Safety and Health Considerations of a Biodigester.

Paper for ‘Gevaarlijke stoffen en veiligheid in de chemische procesindustrie’

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1 INTRODUCTION

This paper is written by a (chemical) engineering student from the Catholic University of Leuven (KUL) who will design and construct a biodigester together with a fellow student. The case is a project named “Development and construction of a biowaste recovery plant in Humahuaca, Argentina”. The foundation of this project lies with Humasol vzw, a non-profit organization which aims to offer humanitarian aid (both technical and financial) in the work field of an engineer. Their local partner, Aldo E. Juarez, contacted them with the question if it would be possible to build a waste processor at his residence.

A machine is being designed and the safety issues concerning this will have to be looked at. Proper safety measures have to be proposed. These things will be discussed in this paper.

The project handles about developing and building a waste (biomass) processor. Different conversion techniques were considered and anaerobic digestion has been chosen (see below 2.1). Microorganisms will convert the biomass into biogas. This gas can be used to cook on.

The purpose of this project is to cover the energy demand of one family needed for cooking; this will be about 20 kWh or 4 m³ biogas a day.

First, the project is situated by explaining the operating principle and design. Second, the composition together with the (eco)toxicity and safety of the biogas, slurry and fertilizer are discussed. The physio-chemical hazards related to these substances are treated as well. Third, a risk assessment is performed, qualitative (HAZOP) as well as quantitative. Next, ways to prevent accidents by applying the layer model are given. Finally, the importance of safety training is explained.

After our project is done, this paper can be used as a foundation for the safety of other digesters. It can also be used as a guide for adjustments to the current digester based on measurements of specific parameters such as biogas composition, etc.

1 www.humasol.be
2 PRINCIPLE

2.1 BIOCHEMICAL CONVERSION

As biomass is a natural material, many highly efficient biochemical processes have developed in nature to break down the molecules of which biomass is composed, and many of these biochemical conversion processes can be used.

Biochemical conversion makes use of the enzymes of bacteria and other microorganisms to break down biomass. In most cases, microorganisms are used to perform the conversion process: anaerobic digestion, fermentation and composting.

A thorough analysis of the advantages and disadvantages of different techniques showed anaerobe digestion to be the most suitable for this project.

2.2 DESIGN CONCEPT

The biomass is collected and then mixed with water in the inlet tank. The created slurry is left in the digester for approximately 45 days. Different bacteria convert it into biogas. This biogas is collected in the gas drum. The gas can be connected directly to the kitchen to cook on or it can be stored in gas bottles. A by-product of the digester is a fertilizer which can be used in agriculture.

Figure 1 Flowchart concept of a biodigester.
The gas drum is made of steel and is designed to move up and down, depending on the amount of gas in the tank. It is guided with rails which gives the drum a maximum and a minimum height and prevents the drum from tipping over or overflowing. The gas holder will rise when gas is produced. The pressure will depend on the weight of the holder and extra weight can be used to increase the pressure. This system assures a constant pressure inside the tank. The sides will have to be insulated well so gas cannot escape.

The dimensions of the drum are the following: height = 1.5m and diameter = 1.4m (for a cylindrical drum) or 1.2m x 1.2m (for a cuboid drum).

The reactor tank is made of brick, reinforced concrete, steel or plastic. It has a cylindrical (diameter = 2m) or cuboid shape (1.4m x 2m) and is 2.5m high.
Anaerobe digestion is a series of biological processes in which microorganisms break down biodegradable material in the absence of oxygen.

\[ \text{biowaste} + \text{water} \rightarrow \text{slurry} \rightarrow \text{biogas} + \text{liquid fertilizer} \]

The first question is: “Are these substances needed?” As they are inherent to the anaerobe process the answer is “yes”.

These different products are discussed below, where composition and properties are given. First the composition of biogas is looked at. Second, the slurry in the tank (before it is fully fermented) is shortly discussed and third, the composition and biosafety of the fertilizer is treated. The hazard vector is applied to these products to identify dangers and to decide which safety measures should be taken.

The hazard vector:

- Toxicity
- Eco-toxicity
- Physio-chemical

Under physio-chemical dangers falls flammability and explosion.

3.1 BIOGAS

3.1.1 COMPOSITION AND PROPERTIES

Biogas consists mainly of methane (CH\(_4\)) and carbon dioxide (CO\(_2\)). Besides these main components several impurities are present. Biogas has specific properties which are listed in Table 1.
 Detailed overview of biogas components:

Biogas may consist of 55 to 75 % methane and 30 to 45 % carbon dioxide. When the level of methane exceeds 45% the biogas is flammable. The percentage of CO₂ can be changed by several measures like using specific biomass (fatty acids) or a longer residence time.

The most important impurity is hydrogen sulfide (H₂S), this gas can be corrosive and can produce SO₂ when not properly burned. The content of H₂S lies between 0 and 0.5 vol%. H₂S levels are generally around 100 to 2000 ppm but extremes such as 2 ppm and 8000 ppm have been measured before. It is hard to predict the percentage of this impurity but for organic waste (or leftovers as in our case) values are mostly low. Additionally, the removal of H₂S is not necessary for small plants like ours.

More impurities and their properties are discussed in Table 2.

---

Table 2 Properties of biogas.

<table>
<thead>
<tr>
<th>Composition</th>
<th>55–70% methane (CH₄)</th>
<th>30–45% carbon dioxide (CO₂)</th>
<th>Traces of other gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy content</td>
<td>6.0–6.5 kWh m⁻³</td>
<td>0.60–0.65 L oil/m³ biogas</td>
<td></td>
</tr>
<tr>
<td>Fuel equivalent</td>
<td>6–12% biogas in air</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Explosion limits</td>
<td>650–750 °C (with the above-mentioned methane content)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ignition temperature</td>
<td>75–89 bar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Critical pressure</td>
<td>−82.5 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Critical temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Normal density</td>
<td>1.2 kg m⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smell</td>
<td>Bad eggs (the smell of desulfurized biogas is hardly noticeable)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar Mass</td>
<td>16.043 kg kmol⁻¹</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2 (D. Deublein, 2008)
### Table 2 Typical components and impurities in biogas.

<table>
<thead>
<tr>
<th>Component</th>
<th>Content</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>25–50% by vol.</td>
<td>- Lowers the calorific value</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Increases the methane number and the anti-knock properties of engines</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Causes corrosion (low concentrated carbon acid), if the gas is wet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Damages alkali fuel cells</td>
</tr>
<tr>
<td>H₂S</td>
<td>0–0.5% by vol.</td>
<td>- Corrosive effect in equipment and piping systems (stress corrosion): many manufacturers of engines therefore set an upper limit of 0.05 by vol.%;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- SO₂ emissions after burners or H₂S emissions with imperfect combustion – upper limit 0.1 by vol.%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Spoils catalysts</td>
</tr>
<tr>
<td>NH₃</td>
<td>0–0.05% by vol.</td>
<td>- NOₓ emissions after burners damage fuel cells</td>
</tr>
<tr>
<td>Water vapour</td>
<td>1–5% by vol.</td>
<td>- Causes corrosion of equipment and piping systems</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Condensates damage instruments and plants</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Risk of freezing of piping systems and nozzles</td>
</tr>
<tr>
<td>Dust</td>
<td>&gt;5 μm</td>
<td>- Blocks nozzles and fuel cells</td>
</tr>
<tr>
<td>N₂</td>
<td>0–5% by vol.</td>
<td>- Lowers the calorific value</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Increases the anti-knock properties of engines</td>
</tr>
<tr>
<td>Siloxanes</td>
<td>0–50 mg m⁻³</td>
<td>- Act like an abrasive and damages engines</td>
</tr>
</tbody>
</table>

#### 3.1.2 SAFETY ANALYSIS

MSDS sheets from the main components were collected, the resulting data is displayed in Table 3. Because in our case the amount of biogas is relatively small, no great dangers are linked to the gas, but certain caution must be applied. The gas will only be handled and stored under low pressure (1 to 3 bar). Hence, liquefaction of the gas is not likely, if not impossible (as shown by the very low boiling points and critical temperatures).

CH₄ and H₂S are “extremely flammable”, this is logical because otherwise it would not be possible to cook on the gas. However, precautions should be taken when the gas is inside the tank or being transported to the kitchen. H₂S is very toxic for humans and aquatic organisms but this component will only be present in small amounts.

When the gas escapes it is difficult to detect because all the components are colorless and when the H₂S is removed it is odorless. For our machine H₂S will not be removed and a

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³ (D. Deublein, 2008)
typical smell of rotten eggs can indicate a gas leak, under conditions that there is enough H\textsubscript{2}S in the gas (around 0.7 ppm).

<table>
<thead>
<tr>
<th>Component</th>
<th>CH\textsubscript{4}</th>
<th>CO\textsubscript{2}</th>
<th>H\textsubscript{2}S</th>
</tr>
</thead>
<tbody>
<tr>
<td>General information</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appearance/Color:</td>
<td>Colorless gas</td>
<td>Colorless gas</td>
<td>Colorless gas</td>
</tr>
<tr>
<td>Odor:</td>
<td>No odor</td>
<td>No odor</td>
<td>Rotten eggs odor can persist. Poor warning properties at high concentrations.</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>16 g/mol</td>
<td>44 g/mol</td>
<td>34 g/mol</td>
</tr>
<tr>
<td>Melting point</td>
<td>-182 °C</td>
<td>-56.6 °C</td>
<td>-86 °C</td>
</tr>
<tr>
<td>Sublimation point</td>
<td>-161 °C</td>
<td>-78.5 °C</td>
<td>-60.2 °C</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>-82 °C</td>
<td>31 °C</td>
<td>100 °C</td>
</tr>
<tr>
<td>Relative density, gas (air=1)</td>
<td>0.6</td>
<td>1.52</td>
<td>1.2</td>
</tr>
<tr>
<td>Relative density, liquid (water=1)</td>
<td>Not applicable</td>
<td>0.82</td>
<td>0.92</td>
</tr>
<tr>
<td>Vapor Pressure 20 °C:</td>
<td>Not applicable</td>
<td>57.3 bar</td>
<td>18.8 bar</td>
</tr>
<tr>
<td>Solubility mg/l water</td>
<td>26 mg/l</td>
<td>2000 mg/l</td>
<td>3980 mg/l</td>
</tr>
<tr>
<td>Other data</td>
<td></td>
<td>Gas/vapor heavier than air. May accumulate in confined spaces, particularly at or below ground level.</td>
<td>/</td>
</tr>
<tr>
<td>Stability and reactivity</td>
<td>Can form explosive mixture with air. May react violently with oxidants.</td>
<td>Stable under normal conditions.</td>
<td>Can form explosive mixture with air. With water causes rapid corrosion of some metals. May react violently with oxidants.</td>
</tr>
</tbody>
</table>

Methane is lighter than air (relative density) so when it escapes outside it will move up and the gas will disperse high up in the air. Depending on the percentage CO\textsubscript{2} and H\textsubscript{2}S, as well as the temperature of the air, the total relative density might be greater than one (heavier than air). In this case the gas will sink to the ground and might travel to an ignition source and flash back to the leak.

The following relative densities for biogas (60% methane, 40% carbon dioxide) are found in function of temperature. A density of 1.2 kg/m\textsuperscript{3} for the biogas is taken. This shows that when it is warm outside (T\textsubscript{air} > 20-25 °C), a leak has to be taken much more seriously because the gas will not easily float up (away from the people on the ground). The wind profile will also play an important role.

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\textsuperscript{4} (Linde-Group, 2010)
Table 4 Relative densities of biogas versus temperature.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>ρ (kg/m³) (at 1 atm)</th>
<th>Relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td>-25</td>
<td>1.423</td>
<td>0.843</td>
</tr>
<tr>
<td>-20</td>
<td>1.395</td>
<td>0.860</td>
</tr>
<tr>
<td>-15</td>
<td>1.368</td>
<td>0.877</td>
</tr>
<tr>
<td>-10</td>
<td>1.342</td>
<td>0.894</td>
</tr>
<tr>
<td>-5</td>
<td>1.316</td>
<td>0.912</td>
</tr>
<tr>
<td>0</td>
<td>1.293</td>
<td>0.928</td>
</tr>
<tr>
<td>5</td>
<td>1.269</td>
<td>0.946</td>
</tr>
<tr>
<td>10</td>
<td>1.247</td>
<td>0.962</td>
</tr>
<tr>
<td>15</td>
<td>1.225</td>
<td>0.980</td>
</tr>
<tr>
<td>20</td>
<td>1.204</td>
<td>0.997</td>
</tr>
<tr>
<td>25</td>
<td>1.184</td>
<td>1.014</td>
</tr>
<tr>
<td>30</td>
<td>1.164</td>
<td>1.031</td>
</tr>
<tr>
<td>35</td>
<td>1.146</td>
<td>1.047</td>
</tr>
</tbody>
</table>

3.1.3 TOXICITY

CO₂ is not considered as toxic, although when concentrations exceed 8% it can make breathing difficult (no rapid circulation). Symptoms may be: headache, nausea and vomiting, and prolonged exposure may lead to unconsciousness.

CH₄ can be asphyxiant, but will most likely explode before any danger by lack of oxygen occurs.

H₂S is much more toxic than the other two components. It can cause damage to the central nervous system, metabolism and gastrointestinal tract. Long exposure to small concentrations can be irritating to eyes and respiratory system and eventually result in pulmonary oedema. It has a LC₅₀(1h)⁵ value of 712 ppm. When the storage tank is placed in a well-ventilated spot (e.g. outside) the risk is reduced. Additionally, if the decomposition produces high amounts of H₂S, a system should be installed to remove it.

Table 5 Toxicity parameters and symptoms.⁶

<table>
<thead>
<tr>
<th>Gas</th>
<th>MIO (1) (ppm)</th>
<th>TVL-TWA (2) (ppm)</th>
<th>TVL STEL (3) (ppm)</th>
<th>Physiological effects</th>
<th>Symptoms of overexposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>-</td>
<td>N.A</td>
<td>N.A</td>
<td>Asphyxiant</td>
<td>Headache, Dizziness, Restlessness, Sweating</td>
</tr>
<tr>
<td>CO₂</td>
<td>-</td>
<td>5,000</td>
<td>30,000</td>
<td>Asphyxiant</td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>0.7</td>
<td>10</td>
<td>15</td>
<td>Poison</td>
<td>Eye irritation, Convulsions</td>
</tr>
</tbody>
</table>

⁵ Lethal dose for 50% of the population for an exposure of 1h.
⁶ (ACGIH, 1987) and (Waish, 1988).
Because \( \text{H}_2\text{S} \) is the most toxic the dose-response relation is given in Table 6. The effects might be different because biogas is a mixture and when biogas escapes, this mixture is diluted by air too.

<table>
<thead>
<tr>
<th>Concentration (in air)</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03–0.15 ppm(^{10})</td>
<td>Threshold of detectability (odor of bad egg)</td>
</tr>
<tr>
<td>15–75 ppm</td>
<td>Irritation of the eyes and the airways, nausea, vomiting, headache, unconsciousness</td>
</tr>
<tr>
<td>150–300 ppm (0.015–0.03%)</td>
<td>Palsy of the olfactory nerve</td>
</tr>
<tr>
<td>&gt;375 ppm (0.038%)</td>
<td>Death through poisoning (after some hours)</td>
</tr>
<tr>
<td>&gt;750 ppm (0.075%)</td>
<td>Unconsciousness and death by apnea within 30–60 min</td>
</tr>
<tr>
<td>Above 1000 ppm (0.1%)</td>
<td>Sudden death by apnea within a few minutes</td>
</tr>
</tbody>
</table>

### 3.1.4 ECO-TOXICITY

Several properties which are relevant to the eco-toxicity are given in Table 7. This shows that when the gas escapes it is harmful for the greenhouse effect. \( \text{CH}_4 \) and \( \text{CO}_2 \) are so called greenhouse gasses. All gasses should be burned and not just be let out in the air. When there is an emergency a pressure release valve might send biogas into the air, this expulsion should be kept to a minimum.

Although \( \text{H}_2\text{S} \) is not a greenhouse gas, it is harmful for the environment, specifically for aqueous systems, and endangers drinking water.

<table>
<thead>
<tr>
<th>General</th>
<th>Lifetime</th>
<th>Global Warming Potential (GWP) time horizon (years) (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>No known ecological damage caused by this product.</td>
<td>12</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>When discharged in large quantities may contribute</td>
<td>Not known</td>
</tr>
</tbody>
</table>

\(^{(D.\ Deublein,\ 2008)}\)
to the greenhouse effect.

<table>
<thead>
<tr>
<th>H₂S</th>
<th>May cause pH changes in aqueous ecological systems.</th>
<th>N.A.</th>
<th>0</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
</table>

Endangering to drinking water.

(1) “Global warming potential (GWP) is a measure of how much a given mass of greenhouse gas is estimated to contribute to global warming. It is a relative scale which compares the gas in question to that of the same mass of carbon dioxide (whose GWP is by convention equal to 1). A GWP is calculated over a specific time interval and the value of this must be stated whenever a GWP is quoted or else the value is meaningless.” (Wikipedia, 2010)

3.2 SLURRY

The definition of slurry is the inserted biomass together with water, the content which stays in the tank for several days (the residence time).

3.2.1 COMPOSITIONS AND PROPERTIES

Because microorganisms convert slurry into fertilizer and biogas, the composition does not stay exactly the same during the residence in the tank. However, an average will be taken.

**Moisture content**

The moisture content provides a transport phase for the microorganisms and nutrients.

For wet fermentation systems, the total moisture content of the biomass slurry is typically more than 88 percent, with 98 to 90 percent most common for wastewater treatment. For the dry fermentation systems, the total moisture content may be less than 80 percent.

The biomass is inserted into our machine with a 1:1 ratio organic waste/water. Because the waste itself has a moisture content of approximately 50 %, the total moisture content of the slurry can be taken around 75% (solid content: 25%).

When the moisture content is higher, the fraction of CH₄ in the biogas will increase. When a solid content of 40% is exceeded (moisture content of 60%), CH₄ production will decrease again (bad mixing conditions).

**pH**

A neutral pH (range of 6.7 to 7.4) is required for methanogenesis. Balanced growth of the fermentative, acetogenic, and methanogenic microbes (different phases in the anaerobe conversion) will maintain pH in the proper range, but perturbations of the process (i.e.,
sudden changes in loading rate, temperature, or feed constituents) may upset the microbial balance. The formation of acids during the acidogenesis phase requires that the subsequent reactions proceed to consume these acids. Once the pH of the digester falls below 6.7, the interactions between these different groups of microbes become unbalanced and digestion begins to fail.

To conclude, a pH range from 6.7 to 7.4 is taken as the average conditions of the slurry.

**Temperature**

We chose to work with mesophilic (20°C to 40°C) conditions. Maximum methane generation rates are achieved at a temperature of 35°C to 37°C for this system. Because of the weather and cold nights in Humahuaca the temperature in the tank can drop to 10°C. When the temperature regularly goes lower, certain measures will have to be taken to keep the elevated temperature. More than 40°C can kill the mesophilic bacteria, so this should be prevented at all times.

![Figure 3 Influence of the temperature upon the time of fermentation.](image)

### 3.2.2 SAFETY ANALYSIS

This paragraph discusses the various risks for persons involved in handling the in- (and outputs) of the biodigester.

When the organic waste is mixed with water in the inlet tank, the person who performs this should wear gloves and wash his/her hands afterwards. This to prevent pathogens from entering the digester, or to prevent the taking in of (dangerous) bacteria through skin or food (secondary contamination).

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8 (D. Deublein, 2008)
The annexes include a list of the different bacteria/pathogens which might enter the digester (9.1.1 List bacteria in sludge). The several sources which might contain these bacteria are given, as well as the uptake (skin, oral,...) and provoked illnesses. This list can be used to predict the contamination risk of the sludge (and afterwards the fertilizer) when the feed is characterized.

Normally the slurry will stay in the digester without human interference. When the plant has to be shut down for maintenance and the slurry has to be removed, the same precautions should be taken.

### 3.2.3 ECO-TOXICITY

When there are no problems or leaks, the slurry will stay in the tank during the conversion to fertilizer. However, eco-toxicity considerations can be taken the same as for the fertilizer, of which the discussion can be found below. Because the anaerobe digestion is not completely finished, the slurry will contain more pathogens than the end product (fertilizer).

### 3.3 FERTILIZER

The end product of anaerobic digestion produces a better fertilizer and soil conditioner than either composted or fresh manure. This fertilizer is a watery substance with usually a dark brown color. In theory it is odorless but in reality it can have a typical smell, which normally is not perceived as smelly.

The liquid effluent contains many elements essential to plant life: nitrogen, phosphorous, potassium and organic substances such as proteins, cellulose, lignin, etc. It also contains small amounts of metallic salts indispensible for plant growth.

### 3.3.1 SAFETY ANALYSIS

When household waste is used, pathogens might be inserted unwillingly into the biodigester. When a latrine is connected to the digester, this chance increases even more. When handling the slurry and fertilizer gloves must be used to prevent contamination through skin or intake by secondary contamination. A good training and awareness of the risk should be established for the people involved in these activities.

In Table 8 the die-off rates of the (most present) pathogens are given after they have passed the entire process and have exited the digester.
Table 8 Survival of pathogens in the anaerobe digestion process.  

<table>
<thead>
<tr>
<th>Organisms</th>
<th>Temperature (°C)</th>
<th>Residence Time (days)</th>
<th>Die-Off (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poliovirus</td>
<td>35</td>
<td>2</td>
<td>98.5</td>
</tr>
<tr>
<td>Salmonella ssp.</td>
<td>22 to 37</td>
<td>6 to 20</td>
<td>82 to 96</td>
</tr>
<tr>
<td>Salmonella typhosa</td>
<td>22 to 37</td>
<td>6</td>
<td>99</td>
</tr>
<tr>
<td>Mycobacterium tuberculosis</td>
<td>30</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Ascaris</td>
<td>29</td>
<td>15</td>
<td>90</td>
</tr>
<tr>
<td>Parasite cysts</td>
<td>30</td>
<td>10</td>
<td>100(^b)</td>
</tr>
</tbody>
</table>

Anaerobe digestion kills most pathogens but contamination is still possible (Polio, Salmonella and Ascaris). This might make the use of the fertilizer dangerous.

3.3.2 ECO-TOXICITY (BIOSAFETY)

Use of fertilizer

Excessive use of the fertilizer might not be good for the environment (ground, water,...) so intelligent use is required.

Methods of applying this fertilizer are numerous and conflicting. The effluent can be applied to crops as either a diluted liquid or in a dried form. Note that although 90-93% of toxic pathogens found in raw human manure are killed by anaerobic decomposition, there is still a danger of soil contamination with its use. The effluent should be composted or pasteurized (heated to 70°C during 1h) before use if the slurry contains a high proportion of human waste. However, when all factors are considered, the effluent is much safer than raw sewage, poses less of a health problem, and is a better fertilizer.

The continued use of the effluent in one area tends to make soils acidic unless it is diluted with water (3 parts water to 1 part effluent is considered a safe mixture). A little dolomite or crushed limestone added to the effluent containers at regular intervals will cut down on acidity. Unfortunately, limestone tends to evaporate ammonia; so it is generally best to keep close watch over the amount of effluent provided to crops until the reaction of the soil and crops is certain.

Because the organic components have already been decomposed, the nutrients are quickly absorbed by the soil and immediately available to the plants. Simultaneously, these nutrients serve as a base for developing soil-organisms which convert the nutrients into a form that can be readily absorbed by plants. The other components (protein, cellulose, lignin, etc.) all contribute to increasing the permeability and hygroscopicity of the soil and contribute to the prevention of soil erosion.

---

(Waish, 1988)
The effluent should be applied to the fields immediately or stored well (covered) otherwise ammoniac can escape (greenhouse gas).

**Effects on crops**

Crop yield is generally higher when fertilizer from a digester is used. However, depending on the kind of crops the effect may be contrary. For example, the yield of most vegetable crops (potatoes, radishes, carrots, cabbage, onions, garlic, etc.), many types of fruit (oranges, apples, guaves, mangos, etc.), sugar cane, rice and jute increases with the use of digester-fertilizer. In contrast, crops such as wheat, oilseed and cotton react less favorably. The effluent is also a good fertilizer for pastures and meadows.

It is difficult to predict the effect of the use of this fertilizer. Data varies and the results depend also on the climate and soil composition, so it would be advisable to test the fertilizer first on a small part of the crop.

**Effects on the environment**

When the fertilizer contains pathogens, too much heavy metals or other harmful components it can be polluting to the ground and the (ground) water. The water table in Humahuaca lies only 1 m under ground level, so water contamination is possible. Moderate use of the fertilizer is advisable when the composition is not known.

### 3.4 PHYSIO-CHEMICAL HAZARDS

Physio-chemical hazards include the possibility of fire (flammable products) and explosion.

#### 3.4.1 FLAMMABILITY

Before a fire can occur, three things are necessary: a fuel (in our case biogas), oxygen and an ignition source.

Examples of ignition sources are open flames, hot surfaces, hot gases or liquids, sparks caused by electric current, electrostatic discharge, lightning and sparks due to friction. Depending on how flammable the gas is, strict measures against exposure to these sources should be taken.

*Parameters of biogas.*

The properties related to flammability of the main components of biogas are given in Table 9 Physical and chemical properties related to flammability.
Table 9 Physical and chemical properties related to flammability.\textsuperscript{10}

<table>
<thead>
<tr>
<th>Component</th>
<th>CH\textsubscript{4}</th>
<th>CO\textsubscript{2}</th>
<th>H\textsubscript{2}S</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIT</td>
<td>595 °C</td>
<td>Not applicable</td>
<td>270 °C</td>
</tr>
<tr>
<td>LFL (vol %)</td>
<td>4,4</td>
<td>Not applicable</td>
<td>4,3</td>
</tr>
<tr>
<td>UFL (vol %)</td>
<td>15</td>
<td>Not applicable</td>
<td>45,5</td>
</tr>
<tr>
<td>MIE (mJ)</td>
<td>0.3</td>
<td>Not applicable</td>
<td>0.068</td>
</tr>
</tbody>
</table>

**Stability and reactivity**

<table>
<thead>
<tr>
<th>Component</th>
<th>CH\textsubscript{4}</th>
<th>CO\textsubscript{2}</th>
<th>H\textsubscript{2}S</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIT</td>
<td>Can form explosive mixture with air. May react violently with oxidants.</td>
<td>Stable under normal conditions.</td>
<td>Can form explosive mixture with air. With water causes rapid corrosion of some metals. May react violently with oxidants.</td>
</tr>
</tbody>
</table>

AIT = auto ignition temperature.
LFL = lower flammable limit.
UFL = upper flammable limit.
MIE = minimum ignition energy.

Flammability limits give the upper and lower boundary of where the gas is flammable. It shows in what relative concentration range (volume percentage fuel in air) it is not safe. The auto ignition temperature is the temperature where the fuel spontaneously ignites from the energy in the environment. The design-temperature (37°C) does not come near the auto-ignition temperature for any of the components. Therefore, this parameter is not relevant in our case.

![Figure 4 Ignition energy.\textsuperscript{11}](image)

As can be seen in Figure 4, the flammability range will increase with increasing spark or ignition energy. Under 0.3 mJ it is impossible to ignite at any concentration.

\textsuperscript{10} (Linde-Group, 2010)
\textsuperscript{11} (Vermant, 2010)
The flammability properties of the main component (methane) is shown in the flammability diagram (Figure 5). This diagram shows also the limiting $O_2$ concentration, which is useful to know what percentage (12 vol%) of $O_2$ is needed in the air before it poses a danger (in combination with $CH_4$).

![Flammability Diagram](image)

**Figure 5 Flammability diagram.**

Of course biogas is a mixture of these components and may have different properties. The UEL (upper explosion limit = UFL) and LEL (lower explosion limit = LFL) of biogas is shown in Figure 6.

---

12 (Toups, 2003)
The methane is diluted by CO₂ which lowers the flammability limits. The amount of water vapor present has a small but noticeable influence.

**Cooking**

Flammability is not only a bad property of biogas. It needs to be optimized to have a good burning flame in the kitchen. For this reason it is necessary to remove most water from the gas. CO₂ will dilute the methane but does not need to be removed, as long as there is a sufficient percentage methane present (40 vol%) the biogas will burn fine.

### 3.4.2 EXPLOSION

Explosion can be defined as a phenomenon where a large amount of energy is released in a short amount of time, leading to pressure waves and projectiles.

There are several types of explosion:

**Physical:**
- Overpressure

---

13 (Waish, 1988)
**Chemical:**

- Rapid combustion (explosive atmosphere) (Restricted space / confined, without obstacles / unconfined)
  - Gas Explosion
  - Dust Explosion (not applicable)
- "Chemical" explosion (not applicable)
- UCVE and BLEVE (not applicable)

**Physical**

When the pressure in a confined space exceeds material strength, the material will rupture. This is treated in more detail further in this paper. However, the pressure in the tank will only increase slowly and there will be cracks in the walls before actually exploding.

**Chemical**

Rapid combustion gas results in a chemical explosion. This can result in a pressure wave.
4 RISK ASSESSMENT

The following simplified machine is used to perform a risk assessment (Figure 7):

*Valve 1 and 2 are open during normal operation, valve 3 has to be opened to start using the burner.

4.1 QUALITATIVE METHODS

A method to control and design the safety of a machine is to use a checklist which is mostly written by people with a lot of experience with these kinds of machines. Numerous checklists can be found in the literature for all aspects of the biodigester (regulations, fire protection, explosion protection, emission prevention, ...). An example out ‘Biogas from Waste and renewable Resources’ by D. Deublien and A. Steinhauser is given below. This example is made for industrial or bigger digesters than ours, but can serve as a foundation.

Checklist for fire protection measures¹⁴:

Measures relating to the design

- Are the prescribed protection distances realized? Are the fire protection zones free of buildings?
- Are metal guards correctly dimensioned?
- Are all openings in fire walls provided with fire-resistant and self-closing covers?
- Are the doors in the fire walls at least fire-retardant and self-closing and/or lockable if they do not lead into the open air?

¹⁴ (D. Deublein, 2008) p 178.
- Is it certain that no gases can settle at any place in the factory?
- Are gas pipes in all areas insulated to give protection against continuous fire and provided with fire protection flaps?
- Are gasholders from flammable materials in fire-protected areas shielded against radiation?
- The shield should be made of non-flammable materials.
- Do escape doors open to the outside?
- Are certified flame traps installed as safety devices in all pipes to and from the gasholder close to the consumer according to the prescriptions of the manufacturer?
- The flame traps must be easily cleaned and correspond to the standards.
- The often used gravel pots must be design-examined.
- Are there adequate and well-marked routes for fire brigade vehicles? Are the roads strongly constructed such that they can be safely used by fire brigade vehicles up to 14 Mg total weight? Are the routes always free?
- Are enough fire extinguishers on plant site? At least 12 portable units of suitable extinguishing agent should be available per plant or per fire protection sector.
- Is a minimum of one portable fire extinguisher available at the gas consumption equipment building, easily seen, easy to reach in case of fire, and always working?
- Are the extinguishing foams stable in contact with alcohol?
- Are there hydrants available which are capable of delivering 1600 L/min water for a period of 2 hours?
- Are all areas clearly marked showing their use?

Measures relating to organization

- Are smoking, naked flames, and storing of flammable materials forbidden in the entire area of the plant?
- Are fire-protection posts set up and suitable fire extinguishers made available when work involving a risk of fire is carried out such as welding, cutting, abrasive cutting, soldering, etc., and use of a naked flame?
- Is storage of flammable materials, flammable liquids, and gases limited to small amounts inside a building? Is no more than 200 kg of engine oil, waste oil, and other flammable materials stored inside the CHP plant area.
- Are all hazardous areas and safety areas marked, e.g., entrances to gasholders?
- Was a responsible person designated for all fire protection measures?
- Are fire protection exercises regularly carried out?
- Is the local fire brigade informed about the entire plant in detail and is a fire brigade plan available in accordance with local regulations, e.g., DIN 14096?
4.1 HAZOP

There are several ways to do a risk assessment, here is chosen for a HAZOP-analysis (Hazard and Operability Study).

The main intentions of the process are identified and for every intention the guide words (no, less, more, ...) are applied. The possible causes of the considered problem are identified as well as the consequences, dangers and possible safeguards (meters, alarms, ...). Several actions are proposed to prevent accidents and to bring the process back to its normal operation.

Additional problems (failing of specific components) are considered and the same method of analyzing is applied (causes, consequences, ...).

Main intentions:

- Pressure in the tank (level of the drum)
- Level in the tank
- Input composition
- Biogas composition

Extra:

- Additional failures
- Conditions in the tank

4.1.1.1 PRESSURE IN THE TANK

NO Pressure = vacuum

See ‘LESS Pressure’: No pressure or vacuum is an extreme case of that.

MORE Pressure

- Causes: Too much conversion for the designed volume.
- Consequences: Rupture of the tank.
- Dangers: Breakage of the tank, gas escapes, toxic and fire hazard.
- Possible safeguards: Pressure meter with alarm, pressure relief valve.
- Actions:
  - When alarm indicates high pressure; tap off gas (burning in the kitchen)
  - Try to lower conversion (lower temperature, extract effluent (smaller content), ...)
  - When release of gas; evacuate the direct surroundings and remove all possible sparks until gas is dispersed in the air.
  - Remove content and repair the tank.
When gas drum reaches its highest position (indicated on the drum) gas should be tapped off and used.

**LESS Pressure**

- **Causes**: Forced draining of the tank (gas as well as fluid).
- **Consequences**: Implosion of the tank.
- **Dangers**: Breakage of the tank, gas escapes, toxic and fire hazard.
- **Possible safeguards**: Pressure meter with alarm, vacuum relief valve.
- **Actions**:
  - **When alarm indicates low pressure**: stop draining the tank.
  - **When release of gas**: evacuate the direct surroundings and remove all possible sparks until gas is dispersed in the air.
  - Remove content and repair the tank.

Normally content is not forced out of the tank, when pressure inside and outside the tank is equal, flow will stop.

AS WELL AS, PART OF, REVERSE, OTHER THAN

Not applicable.

---

**4.1.1.2 LEVEL IN THE TANK**

**NO content**

- **Same as ‘Lower level’**.

**MORE: Higher level (Not enough place for gas)**.

- **Causes**: Too much feeding or no extraction of the effluent.
- **Consequences**: Not enough space for gas, max. pressure reached sooner.
- **Dangers**: Overflow of the reactor, maximum pressure reached.
- **Possible safeguards**: Level indicator (with alarm).
- **Actions**:
  - Stop feeding and remove effluent.

Because the feeding rate is relatively slow, this can easily detected and accidents can be prevented.

**LESS: Lower level (lower than in- and outlet pipe)**

- **Causes**: No feeding and/or (after) removal of content.
- **Consequences**: Gas might escape through inlet and/or outlet pipe.
- **Dangers**: Gas escape, toxic and fire hazard.
- **Possible safeguards**: Level indicator (with alarm).
- **Actions**:
  - Close the inlet/outlet tank.
  - Feed the tank.

→ **When gas escapes, precautions for toxic and fire hazards need to be taken. When feeding the tank after it was closed, beware of gas escaping (don’t hang above the inlet pipe when opening it).**

→ **When there is a low level of slurry in the tank, consequently, there will only be a small biogas production.**

**AS WELL AS, PART OF, REVERSE, OTHER THAN**

Not applicable.

---

### 4.1.1.3 INPUT COMPOSITION

Normally the input of the system will consist of 50% waste, 50% water. The waste should be small enough to enter the digester.

**NO**

→ **Same as less water/waste.**

**MORE water / LESS waste**

- **Causes**: Human mistake.
- **Consequences**: Less conversion/biogas production.
- **Dangers**: No danger.
- **Actions**:
  - No action needed (add correct amount of water next time).

**LESS water / MORE waste**

- **Causes**: Human mistake.
- **Consequences**: Plug in the inletpipe, not possible to add more waste.
- **Dangers**: Overflow of inlet-tank.
- **Actions**:
  - Stop feeding the reactor before plug is removed.
  - Remove plug by pushing it through or use a plunger.

**Water/waste AS WELL AS non-digestible objects**

- **Causes**: Human mistake.
PART OF, REVERSE

Not applicable.

OTHER THAN water or waste

⇒ **Is harmful for the digester, it will fill up the tank and prevent biogas production. Has to be prevented at all times.**

4.1.1.4 **BIOGAS COMPOSITION**

A detailed explanation of the content of biogas is found is ‘3.1 Biogas’. Here an average is taken: 60 % methane \( \text{(CH}_4 \text{)} \), 40 % carbon dioxide \( \text{(CO}_2 \text{)} \) and the hydrogen sulfide \( \text{H}_2\text{S} \) content of 0.1 % or 500 ppm is taken.

**NO CH\(_4\)/CO\(_2\) or H\(_2\)S**

Not applicable.

**MORE CH\(_4\) = LESS CO\(_2\)**

- **Causes**: Better conversion and good gas production.
- **Consequences**: More flammable.
- **Dangers**: Fire hazard.
- **Possible safeguards**: Composition detector.
- **Actions**:
  - No action possible, stricter safety measures.

**LESS CH\(_4\) = MORE CO\(_2\)**

- **Causes**: Bad conversion and gas production.
- **Consequences**: Biogas will become an inert gas and will not burn.
- **Dangers**: No danger, but gas will not be suitable to cook on.
- **Actions**:
  - Try to improve conversion.

**MORE H\(_2\)S**

- **Causes**: Feed contains more waste which becomes \( \text{H}_2\text{S} \) when converted.
- **Consequences**: Biogas is more toxic.
• **Dangers**: Toxicity hazard.
• **Possible safeguards**: H\textsubscript{2}S detector.
• **Actions**:
  - Change feed.
  - Install mechanism to remove H\textsubscript{2}S.

**LESS H\textsubscript{2}S**

→ *Makes biogas a safer gas.*

**Biogas AS WELL AS air (O\textsubscript{2}) in the tank**

• **Causes**: Leakage of the tank, O\textsubscript{2} enters via input or output pipe, tank not well sealed.
• **Consequences**: Mixture may become flammable.
• **Dangers**: Possible explosion and fire hazard.
• **Possible safeguards**: O\textsubscript{2} detector.
• **Actions**:
  - Seal tank properly.
  - Take precautions when filling and emptying the tank.
  - Evacuate the direct surroundings and remove all possible sparks.

→ *Normally the pressure in the tank will be higher than atmospheric pressure and gas will escape instead of air entering the tank.*

→ *O\textsubscript{2} will disappear naturally.*

**PART OF, REVERSE, OTHER THAN**

Not applicable.

### 4.1.1.5 ADDITIONAL FAILURES

Problems with specific components of the machine may occur too. Here the most important parts are discussed.

• **Pipes**
  - Gas
  - Input/output

• **Handvalves**
  - Gaspipe
  - Effluent (no problem when level in the principal tank is high enough)

• **Pressure/vacuum relief valve**

• **Pressure/temperature/gas meter**
Breakage gas pipe

- **Causes:** Maximum pressure exceeded, corrosion.
- **Consequences:** Gas escapes.
- **Dangers:** Toxic and fire hazard.
- **Actions:**
  - Close valve 1 and valve 2.
  - Let remaining gas escape (wait).
  - Repair the pipe when all gas is removed.

Breakage input/output pipe

- **Causes:** Diverse reasons, corrosion.
- **Consequences:** Slurry escapes.
- **Dangers:** Ecological hazard.
- **Actions:**
  - Remove escaped slurry with gloves (prevent infection).
  - Repair or change pipe.

Valve 1 or 2 fails closed

- **Causes:** Diverse reasons, corrosion.
- **Consequences:** Gas cannot be tapped off, pressure will rise.
- **Dangers:** Maximum pressure might be reached (see higher).
- **Actions:**
  - Change or repair valve immediately (caution for escaping gas!).
  - When valve 2 fails, close valve 1.

→ **Valve 1 and 2 are open during normal operation.**

Valve 3 (connection kitchen) fails open

- **Causes:** Maximum pressure exceeded, corrosion.
- **Consequences:** Gas escapes.
- **Dangers:** Toxic and fire hazard.
- **Actions:**
  - Close valve 1.
  - Let remaining gas escape (wait).
  - Repair the pipe when all gas is removed.

Pressure/vacuum relief valve

- **Causes:** Diverse reasons, corrosion.
- **Consequences:** Gas/air cannot escape/enter.
• **Dangers:** Maximum pressure might be reached (see higher).
• **Actions:**
  - Monitoring of pressure meter.
  - Change or repair valve.

**Pressure/temperature/gas meter**

• **Causes:** Diverse reasons, corrosion.
• **Consequences:** No process regulation or indication possible.
• **Dangers:** Diverse hazards (max. pressure, low temperature, ...).
• **Actions:**
  - Repair as soon as possible.

### 4.1.1.6 CONDITIONS IN THE TANK

These include a change in temperature, pH, moisture content, ... . Changes in these factors will be harmful for the process and biogas production may decrease but no safety issues are presented here.

This shows that a HAZOP procedure can be used, not only to identify the safety hazards, but also to detect possible problems with the process.

### 4.1.1.7 SUMMARIZE

All the scenarios are ranked in Table 10 as major, moderate and no hazard. This ranking is based on frequency and impact. 'No hazard' means that there is no physical or material danger but it still might be harmful for the process.

**Table 10** Ranking of hazard scenarios.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Intention</th>
<th>Guide word</th>
<th>Level of danger</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pressure in the tank</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 A</td>
<td>NO Pressure = vacuum</td>
<td>Moderate hazard</td>
<td></td>
</tr>
<tr>
<td>1 B</td>
<td>MORE Pressure</td>
<td>Major hazard</td>
<td></td>
</tr>
<tr>
<td>1 C</td>
<td>LESS Pressure</td>
<td>Moderate hazard</td>
<td></td>
</tr>
<tr>
<td>1 D</td>
<td>AS WELL AS, PART OF, REVERSE, OTHER THAN /</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Level in the tank</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 A</td>
<td>NO content</td>
<td>Moderate hazard</td>
<td></td>
</tr>
<tr>
<td>2 B</td>
<td>MORE: Higher level (Not enough place for gas).</td>
<td>Moderate hazard</td>
<td></td>
</tr>
<tr>
<td>2 C</td>
<td>LESS: Lower level (lower than in- and outlet pipe)</td>
<td>Moderate hazard</td>
<td></td>
</tr>
<tr>
<td>2 D</td>
<td>AS WELL AS, PART OF, REVERSE, OTHER THAN /</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Input composition</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 A</td>
<td>NO</td>
<td>No hazard</td>
<td></td>
</tr>
<tr>
<td>3 B</td>
<td>MORE water / LESS waste</td>
<td>No hazard</td>
<td></td>
</tr>
</tbody>
</table>
### Biogas composition

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3 C</td>
<td>LESS water / MORE waste</td>
<td>No hazard</td>
</tr>
<tr>
<td>3 D</td>
<td>Water/waste AS WELL AS non-digestible objects</td>
<td>No hazard</td>
</tr>
<tr>
<td>3 E</td>
<td>PART OF, REVERSE</td>
<td>No hazard</td>
</tr>
<tr>
<td>3 F</td>
<td>OTHER THAN water or waste</td>
<td>No hazard</td>
</tr>
</tbody>
</table>

#### Additional failures

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5 A</td>
<td>Breakage gas pipe</td>
<td>Major hazard</td>
</tr>
<tr>
<td>5 B</td>
<td>Breakage input/output pipe</td>
<td>Major hazard</td>
</tr>
<tr>
<td>5 C</td>
<td>Valve 1 or 2 fails closed</td>
<td>Moderate hazard</td>
</tr>
<tr>
<td>5 D</td>
<td>Valve 3 (connection kitchen) fails open</td>
<td>Moderate hazard</td>
</tr>
<tr>
<td>5 E</td>
<td>Pressure/vacuum relief valve</td>
<td>Moderate hazard</td>
</tr>
<tr>
<td>5 F</td>
<td>Pressure/temperature/gas meter</td>
<td>No hazard</td>
</tr>
</tbody>
</table>

### 5 Conditions in the tank

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>No hazard</td>
</tr>
</tbody>
</table>

### Summary

**Major hazard**: scenarios 1B, 4D, 4F, 5A and 5B.

**Moderate hazard**: scenarios 1A, 1C, 2A, 2B, 2C, 4B, 4D, 4F, 5C, 5D and 5E.

**No hazard**: scenarios 3A, 3B, 3C, 3D, 3E, 3F, 4C, 4E, 5F and 6.

### 4.2 QUANTATIVE METHODES

#### 4.2.1 RELIABILITY

The reliability of a machine and its components during their lifetime will follow a ‘bath tub’-like course (see Figure 8).
The failure rate (in faults/year) of certain basic components is given in Table 11. These values can be used when selecting components and for maintenance planning.

Table 11 Failure rates of basic components.\(^{16}\)

<table>
<thead>
<tr>
<th>Component</th>
<th>Failure rate (Faults/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hand valve</td>
<td>0.13</td>
</tr>
<tr>
<td>Pressure relief valve</td>
<td>0.022</td>
</tr>
<tr>
<td>Level measurement</td>
<td>1.70</td>
</tr>
<tr>
<td>Pressure measurement</td>
<td>1.41</td>
</tr>
<tr>
<td>Thermometer temperature measure</td>
<td>0.027</td>
</tr>
<tr>
<td>Thermocouple temperature measure</td>
<td>0.52</td>
</tr>
<tr>
<td>pH meter</td>
<td>5.88</td>
</tr>
</tbody>
</table>

### 4.2.2 RELEASE RATE: GAS ESCAPE

The release rate for an accidental gas escape is calculated with the following equations.

\[
\dot{m}_i = C_d A \psi \left[ P_0 \rho_0 \kappa \left( \frac{2}{\kappa + 1} \right)^{\frac{\kappa+1}{\kappa-1}} \right]^{1/2}
\]

\(^{15}\) (Vermant, 2010)

\(^{16}\) (Vermant, 2010)
The value of $\psi$ depends on the situation (subcritical or supercritical). This can be calculated as followed:

$$\frac{P_0}{\rho_0} < \left(\frac{\kappa + 1}{2}\right)^{\kappa} \Rightarrow \psi = \left[\frac{2}{\kappa - 1} \left(\kappa + 1\right)^{\frac{1}{\kappa - 1}} \left(\frac{P_0}{\rho_0}\right)^\frac{2}{\kappa} \left(1 - \left(\frac{P_0}{\rho_0}\right)^\frac{1-\kappa}{\kappa}\right)^{1/2}\right]$$

$$\frac{P_0}{\rho_0} > \left(\frac{\kappa + 1}{2}\right)^{\kappa} \Rightarrow \psi = 1$$

The time-dependent release rate is found when all parameters are filled in.

$$\dot{m}(t) = \dot{m}_i \left[1 + \frac{1}{2} (\kappa + 1) t_R\right]^{\kappa+1}$$

$$t_R = C_D A_u (P_0 \rho)^{1/2} m_0 \beta t$$

$$\beta = \left[\kappa \left(\frac{2}{\kappa + 1}\right)^{\kappa+1} \right]^{1/2}$$

Here the parameters are used:

$\kappa_{(CO_2, 20^\circ C)} = 1,300^{17}$

$\kappa_{(CH_4, 20^\circ C)} = 1,320^{18}$

So a $\kappa$(heat capacity ratio) of 1,310 is taken.

$P_0 = \text{pressure in the tank} = 3 \text{ bar}$

$P_\text{a} = \text{atmospheric pressure} = 1 \text{ bar}$

$\rho_0 = \text{density of biogas} = 1.200 \text{ kg/m}^3$

$m_0 = \text{initial content} = 4$

$C_D = \text{drag coefficient} = 0.63$ (rough hole)

A round hole with a diameter of 0.02 m is supposed here ($A = \text{surface of the hole}$). Initially there is 4 m$^3$ of gas in the reactor.

The results are shown in Figure 9. The release rate decreases drastically in the first few seconds; this can be explained because the pressure in the tank decreases when gas escapes. The remaining gas can only be forced out of the reactor (when this is wanted).

The dispersion of the gas in the air can be calculated as well. This is done by using the plume or puff model. This depends on the weather and many other parameters. These calculations are too complicated to perform for such a small machine. There is always some wind in Humahuaca, so the when gas escapes it will be diluted rather quickly.
SAFETY, PREVENTION AND CONTROL

This part deals with preventing accidents and controlling the process. Following general strategy should be followed:

General strategy:

1. Eliminate the possibility of accident
2. Reduce likelihood of initiating/escalation of accidents
3. Reduce impact

This has to be prioritized in the given order: most important is to try to eliminate the possibility of an accident, then to install control devices and alarms to prevent an accident from starting or escalating. Reducing the impact of possible accidents should be the last safety measure, not the first.

5.1 PROTECTIVE LAYER MODEL

Safety prevention and control is analyzed by using the protective layer model (Figure 10) which consist out of the following protection layers (ranked from most to least important measures):

1. Inherent safer design (Eliminate the possibility of accident)

2. Protective measures (Reduce Likelihood of initiating/promotion of accidents)
   - Basic controls, process alarms, and operator supervision
   - Critical alarms, operator supervision, and manual intervention
   - Automatic action safety instrumented system or electronic shutdown system
   - Physical protection (relief devices)

3. Mitigating measures (Reduce Impact)
   - Physical protection (dikes)
   - Plant emergency response
   - Community emergency response
5.1.1 INHERENT SAFER DESIGN

The substances involved in the process are inherent to anaerobe digestion and therefore cannot be substituted. Removal of H$_2$S might improve the safety. However, as long as the concentration stays low, this adjustment will only make the plant more complicated, which may cause other problems.

The digester is made as basic as possible because it has to be repaired and built by the locals. No pumps or other unnecessary components are used.

Separate measuring devices are installed to make it clear which device represents which parameter. This makes the digester easier to understand. What these values mean will be explained and written down in a short, one-page manual.

The reactor and other components are designed in such a way that they are capable of handling a certain overpressure and vacuum. Of course there are limits to this and additional safety devices should be installed. Furthermore, the plant will be placed close enough to the kitchen to minimize pressure drop but far enough so that if gas escapes people living in the neighborhood will not be harmed.

5.1.2 PROTECTIVE MEASURES

5.1.2.1 BASIC CONTROLS, PROCESS ALARMS, AND OPERATOR SUPERVISION

As mentioned above, several controlling devices will be installed on the reactor. Temperature, pressure and level monitoring will be provided. These meters should be
checked regularly so hazard reducing measures can be performed if necessary (gas tapped off, black tarp put on, feeding stopped or effluent tapped off, ...).

The gas meter will be installed on the gas pipe. This is not for safety but merely to obtain information on how much gas is consumed.

**Alarm / detection - Operator intervention**

Because high or low pressure is an important initiator of accidents, an alarm is connected to the gas meter. The operator will have to intervene to prevent accidents.

An alarm will be installed on the thermometer too, not to prevent accidents, but to keep the process running. As specified above, temperatures above 43 degrees are harmful for the process bacteria.

An O$_2$ detection alarm could be installed inside the tank or a biogas detection alarm outside as well if found necessary. This can indicate leaks and prevent fire or explosion.

**5.1.2.2 CRITICAL ALARMS, OPERATOR SUPERVISION, AND MANUAL INTERVENTION**

The alarms which are mentioned above might only be a light turning on or a more subtle way of indicating a problem. When things become really serious a sound alarm may go off to alert the operator or people nearby. The manuals given with the machine might be needed to (safely) solve the problem.

**5.1.2.3 AUTOMATIC ACTION SAFETY INSTRUMENTED SYSTEM OR ELECTRONIC SHUTDOWN SYSTEM**

*Safety Instrumented Systems (SIS)*

Because the design is being kept simple, no safety interlock systems are integrated. This means that when an alarm goes off, the operator will have to intervene or the accident will escalate.

**5.1.2.4 PHYSICAL PROTECTION (RELIEF DEVICES)**

When the alarms goes off and no operator comes to solve the problem, it can still be prevented by relief devices.

When the problem is overpressure, a pressure relief valve can jump in. However, this should be prevented at all times and may only be used to put off an impending accident.

Similarly, a vacuum valve can prevent accidents due to a lower pressure than the atmospheric pressure.
**Pressure relief valves**

There are two types of relief valves: self-closing and non-self-closing. In this case a non-self-closing type has been chosen: a rupture disc. Self-closing options, such as a spring-loaded safety relief valve, will not have a very long lifetime because of the corrosive nature of the gas. Additionally, rupture discs are mostly cheaper and easy to repair.

The effluent of the safety valve will go untreated to the environment. The use of this device will be prevented as much as possible and if it is used, only relatively small amounts will escape. If a possibility exists to store the escaped gas, this will be done.

In all locations where a closed space may be present, a safety relief valve should be installed. This includes the gas pipes because when these are heated by the sun the gas inside the pipes will expand and this can rupture the pipes.

![Figure 11 Placing of the safety relief valves.](image)

### 5.1.3 MITIGATING MEASURES

Certain mitigating measures have to be taken in case an accident does happen. These measures aim to decrease the damage done by the accident, not to prevent the accident from happening.

#### 5.1.3.1 PHYSICAL PROTECTION

The plant is placed far enough from the houses to keep them safe when something goes wrong. Fire extinguishers will be put near the plant and their use explained. Fire alarms (smoke detection) will indicate fire. Fires mostly start small and a quick reaction can put out the fire and prevent hours of fire fighting.
5.1.3.2 PLANT EMERGENCY RESPONSE

When something happens due to pressure or temperature an alarm will indicate this. When gas escapes the area will have to be evacuated. The gas needs to be allowed some time to escape and disperse in the air before the plant can be inspected and repaired.

5.1.3.3 COMMUNITY EMERGENCY RESPONSE

Due to the size of our machine, this is not necessary.

5.2 PRACTICAL IMPLEMENTATIONS

Safety, prevention and control has to be applied to following conditions:

- Normal operation
- Possible problems, start-up and shut-down
- Maintenance, reparation and changes

Basic safety rules are applied during normal operation, for example the wearing of gloves. When there are problems or during start-up and shut-down special care will have to be taken. At these times accidents are most likely to happen. When a component fails and needs to be repaired this has to be done with great care. It would be best to shut down the entire process and empty the tank before performing serious reparations and is mandatory for reparations which may induce sparks.

Lastly, very different safety rules apply during the construction of the plant. The digester needs to be tested completely before biomass can be inserted and gas produced.
6 SAFETY TRAINING

Because of the size of the plant, human responsibility for safety of the plant is large. To make sure that this is done properly, the supervisors of the plant will receive a proper training.

A compact manual will be written in the local language with the needed response for possible problems and alarms. They will help to build the plant. This way they will have the knowledge needed to do repairs and during the construction, several safety points will be explained.

For the people to understand the inner workings of the digester (the microorganisms etc.) a one-page explanation in their language will be handed out. This text will attempt to explain the inner workings as simply as possible and emphasize parts which are important for the correct use and safety precautions of the digester.

Biogas is flammable, so the label (Figure 12) will be put up around the digester. No smoking signs and a well-defined danger zone will be put up as well.

Figure 12 Flammable gas sign.
7 CONCLUSION

Safety is a difficult concept. How to judge whether something is safe or not is not an easy task.

First, the compositions and safety of the different components were discussed. This showed that biogas is a flammable and mild toxic gas which needs to be treated with care. The effluent of the digester might contain pathogens so when handling this, gloves are mandatory.

A HAZOP showed which parameters are important and need monitoring, these where mainly pressure and temperature. How these accidents are supposed to be prevented is subsequently found by the protective layer model.

Although only a small part is dedicated to safety training, this should not be underestimated. When the people who are responsible for the plant do not fully understand what the dangers might be, they will not perform the safety procedures correctly.
REFERENCES


## 9 ANNEXES

### 9.1.1 LIST BACTERIA IN SLUDGE\(^{19}\)

<table>
<thead>
<tr>
<th>Infectious agent</th>
<th>R</th>
<th>Sources</th>
<th>Uptake and illnesses provoked</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacteria</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Leptospira sp.</em></td>
<td>2</td>
<td>Waste water (urine of rats), livestock husbandry, slaughterhouse</td>
<td>Uptake via the softened and injured skin. Leptospirosis often not discovered, rare but severe illness (fever, ague, meningitis)</td>
</tr>
<tr>
<td><em>Escherichia coli</em></td>
<td>2</td>
<td>Stomach-intestine bacterium, which is excreted.</td>
<td>Oral uptake A possible reason for stomach-intestinal illnesses, diarrhea</td>
</tr>
<tr>
<td><em>Salmonella sp.</em>, <em>Shigella sp.</em>, <em>S. typhi</em></td>
<td>3</td>
<td>Release of salmonellae, water, soil, plants</td>
<td>Smear infection, oral uptake Low risk of infection; only when epidemic, higher risk: diarrhea with vomiting, fever, heart disease</td>
</tr>
<tr>
<td><em>Yersinia enterocoliita</em></td>
<td>2</td>
<td>In stables, especially in piggeries</td>
<td>Oral uptake after contact with meat of pigs or waste water Fever, diarrheea</td>
</tr>
<tr>
<td><em>Klebsiella pneumoniae</em></td>
<td>2</td>
<td>In the stomach-intestine tract, soil, water, cereals</td>
<td>Oral uptake Only with low immunity are urinary passage and airway problems caused.</td>
</tr>
<tr>
<td><em>Pseudomonas aeruginosa</em></td>
<td>2</td>
<td>Widely spread on soil and in water</td>
<td>Contact Infection of the skin, urinary passage, and meningitis</td>
</tr>
<tr>
<td><em>Staphylococcus sp.</em></td>
<td>2</td>
<td>Ubiquitous, not specifically in biogas plants</td>
<td>Injuries and oral uptake Acute inflammation, sanies, food poisoning</td>
</tr>
<tr>
<td><em>Streptococcus sp.</em></td>
<td>2</td>
<td>Livestock (pigs, horses)</td>
<td>Via injuries by direct contact Inflammation of the endocardium, meningitis, arthritis</td>
</tr>
<tr>
<td><em>Trichinella spiralis, Trichinella pseudospiralis</em></td>
<td>2</td>
<td>Domestic and wild animals: e.g., pigs, fox, marten, bear, wolf, rats</td>
<td>Oral uptake, smear infection Fever above 39°C, face edema</td>
</tr>
<tr>
<td><em>Clostridium tetani, C. botulinum</em></td>
<td>2</td>
<td>Ubiquitous, not specifically in biogas plants</td>
<td>Injuries of the skin Tetanus</td>
</tr>
<tr>
<td><em>Bacillus anthracis</em></td>
<td>3</td>
<td>Cattle, sheep, goats, horses, buffaloes, camels, reindeer, mink, very seldom pigs and carnivores</td>
<td>Percutaneous through injuries, aerogenic and oral uptake Danger especially when working with cadavers and fats Anthrax</td>
</tr>
</tbody>
</table>

\(^{19}\) (D. Deublein, 2008)
<table>
<thead>
<tr>
<th>Infectious agent</th>
<th>R</th>
<th>Sources</th>
<th>Uptake and illnesses provoked</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Brucella sp.</em></td>
<td>3</td>
<td>Cows, sheep, goats, pigs, dogs</td>
<td>Injuries of the skin and mucosa through dust expulsion from infected animals into the air. Bacteria-containing milk and milk products Brucellosis, Malta fever</td>
</tr>
<tr>
<td><em>Mycobacterium sp.</em>, <em>Mycobacterium tuberculosis</em></td>
<td>3</td>
<td>Soil, water</td>
<td>Aerogenic, smear infection (sputum, milk, urine, and excrement of infected animals, oral uptake, injuries.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>In the lungs of humans</td>
<td>Abscess of the skin, tuberculosis</td>
</tr>
<tr>
<td><em>Enterobacter</em></td>
<td>2</td>
<td>Ubiquitous</td>
<td>Infection of the urinary passage and airways, meningitis</td>
</tr>
<tr>
<td><em>Erysipelothrix rhusiopathiae</em></td>
<td>2</td>
<td>Pigs, poultry, crustaceans, and fishes</td>
<td>Via injuries to the skin in contact with infectious material, redness (red murrain)</td>
</tr>
<tr>
<td><strong>Fungi</strong></td>
<td></td>
<td>Material from rakes</td>
<td>They are able to cause infections and allergies Depending on the species, different ways of infection possible Risk of infection very low</td>
</tr>
<tr>
<td><em>Candida sp.</em>, <em>Aspergillus sp.</em> <em>(fumigatus)</em></td>
<td>1–2</td>
<td>Material from rakes</td>
<td>They are able to cause infections and allergies</td>
</tr>
<tr>
<td><strong>Parasites</strong></td>
<td></td>
<td>Because of their weight, protozoans and worm eggs sink to the bottom of the bioreactor and are enriched in the residue, where they can survive a long time.</td>
<td>Mainly oral uptake Are able to provoke stomach-intestinal illnesses Low risk of infection</td>
</tr>
<tr>
<td><em>Round worm</em></td>
<td>2</td>
<td>Because of their weight, protozoans and worm eggs sink to the bottom of the bioreactor and are enriched in the residue, where they can survive a long time.</td>
<td>Mainly oral uptake Are able to provoke stomach-intestinal illnesses</td>
</tr>
<tr>
<td><em>Gastrointestinal worm</em></td>
<td>2</td>
<td>Because of their weight, protozoans and worm eggs sink to the bottom of the bioreactor and are enriched in the residue, where they can survive a long time.</td>
<td>Mainly oral uptake Are able to provoke stomach-intestinal illnesses</td>
</tr>
<tr>
<td><em>Hookworm</em></td>
<td></td>
<td></td>
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</tr>
<tr>
<td><em>Distome</em></td>
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<tr>
<td><em>Liver fluke</em></td>
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<tr>
<td><em>Lung worm</em></td>
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<tr>
<td><em>Stomach worm</em></td>
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<tr>
<td><em>Tapeworm</em></td>
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<td></td>
<td></td>
</tr>
<tr>
<td><em>Nematode</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Viruses</strong></td>
<td></td>
<td>Excreted</td>
<td>Oral uptake Diarrhea, polio, meningitis Extremely low risk of infection</td>
</tr>
<tr>
<td>Infectious agent</td>
<td>$R$</td>
<td>Sources</td>
<td>Uptake and illnesses provoked</td>
</tr>
<tr>
<td>----------------------</td>
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<td>--------------------------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Hep.-A Virus</td>
<td>2</td>
<td>High concentration in the waste water in autumn due to travellers coming home</td>
<td>Oral uptake</td>
</tr>
<tr>
<td>Hep.-B Virus</td>
<td>3</td>
<td></td>
<td>Icterus, Certain risk of infection</td>
</tr>
<tr>
<td>Enteroviruses</td>
<td>2</td>
<td>Proliferating in the intestinal mucosa</td>
<td>Transfer from human to human via droplets or dirt fever, flu, meningitis, encephalitis, hepatitis, pneumonia, myo- and pericarditis</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HIV Virus</td>
<td>3</td>
<td>Virus is not stable in waste water</td>
<td>Transfer through blood or other body liquids</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>AIDS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Very low risk of infection</td>
</tr>
<tr>
<td>Rota Virus</td>
<td>2</td>
<td>In excrement</td>
<td>Oral uptake</td>
</tr>
<tr>
<td>Noro Virus</td>
<td>2</td>
<td></td>
<td>Diarrhea with vomiting</td>
</tr>
<tr>
<td>Picorna Virus</td>
<td>2</td>
<td>In saliva, nasal discharge, sperms, and milk of infected animals</td>
<td>Transfer through contact with animals, persons, vehicles via the air</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Virus of aftosa</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>The virus is inactivated by temperatures above 56°C or acids</td>
</tr>
<tr>
<td>Swine fever</td>
<td></td>
<td>In meat of pigs, even in cured and frosted meat</td>
<td>Sputum, secretion of the eyes, breath</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fever, cramps, palsy, bleeding, cardio-vascular disease</td>
</tr>
<tr>
<td>Paramyxovirus</td>
<td>2</td>
<td>Poultry</td>
<td>Avian plague (Newcastle Illness), seldom transferred via air to owner and laboratory personal</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Trachoma, sometimes flu</td>
</tr>
<tr>
<td>Protozoans</td>
<td></td>
<td>Waste water, sewage sludge</td>
<td>Oral uptake</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Epidemic (malaria, sleeping sickness, amebiasis)</td>
</tr>
<tr>
<td>Entamoeba histolytica</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Giardia lamblia</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toxoplasma gondii</td>
<td>2</td>
<td></td>
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</tbody>
</table>