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# ENGINEERING OF THE WASTE COMPARTMENT

ESA contract 15689/01/NL/ND

## TECHNICAL NOTE 71.5

## Gas Loop Design of the Waste Compartment

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# 1. Introduction

Anaerobic digestion is a biological process that consists of a series of reactions, which are carried out by a mixed group of bacteria in the absence of molecular oxygen. Almost all naturally occurring organic matter and many synthetic organic compounds can be fermented, or digested anaerobically. If partial digestion occurs, intermediate compounds may be produced, including many that are odorous. If the process is carried to completion, gaseous products including methane and carbon dioxide are produced with minimal odorous by-products. Through anaerobic digestion, organic matter is converted in a stepwise fashion to stable end products. Usually, anaerobic biological conversion of organic matter is thought to occur in three steps: hydrolysis, acidogenesis, and methanogenesis with each step involving its own unique consortium of bacteria.

The first step involves the enzyme-mediated transformation (hydrolysis or liquefaction) of the higher-molecular-mass compounds into simple, lower molecular weight fermentation end products such as lactate, ethanol, acetate, formate, $H_2$, propionate, and butyrate. The second step (acidogenesis) involves the bacterial conversion of the compounds resulting from the first step into acetate, $H_2$, and formate. The third step (methanogenesis) involves the bacterial conversion of the intermediate organic compounds into simpler end products that are about 65% methane and 35% carbon dioxide, with traces of hydrogen sulphide and ammonia. Of the three steps, the last one is critical because of the slow growth rate of methane bacteria (2 to 22 days per generation) and its sensitivity to environmental changes.

Because the methanogenesis is inhibited in the waste compartment in the Melissa loop, the produced fermentation gases will concern the by-products formed between the acidogenesis and the acetogenesis, mainly $CO_2$, $H_2$, $H_2S$, VFA and other gases in trace amounts. The fermentation gases will be used and further processed in the photoheterotrophic compartment.

The pilot waste compartment will be built at EPAS and convoyed to Barcelona where it will be connected to the other compartments. Actually, EPAS is investigating a prototype waste compartment on which all loops (gas loop, liquid loop and solid loop) are optimised for further use at pilot scale and connection to the MELISSA loop.

The general concept of the waste compartment with highlighting of the gas loop is presented in Figure 1. The present note deals with the characterisation and design of the gas loop as schematised in Figure 2.

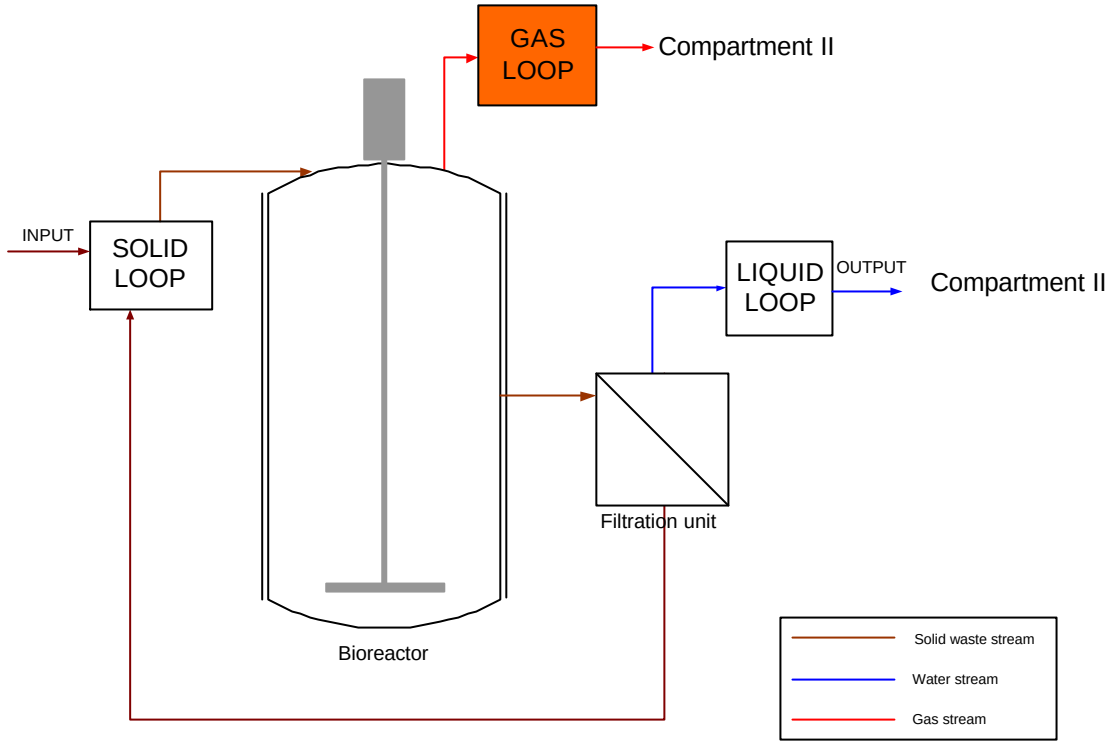


Figure 1: Schematic general design of the waste compartment with indication of the sub-system treated in this technical note

# 2. Concept of the gas loop

## 2.1 Requirements of the gas loop

According to experiments carried out at EPAS, given the feeding parameters of the pilot reactor, a production of gas around 13 L/d can be expected. This biogas should be mainly made out of $CO_2$. The concept of the gas loop has to insure the management and withdrawal of this gas flow.

The composition of the exhaust gases from the fermenter should be determined quantitatively. On-line apparatus are thus needed for this purpose for:

- $CO_2$
- $CH_4$
- $H_2$
- $H_2S$
- $O_2$

## 2.2 Design choices

The choice has been made to design an *active* gas loop, meaning that in all cases, even when no gas is produced, a constant flow of gas will be maintained through the loop. A *passive* design would have meant that only the gas produced would flow through the gas loop by means of a backpressure regulator directly attached to the waste compartment.

The *active gas loop* concept has the following advantages over the *passive* version:

- It adds a level of flexibility for the connection of the gas loop to the next compartments.

  Since a compressor in the gas loop maintains a constant flow of gas through the loop, pressure can be built up in a small buffer vessel. This buffer vessel can provide a driving force for the gas flow through the following compartments of the MELISSA loop thus avoiding any extra compressors or gas pumps. This is however only the case provided a small pressure drop is present between each of the compartments.

- A constant flow through the gas analysers can be maintained.

  Even when the gas production is very low, a constant gas flow can be maintained through the analysers, so in all cases the correct analysis of the gas composition can be monitored.

The following problems need to be tackled when building this gas loop:

- A robust way needs to be worked out to sustain the gas flow under all conditions;
- Since the build-up of pressure brings along the possibility of condensate formation (containing water and probably some VFA), a device to separate the condensate water from the gas and to return it to the bioreactor needs to be present;
- The net production of gas needs to be withdrawn accurately from the bioreactor.

## 2.3 General concept

As mentioned before, the gas loop consists of the withdrawal and dewatering of the fermentation gases and on-line analysis of their composition. The note includes all apparatus and techniques to perform this function. A conceptual design scheme of the gas loop is depicted in Figure 2.

The gases are withdrawn from the bioreactor using a compressor. The flow of the compressor can be regulated using a needle valve at the suction side. The gas is compressed into a smaller pressure buffer vessel, where a higher pressure than the bioreactor pressure is maintained. A pressure of about 3 bar in this pressure vessel is sufficient to suit the needs of the following compartments. The gas in this pressure buffer is used to regulate the bioreactor pressure using a pressure reducing regulator. The pressure in the bioreactor is kept slightly above atmospheric pressure (around 100 mbar) in order to avoid any contamination of the gas phase in the bioreactor. Since the compressor continuously withdraws an amount of gas from the bioreactor, a continuous flow of gas is maintained from bioreactor to buffer vessel and back.

When the bioreactor is controlled at a certain pressure set point, any quantity of gas produced will result in an increase of the pressure in the pressure buffer vessel. This can conveniently be used to withdraw the net gas produced using a backpressure regulator. Using the pressure buffer, no pump is needed to feed the following compartments.

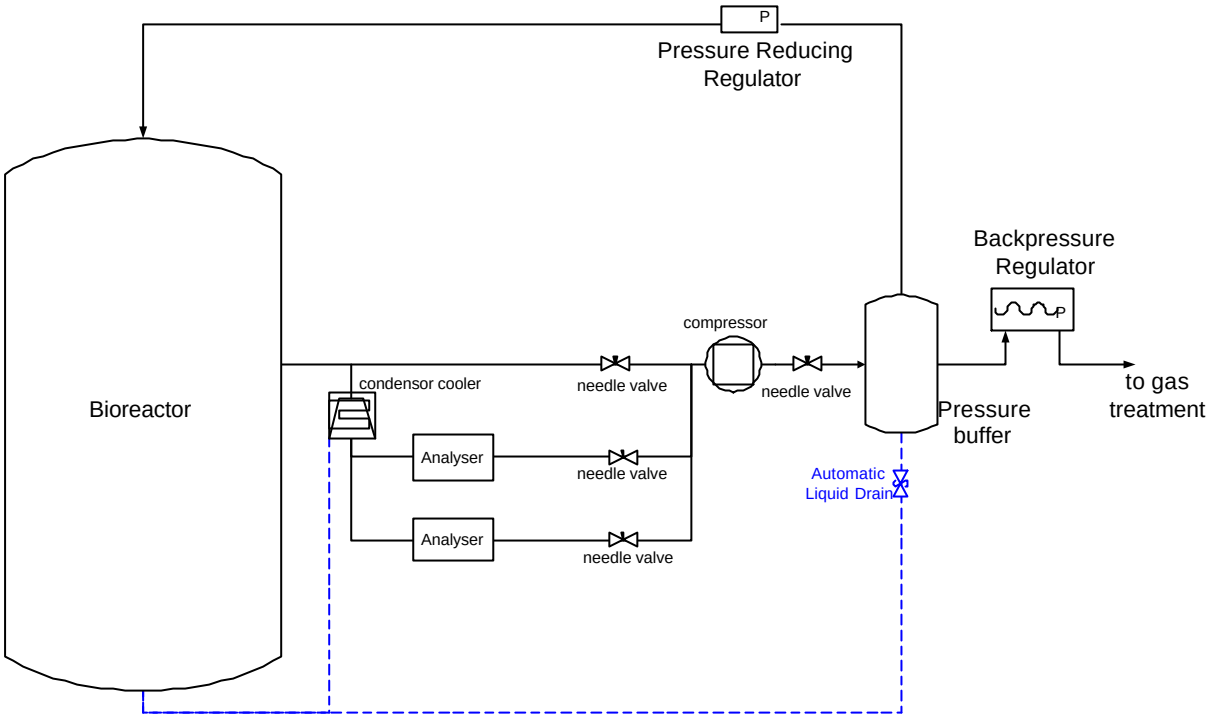


Figure 2: Conceptual scheme of the gas loop of the waste compartment

# 3. Hardware, instrumentation and local control aspects

## 3.1 Tubing

The following requirements should be fulfilled by the tubing used in the gas loop:

- resistant to corrosion
- resistant to chemical disinfection
- non permeable (air tight)

Generally the following statements can be made:

1. Teflon tubing is suitable for gas transport because of its excellent chemical and temperature resistance.

2. Stainless steel tubing is also suitable for gas transport and has largely the same advantages as Teflon tubing although it is not transparent. On the other hand, the material is more rigid and self-supporting which permits easy handling and installation.

3. Nylon tubing does not have the same degree of chemical and temperature resistance compared to fluorinated plastics nor a complete impermeability. It is therefore not recommended for use in this application.

4. No-ox tubing (Alltech): No-ox tubing has a double wall that eliminates re-gassing. The inner wall consists of inert Teflon. The non-wetted outer wall is made from a translucent, flexible polymer with extremely low gas permeability. No-ox cuts re-gassing to negligible levels, while preserving

Teflon's chemical resistance. The small amount of re-gassing through Teflon tubing is however negligible in this application and only of importance in e.g. gas chromatography applications.

Based on these findings, a combination of Teflon and stainless steel tubing will be used for the gas loop.

## 3.2 Gas flow maintenance

Several devices are included to regulate the pressure and to control the gas flow rate. These devices should obviously be constructed corrosion resistant.

### 3.2.1 Exhaust gases pumps

The pumps used in the gas flow should be efficient in handling fermentation gases continuously. They should not only have the necessary mechanical properties such as resistance to a constant output pressure of about 3 bar but also be resistant against chemical attack by a variety of media including the condensate that can be formed. All contamination of the gas with oil or any other substance should be avoided and a maintenance-free operation should be provided.

For these reasons, a diaphragm or membrane compressor was selected. In its simplest form, this type of pump consists of a motor, eccenter, connecting rod, diaphragm, valve system and pump head (Figure 3). The drive motor turns the eccenter, oscillating the connection rod and the diaphragm against the sealed pump chamber. Valves direct the media through the pump in the proper direction. The media of the inlet and outlet ports, the valves, the pump chamber and the diaphragm should be able to withstand the components in the medium and the eventual condensate formed by the pressure increase in the pump.

The type of pump itself fulfils some of the requirements:

- Possibility to continuous pumping against an output pressure;
- Oil-free working principle;
- Sealed pump head preventing contamination of the medium.

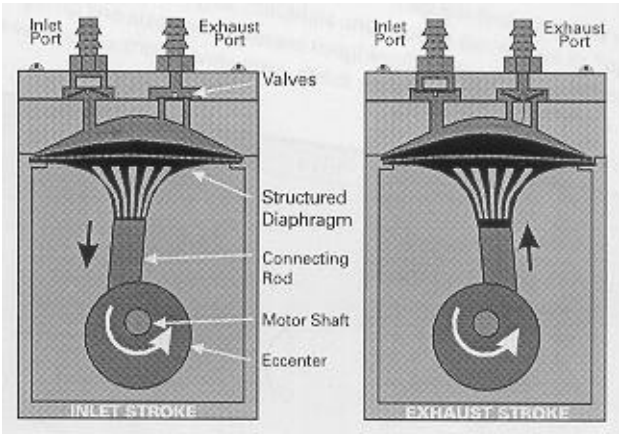


Figure 3: Schematic representation of the principle and components of a diaphragm pump

Through the selection of the materials, the resistance of the pump against gas components and condensate can be chosen.

- Pump head and ports in stainless steal AISI-303;
- Valves in stainless steal AISI-303;

- Membrane in PTFE. Since PTFE itself is a rather rigid material, a thin membrane in PTFE is fixed to a EPDM carrier, making the diaphragm more flexible. The medium only has contact with the PTFE.

The capacity of the pump should be high enough to work together with the selected pressure regulator (see paragraph 3.2.2). A relatively small air flow rate of around 15 to 20 L/min is preferred in order not to oversize the compressor and the pumped air flow.

A type of pump that meets all the above requirements is for example:

COMPTON D/296/416-3E, connections 1/2" NPT, stainless steel body with PTFE membrane and EPDM membrane carrier.

### 3.2.2 Pressure regulators

Pressure regulators are used in a broad range of applications. Yet, only two basic valve types are commonly employed, direct-acting and pilot-operated. Variations in these types consist mainly of methods of loading the seat, different seat and body materials, balanced versus unbalanced designs, and different kinds of pilots (for pilot-operated safety relief valves). The opening action of the regulator may be either direct, where the valve provides an initial rapid flow to relieve pressure, or modulating, where the valve has a variable relieving capacity, generally in proportion to demand.

#### 3.2.2.1 Pressure reducing regulator

For the pressure reducing regulator in the gas loop, the choice has to be made between a purely mechanical solution and an pilot-operated electronic regulator. The choice between these two solutions needs to be done based on the results of prototype testing. The mechanical solution will provide a good pressure control without any chance of failure of electronic components, while the electronic solution will yield a more precise and accurate pressure control.

- The mechanical solution consists of a hand adjustable, spring-loaded pressure reducing regulator. For corrosion resistance, a version needs to be selected where the only materials in contact with the medium are for example Stainless Steel AISI-316 and/or Teflon.

  Important in the selection of a proper pressure reducing regulator are the inlet and outlet pressures and the required flow rate for a given pressure drop.

  Obviously, the inlet pressure needs to be in the range applied in the process. In the case of the gas loop, the inlet pressure is the pressure in the buffer vessel, which will be maintained around 3 bar. The regulator should also be selected with an outlet pressure nearest (yet above) the maximum application pressure, in this case the pressure in the bioreactor of 100 mbar.

  The relationship between the pressure drop and the flow through a valve or regulator is expressed as the $C_v$ value. It is defined as the number of US gallons of water per minute that will flow through a wide-open valve with a pressure drop of 1 psi. This value is however also used for sizing gas valves and regulator. The formulas for valve-sizing are based on the basic equation of liquid flow:

$$Q = K\sqrt{\text{pressure drop}}$$

  More specifically for gases the formula becomes:

$$Q_g = 960 C_v \sqrt{\frac{(P_1 - P_2)(P_1 + P_2)}{G_g (T + 460)}}$$

where:

$C_v$ = valve flow coefficient

$G_g$ = gas specific gravity

$P_{1,2}$ = respectively valve inlet and outlet pressure (psia)

$Q_g$ = gas flow rate (cubic feet per hour at STP conditions)

T = gas temperature (°F)

It can be calculated that for the given air flow rate (about 15 L/min) an inlet pressure of 3 bar (4 bara or 58 psia) and an outlet pressure of about 100 mbar (1.1 bara or 16 psia), a pressure reducing regulator capable of a $C_v$ value of 0.02 or higher should be selected. Several possibilities exist with different brands, for example TESCOM of GO Regulator.

- Tescom 44-5060-240 ($C_v$ = 0.24, outlet pressure subatmospheric 0.067 bara to 2 bara)
- Tescom 44-2660-242-031 ($C_v$ = 0.02, outlet pressure 1.1 to 2.7 bara)
- Go Regulator PR2-2A11A3D121 ($C_v$ = 0.06, outlet pressure 1 to 2.7 bara)

- The electronic solution consists of an electronic pressure controller, combined with a pressure regulator and an external pressure transducer. The solution without external pressure transducer already provides an accuracy of about 1 to 2% for the controlled outlet pressure. An accuracy of 0.25% can be obtained using a pressure transducer as close as possible to or on the bioreactor. The pressure regulator used (selected according to the $C_v$ value and pressure drop) should be available in a dome loaded version. The following possibilities can be proposed:
  - Tescom electronic regulator type ER3000-SI-1 (pneumatic actuator) with analog or digital (RS-232) set point selection, combined with Tescom 44-2260-241-500 ($C_v$ = 0.02, outlet pressure 1.1 to 2.7 bara). Accuracy 1% without, 0.25% with external pressure transducer.
  - Bellofram I/P convertor T-1500 series type 966.713.000 combined with Tescom 44-2260-241-500. Accuracy 2% without, 0.25% with external pressure transducer.

#### 3.2.2.2 Back pressure regulator

The back pressure regulation of the buffer vessel and the withdrawal of the net gas produced can be done with a hand adjustable, spring loaded, diaphragm-sensed back pressure regulator. Again, all parts exposed tot the media should be constructed of corrosion resistant materials as AISI-316 stainless steel and CTFE.

Several possibilities exist with different brands, for example TESCOM:

- Tescom 44-2362-24, pressure inlet pressure max 6.9 bar

## 3.3 Gas-Liquid separation

The exhaust gases from the fermenter will typically be relatively warm (55°C) and will contain water vapour. If the sample lines or the instruments are colder than the sample air and pressure will increase, the risk of condensation must be taken into consideration. Condensed water in the sample lines will eventually end up in the instrument and may damage it.

### 3.3.1 Condensation effect due to pressure build-up

Since the vapour pressure rises with temperature, the gas mixture can contain a high vapour content at elevated temperatures. In such cases, it is useful to examine the possibility of vapour condensation in or

after of the pump. A system to remove this condensate and to drain it back to the bioreactor should be present. It is however very important to decide on which place to remove the vapour in the gas mixture.

#### 3.3.1.1 Gas cooling and condensate evacuation ahead of and after the compressor.

In order to remove vapour from a gas stream, the gas can be cooled so the vapour condenses and can be removed. This way, a gas with a low dew point can be obtained. The dew point is the temperature at which the vapour in the gas condenses. The lower the dew point of a gas mixture, the lower the moisture content of the gas.

Assume the gas coming from the bioreactor has a temperature of 55 °C and is saturated with water vapour. At this temperature and with a pressure of 100 mbar, a moisture content of 12% or 120000 ppm can be expected. When this gas is cooled with a peltier of compressor cooler to a dew point temperature of 5 °C, the moisture content drops to 0.86% or 8600 ppm.

The compressor increases the pressure to 3 bar (or 4 bara). This means a volume compression of a factor 3.6 is applied to the gas and the moisture content increases with a factor 3.6 to 3.1%. This means in the pressure buffer, the dew point is not lower than 24°C. This is relatively high so that the risk for extra condensation in the pressure buffer cannot be excluded completely, and an extra cooler after the compressor should be installed. Also, since the local pressure in the compressor can even be higher than the 3 bar in the buffer vessel, it is likely that still some condensate will be formed inside the compressor

For the gas flow of 15 L/min, quite some cooling capacity should be installed before as well as after the compressor. A more economic solution is to only remove the condensate formed in the pressure vessel by a liquid drain, leading it back to the bioreactor, and to install a separate sample cooler/dryer in front of the gas analysis system.

#### 3.3.1.2 Condensate removal from the pressure buffer

Since condensation in the compressor cannot be excluded, it is important to select a compressor that can handle this (see paragraph 3.2.1). Because of the high cooling capacity needed, the possibility to remove the condensate formed in the pressure buffer without extra cooling combined with a separate cooler for the gas analysers should be evaluated.

To remove the condensate from the buffer vessel a purely mechanical and an electrical solution can be installed. It should be noted that the condensate from the pressure buffer will be drained back to the bioreactor. This way, no separate liquid drain in the pressure buffer is needed.

- The mechanical solution is an automatic condensate drain, designed to remove water from compressed gasses. The system is equipped with a ball float that actuates a valve to remove the condensate gathered in the device. The drain function via gravity. The outlet valve is controlled by a lever mechanism. Te float closes the condensate outlet via the lever mechanism with the valve tip. Due to the rising condensate level, the buoyancy of the float releases the outlet (Figure 4).

  The system is completely constructed out of corrosion resistant materials (stainless steel AISI-316) and can be obtained from different suppliers like M&C (automatic liquid drain AD-SS) and Armstrong (liquid drain 11-LD).

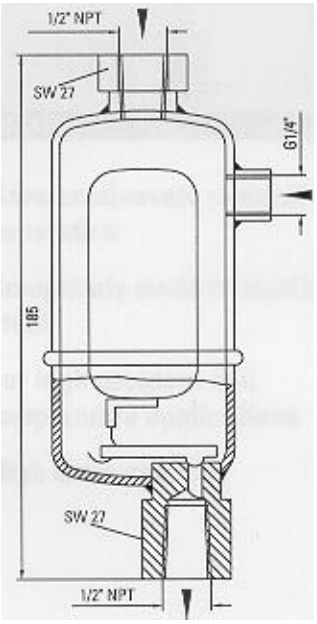


Figure 4: Dimensions of an automatic liquid drain

- The electrical condensate drain works following the same principle (Figure 5). The condensate is gathered in a reservoir (1). A probe continuously measures the level of water in the reservoir (2) and generates a signal when the reservoir is completely filled. On this command, a diaphragm valves opens (3) and the condensate is released (4). The valve is closed in time so as to avoid a spill of air through the drain. The condensate reservoir and the valve can be installed separately or together in one device.

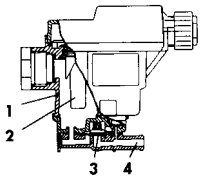


Figure 5: Schematic representation of an electronic liquid drain

A possibility for a separate solution is the Sentinel drain (Model MDV400L), which can operate in response to a liquid level sensor. A complete all-in-one solution can be obtained from BEKO, e.g. the BEKOMAT 12 condensate drain.

The choice between both systems will mainly depend on the durability and the risk of getting air leaks. The leakage of air and a late closing of the valve should be avoided under all circumstances, since this can cause pressure chocks in the bioreactor because the condensate is directly lead back to the bioreactor. The mechanical drain is completely constructed from stainless steel, and a filter element will be included in front of the drain so as to avoid leakage by an incomplete closing of the drain. Therefore, the mechanical drain is selected, unless prototype testing shows that the electrical drain is a better option.

### 3.3.2 Sample gas cooling/drying for the gas analysis system

Different possibilities also exist to separate water vapour from sample gases prior to gas analysis, using the Peltier cooling effect of compressor cooling. The goal of the removal of vapour is to lower the dew point of the sample gas to generally 5 °C so as to avoid condensation in the analysers. A stable dew point is required to avoid water vapour cross-sensitivity and volumetric errors.

The heat exchangers used in gas cooling devices can be constructed out of Duran glass, PVDF or even stainless steel AISI-316 for high pressure applications. A heat exchanger in Duran glass can provide the stablest dew point independent of the gas flow rate. It is however more fragile, compared to a PVDF heat exchanger. The lay-out needs to provide a high degree of precipitation and a reliable condensate separation. The materials of use permit application even in corrosive gas streams. Additionally, the contact time between condensate and sample gas should be kept short to minimise the washing out effect and a possible lowering of the detection limit of gases.

- In a Peltier cooling device, the cooler module normally consists of a heat exchanger packaged as a compact unit suitable for wall or bulkhead mounting. The heat exchanger unit houses a Peltier element. Passing a direct current through the Peltier element causes heat transfer along its length from the "cold" to the "hot" junction. The "cold" section is mounted on top of the heat exchanger and is equipped with a temperature sensor so as to monitor the set temperature of the unit.

  Peltier coolers are rather powerful with a small overall size, making them suitable for integration in (portable) analysis systems for gas monitoring systems with relatively low flow rates. These units can be upgraded with a peristaltic pump for condensate drainage en with a diagnostic device to monitor the Peltier element temperature and the presence of condensate in the outgoing gas flow.

  This type of cooling device can be obtained with different constructors, like the Bühler PKE4 series, the M&C ECP Series or the JCT JCM Series coolers

- When a compressor cooler is used, the cooling capacity is provided by a small compressor chiller (non CFC operating). Compressor coolers are generally somewhat larger than Peltier coolers, but in turn they can guarantee high dew point stability even under changes of inlet dew point and ambient temperature. Again the cooler can be equipped with status and alarm contacts to monitor temperature en condensate in the outlet.

  Compressor coolers can also be obtained with different constructors, like the M&C EC Series or the Thermotechnik MAK-6 Series coolers.

- Compressor and Peltier cooling can also be combined in ultra low gas coolers, in which a dew point as low as –30 °C can be obtained. This is sometimes needed for outdoor measuring devices, where a dew point below the lowest possible temperature in winter should be obtained. An example of this type of cooler is the M&C Series EC cooler, version EC-30.

For the application under study, a compressor cooler will provide the gas analysers with a dry and condensate free sample gas with a stable dew point temperature of 5 °C. For maintenance reasons, a Teflon (PVDF) heat exchanger is preferred over a glass one although this choice is not imperative.

## 3.4 On-line instrumentation

### 3.4.1 Pressure transducer

Many pressure transducers employ the piezo-resistive principle to convert pressure to an electrical signal. The key element is a silicon chip, which has been micro-machined to create a diaphragm around which four resistors are diffused in a bridge configuration. The application of pressure to this silicon diaphragm causes the bridge resistors to change their value creating a differential voltage output proportional to the applied pressure.

There are a variety of pressure transducers on the market. A stainless steel version that can be used in harsh environments and a screw-in connector, which enables proper leakage protection, is very important. Such sensor is e.g. the SensorTechnics PTE2000.

### 3.4.2 On-line humidity sensor

The aim of using the humidity sensor in the gas loop is to control the evaporation of water from the bioreactor to gas phase.

Most humidity sensors consist out of a polymer film that either absorbs or releases water vapour as the relative humidity of the gas rises or drops. The dielectric properties of the polymer film depend on the amount of water contained in it. As the relative humidity changes the dielectric properties of the film change and so the capacitance of the sensor changes. The electronics of the instrument measure the capacitance of the sensor and convert it into a humidity reading.

Various measurement apparatus can be obtained, measuring relative humidity and temperature. Dew point and absolute humidity can be calculated in the transmitter based on a separate pressure transducer or a manual input of pressure on the apparatus. These transmitters are also equipped with analogue outputs.

An example of such sensor is the Vaisala HMP238 sensor, which can be connected to pressurised air lines up to 40 bar. It is supplied with a ball valve that enables disconnecting and reinstalling the probe.

### 3.4.3 Gas-analysers

The composition of the exhausted fermentation gases produced from the biological first compartment should be measured in order to study and to control the biological process. The produced fermentation gases indicate the state of fermentation. Actions can then be taken to orientate the process by applying changes on some parameters like the pH. The analysis of the different fermentation gases should be performed on-line and at regular intervals in order to maintain the system stable.

The expected concentration ranges are listed in Table 1. It should be noted that these concentrations are applicable to steady-state conditions. At start-up, higher or lower $CO_2$ concentrations can be expected depending on the choice to start up the reactor in a $N_2$ or $CO_2$ atmosphere. Furthermore, when full methanogenesis would be preferred at a certain point, higher $CH_4$ concentrations are to be expected. It is therefore mandatory to have gas analysers with a wide measurement range

Table 1. Gas components to be measured in the fermentation gases

| Gas component | Range | Unit | Remark |
|---|---|---|---|
| $CO_2$ | 40 – 80 | Vol % | high or low concentration at start-up |
| $CH_4$ | 0.1 – 20 | Vol % | higher with full methanogenesis |
| $H_2S$ | < 2 | Vol % | |
| $H_2$ | < 1000 | Ppm | |

Obviously, different measurement techniques exist to monitor these components.

#### 3.4.3.1 IR analysis, measurement for $CO_2$, $CH_4$ (and $H_2S$)

Infrared sensors are based on the amount of infrared light that is absorbed by a certain component in the gas. Each component has a specific wavelength at which infrared light is absorbed. A detection mechanism detects the amount of absorption and translates it towards a concentration reading.

- Classic detection mechanism

  The sample gas is pumped through one compartment (the measuring side) of a measuring cuvette. The other compartment (the reference side) is filled with a reference gas. A turning modulation wheel directs the radiation to one side of the cuvette at a time. Behind this cuvette, the rest of the infrared radiation is absorbed in a detector. This detector consists of two optical absorption chambers in series, separated by a thin membrane of synthetic material. This

membrane can slightly move if there is a pressure difference between the two absorption chambers. The chambers are filled with a certain amount of the component of interest ($CH_4$ or $CO_2$ in this case). Due to the unequal absorption of infrared radiation at each side in the measuring cuvette, a time-fluctuating amount of infrared radiation is still to be absorbed in the detector. This fluctuation induces pressure pulses of the membrane that separates the two chambers in the detector, due to unequal heating in both compartments. The amplitude of this fluctuation is used as a measure of the concentration in the sample gas.

This detection mechanism is suitable for the measurement of $CO_2$ en $CH_4$ in the fermentation gas formed. It is a reliable and proven technology and is sufficiently accurate for the application. Weekly calibration of the sensor is recommended. This can be done automatically using a cuvette with a known composition.

Several manufacturers like Siemens, Bühler and Maihak produce this kind of apparatus. A combined $CO_2$, $CH_4$ measurement can be obtained for prices ranging from € 8,000.-- to € 10,000.--. This price does however not incorporate gas pre-treatment steps like cooling and condensate removal as discussed above in paragraph 3.3.2.

- Photo-acoustic spectroscopy (PAS) monitoring

The Photo-acoustic gas monitor also uses a measurement system based on the infrared absorption method. It is capable of measuring almost any gas that absorbs infrared light such as $CO_2$, $CH_4$ and eventually also $H_2S$.

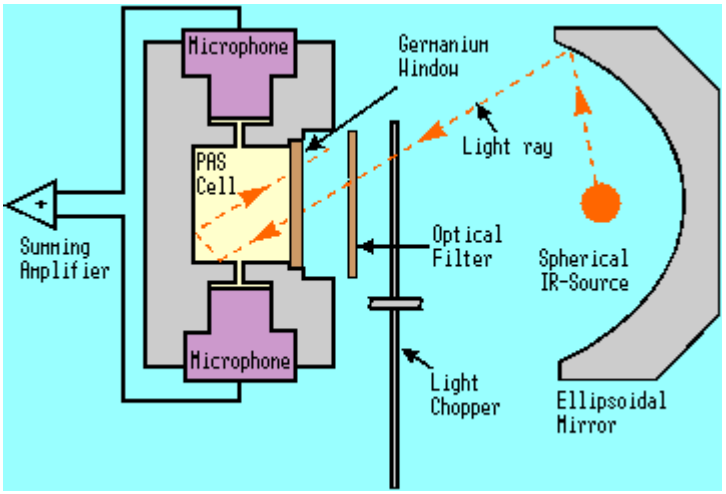


Figure 6. PAS measurement system in the fermentation monitors type 1313 and 1314

In Photo Acoustic Spectroscopy (PAS) the gas to be measured is irradiated by intermittent light of pre-selected wavelength. The gas molecules absorb some of the light energy and convert it into an acoustic signal, which is detected by a microphone (Figure 6). PAS is an inherently very stable method for detecting very small concentrations of gas.

Photoacoustic gas measurement is based on the same basic principles as conventional IR-based gas analysers, namely the ability of gases to absorb infrared light. However there are some important differences between PAS and these conventional techniques.

In a standard IR-analyser, the energy absorbed by the gas sample is measured indirectly, by measuring the transmission through the measurement chamber and comparing it to that through a reference cell whereas, with PAS the amount of infrared light absorbed is measured directly, by measuring the sound energy emitted on the absorption of light. This means that:

- PAS is highly accurate, with very little instability and rarely requires calibration (maximum every 6 months). For example, zero point drift is almost non-existent as *zero* is always reached when there is no gas present.

- With PAS all gases and vapours can be monitored simultaneously in a single measurement chamber as it is possible to make the signal for each substance to be monitored individually detectable.

- Fast response time (rise time of less than 0.2 seconds)

On the other hand, the measurement apparatus is quite expensive (price estimated around € 25,000.--) compared to the above apparatus with a classis detection method. Furthermore, the measurement cell is only capable of measuring relatively low concentrations of the IR components. In order to measure the concentrations in Table 1, a dilution of the sample gas with $N_2$ would be necessary. This is not desirable, since all the sample gas should be recirculated back to the bioreactor. Photoacoustic gas measurement is commercialised by Innova AirTech Instruments (Fermentation Monitor 1313 and 1314).

#### 3.4.3.2 Electrochemical analysis

Some gases like $H_2$ and $H_2S$ can be measured electrochemically, like in the ADOS Biogas Analyser and several gas detection systems from a variety of manufacturers. The electrochemical measurement of $H_2S$ at these high concentration ranges is however very difficult and will result is a fast degradation of the electrochemical cell. Furthermore, care has to be taken in order to avoid cross-sensitivity. It is known that an electrochemical $H_2$ sensor is extremely sensitive towards $H_2S$, so measures have to be taken to absorb $H_2S$ in front of the measurement cell. Therefore, an intermittent analysis of $H_2$ is proposed in case an electrochemical measurement is selected.

Electrochemical sensors can be obtained for prices around € 2,000.-- per component to be measured. This is not including the $H_2S$ trap for $H_2$ measurement.

#### 3.4.3.3 Mass Spectrometry

A Mass Spectrometer measures gas components based on the analysis of ionised fragments in a vacuum. The range of the components to be measured can vary from as low as 1 ppm to 100%. It is a continuous and quick measurement for all components of interest in the off-gas. Up to 32 components can be measured out of several streams using a heated multiport sampling system.

Nowadays, the trend is toward miniaturisation of equipment and analysers. Since a few years, some manufacturers offer MS-equipment that can be installed on-line for pilot testing. Still, this solution remains very costly. Possible options are the AMETEK ProLine Mass Spectrometer or the on-line microMS from Mass Sensors Inc. Both possibilities cost well over € 50,000.--.

#### 3.4.3.4 GC

In a gas chromatograph the liquid or gas sample is injected by means of a micro syringe through a rubber septum and into a flash vaporiser port at the head of a chromatographic column that contains a liquid stationary phase adsorbed onto the surface of an inert solid. The sample is transported through the column by a flow of inert carrier gas. The separation is due to the different retention time of the compounds when they pass through the column. The effluent of the column goes to the detector, which emits a signal that is translated into a serial of peaks (chromatogram). Position (retention time) of these peaks is used in qualitative determination and size (area or height) is related with concentration.

This measurement is stable, can measure all components of interest except $NH_3$. GC can measure $H_2S$ although also in this case the concentration is a bottleneck. One example of a suitable gas chromatograph is the Varian CP-4900 Micro GC. The GC solution is also relatively costly. Prices vary from € 40,000.-- to € 50,000.--.

### 3.4.3.5 Possibilities for $O_2$ measurement

$O_2$ is not a process parameter in itself, since it should be absent under all circumstances. However, it can be an indication of the functioning of the waste compartment and this way it can be used as a check of the gas loop hardware. $O_2$ can be measured in different ways:

- Paramagnetism

  The $O_2$ measurement can be based on the paramagnetic characteristic of oxygen. The measuring cell contains a diamagnetic part, suspended in a permanent magnetic field in such a way that it can rotate out of the magnetic field. However, an opto-electrical compensation circuit is provided to keep the dumbbell in a defined resting position. The paramagnetic characteristic of the $O_2$ in the sample gas will change the magnetic field. This effects an adaptation of the opto-electrical compensation. This compensation difference is used to calculate the $O_2$ concentration.

  Manufacturers like Siemens, Bühler and Maihak regularly incorporate paramagnetic measurements together with IR-analysis for $CO_2$ and/or $CH_4$ (paragraph 3.4.3.1).

- $ZrO_2$

  $O_2$ can also be measured based on the permeability of $ZrO_2$ for $O_2$ at a temperature of 650°C. It is therefore especially suitable for $O_2$ measurements in flue gases. The ions cause a voltage difference that is logarithmically dependent on the $O_2$ concentration. This measurement is very stable and linear. It is suitable for measuring $O_2$ at lower ranges compared to the paramagnetic measurement technique, but also more expensive.

- Electrochemical

  An $O_2$ measurements based on a electrochemical cell is less accurate but also cheaper than the above measurements. Moreover, it needs more calibration. It is suitable for alarm generation.

  Since $O_2$ should not be present in biogas produced by fermentation processes, this type of sensor is sometimes incorporated in biogas monitors, like the ADOS Biogas Analyser 401 (together with IR analysis for $CO_2$ and $CH_4$ and electrochemical analysis for $H_2$ or $H_2S$)

### 3.4.3.6 Conclusion

Mass Spectrometry and GC are not further considered. On the one hand, their price is very high compared to other measurement techniques. Furthermore, although the measurements of these instruments are very precise, this level of precision is not required in this application. The mass balance for $CO_2$ and $CH_4$ can perfectly be closed based on IR-measurements, if the measurement range and the precision of other measurements in the system is taken into consideration.

Components that are present in lower concentrations also do not need to be known with the precision MS and GC can deliver. The measurements of $H_2$ and especially those of $H_2S$ and $O_2$ are considered more as indicators for maintaining a stable process and as alarm generators than they are needed for mass balance requirements.

Theoretically and apart from its capability to measure $H_2S$, GC might be interesting to measure Volatile Fatty Acids directly in the gas phase. However, it is possible to equip the GC described TN71.4 so that it can also measure directly in the gas phase. Measuring VFA both in liquid and gas phase is not useful since there is a pH-dependent equilibrium between the concentrations in the two phases.

Based on these considerations, the following measurement systems will be used:

- $CO_2$ and $CH_4$ will be measured using the IR absorption technique with a classical detection mechanism using a measurement cuvette. Automatic calibration will be foreseen.

- For the measurement of $H_2$, an electrochemical sensors will be used. $H_2$ will be measured in an intermittent way, using a $H_2S$ trap in front of the sensor.

- If desired, $O_2$ will be measured paramagnetically or electrochemically, denpending on the choice of the other equipment. Many biogas analysers incorporate an electrochemical $O_2$ sensor. Here too, automatic calibration is foreseen.

- At the concentration range that is expected, the measurement of $H_2S$ with classical cost-conscious techniques apart from GC is very hard to perform. Further research will be performed in order to find a measurement technique that gives an indication of the $H_2S$ concentration in the gas phase at least in a intermittent way.

# 4. Final design of the gas loop

The necessary information about the equipments required for the design of the gas loop are shown in Table 2.

Table 2. Gas loop equipment

| Reference | Description | Type | Sub-type |
|---|---|---|---|
| **V-G-001** | Regulates the flow through gas loop and gas analysers | Valve | Needle valve |
| **V-G-002** | Regulates the flow through gas loop and gas analyser 1 | Valve | Needle valve |
| **V-G-003** | Regulates the flow through gas loop and gas analyser 2 | Valve | Needle valve |
| **V-G-004** | Safety pressure relief valve on pressure vessel R-G-001 | Valve | Needle valve |
| **V-G-005** | Regulates the flow through gas loop | Valve | Needle valve |
| **V-G-006** | Regulates the addition of $N_2$-gas at reactor start-up | Valve | Needle valve |
| **V-G-007** | Automatic liquid drain on vessel R-G-001 | Valve | M&C AP-SS |
| **R-G-001** | Pressure vessel: buffer for produced gas at 4 bara | Vessel | |
| **PMP-G-001** | Masterpump that generates air flow through gas loop | Pump | Compton D/416 (D/296/416-3E) |
| **PD-G-001** | Precision stainless steel pressure transmitter bioreactor | Transducer | Sensor Technics PTE2005G (4A): 0 – 0.35 bar |
| **PD-G-002** | Precision stainless steel pressure transmitter pressure vessel | Transducer | Sensor Technics PTE2100G(4A): 0 – 5 bar |
| **PR-G-001** | spring loaded, diaphragm-sensed backpressure regulator: regulates pressure in buffer vessel R-G-001, relieves net gas produced | Back-pressure regulator | Tescom 44-2362-24 |
| **PR-G-004** | Self-contained spring loaded pressure reducing regulator with negative bias, regulates bioreactor pressure | Pressure reducing regulator | Tescom 44-5060-240 |
| **FI-G-001** | Rotameter for flow through gas loop and analysers | Indicator | Rotameter |
| **FI-G-002** | Rotameter for flow through analyser 1 | Indicator | Rotameter |
| **FI-G-003** | Rotameter for flow through analyser 2 | Indicator | Rotameter |
| **PI-G-001** | Pressure on suction side of PMP-G-001 | Indicator | Manometer |
| **PI-G-002** | Pressure at outlet gas analyser 1 | Indicator | Manometer |
| **PI-G-003** | Pressure at outlet gas analyser 2 | Indicator | Manometer |
| **PI-G-004** | Controlled backpressure by PR-G-004 | Indicator | Manometer |
| **PI-G-005** | Controlle pressure by PR-G-001 | Indicator | Manometer |
| **PI-G-006** | Inlet pressure to PR-G-001 | Indicator | Manometer |
| **HX-G-001** | Cooler to dehumidify the gas for gas analysis | Heat Exchanger | Compressor Cooler |

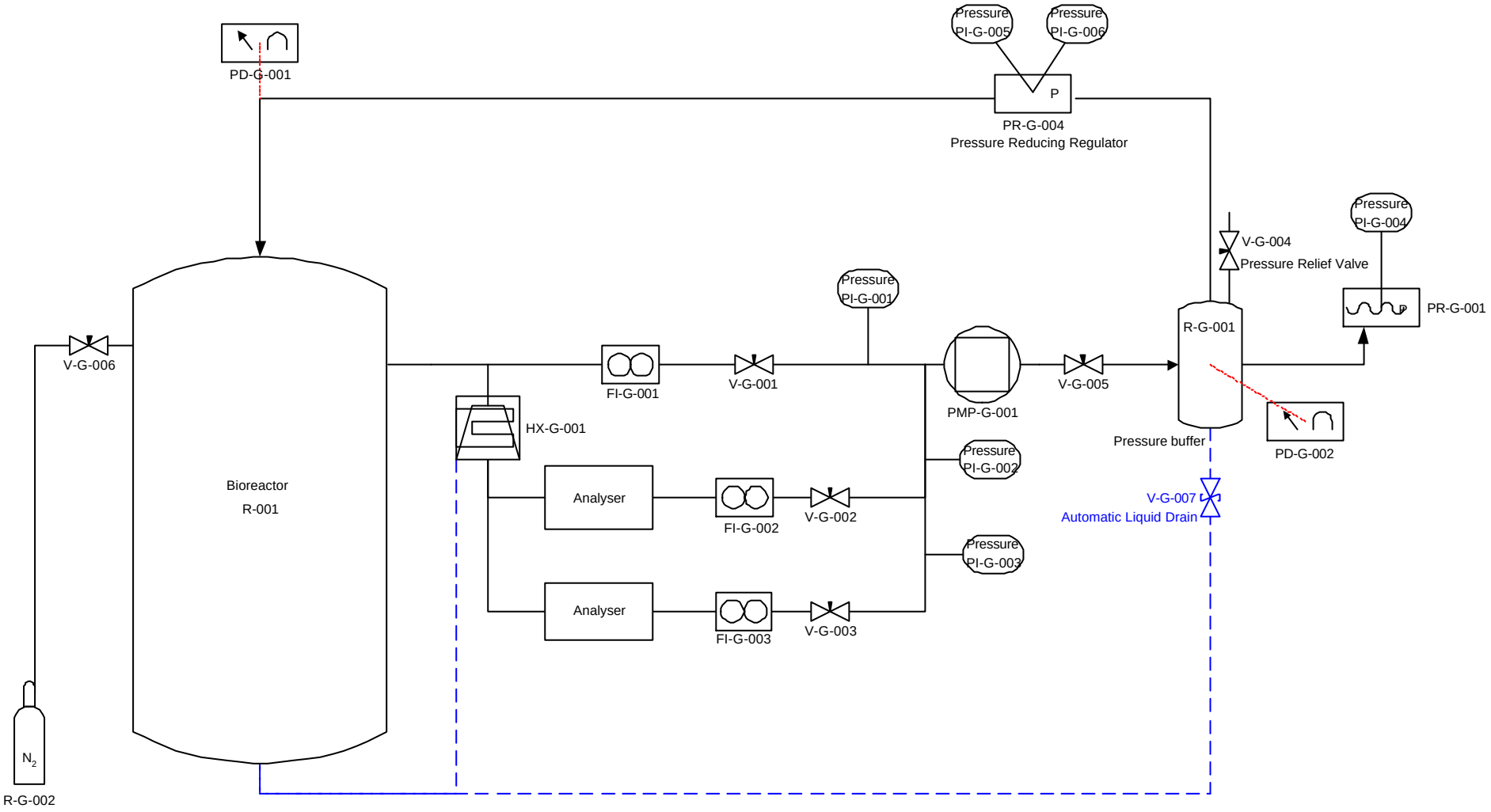


Figure 7: Final gas loop design