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Basics of Anaerobic Digestion - Biochemical Conversion and Process Modelling

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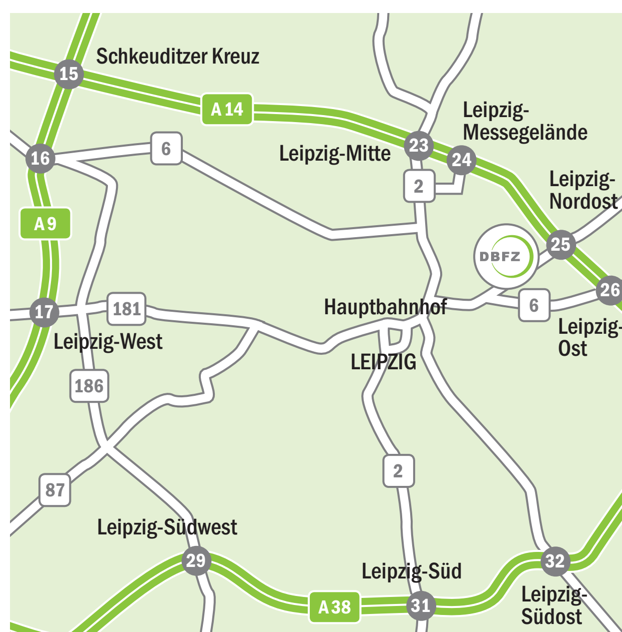

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Biochemical Conversion and Process Modelling

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Table of content

List of abbreviations V

List of symbols VI

List of indices VIII

1 Introduction 10

2 Biochemical conversion 19

2.1 Characteristic process phases 19

2.1.1 Hydrolysis 19

2.1.2 Acidogenesis 21

2.1.3 Acetogenesis 25

2.1.4 Methanogenese 26

2.2 Microbial influencing variables 27

2.2.1 Nutrient supply 29

2.2.2 Temperature 33

2.2.3 pH value and organic acids 36

2.2.4 Inhibitors 40

3 Process modelling 48

3.1 Fundamentals of process modelling 48

3.1.1 Reaction equations 49

3.1.2 Reaction kinetics and growth inhibition 51

3.1.3 Physicochemical reactions 56

3.2 Model structures 58

3.2.1 Literature survey 59

3.2.2 Model simplification 65

3.3 Substrate characterisation 66

3.3.1 Chemical substrate analyses 68

3.4 Parameter estimation 74

3.4.1 Parameter selection 75

3.4.2 Objective function 77

3.4.3 Optimisation procedure 78

List of figures 82

List of tables 84

References 85

List of abbreviations

Abbreviations	Explanation
AAS	Atomic absorption spectrometry
Acyl	Acyl group
ADM1	Anaerobic Digestion Model No. 1
ADP	Adenosine diphosphate
AMP	Adenosine monophosphate
ASM	Activate Sludge Model
ATP	Adenosine triphosphate
CHP	Combined heat and power (cogeneration) unit
CoA	Coenzyme A
CSTR	Continuously stirred tank reactor
DBFZ	*Deutsches Biomasseforschungszentrum*
DLG	*Deutsche Landwirtschaftsgesellschaft*
DLV	*Deutscher Landwirtschaftsverlag*
EEG	*Gesetz für den Ausbau erneuerbarer Energie*
FAD	Flavin adenine dinucleotide
FID	Flame ionisation detector
GC	Gas chromatography
HPLC	High performance liquid chromatography
IC	Ion chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
IR	Infrared
IWA	International water association
KTBL	*Kuratorium für Technik und Bauwesen in der Landwirtschaft*
MPB	Methane-producing bacteria
NAD	Nicotinamide adenine dinucleotide
NADP	Nicotinamide adenine dinucleotide phosphate
NIRS	Near-infrared spectroscopy
OED	Optimal experimental design

PME	Plant methyl ester (biodiesel)
SRB	Sulphate-reducing bacteria
UASB	Upflow anaerobic sludge blanket
UV	Ultraviolet

List of symbols

Symbol	Explanation	Unit
B	Growth parameter	[-]
COD	Chemical oxygen demand	[g O_2 g^{-1}]
DQ	Degradability quotient | Digestibility quotient	[% VS]
DVS	Degradable volatile solids	[g kg^{-1} TS]
DXC	Degradable crude carbohydrates	[g kg^{-1} TS]
DXL	Degradable crude lipids	[g kg^{-1} TS]
DXP	Degradable crude proteins	[g kg^{-1} TS]
e(t)	Error | Model deviation	
eNSE	Extended NASH-SUTCLIFFE -efficiency	[-]
eXC	Carbohydrates of endogenous origin	[g kg^{-1} TS]
eXL	Lipids of endogenous origin	[g kg^{-1} TS]
eXP	Proteins of endogenous origin	[g kg^{-1} TS]
FM	Fresh matter	[kg]
I	Inhibition function	[-]
iXC	Indigestible crude carbohydrates	[g kg^{-1} TS]
iXL	Indigestible crude lipids	[g kg^{-1} TS]
iXP	Indigestible crude proteins	[g kg^{-1} TS]
J_{opt}	Objective function (value)	
k	First-order kinetic constant	[d^{-1}]
K_a	Dissociation constant	[mol L^{-1}]
K_H	Henry constant	[mol L^{-1} bar^{-1}]
K_I	Inhibition constant	[g L^{-1}] | [g COD L^{-1}]
k_La	Volumetric mass transfer coefficient	[d^{-1}]
k_m	Maximum uptake rate	[g COD g^{-1} COD d^{-1}]

K_S	Half-saturation constant	[g L^{-1}] | [g COD L^{-1}]
K_W	Ion product of water	[mol L^{-1}]
MAE	Mean absolute error	
MLSE	Mean logarithmic squared error	
MSE	Mean squared error	
n	Sample size | Quantity	[-]
n(t)	Disturbance	
NfE	Nitrogen-free extracts	[g kg^{-1} TS]
NSE	NASH-SUTCLIFFE-efficiency	[-]
p	Pressure | Model parameters	[bar]
pH_{LL} | pH_{UL}	Lower and upper pH limits	[-]
pK_a	Negative logarithmic dissociation constant	[-]
R	Universal gas constant	[bar L mol^{-1} K^{-1}]
R^2	Coefficient of determination	[-]
RMSE	Root mean squared error	
s	Standard deviation	
S	Soluble or gaseous components	[g L^{-1}] | [mol L^{-1}]
T	Temperature	[°C] | [K]
t	Discrete time	[d]
TIC	Buffer capacity	[g L^{-1}]
TS	Total solids	[% FM]
u(t)	Input variable	
V	Volume	[L]
VFA	Volatile fatty acids	[g L^{-1}]
VS	Volatile solids	[% TS]
X	Particulate components	[g L^{-1}] | [mol L^{-1}]
XA	Crude ash	[g kg^{-1} TS]
XC	Crude carbohydrates	[g kg^{-1} TS]
XF	Crude fibres	[g kg^{-1} TS]
XL	Crude lipids	[g kg^{-1} TS]
XP	Crude proteins	[g kg^{-1} TS]
y(t)	Process output | Measurements	

$\hat{y}(t)$	Model output | Simulation results	
ΔH	Enthalpy of solution	[J mol^{-1}]
$\Delta G^{o\prime}$	Free enthalpy at standard conditions pH 7 | 298.15 K | 1 atm	[kJ mol^{-1}]
ΔG_f^o	Free enthalpy of formation at standard conditions 298.15 K | 1 atm	[kJ mol^{-1}]
μ	Growth rate	[d^{-1}]
μ_m	Maximum growth rate	[d^{-1}]
υ	Stoichiometric coefficient	[-]
ρ	Process rate | Reaction rate	[g L^{-1} d^{-1}] | [mol L^{-1} d^{-1}]
ρ_T	Transfer rate (phase transition)	[g L^{-1} d^{-1}] | [mol L^{-1} d^{-1}]

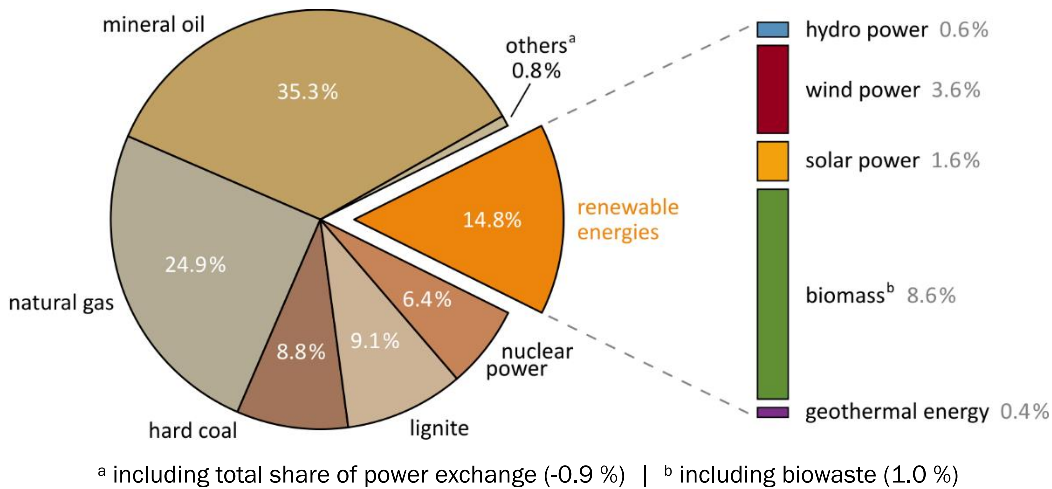
List of indices

Abbreviations	Explanation
0	Initial (concentration)
aa	Amino acids | Acido- and Acetogenesis
ac	Acetic acid
an-	Anions
as	Amino acids and sugars
bac	Bacteria | Microorganisms
bu	Butyric acid
c4	Valeric and butyric acid
cat^+	Cations
ch	Carbohydrates
ch4	Methane
co2	Carbon dioxide
dec	Microbial decay
dis	Disintegration
et	Ethanol
fa | lcfa	Long chain fatty acids
gas	Gas phase
h2	Hydrogen
hyd	Hydrolysis

hco3	Hydrogen carbonate
IC	Inorganic carbon
IN	Inorganic nitrogen
in	Input
la	Lactic acid
li	Lipids
liq	Liquid phase
nh3	Ammonia
out	Output
OS	Organic substances
pr	Proteins
pro	Propionic acid
S	Substrate
sOS	Soluble organic substances
su	Sugars
Tca	Carbonic acid, hydrogen carbonate and carbonate
va	Valeric acid
vfa	Volatile fatty acids
xc	Particulate composites
xOS	Particulate organic substances

1 Introduction

Currently, a large share of the primary energy supply in Germany is provided by fossil fuels [85], Figure 1. These fuels were formed in prehistoric geological times from natural degradation of dead phyto- and zoomass. The rapid exploitation and enduring combustion of these energy sources has led to an increasing imbalance in the global carbon cycle over the last hundred years [437, 482]. Fossil fuels that were compressed over a very long period of time are now being depleted, utilised for energy provision and released into the atmosphere in the form of climate-relevant greenhouse gases.[1]



[a] including total share of power exchange (-0.9 %) | [b] including biowaste (1.0 %)

Figure 1: Primary energy supply (12,832 PJ) in Germany in 2019 [85]

In order to cope with the long-term consequences of finite energy reserves and increasing environmental pollution, low energy consumption and an efficient use of the available energy reserves are required. This includes sensible energy and environmental policies as well as intensive research in the field of modern and efficient energy conversion processes. However, these approaches do not solve the problem of a one-sided primary energy supply based on fossil fuels; instead, they only prolong it. Thus, systematically replacing primary fossil-based energy sources with renewable energies over the long term represents the most important alternative to the conventional energy sector [253, 571].

Renewable or regenerative energies are primary energy forms regarded as sustainable or inexhaustible by human standards. This means that the energy converted from sun, wind, water, geothermal heat, biomass or tides is considered regenerative [253]. Thus, the sustainable exploitation and consistent use of renewable fuels promises to reduce the anthropogenic increase of major greenhouse gases in the long term by supplying climate-neutral energy. Because the area-specific or volume-specific energy density of these energy sources is comparatively low, large-scale systems are required. Furthermore, they depend strongly on specific environmental conditions. Thus, many renewable energies can only be used on a non-continuous basis, since the amount of transformed energy depends on the individual location, weather or season [253, 551, 571].

[1] The combustion of fossil fuels and the effects of land use changes are now regarded as the main cause of the recent increase in carbon dioxide concentrations in the atmosphere [507]. The extent to which the anthropogenic greenhouse effect will have a long-term impact on the climate and the environment has yet to be fully established due to the complex dependencies [344, 482]. As a result, calculation result of numerous climate models predict consequences of varying severity [489].

Energy from biomass

Biomass accounts for the largest share of primary energy supplied from renewable energies, Figure 1. In principle, all matter of organic origin (i.e., carbonaceous matter) is considered as biomass.[2] In terms of the specific utilisation of renewable energy sources, this primarily includes energy crops, harvest residues, organic by-products and waste. A variety of conversion technologies are available today that furnish the chemically bound energy of biomass in the form of solid, liquid or gaseous fuels to provide heat and power, Figure 2.

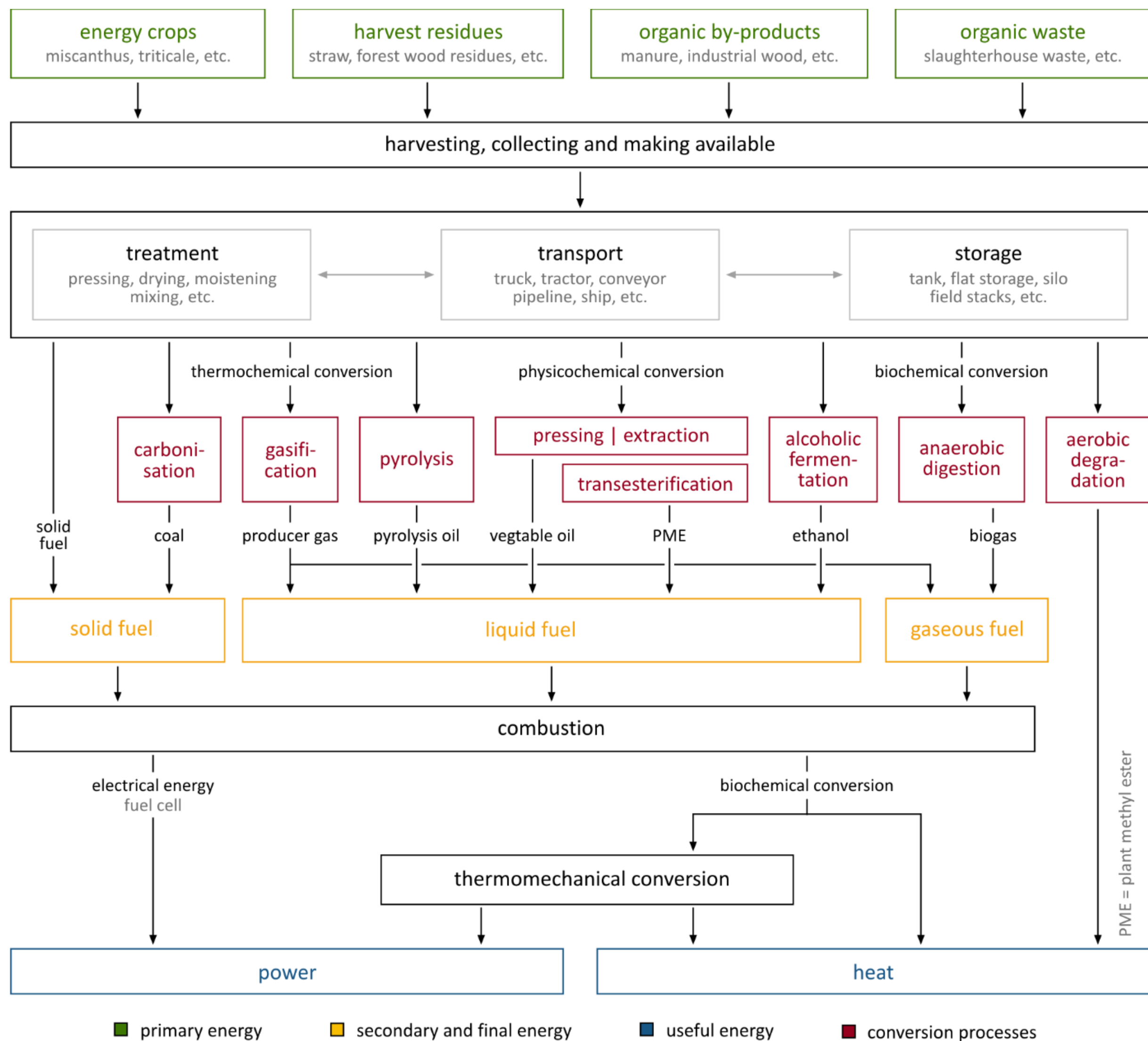
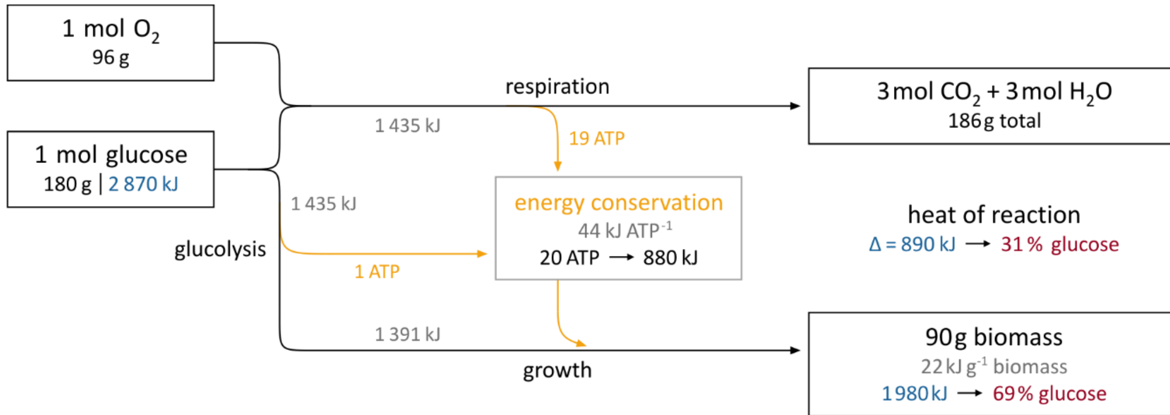


Figure 2: Conversion technologies (pathways) for energetic utilisation of biomass [252]

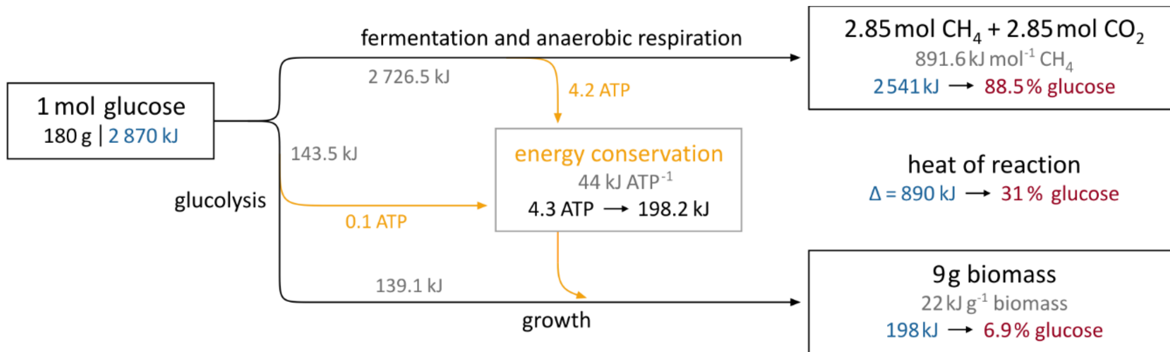
The properties and availability of organic substrates, as well as the resulting technical, ecological and economic requirements or conditions, determine the choice of conversion technology [252]. While solid bioenergy sources containing lignocellulose with a low water content can be converted into sustainable energy carriers by thermochemical carbonisation, gasification or pyrolysis, substrates with a high water

[2] "The differentiation of biomass from fossil fuels begins with peat, the fossil-based secondary product of the degradation process. As a result, peat in the strict sense of this definition no longer counts as biomass." [252, pp. 2]

content can be used efficiently in biochemical conversion processes to provide liquid or gaseous fuels. In addition to the selective use of energy crops like maize or grain silage, complex wastes and by-products from agriculture, industry (food, pharmaceutical or paper industries) and municipality are thus particularly suited for anaerobic or aerobic treatment. Moreover, applied methods of anaerobic fermentation or aerobic respiration differ in their actual reaction conditions, in the microorganisms involved, and in their process-specific degradation products as illustrated in Figure 3.



(a) mass and energy dissipation during respiration of glucose (pH value = 7)



(b) mass and energy dissipation during anaerobic fermentation of glucose (pH value = 7)

Figure 3: Comparison of product formation during (a) aerobic and (b) anaerobic treatment [173]

Biochemical conversion of one mole or 180 g of glucose produces a free enthalpy of ΔG°' = 2780 kJ during complete oxidisation [480]. In the case of high volumetric loads, utilisation of an additional 96 g of oxygen enables 50 % of the glucose to be converted to 186 g of carbon dioxide and water through aerobic respiration, Figure 3a.[3] Based on numerous anabolic reaction pathways of glycolysis (EMBDEN-MEYERHOF-pathway) and utilization of 20 mol ATP, 90 g of microbial biomass is produced. With an energy content of 22 kJ per g of biomass the potential enthalpy of glucose result in 69 % of biomass and 31 % of reaction heat under these reaction conditions [173]. During anaerobic digestion the fermentation of glucose yields only 4.3 mol ATP in total, so that the microorganisms involved gain less energy for growth related processes, Figure 3b. Consequently, a large part (88.5 %) of the free enthalpy of glucose is stored as methane in an energy-rich degradation product.

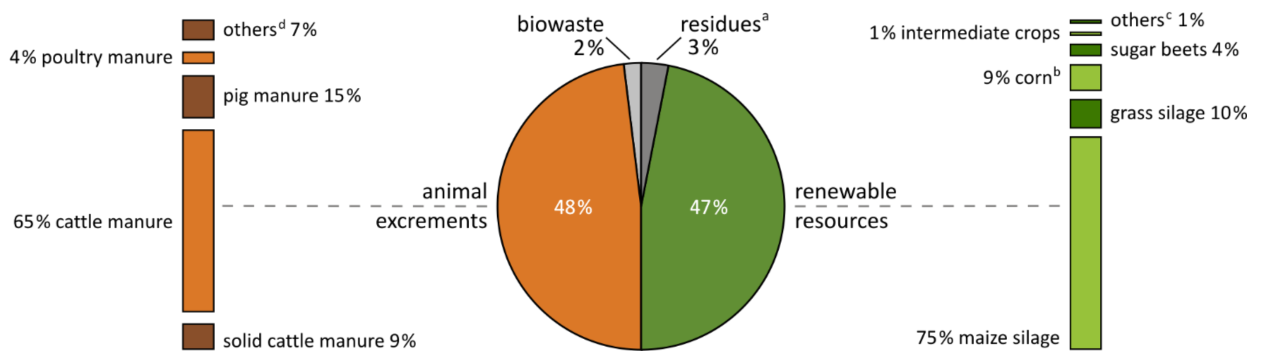
[3] In principle, the product ratio of respiration and bacterial growth shifts depending on the throughput rate of the process. For example, up to 70 % of glucose can be oxidised to carbon dioxide and water at a low organic loading using 4.3 mol or 137.6 g of oxygen [173].

Thus, aerobic conversion processes are generally applied for biomass treatment in the wastewater and waste management sectors, whereas the anaerobic biogas process is suited for valuable energy supply from organic, fermentable substrates or waste [252].

Biogas technology in Germany

Due to more than 9,000 large-scale anaerobic digestion plants, biogas technology is making a significant contribution to the sustainable energy supply in Germany. With a total of around 5,901 MW_{el} of installed electrical capacity (on-site electricity generation), electricity generated from biogas amounted to around 31.6 TWh in 2019 (including 2.6 TWh from biomethane) and thus accounts for over 58 % of total electricity generation from biomass [82, 149].

In Germany, anaerobic digestion plants usually use renewable raw materials and animal excrements (manure and dung) to operate, Figure 4. Anaerobic digestion of municipal biowaste or industrial, commercial and agricultural residues represents only a very small fraction (about 5 %) of mass-specific substrate use in Germany [149].



[a] industrial, commercial and agricultural residues | [b] cereal whole crop silage (7 %) and cereal grain (2 %)
[c] unspecified renewable resources (incl. 0.4 % millet and 0.2 % corn-cob-mix) | [d] unspecified manure and dung

Figure 4: Mass-specific substrate use in German anaerobic digestion (biogas) plants in 2018 [149]

After proper substrate preparation and storage (ensiling), energy crops such as maize, grass or grains are usually used in combination with cattle or pig manure in agricultural biogas plants, Figure 5. Suitable environmental conditions are then created by controlling temperature and mixing of the fermentation medium to allow for anaerobic digestion of the fermentable substrate components used for biogas production.

Biogas is a gas mixture consisting of 45 % to 75 % by volume of methane and 25 % to 45 % by volume of carbon dioxide [477]. Depending on the substrates used and plant operation, the gas may also contain interfering and harmful components such as water vapour, hydrogen sulphide or ammonia – as well as other trace gases of halogenated hydrocarbons or siloxanes – which limit the direct use of the energy carrier [477, 611]. For feeding biomethane into the local natural gas grid, the raw gas must be processed and conditioned to natural gas quality (biomethane) through corresponding purification and separation processes [3, 25, 487].

Usually the biogas undergoes desulphurisation [131, 240, 569, 611] and drying as it is converted into heat and power directly on site in a combined heat and power plant (CHP). Part of the energy can be used for own electricity and heat requirements, while the remaining part can be fed into the local power grid and used to heat local homes, stables or to supply local heating.[4] Depending on the specific nutrient and emission limits [123, 147], the fermentation residues (digestate) can be recycled into fertiliser.

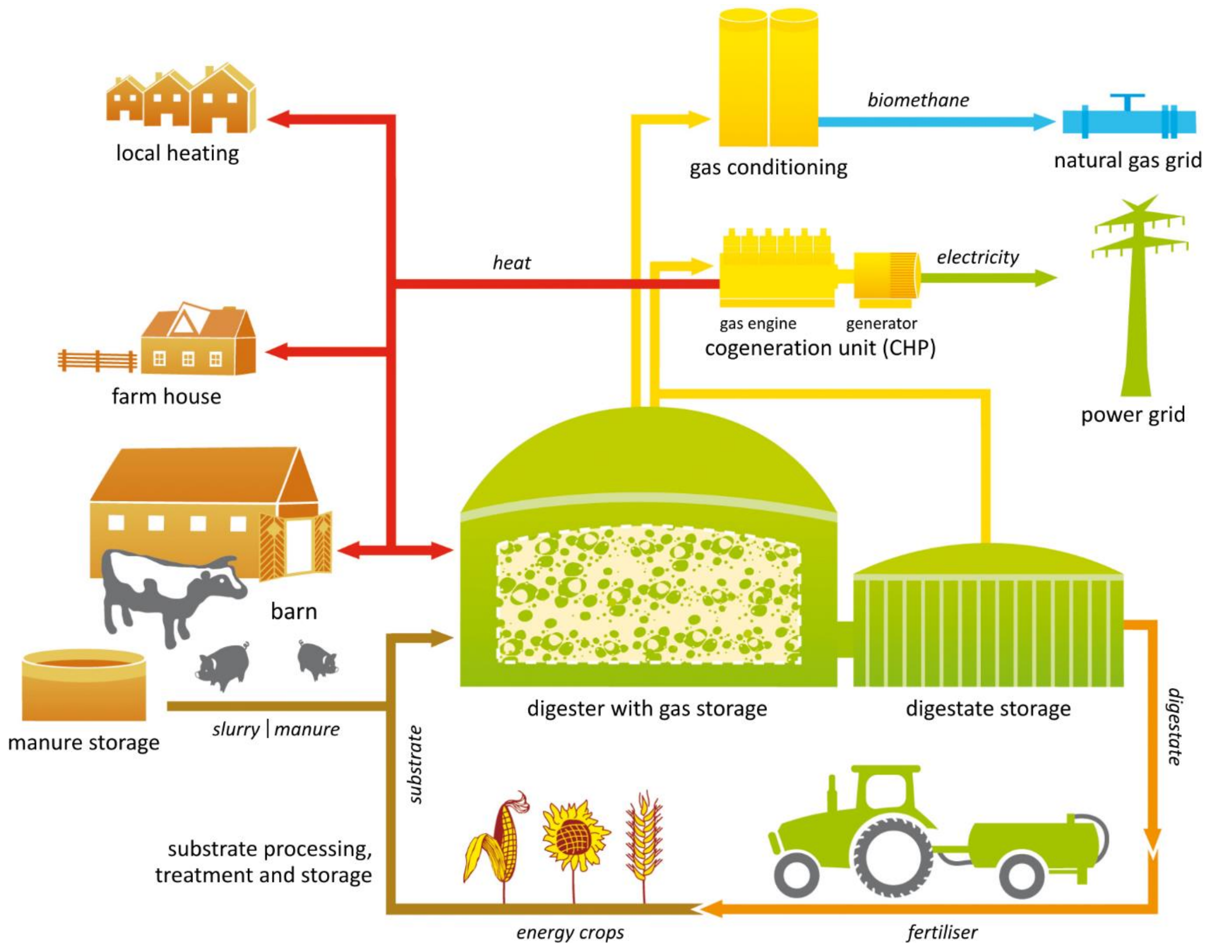


Figure 5: Simplified process scheme of an agricultural biogas plant [148]

The Renewable Energy Sources Act (*Gesetz für den Ausbau erneuerbarer Energie*, EEG) has resulted in a nine fold increase in the number of biogas plants in Germany from around 1,000 in the year 2000 to approximately 9,160 in the year 2020 [149, 463, 464]. However, due to ongoing amendments to the EEG, the original attractiveness of constructing agricultural biogas plants has now declined considerably. For example, the high remuneration for using renewable raw materials and innovative plant technology (including waste heat utilisation) was eliminated in the 2012 version of the EEG [81]. In an updated version from 2014, feedstock-related remuneration has been completely eliminated so that the same basic remuneration is paid regardless of the technology and biomass utilized [588]. Only small liquid manure plants and waste digestion plants continue to benefit from the original remuneration sys-

[4] Due to the various system concepts and measurement methods, the exact percentage of required electricity and heat can vary considerably [144, 464]. For example, the operation of agitators, feed-in technology and combined heat and power units requires between 1.7 % and 23.6 % (operator survey 2015 [464], 7.6 % on average) of the total amount of electricity produced [123]. In addition, 5.5 % and 52.6 % (operator survey 2015 [464], 27.2 % on average) of the waste heat is required to heat the fermenter [123, 464].

tem set forth in the 2012 version of the EEG. There is also increasing support for processing biogas that can be fed into the natural gas grid (biomethane) as well as for participation in direct marketing (market and flexibility premium). The current funding conditions are therefore consciously leading to a considerable decline in plant construction and are specifically directing biogas technology towards decentralised and flexible power generation from biogenic residues and waste materials. The ongoing social and political discourse makes it clear that long-term acceptance for the expansion of biogas technology is only possible when the individual potentials of the different substrates and wastes, and the distinctive advantages of their energetic utilisation in biogas plants are considered.

Usually, the operation of agricultural biogas plants takes into account seasonally fluctuating substrate availability coupled with an almost consistent organic loading rate and retention time for constant biogas production. Current studies show that conventional operation considerably underestimates the potential of biogas technology and its possible contribution to the future energy system. This means that, with the right system configuration and process management, biogas plants can also be used to cover the demand-driven supply of positive or negative control energy [190, 196, 224, 321]. Furthermore, the available potential and technical implementation of efficient fermentation of municipal and industrial wastes [161, 162, 484], as well as the utilisation of alternative energy crops [146] must be examined in more detail.

Dynamic but reliable plant operation with strongly fluctuating substrate qualities or quantities requires analytical methods for characterising substrates and processes, as well as practical methods for efficiency evaluation and process monitoring or control.

Modelling biogas plants

For realistic plant design and optimum process control, the knowledge of the individual degradation behaviour of different substrates at various process conditions is essential. Dynamic modelling of biogas plants - along with sensor data and laboratory analyses - provides a reliable basis for monitoring or prediction of characteristic process parameters and indicators. Thus, simulation results can be used for

- realistic plant design and efficiency evaluation of the digestion process,
- detailed state analysis and process optimisation,
- model-based process control and monitoring in real time,
- planning or even replacement of cost-intensive and complex test series and
- research into bio- and physicochemical dependencies and functions [31, 275].

In practice, model calculations can therefore serve as decision-making tools for plant operators or can be applied as a basis for automated process control and state monitoring for flexible and demand-oriented biogas production. Accordingly, suitable model approaches are required for dynamic process simulation of biogas plants.

A dynamic model is a simplified representation of a complex system and uses mathematical functions to describe time dependencies of characteristic system properties [130, 234]. Based on available measurements and existing information on physical and biochemical processes various modelling techniques are available, Figure 6.

The development of mechanistic *white box* models for simulation of anaerobic digestion processes is obviously not yet feasible, due to complex and partly unknown or unclear dependencies. As a seemingly logical consequence, the biogas process is often regarded as a *black box*. Even if good simulation results can be achieved with the help of artificial neural networks [226, 227, 229, 430, 509, 511], the application of purely experimental modelling methods only makes sense to a limited degree. Thus, empirical findings and physical dependencies cannot easily be integrated into phenomenological models. Moreover, the simulation behaviour depends solely on the informational content of the measured (sensor) data used for modelling (training and/or adaptation) and therefore has a limited transferability to other substrates, operating states or process conditions [601]. Hence, the different shades of *grey box* models offer a good compromise between specific theoretical knowledge and experimental research possibilities. Whereas *dark-grey box* models enable the development of important process variables using vague linguistic statements [379, 423] and adaptive neuro-fuzzy models [364, 516], *light-grey box* models use linear and non-linear differential equations, which are adapted to respective process conditions by suitable parameter estimation procedures.

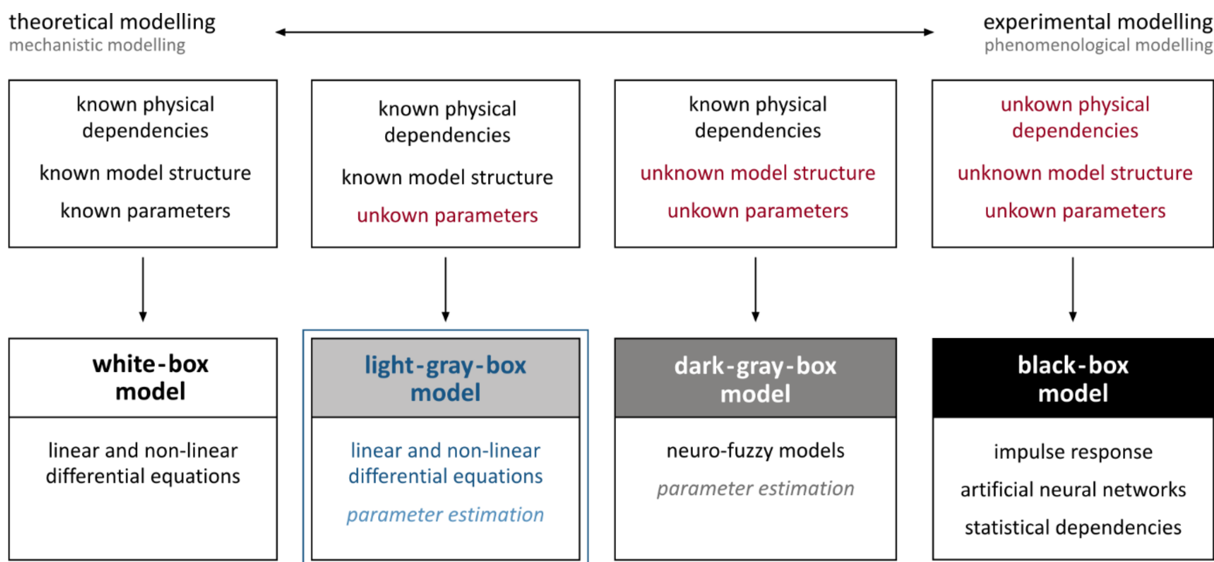


Figure 6: Characteristic modelling techniques to describe dynamic systems [238]

A large number of dynamic models for simulation of different process parameters of anaerobic biogas production have been developed since the late 1960s, Figure 7. The various model approaches differ greatly in the number of modelled state variables and process steps [176, 338]. Simple models are typically bound to a specific process state and can only be transferred to different substrates or operating conditions to a limited degree. Complex models – such as the *Anaerobic Digestion Model No. 1* (ADM1) [33] – are often structurally non-identifiable [125] and cannot yet be utilised as basis for process automation, since usually only a fraction of the measurement data required for model adaptation is available in necessary quantity and quality [553, 580].

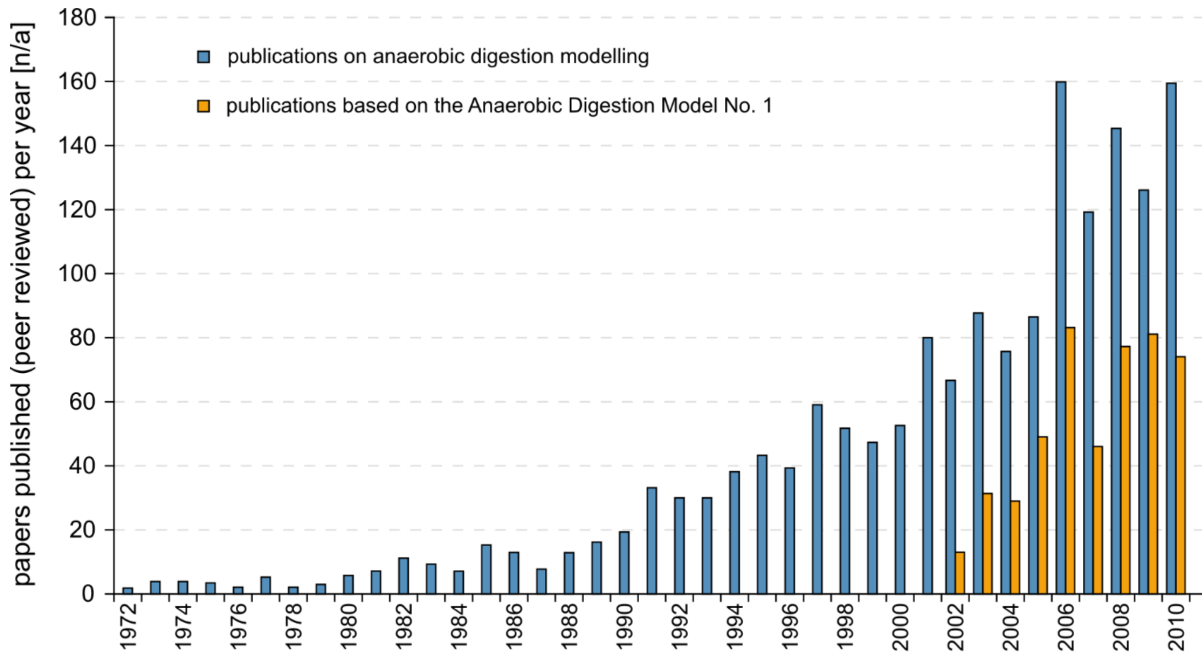


Figure 7: Number of publications on anaerobic process modelling per year [32, 37]

Despite the exiting knowledge and many years of experience in mathematical modelling [32, 39, 176, 338] and process monitoring [247, 389] of anaerobic digestion, model-based state observers or control methods cannot be used as standardised tools in agricultural biogas plants due to complex model structures and individual adaptation procedures required for parameter estimation or substrate characterisation. Current investigations in the field of simulating anaerobic digestion of typical energy crops and manure [168, 279, 331, 334, 474, 478] usually only apply the established ADM1 and do not offer practical approaches for robust application in industrial plant operation. In the context of substrate or efficiency evaluation, single-stage model structures and simplified balances enable kinetic evaluation of discontinuous fermentation tests [74, 127] or a general mass balancing during steady state plant operation [298, 556]. However, these specialised model approaches are rarely applied to simulate dynamic processes. Thus, a comparative evaluation and development of suitable model structures is still needed to enable practice-oriented process simulation in large-scale biogas plants.[5]

Model simplification

Within a doctoral thesis at the University of Rostock, simplified model structures were developed for practical process simulation of agricultural biogas plants [555]. To utilize and refine stoichiometric, kinetic and physicochemical dependencies of the existing model theory, model development focused on the application of ordinary differential equations (ODE) and corresponding *light-gray-box* models, as shown in Figure 6. Thus, the stoichiometric degradation pathways (reactions) and various intermediates (state variables) of the established ADM1 were systematically simplified with respect to practical and robust application in full-scale operation. Individual model structures were evaluated based on laboratory experiments for anaerobic digestion of energy crops, farm manure and industrial residues of agri-

[5] In principle, various models and simplified simulation methods exist in for automated monitoring and control of anaerobic/aerobic wastewater treatment processes [30, 120, 121, 389]. However, due to the typical reference unit of the chemical oxygen demand (COD) and the specialised model structures, such models can only be applied to a limited degree for simulating anaerobic digestion of agricultural substrates and residues (see chapter 3.2.1).

cultural origin (grain stillage). Parameter estimation was performed both on the basis of Monte Carlo analysis in the entire value range of individual model parameters and by numerical optimization procedures. During discussion of results, stoichiometric model properties of implemented model structures (such as the cumulative biomethane potential (BMP) or microbial biomass yields of individual nutrients) were compared with established reference values in available literature. Furthermore, simulation results and estimated model parameters of each laboratory experiment were evaluated in detail. The effect of characteristic parameters on simulation results as well as significant differences of the applied model structures and estimation procedures are presented in conclusion.

This DBFZ report on *Basics of Anaerobic Digestion – Biochemical Conversion and Process Modelling* is a compilation of introductory and methodological chapters of the original manuscript of the German doctoral thesis:

Weinrich, S: Praxisnahe Modellierung von Biogasanlagen: Systematische Vereinfachung des Anaerobic Digestion Model No. 1 (ADM1). University of Rostock, 2017.

https://doi.org/10.18453/rosdok_id00002016

The second chapter on **Biochemical conversion** covers biochemical fundamentals of characteristic process phases and influencing variables during anaerobic digestion of biomass. Suitable methods for process modelling of biogas plants as well as a comprehensive literature review of available reaction models (including model simplifications) are presented in the third chapter on **Process modelling.**

Details on systematic development and evaluation of simplified model structures as well as model validation based on different laboratory experiments for anaerobic digestion of agricultural substrates and industrial residues are provided in the following research papers:

Weinrich, S., Nelles, M. (2021): Systematic simplification of the Anaerobic Digestion Model No. 1 (ADM1) – Model development and stoichiometric analysis. Bioresource Technology. Vol. 333, 125124.

https://doi.org/10.1016/j.biortech.2021.125124

Weinrich, S., Mauky, E., Schmidt, T., Krebs, C., Liebetrau, J., Nelles, M. (2021): Systematic simplification of the Anaerobic Digestion Model No. 1 (ADM1) – Laboratory experiments and model application. Bioresource Technology. Vol. 333, 125104.

https://doi.org/10.1016/j.biortech.2021.125104

2 Biochemical conversion

For development of realistic and precise process models, the understanding of the fundamental biochemical conversion processes during anaerobic digestion is essential. In the following chapters, characteristic process phases as well as relevant influencing factors on microbial growth and substrate degradation (such as nutrient supply, temperature, pH value or typical inhibitors) are presented and discussed in detail.

2.1 Characteristic process phases

During anaerobic digestion, a variety of bacteria and archaea decompose the organic substrate into mainly methane and carbon dioxide [51, 178, 477, 569]. The anaerobic degradation process is generally divided into four characteristic process phases – hydrolysis, acetogenesis, acidogenesis and methanogenesis – which differ with regard to their reaction pathways and metabolites of the microorganisms involved, Figure 8. The individual degradation steps take place simultaneously in a continuous single-stage reactor. This results in narrow limits and high demands on specific environmental and operating conditions for the degradation of complex substrates. Therefore, a detailed understanding of the properties and influencing variables of different degradation pathways is of decisive importance for process optimisation or modelling.

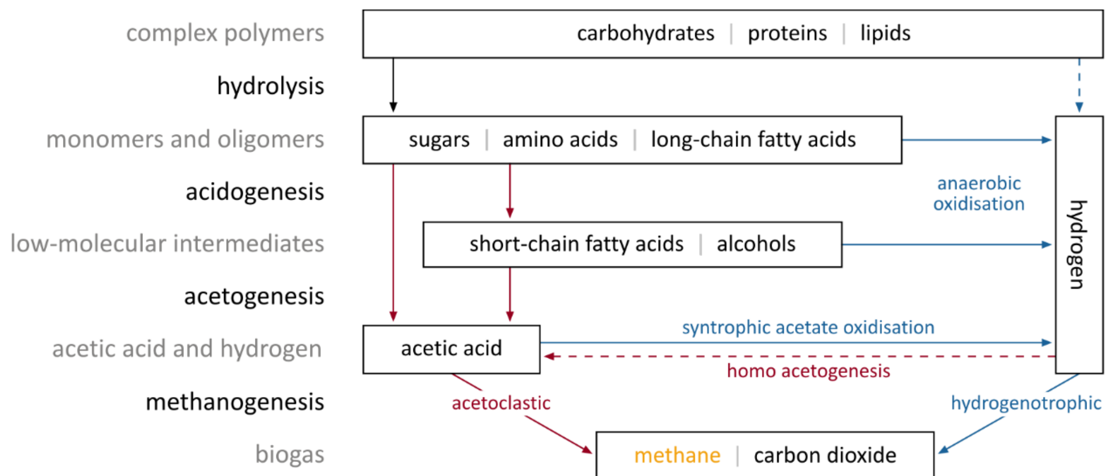


Figure 8: Characteristic process phases during anaerobic digestion [33, 192, 472]

2.1.1 Hydrolysis

During hydrolysis, bacteria break down high-molecular organic polymers, such as carbohydrates, proteins and fats, into their fundamental (low-molecular) building blocks. Extracellular enzymes (hydrolases) catalyse the hydrolytic cleavage of chemical bonds. Depending on the composition and bioavailability of the respective substrate, different proportions of sugars, amino acids, glycerine and long-chain fatty acids are produced during hydrolysis [452, 461].

Hydrolysis of carbohydrates

Carbohydrates include both simple sugars (monosaccharides) and more complex oligo- and polysaccharides, which are mainly formed by the linkage or polycondensation of simple monosaccharides [369]. The most common natural carbohydrates consist of long-chain polysaccharides such as cellulose (hemicellulose and lignocellulose), pectin and starch [175]. During hydrolysis, these chains are then split into their monomeric building blocks, Figure 9.

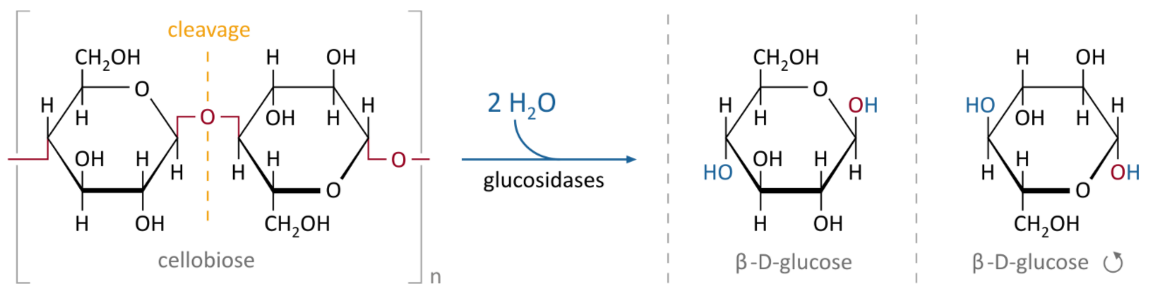


Figure 9: Hydrolysis of carbohydrates (cellobiose)

Simple disaccharides, like sucrose or maltose, can be broken down comparatively quickly, whereas the hydrolysis of cellulose or pectin is slower [51]. Complex lignocellulosic compounds present in many agricultural substrates and residues cannot be completely hydrolysed, since lignin cannot be split anaerobically [75].

Hydrolysis of proteins

Proteins are long-chain macromolecules formed through the linking of 20 different amino acids. The sequence of amino acids determines the structure and properties of the individual protein [369]. During hydrolysis, proteolytic enzymes (proteases) split proteins into polypeptides and amino acids [45], Figure 10. Due to their complex structure, proteins are generally more difficult to hydrolyse than simple carbohydrates [175, 211]. However, the actual decomposition rate depends strongly on the respective structure and the solubility of the protein as well as the individual pH value present [176].

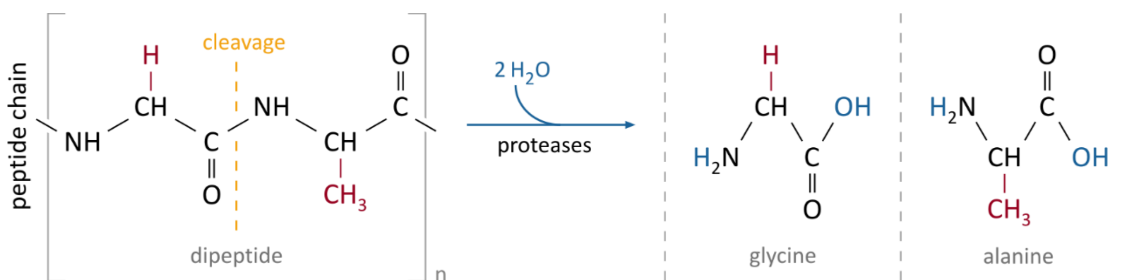


Figure 10: Hydrolysis of proteins (dipeptide)

Hydrolysis of fats

Fats and oils are esters of the alcohol glycerol, which are built of long-chain fatty acids (monocarboxylic acids). Ninety-eight per cent of all natural fats and oils are mixtures of different triglycerides, whereby each of the three hydroxyl groups of glycerol is esterified with one fatty acid [369, 446]. During hydrolysis, lipases (esterases) enzymatically split fats into glycerol and the individual long-chain fatty acids [415], Figure 11. Consequently, fats can be completely hydrolysed, but mostly only at low decomposition rates [51].

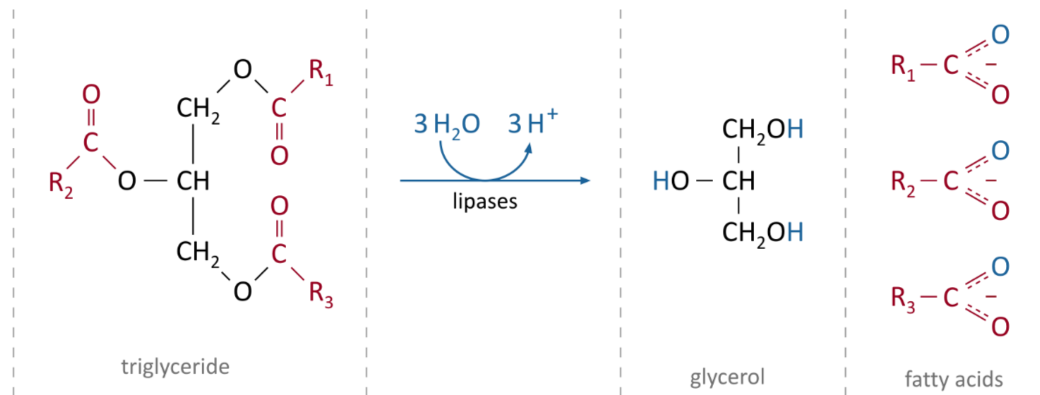


Figure 11: Hydrolysis of fats (triglyceride)

The individual components of the substrates determine not only the distribution of the respective intermediate products, but also the speed of hydrolysis. Dissolved organic compounds, such as those present in municipal sewage sludge or pig and cattle manure, can be used directly in the subsequent fermentation process. During degradation of agriculture substrates or biowaste, which contain complex, particulate and hard-to-degrade constituents or structural components, hydrolysis most often defines the rate-limiting step in the overall digestion process [129, 397, 525, 538]. Furthermore, the rate of hydrolysis depends on substrate composition and on the concentration of microbial biomass, which is proportional to the production of the catalysing enzymes [188]. Research into the application of specific disintegration technologies [88, 208, 291, 485] and the application of hydrolytic enzymes [57, 205, 280, 414] implies that, substrates and waste materials that were previously difficult to ferment will also be able to be utilised by anaerobic digestion in the in the future.

Due to hydrolytic degradation, the dissolved intermediates can now be absorbed through the cell membranes of the microorganisms and are thus available for intracellular metabolism and subsequent process phases of anaerobic degradation [175, 415].

2.1.2 Acidogenesis

During acidogenesis, available hydrolysis products are primarily fermented by various fermentative bacteria to produce short-chain organic acids, hydrogen, carbon dioxide, ethanol, ammonia and hydrogen sulphide. Degradation through microorganisms occurs along various metabolic pathways and is strongly influenced by the respective environmental conditions such as the hydrogen partial pressure and temperature [51, 452].

Acidogenesis of monosaccharides

Glucose is often used as a reference molecule for the stoichiometric description of the acidogenesis of dissolved carbohydrates (monosaccharides) [33, 254, 365, 372]. The energy required for anaerobic degradation of glucose is obtained through substrate phosphorylation (glycolysis). Oxidising the substrate and transferring the separated electron to the carrier molecule NAD^+ obtains the energy required to regenerate ADP to ATP [435]. The catabolism of the fermentation of glucose to acetate, propionate and butyrate can be described as shown in Figure 12.

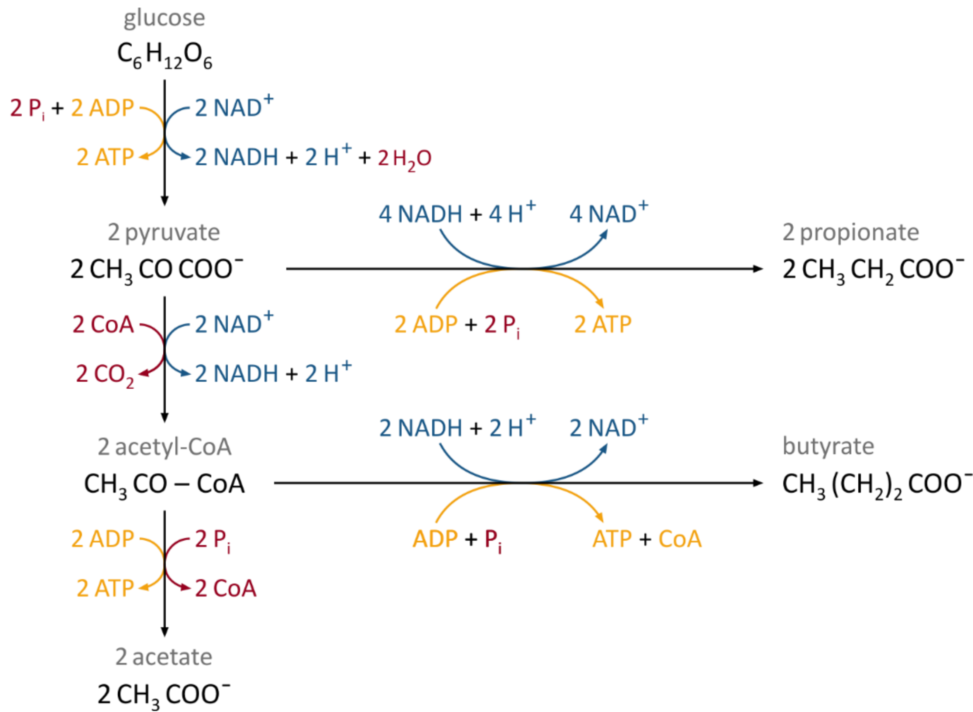


Figure 12: Fermentation of glucose [372, 435]

Among others, the distribution of fermentation products is influenced by the hydrogen partial pressure [76, 372, 521], pH value [151, 517, 610] and temperature [608]. For example, more propionic and butyric acid and consequently less acetic acid, hydrogen and carbon dioxide are formed at high than at low hydrogen partial pressure [75, 360, 435]. In addition to the degradation pathways described above there are other reactions that lead to different intermediates such as ethanol or lactic acid, Table 1.

Table 1: Stoichiometric degradation pathways during fermentation of glucose [33, 379]

Acetic acid	$C_6H_{12}O_6 + 2\,H_2O \rightarrow 2\,CH_3COOH + 2\,CO_2 + 4\,H_2$
Propionic acid	$C_6H_{12}O_6 + 2\,H_2 \rightarrow 2\,CH_3CH_2COOH + 2\,H_2O$
Acetic | Propionic acid	$C_6H_{12}O_6 \rightarrow CH_3CH_2COOH + CH_3COOH + 2\,CO_2 + 2\,H_2$
Butyric acid	$C_6H_{12}O_6 \rightarrow CH_3[CH_2]_2COOH + 2\,CO_2 + 2\,H_2$
Ethanol	$C_6H_{12}O_6 \rightarrow 2\,CH_3CH_2OH + 2\,CO_2$
Ethanol | Acetic acid	$C_6H_{12}O_6 + H_2O \rightarrow CH_3CH_2OH + CH_3COOH + 2\,CO_2 + 2\,H_2$
Lactic acid	$C_6H_{12}O_6 \rightarrow 2\,CH_3CH\,OH\,COOH$
Lactic acid | Ethanol	$C_6H_{12}O_6 + H_2O \rightarrow CH_3CH_2OH + CH_3CH\,OH\,COOH + 2\,CO_2$

Acidogenesis of amino acids

Anaerobic degradation of amino acids takes place either in pairs, as a *STICKLAND reaction* [506], or individually by dehydrating an amino acid using external electron acceptors [433]. Since the combined *STICKLAND reaction* is faster than oxidation of a single amino acid [28], this degradation pathway is often used as a theoretical basis for modelling acidogenesis of amino acids [33]. Various short-chain fatty acids, carbon dioxide, ammonia, hydrogen and (occasionally) hydrogen sulphide can be produced depending on the concentration and structure of different amino acids [432]. The extent to which external electron acceptors (hydrogen-utilizing bacteria) are involved in the degradation of individual amino acids still remains unclear.[6]

The *STICKLAND reaction* describes a redox reaction in which oxidation of one amino acid is bound to the reduction of another amino acid, so that the different amino acids participate in the reaction either as electron donors or acceptors [433]. In several reaction steps, the amino acids are thus degraded through deamination and decarboxylation while generating ATP, Figure 13. Carbon dioxide and ammonia are produced during oxidation in addition to a carboxylic acid that has one carbon atom less than the original amino acid: alanine → acetate. The amino acid utilising hydrogen is usually reduced to ammonia and a carboxylic acid of the same chain length: glycine → acetate.

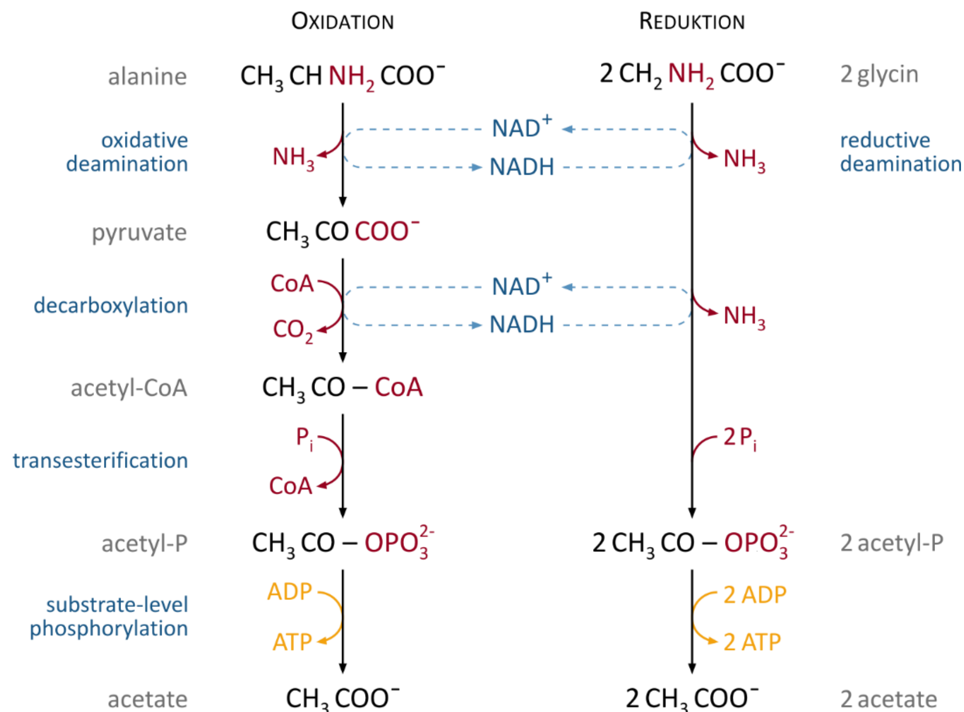


Figure 13: Coupled *STICKLAND reaction* of alanine and glycine [341]

[6] In this matter, two studies contradict one another; RAMSAY and PULLAMMANAPPALLIL [433] have found that the methanogenic bacteria utilising hydrogen play a major role in the degradation behaviour of the amino acids, while NAGASE and MATSUO [382] have found they only have a minor influence.

Acidogenesis of long-chain fatty acids

Long-chain fatty acids are broken down using the process of *beta oxidation*, which depends on the number of carbon atoms and the position or configuration of possible double bonds. Thus, the acidogenesis of even-chain fatty acids primarily produces acetic acid, whereas odd-chain fatty acids also produce propionic acid [360, 415].

In order to enable microbial degradation of fatty acids, catalytic acyl-CoA synthetases activates the fatty acids by forming an energy-rich thioester bond between the carboxyl group of the fatty acid and the coenzyme A to form acyl-CoA. During the actual *beta oxidation*, the activated fatty acids are then reduced by two carbon atoms per reaction cycle through oxidation, hydration and thiolysis (cleavage of acetyl-CoA), Figure 14. In order to completely break down long-chain fatty acids into acetic and propionic acid, this cycle often has to be repeated several times [100, 401, 446].

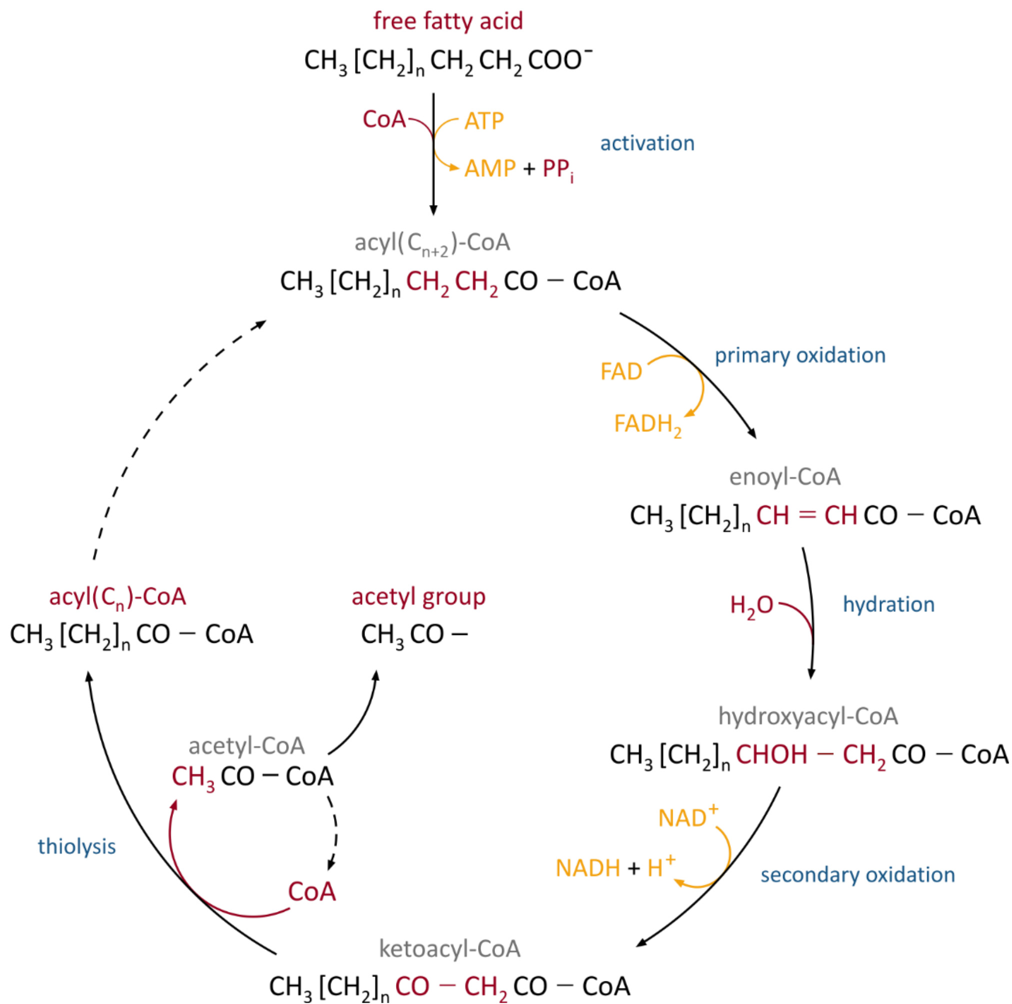


Figure 14: *Beta-oxidation* of long-chain fatty acids [100, 378, 483]

2.1.3 Acetogenesis

During acetogenesis, various metabolic products of previous degradation stages are mainly broken down into acetic acid (acetate), hydrogen and carbon dioxide (hydrogen carbonate). Corresponding to the positive free enthalpy ΔG°', many of the acid-forming reactions are endergonic under standard conditions and therefore do not occur spontaneously, Table 2. In order to shift the state of equilibrium to yield exergonic reactions, the resulting hydrogen must be consumed continuously [473]. Acetogenic bacteria therefore depend on a close symbiotic relationship with hydrogen-utilising archaea during methanogenesis [78, 361, 591].

Table 2: Stoichiometry and free enthalpy of relevant degradation pathways during acetogenesis

Educt	Reaction	ΔG°'
Propionate	$CH_3CH_2COO^- + 3\,H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 3\,H_2$	76.5
Butyrate	$CH_3[CH_2]_2COO^- + 2\,H_2O \rightarrow 2\,CH_3COO^- + H^+ + 2\,H_2$	48.3
Valeriate	$CH_3[CH_2]_3COO^- + 2\,H_2O \rightarrow CH_3COO^- + CH_3CH_2COO^- + H^+ + 2\,H_2$	48.3
Capronate	$CH_3[CH_2]_4COO^- + 4\,H_2O \rightarrow 3\,CH_3COO^- + 2\,H^+ + 4\,H_2$	97.7
Lactate	$CH_3CH\,OH\,COO^- + 2\,H_2O \rightarrow CH_3COO^- + HCO_3^- + H^+ + 2\,H_2$	-4.0
Ethanol	$CH_3CH_2OH + H_2O \rightarrow CH_3COO^- + H^+ + 2\,H_2$	9.6
Glycerol	$C_3H_8O_3 + 2\,H_2O \rightarrow CH_3COO^- + HCO_3^- + 2\,H^+ + 3\,H_2$	-73.1
Hydrogen utilising reactions		
Hydrogenotrophic methanogenesis	$4\,H_2 + CO_2 \rightarrow CH_4 + 2\,H_2O$	-130.7
Homoacetogenesis	$4\,H_2 + 2\,CO_2 \rightarrow CH_3COO^- + H^+ + 2\,H_2O$	-94.9
Sulphate reduction	$4\,H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4\,H_2O$	-152.1

Free enthalpy for standard conditions (pH = 7 and T = 298.15 K) in kJ per reaction, according to [349, 521] and $\Delta G^{o\prime} = \sum \Delta G_f^o(\text{Products}) - \sum \Delta G_f^o(\text{Educts}) \pm n\,\Delta G_f^{o\prime}$ with n = number of protons.

For example, hydrogen produced by the oxidation of butyric acid can be used directly for hydrogenotrophic methane formation, Figure 15. In order to enable a direct hydrogen exchange (*interspecies hydrogen transfer*) between the microorganisms involved, a small interbacterial distance [61] and a narrow range for hydrogen partial pressure [202] are required to create thermodynamically favourable conditions for both acid formation and hydrogen-utilising methane formation, Figure 16.

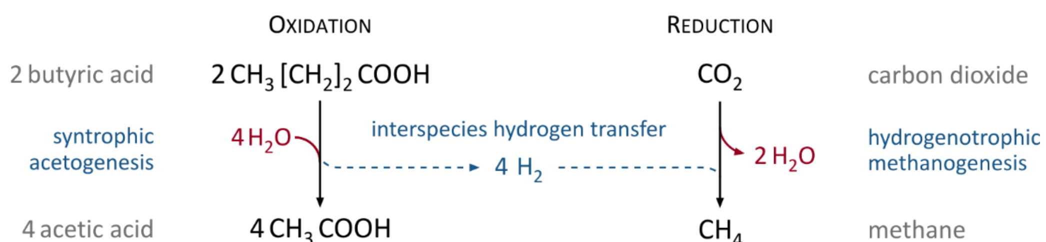


Figure 15: Syntrophic oxidation of butyric acid (*interspecies hydrogen transfer*)

In principle, various reactants are available for synthetic degradation that compete for the available hydrogen, Table 2. During homoacetogenesis [117, 390] the available hydrogen can therefore also be used to reduce carbon dioxide to acetic acid (acetate). In the overall process, however, this reaction is a weak hydrogen competitor [107] and is only able to influence the hydrogen balance under special environmental conditions. For example, homoacetogenic bacteria have an energetic advantage over hydrogenotrophic methanogens in an acidic environment [418] or at low temperatures [104], so that a large part of the available hydrogen is then used for acetate formation. The reduction of sulphate to hydrogen sulphide can also lead to a decrease in the available hydrogen. As a result, there may be less substrate available for methanogen metabolism, which would result in reduced biogas yields, especially at high sulphate concentrations (see chapter 2.2.4). How hydrogen is ultimately used depends strongly on the existing microbial community, the substrate properties and the individual process conditions.

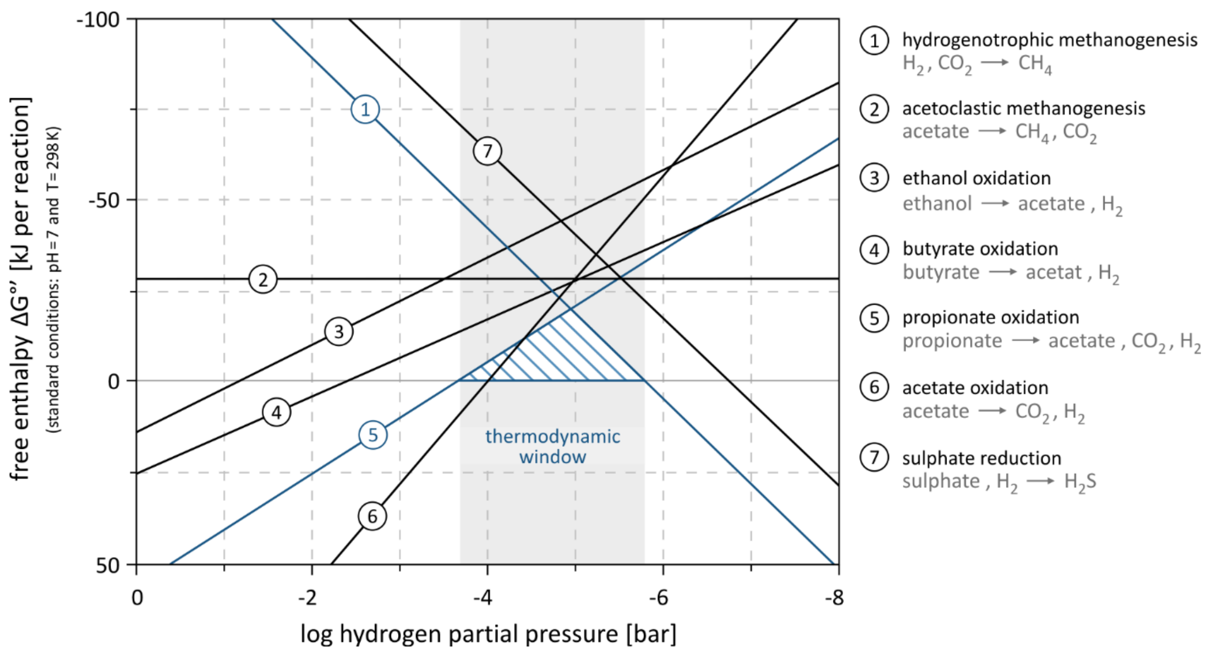


Figure 16: Influence of hydrogen partial pressure on the free enthalpy ΔG°' [466]

2.1.4 Methanogenese

During methanogenesis, obligate anaerobic bacteria convert acetic acid, hydrogen and carbon dioxide to methane, water and carbon dioxide. In principle, there are many formation possibilities. Thus, methane can also be formed through the reduction of carbon dioxide with formate or through the disproportionation of methanol or various methylamines [101]. However, methane is usually produced by acetoclastic and hydrogenotrophic methanogenesis, Table 3.

In natural surroundings, a large proportion of methane is directly produced through cleavage of acetic acid [157, 316]. Due to their strong affinity to acetate, acetoclastic methanogens can outcompete hydrogenothrophic methanogens at long retention times and low acetate concentrations, despite their slower growth rates [246]. This also corresponds to conventional descriptions in available literature on methanogenesis of sewage sludge fermentation. In general, 70 % of the methane is formed by acetic acid degradation and only 30 % through methanation of carbon dioxide by hydrogen reduction [192, 245, 496].

Table 3: Stoichiometry and free enthalpy of relevant degradation pathways during methanogenesis

Educt	Reaction	ΔG°'
Acetate	$CH_3COO^- + 2\,H_2O \rightarrow CH_4 + HCO_3^-$	-31.0
Hydrogen	$4\,H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3\,H_2O$	-135.5
Formate	$HCOO^- + 3\,H_2 + H^+ \rightarrow CH_4 + 2\,H_2O$	-134.2
Methanol	$CH_3OH + H_2O \rightarrow CH_4 + H_2O$	-112.5
Acetate utilising reactions		
Acetat oxidisation	$CH_3COO^- + 2\,H_2O \rightarrow 2\,HCO_3^- + 4\,H_2 + H^+$	104.5

Free enthalpy for standard conditions (pH = 7 and T = 298.15 K) in kJ per reaction, according to [349, 521] and $\Delta G^{o\prime} = \sum \Delta G_f^o(\text{Products}) - \sum \Delta G_f^o(\text{Educts}) \pm n\,\Delta G_f^{o\prime}$ with n = number of protons.

However, under certain environmental conditions, the available acetic acid can also be broken down into hydrogen and carbon dioxide (hydrogen carbonate) through acetate oxidation, Table 3. At high organic acid concentrations [200, 490] or a strong ammonia loads [257, 476, 490, 572] the activity of sensitive acetoclastic methanogens is strongly inhibited so that anaerobic degradation inevitably occurs via synthrophic acetate oxidation and hydrogenotrophic methane formation. High temperatures provides acetate oxidation an advantage over direct acetoclastic methanogenesis at low acid concentrations only [6, 606]. Due to the multi-layered dependencies and the complex analytical investigation methods used to characterise the various degradation pathways, it has not yet been possible to derive specific reference values and universal statements for practical operation. However, current studies clearly show that for anaerobic digestion of renewable resources (biomass) with high volumetric loads and low residence times, the degradation pathway of acetic acid through acetate oxidation shifts considerably in the direction of hydrogenotrophic methane formation [41, 110, 276, 277, 292, 308, 387, 436, 468]

2.2 Microbial influencing variables

For accurate evaluation, optimisation and modelling of reaction pathways and products of individual degradation phases, the understanding of the composition and influencing variables of the microbial community is of crucial importance [587]. Numerous publications describe physiological relationships (metabolism) and phylogenetic relationships (taxonomy) of microbial communities in anaerobic biogas plants. Depending on individual process conditions, a wide range of microorganisms has already been identified. Based on the phylogenetic classification of all living organisms, the entire biocenosis can be divided into fermentative bacteria and methane-forming archaea.

Fermentative bacteria

Various types of facultative and obligate anaerobes are responsible for the different degradation processes during hydrolysis, acidogenesis and acetogenesis [178, 475]. Individual species of the phylum *Firmicutes*, *Proteobacteria* or *Bacteroidetes* are often detected, Figure 17. Various types of *Clostridia* enable the hydrolysis of substrates that contain cellulose and often include the majority of bacteria present [276, 292, 295, 475, 587].

Process Phases	Domain	Phylum	Class | Order
complex polymers	Bacteria	Firmicutes	Clostridia Bacilli Erysipelotrichi
hydrolysis			
monomers and oligomers		Proteobacteria	Alphaproteobacteria Deltaproteobacteria Gammaproteobacteria
acidogenesis		Bacteroidetes	Bacteroidia
low-molecular intermediates		Actinobacteria	Actinobacteria
acetogenesis		Spirochaetes	Spirochaetes
		Thermotogae	Thermotogae
acetic acid and hydrogen	Archaea	Euryarchaeota	Methanomicrobia Methanosarcinales, Methanomicrobiales
methanogenesis			Methanobacteria Methanobacteriales, Methanococcales
biogas			

Frequently identified classes according to [22, 42, 44, 183, 276, 292, 295, 329, 468, 475, 501, 570, 574, 587, 613]

Figure 17: Taxonomic classification of known microorganisms during anaerobic digestion[466]

Methanogenic archaea

Obligate anaerobic archaea (*Euryarchaeota*) are methane-forming microorganisms that can degrade carbon, methyl or acetate-based substrates to carbon dioxide and methane [341]. In contrast to fermentative bacteria, this group of highly specialised methanogens has a limited biodiversity [44, 91, 276, 436, 468]. Thus, the known methanogenic archaea are mainly from the class of *Methanomicrobia* and *Methanobacteria* [574], Figure 17. Furthermore, various studies have shown that *Methanoculleus* (*Methanomicrobia, Methanomicriobales*) plays a dominant role in the methanogenic community of large-scale biogas plants [44, 292, 295, 329, 387, 587].

Apart from detecting and analysing single organisms, the majority of species or the functional relationships between the microorganisms involved in the overall process are still unknown and most often cannot be assigned to a known taxonomic group [22, 276, 292, 329, 436, 475, 501]. Depending on the utilised substrates and specific operating conditions, the ratios of the two domains vary by an average of 15 – 30 % bacteria and 85 – 70 % archaea [22, 469, 587]. However, since the composition of a complex biocenosis also changes continuously during dynamic process operation [110, 156, 308, 468, 501], there is a limited transferability of individual findings of microbiological investigations to the operation of agricultural or industrial biogas plants. Nevertheless, process-specific parameters and fundamental dependencies of the anaerobic digestion process can be discussed and applied for practical modelling techniques, without requiring details on the individual composition of the microbial community.

2.2.1 Nutrient supply

Like any living creature, aerobic and anaerobic microorganisms depend on a sufficient and divers supply of different nutrients [76]. The concentration and bioavailability of the required nutrients thus also has a major influence on the degradation behaviour of individual bacteria and archaea involved. A lack of nutrients usually leads to reduced microbial growth, low biogas rates and high acid concentrations and is therefore – among other factors – often the primary reason for inhibited and unstable process conditions [111, 310, 462, 541]. Very undiversified distribution of nutrients has often been observed during mono-fermentation of energy crops, such as maize or cereals [1, 420]. Therefore, the addition of nutrient-containing co-substrates or supplementary trace elements is recommended to ensure a balanced concentration of individual nutrients to ensure stable process conditions [470, 602].

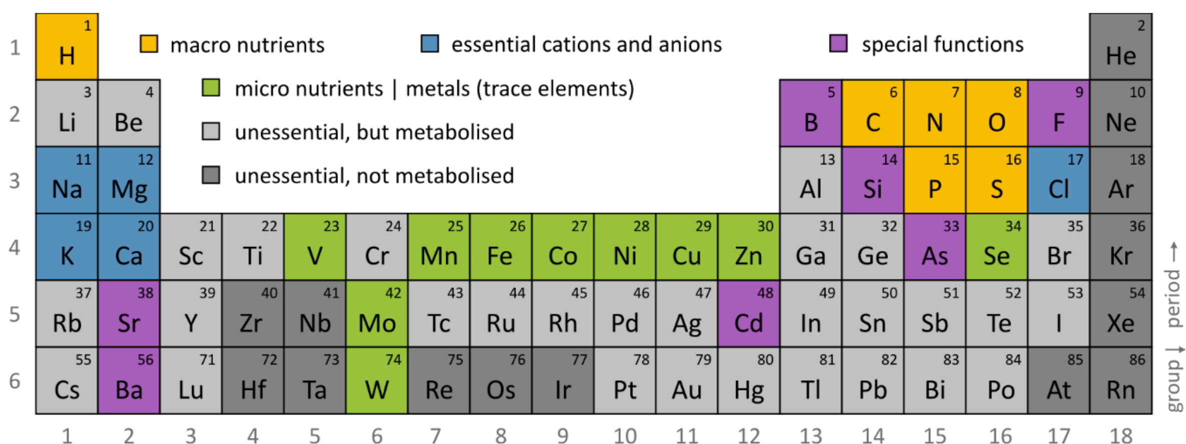


Figure 18: Classification of essential nutrients in the periodic table of elements [341, 546]

The different nutrients are divided into macro- and micronutrients based on their required concentration and their elemental importance for the microorganisms, Figure 18. Nutrients that are needed in larger quantities are referred to as macronutrients, whereas elements that are only required in small concentrations are known as micronutrients or trace elements [341].

Macronutrients and essential cations/anions

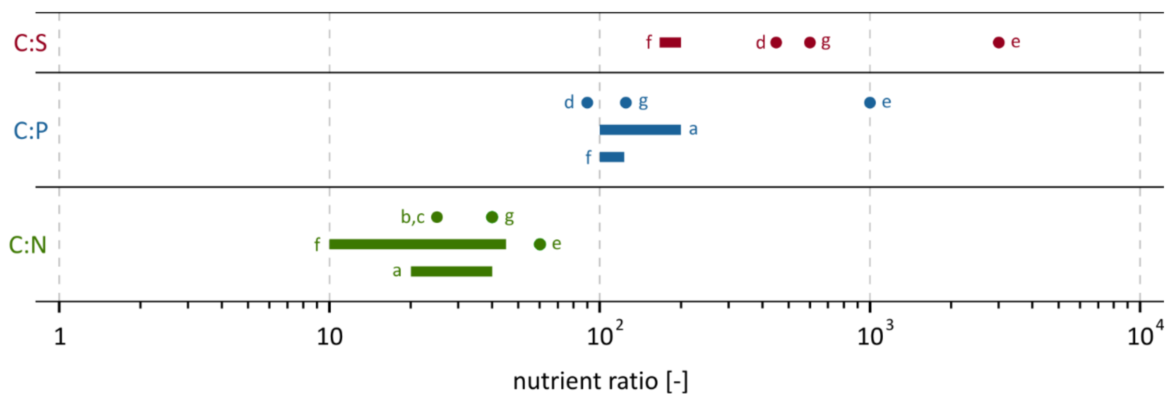
The various macronutrients and ions are crucially important for microorganisms. They are involved in the synthesis of ATP/NADP and important enzymes or form essential components of the cell material, Table 4. Due to low growth rates and small biomass yields during anaerobic digestion, the need for macronutrients is comparatively low and is often already sufficiently supplied by the added substrate [51, 554].

Table 4: Functions and importance of macronutrients during anaerobic digestion

Macronutrients	
C	• Essential component of cell material [a,b,c] • Main energy source of microorganisms [b,c]
N	• Component of many proteins, nucleic acids and enzymes [b,c,d]
P	• Synthesis of energy carriers ATP and NADP [c,d] • Component of many nucleic acids, phospholipids and enzymes [a,b,c]
S	• Component of the amino acids cysteine and methionine [a,d] • Cofactor and component of many enzymes [a,b,c]
Cations and Anions	
K	• Supports nutrient transport and energy balance [b,c] • Important inorganic cation [a,b,c]
Ca	• Component of exoenzymes (amylases and proteases) [a]
Mg	• Cofactor and activator of many enzymes [a,c] • Component of ribosomes, membranes and cell walls [a]
Na	• Formation of ATP (sodium-potassium pump) [c,d] • Nutrient transport within the cell [a,c]
Cl	• Important inorganic anion [a]

[a] GOTTSCHALK [185] [b] KAYHANIAN and RICH [263] [c] TAKASHIMA et al. [514] [d] VINTILOIU et al. [541]

Nevertheless, during unbalanced mono-fermentation of e.g., fodder beets, nutrient deficiency of phosphorus and sulphur can strongly influence process stability and gas production [470]. There exist only a few studies investigating the optimal distribution of macronutrients in substrates. However, individual results of these studies can differ widely, Figure 19. In general, a balanced nutrient ratio of approximately C:N:P:S = 3000:50:3:1 [467] to 600:15:5:1 [554] should be maintained.



[a] BAUER et al. [42] [b] GERARDI [178] [c] HILLS [217] [d] KAISER et al. [250]
[e] SCHERER [467] [f] WEILAND [552] [g] WEILAND [554]

Figure 19: Reference values for optimal ratio of macronutrients in substrates

Micronutrients (trace elements)

Many micronutrients are involved in the formation and activation of important cofactors and enzymes of microorganisms [83, 185, 409, 514, 599]. Furthermore, certain metals, such as iron or manganese, serve as electron acceptors in redox reactions or reduce the inhibitory effect on the anaerobic degradation process by precipitating sulphides [263, 409, 592]. Even if individual elements are only required in small quantities, they play a decisive role in the metabolism of the microbial community and thus influence the biogas process significantly.

Comparative studies on different anaerobic digestions plants prove that the nutrient concentrations vary greatly depending on individual process conditions and applied substrates [314, 326, 462, 541]. Generally, higher nutrient concentrations can be expected during fermentation of complex residues like food waste and pig or cattle manure than during the mono-fermentation of e.g., maize, grass or beet silage [220, 314, 462].

Often a lack of individual trace elements of iron, nickel, cobalt, molybdenum, selenium or tungsten is reported [27, 142, 242, 310, 330, 420, 541, 607]. In many cases, the addition of the missing nutrients resulted in stable plant operation with high gas production rates and low acid concentrations. Excessive and unnecessary addition of trace elements to a process that already has high concentration of nutrients can lead to lower growth rates or even inhibit the microorganisms involved [142, 155, 330], Figure 20. A trace element analysis of the fermentation medium e.g., using the method of OECHSNER et al. [407], should be applied to determine the required quantity of trace elements.

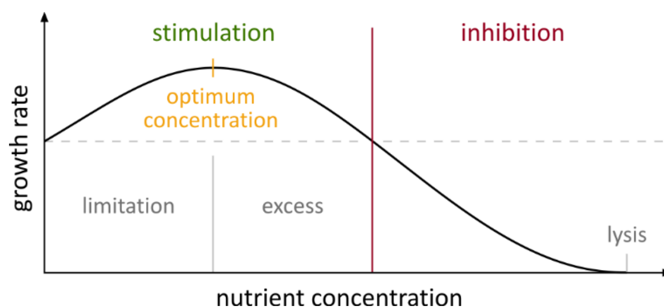
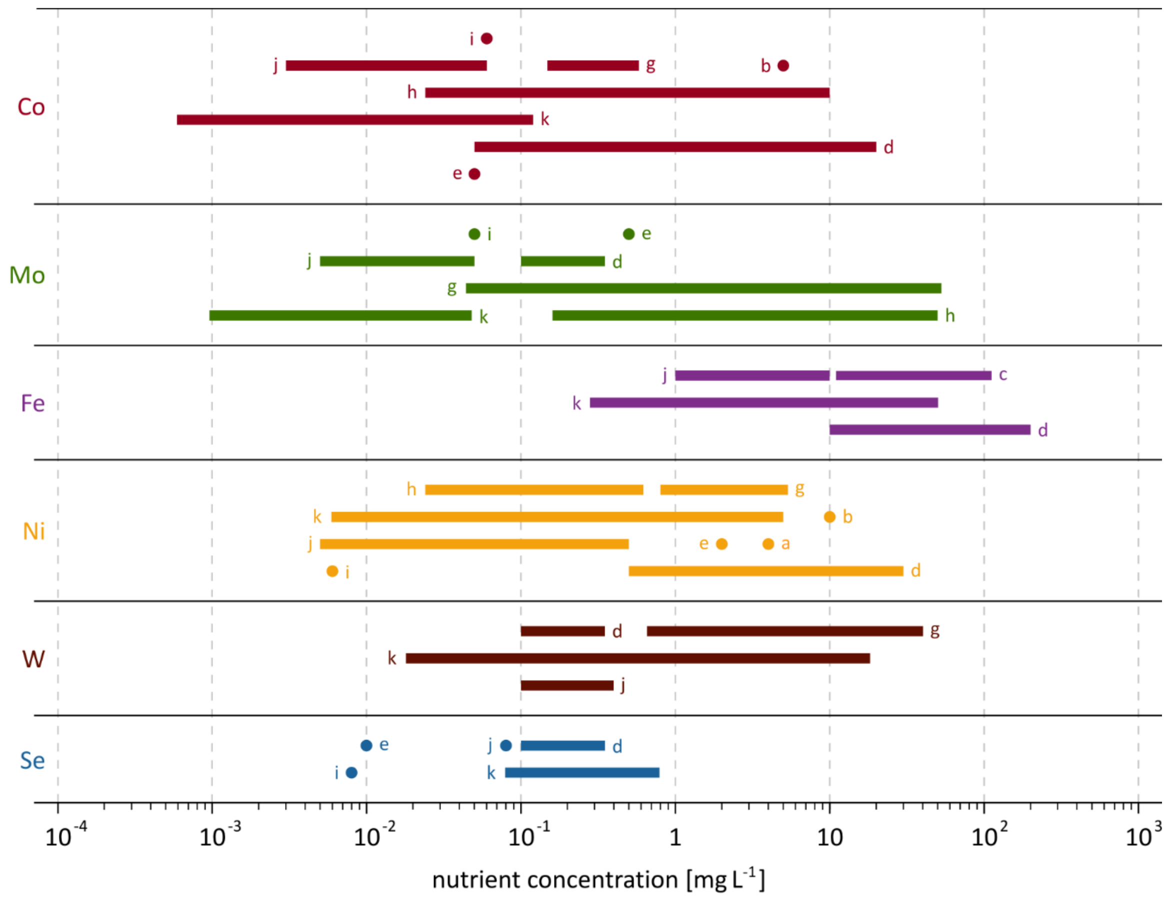


Figure 20: Influence of the nutrient concentration on the microbial growth [353, 409]

However, despite numerous studies on nutrient supply in the anaerobic digestion process, it is still unclear how individual trace elements or complex trace element mixtures precisely influence the activity and metabolism of microorganisms. There exist many different opinions about the exact significance and optimal dosage of supplementary additives during fermentation of common substrates, Figure 21. For most micronutrients, a meaningful concentration range between 0.01 and 10 mg L^{-1} can be defined. Iron is clearly required in larger amounts (up to 200 mg L^{-1}) than other trace elements [341].



[a] Altas [12] [b] Gikas [180] [178] [c] Hoban and Berg [222] [d] Kloss [278] in Schattauer et al. [462]
[e] Lebuhn and Gronauer [309] [f] Lin and Shei [325] [g] Lo et al. [330] [h] Pobeheim et al. [420]
[i] Sahm [452] [j] Seyfried and Bode [488] [k] Takashima et al. [514] [l] Yue et al. [596]

Figure 21: Reference values for optimal concentrations of trace elements in the digestate

Currently no general statements about the complex synergistic and antagonistic effects of the different nutrients on the divers microbial communities of anaerobic digestion can be made [95]. The optimal trace element solution of a certain pure culture can strongly inhibit another species [409]. In some cases adding a single nutrient increases the gas yield, whereas the addition of a complex solution of different nutrients does not result in improvement [607]. Other studies show that a diverse distribution and combination of different nutrients (trace element mixture) has a better effect on the biogas process than adding individual elements, due to synergistic effects [142, 541].

Adding trace elements significantly influences the composition of methanogenic archaea, which are more sensitive to nutrient deficiency than fermentative bacteria [153]. For example, adding iron, copper and nickel increases the concentration of acetoclastic methanogens, so that inhibition of these species may also be traced back to nutrient-related growth restrictions [261].

Regardless of the overall concentration, the bioavailability of respective trace elements influences the nutrient supply of microorganisms and consequently also the anaerobic digestion process [409, 540, 607]. In principle, trace elements and other heavy metals enter the fermenter via the substrate, material abrasion or through process additives in bound and often biologically unavailable forms, Figure 22. These are first dissolved by biochemical degradation in order to be absorbed by the microorganisms involved [42]. The bioavailability of the nutrients depends on the environmental conditions, such as the

pH value or redox potential, and precipitation or chelation of metal ions [86, 409]. Thus, a high pH value in the presence of free phosphate, sulphide or carbonate promotes the formation of hardly soluble compounds, which can only be made available again by removing the complexing agents [42]. Recirculation of digestate often has a positive effect on the nutrient balance, as the retention time of individual trace elements is increased [242].

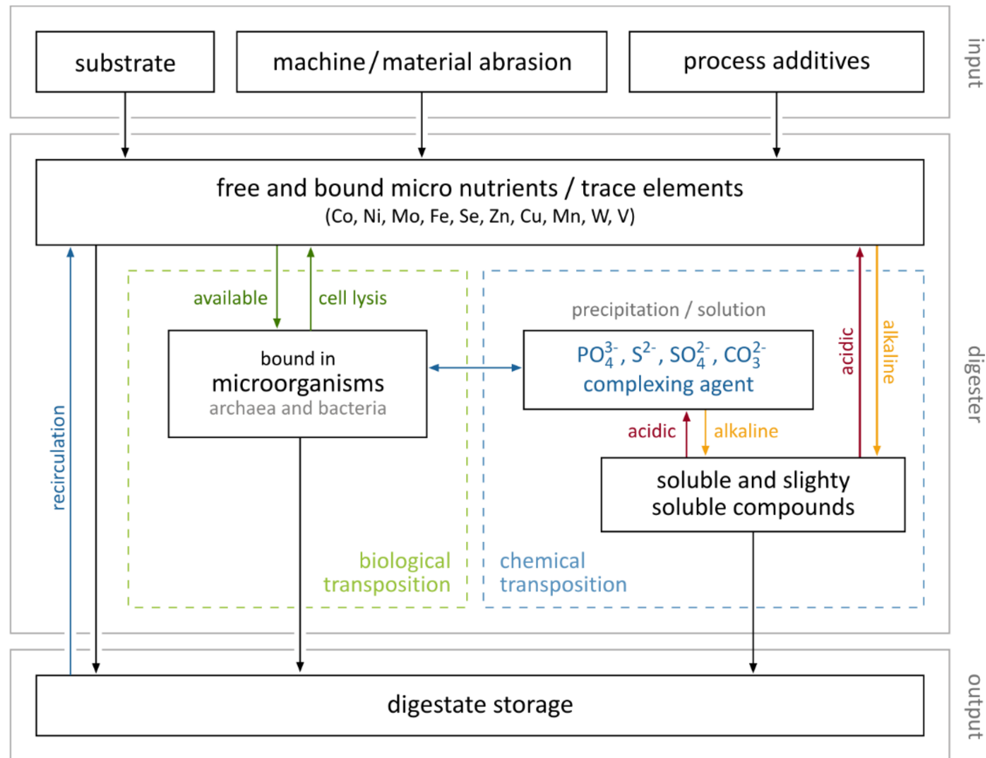


Figure 22: Supply and bioavailability of trace elements in biogas plants [42]

Both the high variance in the nutrient concentrations of different fermenter samples and the different reference values for optimal nutrient distribution (Figure 21) reflect strong differences in the process state of the systems under investigation. Even though there is a repeated emphasis on the positive influence of various additives on the fermentation and activity of methanogenic microorganisms, the respective effects vary greatly depending on substrate composition, inoculum and operating conditions. Since the concentration and availability also changes during operation, no general recommendations can be developed. Instead, the individual process conditions and plant concept should determine whether and how nutrients should be added – either in the form of trace element mixtures or by adding co-substrates that contain required nutrients [111].

2.2.2 Temperature

In addition to nutrient supply, temperature is one of the most important factors influencing the growth and activity of the microorganisms involved. As the temperature rises, the chemical and enzymatic reactions within the cell occur at higher speed, so that growth and metabolic processes of the species constantly increase until a maximum growth rate is reached [341]. Above this temperature, certain proteins can denature irreversibly and thus severely restrict cell functions until there is final thermal decay, Figure 23.

In general, anaerobic degradation also occurs at higher temperatures with faster growth rates and consequently higher gas production rates and shorter residence times. Based on the operating temperature most biogas plants can be divided into psychrophilic, mesophilic and thermophilic fermentation stages.

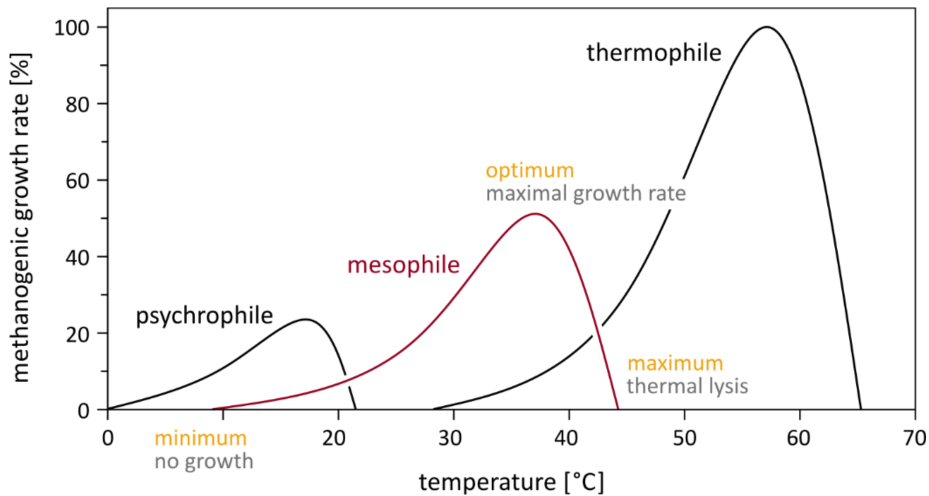


Figure 23: Influence of temperature on methanogenic growth rate [341, 529]

Psychrophilic fermentation (10 – 20 °C)

High acid concentrations (low pH), poor degradation rates and low gas production were frequently observed during psychrophilic fermentation as a result of low growth rates. Hence, weaker process stability and poor biochemical conditions for the anaerobic degradation of different substrates can generally be expected at psychrophilic temperatures [10, 193, 459, 529].

Mesophilic fermentation (30 – 40 °C)

Compared to psychrophilic fermentation, mesophilic temperatures achieve better hydrolysability of complex substrates [282], faster degradation rates and higher organic loading [348], resulting in high gas production rates and higher methane contents [92]. For longer retention times no major differences of the gas yield is to be expected in comparison to thermophilic fermentation at higher temperatures [177]. Furthermore, the wide diversity of mesophilic microorganisms [91, 486] creates a balanced biocenosis and stable process conditions [477]. Mesophilic fermentation therefore appears to represent a good compromise between fast degradation rates, high methane concentrations, good process stability and moderate energy consumption. Thus, it is also the conventional operating temperature of biogas plants in Germany [143, 144].

Thermophilic fermentation (50 – 60 °C)

In addition to the technological advantages, such as the eradication of pathogenic germs (hygenisation) and lower homogenisation times due to low viscosity [328], thermophilic fermentation enables fast degradation and high organic loading rates for short retention times [63, 66, 138, 177, 271, 340, 528, 539, 612]. Even though there have been individual cases of stable and efficient hyperthermophilic fermentation [7, 528], methanogenic archaea are sensitive to temperatures above 60 °C. Reduced gas production, low methane contents and high acid concentrations have frequently been observed for

higher temperatures. Therefore, the optimal operating temperature for thermophilic fermentation of common substrates is below 60 °C [5, 7, 236, 271, 282, 458, 528, 583]. Increasing hydrolysis rates [137] usually result in a higher level of organic intermediates and acids [7, 68, 302], which (in addition to a highly specialised microbial community) leads to a more sensitive process stability [271, 272, 539, 584].

Strong fluctuations and quick drops in process temperatures usually lead to increased acid concentrations and greatly reduced biogas rates [5, 62, 92, 99, 138, 305, 406]. However, depending on the duration and degree of temperature change, the process can be stabilised again within a few hours or days by adjusting feeding and increasing temperatures back to the original operating temperature. Most often this has no lasting impact (long term damage) on the microbial community [5, 62, 92, 99, 138, 305, 406]. Temperature changes within the temperature limits of the microorganisms involved often result in good process stability and only small, isolated increases in organic acids [68, 99]. For example, if the temperature is increased very slowly by 6 °C a^{-1} from 53.9 to 57.28 °C [236], constant process parameters and stable plant operation prove good adaptability of individual microorganisms to temperature [92, 236].

However, a significant change in temperature is likely to lead to reduced gas production rates and strong accumulation of organic acids (especially propionic acid) [68, 99, 327]. In the transition area between temperature zones, from 42 to 48 °C, the thermal decay of mesophilic bacteria and the low activity of the thermophilic bacteria results in low growth rates of the methanogenic population, Figure 23.

It is assumed that during transition, individual mesophilic bacteria do not adapt to higher temperature zones [91]. Instead, thermophilic bacterial strains, which are already present in the fermenter during mesophilic fermentation, become dominant within the population, triggering a change in species within the microbial community [68, 91, 94, 528]. Despite the change in population, the biogas process can adapt to a new temperature zone over the long term through an adjustment in feeding [99]. However, since reduced biogas production and process stability are expected anyway when there is a strong change in temperature, a rapid temperature change (temperature jump) is preferable, as this shortens the critical transition time and re-stabilises the process more quickly [68, 328].

Generally, there is no optimal temperature for anaerobic digestion of organic substrates and waste [328]. Because methanogenic archaea are highly temperature dependent, it is much more important that the process remains at a constant temperature level in order to ensure a stable and efficient degradation [92, 539]. Depending on the utilized substrates and the technological framework conditions of the overall plant concept [349], both mesophilic and thermophilic fermentation have specific advantages for their applications, Table 5. In addition to the basic need for hygenisation, the ammonium concentration [19, 171, 172] or the self-heating potential [327] of individual substrates also play a decisive role in selecting a suitable operating temperature. Furthermore, thermal pre-treatment [177] or temperature adjustment of the secondary digester [59] provides an opportunity to better exploit the gas potential of the utilized substrates or to reduce olfactory parameters, such as odour from sulphur [583].

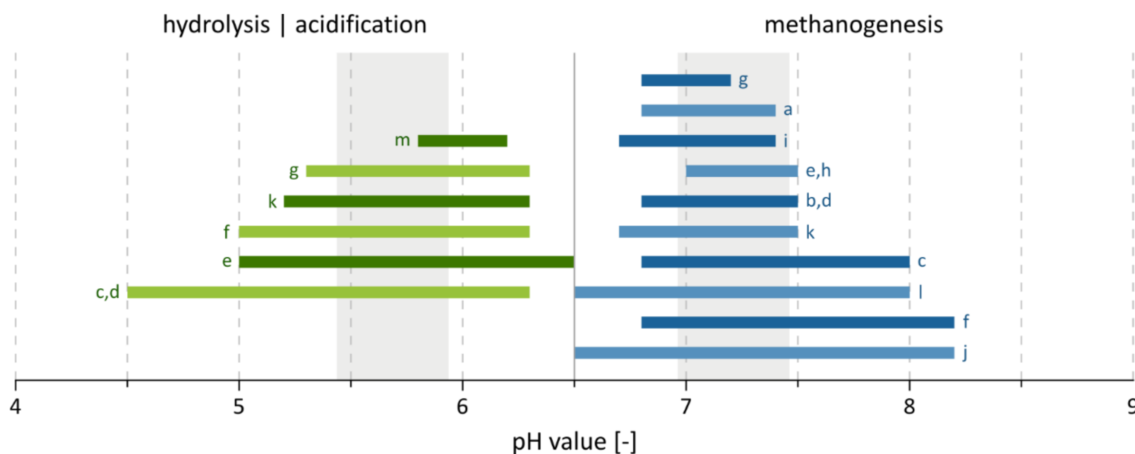
Table 5: Advantages of mesophilic and thermophilic anaerobic digestion [477]

Mesophilic digestion	Thermophilic digestion
High process stability	High reaction rates
Low heating energy	Short retention times
Low ammonia inhibition	Hygienisation
Low water vapour content in the biogas	Low viscosity
Low carbon dioxide content in the biogas	Reduction of sludge volume

2.2.3 pH value and organic acids

The pH value during anaerobic fermentation is derived from the reaction of alkaline or acidic metabolic products and substrate components [71]. Depending on the strength (dissociation constant) and concentration of individual acids and bases, as well as the existing buffer system, the concentration and activity of free hydrogen ions and pH value changes. The pH directly influences growth and composition of the microbial community [134] and also regulates the activity, stability and solubility of important enzymes [93]. A change in pH can influence the morphology and structure of the cell as well as the efficiency of many metabolic functions of substrate and energy conversion [134]. In addition to its direct function of regulating metabolism, pH also controls dissociation of important acidic or alkaline intermediates and thus influences their inhibitory or stimulating effects on the growth conditions of microorganisms [71].

Every organism has a pH range in which growth and metabolism are possible [341]. This means that different pH optima can be defined for different acetogenic bacteria. For example, proteins (gelatine) are usually degraded in the neutral range around pH ≈ 7 [73], whereas the fermentation of carbohydrates (glucose) usually occurs at pH values between 5.8 and 6.2 [610]. The distribution of individual intermediate and end products of the biogas process also changes depending on the activity of the microorganisms and enzymes involved [129, 134, 610].



[a] Braun [71] [b] Eastman and Ferguson [129] [c] Eder and Schulz [131] [d] Kaiser et al. [250]
[e] Scholwin et al. [477] [f] Lemmer and Oechsner [313] [g] Mundrack and Kunst [378]
[h] O'Flaherty et al. [405] [i] Sahm [452] [j] Speece [503] [k] Weiland [552]
[l] Wellinger et al. [569] [m] Zoetemeyer et al. [610]

Figure 24: Optimal pH ranges during anaerobic digestion

According to Figure 24, two pH ranges are common within a diverse microbial community. While the acid-forming bacteria prefer slightly acidic conditions, the optimal pH for methanogens is within the neutral range. However, since the acid-forming bacteria are active within a large pH range [320, 505] and only the methanogenic archaea are inhibited by a strongly acidic or alkaline medium, a pH in the optimal range between 7 and 7.5 [51, 477] often develops automatically in single-stage processes. However, if the plant is designed for a two-stage process, the pH range can be adjusted by adding hydrochloric acid [248, 603], calcium hydroxide [354] or sodium carbonate [51], thus creating the optimal conditions for the respective process phases. Thus, the pH value has been applied as a reference variable (nominal value) in simple control systems in order to guarantee optimum process conditions for the microorganisms involved [206].

Buffer capacity

During anaerobic fermentation, various buffer systems are able to counteract a strong and abrupt change in pH, Table 6. A strong buffer contains a relatively high concentration of a weak acid and its conjugated base, so that the effect of acidic or alkaline substrate components and metabolic products is balanced by the reaction of free H^+ or OH^- ions with the existing base or acid [45, 369]. Within the effective pH range of the buffer system, only the dissociation equilibrium of the components involved shifts, whereas pH values almost remain the same, Figure 25.

Table 6: Dissociation equilibrium of effective buffer systems during anaerobic digestion

Buffer	Dissociation equilibrium	pK_a
Carbonate buffer	$[CO_2 + H_2O \rightleftharpoons H_2CO_3] \rightleftharpoons H^+ + HCO_3^-$	6.35
	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	10.33
Ammonium buffer	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	9.25
Sulphate buffer	$H_2S \rightleftharpoons H^+ + HS^-$	6.99
	$HS^- \rightleftharpoons H^+ + S^{2-}$	12.89

Negative logarithmic dissociation constant pK_a at T = 293.15 K according to [417].

A sufficient carbonate buffer is crucial for methane fermentation [71, 354]. For nitrogen contents in agricultural plants, the ammonium buffer may also have a stabilising effect on the pH value [19, 296, 569]. In this way, substrates with high and divers nutrient concentration, such as liquid manure [554, 569, 602] or kitchen waste [118], strengthen the buffering capacity of anaerobic fermentation processes.

In practice, the buffer capacity is often determined as TIC [7] through titration of a digestate sample with sulphuric acid [399, 440, 545]. The amount of acid consumed indicates the overall effect of the buffers present, which counteracts acidification (titration) up to a pH value of 5.0. Depending on the substrates used, the buffer capacity is an important process parameter for assessing a sustainably constant pH value, hence ensuring stable plant operation [296, 513].

[7] The original meaning of TIC as *total inorganic carbonate* is therefore only partially applicable for use in biogas technology, since the effect of other buffer systems, such as the ammonium buffer, may also be detected during titration [545].

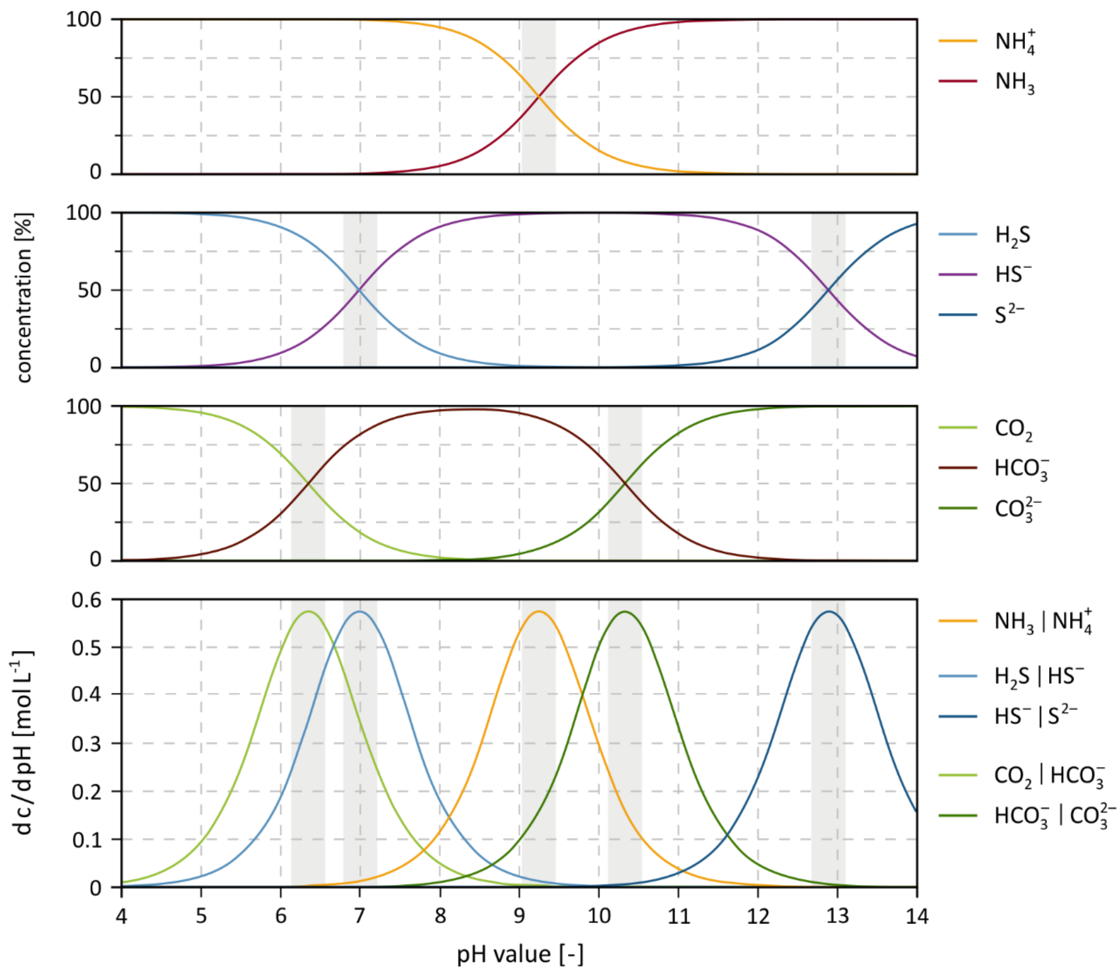


Figure 25: Characteristic buffer systems during anaerobic digestion

Organic acids

Various organic acids, such as acetic, propionic and butyric acids, are important intermediates during anaerobic digestion. Ideally, all fatty acids are broken down by acetogenic and methanogenic microorganisms as soon as they are created. Thus, a balanced process usually evinces a low acid concentration [187, 403, 427].

High acid concentration or a strong increase in individual acids is generally a reliable indicator for process disturbances [8, 187, 350, 359, 427]. However, it may be difficult to distinguish whether individual acids are causing the disturbance themselves or are merely just the indicator. When there is a strong acid load, the resulting pH can lead to an inhibited process state [8, 187, 505, 550]. Furthermore, the growth of the affected microorganisms is sometimes directly influenced by substrate or product inhibition of individual acids, see Section 2.2.4.

Since there is a direct correlation between process stability and acid concentration or acid distribution in the reactor, organic acids provide information about the current process state and degradation behaviour [8, 215, 216, 296, 359]. When combined with other influencing variables, such as buffer capacity or pH, individual acids can be used as important parameters for monitoring anaerobic digestion

plants [8, 58, 342, 419, 513]. However, it is still unclear how and which acids should be used for process evaluation. Depending on the plant concept and substrates under investigation, there are still many different opinions on the significance of individual acids and derived indicators (e.g., acid ratios).

Total volatile fatty acids (VFA)

The influence of different volatile organic acids is often measured via the sum parameter VFA using the titration of a digestate sample up to a pH value of 4.0 [80, 258] or 4.4 [399, 440]. Thus, the current value and, most importantly, the progression of the total acid concentration often provide a first impression of the process state. However, a high acid concentration is not necessarily an indicator of an unstable process. In order to estimate the existing acid content as a function of the effective buffer, the total volatile fatty acid (VFA) concentration is usually related to the buffer capacity (TIC). A critical limit between 0.1 and 0.4 is generally defined for the VFA-TIC ratio [313, 554, 605]. However, during fermentation of renewable resources, a higher VFA-TIC up to 0.6 has been reported during stable process operation [123, 440, 553]. Since the methods used in sample pre-treatment and manual titration differ widely, the timeframe is a more important factor in reliable process monitoring than exceeding fixed thresholds [440, 545]. Generally, the VFA-TIC ratio has already been successfully applied for process monitoring [70] or as a reference variable within a control system [362].

Propionic acid

Propionic acid (propionate) is generally considered to be a reliable and sensitive process indicator [350, 393, 502, 534]. Often an increase in propionic acid can be observed just before a process failure or inhibition. Thus, the content and/or change in propionic acid concentration has been used as an indicator for process monitoring and as an early warning signal [60, 393]. However, high concentrations of propionic acid can also result from strong glucose degradation, even under stable operating conditions, and thus lead to a false indication (false alarm) during process evaluation [427]. In order to scale sensitive propionic acid to acetic acid, a propionate-acetate ratio greater than 1.4 has been proposed [215] and successfully applied for indicating process inhibition [216, 345]. Nevertheless, even an acid ratio that is far below 1.4 can trigger a process failure [393]. Thus, the ratio of propionate to acetate may be less significant under certain process conditions [8].

Butyric acid

The iso-form of butyric acid (butyrate) is also suitable for process monitoring [214, 216] and the ratio of butyrate to iso-butyrate can also be used as process indicator [8]. However, no general statements are possible for this parameter as well, due to a lack of literature references.

Due to their high informative value, organic acids have always been used as a reference variable in various control systems [206]. For example, the acid concentration in the reactor can be controlled by adjusting the substrate feed (dilution rate) using fuzzy control [429] or model-based, adaptive control [439]. The progression of acid concentration is also a successful way to optimise and separate hydrolysis and methanation in a two-stage fermentation plant concept [522]. However, since the biogas or

methane production rate is generally the target value of the process, gas production is a better reference variable in industrial plants than e.g., propionic or total VFA concentration. Nevertheless, individual acids – such as propionic acid – can be used as additional indicators or alarm variables within a control or process monitoring system [60].

In the past, various indicators and critical concentrations for assessing process stability were developed based on various organic acids. Stable operation has also often been observed outside defined limits [7, 19, 392] and thus there is no universal method for monitoring anaerobic processes using individual organic acids [393]. Nevertheless, the dynamic progression of individual acids serves as the basis for reliable process evaluation and is therefore also a crucial element of many established process models.

2.2.4 Inhibitors

Inhibitors are substances that have a restraining effect on growth and product formation of the microbial community [95]. Inhibitors can enter the process as harmful substrate components or (depending on the specific operating conditions and reaction pathways) can be produced as intermediates during anaerobic fermentation. In addition to specific degradation products, antibiotics, disinfectants, herbicides, salts and heavy metals can also have an inhibitory effect on the fermentation process [131, 250, 569].

The inhibitory effect primarily depends on the concentration of undissociated and/or dissolved substances, so that even essential nutrients or trace elements — such as nitrogen or sulphur — can inhibit the anaerobic digestion process in high concentrations [51, 163, 250, 299, 353, 409], Figure 20. There are many mechanisms that strongly influence the activity of cells and enzymes [132], including:

- Chemical reactions with one or more cellular components
- Adsorption or complexation with enzymes, coenzymes or substrates
- Disturbance of important reaction sequences and control functions of the cell
- Change in physicochemical environmental conditions

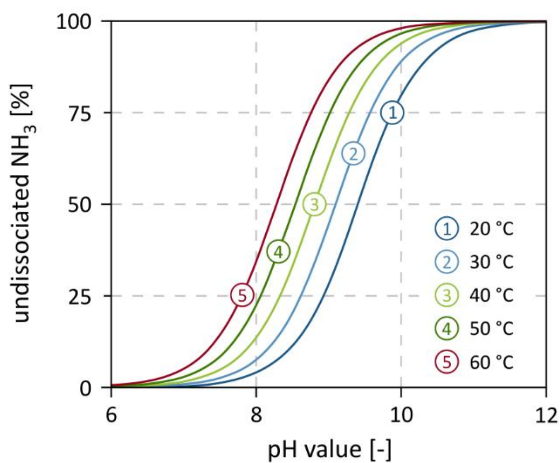
The specific functional relationship is usually determined by the critical concentration of inhibitors at a defined level of methanogenic activity (50 %) or by the resulting biogas production during continuous steady state operation [288, 296].

Available literature includes a wide range of test results and concentration limits that vary strongly as a result of complex synergies/antagonisms, adaptation times and complexation of individual inhibitors related to operating and environmental conditions [95, 477]. For each application, a detailed process analysis must determine whether the concentration of a potential inhibitor should be reduced, for example by applying suitable additives, extending adaptation periods, or by specific treatment of the substrate or recirculate [353].

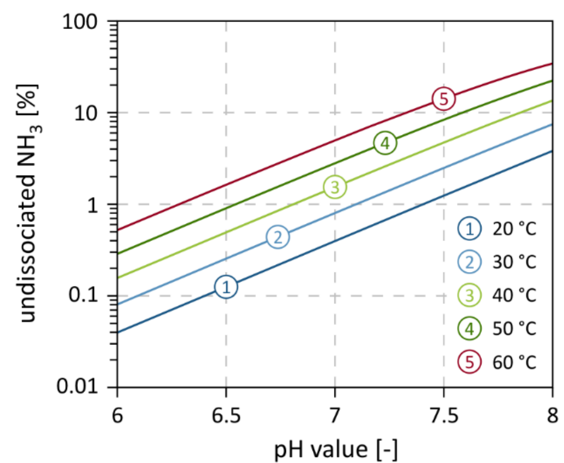
Nitrogen (ammonia)

Nitrogen is an essential nutrient for microorganisms and is mainly released as ammonium/ammonia during hydrolysis and fermentation of substrates that contain proteins. Therefore, fermentation of animal excrements, biowastes or residues from the food industry typically lead to high nitrogen concentrations in the digester [87, 512].

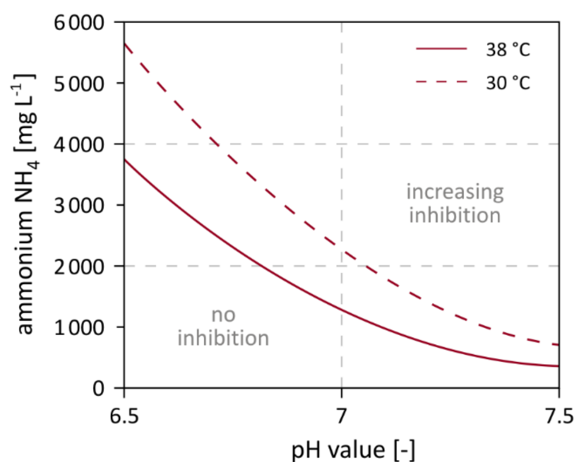
While the ammonium ion NH_4^+ is synthesised by most bacteria for nitrogen supply [71], undissociated ammonia NH_3 inhibits the metabolism and activity of microorganisms [24, 72, 286, 296, 358, 421, 600]. Ammonia diffuses freely through the cell membrane and can thus lead to a change in the intracellular pH value, a higher energy demand or an inhibition of specific enzymatic reactions in the cell [589]. The inhibitory effect mainly affects the sensitive methanogenic archaea [47, 199, 287, 442]. Comparative investigations on the methanogenic community also reveal that high ammonia concentrations strongly influences the growth of acetoclastic methanogens [18, 65, 87, 259, 287, 421].[8]



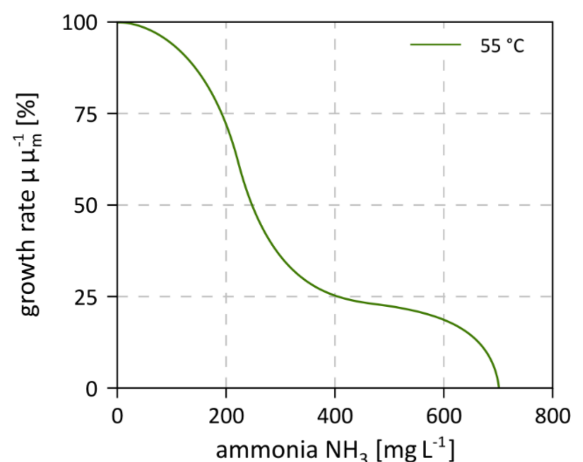
(a) Temperature dependence of the dissociation equilibrium $NH_3 \rightleftharpoons NH_4^+$ in pH range between 6 and 12



(b) Temperature dependence of the dissociation equilibrium $NH_3 \rightleftharpoons NH_4^+$ in pH range between 6 and 8



(c) Permissible ammonium concentration NH_4^+ at two different operating temperatures [297]



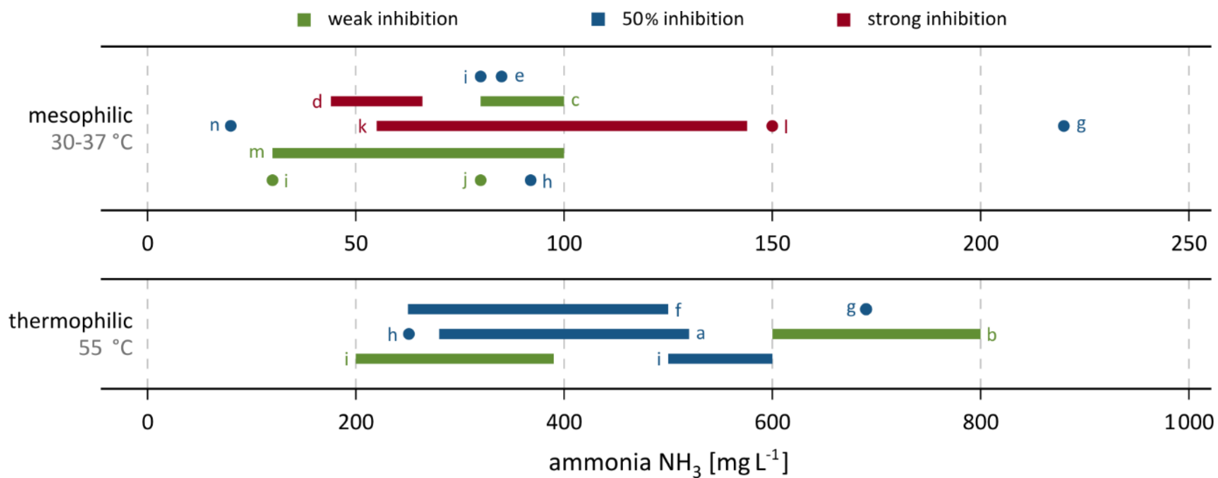
(d) Ammonia inhibition of relative growth rate during acetoclastic methanogenesis [18, 65]

Figure 26: Influencing factors on the dissociation [417] and inhibitory effect of ammonia

[8] Only WIEGANT and ZEEMAN were able to demonstrate a stronger inhibition of hydrogenotrophic methanogens at high ammonia concentrations during thermophilic operation [579].

The effective ammonia concentration is a result of the dissociation ratio between ammonium ⇌ ammonia. Thus, the inhibitory effect is strongly influenced by the specific pH value and process temperature [417], Figure 26a. In a pH range of 6 to 8, the ammonia concentration and corresponding inhibitory effect is stronger at higher temperatures and pH values, Figure 26b. Nevertheless, most of the inorganic nitrogen in this pH range is present in the salts of the ammonium ion NH_4^+ [71]. Based on the pH value, a reliable ammonium concentration can thus be defined for mesophilic operation, Figure 26c. During thermophilic operation, the inhibitory effect on the growth and metabolism of acetoclastic methanogens is often characterised by distinctive inhibition levels, depending on the concentration of ammonia [18, 65, 199, 421], as shown in Figure 26d.

Considering mesophilic and thermophilic temperatures, there is a variety of critical limits for ammonia inhibition on microbial methane production, Figure 27. Individual concentrations sometimes differ greatly depending on the applied experimental conditions, substrates, inocula and microbial community. Moreover, it is difficult to compare contradictory limits, due to imprecise information on the type or strength of inhibition as well as missing information on additional adaptation times. During mesophilic operation, a continuous increase in ammonia inhibition can be expected between 20 and 150 mg L^{-1} NH_3. Even though it is usually assumed that higher temperature leads to higher ammonia load [19, 72, 199, 203], thermophilic microorganisms appear to be able to tolerate significantly higher ammonia concentrations [171, 172]. For thermophilic operation, a concentration range between 200 and 800 mg L^{-1} NH_3 can be defined as onset of ammonia inhibition, Figure 27.



[a] Angelidaki and Ahring [18] [b] Angelidaki and Ahring [19] [c] De Baere et al. [24] [d] Bhattacharya and Parkin [47]
[e] Boardman and McVeigh [56] [f] Borja [65] [g] Gallert und Winter [172] [h] Gallert et al. [171]
[i] Hashimoto [203] [j] Koster et al. [289] [k] Koster and Lettinga [287] [l] McCarty and McKinney [358]
[m] Seyfried and Bode [488] [n] Soubes et al. [500]

Figure 27: Ammonia inhibition of methane formation depending on temperature

Methanogenic microorganisms can slowly adapt to very high ammonium concentrations and thus raise the inhibition threshold [18, 24, 87, 171, 284, 532, 600]. Stable operation at concentrations of up to 11,831 mg L^{-1} NH_4^+ [288] or 1,100 mg L^{-1} NH_3 [199] have been reported. However, it should be noted that such high ammonia concentrations – despite stable process conditions – sometimes strongly inhibit the process and lead to a considerably lower methane production.

Ammonia inhibition can be reduced or controlled based on the shown dependencies. For example, a specific reduction of temperature [19, 72] or pH [72, 284, 286, 508] can lead to lower ammonia loads and more stable process conditions. The presence of individual metal ions, such as Mg^{2+}, Ca^{2+} or Na^{+}, can also reduce the inhibitory effect of ammonia [64, 358, 504]. In order to adapt the microorganisms to high ammonia concentrations in the long term, substrates that contain considerable amounts of nitrogen should be added to the process with low organic loading rates, high C:N ratios and long retention times [47, 72, 262]. Since temperature and pH value are usually kept constant, a direct adjustment of the feed can limit the effects of high ammonia concentrations on the biogas process [171].

Sulphur (hydrogen sulphide) [9]

High concentrations of sulphur are primarily found in industrial wastewaters from paper production or food processing of molasses, alcohols, citric acids, cooking oils or seafood [315]. Sulphur is a component of important enzymes and (in the form of various sulphide compounds) is an essential nutrient for growth and activity of the microorganisms [268, 289]. Analyses of pure culture *Methanosarcina barkeri* show that small amounts of sulphide have a positive effect on methane formation during acute nutrient or sulphur deficiency [373, 471]. Adding sulphide or sulphide forming microorganisms can reduce the availability of various heavy metals (such as cobalt, zinc, nickel or iron) below toxic limits by precipitation as metal sulphides [307]. However, excessive concentrations of sulphur or sulphate can also have negative effects on the anaerobic digestion process [136, 319, 351]:

- Sulphate-reducing bacteria and archaea (desulphurisers) compete with acid- and methane-forming microorganisms for the same substrates, which can result in the deceleration of individual degradation phases and the inhibition of methane formation.
- The reduction of sulphate (desulphurisation) produces sulphide or hydrogen sulphide, which has an inhibitory effect on the growth of anaerobic bacteria and archaea.
- The precipitation of metal ions (metal sulphides) can limit the availability of important trace elements and the corresponding microbial activity.
- A high percentage of hydrogen sulphide in biogas is harmful and can cause corrosion in the affected technical units (gas pipeline and combustion engine).
- High sulphide concentrations in the digestate can severely restrict further utilisation pathways (for example application as a fertiliser) due to toxicity and odour problems.

It is now assumed that competition for available electrons in the substrate is the main cause of process inhibition during high sulphate concentrations [352]. This growth-limiting effect is reinforced by the reduction of sulphate to sulphide or hydrogen sulphide, which additionally inhibits the growth of both methanogenic and sulphate-reducing bacteria, Figure 28.

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[9] Detailed investigations and comprehensive literature reviews describe the multifaceted influence of various sulphur compounds on the anaerobic degradation process [95, 103, 136, 315, 542].

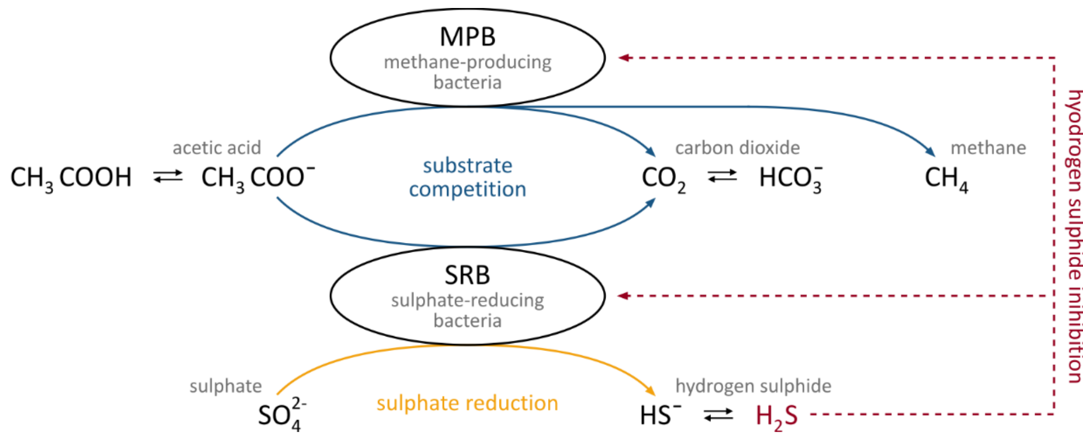


Figure 28: Influence of sulphate-reducing bacteria on methane formation [537]

Compared to methanogenic archaea, sulphate-reducing bacteria have a higher diversity of metabolic pathways [136] and compete for important intermediates during aceto- and methanogenesis, Table 7. When hydrogen, organic acids or alcohols are converted under standard conditions, it can be expected that sulphate-reducing bacteria will outperform methanogenic archaea due to improved thermodynamic conditions (see free standard enthalpy in Table 2 and Table 3) [201, 319, 351, 585].

Table 7: Stoichiometry and free enthalpy of relevant degradation pathways during sulphate reduction

Educt	Reaction	ΔG°'
Hydrogen	$4\,H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4\,H_2O$	-152.1
Acetate	$CH_3COO^- + SO_4^{2-} \rightarrow HS^- + 2\,HCO_3^-$	-47.6
Propionate	$CH_3CH_2COO^- + 0.75\,SO_4^{2-} \rightarrow 0.75\,HS^- + CH_3COO^- + HCO_3^- + 0.25\,H^+$	-37.6
Butyrate	$CH_3[CH_2]_2COO^- + 0.5\,SO_4^{2-} \rightarrow 0.5\,HS^- + 2\,CH_3COO^- + 0.5\,H^+$	-27.8
Lactate	$CH_3CH\,OH\,COO^- + 0.5\,SO_4^{2-} \rightarrow 0.5\,HS^- + CH_3COO^- + HCO_3^- + 0.5\,H^+$	-80.1
Ethanol	$CH_3CH_2OH + 0.5\,SO_4^{2-} \rightarrow 0.5\,HS^- + CH_3COO^- + H_2O + 0.5\,H^+$	-66.4

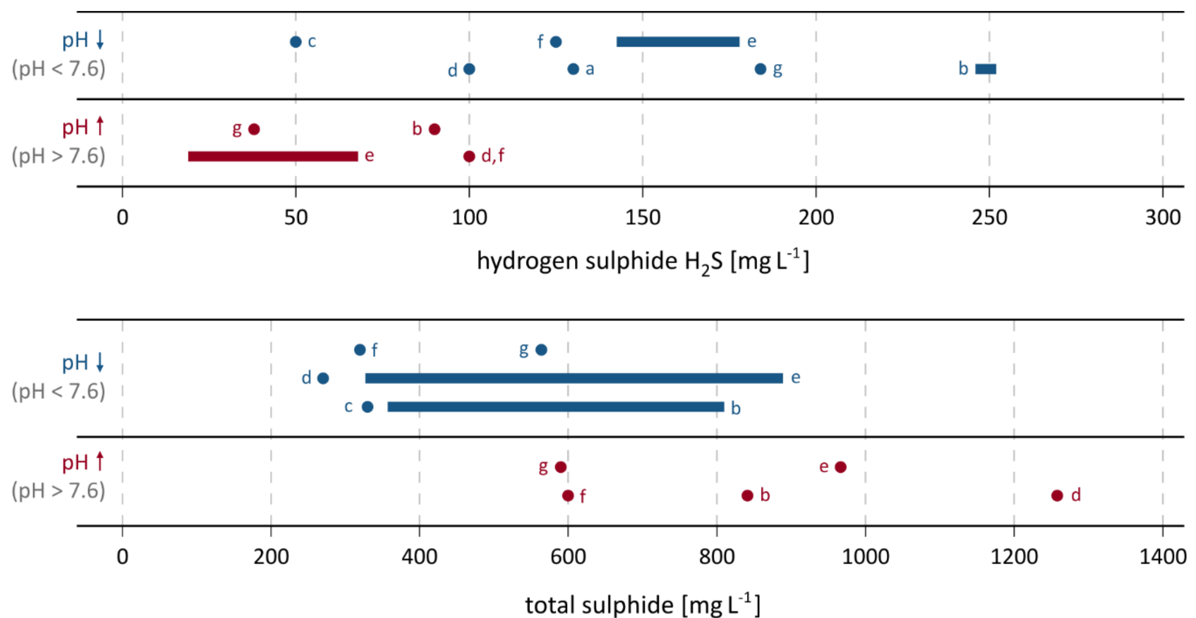
Free enthalpy for standard conditions (pH = 7 and T = 298.15 K) in kJ per reaction, according to [136, 315, 521] and $\Delta G^{o\prime} = \sum \Delta G_f^o(\text{Products}) - \sum \Delta G_f^o(\text{Educts}) \pm n\, \Delta G_f^{o\prime}$ with n = number of protons.

Kinetic investigations of individual bacterial groups also show that various sulphate-reducing bacteria have a higher substrate affinity (small K_S values) and most often faster growth rates (high μ_m values), in comparison to individual methanogens [48, 201, 294, 443, 481, 595]. Due to better kinetic growth conditions (large μ_m-K_S ratios), individual substrates and intermediates are more likely to be degraded by sulphate-reducing bacteria at low substrate concentrations.

It should be noted that competing reactions do not necessarily impair one another and both reaction paths can occur alongside at high substrate concentrations. However, as soon as the primary substrate is limited, the actual degradation path is determined by the degradation and growth conditions of the superior species [48, 294]. During hydrogen utilisation, most of the substrate is degraded by sulphate-reducing bacteria, so that only a limited amount of hydrogen is available to hydrogenotrophic methanogens, which consequently leads to greatly reduced methane yields [11, 77, 201, 404]. Oxidation of propionic acid is also preferably carried out by sulphate reducers, so that an increased degradation of pro-

pionic acid has frequently been observed at high sulphate concentrations [201, 405, 524, 543]. However, despite strong substrate affinities, an advantage of sulphate-reducing over methane-forming microorganisms has rarely been observed during acetate utilisation [11]. Most often acetate is directly degraded by methanogenic archaea [50, 201, 524, 543], due to higher growth rates of individual species [595] or the specific experimental conditions and applied reactor systems [404].

In accordance with ammonia inhibition or the influence of organic acids, sulphur in its undissociated form as hydrogen sulphide H_2S acts as an inhibitor, as the uncharged molecule can permeate cell membranes more easily [103, 136, 289, 405, 408]. Thus, 50 % inhibition of methanogens is expected within a range of approximately 50 to 250 mg L^{-1} H_2S at pH values below 7.6, Figure 29. Microorganisms involved can also adapt to high sulphur concentrations, so that severe growth inhibition may only occur at concentrations above 1,000 mg L^{-1} H_2S [237]. However, in an alkaline environment, most of the sulphur is present in its dissociated form, Figure 25. Thus, for pH values above 7.6, an overall sulphide concentration between 600 and 1,200 mg L^{-1} is considered to cause considerable process inhibition [289, 405], Figure 29.



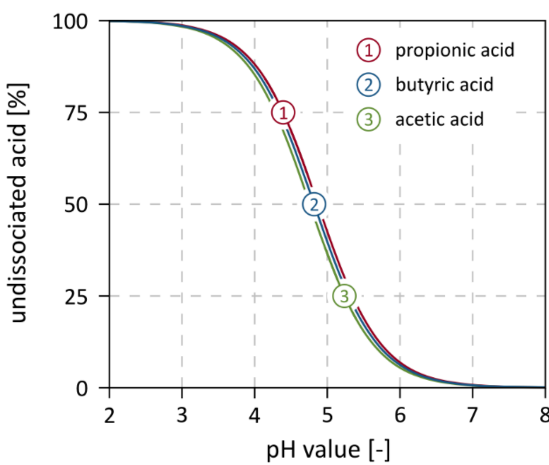
[a] Karhadkar et al. [260] [b] Koster et al. [289] [c] Li et al. [319] [d] McCartney und Oleszkiewicz [352]
[e] O'Flaherty et al. [405] [f] Oleszkiewicz et al. [408] [g] Visser et al. [544] in Lens et al. [315]

Figure 29: Hydrogen sulphide and total sulphide inhibition of methane formation

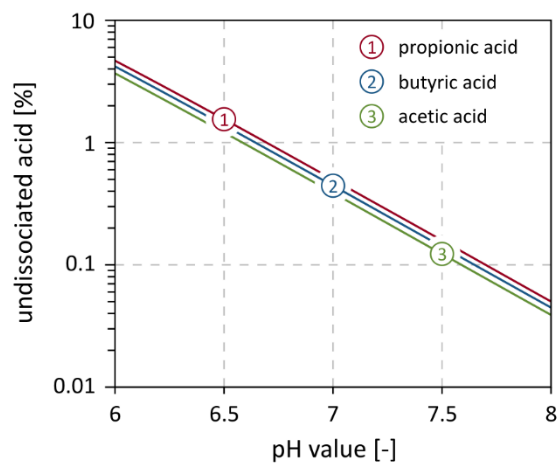
In general, different methods are available to limit inhibitory sulphur concentrations in the liquid and gas phase [131, 240, 425, 569]. In agricultural biogas practice, simple, robust methods of chemical and biological desulphurisation have proven to be effective. Thus, hydrogen sulphide is usually converted to elemental sulphur by injection of air or is bound in sparingly soluble iron sulphides by chemical desulphurisation through the addition of iron salts [145, 240]. Depending on the required gas quality, more complex and expensive procedures, such as activated carbon desulphurisation or gas scrubbing, may also be applied [25, 269].

Organic acids

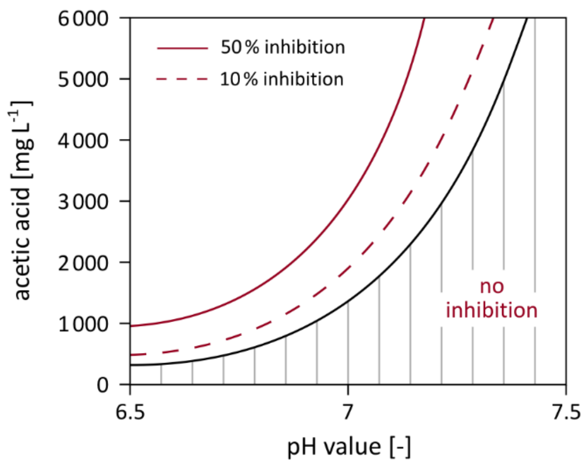
The inhibitory effect of high acid concentrations on the anaerobic degradation process is the subject of various and sometimes controversial scientific investigations and discussions [296, 359]. The low pH value resulting from high acid concentrations is often considered the cause of inhibited process conditions, see Section 2.2.3. However, individual acids can also directly inhibit growth and product formation of the microorganisms involved [4, 350, 359, 370, 609]. The inhibition effect is mainly associated with the undissociated concentration of organic acids [207]. Thus, strength of inhibition varies greatly depending on the specific pH value, Figure 30a. Within a typical pH range between 6 and 8, only a fraction (< 10 %) of the total acid concentration is present in its undissociated and thus inhibiting form, Figure 30b.



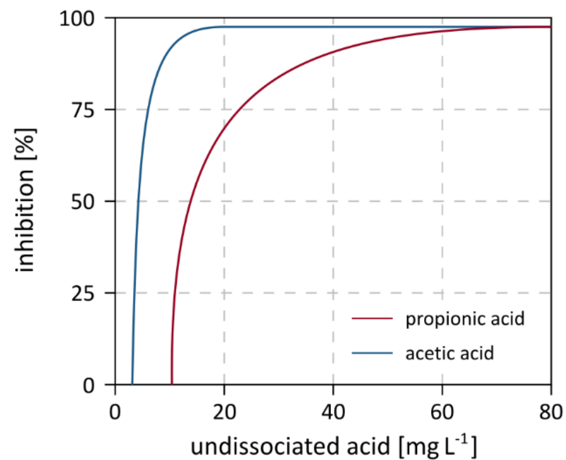
(a) Dissociation equilibrium of different, organic acids in the pH range between 2 and 8



(b) Dissociation equilibrium of different, organic acids in the pH range between 6 and 8



(c) Characteristic inhibitory concentrations of acetic acid in the pH range between 6.5 and 7.5 [297]



(a) Inhibition of undissociated propionic and acetic acid on methane formation [297]

Figure 30: Dissociation equilibrium [283] and inhibitory effects of short-chain organic acids

Acid-forming bacteria are generally more resistant and can tolerate comparatively more acids before product inhibition occurs [505]. Higher propionic acid concentrations have often been shown to inhibit methanogens [4, 29, 223, 400]. High concentrations of acetic acid can also have an inhibitory effect on the breakdown of propionic and butyric acid [9, 166, 184, 350, 527, 609]. In general, a clear distinction can be made between product and substrate inhibition of individual organic acids or inhibiting in-

termediates, Figure 31. Depending of the pH values, critical limits of the total concentration of acetic acid can be defined, Figure 30c. The concentration of undissociated acid determines the strength of inhibition of the affected microorganisms and resulting methane formation, Figure 30d. Usually, the effective concentration for inhibition of methane formation can vary between 1,000 and 3,000 mg L^{-1} total acetic acid [9, 350, 550, 552] or 14 and 80 mg L^{-1} undissociated acid [296, 297, 350]. However, some studies also show stable process conditions at much higher acetic acid concentrations of up to 10,000 mg L^{-1} [4].

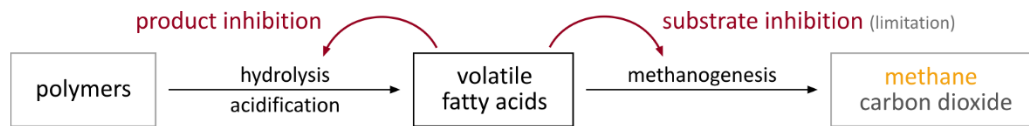


Figure 31: Product and substrate inhibition (limitation) of organic acids [535]

Generally, the inhibitory effect increases with the chain lengths of the various organic acids. Thus, even low concentrations of specific long-chain fatty acids can strongly inhibit the anaerobic fermentation of butyric or propionic acid and methane formation [17, 198, 285, 400, 411, 441].[10]

For a specific (unfavourable) combination of different long-chain fatty acids, synergetic effects can further enhance inhibition by a single acid [285]. Nowadays, the inhibitory effect of long-chain fatty acids is often attributed to the adhesion of individual acids to the cell wall, which influences and limits important transport and protective functions of the cell membrane [233, 416]. Originally, permanent toxic effects and irreversible cell damage of involved acetogenic or methanogenic archaea were assumed [17, 441]. Recent studies have shown that inhibition of long-chain fatty acids is reversible and that the microbiome regenerates even after high acid loads [416].

Suitable adaptation times can also enable the microorganisms involved to adapt to high concentrations of long-chain fatty acids [89, 391, 411, 412]. However, it is still unclear whether the adaptation process is triggered by a structural population change of the microbial community or by phenotypically adapting of the existing population to high acid concentrations (physiological acclimatisation) [411].

Based on individual degradation conditions and adaptation processes, the definition of critical acid concentrations is therefore only of limited use [8]. Nevertheless, depending on the specific substrate composition and operating conditions, different concentration ranges in literature can be applied – at least initially – to characterise an individual reactor sample for process evaluation. In principle, fatty substrates should be introduced slowly and continuously into the fermentation process to enable both adaptation of the microbial community and slow degradation of long-chain fatty acids [89]. Furthermore, high fat concentrations in the substrate can already be reduced during substrate processing by an additional fat separator [400].

[10] Due to their strong inhibitory effect on the anaerobic digestion process, long- and medium-chain fatty acids are frequently applied for food preservation [249, 285] or as a feed additives in animal breeding to reduce methane formation and greenhouse gas emissions in ruminants [54, 124, 339, 498].

3 Process modelling

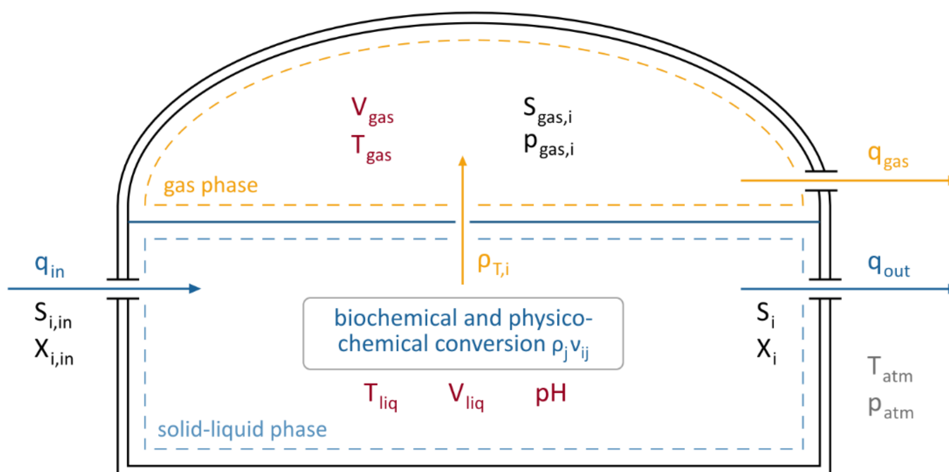
With basic understanding of the fundamentals of biochemical conversion during anaerobic digestion, available methods for process modelling can be derived. This includes biochemical equations, kinetic functions (including inhibitors) and physicochemical dependencies as well as a description of established model structures for simulation of anaerobic processes. In addition, available methods for substrate characterization (model input) and numerical parameter estimation are presented.

3.1 Fundamentals of process modelling

Based on fundamental biochemical and physical dependencies, modelling of material and mass flows offers a range of possibilities to describe influential components and characteristic process phases. The simulation of anaerobic processes is typically limited to the modelling of continuous stirred tank reactors (CSTR).[11] By neglecting the spatial distribution of individual model components, ordinary first-order differential equations can be used for process description [33, 121]. The change of any component over time within the system or phase boundary therefore results in

Change	=	Input – Output	+	Production – Consumption	±	Outgassing.
Derivative		Mass transfer		Biochemical reactions		Phase transition

For balancing a single fermenter, the characteristic components of the solid-liquid or gas phase is illustrate in Figure 32, using the nomenclature of the ADM1 [33].



Temperature T in °C, pressure p in bar, concentration of soluble and gaseous components S in g L^{-1}, concentration of particulate components X in g L^{-1}, volume V in L, volume flow q in L d^{-1}, kinetic reaction or transfer rate ρ in g L^{-1} d^{-1} and stoichiometric coefficients ν in g g^{-1}

Figure 32: Characteristic components for mass balancing a single biogas fermenter

[11] Depending on the reactor design for stirred vessels, fixed bed, fluidised bed or UASB reactors, there are only few process models which describe the spatial derivatives of individual state variables, using partial differential equations (distributed parameter systems) for anaerobic technologies [119, 167, 374, 375, 515, 586].

The change of a state variable S_i (or X_i) in the solid-liquid phase results from the mass balance of all relevant influencing factors, degradation reactions and phase transition processes in

$$\frac{d(V_{liq}S_i)}{dt} = q_{in} \cdot S_{i,in} - q_{out} \cdot S_i + V_{liq} \sum_j \rho_j \nu_{ij} - V_{liq} \cdot \rho_{T,i} \ .$$

Based on the simplified assumption of a volume-stable reaction with a constant filling level and identical inflow and outflow ($q_{in} = q_{out} = q_{liq}$), the time dependence of the reaction volume V_{liq} is eliminated, resulting in Equation 1. In general, direct transition to the gas phase (sublimation) can be ignored (with $\rho_{T,j} = 0$) when balancing particulate components X_i, Equation 2. The gaseous state variables are determined based on Equation 3, presuming that no biochemical reactions and no external inflow of gas occur in the headspace.

General balancing equations

V_{liq} = const. and V_{gas} = const.

Solid-liquid phase

$$\frac{dS_i}{dt} = \frac{q_{liq}}{V_{liq}} \cdot (S_{i,in} - S_i) + \sum_j \rho_j \nu_{ij} - \rho_{T,j} \quad \text{Equation 1}$$

$$\frac{dX_i}{dt} = \frac{q_{liq}}{V_{liq}} \cdot (X_{i,in} - X_i) + \sum_j \rho_j \nu_{ij} \quad \text{Equation 2}$$

Gas phase

$$\frac{dS_{gas,i}}{dt} = -\frac{q_{gas}}{V_{gas}} \cdot S_{gas,i} + \frac{V_{liq}}{V_{gas}} \cdot \rho_{T,j} \quad \text{Equation 3}$$

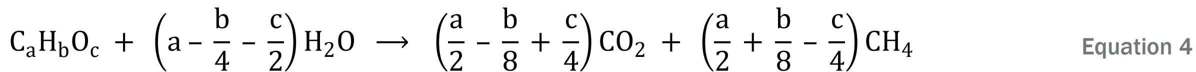
In addition to mass transport via the system boundary, detailed description of stoichiometric pathways, effective reaction kinetics and physicochemical dependencies (dissociation and phase equilibria) are core elements of modelling anaerobic processes.

3.1.1 Reaction equations

There are numerous of biochemical reaction equations that can be applied to describe various metabolic pathways of anaerobic digestion and enable quantitative calculations of specific intermediates and products. In applied research, simple equations have been established to calculate the stoichiometric biogas potential of individual substrates or substrate components [235]. According to BUSWELL [84] and BOYLE [69] Equation 4 and Equation 5 can be used to calculate fermentation products during complete conversion of degradable organic substances. Based on the empirical molecular formula $C_5H_7O_2N$ of microbial biomass, the stoichiometry was extended by MCCARTY [357] to include the proportion of microbial biomass, Equation 6.

Sum stoichiometry

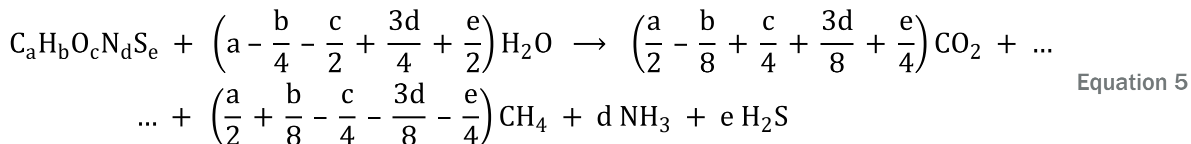
BUSWELL [407]



$$C_aH_bO_c + \left(a - \frac{b}{4} - \frac{c}{2}\right) H_2O \longrightarrow \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4}\right) CO_2 + \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4}\right) CH_4$$

Equation 4

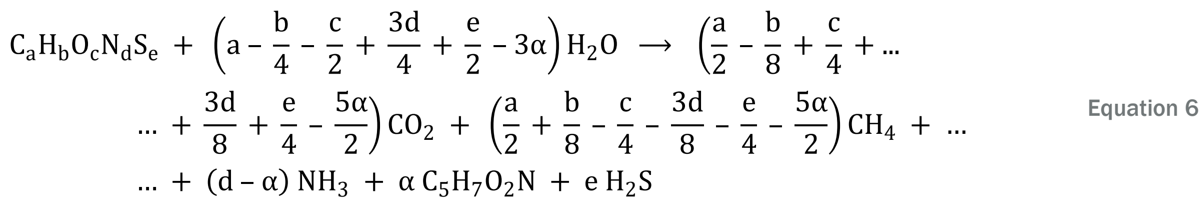
BOYLE [408]



$$C_aH_bO_cN_dS_e + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4} + \frac{e}{2}\right) H_2O \longrightarrow \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8} + \frac{e}{4}\right) CO_2 + \ldots$$
$$\ldots + \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right) CH_4 + d\,NH_3 + e\,H_2S$$

Equation 5

BOYLE [408] | McCarty [409]



$$C_aH_bO_cN_dS_e + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4} + \frac{e}{2} - 3\alpha\right) H_2O \longrightarrow \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \ldots\right.$$
$$\left.\ldots + \frac{3d}{8} + \frac{e}{4} - \frac{5\alpha}{2}\right) CO_2 + \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4} - \frac{5\alpha}{2}\right) CH_4 + \ldots$$
$$\ldots + (d - \alpha)\,NH_3 + \alpha\,C_5H_7O_2N + e\,H_2S$$

Equation 6

Considering thermodynamic and bioenergetic boundaries, individual stoichiometric equations can also be extended to include detailed descriptions of any sub-process and intermediate [355–357]. Thus, numerous reaction equations of the ADM1 [33] can be applied to model the most important degradation phases and to describe individual process conditions by suitable parameterization procedures. During practical modelling, a detailed process characterisation should only be conducted on those reactions and intermediates that are available (or can be calculated) using conventional measurement methods or which describe a growth-limiting process phase or inhibition.

Basically, all methods depend on a realistic characterization of the applied substrate mixture using individual empirical formulas. To transfer the composition of degradable nutrients (carbohydrates, proteins and fats) to the stoichiometric equations, single representative substances or a variety of individual constituents of each nutrient are applied.

With regard to anaerobic digestion of renewable raw materials, detailed reaction equations for the biogas potential of fermentable substrate components of forage and cereal crops have been developed based on extensive data collected on the energetic assessment of fodder in animal nutrition [560–562], which can be used for mass balancing and efficiency evaluation in industrial plant operation [556, 559]. However, individual results cannot be applied for a detailed description of individual process phases or intermediates. Therefore, the stoichiometric basis for detailed simulation of the agricultural biogas process (including different process phases and intermediates) is still based on established process models, such as the ADM1 or preceding models used in waste water technology [176, 338].

3.1.2 Reaction kinetics and growth inhibition

In order to characterise the concentration of individual intermediates and products over time, a fundamental understanding of typical growth of the involved microorganisms is required. Bacteria usually multiply through division, so that the cell population doubles in each generation time (cell division cycle). The cell number of a continuously growing culture is thus exponential in accordance with a geometric progression of 2^n. The typical (idealised) growth curve of a discontinuous culture goes through four characteristic phases [165, 341, 366], as illustrated in Figure 33.

Acceleration phase

Every bacterial culture needs an initial phase (lag phase) to adapt to specific conditions in a new environment. How long it takes to reach the maximum growth rate depends both on the specific properties of the culture and on the availability of essential enzymes and nutrients.

Exponential phase

If unicellular microorganisms divide at a constant rate (minimum generation time), the cell concentration increases exponentially. External factors – such as temperature, pH value or inhibitor concentrations – and the genetic properties of the microorganisms themselves can cause a considerable change in the maximum growth rate.

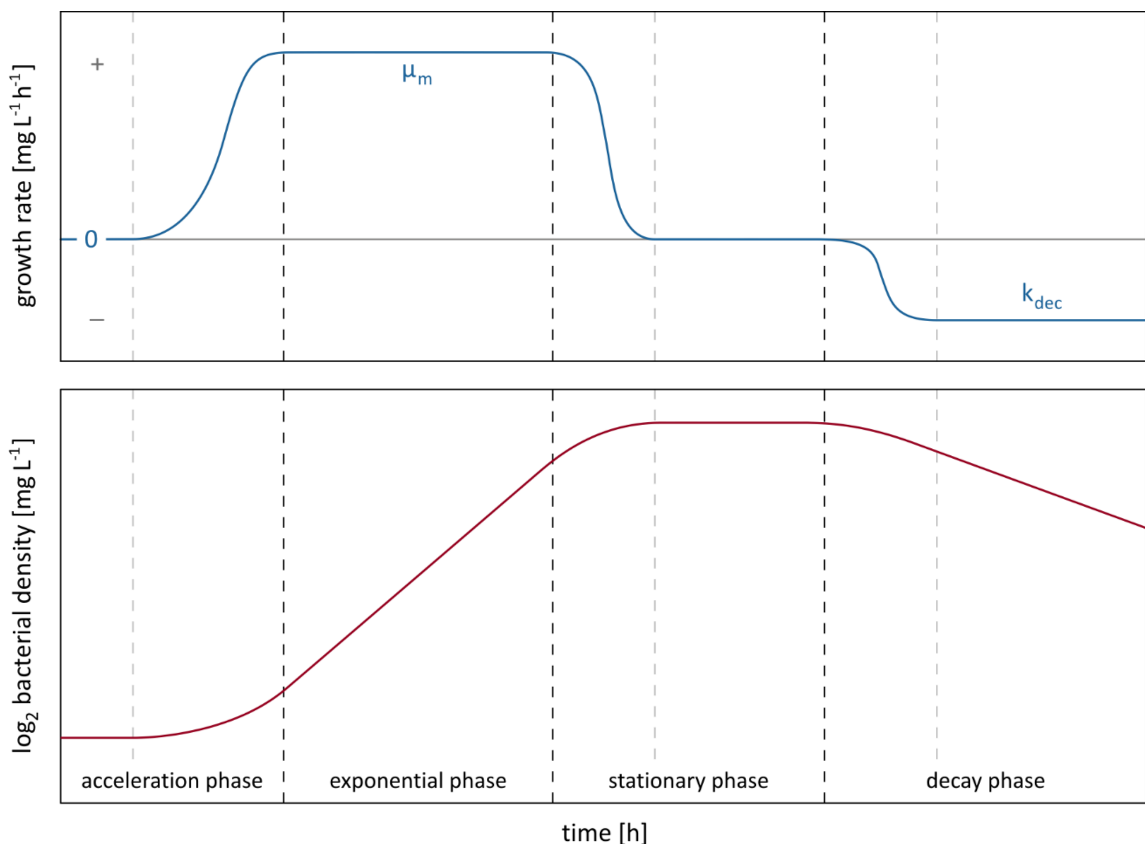


Figure 33: Growth phases of a discontinuous culture [165, 341, 366]

Stationary phase

In a discontinuous culture, growth is limited by the consumption of essential nutrients, a high population density or the accumulation of inhibitory metabolic products. Growth processes occasionally still occur, however their increase of cell number is compensated by cells that are already decaying (cryptic growth).

Decay phase

When all of the medium's nutrient and energy sources are exhausted cells begin to die. Usually the number of living cells also decreases exponentially, but the rate is much slower than in the growth phase.

In a continuous culture, the different life phases occur simultaneously. Therefore, it is necessary to describe the effective growth of individual species, based on characteristic kinetic parameters in order to be able to calculate substrate degradation and product formation of a particular process stage.

Biochemical reaction kinetics

For dynamical modelling of biochemical metabolic processes, a wide range of reaction kinetics can be applied to calculate the progression of the observed variables [176, 415]. The description of the diverse degradation processes involved in enzymatic hydrolysis or decay (lysis) of individual microorganisms is usually characterized by simple first-order reaction kinetics.[12] Thus, degradation and product formation during fermentation of particulate substrates can be directly simulated based on the rate-limiting substrate concentration – regardless of specific biomass growth.

However, biochemical conversion of dissolved substrate components and intermediates, is often described by the metabolism and growth of the microorganisms involved. The specific growth rate of individual species is crucial for modelling individual bacterial populations as well as for the resulting substrate degradation and product formation. Based on the specific substrate, product and biomass concentration or other biological and physicochemical factors (such as pH value, temperature and various inhibitors), numerous growth kinetics were developed for precise depiction of microbial growth behaviour [30, 301]. Many of these mathematical correlations are based on empirical (phenomenological) observations and do not provide mechanistic causality. A small selection of common kinetics – derived from a wide variety of sometimes only slightly varying approaches – has proven to be suitable for practical applications [121, 176, 415], Table 8.

Generally, kinetics chosen to characterise microbial growth rates can be divided into linear and sigmoidal growth functions. The specific growth rate μ_m is primarily influenced by the concentration of the growth-limiting substrate S, Table 8. The established MONOD kinetic [366] also describes biomass growth in relation to the respective substrate concentration S, the maximum growth rate μ_m and half-saturation constant K_S, with $\mu(S = KS) = 0.5\ \mu_m$.

[12] "The first-order hydrolysis function is an empirical expression that reflects the cumulative effect of all the microscopic processes occurring in the digester. (...) A large number of factors affect the rate at which materials can be hydrolysed. Large particles with a low surface-to-volume ratio would be hydrolysed more slowly than small particles. Starches, proteins, and cellulose would certainly be degraded at different rates. (...) Thus the overall hydrolysis function represents the sum of the individual processes taking place in the digesters." [129, pp. 361-362]

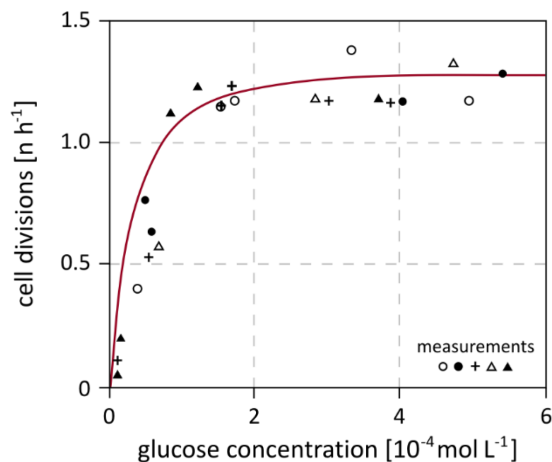
Table 8: Microbial growth kinetics of anaerobic digestion

Linear growth functions				
GRAU [189]	$\mu_m \cdot \frac{S}{S_0}$	BLACKMAN [53]	$\mu_m \cdot \frac{S}{K_S}$ μ_m	$S \leq K_S$ $S > K_S$
Sigmoidal growth functions				
MONOD [363, 366]	$\mu_m \cdot \frac{S}{K_S+S}$	TESSIER [518]	$\mu_m \cdot \left(1 - e^{-\frac{S}{K_S}}\right)$	
MOSER [371]	$\mu_m \cdot \frac{S^n}{K_S+S^n}$	CHEN [96]	$\mu_m \cdot \frac{S}{K_S \cdot (S_{in}-S)+S}$	
CONTOIS [105]	$\mu_m \cdot \frac{S}{B \cdot X+S}$	HALDANE [13, 197]	$\mu_m \cdot \frac{S}{K_S+S+\frac{S^2}{K_I}}$	

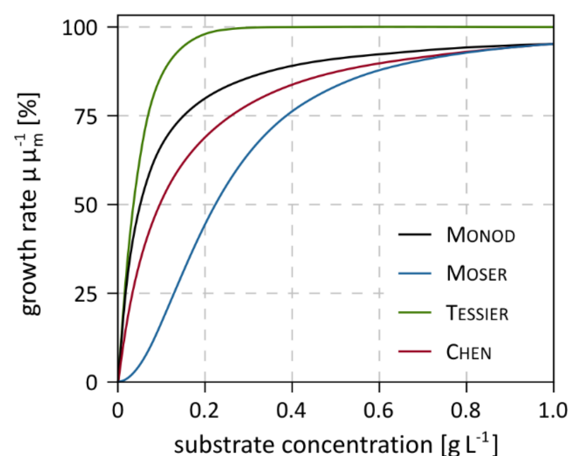
Maximum growth rate in d^{-1}, substrate concentration S in g L^{-1}, inhibition constant K_I in g L^{-1} Half saturation constant K_S in g L^{-1}, microbial biomass concentration X in g L^{-1}, growth parameter B, initial substrate concentration (t = 0) S_0 in g L^{-1} and input substrate concentration S_{in} in g L^{-1}

This growth kinetic is based on the MICHAELIS-MENTEN law [363] that was used to characterise enzyme-catalysed reactions. It was transferred by Monod to describe microbial growth by regression of experimental measurements (without causal evidence), Figure 34a. Thus, other sigmoidal kinetics according to MOSER [371], TESSIER [518] or CHEN [96] clearly allow a precise representation of empirical dependencies as well, Figure 34b.

However, the different functions are unable to describe known effects such as growth reduction at high substrate or biomass concentrations. The HALDANE equation [13, 197] also includes the inhibitory effect of high substrate concentrations, whereas CONTOIS [105] limits the growth rate depending on the biomass concentration, Figure 34c and d. To include the influence of additional inhibitors or growth-limiting substrates, individual kinetics can be extended by suitable inhibition functions.

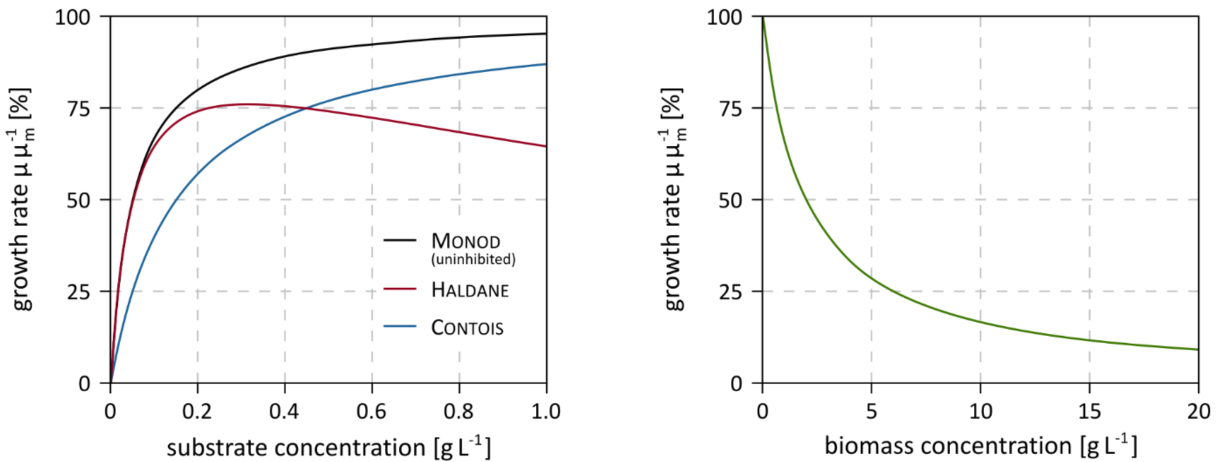


(a) Growth progression (cell divisions per hours) of the pure culture *E. coli* depending on the glucose concentration [366]



(b) Qualitative progression of uninhibited growth functions (K_S = 50 mg L^{-1}, S_{in} = 2 g L^{-1} and n = 2)

Figure 34: Progression of different growth functions of anaerobic digestion (Table 8)



(c) Qualitative course of inhibited growth functions (K_S = 50 mg L-1, K_I = 2 g L-1 and X = 300 mg L-1)

(d) Influence of the biomass concentration on the progression of Contois kinetics (S = 1 g L-1 and B = 0.5)

Figure 34: Progression of different growth functions of anaerobic digestion (Table 8)

Microbial growth inhibition

The anaerobic digestion process is influenced by many (and partly still unknown) factors, which may also strongly inhibit the growth of microorganisms, Chapter 2.2.4. If inhibition is reflected in specific measurements or characteristic process parameters, the effects can also be integrated into available growth functions. In addition to the common inhibitors, such as pH, acid or ammonia concentrations, the influence of ATP supply [43, 365], the availability of the coenzyme NAD [372] and the inhibition of hydrolytic enzyme formation [35] have been modelled in the past. However, even if these possibilities are available from a theoretical perspective, the description of such complex interrelationships, using available laboratory analysis and sensor data, is only of limited use in full-scale plant operation.[13]

In accordance with the development of different growth kinetics, various approaches have been derived to characterize inhibition as well [30, 370, 415]. Concerning the modelled effects, the most important inhibition functions can be divided into three groups, Table 9. Reversible inhibition originates from enzyme kinetics. When applied to microbiological processes, it describes growth inhibition via the influence of individual elements of the characteristic Monod kinetic [52, 312]. Competitive inhibition increases the half-saturation constant and thus slows down the attainment of the maximum growth rate, whereas uncompetitive inhibition influences substrate concentrations and the corresponding maximum growth rate. In the case of the substrate inhibition S_I = S, the uncompetitive inhibition corresponds to Haldane kinetics, Table 9. The most common form of reversible inhibition is non-competitive inhibition, which affects overall Monod kinetics and alters both level and slope of the growth function.

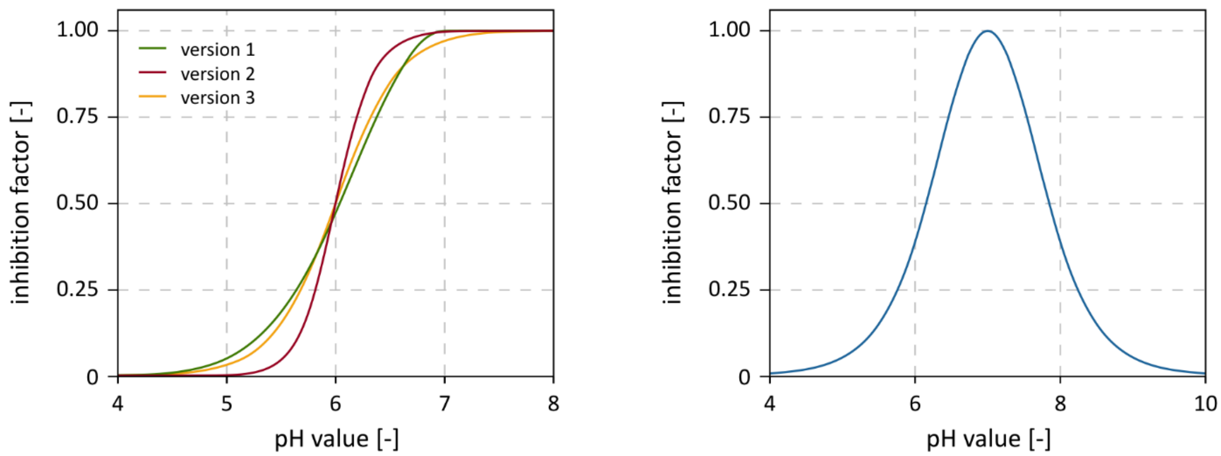
[13] For example, growth inhibition caused by a lack of trace elements can also be implemented in typical process models. However, due to a lack of available measurements the actual influence is difficult to detect or calibrate. Thus, practical application for individual inhibition phenomena is not always guaranteed.

Table 9: Inhibition functions of microbial growth of anaerobic digestion

Reversible inhibition		
Competitive [52, 312]	$\mu = \mu_m \cdot \frac{S}{K_S \cdot \left(1 + \frac{S_I}{K_I}\right) + S}$	
Uncompetitive [52, 312]	$\mu = \mu_m \cdot \frac{S}{K_S + S \cdot \left(1 + \frac{S_I}{K_I}\right)}$	
Non-competitive [52, 312]	$\mu = \mu_m \cdot \frac{S}{(K_S + S) \cdot \left(1 + \frac{S_I}{K_I}\right)}$	
pH inhibition		
Single-sided | version 1 [33, 445]	$I_{pH} = \begin{cases} \exp\left(-3 \cdot \left(\frac{pH - pH_{UL}}{pH_{UL} - pH_{LL}}\right)^2\right) \\ 1 \end{cases}$	$pH < pH_{UL}$ $pH \geq pH_{UL}$
Single-sided | version 2 [337]	$I_{pH} = 1 - \frac{K_{pH}^n}{K_{pH}^n + pH^n}$	$K_{pH} = \frac{pH_{UL}+pH_{LL}}{2}$ $n = pH_{UL} \cdot pH_{LL}$
Single-sided | version 3 [445]	$I_{pH} = \frac{K_{pH}^n}{K_{pH}^n + 10^{-pH \cdot n}}$	$K_{pH} = 10^{-\frac{pH_{UL}+pH_{LL}}{2}}$ $n = \frac{3}{pH_{UL}-pH_{LL}}$
Double-sided [33]	$I_{pH} = \frac{1 + 2 \cdot 10^{0.5 \cdot (pH_{LL} - pH_{UL})}}{1 + 10^{(pH - pH_{UL})} + 10^{(pH_{LL} - pH)}}$	
Substrate inhibition		
Competitive uptake [33]	$\mu = \mu_m \cdot \frac{S}{K_S + S} \cdot \frac{S_I}{S_I + K_I}$	
Secondary substrate [33]	$\mu = \mu_m \cdot \frac{S}{K_S + S} \cdot \frac{S}{S + S_I}$	

Growth rate μ in d^{-1}, maximum growth rate μ_m in d^{-1}, substrate concentration S in $g\ L^{-1}$, inhibition constant K_I in $g\ L^{-1}$, half saturation constant K_S in $g\ L^{-1}$, inhibitor concentration S_I in $g\ L^{-1}$, lower pH limit pH_{LL}, upper pH limit pH_{UL} and inhibition factor I_{pH}

The influence of the pH value can be described by single-sided or double-sided inhibition, Figure 35. Since microbial growth at high pH values is strongly limited by inhibition of ammonia NH_3, left-sided inhibition towards low pH values has often proven to be sufficient [154], Figure 35a. Individual variations of single-sided pH inhibition differ only in their specific mathematical formulation and numerical applicability [445]. Thus, small functional differences can be ignored from a biochemical point of view. Furthermore, the effect of competing or limiting substrates can be integrated into the microbial growth functions of individual process models as well, Table 9.



(a) Progression of different variations of single-sided pH inhibition (pH_{LL} = 5.0 and pH_{UL} = 7.0)

(b) Progression of double-sided pH inhibition according to [33] (pH_{LL} = 6.5 and pH_{UL} = 7.5)

Figure 35: Progression of single- or double-sided pH inhibition of anaerobic digestion (Table 9)

In combination with typical growth kinetics, individual inhibition functions offer a variety of options to influence microbial biomass growth, substrate degradation and biogas formation. Most often it is less important which specific mathematical expression is applied and more important which processes are affected by growth limitation and how these effects can be described by reasonable choice of parameters.

3.1.3 Physicochemical reactions

Modelling of physicochemical processes addresses functional descriptions of non-biological factors and dependencies. In various digestion models, the pH value is typically determined based on the dissociation equilibrium of free ions in the liquid phase. In addition, simulation of phase transition processes between the liquid and gas phases are included in many model structures as well. Precipitation reactions in the solid-liquid phase of substrates or additives with a high concentration of free ions can also have a considerable impact on the anaerobic degradation processes [33].

However, high diversity of potential cations and modelling of corresponding precipitation products - from nucleation to crystal growth, agglomeration and ripening - require detailed kinetic and thermodynamic considerations [194, 526]. As a result, physicochemical processes between the solid and liquid phases are usually neglected in conventional process models. However, as soon as strong precipitants such as Mg^{2+} or $Fe^{2/3+}$ affect the ion balance, potential precipitation reactions must also be taken into account in order to ensure that the pH value and all reaction partners involved are calculated correctly [380, 381, 530].

Dissociation equilibrium and pH value

The pH value is generally calculated from the ion balance of the characteristic dissociation products of organic acids, the carbonate and ammonium buffer, and additional cations or anions, Table 10. Depending on the implemented model components, some models may include additional ions such as SO_4^{2-}, Na^+ or $H_2PO_4^-$ during ion balancing [20, 536]. For simplified and robust process simulation of

agricultural biogas plants, NAUMANN developed a semi-empirical pH model for co-digestion of maize silage and cattle manure [384], Table 10. Depending on the process-specific parameters, the model is best used in a pH range between 6 and 8 for the fermentation of similar substrate combinations.

Table 10: Calculation of the pH value based on ion balancing

Dissociation equilibrium | Ion balance [33]			
Valerate [pK_a= 4.84]	$S_{va^-} = \frac{K_{a,va} \cdot S_{va}}{K_{a,va} + S_{H^+}}$	Butyrate [pK_a= 4.82]	$S_{bu^-} = \frac{K_{a,bu} \cdot S_{bu}}{K_{a,bu} + S_{H^+}}$
Propionate [pK_a= 4.87]	$S_{pro^-} = \frac{K_{a,pro} \cdot S_{pro}}{K_{a,pro} + S_{H^+}}$	Acetate [pK_a= 4.76]	$S_{ac^-} = \frac{K_{a,ac} \cdot S_{ac}}{K_{a,ac} + S_{H^+}}$
Hydrogen carbonate [pK_a= 6.35]	$S_{hco3^-} = \frac{K_{a,co2} \cdot S_{IC}}{K_{a,co2} + S_{H^+}}$	Ammonia [pK_a= 9.25]	$S_{nh3} = \frac{K_{a,IN} \cdot S_{IN}}{K_{a,IN} + S_{H^+}}$
Carbon dioxide	$S_{co2} = S_{IC} - S_{hco3^-}$	Ammonium	$S_{nh4^+} = S_{IN} - S_{nh3}$
$S_{cat^+} + S_{nh4^+} + S_{H^+} - S_{hco3^-} - S_{ac^-} - S_{pro^-} - S_{bu^-} - S_{va^-} - \frac{K_W}{S_{H^+}} - S_{an^-} = 0$			
Semi-empirical pH model [384]			
$S_{Tca} = -S_{vfa} + 2 \cdot p_{co2} \cdot K_{H,co2} - \left(K_{a,ac} + \sqrt{K_{a,ac}^2 + 4 \cdot K_{a,ac} \cdot S_{vfa}}\right) + S_{co3,2^-}$			
$S_{H^+} + \frac{K_{a,co2} \cdot p_{co2} \cdot K_{H,co2}}{S_{Tca} - p_{co2} \cdot K_{H,co2}} + \frac{K_{a,co2} \cdot K_{a,hco3} \cdot p_{co2} \cdot K_{H,co2}}{\left(S_{Tca} - p_{co2} \cdot K_{H,co2}\right) \cdot S_{H^+}} = 0$		with	$S_{vfa} = S_{ac} + S_{pro} + S_{bu} + S_{va}$

[a] Dissociation constant pK_a in mol L^{-1} at 293.15 K (20 °C) according to [417] with $pK_a = -\log_{10}(K_a)$ and S_i in mol L^{-1}.

[b] S_{Tca} as a sum parameter of carbonic acid (H_2CO_2), hydrogen carbonate (HCO_3^-) and carbonate (CO_3^{2-}).

[c] Empirical carbonate concentration $S_{co3,2^-}$ = 0.177 mol L^{-1} and $pK_{a,hco3}$ = 10.32 according to [384].

Phase transition

In chemical engineering, the mass transfer between the liquid and gas phases is typically described by HENRY's law [98, 210]. Accordingly, the steady-state concentration of a soluble component in the liquid phase is proportional to its partial pressure in the gas phase. In an aqueous and unsaturated solution, this linear relationship is defined by the substance-specific and temperature-dependent Henry coefficient K_H according to Equation 7.

$$\bar{S}_{liq,i} = K_H \cdot \bar{p}_{gas,i} \quad \text{for } \bar{S}_{liq,i} \text{ and } \bar{p}_{gas,i} \text{ in steady-state conditions} \qquad \text{Equation 7}$$

Based on the two-film theory developed by WHITMAN [575] and LEWIS [318], this fundamental relationship can be applied to describe the dynamic transfer rate of volatile intermediates and products via the volumetric mass transfer coefficient k_La as illustrated in Equation 8 [33, 139, 510].

$$\rho_{T,j} = k_La \cdot \left(S_{liq,i} - K_H \cdot p_{gas,i}\right) \qquad \text{Equation 8}$$

By selecting appropriate parameters from Table 11, Equation 3 and Equation 8 can be applied to simulate the progression of the resulting gas production from anaerobic degradation of any model substance. This primarily involves the characteristic biogas components of methane, carbon dioxide and hydrogen. Due to its comparatively good solubility (high K_H value), the carbon dioxide content of biogas was already determined on the basis of HENRY's law in the initial models of ANDREWS and GRAEF [15]. For simplification, the methane quantity produced is sometimes defined as insoluble and only included as a volatile component in the gas phase [46, 164].

Table 11: Characteristic HENRY coefficients of anaerobic digestion [460]

	K_H° (298.15 K) [mol L^{-1} bar^{-1}]	ΔH [J mol^{-1}]	ΔHR^{-1} [K]	K_H° (311.15 K) [mol L^{-1} bar^{-1}]
Hydrogen	0.00077	4 157	500	0.00072
Methane	0.0014	13,303	1,600	0.0011
Carbon dioxide	0.035	19,955	2,400	0.025
Hydrogen sulphide	0.1	16,629	2,000	0.075
Ammonia	60	34,089	4,100	34
Acetic acid	4,046	52,381	6,300	1,674

Calculation of the Henry coefficient K_H at a temperature change from 298.15 K (25 °C) to 311.15 K (38 °C) via the enthalpy of solution ΔH using the VAN'T HOFF equation according to [33, 460].

Some models depict the concentration of hydrogen sulphide or ammonia in the gas phase [21, 164, 213, 536]. The hydrogen sulphide content of biogas is often monitored during process and quality control or gas treatment. In consideration of potential inhibition and precipitation, hydrogen sulphide can be included as an additional state variable in the liquid and gas phase for anaerobic digestion of sulphur containing substrates [152]. However, since ammonia (or acetic acid) are predominantly present in a dissolved form (high K_H values in Table 11) and can currently only be detected as trace gases using complex measurement methods [247, 323, 342], phase transition processes of these intermediates are typically disregarded during practical process modelling. If it is possible to continuously analyse even low concentrations of highly dissolved or low volatile intermediates in the gas phase, these process measurements could also be applied as valuable indicators for model validation and process evaluation in the future.

3.2 Model structures

Based on the fundamental concepts for numerical description of the anaerobic digestion process, numerous possibilities are available for the selection of a specific model structure and corresponding set of parameters. For a systematic comparison of existing models, a basic distinction must be made between external requirements and internal model properties, Figure 36. While the external requirements define the practical context for model application, the internal properties specify the characteristics of the resulting model structure. Furthermore, the individual objectives for model application (e.g., for process monitoring, optimization or control) have a considerable impact on the selection of a suitable model structure.

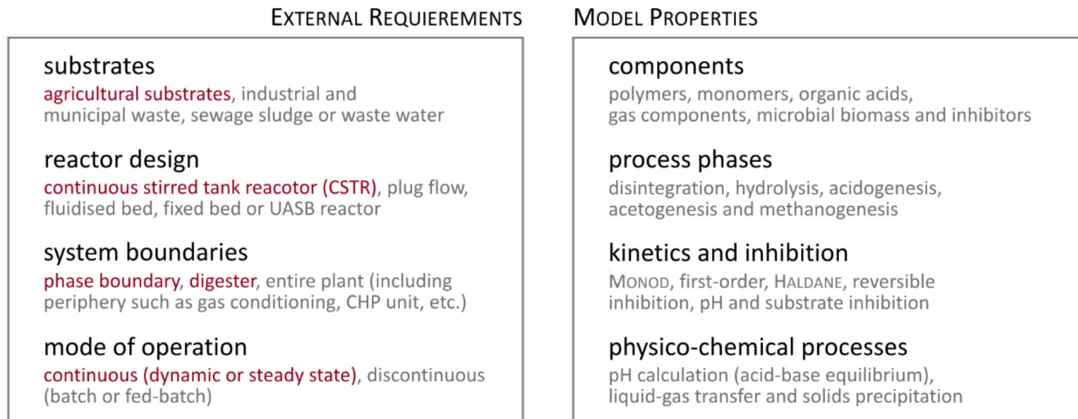


Figure 36: Classification of external requirements and internal model characteristics

3.2.1 Literature survey

Since the first model proposed by Andrews [14], a large number of dynamic models have been developed to calculate various parameters of the anaerobic digestion process, Figure 7. From a modelling perspective, the different simulation models are often evaluated and categorised by the growth-limiting factor or process phase [176, 335, 338]. In practice, however, substrate characterisation – using existing measurement technologies and cost-intensive analyses – has a decisive influence on the applicability and reliability of the applied models. In Figure 37 different model structures are therefore classified based on primary substrate characterisation. Whereas early process models merely describe anaerobic degradation of a single substrate or a single substrate component, such as acetic acid or glucose, subsequent approaches use a complex substrate mixture in the form of undissolved organic composites or individual nutrients to simulate the entire fermentation process. The fundamental stoichiometric degradation pathways of the initial process models are often included in later models as well. Thus, the more complex model structures have often emerged from the chronological development of simple process models. Various publications sometimes only differ in the investigated substrate types or suggest minor changes or extensions to the model structure. As a result, decisive development steps from the first models to the ADM1 can ultimately be traced through a limited number of model approaches.

The first characteristics group of models refers to acetate degradation and includes only the model structure developed by Andrews [14], Table 12. This specific model describes acetoclastic methane formation based on the growth of a single microbial species using Haldane kinetics and also accounts for the dissociation equilibrium between carbon dioxide and hydrogen carbonate at a constant pH value. The description of phase transition process enables the determination of the carbon dioxide concentration in the gas phase. In a later publication by Andrews and Graef the original model structure is extended to include the calculation of varying pH values with the range from 6 to 8 [15].

Modelling of monosaccharide or glucose fermentation forms the second group of models, which can be divided into two classes, Figure 37. While class A only characterises anaerobic glucose degradation to methane using the single intermediate of acetic acid, class B describes the concentration and influence of the extended spectrum of short-chain organic acids. The basic stoichiometric degradation pathways within each class are mostly identical. Thus, structural differences between individual models are mainly caused by the number and combination of the applied kinetic functions (including inhibitors) and the calculation of phase or ion equilibria, Table 12.

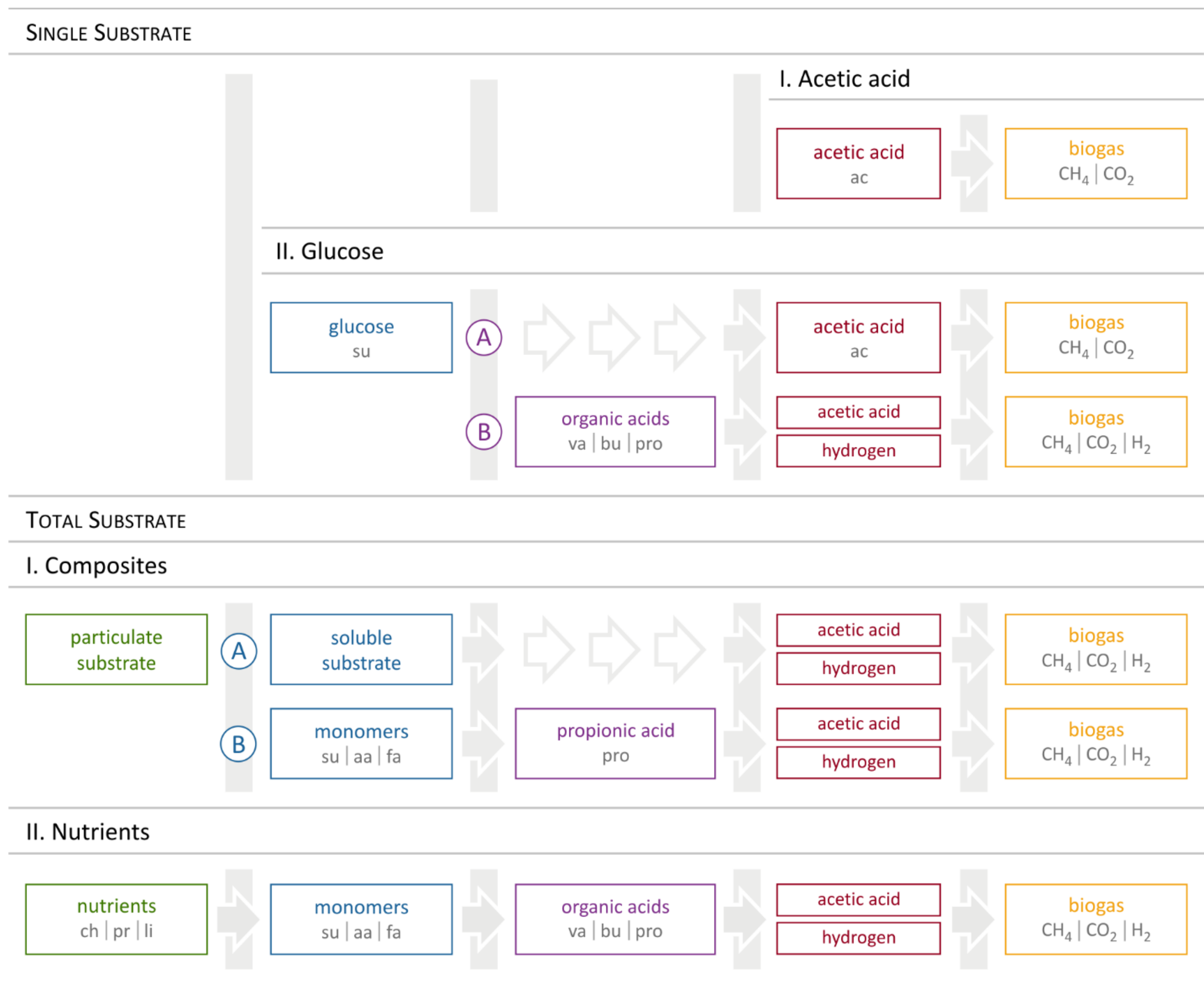


Figure 37: Classification of available process models based on substrate characterisation

Based on investigations of ANDREWS and GRAEF [15, 16], KLEINSTREUER and POWEIGHA [275] developed the first model to simulate glucose fermentation. In addition to simple pH calculations and phase transition processes of carbon dioxide, the model structure also enables the simulation of growth-specific temperature dependencies. The model structure proposed by MOLETTA et al. [365] also includes the definition of energetic boundaries during anaerobic glucose degradation and specifically differentiates between substrate uptake for maintenance and the actual growth of living microorganisms. KIELY et al. [270] enhanced the basic model structure by including ammonia inhibition and a detailed ion balance for iterative determination of the pH value.

Similar differences can be observed in the second class when individual intermediates of glucose fermentation are described. The HILL model [212] depicts the basic kinetic and stoichiometric reaction pathways for the formation and degradation of different organic acids and also includes growth inhibition at high acid concentrations. The model concept of MOSEY [372] focuses on the detailed description of kinetic boundaries during anaerobic oxidation of glucose and characterises the growth limiting influence of the availability of NAD in its oxidised form NAD^+ via the hydrogen partial pressure in the gas phase.

Table 12: Properties of characteristic models for anaerobic digestion of single substrates

Modell	Polymers	Monomers	Acids	Gases	Inhibition	Process steps	Microbial species	Temperature	pH value	Phase transition	Reference unit
I. Acetic acid											
ANDREWS [15, 16]			Ac	CH_4 CO_2	Ac	2	1	○	●	●	mol
II. Glucose											
A. Glucose (Su → Ac)											
KLEINSTREUER [275]		Su	Ac	CH_4 CO_2	Ac Toxic [a]	4	2	●	●	●	mol
MOLETTA [365]		Su	Ac	CH_4	Ac	4	2	○	○	○	kg
KIELY [270]		Su	Ac	CH_4 CO_2	Ac NH^3	4	2	○	●	●	mol kg
A. Glucose (Su → VFA)											
HILL [128, 212]		Su	Bu Pro Ac	CH_4 CO_2 H_2	VFA	11	5	○	○	○	kg
MOSEY [b] [372, 428, 451]		Su	Bu Pro Ac	CH_4 CO_2 H_2	pH H_2 [c]	10	5	○	○	○	mol
COSTELLO [b] [108, 109, 264, 444]		Su	Bu La Pro Ac	CH_4 CO_2 H_2	pH H_2 [c] VFA	12	6	○	●	●	mol
KALYUZHNYI [254–256]		Su	Et [d] Bu Ac	CH_4 CO_2 H_2	pH H_2 [c] Et VFA	10	5	●	●	●	mol kg

[a] The model includes inhibition of unspecified toxic substances.

[b] Subsequent model publications of ROZZI et al. [449], PULLAMMANAPPALLIL et al. [428], RUZICKA [451], KELLER et al. [264] or ROMLI et al. [444] also based on the fundamental stoichiometry of MOSEY [372] and characteristic extensions of COSTELLO et al. [108]. Thus, these (most often identical) model structures are not presented individually.

[c] The partial pressure in the gas phase is used as a measurable indicator for the oxidation state of the coenzyme (redox equivalent) NAD which has a direct influence on the specific reaction rates during glycolysis (EMBDEN-MEYERHOF-PARNAS-Weg) and subsequent fermentation.

[d] The monohydric alcohol ethanol (Et) is assigned to the group of organic acids as a product of acidogenesis.

COSTELLO et al. [108] and PULLAMMANAPPALLIL et al. [428] independently extended the model by MOSEY to include iterative pH calculation and additional inhibitors. The two model structures differ only in the description of the effective dissociation equilibria and the selection of specific inhibition functions of individual organic acids. Furthermore, Costello et al. add lactic acid and lactate, as additional intermediates of acidogenesis. The model developed by KALYUZHNYI [254] is also based on the investigations of MOSEY [372] and additionally describes the specific degradation pathways of alcohol fermentation (ethanol fermentation). In addition to a detailed calculation of the pH value, the model also reflects the influence of various inhibitors [20, 108, 112, 372] on glucose fermentation.

In parallel to the simulation of anaerobic fermentation of single model substances, modelling of the entire metabolic chain during fermentation of complex substrates evolves. In Figure 37, the first group of models characterises the substrate mixture by a single sum parameter for (particulate) organic substrate, while the second group uses individual nutrients of carbohydrates, proteins and lipids for a more detailed description of the substrate composition. Bases on the different intermediates, the first group can be divided into two classes. Class A only differentiates between dissolved and undissolved organic substrate, whereas class B further distinguishes between dissolved monosaccharides, amino acids and long-chain fatty acids. Since the models are already applied in wastewater technology and as there is no specific empirical formula for the stoichiometric description of complex and diverse substrates, the chemical oxygen demand (COD) is often used as the reference unit for substrate characterisation.

A few years after the model of ANDREWS and GRAEF was first published [15], HILL and BARTH present a comprehensive model [213] for simulating the characteristic process phases of fermentation, Table 13. The model describes anaerobic degradation of an organic substrate via dissolved monomers and organic acids to methane. In addition to the iterative determination of the pH value and phase transition processes, the model also includes temperature-induced changes in microbial growth rates and HENRY coefficients. The models of SMITH et al. [495] and NEGRI et al. [385] are mainly based on the combination of already published model components and were originally developed to simulate a plug-flow reactor or multi-stage plant concept.[14] Both model approaches differentiate between rapidly and slowly degradable substrate components, whereby NEGRI et al. additionally model the hydrolysis rate as a function of the available surface of particulate substrate components and the number of hydrolytic enzymes.

Nearly a decade later, BERNARD et al. [46] consciously simplifies existing model structures, to enable the development and evaluation of model-based monitoring and control concepts. Therefore, anaerobic degradation of organic substrate to biogas is described by a single intermediate of volatile organic acids and modelled using a process-specific (empirical) stoichiometry. BERNARD et al. deliberately avoid detailed stoichiometric balancing and simulate the fermentation process by considering only COD and mass conservation. In addition to a simplified ion balance, the resulting model structure only contains the phase transition processes of carbon dioxide, while methane production is described directly in the gas phase due to its comparatively low solubility (see Section 3.1.3).

Within the second class (B. Monomers in Table 13), both BRYERS [79] and SIEGRIST et al. [491, 492] distinguish between simple sugars, amino acids and long-chain fatty acids in dissolved hydrolysis products, to enable a detailed description of propionic and acetic acid. Both model structures are based on the degradation pathways of sewage sludge fermentation proposed by GUJER and ZEHNDER [192]. The model developed by BRYERS includes algebraic calculations of the pH value and the phase equilibrium of carbon dioxide, whereas SIEGRIST et al. additionally consider phase transition processes of all gas components as well as other growth-specific inhibitors and temperature dependencies. The comprehensive model of VAVILIN et al. [536] applies empirical formulas to characterise the stoichiometric degradation pathways of dissolved monosaccharides, amino acids and long-chain fatty acids.

[14] Since the modelling methods used to simulate the specific fermenter and plant configurations are only based on the theory of stirred tanks reactors, the model structures described can also be applied to simulate conventional biogas fermenters [376, 377].

Table 13: Properties of characteristic models for anaerobic digestion of complex substrates

Modell	Polymers	Monomers [a]	Acids	Gases	Inhibition	Process steps	Microbial species	Temperature	pH value	Phase transition	Reference unit
I. Composites											
A. Soluble Substrate											
HILL and BARTH [204, 213, 494]	xOS	sOS	VFA	CH_4 CO_2 NH_3	VFA NH_3	5	2	●	●	●	mol kg
SMITH [b] [495]	xOS	sOS	VFA	CH_4 CO_2	VFA	6	2	○	●	●	COD mol
NEGRI [b] [376, 377, 385]	xOS sOS	sOS	VFA	CH_4	pH	7	3	○	○	○	Kg
BERNARD [30, 46]	OS		VFA	CH_4 CO_2	VFA	2	2	○	○	○	COD mol
B. Monomers											
BRYERS [79]	xOS	AS [c] Fa	Pro Ac	CH_4 CO_2 H_2		9	3	○	●	●	COD mol
SIEGRIST [491, 492]	xOS	Su Aa Fa	Pro Ac	CH_4 CO_2 H_2	pH H_2 Ac	11	5	●	●	●	COD
VAVILIN [454, 536]	xOS	Su Aa Fa	Pro Ac	CH_4 CO_2 H_2 H_2S NH_3	pH H_2 NH_3 H_2S Pro	15	7	●	●	●	kg
II. Nutrients											
ANGELIDAKI [20, 20, 265, 333]	Ch Pr Li	Su Aa Fa	Va Bu Pro Ac	CH_4 CO_2 H_2S	pH VFA Fa NH_3 IN	18	8	●	●	●	kg
BATSTONE [35, 36]	Ch Pr Li	Su Aa Fa	Va Bu La Pro Ac	CH_4 CO_2 H_2	pH H_2 [d]	21	9	○	●	●	mol
ADM1 [e] [33, 34]	Ch Pr Li	Su Aa Fa	Va Bu Pro Ac	CH_4 CO_2 H_2	pH H_2 NH_3 IN	19	7	●	●	●	COD mol

[a] The group of monomers also includes soluble organic substances (sOS), as a collection of individual monomers.

[b] The model distinguishes between rapidly and slowly degradable organic substrate components.

[c] Dissolved intermediates of amino acids and monosaccharides are summarized in a single component (amino acids and simple sugars, AS).

[d] Following the model approach of MOSEY [372], BATSTONE et al. [35, 36] also use hydrogen partial pressure to regulate both reaction rates and stoichiometric composition of intermediates during acido- and acetogenesis.

[d] The ADM1 [33, 34] includes an additional disintegration step (based on first-order kinetics) to depict distribution of particulate composites into carbohydrates, proteins and lipids.

The model structure contains an extended ion balance, detailed gas composition and various inhibitors as well as the competitive reactions of sulphate-reducing bacteria on anaerobic degradation of propionic and acetic acid. Furthermore, it depicts temperature dependencies of individual growth parameters and the influence of extracellular enzymes on the hydrolysis rate.

Process models of the last group (II. Nutrients in Table 13) characterise anaerobic degradation of the characteristic nutrients and provide the basis for numerous investigation on modelling anaerobic processes over the past decades. Based on the stoichiometry proposed by Hill [212], Angelidaki et al. [18, 21] develop a first comprehensive model to provide a complete description of carbohydrate, protein and lipid fermentation. In addition to the detailed calculation of the pH value, phase transition processes and growth-specific temperature dependencies, the model protein (gelatine) also enables the simulation of dissolved and gaseous hydrogen sulphide. Beside numerous inhibition and limiting functions, the model also includes inhibition of high acid concentrations on enzymatic hydrolysis (product inhibition) and the influence of long-chain fatty acids on acidogenesis and acetogenesis (substrate inhibition). Batstone et al. [35, 36] extend the model structure of Mosey [372] or Costello et al. [108] by adding the anaerobic degradation pathways of proteins and lipids [432]. Following investigations of Mosey, Batstone et al. also use the hydrogen partial pressure in the gas phase to regulate both the specific reaction rates and the stoichiometric distribution of individual intermediates during of acido- and acetogenesis. Furthermore, the model includes a differentiated description of hydrolysis rates based on the effective enzyme concentration [232, 239] as well as a charge balancing of dissociated ions to calculate the pH value. To provide a uniform model structure, the ADM1 [33, 34] by the *IWA Task Group for Mathematical Modelling of Anaerobic Digestion Processes* combines established model concepts. With numerous scientific applications, the ADM1 defines the standard of anaerobic process modelling until today, Figure 7. In addition to the characteristic process phases from hydrolysis and/or disintegration to acetoclastic and hydrogenotrophic methanogenesis, the model includes different physicochemical reactions for iterative calculations of the pH value, phase transition processes and temperature dependencies. The detailed model report also offers various options to extend the basic model structure by adding nitrate or sulphate reduction, the inhibition of long-chain fatty acids and additional precipitation reactions as well as the stoichiometric degradation pathways of homoacetogenesis, acetate oxidation and alternative reaction products from acidogenesis of monosaccharide.

The available publications on anaerobic process modelling provide a detailed knowledge base for selecting or developing a suitable model structure for a specific simulation task, Figure 36. Individual models generally apply Monod or Haldane kinetics for the description of microbial growth (and substrate degradation). Enzymatic hydrolysis and biomass decay are typically described by first-order kinetics. The stoichiometric degradation pathways and characteristic intermediates are also largely identical among individual model groups, Figure 37. Due to the representative model substrate (glucose), various degradation mechanisms during fermentation of dissolved carbohydrates are subject of numerous investigations. Anaerobic degradation of proteins and lipids is only described in detail by a few fundamental model structures, which sometimes differ greatly in the applied reference substances and composition of nutritional groups. Thus, even the ADM1 contains a variable stoichiometry for amino acid degradation via coupled Stickland reactions [33, 433], which however can only be determined with great effort based on the specific amino acid composition of individual proteins. In addition to the selection or identification of suitable kinetic functions and stoichiometric yield coefficients, available model structures

primarily differ in type and number of the depicted inhibitory and physicochemical effects. Therefore, simulation results of different models can vary greatly for each process state, depending on the applied inhibition functions and temperature dependencies.

With regard to their practical application, individual models can be characterised by the applied reference unit. Depending on a mol-, mass- or COD-basis of each model structure, the required unit of individual model components can be determined via corresponding conversion factors on the basis of the molar mass or COD content of each component [102, 281, 331, 337, 474].

3.2.2 Model simplification

For application on full-scale anaerobic digestion plants WEINRICH [555] proposes a systematic procedure for successive model simplification of a mass-based ADM1. Individual model structures greatly differ in their number of implemented process phases, characteristic components and required parameters. Simplified model variants combine nutrient degradation and biogas formation based on first-order sum reactions, whereas complex model structures describe individual degradation pathways and intermediates during acido- and acetogenesis in detail. In regard to available measurements on agricultural anaerobic digestion plants [169], simplified model structures show clear advantages for practical application, due to the small number of model parameters required and suitable system characteristics. Thus, individual model simplifications can be applied as robust estimators to predict gas production rates for plant design, process monitoring and control during full-scale plant operation. Complex model variants enable a precise description of characteristic intermediates and allow for a detailed state analysis based on microbial growth conditions (including relevant inhibitors).

Further details on model development and stoichiometric analysis of different simplification of a mass-based ADM1 for process simulation of anaerobic biogas plants are provided in the following research paper:

Weinrich, S., Nelles, M. (2021): Systematic simplification of the Anaerobic Digestion Model No. 1 (ADM1) – Model development and stoichiometric analysis. Bioresource Technology. Vol. 333, 125124.

https://doi.org/10.1016/j.biortech.2021.125124

3.3 Substrate characterisation

Precise laboratory measurements and sensor data of biogas plants is vital for reliable process analysis and also has a decisive influence on model application. Thus, error-free experimental data are required for optimal estimates of unknown model parameters and for realistic simulation results of specific process characteristics. From model development and experimental design to parameter estimation and validation, system theory of dynamic models provides a wide range of effective methods for direct identification of individual parameters. Figure 38.

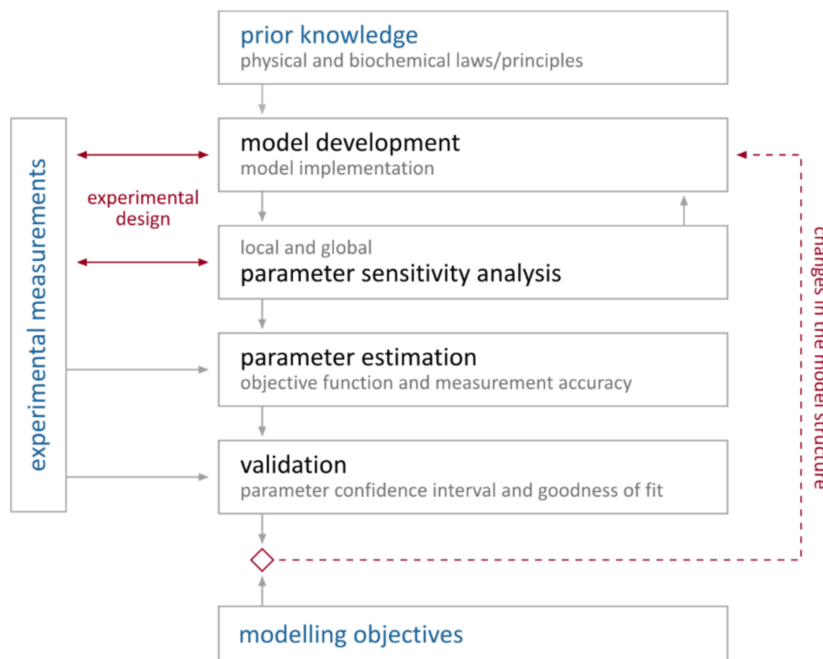


Figure 38: General procedure for parameter identification of dynamic models

Parameter sensitivity on simulation results and parameter estimation can be determined by local or global sensitivity analysis [431, 455–457, 523]. Thus, individual methods can be applied for parameter selection, optimal experimental design (OED) or further model simplification [23, 218, 219, 426, 465]. Considering a specific objective function and measurement accuracy, numerical optimisation procedures enable precise estimation of unknown model parameters [121, 140, 238, 548]. Parameter estimates can be validated based on specific confidence intervals and corresponding model efficiencies. According to the original objective for model application, additional changes of the proposed model structure (including re-evaluation of the revised model and parameter estimates) may be required. Thus, all methods for process simulation of anaerobic digestion rely on the quality of available measurements of the examined laboratory experiment or industrial plant concept.

Generally, every plant operator can choose from a wide range of measurement methods for evaluation of process stability and degradation efficiency during regular plant operation, Table 14. Currently, there is no general standard for adequate measurement equipment on agricultural biogas plants. Based on general recommendation and depending on plant size, operation mode and substrates used, it is within the responsibility of the plant operator to define a suitable measurement scenario for the specific plant concept [133, 186, 209, 388]. Many investors avoid suitable measurement equipment for financial reasons.

Thus, many agricultural biogas plants are often insufficiently equipped with available measurement technologies [145, 300, 324, 553]. In addition, there is often a lack of systematic documentation and evaluation of acquired measurements, so that valuable information is lost or remains largely unused [300, 580].

Table 14: Measurement methods and analytical procedures for process monitoring [320, 324]

Component	Measuring methods [a]	Sensor [b]
Liquid-solid phase		
Mass of solid substrates	Weighing cell	●
Volume of liquid substrates	Inductive flow measurement	●
Total solids	Residue after drying [c]	○
Volatile solids	Loss on ignition [c]	○
Nutrient composition	Weender or VAN SOEST analysis [c]	○
Total VOA	Titration	○
Organic Acids	GC and HPLC	○
VOA/Buffer	Titration [d]	○
pH value	pH electrode [d]	●
Redox potential	Redox electrode	●
Ammonium Nitrogen	Distillation, photometry	
Digester temperature	Temperature sensor	●
Elemental composition	Elemental analysis (combustion analysis)	
Biogas potential	Experimental biogas potential test	
Trace elements	IC, AAS, ICP-OES and ICP-MS	
Gas phase		
Biogas flow rate	thermal, physical or mechanical techniques [e]	●
Methane content	IR spectroscopy, heat tone, FID or GC	●
Carbon dioxide content	IR spectroscopy or GC	●
Hydrogen content	electrochemical analysis, heat tone or GC	●
Hydrogen sulphide content	Electrochemical analysis, UV spectroscopy or GC	●
Biogas temperature	Temperature sensor	●

[a] Atomic absorption spectrometry (AAS), flame ionisation detector (FID), gas chromatography (GC), high performance liquid chromatography (HPLC), ion chromatography (IC), inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), infrared (IR) und ultraviolet (UV).

[b] Online sensor: ● available | ○ generally available, but not state of the art in practice on agricultural biogas plants.

[c] Standardised application of near-infrared spectroscopy (NIRS) for chemical characterisation of animal feed.

[d] Indirect detection of individual parameters by spectroscopic methods based on process-specific calibrations [342]

[e] Thermal techniques: calorimetric flow meter; physical techniques: dynamic pressure sensor or fluidistor oscillator; mechanical techniques: drum, bellows or impeller gas meter.

As a result, many biogas plants are only operated at low organic loading rates or fall victim to process failure during engaged operation and long-term overloading. In regard to reliable and flexible energy supply through renewable energies, the data acquisition will play a more decisive role in the future

[324, 581, 582]. Many characteristic variables and process indicators are still only available on a discontinuous basis (offline), Table 14.[15] In addition to extensive laboratory analyses, inexpensive screening tests are also available to the user, for example to obtain initial information on the FOS-TAC ratio (titration) or the ammonium nitrogen content (photometry) in the digester. Nevertheless, many measurements are only determined on a monthly basis or in the event of a process failure and therefore, do not provide a reliable basis for process monitoring [580]. Furthermore, many agricultural biogas plants lack specific information about the exact amount and specific properties of the substrates used [553, 580], preventing precise process balancing and evaluation. Reliable statements on the concentration, activity or composition of the microbial community and the resulting evaluation methods for process monitoring are also missing. On the one hand, process modelling has to manage with a limited quantity and quality of the available measurements. However, on the other hand it also has to define specific requirements for improvement of accuracy, variety and frequency of measured data, which could decisively improve simulation or balancing results.

3.3.1 Chemical substrate analyses

As a decisive link between the theoretical model structure and the properties of real substrates, substrate characterisation and resulting model input has a considerable influence on the validity of model calculations. It is important to select a suitable measurement method that enables a detailed description of applied substrates. Furthermore, measurement results must be transferred to existing model components. Depending on the substrate type and available analytical procedures, there are various approaches to assign characteristic measurement results to individual state variables (model components) of relevant process models. Examples of established methods based on feed and wastewater analysis, parameter identification from experimental batch tests, model interfaces and literature references are described below.

Animal feed analysis

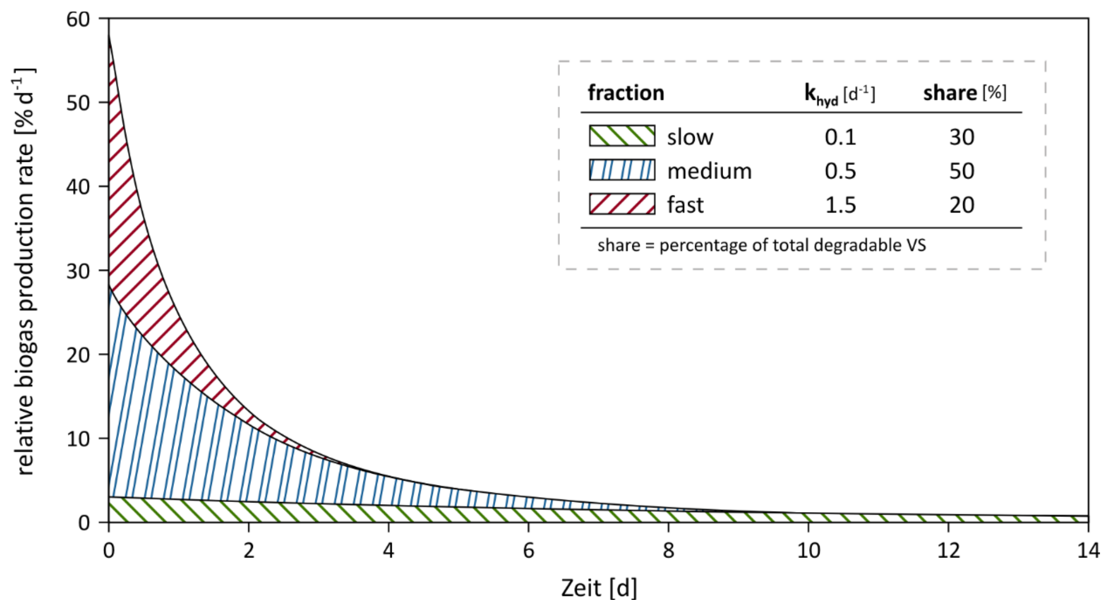
During fermentation of energy crops and agricultural residues, substrate composition of characteristic nutrients is usually determined by the Weender analysis [160, 273, 322]. By converting volatile solids to a corresponding COD equivalent, the input fractionation of carbohydrates, proteins and fats can be calculated for direct application of the original ADM1 [281, 337, 576, 604]. The extended feed analysis according to van Soest [531] enables a differentiated description of different structural carbohydrates (structural substances such as cellulose, hemicellulose or lignin), which can also be used for detailed input characterisation [336].

Parameter identification (batch test)

The substrate-specific progression of biogas or methane production during discontinuous fermentation in anaerobic batch tests can be described by the superposition of individual kinetics of substrate fractions that degrade at different rates, Figure 39. High gas production rates in the first hours and days of an experiment are used to identify rapidly degradable substrate compo-

[15] Bioprocess technology also includes a wide variety of spectroscopic and electrochemical methods [26, 221, 247, 342], which can be used for continuous (online) measurement of individual process variables, Table 14. These sensors have been used in their initial application to monitor biogas plants in the context of applied research projects. Since these methods are often associated with high procurement costs and specific expert knowledge (specialist personnel), they are currently not part of the standard repertoire of measurement technologies on agricultural biogas plants [247, 342].

nents (such as dissolved sugars and amino acids), whereas a low gas production rate at the end of the experiment provides information on slowly degradable constituents [181, 593]. However, the content of organic acids and the composition of individual fractions still need to be determined by chemical analysis. A reasonable application of this method strongly depends on the characteristic gas production curves of individual substrates and the accuracy (and transferability) of the applied batch tests. Further investigations also show the potentials (and limitations) of simultaneous identification of individual hydrolysis constants and degradable substrate fractions based on measured gas production rates during semi-continuous plant operation [40, 230].



Biogas production rate in relation to the total biogas potential of the substrate

Figure 39: Contribution of different kinetic fractions to the (relative) biogas production rate

Wastewater analysis

Detailed balancing combined with chemical properties of individual model components (elementary composition, oxidation state and charge) enables derivation of model-specific feed compositions from typical measurements used in wastewater technology [231, 274, 597].[16] In addition to the share of carbohydrates, proteins and lipids, the empirical sum formula ($C_aH_bO_cN_d$) of the complex substrate [274] or the concentration of simple sugars and short-chain fatty acids in the model input [597] can be determined as well. This method significantly depends on the selection of suitable reference substances, which sometimes differ greatly from the actual substrate composition and resulting biochemical properties.

Model interfaces

In order to simulate entire wastewater treatment plants, suitable interfaces were developed for coupling models of individual aerobic and anaerobic process stages [106, 398, 533]. For example, the input data required for sewage sludge fermentation (ADM1) can be derived from the sim-

[16] For example, the organic nitrogen concentration can be used to determine the corresponding protein content in the feed. The characteristic oxidation state of tripalmitin ($C_{51}H_{98}O_6$) [274] and the specific phosphorus content of phospholipids ($C_7H_{11}PO_8^-$) [597] allow for the calculation of the lipid fraction. The proportion of carbohydrates can finally be determined by subtracting the protein and lipid content from the available organic matter.

ulation results of biological wastewater treatment (*Activated Sludge Model*, ASM) [244, 448, 598]. However, apart from theoretical model investigations, the fundamental problems with a reliable characterization of fermentable substrate components or primary model input of the overall plant concept remain unsolved.

Literature references

Sometimes missing information on the model input is supplemented by practical reference values from available literature [102]. The simulation results more or less reflect the actual condition of the plant based on the process conditions and substrates used. Depending on the process conditions and substrates applied, the resulting simulation results more or less reflect the specific state of the plant.

In addition to the characterisation of organic compounds, all methods need to distinguish between fermentable and non-fermentable substrate components. Thus, stoichiometric and kinetic reaction equations only relate to nutritional components, which are actually degradable under anaerobic conditions. Generally, the established division between organic and inorganic dry matter (ash) can be extended by the definition of degradable volatile solids (DVS) [558, 559, 563]. For a differentiated model description, the total DVS has to be assigned to individual degradable nutrients of carbohydrates, proteins and lipids.

An initial estimate can be achieved by direct determination of non-degradable nutrient components such as lignin. Depending on the substrates applied and available analytical procedures, only the minimum share of non-degradable components (maximum DVS) is measured. Thus, further correction of measured nutrient concentrations is often necessary.[17] Additionally, the results from discontinuous or semi-continuous laboratory experiments can be used to determine degradable substrate components by applying suitable balancing and modelling techniques [40, 230]. However, the validity of this approach is strongly affected by the applied experimental procedures and stoichiometric model assumptions. Thus, it can be difficult to determine whether individual substrate components cannot be completely degraded due to specific operating conditions or the applied model structures, or whether they actually reflect non-degradable substances. Furthermore, numerous dependencies between various model parameters allow only the definition a reasonable value range of DVS [40]. Due to the small number of available measurements (gas volume and gas composition), a detailed and reliable definition of degradable nutrient classes is not possible without additional analysis [181].

In addition to direct measurement of non-fermentable substances or estimation of degradable substrate components on the basis of experimental data, the results of digestion tests from animal feed science can be applied to characterise fermentable nutrient components in renewable raw materials [474]. Thus, KEYMER and SCHILCHER [266, 267] use digestibility quotients from the DLG feed values for ruminants [235, 304] as a basis for the evaluation of degradable substrate components to determine the maximum biogas potential of various agricultural substrates.

[17] LÜBKEN et al. [337], WICHERN et al. [576] and KOCH et al. [281], for example, only consider the share of non-degradable carbohydrates in addition to lignin, whereas the concentration of crude proteins and lipids is defined as being completely fermentable. The content of non-degradable carbohydrates is estimated by means of a mass balance of total VS.

However, without additional adjustments direct transformation of individual coefficients from the feed value table is neither possible nor expedient for achieving a realistic calculation of the biological fermentability of individual nutrients. According to WEIßBACH, "the primary deficiencies of the DLG feed value table and its use for this purpose are as follows:

- The analytical results and digestibility ratios for silage are mainly based on data determined without correction of total solids (TS) for volatile matter. [...] Thus, the digestibility for silage is generally too low.
- The data on the lipid content of silage are mainly based on results obtained using an outdated method in which some of the fermentation products are mistakenly measured as lipids. Therefore, the data on the crude lipid content of silage is generally too high.
- As is customary and useful in animal nutrition, the information on individual degradability quotients only relates to the apparent digestibility. Thus, they are not corrected for metabolic nutrient excretion of the animals and record the biodegradable portion of individual nutrients insufficiently. A subsequent correction of these data is not possible as the methodology of the digestion experiments does not guarantee constant metabolic excretion." [557].

When the digestibility coefficients are directly applied to determine fermentable substrate components in the biogas process, “the apparent digestibility measured in animals is thus wrongly associated with the biodegradability of the nutrients [...]. However, animal faeces do not entirely consist of indigestible substances of the food consumed, but also contain metabolic nutrients excretions of endogenous origin." [558]. A subsequent correction of the apparent digestibility is only possible on the basis of standardised digestion experiments, that guarantee an almost constant excretion of metabolic nutrients [558, 566].

Current evaluations [557, 558] based on extensive test series for energetic feed assessment [567, 568] fulfil these criteria and thus allow for a differentiated and reliable evaluation of biodegradable nutritional components. Considering specific maintenance requirements of animals, the indigestible fraction of characteristic crude nutrients is determined in standardized digestibility tests by examining the different nutrient concentrations in the feed and excreta, Table 15 [557].

The content of indigestible crude proteins and lipids (iXP and iXL) within each substrate type is subject to only minor fluctuations. Thus, average values for indigestible substances of these nutrients are expected for individual substrate groups. The proportion of indigestible crude carbohydrates (iXC) however varies widely and is approximated by a suitable regression function for each substrate type, depending on the content of crude fibres (XF). In order to enable a universal but reliable estimation of indigestible raw carbohydrates, a sufficiently large database with a wide range of digestibility ratios was used.

For example, the resulting regression function (second degree polynomial function) for different harvest products of maize crops is based on 63 digestion experiments, which include whole plant maize silage, ear maize, as well as the residual maize plant after cob harvest and maize straw after kernel harvest.

Table 15: Estimates of nutrient excretions in the digestion experiment [557]

	Nutrient excretions of animals in g kg^{-1} TS					
	iXP indigestible crude proteins		iXL indigestible crude lipids		iXC indigestible crude carbohydrates	
	Mean	s	Mean	s	Regression function	s
Grain and grain silages						
Wheat, rye	29	7	6	2	$35 + 1.89 \cdot XF$	17
Barley, oats	28	5	6	1	$35 + 1.38 \cdot XF$	23
Whole crop maize, maize ear and maize kernels and silages thereof						
Maize	36	4	5	1	$35 + 0.47 \cdot XF + 0.00104 \cdot XF^2$	24
Whole crop cereal silage						
Rye	36	4	6	1	$35 + 0.82 \cdot XF + 0.00022 \cdot XF^2$	24
Wheat	37	4	6	1	$35 + 0.53 \cdot XF + 0.00102 \cdot XF^2$	21
Barley	39	4	6	1	$35 + 0.81 \cdot XF + 0.00006 \cdot XF^2$	23
Other types of green fodder and silage derived therefrom						
Green rye	40	4	10	2	$35 - 0.23 \cdot XF + 0.00230 \cdot XF^2$	22
Green oats	39	4	10	2	$35 - 0.30 \cdot XF + 0.00279 \cdot XF^2$	19
Lucerne	44	5	10	2	$35 + 0.41 \cdot XF + 0.00101 \cdot XF^2$	23
Grass (intensive use)	46	5	10	2	$35 - 0.26 \cdot XF + 0.00300 \cdot XF^2$	40
Sugar beet silage derived therefrom						
Sugar beet	28	-	6	-	$35 - 0.70 \cdot XF$	-

For calculation of the true digestibility within the evaluated digestion experiments [567, 568], average nutrient excretions of endogenous origin were determined according to Equation 9.

$eXC = 35 \text{ g kg}^{-1} \text{ TS}$ — Carbohydrates of endogenous origin — Equation 9a

$eXP = 20 \text{ g kg}^{-1} \text{ TS}$ — Proteins of endogenous origin — Equation 9b

$eXL = 5 \text{ g kg}^{-1} \text{ TS}$ — Lipids of endogenous origin — Equation 9c

Based on the concentration of individual crude nutrients, degradable substrate components can be obtained from the indigestible and endogenous excretions as described in Equation 10.

$DXC = XC - iXC + eXC$ — Degradable carbohydrates — Equation 10a

$DXP = XP - iXP + eXP$ — Degradable proteins — Equation 10b

$DXL = XL - iXL + eXL$ — Degradable lipids — Equation 10c

The sum or combination of individual equations for determination of degradable nutrients corresponds to practical estimation procedures for total DVS according to Weißbach [558, 559, 563].

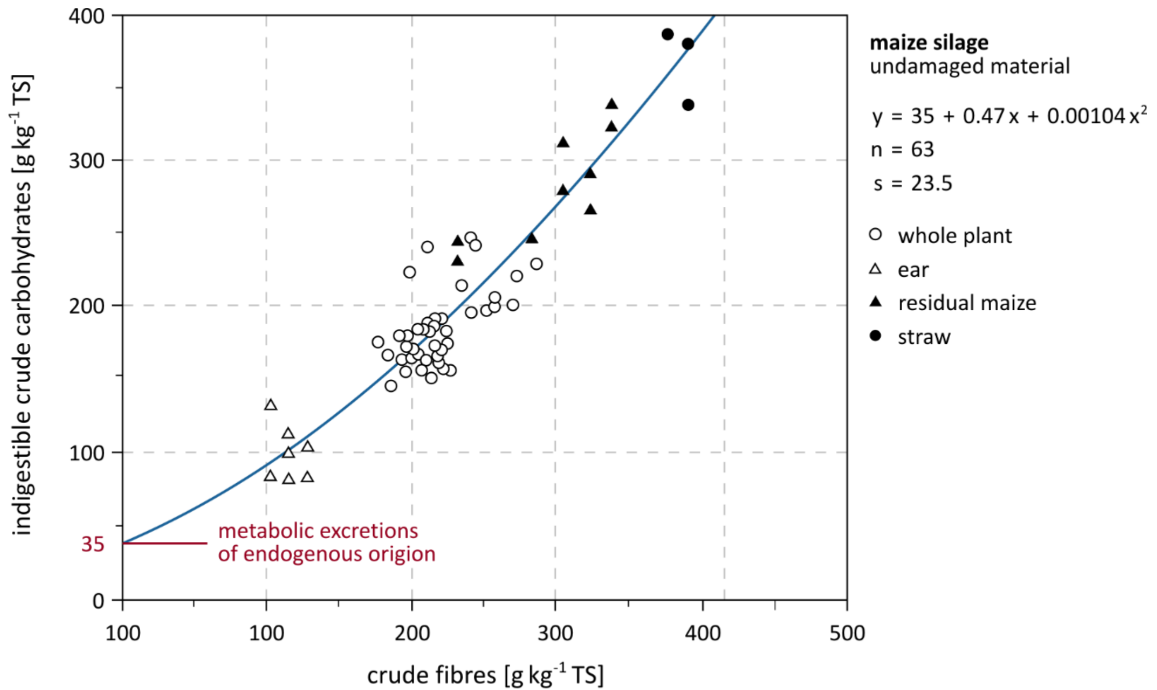


Figure 40: Regression function for indigestible crude carbohydrates of maize silage [557]

No comparable measurements and corresponding estimation formulas are available to assess digestible substrate components of animal excrements. However, WEIßBACH [564, 565] applies specific digestibility quotients of pig and poultry manure to calculate the biogas potential of typical farm manures. Due to standardised test conditions, the corresponding results can also be used to calculate the content of fermentable nutrients. Thus, the indigestible nutrient concentration of comparable excrements or manures can be determined as a function of substrate-specific digestibility quotients (DQ) according to Equation 11.

$iXC = XC \cdot (1 - DQ_{XC})$	Indigestible crude carbohydrates	Equation 11a
$iXP = XP \cdot (1 - DQ_{XP})$	Indigestible crude proteins	Equation 11b
$iXL = XL \cdot (1 - DQ_{XL})$	Indigestible crude lipids	Equation 11c

Equation 9 and Equation 10 are then used to calculate the fermentable nutrients while accounting for metabolic nutrient excretions of endogenous origin.

An additional reference value can be derived on the basis of practical data of typical gas yields of farm manures [557]. If the stoichiometric biogas formation potential of forage and cereal crops is also applied to manure and dung, the degradation quotients of animal excrements can be calculated by dividing the substrate-specific biogas yield of the KTBL reference values [123, 447] by the stoichiometric biogas potential of 809 L kg^{-1} DVS [562], Table 16. Following the usual description of WEIßBACH, it is thus possible to define corresponding estimation equations for calculation to total share of DVS. However, this approach does not allow a differentiated description of individual nutrients. Furthermore, the resulting fermentation quotients are strongly dependent on the informative value of the utilized reference values.

Table 16: KTBL reference values and degradability quotients of farm manure

	KTBL reference values [123, 447]						
	TS [% FM]	VS [% TS]	XA [g kg^{-1} TS]	Biogas [L kg^{-1}VS]	Methane [%]	DQ [a] [%]	Regression function [g kg^{-1} TS]
Cattle manure [b]	10	80	200	380	55	47	DVS = 0.47 · (1000 – XA)
Pig manure	6	80	200	420	60	52	DVS = 0.52 · (1000 – XA)
Solid cattle manure [c]	25	85	150	450	55	56	DVS = 0.56 · (1000 – XA)
Solid Poultry manure [c]	40	75	250	500	55	62	DVS = 0.62 · (1000 – XA)

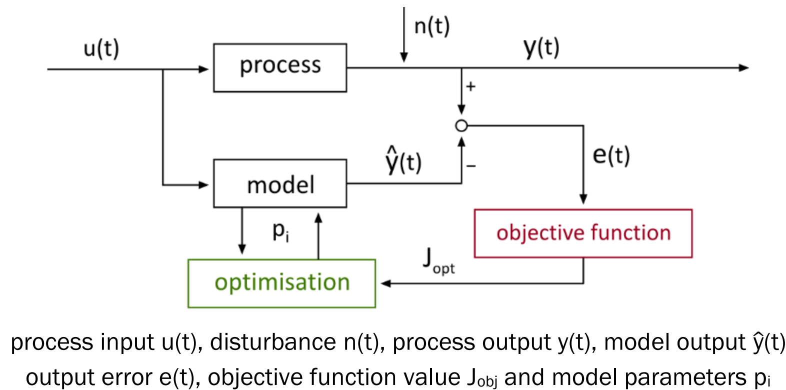
[a] Calculation of the degradability quotient by dividing the specific biogas yield in L kg^{-1} VS of the KTBL reference values by the stoichiometric biogas potential of forage and cereal crops with 809 L kg^{-1} DVS according to WEIßBACH [557, 562].

[b] Cattle manure, including feed remains.

[c] Solid cattle and poultry manure, depending on the straw to feces ratio.

3.4 Parameter estimation

To depict individual process behaviour and simulate the characteristic progression of individual measurements, various methods exist for numerical estimation of unknown model parameters [121, 238, 548]. However, the methodical approach and functional components for identification of parametric models are similar for many established procedures, Figure 41.



process input u(t), disturbance n(t), process output y(t), model output $\hat{y}(t)$
output error e(t), objective function value J_{obj} and model parameters p_i

Figure 41: General block diagram for estimation of unknown model parameters [434, 548]

In each iteration step, the deviation e(t) between measurements y(t) and corresponding simulation results y(t) is determined and summarised in the objective function value J_{opt}. Based on numerical optimisation procedures, individual model parameters θ are then iteratively adjusted to achieve optimal objective values (minimum error). In addition to the selection of variable model parameters and reasonable parameter boundaries, suitable objective functions and powerful optimization procedures are required for assessment and effective minimization of the resulting model deviation.

3.4.1 Parameter selection

Depending on available measurements, individual model parameters must be selected for numerical estimation and precise description of characteristic processes and variables. In system theory, influential parameters can be identified and applied for process simulation using local or global sensitivity analysis [431, 455–457, 523]

During application of the ADM1, local sensitivity indices have been calculated directly via partial derivatives of state equations [102] or percentage changes [182, 311, 577, 578]. To consider the influence of parameter combinations and dependencies between different model parameters, global sensitivity analysis in the entire value range of unknown model parameters is required. In anaerobic digestion process simulation, there are only a few studies [126, 499], that evaluate the global parameter influence using typical indices, such as first-order effects according to SOBOL [497], total effects according to HOMMA and SALTELLI [228] or elementary effects according to MORRIS [368].

A literature survey, consisting of 30 investigation on the application of the ADM1 clearly shows that regardless of substrate types and sensitivity indices, the same parameter groups are usually selected for parameter estimation, Table 17. In general, first-order reaction constants of disintegration or hydrolysis as well as the kinetic parameters of acetogenesis and acteoclastic methanogenesis play a decisive role in the description of individual process behaviour. Characteristic parameters of acidogenesis as well as inhibition constants of nitrogen limitation, hydrogen inhibition or specific limits of the pH function are rarely changed.

Frequency of a parameter change within the sample (Table 17, footnote b) largely corresponds to the overall parameter sensitivity proposed by BATSTONE et al. [33]. Only the limits of pH inhibition rarely change despite their occasionally high sensitivity. Furthermore, kinetic parameters of acetogenesis are often identified during parameter estimation, although their influence on the simulation results (according to BATSTONE et al.) is comparatively low. Considering specific measurements, parameters that tend to be modified during model application are those that also have a large impact on simulation results.

However, influential model parameters are not necessarily identical to a reasonable selection of variable parameters. Thus, identifiability of individual model parameters must be verified (considering the specific model structure, available measurements and reasonable parameter limits). Even under ideal process conditions, individual parameters cannot be clearly identified on the basis of the applied model structure (*structural identifiability*). In addition, identifiability is complicated by experimental procedures and various measurement uncertainties (*practical identifiability)* [121, 547].

Table 17: Parameter selection for parameter estimation during application of the ADM1

	k [d⁻¹]			k_m [g COD g⁻¹ COD d⁻¹]							K_S [g COD L⁻¹]							K_I [g COD L⁻¹]			pH [-]			
	dis	hyd	dec	su	aa	fa	c4	pro	ac	h2	su	aa	fa	c4	pro	ac	h2	IN	nh3	h2	aa	ac	h2	
Biernacki [49]	●	●	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	Maize, grass, green weed silage or glycerine
Blumensaat [55]	●	○	○	○	○	○	○	●	●	○	○	○	○	○	●	○	○	○	●	●	○	○	○	Sewage sludge
Boubaker [67]	●	●	○	○	○	○	○	○	●	○	○	○	○	○	○	●	○	○	●	○	○	○	○	Olive mill wastewater and olive mill solid waste
Cesur [a] [90]	●	○	○	○	○	○	○	●	●	○	○	○	○	○	●	○	○	○	○	○	○	○	○	Pig manure
Chen [97]	●	●	○	○	○	○	○	○	●	○	○	○	○	●	●	●	●	○	○	○	○	○	○	Traditional Chinese medicine wastewater
Cimatoribus [102]	●	○	●	○	○	○	○	○	○	○	○	○	○	○	○	●	○	○	○	○	○	○	○	Sewage Sludge
Derbal [113]	○	●	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	Organic waste and waste activated sludge
Dereli [114]	○	○	●	●	●	●	●	○	●	●	○	○	●	○	○	●	○	○	●	○	○	○	○	Opium alkaloid effluents
El Fadel [135]	●	○	○	○	○	○	○	●	●	○	○	○	○	○	●	○	○	○	●	○	○	○	○	Organic waste
Esposito [141]	●	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	Organic waste and sewage sludge
Feng [a] [154]	●	○	○	○	○	○	●	●	●	○	○	○	○	●	●	●	○	○	●	○	○	○	○	Blackwater and kitchen refuse
Fezzani [158]	●	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	●	○	○	○	○	Olive mill wastewater and olive mill solid waste
Gali [170]	●	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	Fruit pulp, pig manure and glycerine
Girault [182]	○	●	●	●	○	○	○	●	●	○	●	○	○	○	●	●	○	○	○	○	○	○	○	Pig manure
Kalfas [251]	○	●	○	○	○	○	●	●	●	○	○	○	○	●	●	●	○	○	○	○	○	○	○	Olive mill wastewater and olive mill solid waste
Koch [281]	○	●	○	○	○	○	○	○	●	○	○	○	○	○	○	○	●	○	○	●	○	○	○	Grass silage
Koutrouli [290]	○	●	○	○	○	○	●	●	●	○	○	○	○	○	●	●	○	○	○	○	○	○	○	Olive mill wastewater and olive mill solid waste
Lee [311]	●		○	○	○	○	○	●	●	○	○	○	○	○	●	○	○	○	○	○	○	○	○	Dog food and flour
Lübken [337]	○	●	○	○	○	○	●	●	●	○	○	○	○	●	●	○	●	○	○	○	●	○	○	Cattle manure and animal feed
Lübken [334]	○	●	●	○	○	○	○	●	●	●	○	○	○	○	●	○	○	○	●	○	○	○	○	Maize silage
Mairet [343]	○	●	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	●	○	Microalgae (Chlorella vulgaris)
Page [410]	○	○	●	○	○	○	○	○	●	○	○	○	○	○	○	●	○	○	○	○	○	○	○	Cattle manure
Pons [424]	○	●	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	Sewage sludge, cattle manure or glycerine
Schlattmann [474]	●	●	○	○	○	●	○	○	○	○	○	○	○	●	●	●	●	○	○	○	●	●	●	Cattle manure and maize or grass silage
Schön [a] [479]	●	●	●	○	●	●	●	○	●	●	○	●	●	●	●	●	●	○	○	○	○	○	○	Cattle manure or sewage sludge
Thamsiriroj [519, 520]	●	○	○	○	○	○	●	●	●	○	○	○	○	●	●	○	●	○	○	○	○	○	○	Grass silage
Wett [a] [573]	○	○	●	○	●	●	●	○	●	●	○	●	●	●	○	○	●	○	○	○	○	○	○	Pig manure
Wichern [578]	●	○	○	○	○	○	○	●	●	○	○	○	○	○	●	○	●	○	○	○	●	○	○	Cattle manure and animal feed
Wichern [576]	●	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	●	○	●	●	●	○	○	Grass silage
Zhou [604]	○	○	●	○	○	○	○	○	●	○	○	○	○	○	○	○	○	○	○	○	○	○	○	Cattle manure and maize silage
Frequency [b]	■	■	□	·	·	·	□	■	■	·	·	·	·	□	■	□	□	·	□	·	·	·	·	
Sensitivity [c]	■	■	□	·	·	·	·	□	■	·	·	·	·	·	□	■	□	·	□	·	·	■	□	

[a] In addition to estimation of sensitive model parameters, other influencing variables were changed as well (which however are not discussed in detail nor described in the publication).

[b] Frequency of parameter change within the sample (in percentage): · < 6 (less than 20 %) | 6 ≤ □ < 12 (at least 20 %, but less than 40 %) | 12 ≤ ■ (at least 40 %).

[c] Parameter sensitivity according to Table 6.2 in Batstone et al. [33]: · low or no sensitivity | □ some sensitivity or significant sensitivity under dynamic conditions | ■ significant sensitivity under steady-state conditions and critical sensitivity under dynamic conditions.

Assuming ideal process behaviour and error-free measurements, individual state variables and model parameters of the ADM1 are structurally identifiable [306]. However, detailed investigations by NIHTILÄ and VIRKKUNEN [394], HOLMBERG [225] and DOCHAIN et al. [122] prove that even estimation of characteristic growth parameters of original MONOD kinetic – with typical measurement uncertainties and without information on the microbial biomass concentration of the involved species – is not unique or only possible in combination of individual parameters. Based on a small quantity of (partially erroneous) measurements and various state variables and model parameters, considerable uncertainties are to be expected during parameter estimation of established anaerobic process models [125].

In spite of these weaknesses, typical MONOD kinetics are still suitable for functional description of microbial growth behaviour and precise simulation of characteristic measurements. However, the limits of parameter identifiability of anaerobic systems must be taken into account, especially when evaluating and interpreting specific parameter values [225]. Thus, measurement uncertainties can be applied to determine specific confidence regions of individual model parameters [40, 102, 251]. Furthermore, Monte Carlo analysis can provide a graphical representation of the objective function, which can be utilized for evaluation and quality assessment of individual parameter estimates [182].

3.4.2 Objective function

The choice of a suitable objective function and corresponding optimization algorithm significantly affects the outcome of numerical estimation of unknown model parameters [125]. A variety of mathematical functions and quality criteria can be applied for assessment and minimization of the remaining model deviation (with respect to available measurements), Table 18.

Table 18: Objective function and quality criteria for assessment of model deviation [a]

Objective function [125, 367]			
Mean absolute error (MAE)	$\frac{1}{n} \cdot \sum_{i=1}^{n} \lvert y_i - \hat{y}_i \rvert$	Root mean squared error (RMSE)	$\sqrt{\frac{1}{n} \cdot \sum_{i=1}^{n} (y_i - \hat{y}_i)^2}$
Mean squared error (MSE)	$\frac{1}{n} \cdot \sum_{i=1}^{n} (y_i - \hat{y}_i)^2$	Mean logarithmic squared error (MLSE)	$\frac{1}{n} \cdot \sum_{i=1}^{n} \left(\ln(y_i) - \ln(\hat{y}_i)\right)^2$
Model efficiency [293, 367, 383]			
NASH-SUTCLIFFE-efficiency (NSE)	$1 - \frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{\sum_{i=1}^{n} (y_i - \bar{y}_i)^2}$	Extended NASH-SUTCLIFFE-efficiency [b] (eNSE)	$1 - \frac{\sum_{i=1}^{n} \lvert y_i - \hat{y}_i \rvert}{\sum_{i=1}^{n} \lvert y_i - \bar{y}_i \rvert}$

[a] Measurements (y_i), model output ($\hat{y}_i$), arithmetic mean of measurements ($\bar{y}_i$) and number of measurements (n).

[b] Extension of the original NASH-SUTCLIFFE-Efficiency by absolute differences, according to KOCH et al. [281].

During simulation of anaerobic digestion processes, the objective function value is typically determined using (mean) squared differences between individual measurements and the corresponding simulation results [40, 127, 135, 170, 182, 251, 333, 343, 402]. To reduce the considerable influence of extreme values or outliers on the objective function, squared errors (MSE and RMSE) are typically replaced by absolute differences (MAE) [49, 281, 293, 367] or the natural logarithm of individual measurements and corresponding simulation results (MLSE) [38, 195, 576].

Furthermore, the calculation of the objective function can be extended to include parameter-specific and time-dependent weights [125]. Thus, information on measurement uncertainty of individual process variables - for example in the form of the inverse covariance matrix of measurement error (*Maximum Likelihood*) - can be included in the parameter estimation procedure [238, 548, 594]. However, reliable information on measurement uncertainty (and in particular on sampling errors) is rarely available in research or practise. Furthermore, the influence of different value ranges of individual measurements (e.g., during multi-objective optimization) can be addressed by multiplication of additional weights with the squared (or mean) error of each process variable [159, 332].

In addition to typical objective functions, there are numerous quality criteria to assess model efficiency, quantify model precision or compare different simulations results with a given set of measurements [241, 293, 367]. Two variations of the NASH-SUTCLIFFE-efficiency (NSE) have been used during application of the ADM1, Table 18. Based on the similar formula for the coefficient of determination R^2, the original NSE [293, 367, 383] provides an established indicator for evaluation and assessment of simulation results.[18] Thus, a NSE of 1 indicates a perfect description of experimental results by the applied process model. A NSE of 0 shows, that the simulation results contain as much information as the arithmetic mean of individual measurements. For negative NSE values, the arithmetic mean of available measurements is more suitable for (statistical) process description than the corresponding simulation results. By using squared errors, extreme values and outliers can have a considerable influence on the original NSE. Therefore, Koch et al. [281] replaced squared differences in the original NSE with absolute differences, as shown in Table 18.

3.4.3 Optimisation procedure

Based on the applied objection function, unknown model parameter are iteratively determined within reasonable boundaries using suitable optimisation procedures. In general, numerical optimisation algorithms can be divided into local and global procedures [396, 413, 438]. Whereas traditional methods determine the local optimum close to corresponding initial values, global procedures enable identification of the overall optimum in the entire value range of the applied objective function. Furthermore, a clear distinction is made between gradient-based and gradient-free algorithms, Table 19.

[18] The coefficient of determination R^2 characterizes the quality of a linear approximation and is delimited to linear regression models with resulting function values between 0 and 1 [150]. The Nash-Sutcliffe-efficiency (NSE) can be applied for any (non-linear) regression or simulation model and also enables negative function values.

Table 19: Classification of typical optimization procedures in anaerobic process modelling [a,b]

	Local optimization procedures	Global optimization procedures
gradient-based	• NEWTON algorithm • GAUSS-NEWTON algorithm • LEVENBERG-MARQUARDT- algorithm GARCIA-OCHOA [174], DEVECI [116], MARTIN [347], LOKSHINA [332], SIMEONOV [493] • Sequential quadratic programming Sales-Cruz [453], Aceves-Lara [2]	
gradient-free	• Secant method CESUR [90], CHEN [97], KALFAS [251] • Simplex algorithm MÖSCHE [370], SIMEONOV [493], RUEL [450], HAAG [195], GUISASOLA [191], LOPEZ [333], BIERNACKI [49], MAIRET [343]	• Genetic algorithms JEONG [243], ABU QDAIS [430], WICHERN [576] • Particle Swarm Optimization Wolf [590] • Simulated Annealing Haag [195]

[a] Extended summary and application examples for parameter estimation in anaerobic process modelling based on the comprehensive literature review of Donso-Bravo et al. [125].

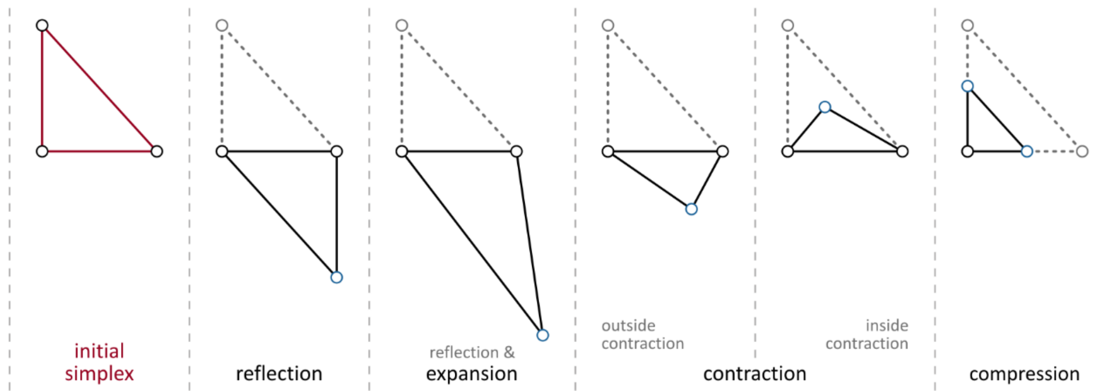
[b] A detailed description of characteristic optimization procedures can be obtained from available literature [179, 395, 396, 413, 438].

Thus, Newton's algorithm requires additional information on the first and second derivative to determine the search direction to the minimum of the objective function [115]. Since it is sometimes difficult to calculate the second derivative (HESSE matrix) in case of nonlinear functional behaviour, the Gauss-Newton algorithm applies the JACOBI matrix to replace the objective function with a linear approximation. This guarantees an explicit and unique solution for each iteration step. The LEVENBERG-MARQUARDT algorithm combines the advantages of both procedures by an additional step-size or damping factor (regularization). The resulting optimisation procedure is more robust than the GAUSS-NEWTON algorithm and yet converges better than NEWTON'S original method [317, 346].[19]

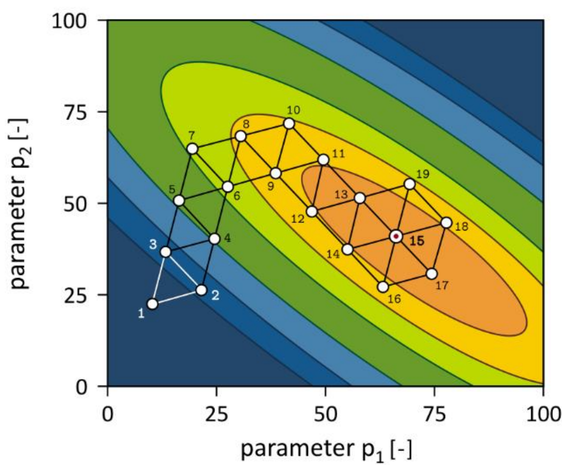
In addition to the LEVENBERG-MARQUARD algorithm, gradient-free procedures such as the secant or simplex method are often used for parameters estimation during simulation of anaerobic processes [125]. Global optimisation procedures generally do not depend on computation of gradients and are rather based on biological or physical phenomena in order to identify the best possible parameter combination in the entire value range of the objective function [179, 395, 422]. For parameter optimisation and model application in anaerobic digestion, individual studies examine the application of nature-inspired optimisation techniques based on evolutionary and/or genetic algorithms, as well as at individual behaviour in animal swarm formation or technical cooling processes, Table 19.

Within the scope of his doctoral thesis, Weinrich [555] applied an extended variant of the gradient-free simplex method of NELDER and MEAD [303, 386, 549] for parameter estimation. For the number n of unkown model parameters, a simplex consists of n + 1 points. Thus, in a two-dimensional parameter space, a simplex is characterized by three points (triangle), Figure 42.

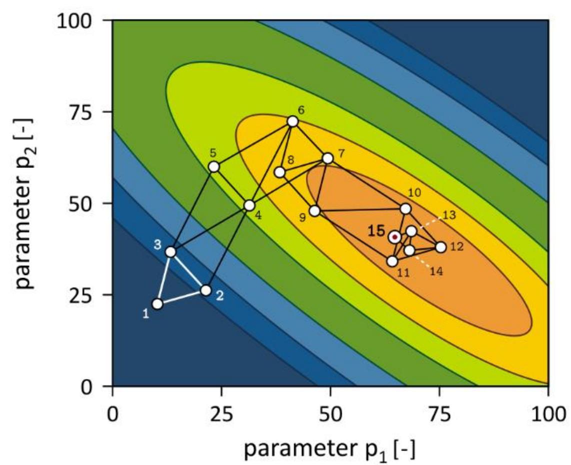
[19] Traditional methods such as the GAUSS-NEWTON or LEVENBERG-MARQUART algorithm have been developed for solving non-linear compensation problems and to minimise squared errors. Thus, the objective function and the corresponding optimisation algorithm cannot be selected separately for these procedures [396, 413, 438].



(a) Transformation of a simplex by reflection, expansion, contraction and compression [303]



(c) Sequential parameter adjustment (optimization) using a fixed simplex [549]



(d) Sequential parameter adjustment (optimization) using a variable simplex [549]

Figure 42: Basic principle of the gradient-free simplex algorithm

Starting from an initial simplex, a new parameter point (or vector) is calculated based on fundamental transformation through reflection, expansion, contraction and compression, Figure 42a. This guarantees a better functional value in the vicinity of the original simplex and in turn defines a new simplex for the next iteration step [549]. By sequentially combining the resulting simplexes, the local minimum (objective value) can be determined iteratively. Optimisation can be performed with continuous reflection of a fixed simplex (Figure 42b) or by application of available operators (Figure 42a) to modify shape of a variable simplex (Figure 42c) during each iteration [549].[20] Compared to the LEVENBERG-MARQUARDT method, the simplex algorithm generally converges more slowly, due to missing gradients. However, this rather simple and gradient-free optimisation procedure reacts less sensitively to local minima and thus enables robust estimation of unknown model parameters [125].

[20] In the example in Figure 42, both methods reach the minimum functional value through 15 parameter combinations. However, for optimization with a fixed simplex, additional iteration steps are required to circle the objective value and guarantee a local minimum (steps 16 to 19).

Further details on the application of the presented estimation procedures for process simulation of continuous anaerobic experiments are provided in the following research paper:

Weinrich, S., Mauky, E., Schmidt, T., Krebs, C., Liebetrau, J., Nelles, M. (2021): Systematic simplification of the Anaerobic Digestion Model No. 1 (ADM1) – Laboratory experiments and model application. Bioresource Technology. Vol. 333, 125104.
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List of figures

Figure 1: Primary energy supply (12,832 PJ) in Germany in 2019 [1] 10
Figure 2: Conversion technologies (pathways) for energetic utilisation of biomass [10]....................11
Figure 3: Comparison of product formation during (a) aerobic and (b) anaerobic treatment [11]....................12
Figure 4: Mass-specific substrate use in German anaerobic digestion (biogas) plants in 2018 [13]......13
Figure 5: Simplified process scheme of an agricultural biogas plant [27] 14
Figure 6: Characteristic modelling techniques to describe dynamic systems [54] 16
Figure 7: Number of publications on anaerobic process modelling per year [61,62] 17
Figure 8: Characteristic process phases during anaerobic digestion [57,82,83]....................19
Figure 9: Hydrolysis of carbohydrates (cellobiose)....................20
Figure 10: Hydrolysis of proteins (dipeptide)....................20
Figure 11: Hydrolysis of fats (triglyceride)....................21
Figure 12: Fermentation of glucose [106,109]....................22
Figure 13: Coupled *STICKLAND reaction* of alanine and glycine [122]....................23
Figure 14: *Beta-oxidation* of long-chain fatty acids [123,125,126] 24
Figure 15: Syntrophic oxidation of butyric acid (*interspecies hydrogen transfer*) 25
Figure 16: Influence of hydrogen partial pressure on the free enthalpy $\Delta G°'$ [139]....................26
Figure 17: Taxonomic classification of known microorganisms during anaerobic digestion[139]...........28
Figure 18: Classification of essential nutrients in the periodic table of elements [122,185] 29
Figure 19: Reference values for optimal ratio of macronutrients in substrates 30
Figure 20: Influence of the nutrient concentration on the microbial growth [195,208] 31
Figure 21: Reference values for optimal concentrations of trace elements in the digestate 32
Figure 22: Supply and bioavailability of trace elements in biogas plants [169] 33
Figure 23: Influence of temperature on methanogenic growth rate [122,222] 34
Figure 24: Optimal pH ranges during anaerobic digestion 36
Figure 25: Characteristic buffer systems during anaerobic digestion 38
Figure 26: Influencing factors on the dissociation [274] and inhibitory effect of ammonia 41
Figure 27: Ammonia inhibition of methane formation depending on temperature 42
Figure 28: Influence of sulphate-reducing bacteria on methane formation [351] 44
Figure 29: Hydrogen sulphide and total sulphide inhibition of methane formation 45
Figure 30: Dissociation equilibrium [376] and inhibitory effects of short-chain organic acids 46
Figure 31: Product and substrate inhibition (limitation) of organic acids [384] 47
Figure 32: Characteristic components for mass balancing a single biogas fermenter 48
Figure 33: Growth phases of a discontinuous culture [122,416,417]....................51
Figure 34: Progression of different growth functions of anaerobic digestion (Table 8) 54
Figure 35: Progression of single- or double-sided pH inhibition of anaerobic digestion (Table 9)............56
Figure 36: Classification of external requirements and internal model characteristics....................59
Figure 37: Classification of available process models based on substrate characterisation 60
Figure 38: General procedure for parameter identification of dynamic models....................66
Figure 39: Contribution of different kinetic fractions to the (relative) biogas production rate 69

Figure 40: Regression function for indigestible crude carbohydrates of maize silage [539] 73
Figure 41: General block diagram for estimation of unknown model parameters [502,546] 74
Figure 42: Basic principle of the gradient-free simplex algorithm 80

List of tables

Table 1: Stoichiometric degradation pathways during fermentation of glucose [33, 379]........................22
Table 2: Stoichiometry and free enthalpy of relevant degradation pathways during acetogenesis 25
Table 3: Stoichiometry and free enthalpy of relevant degradation pathways during methanogenesis...27
Table 4: Functions and importance of macronutrients during anaerobic digestion 30
Table 5: Advantages of mesophilic and thermophilic anaerobic digestion [477]....................................36
Table 6: Dissociation equilibrium of effective buffer systems during anaerobic digestion 37
Table 7: Stoichiometry and free enthalpy of relevant degradation pathways during sulphate reduction...44
Table 8: Microbial growth kinetics of anaerobic digestion 53
Table 9: Inhibition functions of microbial growth of anaerobic digestion...55
Table 10: Calculation of the pH value based on ion balancing..57
Table 11: Characteristic HENRY coefficients of anaerobic digestion [460]...58
Table 12: Properties of characteristic models for anaerobic digestion of single substrates 61
Table 13: Properties of characteristic models for anaerobic digestion of complex substrates................63
Table 14: Measurement methods and analytical procedures for process monitoring [320, 324] 67
Table 15: Estimates of nutrient excretions in the digestion experiment [557]..72
Table 16: KTBL reference values and degradability quotients of farm manure 74
Table 17: Parameter selection for parameter estimation during application of the ADM1 76
Table 18: Objective function and quality criteria for assessment of model deviation [a]............................77
Table 19: Classification of typical optimization procedures in anaerobic process modelling [a,b]..............79

References

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