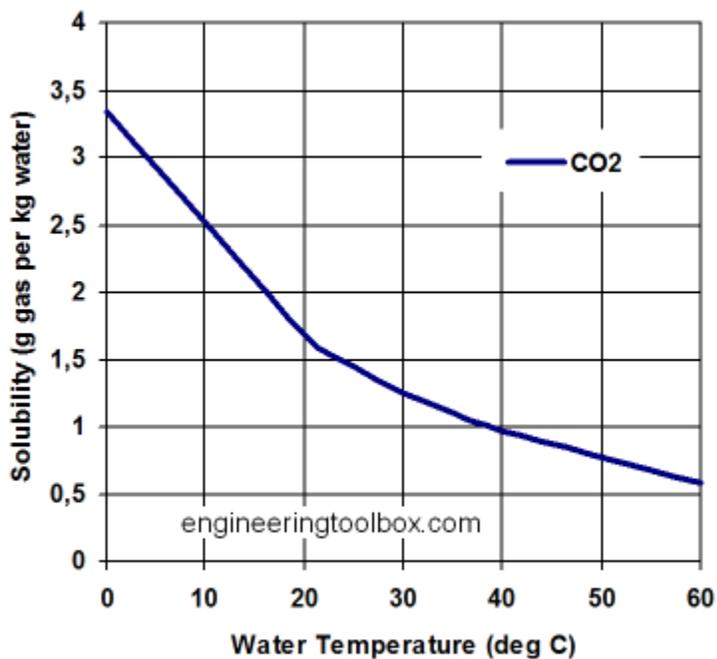
One point of interest is located at (87.4% equivalent, 610 kWh/day). This was the result of a gas pressure at 74 psig and a gas-liquid ratio of 2.74. This is the point with the highest methane equivalent in biogas before the energy output drops in this study's data collection. As stated earlier, natural gas used in models is assumed to be at least 86% methane. For this particular test, hydrogen sulfide was reduced to 4.1 ppm (v). While this is slightly above the

stated maximum for grid injection, future studies may investigate varying these parameters to further reduce hydrogen sulfide while mass-producing this renewable natural gas.

## Discussion

### Uncontrolled variables

While multiple parameters were measured, recorded, analyzed, and used to compare impacts on results, there are still some variables that caused more interference and needed to be compensated. For instance, the water temperature fluctuated between 60 – 70 °F (15.6 – 21.1 °C) during the summer of 2019 testing period at Jones Island, compared to 50 °F during the fall and winter of 2018. Summer tests were conducted outside in June and early July in Milwaukee, when the outside temperature varied between 50 – 80 °F (10.0 – 26.7 °C). Water temperature affects solubility, as seen in the below figure (Solubility of Gases in Water, 2008).



**Figure 21 - Carbon dioxide solubility at different temperatures**

Based on this figure, carbon dioxide solubility fluctuated between 1.75-2 g/L of water.

Water temperature was used in calculations for gas composition and water concentrations, but

there is still variance that may not have occurred had the water temperature remained constant during the entire testing period.

Hydrogen sulfide concentrations in the pre-treated landfill gas also fluctuated. When recording measurements of hydrogen sulfide taken by the gas chromatography spectrometer, the range of recorded measurements was approximately 100 ppm (v). Sets of roughly 30 measurements were taken every 3 hours while testing at Jones Island, then averaged to use in analysis. Additionally, the average hydrogen sulfide concentration varied between 113 – 229 ppm during the testing period. As correlated above, the water wash absorption process is selective towards hydrogen sulfide over carbon dioxide. With all other parameters equal, the absorption column would have removed more carbon dioxide had the hydrogen sulfide concentration in the pre-treated gas been kept lower. ETI reported the fluctuations and the elevated hydrogen sulfide concentrations to MMSD as the gas was simultaneously tested in this study and used by MMSD in their electric generators and turbines. MMSD maintains a factor of safety to minimize the probability of corrosion and to maintain compliance with air discharge permits.

### **Correlating parameters to results**

Though general trends were observed in the data analysis, there were few strong coefficients of determination to support these trends. Coefficients of determination, or r-squared values, of the figures used in sections above are listed in the following table.

**Table 4 - Coefficient of Determination Values**

<b>Figure</b>	<b>Coefficient of Determination</b>
Figure 8	0.1162
Figure 8	0.0086
Figure 9	0.0438
Figure 9	0.0071
Figure 10	0.5972
Figure 10	0.8827
Figure 13	0.6029
Figure 15	0.6968
Figure 16	0.3055
Figure 17	0.4479
Figure 18	0.3016
Figure 19	0.4654
Figure 20	0.3395
Figure 23	0.9986
Figure 23	0.5611

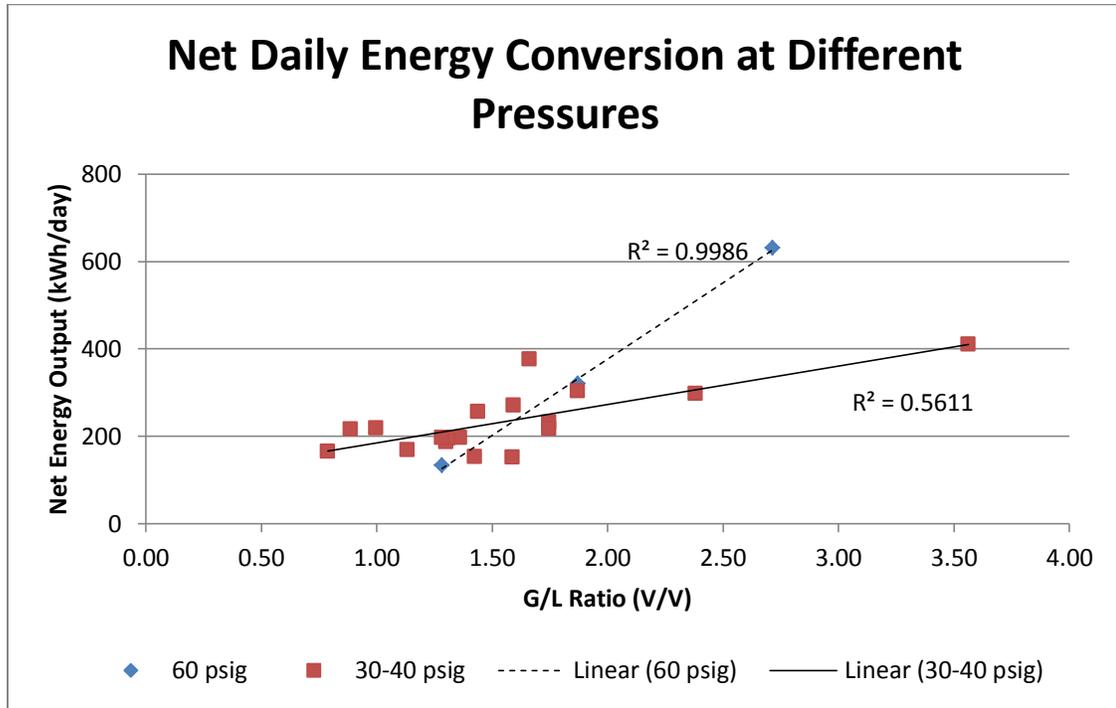
These trends may have received interference from issues described in the previous section. Another possibility is that the trends observed do not have a linear relationship.

## Recommendations

The upgrading process using the water wash method consistently purified the biogas of carbon dioxide and hydrogen sulfide as the water in the column absorbed the gases. However, oxygen and nitrogen gas in the landfill gas from Emerald Park prohibited the actual methane content from reaching 90% or greater in the biogas. This relatively simplistic technology process and is worth investigating further. For example, this process could be applied with anaerobic digester gas used at MMSD's South Shore Wastewater Treatment Plant in South Milwaukee (MMSD, 2019). There, the methane content is the actual percentage of methane in the upgraded biogas' composition, since the amounts of N<sub>2</sub> and O<sub>2</sub> are very small in comparison to landfill gas. Therefore, it is estimated that at MMSD's the South Shore wastewater plant, the purified methane levels could reach potentially into the upper 90% range.

The Jones Island facility can expand the use of a water wash absorber beyond ETI's pilot project. In the results, figure showed that Jones Island could run one pilot absorber and generate over 600 kWh of energy daily. The optimal gas pressure tested to date was determined to be 60 psig. If Jones Island installed an expanded absorber system, they would be able to collect more data and possibly reduce interferences caused by other variables to optimize system performance. The pipeline from Emerald Park landfill is limited to a pressure less of than 100 psig. The Jones Island wastewater treatment plant may at times operate at a lower pressure between in the range of 40 psig, though this may not produce as much of a net energy output as compared to higher operating pressures. Figure 23 plots the same data as figure, though there is a focus on the difference in energy output at the two pressures. Three

points from the testing period are used in the 60 psig series and eighteen points are used in the 30-40 psig series.



**Figure 22 - Energy output generation comparison of 30-40 psig and 60 psig**

While the biogas from the landfill was consistently upgraded to an equivalent methane quality that rivals natural gas, and hydrogen sulfide in the upgraded gas was reduced to level safe for use in vehicles in all cases, the concentration in wastewater could pose a possible aquatic hazard in some cases if discharged into the environment, depending on background levels and other factors. Therefore, future considerations in this field should include ways to reduce the hydrogen sulfide concentration in water by dissociation into bisulfide and sulfide ions or by reactions to convert hydrogen sulfide into elemental sulfur. There are multiple prospective methods, including increasing the pH of the wash water, redox reactions with oxygen, oxidation with bacteria, and chlorination. These potential options would be conducive

to ETI's situation as these are all processes already in use at MMSD's Jones Island Water Reclamation Facility. Another prospective method would be the decomposition of hydrogen sulfide by using ozone and ultraviolet light lamps.

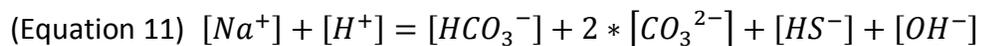
### **Basify the pH**

Gases are trapped in water once they dissociate or react with the water to form new compounds. Increasing the pH would drive these reactions to keep gases from returning to the gas phase. In the case of hydrogen sulfide, this would also neutralize the threat to aquatic species. This could be done for example by adding a sodium hydroxide solution or granular calcium chloride to the wash water either before or after the biogas water wash process. However, this may become an expensive option as the water is not recycled in this case and if ETI scales the tested water wash procedure up to a higher capacity. There will be a larger water supply to basify (Cebula, 2009; Mamrosh, Beitler, & Fisher, 2008). A more helpful option would be to use wastewater effluent from the water reclamation facility, assuming it does have a high pH, to wash the biogas in the absorber (Kennedy, Zhao, Ma, Chen, & Frear, 2015). In this way, there are no additional chemicals needed to increase the fraction of hydrogen sulfide dissociated in the waste solution.

The pH of the wash water outlet water was estimated based on the concentrations of gaseous carbon dioxide and hydrogen sulfide absorbed in the water. The incoming freshwater was assumed to have a pH of 7 and negligible ion concentrations. Balance equations for acid dissociation, ionic charge, and mass of carbon dioxide and hydrogen sulfide absorbed in the water, along with pC-pH curves of the two impurities were used. It was found that the pH was largely influenced by carbon dioxide losing a hydrogen atom to become bicarbonate, as it was

more abundant in the biogas than hydrogen sulfide, even though H<sub>2</sub>S was removed at a higher rate than CO<sub>2</sub>. The water in all tests was estimated to have a pH between 4.5 and 5. Since the dissociation constant for hydrogen sulfide into bisulfide is 7.04, a negligible amount of hydrogen sulfide was assumed to have dissociated into bisulfide. In order to drive this dissociation, use of a base or alkalized water may become necessary. This is assuming that the used wash water remains closed from the atmosphere.

To estimate the molar flowrate of sodium hydroxide necessary to raise the pH to 7.04 and dissociate half of the dissolved hydrogen sulfide into bisulfide, ionic balance and dissociation equations were used. The ionic balance is shown in Equation 11 below, which is based on molar concentrations of each of the ions. The carbonate concentration is doubled due since it has a -2 charge. The sulfide concentration in this modeled estimation is expected to be negligible for two reasons. The first is that there were small concentrations of total sulfide, which includes hydrogen sulfide, bisulfide, and sulfide, dissolved in the process wash water. These concentrations were determined by the mass balance of hydrogen sulfide in the pre-treated and upgraded biogas streams. The second reason is that the dissociation constant for bisulfide into sulfide is measured to be between 12 and 19 on a pH scale. The lowest pH value, 12, is still distant from the pH of interest, 7.04, so little bisulfide is expected to dissolve into sulfide.



Since the objective of this estimation is to determine the amount of base to add to achieve a pH of 7.04, the resulting hydrogen concentration for this equation is  $10^{-7.04}$

moles/liter (M). The hydroxide concentration is inversely related to the hydrogen concentration in water, given in Equation 12.

$$\text{(Equation 12) } [H^+] * [OH^-] = 10^{-14}$$

Following this equation, the hydroxide concentration for each test in the above equation is  $10^{-6.96}$ . The bisulfide concentration at a pH of 7.04 is simply half of the dissolved total sulfide. The bicarbonate and carbonate are estimated using a subset of equations. Equation 13 is a mass balance of the dissolved inorganic carbon species, being dissolved carbon dioxide, bicarbonate and carbonate. Similar to the total sulfide concentrations determined, the total DIC concentrations can be calculated from the difference of carbon dioxide in gas streams.

$$\text{(Equation 13) } DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

The dissociation equations of unstable carbonic acid, which is the product of carbon dioxide and water, to dissociate into bicarbonate, and then bicarbonate into carbonate can be used to reduce the variables in Equation 13. The dissociation equations are shown in Equations 14 and 15. Though Equation 14 has carbonic acid as the denominator, it is representing carbon dioxide as the acid is unstable in that form (Loerting, et al., 2000).

$$\text{(Equation 14) } \frac{[HCO_3^-]*[H^+]}{[H_2CO_3]^*} = 10^{-6.367}$$

$$\text{(Equation 15) } \frac{[CO_3^{2-}]*[H^+]}{[HCO_3^-]} = 10^{-10.33}$$

Rearranging these two above equations to isolate carbonic acid and carbonate, respectively, and inserting the known pH value, Equations 14 and 15 become 16 and 17.

$$\text{(Equation 16)} \quad [H_2CO_3]^* = [CO_2] = \frac{[HCO_3^-]}{4.71}$$

$$\text{(Equation 17)} \quad [CO_3^{2-}] = \frac{[HCO_3^-]}{1950}$$

Using Equations 16 and 17, Equation 13 can be simplified to Equation 18 below to determine bicarbonate concentration for each test.

$$\text{(Equation 18)} \quad DIC = \frac{[HCO_3^-]}{4.71} + [HCO_3^-] + \frac{[HCO_3^-]}{1950} = 1.21 * [HCO_3^-]$$

The bicarbonate concentration can then be used to determine the carbonate concentration using Equation 17 above. With all anions in Equation 11 determined, the sodium molar concentration is solved after subtracting the hydrogen concentration from both sides. The molar flowrate required for each test in Equation 19 by multiplying the sodium molar concentration and the water flowrate together. The ionic sodium concentration is equal to the sodium hydroxide molar concentration, assuming no sodium is already present in the wash water.

$$\text{(Equation 19)} \quad \dot{n} = [Na^+] * Q_{water}$$

Where  $\dot{n}$  is the mass flowrate in moles/min

$[Na^+]$  is the sodium (hydroxide) molarity in moles/liter

$Q_{water}$  is the water volumetric flowrate in liters/min

For the tests conducted in this study, the average required molar flowrate of sodium hydroxide to basify the used wash water was estimated to be 0.124 moles/min, with the maximum being 0.251 moles/min. This requirement may increase if the present water wash absorption column is scaled up to purify more gas and use more water.

### **Redox with oxygen**

In the option that hydrogen sulfide in a waste stream of wash water is blended with waste water treated at the water reclamation facility, the hydrogen sulfide would be exposed to atmospheric pressure. At this point, hydrogen sulfide that has not ionized would be able to reenter the atmosphere. Additionally the water would be exposed to oxygen in the air, which can dissolve in water and oxidize hydrogen sulfide to produce elemental sulfur and water. A caution of this process is that the sulfur would be insoluble making filtration or sedimentation a possible necessary additional step in this process. Another risk would be potential corrosivity of sulfur in water to infrastructure at the plant (McVay, n.d.).

### **Oxidation with bacteria**

Bacteria are able to consume and convert hydrogen sulfide into other sulfur species. The use of biofilters is a common practice by aerating the discharge water. Bacteria are able to grow on a media of wood chips. By supplying the biofilter with the hydrogen sulfide along with nutrients and oxygen for respiration, the bacteria in this biofilter are able to oxidize hydrogen sulfide to elemental sulfur and sulfates (Allegue & Jørgen, 2014; Fischer, 2010). Bacteria used in these biofilters are well-suited for acidic environments (McVay, n.d.). This is one advantage as the used wash water is expected to be acidic from the carbon dioxide and hydrogen sulfide

dissolved and dissociated in it. A disadvantage is that these bacteria will require a long contact time involving a larger biofilter to allow bacteria the time they require, or flowing the wash water through at a slower rate to increase the contact time. Additionally, if hydrogen sulfide is too abundant in the influent flow to a biofilter, there is a possibility of an uncontrollable increase in biomass.

A potential option at the water reclamation facility is to experiment hydrogen sulfide reduction in the aeration tanks for wastewater. Microorganisms in these tanks consume BOD5 flowing into the tank that is aerated with extra oxygen to increase microbial activity (MMSD, 2019). There is a possibility that these microorganisms can be effective at reducing the hydrogen sulfide concentration from the wash water process. However, due to the above shortcomings of this option, the feasibility of this method for Jones Island is unlikely.

## **Chlorine**

Similar to oxygen, chlorine will oxidize hydrogen sulfide to elemental sulfur or sulfates. It will also produce colloidal particles that are corrosive. To aid in this process, hydrogen peroxide can be used to remove hydrogen sulfide. This was recently proven an effective method of completely removing hydrogen sulfide when adding 4.25 mg/L of hydrogen peroxide for every mg/L of hydrogen sulfide in water with a high pH and allowing 40 minutes of contact time (McVay, n.d.). Remaining hydrogen peroxide can then be blended with free chlorine as it disinfects wastewater effluent. This is an attractive option for Jones Island in Milwaukee as a lot of typical downsides are not of concern there. Shortcomings of oxidation with a chemical like chlorine or ozone are the costs, disinfection byproduct formation, and toxic chemical handling (Lebrecht & Hannay, 2015). However, the water reclamation facility already has a

majority of the infrastructure in place, constantly monitors for disinfection byproducts, and implements methods to deter toxic chemicals from entering Lake Michigan. With either of these options for chlorine treatment, the chlorine demand has been increased and should be accounted for when dosing wastewater flows to ensure satisfactory disinfection.

### **Combined ozone and ultraviolet light**

Ozone is able to completely convert all hydrogen sulfide in a water flow to sulfates. It can be added to hydrogen sulfide waters by an in-line injection or fine bubble diffusers. Tests conducted in Orlando found that when ozone was injected in-line, it could remove all hydrogen sulfide in 20 seconds, but it had to be dosed at 7.4 times the concentration of hydrogen sulfide. When diffused in fine bubbles, the dosage was only 2.2 times the concentration and took 60 seconds (McVay, n.d.). This would be expected due to a more even initial distribution of ozone when bubbled into the water than injected at a point. Ozone is a powerful disinfectant, and would be effective at removing hydrogen sulfide with ultraviolet light, which would create hydroxyl radicals to help hydrogen sulfide dissociate (McVay, n.d.). An important consideration for these two methods is the investment and other costs. Jones Island is already using chlorine as a disinfectant, and it is readily available. Ozone is typically produced and stored onsite to prevent it from leaking into the atmosphere. If MMSD adopted this method of removing hydrogen sulfide, it would be practical to use ozone as a disinfectant as well. This would involve removing supplies and equipment to disinfect the wastewater effluent with free chlorine and install equipment to produce, store, and add ozone to effluent and any other water requiring it. Ultraviolet lamps would also have to be installed, which require routine

maintenance to ensure the lamps are functioning correctly. These steps may prevent MMSD from exploring this option further.

### **Struvite management**

Separate from the hydrogen sulfide management methods stated above, the waste wash water could be used in another project. In addition to biogas upgrading, ETI is continuing to investigate phosphorus issues at MMSD's operations and ways to manage struvite precipitation. Struvite, otherwise referred to as magnesium ammonium phosphate, is a mineral formed in municipal wastewater by the following reaction.

Struvite contains magnesium, which promotes chlorophyll growth in plants, as well as nitrogen in ammonia and phosphorus in phosphate, two nutrients (Sircus, 2009). As a result, struvite can be used as fertilizer that slowly releases nutrients to a soil. Jones Island currently produces an organic nitrogen fertilizer, called Milorganite, from recovered biosolids. However, struvite would prove to be a supplement or improvement on Milorganite, since struvite is potentially less costly to produce (Schruender, 2019).

Unfortunately, struvite can precipitate in pipes and other places where it is not easily accessed, causing clogging in wastewater streams. An objective has been to prevent struvite precipitation until it can be harvested. One method of interest is to control the pH of the wastewater to keep the struvite suspended in the wastewater or prevent it from forming in the first place. An acidic solution blended with the wastewater would help achieve this. Water rich in carbon dioxide and hydrogen sulfide would be of use for this purpose (Bashar, 2018). After struvite has precipitated and been harvested, the waste wash water can then be treated at

Jones Island before discharged into Lake Michigan. This offers the chance to repurpose the wastewater for the recovery of other matter and thereby discharging the blended water safely.

## Conclusions

When gas flowrate, water flowrate, and gas pressure were compared for the purpose of correlating various performance indices related to carbon dioxide and hydrogen sulfide removal from the biogas, the pre-treated gas flowrate had the only plausible impact on the performance index. As the gas flowrate increased, there was a decrease in contact time between the gas and the water, and less CO<sub>2</sub> and H<sub>2</sub>S gas was absorbed into the water. The gas that was removed in all tests was predominantly hydrogen sulfide on a percentage removal basis but on a mass basis more CO<sub>2</sub> was removed due to the overall amounts contained in the landfill gas. In all cases, the water wash method simultaneously removed carbon dioxide and hydrogen sulfide from the gas. Although the water wash method is not selective towards hydrogen sulfide, the amount of carbon dioxide removed from the pretreated gas can be affected by the amount of hydrogen sulfide in the gas based on the solubility.

The gas was treated of hydrogen sulfide to less than 10 ppm (v) on average. All gas produced could be used as vehicle fuel without risk of corrosion from hydrogen sulfide. However, not all tests produced gas with less than 4 ppm (v) that would be safe to inject into a natural gas grid.

The water wash process is a low energy intensive process and can net a high energy output. Higher energy outputs occur at higher gas pressures and higher gas-liquid volumetric ratios. However, the high amount of energy can be attributed to the larger flow rate test runs of biogas that processed by this water wash method and subsequently upgraded. Higher gas-liquid volumetric ratios also had lower performance indices, so the methane content of this gas

was comparatively lower. However, the results here provide a basis for upscaling this biogas upscaling this biogas upgrading process to larger scale implementation.

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