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Anaerobic digestion of substrates rich in sulphur and nitrogen

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Summary:

There is an increase interest in producing biogas from organic waste, such as cow manure and fish sludge. The government in Norway is encourages farmers to invest in biogas facilities with financial incentives. A recently started biogas facility is Svanem Biogass AS, which is located at the coast of Trøndelag in Norway. The facility runs on cow manure from several local farmers and fish sludge from the salmon aquaculture in the area. The substrate is rich in nitrogen and sulphur and measures need to be taken to avoid inhibiting the digester due to excess ammonia and reduce the level of hydrogen sulphide in the biogas. It is considered favourable to reduce the hydrogen sulphide in-situ the biogas rector rather than invest in costly equipment for conditioning the biogas. However, the main goal for Svanem Biogass AS is to produce high quality natural fertiliser. The measures cannot affect the quality, nor be too expensive.

To avoid inhibiting the digester due to ammonia, there are two methods that is considered appropriate for Svanem Biogass AS. These methods are slowly stepwise increase of content of fish sludge in the substrate mixture and temperature control. When using a stepwise change in the substrate mixture, the microflora manages to adopt to a change in the substrate. Especially the methanogens need time to adopt to the changes. Temperature reduction within the range of mesophilic condition should be considered when inhibition of ammonia occurs.

Reduction of hydrogen sulphide can be achieved by adding air or oxygen to the head space of the biogas reactor or by adding iron to the substrate. Close to Svanem Biogass AS there is a waterworks with wastewater rich on iron. Simulation shows that with the correct amount of iron added to the substrate, the hydrogen sulphide level can be significant decreased. Adding iron rich water to the substrate is considered as a low-cost measure to reduce the hydrogen sulphide in the biogas without conditioning the biogas afterwards.

Preface

The master's thesis has been conducted at Department of Process, Energy and Environmental Technology at University of South-Eastern Norway (USN) at campus Porsgrunn. The thesis is part of the master program Process Technology, which is part time and where the lectures have been taught online.

The supervisor for the master's thesis has been Associate Professor Wenche Hennie Bergland at the USN. Nirmal Ghimire has also been involved in discussion and attended regularly online meetings during the work with the thesis. Nirmal Ghimire got a PhD in "Methane Production from Lignocellulosic Residues" from USN in 2021 and is Assistant Professor at Kathmandu University in Nepal.

The thesis is a corporation with an external partner, a biogas facility in Trøndelag (Norway) named Svanem Biogass AS. Roar Svanem at Svanem Biogass AS has provided information of the facility and analysis data of the substrate and biogas. This information has been useful to gain a better understanding and assessment of input values for simulations. A visit at the site increased the understanding of the process and challenges for a recently started biogas facility.

The work with the master's thesis made me understand that the anaerobic digestion process is complex and there are no defined rules. The digester ability to adapt to (slowly) changes makes it interesting to continue the reading and try to get a better understanding. However, at the same time the digester can inhibit, and the digestion process stops.

The thesis consists of three main parts: theory, materials and methods and results. The theory includes general considerations of an anaerobic digester, but also more specific regarding inhibition levels of nutrients, transformation of nitrogen, sulphur and phosphorous, method to avoid inhibition of excess ammonia, and method of reduction of hydrogen sulphide in the biogas. In Materials and methods, it is provided information of Svanem Biogass AS, the simulation tool ADM1 extended with sulphur, phosphorous and iron interactions and how input values to ADM1 are estimated. The results of the simulation are presented and discussed with respect to sensitivity of some parameters and variables, variation in fraction of fish sludge and cow manure in the substrate and hydraulic retention time.

Thanks to my family who have been patient with my work on the master's thesis.

Porsgrunn / Brekstad, 29th of October 2023

Kjetil Andersen

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Nomenclature

Alkalinity	The ability to remain an approximately stable pH during changes caused by acidity (the ability to neutralise acids)
Anaerobic	In absence of free oxygen
Assimilation	To change food and other nutrients into a part (fluid or solid) of living organism either by digestion or absorption
Desulphurization	A process of removal sulphur from for example gas or fluid.
Digestate	Organic matter remaining from for example anaerobic digestion
Disintegration	To break down large parts into smaller particles
Dissimilation	Breakdown of more complex substances into simpler ones with release of energy
Inhibition	A condition that prevents a process to happen or continue
Inoculum	A population of microorganisms introduced into another suitable biological material
Inorganic carbon/sulphur/phosphorous	Carbon/sulphur/phosphorous extracted from minerals
Long-Chain Fatty Acids (LCFA)	Fatty acids are carboxylic acid. The acids are with a long unbranched hydrocarbon tail and typically with 13 to 21 carbons.
Micro-aeration	Adding small amount of air or oxygen into an anaerobic process

Microorganisms	Microscopic organisms such as bacteria, fungi, and archaea
Monomers	Atoms or small molecules which can link up to form polymers. Examples of monomers are glucose, vinyl chloride, ethylene and amino acids.
NTP	Normal Temperature and Pressure. Standardisation of gas volume at 20°C and 1 atm.
Oligomers	Polymers with low molecular weight and consists of a few repeating units. The physical properties depend on the length of the chain.
Organic carbon/sulphur/phosphorous	Carbon/sulphur/phosphorous found in plants and living organisms/creature
Substrate	A natural environment in which microorganisms lives. Examples sewage, animal manures, and food waste.
Trøndelag	Region in Norway
Volatile fatty acids (VFA)	VFA are typically acetate, propionate, butyrate, and lactate, and it is produced during anaerobic degradation of organic material.
Volatile	Easily evaporated into vapor
Yield	The return from a process expressed as ratio between produced and consumed. One example is biogas yield which can be expressed as the ratio of biogas produced per unit mass of substrate or volatile solid.

1 Introduction

1.1 Background

Instead of storing digestible organic waste in landfills or keep manure in storage tanks at farms, the energy in the organic waste can be converted into biogas. The biogas from organic waste has potential to contribute to production of energy, for example as heat, electricity, or fuel for vehicles. Cow manure, food waste from households, wastewater sludge, fish sludge/waste and crop residues are examples of organic waste, and can be converted into biogas by anaerobic digestion and be utilised as energy [1].

In the anaerobic process there is a wide range of microorganisms which are digesting the organic waste and transforming it into biogas and digestate. It is not only the biogas that can be utilised, but also the digestate. The digestate is rich on nutrients and can be used as plant fertiliser [1].

The biogas consists mainly of methane, carbon dioxide, water vapour and small amounts of other gases, for example hydrogen sulphide [1]. Methane is a combustible gas, and it is the energy from this gas which can be used as fuel for vehicle or in production of heat and/or electricity. However, the small amount of other gases, especially the hydrogen sulphide, might require the biogas to be conditioned. Hydrogen sulphide is a toxic gas, forming sulphuric acid with the water vapour in the biogas. The sulphuric acid is corrosive to numerous parts in equipment such as pipelines, pumps, compressors, valves and it is reducing the lifetime of the process equipment [2].

1.2 Svanem Biogass AS

In previous years there has been an increase focus on the energy potential of biogas from fertiliser from farmers. In Norway, the government encourages farmers to invest in biogas facilities. The farmers can get support from Innovation Norway for investing in a biogas facility and, in addition, they can also get additional annual support per ton fertiliser used in the biogas facility [3].

Svanem Biogass AS is a biogas production facility located at the coast of Trøndelag in Norway. The facility was official open by the Norwegian Minister of Agriculture and Food 7th of November 2022 [4]. The facility runs on cow manure from several local farmers and fish sludge from the salmon aquaculture in the area. It is also planned to run on fish waste/silage, but due to extra requirements to pre-heat treatment of the fish waste, it is not utilised so far. Because of increased prices on artificial fertilisers, the focus is to produce high quality fertiliser from the digestate and not only biogas [5]. Hence, it is important to control the flow of nutrients like nitrogen and phosphorus, which are the main components of fertilisers. However, also sulphur and salinity are important parameters to control.

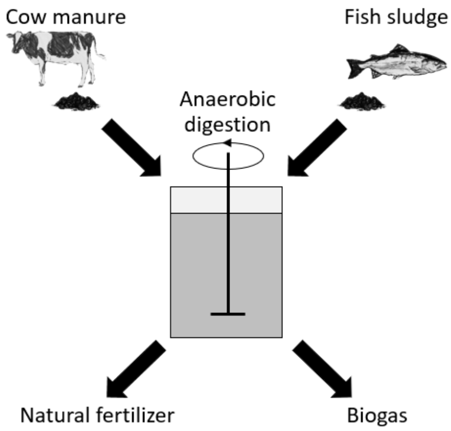


Figure 1.1 Schematic illustration of the concept at Svanem Biogass AS [6]

The facility has not yet decided how to utilise the biogas. The amount of biogas and level of other gases, such as hydrogen sulphide, decides what they are doing further. If possible, the facility will avoid investing in expensive gas conditioning equipment for utilizing of the biogas [5].

1.3 Objective

The objective of this master's thesis is to consider anaerobic digestion of substrates rich in sulphur and nitrogen. The case with Svanem Biogass AS will be the base line for the master's thesis. The sulphur will be assessed with a view of finding methods to reduce the amount hydrogen sulphide gas generated in the biogas reactor. In general, suggest methods for keeping the sulphur in digestate instead of in the biogas. Other nutrients, like nitrogen, phosphorus and salinity must also be considered. Especially concern regarding inhibition due to excess of ammonia. The methods of reducing the amount of hydrogen sulphide or inhibition due to excess of ammonia cannot compromise the quality of the digestate, which shall be used as natural fertiliser.

The master's thesis can be divided into three parts. The first part is theory about biogas from anaerobic process, and how the process depends on different parameters, such as ratio of carbon and nitrogen, pH, temperature, and dry matter content. Nutrients, such as nitrogen, phosphorus, sulphur, and salinity are also considered. Different methods found in literature to avoid inhibition due to excess of ammonia and how to reduce hydrogen sulphide in the biogas are also presented.

The second part of the master thesis is material and methods used in the thesis. Detailed information about Svanem Biogass AS with facility and substrate are presented and discussed regarding how it is implemented in simulations. The simulations are run by using an extended version of ADM1. The extended version which accounts for interactions between phosphorous, sulphur and iron.

The last part is evaluation of simulation results and discussion of findings in literature and simulation results.

2 Theory - anaerobic digestion

Biogas is a product of a process with absent of oxygen (anaerobic) and decomposing, also called digestion, of the substrate by microorganisms. Due to the short carbon cycle, the biogas is considered as a renewable energy even if it releases CO_2 at combustion and at production. The carbon cycle is expected to be between one to seven years [1].

The production of biogas depends on several parameters, such as temperature, ratio between carbon and nitrogen and the substrate used in the bioreactor. The different parameters affecting the anaerobic digestion are discussed in particular in this chapter. Further is among other also digestion steps and transformation of nutrients such as sulphur and nitrogen discussed.

2.1 Digestion steps of organic waste

The digestion steps of organic waste in anaerobic digestion are complicated since there is an interaction between different bacteria and at different state of the process. For example, could waste from some bacteria in previous step be substrate for other bacteria in the next step [7].

The process of digestion is often divided into three to five main steps in the following order: disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis [8]. The last two steps are often considered to run in parallel, as interdependence of two groups of organisms [1]. Hence, sometimes the acetogenesis step is included into the methanogenesis step, as illustrated in Figure 2.1 [7].

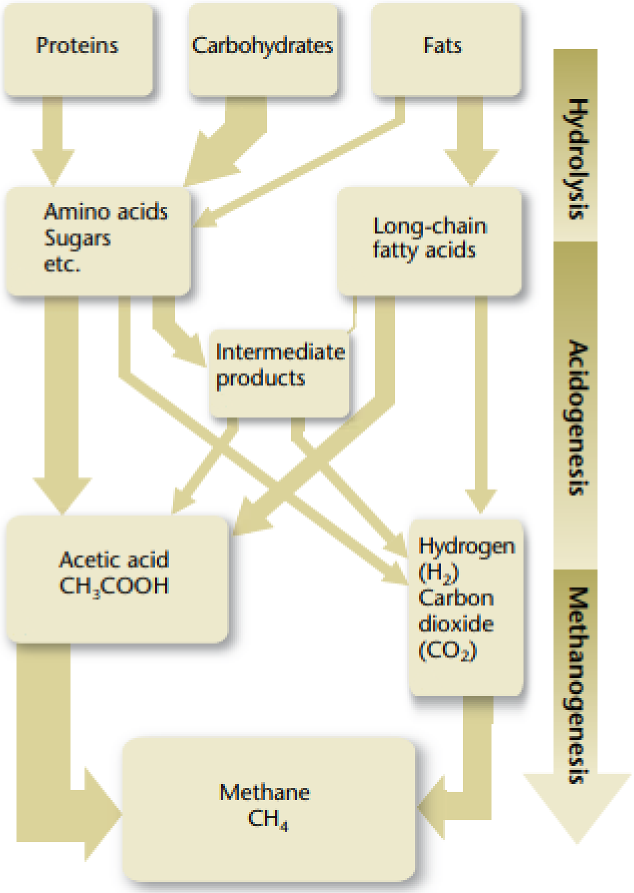


Figure 2.1 Schematic illustration of the anaerobic decomposition of organic waste with different steps [7]

2.1.1 Disintegration

The first step, or also called disintegration, is often neglected when describing the digestion process. The disintegration of the lumped complex solids is due to enzymes, and the products is protein, carbohydrates, fat and inert [8].

2.1.2 Hydrolysis

In the hydrolysis step, microorganisms are secreting hydrolytic enzymes which converting the polymers into monomers and oligomers. Polymers such like carbohydrates (polysaccharide), lipids, nucleic acids, and proteins are decomposed into glucose (monosaccharide), glycerol, purines and pyridines [1]. The decomposition takes place outside the bacteria cell in the liquid and the process is schematically presented in Figure 2.2 [1], [7].

$$\textit{Lipids} \xrightarrow{\textit{lipase}} \textit{fatty acids, glycerol}$$

$$\textit{Polysaccharide} \xrightarrow{\text{cellulase, cellobiase, xylanase, amylase}} \textit{monosaccharide}$$

$$\textit{Proteins} \xrightarrow{\textit{protease}} \textit{amino acids}$$

Figure 2.2 Decomposition of polymers into monomers and oligomers [1]

2.1.3 Acidogenesis (fermentation)

In the acidogenesis, or also called the fermentation, the product of the hydrolysis step is converted into methanogenic substrates by acidogenic/fermentative bacteria [1].

About 50% of the monomers and long-chain fatty acids (LCFA) from the hydrolysis step are converted to acetic acid. Further is about 20% converted to carbon dioxide (CO_2) and hydrogen (H_2). The rest (~30%) is converted to short-chain volatile fatty acids (VFA) and alcohols [1], [7]. However, if there are imbalance in the process, the level of VFA will increase. The VFA-degrading bacteria have a slow growth rate and will not be able degrade the amount of VFA and the process will be interrupted. The degradation of VFA is often one of the limiting factors in the biogas process and is important to keep a steady degradation to avoid inhibition [7].

2.1.4 Acetogenesis

The acetogenesis is run in parallel with the methanogenesis step in the biogas process. The products from previous step and which cannot be directly converted in the methanogenesis step, are in this step converted to methanogenic substrate by bacteria. These products are volatile fatty acids and alcohols and are converted into acetate, hydrogen, and carbon dioxide by oxidation. The products can now be further converted into methane in the methanogenesis step [1], [7].

2.1.5 Methanogenesis

In this step there are production of methane (CH_4) and carbon dioxide (CO_2) and runs in parallel with the acetogenesis step. There are two main paths for production of methane and about 70% of the methane comes from the reaction with acetate. The rest of the methane comes from hydrogen and carbon dioxide [1].

This step is conducted by methanogenic bacteria and they belongs to the kingdom called Archaea [7]. Archaea is single-celled organisms, and two different groups are used in the production of methane. Figure 2.3 summarise the production of methane.

$$\textit{Acetic acid} \xrightarrow{\text{methanogenic bacteria}} \textit{methane} + \textit{carbon dioxide}$$
$$\textit{Hydrogen} + \textit{carbon dioxide} \xrightarrow{\text{methanogenic bacteria}} \textit{methane} + \textit{water}$$

Figure 2.3 Production of methane by two different group of methanogenic bacteria [1]

The growth rate of methanogenic bacteria is slow and with only approximately one fifth of acid-forming bacteria, it could become a limiting factor in the biogas process [7].

2.2 Bioreactor types

There are several different reactor types which is used for anaerobic digestion. The most common reactors are plug flow reactor, continuous stirred-tank reactor, and batch reactor [1]. The different reactors are illustrated in Figure 2.4.

In a plug flow reactor, the particles move evenly through the reactor and pushed through the reactor due to the feed. The retention time in the reactor is depending on the feed rate. However, it is not possible to guarantee that all particles have the same minimum retention time [1].

Continuous stirred-tank reactor (CSTR) is a process where the tank is feed continuously. The substrate in the tank is agitated during the process to ensure a good mixture and approximately the same retention time. The level of substrate in the tank is maintained at the same level. Even with agitation, it is not possible to ensure a minimum retention time in the tank [1].

The batch reactor is a discontinuous process, where the reactor is filled up and then completely emptied before a new batch. This process is cumbersome and is often used for small batches, for example in a laboratory. However, by using a batch reactor, the minimum retention time in the reactor is guaranteed [1].

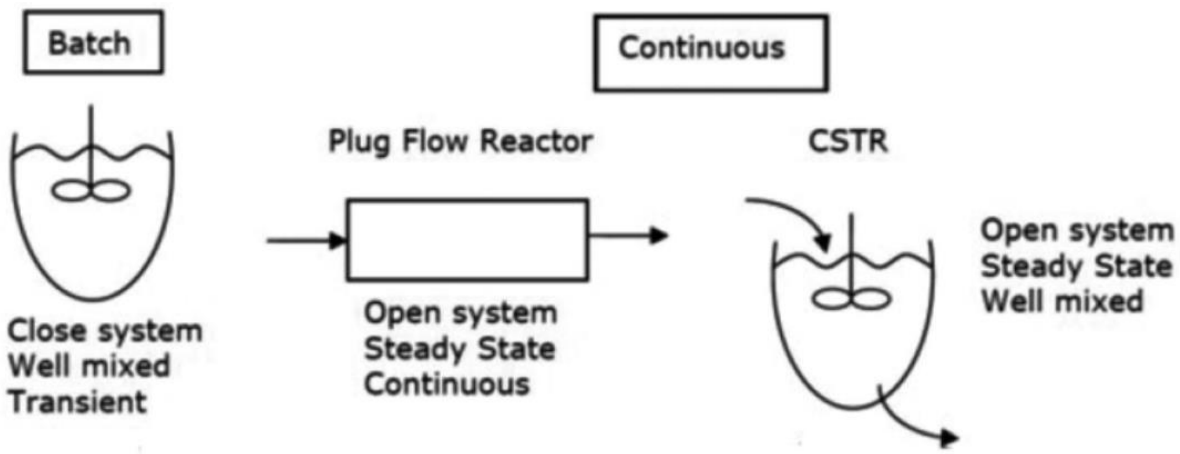


Figure 2.4 Illustration of different reactor types [9]

2.3 Influencing parameters for biogas production in the bioreactor

There are several parameters that influence the efficiency of the bioreactor. By adjusting these parameters, appropriate conditions for the anaerobic process with microorganisms can be provided [1]. The parameters can be divided into two, anaerobic digestion parameters and operational parameters. Examples for anaerobic digestion parameters are temperature, pH-values and ratio of carbon and nitrogen. Operational parameters a typical organic load and retention time.

2.3.1 Ratio of carbon and nitrogen

The ratio of carbon and nitrogen is often used as a measurement of how successful the digestion process is. If the ratio is too low, the process will most likely inhibit. However, if the ratio is too large, the activity of microorganisms will decrease due to lack of nitrogen for bacterial growth [7]. A rule of thumb, the ratio should be between 20:1 to 30:1 for maximum biogas production [10]. Note that the ratio is typically the mass ratio (gram C/gram N) [8].

2.3.2 Ammonia (NH_3)

Nitrogen, as ammonia (NH_3), has significant function in the anaerobic digestion reactor and the main source of ammonia is proteins. Bacteria, especially methanogenic, are sensitive to ammonia, and the concentration of NH_3 should not be more than 80 mg/L [8]. Increasing both the temperature and the pH will increase the fraction of unionised form of ammonia/free ammonia (NH_3) and will increase the inhibition of the process [1].

The relation between free ammonia, total ammonia, pH, and temperature is given by the equation 2.1[1] [1].

$$[NH_3] = \frac{[T - NH_3]}{\left(1 + \frac{[H^+]}{k_a}\right)} \tag{2.1}$$

Free ammonia is the un-ionised form of ammonia (NH_3) and can be calculated by equation 2.1. The $T\text{-}NH_3$ is the total ammonia concentration and is the sum of concentration of ammonium ion (NH_4^+) and concentration of dissolved ammonia gas (NH_3 (aq)) [1], [11]. The k_a is the dissociation parameter and the parameter is temperature dependent [1]. The pH depends on the concentration of H^+.

Even though both NH_3 and NH_4^+ have been reported as concurrent inhibitors of methanogenic activities, it is considered that NH_3 is the most inhibitory form [12]. At high total ammonia concentration, both should be considered as significant inhibitors.

The inhibition of NH_3 in a digester is often expressed as in equation 2.2 and is referred to as non-competitive inhibition [12].

$$I_{NH_3} = \frac{1}{1 + \left(\frac{S_I}{K_{I,NH_3}}\right)} \tag{2.2}$$

The I_{NH3} is inhibition function with a value between 1 and 0, where 1 is no inhabitation and 0 is complete inhibition. The S_I is the inhibitor concentration of NH_3 and where $K_{I,NH3}$ is the 50% inhibitor concentration of the specific methanogenic activity (SMA). Typically values reported

[1] For derivation of the equation, please see Appendix C

for $K_{I,NH3}$ is in the range of 0.05 to 1.4 gNH_3-N·L^{-1} (0.0029 to 0.0824 M) [12]. Where the NH_3-N is the ammoniacal nitrogen and is a measure of the nitrogen content of the ammonia in a sample. In Anaerobic Digestion Model No. 1 (ADM1), an simulation model of anaerobic digestion, the default value of 50% inhibitor concentration ($K_{I,NH3}$) is 0.0018 M [13].

How different values for $K_{I,NH3}$ is affecting the inhibition is plotted in the Figure 2.5. The largest differences are at low concentrations of NH_3. At a low value of $K_{I,NH3}$ it drops quickly to a value close to zero early, i.e., close to fully inhibition. In the plot, it is also marked the concentration of NH_3 when inhibition is reached 50% for different values of $K_{I,NH3}$. Based on the Figure 2.5, the chose of the value of $K_{I,NH3}$ could significantly affect the simulation regarding inhibition in the simulation due to ammonia.

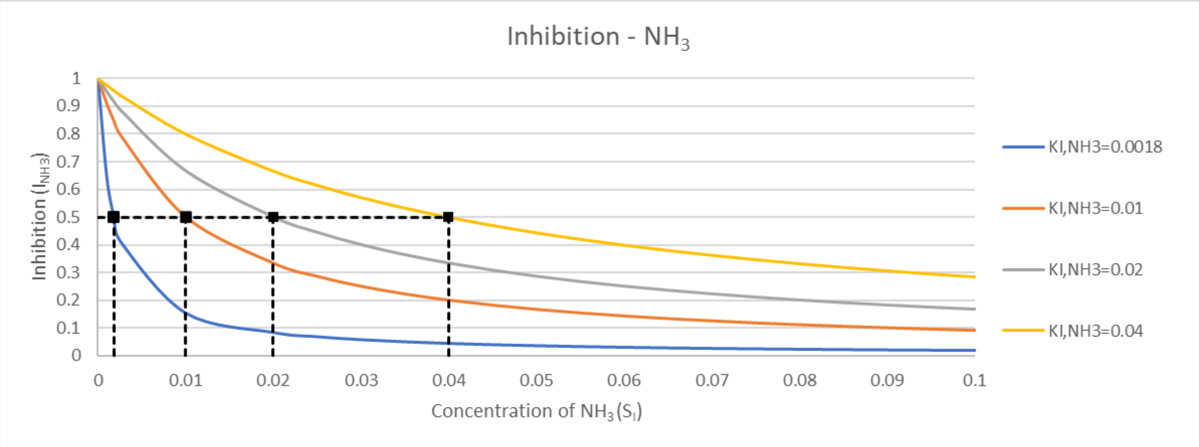


Figure 2.5 Inhibition of NH_3 with difference 50% inhibitor concentration ($K_{I,NH3}$)

2.3.3 Temperature

During anaerobic digestion, a very little heat is generated, since the energy remains mainly in the biogas as methane [1]. Heat must then be added otherwise the process will stop or be very slow. The temperature range used in reactors for organic waste, can be divided into

- Psychrophilic (0 - 25°C)
- Mesophilic (25 - 45°C)
- Thermophilic (45 - 70°C)

The mesophilic temperature range is the most common [8].

Large and rapid changes in temperature should be avoided, due to possible imbalance in the process. The production of acid increases, the pH-value get to low and the process stops. The mesophilic bacteria are less sensitive for temperature fluctuations, than the thermophilic bacteria. Usually, it can be accepted a temperature fluctuation of ± 3°C without a large reduction in methane production [1].

There is a direct relation between the retention time in the reactor and the temperature. Higher temperature decreases the retention time, while lower temperature increases the retention time [1].

2.3.4 pH

The growth of methanogenic microorganisms depends on the pH value and the methane formation has a narrow pH interval. For mesophilic digestion, the optimum interval is between 6.5 to 8.0 and if the pH value is below 6.3 or above 8.3, the process is severely inhibited [1].

The pH in anaerobic digester is controlled by a bicarbonate buffer system, which depends on partial pressure of CO_2 and the concentration of alkaline and acid components in the liquid. The pH value can change rapid when the buffer capacity of the system is exceeded. The buffer capacity for cow manure can also varies with the season. Hence, the pH value cannot be used as a stand-alone parameter [1].

The control of pH value in the bioreactor is mainly dominated by some few species and these are [14]:

$$NH_4^+(aq) \leftrightarrow NH_3(aq) \tag{2.3}$$

$$CO_2\,(aq) \leftrightarrow HCO_3^-(aq) \leftrightarrow CO_3^{2-}\,(aq) \tag{2.4}$$

$$CH_3COOH\,(aq) \leftrightarrow CH_3COO^-\,(aq) \tag{2.5}$$

The control of pH value is complicated due to many species that contributes to increasing and decreasing the pH value. For example, formation of ammonium carbonate ($(NH_4)_2CO_3$) and gaseous CO_2 during anaerobic digestion increases the pH value. Similar with basic cations like Ca^{2+} and K^+ because the electrical charge balance of the solution needs to be neutral. If the cations are increasing, the concentration of H^+ must decrease to be able to maintain a neutral solution. Iron can both increase the pH by removal of hydrogen sulphide and decrease due to precipitation of iron-phosphate [14].

The relation and how each factor are affecting the pH in the solution is illustrated in Figure 2.6.

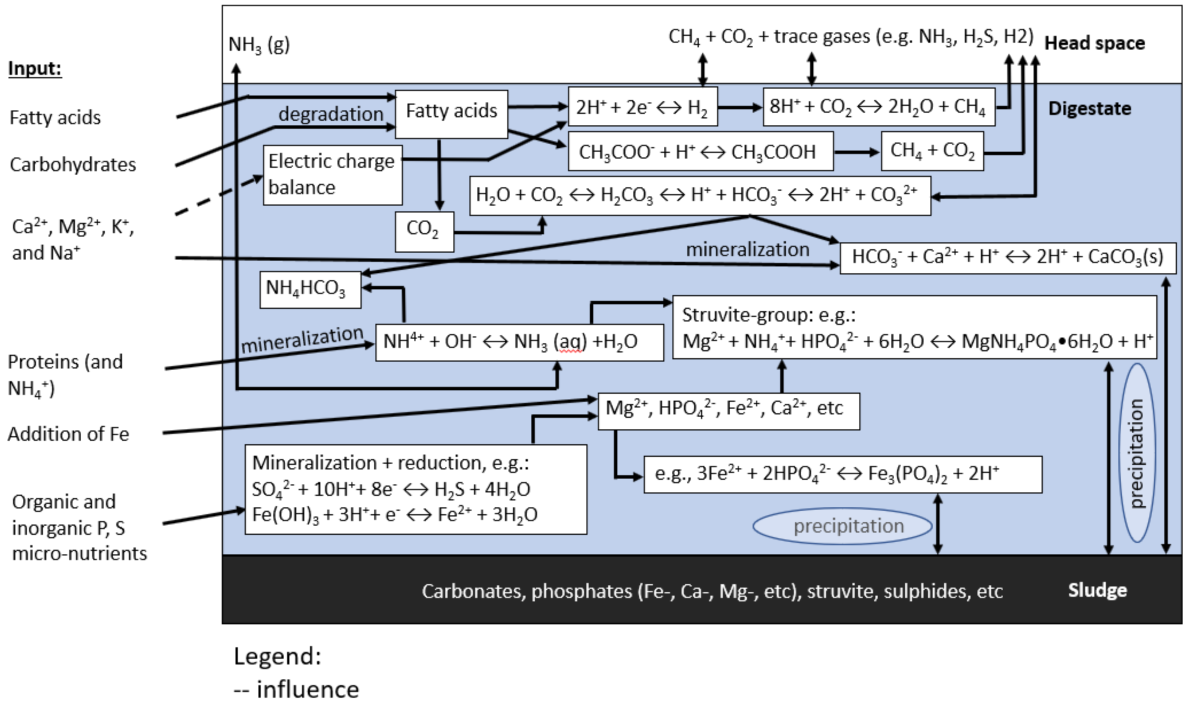


Figure 2.6 Relation for pH in the bioreactor [14]

2.3.5 Volatile fatty acids (VFA)

Volatile fatty acids (VFA) are an intermediate product of the anaerobic digestion, and the stability of the process depends on the concentration of VFA. Volatile fatty acids are typically acetate, propionate, butyrate, and lactate. These acids is produced in the acidogenesis phase (ref Figure 2.1) of the anaerobic digestion [1].

An instability in the digester will usually increase the level of volatile fatty acids, which could result in a drop in pH level. However, as mentioned in chapter 2.3.4, due to buffer capacity of the digester, the pH level will not always drop.

In animal manure there are surplus of alkalinity and the volatile fatty acids could accumulate without detecting it, due to no change in pH-level. When it is detected, the anaerobic digester is usually already inhibited. Similar as for the pH, volatile fatty acids cannot be used as a standalone monitoring parameter [1].

2.3.6 Dry matter content

The content of dry matter is an important parameter when design a biogas plant and it is distinguished between dry and wet digestion. Wet digestion is typically when the dry mater content is maximum 15 % and dry digestion is usually between 20-40% [1].

The dry matter content in the substrate can be described in 3 different ways; total solid (TS), volatile solid (VS), and chemical oxygen demand (COD) [8].

The total solid (TS) is defined as the remaining solid after drying the organic material for 20 hours at 105°C in an oven until steady mass is obtained [15]. Sometimes the total solid (TS) is also noted as dry matter (DM) [1], [15]. The volatile solid (VS) is found by post drying of the total solid (TS) at 550°C for 2 hours. A fraction of the total solid is volatilised, and this fraction is called volatile solid (VS) and consist of mainly organic material. The residual is inorganic material, also known as ash [15]. Please note that there are several oven-drying procedures used worldwide and the temperature and duration vary depending on the procedure. The biogas potential is typically given in per kg volatile solid (VS), for further information see Chapter 2.4. Unit of TS is given as percentage of weight [wt%] and VS as percentage of TS [% of TS], respectively. The third way, chemical oxygen demand (COD), represent the energy content in the substrate and use stoichiometry to find the amount of oxygen needed in the production of biogas. Chemical oxygen content is typically used in cases with mostly dissolved components and low content of suspended matter (few particles) [8]. Units of chemical oxygen demand is mass of oxygen consumed over volume of solution [mg/L or kg COD/m^3].

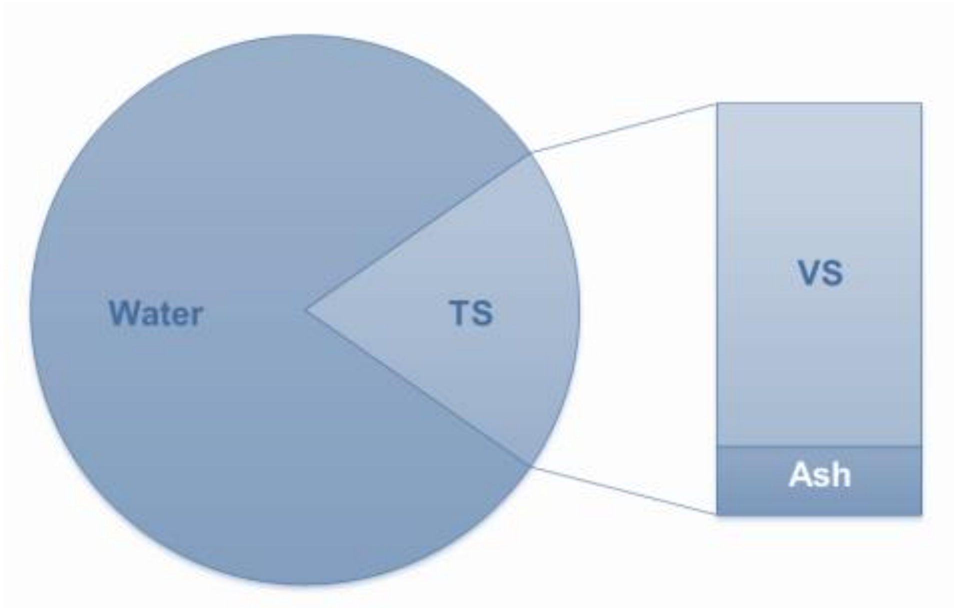


Figure 2.7 Relationship between dry matter contents in substrate [15]

One disadvantages by using the oven-dry method is the possibility of underestimate the dry matter content, i.e., the method underestimate both TS and VS [15]. Several parameters, which are used to evaluate the stability and efficiency of the of the biogas production, are based on TS and VS. Examples of parameters are organic loading rate (OLR) and biogas yield and they will subsequently be underestimated.

During the oven-drying process, volatile substances are lost in addition to water. The volatile substances are typically volatile fatty acids (VFA) and alcohols. Analysis performed confirms that the majority of the loss of total organic carbon (TOC) dissolved in the substrate is VFA (approximately 75%). The remaining 25% is unknown, however not all VFA might have been detected due to limitation of the VFA analysis [15]. Formic and lactic acid is considered not to be detected. Similar with other volatile organic compounds as methanol, ethanol and acetone might also be present in the residual 25% of TOC. The evaporation of volatile substances will result in an error between 3 to 30% in both TS and VS. The error is correlated to the ratio between VFA and TS. That is, if it is high amount of VFA compared to the TS content, the error is increasing [15].

It has been suggested two methods to take account of loss of volatile substances when using oven-drying process to determine TS and VS [15]. The fist method (Method I) is a rough estimation method, and it is suggested for acidic substrates (pH ≤ 5.2). The second method (Method II) is more accurate estimation and should be used to compensate for evaporation of VFAs. A detailed step by step instructions for the two different methods are described in Appendix D.

There are also possible to use other methods than oven-drying process to measure dry matter. Examples of other methods are Karl Fisher titration, infrared drying near infrared reflection spectroscopy (NIR-spectroscopy), freeze drying and microwave oven-drying. These methods do not have the same issue with loss of volatile substances and are more commonly used in the other industries such as forestry and food industry. Still, the oven-drying process is favourable at biogas plants due to its simplicity, non-expensive, and it can examine both TS and VS [15].

2.3.7 Organic loading rate and hydraulic retention time

It will require a long retention time to obtain maximum biogas yield. Hence, the operation of the reactor will be a trade-off between economy and size of reactors and retention time.

The organic load is an important operational parameter and describes the amount of organic fed into the reactor per volume time. The equation for organic loading rate (OLR) is given by

$$OLR_R = \frac{mc}{V_R} \tag{2.6}$$

Where OLR_R is organic load rate of the reactor [kg/(m^3 day)], m is mass of substrate fed per time unit [kg/day], c is concentration of organic matter (VS) in percentage [%] and V_R is the reactor volume of digester [m^3] [1], [8].

The OLR [kg VS/(m^3 day)] can also be expressed by TS and VS (dry matter content), volume of substrate in the reactor and density of substrate [15].

$$OLR_R = \frac{Volume_{substrate}/_{day} * \rho_{substrate} * TS_{substrate} * VS_{substrate}}{Volume_R} \tag{2.7}$$

If the loading rate is too great, the bacteria will not be able to degrade the biomass and the digestate will become acidic and stops [7]. If the loading rate is too small, the capacity of the reactor will not be fully utilised, and the investment will be less favourable.

The hydraulic retention time (HRT) is the average time the substrate stays in the reactor. The reproduction of microorganisms depends on the retention time since some of the microorganism will be part of the effluent. If the retention time is not sufficient, the number of microorganisms in the digestate will be reduced [1].

The hydraulic retention time can be expressed as

$$HRT = \frac{V_R}{V} \qquad (2.8)$$

Where HRT is hydraulic retention time [days], V_R is the reactor volume of digester [m^3] and V is the volume of substrate fed per time [m^3/day] [1].

2.4 Biogas yield and composition of biogas

When comparing different substrate, it is often compared with respect to the biogas yield. The biogas yield is a measurement of the amount of biogas per kilogram Volatile Solid (VS). Sometimes it is also given in other units such as litre per kg organic dry matter. The measured biogas is also often converted into Normal Temperature and Pressure (NTP) to be easier to compare different substrate and it is noted NTP or Nm^3. NTP is abbreviation for temperature and pressure at 20°C (293,15 K) and 1 atm [16].

The biogas does not consist only of methane, but also carbon dioxide, some water etc. The expected number of other gases is important to understand when considering for example the required conditioning of the biogas.

2.4.1 Biogas yield

The gas potential of the substrate can be expressed by specific gas production, also known as biogas yield. The biogas yield is expected to be constant if the inlet feed is with similar substrate mixture. In addition, the biogas yield is normalized to the organic loading rate (OLR) and variation in inlet flow does not influence the value of the biogas yield. The biogas yield can indicate an undergoing process disturbance if changes cannot be related to variation in substrate or substantial changes in OLR [15].

The biogas yield [Nm3 gas/(kg VS)] can be expressed as Equation 2.9 [15].

$$Biogas\ yield = \frac{Volume_{gas}}{Volume_{substrate} * \rho_{substrate} * TS_{substrate} * VS_{substrate}} \qquad (2.9)$$

2.4.2 Biogas yield of different substrate and composition of biogas

Cow manure in biogas production has some advantages, such as there is a natural content of anaerobic bacteria and it is well mixed and have good flowing properties due to high water content [1]. However, the disadvantage is that animal manure has low methane yield compared to other organic waste such as food remains and gras as illustrated in Figure 2.8. This due to digestion process has already started in animal manure. Typically, methane yield is 0.15-0.2 m^3/kg VS for cow manure (wet) while for food remains is about 0.45-0.6 m^3/kg VS [10].

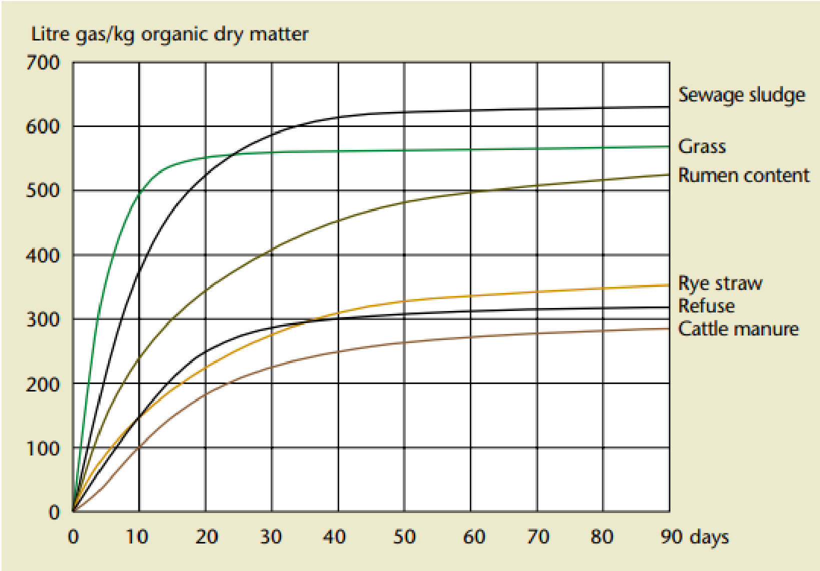


Figure 2.8 Biogas yield at 30°C with different substrate in a bath reactor over 90 days [7]

To increase the methane yield in cow manure, other organic waste can for example be added to the substrate. Fish sludge contains a lot of fat and protein, and must be mixed with other organic waste, to be able to start an anaerobic digestion process. By mixing different organic waste, the substrate can be optimize with respect to the ratio between carbon and nitrogen [10].

The biogas consists of mainly methane and carbon dioxide, and some small amount of other components [2]. Typical volume fraction of each component is summarized in Table 2.1.

Table 2.1 Composition of biogas (anaerobic digestion) [2]

Gas	**Chemical formula**	**Volume %**
Methane	CH_4	40-75%
Carbon dioxide	CO_2	15-60%
Water	H_2O	5-10%
Hydrogen sulphide	H_2S	0.005-2%
Siloxanes		0-0.02%
Halogenated hydrocarbons	VOC	<0.6%
Ammonia	NH_3	<1%
Oxygen	O_2	0-1%
Carbon monoxide	CO	<0.6%
Nitrogen	N_2	0-2%

2.5 Recommended values for different substances in substrate

The amount different nutrients in the substrate are important due to inhibition of the process. Microorganisms in the different digestion steps differ widely with respect to physiology, nutritional needs, growth kinetics and sensitivity to environmental conditions. This is especially for the acid and methane forming microorganisms [17]. As mentioned in chapter 2.3.1, the ratio between the carbon and nitrogen are important for the process. However, also other nutrients can inhibit the process and it is important to keep those within the threshold values. The correct mixture between different substrate is then crucial for the anaerobic digestion.

In the literature, it is reported variation in the optimum and inhibition levels for most of the substances. Anaerobic digestion is an complex process and therefor it is difficult to given any exact optimum or inhibition level for each substance [17].

Light metals ions (Na, K, Mg, Ca, and Al) are often present in substrate and may be released during digestion of the substrate. In other cases, they can be added to the substrate to adjust the pH-level. Moderate level of these metal ions can increase the growth of microorganisms. However, an excessive amount will slow down the growth and at higher concentration even cause inhibition [17].

One challenge by using fish sludge as substrate is sodium ion inhibition. Sodium creates an osmotic pressure difference within the cell compared with the surrounding environment.

Microbes that are not acclimated can then be dehydrated. In addition, excess salinity also affect different enzymes negatively and can also lead to accumulation of VFA [18]. Tests shows that salinity of 35 g/L reduced the amount of methane production by approximately 64% compared with 0 g/L salinity. If the ratio salinity/COD ratio was larger or equal to 0.33 a complete inhibition was then observed [18].

It has also been observed high hydrogen sulphide (H_2S) concentration in substrate with salinity above 15 g/L. The H_2S concentration was measured to over 15 000 ppm in the biogas with this level of salinity. Typically, the H_2S level is between 100 to 10 000 ppm. This is indicating a competition between methanogens and sulphate-reducing bacteria (SRB) in the anaerobic digestion [18].

Heavy metals are not biodegradable and can accumulate in the digestate to a toxic level. The heavy metal can disrupt the enzyme function and the digester will then fail. Chromium, iron, cobalt, copper, zinc, cadmium, and nickel are considered as heavy metal.

Similar for the carbon and nitrogen, there is an optimal ratio of substances carbon, nitrogen, phosphorus, and sulphur. The ratio is considered to be 600:15:5:1 (C:N:P:S) [1]. In this optimal ratio, the carbon and nitrogen ratio (40:1) are higher than recommended for maximum biogas production in chapter 2.3.1 (20:1 to 30:1).

It is important to notice that the threshold values of substances can be increased if the process is exposed by slowly increasing concentrations. Hence, there is no exact concentration to be used, only recommended levels. In addition, the optimum concentration listed in Table 2.2 are for maximising the biogas production.

Table 2.2 Recommended level of different substances in substrate.

Substance	**Recommended level**	**Comments**
Aluminium (Al)	Suggested concentration up to 2 500 mg/L Al^{3+} after acclimation [17]	Effect of aluminium on anaerobic digestion is minimal [17].
Calcium (Ca)	Optimum concentration: ~200 mg/L [17] Inhibiting concentration: ~8 000 mg/L [7]	Important for growth of some strains of methanogens [17].
Magnesium (Mg)	Optimum concentration: ~720 mg/L [17] Inhibiting concentration: ~3 000 mg/L [7]	
Potassium (K)	Optimum concentration: ~400 mg/L [17]	High level of K neutralize the membrane potential [17].
Sodium (Na)	Optimum concentration: 100 – 200 mg/L [17] Inhibiting concentration: ~8 000 mg/L [17]	Essential for methanogens (at low level) [17].
Zink (Zn)	Optimum concentration: 5 mg/L [19] Inhibiting concentration: $7.5 < Zn < 1500$ mg/L [19]	
Cadmium (Cd)	Optimum concentration: 0.1 mg/L [19] Inhibiting concentration: < 1.2 mg/L [19]	

Substance	**Recommended level**	**Comments**
Iron (Fe)	Optimum concentration: <1000 mg/L [19] Inhibiting concentration: - [19]	
Nickel (Ni)	Optimum concentration: 0.8-4 mg/L [19] Inhibiting concentration: 35 < Ni < 1600 mg/L [19]	
Copper (Cu)	Optimum concentration: 5-30 mg/L [19] Inhibiting concentration: < 500 mg/L [19]	
Lead (Pb)	Optimum concentration: < 0.2 mg/L [19] Inhibiting concentration: 67.2 < Pb < 8000 mg/L [19]	

2.6 Transformation of nitrogen, sulphur and phosphorous in the bioreactor

Important nutrients in natural fertiliser are nitrogen and phosphorous. The transformations of these nutrients are important, and especially to avoid precipitations. The plants might not be able to utilise nutrients in precipitations and should be avoided. However, the transformations of nutrients are complex and due to equilibrium between reactions, it is not possible to avoid some loss of nutrients in the digester either as precipitation or as gas. In addition, sulphur transformation is important to understand, due to formation of hydrogen sulphide.

2.6.1 Transformation of nitrogen

The nitrogen in the digester is mineralized from complex organic nitrogen compounds to NH_4^+-N [2]. Microorganisms are using some of the NH_4^+-N for growth and some are reacting to ammonium carbonate ($(NH_4)_2CO_3$) and to struvite ($MgNH_4PO_4 \cdot 6H_2O$). In addition, some of the ammonium carbonate are volatilised in the biogas stream as NH_3 (<1%) [14].

[2] The nitrogen content in ammonium ion and ammonia is noted NH_4^+-N and NH_3-N, respectively.

In fertiliser, the nitrogen available for plants are closely related to NH_4^+-N contents in the manure [14].

In Figure 2.9 it is summarized the transformation of nitrogen in the digester.

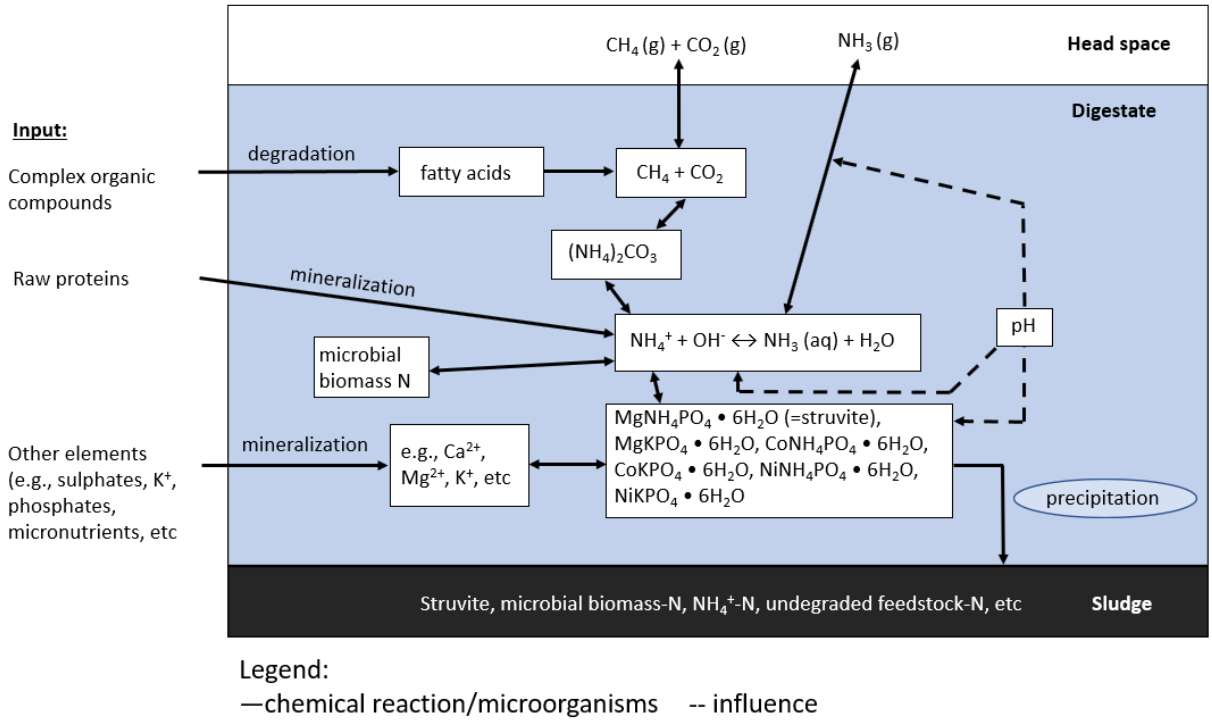


Figure 2.9 Transformation of nitrogen in biogas digester [14]

2.6.2 Transformation of sulphur

The process of transformation of sulphur during anaerobic digestion is complex. Sulphur has a multi-phase nature, either as liquid, solid or in gaseous state, which includes dissimilation, assimilation, and desulphurization. In addition, sulphur has a wide redox state range from -2 to +6. During the anaerobic digestion, there are also many different types of microorganisms which is transforming sulphur. Typically group of microorganisms are hydrolytic bacteria, acidogenic and sulphate reducing bacteria (SRB) [20].

The process of transformation of sulphur in anaerobic digestion can be illustrated as shown in Figure 2.10. In all transformation, both chemical reaction and microorganisms are relevant. For example, desulphurization reaction involves transforming sulphate (SO_4^{2-}) to sulphide, either at HS^-, S^{2-}, or H_2S.

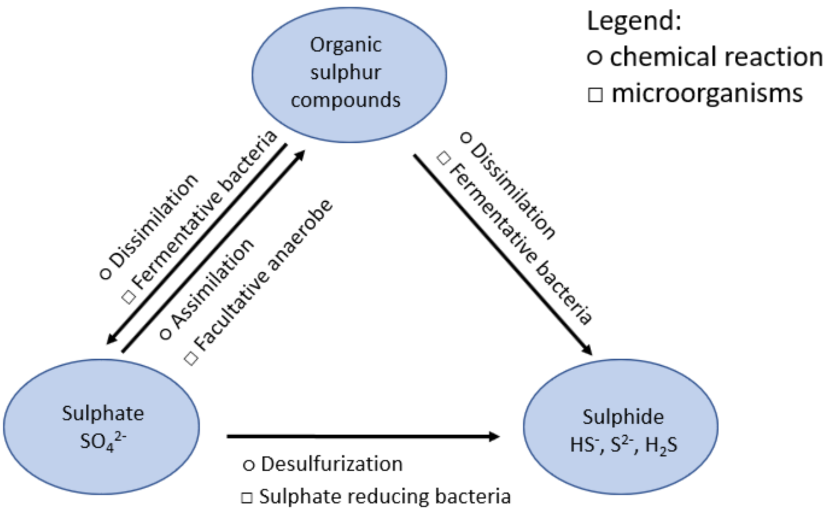


Figure 2.10 Relation between different sulphur transformation in anaerobic digestion [20]

By-products from the transformation of sulphur can inhibit the digestion process. This is due to sulphate reducing bacteria is competing with other bacteria for available nutrients [20]. These other bacteria are for example acetogens and methanogens, which is important for methane production. Sulphate reducing bacteria compete with other bacteria in almost all steps in anaerobic digestion, expect from the hydrolysis step. Figure 2.11 summarize where sulphate reducing bacteria and reactions will create sulphide, such as HS^-, S^{2-} and H_2S.

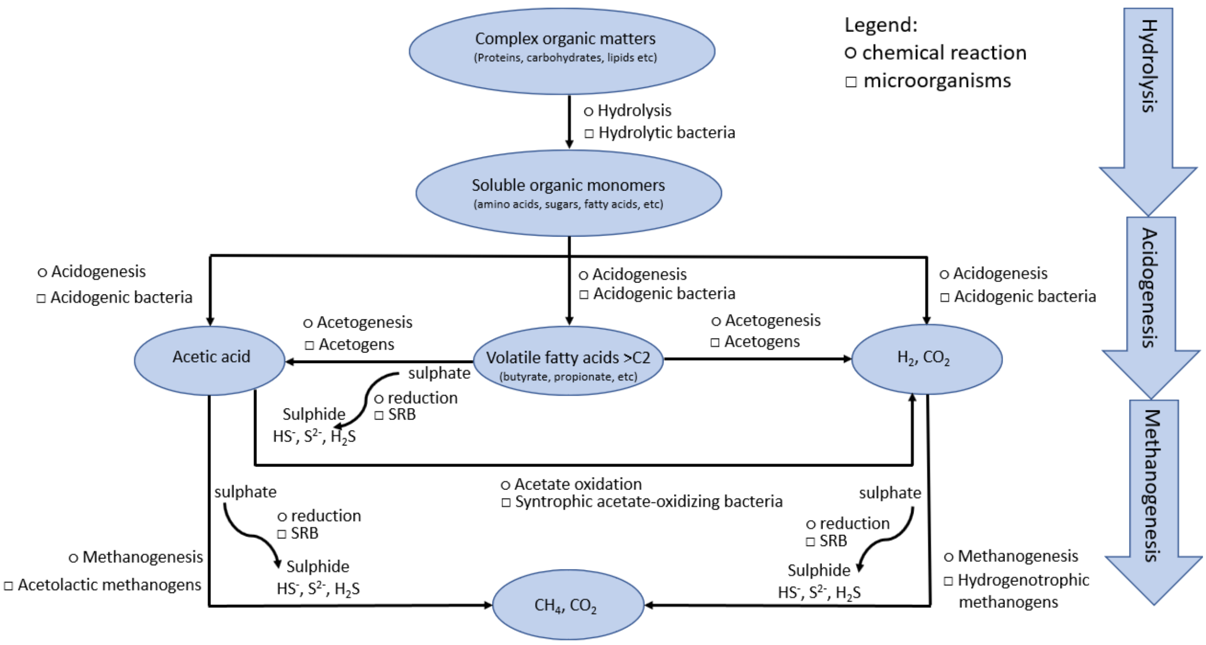


Figure 2.11 Transformation of sulphur in different steps in anaerobic digestion [7], [20]

An overview of reactions which include sulphur in the digester is summarized in Figure 2.12. In general, when the temperature and pH are decreased in the digestate, the H_2S concentration increases [14].

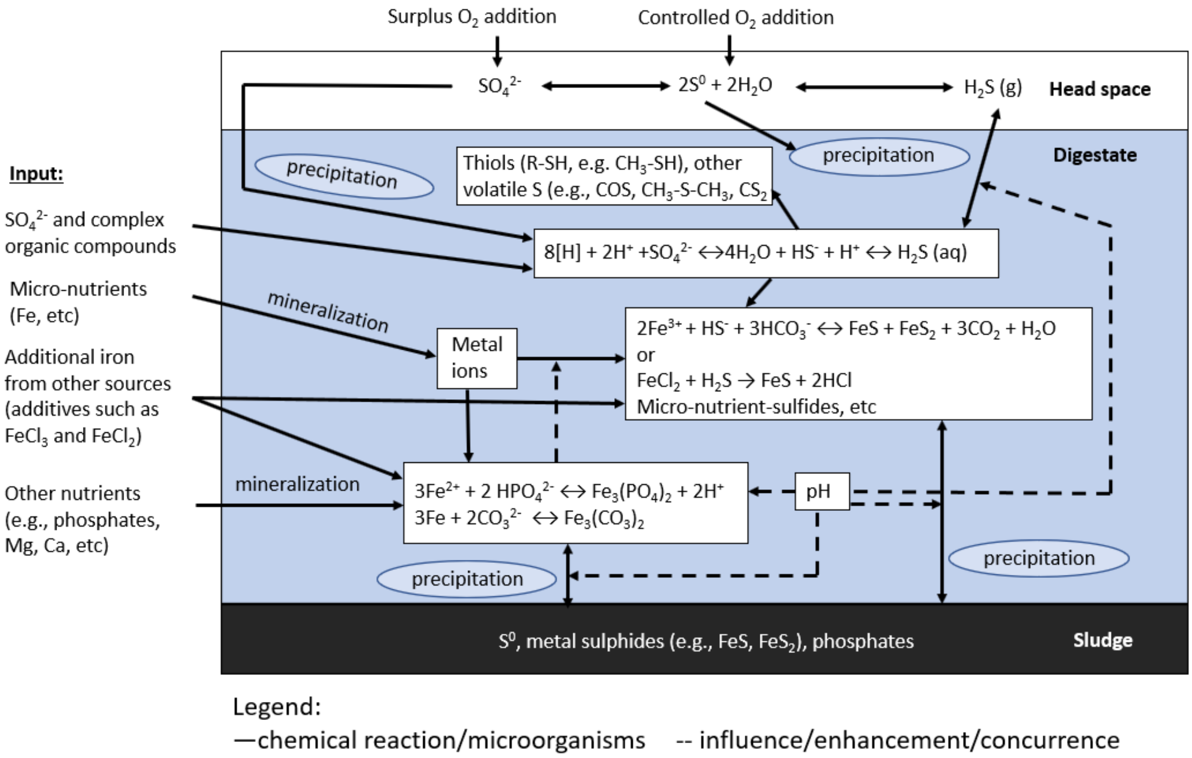


Figure 2.12 Transformation of sulphur in biogas digester [14]

The influent of sulphur to the bioreactor consists of several different composition and it also varies depending on the type of substrate. The determination of the sulphur compositions in the substrate are difficult and complex. Hence, only a few studies has been performed with respect to determine the sulphur composition in the substrate [21]. In Table 2.3 it is summarized the composition of different substrate with respect to sulphur, such as food waste, thickened sludge, and waste active sludge. Thickened sludge is dewatered sludge where the process aims to separate solid and liquid phase. Waste active sludge process is a sewage treatment where air or oxygen is blown into the unsettled sewage and the process is called aeration, and the sludge contains a high content of microorganisms.

Table 2.3 Fractions and species of sulphur in different organic solid waste [21]

Type of waste		**Food waste**	**Thickened sludge**	**Thickened sludge**	**Waste active sludge**	**Waste active sludge**
Characterization methods		Elemental analyser and ICP	XANES	Extraction	XPS	Microwave-enhanced acid digestion
Species and fractions (% of total sulphur)	Organic sulphur	69.7	42 - 73	Particulate organic sulphur: 65 Soluble organic sulphur: 11	74	65 - 88
	SO_4^{2-}	3.8	20-39	4	18	0.9 - 4
	Sulfide compounds	13.9	-	Particulate inorganic sulphur: 20	8	12 - 31
	S^0	-	19.1	-	-	-

2.6.3 Transformation of phosphorus

Phosphorus is an important plant nutrients, and it is found in adenylates, nucleic acids and phospholipids [14]. In soils there are in general little phosphorus, and it is important nutrient in natural fertiliser. There is a common perception that anaerobic digestion will improve phosphorus plant availability, however field experiments indicated no significant effects [14].

During the anaerobic digestion it is expected to be a 10 % loss of phosphorus. In some few papers it is indicated even higher losses, such as up to 25 % and even 36 % [14]. The chemical reactions with phosphorus in the digester are also influenced on the pH-value. By raising the pH-value, the amount of phosphate will also increase. This is due to change in chemical equilibrium between HPO_4^{2-} and PO_4^{3-}. As a subsequent, precipitation such as calcium phosphate and magnesium phosphate will also increase [14]. In Figure 2.13 it is summarized the transformation of phosphorous in the digester.

For waste activated sludge (WAS) of sewage it has been reported that the raw sludge contained approximately 68% inorganic phosphorous and approximate 30% organic phosphorous of total phosphorous [22]. In the study, it was noted that the fraction of inorganic and organic phosphorous did not change much after the digestion. The inorganic phosphorous increased to approximately 77%, while organic was declined to approximately 21%. Another study compared different organic waste such as manure, including pig, horse and cattle manure, and fish sludge. Typically, the organic phosphorous were between 2 to 28% of total phosphorous and there were no significant differences between manure and fish sludge [23].

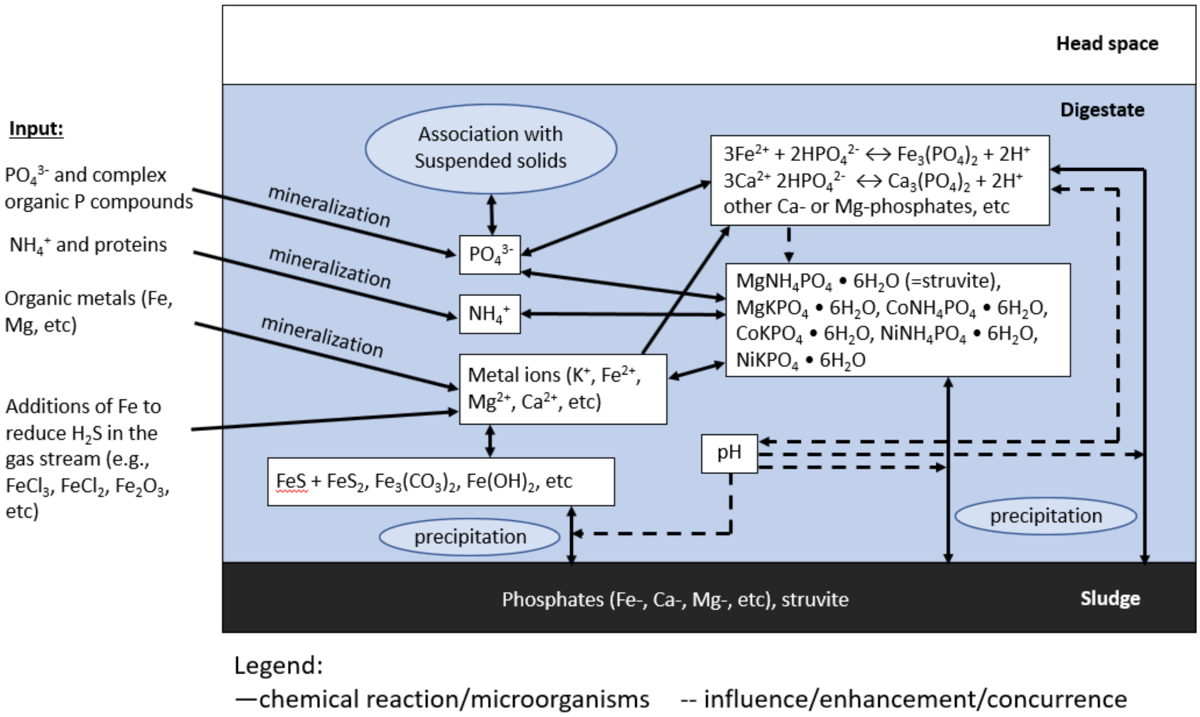


Figure 2.13 Transformation of phosphorous in biogas digester [14]

2.7 Methods to avoid inhibition of anaerobic digestion process by excess ammonia

Excess amount of ammonia (NH_3) can result in inhibition of the anaerobic process in the bioreactor, as discussed in Chapter 2.3.2 and Chapter 2.6.1. The ammonia is the end-product in the anaerobic process of urea, (nucleic) acids and proteins. A high level of ammonia in the digester can decrease the microbial activities and cause reduced performance of the process, i.e., reduced methane production [24].

It has been suggested different remediation techniques in case of ammonia inhibition in the anaerobic digester. However, the methods suggested, such as struvite precipitation, anammox, use of zeolite and carbon fibre textiles, are expensive, especially in a large scale [24]. In general, removal of nitrogen in the digestate is undesirable since digestate shall be used as fertiliser. As mentioned earlier, the nitrogen is a key component in a high-end fertiliser. In the literature, it is suggested different strategies for controlling the ammonia inhibition. The different strategies are discussed in the following chapters.

2.7.1 Stepwise increase of ammonia concentration

The degree of ammonia inhibition can be increased by acclimation of the microflora in the digester. By a stepwise increase of ammonia concentration, the ammonia tolerance could be increased. However, it can take two months or longer for the microbes to adequately adapt. Especially the methanogens need time to adapt [24], [25].

2.7.2 Control of pH in digester

It is known that anaerobic digester can reach an instability due to high level of pH [24]. The equilibrium between ionized ammonium nitrogen (NH_4^+) and ammonia (NH_3), as shown in equilibrium equation 2.10, will shift to the right-hand side when the pH level increases and generate more ammonia [17].

$$NH_4^+(aq) + OH^-(aq) \leftrightarrow NH_3(aq) + H_2O \qquad (2.10)$$

The increased ammonia can inhibit the methanogenic microflora and, as a result of this inhibition, accumulation of volatile fatty acids (VFA) [24]. By an increase of VFA, the pH level decreases, and the ammonia (NH_3) in the digester declines. This interaction between ammonia, pH and VFA could result in a lower methane yield, but with a steady biogas production. This condition is also known as “inhibited steady state” [17], [24].

The ammonia toxicity of microorganisms in the bioreactor can be avoided by proper control of the pH. A pH level in the range of 7.0 to 7.5 seems to be give no ammonia inhibition [17], [24].

2.7.3 Adjustment of temperature

One of the main factors which affects the threshold of ammonia inhibition is the temperature. An increase of temperature often also increases the amount of free ammonia nitrogen (FAN), that is an increase of NH_3. One method to overcome inhibition is to adjust the temperature. An adjustment of the temperature to a lower temperature could result in overcoming the inhibition [17]. This control method is typically used for thermophilic bioreactors, where the temperature is reduced to mesophilic condition to overcome the ammonia inhibition.

2.7.4 Increase of other ions present in the substrate

Other ions present in the digester, such as sodium ion (Na^+), magnesium ion (Mg^{2+}) and calcium ion (Ca^{2+}), seems to have the ability to reduce ammonia inhibition [17]. There is not stated any recommended level of other ions in the digester, other than it reduce the probability of ammonia inhibition. Another reported benefits of additional ions in the digester, is an increase of the methane yield [17]. Especially the combination Na^+, Mg^{2+} and Ca^{2+} has increased the methane yield. Sodium ion (Na^+) alone has shown less increase in the methane yield, than the combination of the three mentioned ions.

2.8 Methods to reduce hydrogen sulphide in-situ biogas

It is favourable to be able to minimize the formation of hydrogen sulphide in the bioreactor, rather than conditioning the biogas afterwards. The general recommended level of hydrogen sulphide is between 200-500 ppm [2]. However, it depends on application and equipment. For combined heat and power installations, the hydrogen sulphide concentration is recommended to be in the range of 65-330 ppm [26] and for natural gas upgrade is less than 4 ppm [2]. Natural gas upgrade, also called natural gas conditioning, is typically used as fuel for vehicles. In addition to have a low level of hydrogen sulphide, the natural gas upgrade also involves removal of water, carbon dioxide and other trace elements. Nevertheless, the service life can be increased and also maintenance can be reduced with lower level of hydrogen sulphide [27].

The amount of hydrogen sulphide developed in the bioreactor depends on the sulphur content in the substrate and if it is in the form of sulphate (SO_4^{2-}) or as sulphur bonded in amino acids [27]. In general, it is the sulphur from the sulphate that forms hydrogen sulphide.

There are 3 control methods of reducing hydrogen sulphide in-situ the biogas; physical, chemical and biological [20]. Physical control is typically increased pressure, use of ultrasound, thermal adjustment, adjustment of the pH or combination of these. Chemical control method is when adding metal or metal salts. The metal will then create a chemical reaction, which reduce the level of hydrogen sulphide. The last one, biological control method, is to favourable growth conditions for sulphur oxidizing microorganisms. This is done by use of air or oxygen into the headspace of the reactor. The efficiency of these 3 methods varies, as illustrated in Figure 2.14, where biological method has the highest removal efficiency [20].

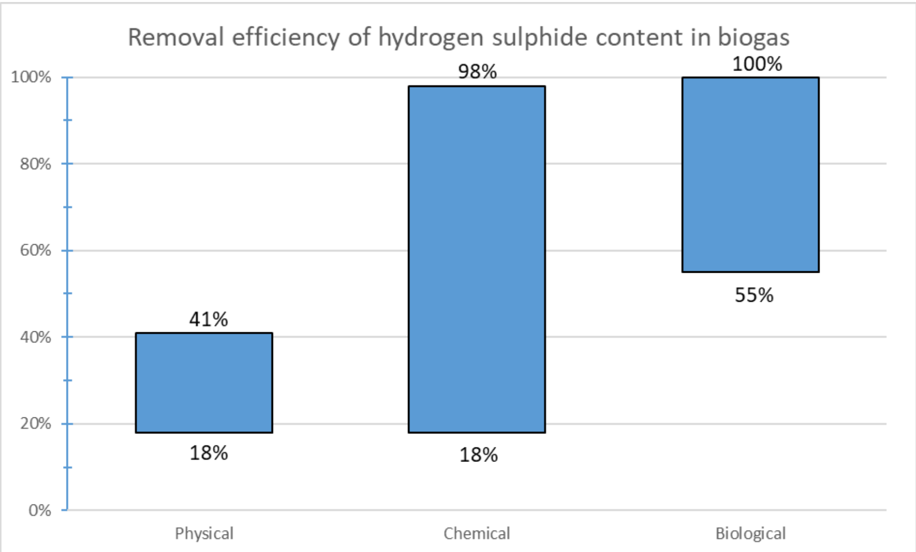


Figure 2.14 Removal efficiency of hydrogen sulphide by physical, chemical and biological control methods [20]

2.8.1 Control of pH in digester

The methane producing bacteria (MPB) and the sulphate reducing bacteria (SRB) have different pH optimum and the reactor pH can play an important role in the amount of hydrogen sulphide and methane. The activity of SRB can be suppressed by adjusting pH and then reduce free sulphide in the reactor. At for example acidic conditions, i.e. low pH, the activity of SRB are high and it is formed H_2S gas from the free sulphide [28]. By increasing the pH level sulphide ions, such as S^{2-} and HS^-, will dominate and inhibition due to H_2S can be avoided. Level above pH > 8, the activity of SRB is less favourable, and it will reduce the rate of sulphate (SO_4^{2-}) and the mitigation of H_2S [28].

The effect of rising the pH-level has been reported to be successful. However, the number of studies regarding pH regulation for H_2S-control are few and often limited to lab-scale experiments. Irrespective, it has been reported 90% lower H_2S content in sewage sludge by increasing the pH to 8 – 8.5 [28].

There has also been a study with high initial alkaline condition at pH 8 of the substrate. In the anaerobic digestion it was used slaughterhouse wastewater sludge and less H_2S was formed by increasing the pH level. By increasing the initial pH level of the substrate from 6.5 to 8, the H_2S content was reduced by approximately 45%. The methane content was also improved, and it was increased by somewhat less than 49% [29].

2.8.2 Micro-aeration

In German farms, they have good experience to add small amount of air into the bioreactor to reduce the level of hydrogen sulphide [26]. The technique is to create a micro-aerobic condition in the gasometer or headspace. Typically, by adding 2-6% air into the headspace where biogas accumulates, microorganisms (Thiobacillus) will then oxidise hydrogen sulphide to sulphur [30]. The microorganisms grow on the surface of the digestate or on the structure surfaces of the digester. It has been reported 99% reduction of H_2S by use of 1.27 Nm^3 air/m^3 feed sludge [20]. The reactions with oxygen are as following [20], [31]:

$$2H_2S\ (g) +\ O_2\ (g) \rightarrow 2S\ (s) + 2H_2O \qquad (2.11)$$

$$2S\ (s) +\ 3O_2\ (g) + 4H_20 \rightarrow 2SO_4^{2-}\ (aq) + 4H^+\ (aq) \qquad (2.12)$$

$$2O_2\ (g) +\ H_2S\ (g) \rightarrow 2H^+(aq) + SO_4^{2-}(aq) \qquad (2.13)$$

$$HS^-\ (aq) +\ 2O_2\ (g) \rightarrow 2H_2O + S_2O_3^{2-}(aq) \qquad (2.14)$$

$$S_2O_3^{2-}\ (aq) +\ 2O_2\ (g) + 2H_2O \rightarrow 2H^+(aq) + 2SO_4^{2-}(aq) \qquad (2.15)$$

However, there are some strengths and weaknesses with this method that need to be addressed.

- The concentration of hydrogen sulphide remaining in the biogas may still be larger than recommended level for the biogas [26]. At the same time it has been shown that the hydrogen sulphide has been reduced by up to 80-95% with an outlet concentration of approximate 10 ppm [30]. Even up to 99% reduction has been reported [20], [31].
- By adding too much air will create an explosive gas mixture in the bioreactor [26], [30]. A mixture of biogas in air (6-12%) is explosive and safety measures have to be taken [31].
- The production of hydrogen sulphide from the digester is recommended to have little variance to ensure efficient removal [26]. That is, the substrate should be as homogenous as possible.
- Blockage may occur due to accumulation of sulphur the bioreactor as shown in Figure 2.15. Air should be added on the opposite side of the biogas output [1].

Figure 2.15 Accumulation of sulphur due to biological desulphurization inside the digester [1]

2.8.3 Adding iron

By increasing the amount of iron in the substrate, it will reduce the level of hydrogen sulphide in the bioreactor [2]. The iron can for example be added either as iron chloride, iron powder or as iron rich substrate typically from waterworks sludge. Iron chloride can be added either in the form of liquid ($FeCl_2$) or as in solid form ($FeCl_3$), and can be dosed straight into the digester or in the influent-mixing tank [2].

Iron chloride is also used in the process in waterworks to enhance coagulation of organic matter from the water. The sludge and/or waste water from this process contains various form of iron, and mostly iron(III) oxide (ferric oxide) [27]. This sludge can be reused in biogas production with the aim of reducing the level of hydrogen sulphide. By adding sludge, about 0.2 – 0.5% of the amount of manure substrate (dry matter), the hydrogen sulphide level is reduced to below 100 ppm in the biogas [27].

Results from laboratory tests shows also good results by adding iron in the form of microscale iron powder. The level of hydrogen sulphide was decreased up to 77% from reference test, and in addition the methane production also improved by up to 57%. The laboratory tests used iron powder at concentration of 100 mg/L to 1000 mg/L, where the highest doses gave the best improvements [27]. The best results is to use nanoscale zero-valent iron, where it has been reported 98% decrease of hydrogen sulphide [20]. However, the nanoscale zero-valent iron is expensive.

Depending on the form of iron added in the digester, the reaction with sulphur will vary. The iron in the substrate will typically react with sulphide by precipitation as ferrous sulphide or it can precipitate as iron phosphate [32]. The sulphide is a result of transformation of sulphate during anaerobic digestion, into sulphide as HS^-, S^{2-}, and H_2S (ref discussion in Chapter 2.6.1) [20].

When adding iron chloride ($FeCl_2$ or $FeCl_3$), it will dissolve in the water to

$$FeCl_2(s) \rightarrow Fe^{2+}(aq) + 2Cl^-(aq) \tag{2.16}$$

$$FeCl_3(s) \rightarrow Fe^{3+}(aq) + 3Cl^-(aq) \tag{2.17}$$

The dissolved iron in the digester will then react with sulphur to iron(II) sulphide (also called ferrous sulphide) and the equilibrium equations are often expressed by [2], [30]

$$Fe^{2+}(aq) + S^{2-}(aq) \rightarrow FeS\ (s) \tag{2.18}$$

$$2Fe^{3+}(aq) + 3S^{2-}(aq) \rightarrow 2FeS\ (s) + S(s) \tag{2.19}$$

Please note that in equilibrium equation 2.19, iron (III) is reduced to iron (II).

The iron in reaction equations 2.18 and 2.19 can also react with hydrosulphide ion (HS^-). The hydrosulphide ion is generated from equilibrium with hydrogen sulphide [33].

$$H_2S\ (aq) \leftrightarrows H^+\ (aq) + \ HS^-\ (aq) \tag{2.20}$$

The equilibrium equation 2.18 can then be written in more detail as [34]:

$$FeCl_2(s) + HS^-(aq) + H^+(aq) \rightarrow FeS\ (s) + 2HCl\ (aq) \tag{2.21}$$

Iron (III) chloride can either be reduced to iron (II) in equilibrium equation 2.19 or also form insoluble precipitate of iron (III) sulphide (ferric sulphide) as shown in equilibrium equation 2.22 [35].

$$2Fe^{3+}(aq) + 3HS^-(aq) \rightarrow Fe_2S_3\ (s) + 3H^+\ (aq) \tag{2.22}$$

or written similar as for equilibrium equation 2.21

$$2FeCl_3(s) + 3HS^-(aq) + 3H^+(aq) \rightarrow Fe_2S_3\ (s) + 6HCl\ (aq) \tag{2.23}$$

In the cases above, the iron will react with hydrogen sulphide ion (HS^-) and decrease the concentration of hydrogen sulphide as seen from equilibrium equation 2.20.

The iron(III) oxide (or ferric oxide) from the water work sludge will react directly with the hydrogen sulphide and form iron(III) sulphide (ferric sulphide)

$$Fe_2O_3(s) + 3H_2S(g) \rightarrow Fe_2S_3(s) + 3H_2O \tag{2.24}$$

Phosphate can, as mentioned earlier, react with iron and form iron phosphate and it is formed from iron(III) and iron(II) [36]. Depending on iron(II) or iron(III), the reaction equation will be

$$3Fe^{2+}\,(aq) + 2PO_4^{3-}\,(aq) \rightarrow Fe_3(PO_4)_2\,(s) \tag{2.25}$$

$$Fe^{3+}\,(aq) + PO_4^{3-}\,(aq) \rightarrow FePO_4\,(s) \tag{2.26}$$

There are some strength and weakness related to adding iron to the substrate. If added iron chloride, the chloride can cause a change in pH and temperature in the digester [2]. The biogas plant needs to ensure that the level of chloride is within acceptable limits all the time, so the digester does not inhibit. The excess of chloride can be avoided by using sludge from waterworks instead of iron chloride. By using the sludge, there will however be a larger transportation cost and the biogas plant need to have iron chloride as a back-up if the amount of sludge is less than expected [27]. Typically, the amount of iron added to the substrate had to be increased by 2.5 to 3 times if added as waterworks sludge compared to adding iron chloride [27]. The sludge is typically dewatered before transportation, and it is important to keep the sludge moistened also during summer when stored due to avoiding iron crystals to form on the sludge surface. The microorganisms in the digester do not manage to utilise these iron crystals [27]. Even though with good results with reducing the level of hydrogen sulphide, the major concern is that the level of iron in the digestate can make phosphorus unavailable for plants when using it as fertiliser [37].

2.8.4 Adding zinc oxide

It has been doing study where zinc oxide nanowires are used to prevent formation of hydrogen sulphide. The zinc oxide and microorganisms worked synergistically to remove soluble sulphide (HS^-) and then also preventing hydrogen sulphide (H_2S) to be created [38]. The zinc oxide act as an inorganic reactive adsorbent. Laboratory batch test shows that the hydrogen sulphide formation decreased to non-detectable level [38]. It needs further experiments, especially in full scale, to determine the effect of adding zinc oxide. There are also concerns for long-term toxicity to microorganisms in the digester.

Norwegian regulation has set a maximum value of several nutrients in fertiliser, among other zinc. The amount of zinc allowed depends on usage of the fertiliser, hence in this case for agriculture the limit is 150 mg/kg-TS [39].

2.9 Anaerobic digestion model no1 (ADM1) extended with P-S-Fe interactions

Simulations in this thesis is based on a validated model and already implemented in a MATLAB script. The simulation model are the Anaerobic Digestion Model No.1 (ADM1) developed by the International Water Association (IWA) [13]. The model used in the thesis is an extended version of the original ADM1 model, which also accounts for phosphorous, sulphur and iron interactions. The scripts have been developed in corporation between the PROSYS centre at Technical University of Denmark (DTU) and the IEA division at Lund

University (LU) in Sweden. The MATLAB-script available from www.github.com and was used to run simulations with [40].

In the original ADM1 it describes organic/inorganic carbon and nitrogen transformation. With the extension, it takes account for phosphorous transformation. However, due to the close link with sulphur and iron, the transformations of these are also implemented. In addition, multiple precipitation are also included in the model [32].

In the model, it takes account of three different extensions compared to the original ADM1. The first one considers phosphorous transformation, with among other phosphorous accumulating organisms and kinetic decay of polyphosphates. The second extensions describe biological production of sulphide, where sulphate reducing bacteria utilise among other hydrogen as electron source. The last extension is using hydrogen and sulphides as electron donor in the chemical reduction from Fe^{3+} to Fe^{2+} [32]. The extended ADM1 describes all main biochemical and physico-chemical processes for P, S and Fe, and in addition take account for the interaction between P, S and Fe and the anaerobic digestion. The latter one, is for example different precipitates and biogas [32].

3 Material and methods

In this chapter the case with Svanem Biogass AS is discussed with respect to among other the biogas facility, bioreactor, and contents of the substrate. This information is used to estimate reasonable values for parameters and variables in ADM1. The ADM1 is used to simulate different cases which could be relevant for Svanem Biogass AS.

3.1 Svanem Biogass AS

The facility at Svanem biogass AS was in a start-up phase and had limited possibilities to do experiments with the substrate. However, during the start-up phase the facility have been running on different fractions of cow manure and fish sludge, where the amount of fish sludge is stepwise increased. Measurements from sensors such as temperature, feed rate, and volume of biogas has been logged during this periode. In end of August 2023, it was sent in samples of substrate and biogas for analysis performed by Svanem Biogass AS and Antec biogas AS (ref Appendix B).

3.1.1 Overview of the biogas facility

The biogas facility at Svanem biogass AS is using reactors from Antec biogas AS. Before the substrate is entering the biogas reactor, the cow manure and fish sludge is combined in a mixing tank. In the mixing tank, there is also a fraction of inoculum (approximately 10%) from two of the biogas reactors (tank 2 and 3). Bioreactor tank 2 and 3 are feed approximately with 150 litres in addition compared with reactor 1. The substrate in the mixing tank is preheated in the mixing tank before entering the biogas reactors [5].

The biogas from the reactors is currently flared and it is not utilised. Further, the digestate is separated into a solid fraction, which contains the majority of the phosphorous, and a liquid fraction, which contains nearly all nitrogen [5]. A schematic presentation of the facility is illustrated in Figure 3.1.

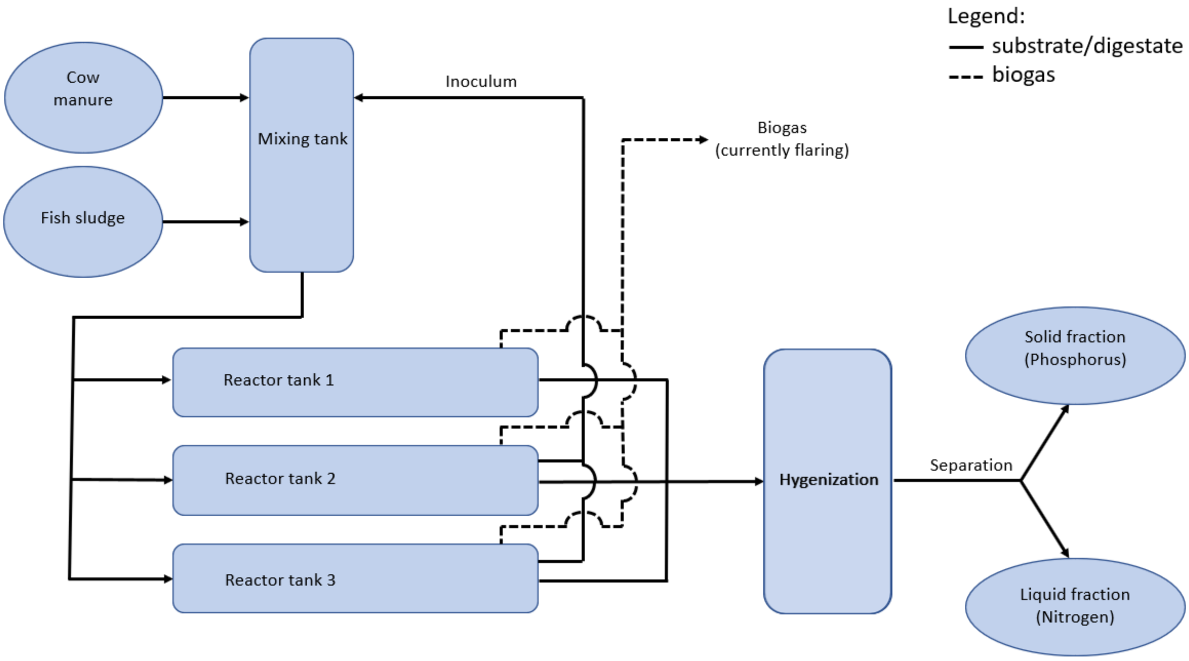


Figure 3.1 Schematic presentation of the facility at Svanem Biogass AS

3.1.2 Reactor type and size

Svanem Biogass AS has invested in a biogas reactor from a manufacture called Antec Biogas AS. According to Antec, the reactor is 5 times faster than traditional plants, i.e., for example the retention time is 7 days instead of 40 days. In addition the gas yield is larger within the same time frame compared to traditional reactors [41]. In general for traditional plants, cow manure is recommended a retention time of 25 to 30 days, and for food waste approximately 15 days [10].

The bioreactor is a horizontal plug flow type reactor where the substrate is continuously fed into the reactor. The reactor has a large surface of biofilm and several chambers. In each chamber, mainly one step of the digestion process occurs [42]. For example, in the first chamber it will mainly be hydrolysis. Compared to a traditional continuous stirred tank reactor (CSTR), there is only one chamber where all the different stages in the digestion occurs. The difference in the reactor tank design is illustrated in Figure 3.2.

The organic waste is pre-treated by being heated to approximately 39 to 41°C and grinded to particle size of 0.6 cm in a mixing tank before entering the Antec reactor [5], [42].

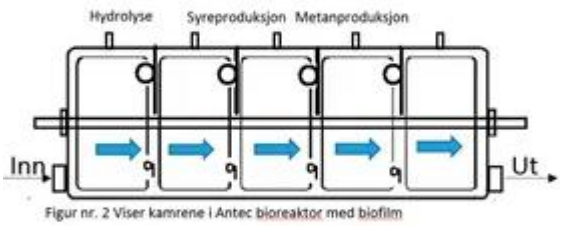
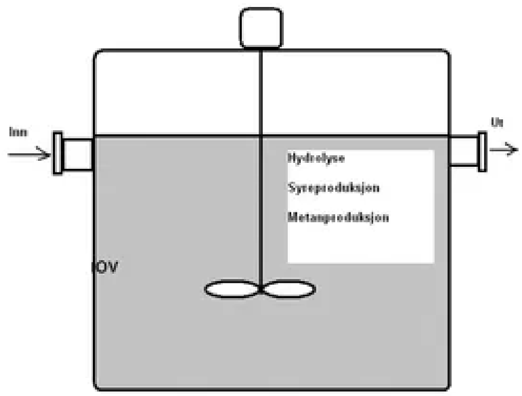
Antec bioreactor	Traditional CSTR
	

Figure 3.2 Antec bioreactor vs traditional CSTR [42]

Technical information for Antec bioreactor at Svanem Biogass AS is given in Table 3.1 [43].

Table 3.1 Technical information and design criteria - Antec bioreactor [43]

Dimension	105 m^3
Headspace (approx. 10% of reactor volume)	~ 10.5 m^3
Digester volume (approx. 90% of reactor volume)	~ 94.5 m^3
Hydraulic retention time (HRT)	~ 7 days
Volume of substrate feed per day	~ 13.5 m^3/day
Temperature (operational)	39°C

3.1.3 Nutrient content in substrate

The substrate at Svanem Biogass AS has been analysed with respect to different nutrients. However, in this report, it will mainly focus on some of them which is especially important for inhibition due to excess ammonia and hydrogen sulphide. For full report of measurements from Svanem Biogass AS, see Appendix B.

Svanem Biogass AS has original planned to use a substrate with 80% cow manure and 20% fish sludge [5]. The fish sludge consists of sludge from salmon, cod and wrasse [44]. Based on the analyse report and information from Svanem Biogass AS, the ratio between cow manure and fish sludge has been varied to see how it will affect the substrate. There are totally 14 different farmers that will deliver cow manure. There are variations in nutrients from each farm, the delivered amount of cow manure, and regularity of delivery. In addition, it is missing assumed number of deliveries from two farmers (farmer #3 and #10), ref Appendix B. I.e., this is neglected in further evaluation of the substrate.

The nutrients are compared with optimum levels for biogas production as discussed in Chapter 2.5. It is further assumed that the density of cow manure and fish sludge is approximately 1000 kg/m^3.

In the figures below it is also plotted one standard deviation in addition to weighted average when presenting the results. The standard deviation is due to variation in the cow manure depending on which farmer who is delivering. Similar with fish sludge from the different aquaculture facilities. Even though with large storage facility of substrate at Svanem Biogass AS there could still be some variations. Further in this report, it will in general be used weighted average values and hence the variation is neglected in simulations.

The substrate is rich on nitrogen compared to carbon, as shown in Figure 3.3. The ratio is about 10:1 (C:N), while the recommended ratio is between 20:1 and 30:1. Likewise, it has been reported satisfactorily results with C/N ratio between 17:1 and 8.5:1 in a mixture of fish waste silage and cow manure [45]. The explanation for tolerance for the low C/N-ratio is that the microorganisms are able to adapt. In the case of Svanem Biogass AS the C/N-ratio is less than recommended values, but slightly larger than 8.5:1 ratio.

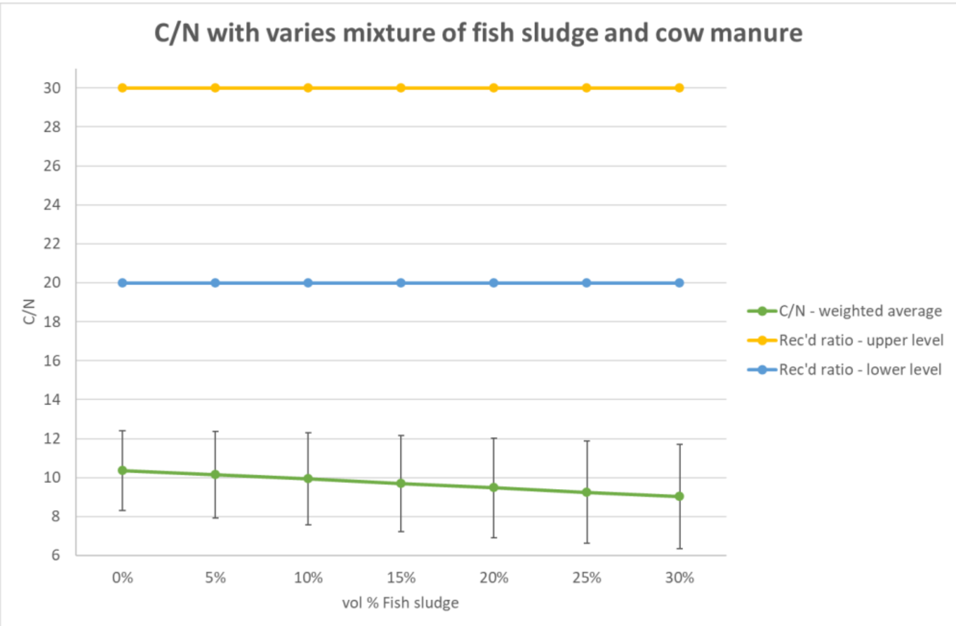


Figure 3.3 C/N with varies mixture of fish sludge and cow manure (weighted average with standard deviation).

Similar ratios are also performed for N/P, N/S and P/S with recommended ratio of 15:5:1 (N:P:S), as mentioned in Chapter 2.5. From the N/P-ratio in Figure 3.4 it shows that the amount of phosphorus is not optimal compared to the amount for nitrogen. The ratio is approximately two times recommended ratio, but the ratio is decreasing when adding fish sludge.

Even though the substrate is rich on nitrogen, the N/S-ratio is lower than recommended value of 15:1 as showed in Figure 3.5. Subsequent the P/S-ratio is also lower than recommended (ref Figure 3.6). The substrate at Svanem Biogass AS is rich on nitrogen, but even more rich on sulphur and phosphorus.

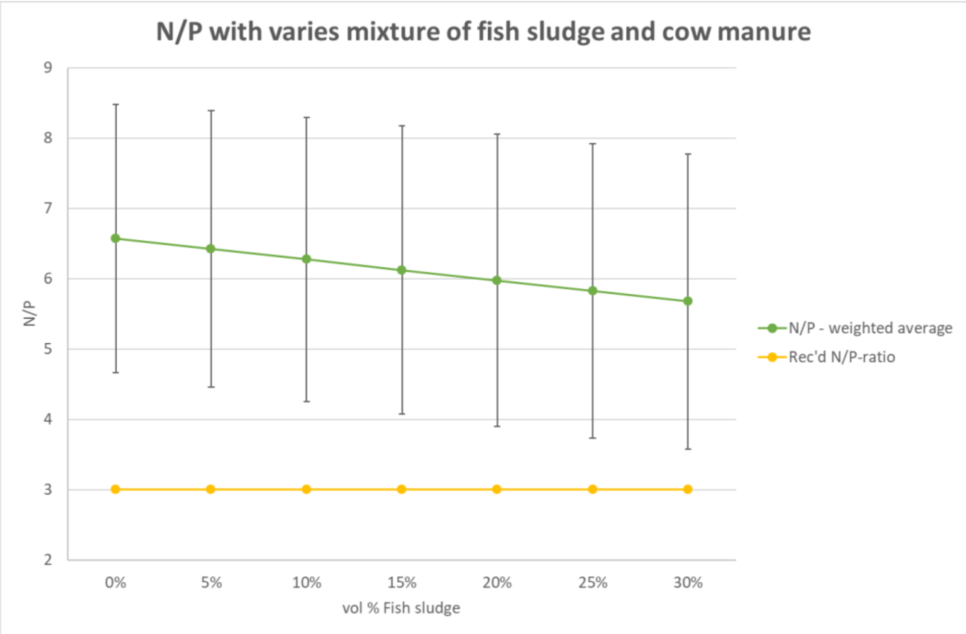


Figure 3.4 N/P with varies mixture of fish sludge and cow manure (weighted average with standard deviation).

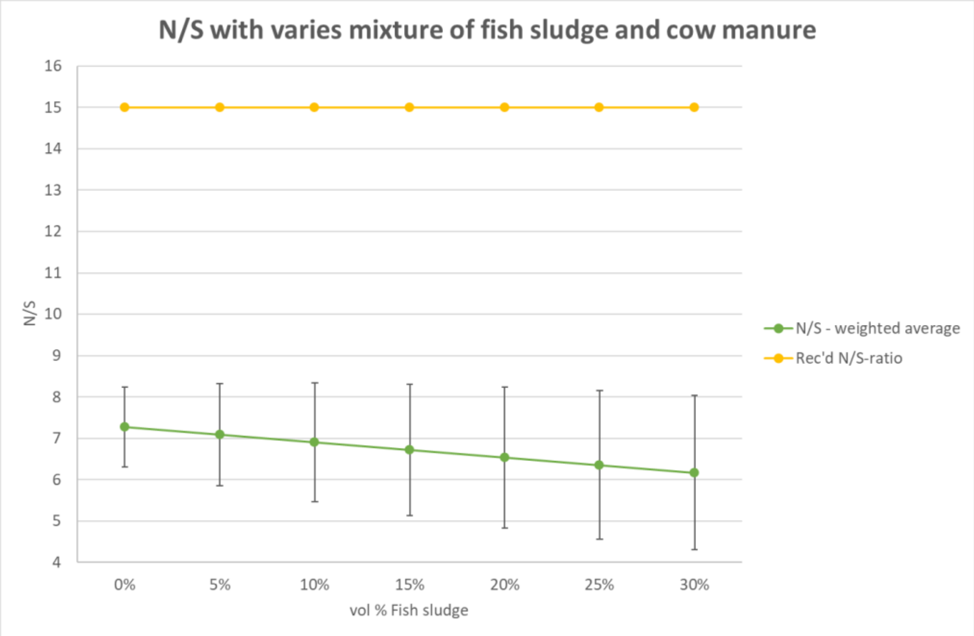


Figure 3.5 N/S with varies mixture of fish sludge and cow manure (weighted average with standard deviation).

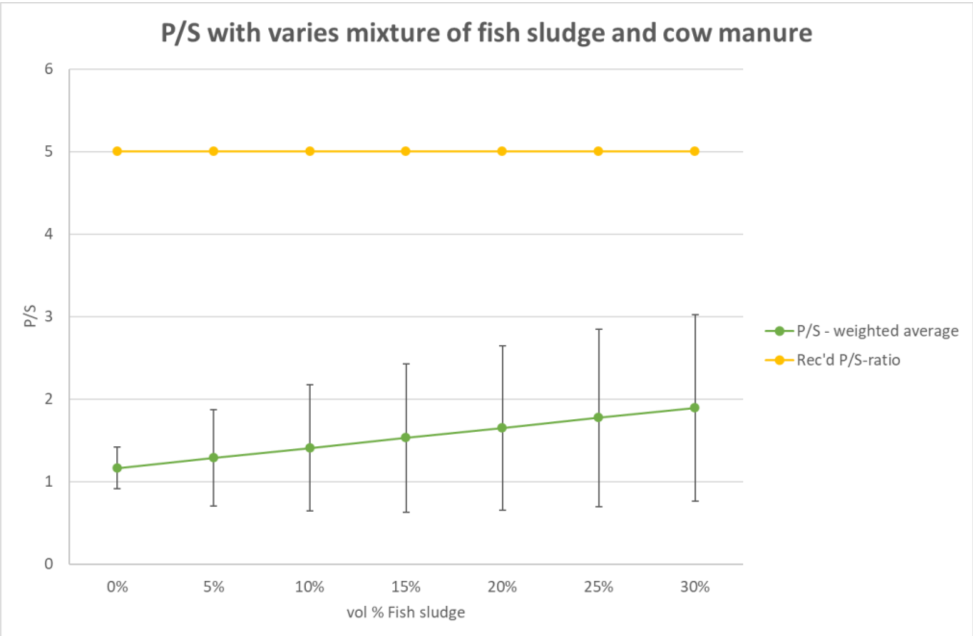


Figure 3.6 P/S with varies mixture of fish sludge and cow manure (weighted average with standard deviation).

The salinity in the substrate also affects the production of methane and hydrogen sulphide. Figure 3.7 shows the plot of the amount of sodium compared with recommended level, and the level in the substrate is more than 3 times the recommended level. Still, it is far from the inhibition level of approximately 8000 mg/L.

It is observed that gras at the coast contains more sodium (Na) than in other places. However, sodium is not an essential plant nutrient, but it is increasing the taste of the gras [46]. A research report has investigated manure and the variations in nutrients in different regions of Norway, among other in Trøndelag [47]. Unfortunately, sodium was not included among the measurements of the nutrients. However, in North Dakota in USA nutrients in solid beef manure has been mapped. The sodium level is in the range of 0.1 – 7.3 lbs/ton and an average of 1.37 lbs/ton [48]. This is equivalent to an average of 685 mg/L, with a range of 50 - 3650 mg/L. The level of salinity at Svanem Biogass AS seems to be at an expected level for cow manure (ref Figure 3.7).

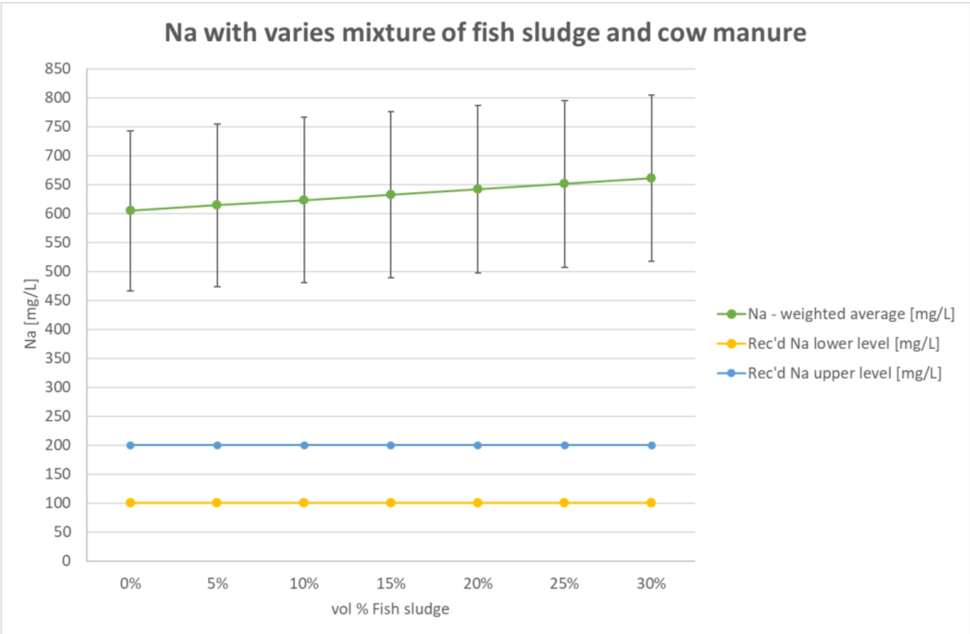


Figure 3.7 Na with varies mixture of fish sludge and
cow manure (weighted average with standard deviation).

The substrate at Svanem Biogass AS is rich on nitrogen, sodium, and sulphur. From the figures in this chapter, it can be concluded that adding the fish sludge in the substrate will increase the concentration of sodium. Further, the concentration of nutrients in fish sludge can be summarized as: phosphorus > sulphur > nitrogen > carbon. However, by adding fish sludge the level of phosphorus will increase in the substrate and this is an important nutrient in natural fertiliser.

The available volume of cow manure is ~13 410 m^3 and fish sludge is ~2 500 m^3, totally approximately 15 910 m^3. That is, the maximum percentage of fish sludge is 15.7 volume %. It is reported that recommended maximum percentage is 20 volume % or 50% of TS of fish sludge in the bioreactor. By adding 20 volume % fish sludge, the amount of methane was also increased by a factor of 2 compared without any fish sludge [49].

With high level of both sodium and sulphur in the substrate, it can be expected high level of hydrogen sulphide in the biogas at Svanem Biogass AS according to findings in literature.

3.1.4 Available resources – iron rich water

Svanem Biogass AS got access to iron rich sludge/waste water from a local waterwork nearby [5]. Eide kommunale vannverk is a waterwork located in Kyrksæterøra and waterwork gets the water from water reservoir in the ground [50]. Groundwater from lose sediments contains usually iron (Fe) and mangan (Mn) [51]. However, it depends on the concentration of oxygen and pH-level. At low-level of oxygen and high level of carbon dioxide, the iron is typically as Fe^{2+} (soluble) [51].

At Eide kommunale vannverk they are aerating the water with oxygen (O_2) for removal of carbon dioxide and sulphur-containing components. At the same time, the oxygen will remove iron and mangan [50]. The iron is oxidized to Fe^{3+} (solid) and non-soluble particulate, and is then filtered from the drinking water by use of a marble filter [50], [51].

3.2 ADM1 – values of variables and parameters

One of the difficulties by using simulation, is that the model needs a several steady-state input variables. Usually, the substrate is only analysed for some nutrients which is not sufficient as input for simulation. For this reason, it is used values from similar cases for the variables and parameters in the ADM1. Analyses of nutrients in the substrate were performed by Svanem Biogass AS and it is given in Appendix B.

If not stated for other parameters and variables in ADM1, default values in the script were used [40], [52].

For running the simulation models, MATLAB (version 9.13) with Simulink (version 10.6) is used.

It was further assumed that the influent variables in the simulation were steady-state. That is, the composition of the substrate does not vary with time.

3.2.1 ADM1 – variables and parameters for cow manure

It was used ADM1 variables and parameters from a similar case, based on cattle manure [53]. The reported properties of the cattle manure are similar to the cow manure at Svanem Biogass AS, and it is assumed that the ADM1 steady-state input variables and parameters from the similar case could be used.

Please note that the ADM1 script used in this report has no variable for inorganic cations (S_{cat}) or inorganic anions (S_{an}), like the original ADM1 has. These variables are accounted for in extension for the physioc-chemical model. The variables sodium (S_{Na}) and potassium (S_K) are equivalent with S_{cat} (equally distributed), and chloride (S_{Cl}) is equal to S_{an} [54].

One variable had to be adjusted, due to unrealistic levels of methane in the biogas when running simulations. It was recommended to use a value of 0.06 for the inorganic carbon (S_{IC}) in the similar case based on cattle manure. This variable was adjusted to 0.15 get a methane level in the biogas to be approximately 65%. For further discussion of adjustment of this variable, see

Chapter 4.3.1 By increasing the value of inorganic carbon (S_{IC}), the amount of CO_2 is increasing in the simulation (biogas). The amount of biogas increases, due to increased CO_2, and the level of methane is reduced, respectively.

The ADM1 steady-state input variables used in the simulation for manure are summarized in Table 3.2. Variables not mentioned in the Table 3.2, are set to zero.

Table 3.2 Cow manure - properties and ADM1 steady-state input variables [53].

Properties – values from Svanem Biogass AS in brackets (weighted average)				
pH [-]	TS [%]	VS [%TS]	NH_4-N [mg/l]	
6.80 (7.38)	5.8 (6.7)	80.80 (-)	2100 (2036)	
ADM1 - Soluble and particulate steady-state input variables				
S_{su} [kg COD/m^3]	S_{aa} [kg COD/m^3]	S_{fa} [kg COD/m^3]	S_{va} [kg COD/m^3]	S_{bu} [kg COD/m^3]
2.53	0.69	2.44	0.72	1.57
S_{pro} [kg COD/m^3]	S_{ac} [kg COD /m^3]	S_{IC} [kmol C/m^3]	S_{IN} [kmol N /m^3]	-
2.94	5.68	0.15*	0.147	-
X_{ch} [kg COD/m^3]	X_{pr} [kg COD/m^3]	X_{li} [kg COD/m^3]	X_{su} [kg COD/m^3]	X_{aa} [kg COD/m^3]
13.62	17.06	4.19	$3.1 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$
X_{fa} [kg COD/m^3]	X_{c4} [kg COD/m^3]	X_{pro} [kg COD/m^3]	X_{ac} [kg COD/m^3]	X_{h2} [kg COD/m^3]
$1.0 \cdot 10^{-5}$	$1.0 \cdot 10^{-4}$	$1.0 \cdot 10^{-2}$	$1.7 \cdot 10^{-3}$	$1.0 \cdot 10^{-2}$
* value adjusted from recommended 0.06 [53] due to unrealistic level of methane in biogas in the simulation				

Some biochemical and stoichiometric parameter values are also required to be changed to represent the response of the digestion for cattle manure in the biogas reactor [53], [55]. The kinetic parameters are given in Table 3.3. For parameters not mention, default values in the MATLAB scripts is used [52].

Table 3.3 Kinetic parameters changed to adopt to cattle manure [53], [55]

Parameter	**Description**	**Unit**	**ADM1 default value**	**Values used in this report**
$K_{m,su}$	Maximum uptake rate of monosaccharides	d^{-1}	30.0	11.9
$K_{s,su}$	Half saturation concentration of monosaccharide uptake	kg COD/m^3	0.5	4.5
$K_{m,aa}$	Maximum uptake rate of amino acids	d^{-1}	50.0	19.8
$K_{s,aa}$	Half saturation concentration of amino acids uptake	kg COD/m^3	0.3	0.3
$K_{m,c4}$	Maximum uptake rate of valerate and butyrate	d^{-1}	20.0	12.2
$K_{s,c4}$	Half saturation concentration of valerate and butyrate uptake	kg COD/m^3	0.2	0.6
$K_{m,pro}$	Maximum uptake rate of propionate	d^{-1}	13.0	3.5
$K_{s,pro}$	Half saturation concentration of propionate uptake	kg COD/m^3	0.1	0.4
$K_{m,ac}$	Maximum uptake rate of acetate	d^{-1}	8.0	11.1
$K_{s,ac}$	Half saturation concentration of acetate uptake	kg COD/m^3	0.15	0.5

Parameter	Description	Unit	ADM1 default value	Values used in this report
$K_{I,nh3}$	50% inhibitory concentration of free ammonia	$kmol/m^3$	0.0018	0.0223
$f_{h2,su}$	Yield of hydrogen from monosaccharides	-	0.19	0.25
$f_{pro,su}$	Yield of propionate from monosaccharides	-	0.27	0.12
$f_{ac,su}$	Yield of acetate from monosaccharides	-	0.41	0.49
k_{dis}	constant describing disintegration phase	d^{-1}	0.5	1.54
$k_{hyd,ch}$	constant describing carbohydrates hydrolysis phase	d^{-1}	10	0.037
$k_{hyd,pr}$	constant describing proteins hydrolysis phase	d^{-1}	10	0.099
$k_{hyd,li}$	constant describing lipids hydrolysis phase	d^{-1}	10	0.225

3.2.2 ADM1 – variables for fish sludge

As input values for the fish sludge, it was not found any similar cases where ADM1 steady-state input variables were given. However, it was found two reports with composition of the fish sludge from a salmon smolt hatching, where one report had COD in the same range as for the analysis at Svanem Biogass AS [44], [56], [57]. Even though the fish sludge at Svanem Biogass AS contains sludge from salmon, cod, and wrasse (ref Chapter 3.1.3), it is assumed that values in the reports with only salmon sludge are valid for this case also. In one of the reports, it was noticed a high feed-coefficient, i.e., the sludge contained extra ordinary high amount of excess feed. When compared to normal feed coefficient, the percentages of VS, protein and fat were twice as high [56]. The feed-coefficient for Svanem Biogass AS is unknown and also the fraction of each fish sludge. For further work, it was used the composition with most similar values for COD and total solid (TS), and for this case it was the sludge containing high amount of excess feed [56].

Table 3.4 Composition of sludge from fish farm effluents [56]

Components – values from Svanem Biogass AS in brackets			
TS [wt%]	VS [% of TS]	Protein [% of VS]	Fat [% of VS]
6.3 – 12.3 (9.7 – 9.8)	78.6 – 86.9 (–)	60 (–)	31 (–)
Carbohydrates [% of VS]	COD_{tot} [g/l]	COD_{sol} [g/l]	-
9 (–)	110 – 193 (157.4 –168.2)	– (31.5 – 56.4)	-

The ADM1 steady-state input variables were then estimated by use values from Table 3.4 and formulas suggested in literature [58], [59]. The formulas are summarized in Table 3.6 and where f_i [% of VS] is the fraction between carbohydrates, lipids, and protein and BFP is the biodegradable fraction in particulates. The fraction between carbohydrates, lipids, and protein are given in Table 3.4. The biodegradable fraction in particulates are not given in available literature and it can be estimated based on Equation 3.1, 3.2, and 3.3 [58], [59].

The method of estimation of BFP includes use of the total biodegradable fraction and reduction of particulates. The total biodegradable fraction (TBF) is found in Equation 3.1.

$$\text{TBF} = 1 - \frac{COD_{out}}{COD_{in}} \qquad (3.1)$$

The reduction of particulates can be found by use of TS_{in} and TS_{out} in Equation 3.2.

$$\text{Reduction of particulates} = 1 - \frac{TS_{out}}{TS_{in}} \qquad (3.2)$$

The biodegradable fraction of particulates (BFP) is the product of TBF and reduction of particulates.

$$\text{BFP} = \text{Reduction of particulates} * \text{TBF} \qquad (3.3)$$

There are several concerns by estimating the BFP as described. When measuring the TS, the soluble will also be in the residual when the water is vaporised [15]. This could overestimate the BFP. The method could give reasonable estimates if the soluble COD (CODs) is small compared to the total COD (COD_T). In this case, the ratio of COD_S and COD_T is in the range of 0.2 to 0.34. Another concern is the measured value of TS. As discussed in Chapter 2.3.6, the

TS is often underestimated due to the oven-dried method which is common to use. The underestimation of the TS is typically in the range of 3-30% [15]. However, if the methods used underestimate both the TS_{out} and TS_{in} to the same extent, the errors of TS could be negligible for the estimation of BFP (ref Equation 3.2). The estimation of BFP can be considered as a rough estimate and further consideration should be done regarding how it affects the results of simulations.

In this case, the BFP is estimated by the method discussed above with available data from literature [56]. From Table 3.5 a rough range of estimate of BFP is presented and the average value of BFP is 0.419.

For use in simulation, a value of BFP equal 0.40 is used for the base case.

Table 3.5 Estimation of biodegradable fraction of particulates (BFP)

for fish sludge based on values from literature [56]

Description	**Measurement I**	**Measurement II**
COD_{in}	160.1	183.4
TS_{in} (wt%)	9.95	12.34
COD_{out}	59.0-68.8	72.0-80.5
TS_{out} (wt%)	3.12	3.33
Total Biodegradable Fraction (TBF)	0.570-0.631	0.561-0.607
Reduction of particulates	0.686	0.730
Biodegradable Fraction of Particulates (BFP)	0.391-0.433	0.410-0.443

It was decided to use average value in the calculation of the parameter if there is given a range in the values. Values for COD_{tot} and COD_{sol} are provided by Svanem Biogass AS (ref Appendix B) and are used in the calculation of variables in Table 3.6.

Table 3.6 Fish sludge - ADM1 steady-state input variables

Parameter	**Content**	**Formula**	**Denomination**
X_{pr}	protein	$f_{pr} * BFP * (COD_{tot} - COD_{sol}) = 0.60 * 0.40 * (162.8 - 43.95) = 28.524$	kg COD/m^3
X_{li}	lipid	$f_{li} * BFP * (COD_{tot} - COD_{sol}) = 0.31 * 0.40 * (162.8 - 43.95) = 14.737$	kg COD/m^3
X_{ch}	carbo-hydrates	$f_{ch} * BFP * (COD_{tot} - COD_{sol}) = 0.09 * 0.40 * (162.8 - 43.95) = 4.279$	kg COD/m^3
X_i	solid inert	$\text{Inert particulates which remains as solid} * (COD_{tot} - COD_{sol}) = 0.57 * (162.8 - 43.95) = 67.745$	kg COD/m^3
S_i	soluble inert	$\text{Inert particulates which dissolves in liquid} * (COD_{tot} - COD_{sol}) = 0.03 * (162.8 - 43.95) = 3.566$	kg COD/m^3
Comments: - Suggested fraction of (COD_{tot}-COD_{sol}) for S_i is assumed to be similar as suggested in literature, i.e., 0.03 [49]. - The fraction of inert particulates which remains as solid in Xi is adjusted such as the sum of X_{pr}, X_{li}, X_{ch}, X_i, and S_i is equal to (COD_{tot}-COD_{sol}).			

3.2.3 ADM1 – variables for sulphur

The extended version of ADM1 also requires input of sulphur, phosphorous and iron. Based on discussion in Chapter 2.6.2 and Table 2.3, it is assumed that thickened sludge analysed by extraction is most relevant for this case. Food waste and activated sludge (with additional oxygen (aeration)), and thickened sludge with high level of elemental sulphur (S^0) are not assumed to be representative for this case.

For sulphur it is assumed that 4% of the total sulphur in the substrate is sulphate (SO_4^{2-}) [kmol S/m^3].

The inorganic sulphur is estimated to 20% of the total sulphur based on Table 2.3. The value of chemical oxygen demand for inorganic sulphur [kg COD/m^3] is found by equilibrium equations 2.11, 2.13, 2.14, and 2.15 and using equation 3.4.

$$\text{COD for inorganic sulphur } [kg\ COD\ /m^3] = 20\%\ of\ total\ sulphur\ [kmol/m^3] * \frac{7\ mol\ O_2}{8\ mol\ S} * 32\ \ kg\ /kmol \qquad (3.4)$$

The elemental sulphur (S^0) [kg COD/m^3] is assumed to be zero in the substrate (ref Table 2.3).

3.2.4 ADM1 – variables for phosphorous

For organic waste it can be expected that 2 to 28% of total phosphorous is organic phosphorous, reference to discussion in Chapter 2.6.3. At Svanem Biogass AS it has been performed several analyses of substrate with respect to among other total phosphorous and phosphorous available for plants (P-AL), where the P-AL can be considered as inorganic phosphorous [60], [61]. The inorganic phosphorous is available for the plants, while organic phosphorous need to be degradable by enzymes before plants can utilise it [61].

The fraction of phosphorous at Svanem Biogass AS for different fish sludge is summarized in Table 3.7. In Table 3.7, the fraction of organic is calculated based on assumption of P-AL is equal to inorganic phosphorous and the remaining is organic phosphorous. When comparing the results in Table 3.7 with discussion in Chapter 2.6.3, the average fraction of organic phosphorous is somewhat larger.

The amount of inorganic phosphorous [kmol P/m^3] is used as an input in the ADM1. In the simulations, it is then used 70% inorganic phosphorous of total phosphorous. This fraction is used for both cow manure and fish sludge, even though it is in the upper level of the reported interval of inorganic phosphorous (ref discussion in Chapter 2.6.3).

Table 3.7 Total phosphorous and P-AL in fish sludge at Svanem Biogass AS [60]

Substrate	**Total Phosphorous [mg/kg TS]**	**Phosphorous (P-AL) [mg/kg TS]**	**Fraction of inorganic phosphorous (P-AL) of total phosphorous**	**Fraction of organic phosphorous of total phosphorous**
Fish slugde – Lumarine Tjeldbergodden	19 000	15 000	~ 79%	~ 21%
Fish sludge – Lerøy Belsvik #29	21 000	11 000	~ 52%	~ 48%
Fish sludge – Lerøy Belsvik #30	26 000	20 000	~ 77%	~ 23%
Fish sludge – Lerøy Belsvik #31	27 000	18 000	~ 66%	~ 34%
Fish sludge – Lerøy Belsvik #33	30 000	21 000	~ 70%	~ 30%
Fish sludge – Lerøy Belsvik #38	34 000	21 000	~ 62%	~ 28%
Fish sludge – Lerøy Botn	17 000	14 000	~ 82%	~ 18%
Average	23 333	16 500	~ 70%	~ 30%
Standard deviaton	6 149	3 891	± 10.6%	± 10.1%

3.2.5 ADM1 – physioc-chemical variables

The values for physioc-chemical variables in the simulations are based on analysed values of the substrate at Svanem Biogass AS (ref Appendix B). Physioc-chemical variables are typically the amount of sodium (Na), potassium (K), magnesium (Mg), chloride (Cl) etc in the substrate. However, there are no values for chloride in the analyses of the substrate provided from Svanem Biogas AS. It was then assumed that the chloride is due to the salinity of the substrate, i.e., from NaCl and the amount of chloride is the same as of the amount of sodium.

The amount of iron was given in analyses of the substrate from Svanem Biogass AS. However, it was not stated if it was iron (II) or iron (III). For the simulations, it was assumed all iron in the substrate was iron (II), due to it is solubility in water.

Input for iron (II) (Fe^{2+}) is given by chemical oxygen demand, and not by kmol/m^3 as for of the other parameters for physico-chemical model, such as for natrium, calcium, choloride, iron (III), etc. The conversion of Fe^{2+} to kmol/m^3 is given in the MATLAB script and it is expressed by equation 3.5 [40].

$$kmol\ Fe^{2+}/m^3 = \frac{kg\ COD/m^3}{8} \tag{3.5}$$

3.2.6 ADM1 – general considerations

The complete ADM1 steady-state input variables used for manure and fish sludge are summarized in Appendix E.

In addition, some changes were done with respect to technical data for the bioreactor, according to Chapter 3.1.2.

There is a disadvantage in the simulation model due to the model is based on a continuous stirred tank reactor (CSTR), while Antec bioreactor is like a plug flow reactor (PFR). In general, a CSTR needs larger reactor volume to achieve the same fractional conversion than a PFR. Referring to Chapter 3.1.2, the Antec reactor is approximately 5 times faster than traditionally reactors with same size Another disadvantage with the MATLAB script is the absence of simulation of the mixing tank before the reactor. The mixing tank receives not only cow manure and fish sludge, but also some inoculum from the bioreactors (ref Figure 3.1). In the ADM1 there is a continuously feed of substrate, but at Svanem Biogass AS it is semi-continuously/stepwise due to only one mixing tank. These effects are not accounted for in the ADM1. It was not considered to modify the script from CSTR to PFR and include a mixing tank, since the script then had to be validated against test data with an Antec reactor and it is out of the scope of this report.

As a validation of the MATLAB-script used in this report, it was run a simulation for cattle manure and compared with results from a previous validated model against measurements from lab-tests [53]. The results show equivalent behaviour as for the validated model. For details, see Appendix F.

3.3 Simulation with ADM1

Based on information from Svanem Biogass AS and discussion in Chapter 3.2, a base case was established for running simulation with ADM1. Even though the ADM1 will not represent the Antec reactor and the configuration at Svanem Biogass AS exactly, the simulations will give a prediction of the behaviour with different substrates.

It was run simulations with parameters and variables for the substrate for the established base case (see Appendix E for details). In addition, varies composition of cattle manure and fish sludge were used and with different loading rates. Some key parameters were further investigated and compared, such as level of pH in the reactor, level of methane and hydrogen sulphide in the biogas.

The following composition of substrate where simulated for the base case:

- 100% cattle manure and 0% fish sludge
- 90% cattle manure and 10% fish sludge
- 80% cattle manure and 20% fish sludge
- 70% cattle manure and 30% fish sludge

The substrate loading is set to be 3.5, 5, 6.5, 8.5, and 9.5 m^3/day, respectively.

The model has not been adjusted or validated with measurements from laboratory test setup or measurements from a biogas facility. Values of variables and parameters used in the simulation is based on values from literature or from analysis of substrate, or in combination of these two. Due to uncertainties regarding some of the estimated parameters and variables based on findings in literature, it was also run cases where sensitivity of these is investigated. For sensitivity simulations it was run cases were following variables and parameters were adjusted.

- Inorganic carbon
- Inorganic sulphur
- Biodegradable Fraction of Particulates (BFP)
- Inhibition coefficient for NH_3

Note that only one variable or parameter were adjusted at the same time. The results were compared with simulation results from the base case.

It was also investigated the effect of additional iron in the substrate, especially the H_2S level in the biogas.

- Additional hydrous ferric oxide

Simulations were run and compared with base case.

4 Results – simulations with ADM1

The simulations were run for 400 days for each case to be sure a steady state condition was then achieved. The solver used is *ode15s* with both *relative error* and *absolute error* set to $1*10^{-11}$ in general. For the case with 80% cow manure and 20% fish sludge at 9.5 m^3/day, it was run with *relative error* set to $1*10^{-11}$ and *absolute error* set to $1*10^{-12}$.

All biogas flow (volume per day) is given in Normal Temperature and Pressure (NTP) at 20°C (293.15 K) and 1 atm.

4.1 ADM1 – simulations with cow manure and fish sludge

It was run simulation for different substrate loading, i.e., different hydraulic retention time (HRT). For the case with 90% cow manure and 10% fish sludge, the results with difference hydraulic retention time are illustrated in figures below.

From the plot of biogas flow (Figure 4.1), a large feed rate gives the largest biogas flow. The difference in biogas flow between a substrate loading rate of 3.5 compared to 9.5 m3/day, is approximately a factor of 1.66. At the same time, the volume percentage of methane in the biogas remain almost the same. In general, the volume percentage of methane is in the range 63.5 to 65.5% as shown in Figure 4.2.

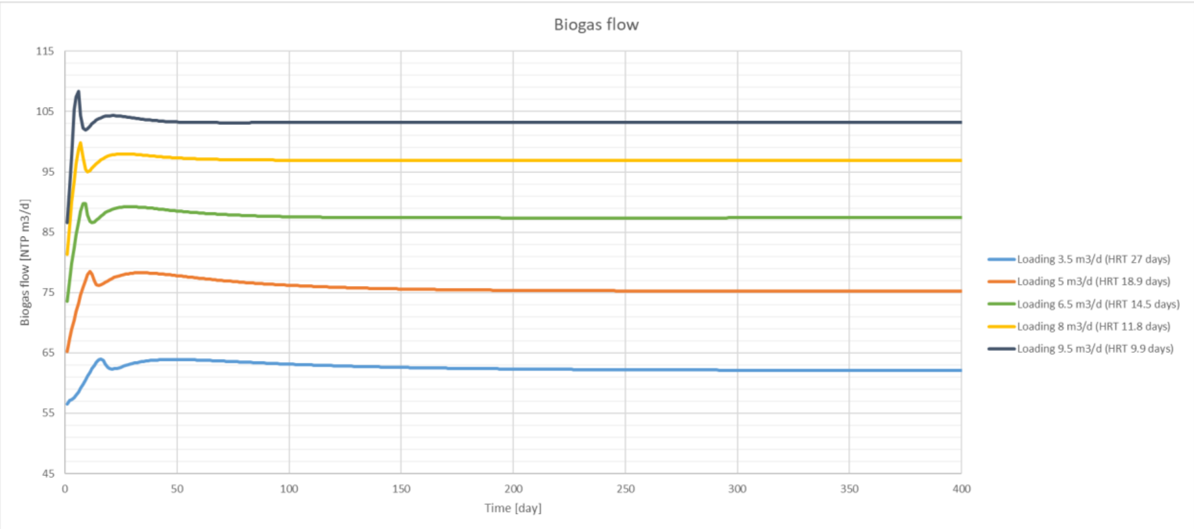


Figure 4.1 Simulation results - biogas flow for substrate mixture of 90% cow manure and 10% fish sludge

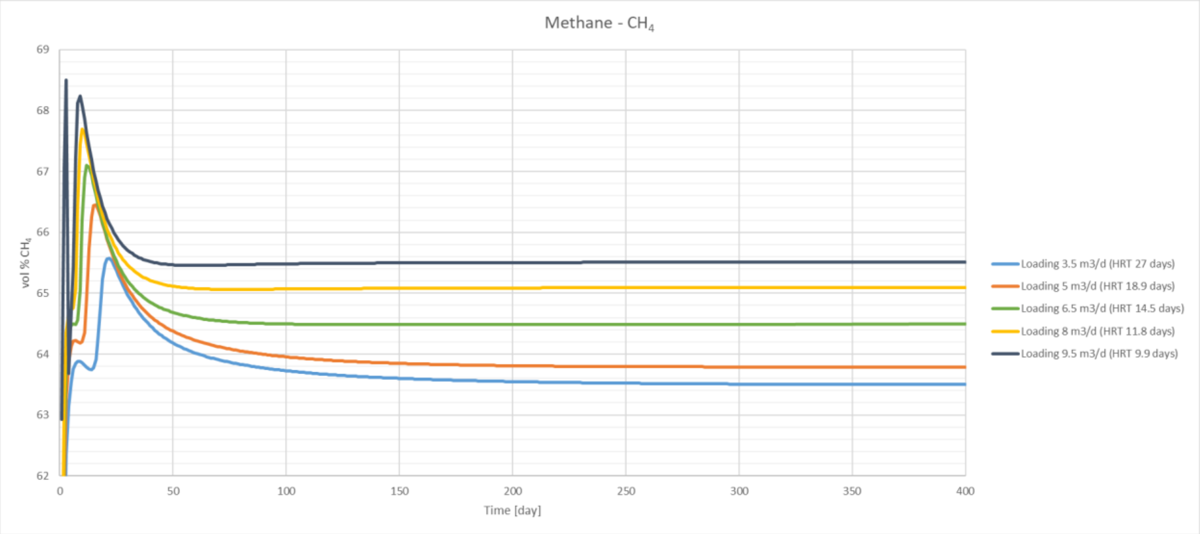


Figure 4.2 Simulation results – volume percentage of methane in biogas for substrate mixture of 90% cow manure and 10% fish sludge

There is in general a small deviation in the pH with a value of about 7.6. As discussed earlier in Chapter 2.8.1, a higher pH gives a lower level of H_2S. This relation can also be seen in the simulation when comparing Figure 4.3and Figure 4.4. In general, the variation pH is small, but still has an impact of the hydrogen sulphide level for the simulations.

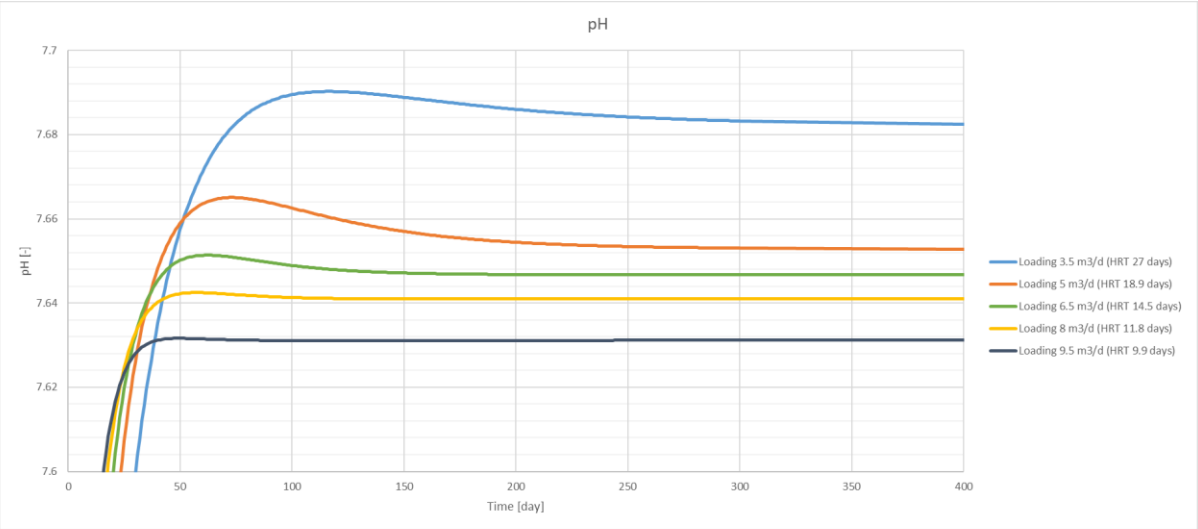


Figure 4.3 Simulation results – pH for substrate mixture of 90% cow manure and 10% fish sludge

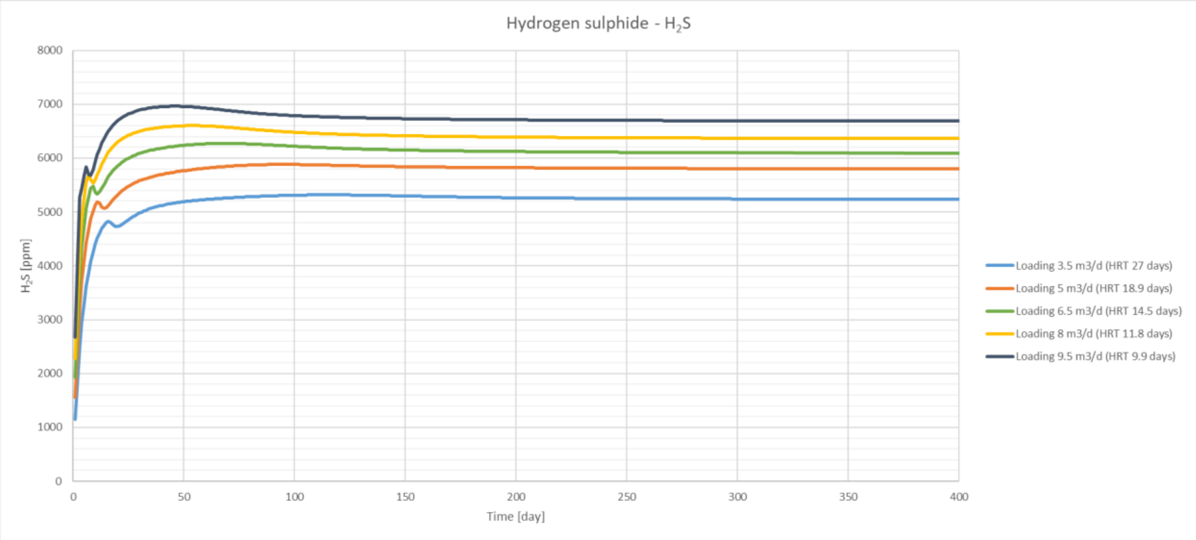


Figure 4.4 Simulation results – Hydrogen sulphide for substrate mixture of 90% cow manure and 10% fish sludge

The inhibition of NH_3 during the simulation is illustrated in Figure 4.5. The inhibition of NH_3 is calculated based on Equation 2.2 in Chapter 2.3.2. In this case, the inhibition of NH_3 is between 0.5 and 0.6 in the simulations.

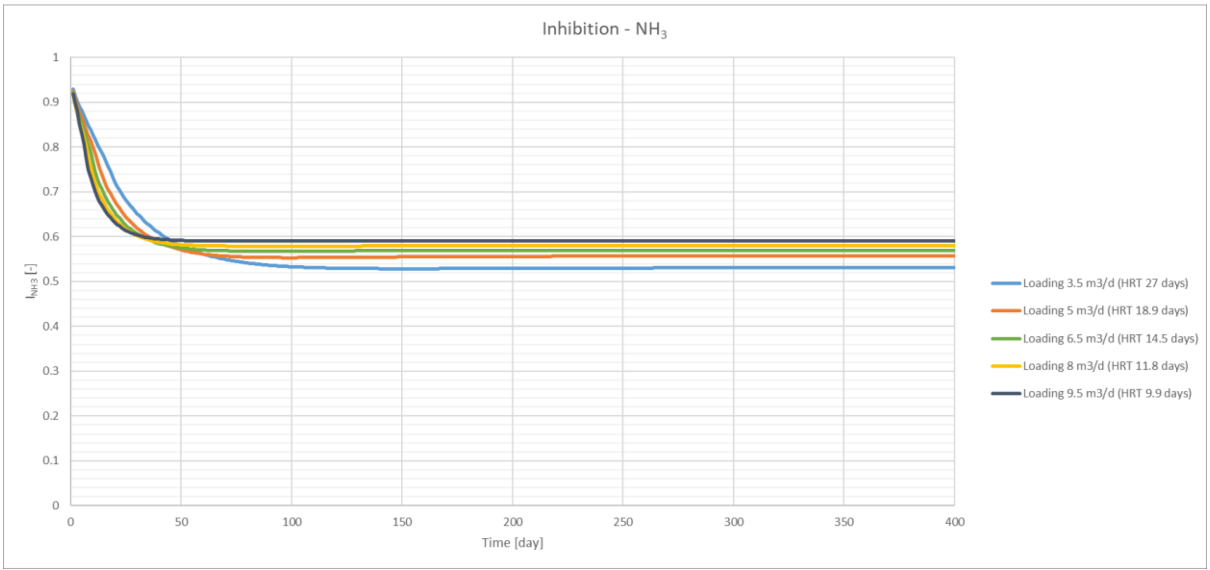


Figure 4.5 Simulation results – Inhibition of NH_3 for substrate mixture of 90% cow manure and 10% fish sludge

The simulations with other composition of substrate shows similar behaviour as for the case with 90% cow manure and 10% fish sludge. The simulations are summarised in figures below, where value at day 400 is used for comparison for each case.

The biogas flow is largest for substrate with pure cow manure. When adding fish sludge to the substrate, the biogas production is reduced, as shown in Figure 4.6. From the plot, it can also be seen that the biogas production increases when the hydraulic retention time is decreased.

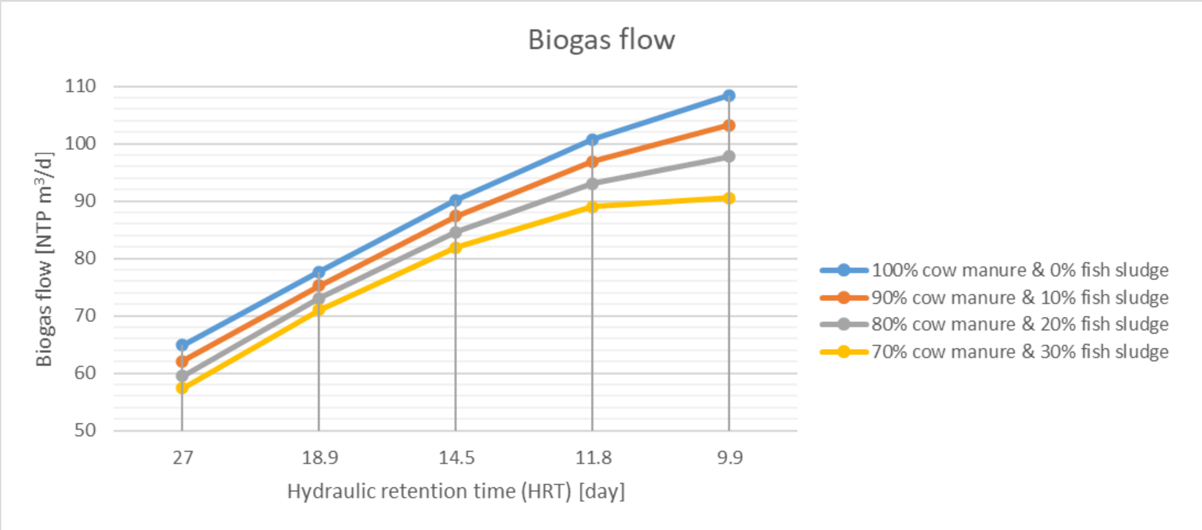


Figure 4.6 Biogas flow with varies composition of substrate after 400 days

The biogas yield for the different composition of substrate is shown in Figure 4.7. The biogas yield from the simulations are compared to typically range of biogas yield for cattle slurry [1]. The results of simulation with cattle manure are in the upper range.

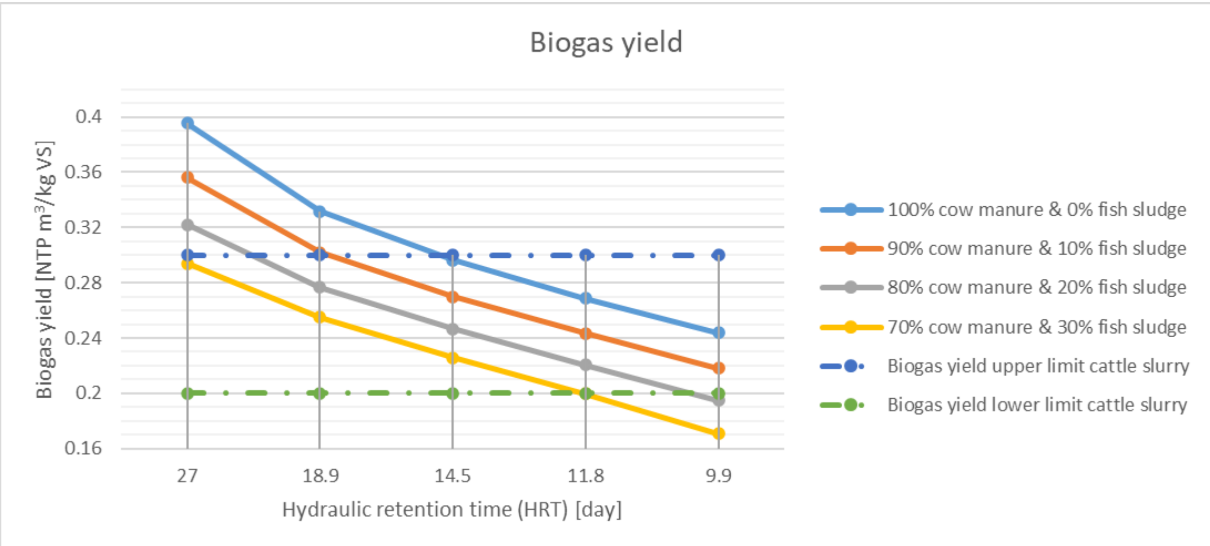


Figure 4.7 Biogas yield with varies composition of substrate after 400 days

In Figure 4.8, the volume percentage of methane in the biogas is in the range of 62 to 66%. The substrate with 100% cow manure has a slightly better fraction of methane in the biogas, which can be seen from the plot. And when adding fish sludge into the substrate, there is a slight reduction of the content of methane in the biogas.

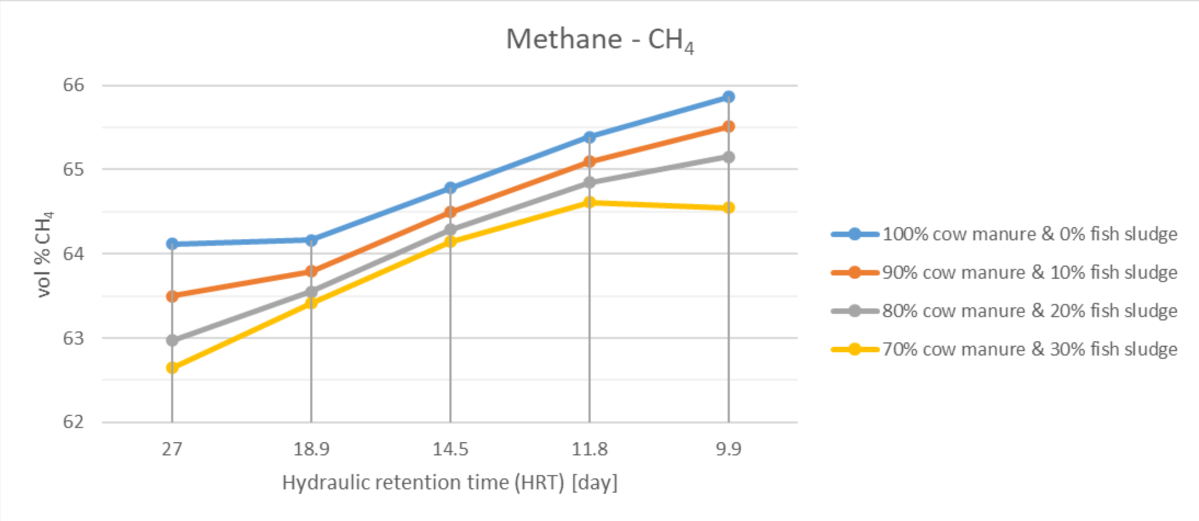


Figure 4.8 Volume percentage of methane in biogas with varies composition of substrate after 400 days

The pH in the bioreactor also depends on the composition of the substrate. In general, the pH level is decreasing as the amount of fish sludge increases in the substrate. This is illustrated in Figure 4.9. The pH level will also be reduced when hydraulic retention time is lowered.

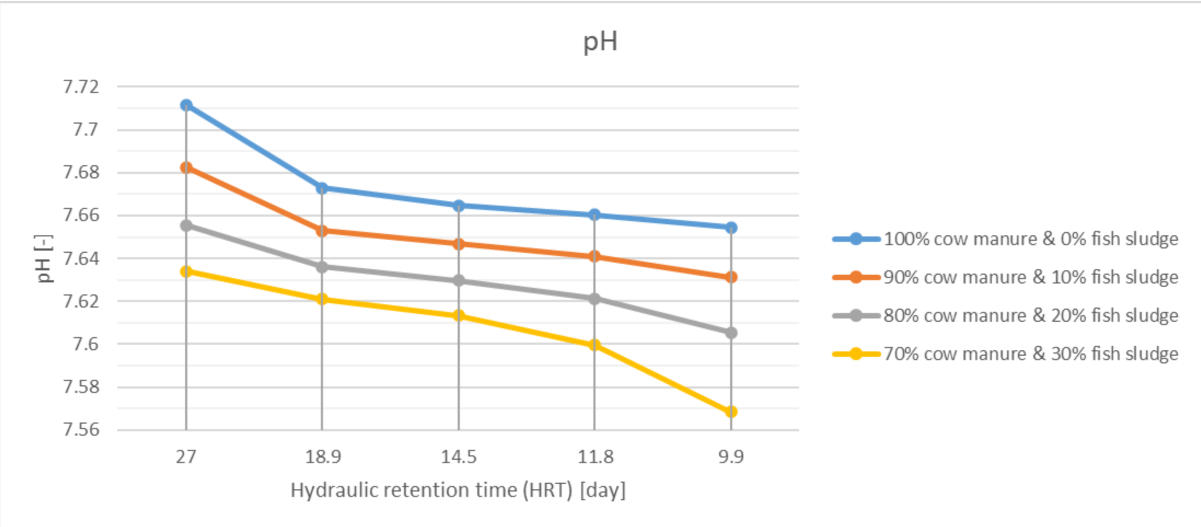


Figure 4.9 pH in bioreactor with varies composition of substrate after 400 days

There is a significant difference in the level of hydrogen sulphide in the biogas with varies composition of the substrate (Figure 4.10). When the substrate is only cow manure, the hydrogen sulphide level is only around 200 ppm. However, already with 10% fish sludge in the substrate, the hydrogen sulphide level is in the range of 5000 to 7000 ppm. The fish sludge is a large contributor to the hydrogen sulphide in the biogas.

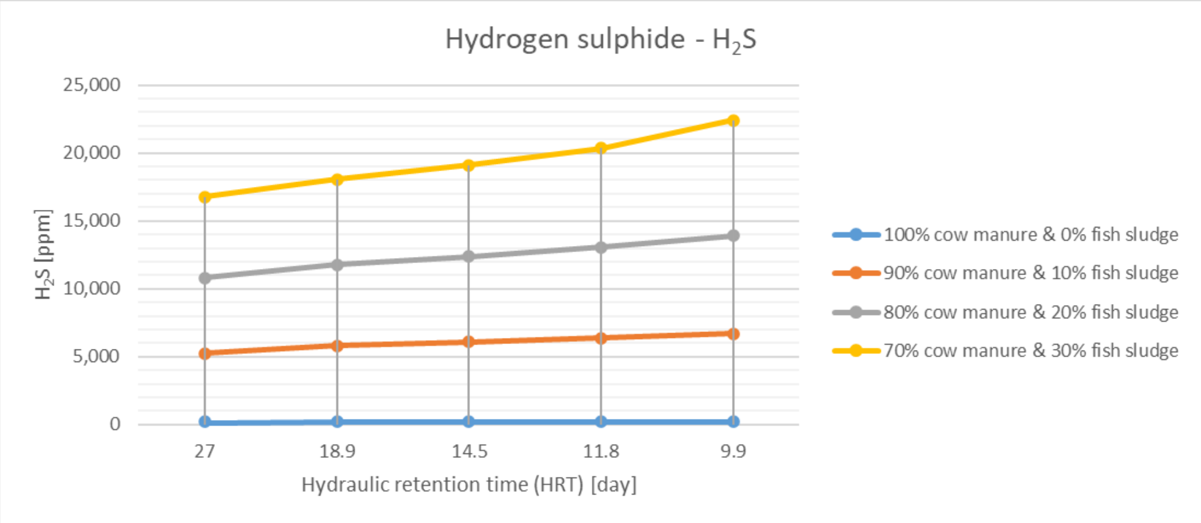


Figure 4.10 Hydrogen sulphide in the biogas with varies composition of substrate after 400 days

The inhibition of NH_3 is between 0.50 and 0.65 during all the simulation cases. From the plot in Figure 4.11, the variation within each composition of substrate has a slightly variation for different HRT. However, the variations in the simulations are in general small.

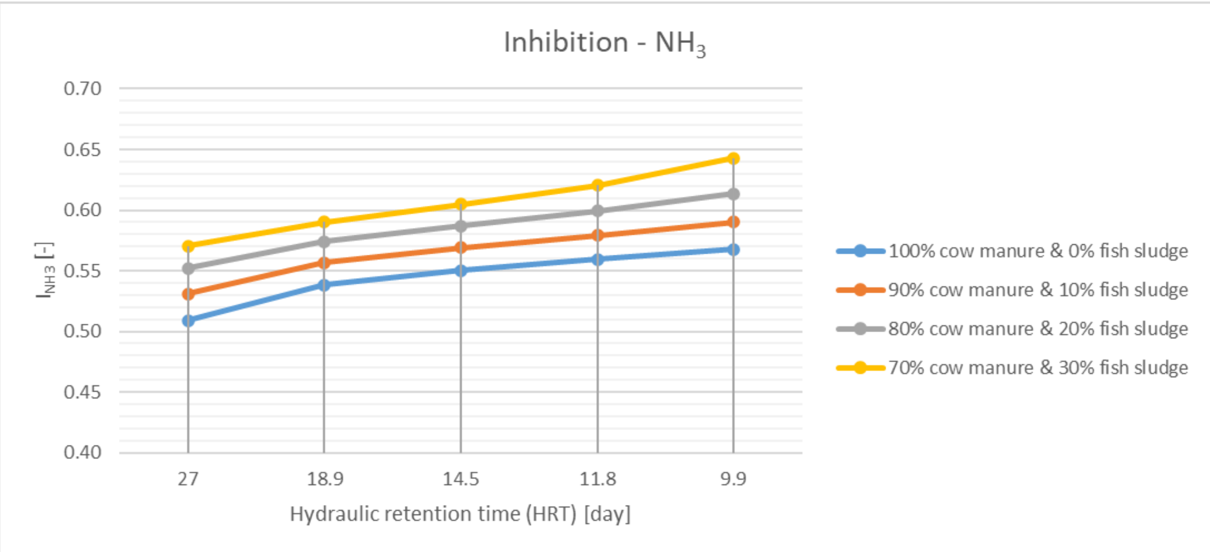


Figure 4.11 Inhibition of NH_3 in the biogas with varies composition of substrate after 400 days

4.2 ADM1 – simulations with added hydrous ferric oxide

Some of the same simulations in chapter 4.2 was re-run with different level hydrous ferric oxide added to the substrate. Hydrous ferric oxide is typically a waste product from waterworks, as mentioned in Chapter 2.8.3. In the simulation it is assumed that the hydrous ferric oxide is monohydrate ($Fe_2O_3 \cdot H_2O$).

The added level of hydrous ferric oxide is calculated based on percentage of TS. The recommended level of hydrous ferric oxide, according to literature, was 0.2% to 0.5% of TS, as discussed in Chapter 2.8.3. However, this was for manure and the simulation in this report is run for 90% cow manure and 10% fish sludge.

4.2.1 ADM1 with added hydrous ferric oxide – estimation

The amount for hydrous ferric oxide to be added was calculated as shown in Equation 4.1.

$$\begin{aligned} &TS\ in\ substrate\ [kg/m^3] \\ &\qquad = \frac{(volume\ of\ substrate * density\ of\ substrate) * \%\,TS}{volume\ of\ substrate} \\ &\qquad = \rho_{substrate} * \%\,TS = 1000 * 7.69\% \ = 76.9\ kg/m^3 \end{aligned} \tag{4.1}$$

Where the density of the substrate is assumed to be approximately 1000 kg/m^3. The percentage TS (7.69%) is for 90% cow manure and 10% fish sludge based on information in Appendix B.

The amount of hydrous ferric oxide is found by Equation 4.2.

$$\begin{aligned} &Ferric\ oxide\ in\ substrate\ [kmol/m^3] \\ &= (TS\ in\ substrate\ [kg/m^3]/molar\ mass\ of\ Fe_2O_3 * H_2O\ [kmol/kg]) \\ &* percentage\ level\ of\ TS = (76.9/117.7) * percentage\ level\ of\ TS \\ &= \ 0.4328 * percentage\ level\ of\ TS \end{aligned} \tag{4.2}$$

In Equation 4.2, it is assumed hydrous ferric oxide (monohydrate) with molar mass of 177.70 kg/kmol.

The percentage level of TS used in simulations are:

- 0.2% (lower range of recommended level with manure, ref Chapter 2.8.3)
- 0.5% (upper range of recommended level with manure, ref Chapter 2.8.3)
- 2.0%

4.2.2 ADM1 with added hydrous ferric oxide – simulation results

From the simulation results in Figure 4.12, the biogas flow does not vary with different level of hydrous ferric oxide in the substrate. There are only negligible changes. The biogas yield has also no variation, because of no change in biogas flow (ref Figure 4.13).

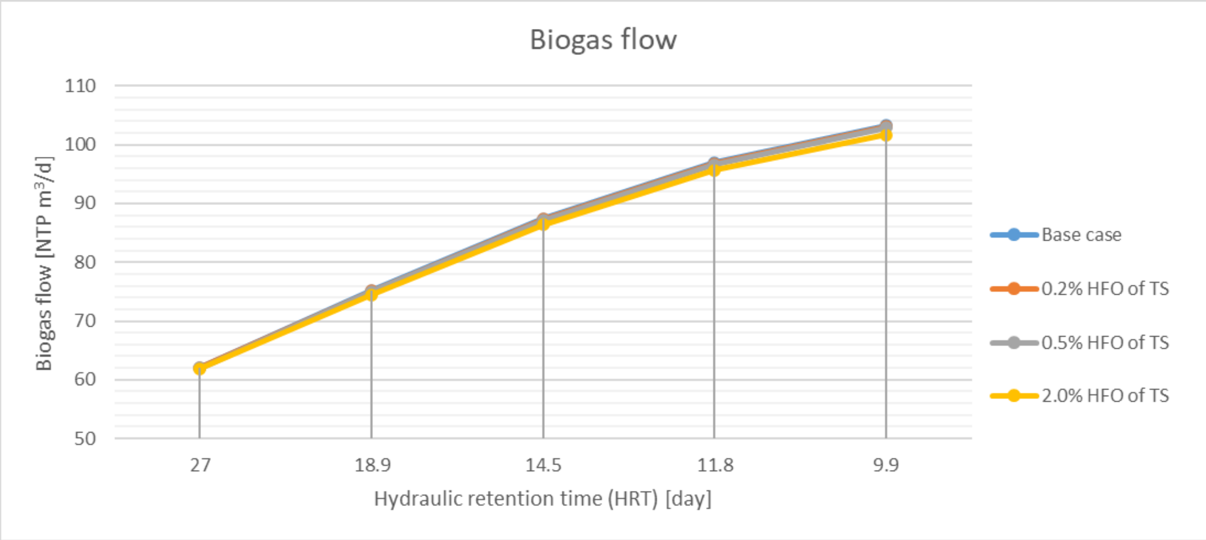


Figure 4.12 Biogas flow with varies level of added hydrous ferric oxide (HFO) after 400 days (90% cow manure and 10% fish sludge)

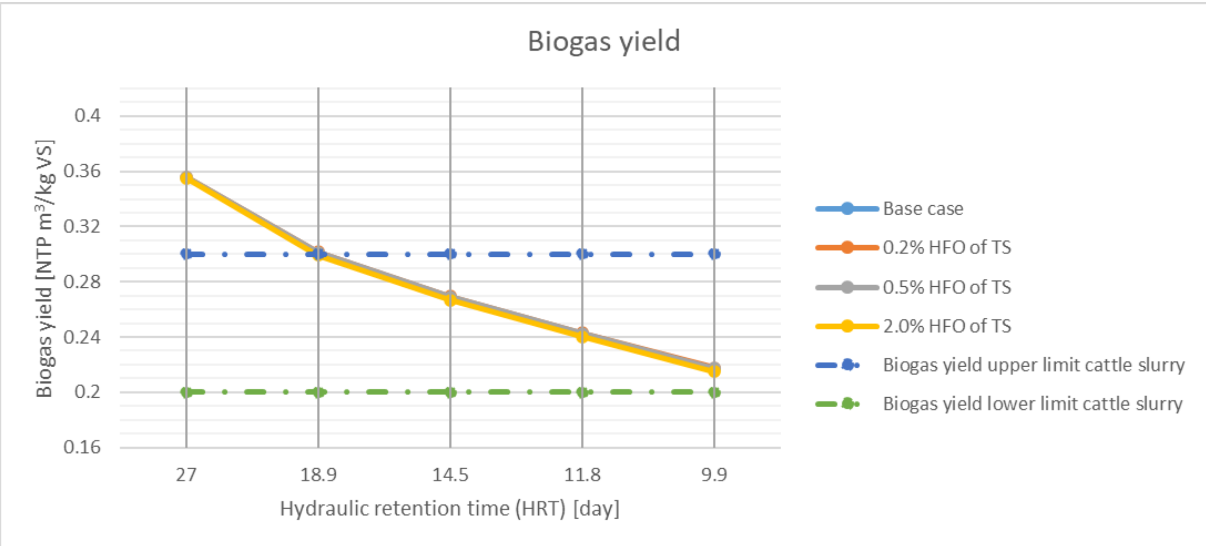


Figure 4.13 Biogas yield with varies level of added hydrous ferric oxide (HFO) after 400 days (90% cow manure and 10% fish sludge)

The methane level increases neglectable for moderate level of hydrous ferric oxide. However, when adding 2% hydrous ferric oxide of TS, the volume percentage of methane is increasing somewhat more (ref Figure 4.14). However, it is not significantly.

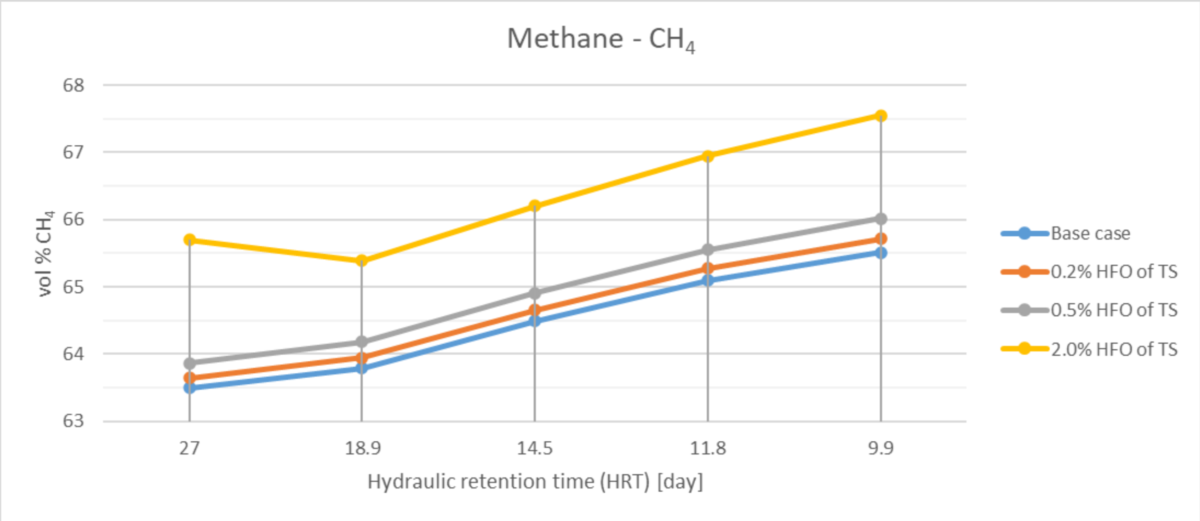


Figure 4.14 Volume percentage of methane in biogas with varies level of added hydrous ferric oxide (HFO) after 400 days (90% cow manure and 10% fish sludge)

The pH level is also maintained at approximately the same level. It is only for 2% hydrous ferric oxide of TS, the pH is slightly increasing as seen in Figure 4.15.

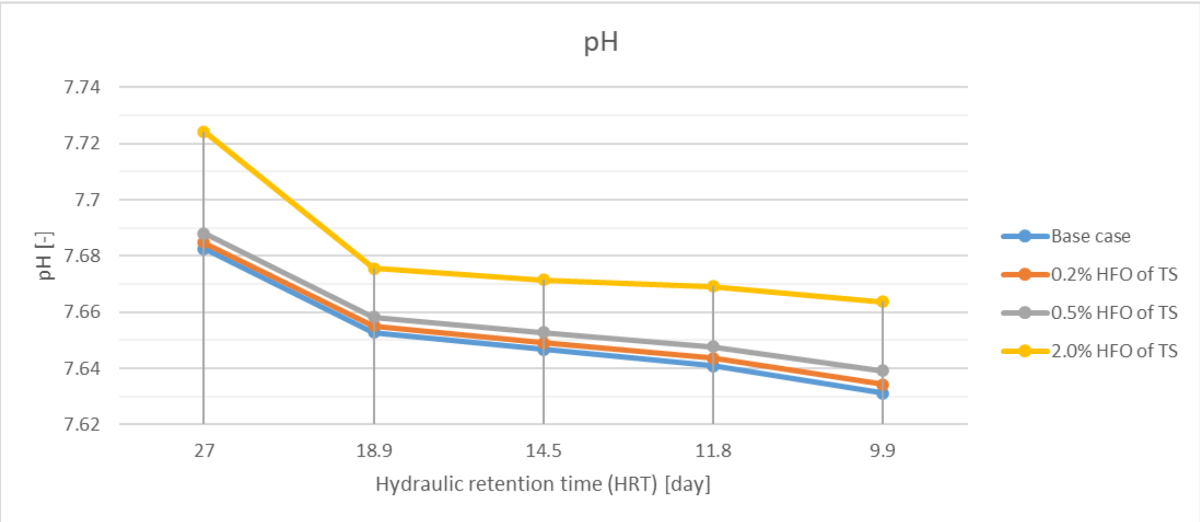


Figure 4.15 pH in bioreactor with varies level of added hydrous ferric oxide (HFO) after 400 days (90% cow manure and 10% fish sludge)

The significantly changes when comparing the results, is for the hydrogen sulphide level in the biogas (ref Figure 4.16). For moderate levels of hydrous ferric oxide added (0.2% and 0.5%), the level of hydrogen sulphide is reduced in the range of 500 to 1000 ppm. However, when increasing the level to 2%, the hydrogen sulphide level is significantly reduced to approximately one tenth of the level. That is, around 500 ppm.

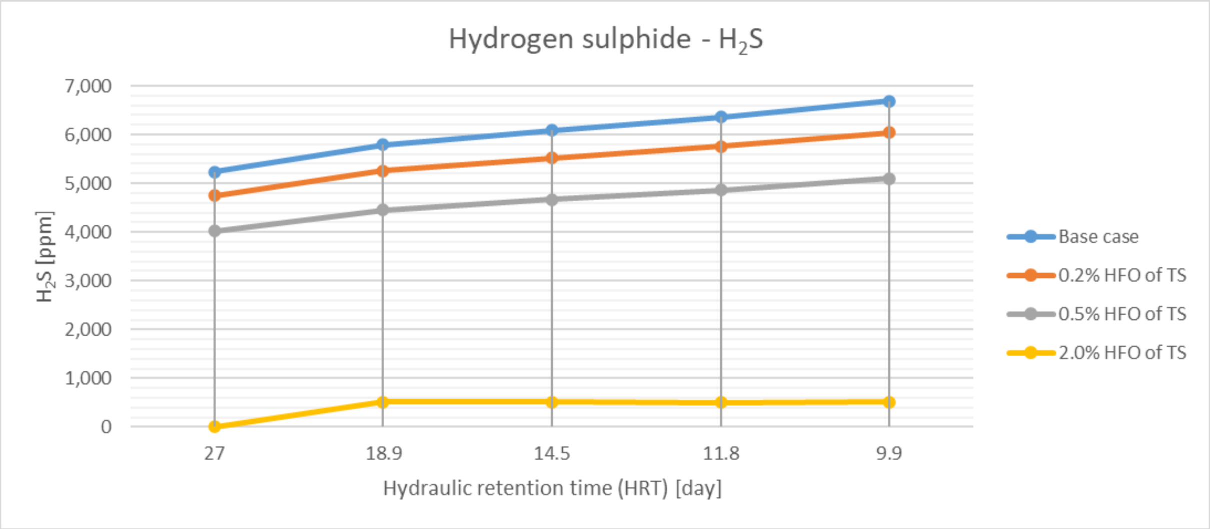


Figure 4.16 Hydrogen sulphide in the biogas with varies level of added hydrous ferric oxide (HFO) after 400 days (90% cow manure and 10% fish sludge)

For the inhibition level of NH_3, there are not significantly changes. Similar for results for pH and volume percentage of methane, only for 2% hydrous ferric oxide of TS the variation is somewhat larger than the rest of the simulated cases.

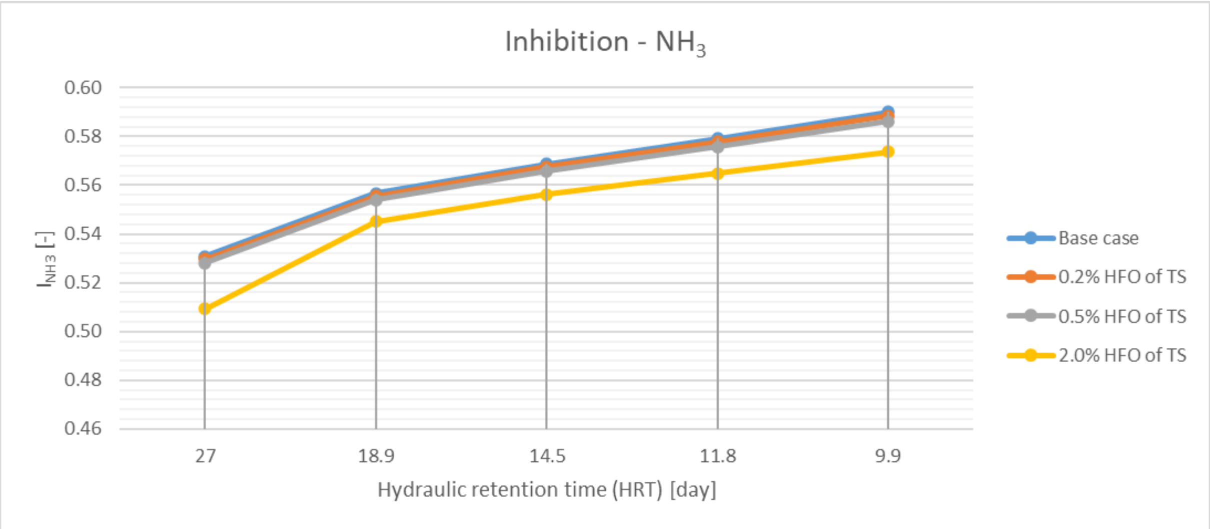


Figure 4.17 Inhibition of NH_3 in the biogas with varies level of added hydrous ferric oxide (HFO) after 400 days (90% cow manure and 10% fish sludge)

The iron ions will react with sulphur and create iron sulphide (FeS) which will precipitate, ref Chapter 2.8.3. As seen in Figure 4.18, the amount of iron sulphide is increasing when adding hydrous ferric oxide.

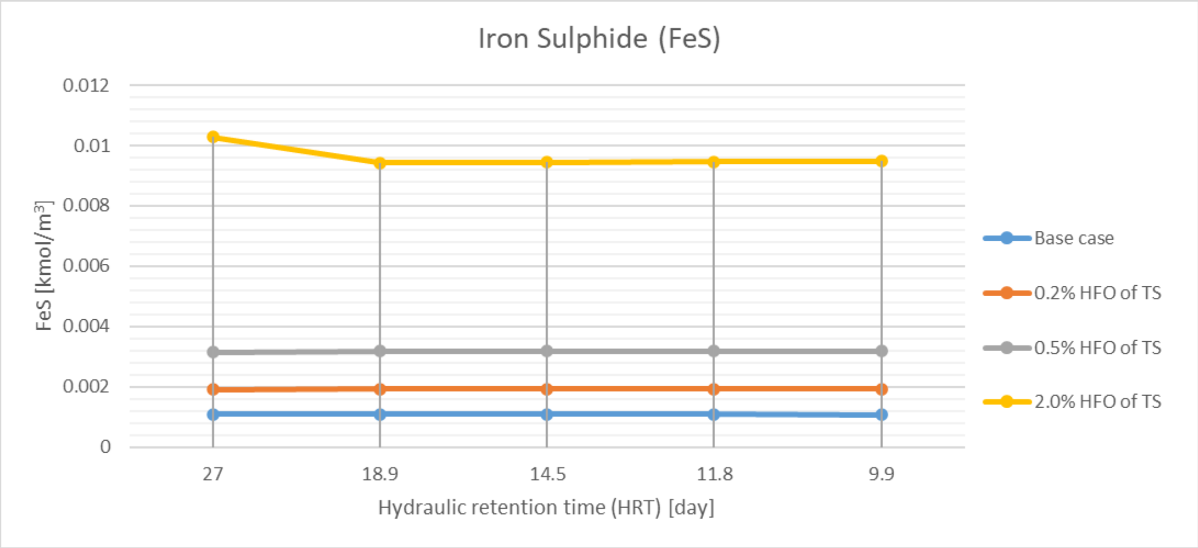


Figure 4.18 Inhibition of NH_3 in the biogas with varies level of added hydrous ferric oxide (HFO) after 400 days (90% cow manure and 10% fish sludge)

4.3 ADM1 – sensitivity of variable and parameter values

For the simulation, it was used values for variables based on evaluation of analysis of substrate and literature. In this chapter it is investigated how sensitive the simulation is for some of the variables. Values for inorganic carbon (S_{IC}) and biodegradable fraction of particulates (BFP) are some of the values looked further into and how it affects the results of the simulations.

4.3.1 Inorganic carbon (S_{IC})

Simulation with 100% cow manure revealed high amount of methane in the biogas, where the range of methane was from 72 to 78% depending on the hydraulic retention time. Typically, the percentage of methane in the biogas for cow manure is in the range of 40-75%, as discussed in Chapter 2.5. For liquid cattle manure it is among other reported a methane yield of 60% [1].

The variable for inorganic carbon (S_{IC}) was adjusted from recommended value of 0.06 to 0.15. This adjustment reduced the amount of methane to approximately the same level as reported in literature. By increasing the value of inorganic carbon (S_{IC}), the amount of CO_2 is increasing in the simulation. That is, due to increase of CO_2, the total amount of biogas increases, and the level of methane is reduced, respectively.

In Figure 4.21 it is compared the volume percentage of methane with variation of the variable S_{IC}. As shown in the plot, an increase of the variable S_{IC} reduce the percentage of methane in the biogas. At the same time, the level of biogas is increased with increased value of S_{IC} as shown in Figure 4.19. From simulation with S_{IC} equal to 0.06 (Figure 4.19), it can be noted that optimum HRT is between 11.8 and 14.5 days regarding biogas flow.

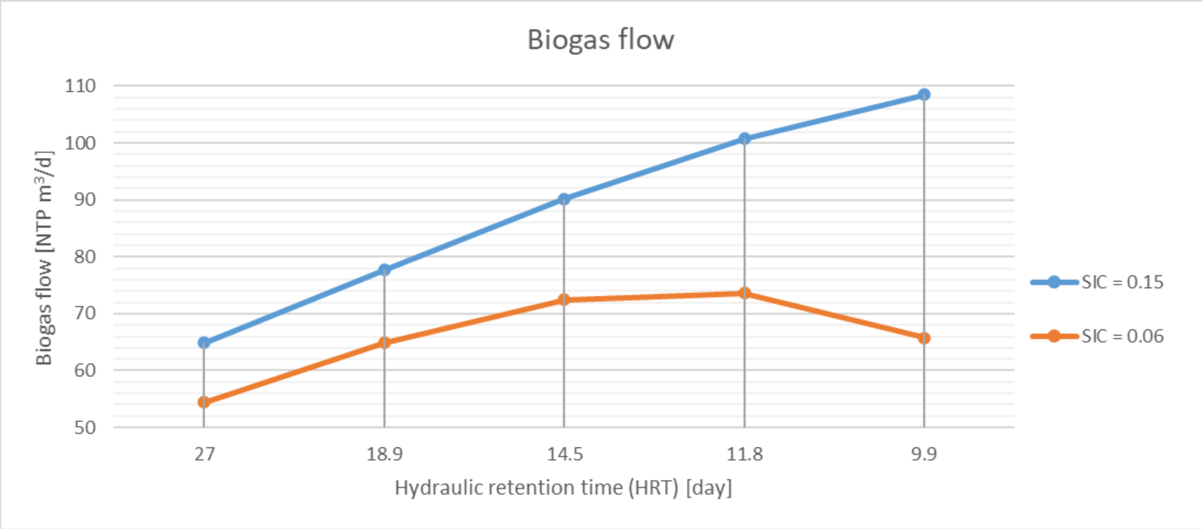


Figure 4.19 Comparison of biogas flow with different S_{IC} (100% cow manure) after 400 days

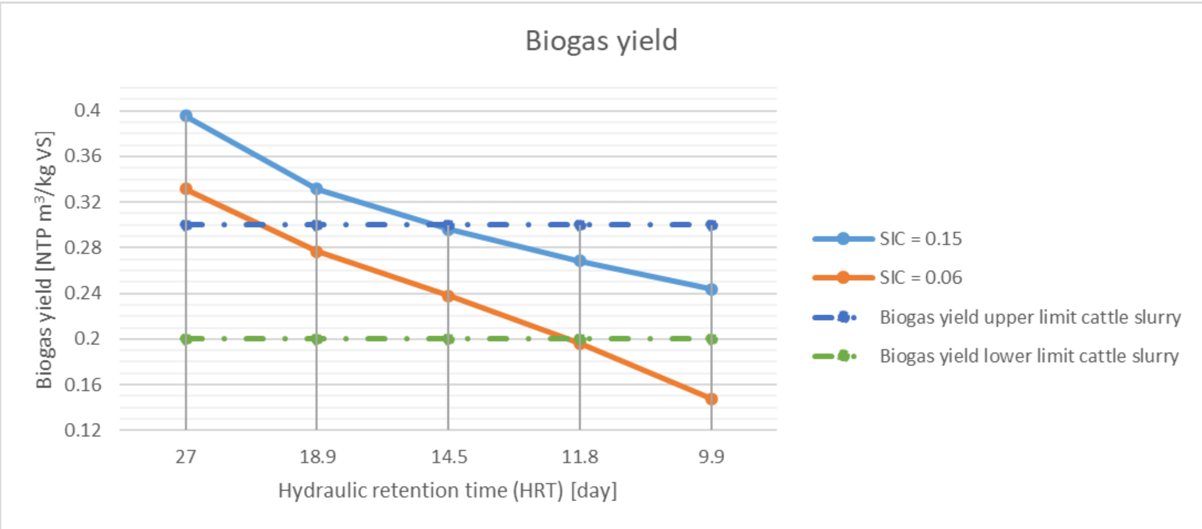


Figure 4.20 Comparison of biogas yield with different S_{IC} (100% cow manure) after 400 days

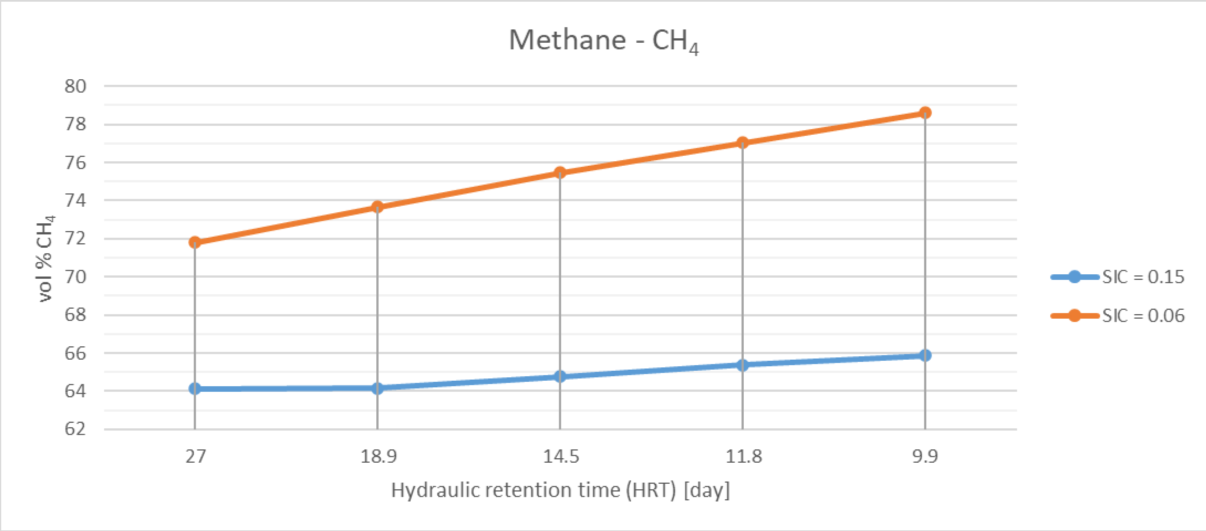


Figure 4.21 Comparison of volume percentage of methane with different values of S_{IC} (100% cow manure) after 400 days

The disadvantages of increasing the variable for inorganic carbon, is that it also affects the pH-level in the digester. The pH level drops somewhat with increasing value of S_{IC}, as shown in Figure 4.22. When the pH decreases, the level of H_2S increases fairly.

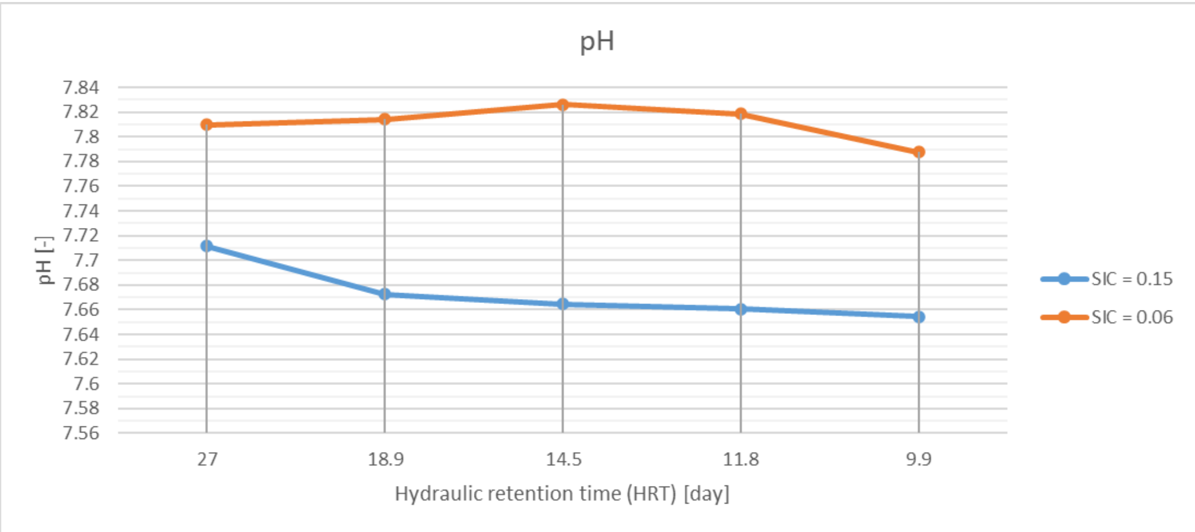


Figure 4.22 Comparison of pH-level with different S_{IC} (100% cow manure) after 400 days

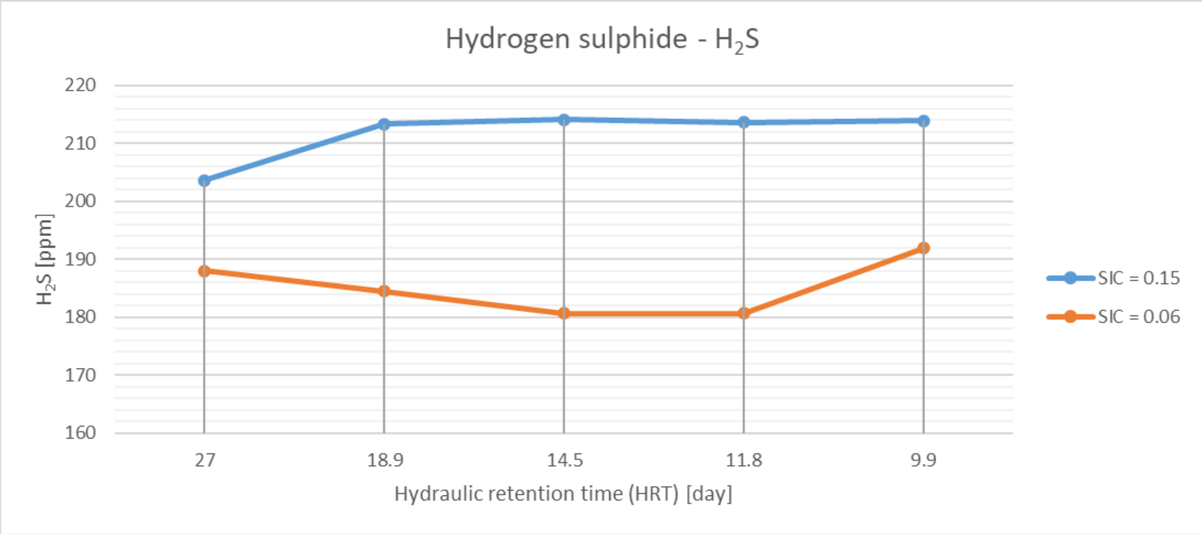


Figure 4.23 Comparison of H2S-level with different S_{IC} (100% cow manure) after 400 days

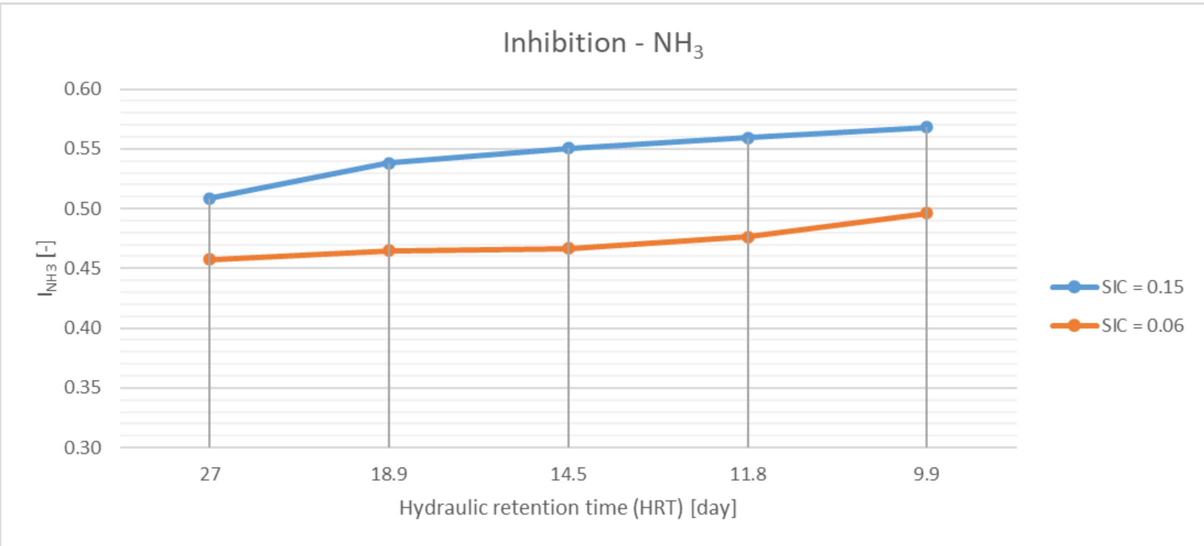


Figure 4.24 Comparison of inhibition-level of NH_3 with different S_{IC} (100% cow manure) after 400 days

By increasing the amount of the inorganic carbon in the simulation, the simulation results agree better with values reported in literature. Without this adjustment, the methane level in the biogas would be considered unrealistic high. An increase of inorganic carbon will have minor effect on the pH level in the digestate, where the change in pH is approximately 2%. However, the hydrogen sulphide level will increase moderately with around 15 to 18%.

For the simulation, it was decided to use S_{IC} equal to 0.15 due to better correlation of methane level in the biogas when compared with values found in literature.

4.3.2 Inorganic sulphur (S_{IS})

The amount of inorganic sulphur of total sulphur was assumed to be 20%, as discussed in Chapter 2.6.2 and Chapter 3.2.3. The sensitivity of this variable was investigated by running simulation with 15% and 25% of total sulphur, respectively. The substrate used in the simulation is 90% cow manure and 10% fish sludge with different loading rate.

As showed in Figure 4.25, the amount of biogas remains the same for all case. That is, the variable does not affect the biogas flow and the biogas yield will be similar (ref Figure 4.26).

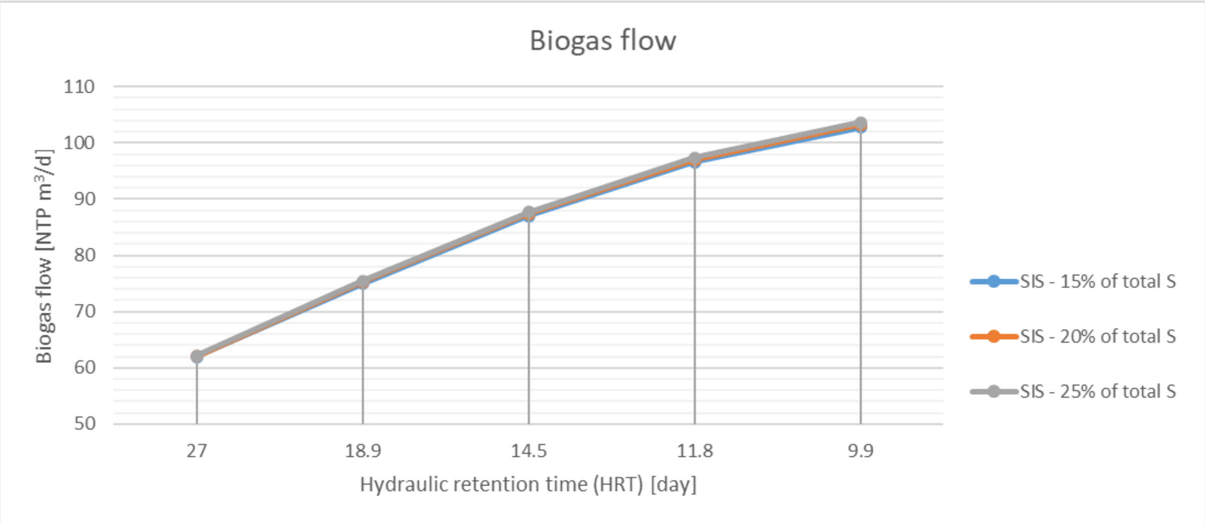


Figure 4.25 Comparison of biogas flow with different S_{IS}

(90% cow manure and 10% fish sludge) after 400 days

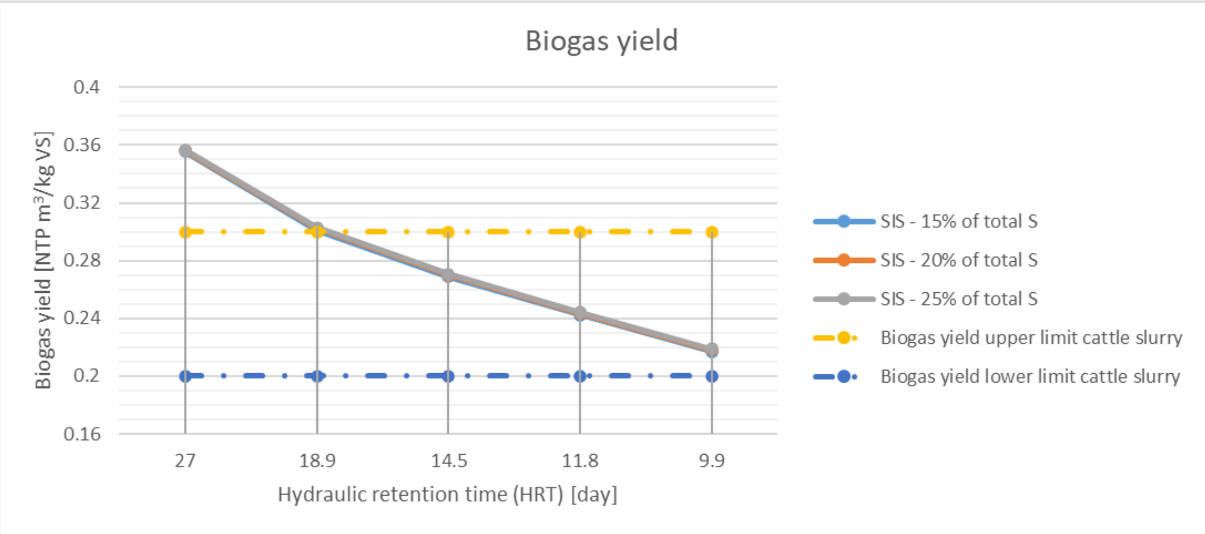


Figure 4.26 Comparison of biogas yield with different S_{IS}

(90% cow manure and 10% fish sludge) after 400 days

The composition of the biogas varies somewhat. From Figure 4.27 and Figure 4.29 it can be observed that the volume percentage of methane and the amount of hydrogen sulphide varies with the change of value of the variable S_{IS}. A change in inorganic sulphur from 20% (base case) to 15% or 25% of total sulphur, involves a change of hydrogen sulphide with approx. ± 30%. The variable for inorganic sulphur, S_{IS}, has an important impact on the amount of hydrogen sulphide in the biogas.

Like other investigated cases, there is a correlation between pH and the amount of hydrogen sulphide (ref Figure 4.29 and Figure 4.28). That is, the amount of hydrogen sulphide is lower when the pH is higher.

The inhibition level of NH_3 remain similar to the value of the base case (20% of total sulphur), as shown in plot in Figure 4.30.

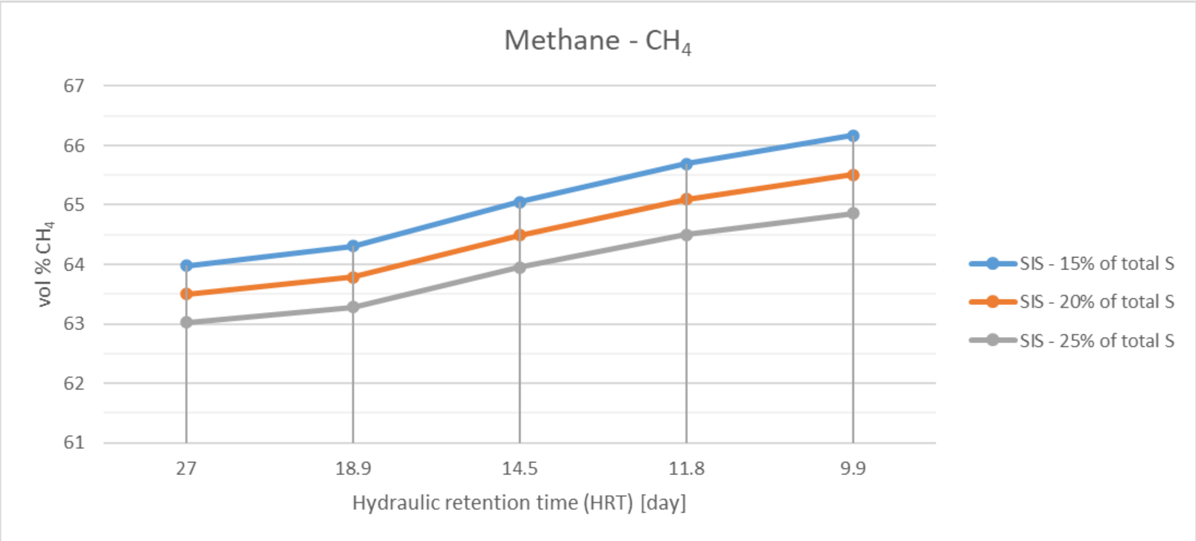


Figure 4.27 Comparison of volume percentage of methane with different values of S_{IS}

(90% cow manure and 10% fish sludge) after 400 days

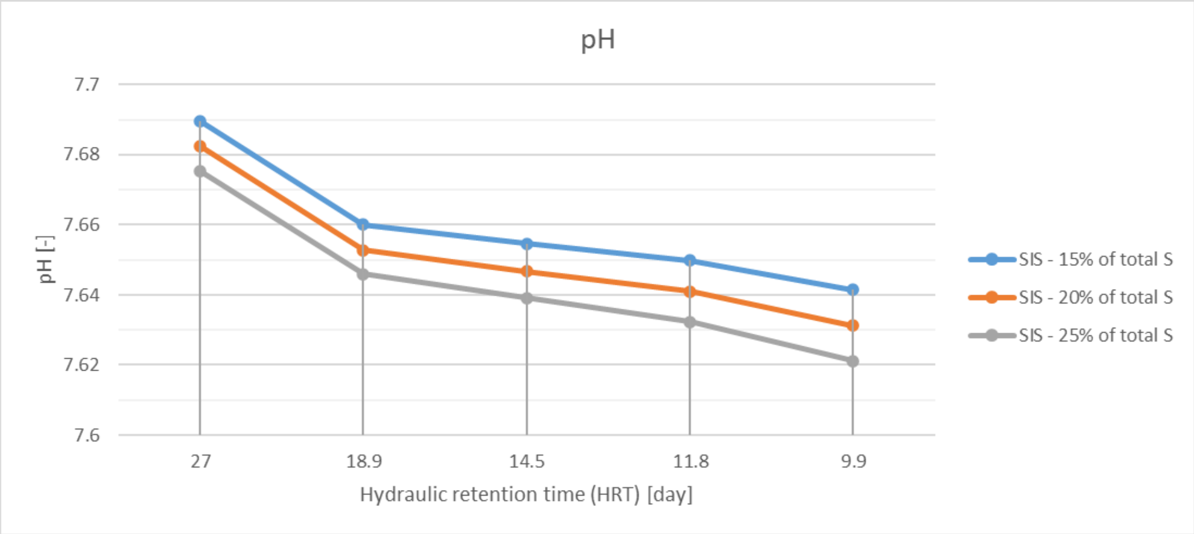


Figure 4.28 Comparison of pH-level with different S_{IS}
(90% cow manure and 10% fish sludge) after 400 days

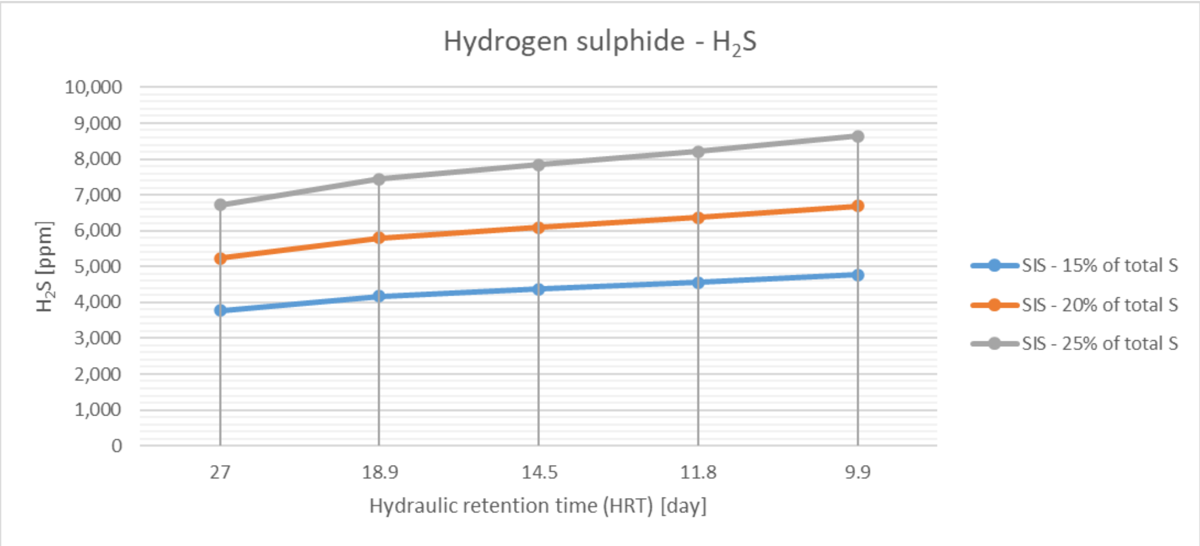


Figure 4.29 Comparison of H_2S-level with different S_{IS}
(90% cow manure and 10% fish sludge) after 400 days

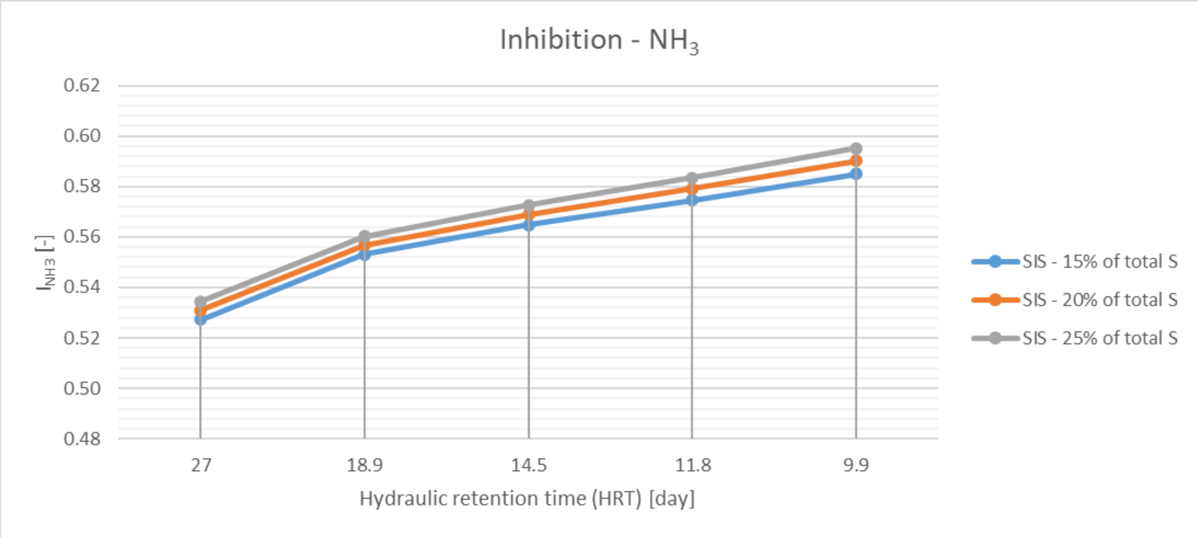


Figure 4.30 Comparison of inhibition-level of NH_3 with different S_{IS} (90% cow manure and 10% fish sludge) after 400 days

4.3.3 Biodegradable Fraction of Particulates (BFP)

The variable biodegradable fraction of particulates (BFP) is used to estimate the variables X_{pr}, X_{li} and X_{ch}, as discussed in Chapter 3.2.2. For the base case it is used a value of 40% (BFP = 0.40). Further it was investigated how sensitive results from simulation is to changes of BFP. It was run additional simulation with BFP equal to 0.50, 0.30, and 0.20, respectively. The values of the variables X_{pr}, X_{li} and X_{ch} were recalculated based on formulas in Table 3.5. From plots in figures below, it can be seen small changes when varying the BFP. That is, values used for BFP has low impact and BFP equal to 0.40 seems reasonable to use.

For the biogas flow, the difference between BFP of 20% and 50% are largest at low HRT, reference Figure 4.31. In general, the differences are small and the BFP is considered to have a small impact on the biogas flow simulation.

All the plots below are simulation with 90% cow manure and 10% fish sludge.

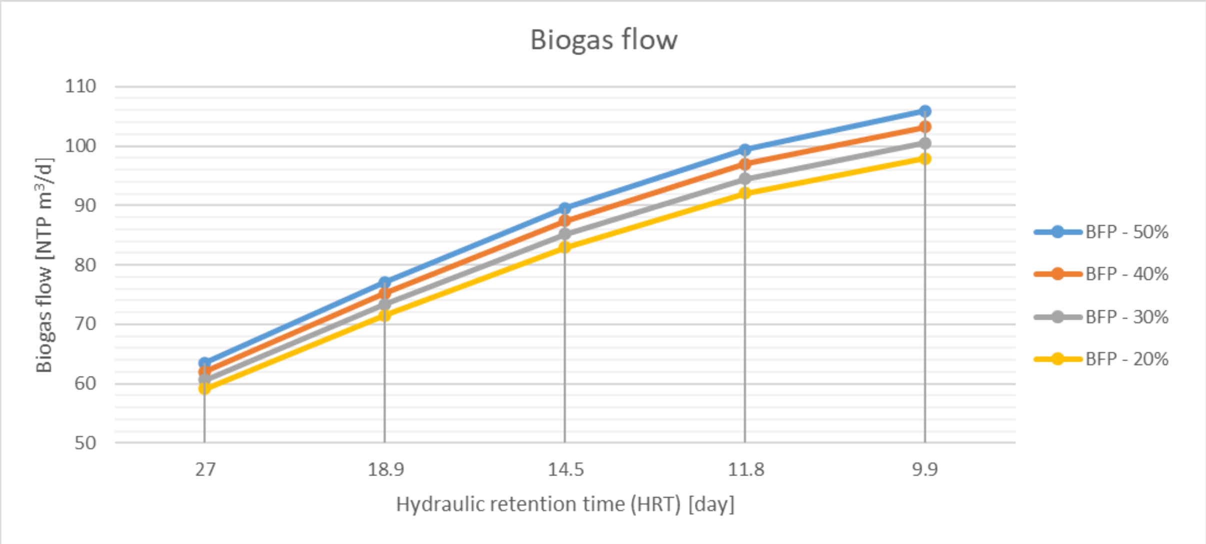


Figure 4.31 Comparison of biogas flow with different

BFP (90% cow manure and 10% fish sludge) after 400 days

Simular to the biogas flow, the biogas yield and volume percentage of methane have small variation with different values for BFP. In Figure 4.32 the biogas yield is plotted and there is small differences. Similar in Figure 4.33 for the plot of volume percentage of methane.

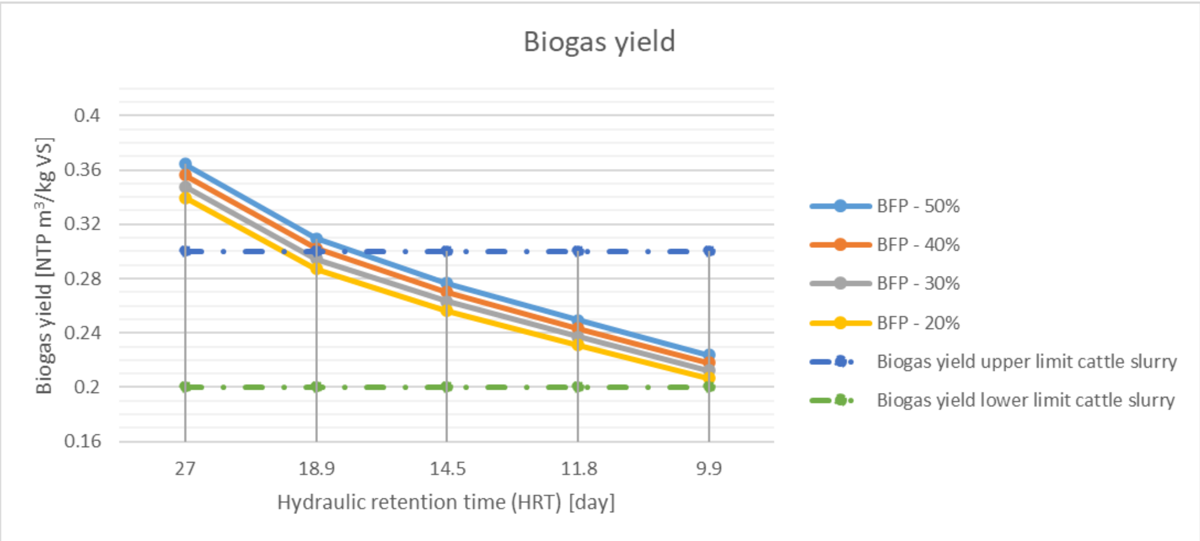


Figure 4.32 Comparison of biogas yield with different

BFP (90% cow manure and 10% fish sludge) after 400 days

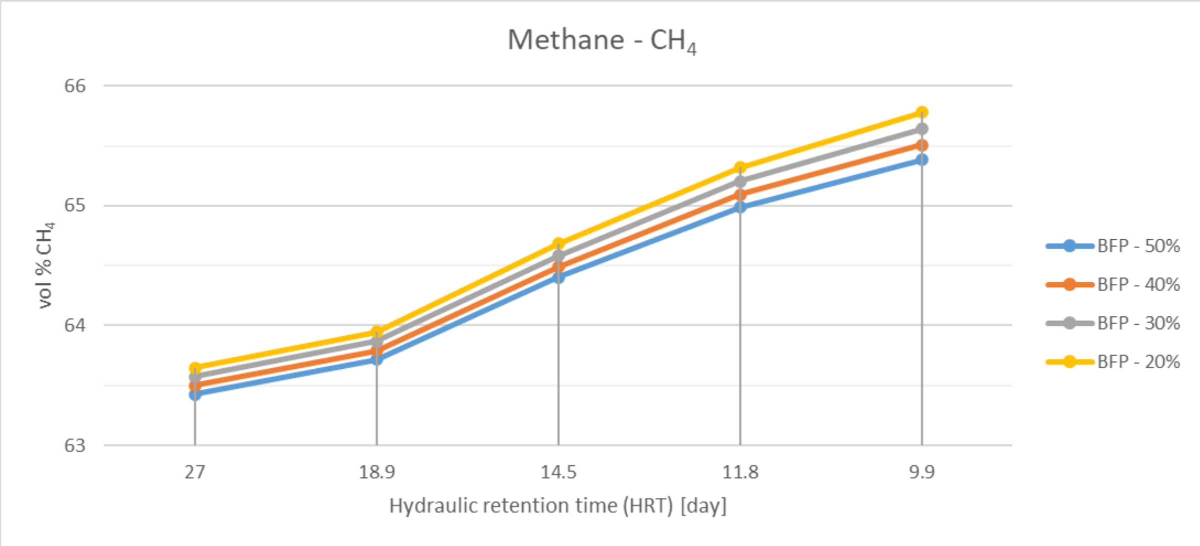


Figure 4.33 Comparison of volume percentage of methane with different values of BFP (90% cow manure and 10% fish sludge)

The variation of BFP has also a low impact on the hydrogen sulphide (H_2S) and pH. In general, the pH varies little for different HRT and BFP-levels, as plot in Figure 4.34 shows. There is some more variation of hydrogen sulphide, as shown in Figure 4.35. Still, the differences are considered small.

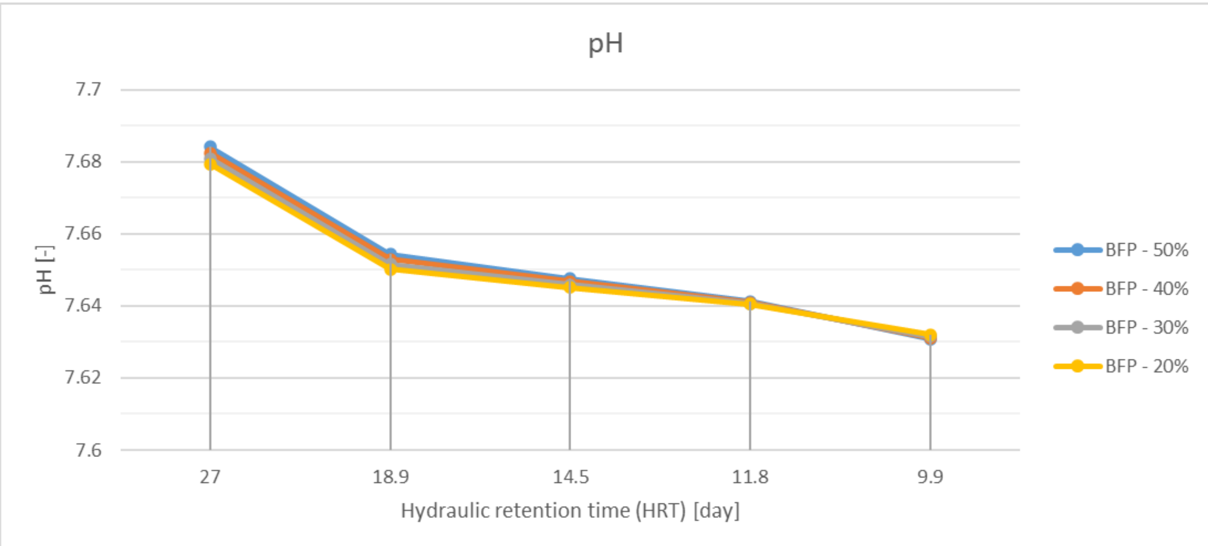


Figure 4.34 Comparison of pH-level with different BFP (90% cow manure and 10% fish sludge) after 400 days

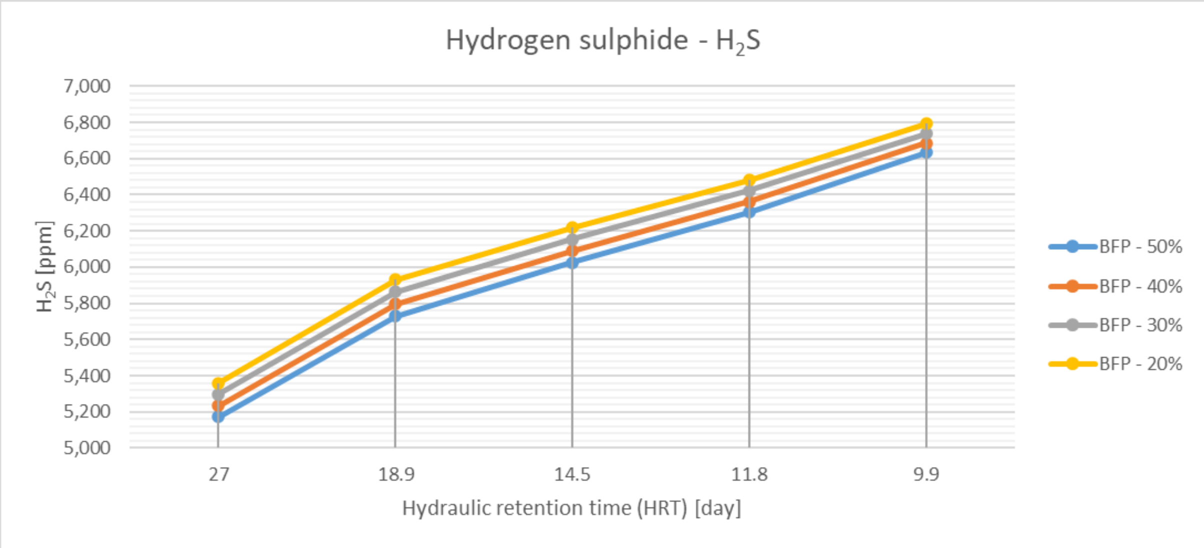


Figure 4.35 Comparison of H_2S-level with different
BFP (90% cow manure and 10% fish sludge) after 400 days

The inhibition of NH_3 have small variations from the base case where BFP equal 40% is used. The results from the simulations are plotted in Figure 4.36.

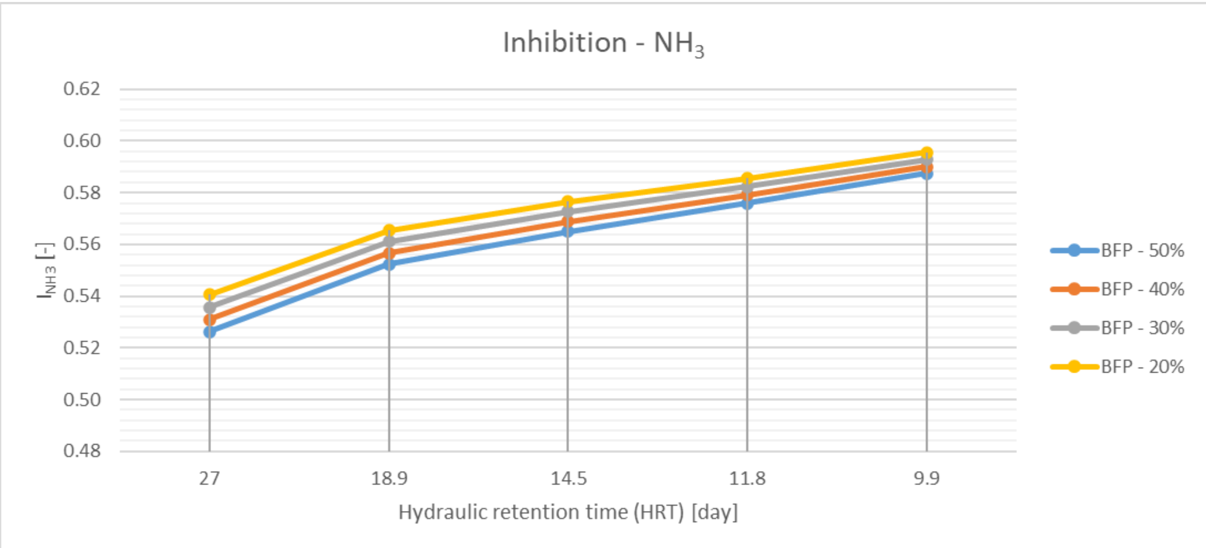


Figure 4.36 Comparison of inhibition-level of NH_3 with different
BFP (90% cow manure and 10% fish sludge) after 400 days

4.3.4 Inhibition coefficient for NH_3 ($K_{i,NH3}$)

The inhibition coefficient for NH_3 can vary as discussed in Chapter 2.3.2. Default value in ADM1 is 0.0018 M, while for the simulation in this report is using a value equal to 0.0223 M. The latter value is recommended to use in combination with the rest of the parameters for cow manure, according to literature [53]. As shown in Figure 4.37 to Figure 4.42, the value of this parameter has a great impact on the simulation results.

A decrease of the value of the inhibition coefficient for NH_3 reduce the biogas flow and biogas yield significantly. Especially at low hydraulic retention time as shown in Figure 4.37 and Figure 4.38. It can also be seen from the plots that there are no values for all the simulated cases. These cases with no value are:

- 80% cow manure and 20% fish sludge at HRT=9.9
- 70% cow manure and 30% fish sludge at HRT=11.8
- 70% cow manure and 30% fish sludge at HRT=9.9

The ADM1 did not found any solution for these cases and are therefore not represented in the plots. A further discussion for these cases later in this chapter.

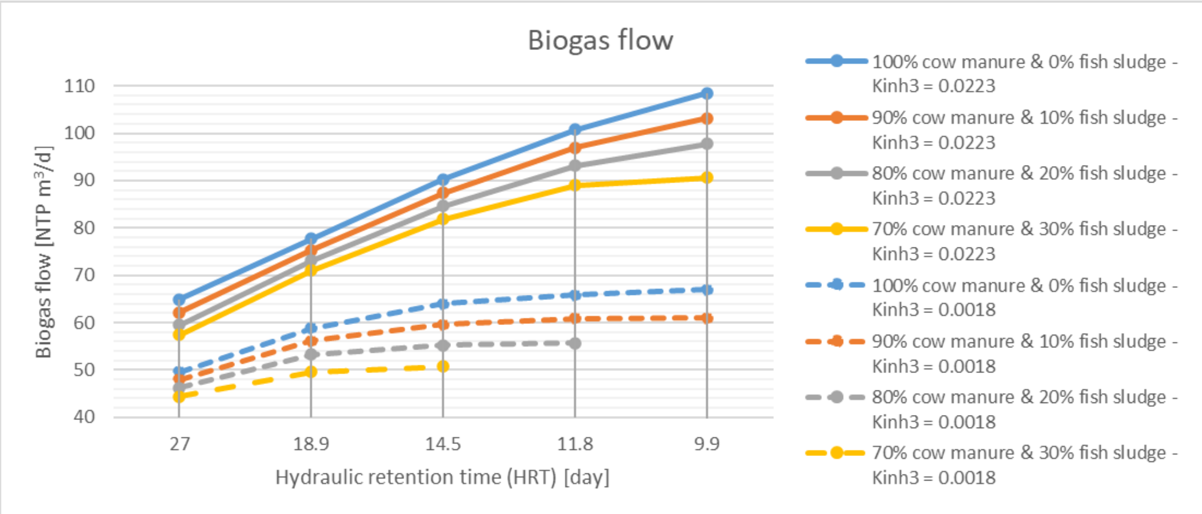


Figure 4.37 Comparison of biogas flow with different value of $K_{i,NH3}$ after 400 days

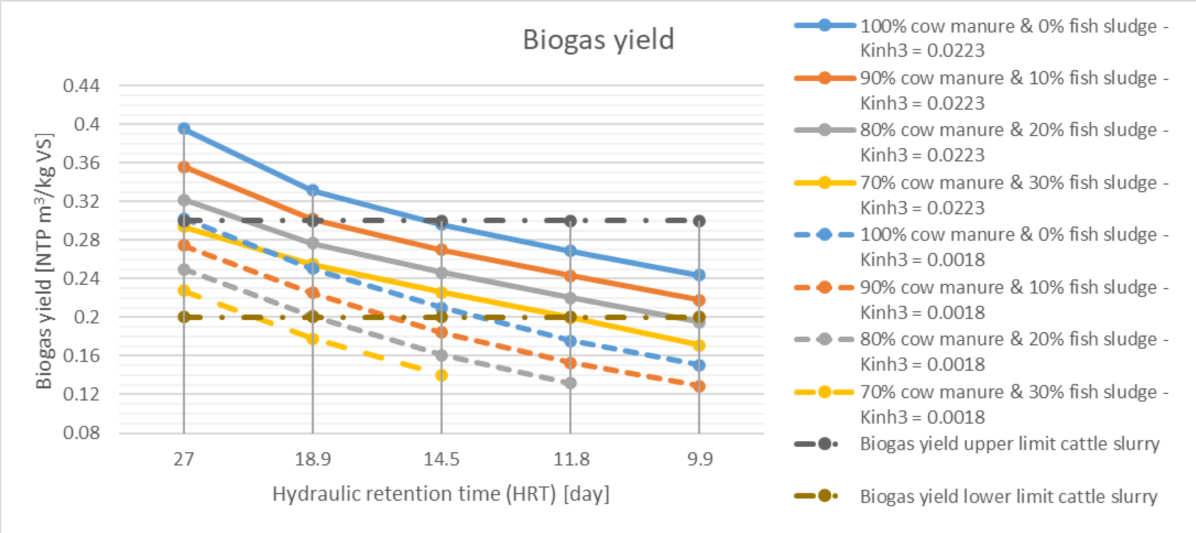


Figure 4.38 Comparison of biogas yield with different value of $K_{i,NH3}$ after 400 days

Similar with biogas flow, the volume percentage of methane in the biogas is also decreasing, as seen in Figure 4.39. From being approximately constant around 65% methane for $K_{i,NH3}$ equal to 0.0223, the methane percentage is dropping below 50% for several cases for $K_{i,NH3}$ equal to 0.0018.

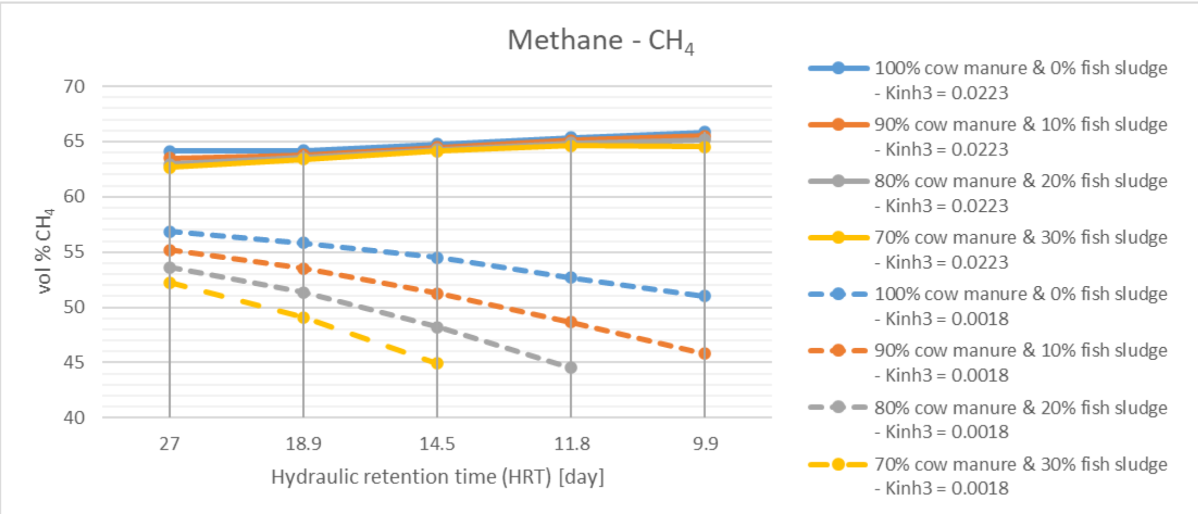


Figure 4.39 Comparison of volume percentage of methane with different value of $K_{i,NH3}$ after 400 days

The pH is varying more and also drops below pH equal to 7 for the cases with $K_{i,NH3}$ equal to 0.0018. For cases with $K_{i,NH3}$ equal to 0.022, the pH could be considered to be more or less constant for all the simulated cases as seen in Figure 4.40.

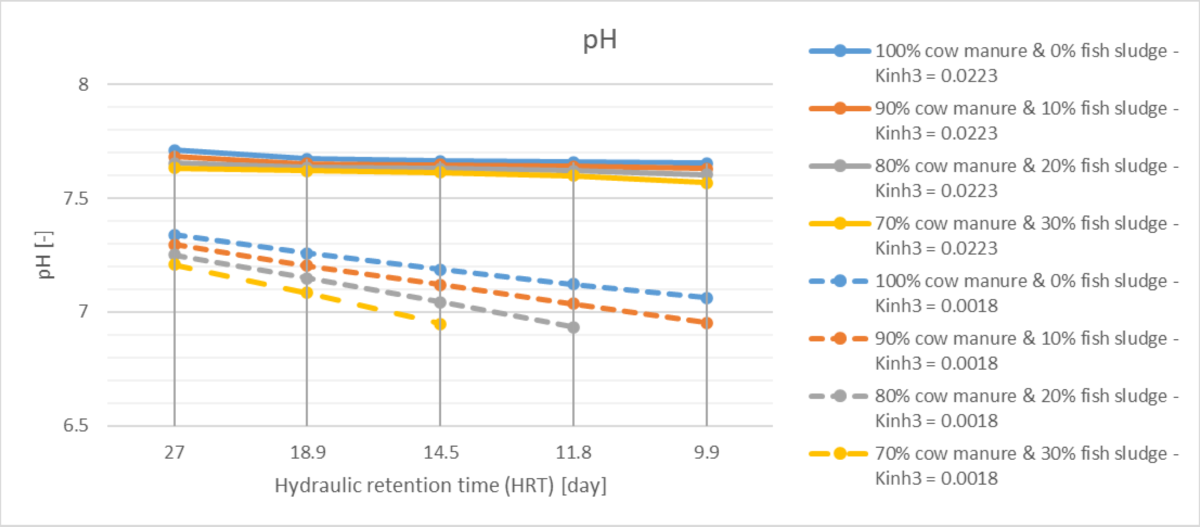


Figure 4.40 Comparison of pH-level with different value of $K_{i,NH3}$ after 400 days

The simulated results of level of hydrogen sulphide (H_2S) in the biogas, is for substrates composition unrealistic high. This is especially for $K_{i,NH3}$ equal to 0.0018 for substrate with 70% cow manure and 30% fish sludge, as illustrated in Figure 4.41. Also, for the most of the simulated cases with 80% cow manure and 20% fish sludge gives very high level of hydrogen sulphide. In general, by using $K_{i,NH3}$ equal to 0.0018 gives significantly higher levels of hydrogen sulphide in the biogas. The exception is for 100% cow manure where the difference is small when comparing the results (ref Figure 4.41).

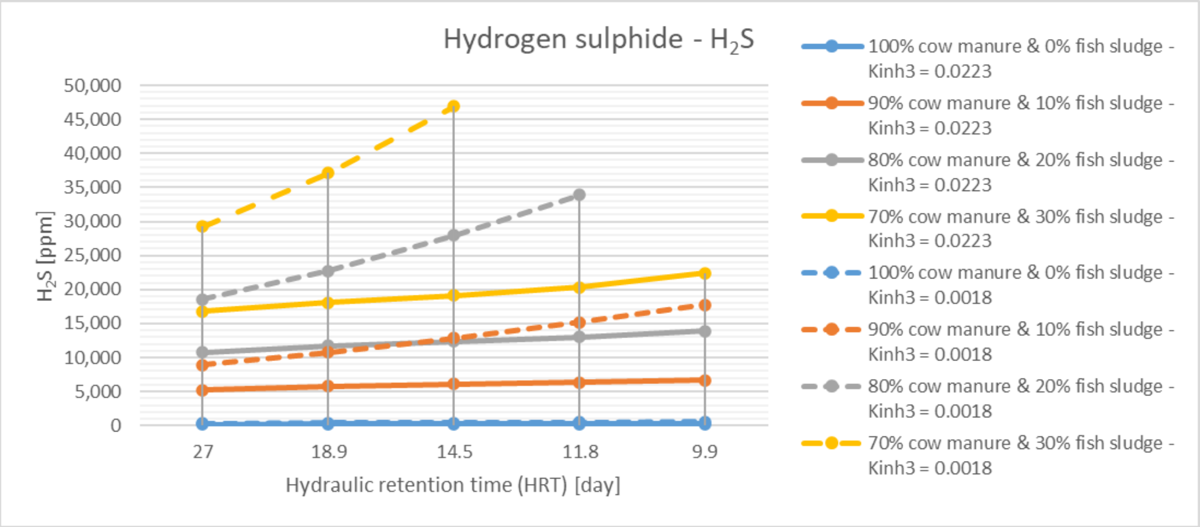


Figure 4.41 Comparison of H_2S-level with different value of $K_{i,NH3}$ after 400 days

Similar for other results, the inhibition-level of NH_3 is also varying when running simulation with different value for $K_{i,NH3}$. In general, the inhibition-level of NH_3 for $K_{i,NH3}$ equal to 0.0018 is approximately half of the level for $K_{i,NH3}$ equal to 0.022 (ref Figure 4.42).

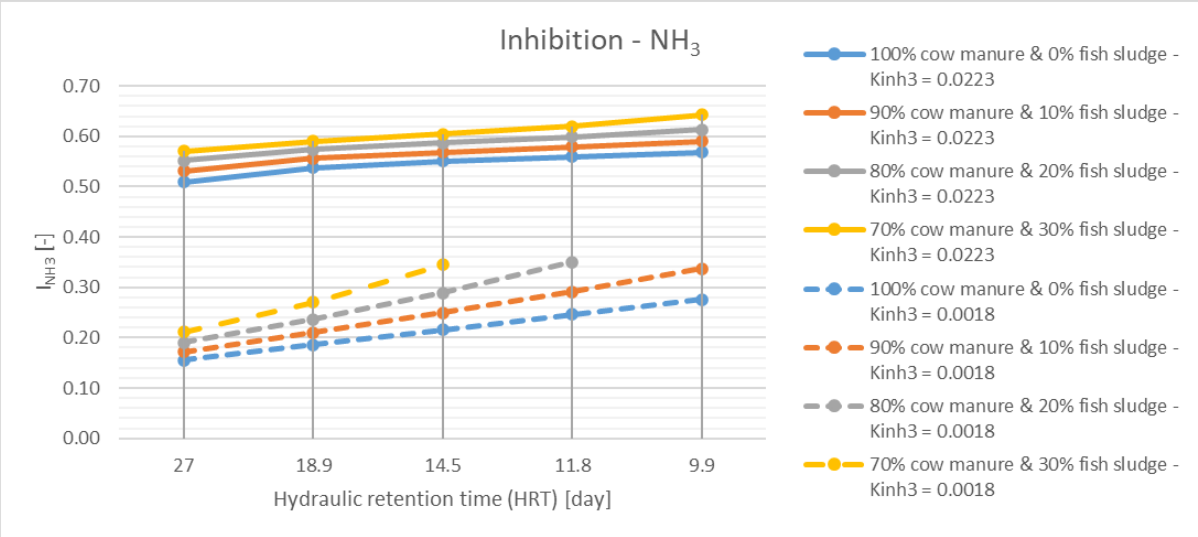


Figure 4.42 Comparison of inhibition-level of NH_3 with different value of $K_{i,NH3}$ after 400 days

As mentioned in the beginning of the chapter, some simulation cases did not give any solution. One of the cases was 70% cow manure and 30% fish sludge with HRT equal to 11.8 days. The simulations fail after 223 days, as shown in Figure 4.43.

The pH and the methane level in the biogas have similar behaviour as for the biogas flow, as seen in Figure 4.44 and Figure 4.45. However, it is the opposite is for the hydrogen sulphide (ref Figure 4.46) and inhibition level of NH_3 (ref Figure 4.47). The level of hydrogen sulphide and inhibition level of NH_3 is increasing due to a decrease in pH. This is expected when equilibrium equations for hydrogen sulphide and ammonia is considered (ref Figure 2.9 and Figure 2.12).

In Chapter 2.3.4 it was discussed the range of pH and the recommended range was between 6.3 and 8.3. When comparing with Figure 4.44, the pH level is not within the recommended range. The pH in the simulation is 6.16 at the end of the simulation when it is failing.

Due to low pH, the methanogenic bacteria will inhibit and there will be a low methane level in the biogas. However, as seen from the Figure 4.44 there a still some generation of methane. There are two methods of generating methane in the reactor, as mentioned in Chapter 2.1.5 and Figure 2.11. In this case, the methane is probably mainly generated from hydrogen and carbon dioxide by hydrogenotrophic methanogens and not acetate and acetolactic methanogens. However, this must be further investigated.

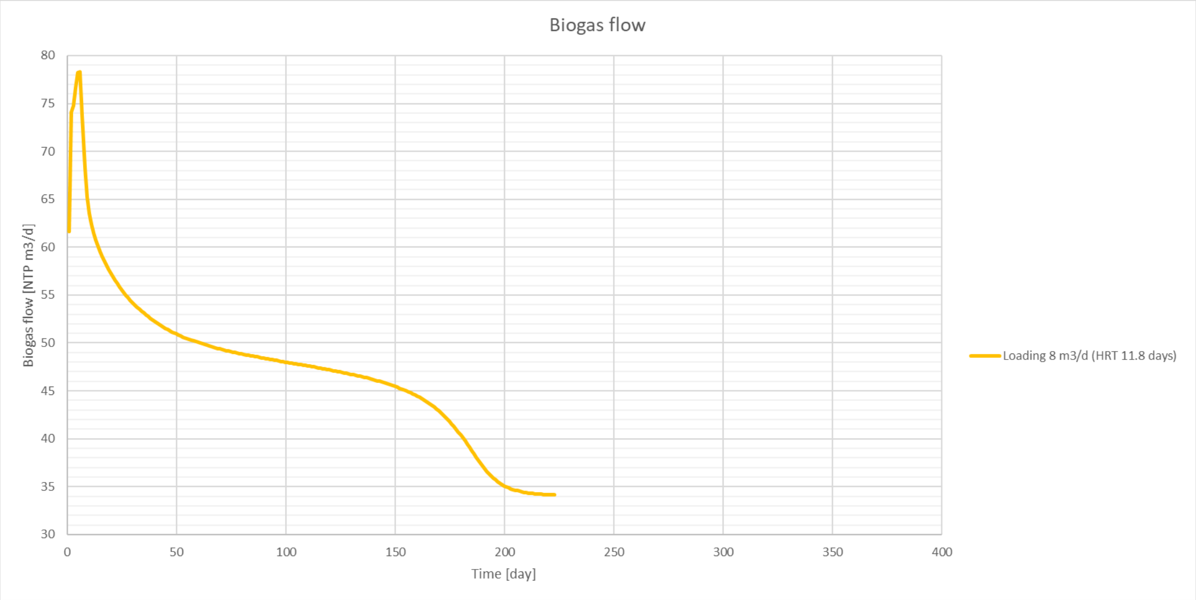


Figure 4.43 Biogas flow with $K_{i,NH3}$ = 0.0018 (70% cow manure and 10% fish sludge)

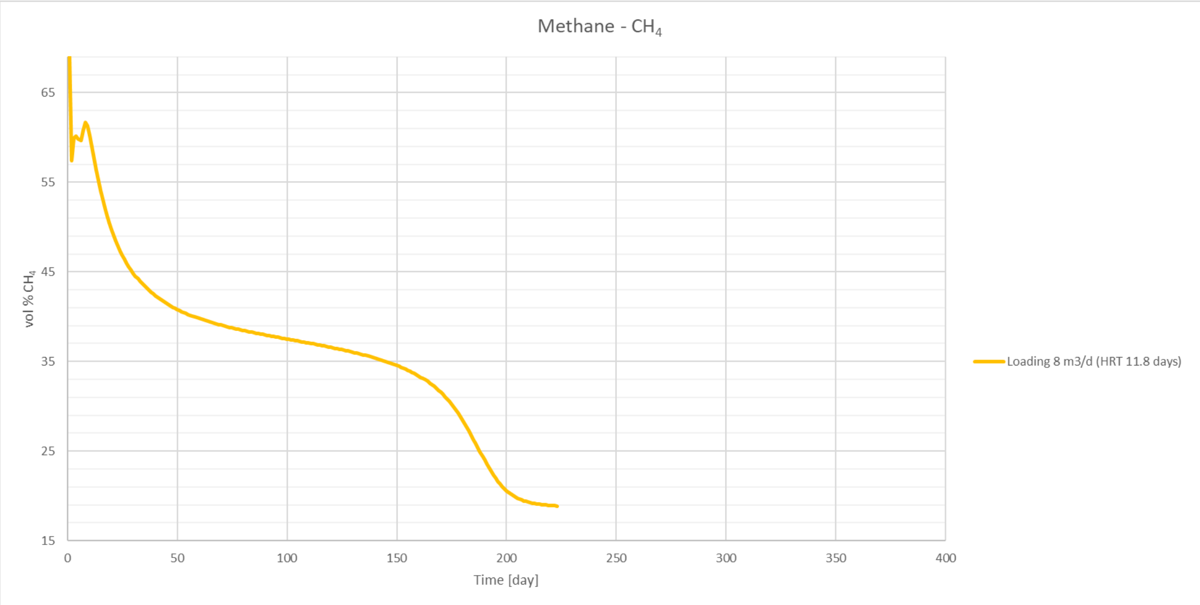


Figure 4.44 Volume percentage of methane with $K_{i,NH3}$ = 0.0018 (70% cow manure and 10% fish sludge)

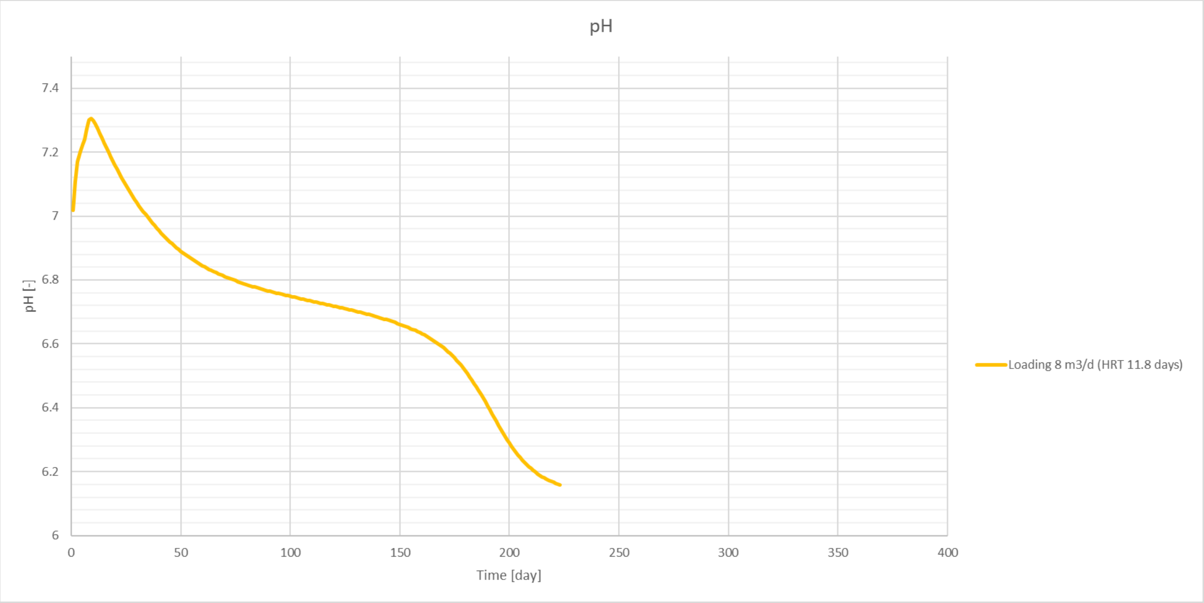


Figure 4.45 pH-level with $K_{i,NH3} = 0.0018$ (70% cow manure and 10% fish sludge)

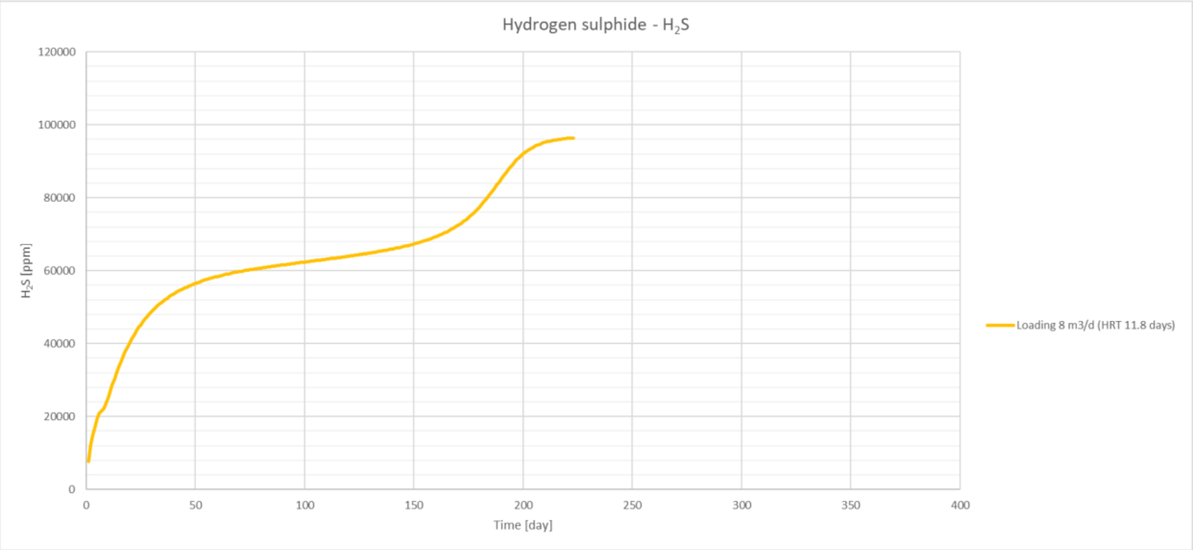


Figure 4.46 H_2S-level with $K_{i,NH3} = 0.0018$ (70% cow manure and 10% fish sludge)

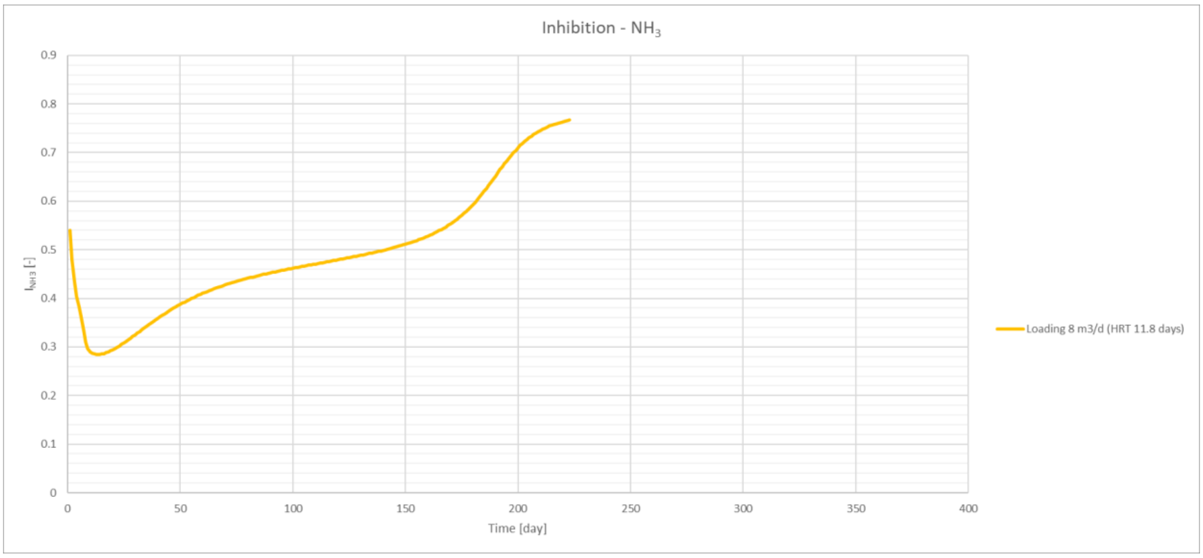


Figure 4.47 Inhibition-level of NH_3 with $K_{i,NH3}$ = 0.0018 (70% cow manure and 10% fish sludge)

5 Discussion

Findings in literature and by simulations with ADM1 shows that there are different methods to reduce the risk regarding use of substrate rich in nitrogen and sulphur. The concern regarding substrate rich in nitrogen is mainly because of inhibition of the digester due to excess of ammonia in the bioreactor. While excess of sulphur is mainly affecting the quality of the biogas and the need of conditioning the biogas before utilising it to for example heating purpose or fuel for vehicles.

5.1 Discussion of simulation results

Several simulations have been run with different substrate content of cow manure and fish sludge in ADM1. The ADM1 version used is an extension from the original ADM1 and where it also accounts for phosphorous, sulphur and iron interactions. A base case has been established based on recommended values for cow manure and fish sludge found in literature. Some values have also been estimated based on suggestion in literature. For the base case, it has been run simulations with different fraction of fish sludge in the substrate and with different hydraulic retention time. It has also been run simulation where some variables values are changed to see the effect on the simulation results and in addition, also been running simulations with additional iron in the substrate.

5.1.1 Base case

The base case was established by using recommended parameters for cow manure found in literature. For fish sludge the parameters in ADM1 were estimated based on COD (total and soluble), Biodegradable Fraction of Particulates (BFP) and formulas for estimating parameters. For parameters such as sulphur, phosphorous and physico-chemical variables it was estimated based on literature and analysis from Svanem Biogass AS. For example, the fraction of inorganic sulphur and sulphate of total sulphur were estimated based on findings in literature. Since it is used values found in literature and/or estimates, there are some uncertainties how well it represents the substrate at Svanem Biogass AS.

From the simulation with different fractions of cow manure and fish sludge and hydraulic retention time, the biogas flow varies. It was run simulation with substrate mixture containing fish sludge from 0% to 30%. The largest biogas flow is found for substrate just containing cow manure and low hydraulic retention time (9.9 days). The biogas flow is reduced when mixing the cow manure with fish sludge. The lowest biogas flow is for substrate containing 30% fish sludge.

For several parameters investigated, there are small variation. The volume percentage of methane remain approximately the same. It is somewhat larger for substrate containing only cow manure. In general, it is in the range of 62% to 66%. Similar for pH in the bioreactor and inhibition of NH_3. The pH is largest for substrate with only cow manure, and it is reduced to some degree when adding fish sludge. The pH is approximately constant, and it is in the range of 7.57 to 7.71. The inhibition-level of NH_3 remain also approximately constant in the range of 0.50 to 0.65.

The main findings for simulation with base case, is the level of H_2S. With substrate containing only cow manure, the H_2S is low and is close to 200 ppm. At this level of H_2S, the biogas can be used to for example heat and power installations without any further conditioning of the biogas (ref Chapter 2.8). However, when adding fish sludge to the substrate, the H_2S level is increasing rapidly. When increasing from 0% to 10% fish sludge, the H_2S is increasing with over 5000 ppm. Further increase of fish sludge up to 30% gives H_2S level between 16000 ppm to 22 000 ppm.

Based on the simulation with base case, there is a larger biogas flow with substrate without fish sludge. The biogas flows are decreasing for substrate with increasing amount of fish sludge. Opposite behaviour is for the H_2S-level in the biogas. The H_2S-level is also dependent on the amount of fish sludge in the substrate, since the fish sludge contains more sulphur. However, the H_2S-level is increasing with increasing fraction of fish sludge. At the same time, the volume percentage of the methane remains in the same range independent of substrate mixture. Simulations shows that measures must be taken before utilising the biogas from a substrate mixture of cow manure and fish sludge.

5.1.2 Adding iron

One method recommended in literature to reduce the H_2S level in the biogas, is to add iron to the substrate. Varies suggestion for adding iron are discussed in Chapter 2.8.3. Since there is available wastewater containing iron from local waterwork, it was run simulation with added hydrous ferric oxide. Simulation results from base case with 90% cow manure and 10% fish sludge was compared with simulation with same substrate, but with varies level of added hydrous ferric oxide. Simulation shows that recommended level of added hydrous ferric oxide found in literature does not reduce the H_2S level significantly. The recommended level is 0.2% to 0.5% hydrous ferric oxide of dry matter (TS) in substrate (ref 2.8.3). However, the recommended level is for substrate with manure. By increasing the amount for hydrous ferric oxide to 2%, the H_2S level is reduced significantly from around 6000 ppm to 500 ppm.

Simulation with correctly adjusted amount for hydrous ferric oxide in the substrate will reduce the H_2S level in the biogas significantly. The iron will react with the sulphur to iron sulphide and will precipitate. In addition, the volume percentage of methane in the biogas is also increasing slightly. Adding hydrous ferric oxide seems to be an easy and low-cost method for Svanem Biogass AS to reduce the level if H_2S in the biogas.

5.1.3 Comparison between simulation and measurement

At the end of the work with the thesis, samples of the biogas were sent for analysis (ref Appendix B). Earlier it had been used a handheld gas measurement unit and the there are some deviations in the measurements. The comparison is presented in Table 5.1.

Table 5.1 Gas measurements at Svanem Biogass AS [44], [62]

Description	**22th of December 2022**	**31st of August 2023**
Substrate	Cow manure	12% fish sludge 78% cow manure 10% inoculum
CH_4	58.9%	63.6%
CO_2	33.8%	36.3%
H_2S	3240 ppm	400 ppm
Biogas flow	No information	128 m^3
HRT	No information	12.7 days
pH	No information	7.7
Comments	Gas contents measured by handheld unit. No information given if substrate also included inoculum	Biogas flow is average during one day and assumed all 3 reactors generate the same amount of biogas. HRT is calculated based on information from Svanem Biogass AS (volume of digester in reactor and feed rate) pH measured in digestate and it is used average value of the measurements (from all the 3 reactors)

The measured values for methane and carbon dioxide are quite similar, with some larger values for the last measurements. However, the difference is small and could be considered as similar. The major difference is the level of H_2S. The level of H_2S has dropped significantly even with substrate which in theory should increase the level of H_2S. If the last measurements are representative regarding H_2S is difficult to conclude, without any further measurements of the gas content.

When comparing the measurements from Table 5.1 with simulation results, it is important to remember that the simulation is using a CSTR while the Antec reactor is more like a plug flow reactor with some additional features. The additional features are a business secret and is not revealed by Antec. This difference can cause a deviation when comparing. In addition, Svanem Biogass AS is using inoculum when mixing the substrate before it enters the bioreactor. This is not accounted for in the simulations.

In Figure 5.1 to Figure 5.4 the measurements from Svanem Biogass AS (31st of August 2023) is plotted with simulation results. Simulation with 90% cow manure and 10% fish sludge is probably most representative and used for comparison of the results. The 10% inoculum is however not taken account for.

Simulation is underestimating the biogas flow as seen in Figure 5.1. Measurements indicate that it is approximately 35% more biogas produced than simulated with ADM1. This might be due to the inoculum and that the Antec reactor is more efficient.

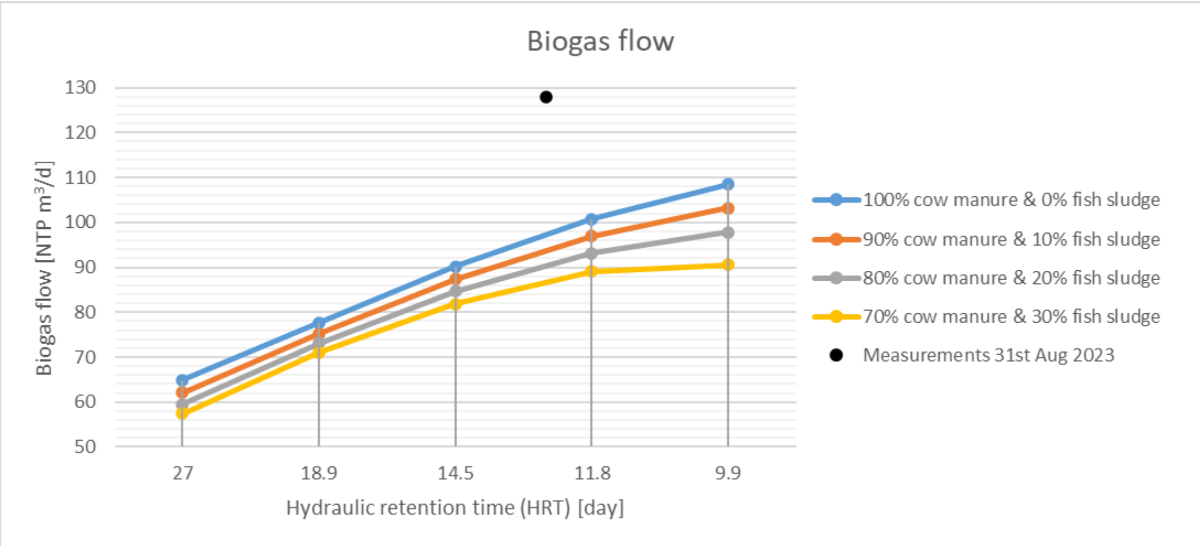


Figure 5.1 Biogas flow - simulated (after 400 days) vs measurements

When comparing methane and pH, the differences are small and can considered to be neglectable as seen in Figure 5.2 and Figure 5.3. The measured methane level is 63.6%, while simulated is around 64.8%. Similar for the pH, where the measured pH is 7.7 while simulated is approximately 7.64.

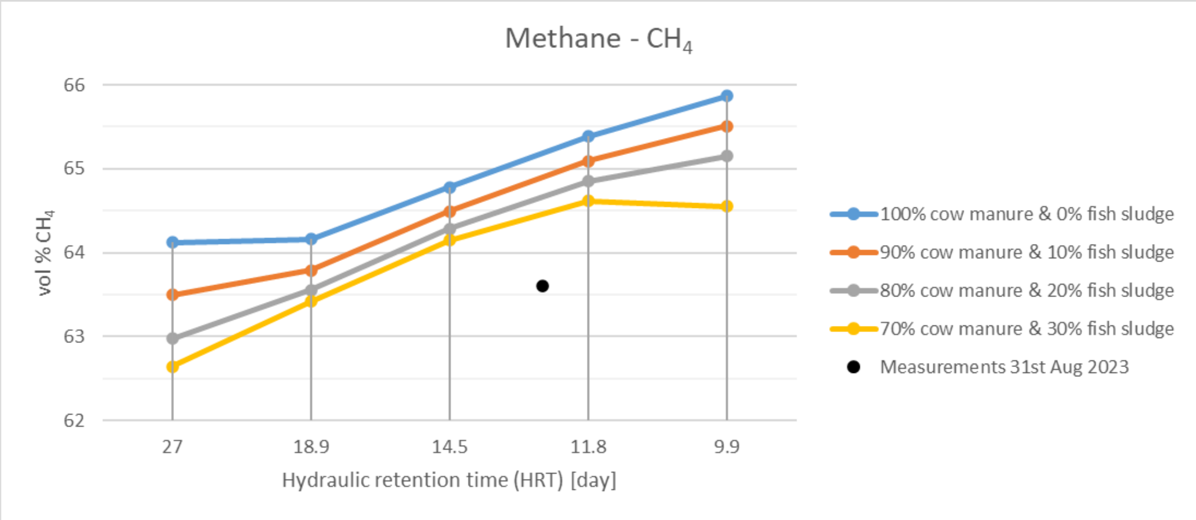


Figure 5.2 Volume percentage of methane in biogas – simulated (after 400 days) vs measurements

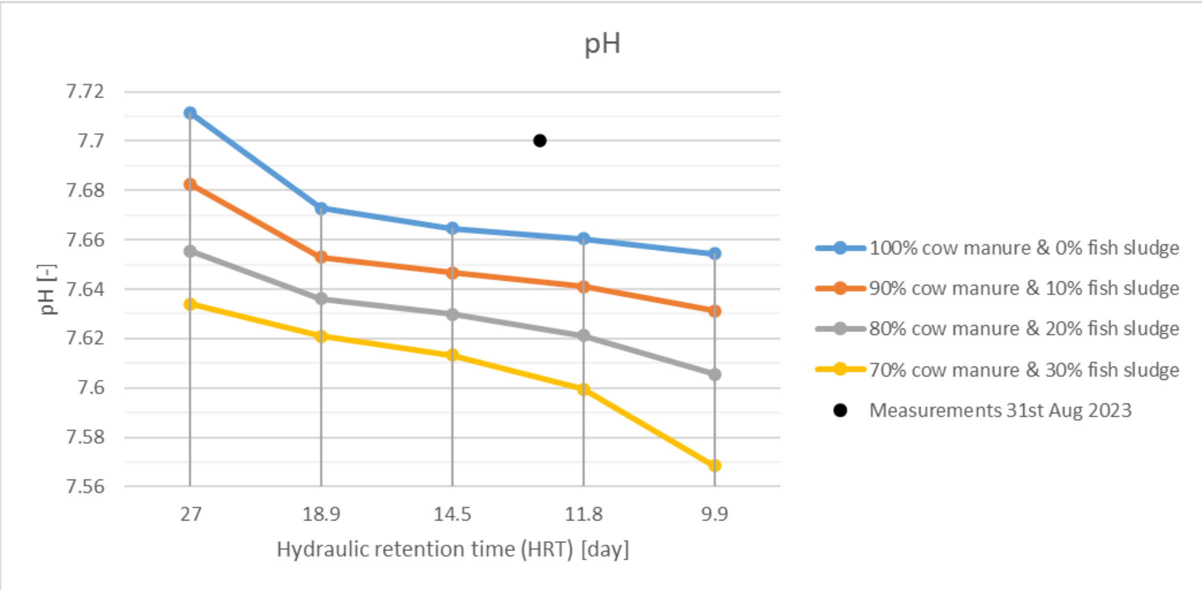


Figure 5.3 pH in bioreactor - simulated (after 400 days) vs measurements

For the hydrogen sulphide, there is a larger deviation as seen in Figure 5.4. It is important to notice that it has been measured twice at Svanem Biogass AS. The first time with a handheld unit, and then the measurements was 3240 ppm. The reason for this large scatter in measurements is not known. If the last measurements from 31st of August 2023 is representative, the H_2S level in the bioreactor is quite low considering substrate used. In addition, the input values for sulphur in the ADM1 must also be adjusted to correspond better with the measurements.

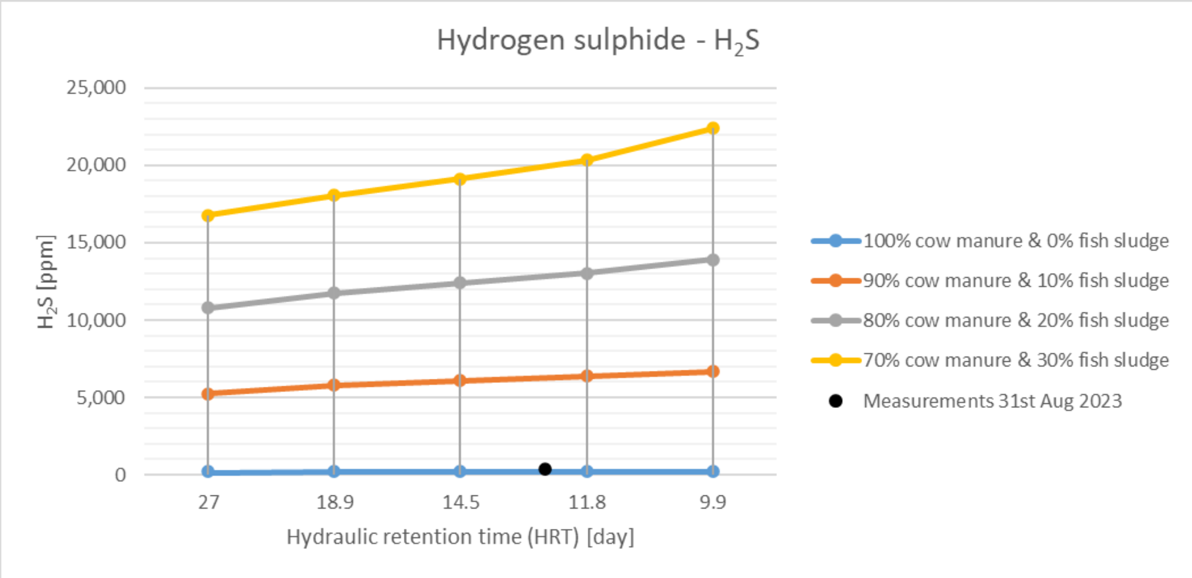


Figure 5.4 Hydrogen sulphide in the biogas - simulated (after 400 days) vs measurements

As seen from the comparison between simulated and measured values, some values correspond quite well while other are deviating. To be able to adjust the model and simulation results, it needs more measurements. One measurement is too little to make any unambiguous conclusion. However, there is an indication how well the model and simulation results fits.

5.1.4 Uncertainty in simulation results

The simulations have not been properly validated or adjusted against measurements from Svanem Biogass AS. For the ADM1 input, it has been used values found in literature for cow manure and fish sludge, estimated based on findings in literature and in combination with information received from Svanem Biogass AS. Some of the assumptions of the input to the ADM1 have been further investigated and how it affects the simulations results. The variables and parameters investigated were inorganic carbon, inorganic sulphur, biodegradable fraction of particulates (BFP) and inhibition coefficient for NH_3.

The inorganic carbon was increased compared to recommended value for cow manure found in literature. By adjusting this value, the amount of biogas flow increased and reduced the volume percentage of methane. The main reason for adjusting this variable was due to very high amount of methane in the biogas. The inorganic carbon was then adjusted until level of methane was within the range reported in literature for substrate containing only cow manure.

The level of inorganic sulphur affected mainly the level of hydrogen sulphide (H_2S) when comparing simulation results for 90% cow manure and 10% fish sludge. For the others results, such as for biogas flow, pH, amount of methane etc, the changes are considered neglectable. However, with only adjusting the level of inorganic sulphur with ±5 percentage points, the level of H_2S varied with approximately with ±33%. This variable has a huge impact on the H_2S level, even with small changes in value.

The value of the biodegradable fraction of particulates (BFP) has low to no impact on the simulation results. The sensitivity of this parameter could be neglected.

The inhibition coefficient for NH_3 has a large impact on the simulation results. The simulation is sensitive to the value used for this coefficient. When using the default ADM1 value for coefficient the biogas flow is significant reduced. The base case is estimating biogas flow in the range of 60 – 110 m^3/day, when using default ADM1 the range is approximately 45 – 70 m^3/day. The volume percentage of methane in the biogas is also significant affected and the volume percentage of the methane level is reduced to only 45% to 58%. The pH level is also reduced, and in some cases the pH level is lower than recommended to avoid inhibiting the digester. For these cases, no simulation solution is found. The inhibition level of ammonia is also reduced compared to the base case. For the hydrogen sulphide level, it is opposite. The level is increased up to 45 000 ppm. There is only with substrate with cow manure that the level is approximately the same.

The examination of the sensitivity of parameters and variables in ADM1 has revealed that some are more important than others. For example, the inhibition coefficient for NH_3 has in general large impact on the simulation results. Similar with variables for inorganic carbon and inorganic sulphur. The inorganic carbon has an impact on the simulation results, especially the biogas flow and the volume percentage of methane in the biogas. The inorganic sulphur has a considerable effect on the hydrogen sulphide level in the biogas and is crucial to estimate correctly. On the other hand, the biodegradable fraction of particulates (BFP) has a minor impact on the results. The BFP is less important to estimate correctly, since it affects the simulation results are neglectable.

5.2 Control methods for excess ammonia

There are different methods to avoid inhibition due to excess of ammonia in substrate rich on nitrogen.

A method, also used in general, is a stepwise increase of substrate with higher contain of nutrients such as nitrogen. The microflora need time to adopt to a change of the substrate contain. Especially the methanogens need time to adopt to the changes. A stepwise increase of substrate containing ammonia is already being used at Svanem Biogass AS. The increase of nitrogenous substrate, i.e., fish sludge, is slowly added to the bioreactor. About half a year after starting up, the fish sludge contains is between 10 to 12% of the volume of the substrate (ref Appendix B and measurements 31st of August 2023).

If the pH is increasing, the amount of ammonia in increasing which also affect the level of volatile fatty acid (VFA). The interaction between ammonia, pH and VFA could result in a lower methane yield, called “inhibited steady state”. Inhibition due to ammonia is not common when the pH level is between 7.0 to 7.5. This is a narrower interval than the general recommended pH range for mesophilic digestion. The optimum pH interval is in general between 6.5 to 8.0 for mesophilic digestion.

However, the pH in the bioreactor could be difficult to adjust, if necessary, in a full-size bioreactor. In a lab-reactor it can be possible to adjust the pH, but in a full-size bioreactor it is considered to not be achievable and/or economical sustainability.

When running a bioreactor in thermophilic conditions, a reduction in temperature to mesophilic conditions could be a solution to overcome inhibition due to ammonia. However, if the temperature is getting too low, the process in the bioreactor will slow down and, in some cases, almost stops. At Svanem Biogass AS they are running at mesophilic condition and only minor temperature adjustment is possible without entering psychrophilic condition. However, temperature reduction within the range of mesophilic condition should be considered when inhibition of NH_3 occurs.

Another option is to make sure that the substrate is containing ions such as sodium, magnesium, and calcium. These ions seem to have the ability to reduce ammonia inhibition. As for the pH, it is not considered to feasible to add more ions such as sodium ion (Na^+), magnesium ion (Mg^{2+}) and calcium ion (Ca^{2+}) into the substrate. However, the ions in the substrate are slightly increasing when increasing the amount of fish sludge in the substrate (ref Appendix B). There are slightly increase of ions in the substrate due to fish sludge and the effect should probably be considered neglectable.

Based on the discussion above, the stepwise increase of substrate with higher contain of nitrogen and temperature adjustment seems to be the most favourable methods for Svanem Biogass AS to avoid inhibiting the digester.

5.3 Control methods for hydrogen sulphide

To avoid high level of H_2S in the biogas, there are 3 control methods: biological, chemical, and physical. The chemical and biological methods are the most efficient.

The physical control method is typically adjusting parameters such as temperature and pH. By increasing the pH up to 8, the H_2S level is reduced. It is the opposite when the pH is reduced, then the H_2S is increasing. Physical control method is reported to only have an efficiency in the range of 18% to 41%. This is not sufficient, and it needs additional purification steps of effluent gas with respect to hydrogen sulphide.

The chemical control method typically adding metals or metal salts. Chemical control method has potential to reduce the formation up to 98%. The metal will create a chemical reaction with the sulphur in the substrate and reduce the H_2S level. Various forms of iron could be added to the digester, such as iron chloride, hydrous ferric oxide, or microscale iron powder. Laboratory tests suggest that also zinc oxide could also be used. However, it would be favourable to use resources considered as waste such as hydrous ferric oxide from waterworks. One concern is that the iron will react with the phosphorus and the plants will not be able to utilise the iron phosphate.

For biological control, it is mainly used micro-aeration and the method has been reported to be the most efficient method, with up to 100% removal of hydrogen sulphide (H_2S). Use of micro-aeration in the bioreactor has been used in Germany for a time and literature are also reporting very good efficiency. It can be used both pure oxygen or air, and it seems like there are small difference in efficiency. By adding small amount for air or oxygen in the head space of the bioreactor, microorganisms will then oxidise hydrogen sulphide to sulphur. The sulphur is solid and will typically accumulate close to the inlet of air or oxygen. This area must be cleaned regularly for sulphur. The concern is the reactor from Antec at Svanem Biogass AS. There is no detailed information of this reactor, and it might not be possible to implement micro-aeration.

The control of pH is an example where recommendation for control inhibition of ammonia is the opposite of recommendation to reduce the level of H_2S in the biogas. The anaerobic digestion is a complex process where there is a trade off when coming to optimising. It should be taken care when trying to optimise for some parameters, since it might affect other parameters which for example slow down the process or in worst case a complete inhibition of the digester.

For Svanem Biogass AS it will probably use of hydrous ferric oxide be favourable. It does not require any modification of the bioreactor, and it is available from local waterwork. However, it depends also on what the biogas is utilised for. The biogas will most likely not be suitable for fuel for vehicle without additional condition due to remaining H_2S. According to literature, it is expected maximum 98% reduction of H_2S and fuel for vehicle requires less than 4 ppm. It requires some more tests and/or simulations to find the correct amount of hydrous ferric oxide to add to the digester and if the level of removal is sufficient.

6 Conclusion

The literature study has revealed that anaerobic digestion is a complex process and adjusting one parameter could affect other parameters and in worst case inhibit the digester. There is in general a good understanding of the main parameters in the digester and how it effects the process. Such parameters are for example pH, inhibition due to ammonia, temperature, and dry matter. In literature it is also tried to establish optimum and inhibition level of several nutrients in the substrate. However, the levels should be considered as guidelines. Several studies have revealed the digester's ability to adapt to different substrate even though certain nutrients is at a higher level than recommended.

The transformation of nitrogen and sulphur in the digester is not elementary due to several dependencies. One important parameter of transformation of nitrogen and sulphur is the pH level in the bioreactor. The pH affects the equilibrium equations of ammonia and hydrogen sulphide, but the digester has also a buffer capacity with respect to change in pH. The pH might not change as expected until the buffer capacity is fully utilised. Then the pH could change rapidly.

A lot of nitrogen in the substrate can result in inhibiting the digester due to excess level of ammonia. There are different methods used to avoid inhibiting the process, among other stepwise increase of substrate with high level of nitrogen and lowering the temperature in case of an inhibition of the digester is occurring. A slowly stepwise increase of substrate with increased level of nitrogen, will be beneficial for the microflora and will then be able to adapt. A reduction in temperature is often used for thermophilic conditions and could be a solution to overcome inhibition due to ammonia. The temperature is then adjusted to mesophilic conditions. However, if the temperature is reduced too much, the digestion process will be slow and, in some situation, also stop. Svanem Biogass AS is running at mesophilic conditions, however it is still possible to reduce the temperature within in the defined temperature range for mesophilic conditions.

Substrate rich in sulphur could culminate in a situation with high level of hydrogen sulphide in the biogas and inhibiting the process due to excess ammonia. The amount of hydrogen sulphide is important to keep as low as possible. The hydrogen sulphide is a corrosive gas and, depending on the utilisation of the biogas, the level must be within some predefined level. If the biogas should be used as fuel for vehicle the level must be 4 ppm or lower. According to literature and simulations in this thesis, the level of hydrogen sulphide could be several thousand times of the recommended level for fuel. There are different methods to reduce the hydrogen sulphide level in-situ the digester. The methods which have the potential to reduce the hydrogen sulphide level significantly is micro-aeration and adding iron to the substrate. Due to the reactor type at Svanem Biogass AS, the methods of adding iron to the substrate will be favourable. There is no need to reconstruct the reactor and there is also a waterworks nearby with iron rich wastewater. Simulation shows that adding additional iron (hydrous ferric oxide) will reduce the hydrogen sulphide level significantly with the right amount of iron added. However, simulations show that adding hydrous ferric oxide will not be able to reduce the level of hydrogen sulphide sufficiently according to the requirements for biogas utilised as fuel. However, the biogas could be used for heating purpose or production of electricity without any further conditioning of the biogas. The amount of hydrous ferric oxide to be added need to be further investigated.

It has been run simulation of the bioreactor with the ADM1 extended with sulphur, phosphorous and iron interactions. Input values for different parameters and variables for the ADM1 was established by use of findings in literature, information from Svanem Biogass AS and estimation. The model is not validated thoroughly with measurements of biogas from Svanem Biogass AS. However, it is compared with a measurement performed in end of August 2023. The level of biogas flow is somewhat underestimated, but the percentage level of methane in the biogas and pH corresponds very well. The measured level of hydrogen sulphide is significantly lower than results from simulations. Based on findings in literature, it was expected to be larger. However, measurements with handheld unit for gas measurement has earlier showed higher value of hydrogen sulphide in the biogas. There are not enough measurements to make any unambiguous conclusion.

Additional simulations have also been run to get a better understanding of how different parameters and variables affect the results of simulation with ADM1. The variable of inorganic carbon affects the biogas flow by increasing the level of CO_2 in the biogas. Another variable is inorganic sulphur, which affects the level of hydrogen sulphide significantly. The level of inorganic sulphur was estimated based on findings in literature, however it seems like it might not be correct for the case with Svanem Biogass AS when comparing measurements and simulation results. The inhibition coefficient for NH_3 has in general large impact on the simulation results and default value in ADM1 is not representative when comparing the result. The value found from literature gives in general better results when comparing with measurements received from Svanem Biogass AS.

For further work it is recommended to validate the input values of parameter and variables in ADM1, especially parameters for sulphur. Results from the simulation shows that some parameters and variable have a significant impact on the results, and it is essential to use correct values. The bioreactor at Svanem Biogass AS differ from the reactor modelled in ADM1, and the simulation should be validated with measurements from a facility with similar mixture of substrate and with a CSTR, and not with a plug flow reactor.

The opportunity of using hydrous ferric oxide at Svanem Biogass AS should be further investigated and tested either in laboratory or in full-scale to compare the effect observed in simulations.

One of the methods found in literature to reduce the amount of hydrogen sulphide in the biogas is micro-aeration. This method is recommended to implement in the ADM1-model, to be able to compare the efficiency of this method with for example adding iron to the substrate.

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Appendices

Appendix A – Project description

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Appendix A – Project description

University of South-Eastern Norway

Faculty of Technology, Natural Sciences and Maritime Sciences, Campus Porsgrunn

FMH606 Master's Thesis

Title: Anaerobic digestion of substrates rich in sulphur and nitrogen

USN supervisor: Wenche Hennie Bergland

External partner: Roar Svanem at Svanem Biogass

Task background:
Svanem Biogass is village pilot from 2022 supported by Innovation Norway containing a biogas and fertiliser production facility run on cow manure and fish sludge as substrates. To obtain high fertiliser quality it is important to control the flow of the nutrients like nitrogen and phosphor but also sulphur and salinity.

Task description:

- Evaluate relevant substrates included nitrogen and sulphur content.
- Make a literature survey of suggested methods for keeping the sulphur in the digestate instead of following the produced biogas.
- Evaluate local available waste streams as sulphur removing aid.
- Simulate the biogas process using the anaerobic model no 1 (ADM1) for evaluation and implement (if necessary) suggested removing aids in the model for evaluation of the effect for chosen scenario.

Student: Reserved for online student Kjetil Andersen

Is the task suitable for online students (not present at the campus)?: Yes

Practical arrangements:
Experimental tests can be done in Campus Porsgrunn. Sampling and data collection can be done at Svanem Biogass.

Supervision:
As a general rule, the student is entitled to 15-20 hours of supervision. This includes necessary time for the supervisor to prepare for supervision meetings (reading material to be discussed, etc).

Signatures:

Supervisor (date and supervision): 30.03.23 Wenche Bergland

Student (write clearly in all capitalized letters): Kjetil Andersen

Student (date and signature): Kjetil Andersen

Appendix B – Analysis and measurements provided by Svanem Biogass AS

Measured values:

Cow manure	m3 (assumed)	pH	NH4-N kg/T	N kg/T	S kg/T	P kg/T	K kg/T	Mg kg/T	Ca kg/T	Na kg/T	C/N ratio	TS [%]	tonne TS	Cu mg/kg-TS	Zn mg/kg-TS	B mg/kg-TS	Mn mg/kg-TS	Fe mg/kg-TS
Farmer #1	600	7.2	1.70	1.70	0.19	0.20	2.40	0.30	0.60	0.46	6.80	2.4%	14.40	30.00	190.00	110.00	390.00	1300.00
Farmer #2	1200	8.1	3.40	5.00	0.62	0.80	7.00	0.90	1.10	0.70	9.20	9.6%	115.20	11.00	130.00	28.00	310.00	570.00
Farmer #3		7.2	2.80	3.70	0.52	0.50	6.00	0.60	0.60	0.72	8.80	7.3%		3.90	370.00	34.00	320.00	950.00
Farmer #4	900	7.5	2.80	3.80	0.50	0.60	5.40	0.60	0.90	0.68	8.20	6.6%	59.40	9.40	160.00	69.00	310.00	780.00
Farmer #5	700	7.4	2.40	2.90	0.37	0.30	3.60	0.50	0.90	0.70	7.50	4.5%	31.50	5.00	190.00	70.00	310.00	490.00
Farmer #6	2000	7.2	1.50	2.00	0.25	0.20	2.70	0.30	0.70	0.42	7.50	3.4%	68.00	22.00	240.00	88.00	370.00	1800.00
Farmer #7	2500	7.0	2.20	3.40	0.50	0.60	2.70	0.60	1.00	0.73	9.70	6.8%	170.00	17.00	210.00	41.00	280.00	570.00
Farmer #8	300	7.0	2.40	5.20	0.68	1.20	2.70	1.30	2.10	0.69	12.00	12.5%	37.50	34.00	260.00	48.00	270.00	650.00
Farmer #9	2000	7.5	1.40	2.00	0.37	0.40	3.00	0.40	1.00	0.44	8.10	4.7%	94.00	2.10	190.00	46.00	260.00	680.00
Farmer #10		7.0	0.80	2.20	0.37	0.60	1.80	0.40	1.10	0.17	14.00	6.5%		1.50	220.00	38.00	380.00	1200.00
Farmer #11	500	7.2	1.90	3.80	0.59	1.00	3.90	0.80	1.80	0.45	14.00	13.3%	66.50	15.00	140.00	25.00	210.00	2700.00
Farmer #12	500	7.6	2.20	4.40	0.63	1.10	4.60	1.00	2.00	0.69	12.00	11.8%	59.00	24.00	200.00	38.00	370.00	830.00
Farmer #13	550	6.9	2.20	3.70	0.48	0.60	3.50	0.60	1.10	0.56	10.00	8.0%	44.00	7.20	160.00	28.00	180.00	570.00
Farmer #14	1660	7.7	1.64	3.71	0.47	0.60	4.80	0.70	1.30	0.76	10.55	8.3%	137.78	40.00	180.00	30.00	290.00	750.00
Sum	13410.00												897.28					
Weighted average with respect to m3		7.38	2.04	3.19	0.44	0.54	3.75	0.58	1.07	0.60	10.37	6.7%	96.82	.	-		-	-
Weighted average with respect to TS		-	-	-	-	.	.	.	.		-	-	-	18.41	184.76	43.98	290.33	903.49
Weighted standard deviation		0.33	0.59	1.03	0.13	0.26	1.36	0.23	0.34	0.14	2.05	2.79%	47.57	11.88	34.89	19.74	48.56	602.28
Fish sludge	2500.00	5.50	2.70	14.60	0.89	3.20	0.70	0.60	6.50	0.79	5.90	16.7%	417.50	8.40	330.00	22.00	130.00	720.00

Calclulated values:

		pH		NH4-N kg/T		N kg/T		S kg/T		P kg/T		K kg/T		Mg kg/T		Ca kg/T		Na kg/T		C/N forhold	
vol % Fish sludg	vol % Cow manure	wavg	std	wavg	std	wavg	std	wavg	std	wavg	std	wavg	std	wavg	std	wavg	std	wavg	std	wavg	std
0%	100%	7.37860	0.33	2.04	0.59	3.19	1.03	0.44	0.13	0.54	0.26	3.75	1.36	0.58	0.23	1.07	0.34	0.60	0.14	10.37	2.05
5%	95%	7.28467	0.52	2.07	0.60	3.76	2.68	0.46	0.16	0.67	0.63	3.60	1.49	0.58	0.22	1.34	1.23	0.61	0.14	10.15	2.22
10%	90%	7.19074	0.65	2.10	0.60	4.33	3.56	0.49	0.18	0.81	0.83	3.45	1.58	0.59	0.22	1.61	1.66	0.62	0.14	9.93	2.36
15%	85%	7.09681	0.74	2.14	0.60	4.90	4.18	0.51	0.20	0.94	0.98	3.29	1.66	0.59	0.21	1.88	1.97	0.63	0.14	9.70	2.47
20%	80%	7.00288	0.81	2.17	0.59	5.47	4.65	0.53	0.21	1.07	1.09	3.14	1.73	0.59	0.20	2.15	2.19	0.64	0.14	9.48	2.56
25%	75%	6.90895	0.86	2.20	0.59	6.05	5.02	0.55	0.22	1.21	1.17	2.99	1.77	0.59	0.20	2.43	2.37	0.65	0.14	9.26	2.63
30%	70%	6.81502	0.90	2.24	0.58	6.62	5.30	0.58	0.23	1.34	1.24	2.84	1.80	0.59	0.19	2.70	2.51	0.66	0.14	9.03	2.67

		TS [%]		tonne TS		Cu mg/kg-TS		Zn mg/kg-TS		B mg/kg-TS		Mn mg/kg-TS		Fe mg/kg-TS	
vol % Fish sludg	vol % Cow manure	wavg	std	wavg	std	wavg	std	wavg	std	wavg	std	wavg	std	wavg	std
0%	100%	6.69%	2.79%	96.82	47.57	18.41	11.88	184.76	34.89	43.98	19.74	290.33	48.56	903.49	602.28
5%	95%	7.19%	3.49%	112.85	83.87	17.91	11.78	192.02	46.46	42.88	19.83	282.31	58.83	894.31	588.39
10%	90%	7.69%	4.00%	128.88	106.26	17.41	11.66	199.28	54.72	41.78	19.85	274.29	66.60	885.14	574.02
15%	85%	8.19%	4.40%	144.92	122.62	16.90	11.52	206.55	61.03	40.68	19.82	266.28	72.68	875.96	559.13
20%	80%	8.69%	4.72%	160.95	135.15	16.40	11.35	213.81	65.95	39.58	19.72	258.26	77.46	866.79	543.67
25%	75%	9.19%	4.96%	176.99	144.84	15.90	11.16	221.07	69.77	38.48	19.56	250.24	81.17	857.62	527.61
30%	70%	9.69%	5.15%	193.02	152.25	15.40	10.94	228.33	72.68	37.39	19.34	242.23	83.96	848.44	510.87

Comments - substance:
- Removed "<" in cells marked with:
- Cells marked with following color is calculated
- Columme tonne TS is caluclated by assumed density of 1000 kg/m3

Analysis provided by Svanem Biogass AS (analysed by Antec Biogas AS)

Prøvene fra 5/6.12.22

	pH [-]	FOS [g HAc/l]	TAC [g CaCO3/l]	FOS/TAC [-]	TS [%]	VS (dw) [%]	COD TOT [g O2/l]	COD SOL [g O2/l]	NH4+ [g/l]
FS 5.12.22	5.8	9175	2455	3.74	9.7 %	77.4 %	168.2	56.4	2.6
FS 6.12.22 (Lastbil)	5.1	2990	175	17.1	9.8 %	88.9 %	157.4	31.5	0.6
RT 1 BI 6.12.22	8.0	1761	2361	0.75	4.3 %	83.8 %	54.3	11.2	0.8

Prøvene fra 2.2.23

	pH [-]	FOS [g HAc/l]	TAC [g CaCO3/l]	FOS/TAC [-]	TS [%]	VS (dw) [%]	COD TOT [g O2/l]	COD SOL [g O2/l]	NH4+ [g/l]
RT 1 BI	8.3	2072	5692	0.36	4.5 %	72.8 %	60.5	15.7	1.9
RT 2 BI	8.2	2654	5646	0.47	4.8 %	74.2 %	69.1	18.6	1.9
RT 3 BI	8.2	2058	5685	0.36	4.5 %	72.9 %	59.7	16.5	1.9

Prøvene fra 12.2.23

	pH [-]	FOS [g HAc/l]	TAC [g CaCO3/l]	FOS/TAC [-]	TS [%]	VS (dw) [%]	COD TOT [g O2/l]	COD SOL [g O2/l]	NH4+ [g/l]
MT	7.8	4554	4452	1.02	5.3 %	75.9 %	79.9	23.5	1.5
RT 1 BI	8.2	2433	5791	0.42	4.4 %	72.1 %	60.9	16.6	1.7
RT 2 BI	8.0	2451	6019	0.41	4.8 %	73.4 %	63.9	16.5	2.1
RT 3 BI	8.0	2381	5802	0.41	4.2 %	71.3 %	61.5	18.5	1.8

Forklaring
BI = Biorest
COD = Chemical Oxigen Demand (TOT = Total, SOL = Soluble)
FOS = Volatile Acids
FS = FiskeSlamm
MT = Mixing Tank
NH4+ = Ammonium
RT = Reaktor Tank
TAC = Total Anorganic Carbon
TS = Torrstoff
VS = Volatile Solids

Evaluering prøvene fra 12.2.23
pH er på en svakt basisk nivå som er bra!
FOS/TAC verdiene er på bra nivå!
COD nedbrytning ligger på ca. 30 %
NH4 er på en akseptable nivå.

Gas measurements 22nd December 2022 (handheld unit, 14 days after starting up)

CH_4 58.9%

CO_2 33.8%

H_2S 3240 ppm

Gas measurements and analysis of substrate 31st August 2023

Samples of the substrate (cow manure and fish sludge), digestate and the biogas were sent for analysis 31st of August 2023.

The biogas facility was running with following mixture of the substrate:

- 12% fish sludge
- 78% cow manure
- 10% inoculum

Other parameters from the facility:

- Feed rate last day: 18 m^3
- Average gas production per hour: 16 m^3
- Last 24 timers it has been 7 sequences out of the reactor (23.8 m^3) and 6 sequences in (20.76 m^3). Average feed per reactor: 7.43 m^3

The following samples was analysed:

- Cow manure (before mixing tank)
- Fish sludge (before mixing tank)
- Digestate from Reactor 1
- Inoculum from Reactor 2
- Digestate from Reactor 2
- Digestate from Reactor 3

The results from the analysis are summarised in Table B.1.

Table B.1 Analysis results of substrate and digestate 31st of August 2023 [62]

Sample Point	***pH*** *[-]*	***FOS*** *[mg/l]*	***TAC*** *[mg/l]*	***FOS/ TAC*** *[-]*	***TS*** *[%]*	***VS (dw)*** *[%]*	***tCOD*** *[g/l]*	***sCOD*** *[g/l]*	***NH4+*** *[g/l]*
CM – Cow Manure	*7.1*	*3704.65*	*3898.45*	*0.95*	*5.9%*	*79.1%*	*81.3*	*23.0*	*1.5*
FL – Fish Sludge	*5.8*	*12194.81*	*2584.93*	*4.72*	*10.0%*	*66.1%*	*159.4*	*61.8*	*3.9*
Reactor 01 Digestate	*7.7*	*1509.55*	*5583.28*	*0.27*	*4.4%*	*72.5%*	*53.0*	*8.4*	*1.7*
Reactor 02 Inoculum	*7.7*	*1638.45*	*4922.77*	*0.33*	*3.4%*	*68.5%*	*44.6*	*8.6*	*1.6*
Reactor 02 Digestate	*7.8*	*1549.72*	*5471.00*	*0.28*	*4.7%*	*73.0%*	*52.0*	*8.9*	*1.7*
Reactor 03 Digestate	*7.6*	*1547.32*	*5535.38*	*0.28*	*4.2%*	*70.9%*	*53.1*	*8.6*	*1.7*

Where:

COD - Chemical Oxygen Demand (t = total, s= soluble)

FOS - Volatile Fatty Acids

TAC - Total Anorganic Carbon

TS – Total Solids

VS - Volatile Solids

In addition to analyses of digestate and substrate, the content of the biogas was also analysed. The biogas had the following composition:

- Methane (CH_4): 63.6%
- Carbon dioxide (CO_2): 36.3%
- Hydrogen sulphide (H_2S): 400 ppm
- Hydrogen (H_2): 0.16%

Appendix C – Derivation of equation for concentration of NH_3

Derivation of equation 2.1 [8].

The reaction equation for NH_3 and NH_4^+ is given by

$$NH_4^+ \leftrightarrow \ NH_3(aq) + \ H^+$$

The dissociation constant (k_a) can be expressed as

$$k_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

Re-arranging with respect to $[NH_4^+]$ and add $[NH_3]$ on each side of the equation.

$$[NH_4^+] + \ [NH_3] = \frac{[NH_3][H^+]}{k_a} + \ [NH_3]$$

$$[T - NH_3] = \left(\frac{[H^+]}{k_a} + 1\right) \ [NH_3]$$

Re-arranging the equation with respect to NH_3.

$$[NH_3] = \frac{[T - NH_3]}{\left(1 + \frac{[H^+]}{k_a}\right)}$$

Appendix D – Methods of correction of VFA in TS and VS

The two methods described in this appendix correct for losses of VFA in oven-dried determination of dry matter (TS and VS) [15]. The methods give different accuracy, and Method I gives a rough estimate. Method I can only be used when pH ≤ 5.2.

Method I – rough estimation [15]:

1) Measure dry matter by use of oven-dried process to TS_m and VS_m. Determination of
    a. TS: in oven for 20 hours at 105°C
    b. VS: dried sample (TS) in oven for 2 hours at 550°C
2) Determine the concentration of VFAs in the substrate sample (VFA_m). The concentration shall be mg VFA/L.
3) Determine a value for the volatility of VFAs in the substrate sample. If unknown, it is preferably to use VFA_{vol} equal to 98%.
4) Estimate compensated dry matter by:

$$TS_{comp}(\%) = TS_m(\%) + \left(\frac{VFA_{vol}(\%)}{100} * VFA_m\left({}^{mg}/_{L}\right) * 10^{-4}\right)$$

$$VS_{comp}\left(\%\ of\ TS_{comp}\right) = \frac{\left(TS_m(\%) * VS(\%)\right) + \left(10^{-4} * VFA_{vol}(\%) * VFA_m\left({}^{mg}/_{L}\right)\right)}{TS_{comp}(\%)}$$

Method II – detailed estimation [15]:

1) Measure weight of initial substrate sample ($m_{sample,\ initial}$)
2) Determine the concentration of VFAs in the substrate sample (VFA_m). The concentration shall be mg VFA/L.
3) Measure dry matter by use of oven-dried process to TS_m and VS_m. Determination of
    a. TS: in oven for 20 hours at 105°C
    b. VS: dried sample (TS) in oven for 2 hours at 550°C
4) Add purified water, for example using a Millipore Milli-Q lab water system, to the dried sample in the beaker. Adjust the amount of water added so that the weight of the substrate sample is approximately the same as before the drying. However, all the dried material should be covered of water and if a lot of dried material is attached to the wall of the beaker it might be necessary to add additional water.
    a. Find the weight the dried sample ($m_{sample,dried}$)
    b. Add purified water (m_{water})to the beaker with dried sample and wait for 30 minutes and then stir the solution for 10 minutes.
    c. Find the concentration of VFAs in the dissolved dried sample ($VFA_{dried,\ dissolved}$).
    d. The concentration of VFAs in the dried sample before dissolved in purified water (VFA_{dried}) is calculated by use of formula below.

$$VFA_{dried}\left({}^{mg}/_{L}\right) = VFA_{dried,dissolved} * \left(\frac{\left(m_{sample,dried} + m_{water}\right)}{m_{sample,initial}}\right)$$

5) The actual volatility (%) of the VFAs in the sample is calculated by

$$VFA_{volatility}(\%) = \left(1 - \frac{VFA_{dried}\left({}^{mg}/_{L}\right)}{VFA_{m}\left({}^{mg}/_{L}\right)}\right) * 100$$

6) The compensated TS_{comp} weight is calculated by

$$TS_{comp}(\%) = TS_{m}(\%) + \left(\frac{VFA_{volatility}(\%)}{100} * VFA_{m}\left({}^{mg}/_{L}\right) * 10^{-4}\right)$$

7) The compensated VS_{comp}(% of TS_{comp}) can now be calculated by

$$VS_{comp}\left(\% \; of \; TS_{comp}\right) = \frac{\left(TS_{m}(\%) * VS_{m}(\%)\right) + \left(10^{-4} * VFA_{volatility}(\%) * VFA_{m}\left({}^{mg}/_{L}\right)\right)}{TS_{comp}(\%)}$$

Appendix E – ADM1 steady-state input variables

ADM1 steady-state input variables and kinetic parameters used for manure and fish sludge. The values used is based on discussion in Chapter 3.2.

Volume of the reactor and volume of headspace were given by Svanem Biogas:
- Volume of digester: 94.5 m^3
- Volume of headspace: 10. 5 m^3

No changes were done for initial values for the simulation with ADM1. It was assumed that default initial values given in the MATLAB script could be used.

Table E.1 Adjusted kinetic parameters for ADM1

Parameter	**Description**	**Unit**	**ADM1 default value**	**Values used in this report**
$K_{m,su}$	Maximum uptake rate of monosaccharides	d^{-1}	30.0	11.9
$K_{s,su}$	Half saturation concentration of monosaccharide uptake	kg O_2/m^3	0.5	4.5
$K_{m,aa}$	Maximum uptake rate of amino acids	d^{-1}	50.0	19.8
$K_{s,aa}$	Half saturation concentration of amino acids uptake	kg O_2/m^3	0.3	0.3
$K_{m,c4}$	Maximum uptake rate of valerate and butyrate	d^{-1}	20.0	12.2
$K_{s,c4}$	Half saturation concentration of valerate and butyrate uptake	kg O_2/m^3	0.2	0.6
$K_{m,pro}$	Maximum uptake rate of propionate	d^{-1}	13.0	3.5
$K_{s,pro}$	Half saturation concentration of propionate uptake	kg O_2/m^3	0.1	0.4
$K_{m,ac}$	Maximum uptake rate of acetate	d^{-1}	8.0	11.1

Parameter	Description	Unit	ADM1 default value	Values used in this report
$K_{s,ac}$	Half saturation concentration of acetate uptake	kg O_2/m^3	0.15	0.5
$K_{I,nh3}$	50% inhibitory concentration of free ammonia	$kmol/m^3$	0.0018	0.0223
$f_{h2,su}$	Yield of hydrogen from monosaccharides	-	0.19	0.25
$f_{pro,su}$	Yield of propionate from monosaccharides	-	0.27	0.12
$f_{ac,su}$	Yield of acetate from monosaccharides	-	0.41	0.49
k_{dis}	constant describing disintegration phase	d^{-1}	0.5	1.54
$k_{hyd,ch}$	constant describing carbohydrates hydrolysis phase	d^{-1}	10	0.037
$k_{hyd,pr}$	constant describing proteins hydrolysis phase	d^{-1}	10	0.099
$k_{hyd,li}$	constant describing lipids hydrolysis phase	d^{-1}	10	0.225

Table E.2 Steady-state input variables for ADM1 - base case

					Simulation #1			Simulation #2			Simulation #3			Simulation #4		
					100%	0%		90%	10%		80%	20%		70%	30%	
Column	**Variable/description**	**Unit**	**Cattle manure**	**Fish sludge**	**Cattle manure**	**Fish sludge**	**Sum**	**Cattle manure**	**Fish sludge**	**Sum**	**Cattle manure**	**Fish sludge**	**Sum**	**Cattle manure**	**Fish sludge**	**Sum**
1	Time	day	0 400		0 400		0 400	0 400		0 400	0 400		0 400	0 400		0 400
2	S_{su} (sugars/monosaccharides)	kg COD/m^3	2.53	0	2.53	0	2.53	2.277	0	2.277	2.024	0	2.024	1.771	0	1.771
3	S_{aa} (amino acids)	kg COD/m^3	0.69	0	0.69	0	0.69	0.621	0	0.621	0.552	0	0.552	0.483	0	0.483
4	S_{fa} (fatty acids/total LCFA)	kg COD/m^3	2.44	0	2.44	0	2.44	2.196	0	2.196	1.952	0	1.952	1.708	0	1.708
5	S_{va} (total valeric acid)	kg COD/m^3	0.72	0	0.72	0	0.72	0.648	0	0.648	0.576	0	0.576	0.504	0	0.504
6	S_{bu} (total butyric acid)	kg COD/m^3	1.57	0	1.57	0	1.57	1.413	0	1.413	1.256	0	1.256	1.099	0	1.099
7	S_{pro} (total propionic acid)	kg COD/m^3	2.91	0	2.91	0	2.91	2.619	0	2.619	2.328	0	2.328	2.037	0	2.037
8	S_{ac} (total acetic acid)	kg COD/m^3	5.68	0	5.68	0	5.68	5.112	0	5.112	4.544	0	4.544	3.976	0	3.976
9	S_{h2} (hydrogen)	kg COD/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	S_{ch4} (methane)	kg COD/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
11	S_{IC} (inorganic carbon)	kmol C/m^3	0.15	0	0.15	0	0.15	0.135	0	0.135	0.12	0	0.12	0.105	0	0.105
12	S_{IN} (inorganic nitrogen)	kmol N/m^3	0.147	0	0.147	0	0.147	0.1323	0	0.1323	0.1176	0	0.1176	0.1029	0	0.1029
13	S_I (soluble inerts)	kg COD/m^3	0	3.566	0	0	0	0	0.3566	0.3566	0	0.7132	0.7132	0	1.0698	1.0698
14	Unknown (X_C (Composite materials)?)	Unknown (kg COD/m3)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
15	X_{ch} (carbohydrates)	kg COD/m^3	13.62	4.279	13.62	0	13.62	12.258	0.4279	12.6859	10.896	0.8558	11.7518	9.534	1.2837	10.8177
16	X_{pr} (proteins)	kg COD/m^3	17.06	28.524	17.06	0	17.06	15.354	2.8524	18.2064	13.648	5.7048	19.3528	11.942	8.5572	20.4992
17	X_{li} (lipids)	kg COD/m^3	4.19	14.737	4.19	0	4.19	3.771	1.4737	5.2447	3.352	2.9474	6.2994	2.933	4.4211	7.3541
18	X_{su} (sugar degraders/monosaccharides degreaders)	kg COD/m^3	0.031	0	0.031	0	0.031	0.0279	0	0.0279	0.0248	0	0.0248	0.0217	0	0.0217
19	X_{aa} (amino acid degraders)	kg COD/m^3	0.021	0	0.021	0	0.021	0.0189	0	0.0189	0.0168	0	0.0168	0.0147	0	0.0147
20	X_{fa} (fatty acid/LCFA degraders)	kg COD/m^3	0.00001	0	0.00001	0	0.00001	0.000009	0	0.000009	0.000008	0	0.000008	0.000007	0	0.000007
21	X_{c4} (valerate and butyrate degraders/C4-degraders)	kg COD/m^3	0.0001	0	0.0001	0	0.0001	0.00009	0	0.00009	0.00008	0	0.00008	0.00007	0	0.00007
22	X_{pro} (total propionic degraders)	kg COD/m^3	0.01	0	0.01	0	0.01	0.009	0	0.009	0.008	0	0.008	0.007	0	0.007
23	X_{ac} (total acetic degraders)	kg COD/m^3	0.0017	0	0.0017	0	0.0017	0.00153	0	0.00153	0.00136	0	0.00136	0.00119	0	0.00119
24	X_{h2} (hydrogen degraders)	kg COD/m^3	0.01	0	0.01	0	0.01	0.009	0	0.009	0.008	0	0.008	0.007	0	0.007
25	X_I (particulate inerts)	kg COD/m^3	0	67.745	0	0	0	0	6.7745	6.7745	0	13.549	13.549	0	20.3235	20.3235
26	Q_{in} (influent flow)	m^3/day	varies		varies			varies			varies			varies		
27	T_{op} (Temperature)	°C	39		39		39	39		39	39		39	39		39
	P extension															
28	S_{IP} (inorganic phosphorus)	kmol P/m^3	0.0119	0.0721	0.0119	0	0.0119	0.01071	0.00721	0.01792	0.00952	0.01442	0.02394	0.00833	0.02163	0.02996
29	X_{PHA} (polyhydroxyalkanoates)	kg COD/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
30	X_{PP} (polyphosphates)	kmol P/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
31	X_{PAO} (phosphorous accumulating organisms)	kg COD/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
32	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
33	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
34	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
35	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
36	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
37	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
	S extension															
38	S_{so4} (sulfate)	kmol S/m^3	0.00056	0.00112	0.00056	0	0.00056	0.000504	0.000112	0.000616	0.000448	0.000224	0.000672	0.000392	0.000336	0.000728
39	S_{IS} (inorganic total sulfides)	kg COD/m^3	0.0784	5.7568	0.0784	0	0.0784	0.07056	0.57568	0.64624	0.06272	1.15136	1.21408	0.05488	1.72704	1.78192
40	X_{hSRB} (hydrogen Sulphate reducing bacteria)	kg COD/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
41	X_{aSRB} (acetate Sulphate reducing bacteria)	kg COD/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
42	X_{pSRB} (propionate Sulphate reducing bacteria)	kg COD/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
43	X_{c4SRB} (Valerate- and butyrate-degrading sulphate reducing bacteria)	kg COD/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
44	X_{S0} (elemental sulphur)	kg COD/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
45	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
46	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
47	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	PCM extension (physico-chemical model)															
48	S_{Na} (sodium)	kmol Na/m^3	0.026	0.034	0.026	0	0.026	0.0234	0.0034	0.0268	0.0208	0.0068	0.0276	0.0182	0.0102	0.0284
49	S_K (potassium)	kmol K/m^3	0.096	0.018	0.096	0	0.096	0.0864	0.0018	0.0882	0.0768	0.0036	0.0804	0.0672	0.0054	0.0726
50	S_{Cl} (chloride)	kmol Cl/m^3	0.026	0.034	0.026	0	0.026	0.0234	0.0034	0.0268	0.0208	0.0068	0.0276	0.0182	0.0102	0.0284
51	S_{Ca} (calcium)	kmol Ca/m^3	0.027	0.162	0.027	0	0.027	0.0243	0.0162	0.0405	0.0216	0.0324	0.054	0.0189	0.0486	0.0675
52	S_{Mg} (magnesium)	kmol Mg/m^3	0.024	0.025	0.024	0	0.024	0.0216	0.0025	0.0241	0.0192	0.005	0.0242	0.0168	0.0075	0.0243
53	S_{Fe2+} (iron (II))	kg COD/m^3	0.008	0.016	0.008	0	0.008	0.0072	0.0016	0.0088	0.0064	0.0032	0.0096	0.0056	0.0048	0.0104
54	S_{Fe3+} (iron (III))	kmol Fe^{3+}/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
55	S_{Al} (aluminium)	kmol Al/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
56	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
57	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
58	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
59	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
60	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
61	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
62	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
63	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
64	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
65	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
67	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
68	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	MMP extension (multi mineral precipitation)															
69	X_{CaCO3} (calcite)	kmol Calcite/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
70	X_{CaCO3} (aragonite)	kmol Aragonite/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
71	$X_{Ca3PO42}$ (amorphous calcium phosphate)	kmol ACP/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
72	$X_{Ca5PO4OH}$ (hydroxyapatite)	kmol HAP/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
73	X_{CaHPO4} (dicalcium phosphate)	kmol DCPD/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
74	$X_{Ca4HPO43}$ (octacalcium phosphate)	kmol OCP/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
75	$X_{MgNH4PO4}$ (struvite)	kmol Struvite/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
76	X_{MgHPO4} (newberyite)	kmol Newberyte/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
77	X_{MgCO3} (magnesite)	kmol Magnesite/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
78	X_{KMgPO4} (K-struvite)	kmol K-struvite/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
79	X_{FeS} (iron sulphide)	kmol Iron sulfide/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
80	$X_{Fe3PO42}$ (iron(II) phosphate)	kmol Vivianite/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
81	X_{AlPO4} (aluminum phosphate)	kmol Aluminum phosphate/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Fe extension															
82	X_{HFO_L} (hydrous ferric oxide with low adsoption capacity)	kmol/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
83	X_{HFO_H} (hydrous ferric oxide with high adsoption capacity)	kmol/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
84	X_{HFO_LP} (XHFO,L with adsorbed phosphate)	kmol/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
85	X_{HFO_HP} (XHFO,H with adsorbed phosphate)	kmol/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
86	X_{HFO_HPold}	kmol/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
87	X_{HFO_LPold}	kmol/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
88	X_{HFO_old}	kmol/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
89	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
90	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
91	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
92	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
93	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
94	X_{ISS0}	kg ISS/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table E.3 Steady-state input variables for ADM1 - variation of S_{IC}

			Simulation #1 - Sic = 0.06			Simulation #2 - Sic = 0.15		
			100%	0%		100%	0%	
Column	Variable/description	Unit	Cattle manure	Fish sludge	Sum	Cattle manure	Fish sludge	Sum
1	Time	day	0 400		0 400	0 400		0 400
2	S_{su} (sugars/monosaccharides)	kg COD/m^3	2.53	0	2.53	2.53	0	2.53
3	S_{aa} (amino acids)	kg COD/m^3	0.69	0	0.69	0.69	0	0.69
4	S_{fa} (fatty acids/total LCFA)	kg COD/m^3	2.44	0	2.44	2.44	0	2.44
5	S_{va} (total valeric acid)	kg COD/m^3	0.72	0	0.72	0.72	0	0.72
6	S_{bu} (total butyric acid)	kg COD/m^3	1.57	0	1.57	1.57	0	1.57
7	S_{pro} (total propionic acid)	kg COD/m^3	2.91	0	2.91	2.91	0	2.91
8	S_{ac} (total acetic acid)	kg COD/m^3	5.68	0	5.68	5.68	0	5.68
9	S_{h2} (hydrogen)	kg COD/m^3	0	0	0	0	0	0
10	S_{ch4} (methane)	kg COD/m^3	0	0	0	0	0	0
11	S_{IC} (inorganic carbon)	kmol C/m^3	0.06	0	0.06	0.15	0	0.15
12	S_{IN} (inorganic nitrogen)	kmol N/m^3	0.147	0	0.147	0.147	0	0.147
13	S_I (soluble inerts)	kg COD/m^3	0	0	0	0	0	0
14	Unknown (X_C (Composite materials)?)	Unknown (kg COD/m3)	0	0	0	0	0	0
15	X_{ch} (carbohydrates)	kg COD/m^3	13.62	0	13.62	13.62	0	13.62
16	X_{pr} (proteins)	kg COD/m^3	17.06	0	17.06	17.06	0	17.06
17	X_{li} (lipids)	kg COD/m^3	4.19	0	4.19	4.19	0	4.19
18	X_{su} (sugar degraders/monosaccharides degreaders)	kg COD/m^3	0.031	0	0.031	0.031	0	0.031
19	X_{aa} (amino acid degraders)	kg COD/m^3	0.021	0	0.021	0.021	0	0.021
20	X_{fa} (fatty acid/LCFA degraders)	kg COD/m^3	0.00001	0	0.00001	0.00001	0	0.00001
21	X_{c4} (valerate and butyrate degraders/C4-degraders)	kg COD/m^3	0.0001	0	0.0001	0.0001	0	0.0001
22	X_{pro} (total propionic degraders)	kg COD/m^3	0.01	0	0.01	0.01	0	0.01
23	X_{ac} (total acetic degraders)	kg COD/m^3	0.0017	0	0.0017	0.0017	0	0.0017
24	X_{h2} (hydrogen degraders)	kg COD/m^3	0.01	0	0.01	0.01	0	0.01
25	X_I (particulate inerts)	kg COD/m^3	0	0	0	0	0	0
26	Q_{in} (influent flow)	m^3/day	varies			varies		
27	T_{op} (Temperature)	°C	39		39	39		39
	P extension							
28	S_{IP} (inorganic phosphorus)	kmol P/m^3	0.0119	0	0.0119	0.0119	0	0.0119
29	X_{PHA} (polyhydroxyalkanoates)	kg COD/m^3	0	0	0	0	0	0
30	X_{PP} (polyphosphates)	kmol P/m^3	0	0	0	0	0	0
31	X_{PAO} (phosphorous accumulating organisms)	kg COD/m^3	0	0	0	0	0	0
32	Unknown	Unknown	0	0	0	0	0	0
33	Unknown	Unknown	0	0	0	0	0	0
34	Unknown	Unknown	0	0	0	0	0	0
35	Unknown	Unknown	0	0	0	0	0	0
36	Unknown	Unknown	0	0	0	0	0	0
37	Unknown	Unknown	0	0	0	0	0	0
	S extension							
38	S_{so4} (sulfate)	kmol S/m^3	0.00056	0	0.00056	0.00056	0	0.00056
39	S_{IS} (inorganic total sulfides)	kg COD/m^3	0.0784	0	0.0784	0.0784	0	0.0784
40	X_{hSRB} (hydrogen Sulphate reducing bacteria)	kg COD/m^3	0	0	0	0	0	0
41	X_{aSRB} (acetate Sulphate reducing bacteria)	kg COD/m^3	0	0	0	0	0	0
42	X_{pSRB} (propionate Sulphate reducing bacteria)	kg COD/m^3	0	0	0	0	0	0
43	X_{c4SRB} (Valerate- and butyrate-degrading sulphate reducing bacteria)	kg COD/m^3	0	0	0	0	0	0
44	X_{S0} (elemental sulphur)	kg COD/m^3	0	0	0	0	0	0
45	Unknown	Unknown	0	0	0	0	0	0
46	Unknown	Unknown	0	0	0	0	0	0
47	Unknown	Unknown	0	0	0	0	0	0
	PCM extension (physico-chemical model)							
48	S_{Na} (sodium)	kmol Na/m^3	0.026	0	0.026	0.026	0	0.026
49	S_K (potassium)	kmol K/m^3	0.096	0	0.096	0.096	0	0.096
50	S_{Cl} (chloride)	kmol Cl/m^3	0.026	0	0.026	0.026	0	0.026
51	S_{Ca} (calcium)	kmol Ca/m^3	0.027	0	0.027	0.027	0	0.027
52	S_{Mg} (magnesium)	kmol Mg/m^3	0.024	0	0.024	0.024	0	0.024
53	S_{Fe2+} (iron (II))	kg COD/m^3	0.008	0	0.008	0.008	0	0.008
54	S_{Fe3+} (iron (III))	kmol Fe^{3+}/m^3	0	0	0	0	0	0
55	S_{Al} (aluminium)	kmol Al/m^3	0	0	0	0	0	0
56	Unknown	Unknown	0	0	0	0	0	0
57	Unknown	Unknown	0	0	0	0	0	0
58	Unknown	Unknown	0	0	0	0	0	0
59	Unknown	Unknown	0	0	0	0	0	0
60	Unknown	Unknown	0	0	0	0	0	0
61	Unknown	Unknown	0	0	0	0	0	0
62	Unknown	Unknown	0	0	0	0	0	0
63	Unknown	Unknown	0	0	0	0	0	0
64	Unknown	Unknown	0	0	0	0	0	0
65	Unknown	Unknown	0	0	0	0	0	0
67	Unknown	Unknown	0	0	0	0	0	0
68	Unknown	Unknown	0	0	0	0	0	0
	MMP extension (multi mineral precipitation)							
69	X_{CaCO3} (calcite)	kmol Calcite/m^3	0	0	0	0	0	0
70	X_{CaCO3} (aragonite)	kmol Aragonite/m^3	0	0	0	0	0	0
71	$X_{Ca3PO42}$ (amorphous calcium phosphate)	kmol ACP/m^3	0	0	0	0	0	0
72	$X_{Ca5PO4OH}$ (hydroxyapatite)	kmol HAP/m^3	0	0	0	0	0	0
73	X_{CaHPO4} (dicalcium phosphate)	kmol DCPD/m^3	0	0	0	0	0	0
74	$X_{Ca4HPO43}$ (octacalcium phosphate)	kmol OCP/m^3	0	0	0	0	0	0
75	$X_{MgNH4PO4}$ (struvite)	kmol Struvite/m^3	0	0	0	0	0	0
76	X_{MgHPO4} (newberyite)	kmol Newberyte/m^3	0	0	0	0	0	0
77	X_{MgCO3} (magnesite)	kmol Magnesite/m^3	0	0	0	0	0	0
78	X_{KMgPO4} (K-struvite)	kmol K-struvite/m^3	0	0	0	0	0	0
79	X_{FeS} (iron sulphide)	kmol Iron sulfide/m^3	0	0	0	0	0	0
80	$X_{Fe3PO42}$ (iron(II) phosphate)	kmol Vivianite/m^3	0	0	0	0	0	0
81	X_{AlPO4} (aluminum phosphate)	kmol Aluminum phosphate/m^3	0	0	0	0	0	0
	Fe extension							
82	X_{HFO_L} (hydrous ferric oxide with low adsoption capacity)	kmol/m^3	0	0	0	0	0	0
83	X_{HFO_H} (hydrous ferric oxide with high adsoption capacity)	kmol/m^3	0	0	0	0	0	0
84	X_{HFO_LP} (XHFO,L with adsorbed phosphate)	kmol/m^3	0	0	0	0	0	0
85	X_{HFO_HP} (XHFO,H with adsorbed phosphate)	kmol/m^3	0	0	0	0	0	0
86	X_{HFO_HPold}	kmol/m^3	0	0	0	0	0	0
87	X_{HFO_LPold}	kmol/m^3	0	0	0	0	0	0
88	X_{HFO_old}	kmol/m^3	0	0	0	0	0	0
89	Unknown	Unknown	0	0	0	0	0	0
90	Unknown	Unknown	0	0	0	0	0	0
91	Unknown	Unknown	0	0	0	0	0	0
92	Unknown	Unknown	0	0	0	0	0	0
93	Unknown	Unknown	0	0	0	0	0	0
94	X_{ISS0}	kg ISS/m^3	0	0	0	0	0	0

Table E.4 Steady-state input variables for ADM1 - variation of S_{IS}

			Simulation #1 - Sis 15% of tot S			Simulation #2 - Sis 20% of tot S			Simulation #3 - Sis 25% of tot S		
			90%	10%		90%	10%	base case	90%	10%	
Column	**Variable/description**	**Unit**	**Cattle manure**	**Fish sludge**	**Sum**	**Cattle manure**	**Fish sludge**	**Sum**	**Cattle manure**	**Fish sludge**	**Sum**
1	Time	day	0 400		0 400	0 400		0 400	0 400		0 400
2	S_{su} (sugars/monosaccharides)	kg COD/m^3	2.277	0	2.277	2.277	0	2.277	2.277	0	2.277
3	S_{aa} (amino acids)	kg COD/m^3	0.621	0	0.621	0.621	0	0.621	0.621	0	0.621
4	S_{fa} (fatty acids/total LCFA)	kg COD/m^3	2.196	0	2.196	2.196	0	2.196	2.196	0	2.196
5	S_{va} (total valeric acid)	kg COD/m^3	0.648	0	0.648	0.648	0	0.648	0.648	0	0.648
6	S_{bu} (total butyric acid)	kg COD/m^3	1.413	0	1.413	1.413	0	1.413	1.413	0	1.413
7	S_{pro} (total propionic acid)	kg COD/m^3	2.619	0	2.619	2.619	0	2.619	2.619	0	2.619
8	S_{ac} (total acetic acid)	kg COD/m^3	5.112	0	5.112	5.112	0	5.112	5.112	0	5.112
9	S_{h2} (hydrogen)	kg COD/m^3	0	0	0	0	0	0	0	0	0
10	S_{ch4} (methane)	kg COD/m^3	0	0	0	0	0	0	0	0	0
11	S_{IC} (inorganic carbon)	kmol C/m^3	0.135	0	0.135	0.135	0	0.135	0.135	0	0.135
12	S_{IN} (inorganic nitrogen)	kmol N/m^3	0.1323	0	0.1323	0.1323	0	0.1323	0.1323	0	0.1323
13	S_I (soluble inerts)	kg COD/m^3	0	0.3566	0.3566	0	0.3566	0.3566	0	0.3566	0.3566
14	Unknown (X_C (Composite materials)?)	Unknown (kg COD/m3)	0	0	0	0	0	0	0	0	0
15	X_{ch} (carbohydrates)	kg COD/m^3	12.258	0.4279	12.6859	12.258	0.4279	12.6859	12.258	0.4279	12.6859
16	X_{pr} (proteins)	kg COD/m^3	15.354	2.8524	18.2064	15.354	2.8524	18.2064	15.354	2.8524	18.2064
17	X_{li} (lipids)	kg COD/m^3	3.771	1.4737	5.2447	3.771	1.4737	5.2447	3.771	1.4737	5.2447
18	X_{su} (sugar degraders/monosaccharides degreaders)	kg COD/m^3	0.0279	0	0.0279	0.0279	0	0.0279	0.0279	0	0.0279
19	X_{aa} (amino acid degraders)	kg COD/m^3	0.0189	0	0.0189	0.0189	0	0.0189	0.0189	0	0.0189
20	X_{fa} (fatty acid/LCFA degraders)	kg COD/m^3	0.000009	0	0.000009	0.000009	0	0.000009	0.000009	0	0.000009
21	X_{c4} (valerate and butyrate degraders/C4-degraders)	kg COD/m^3	0.00009	0	0.00009	0.00009	0	0.00009	0.00009	0	0.00009
22	X_{pro} (total propionic degraders)	kg COD/m^3	0.009	0	0.009	0.009	0	0.009	0.009	0	0.009
23	X_{ac} (total acetic degraders)	kg COD/m^3	0.00153	0	0.00153	0.00153	0	0.00153	0.00153	0	0.00153
24	X_{h2} (hydrogen degraders)	kg COD/m^3	0.009	0	0.009	0.009	0	0.009	0.009	0	0.009
25	X_I (particulate inerts)	kg COD/m^3	0	6.7745	6.7745	0	6.7745	6.7745	0	6.7745	6.7745
26	Q_{in} (influent flow)	m^3/day	varies			varies			varies		
27	T_{op} (Temperature)	°C	39		39	39		39	39		39
	P extension										
28	S_{IP} (inorganic phosphorus)	kmol P/m^3	0.01071	0.00721	0.01792	0.01071	0.00721	0.01792	0.01071	0.00721	0.01792
29	X_{PHA} (polyhydroxyalkanoates)	kg COD/m^3	0	0	0	0	0	0	0	0	0
30	X_{PP} (polyphosphates)	kmol P/m^3	0	0	0	0	0	0	0	0	0
31	X_{PAO} (phosphorous accumulating organisms)	kg COD/m^3	0	0	0	0	0	0	0	0	0
32	Unknown	Unknown	0	0	0	0	0	0	0	0	0
33	Unknown	Unknown	0	0	0	0	0	0	0	0	0
34	Unknown	Unknown	0	0	0	0	0	0	0	0	0
35	Unknown	Unknown	0	0	0	0	0	0	0	0	0
36	Unknown	Unknown	0	0	0	0	0	0	0	0	0
37	Unknown	Unknown	0	0	0	0	0	0	0	0	0
	S extension										
38	S_{so4} (sulfate)	kmol S/m^3	0.000504	0.000112	0.000616	0.000504	0.000112	0.000616	0.000504	0.000112	0.000616
39	S_{IS} (inorganic total sulfides)	kg COD/m^3	0.05292	0.43176	0.48468	0.07056	0.57568	0.64624	0.0882	0.7196	0.8078
40	X_{hSRB} (hydrogen Sulphate reducing bacteria)	kg COD/m^3	0	0	0	0	0	0	0	0	0
41	X_{aSRB} (acetate Sulphate reducing bacteria)	kg COD/m^3	0	0	0	0	0	0	0	0	0
42	X_{pSRB} (propionate Sulphate reducing bacteria)	kg COD/m^3	0	0	0	0	0	0	0	0	0
43	X_{c4SRB} (Valerate- and butyrate-degrading sulphate reducing bacteria)	kg COD/m^3	0	0	0	0	0	0	0	0	0
44	X_{S0} (elemental sulphur)	kg COD/m^3	0	0	0	0	0	0	0	0	0
45	Unknown	Unknown	0	0	0	0	0	0	0	0	0
46	Unknown	Unknown	0	0	0	0	0	0	0	0	0
47	Unknown	Unknown	0	0	0	0	0	0	0	0	0
	PCM extension (physico-chemical model)										
48	S_{Na} (sodium)	kmol Na/m^3	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268
49	S_K (potassium)	kmol K/m^3	0.0864	0.0018	0.0882	0.0864	0.0018	0.0882	0.0864	0.0018	0.0882
50	S_{Cl} (chloride)	kmol Cl/m^3	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268
51	S_{Ca} (calcium)	kmol Ca/m^3	0.0243	0.0162	0.0405	0.0243	0.0162	0.0405	0.0243	0.0162	0.0405
52	S_{Mg} (magnesium)	kmol Mg/m^3	0.0216	0.0025	0.0241	0.0216	0.0025	0.0241	0.0216	0.0025	0.0241
53	S_{Fe2+} (iron (II))	kg COD/m^3	0.0072	0.0016	0.0088	0.0072	0.0016	0.0088	0.0072	0.0016	0.0088
54	S_{Fe3+} (iron (III))	kmol Fe^{3+}/m^3	0	0	0	0	0	0	0	0	0
55	S_{Al} (aluminium)	kmol Al/m^3	0	0	0	0	0	0	0	0	0
56	Unknown	Unknown	0	0	0	0	0	0	0	0	0
57	Unknown	Unknown	0	0	0	0	0	0	0	0	0
58	Unknown	Unknown	0	0	0	0	0	0	0	0	0
59	Unknown	Unknown	0	0	0	0	0	0	0	0	0
60	Unknown	Unknown	0	0	0	0	0	0	0	0	0
61	Unknown	Unknown	0	0	0	0	0	0	0	0	0
62	Unknown	Unknown	0	0	0	0	0	0	0	0	0
63	Unknown	Unknown	0	0	0	0	0	0	0	0	0
64	Unknown	Unknown	0	0	0	0	0	0	0	0	0
65	Unknown	Unknown	0	0	0	0	0	0	0	0	0
67	Unknown	Unknown	0	0	0	0	0	0	0	0	0
68	Unknown	Unknown	0	0	0	0	0	0	0	0	0
	MMP extension (multi mineral precipitation)										
69	X_{CaCO3} (calcite)	kmol Calcite/m^3	0	0	0	0	0	0	0	0	0
70	X_{CaCO3} (aragonite)	kmol Aragonite/m^3	0	0	0	0	0	0	0	0	0
71	$X_{Ca3PO42}$ (amorphous calcium phosphate)	kmol ACP/m^3	0	0	0	0	0	0	0	0	0
72	$X_{Ca5PO4OH}$ (hydroxyapatite)	kmol HAP/m^3	0	0	0	0	0	0	0	0	0
73	X_{CaHPO4} (dicalcium phosphate)	kmol DCPD/m^3	0	0	0	0	0	0	0	0	0
74	$X_{Ca4HPO43}$ (octacalcium phosphate)	kmol OCP/m^3	0	0	0	0	0	0	0	0	0
75	$X_{MgNH4PO4}$ (struvite)	kmol Struvite/m^3	0	0	0	0	0	0	0	0	0
76	X_{MgHPO4} (newberyite)	kmol Newberyte/m^3	0	0	0	0	0	0	0	0	0
77	X_{MgCO3} (magnesite)	kmol Magnesite/m^3	0	0	0	0	0	0	0	0	0
78	X_{KMgPO4} (K-struvite)	kmol K-struvite/m^3	0	0	0	0	0	0	0	0	0
79	X_{FeS} (iron sulphide)	kmol Iron sulfide/m^3	0	0	0	0	0	0	0	0	0
80	$X_{Fe3PO42}$ (iron(II) phosphate)	kmol Vivianite/m^3	0	0	0	0	0	0	0	0	0
81	X_{AlPO4} (aluminum phosphate)	kmol Aluminum phosphate/m^3	0	0	0	0	0	0	0	0	0
	Fe extension										
82	X_{HFO_L} (hydrous ferric oxide with low adsoption capacity)	kmol/m^3	0	0	0	0	0	0	0	0	0
83	X_{HFO_H} (hydrous ferric oxide with high adsoption capacity)	kmol/m^3	0	0	0	0	0	0	0	0	0
84	X_{HFO_LP} (XHFO,L with adsorbed phosphate)	kmol/m^3	0	0	0	0	0	0	0	0	0
85	X_{HFO_HP} (XHFO,H with adsorbed phosphate)	kmol/m^3	0	0	0	0	0	0	0	0	0
86	X_{HFO_HPold}	kmol/m^3	0	0	0	0	0	0	0	0	0
87	X_{HFO_LPold}	kmol/m^3	0	0	0	0	0	0	0	0	0
88	X_{HFO_old}	kmol/m^3	0	0	0	0	0	0	0	0	0
89	Unknown	Unknown	0	0	0	0	0	0	0	0	0
90	Unknown	Unknown	0	0	0	0	0	0	0	0	0
91	Unknown	Unknown	0	0	0	0	0	0	0	0	0
92	Unknown	Unknown	0	0	0	0	0	0	0	0	0
93	Unknown	Unknown	0	0	0	0	0	0	0	0	0
94	X_{ISS0}	kg ISS/m^3	0	0	0	0	0	0	0	0	0

Table E.5 Steady-state input variables for ADM1 - variation of BFP

					Simulation #1 - BFP = 0.40			Simulation #2 - BFP = 0.30			Simulation #3 - BFP = 0.20			Simulation #4 - BFP = 0.50		
					90%	10%	base case	90%	10%		90%	10%		90%	10%	
Column	Variable/description	Unit	Cattle manure	Fish sludge	Cattle manure	Fish sludge	Sum	Cattle manure	Fish sludge	Sum	Cattle manure	Fish sludge	Sum	Cattle manure	Fish sludge	Sum
1	Time	day	0 400		0 400		0 400	0 400		0 400	0 400		0 400	0 400		0 400
2	S_{su} (sugars/monosaccharides)	kg COD/m³	2.53	0	2.277	0	2.277	2.277	0	2.277	2.277	0	2.277	2.277	0	2.277
3	S_{aa} (amino acids)	kg COD/m³	0.69	0	0.621	0	0.621	0.621	0	0.621	0.621	0	0.621	0.621	0	0.621
4	S_{fa} (fatty acids/total LCFA)	kg COD/m³	2.44	0	2.196	0	2.196	2.196	0	2.196	2.196	0	2.196	2.196	0	2.196
5	S_{va} (total valeric acid)	kg COD/m³	0.72	0	0.648	0	0.648	0.648	0	0.648	0.648	0	0.648	0.648	0	0.648
6	S_{bu} (total butyric acid)	kg COD/m³	1.57	0	1.413	0	1.413	1.413	0	1.413	1.413	0	1.413	1.413	0	1.413
7	S_{pro} (total propionic acid)	kg COD/m³	2.91	0	2.619	0	2.619	2.619	0	2.619	2.619	0	2.619	2.619	0	2.619
8	S_{ac} (total acetic acid)	kg COD/m³	5.68	0	5.112	0	5.112	5.112	0	5.112	5.112	0	5.112	5.112	0	5.112
9	S_{h2} (hydrogen)	kg COD/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
10	S_{ch4} (methane)	kg COD/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
11	S_{IC} (inorganic carbon)	kmol C/m³	0.15	0	0.135	0	0.135	0.135	0	0.135	0.135	0	0.135	0.135	0	0.135
12	S_{IN} (inorganic nitrogen)	kmol N/m³	0.147	0	0.1323	0	0.1323	0.1323	0	0.1323	0.1323	0	0.1323	0.1323	0	0.1323
13	S_I (soluble inerts)	kg COD/m³	0	3.566	0	0.3566	0.3566	0	0.3566	0.3566	0	0.3566	0.3566	0	0.3566	0.3566
14	Unknown (X_C (Composite materials)?)	Unknown (kg COD/m3)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
15	X_{ch} (carbohydrates)	kg COD/m³	13.62	4.279	12.258	0.4279	12.6859	12.258	0.320925	12.57893	12.258	0.21395	12.47195	12.258	0.534875	12.79288
16	X_{pr} (proteins)	kg COD/m³	17.06	28.524	15.354	2.8524	18.2064	15.354	2.1393	17.4933	15.354	1.4262	16.7802	15.354	3.5655	18.9195
17	X_{li} (lipids)	kg COD/m³	4.19	14.737	3.771	1.4737	5.2447	3.771	1.105275	4.876275	3.771	0.73685	4.50785	3.771	1.842125	5.613125
18	X_{su} (sugar degraders/monosaccharides degreaders)	kg COD/m³	0.031	0	0.0279	0	0.0279	0.0279	0	0.0279	0.0279	0	0.0279	0.0279	0	0.0279
19	X_{aa} (amino acid degraders)	kg COD/m³	0.021	0	0.0189	0	0.0189	0.0189	0	0.0189	0.0189	0	0.0189	0.0189	0	0.0189
20	X_{fa} (fatty acid/LCFA degraders)	kg COD/m³	0.00001	0	0.000009	0	0.000009	0.000009	0	0.000009	0.000009	0	0.000009	0.000009	0	0.000009
21	X_{c4} (valerate and butyrate degraders/C4-degraders)	kg COD/m³	0.0001	0	0.00009	0	0.00009	0.00009	0	0.00009	0.00009	0	0.00009	0.00009	0	0.00009
22	X_{pro} (total propionic degraders)	kg COD/m³	0.01	0	0.009	0	0.009	0.009	0	0.009	0.009	0	0.009	0.009	0	0.009
23	X_{ac} (total acetic degraders)	kg COD/m³	0.0017	0	0.00153	0	0.00153	0.00153	0	0.00153	0.00153	0	0.00153	0.00153	0	0.00153
24	X_{h2} (hydrogen degraders)	kg COD/m³	0.01	0	0.009	0	0.009	0.009	0	0.009	0.009	0	0.009	0.009	0	0.009
25	X_I (particulate inerts)	kg COD/m³	0	67.745	0	6.7745	6.7745	0	6.7745	6.7745	0	6.7745	6.7745	0	6.7745	6.7745
26	Q_{in} (influent flow)	m³/day	varies		varies			varies			varies			varies		
27	T_{op} (Temperature)	°C	39		39		39	39		39	39		39	39		39
	P extension															
28	S_{IP} (inorganic phosphorus)	kmol P/m³	0.0119	0.0721	0.01071	0.00721	0.01792	0.01071	0.00721	0.01792	0.01071	0.00721	0.01792	0.01071	0.00721	0.01792
29	X_{PHA} (polyhydroxyalkanoates)	kg COD/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
30	X_{PP} (polyphosphates)	kmol P/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
31	X_{PAO} (phosphorous accumulating organisms)	kg COD/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
32	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
33	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
34	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
35	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
36	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
37	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
	S extension															
38	S_{so4} (sulfate)	kmol S/m³	0.00056	0.00112	0.000504	0.000112	0.000616	0.000504	0.000112	0.000616	0.000504	0.000112	0.000616	0.000504	0.000112	0.000616
39	S_{IS} (inorganic total sulfides)	kg COD/m³	0.0784	5.7568	0.07056	0.57568	0.64624	0.07056	0.57568	0.64624	0.07056	0.57568	0.6462	0.07056	0.57568	0.6462
40	X_{hSRB} (hydrogen Sulphate reducing bacteria)	kg COD/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
41	X_{aSRB} (acetate Sulphate reducing bacteria)	kg COD/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
42	X_{pSRB} (propionate Sulphate reducing bacteria)	kg COD/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
43	X_{c4SRB} (Valerate- and butyrate-degrading sulphate reducing bacteria)	kg COD/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
44	X_{S0} (elemental sulphur)	kg COD/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
45	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
46	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
47	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	PCM extension (physico-chemical model)															
48	S_{Na} (sodium)	kmol Na/m³	0.026	0.034	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268
49	S_K (potassium)	kmol K/m³	0.096	0.018	0.0864	0.0018	0.0882	0.0864	0.0018	0.0882	0.0864	0.0018	0.0882	0.0864	0.0018	0.0882
50	S_{Cl} (chloride)	kmol Cl/m³	0.026	0.034	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268
51	S_{Ca} (calcium)	kmol Ca/m³	0.027	0.162	0.0243	0.0162	0.0405	0.0243	0.0162	0.0405	0.0243	0.0162	0.0405	0.0243	0.0162	0.0405
52	S_{Mg} (magnesium)	kmol Mg/m³	0.024	0.025	0.0216	0.0025	0.0241	0.0216	0.0025	0.0241	0.0216	0.0025	0.0241	0.0216	0.0025	0.0241
53	S_{Fe2+} (iron (II))	kg COD/m³	0.008	0.016	0.0072	0.0016	0.0088	0.0072	0.0016	0.0088	0.0072	0.0016	0.0088	0.0072	0.0016	0.0088
54	S_{Fe3+} (iron (III))	kmol Fe^{3+}/m^3	0	0	0	0	0	0	0	0	0	0	0	0	0	0
55	S_{Al} (aluminium)	kmol Al/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
56	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
57	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
58	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
59	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
60	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
61	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
62	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
63	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
64	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
65	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
67	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
68	Unknown	Unknown	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	MMP extension (multi mineral precipitation)															
69	X_{CaCO3} (calcite)	kmol Calcite/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
70	X_{CaCO3} (aragonite)	kmol Aragonite/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
71	$X_{Ca3PO42}$ (amorphous calcium phosphate)	kmol ACP/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
72	$X_{Ca5PO4OH}$ (hydroxyapatite)	kmol HAP/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
73	X_{CaHPO4} (dicalcium phosphate)	kmol DCPD/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
74	$X_{Ca4HPO43}$ (octacalcium phosphate)	kmol OCP/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
75	$X_{MgNH4PO4}$ (struvite)	kmol Struvite/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
76	X_{MgHPO4} (newberyite)	kmol Newberyte/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
77	X_{MgCO3} (magnesite)	kmol Magnesite/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
78	X_{KMgPO4} (K-struvite)	kmol K-struvite/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
79	X_{FeS} (iron sulphide)	kmol Iron sulfide/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
80	$X_{Fe3PO42}$ (iron(II) phosphate)	kmol Vivianite/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
81	X_{AlPO4} (aluminum phosphate)	kmol Aluminum phosphate/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Fe extension															
82	X_{HFO_L} (hydrous ferric oxide with low adsoption capacity)	kmol/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
83	X_{HFO_H} (hydrous ferric oxide with high adsoption capacity)	kmol/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
84	X_{HFO_LP} (XHFO,L with adsorbed phosphate)	kmol/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
85	X_{HFO_HP} (XHFO,H with adsorbed phosphate)	kmol/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
86	X_{HFO_HPold}	kmol/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
87	X_{HFO_LPold}	kmol/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
88	X_{HFO_old}	kmol/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0
89	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
90	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
91	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
92	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
93	Unknown	Unknown			0	0	0	0	0	0	0	0	0	0	0	0
94	X_{ISS0}	kg ISS/m³	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table E.6 Steady-state input variables for ADM1 - variation of hydrous ferric oxide (HFO)

			Simulation #1 - 0.2% HFO of TS			Simulation #2 - 0.35% HFO of TS			Simulation #3 - 2% HFO of TS		
			90%	10%		90%	10%		90%	10%	
Column	**Variable/description**	**Unit**	**Cattle manure**	**Fish sludge**	**Sum**	**Cattle manure**	**Fish sludge**	**Sum**	**Cattle manure**	**Fish sludge**	**Sum**
1	Time	day	0 400		0 400	0 400		0 400	0 400		0 400
2	S_{su} (sugars/monosaccharides)	kg COD/m³	2.277	0	2.277	2.277	0	2.277	2.277	0	2.277
3	S_{aa} (amino acids)	kg COD/m³	0.621	0	0.621	0.621	0	0.621	0.621	0	0.621
4	S_{fa} (fatty acids/total LCFA)	kg COD/m³	2.196	0	2.196	2.196	0	2.196	2.196	0	2.196
5	S_{va} (total valeric acid)	kg COD/m³	0.648	0	0.648	0.648	0	0.648	0.648	0	0.648
6	S_{bu} (total butyric acid)	kg COD/m³	1.413	0	1.413	1.413	0	1.413	1.413	0	1.413
7	S_{pro} (total propionic acid)	kg COD/m³	2.619	0	2.619	2.619	0	2.619	2.619	0	2.619
8	S_{ac} (total acetic acid)	kg COD/m³	5.112	0	5.112	5.112	0	5.112	5.112	0	5.112
9	S_{h2} (hydrogen)	kg COD/m³	0	0	0	0	0	0	0	0	0
10	S_{ch4} (methane)	kg COD/m³	0	0	0	0	0	0	0	0	0
11	S_{IC} (inorganic carbon)	kmol C/m³	0.135	0	0.135	0.135	0	0.135	0.135	0	0.135
12	S_{IN} (inorganic nitrogen)	kmol N/m³	0.1323	0	0.1323	0.1323	0	0.1323	0.1323	0	0.1323
13	S_I (soluble inerts)	kg COD/m³	0	0.3566	0.3566	0	0.3566	0.3566	0	0.3566	0.3566
14	Unknown (X_C (Composite materials)?)	Unknown (kg COD/m3)	0	0	0	0	0	0	0	0	0
15	X_{ch} (carbohydrates)	kg COD/m³	12.258	0.4279	12.6859	12.258	0.4279	12.6859	12.258	0.4279	12.6859
16	X_{pr} (proteins)	kg COD/m³	15.354	2.8524	18.2064	15.354	2.8524	18.2064	15.354	2.8524	18.2064
17	X_{li} (lipids)	kg COD/m³	3.771	1.4737	5.2447	3.771	1.4737	5.2447	3.771	1.4737	5.2447
18	X_{su} (sugar degraders/monosaccharides degreaders)	kg COD/m³	0.0279	0	0.0279	0.0279	0	0.0279	0.0279	0	0.0279
19	X_{aa} (amino acid degraders)	kg COD/m³	0.0189	0	0.0189	0.0189	0	0.0189	0.0189	0	0.0189
20	X_{fa} (fatty acid/LCFA degraders)	kg COD/m³	0.000009	0	0.000009	0.000009	0	0.000009	0.000009	0	0.000009
21	X_{c4} (valerate and butyrate degraders/C4-degraders)	kg COD/m³	0.00009	0	0.00009	0.00009	0	0.00009	0.00009	0	0.00009
22	X_{pro} (total propionic degraders)	kg COD/m³	0.009	0	0.009	0.009	0	0.009	0.009	0	0.009
23	X_{ac} (total acetic degraders)	kg COD/m³	0.00153	0	0.00153	0.00153	0	0.00153	0.00153	0	0.00153
24	X_{h2} (hydrogen degraders)	kg COD/m³	0.009	0	0.009	0.009	0	0.009	0.009	0	0.009
25	X_I (particulate inerts)	kg COD/m³	0	6.7745	6.7745	0	6.7745	6.7745	0	6.7745	6.7745
26	Q_{in} (influent flow)	m³/day	varies			varies			varies		
27	T_{op} (Temperature)	°C	39		39	39		39	39		39
	P extension										
28	S_{IP} (inorganic phosphorus)	kmol P/m³	0.01071	0.00721	0.01792	0.01071	0.00721	0.01792	0.01071	0.00721	0.01792
29	X_{PHA} (polyhydroxyalkanoates)	kg COD/m³	0	0	0	0	0	0	0	0	0
30	X_{PP} (polyphosphates)	kmol P/m³	0	0	0	0	0	0	0	0	0
31	X_{PAO} (phosphorous accumulating organisms)	kg COD/m³	0	0	0	0	0	0	0	0	0
32	Unknown	Unknown	0	0	0	0	0	0	0	0	0
33	Unknown	Unknown	0	0	0	0	0	0	0	0	0
34	Unknown	Unknown	0	0	0	0	0	0	0	0	0
35	Unknown	Unknown	0	0	0	0	0	0	0	0	0
36	Unknown	Unknown	0	0	0	0	0	0	0	0	0
37	Unknown	Unknown	0	0	0	0	0	0	0	0	0
	S extension										
38	S_{so4} (sulfate)	kmol S/m³	0.000504	0.000112	0.000616	0.000504	0.000112	0.000616	0.000504	0.000112	0.000616
39	S_{IS} (inorganic total sulfides)	kg COD/m³	0.07056	0.57568	0.64624	0.07056	0.57568	0.64624	0.07056	0.57568	0.64624
40	X_{hSRB} (hydrogen Sulphate reducing bacteria)	kg COD/m³	0	0	0	0	0	0	0	0	0
41	X_{aSRB} (acetate Sulphate reducing bacteria)	kg COD/m³	0	0	0	0	0	0	0	0	0
42	X_{pSRB} (propionate Sulphate reducing bacteria)	kg COD/m³	0	0	0	0	0	0	0	0	0
43	X_{c4SRB} (Valerate- and butyrate-degrading sulphate reducing bacteria)	kg COD/m³	0	0	0	0	0	0	0	0	0
44	X_{S0} (elemental sulphur)	kg COD/m³	0	0	0	0	0	0	0	0	0
45	Unknown	Unknown	0	0	0	0	0	0	0	0	0
46	Unknown	Unknown	0	0	0	0	0	0	0	0	0
47	Unknown	Unknown	0	0	0	0	0	0	0	0	0
	PCM extension (physico-chemical model)										
48	S_{Na} (sodium)	kmol Na/m³	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268
49	S_K (potassium)	kmol K/m³	0.0864	0.0018	0.0882	0.0864	0.0018	0.0882	0.0864	0.0018	0.0882
50	S_{Cl} (chloride)	kmol Cl/m³	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268	0.0234	0.0034	0.0268
51	S_{Ca} (calcium)	kmol Ca/m³	0.0243	0.0162	0.0405	0.0243	0.0162	0.0405	0.0243	0.0162	0.0405
52	S_{Mg} (magnesium)	kmol Mg/m³	0.0216	0.0025	0.0241	0.0216	0.0025	0.0241	0.0216	0.0025	0.0241
53	S_{Fe2+} (iron (II))	kg COD/m³	0.0072	0.0016	0.0088	0.0072	0.0016	0.0088	0.0072	0.0016	0.0088
54	S_{Fe3+} (iron (III))	kmol Fe^{3+}/m³	0	0	0	0	0	0	0	0	0
55	S_{Al} (aluminium)	kmol Al/m³	0	0	0	0	0	0	0	0	0
56	Unknown	Unknown	0	0	0	0	0	0	0	0	0
57	Unknown	Unknown	0	0	0	0	0	0	0	0	0
58	Unknown	Unknown	0	0	0	0	0	0	0	0	0
59	Unknown	Unknown	0	0	0	0	0	0	0	0	0
60	Unknown	Unknown	0	0	0	0	0	0	0	0	0
61	Unknown	Unknown	0	0	0	0	0	0	0	0	0
62	Unknown	Unknown	0	0	0	0	0	0	0	0	0
63	Unknown	Unknown	0	0	0	0	0	0	0	0	0
64	Unknown	Unknown	0	0	0	0	0	0	0	0	0
65	Unknown	Unknown	0	0	0	0	0	0	0	0	0
67	Unknown	Unknown	0	0	0	0	0	0	0	0	0
68	Unknown	Unknown	0	0	0	0	0	0	0	0	0
	MMP extension (multi mineral precipitation)										
69	X_{CaCO3} (calcite)	kmol Calcite/m³	0	0	0	0	0	0	0	0	0
70	X_{CaCO3} (aragonite)	kmol Aragonite/m³	0	0	0	0	0	0	0	0	0
71	$X_{Ca3PO42}$ (amorphous calcium phosphate)	kmol ACP/m³	0	0	0	0	0	0	0	0	0
72	$X_{Ca5PO4OH}$ (hydroxyapatite)	kmol HAP/m³	0	0	0	0	0	0	0	0	0
73	X_{CaHPO4} (dicalcium phosphate)	kmol DCPD/m³	0	0	0	0	0	0	0	0	0
74	$X_{Ca4HPO43}$ (octacalcium phosphate)	kmol OCP/m³	0	0	0	0	0	0	0	0	0
75	$X_{MgNH4PO4}$ (struvite)	kmol Struvite/m³	0	0	0	0	0	0	0	0	0
76	X_{MgHPO4} (newberyite)	kmol Newberyte/m³	0	0	0	0	0	0	0	0	0
77	X_{MgCO3} (magnesite)	kmol Magnesite/m³	0	0	0	0	0	0	0	0	0
78	X_{KMgPO4} (K-struvite)	kmol K-struvite/m³	0	0	0	0	0	0	0	0	0
79	X_{FeS} (iron sulphide)	kmol Iron sulfide/m³	0	0	0	0	0	0	0	0	0
80	$X_{Fe3PO42}$ (iron(II) phosphate)	kmol Vivianite/m³	0	0	0	0	0	0	0	0	0
81	X_{AlPO4} (aluminum phosphate)	kmol Aluminum phosphate/m³	0	0	0	0	0	0	0	0	0
	Fe extension										
82	X_{HFO_L} (hydrous ferric oxide with low adsoption capacity)	kmol/m³	0	0	0.000866	0	0	0.001515	0	0	0.008656
83	X_{HFO_H} (hydrous ferric oxide with high adsoption capacity)	kmol/m³	0	0	0	0	0	0	0	0	0
84	X_{HFO_LP} (XHFO,L with adsorbed phosphate)	kmol/m³	0	0	0	0	0	0	0	0	0
85	X_{HFO_HP} (XHFO,H with adsorbed phosphate)	kmol/m³	0	0	0	0	0	0	0	0	0
86	X_{HFO_HPold}	kmol/m³	0	0	0	0	0	0	0	0	0
87	X_{HFO_LPold}	kmol/m³	0	0	0	0	0	0	0	0	0
88	X_{HFO_old}	kmol/m³	0	0	0	0	0	0	0	0	0
89	Unknown	Unknown	0	0	0	0	0	0	0	0	0
90	Unknown	Unknown	0	0	0	0	0	0	0	0	0
91	Unknown	Unknown	0	0	0	0	0	0	0	0	0
92	Unknown	Unknown	0	0	0	0	0	0	0	0	0
93	Unknown	Unknown	0	0	0	0	0	0	0	0	0
94	X_{ISS0}	kg ISS/m³	0	0	0	0	0	0	0	0	0

Appendix F – Comparison of ADM1 script with a known case

The MATLAB script version of ADM1 extended with phosphorous, sulphur and iron interaction was compared with a known case [53]. The known case was original focusing on the start-up transition in a bioreactor and had redefined some hydrolysis kinetics (k_{hyd}) constant to be non-constant. This modification was not implemented in the ADM1 script used in this report. When comparing the results, it was focused on the semi-steady state region of the simulation, and it was used constant values for hydrolysis kinetics (k_{hyd}) and disintegration kinetic (k_{dis}) [51]. It was expected to have a larger deviation in the beginning of the simulation when comparing with the known case.

The variables for input are summarised in Table F.1 below [53]. Please note that there is variable influent flow, and one parameter can have several values (correlated to the time). Missing column index in the table below means that the variable is equal to zero (where the maximum column index is 94). Values for S_{cat} is equally distributed between S_{Na} and S_K, and S_{an} is equal to S_{Cl} [54]. Due to different implementation of cations and anions in the MATLAB script used in this report, the value of S_{Na} and S_K were slightly changed to get a better correlation (from 0.053 to 0.062). However, the values used for S_{Na} and S_K (S_{cat}) is in the range of reported values in the compared case [53].

Table F.1 Steady-state input variables for ADM1 [53]

Column	Variable/description	Unit	Cattle manure
1	Time, used if influent is not constant.	Day	0 14 15 16 17 18 19 22 28 29 42 43 85 300
2	S_{su} (sugars/monosaccharides)	kg COD/m^3	2.53

Column	Variable/description	Unit	Cattle manure
3	S_{aa} (amino acids)	kg COD/m^3	0.69
4	S_{fa} (fatty acids/total LCFA)	kg COD/m^3	2.44
5	S_{va} (total valeric acid)	kg COD/m^3	0.72
6	S_{bu} (total butyric acid)	kg COD/m^3	1.57
7	S_{pro} (total propionic acid)	kg COD/m^3	2.91
8	S_{ac} (total acetic acid)	kg COD/m^3	5.68
9	S_{h2} (hydrogen)	kg COD/m^3	0
10	S_{ch4} (methane)	kg COD/m^3	0
11	S_{IC} (inorganic carbon)	kmol C/m^3	0.06
12	S_{IN} (inorganic nitrogen)	kmol N/m^3	0.147
13	S_{I} (soluble inerts)	kg COD/m^3	0
14	X_{C} (Composite materials)	kg COD/m3	0
15	X_{ch} (carbohydrates)	kg COD/m^3	13.62
16	X_{pr} (proteins)	kg COD/m^3	17.06
17	X_{li} (lipids)	kg COD/m^3	4.19
18	X_{su} (sugar degraders/ monosaccharides degreaders)	kg COD/m^3	0.031
19	X_{aa} (amino acid degraders)	kg COD/m^3	0.021
20	X_{fa} (fatty acid/LCFA degraders)	kg COD/m^3	0.00001
21	X_{c4} (valerate and butyrate degraders/C4-degraders)	kg COD/m^3	0.0001
22	X_{pro} (total propionic degraders)	kg COD/m^3	0.01
23	X_{ac} (total acetic degraders)	kg COD/m^3	0.0017
24	X_{h2} (hydrogen degraders)	kg COD/m^3	0.01
25	X_{I} (particulate inerts)	kg COD/m^3	0

Column	Variable/description	Unit	Cattle manure
26	Q_{in} (influent flow)	m^3/day	0 0 0.002 0.002 0.0039 0.0039 0.0052 0.006 0.006 0.0063 0.0063 0.0052 0.0052 0.0052
27	T_{op} (Temperature)	°C	38
	PCM extension (physico-chemical model)		
48	S_{Na} (sodium)	kmol Na/m^3	0.062*
49	S_K (potassium)	kmol K/m^3	0.062*
50	S_{Cl} (chloride)	kmol Cl/m^3	0.02

**Please note that for S_{cat} the value was slightly changed due to different implementation of S_{cat} in the version of ADM1 used in this report. The value was changed from 0.053 to 0.062 and the value was assigned to the variables S_{Na} and S_K.*

In addition some kinetic parameters is adjusted due to cow manure [53], [51]. These are listed in Table F.2.

Table F.2 Adjusted kinetic parameters for ADM1 [53], [51]

Parameter	**Description**	**Unit**	**ADM1 default value**	**Values used**
$K_{m,su}$	Maximum uptake rate of monosaccharides	d^{-1}	30.0	11.9
$K_{s,su}$	Half saturation concentration of monosaccharide uptake	kg O_2/m^3	0.5	4.5
$K_{m,aa}$	Maximum uptake rate of amino acids	d^{-1}	50.0	19.8
$K_{s,aa}$	Half saturation concentration of amino acids uptake	kg O_2/m^3	0.3	0.3
$K_{m,c4}$	Maximum uptake rate of valerate and butyrate	d^{-1}	20.0	12.2
$K_{s,c4}$	Half saturation concentration of valerate and butyrate uptake	kg O_2/m^3	0.2	0.6
$K_{m,pro}$	Maximum uptake rate of propionate	d^{-1}	13.0	3.5
$K_{s,pro}$	Half saturation concentration of propionate uptake	kg O_2/m^3	0.1	0.4
$K_{m,ac}$	Maximum uptake rate of acetate	d^{-1}	8.0	11.1
$K_{s,ac}$	Half saturation concentration of acetate uptake	kg O_2/m^3	0.15	0.5
$K_{I,nh3}$	50% inhibitory concentration of free ammonia	$kmol/m^3$	0.0018	0.0223
$f_{h2,su}$	Yield of hydrogen from monosaccharides	-	0.19	0.25
$f_{pro,su}$	Yield of propionate from monosaccharides	-	0.27	0.12

Parameter	Description	Unit	ADM1 default value	Values used
$f_{ac,su}$	Yield of acetate from monosaccharides	-	0.41	0.49
k_{dis}	constant describing disintegration phase	d^{-1}	0.5	1.54
$k_{hyd,ch}$	constant describing carbohydrates hydrolysis phase	d^{-1}	10	0.037
$k_{hyd,pr}$	constant describing proteins hydrolysis phase	d^{-1}	10	0.099
$k_{hyd,li}$	constant describing lipids hydrolysis phase	d^{-1}	10	0.225

Both the volume of the reactor and volume of headspace were given in the report.

- Volume of digester: 210 litres (0.21 m^3)
- Volume of headspace: 50 litres (0.05 m^3)

The initial values for the simulation with ADM1 was not given in the report. It was assumed that default initial values given in the MATLAB script could be used.

In the simulation it was used ode15S (stiff/NDF) solver with relative tolerance of 1e-9 and absolute tolerance of 1e-10.

The values from the compared case, was extracted from graphs by use of WebPlotDigitizer [63].

The substrate loading, reference Figure F.1, was compared and found to be the same as for the compared case.

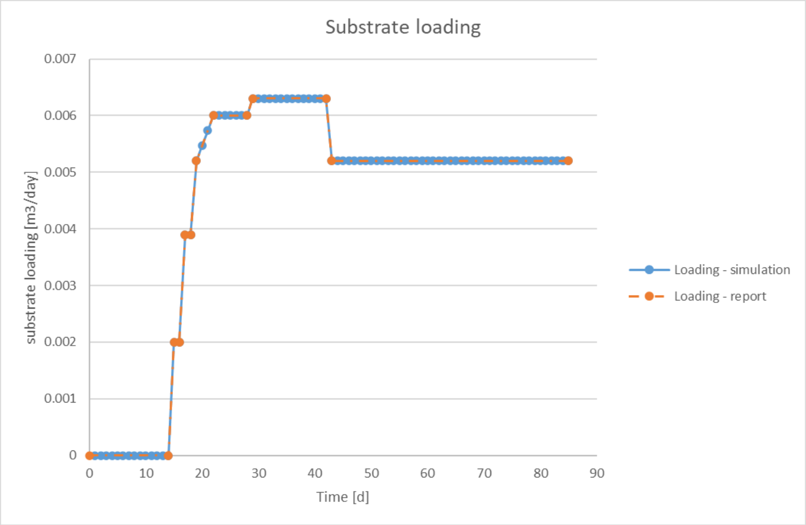

Figure F.1 Comparing substrate loading

The pH was compared both with simulated and measured values from the compared case (Figure F.2). In general, the pH is somewhat underestimated when re-run the simulation the MATLAB script. However, when running the simulation, a bit longer, pH is still increasing and starting the reach the same values as in the compared case.

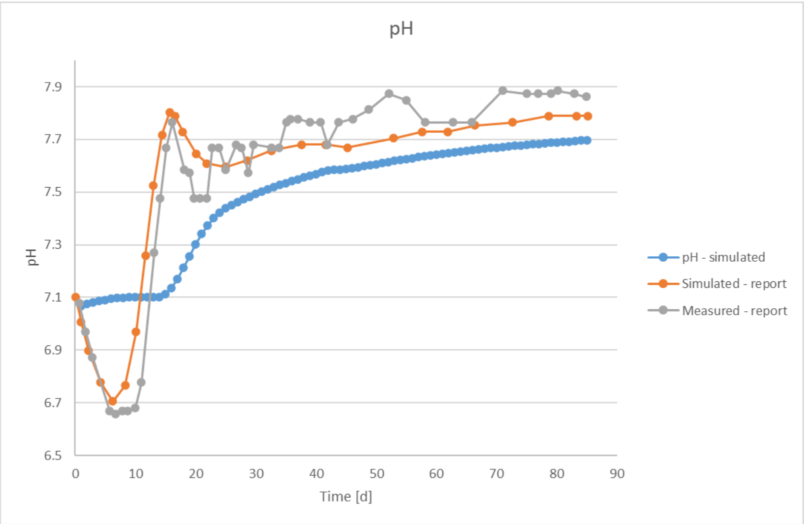

Figure F.2 Comparing pH

It was also extracted values for the volume percentage of methane at standard condition. The simulation with the MATLAB script is overestimating somewhat comparing with results from the compared case. However, it is withing acceptable limits.

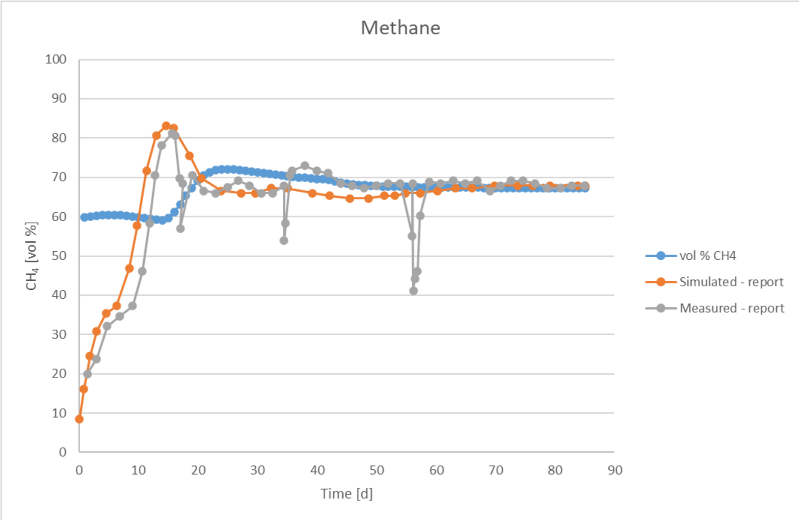

Figure F.3 Comparing methane level

The amount of total biogas seems to also have a good correlation with the compared case (Figure F.4). The biogas was reported in standard condition (STP – 273.15 K and 101.325 kPa) for the compared case.

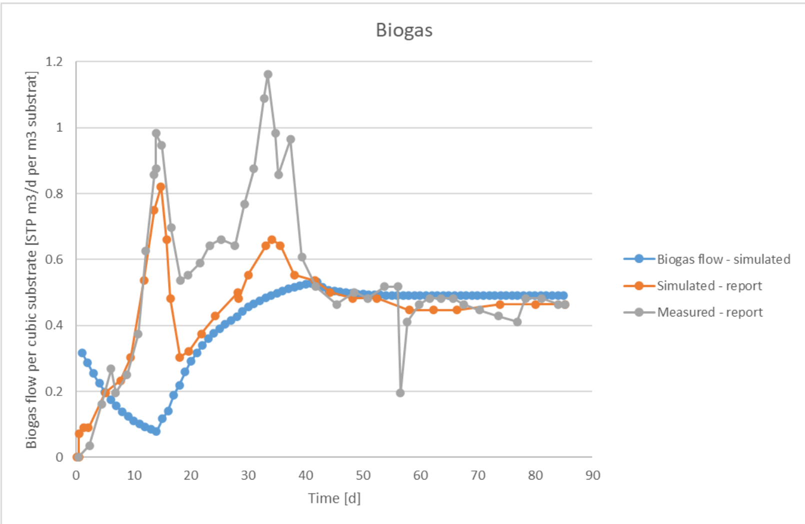

Figure F.4 Comparing biogas level at standard condition (STP)

As mentioned, it was expected that there would be deviations in the beginning of the simulation. However, when the simulation reaches a (semi) steady state condition, the deviation is acceptable. The deviation at (semi) steady state could be due to use of constant value for hydrolysis kinetics (k_{hyd}), while compared case used variable values. There are also some uncertainties due to values of initial parameters for the ADM1, since they were not given in the compared case. This could also have affected the simulation results. Overall, the script reproduces the simulation with an acceptable accuracy when comparing with the given case.