MONITORING REVIEW AND GUIDE

FOR THE OPTIMISATION OF ANAEROBIC DIGESTION AND BIOMETHANE PLANTS

FULL REPORT

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1. Scope of the Report

This report explains the importance and impact of implementing appropriate monitoring of Anaerobic Digestion (AD) and biomethane plants. It provides a review of numerous parameters as well as sampling techniques and monitoring regimes relevant for the AD process itself, the substrates to be digested and for the resultant digestates and biogas produced. This report also includes monitoring information related to biogas clean up and upgrading process technologies. Cost data for a selection of analytical tools and laboratory analyses has also been included. It is outside the scope of this report to review control actions, systems or regimes that can be applied for AD and biomethane plants.

This review and guide provides general information related to key parameters that can be monitored so that an AD plant can be controlled in order to:

a) allow a certain flexibility of varying hydraulic and organic loading of substrates
b) allow some diversification of types of substrates input
c) treat wastes to a high degree (when substrates are classed as wastes)
d) maximise organic conversion efficiencies to biogas/biomethane
e) yield good quality digestates and biomethane
f) access more specific and demanding digestate markets
g) access other markets for the biomethane produced (e.g. transport fuel and gas grid)
h) reduce amount of plant/process downtime
i) reduce plant size and reduce operating costs e.g. chemical dosing and heating loads
j) enhance environmental benefits of the plant and reduce impacts

Ultimately, these benefits will have positive impacts on the economics of AD and biomethane plants and will continue to add to the credentials of the technologies by:

a) delivering technically on a long term basis
b) allowing some operational flexibility
c) allowing these plants to be considered a good neighbour
d) delivering benefits in environmental and economic terms
e) delivering on promises made to government and the public

This will also help new proposals for AD and biomethane systems gain faster acceptability by the public and planning officers and gain further, or continue to receive support from government policies and financial incentives.

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2. Need for Monitoring the AD Process Performance, Substrates and Outputs Characteristics

AD is a biochemical process that occurs in sealed vessels, in which organic matter is mineralised to mainly methane and carbon dioxide through a series of reactions mediated by several groups of microorganisms (Figure 1). The various stages of the process can occur all within one vessel, the digester (sometimes referred to as reactor) or in separate ones. Resultant from the AD process is methane, which can be used to produce renewable electricity, heat or utilised as a vehicle fuel; and also a digestate, which should be low in easily digestible organic content and may contain valuable nutrients. AD for treatment of organic waste and biogas production is an environmentally attractive technology. It has environmental benefits that include waste treatment, pollution reduction, renewable energy generation and improvement of agricultural practices by recycling of plant nutrients. Widening the use and benefits gained from these digestates and nutrients is currently the subject of further R&D. Over 8000 AD plants are currently found throughout the world (not counting micro-scale plants). Europe has currently the largest installed capacity of medium and large scale plants and the deployment is continuing to grow in some regions with the focus of delivering waste treatment and, in many cases, bioenergy production. According to the IEA, over 170 biomethane plants have now been implemented around the world from a variety of substrates for use as a vehicle fuel or for gas grid injection.

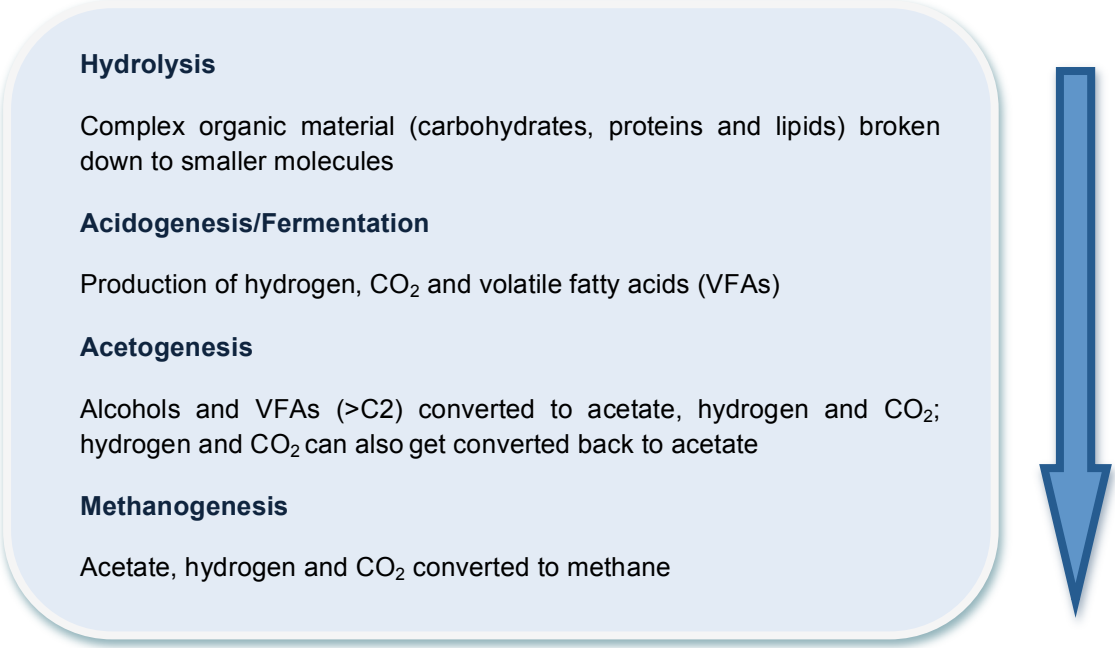

Figure 1 – Simplified diagram of the various stages in the AD process

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AD is a versatile process that is able to degrade a multitude of organic substrates, from a variety of municipal, industrial and agriculture residues and wastes to energy crops. This versatility does however bring some challenges. The process in many cases is required to be able to cope with substrates with a wide range of physical and chemical composition, which may be highly variable even on a daily or weekly basis and can also bring some inhibitions to the process.

In addition to the wide variety of substrates (or feedstocks) that can possibly be utilised, the AD process is delivered by complex and dynamic systems where mechanical, microbiological and physico-chemical aspects are closely linked and influence ultimately the process performance. Research involving the expertise of microbiologists, chemists, engineers and mathematicians worldwide performed largely during the last four decades has resulted in the continued updating of process fundamentals and a greater appreciation of the complexity and diversity of the process as delivered by a mixed bacterial and archae culture with competitive nature. However, not all complexities and action-reaction models related to microbial activities and overall performances are fully understood. Process stability is dependent on the critical balance between the symbiotic growth rates of the principal metabolic groups of bacteria and archae i.e. acid forming bacteria, acetogens and methanogens.

Although inherently stable, the AD process can reach instability by a variety of process perturbations, such as:

a) overload in organic or hydraulic rates
b) presence of toxic or inhibitory compounds, which may hinder digestion due to damage to the active microorganisms or to a reduction in the effectiveness (activity) of enzymes
c) lack of nutrients or trace elements essential for microbes' maintenance and growth
d) deviation from optimum operating temperatures.

It is important to understand that each stage has its inherent characteristics, with hydrolysis and methanogenesis typically being the most challenging. Hydrolysis has been shown to be a rate-limiting step for digestion of particulate substrate and also some fats. The overall hydrolysis rate depends on substrate size and shape, surface area, microbial concentration, enzyme production and adsorption. Methanogenesis is typically the rate-limiting step for more readily degradable substrates where systems may include short retention times potentially leading to a net loss of microbes within the digesters as methanogens are slow growers. One digester may not just suffer from limitations of one set of microbes. Indeed for many systems, limitations can come from more than one group of microbes, and therefore more than one of the digestion stages.

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Spanjers and van Lier (2006) surveyed approximately 400 full-scale AD plants largely for wastewater treatment and found that, at 95% of the plants, in-situ and in-line instrumentation was limited to pH, temperature, water flow, biogas flow, level and pressure. Madsen *et al.* (2011) has also reported that many plants are operated based on ex-situ analysis and only sensors such as pH, redox potential and gas production rates are being employed in-situ or in-line. So far this continues to be also the perception from the authors of this report. However, the industry is showing more motivation to better understand the process and monitor in greater depth, and even remote monitoring techniques are starting to be implemented.

In many cases, process instability has been avoided by operating the AD process far below maximum capacity with reduced substrate throughputs. This however, means larger plants than necessary are built and operated with higher capital and running costs and inherent inefficiencies. It is important instead to consider that as a microbial mediated process that requires organic substrates as feed, those microbes only grow if conditions are adequate. Therefore, underfeeding and operating long retention times in digesters do not necessarily yield improved waste treatment and higher conversions to biogas as the growth of the microbial culture will also be limited due to lack of feed. The microbiology within the AD process is even more complex as in addition to food : microorganisms ratio, higher conversion rate microbes will only develop if the system loading is relatively high or when the digester is suffering from certain impairments. This is the case for methanogens of the *Methanosarcina sp*. (e.g. De Vrieze *et al.,* 2012) for example. Despite the high conversion rates, when digesters are dominated only by these microbial species, these may produce a reduced quality digestate, and there may be a requirement for a digestate polishing step (anaerobic or otherwise), as digestate may suffer from relatively high organic load and odours related to high volatile fatty acid content, which can then cause plant phytotoxicity when utilised on land.

There are also important differences brought about from substrate pretreatments (e.g. storage conditions or more complex pretreatments) performed to actively increase hydrolysis rates of the substrates, and these can have a direct influence on for example, pH, ammonium and VFA levels when substrates enter the digester. In addition, there are a number of other factors that contribute to decisions on how to operate digesters, and the type of digestion process is certainly an important factor. For example, high rate digesters such as Upflow Anaerobic Sludge Blanket (UASB) reactors normally designed to operate on low level of suspended solids and fats are normally able to accommodate a higher organic loading rate (OLR) and reduced Hydraulic Retention Times (HRTs) when compared to the more conventional Continuously Stirred Tank Reactors (CSTRs). This is due to their ability to retain microbes within digester granules reducing significantly the potential for microbial wash out. In addition, the granular structure allows some protection (e.g. higher internal pH of the granules (Angenent and Dague (1995)) for

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the sensitive methanogens which are normally situated at the core of the granule (Arcand *et al*. (1994)).

There is a significant amount of literature that refers to some known inhibition conditions for AD systems and a number of ways of optimising system's performance (e.g. Chen *et al.,* 2008; Fricke *et al.,* 2006). However, in addition to the variations in substrates and the highly complex biochemical process, a number of biochemical interactions can have antagonistic as well as synergistic effects. All these factors make process performance in some cases difficult to predict. Some of these complex effects occur for example when digestion takes place in the presence of various metals and ammonia, which then imposes difficulties in identifying a definite value of the element that is either required or is in excess. There are also other important factors such as the bioavailability and bioaccessibility of certain compounds e.g. essential trace metals, which may be stated by analysis to be present. However, it is more difficult to define their availability/accessibility to the microbial culture, and even certain compounds (added as part of the substrate or through chemical dosing e.g. alkalinity or H_2S control) may alter essential elements availability and induce for example their precipitation.

With all these potential differences and complexities, instead of designing and operating oversized digestion processes to try and buffer potential problems, there are other ways of increasing efficiencies of an AD plant. These can be achieved by actively and frequently monitoring substrates as well as the AD process matrix and its outputs. Understanding their AD process efficiencies, capabilities and trends are key for operators to being able to make appropriate control decisions. These may be related to changing substrates, adding a pH buffer, nutrients and trace elements, altering the organic and hydraulic load rates, introducing substrate pre-treatments or digestate post-treatments, or operating (on intermittent basis) an ancillary process of ammonia removal among other actions.

It is important that research continues so that further understanding of the process develops, and techniques for monitoring and control AD plants are optimised and even costs reduced. It is also important that further learning is not only achieved in laboratory conditions but also from industrial and full-scale experiences, where operating conditions are in general more variable and the monitoring and control regimes are widely stretched and therefore are able to be more fully evaluated.

There are obviously also limits as to what monitoring and control regimes can achieve. It is important to understand that it is not always possible to operate on significantly different substrates, or operate differently from the general specification of the plant, unless considerable

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design changes are made that may take some time to be implemented, and may cause some disruption to normal process operation and may even require significant investment.

In addition, to performing monitoring and control activities for the benefit of improving the digester operation and efficiency, there may be also reasons to monitor digestate quality to meet for example effluent discharge conditions or end of waste criteria requirements.

Similarly, biogas and biomethane quality must be monitored continuously or frequently at least. Clearly, the quality of the produced biomethane has to be guaranteed anytime, thus it is an obligation to monitor and store the relevant data quality and quantity parameters depending on the final utilisation of the biomethane. As one would expect, the most restrictive obligations have typically to be met when biomethane is injected to the natural gas grid. Also a certain amount of monitoring is required when providing biomethane as a vehicle fuel that will be stored at high pressures. In addition to the legal requirements, a certain set of biogas upgrading plant parameters should be monitored and stored for later verification and interpretation and these will depend on the chosen upgrading technology. Monitoring is required not only during plant commissioning but also during plant operation. Monitoring data is useful and may indicate any performance deterioration of the plant when analysed over the plant service lifetime. This data may also provide the possibility of performance augmentation, efficiency enhancement, reduction of utilities or debottlenecking. Finally, a properly maintained data set of typical plant parameters supports predictive maintenance and appropriate service scheduling (i.e. service of machinery, replacement of consumables, replenishment of chemicals), and thus, helps to maximise overall plant availability.

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3. Guide for Monitoring Parameters and Regimes

There are numerous parameters that can be monitored within each matrix/stage of the AD and biomethane plant (Figure 2). Monitoring parameters identified have been selected by the authors of this review based on literature information as well as on the years of practical experience in researching AD and biogas upgrading processes and working with full-scale plants throughout Europe.

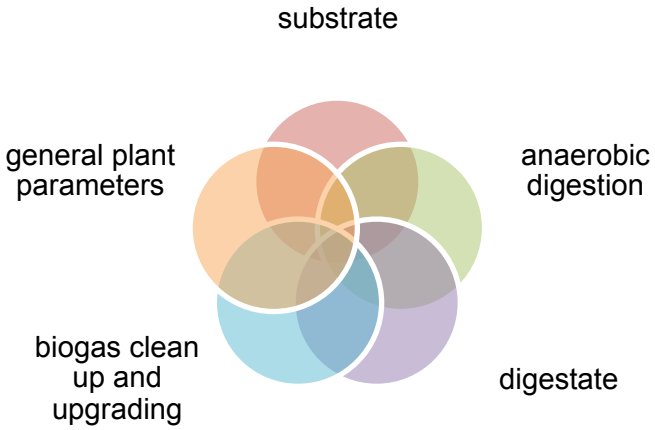

Figure 2 – Interaction of the various stages within an AD and a biomethane plant

Parameters have been distinguished according to the matrix/stage of the AD and biomethane plant in which they can be measured (Figure 3). A more complete explanation of each parameter is included in later sections of this report. The combination of a number of these parameters will provide a good understanding of the operation of the plants and will allow a number of benefits including the optimisation of biogas and biomethane production. Not all parameters are required to be measured for all the plants. However, in some cases additional ones may still need to be measured depending on specific circumstances.

Specifically in regards to the AD plant, substrates and digestates, no standard monitoring regime has been defined by the research community or operators i.e. no agreement has been achieved as to the best selection of parameters to use for monitoring, and only for a few have optimum levels and concentrations been defined. The optimum or minimum frequencies of measurement have also not been defined. Increased frequencies would be beneficial, however, it is recognised that this comes with additional costs e.g. external analytical laboratory costs, investment in sensors and analysers to be based at the plant or staff costs related to performing ex-situ analysis or sensor calibration and maintenance. Once a monitoring regime is

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implemented, there is also the need for operators to be able to interpret sensorial data or biochemical analyses results, then correlate them, and identify any possible analysis interferences and conclude on the status of the plant so that control action(s) or remedial step(s) can then be implemented. To add to the challenges, all of this should be performed rapidly otherwise process functionality can deteriorate.

The AD process status and performance can be monitored by measuring substrate conversion (Chemical Oxygen Demand (COD), dry matter or total solids (TS), or organic dry matter or volatile solids (VS) removal), intermediates accumulation (Volatile Fatty Acids (VFAs), pH, alkalinity, H_2, CO), and product formation (gas production rate, CH_4, CO_2). In brief, individual VFAs have generally been agreed to be valuable as monitoring parameters for AD plants. pH has been found to have a delayed response and the extremely variability of H_2 partial pressures pose in many cases a difficulty in interpretation. Additional parameters can also be measured and are related to microbial communities (abundance and diversity of populations) and microbial activities. Lately these microbial analyses have been gaining considerable interest. Figure 4 illustrates possible monitoring parameters that can be utilised to evaluate performance of digesters and many of those parameters are described in more detailed in later sections.

Monitoring protocols regarding biomethane production have partly been defined and are operational but the situation in each country is significantly different. Typically, biomethane quality monitoring is well defined and there are limits for certain compounds i.e. usually unwanted components like carbon dioxide, hydrogen sulphide, total sulphur, ammonia, oxygen, and moisture. Methane is actually not mentioned directly in most cases and gas characteristics and quality are specified in terms of requirements in terms of heating value, Wobbe index, density or relative density. The monitoring frequency and requirements related to data records can vary and parameters do not always have to be monitored continuously (measurement intervals of 15 minutes are often sufficient). However, the exact monitoring approach and protocols are usually as described by law or required by the natural gas grid operator.

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Figure 3 – Monitoring parameters for each stage/matrix relevant to the operation of an AD plant

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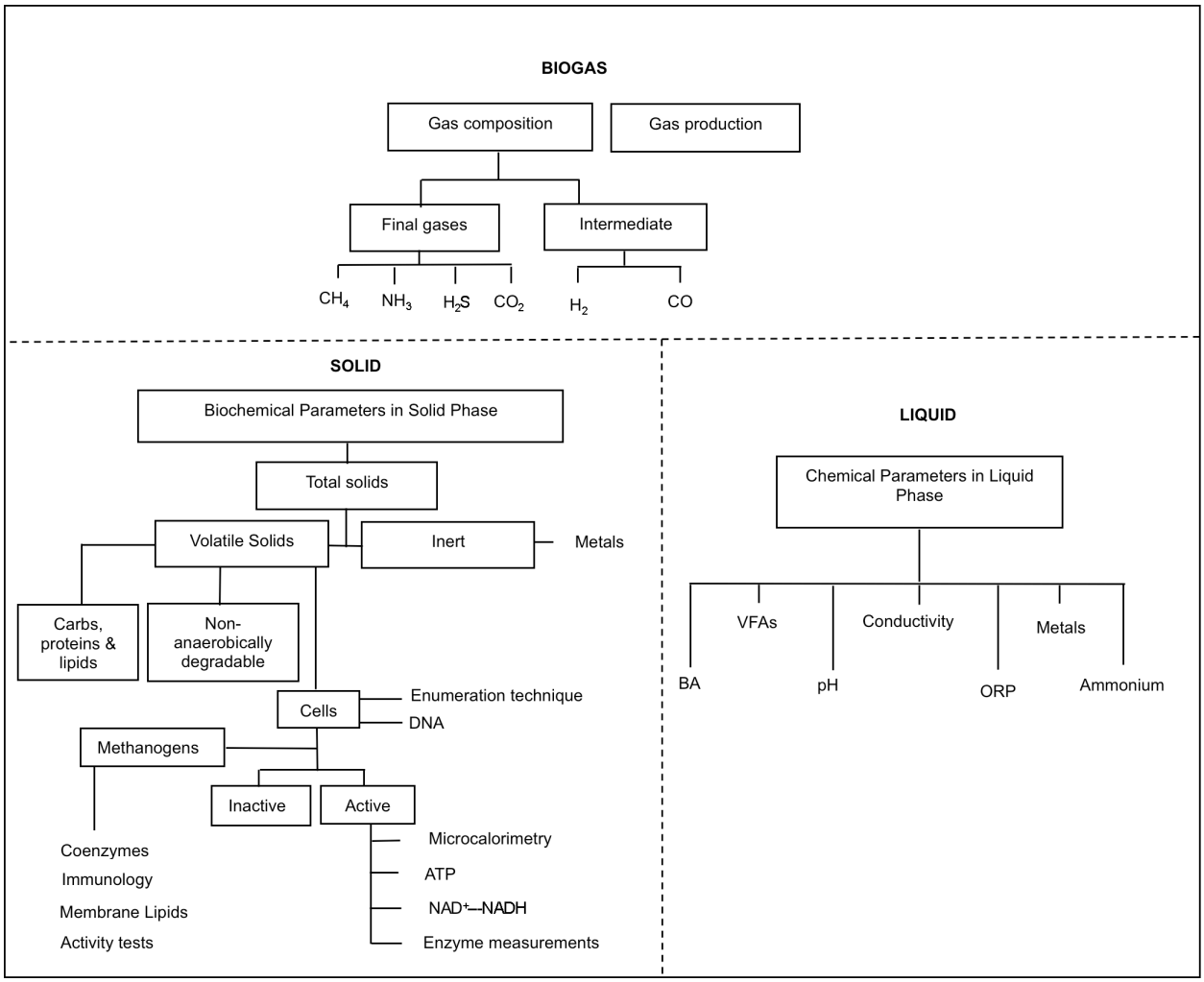

Figure 4 - Characterisation tests for the 3-phases of anaerobic digesters

Figure 5 introduces the terminology used typically to define how monitoring and data acquisition can be performed, in this case exemplified when monitoring the matrix within a digester.

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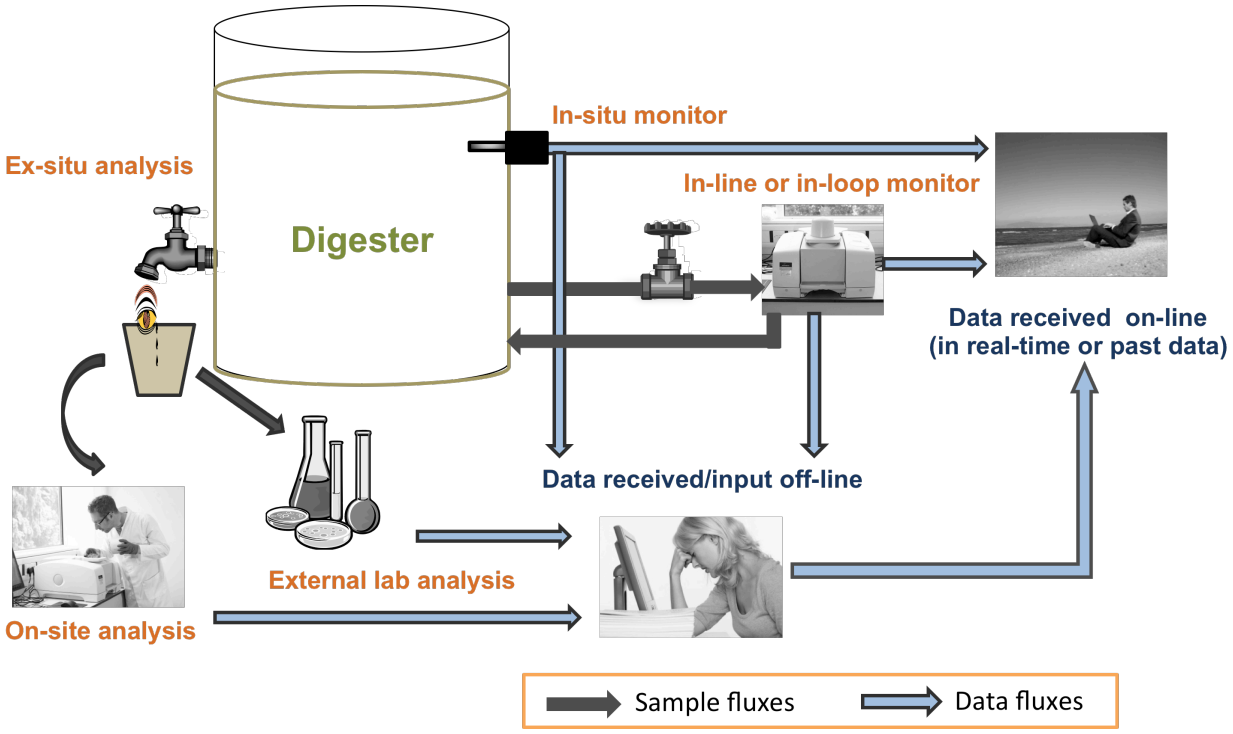

Figure 5 – Concepts/terminology used to define sample monitoring and data gathering regimes

The success of any process monitoring system is also determined by the appropriate placement of sensors and adequate sampling regimes or protocols. This will apply to any matrix or stage within the AD plant, with a greater effect when matrices are significantly heterogeneous and for samples for which time and storage conditions can influence their characteristics, which is largely the case in AD systems. With in-situ monitoring, although sensors are least prone to sampling quality issues and to measuring non-representative samples (when digester is well mixed), they do suffer in many cases from fouling problems, especially for sensors in contact with the liquid/solid matrices. In addition, an important decision aspect is the location of the sensor/or probe or the sampling port. Fouling of sensors placed in-situ and in-line in contact with solid and liquid matrices is likely to occur and clean up and maintenance regimes need to be performed frequently unless sensor self-cleaning takes place. Sensors may sometimes be placed in locations where digester contents mixing is poor or some inorganic material deposits may be occurring, or at the top of digesters where foam and crust formation can interfere with readings, unless the sensor role is to measure those specific conditions. For all these reasons the placing of sampling ports and sensors needs to be thought out carefully and some flexibility for positioning ports and sensors should be built in during the plant's design phase. All these make multi-location sampling, multi-parameter and frequent monitoring a good strategy to follow, allowing for compensation of some sample heterogeneity, sensor fouling and other interferences.

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Ideal monitoring methods should be in-situ or in-line, automated and performed continuously, providing real-time data. This would result in minimal interferences and give early indications of imbalance and of important changes in the microbial status and performance of the system. This would also allow immediate control actions to take place even at a distance. Currently, however, not all important parameters can be automatically measured in-situ or in-line on a continuous basis and in real-time with data acquired on-line. Some technical difficulties and costs make this impractical i.e. in some cases the purchase and operation of sensors, probes or analysers is relatively expensive and also in some cases pre-processing of the sample may be required in order to avoid for example fouling situations specially when measuring samples with particulate matter.

When selecting a measuring method one should keep in mind the required accuracy of measurement and the quality of the instrument. Instruments to be applied to this field may require maintenance and calibrations on a regular basis. Close attention should be paid to the principle of measurement and possible interferences, and instruments or sensors should only be operated in the environment for which they were designed for.

Sampling methodologies affect mostly ex-situ analysis as well as in-line monitoring (mostly when operated intermittently) as representativeness and freshness/conservation of the sample can sometimes be difficult to guarantee. Additionally, if feeding of substrates is intermittent during the day or throughout the week, there will be various differences found when monitoring the digester contents and biogas during that period. For example, if a digester is not fed over the weekend or feeding is significantly reduced, then the digester contents and biogas profiles will be different on a Monday as opposed to a Thursday by when the digester has been fed more intensively for the previous days.

Intermittent or inefficient digester mixing regimes can allow also some uneven contents within the digester. This can therefore have an impact on the homogeneity of the sample collected. Also samples removed from the digester and allowed to release dissolved gases such as CO_2, will result in an impact on measurements such as pH and alkalinity. Other aspects are worth referring to as well. Plastic containers used for collection of samples can absorb a small portion of VFAs and other compounds.

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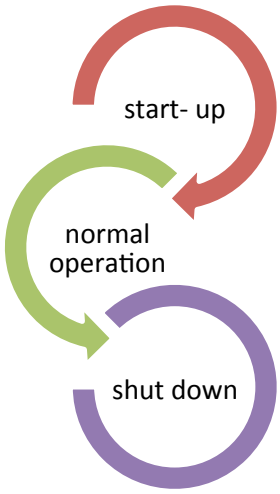
To summarise, the reason for non-standard monitoring regimes in terms of selection of parameters and frequency of analysis is largely due to the complexity of the AD process and the wide variation of substrates used, digester types, operating conditions and aims of the plant. Different monitoring regimes also apply depending on the operating stage of the plant. An AD plant's monitoring regime can be separated into three phases: 1) Start-up, 2) normal operation which will include '*quasi* or almost steady state' as well as more transient operating conditions, and 3) shut down.



Each phase of the operation has special requirements in terms of monitoring. The frequency of monitoring may be more relaxed in case of normal operation at 'almost steady state conditions' e.g. for a number of biogas plants operating regularly on specific energy crops. However, monitoring regimes need to rely on more frequent measurements and with a wider parameterisation during start-up (especially when the source of inoculum is from digester(s) operating differently), and during transient operating conditions e.g. for a number of AD plants utilising biowastes where frequent changes in substrate input is a norm.

It is also important to understand that some changes induced by substrate input or changes in operating conditions can take time to alter significantly the performance of the AD plant, so monitoring periods may be required well up to three hydraulic retention times (HRTs), which can be for some AD plants many months. In such cases, monitoring needs to be fairly frequent for those periods (i.e. a number of parameters monitored at least a couple of times per week). In these cases, monitoring parameter trends become more valuable than only avoiding certain levels/limits. Delays in the manifestation of sub optimal digester performance can be related to the time required for building up concentrations within the digester of a compound, for example light metal ions of sodium, calcium and potassium, or ammonium, which may only achieve excess levels able to create significant inhibitions after some time. However, trends of increasing concentrations would demonstrate that problems are likely to start to occur at some point. Also, it is not always the case that deterioration of performance occurs with time. Indeed, certain substrates and operating conditions may not initially be tolerated, but after a moderated feeding regime that allows microbial population adaptation and shift, the digester may subsequently be able to accommodate certain levels of those compounds or operating conditions.

It is difficult to generalise what parameters and appropriate monitoring frequencies are required for all AD plants due to the influence of all the factors explained above. Operators should reflect

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about a number of technical operation aspects frequently. Figure 6 was compiled with a number of questions that operators should routinely answer. The more 'YES' answers an operator may have, the more comprehensive monitoring regime will need to take place at the AD plant.

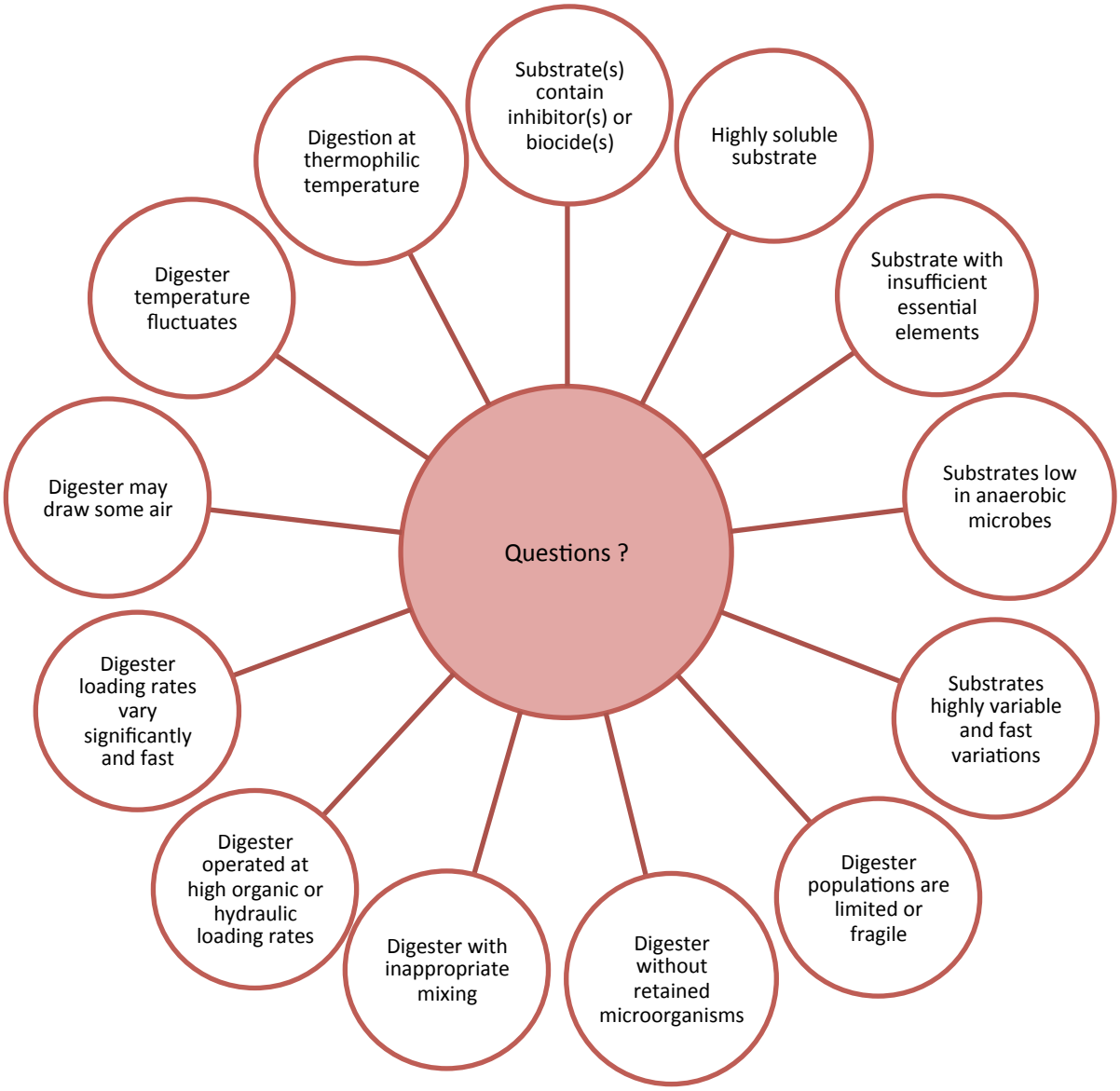

Figure 6 – Some questions that operators should answer regularly

In addition, an effort has been made here to indicate three broad classes of digester operation, which indicate a level of risk and for which an indicative monitoring regime is suggested. In all

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cases, temperature should be monitored and maintained within the optimum range (either mesophilic or thermophilic) and no air ingress to the digester should take place. Inoculation of a digester should take place from a well operating digester(s) ideally operating on similar substrates in order to bring an adapted culture and some good diversity. In some cases more than one type of inoculum can be mixed in order to make sure a wide variety of microbes is present. Inert material should be removed as much as possible prior to entering the digester or have an appropriate removal programme. Otherwise, digesters with time can fill up with sand and precipitates, reducing the working volume of digesters and alter mixing efficiencies.

Class A – Optimised AD plant operating on steady state conditions – Low Risk

Monitoring regimes may be more relaxed in terms of diversity of parameters and also less frequent when AD plants:

- are in optimal operation and are not pushed to the maximum or above organic or hydraulic loading rates for the type of digester and substrates utilised,
- are operating on pretty much steady state conditions for long periods i.e. operate on the same type and loading rate of substrate(s), and
- when operation is without inhibitory conditions (e.g. nutrients and metals are sufficient but not in excess, no biocides are introduced and buffering capacity is adequate).

In these conditions, measurements could be performed on continuous or on very regularly basis for biogas flowrate and composition, and supported by weekly measurements of pH (see however in Section 7.4.3 the explanation of its drawbacks as a monitoring parameter) as well as bicarbonate alkalinity and at least total concentration of VFAs. This would allow a reasonable assessment of the digester(s) performance. In addition, characterisation of the substrates could also take place weekly and that would include as a minimum solid content (TS and VS or COD) in order to verify loading rates to the digester. Other parameters may be measured occasionally to verify overall performance or according to national regulatory requirements, such as for example in demonstrating digestate quality. Further monitoring would be required if performance starts to change as indicated by total acids and alkalinity levels, biogas measurements and changes in substrates or digestates characteristics. This monitoring regime for these types of plants is likely to avoid significant failures.

Class B – AD plant operating on some transient conditions – Medium Risk

The following monitoring regime is likely to be appropriate when AD plants are not pushed to the maximum or above the organic or hydraulic loading rates for the type of digester and substrates utilised but are operated for some periods on transient conditions e.g. variations in type of substrates and organic and hydraulic loading rates. In order to optimise the operation i.e. loading rates and any potential inhibitions, substrate characterisations should be as a minimum

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once a week for solid content and more frequently for any significant change in substrate. For any significant change in substrates the following characterisation should also take place:

- C:N:P:S ratio
- metals including calcium, sodium and potassium depending on the types of substrates.

Monitoring of the biogas flowrate and gas concentrations should be continuously and digester contents should be monitored around 3 times per week for parameters such as alkalinity, individual VFAs (i.e. acetic, propionic, butyric, iso-butyric, valeric and iso-valeric acids) and pH. Some other measurements in the digester such as trace elements, ammonia and some alkali (earth) metals depending on the substrates utilised may need to be measured with frequency as well. If performance demonstrates to be sub-optimal, wider parameterisation might be required and more frequent monitoring undertaken so that control actions can take place more effectively.

Class C – AD plant operating at maximum loading rates (including high rate digestion systems with low HRTs) with significant transient conditions – High Risk

Other AD plants will require more stringent monitoring regimes. For example, when a digester combines a number of these operational scenarios:

- operates very close to the maximum organic loading rate or to the lowest retention time as per design specifications,
- conditions exist that may in some cases result in a lack in essential nutrients and trace elements,
- there is potential for inhibitory compounds to be fed or generated such as significant levels of alkali (earth) metals, long chain fatty acids, ammonia or certain biocides e.g. from cleaning agents,
- when significant changes in substrate composition takes place very rapidly.

In these cases, monitoring of a combination of parameters that relate to the biogas, substrate(s) and the digestate will be fundamental and there will be benefits if these are measured continuously, or semi-continuously on very frequent basis, in-situ or in-line with data received almost on real-time basis. If ex-situ analysis or if manual biochemical analysis are required then those should be performed with results acquired very rapidly so that, if required, control actions can be implemented quickly. In addition to on-line monitoring of biogas flowrate, methane and H_2S content (depending on the type of substrates), a minimum of once a day analysis of parameters such as organic removal efficiencies, alkalinity, individual VFAs, ammonia and

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some alkali (earth) metals (depending on substrates) is likely to be required. Frequent measurements of trace elements are also required. In addition, bacterial enzyme activity and microbial profiling may also be of benefit, especially when the need for diagnosis of the cause for a decrease in digester performance is not apparent with other measurements. A number of high rate digesters operating on low HRTs (e.g. below 4 days) on low suspended solid content substrates with immobilised microbial consortium will also normally require this type of monitoring regime, as even within a week, significant impact to the biochemistry of the digester can occur. Other more relaxed mode of monitoring will prove to be limiting in terms of plant optimisation following different and rapidly changing operating conditions, and will limit the ability of identifying with confidence the cause of sub-optimal performance or failure.

In any case, it is important to have in mind that the more parameters that are monitored, the greater the handle of process conditions and the greater the flexibility to control operation. There is never too much information, and the faster the information becomes available the quicker a control action is likely to take place.

With living microorganisms performing the essential tasks, time is of the essence. It is also important that the data is analysed and understood, and therefore the operator's knowledge and experience cannot be overlooked. A good monitoring practice gives operators a picture of what is happening in the AD process and resultant digestate characteristics. Monitoring specific parameters at regular intervals allows for trends to be deduced and gives operators a chance to identify a critical situation in advance, leaving time to take precautionary measures is key to long term successful operation. If AD plants are not monitored for at least key parameters it is very difficult to achieve important benefits of the system. It is similar to 'driving a car without a windscreen or a steering wheel'. It becomes difficult to benchmark operation and to optimise delivery of the plant. It is also difficult to understand what would be the main contributing factor(s) if there is a process breakdown, which consequently limits the ability of providing fast (and in some cases cost effective) remedial action(s).

In cases where plants are not monitored and controlled effectively, digester performance is likely to be sub-optimal and, as a worst case, the biochemistry within a digester can fail. The need for re-inoculating and start-up of the digester again may delay operation for some time even months. For example, if an acceptable conversion of the organic materials to biogas is not achieved, then in addition to reduced generation of energy, there will also be an increase in potential emission losses to the environment, which should be avoided. It is therefore imperative that a good understanding of the status of the process exists at an operational level.

In addition to the value of multi-parameter and frequent monitoring, value can also be gained from keeping good records and storing data for long periods. This information should be catalogued in a format, which can be easily retrieved and understood even by a different

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operator. It is common that changes made in substrate type and loadings as well as modes of operation are not always recorded, so interpreting changes in process response and performance data becomes difficult. For AD plants that do not undergo a significant monitoring regime, in order to conclude why certain changes may have started to occur, a number of small samples can be stored in a dedicated freezer for a few months so that they can be analysed if required.

A number of researchers have reviewed monitoring parameters and regimes for AD (e.g. Madsen *et al.,* 2011; Boe *et al.,* 2010, Monson *et al.,* 2007). Further developments in the field are continuing, both in terms of the understanding the process biochemistry and parameter responses, and also in terms of further developing new monitoring techniques and improving robustness and reducing the cost of various monitoring techniques. It is therefore, worth continuing to review academic and trade literature and keeping an eye out for new monitoring techniques / sensors / analysers that will be available in the market in the future that may be less prone to interferences, fouling and may be automated and provide data in real-time.

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4. General Plant Parameters (design, operation and performance)

AD plants are normally described by a series of parameters that have been listed below. These describe design parameters, typical operation performance and include annual production and utilisation of energy. This information is normally used to summarise the AD plant profile and allows benchmarking between processes and plants to take place as well as to map out AD capacity in regions. These figures are normally compiled at design stage and based on projected performance but can be revised if substrates, performance and process response changes. These revisions can be compiled based on the operator's documentation. The information typically provides a general overview of the type and performance of the AD and biomethane plant. This information should include:

Identification of the type(s) of substrate used

Type of digestion system (wet or dry, mesophilic or thermophilic, batch or continuous, plug flow or continuously mixed, one or more stages/multi-digesters retained or suspended microbes)

Degree of degradation by the digestion process (% VS or COD destroyed)

Digestate output (tonnes per annum)

Specification of markets for digestate (whole, separated fibre or liquor)

Annual or daily throughput of feedstock (e.g. tonnes per annum)

Organic loading rate (OLR)

Quantity of volatile solids that is loaded per volume of working digester per day (kg VS or COD/m^3.d)

Volumetric loading rate (VLR)

Quantity of feedstock (wet weight) loaded per volume of working digester per day (kg of feedstock (ww)/m^3.d)

Hydraulic retention time (HRT)

Average time the substrate remains in the digester
(working digester volume m^3 / substrate daily feed rate m^3/d)

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Annual or daily biogas/biomethane production (e.g. m^3_{STP} CH_4/annum)

Methane yields

CH_4 produced per tonne of substrate (wet weight or VS or COD) added and destroyed (m^3_{STP} CH_4 / tonne VS added or destroyed)

Methane or biogas produced per digester volume per day (e.g. m^3_{STP} CH_4 / m^3 digester.d)

Standard Temperature and Pressure (STP) conditions normally 273 K, 1013 hPa

Energy conversion, parasitic and uses

Type of biogas utilisation e.g. CHP (heat and electricity) or biomethane upgrading unit (for gas grid or vehicle fuel)

Engine or turbine power rate (MW_e)

Biomethane upgrading unit capacity (m^3_{STP} biogas/h) and production (m^3_{STP} biomethane/h)

Annual or daily electricity or heat production (e.g. MWh_e or MWh_{th}/annum)

Annual or daily parasitic electricity or heat loads required (e.g. kWh_e or kWh_{th}/annum)

Additional fuel/energy requirements (kWh_e or kWh_{th}/annum) of natural gas, oil or electricity

The compilation and logging of this information is part of general good practice and in many cases are required by national environmental regulations as well as related to returns on renewable energy that has been incentivised through government schemes.

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5. Measurement Principles and Techniques Used for Monitoring AD and Biomethane Plants

Monitoring of AD and biogas processing plants relies on a number of analytical methods and techniques that have been developed and are applied in many other biotechnology, chemical and engineering processes. However, in some cases a specific methodology has been devised so that widely applied measuring principles could also be used specifically for biogas systems. In many cases for example, sample preparation has been required due the biofouling and the high suspended solid content of the AD related samples.

Measurement principles rely on a number of physical, chemical or biological techniques, or combinations of these. Some measurement principles can be used to assess more than one parameter while some parameters can be measured using various principles. The choice of which principle to use for monitoring may be made based on costs, accuracy, time required for analysis, possible interferences and requirements for sample preparation. Some of the most significant measurement methods that have been applied to AD systems comprise of:

1. Gravimetry
    - Simple method to quantify compounds based on mass (that may in some cases be combined with pre-treatment(s) e.g. heat to drive off moisture for TS characterisation

2. Chromatography
    - separation of substances by their different affinity between a mobile phase and a stationary phase (based on relative solubility, adsorption, size or charge)
    - can be used for liquids or gases and can be used to measure individual VFAs and gas composition
    - Techniques are divided in Gas Chromatography (GC), Headspace Gas Chromatograph (HS-GC) and High Performance Liquid Chromatography (HPLC)

3. Electrochemistry
    - based on the measurement of electrical potential, current or resistance using electrodes
    - can be used for liquid samples to measure pH, redox, conductivity and a number of ionic species such as ammonium, calcium, various heavy metals, carbonate and sulphide. It has also been used to measure dissolved hydrogen

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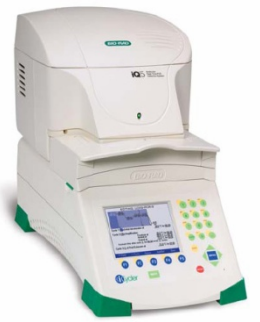
4. Titrimetric
    - measurement of the amount of reagent that reacts with the component to be assessed
    - can be used to measure alkalinity and be used as a surrogate method for measuring total VFAs

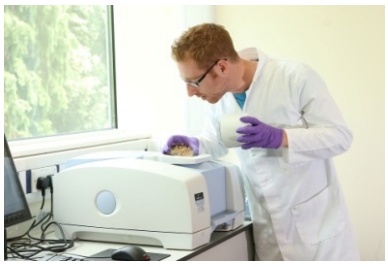
5. Biosensors
    - Combine the selectivity of biological substances with microelectronics and opto-electronics
    - Can be used to measure BOD, and more recently ammonia and total VFAs

6. Electronic noses for gas measurements
    - The use of arrays of electronic gas sensors, so-called 'electronic noses' or volatile compound mappers have been used to measure metabolic activity, indirectly.
    - This type of sensor may have a promising potential in AD as they are non-invasive, however, the liquid-gas phase equilibrium is limited in anaerobic systems, and more research still needs to be performed if electronic noses are to be used in this field

7. Microbiology and molecular tools
    - Techniques that can be used for enumeration of microbes or for DNA/RNA related analysis; these include microscopy, fluorescence in-situ hybridisation (FISH), Denaturing Gradient Gel Electrophoresis (DGGE), real-time polymerase chain reaction (qPCR) and DNA sequencers
    - These techniques have made significant progress in the last few years and their application is likely to become more widespread in AD systems in the future



8. Spectrometric
    - measure the absorbance, transmission, diffusion, or fluorescence of radiation in the ultraviolet (UV), visible (VIS) and infrared (IR) range
    - molecular spectroscopy measures liquids, while atomic spectroscopy measures components in the gas phase
    - Depending on the analysis performed photometrically measured concentrations e.g. COD, NH_4-N and VFAs can suffer from interferences from particulate matter and inherent coloration of the sample
    - Significant applications for AD of these techniques have been researched in the last decade



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Some of the measurement principles above have, or can be applied in theory, to construct instruments to measure parameters in-line within AD systems. A number of them have been built and operated in laboratories, but in some cases they have not yet been fully developed as commercial instruments (e.g. an online HS-GC based sensor for VFA measurements (Boe *et al.,* 2007) and the intermittent bicarbonate alkalinity analyser reported by Esteves *et al.* (2000) based on the principle described in Guwy *et al.* (1994) where continuous stream of substrate was saturated with gaseous CO_2, acidified by the addition of excess acid, and the rate of CO_2 evolution, was proportional to the concentration of bicarbonate/carbonate in the liquid flow, continuously measured by a sensitive gas meter).

Also recent trends in monitoring utilise Infra-Red (IR) Spectroscopy and multivariate analysis techniques for estimating a number of AD related parameters. IR spectroscopy has been utilised for example for monitoring VFAs, alkalinity (partial and total), COD, Total Organic Carbon (TOC), TS and VS, identification of primary sewage sludges vs. secondary sludges, as well as biomethane potential in some cases for a number of different substrates and digester operation by researchers including Steyer *et al.* (2002), Lomborg *et al.* (2009), Jacobi *et al.* (2009), Reed *et al.* (2011) and Lesteur *et al.* (2010). One analyser based on IR Spectroscopy that requires low maintenance has been able to deliver multi-parameters and results that have been fairly reliable. However, in some cases preparation of the sample using filtration or drying was performed, which meant that the technique could not be used in-situ or in-line for on-line data acquisition. However, these pre-processing requirements have not been universal. Data models need however to be built and calibrated for the desired correlations, which in many cases mean significant time investment, and as one model may not necessarily fit the correlation(s) for different types of substrates this may defer the use of these techniques by industry. But once the model(s) have been calibrated, the measurement cycle time is in the order of minutes. Significant R&D related to this is continuing to be performed and some models have already started to be commercialised, and a variety of models have been produced by a number of academic institutions and companies. Raman spectrometry has also started to be utilised. Acoustic chemometrics are being researched and may have some potential for use in AD systems (e.g. Lomborg *et al.,* 2009 and Lhunegbo *et al.,* 2012).

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6. Relevance of Parameters for Substrates Characterisation

Various substrates or feedstocks such as organic municipal, industrial and agricultural wastes, sewage sludge, as well as some energy crops can be exploited in order to produce biogas/biomethane and in the case of wastes perform a significant degree of organic load reduction, along with other resultant benefits such as odour and emissions reduction and even some pathogen kill and enhanced nutrient availability. AD is a conversion process that allows a number of substrates to be co-digested, which can benefit local-based waste management and bioenergy generation approaches.

Some substrates may require some preparation steps before undergoing digestion. That may include size-reduction, homogenisation, removal of inert material and contaminants (e.g. sand, stones, glass, metal, plastic, wood, and bones), increase pathogen kill, suspension, dilution or more specialised pretreatments associated normally with requirements for enhancing hydrolysis of organic material such as mechanical, chemical, biological or thermal disintegrations. A combination of these processes may indeed be required. These pre-treatments and storage conditions for the substrates will then also influence the biochemical characteristics of the substrates. In addition, some wastes will need to follow legislative requirements when treated at AD plants e.g. maximum particle size and pasteurisation requirements in order to comply with hygenisation requirements and the Animal By-Products Regulations. These include animal by-products such as semi-liquid manure or dung, waste from slaughterhouses, and food waste from restaurants and canteens. These substrates may contain parasites, viruses, or other pathogens. The pathogenic potential of the substrates must be taken into particular consideration in sampling, transportation of samples, sample storage, sample preparation, and in carrying out tests.

The digestion process itself brings about some reduction of some pathogens. This is particularly marked in the case of thermophilic digestion (approx. 55 °C). When substrates associated with health issues are processed, special precautions will therefore need to be taken to prevent the transmission or dispersal of pathogens. These precautions concern building- and organization-related measures in the biogas installations as well as process control and process documentation themselves.

The regulatory frameworks surrounding the production and utilization of digestates and end-of-waste criteria in the various countries may also limit the digestion of certain substrates.

The starting point on any decision whether a substrate should enter an AD plant should be a comprehensive biochemical characterisation of that substrate. In general, the more variable the

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substrate is, the more frequent analyses need to be performed. As referred to in previous sections, this step is of great importance when considering particularly AD plants that treat organic wastes or industrial wastewaters. For these, the raw materials that enter the plant may have significantly different chemical compositions due to the varying waste and wastewater flows. In order to maintain a good stability and performance, operators must be able to determine the different chemical characteristics of the substrates and define if the plant as designed is able to accommodate them, predict plant performance and make any necessary changes to the plant and in operation. Upon delivery, the feedstock's quantity and quality should also be regularly verified.

It is vital that feedstocks for an AD plant are fully characterised. Chemical analysis can provide important information and indicate necessary AD plant design and operational requirements:

a) Choice of reactor system and system sizing
b) Waste variability and potential contamination
c) Need for dilutions, co-digestion, additional chemicals, pre and post-treatment requirements
d) Need for odour and emissions control and biogas cleaning requirements
e) Bio-energy generation potential and sizing of biogas storage and utilisation systems
f) Anaerobic digestion process inhibition potential – requirements for monitoring and control
g) Quality of digestate and needs for further treatment

If the characteristics/effects of adding a new feedstock are unknown the following characterisation may be required. Organic and moisture contents, pH, C:N:P:S ratio, COD, carbohydrates, lipids, proteins, lignin and hemicelluloses fractions, heavy metals and light metal ions content and biogas potential. Analyses related to nitrogen such as Total Kjeldahl nitrogen (TKN), NH_4-N, as well as VFAs may need to also be performed, as due to analytical methodologies some of these components are lost when conducting elemental analysis or solid content. TKN provides information related to the sum of organically bound nitrogen together with ammonium (NH_4^+) and ammonia (NH_3), by a thermal acidic extraction and water vapour distillation. While ammoniacal nitrogen (NH_4-N) indicates decomposition of proteins and urea, using water vapour distillation or ion chromatography. VFAs within the feedstock will also indicate an additional portion of organic load which may have not been accounted for when TS and VS content is characterised. The measurement of VFAs is treated in detail in Section 7.4.3.

Measuring the pH value of substrates by using electrodes is important as methanogenic requirement is around the neutrality. However, it is also important to understand that depending on the feedstocks used, substrates with an acidic or an alkaline pH may not always require an

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adjustment based on the substrate pH levels unless if significantly deviating from neutrality, as degradation in the digester will alter those requirements (e.g. VFAs are produced which will lower the pH and pH can increase through the breakdown of proteins). Therefore, it is more appropriate to carry out adjustments based on pH, alkalinity and VFA levels measured in the digester contents, instead (See Section 7.4.3).

6.1 Substrate Solids and Organic Content

Anaerobic substrate input is normally measured in terms of total solids (TS) or dry matter (performed by drying the samples to a constant mass at 105±2^{o}C), which include in addition to the organic content also inorganic and inert material. In terms of total volatile solids (VS) or sometimes defined as the organic or volatile dry matter (termed also as loss of weight on ignition – dried samples are ashed at 550±25^{o}C until constant mass is achieved), which tend to reflect the maximum exploitable organic content of a substrate. For more liquid substrates, the chemical oxygen demand (COD) concentration (measure of the content of oxidisable compounds in the substrate) is used instead of the solid content. The analytical methodology is based on an oxidation and titration or colorimetric procedure.

It is important to distinguish between available degradable fraction and the non-degradable fraction, as a fraction of the input COD or VS may not be anaerobically degradable, such as the lignin content or in non-biodegradable plastic, which will contribute towards a VS content measurement, but which will not degrade. Higher amount of TS and VS will cause increase in loading rate to the digester and it may or may not be able to cope with such a load, may require a different pumping system and may increase the load on agitators or recirculators used for digester mixing.

The level of carbohydrate, protein and lipids content in the substrates can provide an indication of nitrogen and sulphur contents and potential for ammonia and sulphate/sulphide toxicity. It could also indicate how useful certain pretreatments would be as proteins and lipids take longer to degrade than carbohydrates. It can also indicate a range of expected biogas and methane composition. In addition, the measurement of relatively high levels of lignin and hemicellulose content for plant based materials (e.g. straw) will indicate the need for a pre-treatment that may enhance the hydrolysis phase prior to entering the digester and that could improve digestion performance. Hemicelluloses bind cellulose fibres to form and enhance the stability of the cell wall. Lignin is particularly difficult to biodegrade, and in addition reduces the bioavailability of the other cell wall constituents. At the same time however, phenolic breakdown products from lignin degradation through the use of powerful hydrolysis pretreatments may also inhibit the digestion process.

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6.2 Substrate Elemental Analysis

Quantitative elemental analysis (performed by gravimetry, by optical atomic spectroscopy or via combustion and reduction in the presence of a catalyst and detection via thermal conductivity) of the elements C, H, O, N and S are particularly useful. The Carbon to Nitrogen (C:N) ratio is an important parameter in predicting ammonia toxicity as typically optimal ratios are around 20-40:1. The levels of sulphur will also provide an indication of the likely potential toxicity and requirements for desulphurisation of biogas. It is however important to note that not all these elements may be accessible by the microbes and therefore measurements of the ammonium content in the digester liquid as well as H_2S in the biogas produced will be useful.

In addition, the elemental composition can provide a theoretical indication of maximum biogas yields (see below). The theoretical determination of biogas yield and composition is relatively simple to calculate based on stoichiometry, knowing the main elements which make up the substrate i.e. C, H, N, S and O, according to the extended equation (1) from Buswell and Mueller (1952) defined later by Boyle (1976) to account for substrates containing sulphur and nitrogen. The make-up of substrates will influence the theoretical maximum methane yields, with proteins and fats producing a higher yield of methane. For substrates rich in carbohydrates, proteins and fats, theoretical methane yields may be around 375, 480 and 1000 m^3/ tonne VS, respectively.

$$C_cH_hO_oN_nS_s + \left(c - \frac{h}{4} - \frac{o}{2} + \frac{3n}{4} + \frac{s}{2}\right)H_2O \rightarrow \left(\frac{c}{2} + \frac{h}{8} - \frac{o}{4} - \frac{3n}{8} - \frac{s}{4}\right)CH_4 + \left(\frac{c}{2} - \frac{h}{8} + \frac{o}{4} + \frac{3n}{8} + \frac{s}{4}\right)CO_2 + nNH_3 + sH_2S$$

(Equation 1)

However, the theoretical (maximum) biogas yield as well as the various gas concentrations in the biogas will not necessarily match actual amounts obtained as there will be a number of interfering factors such as: a) elements may be part of inorganic and non-biodegradable molecules; b) part of the substrate may be converted to bacterial cells; c) part of the substrates may not go full conversion during the digestion period (this is typical of proteins and fats as they take longer to convert as opposed to carbohydrates); d) some CO_2 and H_2S gases are more soluble than CH_4; e) alkalinity will be generated; f) there will also be some precipitation reactions; g) there could also be some factors of inhibition; h) not enough time for the

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conversion to take place; i) not enough microorganisms to perform the conversion. So these calculations should be used as a guide only and it is therefore likely that the theoretical maximum methane yield will not be achieved at full scale operation. Elemental analysis of substrates and digestates can also be used for mass balances within a plant together with biogas results gathered from the plant.

6.3 Inhibition – Excesses and Deficiencies

Sufficient nutrients and trace elements are also important to microbial cell growth and activity, otherwise cells stop multiplying and then quantity and diversity of microbes will reduce in digesters. Macro-nutrients such as carbon, hydrogen, nitrogen and oxygen are the main components in microbial cells; phosphorus, sulphur and potassium then follow. Other elements such as calcium, magnesium, iron and sodium are required for specific proteins, while micro-nutrients such as nickel, cobalt, molybdenum, selenium and copper are required for enzymatic activity in small amounts (in the mg and g /m^3 range). Some of these elements can be present in lower amounts than that required (i.e. in deficiency) and therefore should then be added. Their exact required concentration is difficult to define and many studies have and continue to take place to identify better the required concentrations. Another important note is also that not all of these elements will become available to the microbes as per measurements done on the substrates, some will be bound in components that may not degrade or they can precipitate and can be even in a chemical state that will not be bioavailable. Measuring them in the liquid phase in the digester contents will provide a better insight of their concentrations as soluble metals.

Most nutrients can also be inhibitory if present in higher concentrations than required. All of these elements that do not end up in the biogas phase will remain in the digestate and therefore substrates characterisation can also indicate their potential content in the digestates unless for some metal precipitates, that may deposit in pipes, tanks and digesters. Excesses must also be avoided. When dealing with a substrate which has a potentially high in protein content or in urea (i.e. blood, slaughter house and poultry wastes) one must be aware that this may cause a nitrogen build up that may inhibit the AD process due to an increased pH value in conjunction with increased NH_4-N concentrations. Nitrogen levels can be measured by elemental composition (i.e. total N minus some fraction of the ammonium), as well as indicated by proteins levels and via the measurement of TKN.

Potassium and calcium levels are in some cases above the lower end of moderately inhibitory for anaerobic digestion processes (around 2.5 g/l) and sodium levels can also be above the

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lower end of toxicity, which is typically stated to be around 3.5 g/l. Further additions for pH and alkalinity control of chemicals based on these elements when already at high levels would need to be avoided. It is also important that returned liquors from the digester to moisten new substrates can with time concentrate a number of these elements.

Heavy metals can also have an inhibitory effect on digestion and can be found in some industrial and domestic wastewaters. Co-digesting with domestic sewage sludge has typically been the main source of heavy metals, but some can also be found in non segregated food waste. Heavy metals are bio-available and toxic when present in ionic form, however they do not cause substantial problems, since the ionic concentration is kept low due to sulfide and carbonate precipitations. They tend to cause more of an impact when present in some significant quantities in digestates that might be used in agriculture land.

Metal analysis can be performed by acid digestion (normally in conjunction with heat and microwave energy) followed by inductively coupled plasma spectrometry, or in case of soluble metals ions through liquid ion chromatography.

Long chain fatty acids (LCFA) such as oleic and linoleic acid can also be inhibitory even at low concentrations of 1.5 g/l, as they adsorb on the bacteria cell wall, and inhibit the transport of essential nutrients (Angelidaki and Ahring, 1992; Templer *et al.,* 2006).

Inhibitors for the AD process can also include biotoxic substances such as disinfectants, biocides and antibiotics. These can severely disrupt the digestion process and at high enough doses can even stop it entirely. Disinfectants are particularly prone to being available within industrial based substrates. Antibiotics may come from substrates generated by the pharmaceutical industry, domestic wastewater and in animal excretory slurries.

Oxygen and nitrate are also inhibitory to methanogens. However, when present at small concentrations, oxygen and nitrate are generally depleted by oxidation of readily available substrate or sulfide.

6.4 Batch and Continuous (Laboratory) Digestion Tests

In many cases batch anaerobic degradability tests and even continuous laboratory (or even pilot scale) experiments may be necessary to fully understand possible effects and prepare to take appropriate actions. Batch tests or discontinuous anaerobic degradability tests in which organic substrates or co-substrates are subjected to anaerobic digestion under defined conditions can provide information regarding anaerobic degradability, and qualitative information regarding the rate

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of degradability and potential inhibition effects as well as gas yield. However, these tests do not provide information regarding: process stability in digesters which are continuously fed, biogas yields under practical conditions due to possible negative or positive synergistic effects, the mono-substrate digestability e.g. as nutrient and trace elements may take place, or the limits of the organic loading rate per unit volume. The result of a batch digestability test depends on the type of substrate, but also the microbial activity of the seeding sludge or inoculum being used, the availability of buffering as well as nutrients and trace elements, the temperature, the length of digestion time and last but not least the effectiveness and sensitivity of the gas measurement system used.

Continuously operated digesters at a size that deals with representative substrate samples and follow the same operational regimes as the full-scale plant provide wider conclusions. These can provide vital information for identifying the appropriate loading rates; needs for bringing in other substrates for co-digestion; needs for pre-treatments; needs to alter mixing regimes; needs for alkalinity or other nutrient or trace element additions; impact on settlement/precipitations, foaming, floating and crust layers, biogas and methane yields and possible problems related to inhibition.

6.5 HRT and OLR

All the above monitoring parameters can define and be used to control more appropriately HRTs and OLRs. Typical OLRs and HRTs used for specific digester types will need to change to accommodate more difficult substrates e.g. requiring a long hydrolysis phase or when inhibitors are present, or even when essential elements are limited. However, as stated above exact appropriate initial HRTs and ORLs are defined at plant design stage, but operational changes occur, feedstocks can change slightly for example. And therefore these need to be continually modified also taking into consideration characterization of feedstocks and actual response from the digester. For example, the microbial consortia can be made fragile by previous sub-optimal operation and with a reduced quantity and diversity in the populations. Also there are complex antagonistic and synergistic effects that occur within the digester that are difficult to fully anticipate. Therefore, the control and operation of an AD plant should combine substrate characterisation with digester response and digestate monitored characteristics. Parameterisation for the latter two is covered in the following two sections.

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7. Parameter Selection Guide for the Characterisation of the Anaerobic Digestion Process

A stable AD process that is also not suffering from inhibition is a prerequisite for efficient biogas and biomethane production. Monitoring the status of the process is therefore essential. As stated in earlier Chapters, many researchers and operators have found that no single parameter can be used as a control measure of the AD process as the degradation of organic matter is performed by a complex microbial population, and that can also adapt and through competitive processes also change. The AD process has typically been modelled as a three-phase process (solid-liquid-gas) as per Figure 4, where each phase is interrelated by physico-chemical relationships. A number of parameters monitored in these phases have been suggested as process indicators. An overview of the parameters most important for monitoring the performance of anaerobic treatment processes and the techniques used to monitor them is described below. In addition to monitoring parameters that identify stability, there are others such as temperature that also requires control.

7.1 Temperature

Temperature represents one of the essential factors affecting AD operation. This parameter is very often constant or at least attempted to be kept constant. Anaerobic digesters can be operated optimally within mesophilic (35-42°C) or thermophilic (55-58°C) temperatures as methanogens grow optimally at those temperatures.

Temperature has a direct effect on physical-chemical properties of all components in the digester and also affects thermodynamics and kinetics of the biological processes including methanogenesis. Temperature determines if a specific reaction is favorable. Increasing temperature has several advantages e.g. increase solubility of organic compounds which makes them more accessible to the microorganisms; increase chemical and biological reaction rates, thus, accelerates the conversion process so the digester can be smaller and can run with shorter HRT; improve several physical-chemical properties such as improve diffusivity of soluble substrate, increase liquid-to-gas transfer rate due to lower gas solubility, decrease liquid viscosity, which makes less energy required for mixing and also improve liquid-solid biomass separation; increase death rate of pathogenic bacteria especially under thermophilic conditions, which decreases retention time required for pathogen reduction; moreover, the organic acid oxidation reactions become more energetic at higher temperature, which advantages the degradation of LCFA, VFA and other intermediates.

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Nonetheless, operating at thermophilic temperatures can also have some negative effects. In addition to requiring more heat energy, increasing temperature decreases the pKa (in a simplified form the dissociation constant) of ammonia, thus, increases the fraction of free-ammonia (NH_3), which is inhibitory to microorganisms. In addition, increasing temperature increases pKa of VFA, which increases its undissociated fraction, especially at low pH (4-5) such as in the acidogenic stage. This makes the thermophilic process more sensitive to inhibition. The microbial population is less diverse and as the optimum range is within a narrower band so even small temperature changes will have an impact. Thermophilic operation has however been utilised in some situations and where ammonia inhibition is not a major consideration.

7.2 Inhibiting Compounds Formed in the AD Process (VFAs, LCFA, ammonia and sulphide)

In addition to inhibitors that may already be present in the substrate (e.g. LCFA, heavy metals and antibiotics); the most common inhibitors are actually formed during degradation of the substrate, such as VFA, LCFA, ammonia and sulfide.

VFAs are the main intermediates in the AD process and accumulate under process imbalance. At lower pH, VFAs become more toxic due to an increase in its undissociated fraction. The undissociated VFA can freely cross the cell membrane, then dissociate which lowers internal pH and disrupts homeostasis. Therefore, maintaining an appropriate buffering capacity would help. These parameters are discussed further in Section 7.4.3.

LCFAs in addition to being in high concentrations in hydrolysed vegetable fats, are also formed during degradation of fat and lipids, and as stated before LCFA can cause inhibition even at low concentrations.

Ammonia comes from the degradation of high nitrogen content feedstocks e.g. sewage and protein-rich waste, and although ammonia and the ionised form ammonium are important cell nutrients, ammonia can also be a significant factor affecting the process stability and therefore monitoring and control of its concentration is necessary. Ammonia toxicity increases at high pH and high temperature due to higher concentration of free ammonia, which is known to be inhibitory. Under high ammonium concentration, the inhibitory effect on methanogens is lowest at pH 7.0-7.5. High pH and temperature both lead to a higher fraction of free ammonia. Operating at mesophilic rather than at thermophilic temperature is often performed to overcome ammonia inhibition. Inhibition of methanogenic bacteria has been reported for concentrations of free ammonia above 100 mg N l^{-1}. Methanogens, can however be slightly acclimated to ammonia, or methanogenic dominant populations can shift where for example *Methanosarcina sp*. can operate at higher ammonia levels than *Methanosaeta sp*. Ion chromatography can be used to measure ammonia. Electrodes based techniques or colorimetric/photometric methods

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are also available for ammonia measurement, however, these techniques work better for matrices with a low content of suspended solids.

Sulfate and sulfur compounds are also present in protein waste. Both acetogenic and methanogenic organisms are affected by the presence of sulfate. At low concentrations of sulfate, sulfate-reducing bacteria compete with methanogenic archaea for hydrogen and acetate, and at high concentration the sulfate-reducing bacteria also compete with acetogenic bacteria for propionate and butyrate. Sulfate-reducing bacteria can easily outcompete hydrogenotrophic methanogens for hydrogen. Sulfide (total and H_2S) produced from sulfate reduction also has inhibitory effect at even low concentrations. The toxicity of sulfide has been related to the undissociated species, H_2S, since the neutral molecule can pass unopposed through the cell membrane. However, others have claimed that the toxicity should rather be related to total sulfide concentration at pH higher than 7.2 (O'Flaherty *et al*., 1998).

7.3 Solid Phase Characterisation

Solid phase is the combination of non-soluble materials immersed in the liquid phase. This mixture is composed of some organic solids and microbial cells as well as inorganic solids. The active cell measurements and their metabolic activity status are very important parameters in defining control strategies, as chemical parameters in the liquid phase provide only some information about the metabolic status of the microorganisms. However, solid measurement techniques are generally elaborate, time consuming and difficult to use in real time control as samples are taken and analyses performed ex-situ with data provided off-line.

7.3.1 Microbial Techniques and Chemical Indicators (enzymatic activity)

The monitoring of microbial community is based on the number and identification of organisms, especially archaea, as they are the most sensitive and the ones delivering the final gaseous CH_4 product. The number and diversity of methanogenic populations can be identified, and therefore a densely populated digester (>10^8 cells/ml methanogens and >10^{10} cells/ml Eubacteria) correlates generally with high methane production. Microbial identification can be done using fluorescence *in-situ* hybridisation (FISH). Measurement of microbial diversity and community structure can be done by the genetic fingerprinting techniques such as denaturing gradient gel electrophoresis (DGGE), temperature gradient gel electrophoresis (TGGE) and terminal restriction fragment length polymorphism

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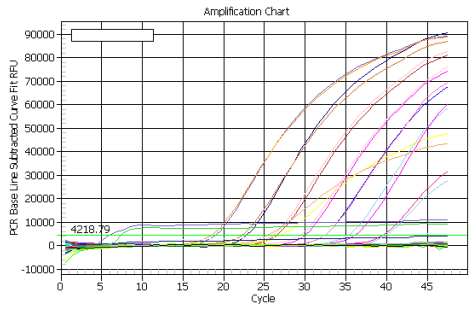

(TRFLP). In addition, qPCR has started to be utilised and is proving a useful technique to measure bacteria and archae as it is able to identify in addition to microbial diversity also the quantity of microbes. Also as sequencers improve in performance and accuracy and reduce in price and runtime, allowing analysis to become more economic, they could be used to provide an identification of species present in digesters. Both immunological techniques and techniques based on RNA and DNA probing are used for identification and can be used for quantitative determinations. However, all molecular techniques are still rare and only performed ex-situ and currently require significant amounts of laboratory work and costs.

It has also been reported that near-infrared spectroscopy (NIR) is also able to measure methanogenic density (Zhang *et al.*, 2002).

Activity measurement focuses on the status of microbial metabolisms. Microbial activities can be directly measured in batch tests such as specific methanogenic activity (SMA). Cell-produced chemical indicators such as enzymes or phospholipid fatty acids have also been extensively examined. The level of specific co-enzymes relating to cell metabolism such as F420 and NADH have also been used to correlate with microbial activities or the number of active organisms in the digester. The quantification of F420 in anaerobes has received much attention in recent years. HPLC has been used for measuring F420 concentrations. However, expensive instrumentation and sophisticated laboratory protocols are necessary; furthermore on-line analysis necessary for control systems is extremely difficult. Fluorescence detection has also been trialled without the need for extraction procedures. The detector was effective on pure bacterial cultures, but was affected severely by the darkness of the digester contents. But further work and evaluation of correlations is continuing using fluorescence techniques at least for ex-situ analysis. Nordberg *et al.* (2000) used near-infrared spectroscopy (NIR) for measuring phospholipid fatty acids correlating to the biomass density. There are also methodologies that can be applied ex-situ to measure hydrolytic bacteria related enzymatic activity such as cellulases, proteases and lipases.

Most of the above methodologies are only available for ex-situ analysis, and require specialist equipment and expertise, and analyses are not performed on-site. Currently, the monitoring of microbial communities and their specific activities is done generally for describing process behavior or to correlate with other liquid and gaseous measured parameters and not yet directly for control purposes.

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7.4 Liquid Phase Characterisation

Parameters used to characterise the chemical status of the liquid phase are more commonly used for monitoring digesters as compared to solid phase. It has been stated in general that monitoring parameters should, preferably, refer to the liquid phase, instead of the gas phase, as the environment to be controlled is the mixed liquor, which contains the anaerobic microorganisms. However, for in-situ and in-line monitoring, fouling is still a significant problem. In-situ or in-line monitoring of most of the liquid phase parameters using chemical and optical probes can be implemented, but calibration and maintenance problems make their long-term performance difficult.

7.4.1 Oxidation-Reduction Potential (ORP)

ORP, or redox potential, is an indication of the oxidation state of a specific system. ORP measurements are relatively simple and quite accurate. However, they are not typically used for monitoring and controlling AD processes and have been stated to be insensitive and slow to react. It is however an interesting parameter to monitor that could identify infiltrations of air/oxygen in the anaerobic system.

7.4.2 Dissolved H_2 Concentration

Hydrogen is formed during the breakdown of complex organic matter to VFAs and again during the further conversion of these acids to acetic acid and CO_2. Theory has stated that below ca. 10^{-4} atm of hydrogen is necessary for degradation of propionate and butyrate, respectively (McCarty and Smith, 1986). Hydrogen is a key intermediate in methanogenesis and since the beginning of the 1980s several researchers investigated how to use H_2 concentration (either in the gas phase or dissolved in solution) in anaerobic process control. The online measurement of dissolved hydrogen has been studied. Findings have demonstrated that measurements are very sensitive to the addition of easily degradable organics and that in addition responded also to other disturbances such as slight air exposure which had no significant impact on process performance (Boe *et al.*, 2010).

Platinum black electrode for direct measurement of dissolved H_2 concentration has been used as well as membrane diffusion techniques to extract dissolved hydrogen (challenges however came from the suspended solid nature of the matrix) and measurement with different sensors,

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such as mass spectrometry, hydrogen/air fuel cell detectors, hydrogen electrodes, gas chromatography and a palladium-metal oxide semiconductor sensor.

Further reference to H_2 measured in the gas is included in Section 7.5.2.

7.4.3 VFAs, Buffering Capacity and pH

The parameters VFA, alkalinity content and pH, are closely inter-related in digesters. Alkalinity or buffering capacity and levels of VFAs are typically fast indicators of changes in digestion. In a low buffered system, pH, partial alkalinity and VFA measurements are useful for process monitoring whereas in highly buffered system only VFA is reliable for indicating process imbalance.

Volatile Fatty Acids (VFAs) concentration

All organic acids contain the carboxyl group written as –COOH. They are weak, ionise poorly and have sharp penetrating odours. Acids with up to nine carbons are liquids but those with longer chains are greasy solids, hence the common name fatty acid. VFAs are the most important intermediates in the AD process. VFA accumulation during process imbalance directly reflects a kinetic uncoupling between acid producers and consumers (Switzenbaum *et al.*, 1990). Additionally, then the unionised VFAs seem to be able to enter the membrane of the bacteria and uncouple the process of adenosine triphosphate synthesis (Zoetemeyer *et al.*, 1982).

VFA concentrations have been indicated for a long time as potential process performance indicators (i.e. acetic, propionic, butyric, iso-butyric, valeric and iso-valeric acids). In principle, the concentration of individual VFAs can be considered as the best control parameters in the liquid phase, as they give indications about the metabolic state of the most delicate microbial groups. However, it is worth mentioning that a high VFA level is the result and not the initial cause of the digester imbalance. In a well operated digester, VFAs should either not exist or at least not accumulate significantly. The accumulation of VFAs in digestion mixed liquors never appeared beneficial either to the CH_4 productivities or to the reliability with time of the digestion system.

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Individual VFAs can give more important information as an early warning before process failure and would provide a good basis for a process control strategy. Acetic acid is usually the predominant VFA present and its moderate accumulation in many cases appears harmless. A rise in the levels of propionic, butryric, iso-butyric and iso-valeric acids have been suggested as good indicators of stress level in advance of process failure. Some have suggested to use the variation in propionic:acetic acid ratio as an indicator for impending failure. Propionic acid is known to be the most thermodynamically unfavorable and many researchers and operators look at propionic acid level as the most important process indicator, as it also remains for long periods after an organic load or an inhibition period. A mathematical model developed by Mosey (1983) proposed that the increase in H_2 as a result of overloading the system would produce a larger increase in propionic acid than acetic acid. High concentrations of acetate and H_2 inhibit the conversion of propionic acid to those end products. Such inhibition leads to a build-up of VFAs, which leads to a decrease in pH if the buffering capacity of the system is exceeded, and inhibition increases with decreasing pH. For example, methanogenic populations were demonstrated to be inhibited at propionic acid concentrations in excess of 1000 mg l^{-1}, while they could tolerate acetic and butyric acids of up to 10 000 mg l^{-1}.

Some researchers state that TVFAs should not be above 500 mg/l, others however state that some systems can cope well up to 3000 mg/l. It is not feasible to define an absolute VFA level indicating the state of the process. Anaerobic systems have their own levels of VFAs, determined by the composition of the substrate digested, by operating conditions including buffering capacity, as well as microbial populations. The overall upper limit of 2000 mg VFA l^{-1} seems to have been over emphasised, however above these values it may well mean that a shift in methanogenic populations may need to occur. Also with higher VFA levels reduced waste treatment would take place, increased odours as well as plant phytotoxicity as well as significant losses of methane potential could occur if VFAs are elevated in the digestates.

Many researchers prefer instead the use of sudden changes in a relatively constant value of the VFA content as a control parameter, rather than setting levels for ‘safe’ digestion. The precise cause of high VFAs can also be difficult to determine as for example the symptoms of toxicity and of trace metal deficiency are often relatively similar. Another important aspect is that although VFAs are excellent for indicating an organic overload, the VFA response is however unclear under a toxic stress where acid producers are also inhibited, for example, under high concentration of LCFA.

Individual VFAs are commonly measured ex-situ by GC with flame ionization detectors (FIDs), thermal conductivity detectors (TCDs) or by the use of HPLC. VFAs can also be measured

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accurately using GC-MS but the cost is usually prohibitive. Effective VFA monitoring has been proven where filtration is avoided based on the use of the headspace GC (HS-GC) technique (Cruwys *et al.*, 2002), where filtration of the sample is avoided. Static HS-GC involves the equilibration of liquid or solid sample in a closed vial at high temperature to extract VFA into the gas phase, and injection of headspace gas with a gas tight syringe into the GC. VFAs measured include acetic, propionic, butyric, iso-butyric, valeric and iso-valeric acids.

Several authors have suggested different variants of titration methods. However, this methodology is only indicative of total VFAs and only worth pursuing for AD plants that are not interested in detailed information about the relative abundance of individual VFA acids, but merely seek a measure for total acidity. For ex-situ measurement of total VFAs (as well as alkalinity), titration has been widely used as an indirect method, which is only semi-quantitative. This method has been largely used for monitoring TVFAs at full scale biogas plants, which is cheaper than GC and HPLC. However, several contaminants have an effect on the buffering subsystems. These are carbonic acid, phosphate, sulphate and ammonium. Many titration methods for determination of total VFA have been proposed, e.g. a simple titration (Anderson and Yang, 1992), a 5-point titration (Moosbrugger *et al.*, 1993), and an 8-point titration (Lahav *et al.*, 2002). Two of the most widely used today are the two endpoint titrations proposed by Ripley *et al.* (1986) and Nordmann (1977), with endpoints pH 5.75 and 4.3 and pH 5 and 4.4, respectively. There have been several attempts to automate the measurement of TVFAs e.g. the titration method as per Nordmann (FOS/TAC) has been automated, however the differences in sample preparation have also cause interferences. Feitkenhauer *et al.* (2002) automated the Anderson and Yang (1992) two-point titration method (pHs 5.1 and 3.5). Analysis can be performed every 30 minutes. However, the usefulness of the titrator could be greatly reduced if there is a high carbonate value in the digester (resulting in increased buffering capacity) as it becomes difficult to estimate the VFA concentration from pH measurements.

Another method for measuring TVFA involves the esterification of the organic acids in the sample at 100°C according to Montgomery *et al.* (1962) followed by a photometric measurement. Although it is a simple procedure, it has been stated to be of poor accuracy at low concentrations and the analyses are rather sensitive towards residual colour.

Typically only titration or colorimetric based analyses have been used to routinely monitor VFAs at full scale plants, and in many cases samples are sent out to external laboratories. The ex-situ nature of these analyses does however mean that there could also be a time delay between the sampling and the analysis, during which digester has not been appropriately monitored and controlled.

There have also been some attempts to measure individual VFAs through automated and in-line techniques which have been based on sample preparation by membrane filtration, and subsequent conventional analysis using HPLC and GC. These have normally been used for soluble substrates with limited use for particulate samples. Most of the in-line VFA monitoring

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systems available are based on filtration for sample preparation, which suffers from fouling, and require extensive maintenance. Boe *et al.* (2007) have indicated that the HSGC method could be used as an in-line sensor, however it is currently not commercialised. A microchip capillary electrophoresis (CE) based method seems to be currently at commercial demonstration stage for in-line monitoring of individual VFAs, and filtration and maintenance requirements as well as costs and reliability performance should be available shortly when analyzing both low and high suspended solids rich samples.

Some VFA based biosensors have also been used based on correlations with microbial respiration and denitrification. There have also been reports related to possible in-line measurement of individual VFAs by near-infrared spectroscopy (NIR); however this requires models that had to previously been generated.

In-line individual VFA analysis methodology with real-time data generation would be ideal for the control of anaerobic digesters. However, taking into consideration the instruments in the market further developments seem to be required.

Buffering Capacity

Buffering capacity, or alkalinity level within the contents of a digester is the measure of its capacity to neutralise acids, in other words to absorb hydrogen ions without a significant pH decrease. Appropriate alkalinity is therefore also important for process stability. If VFA production/consumption balance becomes too severe the buffering capacity will become inadequate, the pH drops and the digester 'sours' and methanogenic bacteria become inhibited. Since the alkalinity is mainly due to the bicarbonate buffer (sodium and calcium bicarbonate), it has been proposed since the early sixties that its measurement can be used in control strategies for anaerobic digestion with a general rule that every mol l^{-1} of VFA that is allowed to build up will destroy (and replace) an equivalent concentration of bicarbonate.

The main buffer in anaerobic digesters is bicarbonate (HCO_3^-). The bicarbonate ion provides buffer capacity over an approximate pH range from 5.3 to 7.3 (Stumm and Morgan, 1981). For historic reasons alkalinity is measured as mg of $CaCO_3$ l^{-1} to a specified pH. Suggested concentrations of bicarbonate range from a recommended minimum of 1000 up to 5000 mg l^{-1} as $CaCO_3$ to maintain the reactor pH above 7, but some researchers suggest increasing the lower level to around 3500 mg $CaCO_3$ l^{-1}. The naturally occurring buffering capacity in anaerobic digesters can vary considerably depending on the waste type. In an anaerobic digester that is working well the VFA:BA is normally 0.3 or less (Ross *et al.*, 1992). If the ratio increases above this, the system is deemed to be unstable.

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Other compounds normally found in the digester also influence the pH balance if present at high concentration, for example, ammonia, hydrogen sulfide and hydrogen phosphate. For example, manure digesters normally have high feed bicarbonate buffering capacity and a high ammonia content, which makes the pH stable around 7.5-8.0 and the system can tolerate rather high concentration of VFAs before pH drops. Therefore, relying on pH measurements as indicators of failure for systems with this level of buffering would only provide a delayed response. Alkalinity or buffering capacity is a better alternative than pH for indicating VFA accumulation, since the increased VFA will directly consume alkalinity before large pH changes occur.

The pH endpoint in the alkalinity titration is the subject of some dispute, values of 5.75 (Jenkins *et al.*, 1983), 4.3 (Ripley *et al.*, 1986), and 4.0 (McCarty *et al.*, 1964) have been suggested in the past. The definition of alkalinity is somewhat circular since selection of a pH endpoint and, consequently, the value obtained for the alkalinity of a sample depends upon prior knowledge of the alkalinity (Powell and Archer, 1989). The buffering capacity of acetic and propionic acids is a useless part of the alkalinity in anaerobic digestion that operates in the pH range 6.5-7.5 (Jenkins *et al.* 1983). Therefore, the distinction between bicarbonate alkalinity (BA) and total alkalinity (TA) is of critical importance. BA refers to the TA minus the TVFA. It is common practice in the operation of an anaerobic reactor to use the VFA:TA ratio as a control parameter (Speece, 1996).

However, TA measured by titration of the sample to pH 4.3 was proved to be insensitive since the combination of VFA and bicarbonate results in a stable TA level. Intermediate alkalinity (IA), the alkalinity between pH 5.75 and 4.3 has been shown to be semi-quantitative to TVFA (Ripley *et al.*, 1986). BA measured by titrating the sample to pH 5.75 has empirical correlation to VFA accumulation (Hawkes *et al.*, 1994). However, this relationship is not observed during VFA accumulation in response to ammonia overload, as the ammonia adds alkalinity to the system (Björnsson *et al.*, 2001). Other authors suggested the ratio of VFA/TA as an indicator where the healthy digester should have the ratio in the range of 0.1-0.35 (Switzenbaum *et al.*, 1990).

Monitoring of pH

pH level influences enzymatic activity of bacteria, since each enzyme is active only in a specific pH range and has maximum activity at its optimal pH. Each group of microorganisms has different optimal pH ranges. Methanogens can function in a quite narrow pH interval from 5.5-8.5, but not all methanogens work at these pHs and the optimal range has normally been defined as 6.6-8.0. Fermentative bacteria can however function in a wider pH range from pH 4 to 8.5 and their products are acids such as acetic, butyric and propionic.

In digesters, and although the feedstock pH can affect the level of pH in the digester, pH is typically held within a neutral range by natural processes. A too strong acidification is avoided by the CO_2/hydrogen carbonate/ carbonate buffer system i.e. with lower a pH more CO_2 gets

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dissolved in the substrate as uncharged molecules. Reversibly, the equilibrium between carbonic acids, bicarbonate alkalinity and carbonate alkalinity as well as ammonia and ammonium ions is a function of digester pH. And as described previously, the pH level also affects acid-base equilibrium of different compounds in the digester. At low pH, free VFA can cause weak acid, while at high pH, free ammonia can cause weak base inhibition.

pH is relatively easy to measure, and often the only liquid-phase parameter that is measured online. The change in pH can be both an indicator, and the cause of process imbalance, since the microorganisms can function only in a specific range of pH. The use of pH as a process indicator is normally based on the fact that a pH drop corresponds to VFA accumulation. Some anaerobic systems apply pH monitoring and control where acid or base are added to ensure suitable pH for microbial growth. In a digester with low buffering capacity and no pH control, VFA accumulation can decrease pH quickly, and pH can be an effective process indicator. However, it is not recommended to use pH for indicating process imbalance in a well buffered system where the change of pH from VFA accumulation is often slow and too small. The high buffering capacity will resist pH change and the pH drop will often occur after the process is severely imbalanced. pH measurements are simple and inexpensive through the use of pH electrodes. But in addition to the delay in measuring a decrease in pH because of alkalinity, it is also logarithmic rather than an arithmetic function and pH is therefore less sensitive to small fluctuations in pH. Signal drift is possible and therefore the probe requires frequent re-calibration and fouling makes necessary frequent washing and other cleaning (e.g. ultrasonic) systems. Xerolyte combined pH electrodes are typically less susceptible to fouling and retain calibrations for longer.

In-situ or in-line pH monitoring of an anaerobic digester is more representative of the pH contents than off-line due to the loss of CO_2. If the sample is allowed to stand exposed to the air for a few minutes the dissolved CO_2 will be liberated, causing a pH change.

7.5 Gas Phase Characterisation

The use of gas phase indicators for real-time data acquisition has been investigated as they have the advantage of having a relatively fast response time to stress of the anaerobic microorganisms as well as being non invasive measurements and therefore less susceptible to fouling and generally more reliable and reasonably more economic when compared to others. Biogas rate and composition will depend on the content of organic compounds (including fats, protein, carbohydrates) being digested, but also due to other process parameters of the digestion as well as the potential for inhibition. The biogas yield may range from a few litres to more than 1000 l per kg of substrate. Very high biogas yields can be obtained with substrates

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such as fats or glycerol, however attention is required as OLRs need to be appropriate as otherwise stability can be compromised.

7.5.1 Biogas Production Rate and Yield

Biogas production is the most common parameter to be measured. It can be expressed in terms of rate (volume gas produced per unit time, e.g. m^3 biogas/day), or yield (volume gas produced per unit feed or per unit of dry or organic dry feed, e.g. m^3 biogas/tonne of substrate or m^3 biogas/tonne VS of substrate added or destroyed).

Biogas rate is an important parameter as it indicates overall performance of the process. However, it is difficult to use it on a stand-alone basis for indicating process imbalance since the change in biogas production rate depends on VLR and OLR, as well as substrate composition. For example, the initial increase in gas production during an overload is also a function of the CO_2 produced by the destruction of bicarbonate. In addition, and specifically for high rate and low HRT type of digesters, biogas rate demonstrates a low sensitivity to overloading compared to other process indicators and a decrease in biogas production can occur only after the process is severely inhibited. Therefore, using only a biogas rate measurement, a cause of process instability would be difficult to determine. This measurement together with knowledge of the organic input to the system, as well as biogas composition and bicarbonate alkalinity (BA) and/or VFAs would then support a decision whether there was instability or not. On-line biogas rate measurement systems include mass flow and differential pressure sensors.

7.5.2 Biogas Composition (CH_4, CO_2, H_2, H_2S)

The response time for gas composition monitoring depends on the head-space volume, rate of biogas production and gas solubility. The composition of the biogas is a more useful indication of the anaerobic digester status than the biogas production rate alone as it reveals information about the activity of methanogens.

Biogas CH_4 and CO_2 Rates and Yields

The biogas consists mainly of CH_4 and CO_2. The ratio of CH_4 to CO_2 is normally stable in the digester and a change of the ratio can be due to process imbalance. However, this ratio also depends on substrate composition, temperature, pH and pressure. Since the dissolution of CO_2 is strongly dependent on pH, fluctuation of pH can also change gas composition. A better indicator is therefore methane production, as methane has a low solubility in the liquid and does

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not undergo any chemical reactions. Example of methods used to analyse CH_4 and CO_2 include gas chromatography and infrared sensors.

Methane production combines biogas production to the measurement of methane percent. The methane content is usually measured at 50 to 75 % by volume. If there is a high pH value in the digester medium, a comparatively high proportion of carbon dioxide and hydrogen sulphide will remain dissolved in the digestion medium. For this reason with a high pH value, a comparatively high methane content will be measured in the biogas. Methane production rate (m^3 CH_4/day) depends on digester loading, not only the status of the process and therefore methane yield (m^3 CH_4/g VS added) would be a better indicator. However, particularly when feedstocks vary frequently, the VS content of the substrate at that particular time does not necessarily correspond to the methane that is currently being produced. In addition, changes in the methane yield can be small at an outset of an inhibition and significant changes may have already occurred in the digester.

The CO_2 composition can fluctuate substantially even when the increase does not approach digester failure. The suitability of $\%CO_2$ as a control variable is questionable as it varies for physico-chemical reasons (for example the destruction of bicarbonate ions, a change of pH or ammonia concentration) as well as metabolic reasons (for example an increase in fermentative activity without methanogenic activity). However, a change in CO_2 does not always indicate a cause for concern; however, if the CO_2 increase is related to the loss of bicarbonate, it is an occurrence worth investigating.

Biogas Trace Gases (H_2, H_2S, NH_3, CO, Si compounds)

Secondary gases at low concentrations include hydrogen, hydrogen sulphide, ammonia and various trace gases. The noxious gases hydrogen sulphide and ammonia originate in protein breakdown and particular attention must be paid to them. Problems can also arise in utilisation of the biogas in engines if the substrates contain volatile organosilicon compounds, as these may cause permanent damage to engines. Organosilicon materials can be present in substrates from the cosmetics industry or be input via process additives such as defoaming agents.

Hydrogen

As referred to above, hydrogen is important as both an intermediate and electron carrier in the digestion process. H_2 is believed to be responsible for 1/3 of the electron transfer between fermenting and methanogenic bacteria. Hydrogen concentration affects thermodynamics and the degradation pathways of the anaerobic degradation process. High hydrogen concentration can inhibit volatile acids degradation, resulting in VFA accumulation. Thus, hydrogen accumulation has been suggested as an early stage indicator for process imbalance by many

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researchers. However, since hydrogen is formed in the liquid phase, the sensitivity of hydrogen in biogas is also limited by the liquid-to-gas mass transfer rate.

The ability of hydrogen to be classed as an early indicator of digestion stress has had mixed statements from the research community. Dissolved hydrogen concentration seems to have shown a better correlation with the build-up of propionic acid but not the hydrogen measured in the gas phase.

The sensitivity of hydrogen seems to depend on several factors; type of digesters, substrates and the intensity of the organic overload. There has been however some consensus that hydrogen responds rapidly to an overload of readily degradable organics, but is less sensitive to slowly degradable material. But even with readily degradable material, there can be a significant variation of hydrogen in the gas phase without a significant stress conditions by the digester (Esteves *et al*., 2000) and therefore this reactive nature of this parameter makes its safe levels difficult to specify and even correlate. For example, not always VFAs increase with an increase in hydrogen. Also a short exposure to air could increase dissolved hydrogen without any change of VFA or biogas.

Although hydrogen is sensitive to organic overloads, it does not seem to maintain high levels as compared to VFAs, even when the organic overload is still occurring. Rapid hydrogen variations have been associated with a natural response to an almost normal microbial activity, rather than an indicator of significant problems. It is also dependent on whether the substrates have been pre-fermented or not. A number of researchers have concluded that the variation in hydrogen concentration was a short-term event, with no correlation to other indicators, or reactor performance. Thus hydrogen has not been recommended as a stand-alone indicator, but rather in combination with other parameters.

It has been shown that gaseous H_2 is extremely sensitive, and responds fast and in many cases significantly to any disturbance to the system, and also to increases in organic loading rate (Esteves *et al.,* 2000). However, H_2 in the gas varied considerably and unpredictably from 0 ppm to over 1800 ppm, but there was typically a correlation with the increase of the organic load. It is important that parameters chosen are not too over sensitive and react significantly to numerous changes including ones that do not impact significantly on the status of the digester. An example of this is the hydrogen concentration in the biogas phase, which seemed to be over sensitive to easily biodegradable carbon loaded as well as for very small changes in temperature, but for which the digester was still coping well (e.g. Esteves *et al.,* 2000).

The H_2 concentration in the biogas can be determined by a GC using specific detectors e.g. the mercuric-mercuric oxide detector. There are also palladium metal oxide semiconductors (Pd-MOS) and electrochemical detectors. Scrubbing H_2S from the biogas before entering the monitor may be necessary, for others no flow of oxygen is allowed as it will poison the cell.

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Carbon Monoxide

Carbon monoxide has been stated to be a possible intermediate in the metabolic pathway of both acetogens and methanogens and it has been reported to be evolved during methanogenesis from acetate. Carbon monoxide was found in significant levels during toxic inhibition by heavy metals. It has also shown good potential for indicating organic and hydraulic overloads in a sewage sludge digester. The level of gaseous carbon monoxide has been reported to be directly related to acetate concentration, and inversely related to methane concentration. However, the response of carbon monoxide could also be dampened by solids hydrolysis, in a similar manner to hydrogen. Puñal *et al.* (1999) concluded that the monitoring of CO concentration did not allow a prediction of digester instability. Further applications of CO as a process indicator or for control purposes have not been found.

H_2S

Little has been published on H_2S monitoring. Sulphide volatilisation is a function of many digester operational parameters including pH, sulphate loading rate, metal concentration and biogas production rate. Hydrogen sulphide in small concentrations of 1000-3000 ppm has been found. The incorporation of H_2S gas as a parameter into a control strategy may be of use for wastes which contain high concentrations of influent sulphur.

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8. Parameter Selection Guide for the Additional Gas Phase Monitoring Relevant for Biogas Clean Up and Upgrading Systems

The biogas produced in the digester contains considerable water vapour (around 3% at 25°C and 1 atm). The gas temperature and the water vapour content must be taken into account when dimensioning biogas pipework. Depending on the various elements within the substrate and on factors such as pH, temperature and potential inhibition, the quality (composition CH_4, CO_2, H_2S) of the biogas may vary. H_2S content of the biogas may vary from 0.01% up to 3% when substrates rich in sulphur are used. If sewage sludge is used as a substrate, the presence of siloxanes in the biogas is possible and should be monitored, as they can cause problems in combustion appliances such as gas-engines.

Table 1 contains typical gas compositions of biogas and these values are compared to the Danish, UK and German natural gas standards.

Adsorption and oxidation are two processes available to desulphurise the biogas. Adsorptive processes like desulphurisation using activated carbon, iron oxide or zinc oxide are commonly used technology. In case of a digester integrated desulphurization, the extracted sulphur (H_2S) remains in the digester (sludge) as elemental sulphur (S) and will exit the system with the digestate. If an external washing tower is in place and sulphur is floated, it can be skimmed off the surface and utilised.

An additional option to the cleaning process is the enrichment of methane in the biogas. Before the enrichment process, biogas must be desulphurised and dried. Afterwards, the carbon dioxide is removed from the biogas in order to produce a biomethane gas stream with enhanced heating value. Numerous technologies are available for this main task such as Pressure Swing Adsorption (PSA), pressurised water scrubbing, membrane separation or amine scrubbing. Please refer to the document “Biogas to biomethane technology review” provided as deliverable D3.1.1. for more detailed information on biogas upgrading technologies.

If biogas is upgraded for the injection into the national gas grid or to be used as fuel, a series of control parameters are of great relevance. The control parameters vary with the type of upgrading technology that is used. Table 2 gives the most important parameters that have to be monitored to allow for a stable, continuous and safe operation of the biogas upgrading plant.

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Table 1 - Typical gas compositions of biogas compared to gas networks in Europe

Parameter	Biogas	Natural gas (Danish)	Natural Gas (UK) GS(M)R 1996	Gas Network Germany (DVGW G260)
Methane [vol%]	60-70	89		
Other hydrocarbons [vol%]	0	9.4		
Hydrogen [vol%]	0	0	≤ 0.1% (molar)	≤ 5
Carbon dioxide [vol%]	30-40	0.67		< 6
Nitrogen [vol%]	up to 1	0.28		
Oxygen [vol%]	up to 0.5	0	≤ 0.2 % (molar)	< 3
Hydrogen sulphide [ppmv]	0-4000	2.9	≤ 5 Total sulphur content (≤ 50)	< 30 (total sulphur)
Ammonia [ppmv]	up to 100	0		
Siloxane [mg/m^3]	*< 0.1- 5			
Lower heating value [kWh/m$^3_{STP}$]	6.5	11.0		
Wobbe Number (MJ/m^3)			47.2-51.41	37.8–46.8 (L gas grid) 46.1–56.5 (H gas grid)
Odour			<7 barg will need an odorising agent	

* Found in biogas from sewage sludge digesters

[*Sources*: *Gas Safety (Management) Regulations 1996, Petersson and Wellinger, 2009]*

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Table 2 - Key parameters to be monitored and controlled in order to efficiently operate a biogas upgrading unit including possible measurement techniques and measurement frequencies:

Parameter	Unit	Sampling method	Exemplary methodology of analysis
Biomethane Volume Flow rate	m^3_{STP}/h	continuous	displacing counter, velocity sensor
Biomethane CH_4-content	%v/v dry	continuous or up to every 15 minutes	non-dispersive infrared sensor (NDIR), GC-Thermal Conductivity Detector (TCD)
Biomethane CO_2-content	%v/v dry	continuous or up to every 15 minutes	NDIR, GC-TCD
Biomethane O_2-content	%v/v dry	continuous or up to every 15 minutes	paramagnetic, GC-TCD
Biomethane H_2S-content	mg/m^3_{STP}, ppmv	continuous or up to every 15 minutes	electrochemical, colorimetric, pulsed flame photometric detector, GC-sulfur chemiluminescence detector
Biomethane H_2O-content	%v/v, ppmv, dew point	continuous or up to every 15 minutes	Aluminaoxide sensor, GC-TCD, Interferometry
Total electricity consumption	kWh	continuous	electricity meter
Hot utility energy consumption	kWh_{th}	continuous	mass flow and temperature
Cold utility energy consumption	kWh_{th}	continuous	mass flow and temperature

The continuous and traceable monitoring of a part of these parameters is typically mandatory for grid injection as well as for the production of vehicle fuel (minimum quality requirements and documentation). The other parameters provide information on the plant's efficiency and economic performance. Having deeper technological insight, one would be able to perform a parameter variation with these data in order to obtain an economically and technically optimised plant operation. To do so, wider operational parameters have to be monitored and the plant

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operator would need to know about the physical principles of the separation task itself to know which parameters to adjust to enhance efficiency or the plant economics. A complete matrix of the relevant monitoring parameters to perform the task of plant optimization is given in Appendix 1. It has to be noted, that not every single denoted parameter out of this list has to be monitored to operate a biogas upgrading plant in an efficient way. The given parameters can be used to describe the whole separation process performed in the plant regarding mass, species, heat and energy balances on a very detailed level. The efficient operation of a biomethane production plant requires only a few major parameters to be monitored and controlled carefully and these parameters depend on the applied separation technology.

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9. Parameter Selection Guide for Characterisation of Digestates

During the digestion process organic wastes undergo chemical-physical changes. Positive effects of this process are: particle size of the organic waste is reduced, potential emissions are significantly reduced, nutrients are significantly more available, the dewatering potential has increased, the unpleasant odour reduced and sanitation improved with some associated pathogen kill (better when digestion occurs at thermophilic temperatures or an additional pasteurisation step take place). In the digestion process the majority of carbon contained in the feedstock/ substrate is converted to biogas. The nitrogen, phosphorus, potassium among other inorganic elements remains in the digestate as well as recalcitrant organic material, humic substances and anaerobic bacteria. Different elements may be found in the liquor fraction or in the solid fraction. Depending on the digester, between 80-98% of whole digestate is water. Digestates can then be dewatered with a number of technologies with or without the aid of coagulants and flocculants. Techniques for the concentration of nutrients such as the use of membranes, reverse osmosis and struvite formation are only occasionally performed and that depends on the characteristics of the digestate and its market. Digestates have typically been used as soil conditioners and fertilizers for agricultural land as whole digestate, or as separated liquor or solid fraction after periods of storage that related to legislative or best practice requirements. Due to in some cases lack of quality, transport requirements, seasonal or nitrogen land use related limitations, other uses have also started to be investigated.

There are many industrial applications in which the main purpose of the AD process is to treat organic waste. For this purpose, the organic removal, which is the difference between the organic content before and after treatment, is an important parameter to be monitored. The organic removal in AD has been reported to be measured in terms of TS, VS, TOC, COD or BOD. These parameters are suitable for monitoring of AD applied to the wastewater treatment systems with soluble organic matter, such as high-rate systems. For solid and slurry wastes treated by suspended system where biomass are washed out with the effluent, it is difficult to distinguish between residue undigested particulate organics and the biomass from the reactor.

There are three reasons to monitor the characteristics of the digestate resultant from an AD plant, as whole, as well as the liquor and solid fractions in cases where they have been separated:

a) evaluate characteristics that indicate how effective the digestion and ancillary processes have been, with some of them taking into account a comparison with the feedstocks initial characteristics e.g. TS, VS or COD destruction, residual VFAs, residual methane

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potential; quantification of removal of contaminants and pathogen kill – so that changes in design and operation can be made and performances increased;

b) characterise and quantify its contents so that appropriate markets or discharge outlets can be found throughout the year, or change quality and characteristics for example through the implementation of a post-treatment e.g. dewatering, drying, concentrating, further stabilization, in order to meet better market demands/reduce transport requirements;
c) optimise digestate processing processes e.g. dewatering – polymer use and solids removal
d) comply with environmental legislation or with voluntary quality standards for digestates and specific uses. Different parameters and levels/limits apply from country to country, depending on the type of digestate and its use. When digestate liquors are discharged to the sewerage system, discharge consents must be met. The European Commission may be implementing shortly an End of Waste Criteria that is likely to be common in Europe for digestates.

Typical parameters required to be measured whether limits are prescribed or they are only declaration parameters are summarized as:

- hygenisation and animal by-products regulation compliance (this may include conditions related to particle size, retention time and temperatures achieved during pasteurization or AD process; as well as *Salmonella*, *E coli* and *Enterococci* analysis;
- Impurities such as stones, glass, plastics and metals
- Stability indicated through residual methane or biogas potential, organic acids and organic dry matter or VS;
- Heavy metal content (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn)
- Declared parameters such as bulk density, organic matter, pH, salt content, nutrients such as N, P, K, S, Ca, Cu and Zn; water soluble nitrogen, sodium and chloride
- Germination tests

Most of these analyses are typically performed ex-situ and sent to external laboratories and some of the techniques used have been described in earlier sections of this report. Except for the biogas or methane potential and organic acids measurement, all the others follow typically International or European analytical standards.

Covered storage of digestates is beneficial not only to reduce ammonia losses, but also to reduce odour emissions. In addition, it has been determined that values up to 15% of the

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methane potential from the initial feedstock can be recovered from digestate store tanks. Obviously this will depend on their characteristics especially stability leaving the digestion plant as well as temperature and residence time in the store.

In case the liquor digestate (or even after a post-treatment) is to be discharged to the sewer system or an aquatic environment under a discharge consents or a licence, a number of parameters may require monitoring with regular frequency and these may be related to organic, solids and nutrient loads as well as sulphide. A few of these measurements may then be required:

Biological Oxygen Demand (BOD) is a measure of the biodegradable organics levels using suspended microorganisms carried out during aerobic degradation. It is the classical parameter to define the organic 'strength' for a sample. It is carried out by measuring the oxygen during an incubation period of five days (BOD_5) or in some countries seven days (BOD_7) at 20 °C. Depletion of oxygen in the test bottle is directly related to the amount of degradable organic matter. Tests on real effluent samples can show standard deviations of 10-20 %. Automation of the test using a biosensor has been developed where a short BOD test is correlated to a BOD_5. However, the instrument has not yet had wide application.

COD is widely used to characterise the organic strength of samples. The test measures the amount of oxygen required for chemical oxidation of organic matter in the sample to CO_2 and H_2O. The laboratory test procedure is performed by chemical oxidation at destructive temperatures. The COD value is normally greater than the BOD of the same sample and can be conducted in a few hours. At normal conditions of temperature and pressure, 1 kg COD removed corresponds to 0.35 m^3 of CH_4, but there is also recalcitrant COD that is not converted during anaerobic conditions. And therefore, the conventional COD test, cannot distinguish between biodegradable and inert organic matter. The analytical error is typically less than for BOD, however the method also suffers some interferences and the conventional methodology is not appropriate for samples with high levels of suspended particles. But newer methods have been proposed to increase homogeneity of samples allowing for measurements to be carried out for higher particulate content feedstocks and also reduce the loss of volatile organic compounds (e.g. Noguerol-Arias *et al.* (2012)). There are now various commercial in-line COD monitors in the market but only for samples with low levels of suspended particles.

Total Organic Carbon (TOC) measures the organically bound carbon in a sample. Unlike BOD or COD, TOC is independent of the oxidation state of the organic matter and therefore it does not provide the same kind of information. TOC does not measure other organically bound

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elements such as nitrogen, hydrogen and inorganics that can contribute to the oxygen demand measured by BOD and COD. TOC is an instrumental analytical method that analyses a sample in a few minutes, and its central principle is to convert organic carbon to CO_2 and measure this product in the evolving gas phase. Inorganic carbon (IC) must be eliminated or compensated for since it is usually a very large portion of the total carbon (TC) in a sample. The determination of TC and IC with the estimation of TOC by difference is a common procedure. Particulate matter is to be avoided because the retention time in the reaction chamber is insufficient to allow complete combustion. Moreover clogging may be a problem. Pre-filtration of the samples is therefore essential for proper operation. Correlations between TOC, COD and BOD can change depending on the samples.

Total Oxygen Demand (TOD) is a measurement at high-temperature (900^{o}C), rapid (5 minutes) combustion method, which makes use of zirconium oxide or platinum lead fuel cell. TOD offers the advantage of simplicity of hardware because the analysis requires no reagents and is not affected by IC concentration and does not require acidification or sparging. TOD also offers the advantage of determination of non-carbon substances e.g. ammonia, nitrates, sulphites, iron, and purgeable organics in the sample, which can also be a disadvantage. TOD reflects the oxidation state of the chemical compound and can be used for on-line measurements. However, the sample needs filtration and tight maintenance requirements. Esteves *et al.* (2000) found that the instrument used may not be able to be used for industrial wastewaters containing significant mineral content due to the frequent blockages of the injection system.

Optical Sensing for Measuring Organic Strength

Absorption spectrometry and optical fluorescence at particular wavelengths have been found to correlate well with BOD, COD and TOC values. However, instruments based upon absorption require optical components to be in constant contact with the sample. In addition, such instrumentation usually requires pre-sample filtration and frequent washing leading to increased maintenance in order to avoid fouling.

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10. Summary of Actions for Improving Biogas and Biomethane Production

A description of control strategies is outside the scope of this report. Control actions can be performed manually or via supervisory control and data acquisition (SCADA) systems with programme logic controllers (PLCs) for example. Controllers can be based on on-off set-points, proportional – integral – (derivative) (PI+D) controller, expert systems, fuzzy logic and neural networks. For example, artificial intelligence based systems have been successful in incorporating non-linear dynamics of the AD process and have even demonstrated ability to tolerate sensor failure e.g. Esteves *et al.* (2001) where conventional on-off or PID based control systems would fail. But largely artificial intelligence based control systems have only been implemented in laboratory based processes. At full scale as referred in previous sections, only a couple of parameters are typically monitored in real-time and control actions are generally related to feed rates, level and pressure controls. Interest is only starting for monitoring and control based approaches at full scale plants and therefore it will be interesting to see in a few years time what strategies will be implemented.

This section describes a number of actions that can be undertaken to optimise biogas and biomethane production. These have been listed below in a summarised form.

10.1 Substrate Control, Co-Digestion and Substrate Pre-Treatments

It is important to prepare and utilise substrates to meet the engineering design requirements of the plant and all ancillary equipment otherwise equipment and integration specification may be required to change e.g. removal of inert material such as sand prior to digestion, reduce the size of the substrates to facilitate hydrolysis, reduce heterogeneity of substrates by good mixing prior to digestion, maintain appropriate viscosity and solid contents appropriate for pumping systems among others.

It is also important to reduce fermentation of easily fermentable substrates with potential for some methanisation before entering the digesters or before capture of the gas is performed, and therefore the reduction of storage times is important. On the other hand, for more difficult to hydrolyse substrates (e.g. substrates rich in ligno-cellulosic contents or substrates rich in bacterial cells and polymeric substances such as waste activated sludge) performing substrate pre-treatments can increase the biodegradability and enhance the rate of hydrolysis and acidogenesis. Pre-treatments might be based on chemical, biological, mechanical or thermal processes. It may also be beneficial to recover the gases produced during pretreatments if rich

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in hydrogen and some methane. Obviously for this, low levels of oxygen would need to be guaranteed.

Co-digestion can be a technique that can support optimisation of AD plants in a number of ways:

- enhance biogas production by increasing organic content to be digested;
- gain best operating substrate mixes with optimised C:N:P:S ratios;
- increase alkalinity;
- reduce the impact of high nitrogen content substrates;
- avoid trace element deficit;
- provide a supply of methanogens for example when using cattle slurry as a substrate;
- decrease the solids concentration in certain substrates (for example by using organic rich wastewaters)

Having on-site some temporary storage facilities for substrates with different characteristics and also homogenisation tanks so that appropriate blends can be performed prior to digestion is advised.

Reduce or increase retention time and organic loading rates as appropriate. For example at digester start-up or during significant substrate change, the microbial community must be acclimatised in order to become active towards the substrate with the generation of enzymes and growth of microbes, so slow changes and step wise increases in loading rates are advised. Low organic loads are not always advised as microorganisms will be lacking the food and therefore also not growing. Overfeeding is also not advised as microorganisms may not grow at the rate required to degrade the substrates and it is important to remember that feeding more does not always mean more methane production.

Reduce or stop using certain substrates that can bring toxic and inhibitory substances and other contaminants e.g. solvents, detergents, heavy metals, biocides, sulphates, and light metals in excess such as Na, Ca and K.

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10.2 Digestion Process Design and Operation

There are a number of environmental requirements that allow the optimisation of the digestion process. Table 3 summarises the levels for temperature, pH, alkalinity, redox and nutrients and trace elements. These values should be used for guidance only.

Table 3 - Environmental requirements by different microbes in AD process

Parameter	Hydrolysis and Acidogenesis	Methanogenesis
Temperature	25 - 35^{o}C	Mesophilic 35-42^{o}C; Thermophilic 55-58^{o}C
pH	5.2 – 6.3	6.7 – 7.5
C:N:P:S ratio	500:15:5:3	600:15:5:3
Redox potential	+400 to – 300 mV	< – 250 mV
Alkalinity mg/l as $CaCO_3$		1500 – 3000 and above
Nutrients and Trace Elements	N, P, S, Fe, Co, Ni, Mo, Se, Cr, Pb, Mg, Mn, Ca, Na, K, W and vitamin B	

10.2.1 Digester Configuration Improvement

As indicated by Table 3, microbes operate optimally at different environmental conditions, and sometimes uncoupling the methanogenic stage from the hydrolysis and acid phase can prove beneficial so that environmental conditions are optimised for those stages. A two stage system could be an acidogenesis based system performed in the first vessel and the methanogenesis stage in the second vessel, with the first being typically smaller than the second.

Also CSTRs, due to their design nature are normally associated with a % loss in degradation potential. This is both because microbes are suspended and continually being lost, and because some of the substrates may leave the digester undigested due to the continuous mixing process undertaken. Therefore, a remedial configuration is having more than one CSTR operating in series where typically the first digester is larger or equal to the second digester. This configuration allows a high loading rate and will still allow good degradation rates and ensure

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low VFA concentration in the digestate recovered from the second digester, resulting in more recovery of biogas and reducing methane emissions as well.

10.2.2 Digestion Temperature Control

It is important to maintain tight control of the digestion temperature at all times.

Increasing temperature (within the optimum ranges) can allow a significant improvement of biogas production rate for some substrates especially those difficult to hydrolyse. Thermophilic operation increases generally the rate of degradation and increases pathogen kill. It is possible to change operation from mesophilic to thermophilic temperatures in case a faster rate of digestion is desired, but this is not something to do routinely. This is a significant change where microbial communities need to be grown or in many cases new inoculum would be better to import; thermophilic operation requires however, higher thermal energy input, the microbial population is less diverse and the optimum range is within a narrower band so even small temperature changes will have an impact. Also a change from thermophilic temperatures to mesophilic ones is possible if substrates changed for example to one more rich in nitrogen as ammonia toxicity is more severe at higher temperatures where ammonium/ammonia dissociation is greater. Again, a digester temperature change is not something to be done routinely and re-inoculation with a mesophilic culture may be the faster method to get the digester operational. In either case, it is important to ensure that the digester heating system is capable of delivering either the increased or decreased heat load.

10.2.3 Digester Mixing Control

It is important to ensure adequate mass transfer and sufficient contact time between substrate and bacteria. Adequate mixing also reduces digester contents' stratification where only a few parts of the digester would then be active. This will help avoid settlement of more dense materials including inert material at the bottom of the digester and the formation of floating/crust layer at the top of the digester.

It is also important however not to cause over sheer of the bacteria flocs as these can contain whole consortia based functionality. There has also been some evidence that in some cases a reduction of mixing helps, a) during high organic loads in order to reduce the inhibition of syntrophic oxidation of VFAs and reduce the level of propionic acid, and b) during feeding times in order to reduce the loss of microbes and increase microbial retention as well as decrease the impact of high ammonium content substrate.

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10.2.4 Microbial Consortia Retention or Replacement

The loss of methanogens (as they are slow growers) in digesters without a mechanism for microorganism retention is a common problem. Increasing hydraulic retention times can help reduce the loss of these microbes. With CSTR systems recirculation of the settled or separated sludge can help bring back bacterial communities to the digester. Also as indicated above reduced mixing just before feeding of substrates/emptying to allow some settlement of the bacterial culture can also reduce its loss (in the case where digester discharge is not performed from the bottom of the digester).

With low suspended solids substrates, it may be possible to utilise high-rate reactors such as anaerobic filters, UASB reactors, fluidised beds among others instead of the conventional CSTRs. This will improve process efficiency and stability and will allow a higher loading rate per volume of digester.

In cases when, either through organic or hydraulic overloads or toxic or temperature shocks, the diversity, density or activity of microbial consortia becomes limited, additional inoculum may be required in the digester. In very severe situations a complete emptying of the digester contents and a re-loading of a healthy consortium inoculum and a process re-start may be required. In many cases this will bring the digester back to normal operation quicker than trying to re-establish operation through chemical additions and slow organic loadings.

10.2.5 Adjustment of Alkalinity and Trace Elements Availability

Alkalinity as referred above is a ‘safety net’ in AD systems, which will allow some VFAs to be produced without a drastic reduction of pH in the digester contents, which otherwise would inhibit methanogens. Certain substrates may provide enough buffering, but others will not. Levels of alkalinity should be monitored and in some cases addition of alkalinity to a digester is common, either temporarily or on a more long term basis. The following chemicals can be added NH_3, NaOH, CaO, $Ca(OH)_2$, Na_2CO_3, $KHCO_3$, $CaCO_3$ and $NaHCO_3$. In cases when certain cations (e.g. Na and Ca) would result in the limits being exceeded then the removal of CO_2 by bubbling N_2 is also a possibility, but this method is not typically performed.

A number of trace elements may become available when substrates are degraded in the digester, but it is typical to find deficiencies in the substrates. Trace element additions may then need to take place in order to make sure essential elements are available for microbes to grow and perform their functions. It is important as well that those elements will be available to the

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microbes, rather than being in insoluble precipitates or in complexes difficult to access by bacteria. Optimal levels of soluble metals are difficult to fully establish and it will depend on the substrates, OLRs and HRTs and the microbial consortia in place and required. Some research efforts have been dedicated to this aspect but further evaluations are still necessary. It is not only methanogens which require these elements but also hydrolytic/acidogenesis/acetogenesis bacteria; so for example different concentrations will therefore be required when difficult to hydrolyse substrates, or when other inhibitions, are in place as compared to when easily biodegradable substrates are used and when no inhibitions occur. In many cases a slight overdose may apply as long as toxic levels are not reached and also digestate characteristics for specific markets are not compromised.

10.2.6 Removal of Toxic or Inhibitory Components

In the cases when toxicity and inhibition are severe, the digestion process may continuously deteriorate until a complete failure. However, when the toxicity or inhibition is not severe, the digestion process can operate in a so-called inhibited steady-state. This may mean a reasonably stable operation, but with lower methane yields and unless the toxic or inhibitory compounds are removed the methane production would not be optimal. In previous chapters inhibitory compounds such as ammonia, LCFAs and sulphate and sulphide compounds have already been discussed.

Ammonia level can be decreased by stripping free-ammonia or by decreasing pH (so that less free ammonia is available or by co-digestion with other feedstocks with less nitrogen-rich compounds. Bentonite or some zeolite addition has also been reported to decrease inhibition from high ammonia levels. However, the potential for light metal ions toxicity i.e. Ca, Na and Mg must also be considered. Bentonite and activated carbon have also been reported to be able to adsorb LCFAs decreasing the problem of inhibition.

Sulphate and sulphide levels can be decreased by ferric chloride ($FeCl_3$) or ferrous chloride ($FeCl_2$) to precipitate sulphate/sulphide in the form of ferrous sulphide. By using ferric chloride alkalinity and pH is likely to decrease. Also by using these precipitating agents other ions may also precipitate, which may be positive if those are in excess or even creating inhibition. However, it may also be a negative effect as essential compounds such as trace elements can then become unavailable to microbes.

Oxygen ingress needs to be reduced both due to inhibition and due to safety reasons. Existence of oxygen in the digester liquid matrix will inhibit methanogenic activity. In the cases where oxygen is introduced at the top of the digester for H_2S removal, it is vital that oxygen does not flow through the microbial matrix (greater risk exists when digester content mixing is performed using the biogas) and does not carry over in concentrations in excess of the ones that biomethane applications prescribe.

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10.3 Biogas Upgrading Plant Design and Operation

The task of final biogas upgrading can be simplified to a significant extent if certain measures are taken into account in the upstream process. Extensive nitrogen content in the gas is a severe problem during biogas upgrading as it cannot be easily removed from the methane using standard upgrading technologies. Therefore, all measures have to be taken to avoid nitrogen to enter the biogas system. Typically, biogas desulphurisation is performed internally or in an external column by the addition of air and this step has to be eliminated if biogas upgrading is aspired. Furthermore, any other leaks or sources of air or nitrogen within the biogas production plant have to be traced and eliminated.

Prior to the design of the biogas upgrading plant it is very important to know about the raw biogas composition in great detail. Not only the main constituents but also the minor and trace components are very important. Additional cleaning steps have to be applied in case of the presence of siloxanes, ammonia, volatile organic components (VOCs like fatty acids, terpens, higher alcohols or hydrocarbons) and this information is required already in an initial phase of the plant design.

Furthermore, the plant capacity is a very crucial point. As biogas plants often operate in a certain range regarding volume flow (and even gas quality), the amount of possible fluctuations (daily, monthly and annual) has to be assessed and accounted for during the design of the biomethane production site. An upgrading technology has to be chosen that provides sufficient flexibility towards the turn-down ratio of the upgrading plant's capacity. Additionally, other relevant parameters of the plant site have to be considered like delivery pressure requirements, maintenance possibilities, personnel and the integration of the upgrading plant into the AD plant.

Finally, every biogas upgrading technology possesses an optimal operational range or a most economic operation characterised by a set of parameters (regarding the type of technologies these parameters include pressures, temperatures or stage-cuts). The absolute values of these parameters at the optimum often depend on the local conditions of the plant assemblage. Therefore, the plant operation can often be optimised after commissioning by the deviation of crucial parameters together with a precise monitoring and analysis. Factory settings usually provide a good start for the initial plant operation but the performance and efficiency of any plant (not only biogas upgrading plants) can be significantly improved with growing knowledge of the plant's behaviour and operational experience. Consistent monitoring and documentation and a well-structured approach are the keys to success regarding operational optimisation.

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10.4 Costs and Benefits in Monitoring AD and Biomethane Plants

Real-time monitoring of a variety of biochemical parameters related to digester operation would be helpful in addition to biogas flowrate and composition. However these are not always performed and reasons include the non availability of such analytical tools or due to costs for real-time analyzers as described above.

Cost data related to monitoring sensors and analyzers as well as laboratory analysis and plant monitoring contracts are difficult to compile. This is due to the different situations and different regional framework conditions. A selection of cost information has however been gathered from a number of European countries and has been summarized here.

10.4.1 Typical Costs of Analytical Equipment, Laboratory Analysis and Plant Monitoring Contracts

The real time analyzers that are most commonly used measure biogas and biomethane flowrates and composition. Capital costs for multicomponent gas analysers that measure gas concentrations of CH_4, CO_2, O_2 and H_2S vary from € 20k-80k depending on the analyser's measuring principle and accuracy and if they provide measurements off-line or on continuous basis and perform automated calibration and gas drying. Biogas and biomethane volume flow measurements, compensated for pressure and temperature can be performed with analysers with costs that vary around € 5k-12k depending on the gas flowrate. The measurement of pH can typically be performed either real-time or ex-situ and costs of pH probes will be around the € 300 but the signal transmitter box will require an additional € 700-900.

Ex-situ analyses can typically be performed related to biochemical parameters relevant for the monitoring of feedstocks, digester contents and digestates characteristics. These analyses can be performed using analytical equipment or analytical methodologies on-site or by sending samples to external laboratories. For example, the costs of purchasing a VFA analyzer that provides concentrations of a number of VFAs including acetic, butyric and propionic acids may cost in the region of € 35k, while a titrator for measuring alkalinity and total VFAs may be in the order of € 1700-3800. Additional running costs are associated with the performance of these analyses that will include consumbles, maintenance and operator's time.

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Table 4 summarises the costs compiled from a variety of laboratories across Europe. Costs seem to vary depending on the methodologies used, as well depending on the country's level of income. It is worth stating that in a number of countries, the availability of provision of these analysis is not widespread. For a selection of parameters such as microbial populations and even VFA analysis and biogas or biomethane potential, the analysis is largely performed by Universities or research institutes, and provision from commercial laboratories is still limited. Annual plant performance monitoring contracts vary in specification and costs but typically cover basic information to help avoid digester failure and to meet regulatory compliance that can be in the order of € 5 k - 40 k, for the higher level of costings the goal is not only to avoid digester failure but also to support the continual optimisation of the plant based on technical advice and laboratory analysis. These values however, should be treated as a guide only, as each plant is different, with more or less of a variable operation and the type and frequency of analysis and suggested modifications can be also different significantly.

The report produced entitled 'European Case Studies of Anaerobic Digestion Plants Showcasing their Monitoring Practices' (with the deliverable ref. Task 5.1) includes some reference to monitoring and related costs for a number of AD and biomethane plants in Europe.

Table 4 – Costs of analysis of relevant parameters by external laboratories (costs are per sample unless specified)

Parameters	Laboratory Costs
Biogas/biomethane potential for feedstocks and digestates (batch test typically around 30 days; methodology can vary and results may include solid content as well as biogas composition; pH and VFAs can be monitored at the end of the test and a control run can be performed in parallel)	€ 520 – 800
Biogas composition (CH_4, CO_2, H_2S, O_2)	€ 20 -30 /compound
pH	€ 5 - 10
TS	€ 6 - 40
oTS (VS)	€ 9 - 40
COD	€ 30 - 60
Nutrients (N, P, K)	€ 35 - 85
Elemental Analysis (Carbon, Hydrogen, Nitrogen, Sulphur and Oxygen)	€ 210
TKN	€ 14 - 45
NH_4 contents	€ 15 - 40

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VFAs	€ 50 – 100 (Total) Speciated into 6 VFAs €120 Per compound €30
Heavy metals (As, Cd, Cr, Cu, Ni, Pb and Zn)	€ 65 - 129
Cations and anions (sodium, potassium, ammonium, phosphorous, chloride, nitrate, nitrite)	€ 80 - 125
Trace elements (cobalt, nickel, selenium, molybdenum, iron, tungsten)	€ 50 - 135
Hygienic parameters (salmonella, E coli, Enterococci)	€ 150 - 210
Microbial population profiling via qPCR (Eubac and methanogens) 16 S pyro sequencing (depending on the sequencing length and size of data) Metagenomic analysis (1 GB data)	€ 470 € 720 - 1650 € 1200
Specific Methanogenic Activity (depending on the methodology and the number of substrates tested)	€ 75 – 280

Note: Analyses are typically performed in triplicate and costs exclude national government taxes.

A 10-20% discount can be typically offered for long term monitoring contracts or for multiple samples. Some laboratories also have minimum charges.

10.4.2 Example of Economic Benefits When Plant Performance Increases as a Result of Monitoring

Two simplified examples have been included here to demonstrate the cost benefits when biogas production increases as a result of monitoring.

Agricultural Feedstocks based AD plant (Operating in Austria)

Power Rating (initial)	500 kW
Feedstocks (annual throughput)	pig slurry (1,600 tons), clover (175 tons) and energy crops (corn-whole crop silage 8,500 tons
Feed-in tariff	€ 170.2 / MWh
Electric energy fed into (initial)	4,077 MWh

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Biogas yield crop silage per tonne oTS	600 m³/ t oDM
Heat revenue	€22.5 / MWh
Sellable heat quantity (initial)	1,937 MWh
Price crop silage	62.5 €/ t TS
Investment costs	€ 2,041,000

Without taking into account taxation of annual profit or any major costs in terms of capital expenditure in order to allow the improvements to take place, a better managed plant could potentially result in an increase in biogas production of 10%, which would result in an increase in annual income of €72,000 or an increase of €150,000 if the increase was 20% in the biogas produced.

AD plant Treating Food Waste (Operating in the UK)

Power Rating (initial)	1 MW
Feedstocks (annual throughput)	30,000 tonnes of source segregated food waste
Feed-in Tariff	9.24 p/kWh
Export tariff electricity and heat	4.64p/kWh and 2p/kWh

As an example, a 20% increase in biogas production for this AD plant would equate to an increase in revenue of approximately £200,000 per annum from heat and electricity export and electricity feed-in tariff. Increased revenue would result when the heat would also be eligible for the renewable heat incentive. It is also possible that as a waste treatment plant an increase in biogas production would result in an increase in waste treatment and an increase in waste throughout could also result in associated increase in gate fee income generation.

Increases of methane production of more than 10% are being demonstrated as part of this project at a selection of AD plants and reports will soon be issued as part of the deliverable of Task 5.3.

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10.4.3 A Special Note on Monitoring in AD Upgrading Plants

First of all, monitoring and storing relevant biomethane quality and quantity parameters is obligatory depending on the final utilisation of the biomethane. Most restrictive obligations have to be met for natural gas grid injection. Furthermore, acquisition and storage of relevant plant performance parameters prove to be highly valuable for an efficient plant operation. First, these parameters may indicate any performance deterioration of the plant when analysed over the plant service lifetime strongly supporting predictive maintenance and service. Secondly, during plant commissioning but also at later points of time during the plant lifetime, this data may provide the possibility of performance observation (checking for compliance to design specifications), efficiency enhancement or debottlenecking.

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11. Conclusions

The measurable parameters for AD plants and biogas upgrading technologies are numerous. There are however still a number of parameters that are not being measured in-situ and in real-time. This in some cases relates to analytical difficulties, in other cases due to the significant maintenance and cost requirements. In this monitoring guide, multiple parameters have been chosen and defined that would allow an effective approach to monitoring. These key monitoring parameters have been chosen by experts based on R&D and practical experience in working with AD and biogas upgrading plants throughout Europe. Different monitoring parameters can apply depending on the objective of the AD and biogas upgrading plants, whether control is to be performed, the type and characteristics of substrates used, the type of conversion technologies and the markets of the digestate and biomethane produced.

The types and characteristics of the substrates, their preparation and storage and the digester design will have a significant impact on the performance of the AD plant. In addition, each multi-bacterial consortium can be unique (in diversity and quantity) and chemical reactions are also complex. Therefore, and although there are similarities in performance, digesters are not equal and do not respond always in the same way. While there are general guidelines for operating digesters, exact optimum levels for various biochemical components cannot be fully defined. In general, frequent characterisation of the substrates (organic and moisture contents, biodegradability, nutrient and trace elements and possibly inhibitory compounds) that lead to an appropriate digestion design and operation, together with feedback response from the digester performance i.e. in terms of methane flowrates, as well as residual individual VFAs and alkalinity, would be ideal monitoring parameters. These parameters in conjunction are able in most cases to dictate appropriate and fairly rapid control actions necessary to optimise the digester performance. Sometimes, however, in order to fully understand the reasons for poorer performance more thorough parameterisation must be performed including the evaluations of the activity, diversity and quantity of the various microbial populations. In addition to performing monitoring and control activities for the benefit of improving the digester operation and efficiency, there may be other reasons to monitor digestate quality i.e. to meet for example effluent discharge conditions or end of waste criteria requirements.

Similarly, it has been shown that monitoring biomethane quality and quantity as well as several biomethane production plant parameters provide significant input to efficient, safe and reliable biogas upgrading plant operation. The monitoring and storing of data from a number of biomethane quality parameters is an obligation for either natural gas grid injection or for vehicle fuel supply but the exact criteria differ in each country. Nevertheless, a complete and traceable documentation of the produced biomethane is mandatory and should also be seen as an asset during plant operation. Depending on the biogas upgrading technology applied, the monitoring

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and storing of some plant operation parameters allow for the identification of plant performance deterioration or possibilities for efficiency enhancement. Additionally, predictive maintenance and servicing of the plant and its components are supported by a comprehensive monitoring regime, leading to maximised plant availability.

Considering renewable energy related incentives in many countries in Europe and based on the data presented in this report related to the cost of analysers, external laboratory analysis and annual monitoring contracts for AD and biomethane plants, when the implementation of monitoring programmes would allow improvements in biogas production for both agricultural feedstocks as well as municipal and industrial wastes based AD plants of even just over 10%, the additional biogas production related income is very likely to outweigh the investment in monitoring programmes even on medium size AD plants.

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Appendix 1 - Parameters Relevant for Biogas Upgrading Systems

Gas Inlet, Product and Off Gas Parameters

Raw Gas Inlet Parameters	Unit
Raw gas volume flow rate	m^3_{STP}/h
Raw gas temperature	°C
Raw gas pressure	bar(g)
Raw gas CH_4-content	%v/v dry
Raw gas CO_2-content	%v/v dry
Raw gas O_2-content	%v/v dry
Raw gas N_2-content	%v/v dry
Raw gas H_2-content	%v/v dry
Raw gas H_2S-content	mg/m^3_{STP}, ppmv
Raw gas NH_3-content	mg/m^3_{STP}, ppmv
Raw gas siloxane-content	mg/m^3_{STP}, ppmv
Raw gas volatile organics-content	mg/m^3_{STP}, ppmv
Raw gas mercaptane S-content	mg/m^3_{STP}, ppmv
Raw gas COS-content	mg/m^3_{STP}, ppmv
Raw gas total S-content	mg/m^3_{STP}, ppmv
Raw gas halogen-content	mg/m^3_{STP}, ppmv
Raw gas H_2O-content	%v/v, ppmv, dew point
Raw gas particle content	mg/m^3_{STP}
Raw gas droplet content	mg/m^3_{STP}
Raw gas upper heating value	kWh/m^3_{STP}, MJ/m^3_{STP}
Product Gas Outlet Parameters	
Product gas volume flow rate	m^3_{STP}/h
Product gas temperature	°C
Product gas pressure	bar(g)
Product gas CH_4-content	%v/v dry
Product gas CO_2-content	%v/v dry
Product gas O_2-content	%v/v dry
Product gas N_2-content	%v/v dry
Product gas H_2-content	%v/v dry
Product gas H_2S-content	mg/m^3_{STP}, ppmv
Product gas NH_3-content	mg/m^3_{STP}, ppmv
Product gas siloxane-content	mg/m^3_{STP}, ppmv
Product gas volatile organics-content	mg/m^3_{STP}, ppmv
Product gas mercaptane S-content	mg/m^3_{STP}, ppmv
Product gas COS-content	mg/m^3_{STP}, ppmv
Product gas Total S-content	mg/m^3_{STP}, ppmv
Product gas Halogen-content	mg/m^3_{STP}, ppmv
Product gas H_2O-content	%v/v, ppmv, dew point
Product gas particle content	mg/m^3_{STP}
Product gas droplet content	mg/m^3_{STP}
Product gas upper heating value	kWh/m^3_{STP}, MJ/m^3_{STP}
Product gas Wobbe Index	kWh/m^3_{STP}, MJ/m^3_{STP}

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Offgas Gas Outlet Parameters	
Offgas gas volume flow rate	m^3_{STP}/h
Offgas gas temperature	°C
Offgas gas pressure	bar(g)
Offgas gas CH_4-content	%v/v dry
Offgas gas CO_2-content	%v/v dry
Offgas gas O_2-content	%v/v dry
Offgas gas N_2-content	%v/v dry
Offgas gas H_2S-content	%v/v dry, ppmv
Offgas gas H_2O-content	%v/v, ppmv, dew point
Offgas gas upper heating value	kWh/m^3_{STP}, MJ/m^3_{STP}

Plant Specific Parameters (All Plants)

Parameter	Unit
Total electricity consumption	kW
Hot utility temperature	°C
Hot utility pressure	bar(g)
Hot utility volume flow	m^3_{STP}/h
Cold utility temperature	°C
Cold utility pressure	bar(g)
Cold utility volume flow	m^3_{STP}/h

Plant Specific Parameters (Pressurised Water Scrubbing)

Parameter	Unit
Water pump electricity consumption	kW
Scrubbing water circulation flow rate	m^3/h
Scrubbing water temperature	°C
Operating pressure	bar(g)
Operating gas temperature	°C
Stripping air flow rate	m^3_{STP}/h
Stripping air temperature	°C
Stripping air pressure	bar(g)

Plant Specific Parameters (Pressure Swing Adsorption)

Parameter	Unit
Operating pressure for adsorber *n*	bar(g)
Operating gas temperature for adsorber *n*	°C
Switching time intervals	s
Stripping air flow rate	m^3_{STP}/h
Stripping air temperature	°C
Stripping air pressure	bar(g)

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Plant Specific Parameters (Amine Scrubbing)

Parameter	Unit
Amine solution pump electricity consumption	kW
Amine solution circulation flow rate	m^3/h
Amine solution temperature	°C
Operating pressure	bar(g)
Operating gas temperature	°C
Electricity consumption gas drying	kW
Stripping air flow rate	m^3_{STP}/h
Stripping air temperature	°C
Stripping air pressure	bar(g)

Plant Specific Parameters (Gas Permeation Plants)

Parameter	Unit
Gas compressor electricity consumption	kW
Operating temperature for membrane stage *n*	°C
Operating pressure for membrane stage *n*	bar(g)
CH_4-content feed for membrane stage *n*	%v/v dry
CH_4-content retentate for membrane stage *n*	%v/v dry
CH_4-content permeate for membrane stage *n*	%v/v dry
Internal gas recirculation volume flow rate	m^3_{STP}/h

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