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# Acid Rain in Distilleries in Pakistan

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**Abstract.** This study highlights the damaging effects of Hydrogen Sulphide ($H_2S$), a gas produced in bio-digesters of all distilleries that escapes from de-gassing stations, or from other leak points, to react with oxygen and water to form a corrosive acid, i.e. "Acid Rain". It is vital that distilleries are equipped adequately to combat these corrosive actions in order to make distillery functioning more cost-effective.

**Keywords:** spent-wash, methane, digesters, hydrogen sulphide, scrubber, solubility, bio-gas

## 1. Introduction

During the production of ethanol, Sulphuric acid ($H_2SO_4$) is used to control the reactionary pH. However, its use leads to the production of $H_2S$. In a 100, 000 liters/day capacity ethanol distillery, about 1260 $m^3$ of treated spent wash is produced daily. This is cooled down in cooling pits and then pumped to the bio digesters where manure (cow-dung) is fed to create bacteria at a temperature of 38-40 $^0$C.

Generally bio-gas contains 50-55% methane, 40-45% carbon dioxide and 2-3% hydrogen sulfide along with moisture and impurities.

## 2. Background Information

### 2.1. Chemical Reactions Involved

Methane can be derived from spent wash in two ways;

- Thermal Conversion
- Biological Conversion

By and large the second method used for the thermal conversion requires a large amount of energy. Methano-genic bacteria are utilized to convert higher organic compounds to methane as it requires less energy. The microbial process of anaerobic digestion and methane production occurs through a complex action of interdependent microbial communities as shown in Figure 1.

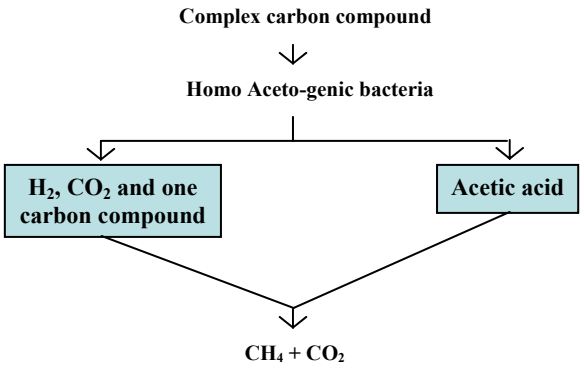


Fig. 1: Methano-genic bacterial reaction (Chynoweth and Issacson 1987) [1]

Factors that influence the process of digestion in the digesters are:

- Temperature
- Bacterial consortium (association)
- Nutrient composition
- Moisture
- pH
- Residence time (time required for spent wash to be kept in the digesters for reaction)

**There are 4 key biochemical reactions in anaerobic digestions:**

- Hydrolysis: The process of breaking higher molecular weight compounds such as proteins, cellulose, lignins, and lipids into smaller molecules (simple sugars, amino acids, fatty acids and glycol).
- Acido-genesis: Further breakdown of molecules. This process is similar to milk sour (formation of ammonia, $CO_2$ and hydrogen sulphide).
- Aceto-gensis: When acetic acid, propionic acid, butyric acid, $CO_2$ and hydrogen are produced. Under a relatively high partial pressure of $H_2$, acetate formation is reduced and the substrate is converted to propionic acid and butyric acid, rather than methane.
- Methano-genesis: This step is one which makes the majority of bio-gas. It is sensitive to both low and high pH and occurs between 6.5-8 pH. It is a slow process and can take up to 2-3 days (at 35˚ C) to 50 days (at 10˚ C). About two-thirds of methane is derived from acetate conversion by methano-genesis.

At low concentration, $H_2S$ is unpleasant whereas in a high concentration, it can even be life threatening. The recommended exposure limit is 300 parts per million (ppm) has immediate danger to life [2].

Hydrogen sulfide is poisonous, odorous, and highly corrosive. Some characteristics of $H_2S$ are described here in Table 1. Because of these characteristics, hydrogen sulfide removal is usually preferred at the gas-production site.

Table 1: Physical, Chemical and Safety Characteristics of Hydrogen Sulfide [2]

| | |
|---|---|
| Molecular Weight | 34.08 |
| Specific Gravity (relative to air) | 1.192 |
| Auto Ignition Temperature | 250° C |
| Explosive Range in Air | 4.5 to 45.5 % |
| Odor Threshold | 0.47 parts per billion |
| 8-hour time weighted average (TWA) (OSHA) | 10 parts per million |
| 15-minute short term exposure limit (STEL) (OSHA) | 15 parts per million |
| Immediately Dangerous to Life of Health (IDLH) (OSHA) | 300 parts per million |

reas in distillery which are mostly affected are:

- Boiler-water tubes and chimneys which are made of steel, nickel and chromium.
- MS and SS piping and all MS and SS vessels
- Instruments which are exposed and come in contact with this gas when wind direction changes towards the main plant
- Air blower and compressors
- All steel structure and supports exposed to the gas
- $H_2S$ has higher solubility than methane and $CO_2$

## 2.2. Control and Removal of $H_2S$.

It goes without saying that “prevention” is better than “cure”.

Best way to avoid acid rain is to prevent or minimize $H_2S$ formation by controlling sulphuric acid dosing in fermentation process of molasses sugar to control pH. Use of phosphoric acid along with sulphuric in 1: 10 ratio can be most effective system

In situ (Digester) Sulphide Abatement; Ferric chloride is added directly to the digesters to form soluble iron sulphates and iron sulphides. But this method can partially control the formation of $H_2S$.

## 2.3. Using water scrubber for $H_2S$

Solubility of $H_2S$ is 3 gm /kg of water at 30˚ C, which is higher than that of methane (0.017gm/kg). Counter-current contact of bio-gas with water can be made at ambient temperature and pressure to dissolve $H_2S$ from bio-gas.

## 2.4. Wet Scrubber Basic Configurations

The basic scrubber configurations are:

- Orifice scrubbers - air or gas velocity is increased through an orifice - increased turbulence atomize the water droplets
- Venturi scrubbers - air or gas velocity is increased through a venturi shape - increased turbulence atomize the water droplets
- Fibre-bed scrubbers - air passes through wet-laden fibre mats where mists are collected. Not suited if solid particles are present in the air since the fibre mats may plug
- Mechanical scrubbers - a mechanical driven rotor produces the fine water droplets in the air
- Impingement-plate scrubber - vertical scrubber with horizontal plates, air flows from bottom to top, water flows from top to bottom
- Spray nozzle scrubbers - water are sprayed with high pressure through nozzles to produce the droplets in the air

Removal or inhibition of $H_2S$ from bio-gas in distilleries is most essential and system to trap $H_2S$ must be installed.

$H_2S$ dissolved in water during scrubbing treatment will produce Sulphurous acid ($H_2SO_3$) and the scrubber no doubt will be corroded quicker than its normal life. However, the cost of implementing this proposition of water scrubber and its maintenance is much less expensive than the replacement of instruments, MS pipes, vessels and boiler tubes that would otherwise corrode. All distilleries therefore, must optimize the use of sulphuric acid in fermentation of molasses and should install a water scrubber on the very first day of distillery installation in order to protect their plant and its profitability. Replacement of corroded instruments, pipes, structures is estimated to be 15 times higher than the cost of controlling its production. In addition to the absorption of $H_2S$ by the scrubber, $CO_2$ produced in the same reaction and which hinders combustion, will also be dissolved in water by the scrubber and will improve the efficiency of boiler by 30-35%.

# 3. Acknowledgements

I acknowledge the invaluable information provided to me by Mr Bezard “Proserpol” and the assistance that I received from Biogas Department at Unicol.

# 4. References

[1] Chynoweth and Issacson 1987.

[2] (OSHA-2002) Occupational Safety and health Administration).